STUDIES ON ADHESIVES FOR BONDING RUBBER TO RUBBER AND RUBBER TO TEXTILES

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BY
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"Thus far the Lord has helped us"

DECLARATION

I hereby declare that the work presented in this thesis is based on the original work done by me under the guidance of ***Dr.Rani Joseph***, Professor, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, and that no part of this thesis has been included in any other thesis submitted previously for the award of any degree.

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Certificate

This is to certify that the thesis entitled, **"Studies on adhesives for bonding rubber to rubber and rubber to textiles"** *is based on the bonafide work done by* **Ms.Lynta Job** *under my supervision and guidance in the Department of Polymer Science and Rubber Technology and that no part thereof has been included in other thesis submitted previously for the award of any other degree.*

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List of Abbreviations

NR	Natural rubber
PB	Polybutadiene rubber
NBR	Acrylonitrile-butadiene rubber
CR	Chloroprene rubber
CNR	Chlorinated natural rubber
NR latex	Natural rubber latex
VP latex	Vinyl pyridine terpolymer latex
ZnO	Zinc oxide
Vulkanox HS	1,2,-dihydro-2,2,4-trimethyl quinoline, Polymerized
Vulkanox 4020	N (1,3- dimethyl butyl N'- phenyl - p- phenylene diamine)
HAF, N- 330	High abrasion furnace black
VGC	Viscosity gravity constant
MgO	Magnesium oxide
MOR	Benzthiazyl-2-sulphenmorpholide
TMTD	Tetramethyl thiuram disulphide
TMTM	Tetramethyl thiuram monosulphide
NA 22	Ethylene thiourea
PF	Phenol formaldehyde
CNSL	Cashew nut shell liquid
ZDC	Zinc diethyl dithiocarbamate
MBTS	Dibenzthiazyl disulphide
$T_{10\,min}$	Scorch time-The time taken for attaining 10% of the maximum torque.
T_{90min}	Optimum cure time -The time taken for attaining 90% of the maximum torque
ΔM	Mass loss
ρ	Density of sample.

kg-f	Kilogram force
N/mm	Newton per millimeter
N/mm^2	Newton per millimeter square
psi	Pounds per square inch

Chapter I

INTRODUCTION

When two solids with plane surfaces are brought together they make contact on the molecular scale only at rare points at their common interface. The application of force across the interface can cause distortion of the contact points making them into areas but some of the energy applied in doing this is stored as elastic energy and on removal of the load, it is utilized in breaking any union formed. The introduction of a liquid to displace the air can create a situation in which real contact is made throughout the interface but not between body and body, but between body and liquid. If this liquid can solidify, the desired state of solid body contact is achieved although the solid body contains a plane of chemically different substances. This material used to bring about the change from occasional touch to intimate contact is an adhesive.

Adhesion refers to the state in which two dissimilar bodies are held together by intimate interfacial contact such that mechanical force or work can be transferred across the interface. The interfacial forces holding the two phases together may arise from van der Waals force, chemical bonding or electrostatic attraction. The mechanical strength of the system is determined not only by interfacial forces, but also by the mechanical properties of the interfacial zone and two bulk phases. Various other definitions for adhesion have been proposed [1-7]. However, none is completely satisfactory or generally accepted. Any satisfactory definition must account for both the thermodynamic and mechanical aspects of adhesion.

Thermodynamic adhesion refers to equilibrium interfacial forces or energies associated with reversible processes, such as ideal adhesive strength, work of adhesion, and heat of wetting. The term was first proposed by Eley [3]. Chemical adhesion refers to adhesion involving chemical bonding at the interface. Mechanical adhesion arises from microscopic mechanical interlocking over substantial portions of the interface.

Adherend, a term coined by de Bruyne [8], refers to a body that is bonded to another body with an adhesive. Substrate refers to any material on which an adhesive is applied.

The science of adhesion is divided into two categories one dealing with the chemistry and physics of surfaces and interfaces, and the other with the mechanics of fracture of adhesives joints. The former is concerned with bond formation, i.e., wetting, adsorption, chemical interlinking, etc, and predicting the magnitude of the intrinsic strength of adhesion across an interface, whereas the latter deals with the mechanical analysis of the strength of adhesive joints and the development of test methods to measure their strength.

The first step in the formation of an adhesive bond is the establishment of interfacial molecular contact by wetting. The molecules will then undergo motions toward preferred configurations to achieve the adsorptive equilibrium, diffuse across the interface to form a diffused interfacial zone, and/or react chemically to form primary chemical bonds across the interface chemical constitution.

The recent development of the theory of adhesion [9-11], has lead to a rational definition of the prevailing causes of adhesion phenomena, which may be classified into three categories: Mechanical keying, interdiffusion and physiochemical bonding.

The extent of molecular or local segmental diffusion across the interface determines the structure of the interfacial zone, which initially affects the mechanical strength of an adhesive bond. Negligible diffusion will give a sharp interface. In this case, if the interfacial attraction consists mainly of dispersion force, the adhesive strength will be low because of interfacial molecular slippage under applied stress. For a sharp interface, high adhesive strength can be obtained only when strong polar interactions or chemical bonds exist across the interface. But, if the interface is sufficiently diffuse as a result of extensive diffusion, dispersion force alone will give high adhesive strength.

Wetting can affect adhesion in two ways. First, incomplete wetting will produce interfacial defects and thereby lower the adhesive bond strength. Second, good wetting, can increase the adhesive bond strength by increasing the work of adhesion , which is directly proportional to the fracture energy. Stress concentration will occur around an unwetted interfacial defect as an adhesive bond is stressed[12,13]. When the local stress exceeds the local strength, the adhesive bond will fracture.

It has been established that solids can be made to adhere strongly by wetting each surface to be joined with a thin layer of a liquid that gets hardened or solidified gradually during contact. However, until this century the selection of suitable adhesives and application techniques was an art depending on the use of glue formulations made from fish and animal products or cements made from inorganic slurries or solutions. The advent of synthetic polymeric adhesives having better and more reproducible properties promoted a wider use of adhesives in the past thirty years and increased interest in converting the art into a science.

In the past several decades important contributions to the subject of adhesion have included the nature of the molecular forces responsible for adhesion, the relation between adhesion and friction, the effects of not matching the physical properties of adhesive and adherend, the effect of voids and occlusions on the development of stress concentrations and the role played by adsorbed films and inadequate wetting on joint strength as well as on the location of fracture. The work done in understanding adhesion and adhesives is well evidenced in the excellent collections of papers edited by de Bruyne and Houwink[14], Eley[15], and Weiss[16].

When two dry, hard solids are pressed together, little effort is required to pull them apart and according the Holm[17] and Bowden[18] this occurs because the real area of contact is generally a small fraction of the apparent area. Strong adhesion between carefully polished contacting solids have been shown to result from a surface-tension effect caused by the presence of a thin layer of liquid between them.

Two solids in contact may develop a degree of adhesion depending on the type of interactions operative between them[19]. After the first stage of wetting the two surfaces are in intimate contact, and the chains are then free to move across the interface by diffusion, creating chain entanglements[20]. In the case of a sharp interface, interfacial chemical bonding is favoured[21]. Wool et al[22], Kline and Wool[23] examined the strength development at polymer-polymer interface, and related the time dependent nature of the interface to the molecular dynamics of macromolecular chains, chemical compatibility and the fractal nature of the diffused interface. Different reactive functional groups have been introduced into different adherends with the objective of formation of chemical linkages[24]. There are evidences of interfacial chemical bonding and interchange reactions between different functional groups in blend systems[25-28].

Dynamic mechanical analysis has been used to characterize adhesion in a tire cord-rubber system[29]. Zorowski and Murayama[30] have shown that an important property of the interface is the degree of adhesion between the two phases and that more energy will be dissipated at poorly jointed interfaces than an intact interface. Recently Bhattacharya and De[31] have shown that adhesion of aluminium surface to rubber can cause changes in the dynamic mechanical properties of the rubber.

A monomolecular layer of oxide or of organic contamination can decrease greatly the adhesion of solids. The effect of this monomolecular layer can be, that if removed by appropriate means, the solids can readily be made to adhere on contact. This fact is well exemplified by Anderson's simple experiment[32], in which two gold spheres are pressed together in a high vacuum.

Bowden and Tabor[18] have proved that in addition to the influence of adsorbed films in decreasing the adhesion of dry solids, there is a loss of adhesion following elastic recovery or release of elastic strains, on removing the load pressing two solids together.

When two flat, smooth solid surfaces (adherends) are separated by thin layer of a liquid having a zero contact angle, strong adhesion will result. This effect arises from the liquid surface tension (γ_{LVo}) and the fact that there will be a concave meniscus at the liquid/air interface. If the area of contact of the liquid with the solid is circular having radius R and thickness d, and if the liquid layer is thin enough so that the meniscus can be treated as a circular toid of radius r=d/2 the Laplace equation of capillarity leads to the following expression:

$$\rho_L-\rho_A = \gamma_{LV_0}(1/R-1/r)$$

If r<<R, then $\rho_L-\rho_A$ will be a large negative quantity and there will be a greater pressure P_A in the air outside the liquid than the value P_L inside. Hence the two plates will be pressed together under the pressure difference P_A-P_L. In short, a thin layer of a liquid that completely wets two flat solids can serve as an adhesive. The above equation has been confirmed experimentally by Budgett[33], by Harely [34], by Bastow and Bowden[35] and later by de Bruyne[36,37].

If the contact angle of a liquid adhesive with each adherend is not large, a prompt adhesive action is obtained upon pressing them together, even though imperfectly fitted until they are separated by only a thin liquid layer. There after, a stronger and more useful joint will be formed, if the viscosity of the liquid layer is increased greatly through any of the various mechanisms such as solvent permeation or evaporation, polymerization and cooling until solidification occurs. If properly designed, the resulting joint can have high resistance to both tensile and shearing stresses.

When a liquid adhesive solidifies, the reversible work of adhesion of the adhesive to the adherend would still be close to the value for the adhesive in the liquid state if it were not for the development of stress concentrations. This conclusion follows from the highly localized nature of the attractive field of force causing adhesion. Since this attractive force is effective little more than the depth of one molecule in both the adhesive and the adherend, it will be unaffected by changes of state so long as allowance in made for any resulting alteration in the surface density or molecular orientation occurring at the joint interface[38]. The former can be estimated from the change of density on solidification, but the latter may be difficult to compute since reorientation effects could originate through a crystallization process starting from some nucleus not located in the interface. Internal stresses and stress concentrations usually develop on solidification of the adhesive, the most common cause being the difference in the thermal expansion coefficients of the adhesive and the adherend.

There is a considerable interest in the relation between the adhesion and friction of rolling or sliding rubber surfaces. It has been shown in earlier studies[39] that rubber surfaces made optically smooth can be brought into intimate contact, and under these conditions adhesion is observed between the joined surfaces. The force to separate them can be predicted[40] under equilibrium conditions.

