DEVELOPMENT OF NOVEL POLYMER BASED ADHESIVES

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To

My

Beloved

Haynes

Declaration

I hereby declare that the thesis entitled " Development of Novel Polymer based Adhesives" is the original work carried out by me under the supervision of Dr. Rani Joseph, professor, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Cochin 682022, and no part of this thesis has been presented for any other degree from any other institution.

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Certificate

I hereby certify that the thesis entitled " Development of Novel Polymer based Adhesives" is based on the original work carried out by Smt. Neetha John under my supervision in the Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Cochin 682022, and no part of this thesis has been presented for any other degree from any other institution.

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LIST OF ABBREVIATIONS

Polymers

NR	Natural rubber
NBR	Nitrile rubber
CR	Chloroprene rubber
SBR	Styrene butadiene rubber
XNBR	Carboxylated nitrile rubber
PVC	Poly vinyl chloride
PU	Poly urethane rubber
VP	Styrene butadiene vinyl pyridine
CNR	Chlorinated natural rubber

Additives

ZnO	Zinc oxide
MgO	Magnesium oxide
ZDC	Zinc diethyl dithiocarbonamide
HAF	High abrasion furnace black
GPF	General purpose black
RF	Resorcinol formaldehyde

Abstract of the Thesis

Novel latex based and solution based adhesives were prepared and evaluated for wood to wood bonding. These adhesives were found to be superior to commercial adhesives like fevicol and dentrite. Novel adhesives were prepared for leather to leather bonding and these were also found to be more efficient than the polyurethane type and dentrite adhesives used commercially. A novel strip adhesive system employing very low amount of solvents was tried successfully for rubber-to-metal bonding. Further, a novel adhesive system was investigated successfully for bonding copper coated bead wire and steel cord to rubber by modifying it with chloroprene rubber.

Chapter 1

INTRODUCTION

Chapter one

Introduction

Adhesion

Adhesion is the state in which two surfaces are held together by interfacial forces of attraction, owing to the interactions of molecules, atoms and ions on the two surfaces[1]. Adhesion is a branch of Zygology, the science of joining things together; others include welding, riveting and all forms of mechanical joining [2]. The term adhesion is used to describe the common phenomenon or state where two bodies are stuck together[3]. The term adhesion is used both for the fundamental atomic and molecular forces responsible for holding two phases together and for quantities obtained from destructive tests[4]. The science of adhesion, is a many-faceted subject requiring an understanding of inter atomic forces, chemical composition and physical properties of materials, and the forces to which a final structure will be subjected [2]. 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, which are formed whenever two substances are placed in intimate contact [5-9]

The science of adhesion can be studied in two ways: From the chemistry and physics of surfaces and interfaces and from the fracture mechanics of adhesive joints[10]. Adhesion occurs by physical or chemical bonding. Physical bonding is due to mechanical interlocking and chemical bonding is by covalent or ionic bonds between adhesive and the substrates[10].

Mechanisms of adhesion are follows:

1) Mechanical interlocking: It occurs when the adhesive flows into pores or adhesive solidify around the projections. Adhesive acts as a mechanical anchor because it flows into the minute openings and crevices on the adherend surfaces [2]. The adhesive diffuses into to the substrates and bonds are formed not just on the surfaces but deeper inside them.

Mechanical interlocking is applicable to porous substrates like wood, paper, textiles etc. There may be hook and eye joints where adhesive molecules seep into the interstices of the two surfaces. This gives fixed joints that cannot be fractured without either physically breaking the adhesive, or the surfaces of one of adhering components [2].

2) Inter diffusion technique: In this adhesive dissolves and diffuses into the substrate material. The extent of diffusion depends upon the affinity of the different types of molecules for one another[10]. This inter diffused molecules form a layer which may be thin (0.5-10 nm) for high molecular weight adhesives and thick for low molecular weight adhesives. This is different from mechanical interlocking, involving penetration of adhesive at the molecular level whereas in mechanical interlocking adhesive enter into pores which are much larger than molecules.

3) Adsorption: In which adhesive molecules are attracted to a specific site on a solid surface. The attraction may be by Van der Waal's forces or specific donor - acceptor interactions. Chemisorption may occur if the adhesive and substrate molecule have chemical character.

4) Electrostatic attraction: Electrostatic forces develop at the interface between materials and electrostatic attraction takes place[11]. These forces are attributed to the transfer of electrons across the interface, thus creating positive and negative charges that attract one another[12].

Surface and interfacial properties: -

The main factor affecting on adhesion are

(a) Surface Topography: - The surface of adherends will be rough even after polishing,[13] so when two solids are made to contact, intimate contact will not occur. There will be adsorbed or entrapped gases which may cause the separation of molecules from true molecular contact. For molecules to get attracted less than 0.3 nm distance is required[14].

(b) Surface Tension and Energy: - Molecules at surface of a solid or liquid are different from those in the interior. Molecules at the surface are not equally attracted in all directions so they are attracted inwards by the molecules below the surface. This attraction gives rise to surface tension of liquids.

(c) Wetting and Setting: - The adhesive should give intimate contact with the surface and spread freely upon them. So the adhesive must be applied in liquid state and with sufficient pressure in order to flow into the small crevices of the solid surface. It must displace or dissolve the adsorbed impurities such as water or oxygen. The adhesive must be capable of setting to a tough solid. There should be large changes in volume of the adhesive during solidification. The thermal expansion coefficients of the adhesive and adherends must be similar. Setting occurs by cooling, by solvent removal or by chemical reaction. Solvent adhesives have greater shrinkage during solidification. The degree to which liquid wets a solid is measured by the contact angle[15]. When contact angle is zero then liquid spread the surface freely, and it is said to be completely wet. Surface tension is related to contact angle[16] by the equation

$$V_{sv} = V_{sl} + V_{lv} \cos\theta$$

V_{sv} - Surface tension of solid vapour

V_{sl} - Surface tension of solid liquid

V_{lv} - Surface tension of liquid vapour.

θ - contact angle

S_{sl} = spreading coefficient $= V_{sv} - V_{sl} - V_{lv}$

For measuring surface tension contact angle measurement is widely used [17]. When Cos θ against surface tension is plotted and curve extended to Cos θ axis then we will get critical surface tension Vc. Any liquid with a surface tension less than Vc will completely wet the solid surface. Polar solvent gives higher Vc[18].

Thermodynamic work of Adhesion:

If liquid and solid has no inter action then the interfacial tension V_{sl} will be the sum of surface tensions of liquid V_L and solid Vs. But there will be interactions, so then V_{SL} less than V_L + Vs.

The extent of the decrease is a direct measure of the strength of the interfacial attraction, which is the thermodynamic work of adhesion, Wa

$$Wa = V_L + Vs - V_{SL}$$

This expression first given by Dupre States that reversible work Wa of separating a liquid and a solid in vacuum must be equal to the free energy change of the system [19,20].

Wc = Work of cohesion

$$Wc = 2V_{LV}$$

$$S = Wa - Wc$$

Higher the value of S the greater is the thermodynamic work of adhesion compared to the cohesive energy of the adhesive [21,22]. Even though after solidification of the adhesive these thermodynamic quantities are modified, but the overall features will remain similar. Weak part of an adhesive bond tends to be interface, a high value of S will favor cohesive failure within the adhesive rather than interfacial failure and in turn will tend to lead to more reliable junction.

$$\Phi = \frac{Wa}{(Wcl \times Wcs)^{\frac{1}{2}}}$$

Wcl, Wcs - work of cohesion of liquid and solid respectively.

For simple interaction $\Phi = 1$. For systems in which there are different types of intermolecular force in the two substances, Φ will be less than unity.

$$V_{sl} = Vs + V_l - 2\Phi(Vs\,V_l)^{1/2}$$

$2\Phi(Vs\,V_l)^{1/2}$ is the surface tension owing to molecular attraction between the liquid and solid. The effective adhesion depends critically on the liquid adhesive displacing the third phase and spreading into all the space between the two solid surfaces to be attached to one another. If there is no affinity between the adherends, then there is certainly no mechanical strength for the adhesive bond [23]. In a good solvent the external layers are oriented and create a certain energetically enhanced surface layer [24-25], which will increase wetting and bond strength. The best adhesion characteristics are achieved in bonds obtained from a good solvent, which is due to the energy state of the adhesive surface when formed on appropriate substrates.[26]

Interfacial Chemical Bonding:

Adhesive joints with chemical bonds between the adherends gives rise to better bonding. The adhesive joints will withstand severe conditions of high temperature and high humidity if coupling agents or adhesion promoters are employed. They have dual chemical functionality, capable of inter linking the two adherends by reacting with the surfaces molecules of both substrates[27]. Specific coupling agents have been developed for bonding specific adherends. The work of adhesion was measured over a wide range of temperatures and rates of separation. The work of detachment was greater for chemically treated than for untreated surfaces. The chemical treatment gives unsaturated groups in the surface, which forms primary chemical bonds during the crosslinking reaction. There is direct ratio between work of detachment and density of chemical bonding at the interface under high temperature and low rates of peeling[28]. The joint strength of a sheet with more crosslinking agents will be lower than those prepared with smaller amount. When the length of molecular strands between crosslinks[29] are long, they contain a large number of bonds that must be highly stressed in order to break or detach one of them. When material is highly crosslinked and molecular strands are short, then it is less extensible and weaker.

Coupling agents are widely used to enhance chemical bonding between different materials. Silane is a good example for coupling agent[30]. The detachment work was found to increase steadily with the amount of interfacial chemical bonding. The adhesion strength is also influenced by the polymeric nature of the adhesive[31]. In high molecular weight elastomeric adhesives, many other bonds must be stressed in order to break the interfacial link.

Viscoelastic effect in Adhesion:

The strength of joints made with elastomeric adhesive depends on viscosity, elasticity, yield value and their dependence on shear rate [32].

$F/A = \eta\, dv/dx$ Where F-Force, A-Area

$\sigma = \eta \dot{\gamma}$, and η-Viscosity

$\gamma. = dv/dx$ -Shear rate

$$\sigma = F/A$$

The ultimate properties of the adhesive are proportional to the viscous effects. The strength of the adhesive joints increases as the temperature is decreased or as testing rate is increased[32]. Many adhesive joints fail cohesively within the adhesive layer at high temperature or low rate of separation [33]. As temperature is lowered, the cohesive strength of the adhesive increases. When it exceeds the interfacial strength, the path of least resistance to fracture becomes the interface. Test temperature and test rate have opposite effects. The effect caused by test temperature can be overcome by decreasing test rate [32]. This is the principle of rate-temperature equivalence. For amorphous glass forming liquids it is above the glass transition temperature. The WLF equation [34].

$$\text{Log } a_{T_g} = \frac{17.4(T-Tg)}{51.6+(T-Tg)}$$

a_{T_g} = ratio corresponding test rates at temperature T and Tg and rates of Brownian motion of molecular segments at T and Tg. From this equations we can predict the rate dependence of the work of detachment over a wide range of peel rates using only limited data obtained at various temperatures over a narrow range of rates. This WLF equation is only applicable to simple viscoelastic substances, not for semi crystalline or glassy adhesives. The shift factor a_T is determined empirically for each type of adhesive.

Energy dissipation and Plasticity:

Energy conservation during steady state peeling requires that work Ga done in detachment = thermodynamic surface detachment energy + energy dissipated within the adhesive + energy dissipated within the stripping member [35,36].

Thermodynamic surface detachment energy is the measure of intrinsic bonding across the interface, which is independent of detachment rate and temperature. Adhesive joints tested at normal rates and temperatures deformations are not perfectly elastic, and the detachment energy can be several orders of magnitude larger than the surface energy because of energy dissipation within the adhesive or bonded members or both.

When an adhesive joint is peeled then tensile stress reaches a maximum at the time of detachment and decays rapidly in the direction of the still attached portion of the bond [36]. There will be two curves an extension curve and a retraction curve, which form a hysteresis loop. Retraction curve lies below the extension curve. The area enclosed by the loop defined as hysteresis. The total volume of adhesive that experiences this cycle deformation upon peeling a distance ΔC.is given by $Wt \Delta C$.

W = test piece width

t = test piece thickness.

The energy dissipated within the adhesive on peeling a distance ΔC is $H\ Wt\Delta C$. This energy provided directly by the peel force. So peel force will be high for adhesives that are capable of dissipating large amounts of energy during detachment, and for thicker adhesive layers, this provides a greater volume of material in which dissipation occurs[37].

Adhesives:

An adhesive is a material that brings two materials together [38,39]. Adhesives and glues have been used for thousands of years, and up to the early 20th century, the only one of major importance were animal and vegetable origin. Since 1930s the synthetic glues has greatly increased. Their main advantage is their resistance to moisture and mould, and their ability to adhere in extreme temperatures and when structures are continually being flexed or bent. Towards the end of 19th century phenol resins made an appearance and by early 20th century phenol-formaldehyde resins came on the scene. Phenol-formaldehyde resins became the first synthetic resins to be used as adhesives and later on epoxy resins were introduced that were at least as strong as traditional glues [40].

Today, the number of applications for adhesives is growing fast. They range from industrial processes requiring large quantities of adhesives, to the assembly of components requiring only small amounts. Paper, packaging, footwear and woodworking remain the major applications. The usage has increased significantly in other areas, for construction work to fix window frames into walls, in vehicle manufacture to joint plastic components such as dashboards to a metal chassis, in electrical assemblies to fix components to circuit boards and in space to cement solar panels to satellites. The new adhesives have been developed with more efficient way of applying evenly and spreading them on large surfaces. So adhesives are used for joining metal to metal and other materials in load-bearing structures, such as bridges, and for a wide variety of other purposes [41].

The basic function of an adhesive is to fasten the components of an assembly together and maintain the joined parts under the service conditions specified by the design requirements. Adhesive material provide the answers to many joining problems, simplify and expedite assembly techniques, and reveal opportunities for design in new areas. Following are the advantages of using an adhesive in joining components [40].

1. Ability to bond a variety of materials, which may be dissimilar and of different modulus and thickness. Thin sheet materials may be bonded where other joining method would cause distortion.
2. Fabrications of complex shapes where other fastening methods are not feasible.
3. Appearance of finished product improved by smooth external joint surfaces and contours eliminate of voids, gaps and protecting fasteners such as rivets, bolts etc.
4. Versatility of adhesive forms and methods of applications permits their adaptation to many production processes.
5. Economic and rapid assembly and possibility of replacing several mechanical fasteners with a single bond, concurrent bonding of may components.
6. Strength of assembly is often higher and cost lower than for joints produced by alternative methods.
7. Uniform distribution of stresses over entire bonded area, stress concentration minimised, and fatigue resistance under alternating loads is improved. Joint continuity allows full use of component strength.
8. Weight reduction can often be effected by the use of adhesives instead of bolts, rivets, use of higher structural materials is allowed with more uniform stress distribution.

9. Elongation qualities of many adhesives allow stress to be absorbed, distributed or transferred; vibration damping and flexibility of properties are good.
10. Ability to join heats sensitive materials which brazing over welding would distort or destroy.
11. Prevention or reduction of galvanic corrosion between dissimilar materials.
12. Good sealing and insulating properties, barrier seal against moisture and chemicals, in many cases adhesive layer insulates against electricity, heat or sound.

The adhesives usually have the following disadvantages too:

1. Process became complicated, by need for surface preparation before joining and maintains clean components, preparation and application of adhesives, processing temperature/pressures and humidity conditions, relatively long curing times, jigs and other equipment.
2. Optimum bond strength usually not realised instantaneously as for spot welding assembly.
3. Difficult to provide enough inspection of adhesive joints.
4. Careful design required minimising peel and cleavage stresses as well as those due to differential thermal expansion.
5. Temperature limitations restrict use of bonded structure to certain service temperatures.
6. Poor electrical and thermal conductivity of many adhesives unless modified by fillers.
7. Possible degradation of bond by heat, cold, biodegradation, chemical agents, plasticisers etc.
8. Differently in dismantling bonded structures for repair.
9. Assembly hazards such as fire or toxicity are one feature of many solvent-based adhesives.

10. Tendency to creep under sustained loading, low peel strength of many thermosetting adhesives.
11. Some assemblies often joined by conventional methods are more economical.

Bonding Process:

Adhesive bonding involves the following interdependent basic steps.

1. Designing the joint specifically for adhesive bonding. The determination of joint stresses, type and size, together with strength requirements, will point to preferred adhesive materials.
2. Selection of adhesives. Take the performance requirements for the bonds.
3. Selection of surface preparation methods. It is necessary to consider suitable adherend pretreatment.
4. Fabrication of the assembly. This is adhesive application and final curing of the bond under controlled conditions.
5. Process control and the establishment of testing procedures to ensure reliability and permanence of the bond.

Classification of Adhesives:

There is no single system for the classification of adhesives. The adhesive industry has generally employed classifications based on end-use, such as metal-to-metal adhesives, wood adhesives, general-purpose adhesives etc. Particular end-use adhesives may be useful in several other fields also.

Adhesives can also be classified according to their physical form, chemical compositions, and method of application, various processing factors and their suitability for particular working requirements.

1. Classification based on bonding temperature[42]: Adhesives are classified as cold setting (below 20° C), room temperature setting (20-30°C), intermediate temperature setting (31-100°C) and hot setting (above 100° C).

2. Classification by origin[38]: Adhesives classified as naturally occurring and synthetic type. The naturally occurring are animal, vegetable and mineral adhesives. Synthetic adhesives are elastomeric, thermoplastic and thermosetting.
3. Classification by bonding methods[41]: Adhesive bonding can be done by pressure setting, hot melt, chemical setting, or by solvent release.
4. Classification by bond strength[41]: Adhesives can be structural (higher than 1000N/cm^2) and nonstructural (lower than 1000N/cm^2).
5. Classification by chemical nature: Thermosetts are UF, PF, MF, PU, Epoxides, Polyesters etc. Thermoplastics are EVA, PVC, PVA, Acrylics, Cyanoacrylic etc.

Surface Treatment :

In order to obtain a strong and durable adhesive joint, surfaces are pretreated[44]. The surface treatment alter the surface region on either by removal of a weak boundary layer or change in surface topography, change in chemical nature of the surface or modification of the physical structure of the surface[45].

All adhesives have surface tensions too great to allow them to wet the surfaces of solids with low surface energies. These are the methods to modify surfaces of these materials to get strong bonds.

(a) Casing or Plasma treatment: In this method, surface is bombarded with ions of an inert gas at low pressure. This casing causes crosslinking reactions in the surface region of the polymer. When a polymer is cooled from the melt, a low molecular weight fraction is pushed to the surface ahead of growing crystallites nucleated in the interior [48]. This results in weak boundary layer in an adhesive joint. Crosslinking the surfaces increase its strength and can increase joint strength [49].

(b) Corona Discharge: The material is exposed to corona discharge, usually in air and at atmospheric pressure. By this method C=C unsaturated double bonds are introduced into the surface [50]and the surface get roughened. This indicates that the corona can degrade and remove the portions of the surface material in a non-uniform way. Surface oxidation also occurs during corona discharge [51].

(c) Acid Etching: Acid etching is usually done by chromic acid. When etching time increases the depth of surface oxidation increases and bond strength improves significantly[49,52]. Increase in joint strength after acid etching is attributed both introduction of polar groups and increased roughness of the surface. Some etchings make carbonaceous residue resulting in darkening of surfaces. They increase wettability and which leads higher adhesion strength [53].

(d) Transcrystalline Growth: The ability to bond polyolefins is also improved by moulding them against a high-energy metallic substrate that induces transcrystalline growth in the surface regions[54]. The substrate induce profuse nucleation of crystallalitics at the surface and this results in the formation of rod like or columnar spherulites that grow inwards from the interface. This causes the increase in bond strength [55]. The shear strength of the specimens with transcrystalline surfaces is two to ten times higher than those of specimens without transcrystallinity [56]

(e) Surface Grafting: Surface grafting with suitable chemical species is another technique [57-59]. Bond strength increases by this pretreatment significantly.

Strength of Adhesives and Joints

Fracture Mechanics: Adhesive joints usually fail by initiation and propagation of flaws. The pressure of flaws [60] governs the strength of most real solids. The strength of adhesive joint is a function of the loading mode, dimensions, elastic properties of the bonded components, and the intrinsic strength of the interface. The aim of fracture mechanics theories is to analyse mathematically the loads, which the flaws propagate and describe the manner in which they grow. The source for naturally occurring flaws, which is termed as intrinsic flaws may be voids, cracks, dirt particles, additive particles in homogenates in adhesives etc., which may be initially present at a critical size or develop during the fracture test. Fracture mechanics has uses in characterising the toughness of adhesives, identifying mechanisms of failure and estimating service life of structures. The damages may be in form of cracks, air-filled voids,[60] debonds etc.

One method of analysis uses a simple energy criterion for fracture in terms of a characteristic work of detachment for breaking apart the interface. It is proposed brittle fracture for elastic solids [61], a energy criterion for fracture has been successfully applied for materials that b ecame locally dissipative [62,63], highly elastic materials[64] and to the separation of two adhering solids [65-75]. Another method consists of evaluating the stresses set up at the site of fracture, and then invoking a characteristic fracture stress as the criterion for rupture [76,77].

In applying an energy criterion to adhesive failure, it is necessary to identify an initial site of separation, a flaw or region of high stress concentration at the interface between the two adhering solids. Failure is then assumed to take place by growth of this initially debonded region until the joint is completely broken. An energy balance is taken for a small growth of the debond, changes in the strain energy of the joint and the potential energy of the loading device are equated to the characteristics work of detachment. This energy balance provides the required relation between the breaking load and the properties of the two adhering solids and the dimensions of the joint. Strain energy is supplied by a loading device and started in the deformable material. Failure occurred in two ways by supplying the work of fracture or detachment and by deforming material that was previously deformed. By equating the energy available to that required propagating fracture or detached zone, the magnitude of the stored strain energy at the moment of fractures deduced, and hence the . the applied stress(σ_b)at break.

The energy criterion arises from Griffith's work[78], which 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 came from stored elastic or potential energy of the loading system can be calculated for any type of test piece[79]. Energy required extending a crack over unit area and is termed as fracture energy or critical energy release rate is denoted as Gc[80].

$$Gc = \frac{Fc^2}{2b}\,\frac{dC}{da}$$

b- specimen thickness

a- crack length

C - compliance of the structure

Fc - load at the onset of crack propagation.

This equation is the foundation of many linear-elastic fracture mechanics: C is determined as a function of a. If bonded structure does not exhibit bulk linear-elastic behaviour then the fracture energy approach is in a different form of equation [81,82].

Mode of failure:

(a) Peeling separation. The elastic energy of deformation of the adherends changes very little as peeling proceeds. This is because most adhering layers do not stretch significantly under the force of peeling, and the amount of material subjected to bonding does not alter.

For peeling at 90° $P = G_a$

G_a - Work of detachment per unit area.

P - Peel force.

For peeling at 180° $P = G_a / 2$

(b) Lap Shear: A deformable adhering layer is subjected to a force applied parallel to the bond plane then a layer becomes stretched after detachment [70,77].

$$P^2 = 2t\,E\,G_a$$

The tensile stress $\sigma_b^2 = 2e\,G_a / t$

For a bar containing a small circular cavity of radius r,

$$\sigma_b^2 = E\,G_c / 3r$$

G_c - work required to propagate a fracture plane [61]

As flaw grows and its radius increases, the stress required for fracture is predicated to decrease. If the applied stress is large enough to cause the small initial flaw to grow, then it will be sufficient to make the process continue. Shearing detachment is therefore predicted to take place continuously at a constant tensile stress in the deformable layer related inversely to its thickeness[70]. This theory has been used for unequal adherends and for prestressed layer also[77].

c) Pullout test: Pullout force P for a fiber embedded in a cylindrical block of radius R [74] is

$$P^2 = 4\pi^2 R^2 r E G_a$$

r- fiber radius

R- adherend cylinder radius.

If both radii are same then,

$$P^2 = 4\pi^2 r^3 E G_a$$

The pullout forces increase as radius of the fiber increased [101]. The surface area to be debonded and the energy required to do so are both greater for fibers or cylinders of larger diameter and pullout force increased [73,31]. For spherical inclusions, the amount of highly stressed material in the vicinity of the debond which provide the energy needed for propagating the debond also increases as the size of inclusion is increased. The highly stressed volume grows in proportion to r^3, whereas the area to be debonded [73]only grows in proportion to r^2.

When a number n of fibers are embedded in a single block of elastomer and they are all pulled together, then the work required for detachment is larger than for a single fiber by a factor of **n**. The strain energy stored within the block must therefore be larger than before, by a factor of n, and the total force applied for pullout must be increased by a factor of $n^{1.2}$. The total force that required to pullout **n** fibers simultaneously forms a single elastic block until increase[73] in proportions to $n^{1.2}$.

Design of Adhesive bonds.

Bonds are made after considering many important factors. Depending upon the bonding method there are several design factors to be considered[83].

(a) Uniform stress distribution it is the most important of all of them. The strength of the joint may affect by the stress concentration over the bonds. In shear stress to a bond, force is directed so as to slide one substrate part another without increasing the bond thickness. Tensile stress tends to increase the bond gap. The optimum directions for these two stresses are perpendicular. The bond will be the combination of shear and tensile stress if the stressing force is not exactly in either the shear or tensile direction. If there is no sharp stress gradients then the bond strength will be the experimental strength on testing.

(b) Self-Alignment: The alignment of the substrates should be proper. In mechanical bonding it is essential that ridges, grooves etc. is essential for better alignments[74].

(c) Self-Fixturing: Load should be applied over the bond line to correct for any dimensional shrinkage of the melt or adhesive. Self-fixturing features eliminate the productivity loss caused by the clamping load.

(d) Ability to Clamp: Clamping force is applied over the adhesive bonds. So the bonds should have the ability to hold the clamping force.

(e) Vertical Insertion: The second substrate must be vertically down upon the first substrate. If more than two joints are made simultaneously in different planes, changes in bond design might be required to satisfy vertical insertion.

(f) Bond gaps Control: Bond strength is higher when bond line is thinner. The bond line should be horizontal to avoid flow of adhesive. Adhesive thickness is controlled by any method, which does not affect bonding.

For maximum effectiveness, adhesive bonds should be designed with (a) Stress the adhesive in the direction of maximum strength (b) Provide maximum bond area (c) Make adhesive layer as uniform as possible (d) Maintain thin and continuous adhesive layer (e) Avoid stress concentrations.

Failure:

Each polymer material has its own unique set of properties and the exact mode of potential failure is unpredictable[86]. In order to predict the failure one must know the material contributions, temperatures, stress and environmental conditions that cause bond strength deteriorating effects. When metal is bonded to fiber reinforced plastic[87] (FRP), metal expand quickly and FRP is slow, to catch up and on cooling, metal contracts faster than FRP. Solution for this is to increase the gauge of faster expanding substrate for slowing the rate or using low modulus adhesives or flexible bonding techniques. Chemical reactivity of the substrates may cause problems of failure. Outgassing of unreacted monomer,moisture or chemical fragments of decomposed initiators may lift adhesives from their bond surface. If substrates are exposed to heat, the additives chemically not bound to the substrate polymer will migrate. Thermal and rheological conditions of the adhesives can also alter the adhesive properties[88]. A durable joint will result if the selected adhesive layer is compatible with mobile ingredients and securely bonds to the second substrates.

Wood Adhesives:

Properties of Wood: Wood is naturally occurring, polymeric composite material. The chemical and anatomic structure of wood affects strength properties, appearance, resistance to penetration by water, chemicals and decays, pulp quality and chemical reactivity [89,90]. Hardwood and softwood forms are the two categories of wood. The principle chemical components of wood are carbohydrates 70-80%, lignin 20-30% and extraneous materials 5-10%. In soft wood lignin content is higher than hardwood. Carbohydrates consist of primarily cellulose (40-50%). The chain length of wood cellulose polymer is between 70,000 and 10,000 glucose units. Wood cellulose is crystalline and resistant to the attack of dilute acids[91]. Lignins are complex phenolic polymers of irregular structure[92]. Extraneous materials in wood are non-polymeric, low molecular weight substances that can be removed by a solvent without being chemically modified [93].

Physical properties of wood include some that are directly related to water content and movement, such as hygroscopicity, mechanical, electrical and thermal properties, corrosiveness and chemical resistance. Moisture content in wood has great effect on adhesion, so it is dried before use. The amount of moisture absorbed depends on the relative humidity and temperature. Relative humidity changes in atmosphere cause corresponding changes in the moisture content of wood [94].

The adsorption and desorption of water in wood is accompanied by external volume changes. The volume change or change in shape may occur because of the development of moisture gradients and stresses, and these stresses can be minimised by drying the wood under controlled conditions [95]. The degree of shrinkage is proportional to the specific gravity of wood[96]. Swelling and shrinkage changes with direction. Tangential swelling is greater than radial swelling and tangential shrinkage is higher than radial shrinkage. Longitudinal shrinkage and swelling are smaller in wood [97].

Permissibility of wood is higher. Wood is a porous material with 60-70% void volume. Permissibility may vary due to the highly anisotropic shape and arrangement of the component cells and the microscopic channels between cells which form a complex capillary network [98].

Wood consists of a series of tubular fibers or cells cemented together; each fiber is composed of various quantities of polymers. These are the cause for the physical and chemical properties of wood. Wood is an anisotropic material and has mechanical properties in longitudinal, radial and along the tangential axis. Mechanical properties are higher when moisture content is lower and when heated mechanical properties deteriorate [99,100].

Electrical properties like conductivity will be higher when moisture content is higher [101]. Conductivity increases when temperature increased and is affected by moisture. Dielectric constant is higher when moisture content is higher [102].

Softwood is chemically more resistant than hard wood. The wood may get corroded depending upon the wood species. Wood is slightly acidic, which may cause corrosion [103]. Corrosion also depends on the external corrosive agents. Some chemically treated wood is usually more corrosive than untreated wood [104].

Requirements of Adhesive:

The adhesive should penetrates into the wood surface and solidly attach the wood fibers. The adhesive should not destroy the continuity of the adhesive remaining in the glue line and one of the adhesive on wood surface should be wetted. The adhesive must be molecularly compatible with the interfaces. The diffusion of solvent or water in the adhesive into the wood is essential for the adhesive. The solvents initially wet the wood surface and pass into the cell walls. The adhesive must migrate sufficiently into the cell walls to form molecular bonds to hold on the wood constituents. To get better adhesion the adhesive must have the properties like physical and chemical characteristics, molecular weight distribution and molecular geometry in balance [105].

Certain process variables are there for getting good adhesive joints for wood. Assembly time- the time between the adhesive applied and pressure applied. If assembly time is short adhesive could not flow inside the gross capillaries of wood and form better joint. If assembly time is too large then mobility of the adhesive is greatly reduced and insufficient penetration occur. If the adhesive applied to one surface only then too much solvent will be lost and there will be insufficient adhesive for wetting the unspread surface. Adhesives should spread evenly over the surfaces. The thickness of glue depends on pressure applied time of pressing and compressibility of wood species. Moisture content of the wood is another process variable. Bonding difficulties may arise if moisture content is very high. The quality of bond will reduce if drying temperature goes higher. The adhesive should be applied as soon as the surfaces are prepared. As the time after surfacing increases the bond quality diminishes. The rate of temperature increase on glue line will affect the bond quality [106]. The applied pressure over the bond depends on the relative roughness of the surface and surface area of contact[107], compressibility of wood, the gap filling capability of the adhesive and amount of glue spread [108]. Small amount of pressure required for smooth surfaces whereas higher pressure is required for rougher surface and larger areas of bonding [109].

The performance of adhesive in service is dependent on the quality of original bond, the physical and chemical characteristics of the cured adhesive, and the stresses in the adhesive joints. The quality of original bond depends on various factors related to the wood surface. Grain orientation, moisture content, quality of wood surface and species of wood used etc. are the main factors. The physical and chemical characteristics of cured adhesives are its water resistance, heat resistance and resistance to biological attack. The glue line is subjected to shearing stresses across the grain as a result of differential swelling or shrinking of adjacent laminae. This differential swelling or shrinkage occurs due to changes in grain orientation, initial difference in moisture content and due to specific gravity difference. They cause cracking or delamination of wood joints [105].

Leather Joints

Leather is animal hide or skin that has been processed for use by man. The hide or skin is composed of water and proteins and unless preserved decays quickly [110].

Leather is made from raw hide in three steps (1) Removal of undesirable constituents such as hair, flesh, fat and some interfibrillary matters, leaving a concentrated network of high protein collagen fibers, greatly softened and interspersed with water. (2) Tanning: treating the hide with an agent called tannin that displaces the water and then combines with the coats and the collagen fibers. Tanning increases resistance to heat, hydrolysis and microorganisms. (3) Finishing to obtain proper thickness, moisture, lubrication and aesthetic appeal. The leather is essentially animal skin protein combined with Tannins, small amounts of oils, dyes, finishes, and moisture. The relative properties and distribution of constituents varies with the type of leather [111,112].

The properties that suited for leather footwear are resistance to abrasion, flexing, deforming and stretch, tensile, tear and burst strength, suitability for cementing, vulcanizing, and molding, wearing comfort, permissibility of air and water vapours storage capacity for perspiration, thermal insulation, suppleness, appearance, color fastness, resistance to wet and dry rubbing, easy care etc [113].

Leather is processed either by vegetable tanning or chemical tanning. Leather should be protected against excessive heat, humidity, rain and pests. Raw hides are cured or preserved to prevent decay. Curing consists of dehydration without disturbing skin structure.

Vegetable tanning materials are tannin -- complex mixtures of polyphenols and non-tanning materials are carbohydrates, salts and acids. The tanning material is ground, leached with water concentrated into solid or powdered extract. The delimed skins are pickled or preheated with tannin and tanned in paddles or drums, with a blend of tan extracts for three or six months[114].

At present a wide variety of synthetic tannins are available. They are 1) auxiliary tans, strong simple sulfonic acids 2) combination of tans, sulfonic acid of complex phenolic materials used for light tanning and for white leathers, 3) exchange or replacement tans, weak acids containing a large number of phenolic groups to substitute vegetable tans and to produce white, light fast leathers. These leathers then dyed to get colours, and then lubricated. Dyed leathers are treated with oils and fats for lubrication, softness, strength and water proofing[115]. The leathers then dried to 14% moisture, and then they are subjected to finishing operation. Some leathers are impregnated with synthetic resins to improve their properties. Polyurethanes give best scuff resistance. Leather is further finished by coating the grain surface. Water resistance is obtained by treating leather with silicones and waxes[116].

Leather Adhesives:

Adhesion between two surfaces depends upon the inherent attractions of atoms and molecules when brought close enough together[110]. Even though solid surfaces were smooth enough to achieve molecular contact, layers of gas molecular form a barrier to material contact. Rough surfaces must be wetted to ensure good adhesion. Material must flow to achieve good contact at the interface; the solid surface must be clean of interfering substances[117].

In most adhesive bonds in leather goods, very high strength is not required[118]. The adhesive must be strong enough to resist tearing, but flexible enough to resist fracture. Adhesive generally must be liquid at the time of application. They clearly undergo a change of state, in converting to the solid. The change of state brought about by a loss of solvent or by a cooling and solidification of a melt adhesive usually involves a change in volume[119]. The adhesive shrinkage causes stress in the joint. The adhesive must be compatible with the surface to which it should stick. The attraction of the solid surface molecules for the adhesive must be at least as great as the adhesive molecules for each other.

Bonding process initially involves the roughening of leather[120]. The grain layer has to be removed completely and on the flesh side all loose fibers have to be removed. The grain layer can also be wiped with a solvent[121]. Next is adhesive application, depending upon the type of adhesive used, different methods of adhesive application is possible. The adhesive must apply within one hour after the preparation of the surfaces to be bonded. The adhesives have to dry after applying. There are wet bonding where, these surfaces are brought together in the wet state. Contact bonding is another type. In this case adhesive applied to both surfaces and after a certain length of time the adhesive layer apparently dry then they are put together under slight pressure[122]. Heat activated bonding in which adhesive is heated sufficiently to get tacky.

Similarly wiping with solvents also activates adhesives. The bonds between two components are pressed by rolling or on a press. There will be failure of adhesive joints when insufficient pressure, if too longer intervals between cementing and assembly, high grease content in the leather, excessive penetration of adhesive, in compatible adhesives on leather, too short drying time of the adhesive etc[123].

Rubber to metal bonding:

The technique of rubber- to- metal bonding is utilised by the rubber industry as early as the rubber industry has been using the process of vulcanization [124,125]. Early bonding techniques is ebonite and brass bonding which is still used for industrial applications. Many developments have occurred over the years in this field, one of the most significant of which is the introduction of chemical bonding agent systems [126,129].

The unique utility of rubber-to-metal assemblies began to be appreciated around the turn of the century through applications that helped cushion motion and deaden noise [127]. The rubber-to-metal composites came to be employed in the mechanical world not only to minimise the damaging effects of vibration and protection against shock, but also to seal against shock, leakage of oil and other fluids, and to simplify assembly by providing a tolerance for misalignment [128,129]. The automobile industry is by far the biggest user of bonded elastomer components [130]. Applications such as engine mounts, suspension bushing, transmission and axle seals, couplings and body mounts etc. are some of them[131]. Manufacture involves molding of the elastomer to shape vulcanization and bonding all in a single-stage press operation [132,133]. In aerospace sector advanced R-to-M technology has resulted in such highly specialised devices as low maintenance rotor bearings embodying alternating layers of rubber and metal in special geometric configurations. R-to-M assemblies are for non aeronautical vehicles of war-tanks, submarines and for rail and rapid transit rolling stock, as well as for track beds and rail crossings. Bonded parts are essential for materials handling machinery, shipping containers, construction and agricultural equipment, leisure devices, air systems and business machines of various types[134].

In order to evaluate the performance of rubber-to-metal bonds it is necessary to consider the structure of the surface of the metals[135]. Most of metals form oxide layers on their surfaces, some of which are porous, like iron oxide and this continual oxygen ingress enables the oxide layer to increase continually whilst in aerobic conditions [136,137]. Metals like aluminum form a dense oxide film, which does not permit oxygen ingress, and this protects the metal underneath from further oxidation [138].

The bonding mechanisms of the multiphase systems involved in the formation of a rubber to metal component are complex [125,131]. Bonding incorporates a primer and an adhesive layer, and interactions, which may occur at each interface. In the region of contact with metal, the interactions are a combination of mechanical and chemisorption process [139,125]. The primers used in rubber-to-metal bonding contain a variety of halogenated rubber and resins, which have good ability to wet out metal surfaces, thus ensuring the greatest possible degree of interfacial contact [140-143]. These rubbers and resins act as barriers to the migration of corrosion catalysts. The resins and rubbers form inters penetrating network of polymer chains within the adhesive system, thus giving strength and structure of the primer coat. Between the primer and the adhesive there will be adsorption and interdiffusion at the interface. The other ingredients of the bonding agents may form cross bridging reactions between the two parts of the bonding system together into an integral unit [125]. The ingredients in the bonding coat will carry out two related series of reactions, the first to form crossbridging links with the rubber surface during its own and the crosslinking of rubber. There will be interdiffusion of sulfur and accelerator entities between the rubber and the bonding agent; become highly activated by the elevated temperature. The second process will be the vulcanisation reactions within the bonding adhesive. Chemical reactivity at the polymer bonding agent interface includes chemisorption, crossbridging and mechanical interlocking effects. The bond quality greatly depends to a large extent upon the ability of all interfaces to freely exchange chemical entities. Any contamination will upset the surface chemistry at that point and will reduce the bond strength [144,145].

Production of bonded parts:

Bonding rubber to metals during the vulcanisation of the rubber makes engineering products for a wide range of applications. The bond achieved must be of sufficient integrity; it should be stronger than the rubber constituent of the component[131]. Components consisting of moulded rubber to metal during high temperature vulcanisation can give rise to inherent stresses, simply due to shrinkage of the rubber when removed from the influence of vulcanisation temperature and the coefficient of thermal expansion relationship of the rubber to metal combination [146]. The shrinkage of the rubber in the system will vary according to the type of elastomer being used, and is also dependent upon the compound hardness or degree of filler present. Allowances for the mould runner shrinkage must be made in determining the shape of the mould cavity and hence the component's final shape. Some oil and solvent environments will penetrate a bond at the interface and this may weaken or destroy the integrity of the bond until the stress is relieved by failure [147].

To effect good long lasting bonds between rubber and metals it is essential that both materials presented to the interface be clean and free from dirts and oil. The possibility that compounding ingredients can exude or bloom from the rubber surface, life of the component must also be taken into consideration at the stage of ingredient selection [131].

The characteristic surface energy of a material controls the contact characteristics of a droplet of liquid at rest on it [148]. A liquid droplet in free space assumes a spherical shape. In contact with the surface of a solid material a liquid will assume a droplet shape characteristic of the relationship between the surface material and the droplet material [149]. When two materials are brought into contact, there will be a change in free energy at the interface which is known as the work of adhesion, [150] and tends to increase the wetting of a solid with a net increase of the surface area of the liquid. Cohesive forces have an opposing effect, which will tend to minimize the surface area of the liquid. By combining the work of adhesion and cohesion one arrives at the spreading coefficient. The spreading coefficient can be either negative in nature, indicating poor wetting of the interface, or can be positive, indicating a good surface wetting [150,151]. Organic solvents readily wet out the metal surfaces much more than water does[152].

The choice of rubber and filler are often constrained by end user or customer specification, but other ingredients such as curing systems may often be variable and able to address limitations. Ingredients, which act by causing, surface blooming, such as waxes and antiozonants can be troublesome in bonding applications. Excessive quantities of certain materials such as plasticisers, oils, antidegradants, fatty acids and fatty acids soaps can bloom to the surface of the rubber and in all probability will also bloom to the interface. Plasticisers can exude, owing to incompatibility with the polymer or simply because they are present in too high a concentration. Some plasticisers can migrate over long periods of time through the bonding agent layers, and cause corrosion or complete bond failure many years after the bond was originally effected.

Curative systems has a very strong influence on the nature of a bond, and often the system required by the compound to meet the specification may result in an adequate ability to bond, for example efficient vulcanisation systems which have low sulfur contents[153].

Metal preparation:

Metals must be suitably pre-treated for satisfactory bonds to be achieved with rubbers. The significance of the pre-treatment of the metallic surfaces is often underestimated, but it is an important factor in determining quality. Pre-treatment means bringing surfaces to a suitable state for further operational processes without material being removed from the component. The material being subjected to selective attack,without the formation of internal stresses and micro cracking increasing [154].

There are various types of impurities, which vary greatly in their behavior and consequently cannot be removed by a single universal procedure[155]. The most effective and economically viable pre-treatment method has to be selected individually for each case. The selection of the correct cleaning method should ensure that the surface quality is suitable for the production process. The cleaning must be inexpensive, safe to use and environmental friendly. According to Sinner's circle, cleaning is influenced by four parameters [156] (a) Mechanics, (b) chemistry (c) temperature (d) duration of the treatment. The cleaning effect of bath cleaning may be increased by moving the bath liquid or the item being treated to a greater or lesser degree. High-pressure injection and ultrasound cleaning intensify mechanical attack of the cleaning media. The choice, composition and concentration of the cleaning chemicals have a decisive effect on the effectiveness of cleaning with liquids[157]. Cleaning take place in three stages (1) wetting of impurities (2) detaching from the substrate surface (3) dispersion of impurities. Cleaning requires sufficient time to allow their processes to take place. According to Arrhenius theory, the rate of reaction increases as the temperature rises, in addition the viscosity of the cleaning solution, greases and oil to be removed is reduced, which produces better wetting and finally results in the removal of the impurities and reaction products[158]. But due to the energy costs and the problems with vapor formation low temperature cleaning are preferentially selected. Cleaning effect is achieved by the interaction of all factors [159].

Metal preparation areas, and holding areas for treated metals prior to moulding shop use, must be atmospherically isolated or be protected by a positive air pressure system from any moulding area. The bonding agents must be stirred frequently. Application of primers and bonding agent can be carried out by hand brushing, spraying or dipping. In general conventional moulding methods can be used for the production of rubber to metal components.

Metal reinforced rubber products:

Two major types of materials are used as integral reinforcements for composite rubber structures are textiles, metal fabrics and cords, steel in rod or wire form has been used for many years as reinforcement in composite of various types for a number of industrial products. From 1940s steel or other metal wires replaced the reinforcement by textile. The development of the radial tyre, with its higher running speeds and temperature, led to the progression from textile reinforcements for tyres through nylon, glass and aramid to steel cords[160].

Rubber will not bond directly to the surface of steel, requiring chemical treatment of steel surface or chemical modification of the rubber compound to induce adhesion. Steel filaments are drawn from thicker gauge wire being passed through a die or series of dies, with heat treatments to give progressive gauge reduction. Before the final gauge reduction, the wire is coated with brass or zinc [161]. Wake points out that preferred composition of brass applied, as die lubricants/ rubber adhesion layer, in tyre cord production is 60/40 (copper/zinc). The brass thus deposited into the steel has a crystal form which is much distorted by the drawing process, which enhances the activity of the copper atoms towards that found in an electrolytically deposited 70/30 brass in an undrawn form.

The current accepted brass-coating thickness appears to fall in the range of 5-8 $\times 10^{-6}$ mm for good adhesion. These type of steel fabric construction can be used in a wide range of applications, including belting and hoses. The brass coating prevent corrosion through water ingress and to facilitate bonding [162-164].

In common with other types of rubber to metal bonding the choice of rubber compounding ingredients plays a considerable role in the achievement of good adhesion between tyre compounds and cords. Ultra accelerators and low sulphur vulcanising systems cannot be used. Sulphur levels of at least 3 phr must be used and the preferred accelerator system. Delayed action accelerator system is required [165].

Objectives and scope of the present work

The primary objective of the present study has been to develop novel, low cost adhesives for bonding wood to wood, leather to leather and rubber to metal substrates due their significance. In the rubber to metal bonding field, at present imported varieties such as polylock, chemlock and desmodour predominate, while latex based or solution based adhesives dominate in the wood to wood and polyurethane based adhesives in the leather to leather bonding field. It is proposed to develop novel latex based and solution based adhesives for these substrates. Due to the industrial importance of rubber to metal bonded systems, it is proposed to try novel methods such as rubber strip adhesion in them. This will be more environment friendly than the solution based adhesives available commercially. Adhesive strips based on polymer blends are also proposed to be developed in order to make them more efficient and cost effective. The conventionally used adhesive systems for wood to wood bonding lack water resistance. Hence adhesive systems with improved water resistance are proposed to be developed for wood to wood bonding. Also, in the case of leather to leather substrates, the conventionally used polyurethane based adhesives lack the necessary strength for critical applications in addition to being expensive. Hence novel adhesives which can contribute to higher strength for these substrates are proposed to be developed. The objectives of the proposed study may be summerised as follows,

1. To develop novel and water resistant systems for wood to wood bonding
2. To develop more efficient and low cost adhesives for leather to leather bonding.
3. To develop a novel strip adhesive system for rubber to metal bonding. It is also proposed to develop novel adhesive systems for steel tire cord/ rubber adhesion and bead wire/rubber adhesion replacing the conventional methods.

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Chapter 2

EXPERIMENTAL

Chapter 2

Experimental Techniques

Materials

Elastomers:

1. Natural Rubber(NR): ISNR-5 was supplied by the Rubber Research Institute of India, Kottayam . The Indian standard specifications for this grade of rubber are given below:

Mooney Viscosity, ML(1+4) at 100°C	82.00
Dirt content (% mass)	0 .05 (Max)
Volatile matter (% mass)	1.0 (Max)
Nitrogen (% mass)	0.7 (Max)
Ash (% mass)	0.6 (Max)
Initial Plasticity Po	30.0(Min)
Plasticity retention index PRI	60.0(Min)

2. Acrylonitrile butadiene rubber (NBR): Acrylonitrile - butadiene rubber was obtained from Apar Polymers Ltd, India.

Grade	N 553
Acrylonitrile content	33%
Mooney viscosity ML(1+4), at 100°C	45

3. Styrene Butadiene Rubber (SBR): Styrene butadiene rubber (SBR, 1502) was obtained from Japan Synthetic Rubber Ltd. Tokyo.

Mooney viscosity, ML(1+4), at 100°C	45

4. Chloroprene Rubber (CR): AD (adhesive grade) type supplied by E.I. Dupont, Akron, Ohio.

Mooney viscosity, ML(1+4), at 100°C	45

5. Chloroprene Rubber(CR): W Type supplied by E.I Dupont Akron Ohio.

Mooney viscosity, ML(1+4), at 100°C	45

6. High Styrene Rubber (HSR): Synaprene 1958 supplied by Synthetics an Chemicals Ltd., Bareily U.P.

Styrene content	50%

7. Carboxylated nitrile rubber (XNBR): KRYNAC-X-7.50, 7% mole carboxyl group.

Plastics

1. Polyvinyl Chloride(PVC): Suspension PVC K Value 65 supplied by Reliance Industries, Gujarat, India.
2. Ethylene vinyl acetate (EVA): Ethylene vinyl acetate co polymer used in this study had a vinyl acetate content of 30% and melt flow index of [MFI (190/5)] 200. It was supplied by NOCIL, Bombay, India.

Latices

1. Natural Rubber Latex: Natural Rubber Latex (centrifuged) was obtained from Rubber Research Institute of India, Kottayam and had following specifications:

Hydrocarbon content	60% (Min)
Total solid content	61.5%(Min)
Coagulam content	0.05%(Max)
Sludge content	0.01%(Max)
Alkalinity	1.6% (Min)
KOH No.`	1(Max)
Mechanical stability time, sec.	475 (Min)
Volatile fatty acid number	0.15

2. Styrene Butadiene vinyl pyridine terpolymer latex (VP Latex): was supplied by Asian Paints, Bombay, India and had the following specification.