Photoelastic studies of Mylonas[41] and Mylonas and de Bruyne[42], which led to the conclusion that in a lap joint , poor wetting of the adherend tends to produce a greater stress concentration at the free surface of the adhesive where failure is most likely to be initiated. As the contact angles becomes large, the maximum stress concentration increases and moves towards the linear boundary where the adhesive and atmosphere make contact with the adherend and stress concentration factor increases. Griffith[43] has proved that failure of adhesive may occur at a relatively small applied stress if there are air bubbles, voids, inclusions or surface defects; it occurs because stress concentrations that result are much higher than the mean stress applied across the specimen. This conclusion is especially important when considered in terms of the probable effect of poor wetting on the development of air pockets at the adhesive-adherend interface.

In adhesives technology it is common practice to roughen the surface of each adherend, or "give it tooth" so as to obtain a stronger joint. If gas pockets or voids in the surface depressions of the adherend are all nearly in the same plane and are not far apart, there may be crack propagation from one pocket to next, and the joint may break as if it had a built in "Zipper".

The history of an adhesive joint comprises of three periods. In the first the adhesive is applied to the adherends and the joint is formed; in the second the adhesive sets and in the third, the properties of the joint remain sensibly constant. The three components of the joint during the three periods of its history depend on the type to which the joint belongs. The three types are the hooking joints, improper joints and proper joints.

Hooking joints are common with fibrous adherends such as paper, paperboard or fabrics. When the adhesive is applied as a liquid, it penetrates into the pores or voids between the fibers and, after setting, forms hooks or loops around these fibers, thus mechanical interlocking ensues. If the adhesive is a Newtonian liquid of viscosity η and the pores are slits of width δ, the rate of capillary penetration is given by the following equation:

$$z/t = \delta \gamma \cos\theta_A / 3\eta z$$

Where z is the depth of penetration reached after time t, γ is the surface tension of the liquid and θ_A is the advancing contact angle[44].

Improper joints contain a weak boundary layer in which rupture takes place when an external force is applied to the joint. The weak boundary layers may be of many kinds and can form during the formulation or during the setting periods. Proper joints do not contain this weak layer. In proper joints as in looking joints, either the adhesive or the adherend breaks.

In order to have good bonding between adhesive and substrate, there must be a decrease in free energy when the two are brought into contact. In addition, the adhesive must be sufficiently fluid to wet the surface completely. To meet this requirement the adhesive must be low in viscosity at the time of application. The setting of an adhesive may take place in several ways, such as, cooling of a hot melt, release of solvent and polymerization in situ.

The organic adhesives are all high polymers; the oldest are those of natural origin. Animal glues and starches have been in use since ancient times, cements based on natural rubber and pyroxylin (cellulose nitrate) became available during the 1800s. Resins based on phenol-formaldehyde and urea formaldehyde were developed in the early twentieth century. The greatest advance in adhesives, is the development of adhesives based on synthetic rubbers, on other vinyl-type polymers and on the epoxy resin which has occurred within past few decades.

Rubber based adhesives[45,46] are used both as lattices and as solvent cements. Latex adhesives, with their low viscosity and high solids content, are advantageous in the manufacture of shoes, books and textile laminates. Tire cord is bonded to rubber with mixtures of rubber lattices and resorcinol formaldehyde resin. Most rubber for adhesives is utilized in solvent-cement form. The rubber is dissolved in the solvent by high-speed mixers, other ingredients may include tackifying resins, fillers, softeners, antioxidants, vulcanizing agents and sequestering agents.

The industrial utilization of rubber paved the way of general acceptance of rubber adhesives. Macintosh obtained a patent in 1823 for rendering two fabrics waterproof by uniting them with a solution of rubber in different solvents. Rossman reviewed many of the early patents taken out in the United States dealing with some rubber cements, describing some 105 references on them up to 1935[47]. Among some of the earlier patents of note was the rubber cement prepared by Jeffery, who dissolved shredded rubber in naphtha. On heating this combination small amounts of shellac were introduced[48]. Hayward described the technique of bonding rubber to rubber with the aid of a rubber cement followed by vulcanization[49]. Grout prepared useful cements from unvulcanized rubber, benzene, turpentine, and Collodion[50]. Kelly indicated the trend of the art toward vulcanizable compositions by adding sulfur, sodium silicate and white lead to the rubber[51].

Zimmerli and Havenhill prepared a solution of calcium resinate, rosin, and rubber in preparing a cement where reclaimed rubber was employed throughout[52]. Prolonged milling and aging of natural rubber accompanied by the addition of coumarone-indene resin form the basis of various rubber adhesives, according to Malone[53]. McCortney added calcium resinate, rosin and an organic peroxide to rubber to prepare adhesive products[54]. The role of the benzoyl peroxide used was to effect some depolymerization of the rubber. Blends of shellac and rubber make useful adhesives. The hardness and elasticity may be controlled by various proportions though as much as 40 percent of shellac may be present[55].

Pragoff developed improved adhesives involving rubber and rosin derivatives[56]. According to the reports made by him, in as much as rosin is an unsaturated acid it is quite susceptible to oxidation and that when exposed to atmospheric conditions rubber-rosin base adhesives deteriorate and lose their adhesive qualities. Consequently in place of rosin, he employed a heat-treated rosin, processed in the presence of nickel, platinum, or copper chromite catalysts which effect an intramolecular rearrangement to yield compounds rich in dehydroabietic acid. These acids or their esters present to the extent of 20 to 30 per cent of the weight of the rubber yield adhesives which have good aging resistance and retain their tack and adhesion, Further, 80 to 20 parts of dehydrogenated rosin and 10 to 15 percent of lanolin[57].

Campbell discovered that rubber cements with a halogenated nitroparaffin containing less than 8 carbon atoms greatly retarded the gelling of vulcanized cement on standing[58]. The solvent, 1-chloro-1-nitropropane is used as one such stabilizer. The nitroparaffins similarly inhibit the gelling of synthetic rubber cements formulated as Buna-S or Hycar or greatly extending the shelf life after activation.

Thies employed a starch-impregnated fabric sheet, in conjunction with a cured rubber sheet, surfaced on one side with gum rubber and a cold patch cement on the other side[59]. Crawford has improved the adhesion of rubber to cotton fabrics by treating the cotton with a shellac amine soap, applying the vulcanizable rubber and vulcanizing the assembly[60]. In cementing rubber- impregnated fabric to fabric free of rubber it has proved desirable to soak the fabric in a volatile rubber solvent for a few minutes[61].

Cyclized rubber is being used extensively in adhesives, but is not always necessary to use cyclized rubber as the adhesive agent in bonding two sheets of rubber together, as in some circumstances very effective results may be obtained by cyclization of the rubber surface just before applying the adhesive, which may be a thermosetting synthetic resin.

Treatment of rubber with strong acids in the presence of phenol has been observed by Fisher to yield strongly adhesive products[62]. Williams examined a large number of phenols in combination with rubber and produced a group of thermoplastic derivatives of phenol-modified rubber, which was accepted as adhesive materials[63].

Chlorinated rubber and rubber hydrochloride have long been prominent in the field of adhesives. Chlorinated rubber has proved suitable for bonding various types of rubber. One of the first adhesives prepared from chlorinated rubber was Peachey's[64], the chlorination of rubber was done in carbon tetrachloride solution. Ellis also prepared a number of chlorinated rubber adhesives, in one instance dissolving the material in carbon disulfide[65] and in another case dissolving the material in carbon tetrachloride or naphtha for use as an adhesive[66]. Besides chlorinated rubber, brominated rubber adhesives have been prepared by Warner, who described a partial bromination[67] of rubber.

Winkelmann did a thorough job in preparing a number of adhesives employing rubber hydrochloride as a base material[68-70]. It was specifically described as a good adhesive for rubber. Neoprene bonded to various metals was made possible by adhesives prepared from halogenated rubber derivatives and vulcanizing agents, according to Winkelmann[71].

Various synthetic resins aid the cementing of rubber products. Knopp and Miedel employ phenol-formaldehyde and urea-formaldehyde as intermediate layers in the bonding of hard and soft rubbers[72]. Improved adhesion was noted by adding iron oxide to urea-formaldehyde. A heat- hardenable reaction product of m-aryl diamine and formaldehyde with rubber latex has aided the bonding of rubber to fibrous materials[73].

The strength of adhesion between two elastomer layers vulcanized in contact is important for various practical applications; tires, conveyor bells, etc. Various studies done by Bhowmick and Gent have shown the relation between the strength of adhesion and the density of chemical interlinking at the interface. The materials studied were polybutadiene and an ethylene-propylene copolymer, crosslinked and interlinked by covalent chemical bonds. The strength of adhesion was determined by peeling the layers apart under threshold conditions, i.e., at low rates of peeling and at high temperatures, and sometimes in the swollen state, so that viscous contribution to the work of detachment were minimized. Under these circumstances, the work G_a of detachment per unit of interfacial area was found to be directly proportional to the degree of chemical crosslinking at the interface over the entire range, from purely van der Waal's attractions with no covalent interlinking, up to the fully-interlinked state when the work of "detachment" became the work of cohesive rupture (tearing). Moreover, at any degree of interlinking, the work of detachment was lowered with interlinking molecular strands of lower molecular weight, in accordance with the theoretical predictions of Lake and Thomas[74] for the threshold strength of elastomeric materials. Bhowmick and Gent have also carried out studies on styrene-butadiene copolymer and a polychloroprene elastomer.

Studies of the strength of adhesion of a simple elastomeric system have already been reported[75]. The system consisted of crosslinked butyl rubber containing a proportion of uncrosslinked linear polyisobutylene. In such a system, the dissolved linear molecules can presumably diffuse readily across an interface into any compatible rigid material, was relatively low and much the same whether linear polyisobutylene molecules of high molecular weight were present or not the changes in the strength of adhesion with composition, or with the effective rate of peeling composition, or with the effective rate of peeling might have arisen from stress induced crystallization[76]. Results over a wide range of temperature were found to obey reasonably well with the rate-temperature equivalence proposed by Williams, Landel, and Ferry for simple amorphous viscoelastic substances[77] and this suggests that effect due to crystallization, if any, were relatively small.

Diffusion of polymer molecules across an interface has been proposed as a major factor in adhesion[78,79]. Certainly the development of self-adhesion or "tack" between two layers of materials seems likely to involve the diffusion of molecules across the interface after the layers have been brought into intimate contact[80-86]. The development of intimate contact is, itself, a relatively slow process and could be the rate determining step in self-adhesion[87]. Indeed, molecular interdiffusion may not be required at all, molecular contact may be sufficient for strong adhesion between layers of the same, or even of different polymers[88,89].

The ability to bond various rubbers is a primary requirement for engineering end uses and many composite products including tires, belts, hoses, etc. The properties of a composite will depend to a large extent on the adhesion between components. Most of the studies in rubber to rubber adhesion have been directed towards adhesion of uncured rubber to uncured rubber, especially on autoadhesion. A review by Hamed[90] on the subject of autoadhesive and adhesive tack has been published. Recently adhesive tack of various rubbers was investigated and the effect of fillers and tackifiers on the tack properties[91] was examined. It was observed that the existing theories for molecular dependence and contact time apply to adhesive tack phenomena[92]. The effect of fillers on the deformation behavior of rubbers, on the rheological properties of rubber solutions and on the cold flow of adhesive coatings was investigated by S.A. Potievskaya[93]. A relationship was observed between the rheological properties of natural rubber and styrene-butadiene rubber solutions and the method of introducing the fillers. An adhesive compound was also developed which gave coatings with low cold flow characteristics, suitable for the manufacture of adhesives.

In actual applications, however, various compounding ingredients are added to the rubber and the mixture is subjected to vulcanization. When dissimilar rubbers are used in a compound, the properties of a vulcanizate will be a function of the adhesive strength between various rubber components used. This is also true when premixed compounds are used in a repairing operation after long storage. Considering the importance of the subject, few studies have been done on rubber to rubber adhesion[94,95]. These preliminary studies examined adhesion of two rubber compounds before and after vulcanization and adhesion between cured rubbers. Only recently has the importance of interfacial bonding on the rubber to rubber adhesion has been highlighted[96-98]. One of the reasons for such limited data is the lack of proper test method. In the testing of rubber to rubber adhesion, failure is rarely interfacial. It starts from the interface and goes to one of the substrates. Width changes in this process as the peel front changes length due to irregular breakage. There is uncertainty in the measurement of width and hence adhesive strength. This problem is obviated by modifying the peel joint with the incorporation of a perforated plastic sheet inside[99].

Bhowmick et al[100] have studied the adhesion between natural rubber and polybutadiene rubber by a modified peel test for various compositions. The studies were done using different gum compounds, carbon black and silica filled compounds. The order of gum joint strength is NR-NR>BR-BR>NR-BR. Adhesive strength was related to the modulus, tensile strength and elongation at break of the weaker adherend. The higher the tensile properties, the higher was the adhesive strength.

Voyutskii[101] reported autohesion and adhesion of unvulcanized rubber. Bhowmick et al[102,103] also extended the studies to various synthetic rubbers and described a compounding approach to improve rubber to rubber adhesion. The strength of interface has been correlated with the interlinking density by Gent et al[104,96].

Temperature changes in adhesive bonded joints cause a wide variety of different stress state for several reasons. First, consider the manufacturing process. As the adhesive is heated, its viscosity is reduced, thus enabling it to flow and wet the surfaces. But the temperature rise will also generally lead to cure when the polymer develops cross-links and changes from a liquid to a solid. In the process of solidifying the adhesive shrinks, the cure shrinkage induces stresses in the adhesive by reaction against the adherends.

For a hot-curing adhesive, some creep will occur as the cure shrinkage takes place. Thus, the net effect on the internal joint stresses is less than might be implied from contraction measurements made on an unrestrained block of the adhesive. However, as the hot-cured adhesive cools to its operating temperature say from 15^0C to 20^0C, there will be differential thermal expansion effects. Most polymers have a high coefficient of thermal expansion compared with metals, and adhesives are no exceptions.

Another effect is that adhesives have different stress/strain behaviors at different temperatures. An adhesive designed for use at ambient temperatures (20^0C) might be strong but brittle at -100^0C, and Adams et al, have shown that thermal effects, whether due to mismatch of the adherends or to adhesive contraction by temperature or cure, lead to significant changes in the stress state of lap joints. At the same time, the stress/ strain properties of the polymeric adhesives also change enormously with temperature. The optimum results will always be obtained in the temperature range for which the adhesive has been designed for, where it has 'acceptable' strength and strain to failure. At high temperatures, the strain capability is high but the load capability is low. At low temperatures the reverse process is found to occur.

Bhowmick and Gent have studied the adhesive strength for SBR-SBR and CR-CR joints[96] under threshold conditions. The adhesive strength increases with reduction in pressure time due to enhanced interlinking density across the interface.

The use of ultra-violet (UV) curable adhesives in industrial manufacturing process began in the early 1970's. Some of the most important markets include packaging, electronics, glass bonding and laminating, security applications and plastic bonding. The technology can be broadly classified into two types: free radically cured and cationically cured. Although in some cases mechanisms go on separately and simultaneously in what is termed hybrid formulations, most common formulations are cured by free radical polymerization. In recent years cationic polymerization has gained popularity. In both cases, formulations which are free from solvents are converted to high molecular weight polymers with varying degrees of crosslink density.

Since UV adhesives have found their way into a large number of diverse applications it is difficult to describe a typical UV formulation. Such products normally contain monomers, prepolymer, photoinitiators, fillers, adhesion promoters and stabilizers. Highly significant factors in determining the performance of a UV curable adhesive are the nature and concentration of the photo-initiator and the spectral emission of the source. Unlike thermal initiators where increasing the concentration of the initiator affects the initiation process uniformly throughout the bulk of the product, varying the concentration of photoinitiator affects where the radiation is absorbed within the adhesive and where the initiating species are generated. Accordingly, determining the optimum photoinitiator level is complicated. At the present time this is largely carried out by trial and error[105].

There are four commercially available sources of UV radiation, namely fluorescent lamps, flashed xenon lamps, medium pressure mercury lamps and electrodeless mercury lamps. The intensity of the radiation source directly affects the cure speed of the adhesive as the rate of generation of initiating species is related to the intensity of the radiation.

Understanding the mechanisms of adhesion led to a great many ways of improving adhesive bond strengths; changing the polarity of the polymer, lowering the internal stresses in the area of the adhesive joint choosing the adhesives so that the coefficient of linear expansion is close to that of the substrate, creating homogeneous structures in the polymers, influencing the adhesive/substrate system by external electric or magnetic fields or their combination etc. The last phenomenon follows from the concepts of the electromagnetic theory of addhesion[106]. Studies show that there is a common electrostatic background with a range of molecular bonds at the phase boundary in all cases of contact between two solids. In the areas of close contact the action of molecular (short range) forces is observed, but in the areas where there is not close contact, interaction is reduced to practically zero as the distance apart is more than 10-20nm. Electrification takes place over the whole area of the surface, so electrostatic forces provide a considerable force between the two surfaces. In other words, two electric quasi-double-layers are formed by induction as indicated which contribute to the total strength of adhesion. Different examples of the dependence of adhesion strength on the conditions of making and breaking adhesion contact are explained by various authorities[106-109] according to the ideas which have already been developed[106, 110-112].

Composite rubber and textile products are a considerable portion of all rubber products. Adhesion is an important factor in using textile materials together with rubber as well as the individual properties of each material. Tires, conveyor belts and transmission belts are used under severe conditions and a very high level of adhesion are required. In general, strong adhesion is obtained through adhesive treatment of the textile or through addition of bonding agents to the rubber compound. Hose and coated fabric do not require such high adhesion. Therefore the mechanical keying effect of textile to rubber gives sufficiently good results for these uses. Though several methods are available to bond textiles to rubber, it is necessary to select an adequate method according to the raw materials and the application.

There is an interesting history of evolution for the tire cord adhesion. In the early 1890-1920's cotton was used with no adhesive treatment or rubber cement treatment. As loads, horsepower and operating speeds of automobiles increased, needs grew for stronger and cooler running tires. Therefore rayon filament was introduced. Rayon has good mechanical property but lacks adhesion. Initially reclaimed-rubber-casein-latex adhesive was examined to improve this defect but it failed to satisfy requirements of the tire industry[113] therefore studies on adhesives based on latex and thermosetting progressed and led to the finding of resorcinol-formaldehyde latex adhesive, commonly called RFL. In 1947 nylon 66 was introduced as a tire reinforcing material in the United States. RFL adhesive is also effective for nylon. At present this adhesive is used extensively for rubber to nylon and rayon cords bonding. Polyester and glass fibers have also been used in the tire industry replaced by synthetic rubbers and new materials such as cis-1,4- polybutadiene and ethylene propylene rubber have been introduced in the rubber industry.

The rubber to textile bonding may be due to the adhesion based on mechanical keying effects or adhesive treatment of the textile material or addition of bonding agents to rubber compounds. Mechanical interlocking is brought about by protruding fiber ends or fabric opening has an important role in rubber to textile bonding. Borroff and Wake investigated the function of staple fiber in adhesion[114,115]. It was found that the bond strength is remarkably affected by amount of staple yarn as well as type of rubber cement and kind of textile material. The effect of staple yarn may be due to mechanical keying around the protruding fiber ends. Also rubber to textile adhesion varies with nature of the weave. Adhesion to a fabric woven from continuous filament yarn is related to its interfacial surface area. Difference in surface area can be secured by differences in weave[116]. Use of very bulky yarn enables rubber to bond to fabric without any adhesive treatment[117].

To improve the adhesion of polyesters to rubber, modification of the existing RFL adhesive was the first attempted[118]. But this approach proved inadequate because adhesion between fiber and RFL was insufficient influence. Poor adhesion may be due to reduced ability to form hydrogen bonds[119], lack of reactive hydrogen in the polyester molecule and its hydrophobic nature[120].

In selecting the elastomer compound and textile, it is necessary to ensure that the overall properties will satisfy service conditions. This requires knowledge not only of the properties of the compound and of the textile but also of the adhesive system that has been used to unite the two into a coherent unit.

In making the correct choice of adhesive system it is necessary to be aware not only of those available but also of other factors affecting adhesion, such as the effects of compound variation of the various processes to be used and aging effects. Also, where possible some insight, into the mechanism where by adhesion is obtained is advantageous.

In considering various adhesive system the choice is primarily governed by the type of textile to be used, as the adhesives are generally more specific to the textile than to the elastomer used except when dealing with certain of the specialty elastomers.

Although the mechanisms where by adhesion is obtained are not fully understood, both chemical and physical interactions have been shown to occur at the textile-adhesive and adhesive-rubber interface. The adhesive films applied to the textile are susceptible to degradation on exposure, resulting in loss of adhesion and care must be exercised in storage of treated fabric to minimize this.

Rubber adhesive bonded to textiles is, however one of the exceptions where mechanical interlocking has been shown to be important. If a true interface exists the same molecular conditions apply as in any other adhesive-adherend system, but the influence of changes in the specific surface adhesion is completely overshadowed by the influence of mechanical factors, such as the form of the weave or the strength of the fiber as reported by Borroff and Wake[121], in which the adhesion in a direct tension test was measured for a series of textiles so constructed that the differences between them were almost entirely in the actual filament constitution or in the use of spun staple yarn where indicated.