Butadiene	70%
Styrene	15%
Vinyl pyridine	15%
Total solid content	40%(Min)

3. Carboxylated NBR Latex: (XNBR Latex): Carboxylated acylonitrile butadiene latex was supplied by Apar Polymers Ltd, Bombay India and had the following specifications

Carboxyl group.7mole%

Total solid content	40% Min

Additives

1. Zinc Oxide (ZnO): Zinc Oxide was supplied by M/s, Meta Zinc Ltd., Bombay. It had the following specifications:

Specific gravity	5.5
Zinc Oxide content	98%
Acidity	0.4%(Max)
Heat loss (2h at 100°C)	0.5%(Max)

2. Stearic Acid: Stearic Acid was supplied by Godrej Soap (Pvt) Ltd, Bombay, 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)

3. N-Cydo hexyl-2-benzthiazyl sulphenamide (CBS):The sample had the following specifications:

Ash	0.5%(Max)
Moisture	0.5%(Max)
Specific gravity	1.27

4. Sulphur: Sulphur was supplied by Standard chemical company private Ltd, Madras and had the following specifications:

Specific gravity	2.05
Acidity	0.01%(Max)
Ash	0.10%(Max)
Solubility in CS_2	98%(Max)

5. Magnesium oxide (MgO): The sample used in the study was commercial grade with a specific gravity of 3.6.

6. Benzthiazyl2sulphenmorpholide(MOR): Benzthiazyl 2 sulphenmorpholide was supplied by ICI India Ltd West Bengal and had a

specific gravity of	1.34.

7. Ethylene thiourea: Ethylene thiourea (Na-22) was commercial grade supplied by ICI India Ltd, West Bengal.

8. Dicumyl Peroxide (DCP): DCP used was crystal with 99% purity, and density 1.02gm/cm3. The recommended processing temperature of the material is 160-200°C.

9. Mercaptobenzthiazole(MBT): Mercaptobenzthiazole having the following specifications was supplied by Bayer India Ltd Bombay.

Specific gravity	1.45-1.52
Melting point	160-180 °C

10. Dibenzthiazyl disulphide(MBTS): Dibenzthiazyl disulphide having the following specification was supplied by Bayer India Ltd Bombay.

Specific gravity	1.34
Melting point	165 °C

11. Tetra methyl thiuram disulphide (TMTD): Tetramethyl thiuram disulphide was supplied by NOCIL. Bombay, India. It had the following specification:

Specific gravity	1.4
Melting point	136°C

12. Tetra methyl thiuram mono sulphide (TMTM): The sample was supplied by Flexsys, Netherlands.

13. Zinc diethyl dithio carbamate(ZDC): The sample used was supplied NOCIL Bombay, India. It had the following specification :

Specific gravity	1.5
Melting point	178°C

14. Aromatic oil: Was supplied by Hindustan Petroleum Corporation.It had the following specification :

Specific gravity	0.95-0.98
Aniline point	38°C
Viscosity gravity constant	0.907

15. Dioctyl phthalate (DOP): Dioctyl phthalate was commercial grade, with the following specifications:

Specific gravity	0.986
Viscosity	60cps

16. Vulcanox HS : Commercial grade antioxidant Vulcanox HS (polymerised 1,2 - dihydro 2, 2, 4 - Trimethyl- Quinoline,) was obtained from Bayer India, Ltd.Bombay and had a Specific gravity of 1.1

17. Pilflex 13: Commercial grade antioxidant Pilflex 13 (n-(1,3-Dimethyl butyl)-N'-Phenyl-p-phenylene-diamine) was obtained from NOCIL India,and had a Specific gravity in the range of 0.986- 1.0

18. Phenol: Phenol was supplied by S. D. Fine Chemicals, Bombay India, and had the following specifications:

Specific gravity	1.071
Melting point	41° C

19. Dispersol VL: This is a nonionic stabilizer for latex compounds and was supplied by ICI India Ltd West Bengal,having a specific gravity 1.0 at 25°C

20. Diphenyl guanidine(DPG): Di phenyl guanidine was supplied by Flexsys , Netherlands and was a white powder soluble in Chloroform. It had the following specifications:

Specific gravity	1.15
Melting point	145°C

21. Accinox TQ: Polymerised 1,2 dihydro2,2,4-Trimethyl Quinoline and was supplied by ICI India Ltd West Bengal. It had the following specifications:

Specific gravity	1.08
Melting point	78-90° C

22. Hexa methylene tetra amine (Hexa): The sample used was commercial grade.

23. PF resin : Phenol formaldehyde resin supplied by Bakelite Hylam. Hyderabad The used grade was 6417(adhesive grade),having the following specifcations:

Specific gravity	1.085- 1.105
Softening point	88-102° C
Methylol group	14-16%

24. Coumarone Indene resin(CI resin): The sample used was commercial grade with a melting point in the range of 65-110°C .

25. Wood Rosin: Rosin of 90 % abietic acid,and not soluble in water was used. It is a solvent extract from aged pine trees having the following specifications:

Acid No.	163
Softening Point	73 °C
Saponification No.	168
Refractive Index	1.545 at 20 °C
Specific Gravity	1.067

26.4 -4' Diphenyl methane Diisocyanate (MDI): MDI of purity 98% and 4-4' isomer greater than 96% was supplied by Manali Petrochemicals, Bombay, India.

Fillers used:

1. Carbon black HAF N330: High abrasion furnace black was supplied by Phillips carbon Ltd. Kochi .It had the following specifications:

Iodine adsorption number	80mg/g
DBP absorption	105cm^3/100g
Mean particle diameter	32nm

2. Carbon black GPF N660: General purpose furnace black was supplied by Phillips carbon Ltd. Kochi .It had the following specifications:

Iodine adsorption number	36 mg/g
DBP absorption	91cm^3/100gm
Mean particle diameter	50nm

3.Precipitated silica: Precipitated silica VN3 Gran Ultrasil was supplied by Insilico. Spray dried precipitated silica had the following specifications:

Specific gravity	1.98
Heat loss	4.7%(2hrs at 100°C)
Ignition loss	3.6% (2hrs at100°C)
N_2 surface area	155-195mm^2/gm
pH	5.6-6.8
Residue 45m sieve	3%
SiO_2	93%

4. China Clay: was commercial grade supplied by English Indian Clays, Veli, Trivandrum, having a specific gravity of 2.6.

Solvents: Toluene, Cyclohexanone, Ethylene dichloride(EDC), Tetra hydrofuran(THF), Xylene, Benzene, Methyl ethyl ketone(MEK), Carbon tetra chloride(CCl_4), Naphtha etc. were commercial grade.

Other Chemicals: Hydrochloric acid, Silver Nitrate, Potassium Carbonate, Sodium Carbonate, Sodium Peroxide, Potassium permanganate Sodium Silicate, Starch, Carboxy Methyl Cellulose, Casein, Potassium Hydroxide, Resorcinol, Formaldehyde, Sodium hypochlorite, Nitric acid, Ferric alum, Thymole blue indicator etc. were laboratory grade.

Adherends:

1. Wood : A kind of soft wood (Acacia) of carpentry grade.
2. Upper leather and sole leather Supplied by Central Leather Research Institute, Chennai.
3. PVC sheets : Opaque PVC sheets of commercial grade.
4. G. I. Sheets : Galvanized mild steel sheets of 1.6 mm thick used were of engineering grade.
5. Aluminium sheets: Anodized aluminium sheets of 1.6mm thick used were of engineering grade.

6. Stainless steel sheets: Steel sheets used were engineering grade from Salem steel.

7 Bead wire: Copper coated steel bead wire used for tyre manufacturing was supplied by Tata Steel ,Bombay having a thickness of 0.98 mm.

8. Steel cord: Brass coated steel cord used for steel radial tyre manufacturing was supplied by Societa' Pneumatici Pirelli, U.S.A. Business unit steel cord for passenger tire with the following specifications:

Construction	2+2x0.25
Plating wt (Brass)	3.4g/kg
Copper in brass plate	63.5%
Zinc	36.5%
Breaking load	49Kgf(min)

Experimental Techniques:

1. Preparation of Chlorinated Natural Rubber (CNR): Natural rubber (NR) was masticated for 30min. in a laboratory two roll mill. Masticated NR was then dissolved in carbon tetra chloride to get a 5% solution, which was then reacted with chlorine gas produced in laboratory for 4-5 hours continuously. A uniform stirring was given to this solution while reaction proceeded. When reaction was complete a thick layer was separated over the solution, with a light yellow clear bottom solution. This was then poured into hot water at 90° C for separating the remaining CCl_4. The white colored mass was then taken out from water dried at 70°C for 2-3 hours and powdered.This was again washed to remove traces of HCl and then dried in an air oven for 24hrs at 70 °C.

The chlorinated natural rubber was characterized by the following methods.

a) Determination of chlorine content: Chlorine content was determined by volumetric analysis. About 0.1 gm of the sample was fused with a mixture of sodium carbonate and potassium carbonate and sodium peroxide in the ratio (1:1: 0.5) in a platinum crucible at 850°C for 4 hrs. The fused mass was extracted with water and neutralized with concentrated nitric acid and to the neutralized solution a known volume of silver nitrate was added. The precipitate was filtered and treated against sodium thiocyanate solution using ferric alum indicator and chlorine content was calculated as

$$\%\text{Chlorine content} = \frac{(\text{Blank- Sample volume}) \times 35.5 \times N \times 100}{w \times 1000}$$

N- Normality of thiocyanate solution

w- Weight of sample.

b) Fourier Transform Infrared Spectroscopic (FTIR) analysis: In order to determine the various chemical groups present in the product FTIR spectrum of the chlorinated natural rubber (CNR) was taken using Shimadzu FTIR spectrometer model D8001. A commercial sample of CNR was also studied by this method.

c) Thermo gravimetric analysis (TGA): The thermal stability of chlorinated natural rubber was studied on a Shimadzu (TGA 50) thermogravimetric analyzer. TGA for commercial CNR was also done.

2. *Optical microscopic analysis:*

Carl Zeiss optical microscope model Stemi 2000-C with 100 x magnification was used to take the optical photographs of the adherends wood, mild steel, upper leather, sole leather, rubber sole, microcellular sole, bead wire and steel cord. The roughened surfaces and the peeled off surfaces of these adherends were examined and compared with those of commercial adhesives.

3. *Preparation of Phenol formaldehyde (PF) resin:*

Phenol and formaldehyde were taken in the ratio (1:1.5)in a flask fitted with water condenser. The mixture was distilled for 1 hour in alkaline medium . The resin was dried under vacuum kept in a desciccator.

4. *Preparation of resorcinol formaldehyde (RF) resin:*

Resorcinol and formaldehyde were taken in1:1 mole ratio and reacted in flask fitted with water condenser and a magnetic stirrer. The reaction was carried out by adding formaldehyde drop wise for about 2 hours. Temperature was kept at 90°C and care was taken to keep the solution temperature below boiling point. The reaction was stopped by the addition of oxalic acid or sodium hydroxide. The resin was then dried in vacuum oven at 70 °C and kept in a desciccator.

5. *Preparation of blocked MDI:*

A solution of MDI (25%) was prepared in ethylene dichloride (EDC) and to this phenol was added in 1:1 ratio and stirred.

6. *Preparation of ammonium caseinate:*

Casein was taken in water with 10% solid content and ammonia solution was added and heated till casein got dissolved to obtain a uniform solution of ammonium caseinate.

Mechanical properties

1.Mixing and homogenization:

Mixing and homogenization of elastomers and compounding ingredients were done on a laboratory size (15x33cm) two roll mill at a friction ratio 1:1.25. The elastomer was given one pass through a close nip. Then it was given 2 passes through a wider nip. The temperature of the rolls was maintained at 70±5 °C during mastication. After the disappearance of nerve,the compounding ingredients were added as per ASTM D 3184(80)and ASTM D3182(82) in the order activators, fillers, accelerator and curing agents. Before the addition of accelerator and sulphur the batch was thoroughly cooled.

After completion of the mixing, the compound was homogenized by passing six times endwise through a tight nip and finally sheeted out at a nip gap of 3mm.

2. Determination of cure characteristics.

The cure characteristics of the elastomers were determined using a Goettfert elastograph model 67.85. It is a microprocessor controlled rotorless cure meter with a quick temperature control mechanism and well defined homogeneous temperature distribution in the die or test chamber. A specimen of definite size was kept in the lower half of the cavity which was oscillated through a small deformation angle (±2°). The frequency was 50 oscillations per minute. The torque was measured on the lower half of oscillating die and a torque Vs time curve was obtained from the instrument. From this torque , scorch time t_{10}, and cure time t_{90} were determined. The elastograph microprocessor evaluates the vulcanisation curve and print out these data after each measurement.

Moulding of test specimens:

The test specimens were prepared in standard mould by compression moulding on single day light , electrically heated press having 75x75 cm plates at a pressure of 200 Kgf/ cm^2 on the mould. The rubber compounds were vulcanised up to their respective optimum cure times at 150°C unless otherwise specified. Mouldings were quenched in water at the end of the curing cycle and conditioned 24hrs for subsequent testing.

a)Tensile properties:

Tensile properties of the vulcanisates were determined according to ASTM D 412 (80) using dumbell specimens on a Zwick universal testing machine model 1445. All the tests were carried out at ambient temperature . Specimens were punched out from the compression moulded sheets using a dumbell die. The thickness of the narrow portion was measured by a dial thickness gauge. The specimen was held tight between the two gripsof the machie , the upper grip of which was fixed. The rate of separation of the power actuated lower grip was fixed at 500mm/min for elastomeric specimens. The tensile strength , elongation at break and modulus were printed out after each measurement by the microprocessor of the machine.

b) Tear strength:

This test was carried out as per ASTM D 624 (81) using unnicked 90° angular test pieces. The samples were cut from the compression moulded sheets parallel to the mill grain direction. The test was carried out on a Zwick universal testing machine at a speed of 500mm/min at ambient temperature.

c) Hardness:

The hardness (Shore A) of the moulded specimens were tested using Zwick 3115 hardness tester in accordance with ASTM D 2240 (81). The tests were performed on a mechanically unstressed specimens of 300 mm diameter and minimum 6mm thickness. A load of 12.5 N was applied and the readings were taken after 10 seconds of indentation after firm contact has been established with the specimens.

d) Brookfield viscosity:

The viscosity of adhesives (solution type) were determined on a RVT spindle type viscometer using the spindle number 5. The spindle was allowed to rotate for one minute and corresponding reading on the dial was noted. The viscosity was then expressed in centipoise by multiplying with the correction factor on the chart provided.

e) Total solid content :

The total solid content of latex based adhesives were estimated as per IS standards. A specific amount of the latex taken in previously weighed petri-dish was dried in an air oven at 100 °C for 2 hours till disappearance of white patches. The sample was cooled and weighed. The difference in weight divided by the original weight of the sample gives the total solid content which is expressed as percentage .

Chapter 3

WOOD TO WOOD BONDING

Chapter 3

Part 1 Studies on wood -to wood bonding adhesives based on natural rubber latex.

Adhesives are used in construction application for bonding wood pieces[1]. The mechanism of wood adhesion is related to the complex physical structure and chemistry of the substrates. Wood is largely composed of cellulose and lignin and to a lesser degree of extractables which differ greatly in their reaction to adhesives[2]. Some wood adhesives promote strong forces of covalent bonding, while in the case of others, weaker adhesion forces such as van der waals forces and hydrogen bonding operate and /or mechanical inter locking may occur [3,4].

Generally, latex based adhesive offer a great advantage over other adhesive systems for joining porous substrates. The water phase of these adhesives tend to penetrate into the material and hence results in faster drying of the adhesives[5].

Natural rubber latex and synthetic latices once produced as water -dispersed adhesives cannot be redispersed in water after they have been dried out. A forced drying occurs while drying latex adhesives [6,7]. The most consistent theory for the film formation of water dispersed adhesives is the one proposed by Vanderhoff et al [8].

Water based adhesives are more advantageous than solvent based adhesives because organic solvent emitted into air are pollutants and are toxic in nature, and may cause explosion hazard. Furthermore, solvent recovery and recycling require more expensive equipment, compared to water [9].

In this part of the work we propose to prepare NR latex based adhesives and to study their efficiency as a bonding agent for wood to wood bonding. Different formulations based on NR latex are proposed to be used for wood bonding. The effect of degree of prevulcanisation on bond strength is also proposed to be studied. The effect of the amount of carboxymethyl cellulose, ammonium caseinate, phenol formaldehyde resin(PF), cooked starch, etc. on bond strength also will be investigated. The changes in bond strength with aging of the adhesive are also proposed to be studied.

Experimental

Fevicol was supplied by Pidilite Industries, Bombay, India. Wood used was a kind of soft wood of carpentry grade.

The centrifuged latex was deammoniated to 0.2% ammonia content. All water insoluble ingredients were added as dispersions in water. The compounding ingredients were added as per two formulations, L1 and L2 (Table 1), with formulation L1 used as base formulation.

Wood pieces were cut into 25x300x3 mm strips. These wood pieces were dried and polished using sand paper No. 60 (250μm), and then the adhesives were applied to a thickness of 0.2 mm on the two wood pieces and bonded as a lap joint, applying a load of about 1kg for 24 h. The lap joints were conditioned for 7 days at room temperature. The tension shear strength (N/cm^2) of the bonded joints was tested on a Zwick UTM model 1445 at ambient temperature according to ASTM D 903-49 (72).

Table 3.1.1 Formulation

Ingredients, Phr	**L1**	**L2**
NR latex (60% DRC)	100	100
KOH(10%)	0.1	0.1
Dispersol VL	0.5	0.5
CMC	0.0	3.0
Ammonium caseinate	3.0	0.0
Sodium silicate	5.0	5.0
Starch	3.0	3.0
Sulphur(50%)	1.5	1.5
ZDC(50%)	1.0	1.0

Latex compound L2 was subjected to prevulcanisation for different times varying from 12 to 45 min at a constant temperature(70 °C). The prevulcanised compounds were then used for bonding wood pieces and the lap shear strength was determined as described earlier. The optimum prevulcanisation time for different compounds were determined. The extent of prevulcanisation was determined by chloroform coagulation test. Latex was stirred with a fixed proportion (equal volumes) of chloroform and degree of vulcanisation was judged from the appearance of the coagulum formed. When the degree of crosslinking increases , the rubber particles coalesce together less rapidly to form a coherent coagulum. As the degree of vulcanisation increases the coagulum changes from soft to a crumbly material [11]. Here the coagulum is a weak lump which breaks easily when stretched.

The effect of varying the amount of thickening agent, carboxy methyl cellulose, from 1 to 5 phr in formulation L2 (Table 1) on the bond strength was studied. The latex compounds were prevulcanised for 30 min at 70°C prior to joint strength determination.

The lap shear strength of bonded specimens with amounts of ammonium caseinate varying from 1 to 5 phr was also determined as above. These latex compounds were also prevulcanised for 30 min at 70 °C.

Similarly, the variation of PF resin from 10 to 60 phr and cooked starch from 2 to 5 phr in formulation L1 (Table 1) was studied. The bond strength of lap joints using prevulcanised latex compounds was also measured as described above.

The water resistance of the bonded samples was determined by accelerated aging methods involving sample exposure to cold water(30°C), and hot water (100°C). Some bonded pieces were placed in cold water for 1 day at room temperature and then dried prior to lap shear testing. Similarly , some bonded pieces were placed in hot water for 1 hr and lap shear strength was determined. The water resistance test was conducted according to ASTM D 1151 (72) procedure.

Latex compound L1 was aged for 30 and 45 days at room temperature and subsequently used to make lap joints of wood, and lap joint shear strength was determined.

Results and Discussion

The lap shear strength is found to increase with the prevulcanisation time, attain a maximum value and then decrease (Figure3.1.1). This shows that prevulcanisation time increases, good bonding develops, but as the extend of prevulcanisation increases the inter particle bonding decreases [11], resulting in a reduction in the lap shear strength. This trend shows that there is an optimum level of prevulcanisation time which results in maximum bond strength. Conventional sulphur vulcanisation occurs in each rubber particle.

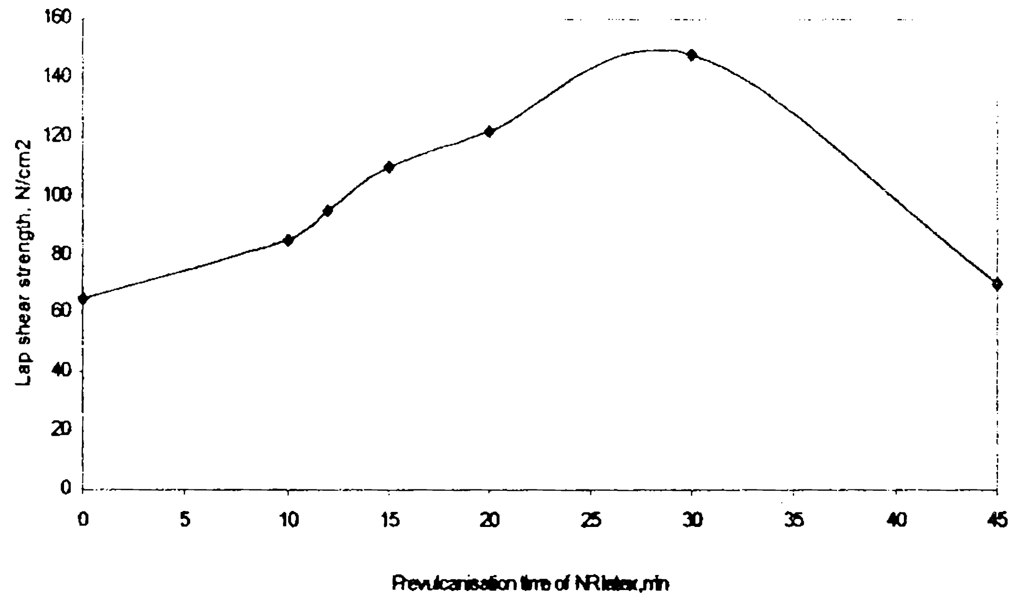

Fig.3.1.1 The effect of prevulcanisation time on lap shear strength

The lap joint strength increases as the carboxy methyl cellulose (CMC) content increases to 2 -3 phr and then decreases (Figure 3.3.2). This shows that CMC can be used to get excellent wet adhesion strength. It can be used as core binder. This trend may be due to the increase in the viscosity of the latex compound as the CMC acts as a thickening agent. This further shows result shows that there is an optimum viscosity for a latex based adhesive for obtaining maximum bond strength The bond strength of prevulcanised latex compounds show a trend similar to that for unvulcanised latex compounds(series1), with prevulcanised being (series2) slightly better in strength.

As the amount of ammonium caseinate increases , the lap joint strength increases (Figure 3.3.3). This shows that ammonium caseinate can act as a tackifier in NR latex based adhesives. Ammonium caseinate also acts as thickener for NR latex, which increases the viscosity thus preventing streaming when applied to vertical surfaces [11]. The bond strengths of prevulcanised

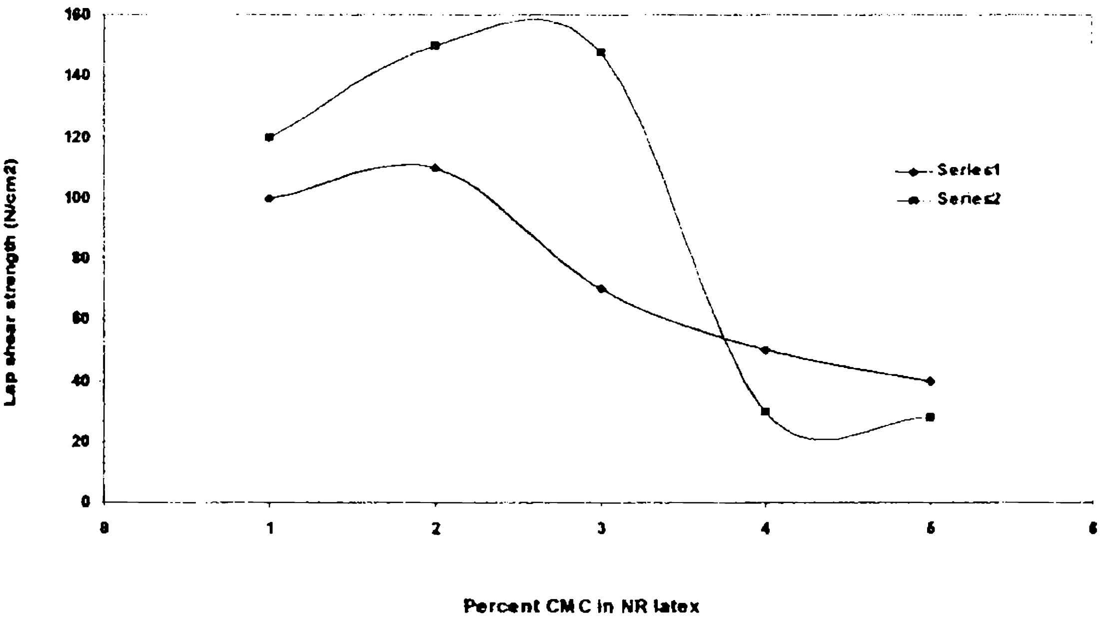

Fig.3.1.2 Variation of lap shear strength with amount of CMC

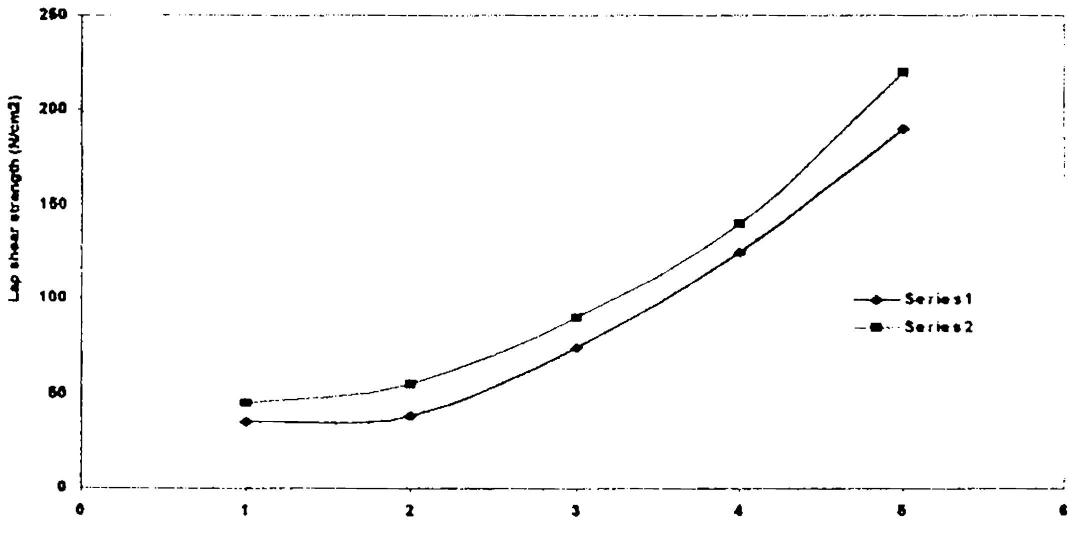

Fig.3.1.3 Variation of lap shear strength with ammonium caseinate content

latex(series2) and unvulcanised latex (series 1) show the same pattern of joint strength. The slight reduction in bond strength in the case of prevulcanised latex may be due to over cooking of the ammonium caseinate while prevulcanising the latex. Ammonium caseinate enhances the durability of wood joints because of its higher molecular weight. The ammonia present will escape easily, resulting in insoluble casein [6]. The active amino acid group is-CONH, which has higher molecular weight and superior water resistance.

Phenol formaldehyde (PF) resin modifies the viscoelastic properties of the rubber components so that immediate wetting and bonding occur. The lap joint strength increases as the amount of PF resin increases up to 50 phr, after which the bond strength decreased with increasing amount of PF resin (Figure 3.1.4). This result may be due to the phase change, i.e. the PF resin phase becoming the continuous phase [9], resulting in higher modulus, due to poor wetting. Series1 unvulcanised and series 2 prevulcanised in figure.The bond strength of the prevulcanised latex shows a pattern similar to that of unvulcanised latex compounds but displays only a lower joint strength.

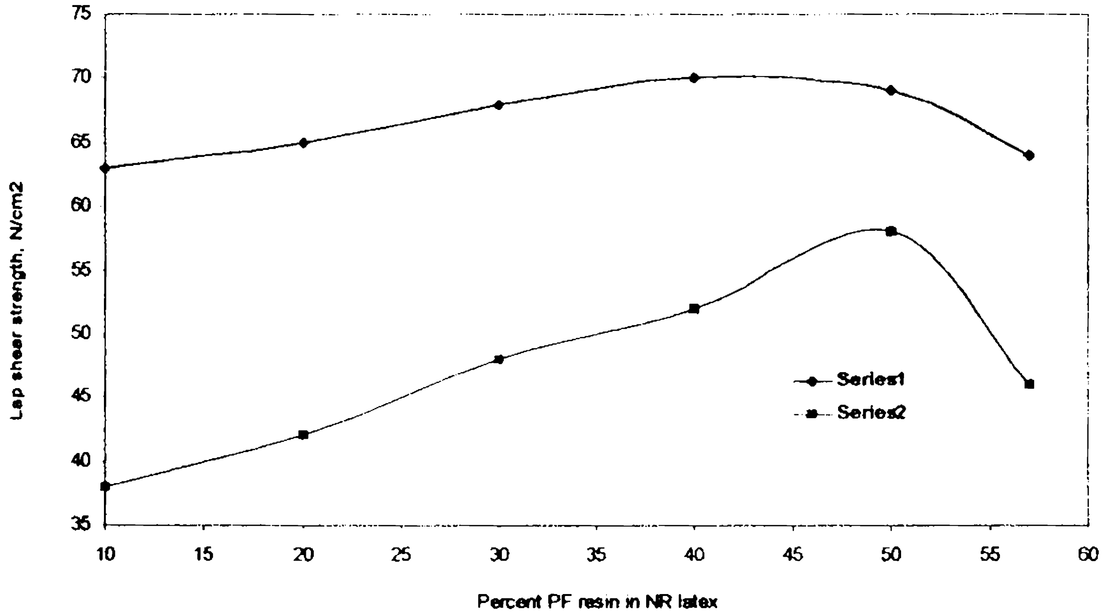

Fig.3.1.4 Variation of lap shear strength with amount of PF resin.

In the dispersed form, starch has a higher degree of spreadability and filmness and is capable of wetting polar surfaces such as cellulose, penetrating crevices and pores, and forming strong adhesive joints.

It is the result of both mechanical interlocking and the interaction of secondary bond forces (van der Waal's and hydrogen bonding)[12]. The variation of lap shear strength of prevulcanised(series 2) and unvulcanised (series 1) latex compounds with the amount of starch is shown in figure 3.1.5. This result shows that starch can increase the bond strength of latex- based adhesives, and there is an optimum amount of starch which can give the maximum bond strength .

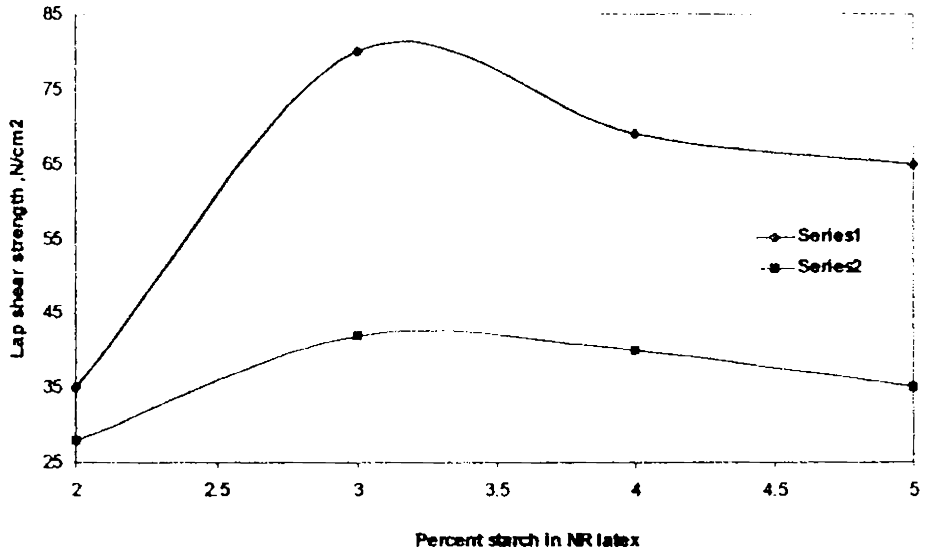

Fig.3.1.5 Variation of lap shear strength with starch content

Table 3.1.2 shows the water resistance of the bonded samples using a commercial adhesive (Fevicol) and NR latex- based adhesive (L1). The NR latex based adhesive shows higher retention in bond strength, both in cold and in hot water. In hot water, the unvulcanised latex- based adhesive shows better results. This may be due to the crosslinking efficiency of the latex film in between the wood pieces in hot water.

Table 3.1.2 Percent retention of dry strength vs accelerated ageing shear strength.

Property	Commercial	Unvulcanised(L1)	Vulcanised(L1)
Lap shear strength(dry), N/cm^2	181.5	90.9	66.7
Shear strength after 1 day in cold water, N/cm^2	45.8	44.7	41.0
% Retention	25	49	62
Shear strength after 1 h in hot water, N/cm^2	0	33.7	23.5
% Retention	0	37	35

The effect of room temperature aging on bond strength is shown in Table 3.1.3. The slight reduction in bond strength observed may be due to the natural destabilization of the latex during storage.

Table 3.1.3 Lap joint strength using the room temperature- aged NR latex

NR latex type	Fresh	After 30 days	After 45 days
Unvulcanised (L1) lap shear strength (N/cm^2)	90.9	68.4	58.8
Vulcanised (L1) lap shear strength(N/cm^2)	66.7	38.4	30.5

Conclusions

1. A natural rubber latex compound can be used as an adhesive for wood - to - wood bonding.
2. The bond strength of NR latex adhesives can be improved by prevulcanising the latex compound to an optimum level.
3. Modification of NR latex compounds using ammonium caseinate and carboxy methyl cellulose improves the lap shear strength.
4. The addition of PF resin enhances the bond strength.

5. The NR latex adhesives show higher resistance both in cold and in hot water, compared with a conventional latex based adhesive, Fevicol.

This part of the work published in *J. Adhesion Sci. Technol*, vol. 11, No.2, pp225-232 (1997).

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Part 2 Use of styrene butadiene vinyl pyridine copolymer latex based adhesives for bonding wood.

Experimental:

Wood pieces were bonded using VP latex compound as per the procedure described in part 1. The formulations for VP latex compound is given below in Table 3.2.1.

Table 3.2.1 Formulations of VP latex compounds, Phr

INGREDIENTS	V	V1	V2	V3	V4	V5
VP LATEX	100	100	100	100	100	100
AMMONIUM CASEINATE	0	30	0	0	0	0
STARCH	0	0	30	0	0	0
CMC	0	0	0	30	0	0
RF1	0	0	0	0	10	0
RF2	0	0	0	0	0	10
SULPHUR	1.5	1.5	1.5	1.5	1.5	1.5
ZDC	1.0	1.0	1.0	1.0	1.0	1.0

The latex compound was prevulcanised for different times ranging from 10 to 40 min. at a constant temperature (70°C). The prevulcanised latex compounds were used for bonding wood pieces and strengths were determined as in part 1of this chapter.

The effect of varying the amount of thickening agent ammonium caseinate and carboxy methyl cellulose and modifiers like cooked starch , RF1(slightly alkaline) and RF 2(slightly acidic) resins in the VP latex compound on joint strength was determined. These latex compounds were prevulcanised for 30 min. at 70° C and joint strengths were studied as in the case of NR latex in part 1.

A mixed system with different combinations of ammonium caseinate and cooked starch were prepared and added to the latex and lap shear strength was determined. The effect pH change on lap shear strength was also studied. The pH value was changed by the addition of dilute ammonia solution. The compounded VP latices were kept for one month and lap shear strength was determined after equal intervals of time.

The wood joints with the VP latex adhesives were kept immersed in cold water (30°C) for 24 hours, in hot water (100°C) for 2 hours, in acid (80°C) for 2 hours and in alkali (80°C) for 2 hours and joint strength was determined after taking out the specimens and drying as per ASTM 1151 (72). Same tests were conducted using commercial adhesive also.

Optical photographs of the wood surfaces before adhesive application and after peeling were taken.

Results and Discussion

Figure3.2. 1 shows the effect of lap shear strength of wood joints bonded with VP latex compound V1 (Table 3.2.1) with varying time of prevulcanisation. Lap shear strength increases, reaches a maximum value and then decreases as prevulcanisation time increases which may be due to lower film strength of the latex after attaining a required prevulcanisation[9].

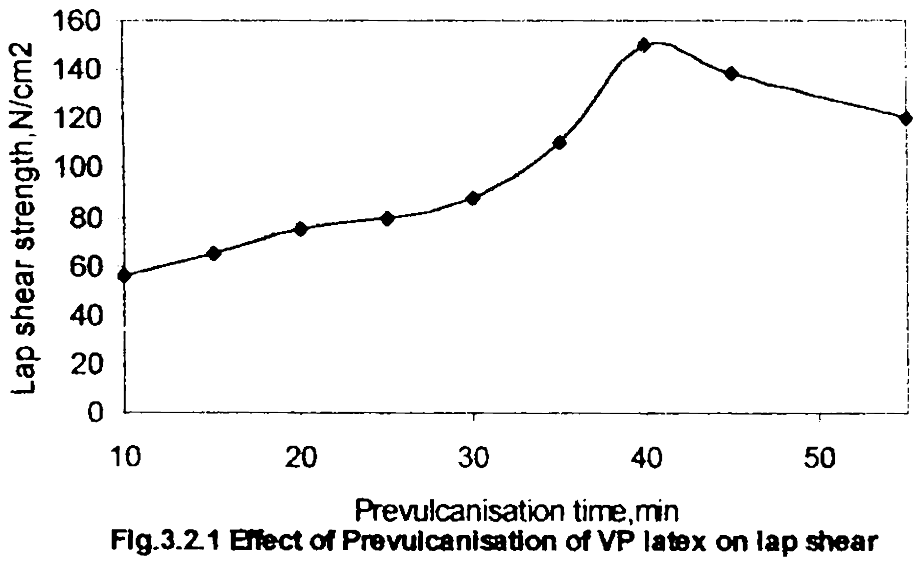

Fig.3.2.1 Effect of Prevulcanisation of VP latex on lap shear strength

Figure3.2.2 shows the prevulcanisation time for different VP latex compounds. For the compounds with CMC the lap shear strength increases when prevulcanisation time increases. In the case of ammonium caseinate, cooked starch and resorcinol formaldehyde resins(RF1 &

RF2) the joint strength increases, reaches a maximum and then decreases. The increase in lap shear strength with prevulcanisation may be due the increased film strength, but after attaining a state of prevulcanisation the particle coalescence becomes poor, resulting in decreased lap shear strength [9].

The lap joint strength increases as the carboxy methyl cellulose (CMC) content increases to 7.5 phr and then decreases (Figure3.2.3). This may be due to the increase in the viscosity of

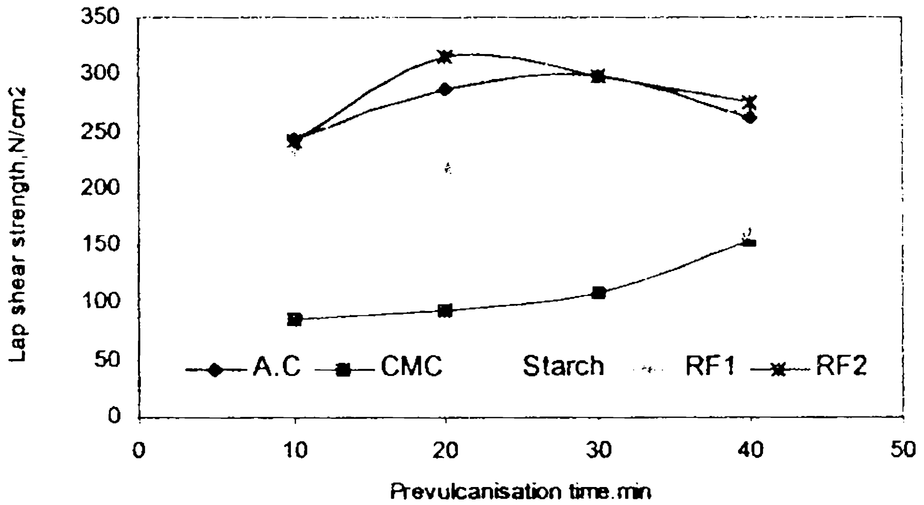

Fig.3.2.2 Variation of Prevulcanisation time with lap shear strength

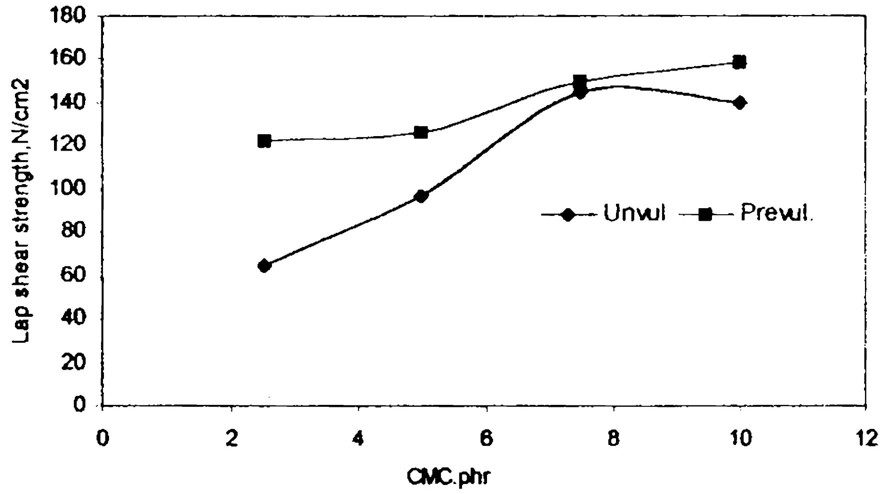

Fig.3.2.3 Variation of lap shear strength with CMC content.

latex compound as CMC acts as a thickening agent. This result shows that there is an optimum viscosity for latex based adhesives for obtaining maximum bond strength. Bond strength of prevulcanised latex compounds (prevulcanised for its optimum prevulcanisation time) show almost similar trend as that of unvulcanised latex compounds but show higher joint strength. This may be due to the increased film tensile strength of prevulcanised latex film.

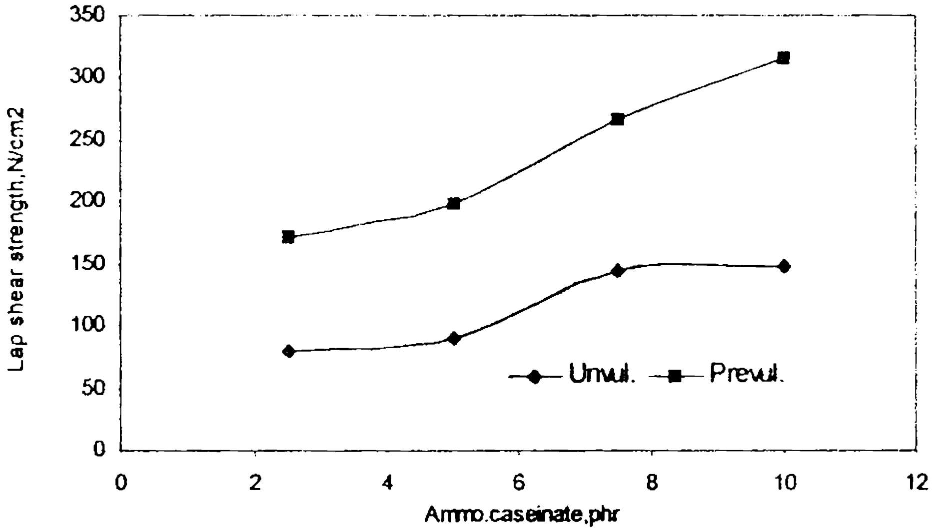

Fig.3.2.4 Variation of Lap shear strength with Ammo.caseinate.

As the amount of ammonium caseinate increases, the lap joint strength increases (Figure3.2.4).This shows that ammonium caseinate can act as a thickener in VP latex based adhesives. The bond strength of prevulcanised latex and unvulcanised latex show the same pattern. Ammonium caseinate increases the durability of wood joints because of its higher molecular weight. Ammonia present will be lost easily, resulting in insoluble casein [5]. The use of thickener is to increase viscosity which can prevent streaming when applied to vertical surfaces. It may also suppress any tendency for the aqueous phase of the adhesive to separate out of the adhesive when applied to porous surfaces. The separation of aqueous phase may prevent the development of optimum bond strength cause staining of the adherends[10].

In dispersed form, starch has high degree of spreadability and filminess and is capable of wetting polar surfaces such as cellulose, penetrating crevices and pores, and forming strong adhesive joints. It is the result of both mechanical interlocking and the interaction of secondary bond forces[15]. The variation of lap shear strength of prevulcanised and unvulcanised latex compounds with the amount of starch is shown in Figure3.2.5. This shows that starch can increase the bond strength of latex based adhesive and when prevulcanised there is a decrease in bond strength which may be due to the over cooking of starch while prevulcanising.

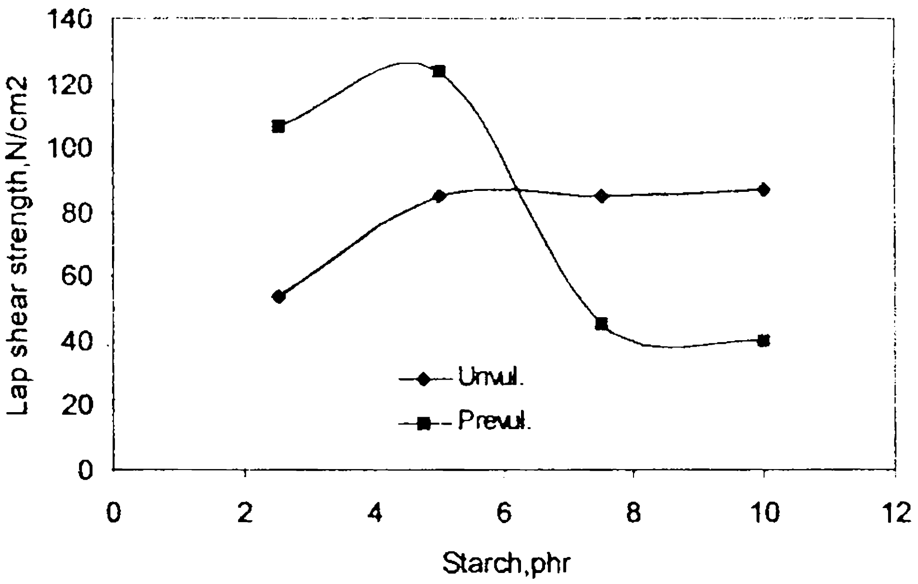

Fig. 3.2.5 Variation of lap shear strength with starch content.

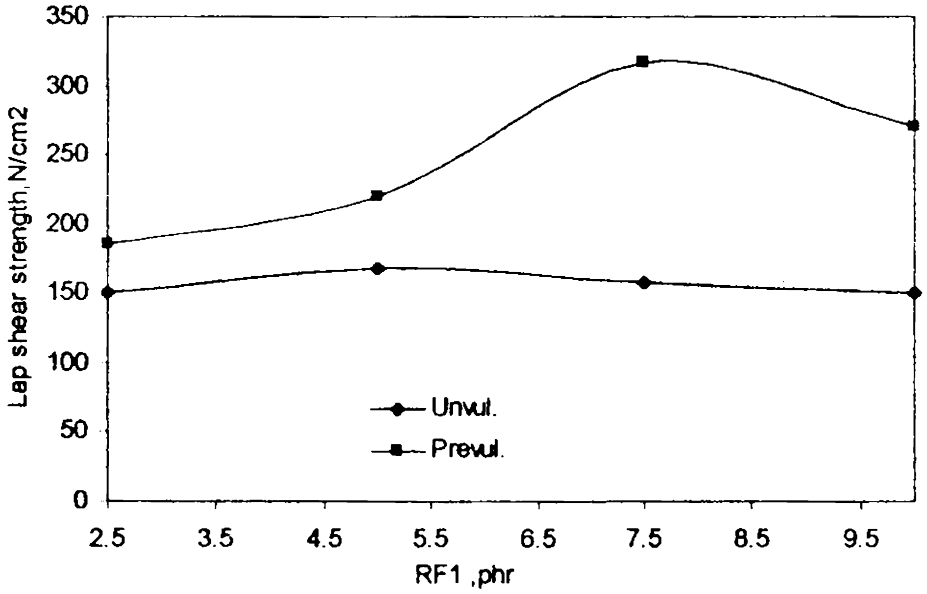

Fig.3.2.6 Variation of Lap shear strength with RF1 resin content

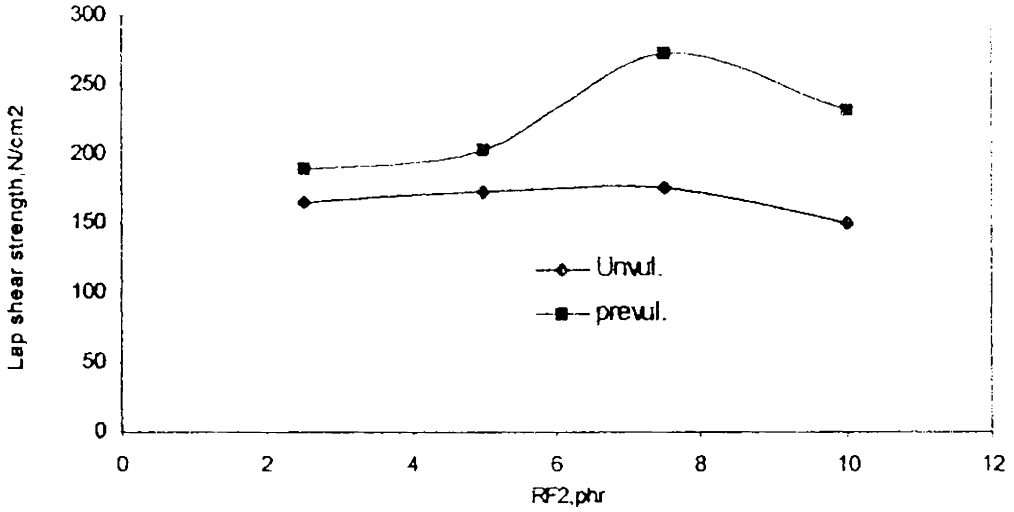

Fig.3.2.7 Variation of Lap shear strength with RF 2 resin content.

Figure3.2.6 and Figure3.2.7 show the effect of variation of RF1 and RF2 resins in VP latex compound respectively. Both resins show similar trend in prevulcanised and unvulcanised state. There is an optimum amount of RF resin which gives maximum joint strength.