The area of the interface between rubber and textile is also important to be considered. Methods are available to measure the surface area of fabrics and have been applied by Khot, Gundavda and Wake[122] to the measurement of the areas of a number of fabrics before and after rubberizing when one face of a fabric is coated by spreading from a solution the percentage covered seems to depend on the thickness (weight) of the fabric. The surface area so considered is the effective surface area or, the outside of the fabric. Fabrics have also an inside or internal surface area, some of which may be accessible to rubber and be wetted by it. Adhesion to a fabric woven from continuous filament yarn is broadly related to the interfacial surface area, differences in surface area having been secured by differences in weave.

The adhesion of rubber to woven fabric does vary with the nature of the weave. The amount of penetration into the interstices was not very important when the rubber was soft enough, as it usually is in cements, to deform easily in separating from the textile.

The adhesion between textile cords and rubber is very important question of the rubber industry. The field was reviewed by Takeyama and Matsui[123] and recently by Renner and Langenthal[124] as well as by Darwish[125]. The adhesion between cord and rubber has been discussed by many authors under static and dynamic conditions.

Weber and Schilo[126] have carried out work on polyester and aramid fiber for, e.g., tires and PVC coated fabrics were subject to surface treatments and the effect of modifications was evaluated using peel test. Standard methods in terms of static adhesion to rubber at room temperature and at 120^{0}C. The tire yarns studied were

Dioten polyester and Twaron 1001 aramid, the fibers were exposed to fluorine gas atmosphere in a ventilated chamber. Both types fiber showed significantly improved adhesion to rubber and PVC after the fluorine treatment, but the improvement was not sufficient in comparison to conventional two bath dip treatment. Use of a vulcabond adhesion agent did not improve adhesion and in the case of Diolen, the treated fiber had poorer adhesion that the untreated fiber and vulcabond alone were used. The surface treatment did not effect other properties such as tenacity, elongation or shrinkage and this process also does not show are environmental impact.

S.N. Lowandy et al[127], have used an adhesion promoter system composed of hexamethylenetetramine, resorcinol and hydrated silica and compounded it butyl rubber mix. This mix was spread over treated polyester fabric. The resorcinol was also replaced by o-aminophenol, m-aminophenol or m-phenylenediamine. The rubber fabric materials were subjected to aging or exposed to ionizing radiation and dynamic properties such as peel strength, permeability, dielectric constant and electric resistivity were examined.

A heavy responsibility of rubber-textile bonding is placed upon the adhesive component, an optimum adhesion of which binds up surfaces of textiles and rubber together without appreciably stiffening or tendering the fiber, and without effecting the vulcanization characteristics of the rubber. This technical problem remains solved with the present day use of resorcinol formaldehyde latex (RFL) dip but with many diversification in its applications and scope of improvement.

Various types of adhesives have been developed for rubber bonding with different textile fibers. They include the latex-proteine-adhesives for bonding rubber to rayon cord, latex-polyisocyanate adhesives developed for or rubber-polyester bonding and resorcinol-formaldehyde-latex adhesives which is the most important group rubber-textile bonding adhesives, used at present by tire manufactures for rubber to textiles such as rayon, nylon 6, nylon 66, vinylon and easy to adhere types of polyester.

If latex alone is employed as an adhesive good rubber to textile adhesion cannot be obtained because of lack of active groups in the latex and weak tensile properties of the adhesive coating film. Addition of a resin into the latex is found to improve the mechanical properties of the latex. Several thermosetting resins were used for this purpose. Phenol formaldehyde[128], urea formaldehyde[129], aniline formaldehyde[130], and ketone formaldehyde resin[131] were patented. Among them resorcinol formaldehyde resin was selected to be used as an aqueous adhesive incorporated into latex because of its superior adhesion and ease of processing[128].

The nylon-6 cords used were subjected to heat treatment prior to rubberization on a calender on the course of which further heat treatment and mechanical treatment were carried out. Shrinkage of nylon cord is liable to occur under rising temperature conditions. If shrinkage is prevented as a result of mechanical counter measures, shrinkage stress will develop in the cord fibers and the magnitude of this stress will be temperature dependent. Insufficient tensioning of the cord after heat treatment may lead to partial or indeed total shrinkage resulting in a partial or total nullification of the thermal drawing effect. Differences in the temperature and in degrees of tensioning in the width of the cord fabric may likewise lead to non-uniform shrinkage of fibers and to defects in the material. Data have been published in regard to the determination of the internal stress and shrinkage of cord fibers occurring in the course of dipping and drying operations[132]. Studies have also been carried out to determine the changes occurring in the internal stress and deformation of nylon-6 cords that have been subjected to preliminary dipping in a latex-resorcinol-formaldehyde dipping compound and to heat treatment.

Iyengar[133] measured the static and dynamic adhesion of nylon cord in compounded dynamic adhesion of nylon cord in compounded stocks based on NR. He used the conventional resorcinol formaldehyde latex(RFL) system. He applied the 'H'- Pull out test for static measurements whereas for dynamic adhesion fatigue the Dynamic shear Adhesion (DSA) and Scott Flex text were used. He concluded that NR stocks in which a long scorch time was obtained showed good adhesion. He also concluded that a highly polar material in rubber promotes the adhesion only if the scorch time of the stock is long enough.

De Jong[134] discussed bending under tension for a Neoprene compound reinforced with polyester cord. He concluded that the smaller is the bending radius the shorter is the running time to failure. He also used a disc fatigue test in which compression is applied and concluded that the dip recipe has influence on the residual strength of the composite after the compression fatigue test, when he used the Mallory tube test in which the compression and the heat generation take place, he concluded that the twist factor and the type of reinforcing material were dominating parameters. Brodsky[135] tried to measure adhesion fatigue on H-type test specimen, but the results were badly scattered and he concluded that the H-type test is not suitable for dynamic testing of rubber/textile cord adhesion. He developed another test method called three cord shear Adhesion (TCSA) for testing cords-to rubber adhesion under static and dynamic conditions.

W. Parasiewicz[136] has reported the effects of epoxidised NR and epoxy resin on adhesion of rubber mixture applied in tire industry to polyamide and polyester fibers. Epoxies were added in varying amounts to the typical rubber mix and the force needed to pull out of the fiber from the 'H' sample was measured. An improvement in adhesion was observed and was supported by spectroscopic investigations.

Many technical rubber products such as tires, hoses and conveyor belts contain textile reinforcements for high strength and dimensional stability. The classical way to obtain good adhesion between rayon or nylon to rubber is to dip the cords in a RFL suspension[137].

Additives for improving tire cord adhesion and toughness of vulcanized rubber compositions without the need of resorcinol was investigated by B. Singh[138]. Derivatives of melamine, acetoguanamine, benzoguanamine, cyclohexylguanamine and glycoluril substituted with at least two vinyl terminated radicals were used, preferred compound may also be substituted with at least one radial having a carbamylmethyl group.

It has been shown by M.Z. Levit[139] that the value of adhesion at the interface in rubber-fabric materials and the viscoelastic properties of the elastomer determine the work expanded on it deformation in failure. Increased adhesion strength will be found in composite products where the magnitude of this work is the greatest.

The relationship between ozone levels ranging from 0 to 20 parts per hundred million and adhesion of rubber to polyester tire cords at various temperatures, humidity levels and exposure times was investigated by E. K Bradley[140]. The data obtained indicated that losses in adhesion ranged from 7.5 to 54% at the 5 parts per hundred million ozone level depending upon exposure conditions, the effect of humidity on adhesion loss was greater at lower temperatures and that temperature promoted the effect of ozone more than humidity or time.

The effect of high energy irradiation doses on the adhesion of butyl rubber and nylon 6 fabric was studied by S. N. Lawandy[141] various factors affecting adhesion and radiation such as filler content, curing system and method of vulcanization were considered. The radiation was applied after vulcanization to enhance bonding.

W.E. Weening[142] has reported the adhesion of polyester to rubber and the effects of thermal aging. After a brief consideration of the reasons for the poor adhesion of polyester cords to rubber in comparison with nylon and rayon, various methods of improving adhesion have been discussed: use of pretreated cords; use of rubber containing adhesion promoters, a two-bath system for treating the polyester, a pre dip containing an epoxy compound followed by the normal resorcinol formaldehyde treatment and a single bath system using a modified resorcinol formaldehyde latex etc. The influence of treatment conditions and the rubber mix on adhesion and cord tenacity is presented in the second part of the article. The various types of thermal and chemical degradation which can occur during vulcanization and service life are also briefly mentioned; the most important, nucleophilic attack on the polyester due to the presence of amine in the mix and water content is discussed in more detail and the use of stabilizers in NR and SBR is assessed. Finally degradation of the adhesive interface is also discussed.

The influence of different chemical impurities on the physical-mechanical indexes of the gumming composition in NR was studied by C. Rusu[143] and the effects on the adherence to viscose, polyamide and polyester (impregnated and non-impregnated) cord was also studied.

Objectives and Scope of the present work

The present work has been undertaken to fill the gaps in the various systems of adhesives available commercially for bonding different types of rubbers and to develop a novel RFL system for textile bonding, cost reduction being one of the motivating reasons. The elastomer combinations that are proposed to be particularly looked into are NR to NR, NR/PB to NR/PB (due to their importance in tire retreading), CR to CR (due to their importance in marine applications) and NR to NR and NR to NBR (due to their general importance). In rubber to rubber bonding we propose to develop novel adhesives based on NR, NBR, CR and reclaimed rubber. The reclaimed rubber is proposed to be made from waste latex gloves since it contains lightly crosslinked and unfilled rubber hydrocarbon of high purity. The effect of modifying CR and NR based adhesives with chlorinated natural rubber is also proposed to be investigated. The effect of the type and concentration of the resin and concentration of the HAF black in the adhesives are the other important parameters proposed to be investigated. The efficiency of these novel adhesives is proposed to be compared with that of commercially available adhesives.

In rubber to textile bonding we propose to investigate the efficiency of different types of RF resin in modifying the RFL adhesive, one of the objectives being a higher shelf life for the RFL adhesive without affecting the bond strength of the rubber to textile. Also, we propose to modify the rubber compound used for bonding the textile using commercially available and novel resins. The effect of replacement of RF resin in the RFL by other potential agents is also proposed to be investigated.

The present study on the adhesives for bonding rubber to rubber and rubber to textiles used in the manufacture of tires, belt and marine products, etc. have been undertaken with the following objectives:

1. To develop adhesives based on natural rubber and waste latex reclaim for bonding vulcanizates of NR with NR and NR/PB with NR/PB.
2. To develop low cost adhesives for precured retreading process.
3. To evaluate the bonding and aging behaviour of vulcanizates of CR with CR, NR with NBR and CR with NR using different elastomer based adhesives.
4. To develop room temperature curable adhesives for bonding vulcanizates of CR with CR and NR with NR.
5. To improve the bonding of nylon tire cord to rubber.
6. To improve the bonding of rayon tire cord to rubber.
7. To study the effect of replacement of RF resin in the RFL adhesive partially and wholly by other potential agents.

8. To compare the efficiency of the novel adhesives developed with that of commercial adhesives.

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Chapter II

EXPERIMENTAL TECHNIQUES

The Materials used and the experimental procedures adopted in the present investigations are given in this chapter.

2.1 Materials used

2.11 Elastomers

(1) Natural rubber (NR)

ISNR-5 was supplied by the Rubber Research Institute of India, Kottayam, Kerala. The Indian standard specifications for this grade of rubber are given below.

Mooney viscosity [ML (1+4) at 100^0 C]	82.00
Other parameters	Limit
Dirt content ,% by mass, max.	0.05
Volatile matter, % by mass, max.	1.00
Nitrogen, % by mass max.	0.70
Ash, % by mass, max.	0.60
Initial Plasticity, min.	30.00
Plasticity retention index, (PRI) min.	60.00

(2) Polybutadiene (PB) rubber

Polybutadiene rubber was obtained from Indian Petro Chemicals Corporation Ltd., Baroda. The grade used was Cisamer 1220 having a Mooney viscosity [ML (1+4) at 100°C] of 45.

(3) Latex Product waste

Waste examination gloves was supplied by Midland Rubber Products Ltd., Kakkanad, Kerala, India.

(4) Acrylonitrile-butadiene rubber (NBR)

Acrylonitrile-butadiene rubber was obtained from Apar Polymers Ltd., India. The sample used was grade N 553 with 33% acrylonitrile content and having a Mooney viscosity [ML (1+4) at 100°C] of 45.

(4) Chloroprene rubber (CR)

Chloroprene rubber, was obtained from Du Pont, Akron, Ohio, USA. The rubber was having a Mooney viscosity [ML (1+4) at 100°C] of 45.

(5) Natural rubber latex

Centrifuged natural rubber latex was obtained from Rubber Research Institute of India, Kottayam and had the following specifications:

Dry rubber content	60% min.
Total solids content	61.5% min.
Coagulum content	0.05% max.
Sludge content	0.1% max.
Alkalinity	1.6 min.
KOH No.	1 max.
Mechanical stability time	475 min.
Volatile fatty acid number	0.15

Copper content	8 (ppm) max.
Manganese content	8 (ppm) max.

(7) Vinyl pyridine terpolymer (VP) latex

Vinyl pyridine terpolymer latex had the following specifications:

Styrene (wt %)	15
Butadiene (wt %)	70
Vinylpyridine (wt %)	15

(8) Buffed tires

Used car tires were buffed at the TVS Retreading Unit, South Kalamassery, Cochin, Kerala.

(9) Precured retread

Precured tread was supplied by Nelpurayil Rubbers, Industrial Estate, Kalamassery, Cochin, Kerala.

2.12 Compounding ingredients

(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%
Heat loss max. (2h at 100^{0}C)	0.5%

(2) Stearic acid

Stearic acid used in the study was supplied by Godrej Soaps Pvt. Ltd., Bombay and had the following specifications:

Specific gravity	0.85±0.01
Melting point	50-69°C
Acid number	185-210
Iodine number	9.5 max.
Ash content	0.1% max.

(3) Vulkanox HS

Commercial antioxidant vulkanox HS (1,2,-dihydro-2,2,4-trimethyl quinoline, polymerized) was obtained from Bayer India, Ltd., Bombay. It had a specific gravity of 1.1.

(3) Vulkanox 4020

Vulkanox 4020 N (1,3- dimethyl butyl N'- phenyl - p- phenylene diamine) was obtained from Bayer India Ltd., Bombay. It had a specific gravity of 1.1.

(4) Renacit -7

Renacit - 7 - was supplied by Bayer India Ltd., Bombay.

(5) High abrasion furnace black (HAF, N- 330)

High abrasion furnace black was supplied by M/s Carbon and Chemicals (India) Ltd., Kochi. It had the following specifications:

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

(6) Precipitated silica

It was obtained from Lunar Chemicals, Kanpur, India. The specific gravity was 1.95.

(7) Aromatic oil

Aromatic oil was supplied by Hindustan Petroleum Corporation. It had the following specifications:

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

(8) Magnesium oxide (MgO)

Magnesium oxide used in the study was commercial grade with a specific gravity of 3.6.

(9) Benzthiazyl-2-sulphenmorpholide (MOR)

Benzthiazyl -2-sulphenmorpholide was supplied by ICI Ltd., India. It had a specific gravity of 1.34.

(10) Tetramethyl thiuram disulphide (TMTD)

Tetramethyl thiuram disulphide was supplied by polyolefins Industries Ltd.,Bombay. It had a melting point of 136°C and specific gravity of 1.4.

(12) Tetramethyl thiuram monosulphide (TMTM)

Tetramethyl thiuram monosulphide was supplied by Flexys, Netherlands. It had the following specifications:

Melting point	108°C
Moisture content	0.12%
Ash	0.03%

(13) Ethylene thiourea (NA 22)

Ethylene thiourea was commercial grade supplied by Alkali and Chemical corporation of India , Ltd., Rishra.

(14) Hexamethylenetetramine

Hexamethylenetetramine was supplied by LOBA Chemie, Bombay, India. It had the following specifications:

Minimum assay (acidimetric)	99%
Sulphated ash, max	0.05%
Lead (Pb), max	0.0002%

(15) Phenol formaldehyde (PF) resin

Two grades of phenol formaldehyde resin were used.

(i) Phenol formaldehyde resin - 6414 was supplied by Bakelite Hylam, India. It had the following specifications:

Specific gravity	1.085 -1.105
Softening point	88 - 102°C
Methylol content	12-16%

(ii) Phenol formaldehyde resin - PR/307 was supplied by Indian Plastics Limited, Bombay.

(16) Wood rosin

Wood rosin used was commercial grade. It contains a mixture of acids, the major part being abietic acid, (a product from destructive distillation of aged pine wood by removing turpentine fraction. The sample used had the following specifications:

Solubility in water	Insoluble
Acid number	163
Softening point	73°C
Saponification number	168
Refractive index at 20°C	1.545
Specific gravity	1.067

(17) Cashew nut shell liquid (CNSL) resin

Cashew nut shell liquid resin is a phenolic resin derived from cashew nut shell liquid and phenol. This resin was prepared by condensation of a mixture of CNSL and phenol with a molar excess of hexamethylenetetramine. This resin is resole type and can be cured by heating.

(18) Sulphur

Sulphur was supplied by Standard Chemical Company (Pvt.) Ltd., Chennai. The sample used had the following specifications:

Specific gravity	2.05
Acidity	0.01% max.
Ash	0.01% max.
Solubility in CS_2	98%

(18) Zinc diethyl dithiocarbamate (ZDC)

Zinc diethyl dithiocarbamate was supplied by Polyolefines Industries Ltd., Bombay. It had a melting point of 178°C and a specific gravity of 1.50.

(19) Dibenzthiazyl disulphide (MBTS)

Dibenzthiazyl disulphide was supplied by Bayer Chemicals, Bombay. It had a melting point of 165°C and a specific gravity of 1.34.

(21) Pine tar

Pine tar used was commercial grade.

(22) Resorcinol

Resorcinol was supplied by Sahyadry, Calcutta. It had the following specifications:

Freezing point	110°C
Ash	0.1%
Resorcinol content	99%min.

(23) Chlorinated Natural Rubber (CNR)

Chlorinated Natural Rubber was supplied by Rishiroop industries, Bombay. It had a chlorine content of 65%.

2.13 Other additives

Sodium hydroxide used was of analytical grade.

Solvents

Toluene, acetone, hexane, benzene, methyl ethyl ketone, formaldehyde, ammonium hydroxide and naphtha used were analytical grade.

2.2 Experimental methods

2.21 a) Mixing and homogenization using mixing mill

Mixing and homogenization of elastomers and compounding ingredients were done on a laboratory size (15x33cm) two roll mill at a friction ratio of 1:1.25. The elastomer was given one pass through a nip of (0.002x100)". Then it was given two passes through a nip of (0.002x10)" and allowed to band at a nip of (0.002x55)". The temperature of the rolls were maintained at 70-50°C during the mastication. After the nerve had disappeared the compounding ingredients were added as per ASTM D 3184 (1980) and ASTM D 3182 (1982) in the order activators, fillers, accelerators and curing agents. Before the addition of accelerators 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.

b) Determination of cure characteristics

The cure characteristics of the elastomers were determined on a Goettfert elastograph model 67.85. It is a microprocessor controlled rotorless cure meter with quick temperature control mechanism and well defined homogeneous temperature distribution in the die or the test chamber. In this instrument a specimen of definite size is kept in the lower half of the cavity which is then oscillated through a small deformation angle ($\pm 0.2^0$) at a frequency of 50 oscillations per minute. The torque is measured on the lower oscillating die half. The following data can be taken from the torque time curve:

1. Minimum torque - Torque shown by the mix at the test temperature before the onset of cure.
2. Maximum torque - The Torque recorded after curing of the mix is completed.
3. Scorch time (T_{10}) - The Time taken for attaining 10% of the maximum torque.
4. Optimum cure time (T_{90}) -The Time taken for attaining 90% of the maximum torque.
5. Cure rate: Cure rate was determined from the following equation

$$\text{Cure rate (Nm/min)} = L_{max} - L_{min} / T_{90} - T_{10}$$

Where L_{max} and L_{min} are the maximum and minimum torque respectively and T_{90} and T_{10} the times corresponding to the optimum cure time and scorch time respectively.

The elastograph microprocessor evaluates the vulcanization curve and prints out these data after each measurement.

2.22 Moulding of Test Specimen

The test specimens were prepared in standard moulds by compression moulding on an electrically heated press having 30x30 cm platens at a pressure of 120kg/cm^2 on the mould. The rubber compounds were vulcanized upto their respective optimum cure times at 150^{0}C unless otherwise specified. Mouldings were cooled quickly in water at the end of the curing cycle and stored in a cold and dark place for subsequent physical tests.

2.23 Preparation of adhesive and adhesive dough

The different adhesives based on NR, Latex reclaim waste, NBR and CR were prepared by mixing the elastomers and other compounding ingredients as per the ASTM standards mentioned. The cure time of the matured compounds were determined using a Goettfert elastograph. The adhesive strips were sheeted out at different thickness and wound over cellophane paper. The different adhesive dough were made by preparing solution of the adhesive used to a required concentration in suitable solvent or solvent mixture. The adhesive dough was stored in a cool and dark place in air tight containers.

2.24 Preparation of the adherend pieces

The compounds moulded at the required temperature up to the optimum cure time were cut into pieces of dimensions 120x25x2mm. The surfaces of the adherend pieces were cleaned by using solvent naphtha.