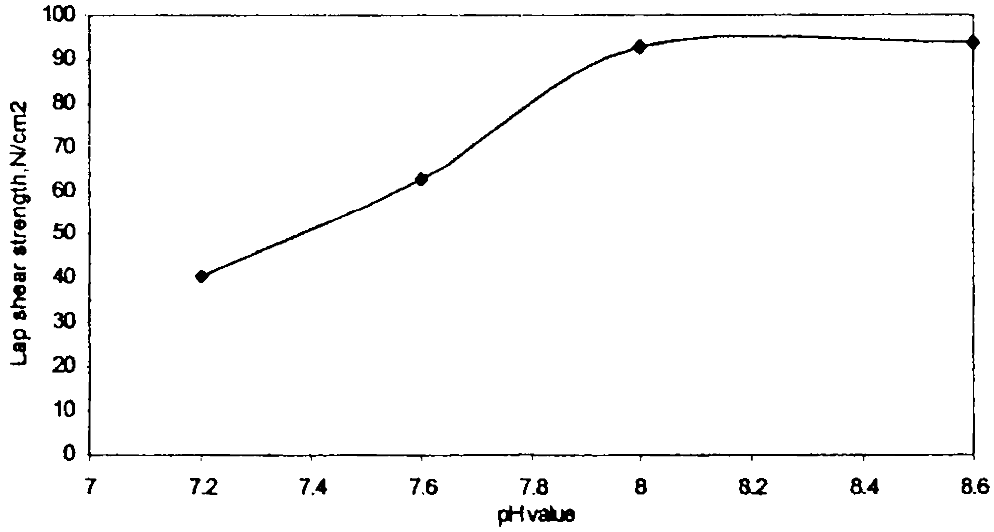

Fig.3.2.8 Variation of lap shear strength with pH value of latex

Figure 3.2.8 shows the effect of pH value on lap shear strength. As pH increases from 7.2 to 8.2 the lap shear strength increases [11-13]. The pH value in the alkaline range gives more adhesion strength.

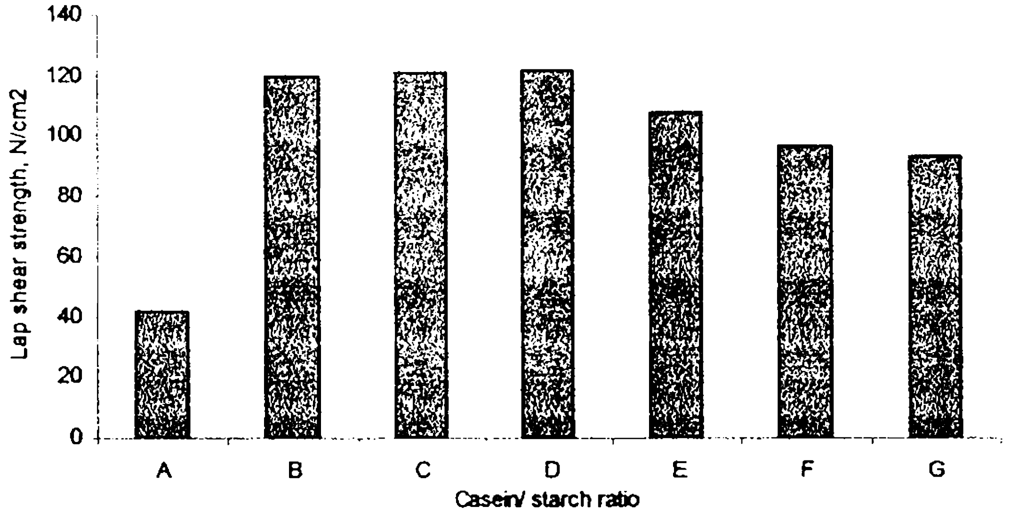

Fig.3.2.9 Variation of lap shear strength of mixed systems

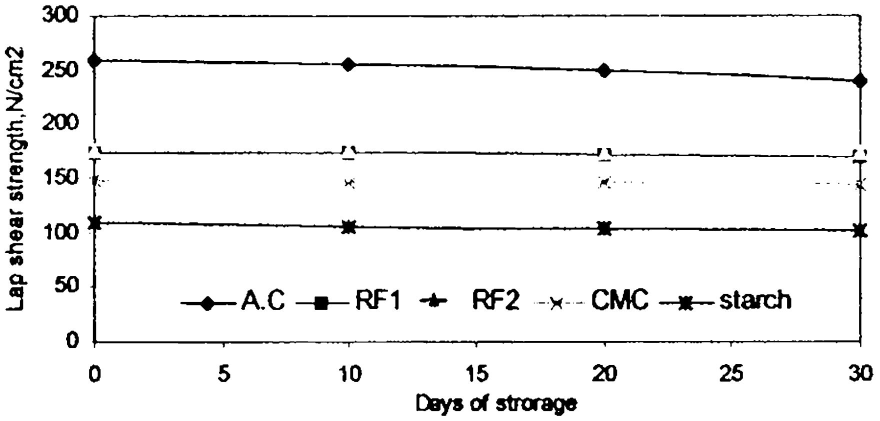

Fig.3.2.10 Variation of Lap shear strength with days of storage

Figure3.2.9 shows the lap shear strength of different combinations of ammonium caseinate and starch in VP latex. The different combinations do not give a higher strength compared to when they are used individually.

Figure3.2.10 shows the variation of lap shear strength with the number of days of storage. Even after 30 days of storage the lap shear strength of the adhesives are not changed much. This shows that the VP latex based adhesives posses good shelf life.

Table 3.2.2 shows the resistance of VP latex based adhesives in cold water, hot water, acid and alkali compared to natural rubber latex and commercial latex based adhesive, Fevicol. VP latex based adhesives show much higher retention in strength compared to natural rubber based wood adhesive[16] and Fevicol.

Table 3.2.2 Lap shear strength of latex adhesives under different environments.

	Strength after soaking in (N/cm^2)				
Adhesive	**Original**	**Water**	**Hot water**	**Acid**	**Alkali**
V1	260.2	259.2	145.7	244.4	234.8
V2	109.2	28.6	27.7	97.1	96.9
V3	148.3	118.6	45.2	109.6	108.6
V4	174.1	119.7	57.8	151.0	150.5
V5	176.59	100.23	50.6	181.31	180.6
FEVICOL	200.6	58.5	0.0	6.3	0.6
NR LATEX	90.9	44.8	33.7	30.8	31.2

Photograph 3.2.1 shows the roughed wood surface used for adhesive application . Photograph 3.2.2 and 3.2.3 shows the peeled off wood surface with laboratory adhesive and commercial adhesive(Dentrite) respectively. From the photograph it can be observed that the rubber film adhering to the surface is more in the case of laboratory adhesive so we get more adhesion strength. Here adhesive failure occurred during separating the adherends.

Photograph 3.2.1 Roughed wood surface before adhesive application.

Photograph 3.2.2 Peeled off wood surface with laboratory adhesive.

Photograph 3.2.3 Peeled off wood surface with commercial adhesive.

Conclusions

1. VP latex based adhesives can be used for bonding wood pieces.
2. An optimum amount of ammonium caseinate, CMC, starch and RF resin in VP latex adhesives gives maximum bond strength in wood joints.
3. Prevulcanisation of the latex improves bond strength.
4. VP latex based wood adhesives have good shelf life.
5. The resistance of VP latex based adhesives to water, acid and alkali are found to be superior to that of commercial adhesive.

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Part 3 Rubber solution adhesives for wood to wood bonding

The performance or behavior of wood adhesive system is dependent on a wide range of variables, such as surface smoothness of wood substrate, pH, presence of extractables, amount of debris present and others which are related to the environment conditions such as temperature and relative humidity[1]. The bonding mechanism of wood adhesives is related to the complex chemistry of the substrates[2]. In some cases, strong forces of covalent bonding may occour which in others weaker forces such as Van der waal's forces and Hydrogen bonding may operate or mechanical interlocking may occur [3,4].

Adhesives based on urea formaldehyde (UF) and phenol formaldehyde (PF) are the major adhesives used for bonding wood [5,6,7]. But these adhesives are very sensitive to hydrolysis [8,9] and stress scission[10]. The UF and PF adhesives produce health hazards due to formaldehyde release[11]. Isocyanate type adhesives have disadvantages like shorter pot life, higher cost, limited durability and lack of tack etc.[12].

In this part of the study development of solution based wood adhesives based on chloroprene rubber and natural rubber and their evaluation are proposed.

Experimental

Adhesives used:

A -Adhesive prepared in laboratory.

B -Dunlop adhesive supplied by Dunlop India Ltd, Calcutta.

C -Superbond adhesive supplied by Superchem MIDC, Thane.

D -Dentrite adhesive supplied by Chandra's chemicals enterprises, Calcutta.

E -Fevibond adhesive supplied by Pidilite Industries Ltd, Bombay.

Adhesive preparation:

Rubber compounds were prepared on a laboratory two roll mill(15x30)cm as per the formulations in Table 3.3.1. The compound was sheeted out from the mill and cut in to small pieces and dissolved in toluene to make a 40 percent solution. The solution was kept for two days and stirred vigorously for getting a uniform solution using a high speed mechanical stirrer.

Table 3.3.1 Formulations of rubber compounds, phr

Ingredients	CR AD type	CR W type	NR
Neoprene AD	100	0	0
Neoprene W	0	100	0
NR	0	0	100
MgO	5	5	2
Wood rosin	10	10	20
PF resin	20	20	20
Accinox TQ	1	1	1

Wood preparation:

Wood pieces were cut into 25x300x3 mm strips and polished using sand paper grit no.60(250μm).

Wood bonding and testing:

Using a brush the adhesive solution was applied on both pieces to a thickness of 0.1 mm and lap joined for 25x30 mm area of overlap. A load of about 1kg was placed over the joint and kept for 24 hours. Then the that wood joints were kept at room temperature (30°C)and relative humidity(RH) of 50±5 for 7 days.

These wood joints were tested for lap shear strength on a Zwick UTM model 1445 as per ASTM D 906-49 (72).

Effect of CNR and PF resin:

The effect of chlorinated natural rubber (CNR) on lap joint strength was measured by varying its amount from 10 to 60 phr in the formulations in Table 1.Similarly the amount of PF resin was varied from 20 to 45 parts and change in lap shear strength was determined.

Replacing CR AD type with W type CR and NR:

Adhesive grade neoprene was partially replaced by W type neoprene and lap shear strength was determined. Similarly neoprene AD was replaced by natural rubber and its effect on lap shear strength was studied.

Shelf life of the adhesive:

The neoprene based adhesive was kept for two months and lap shear strength was determined at equal intervals of time in order to determine the shelf life of the adhesive.

Comparison with commercial adhesives:

The adhesive showing maximum bond strength was compared with the commercial adhesives for lap shear strength. The solid content of the adhesive prepared in laboratory was reduced 25 from 40% by adding more solvent to the solution as the commercial adhesives are having 25% total solid content only.

Resistance of the wood joints:

Wood pieces bonded with the adhesive prepared in laboratory and some of the commercial adhesives were kept in cold water(30°C) for one day. Then they were taken out, dried at room temperature(30°C and RH 50±5) for one day and the lap shear strength was determined. Similarly bonded pieces were immersed in hot water at 100°C, in acid (pH 2) and in alkali (pH 10) both at 80°C for one hour. Then the lap shear strength was determined as described earlier. The bonded wood pieces were kept for one month at room temperature and lap shear strength was measured for determining the ageing resistance of the wood bonds were determined.

Direct shear method:

Wood pieces were cut into 60x60x20 mm size, dried and polished using emery paper no.60 (250μm).Adhesives were applied on both pieces to full area to a thickness 0.1 mm. A load of 1kg was placed over it for one day and then it was kept for seven days at room temperature. These wood joints were tested on a direct shear machine and the load required for shearing one piece over the other was measured and the result was expressed as N/cm^2 by considering the area of the wood pieces. The test was conducted as per IS 2720 (1972) part XIII.

Relationship between solid content and viscosity:

The effect of solid content and viscosity on the adhesive with varying amounts of resin content and rubber content was studied. To the adhesive solution the amount of resin and rubber content varied and the effect of viscosity and solid content was estimated.

Adhesive with different solvents:

The rubber solution with different solvents were also tried. Solvent mixtures were also used to make the adhesives. These adhesive solutions were tried on wood joints and lap shear strength was estimated.

Results and Discussion

Figure3.3.1 shows the effect of variation of chlorinated natural rubber in the adhesive solutions on the lap shear strength. Lap shear strength increases as the amount of chlorinated natural rubber increases, reaches a maximum and then decreases. In the case of natural rubber solution the highest strength is obtained at 50 phr CNR. This shows that there is an optimum concentration of NR which gives maximum bond strength. At higher concentrations CNR may form the continuous phase and the bond joint looses its elastomeric nature. There is no visible phase separation. The solution is homogeneous in nature. In the case of W type CR based adhesive also the lap shear strength initially increases in reaches a maximum and then decreases similar to that of Neoprene AD type adhesive. But W type Neoprene based adhesive shows lower lap shear strength relative to Neoprene AD. This may be due to the slower crystallizing nature of Neoprene W type [13]. NR based adhesive shows only a marginal increases in lap shear strength

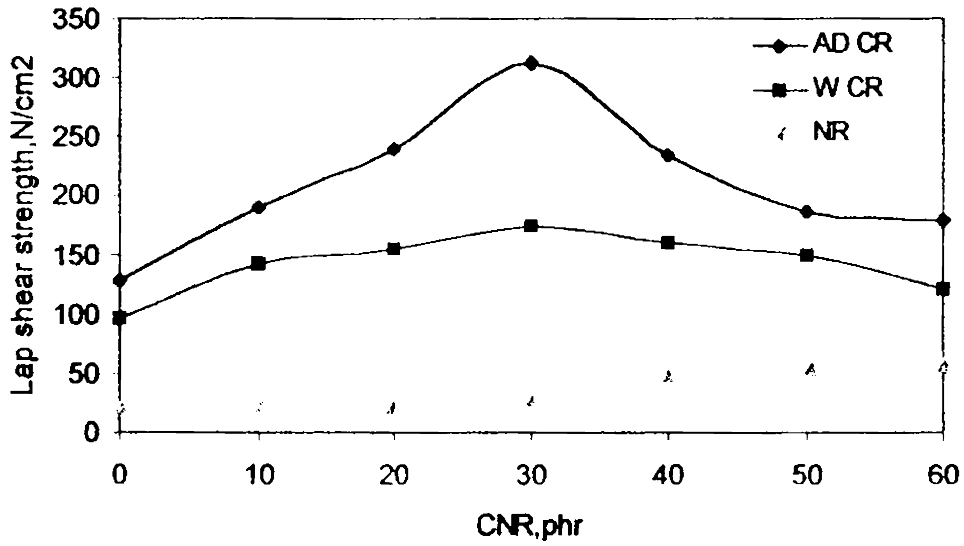


Fig.3.3.1 Variation of lap shear strength with CNR content

even at 50 phr CNR. This may be due to the low compatibility of polar CNR and nonpolar NR.

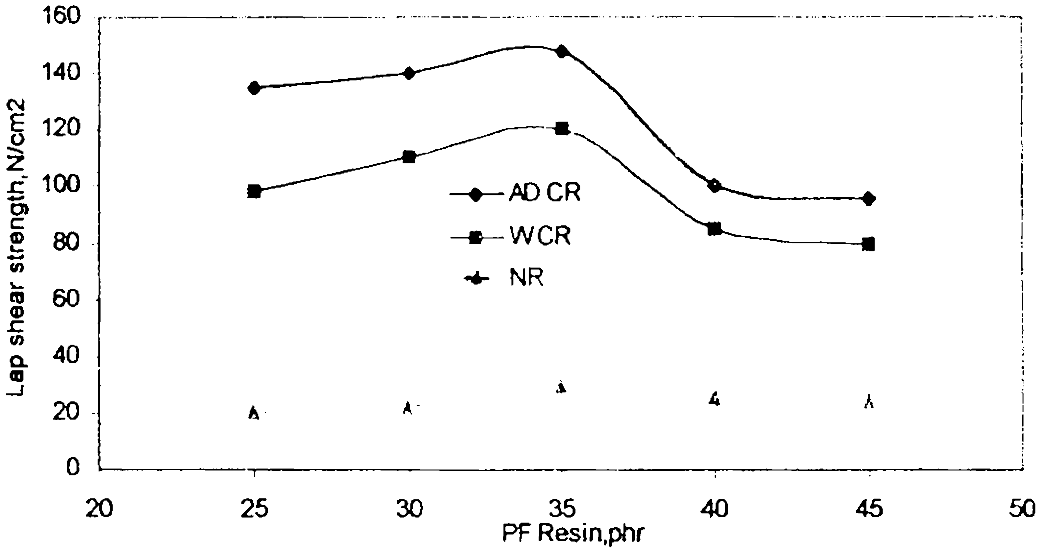


Fig.3.3.2 Effect of PF resin on lap shear strength.

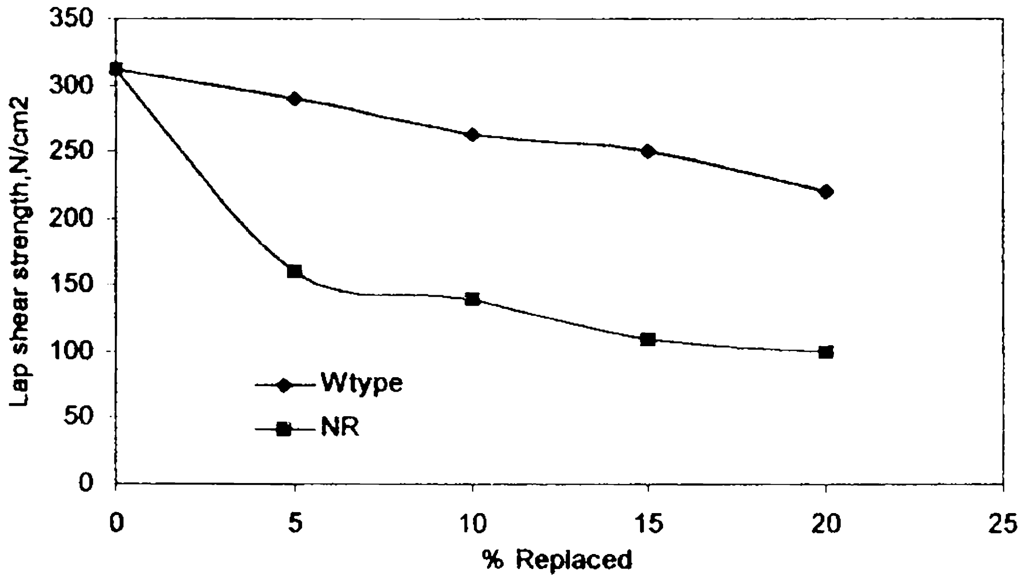
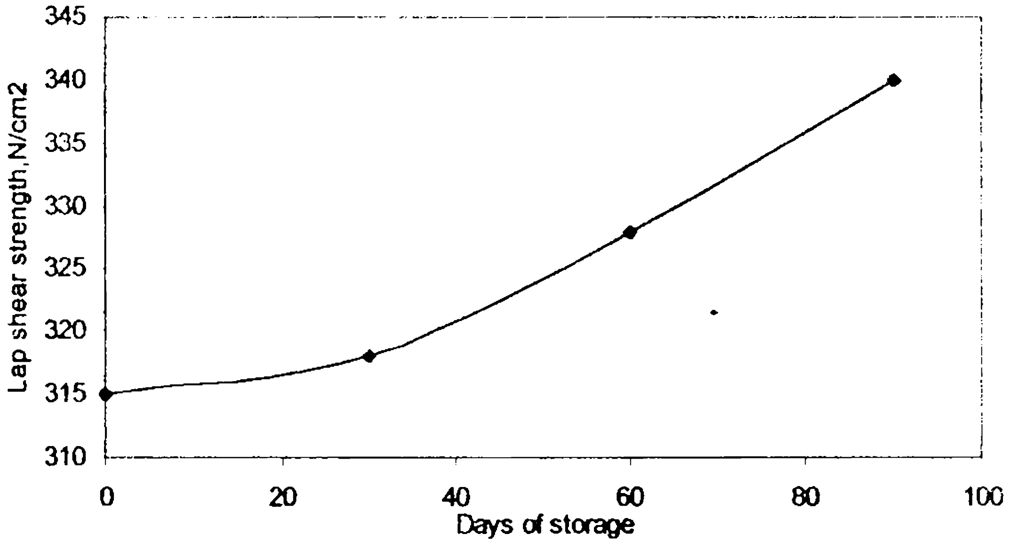


Fig.3.3.3 Lap shear strength with % replacement of CR AD type

In Figure3.3.2 shows the effect of variation of PF resin in the adhesive solutions on lap shear strength . Lap shear strength increases initially and then decreases. This may be due to the phase change [14] in the solutions when PF resin becomes the continuos phase . CR AD type, CR W type and NR based adhesives show the same trend when the amount of PF resin is varied.

The decrease in lap shear strength when part of adhesive grade CR is replaced by W type CR is shown in Figure3.3.3.



Fog.3.3.4 Variation of Lap shear strength with days of storage

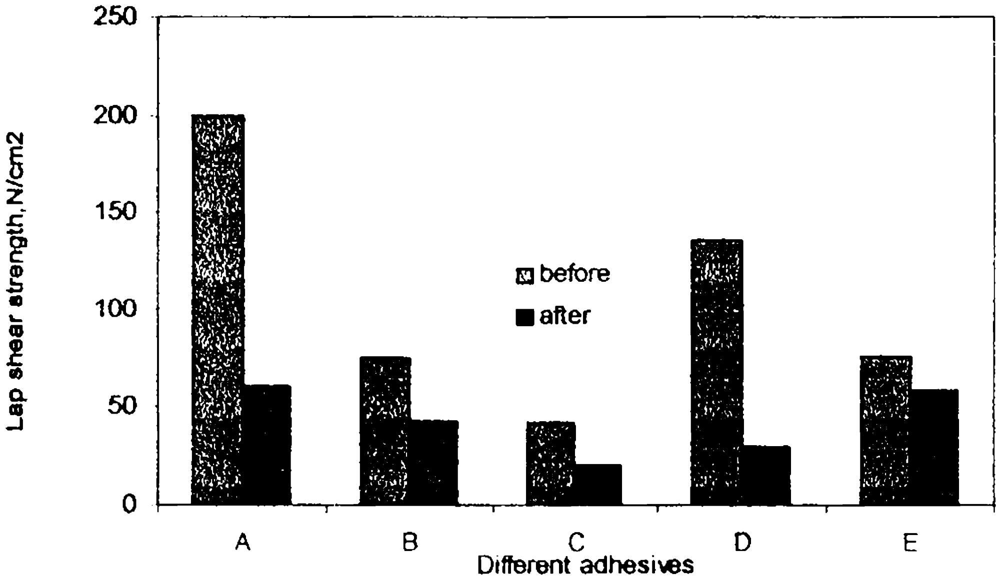


Fig.3.3.5 Effect of water on wood joints

CR AD type crystallizes much faster than CR W type[14] and so W type CR gives lower strength compared to CR AD type. This figure also shows that the decrease in lap shear strength is more pronounced when adhesive grade CR is replaced by natural rubber. This may be due to the nonpolar nature of NR. Polar adhesives are likely to give higher bond strength with polar adherends like wood.

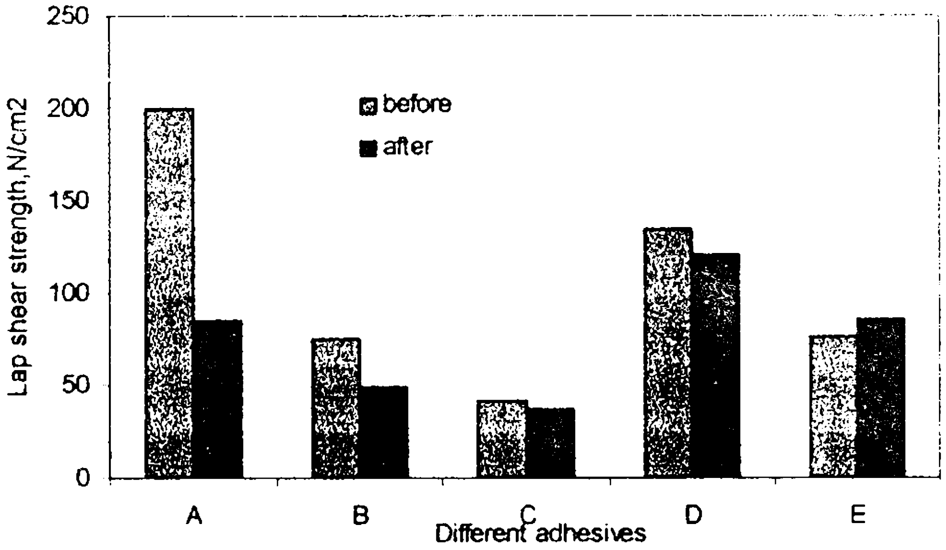


Fig.3.3.6 Effect of hot water on wood joints

Figure3.3.4 shows the variation of lap shear strength of the adhesive with days of storage. The joint strength is found to increase with the length of storage of adhesive solution. It may be

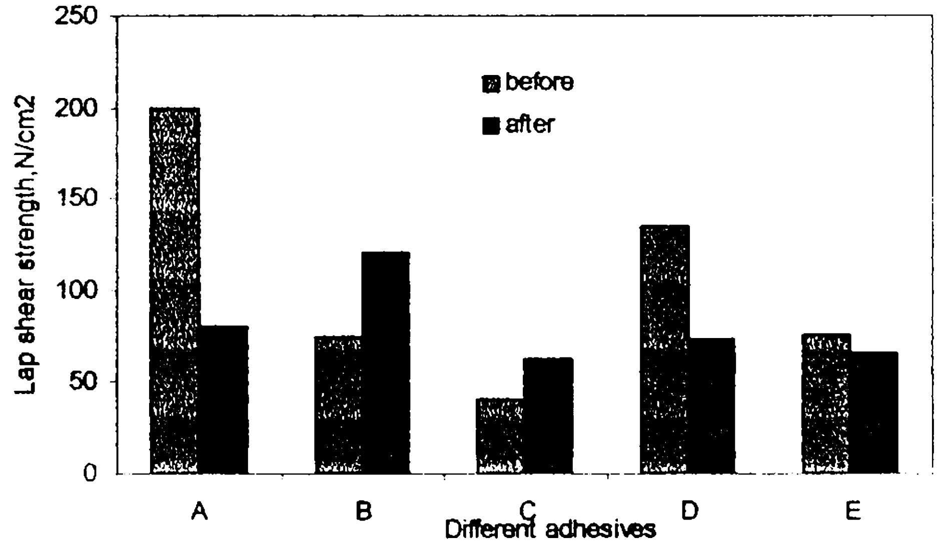


Fig.3.3.7 Effect of acid on lap shear strength

due to the increase in solid content due to the slight evaporation of solvent and partial precuring of the solution during storage.

The water resistance of joints prepared with the commercial adhesives and the adhesive prepared in the laboratory is shown in Figure3.3.5. Compared to commercial adhesives the water resistance is found to be superior for the adhesive prepared in the laboratory.

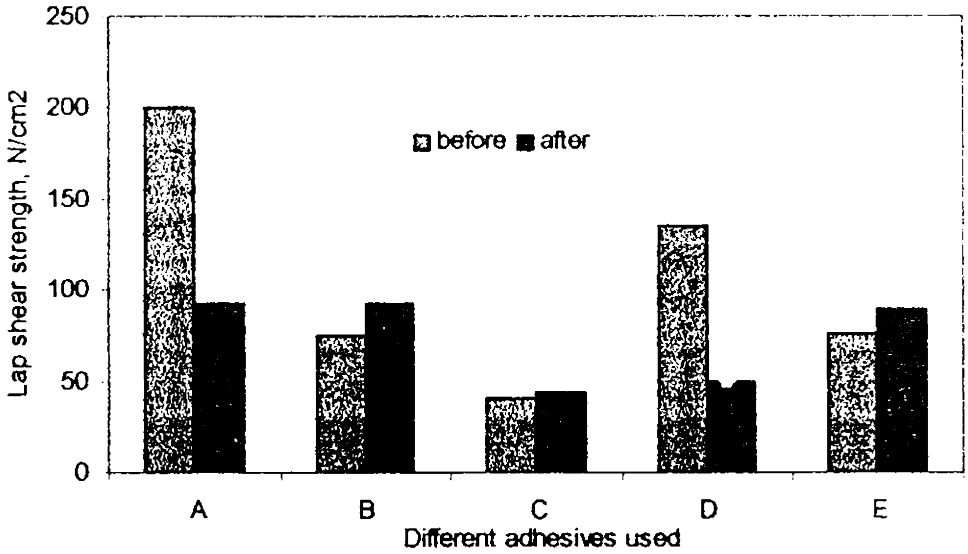


Fig.3.3.8 Effect of alkali on wood joints

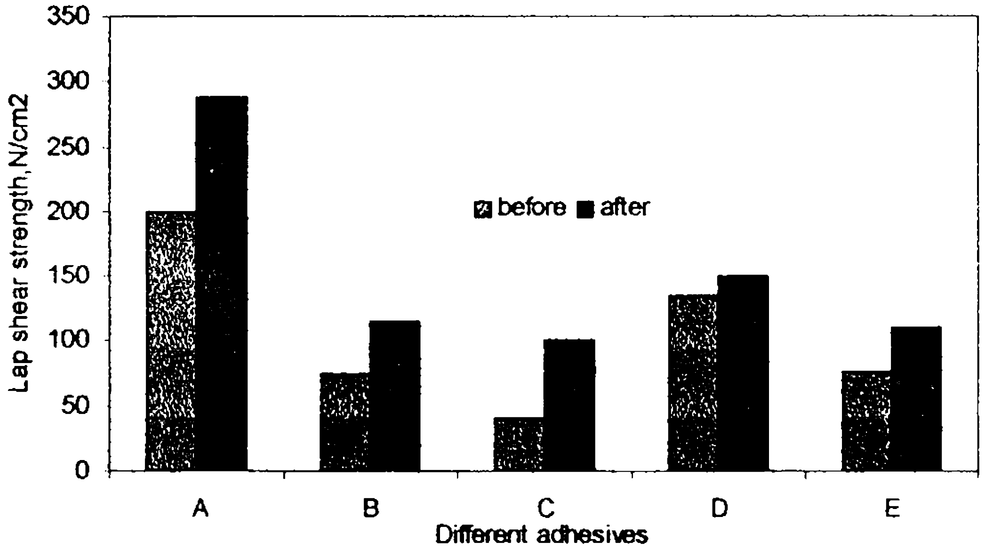


Fig.3.3.9 Effect of ageing lap shear strength of wood joints

Figure3.3.6 shows the hot water resistance of the adhesives. There is a slight increase in bond strength for some of the joints. This may be due to the slight crosslinking of adhesive film in boiling water. The adhesive prepared in laboratory is found to be comparable to that of commercial adhesives.

Acid and alkali resistance of the adhesives are shown in Figure3.3.7 and Figure3.3.8 respectively. The adhesive prepared in laboratory gives better resistance compared to other adhesives.

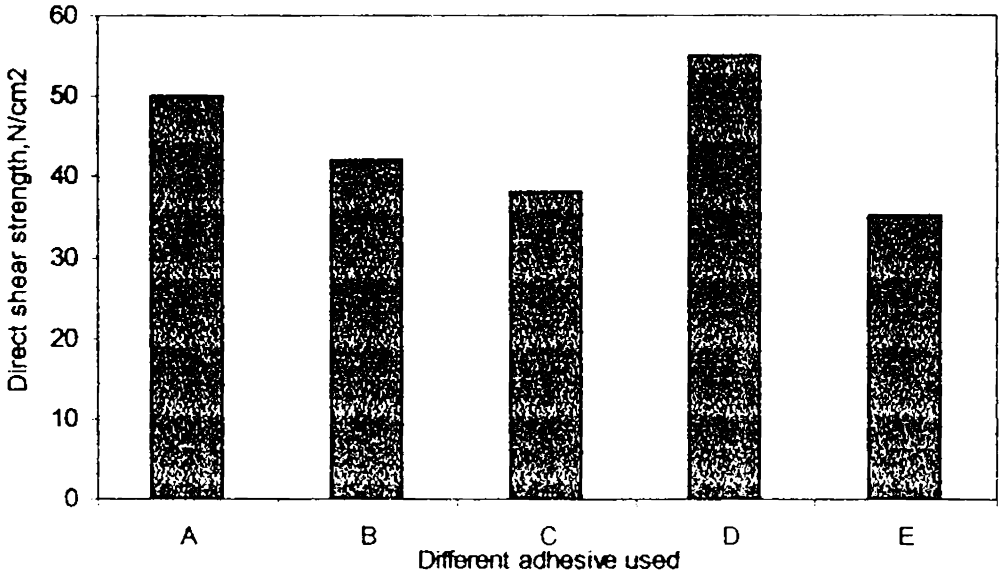


Fig.3.3.10 Direct shear strength of different adhesives

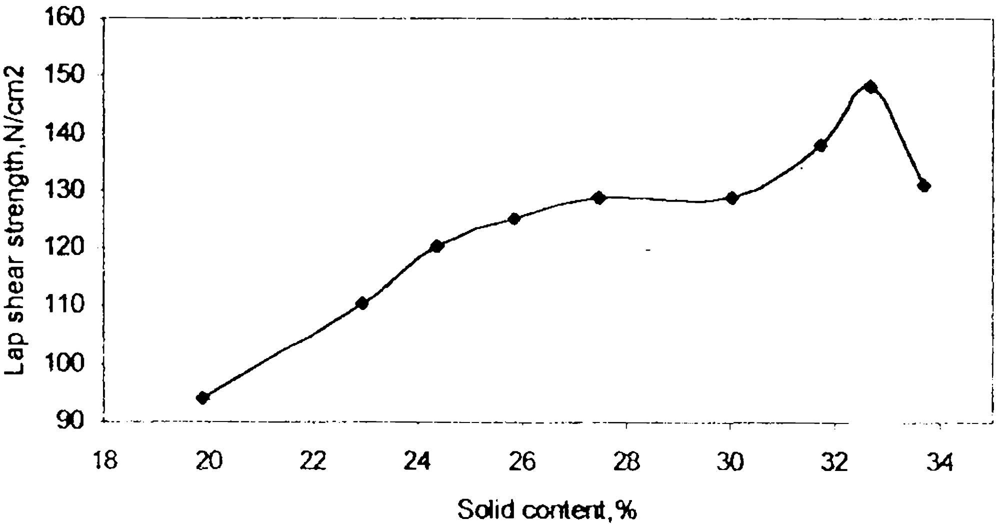


Fig.3.3.11 variation of Lap shear strength with solid content

Figure3.3.9 shows the results of room temperature ageing of the wood joints for one month. Results show an increase in joint strength which may be due the crosslinking of the adhesive film during storage.

Direct shear strength of different adhesives are shown in Figure3.3.10 Adhesive prepared in laboratory shows better direct shear strength compared to other commercial adhesives.

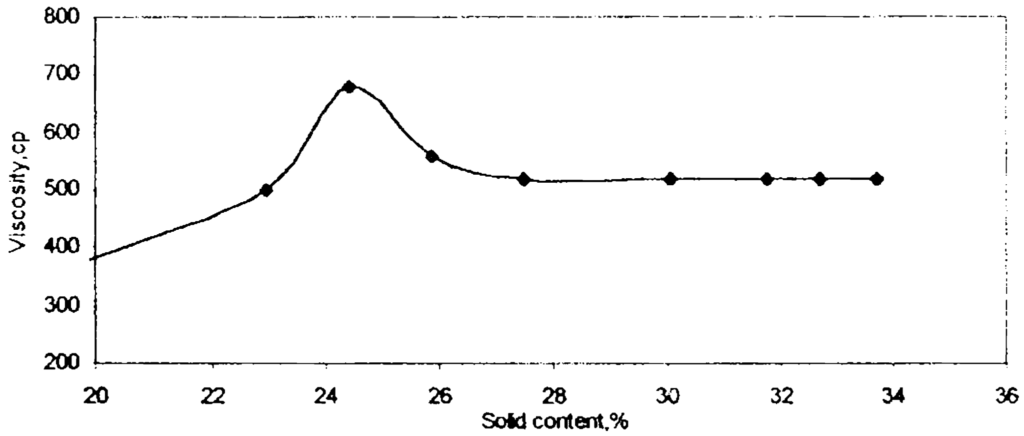


Fig.3.3.12 viscosity variation with solid content

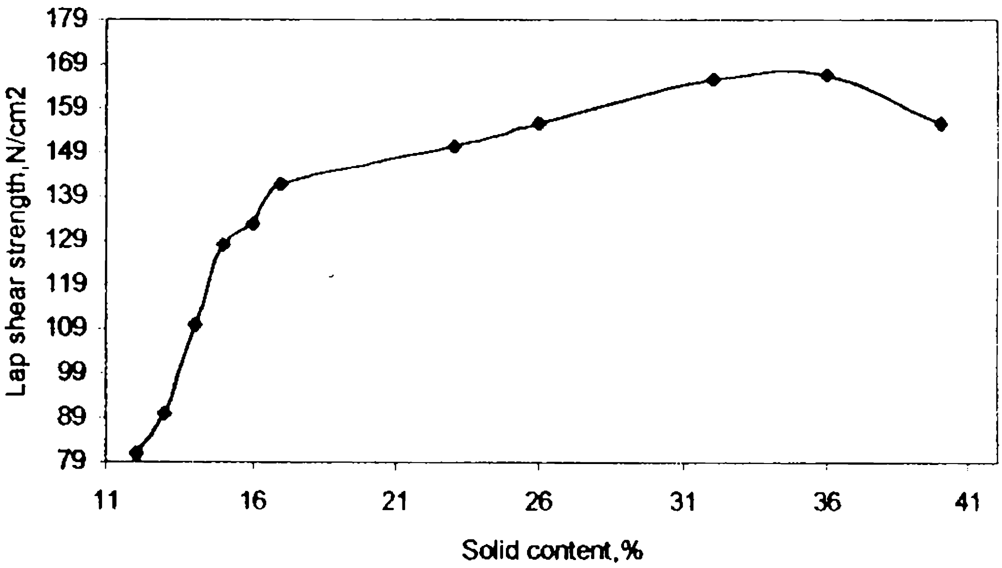


Fig.3.3.13 variation of Lap shear strength with solid content

Figure 3.3.11 shows the effect of total solid content on lap shear strength as resin content increases. Lap shear strength increases reaches a maximum and then decreases. The resin forms the continous phase when used in higher amounts.

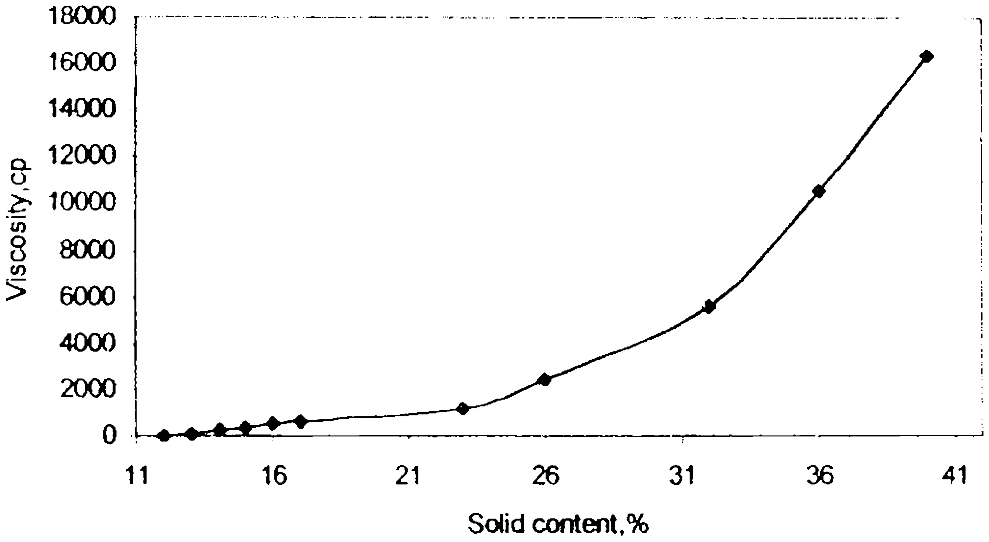


Fig.3.3.14 change in viscosity with solid content

Figure 3.3.12 shows the effect of viscosity change when resin content increases. As the amount of resin increases viscosity increases, reaches a maximum and then decreases and levels off to a particular viscosity. Due to the lower molecular weight of PF resin there will not be any change in viscosity after a particular level of resin. Molecular weight is a factor that directly affects the solution viscosity of polymers.

Figure 3.3.13 shows the effect of lap shear strength of wood joint when the amount of rubber content is varied in solution adhesive. As the rubber content increases the strength increases reaches a maximum and after that slight reduction in lap shear strength is observed. This may be due the large increase in viscosity which decreases the spreadability of the adhesive film and hence makes it more difficult to wet the wood surfaces.

Figure3.3.14 shows the effect of rubber content in the viscosity of rubber solution adhesive. Viscosity increases significantly as the rubber content increases, as expected, since molecular weight of rubber is very high.

Table 3.3.2 shows the lap shear strength of rubber solutions with different solvents. Results from solvent mixtures are also shown in this table. Toluene/ EDC mixer shows the best results.

Table 3.3.2 Lap shear strength (N/cm^2) of adhesives with different solvents.

Xylene/Naptha(%)	25/75	28.2
	50/50	29.27
	72/25	34.53
Toluene/ Naptha(%)	25/75	28.16
	50/50	57.22
	75/25	162.68
EDC/Toluene (%)	25/75	114.5
	50/50	168.71
	75/25	198.65
Xylene(%)	100	20.23
Naptha(%)	100	Not soluble
EDC(%)	100	147.53

Conclusions

1. Adhesive solution prepared with Neoprene AD type is found to give superior bonding than commercial wood adhesives.
2. Optimum amounts of CNR (30%) and PF resin (35%) improves adhesive strength of neoprene based adhesives.
3. Neoprene AD based adhesive solution is found to have better resistance to cold water, hot water, acid and alkali compared to the commercial adhesives.
4. Shelf life of the adhesive is found to be comparable to that of commercial adhesives.

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Part 4 Novel adhesives based on thermoplastic elastomers for wood to wood bonding

Thermoplastic elastomer shows properties of plastic as well as elastomer[1]. Thermoplastic elastomers are widely used in different mechanical applications due to its toughness and also its flexibility [2]. They are used in many hot melt adhesives [3-5]. Use of hot melt adhesives need complex mechanism for heating and cooling the adhesive joints. In the case of wood joints heating of the joints is not usually practised.

In this study solutions of thermoplastic elastomers are proposed to be used for bonding. Use of solutions avoid the need for heating and cooling and thus make the process simpler and comparatively cheap.

Experimental

The adhesives were prepared from themoplastic based on rubber plastic blends. This part of the study is being patented and author request to excuse for not providing the exact details.

Commercial Adhesive used for comparison was Dentrite adhesive supplied by Super chem.

Optical microscopy photogaphs of the wood adherends were taken before applying the adhesives and after peel off.

Results and discussion

Figure3.4.1 shows the effect of thermoplastic content in the adhesive on lap shear strength of wood joints. When thermoplastic content increases lap shear strength increases. But when the thermoplastic or the elastomer is used alone the lap joint strength is lower. This shows there is an optimum amount of the thermoplastic and elastomer in the adhesive to get maximum joint strength for wood pieces. In both types of thermoplastic elastomer studies the same trend is observed.

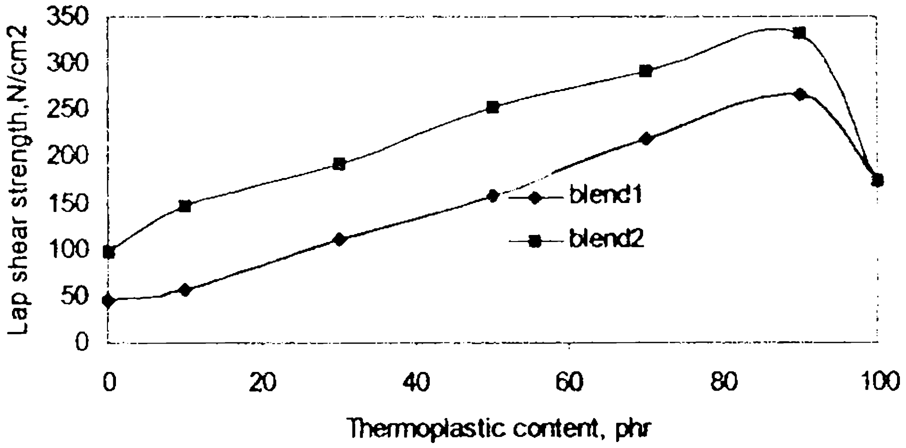

Fig.3.4.1 Effect of thermoplastic content in lap shear strength

Figure 3.4.2 shows the effect of tackifier resin in the thermoplastic elastomer based adhesive for wood joints. When the tackifing resin content increases lap shear strength increases reaches a maximum and then decreases. When the resin content is above an optimum level there may be phases change of the adhesive film to a more brittle nature thus reducing the lap shear strength.

Figure 3.4.3 shows the effect of plasticiser on lap shear strength of thermoplastic elastomer based adhesives on wood bonding. As the amount of plastisicer increases lap shear strength reduces due the lowering of film strength of the adhesives. When the amount plastisicer increases it reduces the inherent strength of thermoplastic elastomer.

Figure3.4.4 shows the variation of lap shear strength by changing the viscosity of the adhesives. As viscosity increases lap shear strength increases but after a particular viscosity spreadability of the adhesive film decreases and hence it cannot be handled easily.

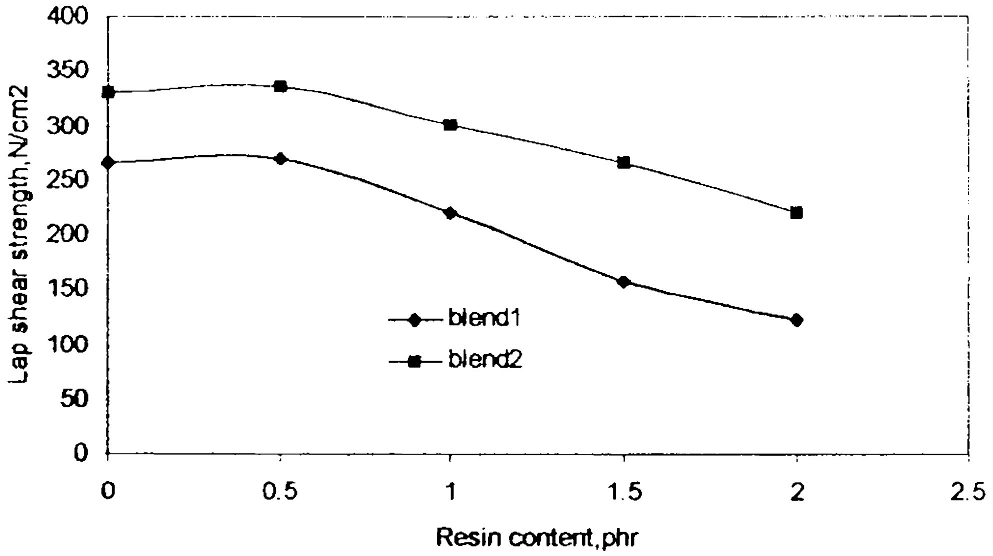

Fig.3.4.2 Effect of resin on lap shear strength

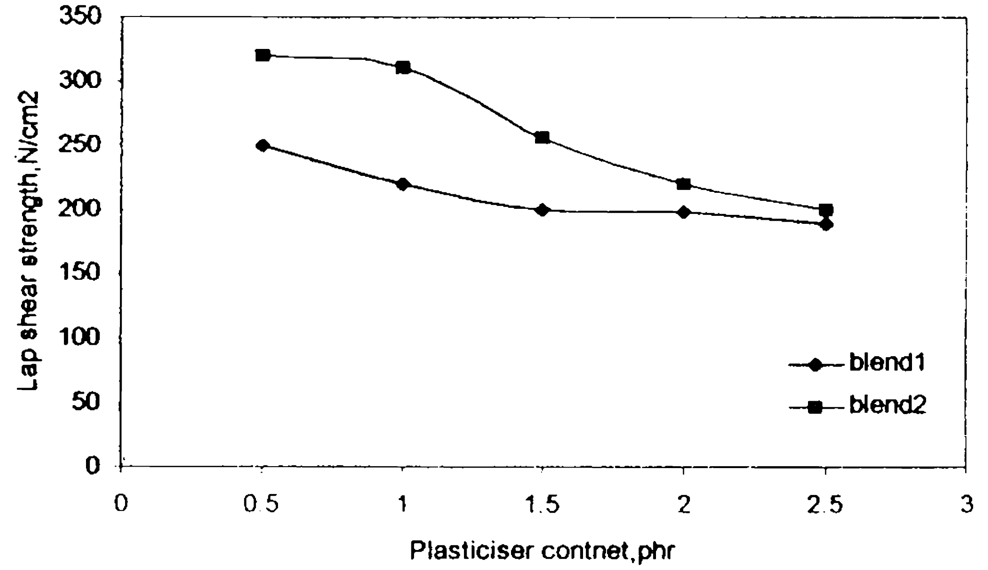

Fig.3.4.3 effect of plasticiser on lap shear strength

Figure 3.4.5 shows the effect of storage of the adhesives for 5 weeks on lap shear strength of wood joints. On storage the lap shear strength of both the adhesives increases slightly which may be due to the evaporation of solvent leading to higher solid content. From this it is clear that adhesives have enough storage life.

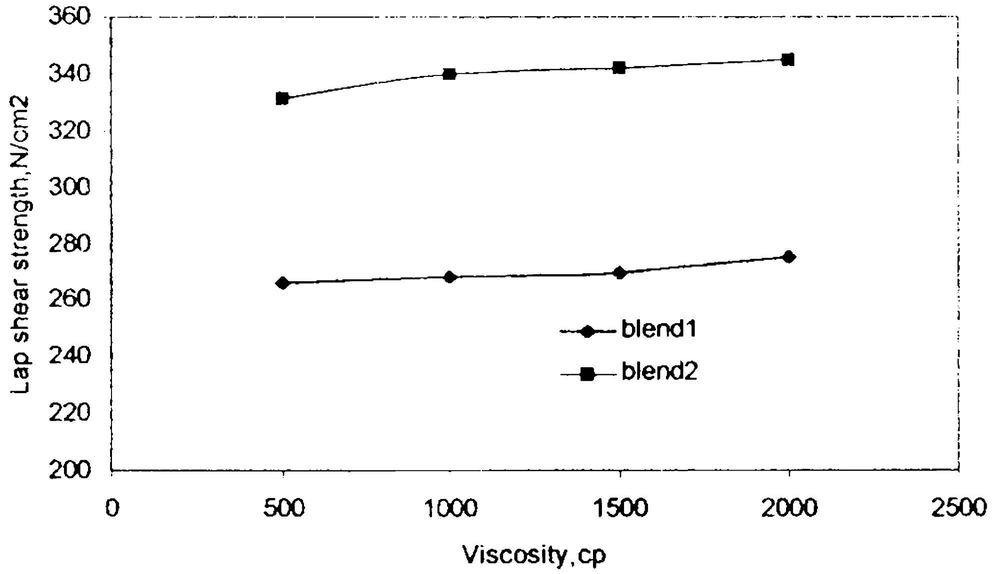

Fig.3.4.4 effect of vicosity on lap shear strength

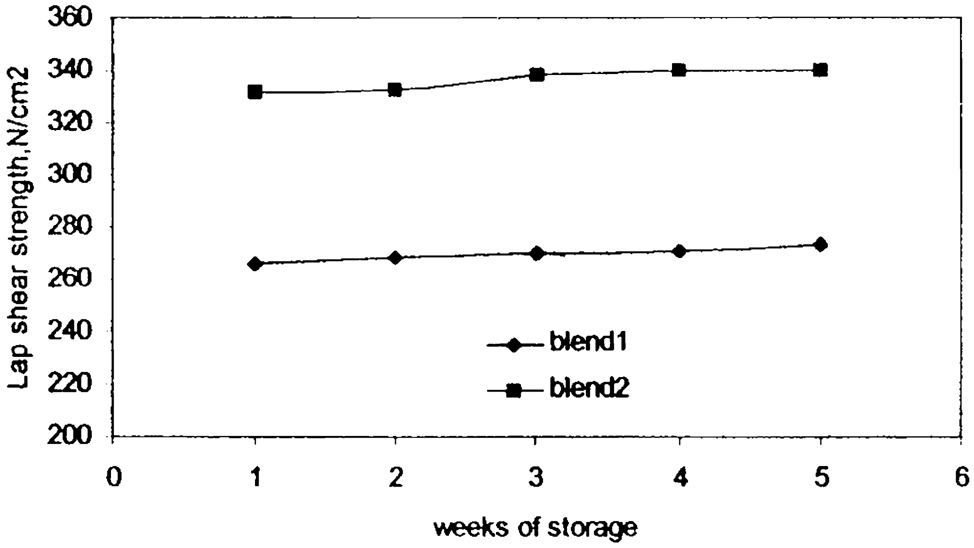

Fig.3.4.5 effect of storage on lap shear strength

Figure 3.4.6 shows the lap shear strength of the wood joints made of two types of thermoplastic elastomer based adhesives and commercial adhesive before and after soaking in cold water. There is slight reduction in lap shear strength in all cases, but here commercial adhesives show much more reduction in strength compared to the adhesives based on thermoplastic elastomers.

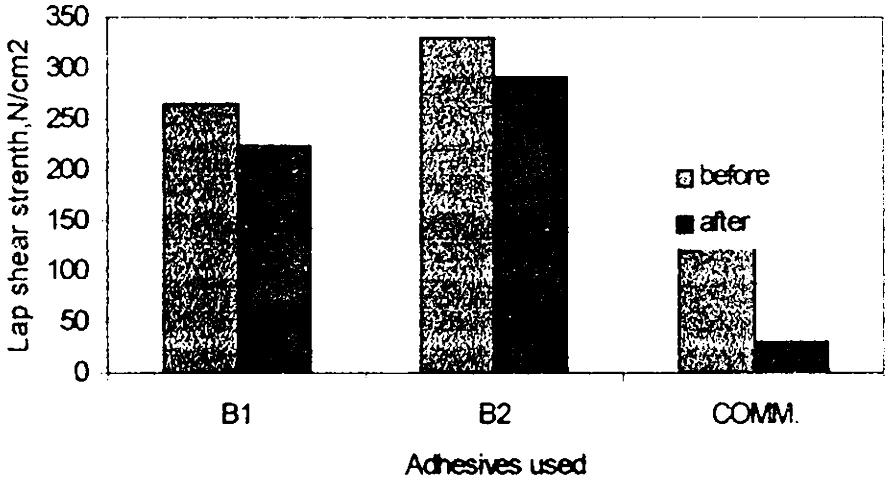

Fig.3.4.6 Variation of lap shear strength of wood joints before and after soaking in water

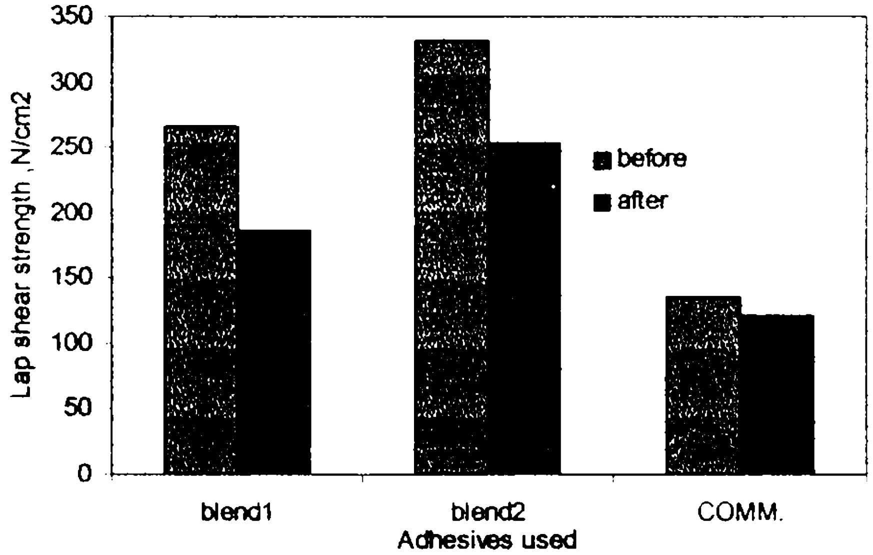

Fig.3.4.7 Effect of hot water on lap shear strength

Figure 3.4.7 shows the effect of hot water on lap shear strength of the adhesives. Adhesives based on thermoplastic elastomers show better retention in strength compared to commercial adhesives. Thermoplastic elastomer based adhesives show better properties due to the hard domains present in the molecule making it resistant to different environments [2]

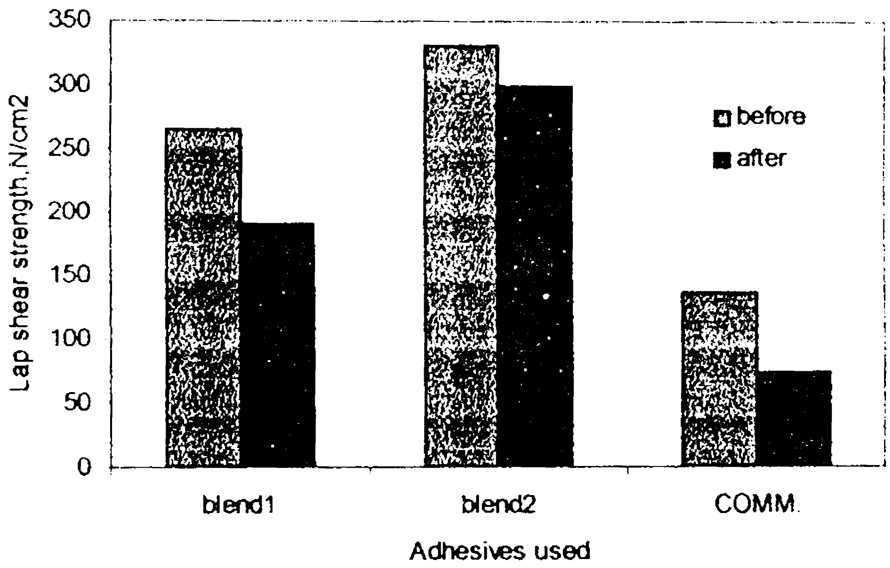

Fig.3.4.8 Effect of acid on lap shear strength

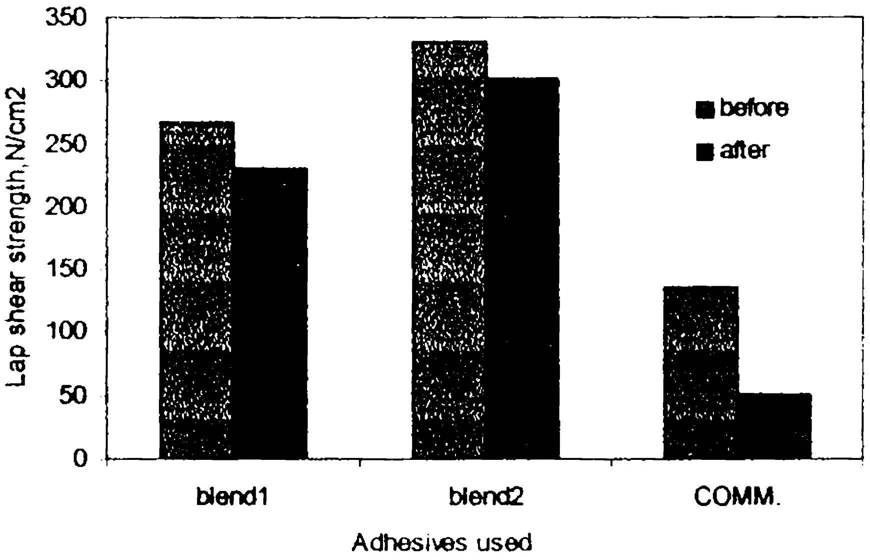

Fig.3.4.9 Effect of alkali on lap shear strength

Figure3.4.8 shows the lap shear strength of the wood joints before and after soaking in hot acids. The adhesives prepared in laboratory show better strength retention compared to commercial adhesives. The chemical resistance of thermoplastic elastomer based adhesives is much better than ordinary elastomer based adhesives.

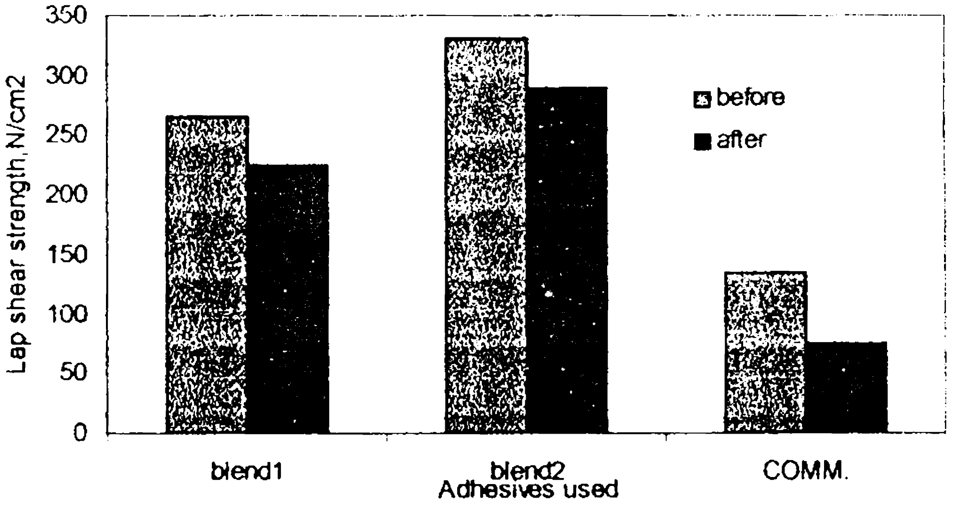

Fig.3.4.10 Effect of ageing on lap shear strength

Figure 3.4.9 shows the effect of hot alkali on lap shear strength of wood joints. Thermoplastic elastomer based adhesives show superior resistance to alkalis compared to commercial adhesives.

Figure 3.4.10 shows the ageing resistance of the adhesive joints. Commercial adhesive shows lower resistance than thermoplastic elastomer based adhesives. Thermoplastic elastomer based adhesives have better heat resistance compared to other elastomers due the presence of hard domains.

Photograph 3.4.1 shows the roughened wood surface before adhesive application. Photographs 3.4.2 and 3.4.3 show the peeled off surfaces of adhesive prepared in laboratory and one commercial adhesive respectively. From the photographs it is evident that former leaves more polymer residue over the wood surface which may be the cause for more adhesion strength.

Photograph 3.4.1 Roughed wood surface before adhesive application.

Photograph 3.4.2 Peeled off wood surface with laboratory adhesive.

Conclusions

1. Thermoplastic elastomer based adhesives can be used for wood to wood bonding.
2. Optimum amount of tackifier resin and plasticiser can improve the adhesion strength of wood joints with thermoplastic elastomer.
3. The thermoplastic elastomer gives very good storage life and so it can be commercialized.
4. The resistance of this adhesive in different environment like water, acids, alkalies and high temperature etc. is found to be superior compared to commercial adhesives.
5. Optical microscopic studies give evidence for superior strength to thermoplastic elastomer based adhesives.

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Chapter 4

LEATHER BONDING

Chapter 4

Part I Studies on Polymeric Solution Adhesives for Bonding Leather

The footwear manufacture involves joining of many intricate parts using adhesives[1]. The forces of attraction may be strong chemical bonds or the weaker forces known as Van der Waal's attraction [2,3]. Bonding may also results from mechanical interlocking or by penetration of adhesive molecules into the substrates by diffusion[4].

Neoprene rubber, nitrile rubber, polyurethane rubber [5,6] and natural rubber based adhesives are common in shoe industry [7]. Disadvantage of nitrile based adhesives is that, it is necessary to activate the substrates at higher temperature (70-80 °C) to get better bonding strength.

In this work we developed three different types of novel solution adhesives are proposed to be tried for leather to leather bonding. The peel and shear strength of the adhesive joints are proposed to be compared with joints made with commercial adhesives.

Experimental:

Materials used:

Commercial No1: Poly urethane based commercial adhesive supplied by CLRI Madras.

Commercial No2: Dentrite adhesive supplied by Superchem

Adhesive preparation:

1. PVC based: Suspension grade PVC was dissolved in either cyclohexanone or tetrahydro furan. The solid content of the solution was 10 percentage.
2. CR based: Chloroprene rubber was compounded as per the formulation in Table 4.1.1. This compound was then put in a solvent (usually toluene) and kept for two days. After that a mechanical stirring was given to make the solution uniform, the total solid content was about 20 percentage.
3. NR based: Natural rubber was compounded as per the formulations in Table 4.1.1. This was then dissolved in solvent and the adhesive was prepared explained above.

Table 4.1.1 Formulations of leather adhesives, phr

Ingredients	NR adhesive	CR adhesive	NR sole	SBR sole	MC sole
NR	100		100		
CR		100			
SBR				100	
NBR					50
PVC					50
ZnO		5	4	4	5
MgO	2.0	4			2
Stearic acid			2	2	2
Accinox TQ	1.5	1.0	1.0	1.0	
Clay					80
Silica					20
HAF			45	40	
Aromatic oil			2	2	
MBTS			1.5	1.5	
TiO2					2
DNPT					10
PF resin	20	20			
Wood rosin	20	10			2
DEG					1.5
DOP					5
Vulcafor F					1.5
Sulphur			2.5	2.0	1.5
TMTD			1.0	1.0	0.5

Commercial adhesive 1: The polyurethane based adhesive chips supplied by CLRI was dissolved in THF to get a 20 percentage solution. This was used as the commercial adhesive in this study.

1. Upper Leather to Upper Leather bonding:

Leather pieces (*hereafter mentioning of leather means upper leather*) were cut into 120x 25 mm size. These pieces were roughened using sand paper no.50 and wiped with MEK and dried. These specimens were treated with the adhesives so that the pores, completely filled and there was a uniform layer of the adhesive formed. When the adhesive surface is dried another layer of adhesive was applied in the same manner. When the second adhesive film is dry to a point there is still an aggressive tackiness but no tendency for the film to lift when tested with a finger. The coated surface of the two strips were aligned face to face carefully, without entrapping air, in such a way that the free ends of the strips lie in opposite direction for shear strength and lie in the same direction for peel strength testing. The pieces were pressed together by applying a pressure of around 10-12 kg/cm^2. The test specimens were conditioned for 48 hours. For peel strength testing adhesive was applied over an area 2.5x2cm at one of the buffed surface of the strips. For shear strength testing adhesive was applied over an area of 2.5x 4cm at one of the buffed surface of each strip.

All the three types of adhesives prepared with two commercial adhesives were used for bonding the adherends to determine the peel and lap shear strength. Adhesion strengths were tested on a Zwick UTM model 1445 with a cross head speed of 50 mm/min. at room temperature as per ASTM 1876(89) - adhesive strength for two flexible adherends. For each result six specimens were tested and the mean was taken.

The leather to leather joints made were kept immersed in water at room temperature for 24 hours. After that the specimens were taken out, dried and thier strengths were determined as per ASTM D 1137 (90). Leather joints were kept in an air oven at 50°C for 24 hours. The specimens were then taken outside, conditioned and strength were determined. The leather pieces were tested after 30 minutes of joining in peel or lap shear form so that the quick stick of the adhesives were obtained. Flexing was given to the leather joints on Ross flex instrument. Number of cycles to failure were noted. Leather in both peel and shear joints were tested for the flex resistance.

2. Bonding of different leather foot wear components:

Types of joints tested:

1. Upper leather to sole leather
2. Upper leather to vulcanised natural rubber sole
3. Upper leather to vulcanised synthetic rubber(SBR) sole
4. Upper leather to microcellular (MC)sole
5. MC to vulcanised natural rubber sole
6. MC to vulcanised synthetic rubber sole.
7. Upper leather to plastic sole
8. Sole leather to plastic sole

Natural rubber (NR) sole, synthetic rubber (SBR) sole and micro cellular (MC) sole were prepared in the laboratory as per the formulations in Table4.1.1. The compounds were prepared on a two roll mill (15 x 30 cm). The optimum cure time was determined on Goefertt elastograph and they were vulcanised on a hydraulic press at 160°C for their optimum cure times. Vulcanised soles were then conditioned for 24 hours and hardness of the soles were measured on a Zwick durometer.

Leather pieces were cut into 150x25 mm size and vulcanised rubber soles were cut into 25x 25 mm size. The leather and rubber pieces were bonded as per IS 4663(68). Rubber and leather pieces were abraded with sand paper no.50 and wiped with MEK solvent and dried. Two leather pieces were taken and in between these pieces the rubber piece was kept and bonded in a sandwich model. The rubber piece was coated with the adhesive on both sides and jointed with the leather pieces. Both peel and lap joints were prepared for strength measurement. For joining MC and leather both the adherends were cut into 150x25mm size. Rubber and MC joints and upper leather to plastic sole were also prepared as above. In all the different types of joints the adhesives prepared were used and strength were determined as above.

Optical microscopic studies

Optical microscopic examination of the roughened and peeled off surfaces of upper leather, sole leather, rubber sole and microcellular sole etc. with CR adhesive was examined. The peeled off surfaces with commercial adhesive Dentrite were also studied by optical photographs.

Results and Discussion:

Figure 4.1.1 shows effect of total solid content on peel and lap shear strength of leather to leather joints. As the solid content increases peel strength increases, reaches a maximum and then decreases. Lap shear strength also shows same trend in this figure. This may be due to lower penetration of adhesives when solid content is very high.

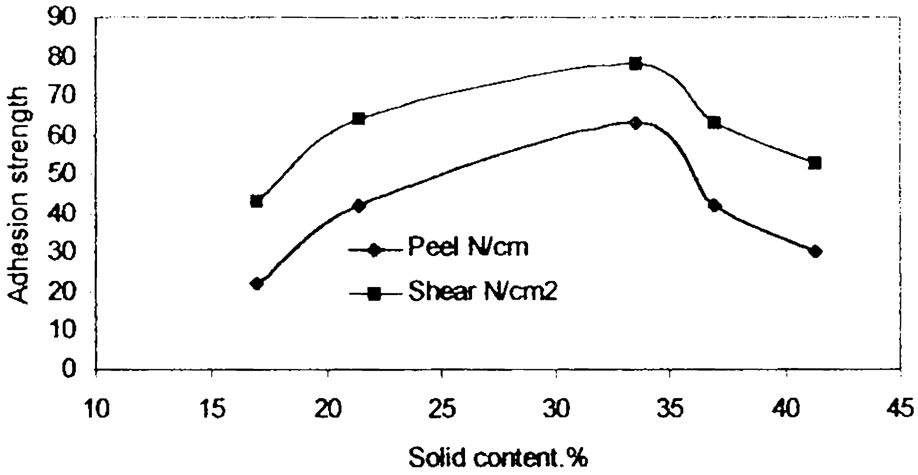


Fig.4.1.1 Effect of solid content on adhesion strength

Figure 4.1.2 shows the effect of viscosity of adhesive to the peel and shear strength of leather to leather joints. When the v iscosity increases joint strength both in peel and shear increases to some extent and then decreases. However,when the viscosity is higher the penetration of the adhesive solution is restricted, resulting in lower peel (series 1) and shear strength (series 2).

Figure 4.1.3 shows the peel strength of different adhesives used for bonding upper leather to upper leather before and after soaking in water. Commercial adhesives show inferior properties compared to the adhesives prepared in laboratory.

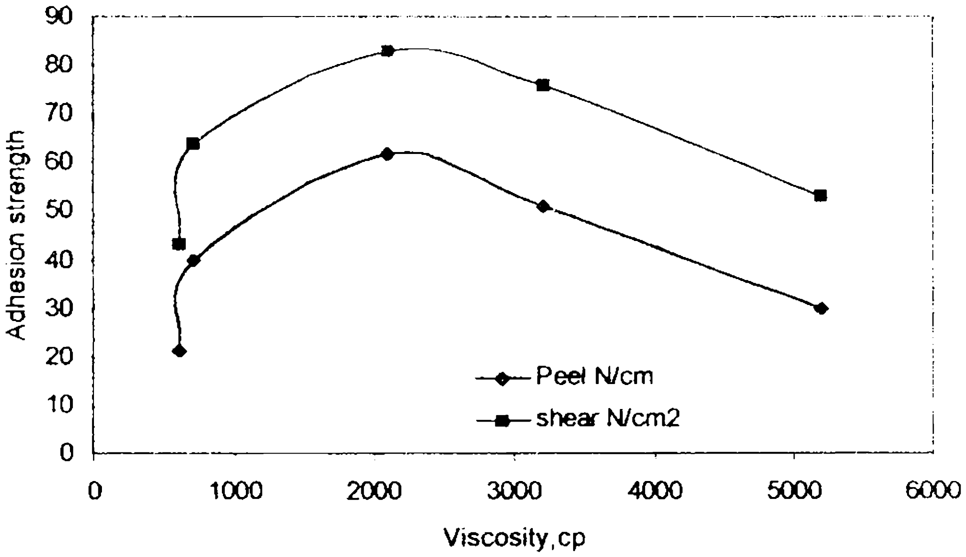


Fig.4.1.2 Effect of viscosity on adhesion strength

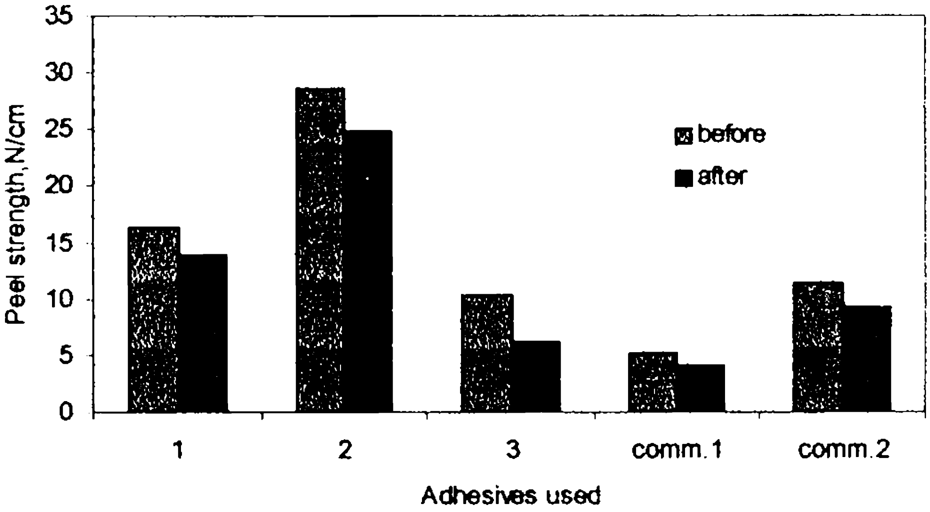


Fig.4.1.3 Effect of water soaking on peel strength of leather joints

Figure 4.1.4 shows the shear strength of leather joints before and after soaking in water. Shear strength of commercial adhesives are found to be much lower than adhesives prepared in laboratory. In both peel and shear strength NR based adhesives show lower strength compared to PVC and CR adhesives. This may be due to the higher polarity of PVC and CR than NR which gives more adhesion strength.

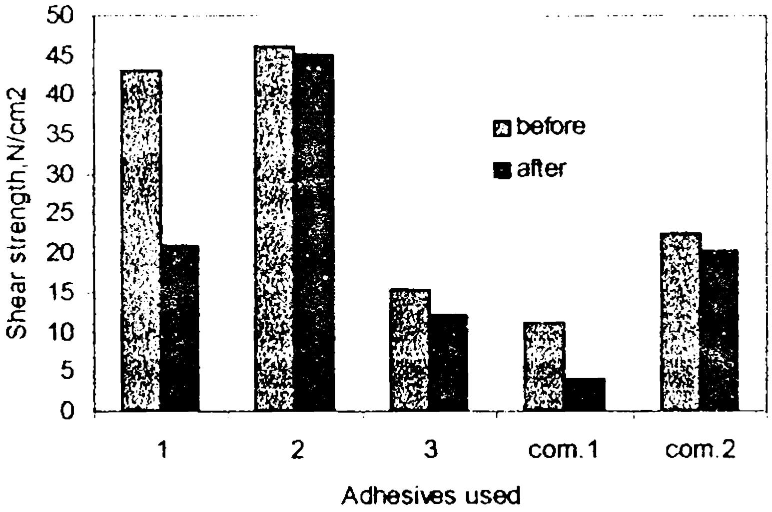


Fig.4.1.4 Effect of hot water on shear strength of leather joints.

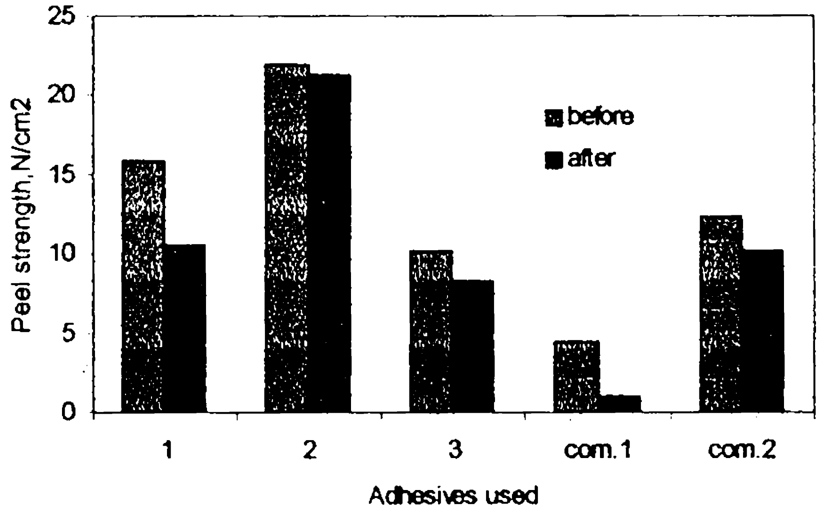


Fig.4.1.5 Effect of ageing on peel strength of leather joints

Figure 4.1.5 shows the peel strength of different adhesives before and after ageing. Adhesives prepared in laboratory are found to be better in ageing resistance compared to commercial adhesives.

Figure 4.1.6 shows the shear strength of different adhesives before and after ageing. Natural rubber solution based adhesive show lower resistance compared chloroprene and PVC based

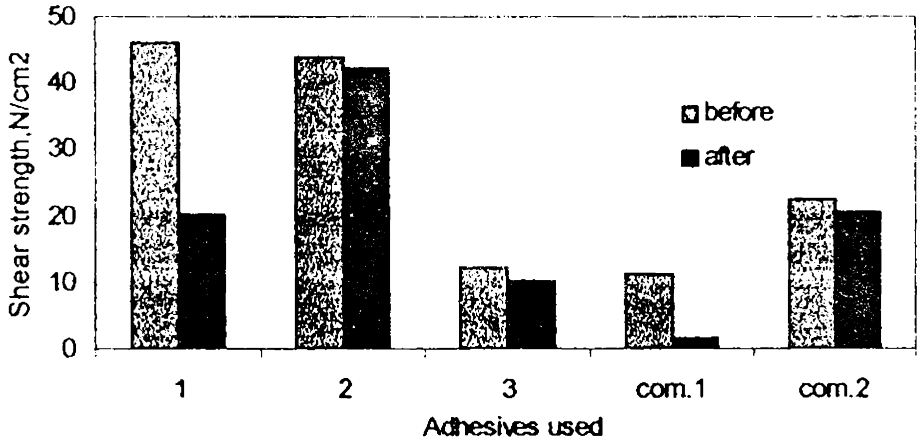


Fig.4.1.6 Effect of ageing on shear strength of leather joints

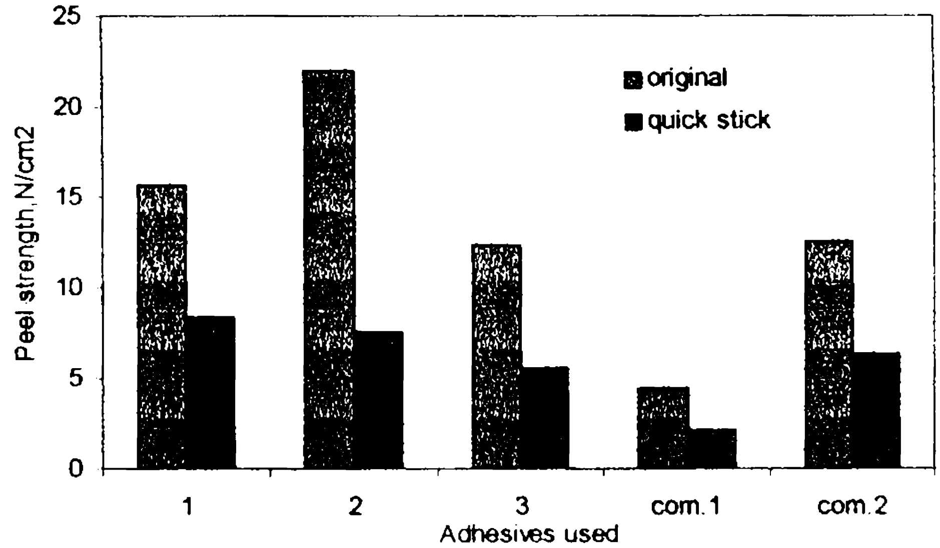


Fig.4.1.7 Quick peel strength of leather joints

adhesives. This may be due to the better ageing resistance of CR and PVC than NR solution. Commercial adhesives show lower ageing resistance compared to adhesive prepared in laboratory.

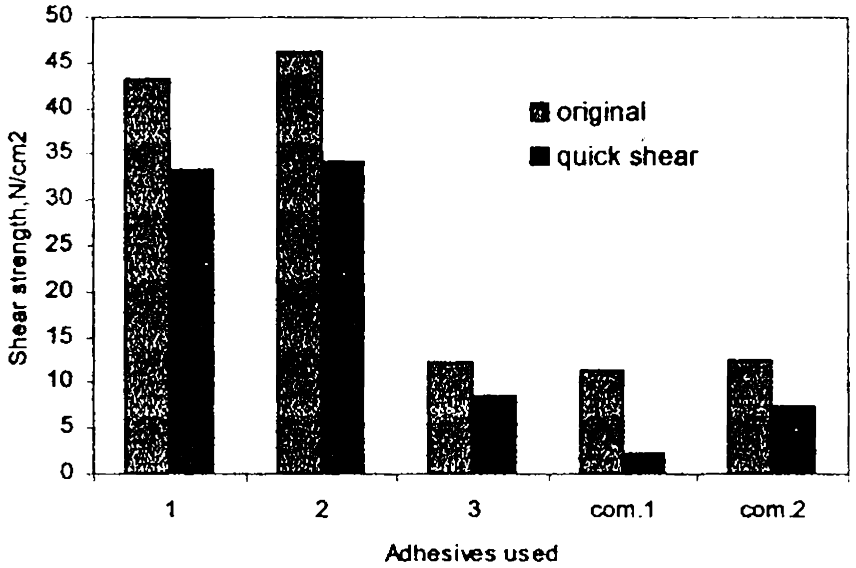


Fig.4.1.8 Quick shear strength of leather joints

Figure 4.1.7 and 4.1.8 show the quick stick values of the different adhesives in peel and shear joints respectively. The quick stick strength in both peel and shear test shows that the adhesives prepared in laboratory are superior to commercial adhesive. The adhesives prepared in laboratory gained the adhesive strength within 30 minutes of time.

Table 4.1.2 shows number of cycles to failure of adhesive joints were failed. The adhesive prepared in laboratory are found to be more resistance to flexing. Flex resistance of commercial adhesives are found to be poor compared to adhesives prepared in laboratory.

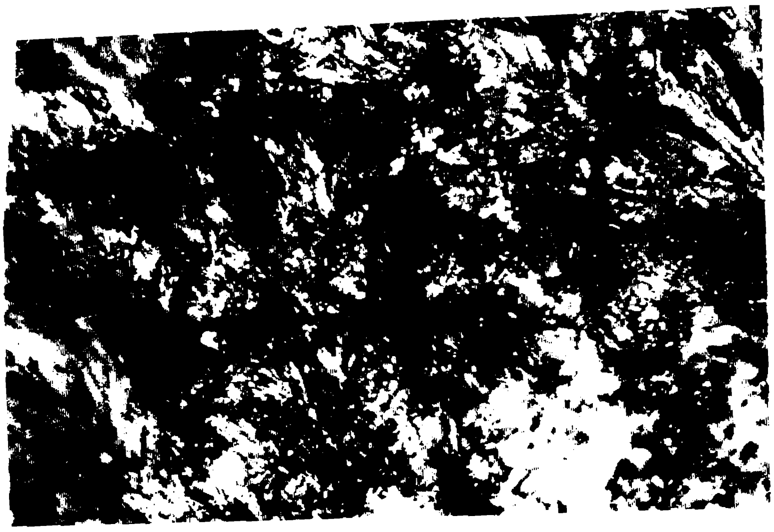
Table 4.1.2 Flex test results:

Adhesives	No. of cycles to failure	
1	peel	2856
	shear	Above 1 lakh
2	peel	15081
	shear	Above 1 lakh
3	peel	16446
	shear	Above 1 lakh
Commercial 1	peel	50
	shear	200
Commercial 2	peel	15046
	shear	Above 1 lakh

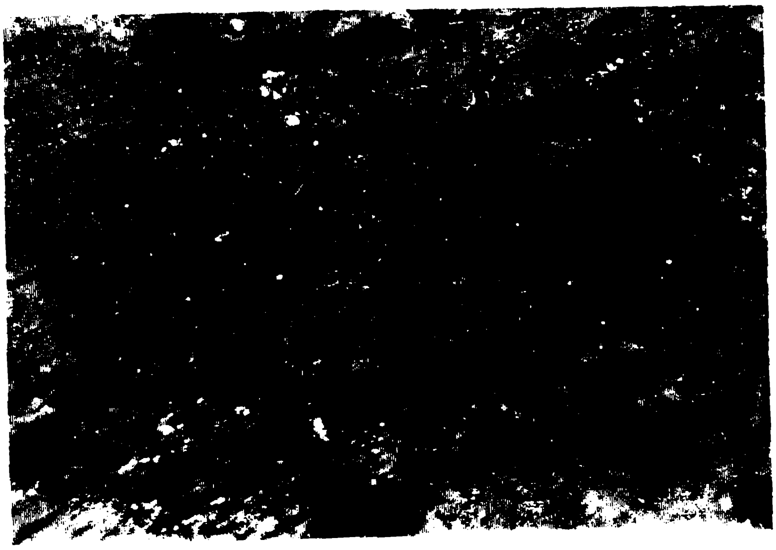
Table 4.1.3 shows the strength of different foot wear components which were jointed with the adhesives prepared in the laboratory. It may be observed that the adhesive prepared in laboratory shows much superior bonding compared to commercial ones.

Table 4.1.3 Strength of the joints of different leather foot wear components

Adhesive	1		2		3		Comm.1		Comm.2	
	peel	shear	peel	shear	peel	shear	peel	shear	peel	shear
1.	11.5	59.5	15.7	43.1	1.44	4.9	1.2	8.6	9.8	25.8
2.	5.8	24.1	12.7	47.0	3.0	8.4	2	8.8	6.8	29.4
3.	4.6	31.7	8.6	22.9	3.5	6.4	0.2	0.4	6.2	24.6
4.	16.4	24.9	13.3	19.9	1.3	5.4	1.5	6.3	10.3	19.5
5.	10.2	28.0	9.5	22.5	5.2	8.1	0.6	2.9	11	18.4
6	12.6	29.4	8.3	27.8	10.6	18.7	0.5	6.1	11.7	18.2
7.	12.6	29.4	8.3	27.8	10.6	18.7	0.5	6.1	11.7	18.2

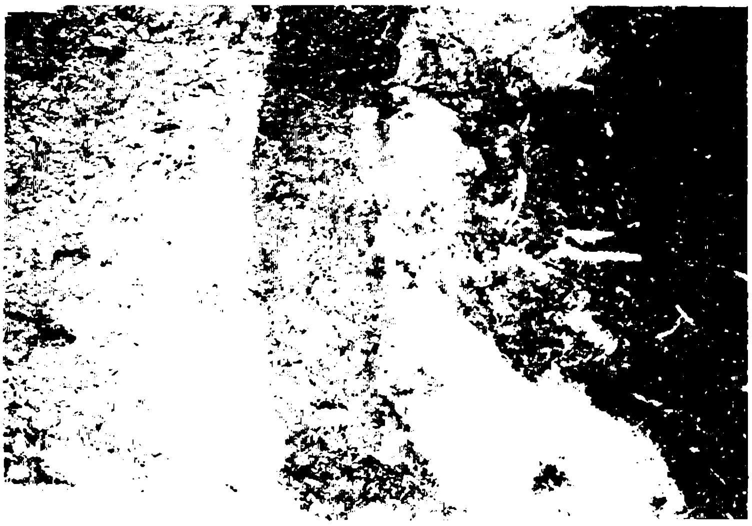


Photograph 4.1.1 Roughed upper leather surface before adhesive application.

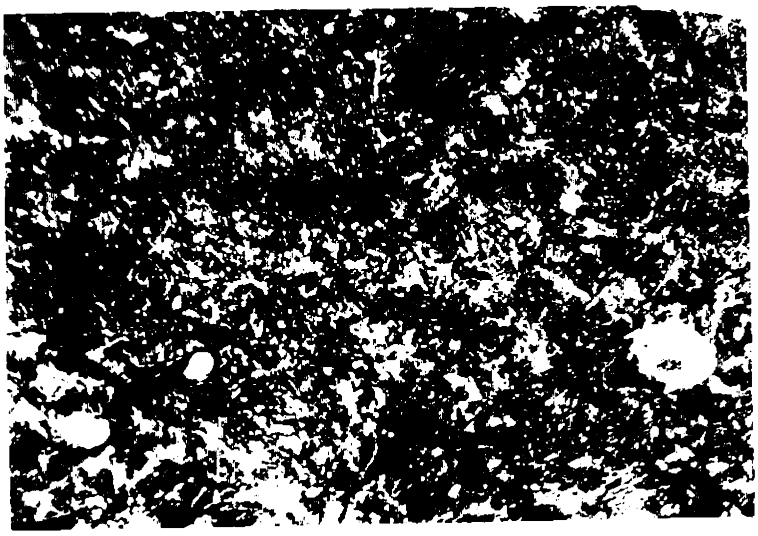


Photograph 4.1.2 Peeled off upper leather surface with laboratory adhesive.

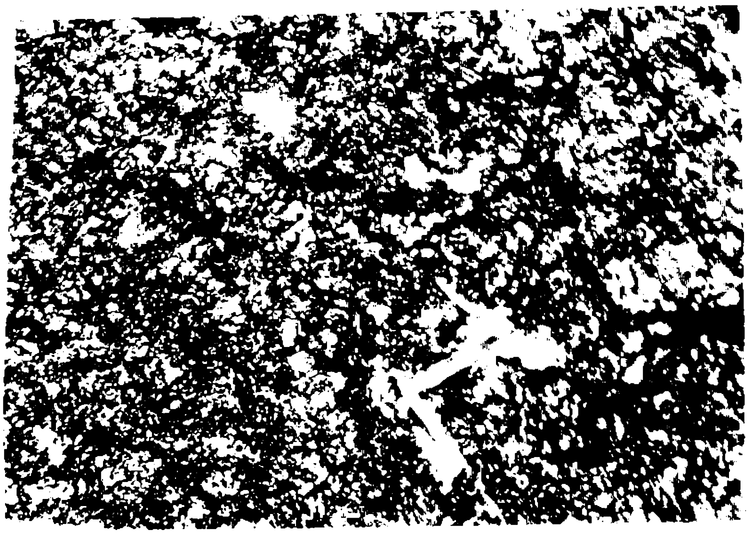
Photograph 4.1.3 Peeled off upper leather surface with commercial adhesive.



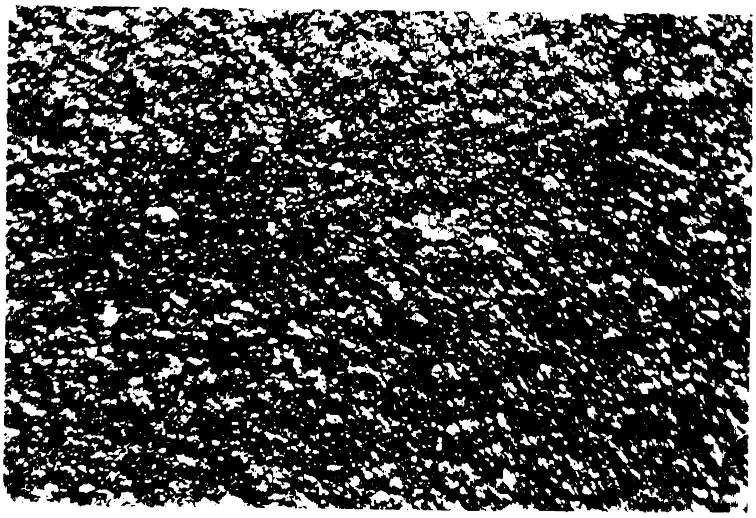
Photograph 4.1.4 Roughed *sole* leather surface before adhesive application.



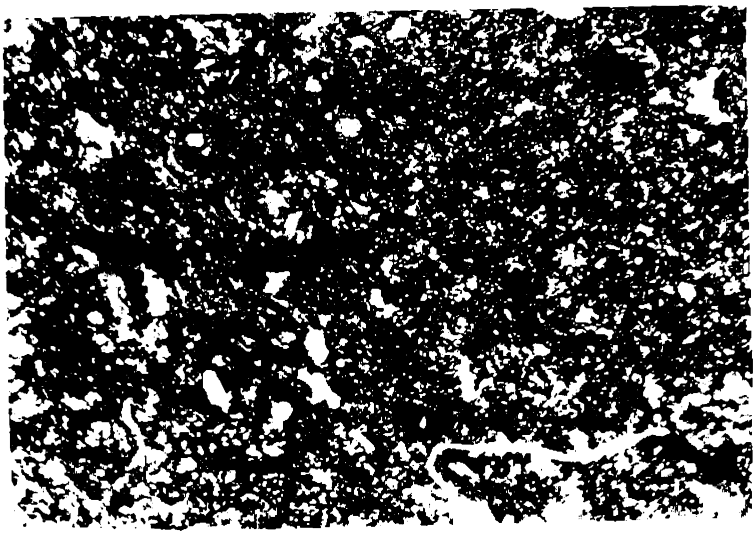
Photograph 4.1.5 Peeled off *sole* leather surface with laboratory adhesive.



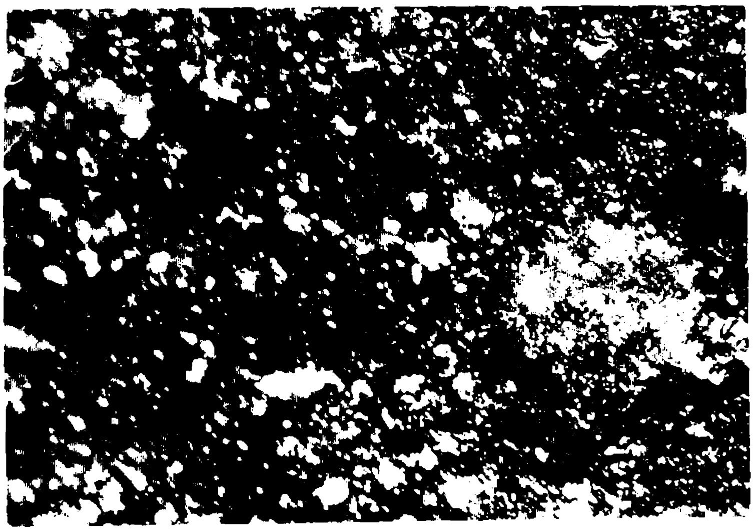
Photograph 4.1.6 Peeled off *Sole* leather surface with commercial adhesive.



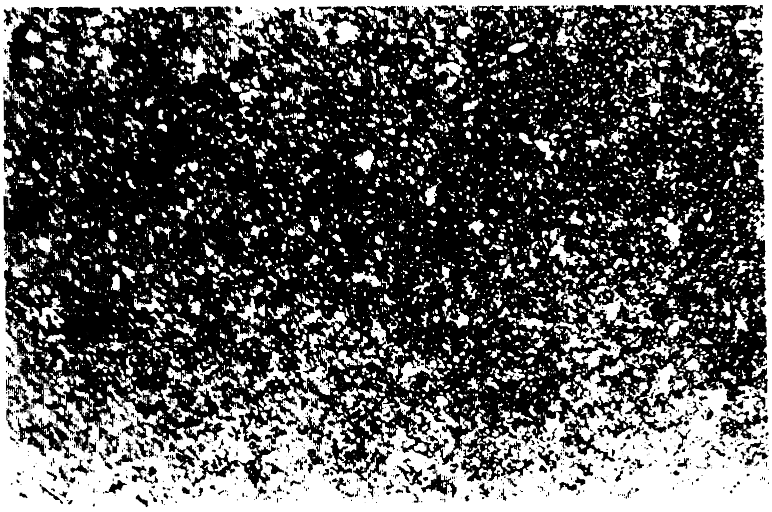
Photograph 4.1.7 Roughed rubber surface before adhesive application.



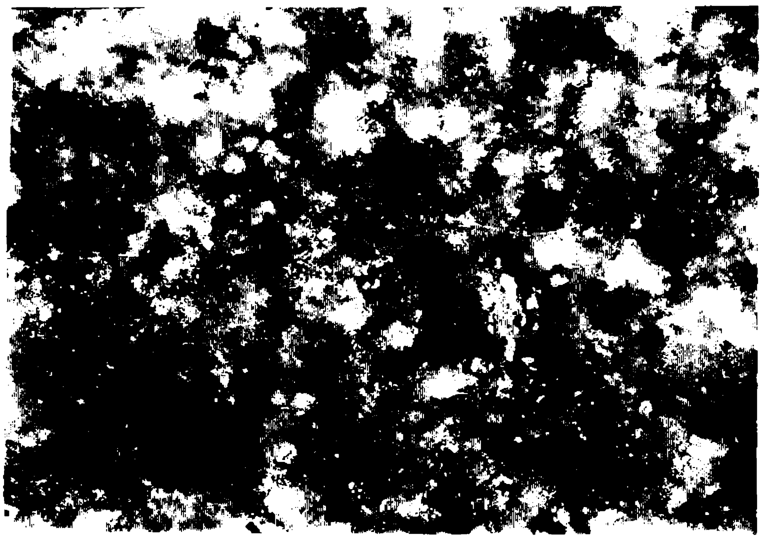
Photograph 4.1.8 Peeled off rubber surface with laboratory adhesive.



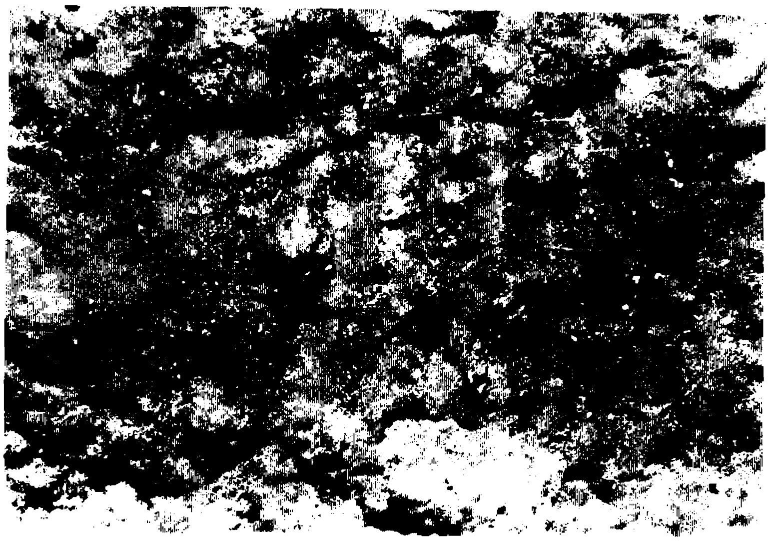
Photograph 4.1.9 Peeled off rubber surface with commercial adhesive.



Photograph 4.1.10Roughed M C surface before adhesive application.