2. 25 Preparation of resorcinol formaldehyde latex (RFL) dip solution

Two methods were adopted to prepare the resorcinol formaldehyde latex dip solution:

Method -I

Materials used:

Resorcinol - 100gms
Formalin - (37%) 45.45gms
NaOH - .02gms

Procedure: - 100gms of resorcinol was added to 15.45gms of formalin solution in a reaction flask kept on a magnetic stirrer fitted with a reflux condenser. The mixture was gradually heated to 80^{0}C. As the resorcinol got dissolved large amount of heat was liberated and the temperature rose to 100^{0}C. Then heating was stopped for a while and the remaining 30gms of formalin was added in increments over two and a half hours. During this addition, the temperature was controlled so as not to exceed 110^{0}C. During the last addition of formalin to the partially reacted mass, the rate of reaction slowed down. After the reaction 0.02gms of sodium hydroxide dissolved in 1ml water was added. The mass was dried in vacuum at room temperature.

A 7.5% solution of the dried resin was prepared in distilled water. A definite weight of this solution was mixed with the latex and distilled water to get the resorcinol formaldehyde latex dip solution of the desired concentration.

Method -II

Materials used:

Resorcinol	- 100gms
Formalin	- (37%) 147.3gms
Water	- 2166gms
Sodium hydroxide	- 2.88gms

The sodium hydroxide was dissolved in 100ml distilled water. The temperature was brought down to 20-15^{0}C by adding the rest of the water. Then the resorcinol and formalin were added under continued stirring at 20-15^{0}C. The solution was kept for maturation for 4h to get the masterbatch solution.

The final solution was prepared with the following ingredients:

Master batch	100 gms
Latex	91.18 gms
Water	12.23 gms
Ammonium hydroxide	4.45gms (27% liquor ammonia)

The latex, masterbatch and water were stirred for 15min. After maturing for 2hs the solution was used as resorcinol formaldehyde latex dip solution.

2.26 Physical testing methods

Testing of Adhesive bond

a) Peel test

The 180° peel test for rubber to rubber bonded samples was carried out on a Zwick universal testing machine (UTM) model 1445 according to ASTM D (413) - 82. All the tests were carried out at room temperature (28±20°C). A layer of the adhesive strip was placed between the two adherend pieces punched out from compression moulded sheets using a die of dimensions 120x25mm. The free ends of the samples were held tight by the two grips. The rate of separation of the power-actuated grip was 0.8mm/s. The peel strength was evaluated and printed out after each measurement by the microprocessor.

b) H-Test

The H-test is designed to measure the force required to pull a cord in the direction of its axis, from a strip of rubber in which the ends of the cord are embedded according to the ASTM D 2138 - 83. The property measured is the shearing force acting at the cord / rubber interface. In the H-test, the two ends of the strip of rubber with the interconnecting cord form a specimen resembling the letter "H". All the tests were carried out at room temperature (28 ± 2^0C). The reported value is the arithmetic mean of five test results.

c) Tensile stress-strain behavior

Tensile properties of elastomers were determined according to ASTM D - 412 (1980), using dumbbell specimens on a Zwick universal testing machine model 1445. All the tests were carried out at room temperature (28 ± 2^0C). Samples were punched out from compression moulded sheets using a dumbbell die (C-type). The thickness of the narrow portion was measured by bench thickness gauge. The sample was held tight by the two grips, of which the upper grip was fixed. The rate of separation of the power actuated lower grip was fixed at 500mm/min for elastomeric specimens. The tensile strength was evaluated and printed out after each measurement by the microprocessor.

d) Abrasion resistance

The abrasion resistance of the samples was tested using a DIN abrader. Samples having a diameter of 20± 0.2mm and a thickness of 16 to 20mm, were kept on a rotating sample holder and 10N load wad applied. Initially a pre-run was given for the sample and its weight was taken. The weight after the final run was also noted. The difference in weight is the weight loss of the test piece after it travels through 42m on a standard abrasive surface. The result is expressed as volume loss (cc/h).

$$\textbf{Abrasion loss} = \Delta M / \rho$$

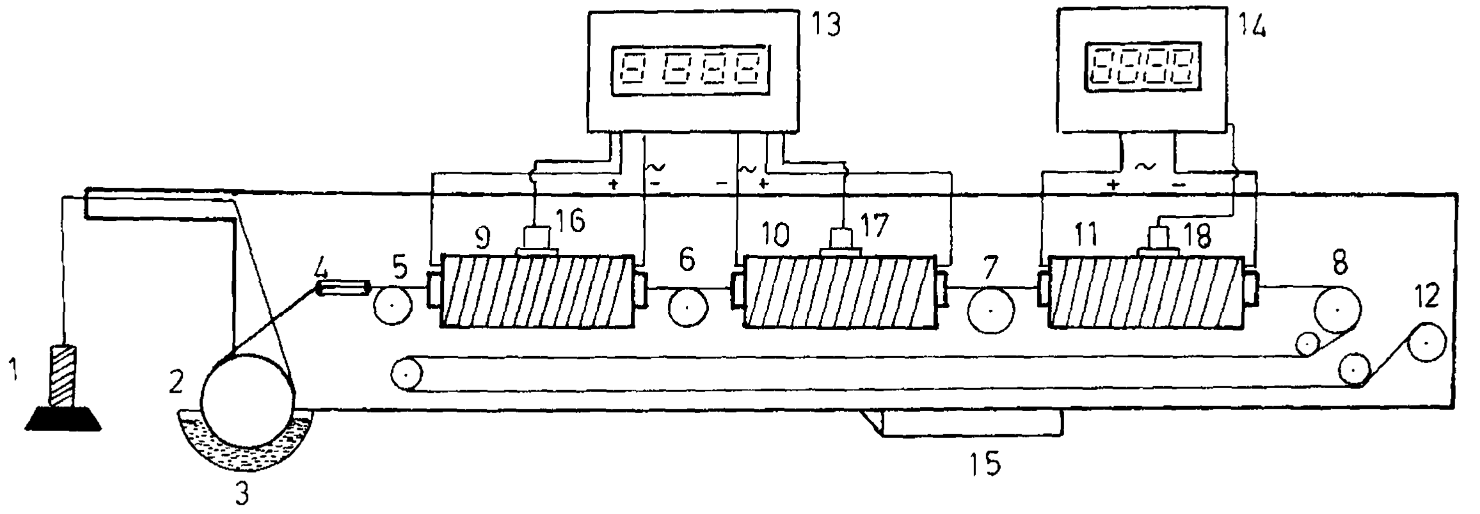
Where ΔM is the mass loss, ρ the density of the sample.

e) Storage life of the adhesive strip

The storage life of the adhesive strips was determined by keeping the strips for five weeks at room temperature in sealed cellophane packets and then measuring the peel strength of standard adherends using the adhesive strip.

2.27 Fabrication of the dipping unit

The dipping unit was designed and fabricated in the laboratory. It consists of three zones: the first and the second zones are drying zones and the third, the curing zone. The temperature of each zone can be varied from 25°C to 210°C. Each zone has a length of 33.33cm. The unit was used for dipping as follows: The textile cord was initially dipped in the RFL dip solution, the excess solution was squeezed through the squeezer and the cord was then passed through the drying and the curing zones. Finally it was wound over a pulley. The cords were stored in polythene covers and stored in a moisture and dust free place. A schematic diagram of the unit is shown in figure 2.1.



1. Textile cord spindle
2. Dipping pulley
3. RFL dip solution tub
4. Squeezer
5-8. Pulleys
9,10. Drying zone
11. Curing zone
12. Cord winding pulley
13,14. Digital temperature display
15. Motor
16-18. Temperature controller (PT 100)

Fig. 2.1 A schematic diagram of the dipping unit

Chapter III

Part I

STUDIES ON ADHESIVES BASED ON NATURAL RUBBER AND WASTE LATEX RECLAIM FOR BONDING VULCANIZATES OF NR WITH NR AND NR/PB WITH NR/PB BLEND

Natural and synthetic rubbers and their derivatives have been utilized in the preparation of many adhesives. The development of rubber adhesives from natural rubber precedes by a number of years the efforts made with synthetic resins, though today both groups are the subject of active attention in the adhesive field. Rubber like materials possess peculiar advantages over the more rigid synthetic resins as adhesives. Not only are they capable of developing good adhesion for various surfaces but also their high elongation permits the adhesive film to absorb much of the strain.

When a layer of adhesive is sandwiched between two surfaces of the same rubbery polymer, they adhere with a strength that depends on the time of contact. This can be attributed to either increased interdiffusion of molecules across the interface or an increase in the true contact area with time.

Most studies on the effect of contact time on the strength of autoadhesion have been carried out on a time scale ranging from seconds to hours. Anand and *et al* studied the auto adhesion of polystyrene and considered it to be mainly a process of developing good contact between surfaces that are not molecularly smooth[1-6].

Ellul and Gent compared the autoadhesion and adhesion of isobutylene and ethylene-propylene polymers over a wide range of peel rates and test temperatures[7,8]. Their results show that interdiffusion of molecules contribute significantly to the strength of autoadhesion only over a certain range of peel rates and temperatures. Outside this range their contribution is rather small. A surprisingly high adhesion strength is found with inert substrates like poly (ethylene terephthalate) (Mylar 300A), when interdiffusion is quite improbable.

Bruce and Blake pointed out that tackiness of rubber adhesives is due largely to the action of light and oxygen[9]. Houwink also reviewed the oxidation of rubber, pointing out that in many experiments the amounts of oxygen present is in question[10].

Rubber to rubber bonding is common in the tire industry. In this study we propose to develop novel adhesive compounds for bonding natural rubber vulcanizates and NR/PB blend vulcanizates by replacing natural rubber in the conventionally used adhesives, either partially or fully by utilizing reclaim rubber prepared from waste latex products[11] for cost reduction.

Experimental

The polymers used were natural rubber (NR), polybutadiene (PB) and latex reclaim. The compounding ingredients viz., resins, zinc oxide, stearic acid, accelerator, antioxidants, HAF black and sulphur were commercial grade. NR and NR/PB blend were mixed with other compounding ingredients according to the formulation given in Table 3.11, as per ASTM D 3182 (1982).

Table 3.11 Formulation of rubber sheets for bonding

Ingredients	NR sheets	NR-PB blends Sheets
Natural rubber	100	70
Polybutadiene	—	30
Zinc oxide	5.0	5.0
Stearic acid	2.0	2.0
HAF black	40	50
Aromatic oil	5.0	6.5
MBTS	0.6	—
TMTD	0.2	—
MOR	—	1.0
Vulkanox HS	1.0	0.5
Vulkanox 4020	—	1.0
Sulphur	2.5	2.25
*T_{10}, min	1.9	3.7
*T_{90}, min	3.6	9.6
Maximun torque, Nm	0.494	0.657

*Cure characteristics

The optimum cure time (T_{90}min) and the scorch time, (T_{10}min) were determined on a Goettfert Elastograph model 67.85. The compounds were then moulded at 150°C up to the optimum cure time. Rubber pieces (120 x 25 x 2mm) to be used as adherends for bonding studies were cut from the moulded sheets.

The adhesives were compounded on a laboratory two-roll mixing mill using the formulation given in Table 3.12. While compounding the adhesive, the rubber was first masticated on a laboratory-mixing mill for 5min to facilitate the mechanical breakdown of the rubber, followed by the addition of other compounding ingredients. After compounding the cure times of the matured compounds were determined using a Goettfert Elastograph as before.

Table 3.12 Formulations of NR and latex reclaim based adhesives

Ingredients	Adhesive						
	1	2	3	4	5	6	7
Natural rubber	100	100	100	100	—	50	—
Latex reclaim	—	—	—	—	100	50	100
Renacit-7	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0
HAF black	40.0	40.0	30.0	50.0	40.0	40.0	40.0
Pine tar	8.0	4.0	8.0	8.0	8.0	8.0	8.0
PF resin	—	4.0	—	—	—	—	—
Wood rosin	2.0	2.0	2.0	2.0	2.0	2.0	2.0
MOR	0.8	0.8	0.8	0.8	0.8	0.8	0.8
TMTM	0.7	0.7	0.7	0.7	0.7	0.7	—
Vulkanox HS	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Insoluble sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5
*T_{10}, min	4.4	2.6	3.9	3.8	1.4	1.5	1.3
*T_{90}, min	8.8	7.0	7.4	7.2	4.8	5.8	6.4
Maximum torque, Nm	0.553	0.611	0.434	0.714	0.777	0.601	0.737

*Cure characteristics

The bonding characteristics were evaluated by peel strength test on a universal testing machine at a speed of 50mm/min. The samples for testing were prepared by placing the adhesive strip (25mm widex80mm long), between the adherend pieces and moulded at 140°C.

The conditions for bonding were standardized using adhesive 1 (Table 3.12). The bonding characteristics of adhesive 1 for different thickness varying from 0.5 to 1.80mm were studied by placing the adhesive between vulcanized NR-NR pieces or NR/PB-NR/PB blend pieces and pressing in a mold at 140°C. The optimum thickness for bonding of the cushion compound with NR-NR and NR/PB-NR/PB sheets were standardized.

The effect of temperature on the bonding of NR-NR pieces or NR/PB-NR/PB pieces with the cushion compound for the optimized thickness was studied at temperatures varying from 130° to 170°C.The effect of increasing the bonding time was also studied for vulcanized NR-NR pieces using adhesive. In the first trial bonding time was kept same as the optimum cure time of the adhesive compound. In the second trial, a bonding time of 1.5 times the optimum cure time was given at each temperature. After standardizing the thickness, temperature, and bonding time, the studies were extended to different adhesives using the formulations given in Table 3.12, for NR-NR and NR/PB-NR/PB pieces.

In one adhesive formulation part of pine tar (formulation 2) was replaced by PF resin to study its effect on peel strength. In adhesives 3 and 4, the amount of carbon black was varied to study its effect on the peel strength. In adhesive 5, NR was completely replaced by latex reclaim. In adhesive 6, 50% of NR was replaced by latex reclaim. In adhesive 7, NR was completely replaced by latex reclaim and the amount of accelerator was reduced to study its effect on the peel strength.

In order to study the shelf life of each adhesive, the adhesives were kept for 5 weeks at room temperature covered with cellophane paper and the peel strength was determined after bonding NR-NR pieces and NR/PB-NR/PB pieces with each sample. The study was conducted at the optimum thickness, temperature, and bonding time determined using adhesive 1.

The effect of replacing part of insoluble sulphur by soluble sulphur in the adhesives was also evaluated. The formulations of the cushion compound is given in Table 3.14.

Table 3.14 Formulations of adhesive varying in ratio of insoluble to soluble sulphur

Ingredients	Adhesive		
	7	8	9
Natural rubber	100	100	100
Renacit-7	0.2	0.2	0.2
Zinc oxide	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0
HAF black	40.0	40.0	40.0
Pine tar	8.0	8.0	8.0
Wood rosin	2.0	2.0	2.0
MOR	0.8	0.8	0.8
TMTM	0.7	0.7	0.7
Vulkanox HS	1.0	1.0	1.0
Insoluble sulphur	0.5	1.0	1.25
Soluble sulphur	2.0	1.5	1.25
*T_{10}, min	3.6	2.8	2.8
*T_{90}, min	6.5	6.2	12.0
Maximum torque, Nm	0.682	0.757	0.807

*Cure characteristics

The peel strength was determined after bonding the vulcanized NR-NR pieces and NR/PB-NR/PB pieces with the adhesives. The adhesives were kept covered in cellophane paper. The shelf life of the adhesive was also determined by measuring the peel strength of the samples bonded with the adhesive after intervals of one week upto seven weeks.

Results and Discussion

Table 3.11 shows the scorch time and cure time of the NR compound and NR/ PB blend compound. The NR based compound cures faster than the NR/PB blend compound as expected. The scorch time and cure time of adhesives 1-7 are listed in Table 3.12. The scorch time and cure time are reduced when part of pine tar is replaced by PF resin, which may be due to the accelerating effect of the PF resin.

When the carbon black level is changed to 30phr or 50phr, there is not much change in the scorch time or cure time, but when NR is replaced by latex reclaim, there is an appreciable reduction in the scorch time as well as in the cure time. This may be due to the presence of crosslink precursors and/or unreacted curatives in latex reclaim[12] and particularly because fast-curing accelerators like ZDC or ZMBT are used in latex compounding. Adhesive 7 cures as fast as adhesive1, even when accelerator-2 is avoided. The maximum torque value is almost the same for all compounds except adhesive 4, where the amount of carbon black is 30phr. This is due to the lower modulus of this compound.

Figure 3.11 shows the variation of peel strength with thickness of the adhesive at 140°C.The peel strength increases when the adhesive thickness is increased from 0.50 to 1.30mm and then decreases with a further increase in the thickness. This shows that there is an optimum thickness for the adhesive to provide good bonding. Further increase in adhesive thickness results in lower bonding strength, probably due to the undercure of the thick adhesive layer. The need for an optimum adhesive thickness is also found in the case of NR/PB blend sheets.

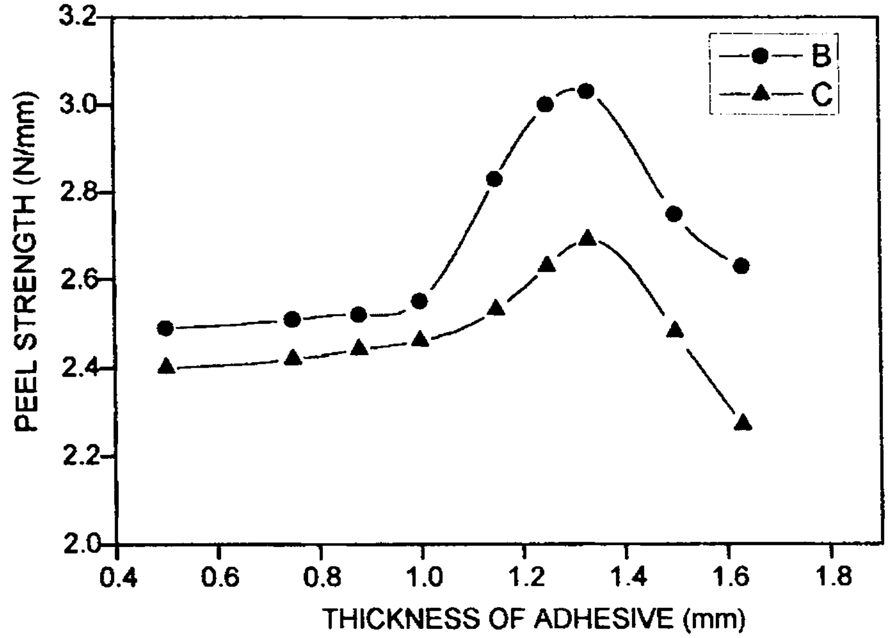


Fig. 3.11 Variation of peel strength with thickness of adhesive 1 at 130°C for NR-NR- (B) and at 140°C for NR/PB-NR/PB - (C) pieces.

Figure 3.12 shows the variation in peel strength with temperature. The NR based sheets show maximum peel strength at a bonding temperature of 130°C, and the NR/PB blend sheets at 140°C. This may be due to the fact that diffusion of the adhesive in an NR based test piece is easier than in an NR/PB blend test piece, since the NR based test pieces have a lower modulus compared to the NR/PB blend (as seen by the maximum torque value shown in Table 3.11). Further, the NR/PB blend compounds are fast curing than NR based compounds.

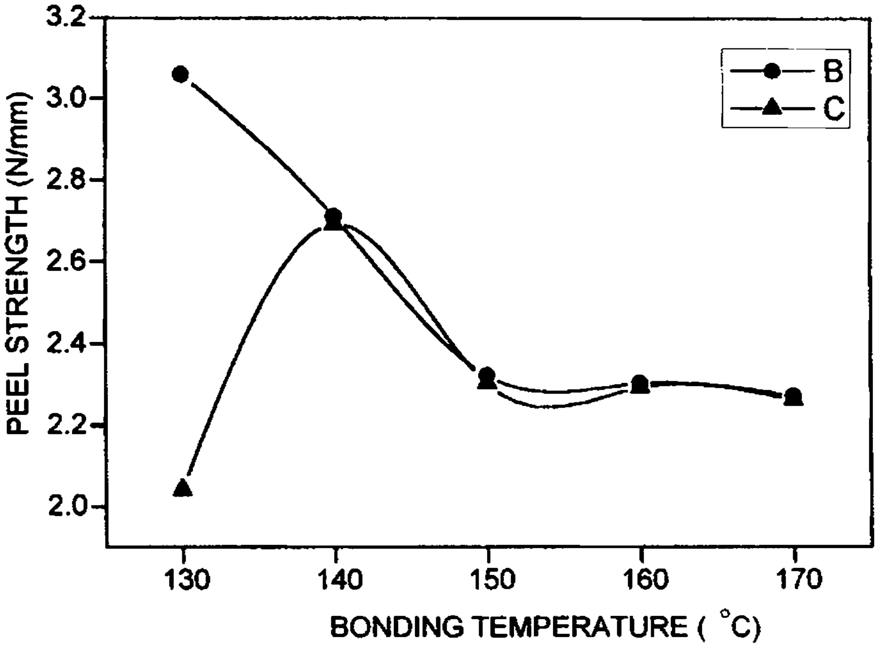


Fig. 3.12 Peel strength as function of the bonding temperature for NR/NR -(B) and NR/PB-NR/PB -(C) pieces using adhesive 1.