Photograph 4.1.11 Peeled off M C surface with laboratory adhesive.



Photograph 4.1.12 Peeled off M C surface with commercial adhesive.

1. Upper leather to sole leather	5. MC to NR sole
2. Upper leather to NR sole	6. MC to SBR sole
3. Upper leather to SBR sole	7. Upper leather to plastic sole
4. Upper leather to MC sole	

Photograph 4.1.1 shows the roughed upper leather surface and photographs 4.1.2and 4.1.3 show the peeled off surfaces with CR adhesive(laboratory) and commercial (Dentrite) adhesive respectively.

Photograph 4.1.4 shows roughed sole leather surface. Photograph 4.1.5 and 4.1.6 show peeled off surfaces of sole leather with CR adhesive and commercial adhesive respectively.

Photo graph 4.1.7 shows roughed rubber surface. Photograph 4.1.8 and 4.1.9 show peeled off surfaces with CR adhesive and commercial adhesives respectively..

Photograph 4.1.10 shows roughed surface of MC sole. Photograph 4.1.11 and 4.1.12 show peeled off surfaces with CR adhesive and commercial adhesives respectively.

In all the photographs the surfaces of CR adhesives and commercial adhesive are found to be comparable.

Conclusions:

1. Natural rubber, chloroprene rubber and polyvinyl chloride based solution adhesives superior to costly polyurethane based adhesives for bonding leather substrates.
2. The water resistance and ageing resistance of such adhesives are found to be superior compared to the commercial adhesives.
3. Quick stick strength and flex resistance of these adhesives are also superior to commercial adhesives.

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Part 2 Aqueous adhesives for bonding leather components

In recent years concern for the environmental effects of solvents is growing. The increasing awareness of the impact of solvent emissions is leading to greater restrictions on solvent usage[1].

Volatile organic solvent containing preparations such as adhesives and finishes are being restricted nowadays Chlorinated solvents used as cleaners and propellants lead in depletion of the ozone layer in the upper atmosphere which protect us from harmful UV radiations[2]. Solvents participate in photochemical reactions involving nitrogen oxides and sunlight to produce ozone in the lower atmosphere which is harmful to biological processes and a major contribution to smog. Two methods which may be used to avoid such pollution are to use solvent free adhesives and to contain or destroy solvent vapours. Non solvent adhesives such as latex and hot melts are used in footwear industry [3].

In this study, latex based adhesives for bonding leather components are proposed to be developed. The peel and shear strength of the adhesive joints are proposed to be tested and the resistance of the joints under different environments and shelf life of the adhesives are also to be determined.

Experimental

NR ,VP and XNBR latices were compounded according to the formulations in Table 4.2.1. Leather pieces were bonded using these compounds and their peel and shear strengths were determined as explained in part 1 of chapter 4.

Table 4.2.1 Formulations for latex adhesives, Phr

Ingredients	NR latex	VP latex	XNBR latex
NR latex	100		
VP latex		100	
XNBR latex			100
KOH	0.1	0.1	0.1
Ammo. caseinate	5	5	5
Starch	2.5	2.5	2.5
RF resin	7.5	7.5	7.5
CMC	10	10	10

In order to compare the adhesion strength with a commercial latex based adhesive, joints made with Fevicol were tested for peel and shear strength.

Results and Discussion

Figures 4.2.1 and 4.2.2 show the effect of ammonium caseinate in NR,VP and XNBR latices for peel and shear strength of leather joints respectively. Ammonium caseinate acts as a thickener in latices and increases the adhesion strength of the bonds initially, but after an optimum amount there is a reduction in adhesion strength. When the amount of thickener increases above the optimum level the inherent tackiness of latex molecules may get affected reducing the bond strength .

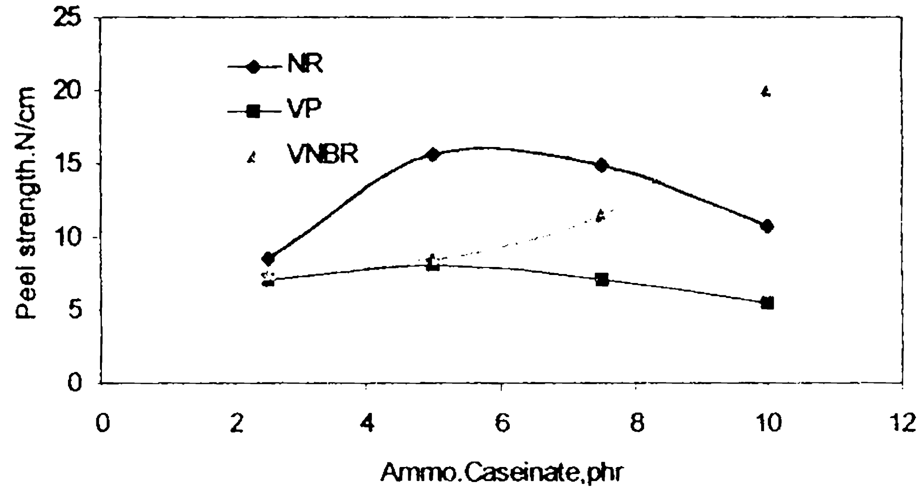

Fig.4.2.1 Effect of ammo.caseinate on peel strength

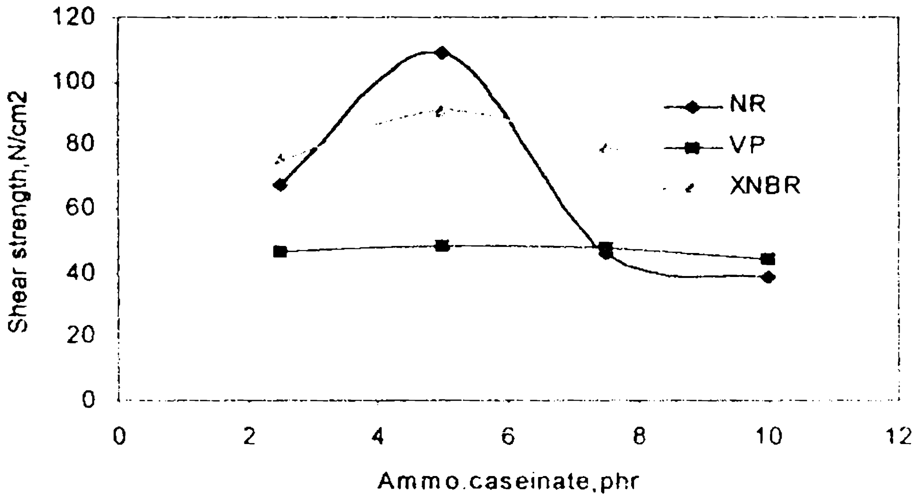

fig.4.2.2 Effect of Amm.caseinate on shear strength

Figures 4.2.3 and 4.2.4 show the effect of carboxy methyl cellulose in NR, VP and XNBR latices on peel and shear strength respectively. CMC is found to increase the tackiness of latex particles thereby enhancing the adhesion strength. As the amount of CMC increases above 10 phr there is an increase in the viscosity of the adhesive and lacks its spreadability.

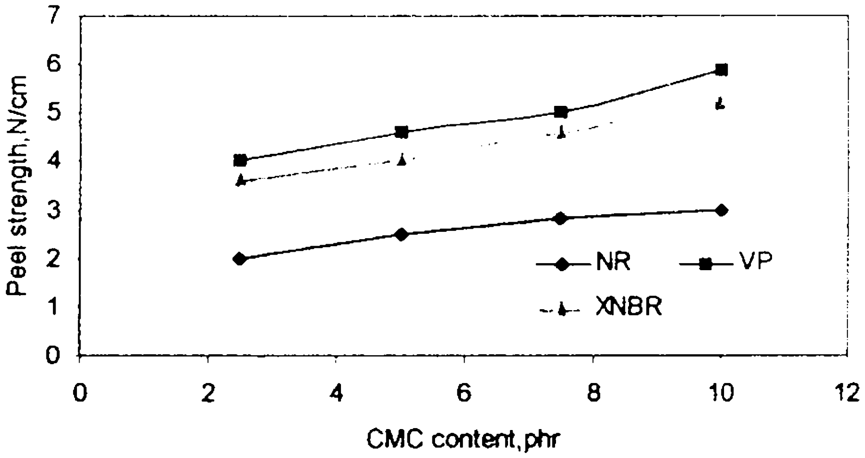

Fig.4.2.3 Effect og CMC on peel strength of leather joints

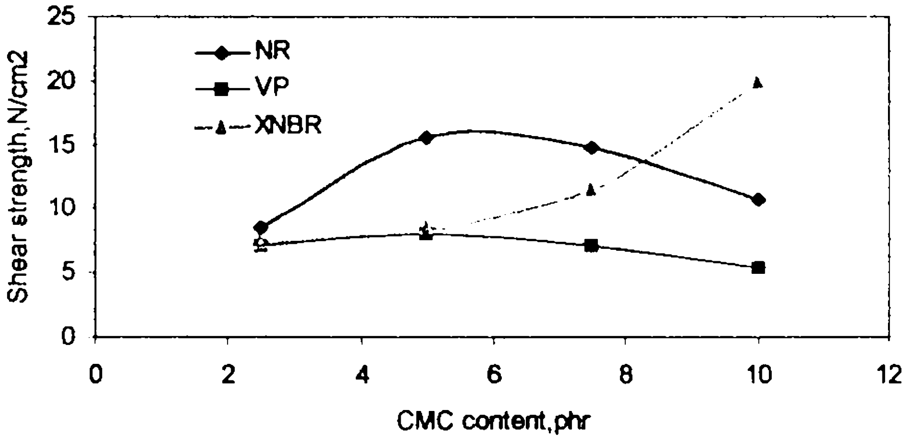

Fig.4.2.4 Effect of CMC on shear strength

Figures 4.2.5 and 4.2.6 show the peel and strengths of leather joints with the variation of resorcinol formaldehyde (RF 1) resin content in the latices. When the RF resin content increases peel and shear strength of leather joints increase, reach a maximum and then decrease. Resin increases adhesion strength up to an optimum level, but further increase of resin may increases the modulus of the adhesive films resulting in stiffening of the adhesive joints thus reducing the adhesion strength [4]. The same pattern is observed for all the three cases, NR latex based shows highest adhesion strength followed by VP and XNBR.

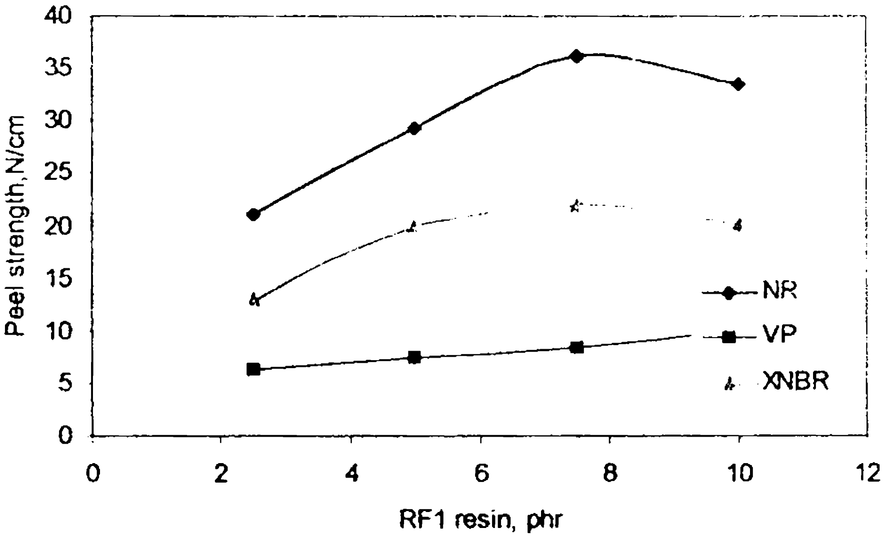

Fig.4.2.5 Effect of RF1 resin on peel strength of leather joints

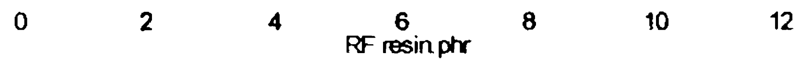

Fig4.2.6 Variation of shear strength with RF 1 resin content

The variation of cooked starch content in NR, VP, XNBR latices on peel and shear strength is shown in figures 4.2.7 and 4.2.8 respectively. There is a slight reduction in bond strength as the amount of starch is increased from 2.5 to 10phr as expected. In leather joints starch causes slight reduction in bond strength and water resistance [5].

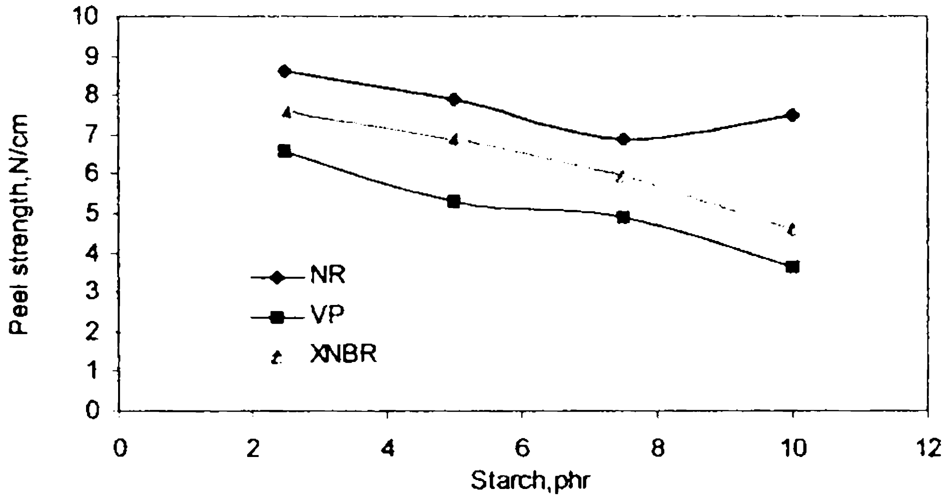

Fig.4.2.7 Effect of starch on peel strength of leather joints

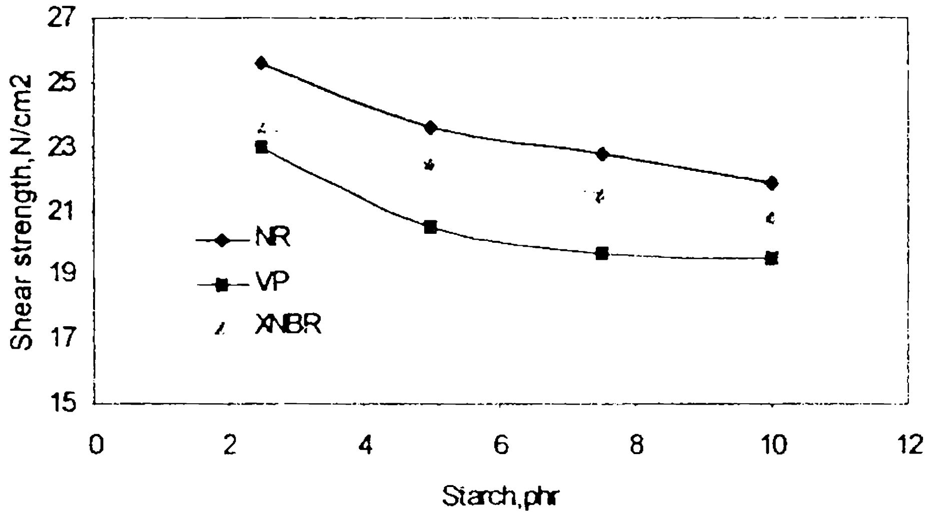

Fig.4.2.8 Effect of starch on shear strength

Figures 4.2.9 and 4.2.10 show the peel and shear strength of leather joints before and after soaking in water. From this it is clear that NR latex based adhesive shows highest strength compared to other latices. This may be due to the higher solid content of NR latex. XNBR latex based adhesive shows better bonding strength compared to VP latex. However, there is some reduction in adhesive strength for all the adhesives due to the presence of water.

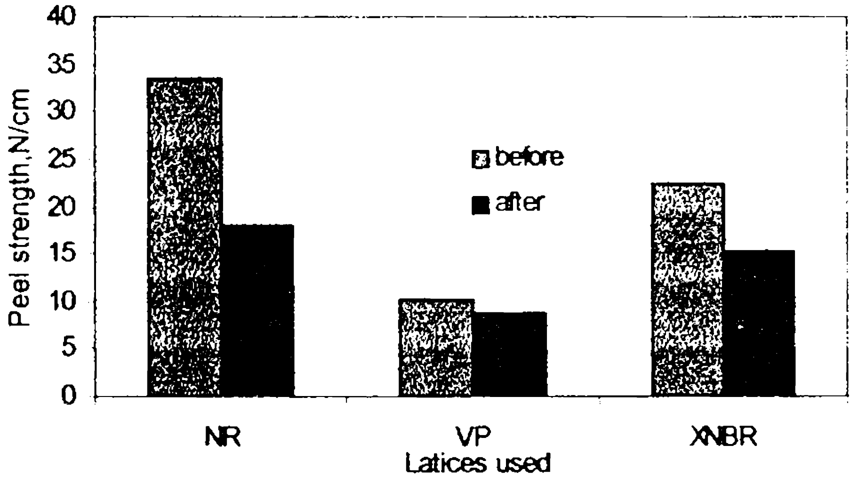

Fig.4.2.9 Effect of water soaking on peel strength

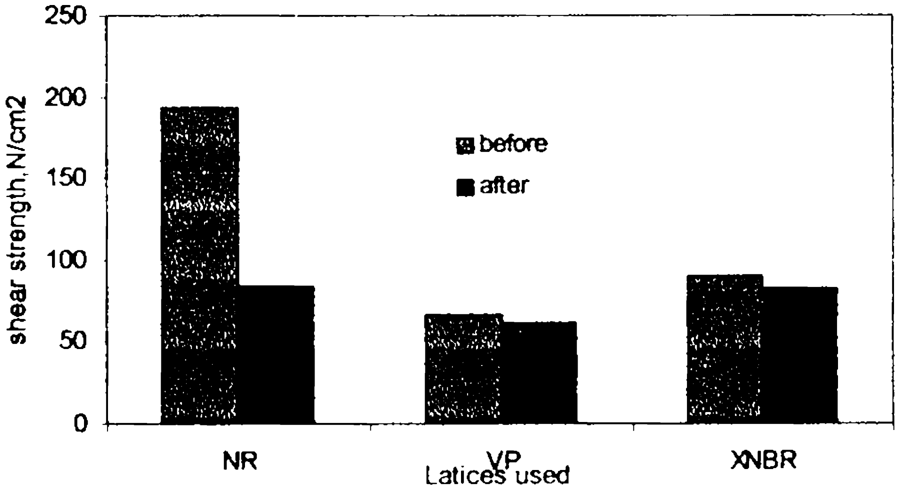

Fig.4.2.10 Effect of water soaking on shear strength of leather joints

Figures 4.2.11 and 4.2.12 show the peel and shear strength of joints before and after soaking in hot water at 80°C. In the cases of VP and XNBR latices slight crosslinking may occur which may be the reason for increase in adhesion strength. But in NR latex slight decrease in strength is observed which may be due to naturally occurring easily decomposable materials present in NR latex.

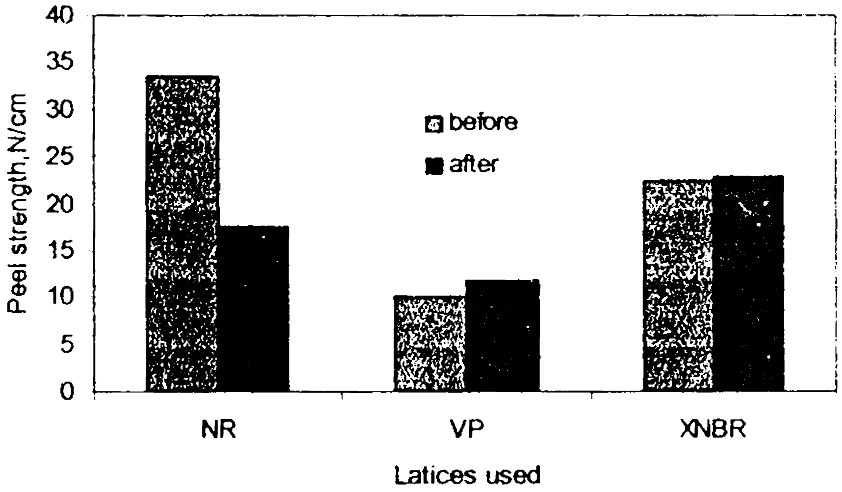

Fig.4.2.11 Effect of hot water on peel strength

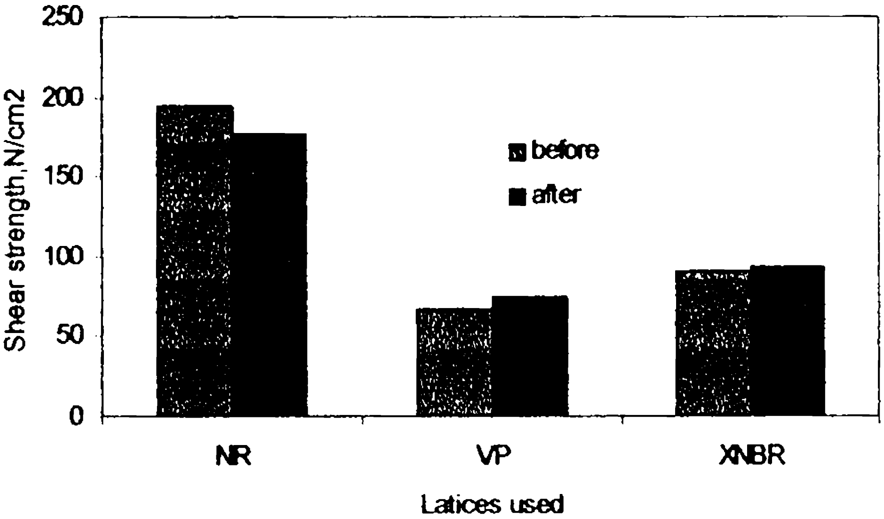

Fig.4.2.12 Effect of hot water on shear strength

Figures 4.2.13 and 4.2.14 show the peel and shear strength of leather joints before and after ageing in air oven at 50 °C. Leather pieces joined with NR latex based adhesive show more decrease in strength compared to other two latices. This may be due to the higher degradation of NR latex.

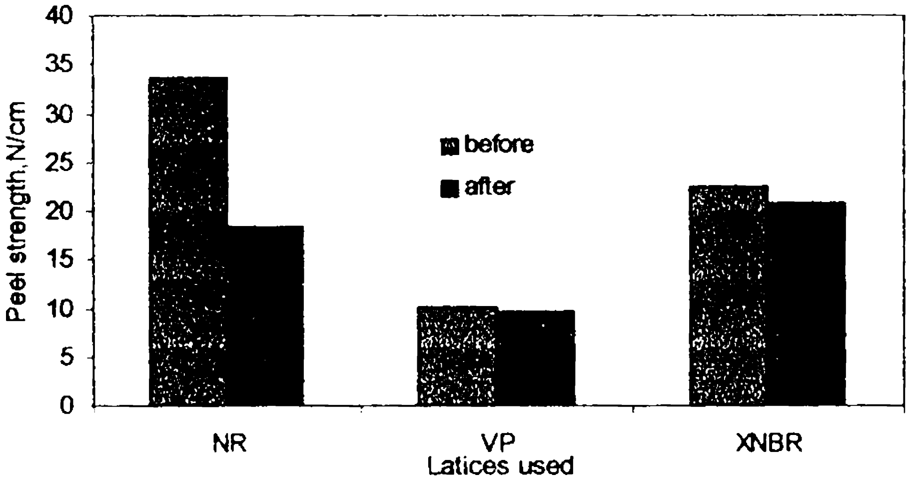

Fig.4.2.13 Effect of ageing on peel strength

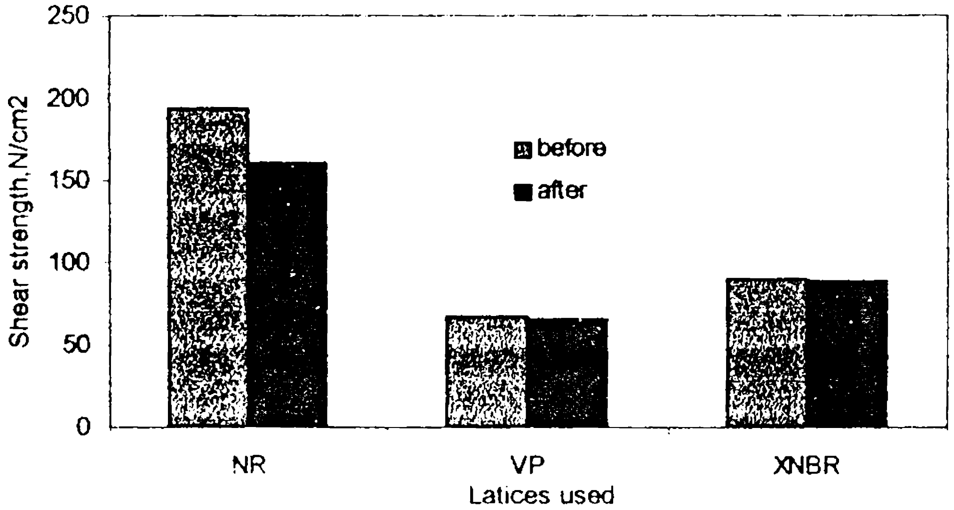

Fig.4.2.14 Effect of ageing on shear strength

The quick peel and shear strength of latex based adhesives are shown in figures 4.2.15 and 4.2.16. All the three latices attain almost full joint strength within 30 minutes.

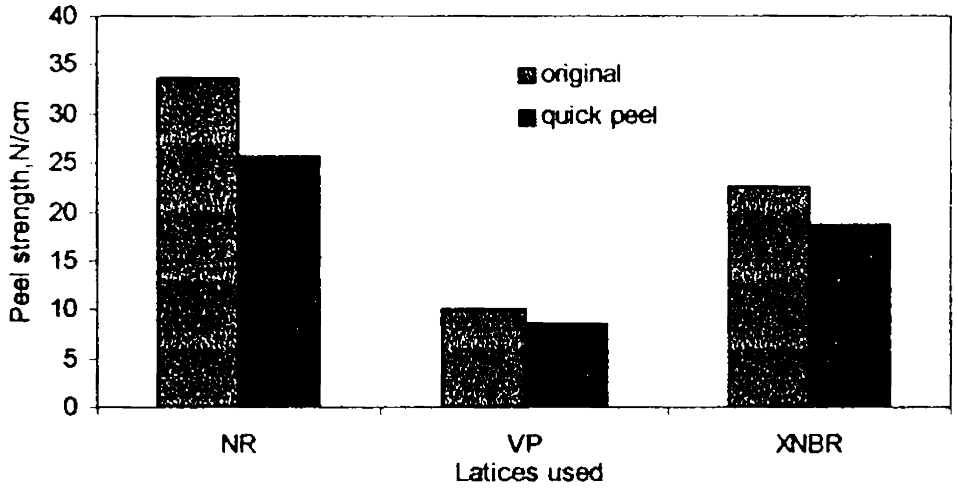

Fig.4.2.15 Quick peel strength of leather joints

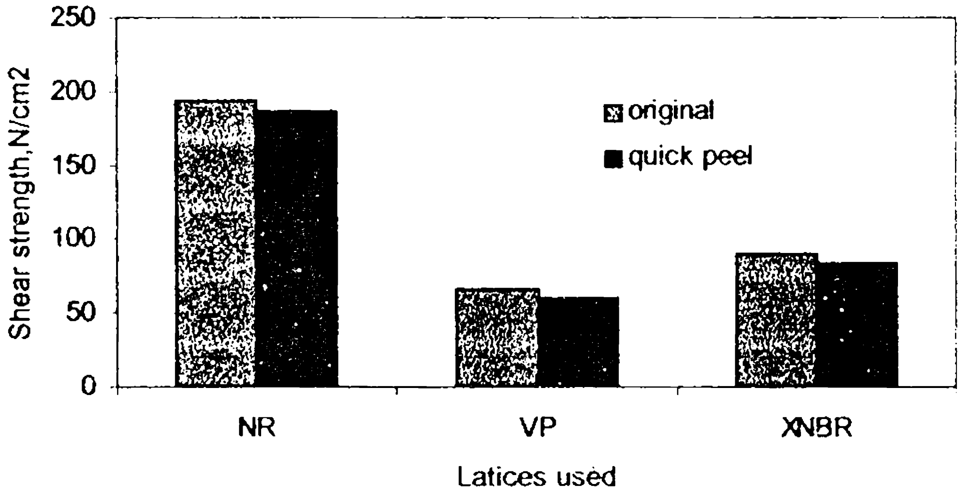

Fig.4.2.16 Quick shear strength of leather joints

The peel and shear strength of latices stored for one to four weeks are shown in figure 4.2.17 and 4.2.18. NR latex shows slightly more reduction in peel and shear strength compared to VP and XNBR latices. This may be due to the comparatively low storage stability of NR latex. So for better storage stability synthetic latices may be preferred to natural latex.

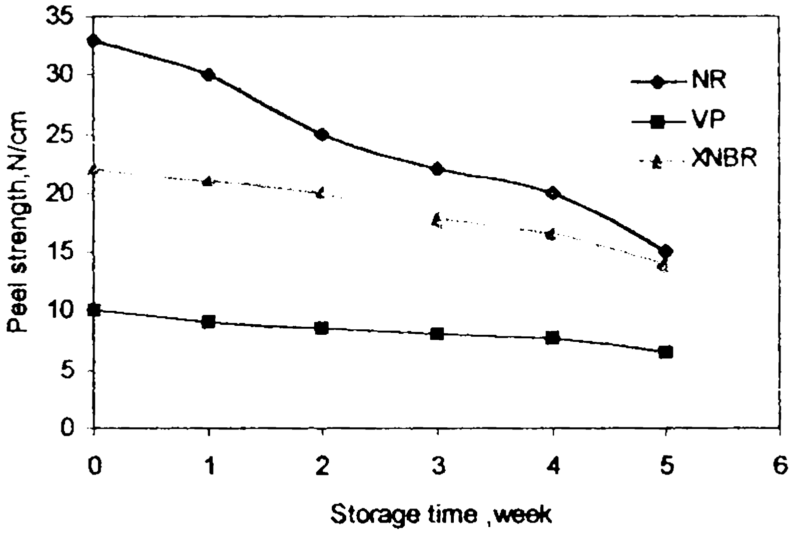

Fig.4.2.17 Effect of storage of latices on peel strength

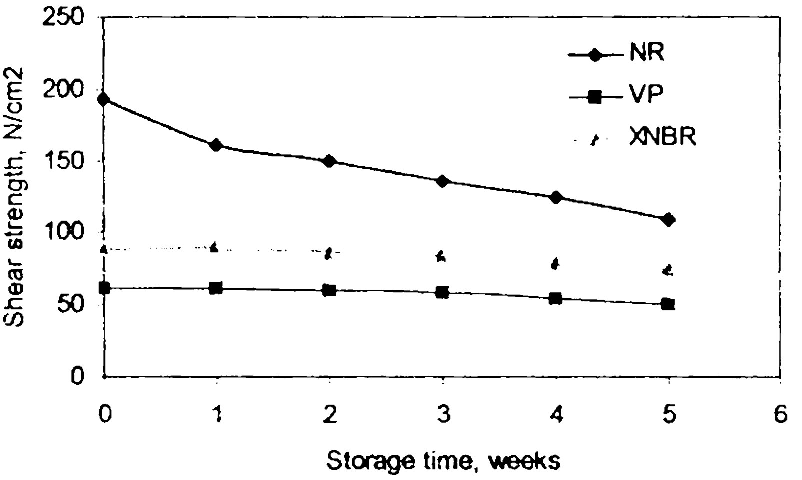

Fig.4.2.18 Effect of storage of latices on shear strength

Table 4.2.2 shows the peel and shear strength of different leather components jointed using the latex based adhesives. The strength of joints made of NR latex based adhesives are found to be superior compared to other two latices. This may be due to the highest solid content of centrifuged latex.

Table 4.2.2 adhesion strength of different components by latex adhesives

Adhesives	NR latex		VP latex		XNBR latex	
	peel N/cm	shear N/cm^2	peel N/cm	shear N/cm^2	peel N/cm	shear N/cm^2
Upper leather to sole leather	3.5	68.2	5.3	44.4	10.9	70.7
Upper leather to NR sole	3.4	28.4	5.0	20.3	8.91	25
Upper leather to SBR sole	3.5	28.5	5.4	23.0	9.0	17.7
Upper leather to Mc sole	9.4	24.3	9.3	13.8	10.1	10.9
Mc to NR sole	4.3	16.9	8.4	12.2	8.3	10.9
Mc to SBR sole	6.4	10.9	8.0	11.1	8.1	11.9
Upper leather to plastic sole	10.2	25.6	8.2	23.2	8.3	20.3

Table 4.2.3 shows the results in comparison with the commercial latex based adhesive-Fevicol. The peel and shear strength of upper leather to upper leather is shown here.

Table 4.2.3 Comparison of latex adhesives

Latex adhesives	Peel strength, N/cm	Shear strength,N/cm^2
NR	30.5	193.5
VP	12.2	61.5
XNBR	20	90.8
Fevicol	12.1	120.3

Conclusions

1. Latices of NR, VP and XNBR can be used to prepare adhesives for bonding leather components.
2. Ammonium caseinate and CMC can be used as modifiers to increase the adhesion strength.
3. Starch can be used as a filler in latex based adhesives without much deterioration in properties.
4. An optimum level of resorcinol formaldehyde resin can increase bond strength.
5. Compared to synthetic latices natural rubber latex shows marginally lower ageing resistance.
6. NR latex based adhesive for leather shows superior bond strength compared to commercial latex based adhesive-Fevicol.

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Part 3 Studies on novel low cost adhesive system for bonding different components in leather products.

In leather product industry many dissimilar adherends are jointed using different types of adhesives. The joining mechanisms relate to include the complex chemistry of the adherend surfaces[1].

Polyurethane based adhesives are widely used in the leather industry. These adhesives have disadvantages like low tack, shorter pot life and limited durability[2] In foot wear manufacture different adherends like upper leather, sole leather, rubber sole, plastic sole, micro cellular sole s etc. are bonded using adhesives[3]. The adhesive used should be compatible with all the adherends used and must comprise of low cost and easily available components[4]

In this part of the study, adhesives from blends of thermoplastic elastomer solutions are proposed to be developed and evaluated for bonding leather.

Experimental

Two types of adhesives based on thermoplastic elastomers from rubber/plastic blends were prepared and investigated for leather to leather bonding. The efficiency of such adhesives was compared with those of commercial adhesives. Polyureathane based (Commercial 1) and dentrite (Commercial 2).

This part of the study also being patented The auther requests to be excused for not giving the details of the materials and formulations.

Leather components were jointed with the adhesives prepared and also with the commercial adhesive(Dentrite). The peel and shear strengths of the joints were determined as per procedures explained in part 1 of this chapter.

Results and discussion

Figure 4.3.1 shows the variation of peel and shear strength of leather joints when the viscosity of the adhesive blend type 1 changes. This shows that on decreasing the viscosity the adhesion strength decreases. On reducing the viscosity the solvent content increases and solid content decreases thus adhesion strength reduces. Similar behaviour is observed for blend 2

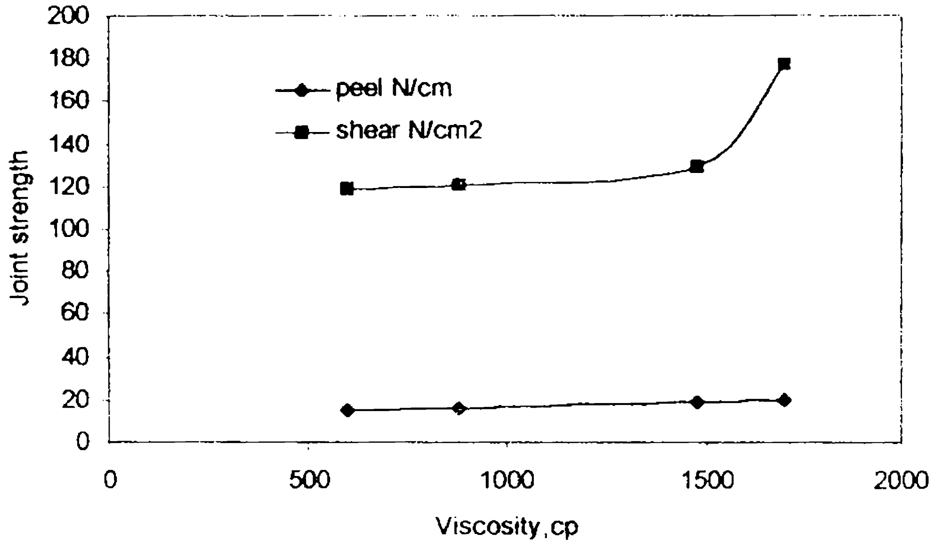

Fig.4.3.1 Effect of viscosity on joint strength of blend1 adhesive

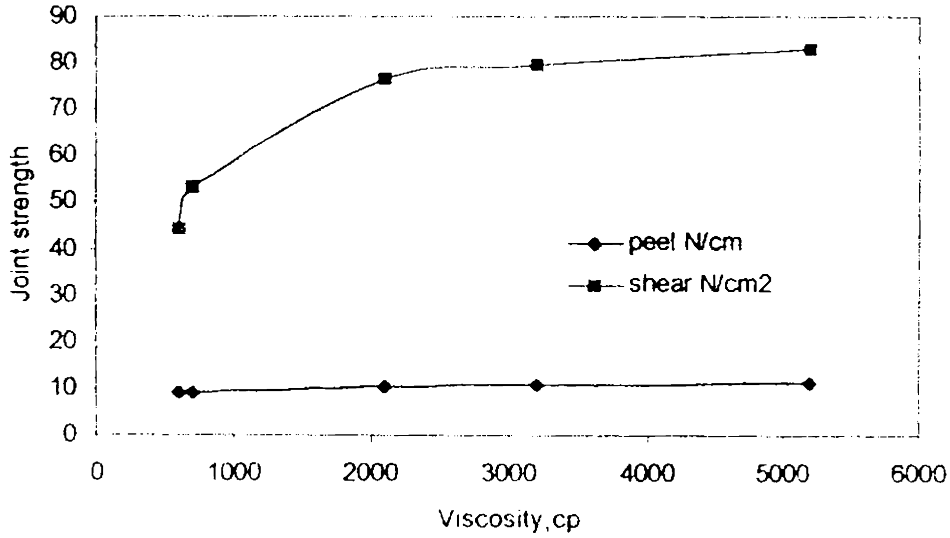

Fig.4.3.2 Viscosity of blend2 adhesive on joint strength

(figure 4.3.2) also. Higher viscosity if preferred for better strength but when viscosity increases more than an optimum level the spreadability of the adhesive over the adherend decreases. So we maintain a viscosity of around 1000cp.

Figure 4.3.3 shows the effect of peel strength of leather joints when the amount of thermoplastic content varied. When thermoplastic content is zero strength were very low in both types blends. But when TP content increases peel strength increases as modulus of the adhesive film increases [5] Thermoplastic alone is used then also peel strength is lower. This may be due to the unique property of thermoplastic elastomers. In blend 2 the strength of adhesive film is low so that adhesion strength also found to be lower. Similar behaviour was obtained as in the case of shear strength also in figure 4.3.4.

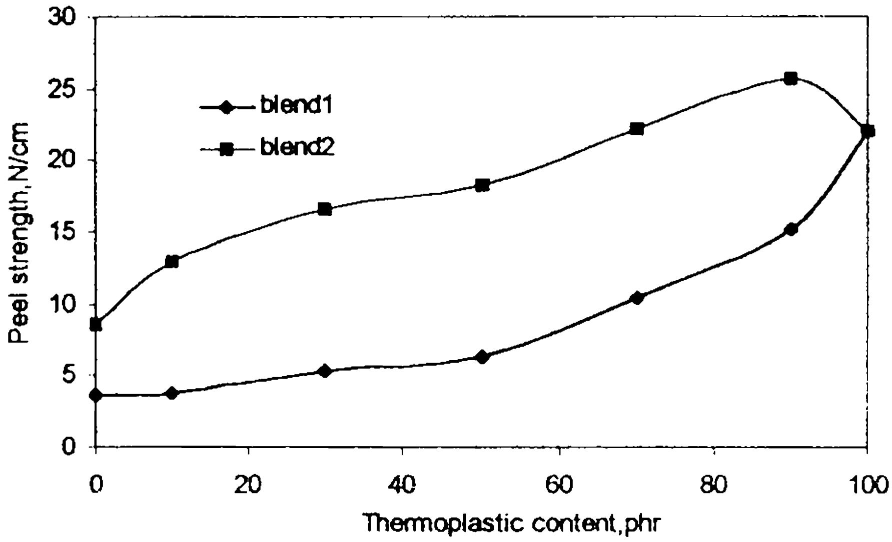

Fig.4.3.3 Effect of thermoplastic content on peel strength of leather joints

Figures 4.3.6 and 4.3.5 show the effect of tackifier resin in peel and shear strength of leather adhesives based on thermoplastic elastomer solutions respectively. Peel strength of the joints decreases as resin content increases but as resin content increases shear strength (fig.4.3.5)

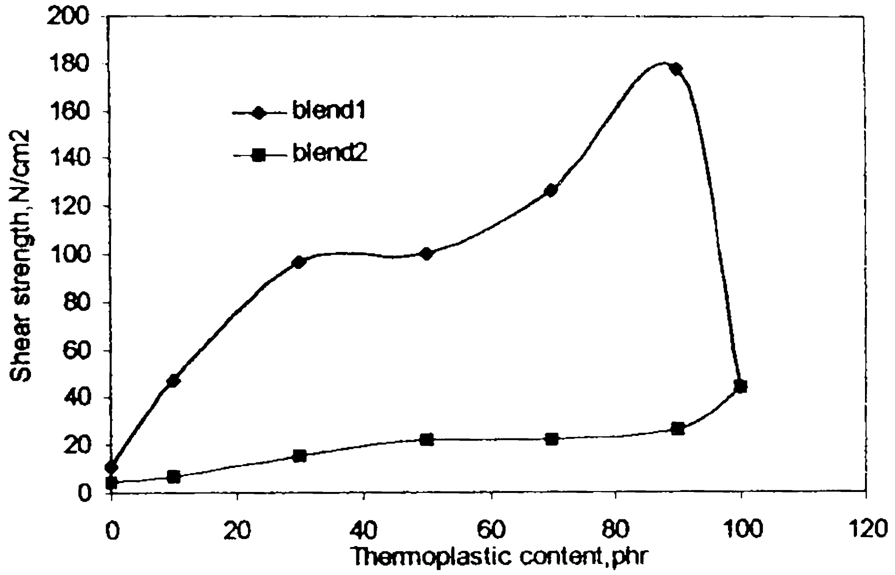

Fig.4.3.4 Effect of thermoplastic content on shear strength

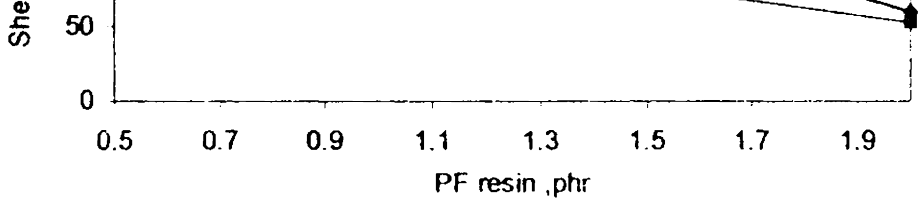

Fig.4.3.5 Effect of PF resin on shear strength of leather joints

increases reaches a maximum and then decreases in both types of adhesives.Thi shows that resin present cannot increase the inherent strength of thermoplastic elastomers. As solid content increases peel strength does not increases as in the case of shear strength[6] . So shear strength initially increases when the resin is added to the adhesive.

Figures 4.3.7 and 4.3.8 show the effect of a plastisicer in the thermoplastic elastomer based adhesives on peel and shear strength of leather joints respectively. As the amount of

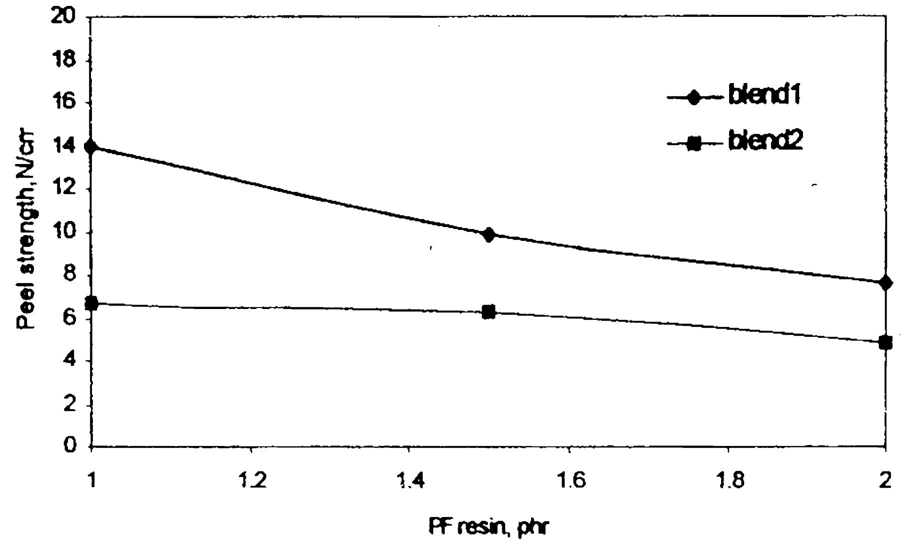

Fig.4.3.6 Effect of PF resin on peel strength

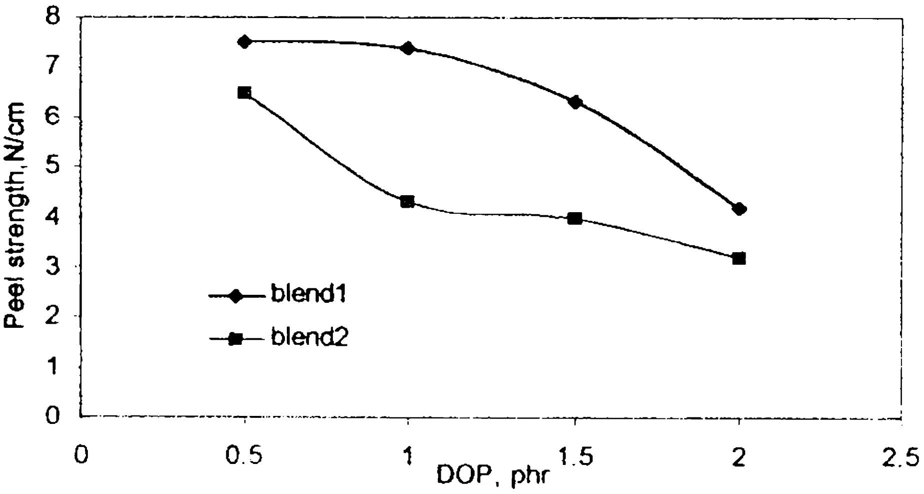

Fig.4.3.7 Effect of DOP on peel strength of leather joints

plastisicer increases peel and shear strength of both the blends decreases. Plastisicers are used to flexibilise the adhesive bonds but it reduces the adhesion strength of the joints [7]. This may be due the more cohesive nature of the adhesive while plastisicer content increases.

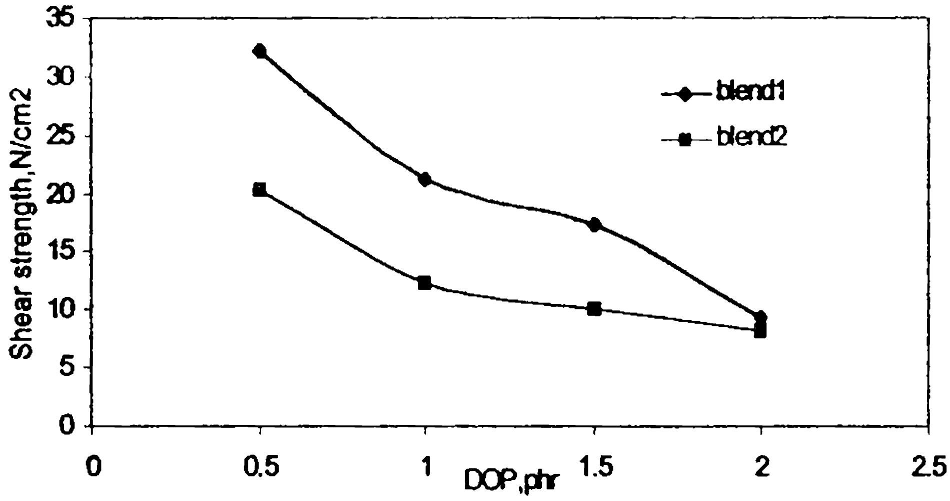

Fig.4.3.8 Effect of DOP on shear strength

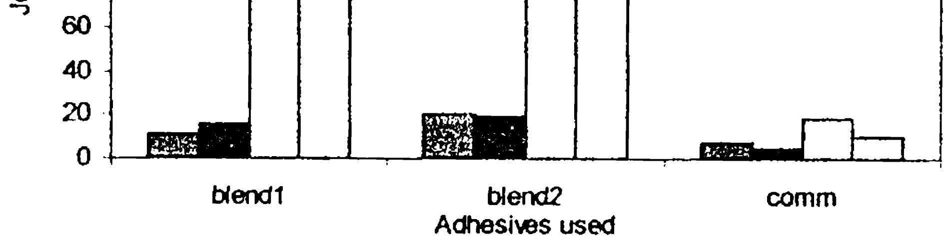

Fig.4.3.9 joint strength variation after soaking in water

Figure 4.3.9 shows the peel and shear strength of leather joints before and after soaking in water. Strength of commercial adhesive(2) is also shown in the figure for comparison. Adhesives based on thermoplastic elastomers are found to display much improved water resistance.

Figure 4.3.10 shows the effect of peel and shear strength of leather joints before and after soaking in hot water. This figure also shows the superior water resistance of the thermoplastic elastomer based ashesives to commercial adhesive(2) ones.

Figure 4.3.11 shows the ageing behaviour of the adhesives. Both types of thermoplastic elastomer based adhesives show better ageing resistance than commercial adhesive(2). Here

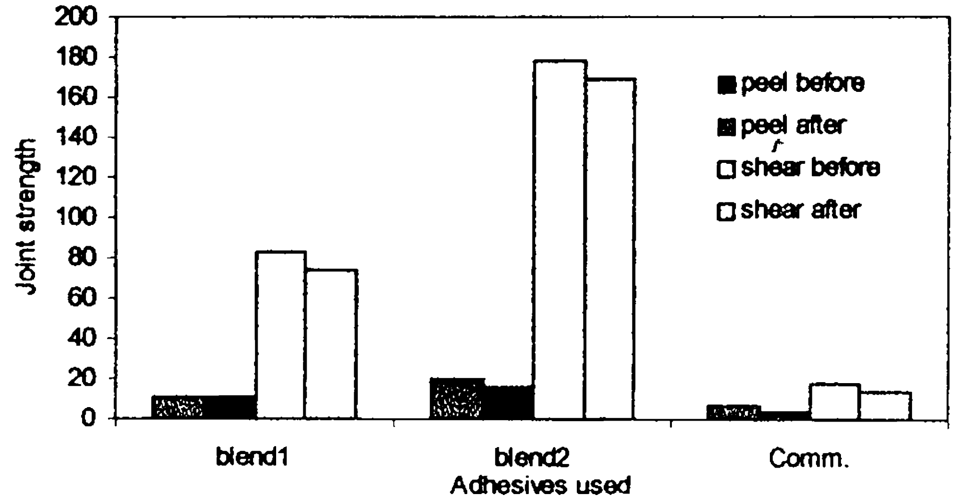

Fig.4.3.10 Effect of hot water on joint strength of leather bonds

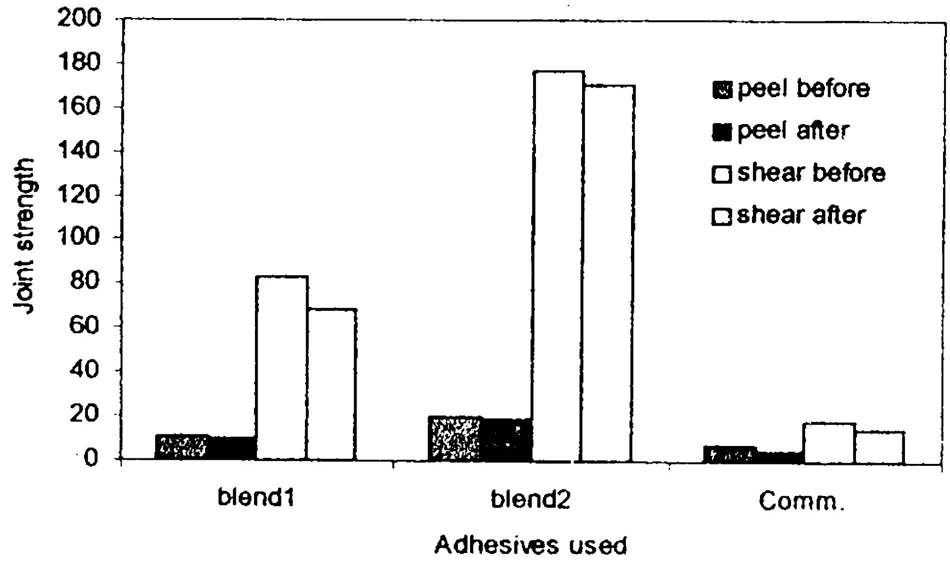

Fig.4.3.11 Effect of ageing on joint strength

also the thermal and ageing resistance of the thermoplastic adhesives are evident.

Figure 4.3.12 shows the quick stick resistance of the adhesives. In this case we can see that thermoplastic elastomer based adhesives attain 80 % of their original strength within 30 minutes of bonding. Commercial adhesive(2) have only lower strength compared to the thermoplastic elastomer based adhesives. Thermoplastic elastomer based adhesives are found to be quick drying and attain the ultimate strength quickly. So the production rate with this type adhesives can be higher.

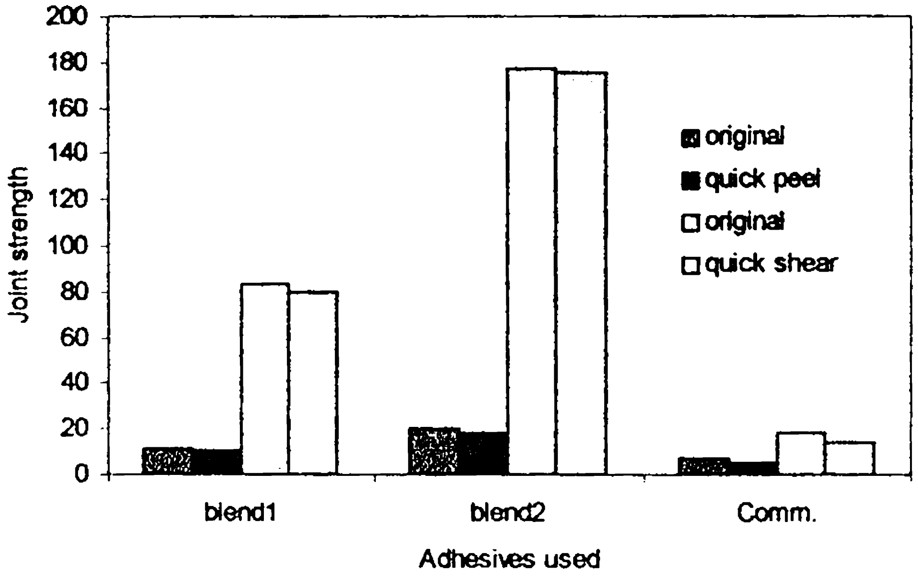

Fig. 4.3. 12 Quick stick strength of leather joints

Figure 4.3.13 shows the effect of storage on peel strength of leather joint with thermoplastic elastomer based adhesives. When these adhesive are stored adhesion strength is found to be increasing. This may be due the slight increase in solid content due the evaporation of solvents. From this figure it is evident that on storage the strength of the adhesives does not get dreduced as so they have enough storage stability. Figure 4.3.14 shows the effect of shear strength on storage of the adhesives.

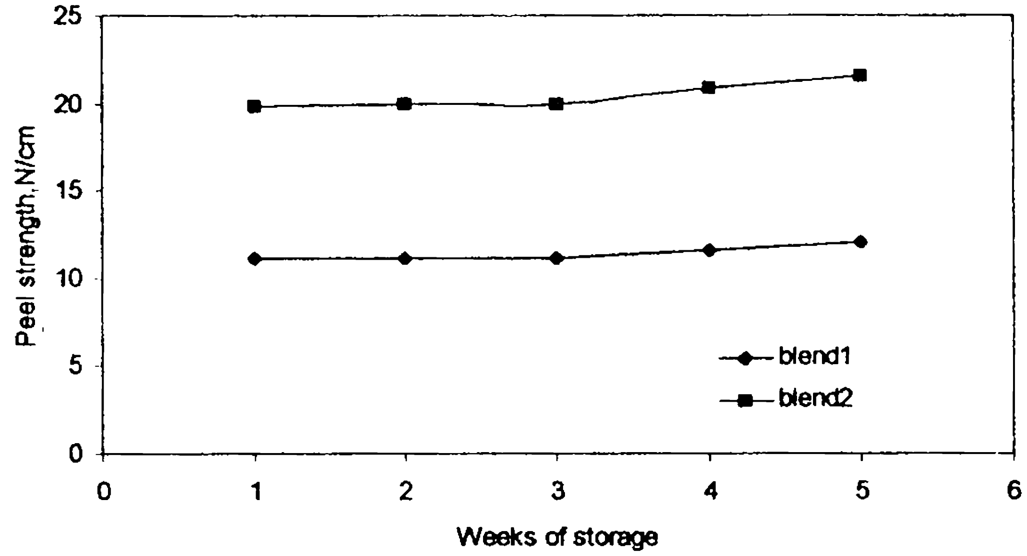

Fig.4.3.13 Effect of storage on peel strength

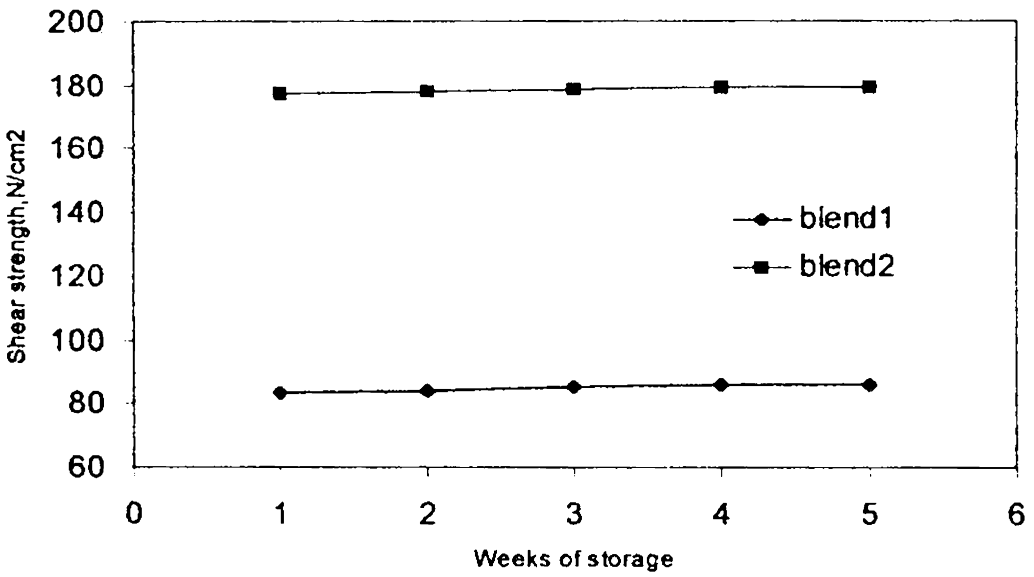

Fig.4.3.14 Variation on shear strength on storage of adhesives

Table 4.3.1 shows the number of flex cycles to failure of the adhesive joints The adhesives based on thermoplastic elastomer solutions withstand much larger number of cycles than commercial adhesive.

Table 4.3.1 Flex cycles after leather joints failed

Adhesive joint	Adhesive type	Peel strength, N/cm	Shear strength, N/cm^2
Leather to leather	Blend1	16464	Above 1 lakh
	Blend 2	53656	Above 1 lakh
	Comm.1	200	1600
	Comm.2	20646	83456
Leather to plastic	Blend1	10246	Above 1 lakh
	Blend 2	43264	Above 1 lakh
	Comm.1	150	1500
	Comm.2	10489	64346

Table 4.3.2 shows the peel and shear strength of different leather components jointed using these adhesive solutions. These are the main components used in leather products. In all the types of adhesives thermoplastic elastomer based adhesives show better adhesion for bonding applications in leather product industry.

Table 4.3.2 Adhesive strength of different foot wear components

	Blend1		**Blend 2**		**Comm.2**	
Adhesive joint	**Peel N/cm**	**Shear N/cm^2**	**Peel N/cm**	**Shear N/cm^2**	**Peel N/cm**	**Shear N/cm^2**
1	22	83	30	178	10	30
2	21	85	30	128	20	43
3	15	56	32	61	12	41
4	18	51	28	62	21	33
5	15	61	21	92	14	50
6	20	42	29	48	23	30
7	23	39	25	49	22	31
8	14	35	25	43	10	28
9	20	64	47	81	11	32

1-Upper leather to upper lather; 2- Upper leather to sole leather; 3- upper leather to NR sole; 4- Upper leather to SBR sole; 5 -Upper leather to M/C sole; 6 -M/C to NR sole; 7 -M/C to SBR sole; 8 -Upper leather to plastic sole; 9- Sole leather to plastic sole.

Table 4.3.3 shows the peel and shear strength of upper leather to plastic soles jointed using the adhesives before and after exposed to different environments.

Table 4.3.3 adhesion strength retention of leather to plastic soles. Peel (N/cm)and Shear (N/cm^2) strength.

	Blend1		Blend2		Comm.2	
	Peel	Shear	Peel	Shear	Peel	Shear
Normal	14	35	25	43	10	28
Water soaking	11	35	23	40	7	18
Hot water soaking	5	32	9	41	3	9
Ageing	9	36	10	42	5	20
Quick stick	12	33	23	40	4	18

Conclusions

1. Thermoplastic elastomer solutions can be used as efficient adhesives in leather product industry.
2. Thermoplastic elastomer based adhesives show much superior bonding compared to commercial adhesives.
3. Thermoplastic elastomer adhesive solutions show better resistance to different environment compared to commercial adhesives.
4. The shelf life of the thermoplastic elastomer based adhesives are found to be very good

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Chapter 5

RUBBER TO METAL BONDING

Part 1 Rubber to metal bonding studies using rubber compound strip adhesive system

Rubber- to- metal bonds account for a considerable proportion of the entire elastomer processing industry. Rubber-to- metal bonds are found in all rubber products where metal parts are used as reinforcing elements or for load application or connection to other structures. This includes products in covering to protect against wear or corrosion[1,2]. The rubber-to- metal assemblies form an essential component of engineering application that helps to cushion motion and deaden noise. The rubber-metal composites used in mechanical world not only minimise the damaging effects of vibration but also protect against shock and seal leakage of oil and other fluids, and simplify assembly by tolerance for misalignment[3]. The patent literature indicates that rubber-to-metal adhesive formulations contain six to eight components in addition to the solvent[4,5]. Some of these ingredients are capable to become chemically active at elevated temperatures. So more than one mechanism of bonding or chemical reactions across the rubber-adhesive interface may occur[6]. Cross bridging can occur in between the layers depending on the rubber and vulcanization system[7-9]. The effect of compounding ingredients[10] and accelerators on bonding has been studied[11].

The literature points to a widespread use of various halogen -containing polymers in primers and overcoats for rubber - to -metal bonding[4,12-15]. The surface modification of rubber adherend strip by chlorinating was also effective. Chlorinating seems to produce changes in the chemical composition of the elastomer surface according to both ionic and free radical mechanisms, taking place at a one nm surface depth[16]. Chlorinating effectiveness depends to a high degree, on the conditions of the realisation of the reaction (strip thickness, chlorine content, temperature, time, etc)[17].

In the present study the use of a primer and a solid rubber compound strip for bonding rubbers to metal is proposed. This procedure may make the adhesive system simpler to apply and more environment-friendly since it uses lower amount of solvents. The efficiency of the system is proposed to be compared with that of a commercially available solution adhesive -Polylock.

Experimental

Adherends used:

A. Galvanised mild steel(ms) of thickness 1.6mm used .

B. Aluminium sheets of thickness 1.6mm used.

C. Stainless steel sheets of thickness 1.6 mm used.

Commercial adhesive used was Polylock supplied by Bombay Chemicals, India.

Preparation of chlorinated natural rubber as explained in chapter 2, experimental.

The chlorine content was estimated as per standard procedures described in chapter 2. In order to characterise chlorinated natural rubber thermo gravimertic analysis(TGA) and fourrier transform IR of the prepared CNR and commercial CNR were taken and compared.

Preparation of steel surface: The mild steel pieces were cut into rectangular strips of 304.8x25mm size as per ASTM D 903 29(72). The surfaces of the plates were abraded using emery paper no.60, etched with dilute HCl(1N), washed with running cold water and dried by placing in oven for 1hr. at 50°C.

Preparation of primer: A 70% solution of chlorinated natural rubber solution in toluene was used as a primer for mild steel adherend, which was applied over the polished surface of the steel pieces. These were then dried and used for bonding studies.

Preparation of rubber compound strips for adhesion studies: Rubber compounds were prepared as per the formulations in Table.5.1.1 A. The mixing of the rubber and the ingredients was done on a laboratory two roll mill (15 x30)cm. The compound was then sheeted out at different thickness and wound over cellophane paper.

The adherend rubber compounds for bonding to steel were prepared as per the formulations in the Table 5.1.1 B. The compounds were then sheeted out to a thickness of about 1.9mm. Thin strips of the compounded rubbers were cut into304.8x25mm size for bonding.

Table 5.1.1A Formulation of strip compounds

Ingredients(phr)	NR STRIP	NBR STRIP	CR STRIP
Natural rubber	100	0	0
Nitrile rubber	0	100	0
Chloroprene rubber			100
Zinc oxide	5	5	5
Stearic acid	2	0	0
MOR	0.8		
TMTD	0.5	0.5	
Wood rosin	2.5		
Sulphur(insoluble)	2.5	1.5	
HAF (N 330)	30	30	30
MBTS		1.0	
DOP		3	3
Aromatic oil	4		
Magnesium Oxide			4
NA 22			0.5

Table 5.1.1 B Formulations of bonding adherends

	NR	NBR	CR
Natural rubber	100		
Nitrile rubber	100		
Chloroprene rubber	100		
Zinc Oxide	5	5	5
Stearic acid	1.5	1.5	
HAF (N330)	45	40	40
Pilflex 13	1.0	1.0	1.0
Sulphur(soluble)	2.5	1.5	0
CBS	0.8		
MBTS	1.0		
NA 22			0.5

Bonding of rubber to steel : The rubber compound adhesive strip was placed over the primer coated steel pieces. The rubber compound to be bonded was then placed over the strip and this assembly was placed in a hydraulic press at a pressure of 30 MPa and a temperature of 150° C for 10 minutes. The press was then opened and bonded samples were taken out. Different rubber strips were used for bonding different rubber adherends as shown in Table 5.1.2.

Determination of peel strength.: The 180° peel test for rubber-to-steel bonded samples were determined on a Zwick UTM model 1445 as per ASTM D 903 29(72)- standard test for joints with one flexible and a rigid adherend. The formulation of the compound strip which gave maximum joint strength was selected as the standard for further studies. The amount of carbon black in NBR, CR and NR strip compounds was varied from 10 to 40 phr and using these strips NBR ,CR and NR adherends were bonded and peel strength was determined as earlier.

The strip compounds based on NBR, CR and NR were modified with adhesive grade PF resin in different amounts from 10 to 40 phr and bonding studies were carried out. From this, the best adhesive system was determined and further studies were done using that particular strip and adherend.

The variation of peel strength with temperature of bonding (from 140 to 160°C) was determined. The thickness of strip used was varied from 0.5 to 2.8 mm and peel strength was determined. The optimum strip thickness and bonding temperature were used for further studies.

Ageing resistance: The rubber-to-steel bonded samples were kept in a vacuum oven at different temperatures from 80° C to 140°C for 30 minutes. Then the samples were taken out and conditioned for 30 minutes at room temperature and peel strength was measured on the Zwick UTM Model 1445. Samples bonded with Polylock adhesive were also aged and tested as per ASTM D 896 (66).

Salt water resistance: The bonded samples were soaked in a 30% NaCl solution for different periods from 5 days to 20 days. After 5 days of soaking the bonded samples were taken out from the salt solution, dried and conditioned. Then the peel strength of these samples was determined. Similarly, peel strength was also measured after 10,15,20 days of soaking. Polylock adhesive was also tested for salt water resistance as per ASTM D 1151 (61).

Storage life of the adhesive strip: To study the storage life of the adhesive strips, the strips were kept for few weeks at room temperature in sealed cellophane packets and then the peel strength was determined.

Strip compound based on elastomer blends: Three types of blends were prepared using NR/BR (blend 1), NR/NBR (blend 2) and NBR/CR(blend 3) as per the formulations in Table 5.1.a. Rubber compound strips were prepared using these blends and used for bonding different adherends.

Table 5.1.a Formulations of adhesive strips by blends of elastomers

Ingredients, phr	**Blend 1**	**Blend 2**	**Blend 3**
NR	50	50	
BR	50		
NBR		50	50
CR			50
Zinc oxide	5	5	5
Stearic acid	1.5	1.5	1
HAF	40	40	40
Aromatic oil	2	2	2
TMTD	0.5	0.5	0.25
MBTS		1.0	0.5
MgO			4
Na 22			0.25
Sulphur(insoluble)	2.5	2.0	1.0
MOR	0.8		

Adhesion studies using different metals: Adhesive bonds were prepared using metals like aluminium and stainless steel other than mild steel. The strips prepared from single elastomer and blends of elastomers were used in these metals with the different adherends like CR, NBR and NR.

Mechanical properties of the compounds used as strips and adherends: Mechanical properties like tensile strength, elongation at break, modulus at 300% elongation and tear strength were determined for the different strip compounds and adherends. The effect of each properties when the amount of carbon black and PF resin content changes were estimated.

Optical microscopic analysis of metal surfaces: The metal surface were studied with an optical microscope having 100 times magnification. The polished metal surface and the surfaces which are peeled off were examined and photographs were taken.

Peel strength of solution adhesives: Solution types adhesives were prepared and applied over the primer coated metal surfaces and allowed to dry completely. Over this adherends were placed and compression moulded as explained earlier. Blocked MDI was prepared as per the procedure in chapter 2.

Results and Discussion

Table 5.1.3 shows the peel strength of joints with different strip compounds based on NR, NBR and CR with different adherends based on the above mentioned rubbers. The joint strength is found to be maximum for an NBR strip with CR adherend. In most cases the joints failed at the interface between the strip adhesive and the adherend rubber. No adherend failure occurred here.

Table 5.1.3 Peel strength of joints with different adhesive strips

Strip	Adherend	Peel strength N/mm
NBR	CR	5.25
NBR	NBR	3.32
NBR	NR	0.44
CR	CR	2.05
CR	NBR	1.64
CR	NR	0.32
NR	NR	0.35

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------------------------ PARAMETERS OF SPECTRUM -- 1998/10/06 11:57:03 ---
          MEASURING MODE ;   %T
              RESOLUTION :   4.0 cm-1
            ACCUMULATION ;   40
                AMP GAIN ;   AUTO
                DETECTOR :   DETECTOR 1 (2.8 mm/sec)
            APODIZATION ;   HAPP-GENZEL
                 REMARKS ;
                 ANALYST
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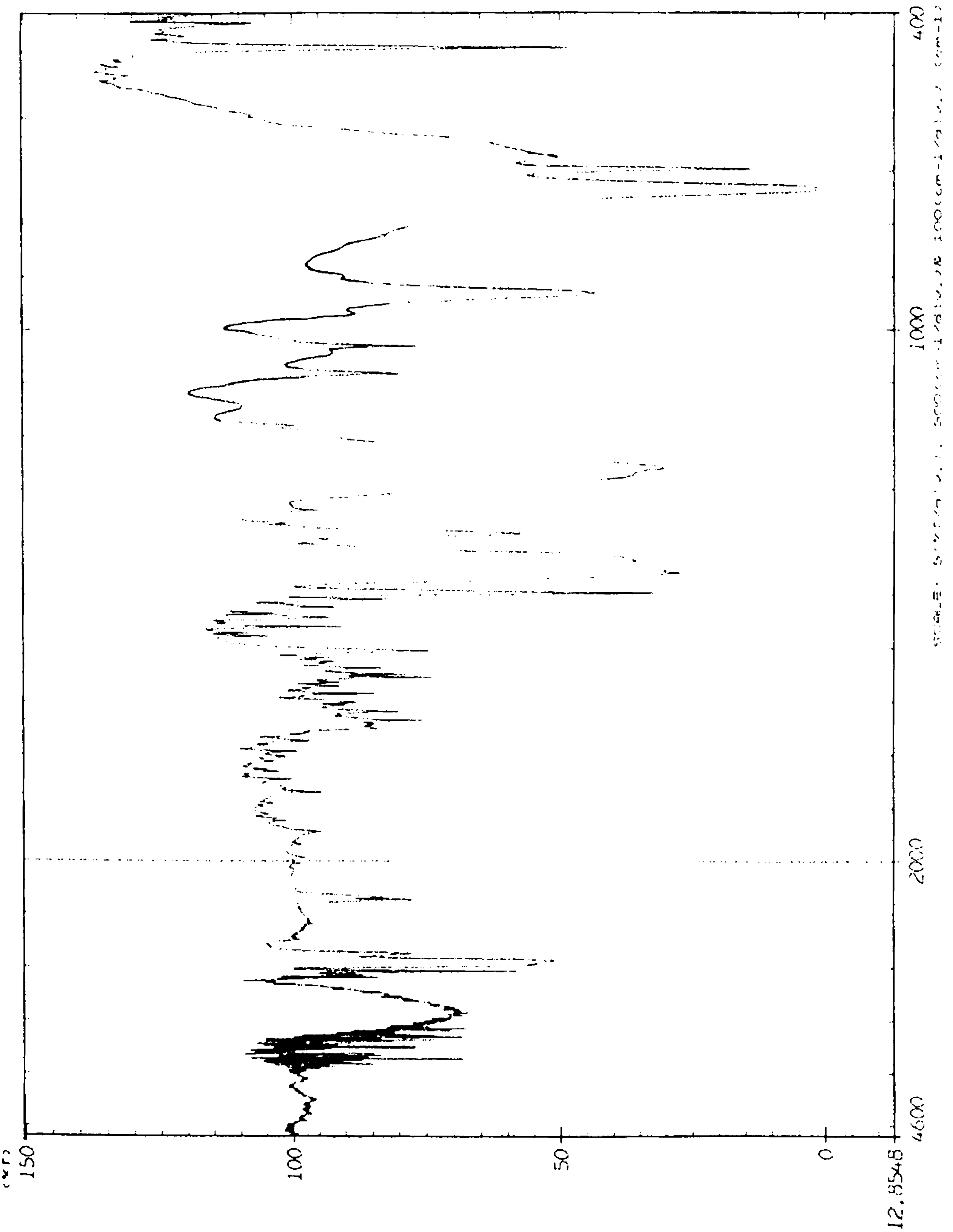


Fig. 5.1.3 shows the FTIR curve for CNR prepared in laboratory

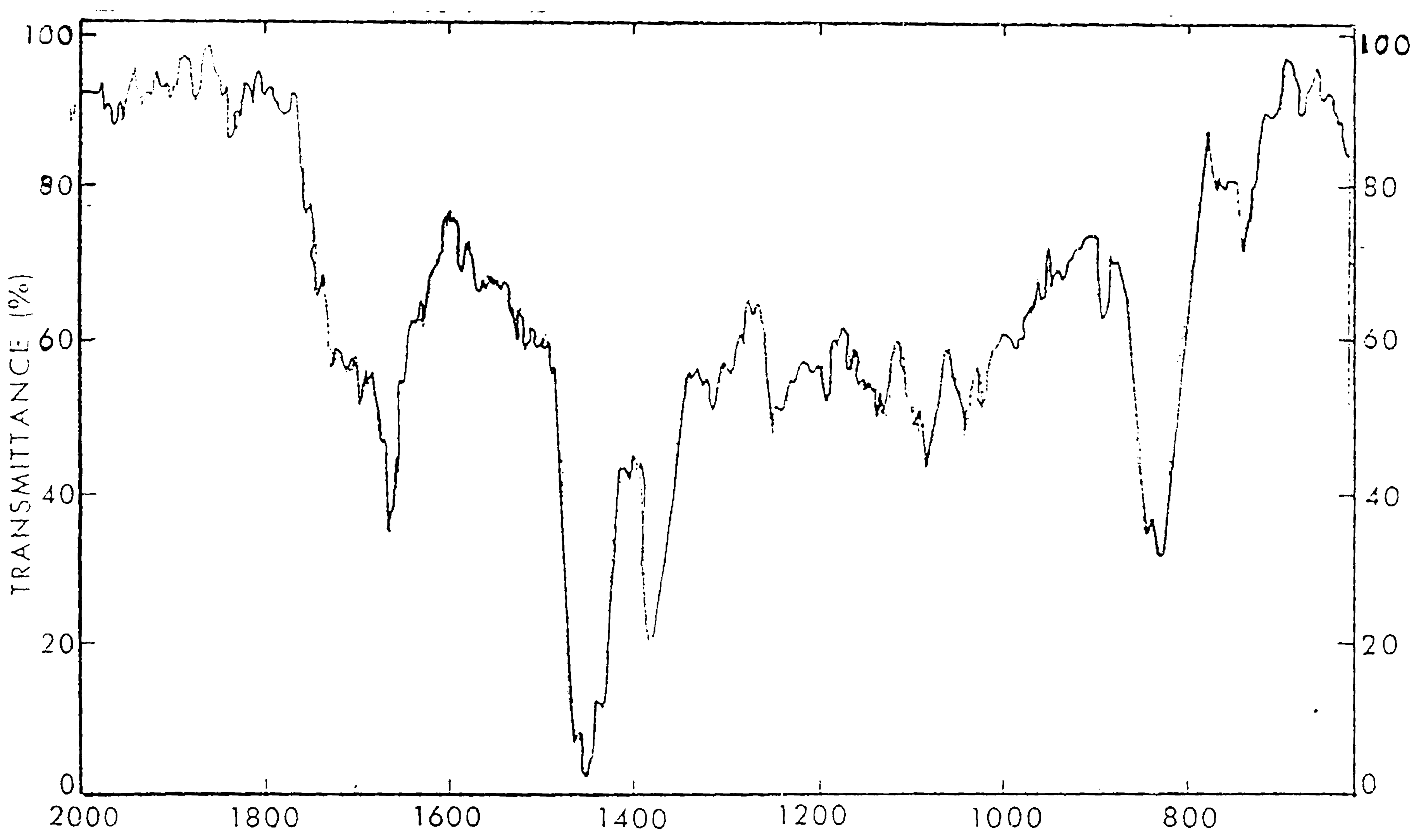


Fig5.1.4 shows the FTIR curve for commercial sample

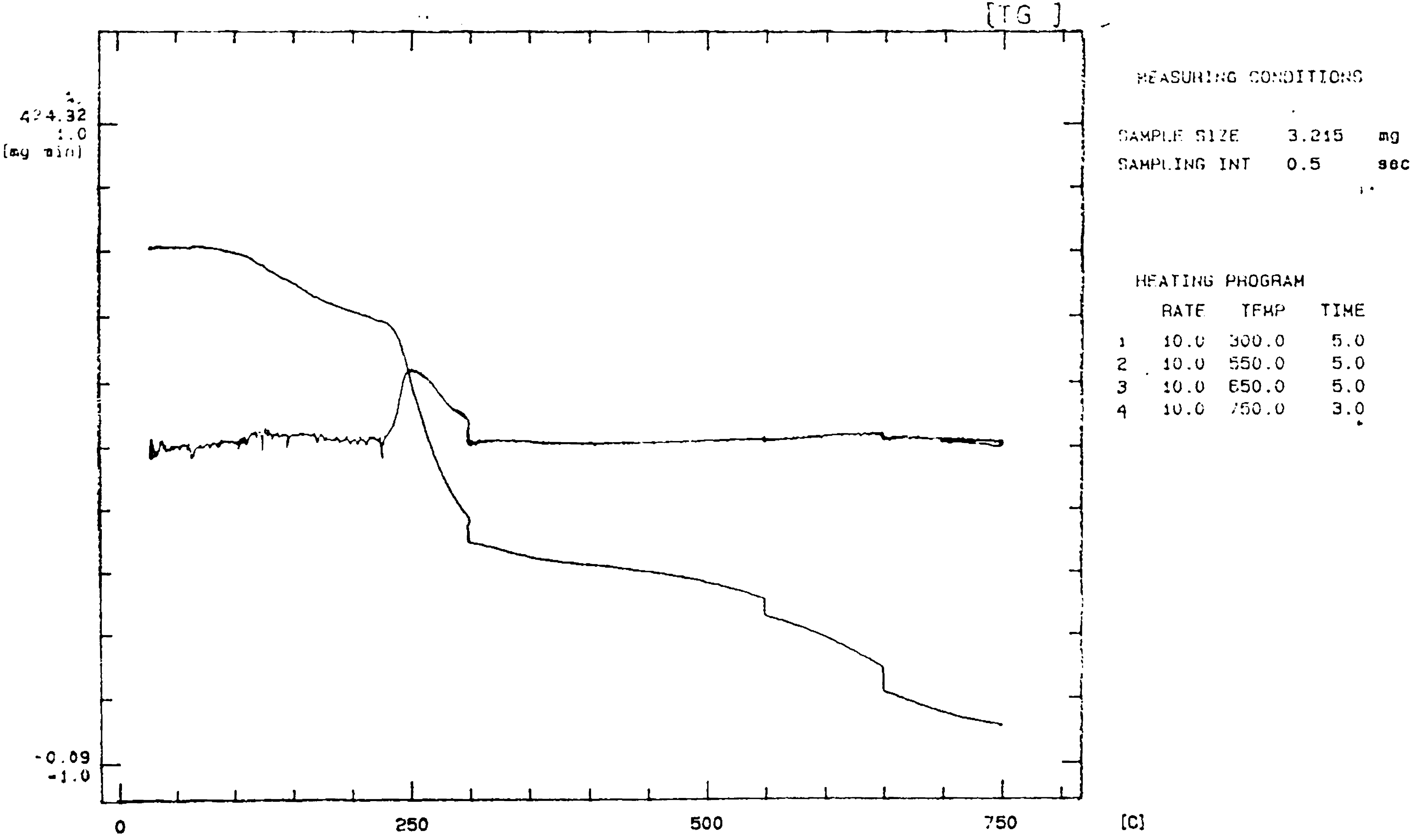


Fig.5.1.1 shows the TGA curve for CNR prepared in the laboratory

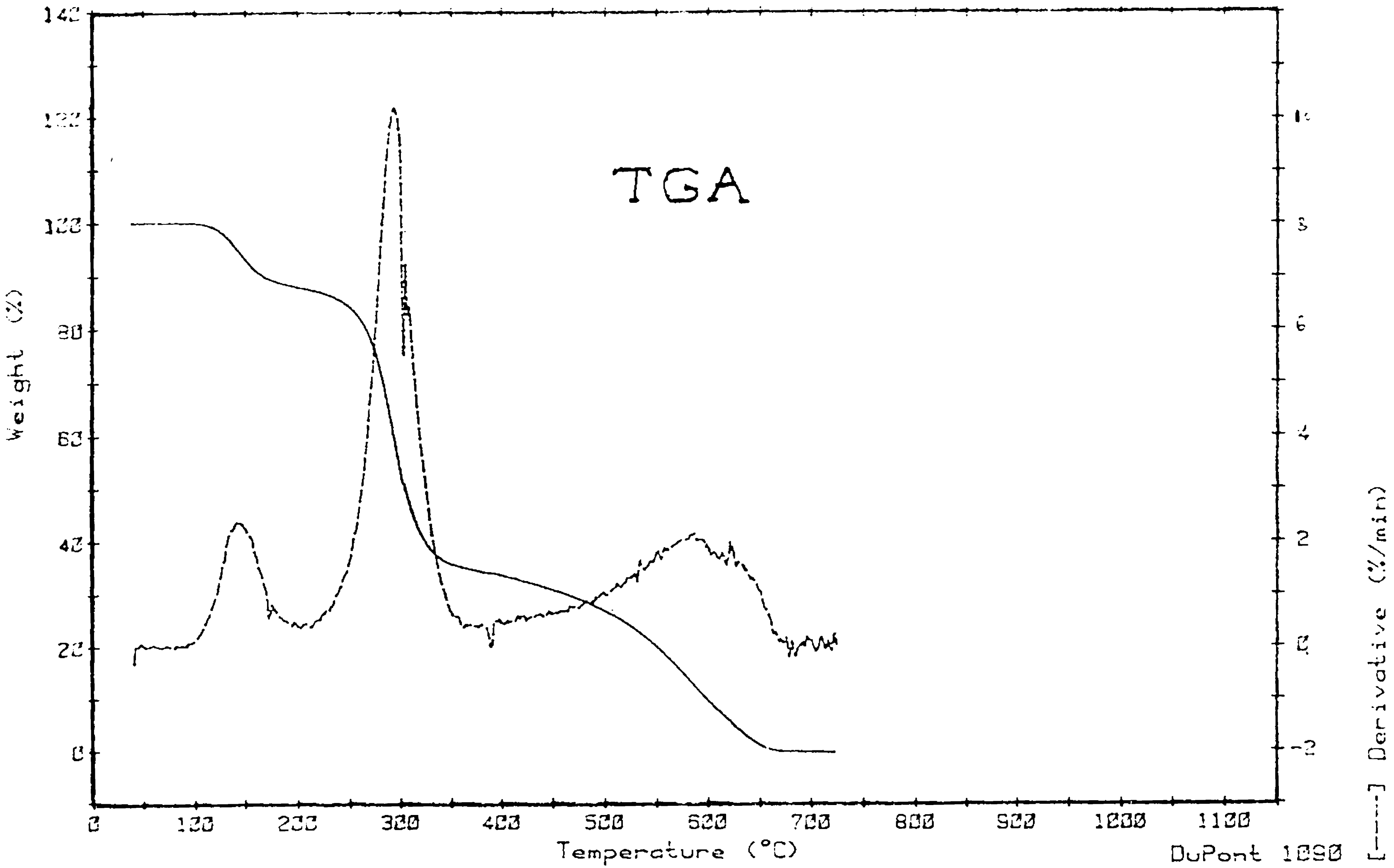


Fig. 5.1.a shows the TGAcurve for commercial CNR sample.

Figure 5.1.1 shows the Thermo-gravimetric curve for the chlorinated natural rubber prepared in laboratory and Figure 5.1.2 TGA is for commercial CNR sample. In both thermal degradation has three distinct regions. The initial phase of degradation occurs between 100-150°C. This degradation is due to the evolution of HCl from the CH_2Cl group (Van Amerongen et. al 1951), which shows samples are stable up to 150°C. The second region of degradation starts between 250-300°C and this is attributed to the degradation of CHCl and $CHCl_2$ groups. The third and the final stage of degradation is attributed due to the degradation of organic material which takes place around 750°C. Thus it may be noted that the degradation of the sample prepared in the laboratory and the commercial sample follows the same pattern.

Figure 5.1.3 and Figure 5.1.4 show the FTIR spectrum of CNR prepared in laboratory and that of the commercial CNR sample. In both spectrum the peak between 625-800cm^{-1} shows the C-Cl frequency.

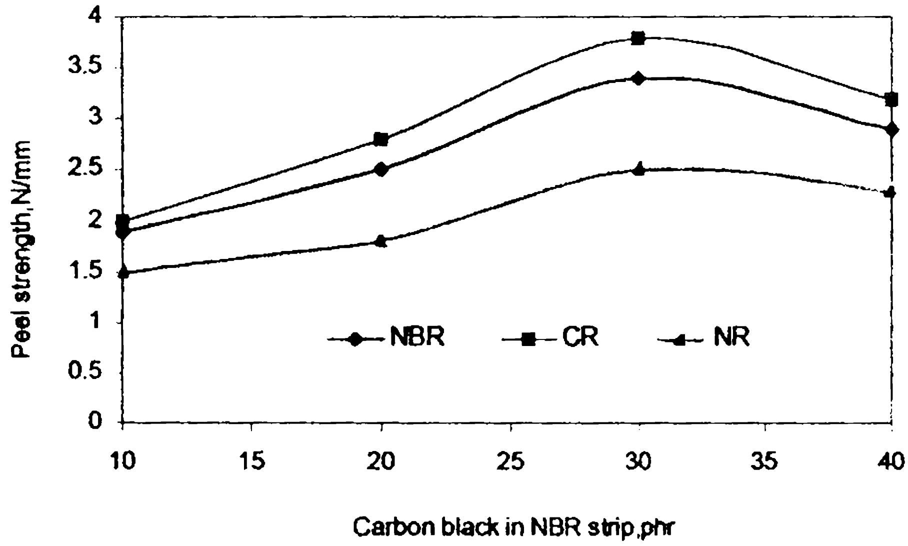


Fig5.1.5 Peel strength variation with carbon content

Figure 5.1.5 shows the effect of the variation of the amount of carbon black in the adhesive strips of NBR compound on peel strength of rubber-to-steel joints. As the amount of carbon black increases, the joint strength increases, reaches a maximum and then decreases. This shows that there is an optimum amount of carbon black which gives maximum peel strength. When the carbon black content is increased to 40 phr there is a reduction in the peel strength. This may be due to the lower adhesive property when carbon black is more in the compound. In the case of the CR strip as the concentration of carbon black increases peel strength decreases a shown in Figure5.1.6. This is because HAF produces lower reinforcement in CR compound compared to NBR[18]

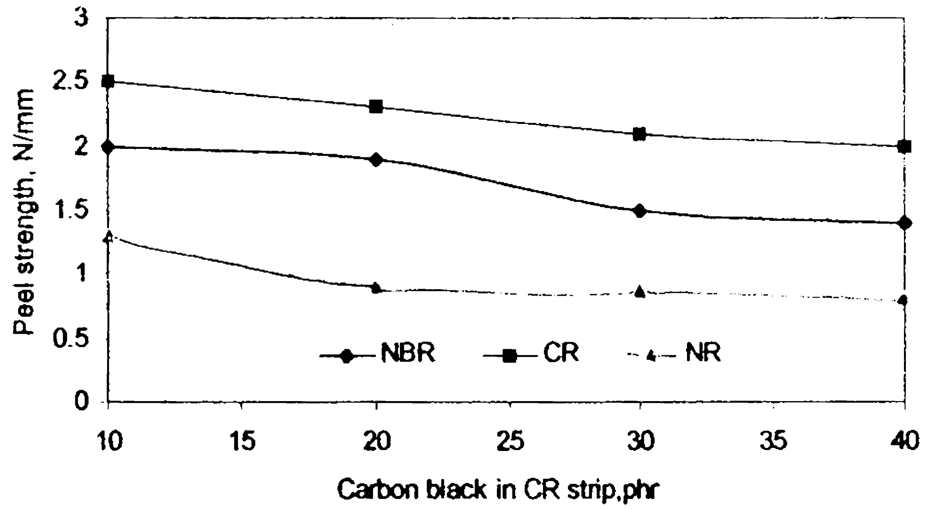


Fig.5.1.6 Effect of carbon black on peel strength

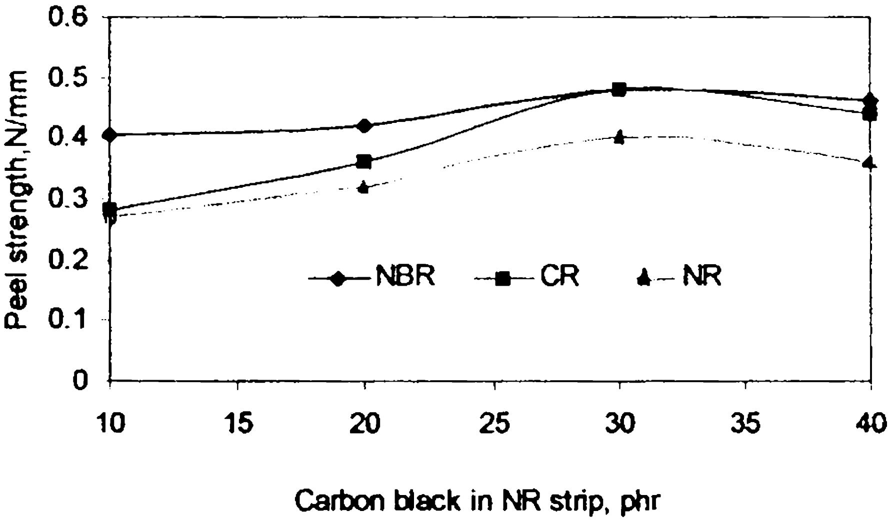


Fig.5.1.7 Effect of carbon black on peel strength.

Figure 5.1.7 shows the effect of variation of the amount of carbon black in the NR compound strips on peel strength. Peel strength increases, reaches a maximum and then decreases similarly to that for the NBR compound. But the peel strength value is found to be low for NR strip which this may be due to the non polar nature of NR.

As the amount of the PF resin increases peel strength increases reaches a maximum and then decreases[19,20]as shown in Figures 5.1. 8, 5.1.9 and 5.1.10 for NBR, CR and NR strip compounds, respectively. As the resin content increases, a phase change may occur in the compound from elastomeric to plastic resulting in a reduction of peel strength.

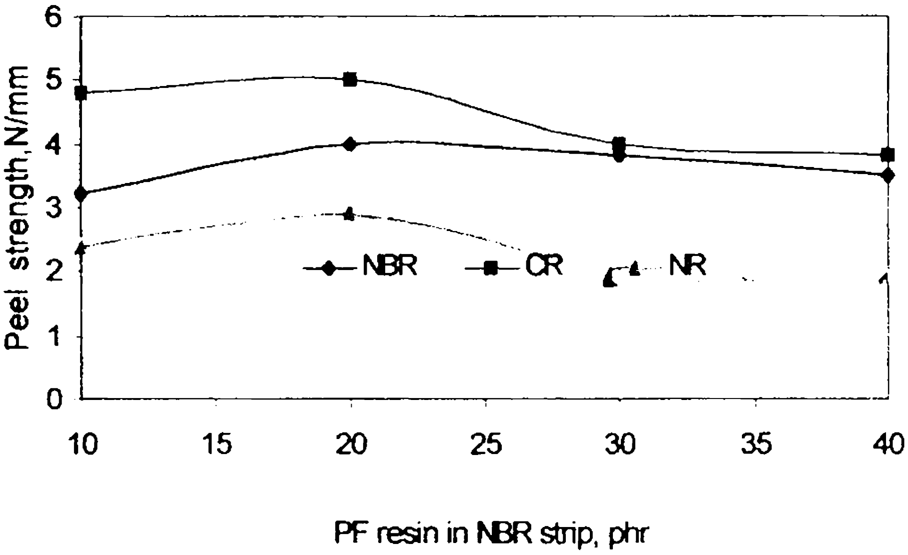


Fig.5.1.8 Effect of PF resin on peel strength

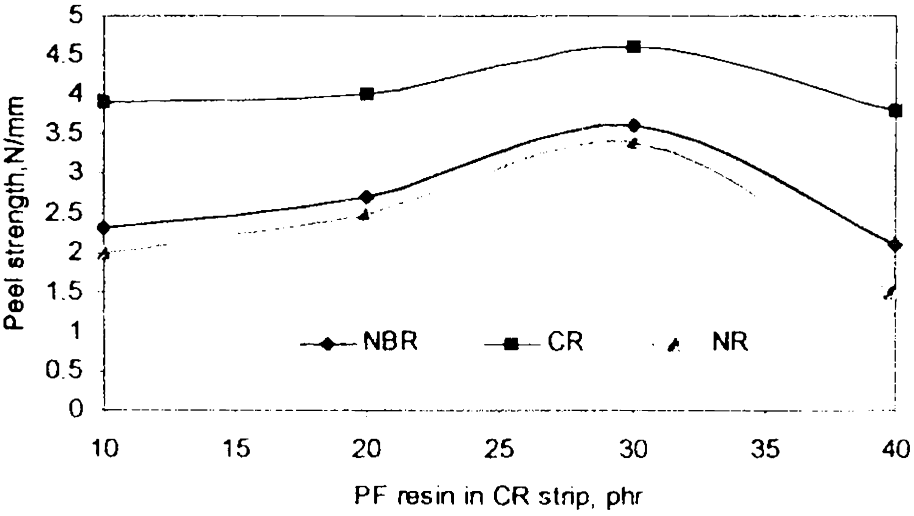


Fig.5.1.9 Effect of PF resin on peel strength

Figure 5.1.11 shows the effect of moulding temperature on peel strength. As the temperature is increased to 150°C, the peel strength increases, reaches a maximum and then decreases for strip bonding. The decrease may be due to over curing of the strip compound at higher temperature. For the commercial adhesive the maximum peel strength is obtained at 140° C while at higher temperature there is reduction in peel strength.

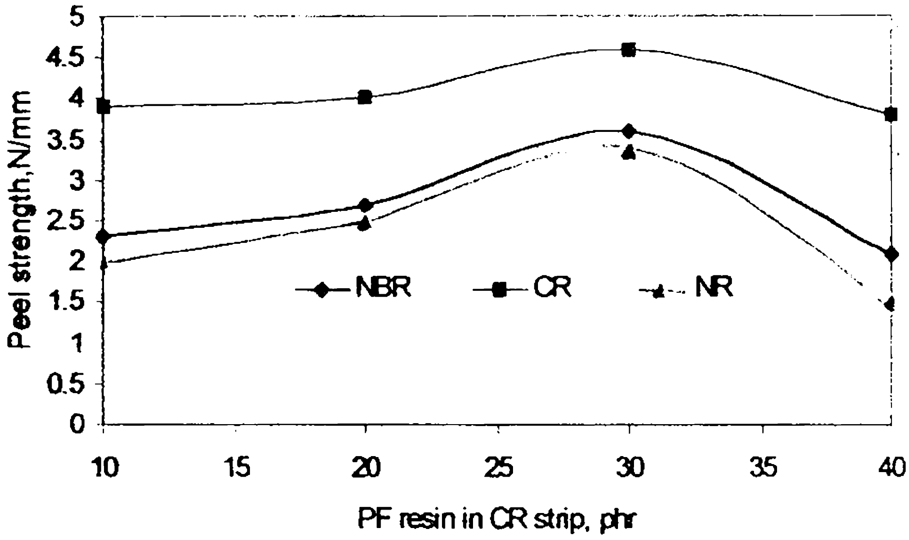


Fig.5.1.10 Effect of PF resin peel strength

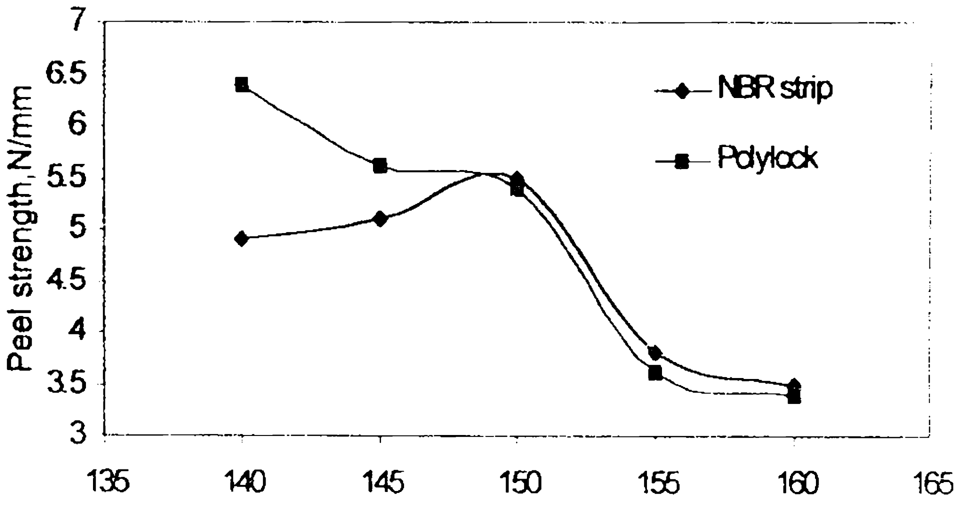


Fig.5.1.11 Effect of bonding temperature on peel strength

Figure 5.1.12 shows the effect of the strip thickness on peel strength. As the thickness of adhesive strip compound increases, peel strength also increases upto an optimum thickness, after which the peel strength is found to be decreasing. The strip compound may not get fully cured when the thickness is high.

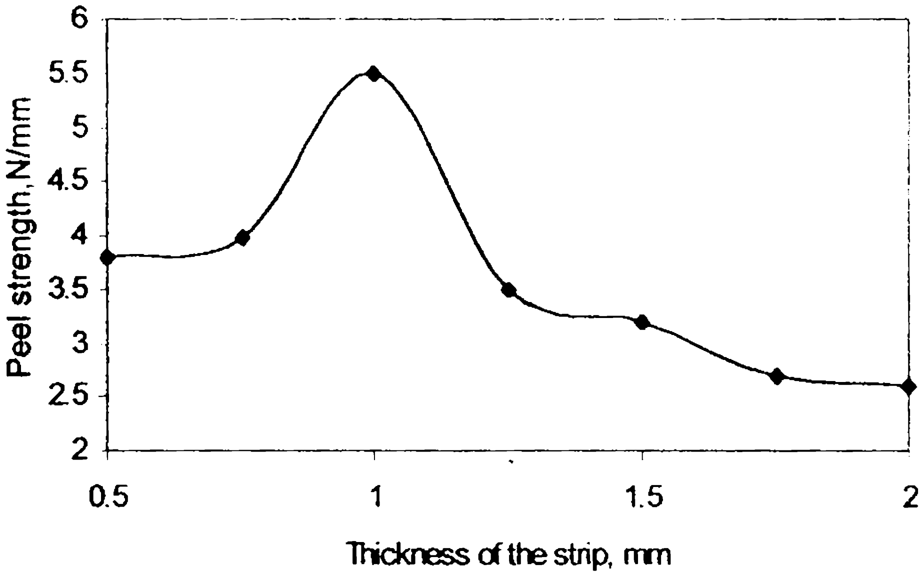


Fig.5.1.12 Peel strength variation with strip thickness

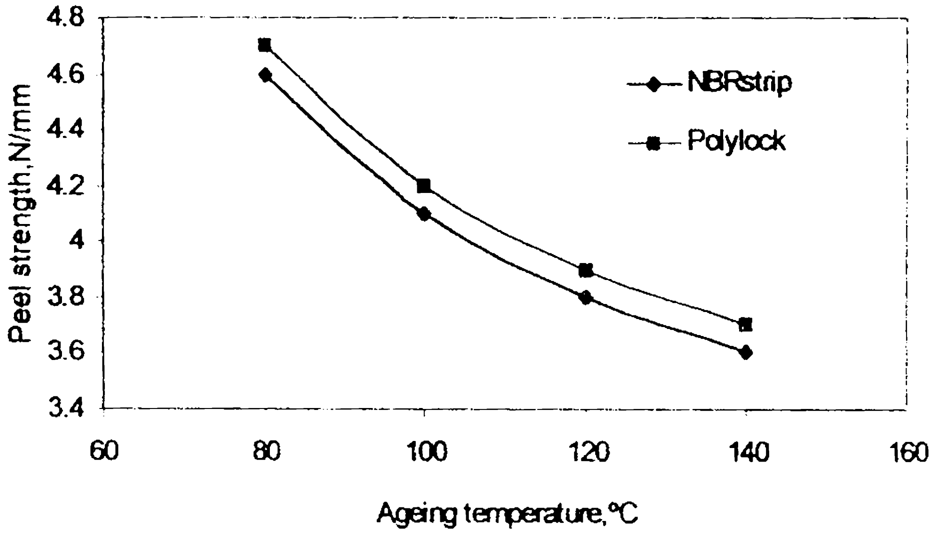


Fig 5.1.13 Effect of ageing on peel strength

Figure 5.1.13shows the effect of ageing on bond strength. When the temperature of ageing increases from 80 to 140°C, the peel strength decreases, which may be due to the degradation of bonding layer at higher temperatures [21].

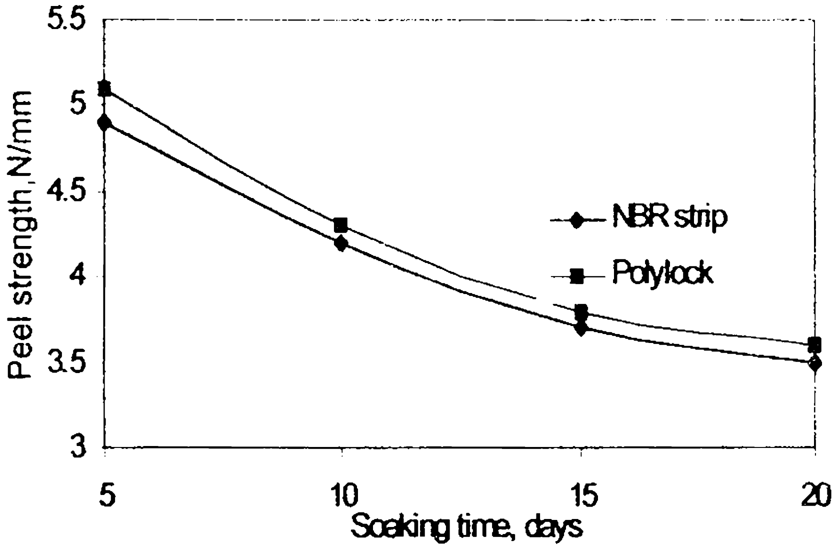


Fig.5.1.14 Effect of salt water soaking on peel strength

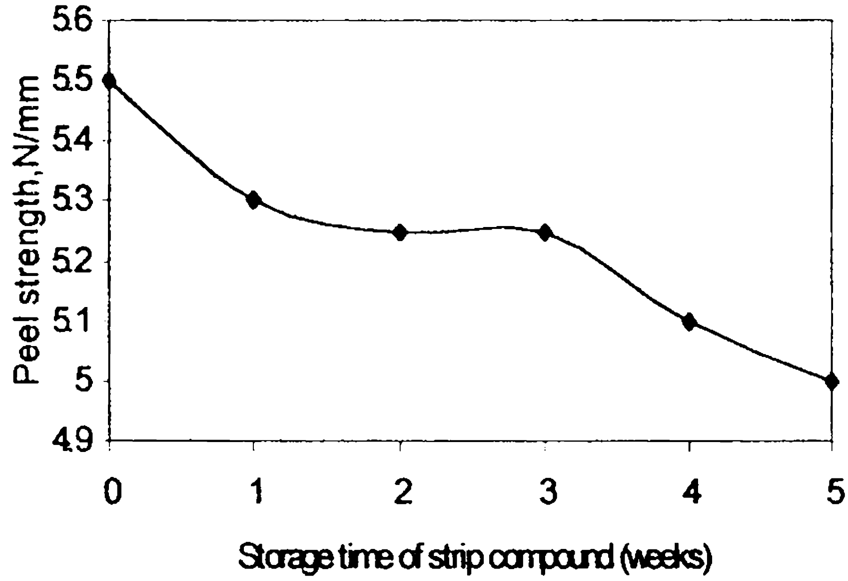


Fig.5.1.15 Effect of storage of strip on peel strength

Figure 5.1.14 shows the salt water resistance of the bonded samples. The peel strength decreases with the number of days. This shows that salt water slightly weakens the bonds[22].

Figure 5.1.15 shows the ageing resistance of the strip compound at room temperature. There is not much decrease in peel strength after five weeks. The strip compound possesses good storage stability.

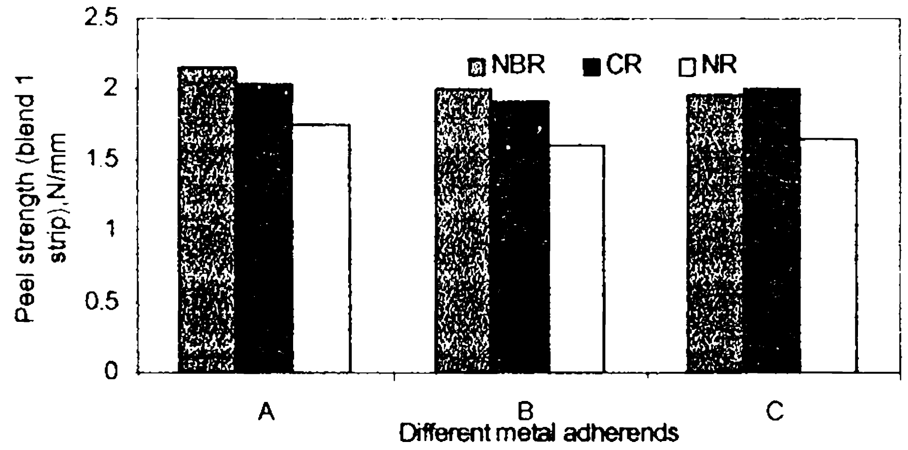


Fig.5.1.16 Peel strength of different metal rubber adherends with rubber strip (blend 1)

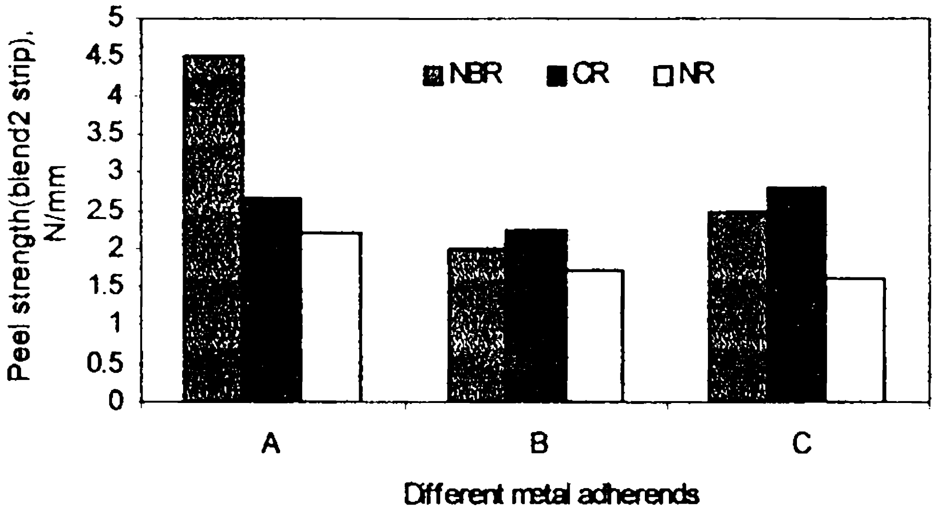


Fig.5.1.17 Peel strength of different metal rubber adherends with rubber strip (blend2)

Figure 5.1.16 shows peel strength of different metal and rubber adherends using rubber strip made from blend1(NR/BR). Generally NBR shows highest adhesion, followed by CR and then by NR. A-m s, B- aluminium and C - s s respectively.

Figure 5.1.17 shows the peel strength of metals- rubbers adherends using rubber strip made from blend 2 (NBR/NR). With steel ,NBR shows the highest adhesion, while for aluminium and stainless steel CR shows the highest adhesion A- m s, B- aluminium and C- s s respectively.

Figure 5.1.18 shows peel strength of metals - rubbers adherends using rubber strip made from blend 3 (NBR/CR). In this case also NBR shows the maximum adhesion to mild steel, while CR shows maximum adhesion to stainless steel . A-m s, B- aluminium and C - s s respectively.

Figure 5.1.19 shows peel strength of different metals - rubbers adherends using NBR strip. In this case CR shows the maximum adhesion to all the three metals . A - ms , B - aluminium and C - ss respectively.

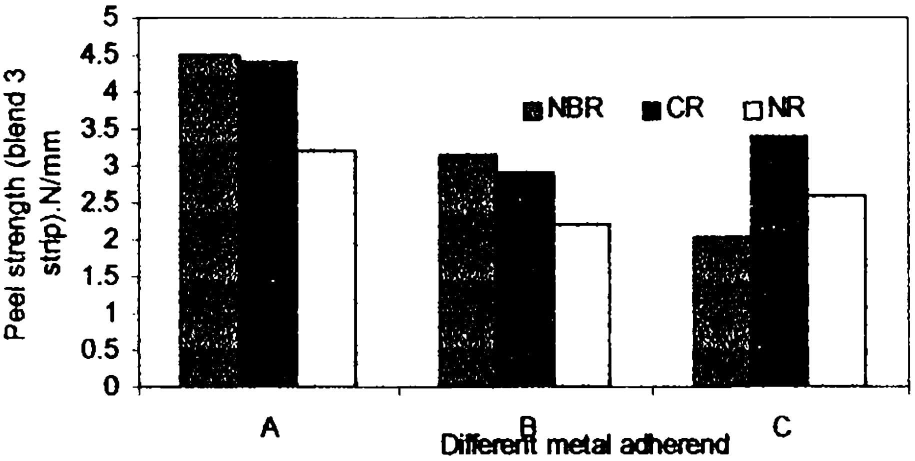


Fig.5.1.18 Peel strength of different metals-rubber adherends with rubber strip (blend3)

Figure 5.1.20 shows peel strength of different metals- rubbers adherends using CR strip. In this case also CR shows the maximum adhesion to all the three metals. A-m s, B- aluminium and C- s s respectively.

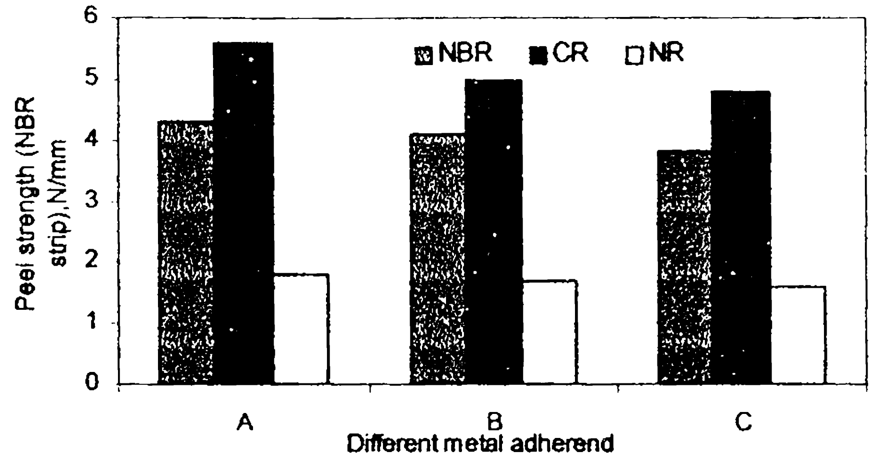


Fig.5.1.19 Peel strength of different metal rubber adherends with NBR strip

Figure 5.1.21 shows peel strength of different metals - rubbers using NR strip. The peel strength values are found to be lower in this case as expected which may be due the nonpolar nature of NR. A-m s, B- aluminium and C- s s respectively.

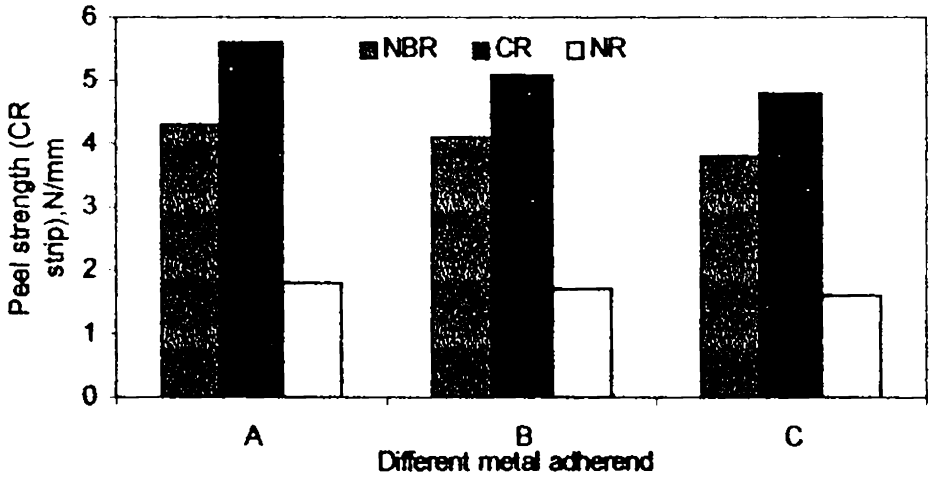


Fig.5.1.20 Peel strength of different metal rubber adherends with CR strip

Figure 5.1.22 shows the effect of carbon black content in the strip compounds on tensile strength. As the amount of carbon black increases tensile strength increases reaches a maximum and then decreases for all the strip vulcanisates. When carbon black content is more it results in increased stiffness and reduced strength.

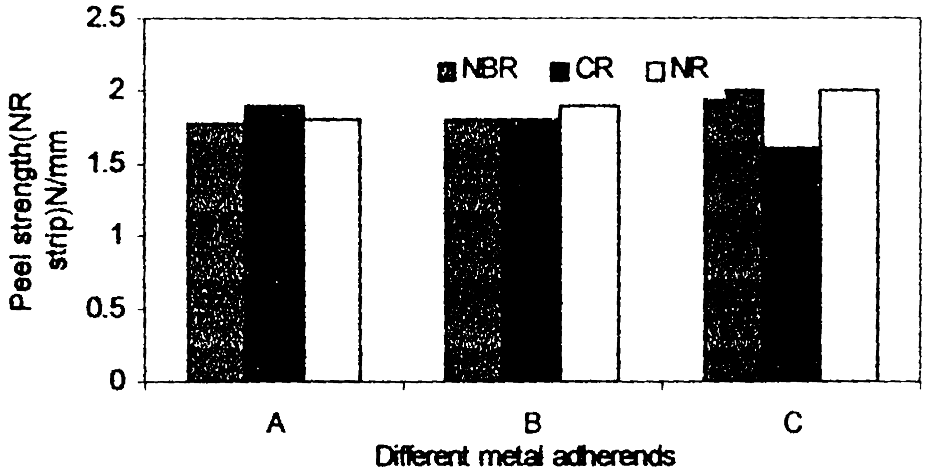


Fig.5.1.21 Peel strength of different metal rubber adherends with NR strip

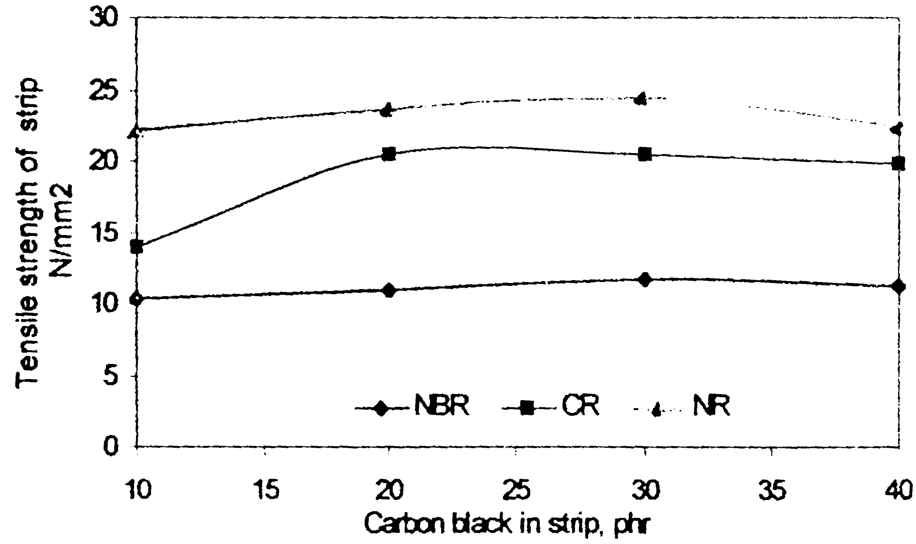


Fig.5.1.22 Effect of carbon black on tensile strength of strip vulcanisates

Figure 5.1.23 shows the effect of carbon black in the strip compounds on elongation at break of strip compounds. Here the elongation at break values do not vary much as the amount of carbon black increases.

Figure 5.1.24 shows the effect of carbon black in strip compounds on modulus at 300% elongation of strip vulcanisates. Modulus values increase as the amount of carbon black increases but decrease after a particular level in all the strip compounds. This may be due the dilution effect of the filler at higher dosages.

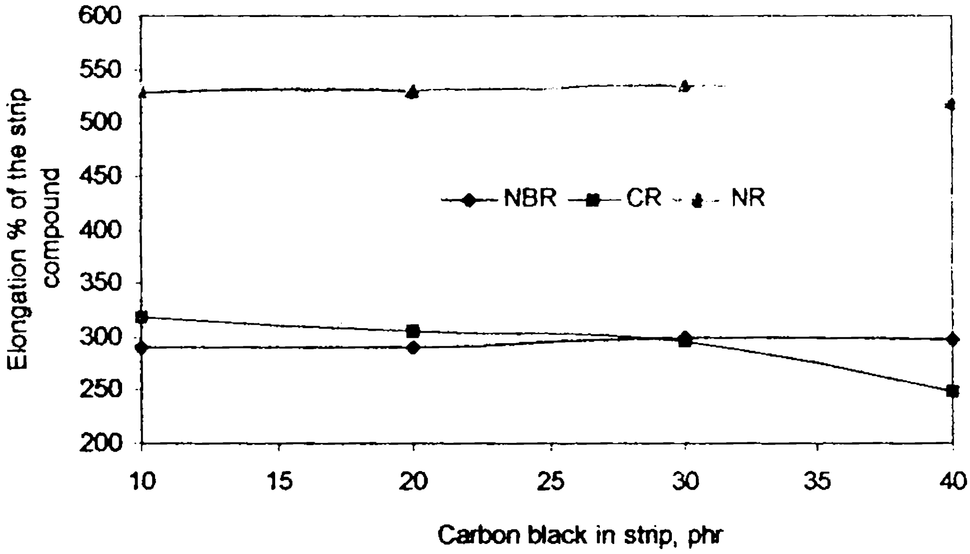


Fig.5.1.23 Elongation at break of strips with carbon black content

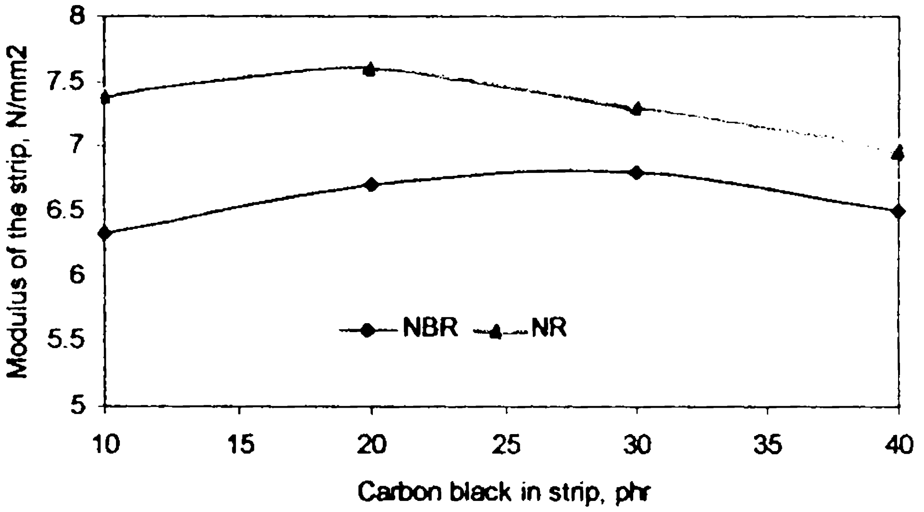


Fig.5.1.24 Effect of 300% modulus with carbon black content

Figure 5.1.25 shows the effect of carbon black in the strip compounds on its tear strength. Tear strength increases as the carbon black content increases and after an optimum level tear strength decreases in the cases of NBR and NR strip compounds. But in CR strip there is not much effect on tear strength as the amount of carbon black increases.

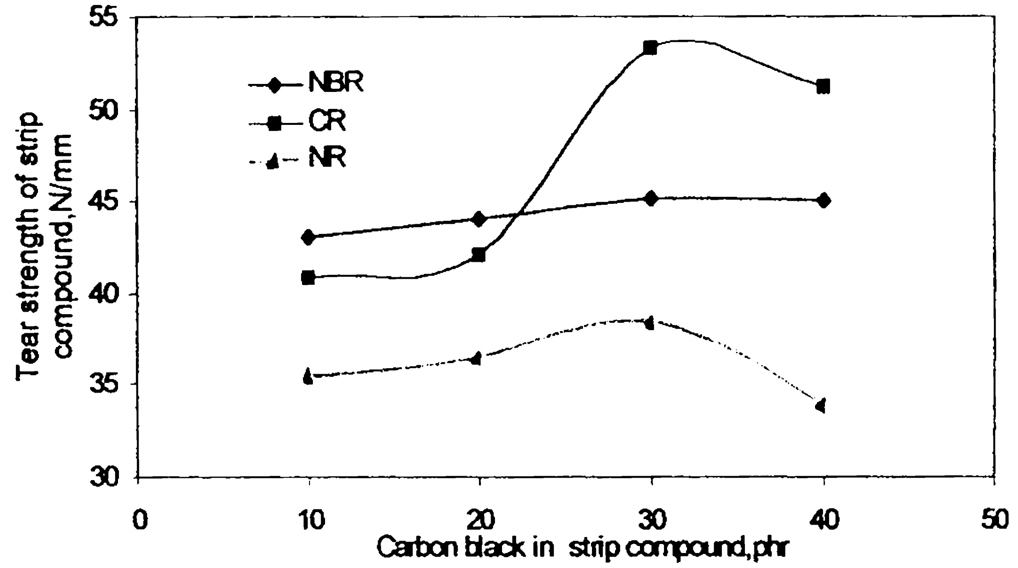


Fig.5.1.25 Effect of Carbon black on tear strength of strip

Figure 5.1.26 shows the effect of PF resin in the strip compounds on thier tensile strength. Tensile strength increases initially attains a maximum value and then decreases for all the strips. Increase in PF resin content results in a phase change at higher resin levels, thus causes brittleness leading to reduced tensile strength.

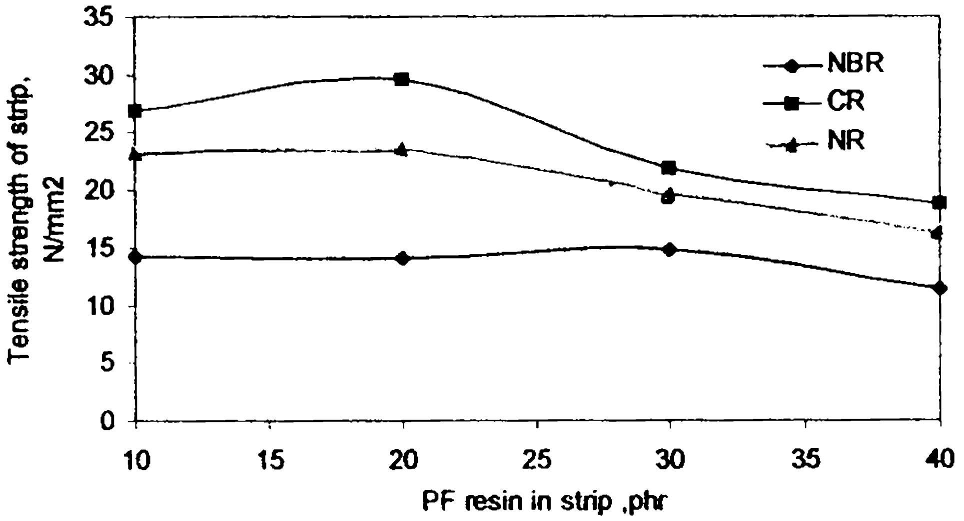


Fig.5.1.26 Effect of PF resin on tensile strength of strip vulcanisate

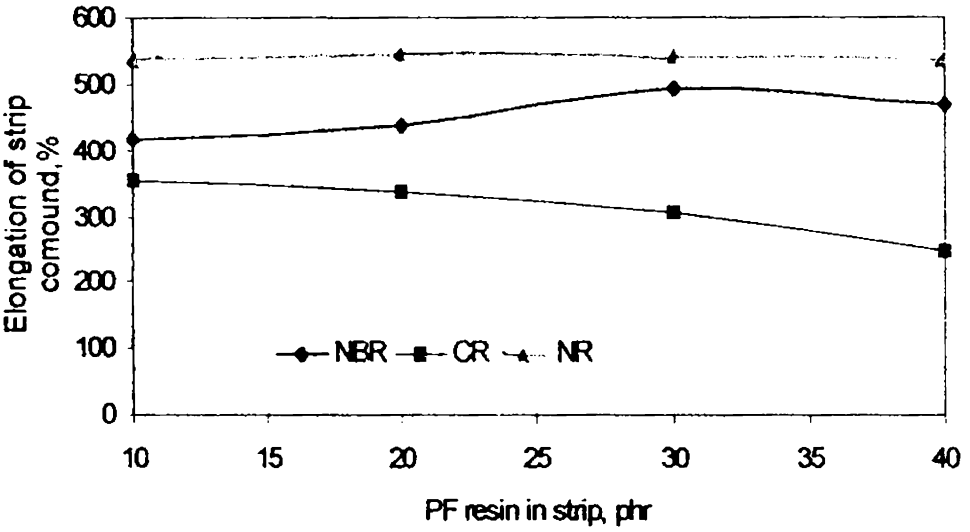


Fig.5.1.27 Effect of PF resin on elongation at break of strip vulcanisates

Figure 5.1.27 shows the effect of PF resin in the strip compounds on its elongation at break . Elongation at break does not vary much as the amount of PF resin increases only a slight reduction is observed. This may due to the slight increase in brittleness of the vulcanisates.

Figure 5.1.28shows the effect of PF resin on modulus of the strip compounds. Modulus values decrease as the amount of resin increases.

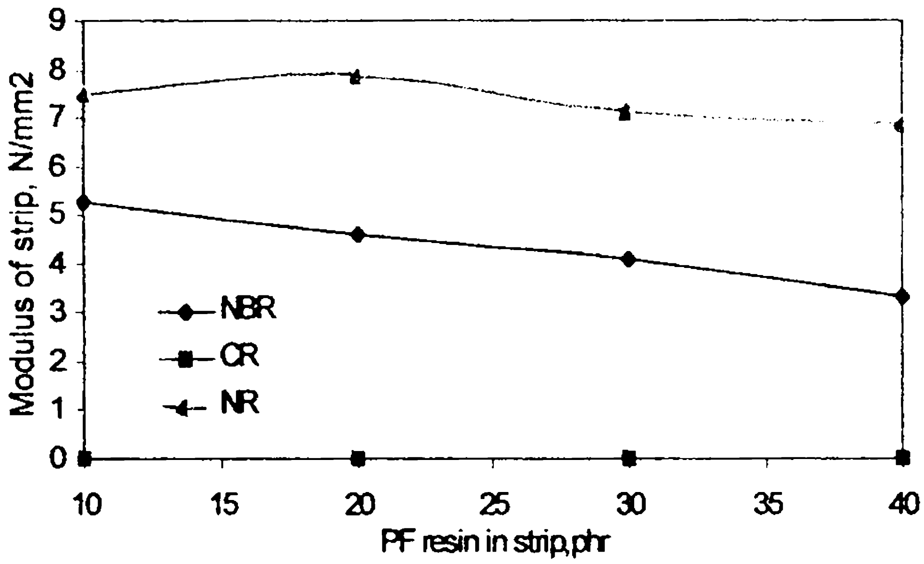


Fig.5.1.28 Effect of PF resin on 300% modulus of strip vulcanisates

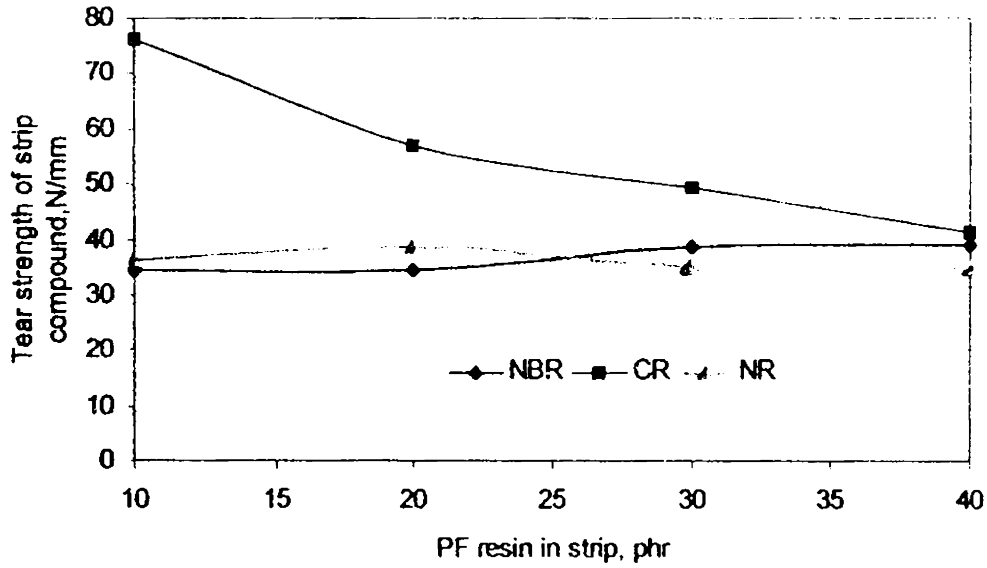


Fig.5.1.29 Variation of PF resin on tear strength of strip vulcanisates

Figure 5.1.29 shows the effect of PF resin on tear strength of strip compounds. As the amount of resin increases tear strength decreases which also may be due to the more brittle nature of the vulcanisates.

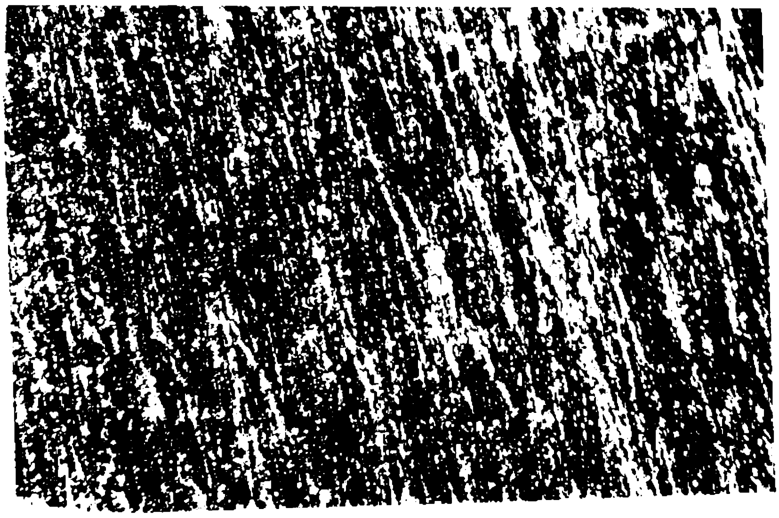
Table 5.1.4 shows the tensile properties of the adherend rubber compounds used for bonding rubber to metal in this study.

Table 5.1.4 Tensile properties of adherends

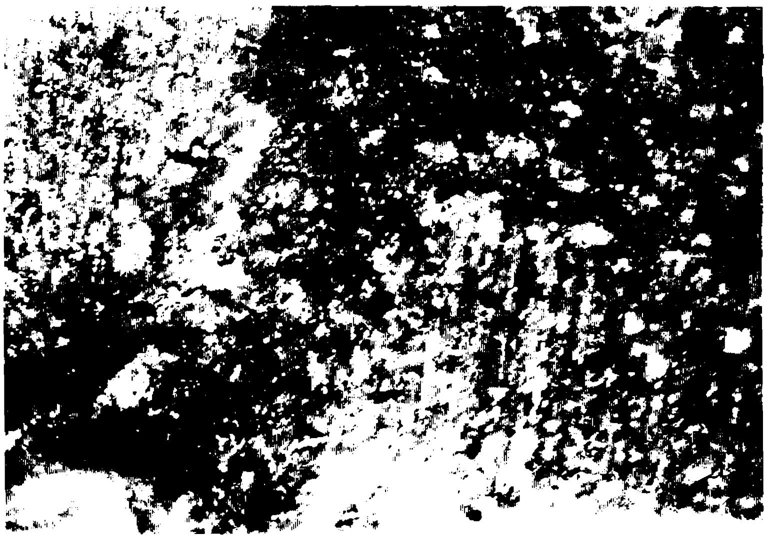
Adherends	**NR**	**NBR**	**CR**
Tensile strength N/mm^2	23.7	18.9	26.9
Modulus at 300% Elongation N/mm^2	7.5	6.6	2.5
Tear strength N/mm	66.5	52.8	53.8
Elongation at break %	537	603	319

Photograph 5.1.1 shows the polished galvanised mild steel surface and Photograph 5.1.2 shows the steel surface which was bonded using the strip adhesive system after peeling off. Photograph 5.1.3 shows the surface bonded using polylock adhesive. In both photographs the surface after peeling is found to be similar. The peel strength obtained are also found to be comparable as expected.

Table 5.1.5 shows the peel strength of some solution adhesives. When MDI is used we get higher strength but due to lack of storage life it can not be used for long term applications. Blocked MDI gives better storage life but the peel strength is found to be lower due the presence of blocking agent and the diluent. This method uses more amount of solvents which is hazardous.



Photograph 5.1.1 Roughed metal surfaces before adhesive application.



Photograph 5.1.2 Peeled off surface strip adhesive system.

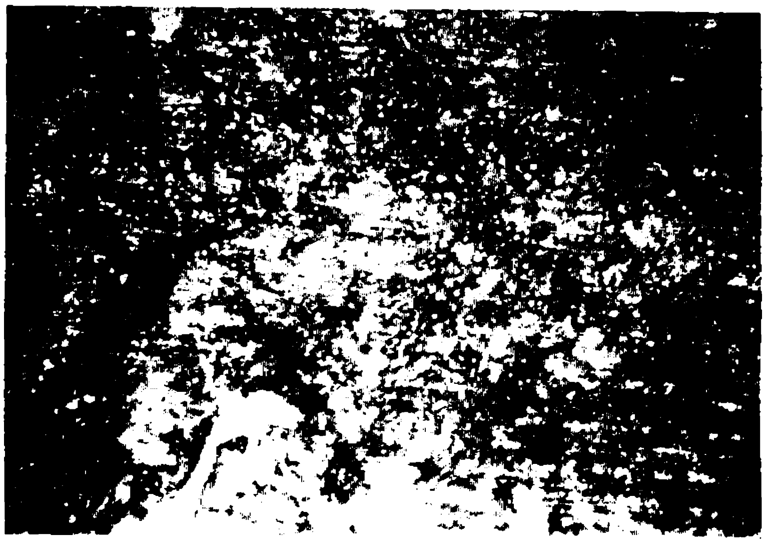


Table 5.1. 5 Peel strength of solution adhesives

	Adhesive Type	Primer used	Peel strength N
Type 1	CR	CNR	24.8
	CR	CNR/EVA	19.4
	CR/EVA	CNR	20.3
	CR/EVA	CNR/EVA	23.1
	CR/CNR	CNR	21.6
Type 2 With MDI in solution	CR	CNR	22.7
	CR/EVA/CNR	CNR	37.1
	CR/CNR	CNR	45.1
	XNBR/CNR	CNR	27.6
	XNBR	CNR	35.1
	NBR	CNR	38.1
Type 3 Without MDI	CR/CNR/XNBR	CNR	25.6
	CR/PF	CNR	28.1
	CR	MDI	78.6
	CR/CNR	CNR	25.5
	CR	CNR/MDI	32.4

Conclusions

1. A rubber compound strip can be used in place of adhesive solutions for bonding rubber to mild steel.
2. For bonding chloroprene rubber to mild steel nitrile rubber strip is found to be the most effective.
3. There is an optimum amount of carbon black and phenol formaldehyde resin in the strip compound for obtaining maximum joint strength.
4. This technique of bonding rubber to steel causes less pollution because of the lower amount of solvents used.

5. Rubber strip compound shows acceptable shelf life.
6. Other metals (SS, Aluminium) also show bonding comparable with the different strips and adherends.
7. Tensile strength, Tear strength, modulus and elongation at break values of the strip compounds are affected by the variation of carbon black and PF resin.

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Part 2 Improvement of bead wire adhesion to styrene butadiene rubber by the addition of chloroprene rubber.

Adhesion of bead wire to the rubber compound is of great importance in the tire industry[1]. The bead wires are coated with brass containing 70% Cu and 30% Zn. Which proportions give the crystalline structure of brass [2,3]. Good adhesion requires high levels of sulfur and high sulfur to accelerator ratio [4-8]. Van Ooij postulate that Cu_xS acts on adhesive at vulcanization reaction [9].

In this part of the study it is proposed to evaluate the effect of different ingredients like chloroprene rubber, resorcinol formaldehyde resin, blocked isocyanate, precipitated silica and insoluble sulfur with rubber compound for improving adhesion of bead wire to rubber.

Experimental

Rubber compound was prepared on a laboratory two roll mill with a friction ratio 1:1.25 as per the formulations in Table5.2.1. Cure time was determined on Goeffert Elastograph model 67.85.

TCAT specimens: A four cavity mould was used for preparing the rectangular block specimens of dimension 12.7x12.7x63 mm and the bead wire embedded in the block. Strips of rubber (12.7x7.6 mm) were placed in the major grooves of the mould cavities. A brass coated bead wire was put symmetrically on top of each rubber layer such that the embedment depth was 19 mm. Other rubber strips were then placed over the cords, thereby surrounding them. Curing was carried out at t_{90}+7min at 150°C. After moulding any flash was removed with a razor blade. A final test piece is shown in figure5.2.1. To test the pull out strength the two emergent cords were clamped in a UTM model 1445 and pulled at a rate of 50mm/min as per the ASTM D2229 (89). Initially only the block deforms, but at a critical load, one of the cords is pulled out. The maximum force is the pull out force.

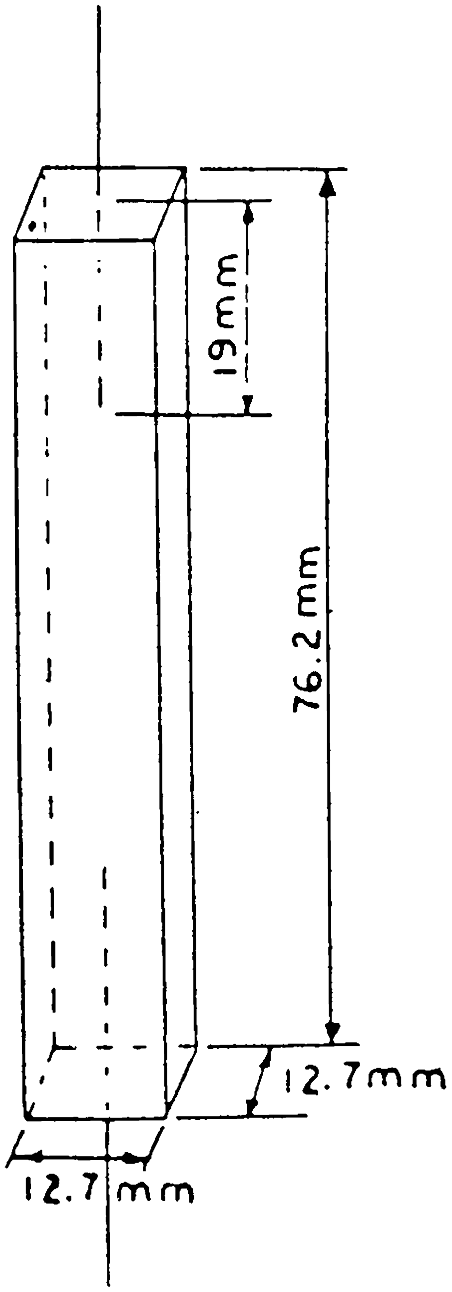

Fig. 5.2.1 -TCAT test specimen showing two emergent, bonded cords.

$$\text{Secant Modulus} = \frac{P_{10} L_0}{L A_0}$$

Where P_{10} = force of displacement, L =10mm

L_0 = distance between ends of the cord in TCAT specimen

A_0 = cross sectional area.

The rubber coverage on the bead wire was measured by visual examination.

In formulation No 1 in Table 5.2.1 the amount of blocked MDI, RF resin, sulfur, d CR content were varied. A part of GPF was replaced by precipitated silica and the effect n bond strength was studied. Compound containing optimum amount of these additives was ken as compound No 4 which is used to compare with conventional bonding compounds.

Table 5.2.1 Formulations of the compounds

Ingredients, Phr	**Compound No 1**	**Compound No2**	**Compound No3**
Natural rubber		25	
SBR 1502	100	25	80
OESBR 1712		68.75	68.75
ZnO	4	3	3
Stearic Acid	2	1	1
GPF	100	55.5	57
HAF		21.5	57
HS	2		
CBS	1		
Sulfur	3.6	3.75	3
Aromatic oil	10	13	7
Wood rosin	5		
PF resin		6	6
MOR		1	1
CI resin		2	2

Formulations of Compound No 2 and 3 are similar to conventional bead wire ompound . Ageing studies were carried out for the specimens at different conditions like at 0°C for 2 and 4 weeks in an air oven , in cold water for 2 and 4 weeks at ambient temperature, in salt water (10% NaCl) for 2 and 4 weeks and steam ageing for 8 and 16 hours for all the compounds. Storage life of the compounds were investigated after 1 month and 2 months of storage. Tensile properties of the vulcanisates on a Zwick UTM model 1445 the ASTM D 412 (90).

The optical microscopic examination of the bead wires were conducted at 100 times magnification using an optical microscope.

Results and Discussion

Table 5.2.2 shows the cure characteristics of the compounds. The compound 4 shows lower scorch time and cure time compared to compound 2 and 3.

Table 5.2.2 Cure characteristics of the compounds

Compounds	t2, min	t90, min
Compound No 4	1.8	9.6
Compound No 2	4.5	20.9
Compound No 3	4.8	23.6

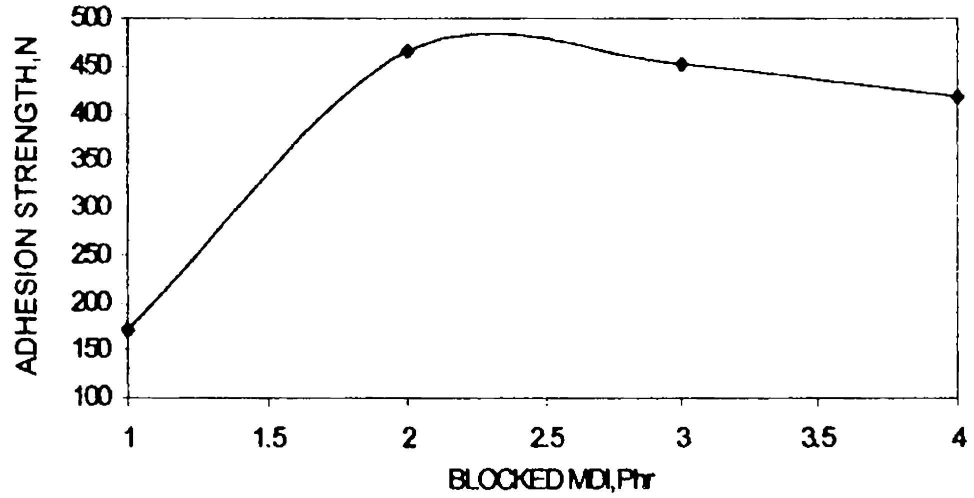

Fig.5.2.2 Effect of blocked MDI on adhesion strength

Figure 5.2.2 shows the effect of blocked MDI in the compound. Pull out strength increases when blocked MDI is added due to the presence of isocyanate group which improves adhesion [9,10]. But after a certain concentration the strength reduces due the presence of blocking agent and the solvents.

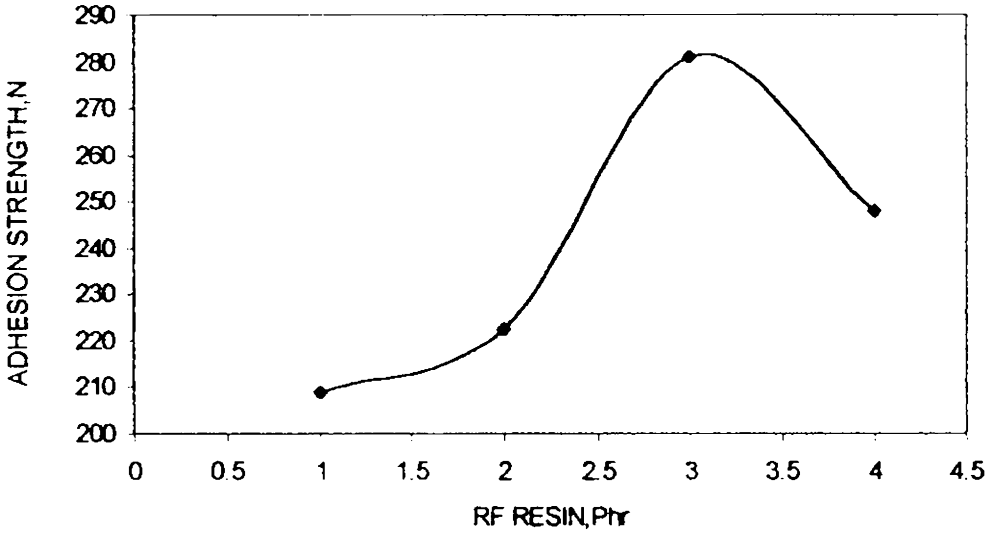

Fig.5.2.3 Effect of RF resin on adhesion strength

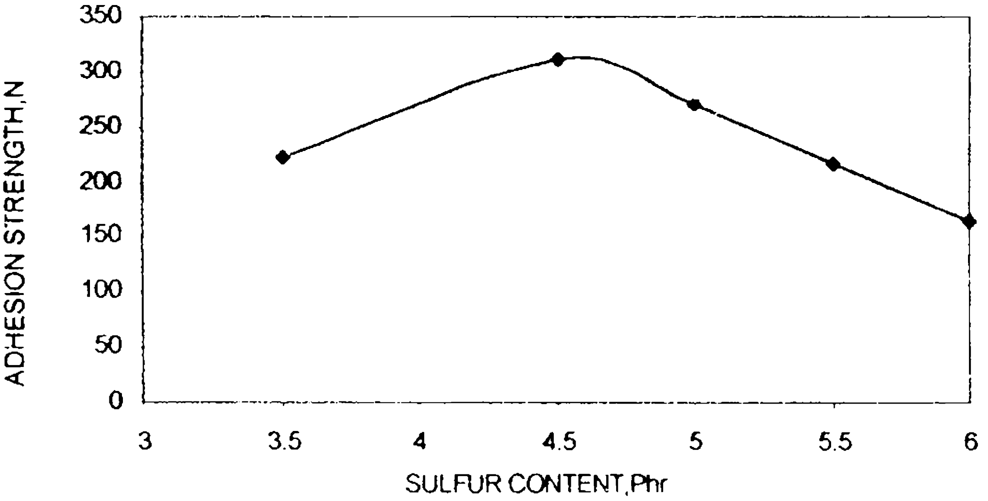

Fig. 5.2.4 Variation of adhesion strength with sulfur content

Figure 5.2.3 shows the effect of RF resin in the compound. As the amount of RF resin increases adhesion strength increases [11-13], reaches a maximum and then reduces. This shows that there is an optimum amount of RF resin which give maximum adhesion.

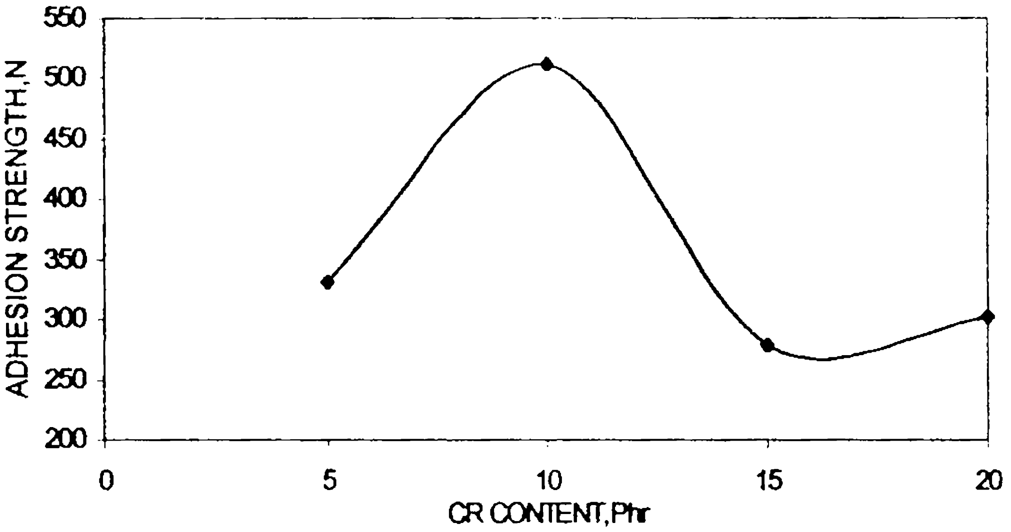

Fig. 5.2.5 Variation of adhesion strength with CR content

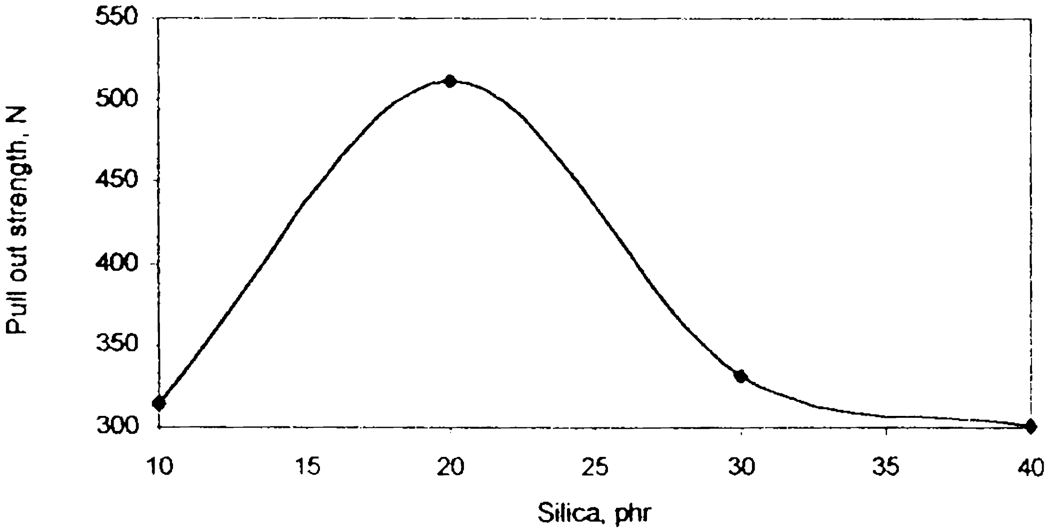

Fig. 5.2.6 Effect of silica in adhesion strength

Figure 5.2.4shows the effect of insoluble sulfur, when amount of sulfur increases adhesion strength increases reaches a maximum and then decreases. This may be due high degree of crosslinking which makes the compound more stiff leading to a reduction .

Figure 5.2.5 shows the effect of CR content in the compound. Presence of CR improves adhesion to metal [14],increasing the pull out strength . But after an optimum amount of CR the compatibility of CR with SBR reduces and hence adhesion strength diminishes.

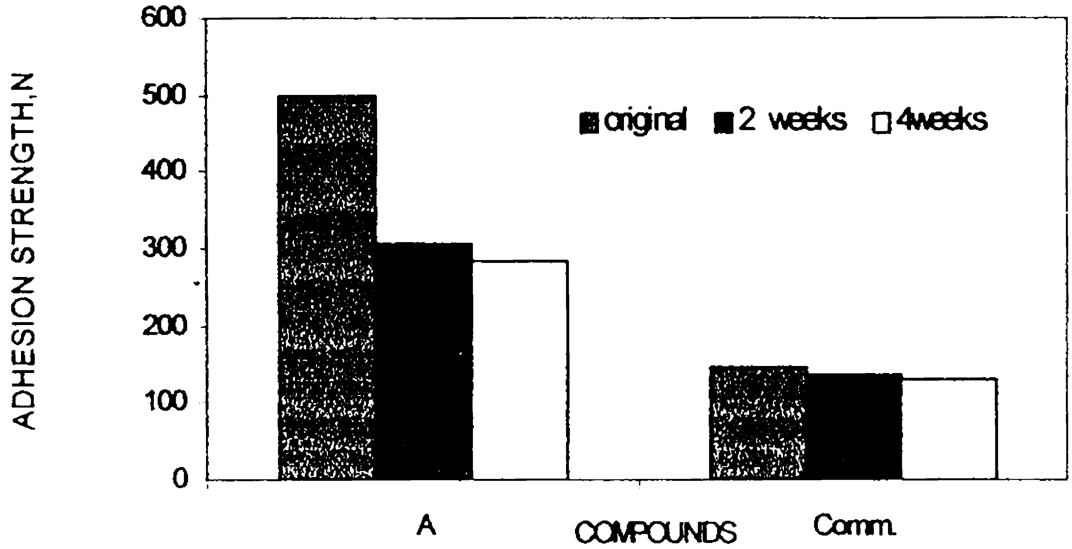

Fig. 5.2 7 aerobic ageing of the specimens.

Figure 5.2.6 shows the effect of silica filler in the compounds. As silica is added to the compound adhesion strength improves, reaches a maximum and then decreases. The improvement in adhesion is due to the reinforcement [17].

Figure5.2.7 shows the aerobic ageing resistance of TCAT specimens prepared from laboratory and the conventional compounds. Results show that compounds prepared in laboratory show comparable results to the conventional compounds. Chlorine present in the test compounds may give good heating resistance resulting in better adhesion strength after ageing.

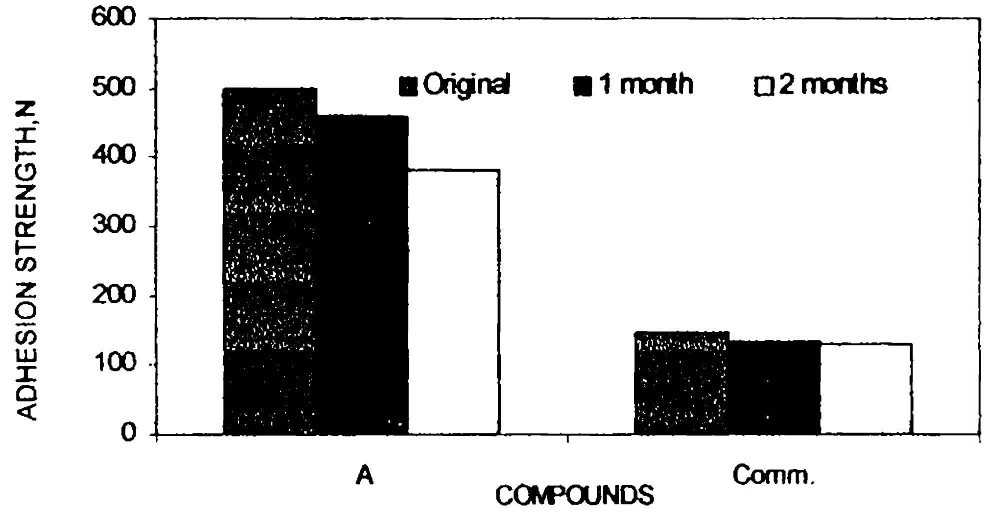

Fig.5.2.8 room temperature ageing of the specimens

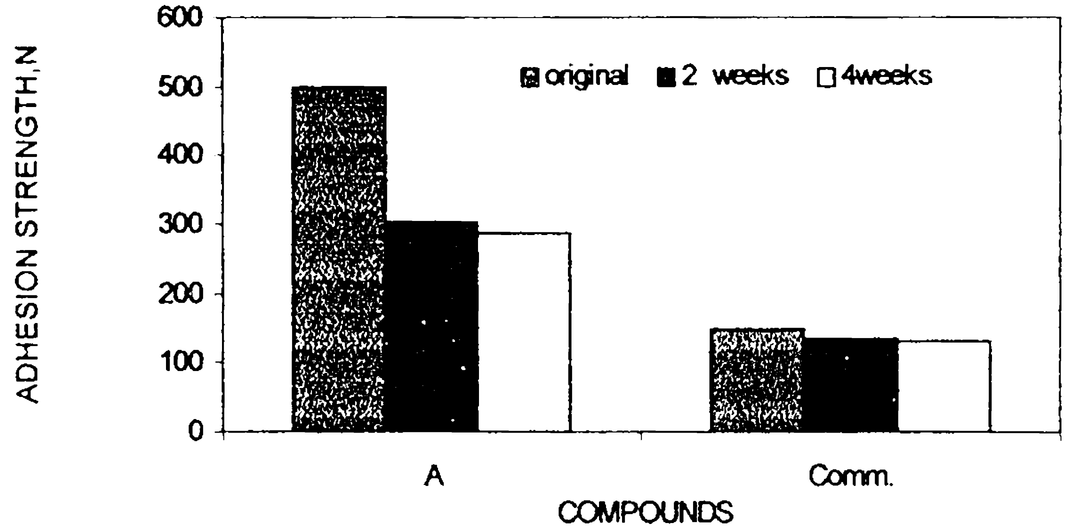

Fig. 5.2.9 salt ageing of the specimens

Figure5.2.8 shows the effect of room temperature ageing of the TCAT specimens prepared from test compounds and conventional compounds. Test compounds show comparable strength to that of conventional compounds.

Figure5.2.9 shows salt ageing resistance of the specimens. Test compound shows better strength when compared with conventional compound. The TCAT specimens prepared using test compounds show better corrosion resistance in contact with salt water.

Figure5.2.10 shows steam ageing studies on the specimens. Similar results as in the previous case are observed in this case also. Specimens prepared from test are resistant to steam due the presence of chloride linkages.

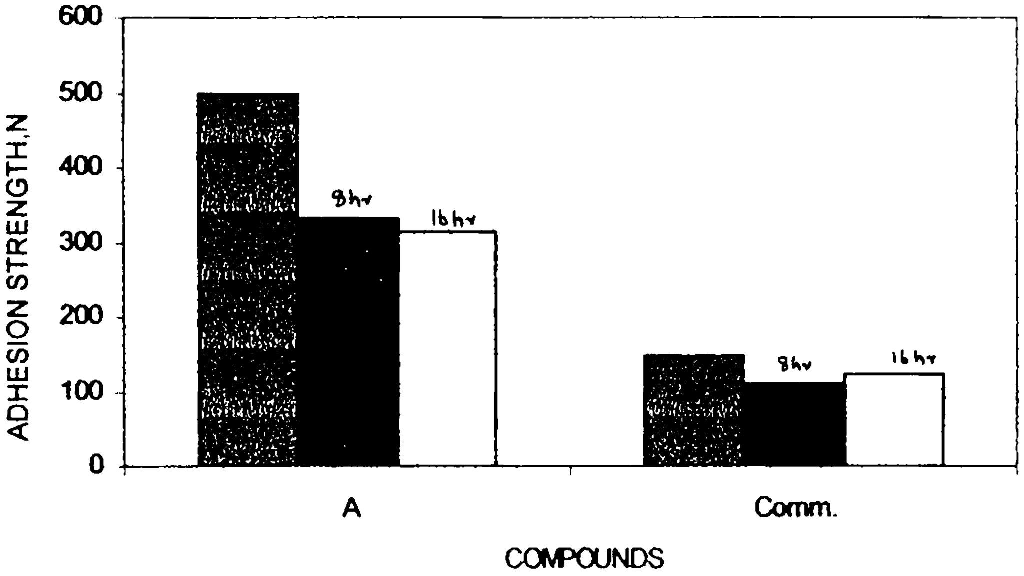

Fig. 5.2.10 steam ageing of the specimens

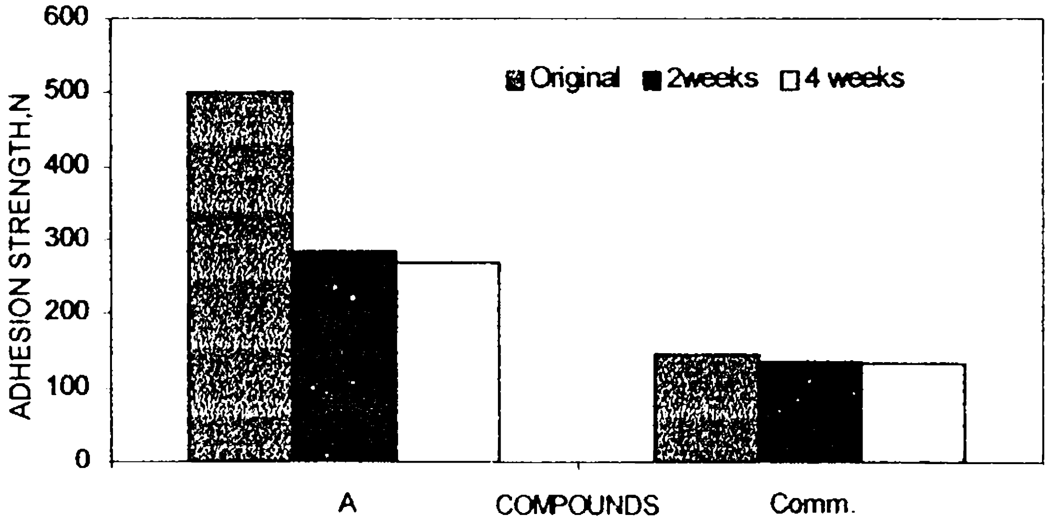

Fig.5.2.11 humid ageing of the specimens

Figure5.2.11 shows humid ageing resistance of the specimens. Results are comparable with the conventional compounds. Here also specimens prepared from test compounds show resistance to humidity so adhesion strength does not change widely when in contact with water.

Table 5.2.3 shows the properties of the specimens like secant modulus and rubber coverage. The modified compounds show higher secant module and rubber coverage.

Table 5.2.3 Properties of adhesion specimens

Conditions	Adhesion strength, N		Secant modulus, N/cm^2		Rubber coverage %	
	Comp.4	Comp.1	Comp.4	Comp.1	Comp.4	Comp.1
Unaged	512	148	6.38	1.8	82	80
RoomTemp. ageing	382	138	4.76	1.7	81	79
Aerobic ageing	285	130	3.6	1.6	82	80
Salt ageing	315	111	4.0	1.4	82	80
Humid ageing	269	136	3.4	1.7	81	79
Steam ageing	250	128	3.1	1.6	81	78

Table 5.2.4 shows the tensile properties of the compounds. Results for the compounds were comparable.

Table 5.2.4 Tensile properties of the compounds

Compound	Tensile strength	Modulus@ 300% elong. (N/mm^2)	Elong. @ break % (N/mm^2)	Tear strength	Hardness Shore A (N/mm)
Compound No 4	15.2	7.0	404	68.8	85
Compound No 2	12.6	6.8	606	56.3	82
Compound No 3	12.4	6.8	518	58.6	85

Photograph 5.2.1 Bead wire surface before adhesive application.

Photograph 5.2.2 Pulled off bead wire surface with commercial adhesive.

Photograph 5.2.1 shows the optical microscopic photograph for bead wire specimens. Photograph 5.2.2 shows the bead wire sample after pulled out from the compound and photographs 5.2.3shows the pulled out specimen from conventional compound. From the photographs we can see that both show almost identical surfaces after pulled out.

Conclusions

1. Blocked MDI in SBR compound improves the pull out strength of bead wire.
2. RF resin and CR improve the pull out strength.
3. Sulfur level in the SBR compound gives better adhesion strength
4. Ageing resistance of test compunds are better compared to conventional compounds.
5. Mechanical properties of both conventional and test compound are comparable.
6. The compound prepared in laboratory shows better results in secant modulus and rubber coverage than conventional compounds.

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Part 3 Studies on the Effect of Chloroprene Rubber in Steel Cord Adhesion

Steel belted tyre are now a days very popular[1]. Due to higher modulus of steel wire it gives very high reinforcement to tyre compound [2]. In order to improve the reinforcement, adhesion of steel cord to the rubber is very essential [3]. Adhesion was improved by the addition of cobalt and its derivatives to the compounds [4,5]. The availability of cobalt compounds are very difficult and it is found to be very expensive also. In another method the steel cord used was coated with brass to get better bonding [6,7]. Polar compounds containing chlorine can influence rubber - to steel cord adhesion[8].

In this part of the study of adhesion of steel cord to rubber compounds the addition of chloroprene rubber to the natural rubber compounds is proposed for improving its adhesion .Due to higher polarity of chloroprene rubber it may provide better bonding to steel cords.

Experimental

Steel cord used for adhesion was brass coated used in passenger tire manufacture. It was supplied by Societa' Pneumatici Pirelli, Business unit steel cord, United States of America with the following construction 2+2x0.25.

Chloroprene rubber compound prepared as per the formulations (Table5.3.1) and was blended with natural rubber in different proportions with the ingredients for natural rubber (Table5.3.1) and compound was prepared. These compounds were used for the adhesion studies with steel cords. Specimens for TCAT (Tire cord adhesion test) were prepared as described in part 2 of this chapter.

Table 5.3.1 Formulations of cord adhesion compounds

Ingredients , Phr	Base compound	CR compound
Natural rubber	100	0
Chloroprene	0	100
Zinc Oxide	5	5
Stearic acid	1.5	0
HAF(N330)	80	40
Aromatic oil	2	0
Pilflex 13	1	1
Sulphur	4.5	0
RF resin	3.0	0
MOR	0.8	0
Ethylene Glycol	1	0
Na22	0	0.5
Magnesium Oxide	0	4
Precipitated Silica	10	0

Results and Discussion

Figure 5.3.1 shows the effect of adhesion strength of steel cord to natural rubber compound when amount of chloroprene rubber compound varied. Adhesion strength increases and reaches a maximum and then almost levels off at 25 phr level. The chloroprene rubber present in the compound make it more polar and thus the adhesion to metal increases. There may be weak linkages between the chloride and the copper or zinc present in the coating of steel cord. Adhesion strength may increases due to this. When chloroprene content increases more than 25 phr there will be difficulty in the compatibility of chloroprene rubber and natural rubber due to their large difference in polarity. Which may be the cause for the strength to levels off and no further increase. So the improvement in property is only upto 25 phr level.

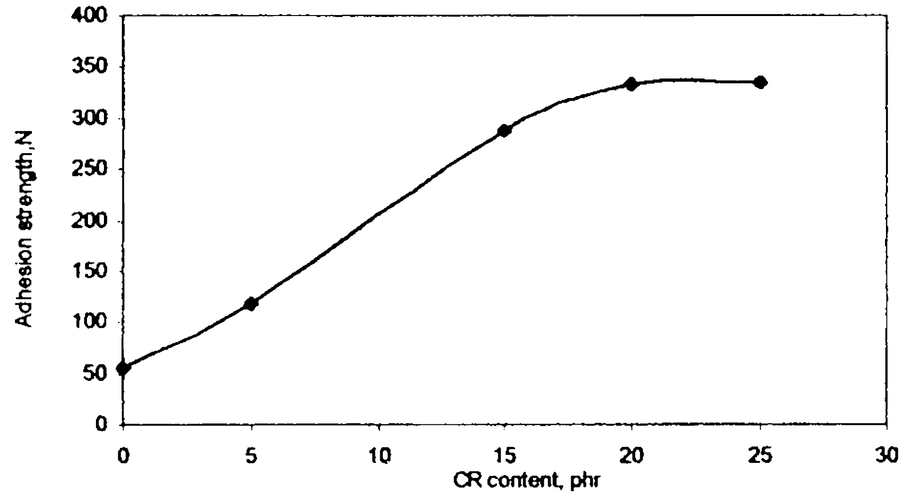

Fig.5.3.1. Variation of adhesion strength with CR content

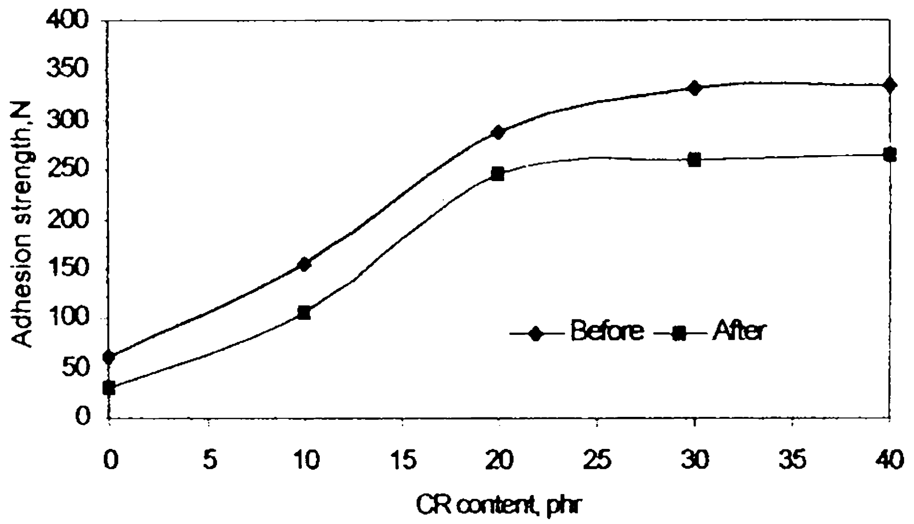

Fig.5.3.2 Adhesion strength with CR content before and after soaking in water (2 weeks)

Figure 5.3.2 shows the water resistance of the specimens made of compounds containing chloroprene rubber. Series 1 shows the strength before soaking in water and series 2 shows the strength after. There is reduction in adhesion strength due the effect of water on Cu++ and Zn++ ions which may cause dezincification due the formation of $Zn(OH)_2$ as a result of this lowering of adhesion strength [5].

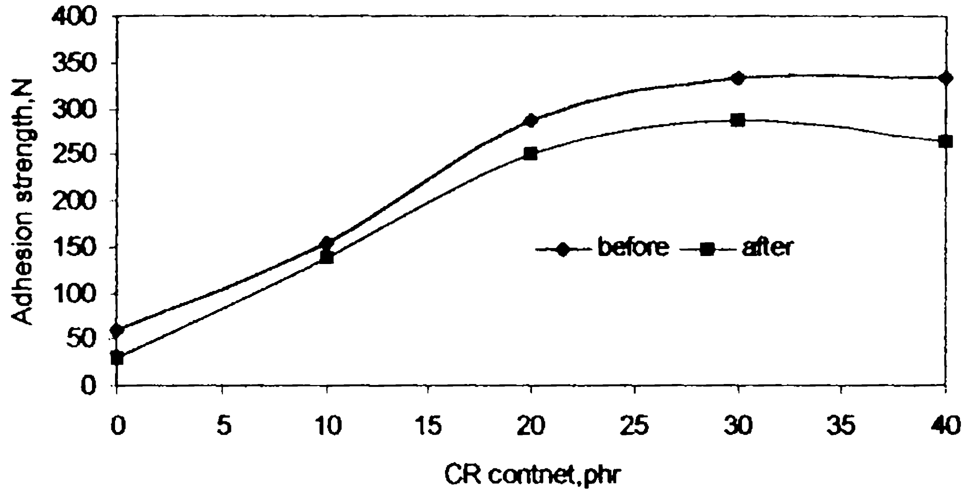

Fig. 5.3.3 Adhesion strength with CR content before and after steam ageing (16 hrs)

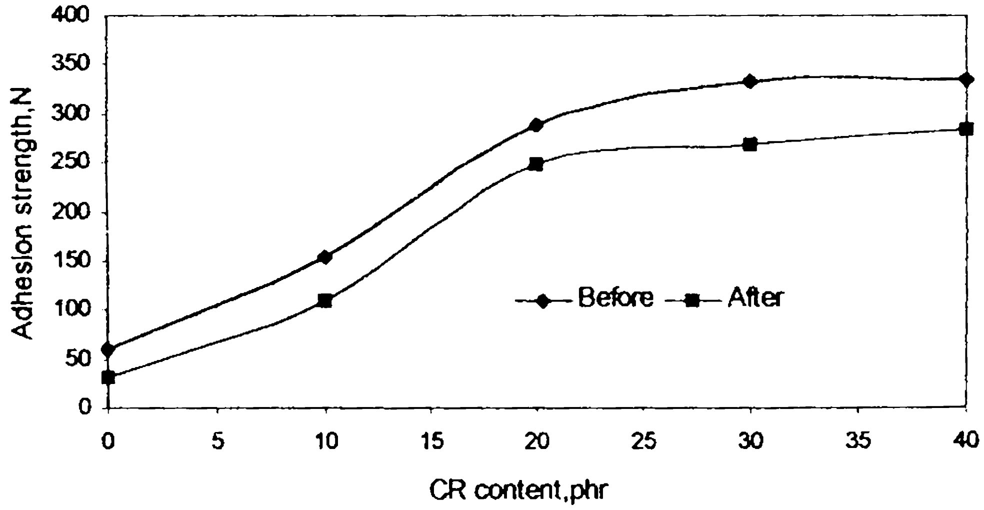

Fig.5.3.4 adhesion strength with CR content before and after aerobic ageing (4weeks)

Figure5.3.3 shows the effect of steam on the TCAT specimens with chloroprene rubber present. Reduction in adhesion strength is observed due the effect of latent heat of steam and also the effect of moisture present.

Figure 5.3.4 shows the effect of aerobic ageing of the specimens as the amount of chloroprene rubber content increases. Strength is found to be decreasing as expected. There may be thermal degradation due the temperature of ageing.

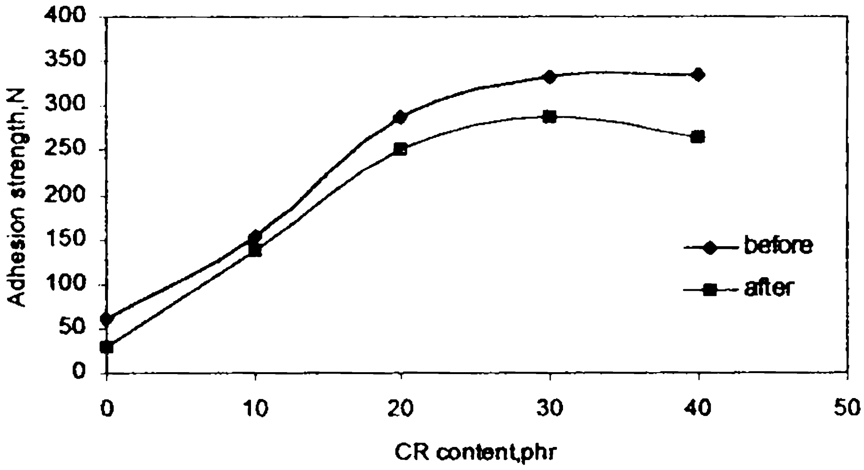

Fig.5.3.5 Adhesion strength with CR content before and after salt ageing (4 weeks)

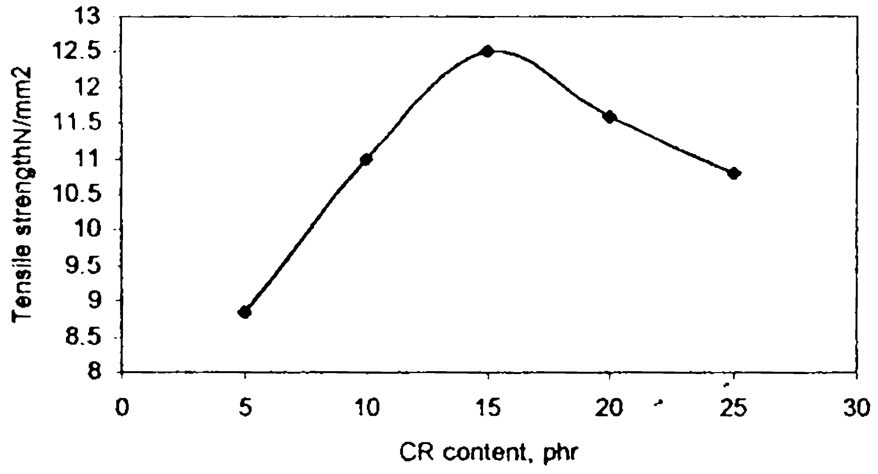

Fig.5.3.6 Tensile strength with CR content

Figure 5.3.5 shows the effect of salt ageing on the adhesion strength of steel cord to rubber compounds. All specimens with varying amounts of chloroprene rubber show decreases in strength. The sodium chloride present cause the formation of another layer contains zinc hydroxide or zinc chloride this is called dezincification process which will reduce the adhesion ^{5}.

Figure 5.3.6 shows the variation in tensile strength as the amount of chloroprene content in the natural rubber compounds. The initial tensile strength was found to be slightly lower due the higher dosage of filler(formulation in Table5.3.1). Tensile strength increases as amount of chloroprene rubber but after 15 phr strength was found to be decreasing. This may be due the large difference in polarity of these rubber, which cause incompatibility.

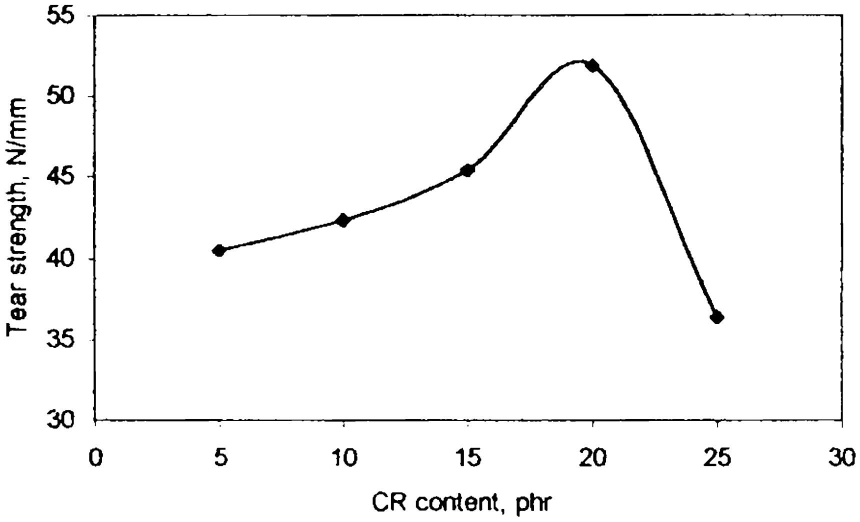

Fig.5.3.7 Tear strength with CR content

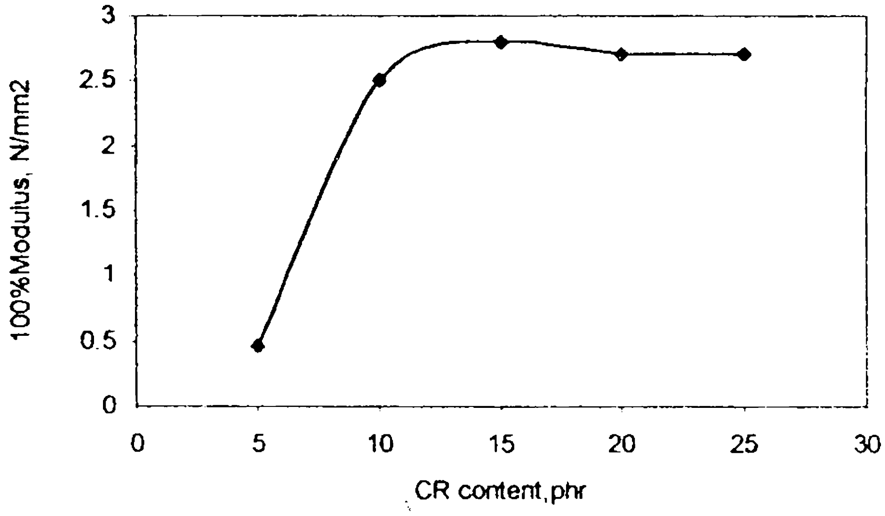

Fig.5.3.8 Modulus at 100% elongation with CR content

Figure 5.3.7 shows the tear strength of the compounds containing chloroprene rubber. Here also the initial tear strength was found to be lower than a usual NR compound due the very high loading of fillers. But the results are comparable with conventional cord adhesion compound .Tear strength increases in the initial state but after that it decreases. Similarly modulus at 100% elongation and elongation at break also shows the same trend as chloroprene rubber content increases (Figure 5.3.8 and Figure 5.3.9).

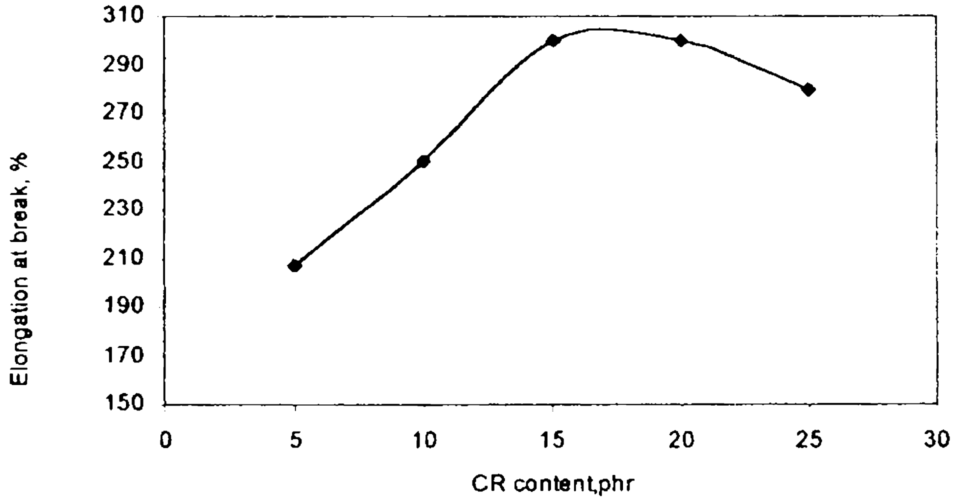

Fig.5.3.9 Elongation at break with CR content

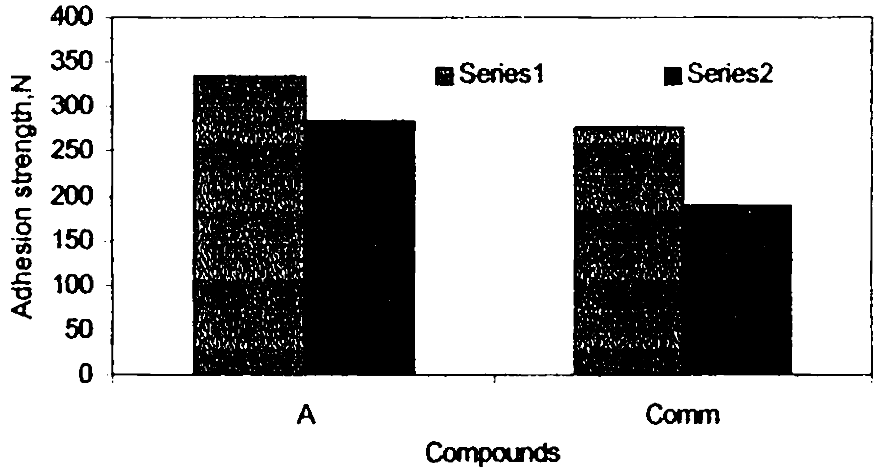

Fig.5.3.10 Effect of water soaking on adhesion strength, series1 before and series 2 after soaking

Figure 5.3.10 shows the water resistance of the TCAT specimens. Conventional compound containing cobalt salts also tested and the results shows that specimens from laboratory compound shows better resistance than conventional compounds. By the addition of chloroprene rubber the water resistance of the compounds increases due to its higher molecular weight due to this compounds shows better resistance than conventional compounds.

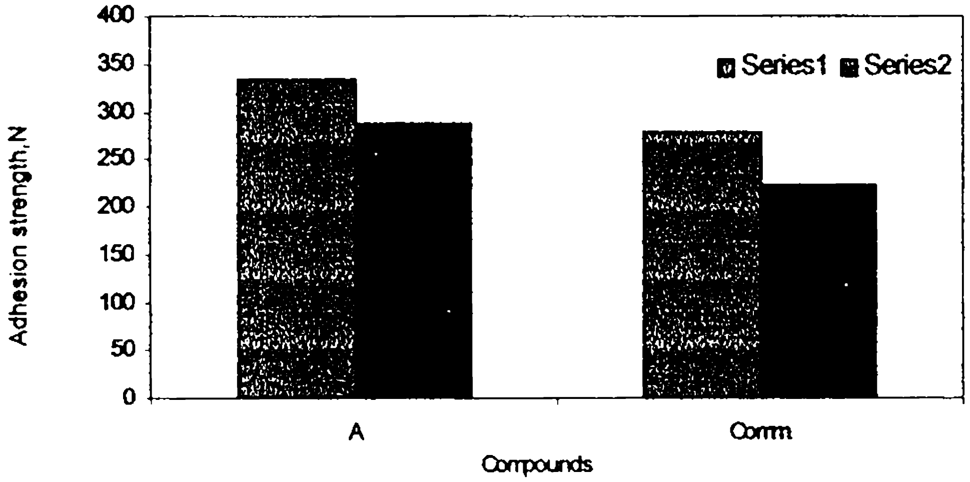

Fig.5.3.11 Effect of aerobic ageing on adhesion strength before(series1) and after(series2) aerobic ageing

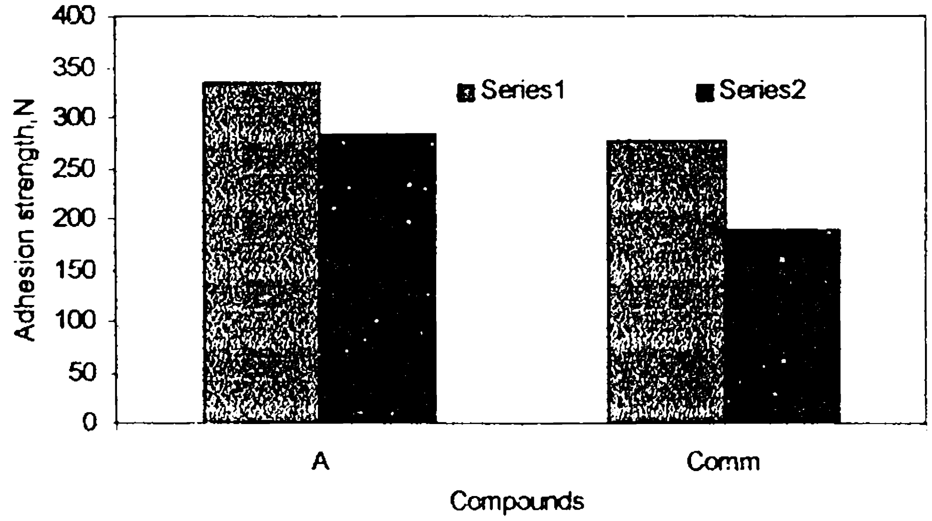

Fig.5.3.12 Effect of steam ageing before(series1) and after(series2) on adhesion strength

Figure 5.3.11 shows the aerobic ageing of the TCAT specimens. In this figure specimens prepared from laboratory compounds show better results than conventional compounds. The chloroprene rubber present in the compound increases its thermal resistance so we get better results for the compounds prepared in laboratory.

Figure5.3.12 shows effect of steam ageing to the specimens. Specimens prepared using laboratory shows better results in this cases also. Figure 5.3.13 shows the comparison of salt ageing to laboratory and conventional compounds. Laboratory compounds shows comparable results in this cases also.

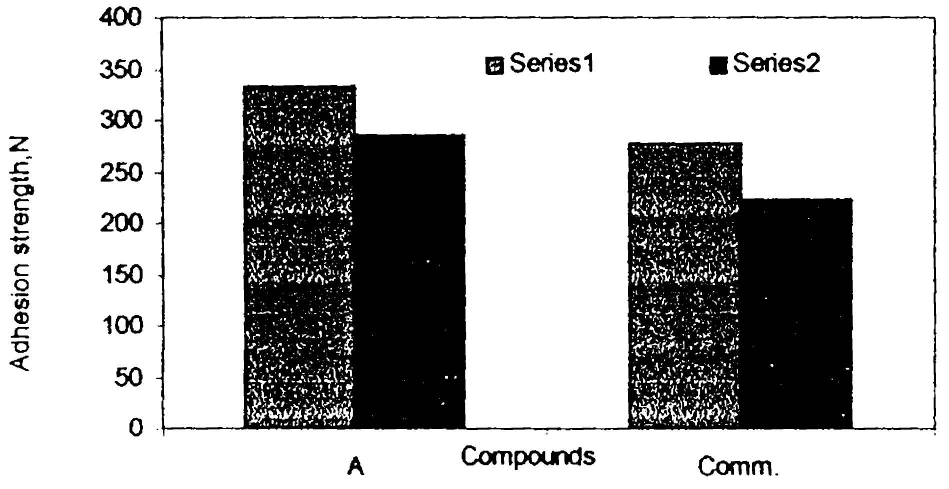

Fig.5.3.13 Effect of adhesion strength before(series 1) and after (series2) salt ageing

Table 5.3.2 shows the values of secant modulus and rubber coverage of TCAT specimens. The compound prepared in laboratory shows more secant modulus than conventional compounds. This may be due the increase in modulus of the compound by the addition of chloroprene rubber. Rubber coverage increases which is evident from the adhesion strength results.

Table 5.3.2 The properties of TCAT specimens

Condition	Adhesion Strength, N		Secant Modulus, N/mm^2		Rubber Coverage, %	
	1	2	1	2	1	2
Unaged	334	277	4.16	3.46	90	88
Room Temp. Ageing	300	250	3.74	3.12	90	88
Humid Ageing	248	202	3.09	2.52	89	88
Aerobic ageing	287	223	3.58	2.79	90	88
Steam ageing	265	200	3.31	2.49	88	87
Salt ageing	283	189	3.53	2.36	87	86

1- Modified laboratory compound and 2 - Conventional compounds.

Table 5.3.3 shows the tensile strength of both laboratory compound and conventional compound. Similar results for tensile strength, tear strength, modulus and elongation at break were obtained.

Table 5.3.3 Tensile properties of cord adhesion compounds

Properties	Modified	Conventional
Tensile strength, N/mm^2	12.5	14.66
Tear strength, N/mm	51.95	39.1
Modulus at 100% elongation N/mm^2	2.8	4.2
Elongation at break, %	300	468

Photograph 5.3.1 Cord wire surface before adhesive application.

Photograph 5.3.2 Pulled off cord wire surface with laboratory adhesive.

Photograph 5.3.3 Pulled off cord wire surface with commercial adhesive.

Photographs 5.3.1, 5.3.2 and 5.3.3 shows the cord wire before adhesion, cord specimen after peeling with the modified compound as well as the conventional compound respectively. Photographs are found to give comparable results in both cases. So this modified compounds can be used in tyre cord adhesion.

Conclusions

1. Chloroprene rubber can be added to the natural rubber compounds to get better adhesion to steel cord.
2. There is an optimum level of chloroprene content up to which we can improve adhesion of steel cord to rubber.
3. By the addition of chloroprene rubber we can improve water resistance, aerobic ageing resistance , steam ageing and salt ageing resistance.
4. The secant modulus and rubber coverage values are found to be much better in case of laboratory compounds.
5. The adhesion strength of compounds containing chloroprene rubber are found to be better than that of conventional compounds.

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Chapter 6

SUMMARY AND CONCLUSIONS

Chapter 6

Summary and Conclusions

The primary objective of the study was to develop novel , more efficient and indigenous adhesives to replace expensive,commercial adhesives for wood to wood, leather to leather and rubber to metal bonding The results of the study may be summarised as follows :

Adhesives for wood to wood joints :

Natural rubber latex based adhesives found to be efficient and cost effective systems for bonding wood. The effect of prevulcanisation of NR latex and the effect of different ingredients on adhesive efficiency were investigated . Natural rubber latex based adhesives were also found to be superior in water resistance compared to the commercially available latex based wood adhesives.

Styrene butadiene vinyl pyridine copolymer latex adhesives were also tried as wood adhesives. VP latex was also found to be an efficient adhesive for wood joints. Adhesion strength could be improved by modifiers such as RF resin,ammonium caseinate and CMC. The efficiency of wood joints employing these adhesives was found to be superior to that compared to commercial latex based adhesives.

Solution based wood adhesives were also prepared from natural rubber and synthetic rubbers and their blends. Chlorinated natural rubber was prepared and characterised and compared with commercial CNR. Solution adhesives were modified by CNR and lap joint strength improved significantly . Wood joint strength employing these adhesives was found to be superior than some of the commercial solution based wood adhesives. Durability of the wood joints when in contact with water, hot water, acid and alkali was also found to be much higher than commercial adhesives. Shelf life of the adhesives prepared was also found to be adequate .

Novel thermoplastic elastomer based adhesives were prepared and tried as wood adhesives. Lap shear strengths using these adhesives were better than that of commercial adhesives. The effect of solid content and viscosity on lap joint strength were estimated. Optical microscopic investigation of the peeled surfaces was done to investigate the mode of failure .

Adhesives for leather to leather joints :

Natural rubber, chloroprene rubber and polyvinyl chloride based solution adhesives were prepared for bonding different components in leather products. The peel and shear strength of the joints using these adhesives were much higher than those of commercial adhesives. Resistance to water, hot water , ageing and flexing etc. were also found to be superior for the test adhesives to those of commercial adhesives.

Leather joints were prepared with latex based adhesives also. NR, VP and XNBR latices were compounded and tried in leather joints. Joint strength under different environments and shelf life were evaluated and compared with commercial adhesive.

Thermoplastic elastomer based solution adhesives were tried for leather joints also. Adhesion strength of the joints were significantly higher than those of commercial adhesives. Ageing resistance of the bonded specimens were also superior . The peeled off surfaces were examined under an Optical microscope to study the mode of failure .

Adhesives for rubber to metal bonding :

A low solvent rubber compound strip adhesive system was developed in place of solvent adhesives for rubber -to- metal bonding. Peel strength of the joints were compared with those of the commercial adhesive -polylock and results were comparable. The rubber compound strip used for bonding was modified with different ingredients and also with blends of elastomers. The efficiency of different rubber strips based on different elastomers on different adherends was investigated. Using the results, it may be possible to select a particular rubber strip for obtaining maximum adhesion depending upon the type of substrates .

Adhesion of the bead wire-to-rubber was also investigated by modifying the rubber compounds. The effect of different ingredients in the compound was studied. The SBR compound which contain CR gave the maximum adhesion to bead wire. The resistance of the specimens to adverse environments were studied and found to be comparable with conventional bead wire compounds.

Adhesion of steel cord to NR compounds was also found to be improved by the addition of chloroprene rubber. Accelerated ageing of the bonded specimens under different service conditions were studied. The adhesion strength was comparable with conventional compounds containing cobalt adhesion promoters.

The pulled off bead wire and steel cord were examined using an optical microscope to study the mode of failure

The major highlights of the study are :

1. Development of water resistant latex based adhesives for wood to wood bonding
2. Development of superior strength adhesives based on thermoplastic elastomers for leather to leather bonding .
3. Development of rubber strip adhesion system for rubber to metal bonding . Modification of the matrix using polychloroprene rubber for improving the bead wire and steel cord adhesion to rubber.

List of publications from present work

1. Studies on wood to wood bonding using natural rubber latex, Neetha John and Rani Joseph, J. Adhesion . Sci. Technol, Vol.11, p 225-232, no.2, (1997).
2. Novel adhesive system for rubber to metal bonding, Neetha John and Rani Joseph, Proce. Ninth Kerala Science Congress ,p423, (1997).
3. Rubber solution adhesives for bonding wood joints, Neetha John and Rani Joseph, J. Appl. Polym. Sci. Vol.68, no.7, p 1185, (1998).
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5. Studies on polymeric adhesives for bonding leather, Neetha John and Rani Joseph, J. of American Leather Chemists Association (1998), Vol 93, No. 5.
6. Improvement of adhesion of copper coated bead wire to styrene butadiene rubber by the addition of neoprene rubber and other additives, Neetha John and Rani Joseph, Proce ,National seminar on advances in polymer technology (APT'98) ,p 14,(1998).
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