Figure 3.13 shows the variation of peel strength with time of bonding. The increase in bonding time does not produce much change in the peel strength at low temperatures, but the peel strength increases with the time of bonding when the bonding temperature is raised to 150°C. This shows that at 150°C, the optimum cure time is not sufficient to produce proper bonding.

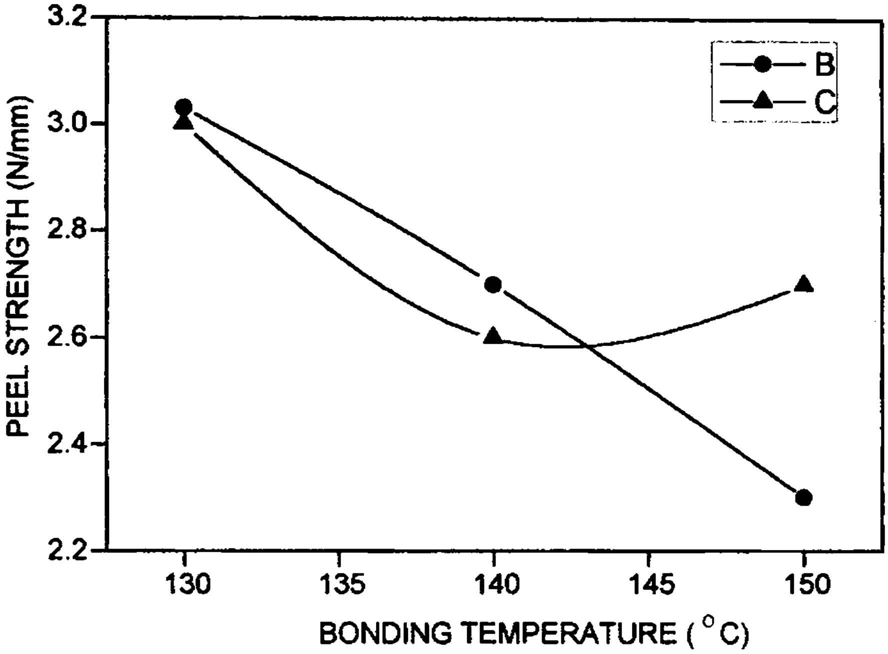


Fig. 3.13 Peel strength vs. Bonding time at different temperatures using adhesive1 for NR/NR. (B) - Optimum cure time ; (C) - 1.5 times of optimum cure time.

Table 3.13 shows the peel strength of NR and NR/PB with different adhesives, adhesive 2 shows a lower peel strength compared with adhesive1. Thus, the use PF resin does not improve the rubber to rubber bonding. At lower and higher carbon black levels, the adhesive produces a slight reduction in peel strength. Therefore 40phr of carbon black may be the optimum level for obtaining good bonding in both NR-NR sheets and NR-PB/NR-PB sheets. The peel strength values for adhesives 5, 6 and 7 are higher for the NR/PB blends compared with the NR based test pieces, as shown in Table 3.13. This may be due to the faster curing rates of these adhesive formulations, as the latex reclaim cures faster than NR[9,10]. The peel strength values for NR-NR sheets are only marginally reduced when natural rubber is replaced by latex reclaim (adhesives 5, 6 and 7). This shows that latex reclaim can replace NR either partially or fully.

Table 3.13 Variation of peel strength with aging at 30°C for 5 weeks

Adhesive	Peel strength (N/mm) for NR sheets bonded at 130°C		Peel strength (N/mm) for NR-PB blend sheets at 140°C	
	Before aging	After aging	Before aging	After aging
1	3.03	2.73	2.69	2.07
2	2.30	2.30	2.15	1.95
3	2.72	2.52	2.52	2.20
4	2.66	2.09	2.36	2.36
5	2.32	2.31	2.90	2.42
6	2.38	2.16	3.19	2.95
7	2.44	2.25	3.02	3.01

Table 3.13 also shows the peel strength of adhesives 1-7 after 5 week's aging at room temperature. There is not much drop in peel strength for any of these adhesives. Thus, it may be concluded that migration of the ingredients from the bulk to the surface of the adhesives is not a significant factor.

The effect of replacing part of insoluble sulphur with soluble sulphur on the peel strength is shown in figures 3.14 and 3.15. It is seen that when vulcanized pieces of NR-NR and NR/PB-NR/PB pieces were bonded at 130°C and 140°C the peel strength decreases gradually for NR-NR sheets for all ratios of insoluble to soluble sulphur upto three weeks, followed by a period of constant peel strength upto six weeks after which there is a drastic fall in the peel strength. But as the ratio of soluble to insoluble sulphur increases, the peel strength decreases more rapidly with time.

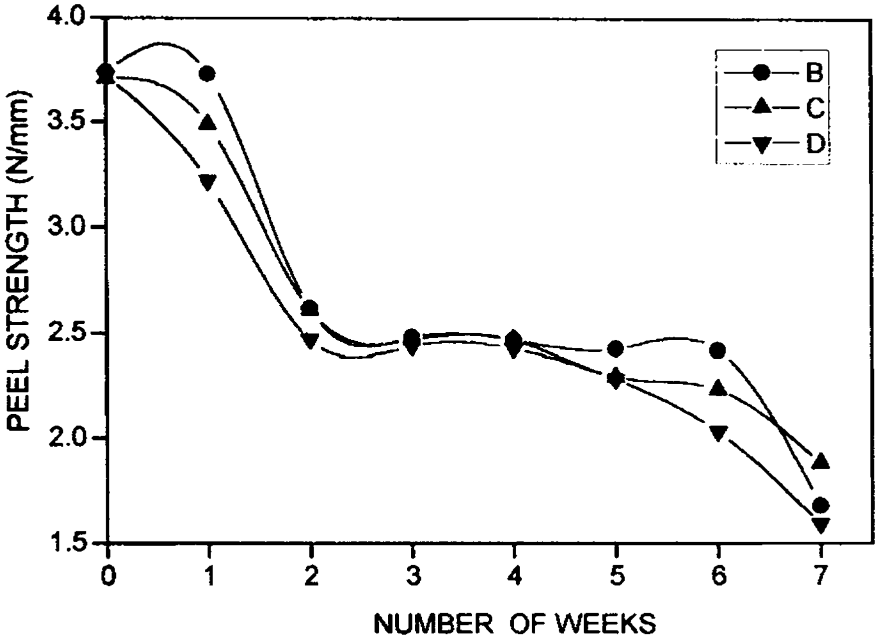


Fig. 3.14 Variation of peel strength with ratio of insoluble to soluble sulphur for NR/NR at 130°C. (B) - 1.25/1.25; (C) - 1/1.5; (D) - 0.5/2.0.

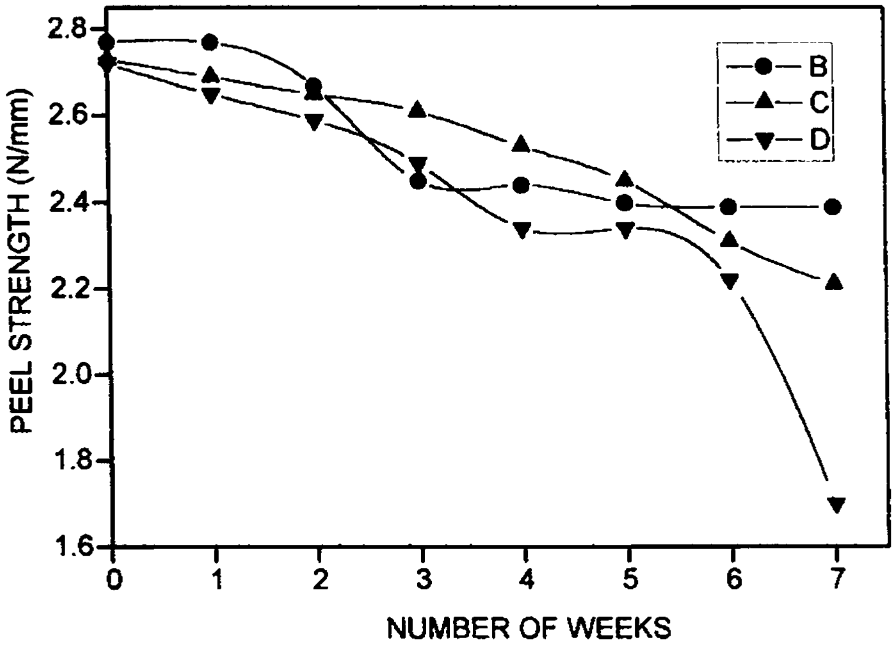


Fig. 3.15 Variation of peel strength with ratio of insoluble to soluble sulphur for NR/PB-NR/PB blend sheets at 140°C. (B) - 1.25/1.25; (C) - 1/1.5; (D) - 0.5/2.0.

For NR/PB blend vulcanizates at the 1:1 ratio the peel strength shows a slight decrease initially and then remains more or less constant as shown in figure 3.15. But for higher ratios of soluble to insoluble sulphur there is a more rapid decrease. This may be due to the blooming effect of soluble sulphur. But a partial replacement of insoluble sulphur by soluble sulphur is possible.

Conclusions

1) The natural rubber-based adhesive formulations tried are efficient for bonding NR-NR and NR/PB-NR/PB vulcanizates.
2) Natural rubber can be replaced by latex reclaim either partially or fully without any serious reduction in peel strength.
3) The optimum level of carbon black in the adhesive is about 40phr for maximum peel strength in the present system.
4) Partial replacement of pine tar with PF resin does not improve the peel strength.
5) Partial replacement of insoluble sulphur by soluble sulphur does not affect the peel strength of the bonded samples.

Part -II

DEVELOPMENT OF LOW COST ADHESIVES FOR PRECURED RETREADING PROCESS

Rubber to rubber bonding is very important in the tire industry[13,14]. In the precured retreading process vulcanized components are bonded together. Natural rubber based adhesives are commonly used in this area for developing cushion compounds for bonding precured tread to the casing. Reclaim rubber can also be used in such adhesive formulations since this can bring down the material cost. However, the reclaimed rubber mainly derived from used tires may contain a mixture of elastomers, such as natural rubber, styrene butadiene rubber, polybutadiene rubber, etc and adhesives based on such elastomer mixtures are usually not very efficient. Unlike dry rubber products, latex products are only lightly crosslinked and contain rubber hydrocarbon of very high quality without any filler. Hence the latex products reclaim may be a potential source for preparing low cost adhesives for rubber to rubber bonding. Many techniques have been developed for reclaiming waste latex products[11,15,16]. In this study reclaim from latex waste products is proposed to be utilized for preparing adhesives for rubber to rubber bonding. The efficiency of such adhesives is proposed to be compared with adhesives prepared from raw natural rubber.

In the precured retreading process a solution of natural rubber compound (dough) is applied over the buffed casing, a thin piece of solid adhesive is then placed over it and finally the precured tread with the coating of dough above it for curing.

The dough and the adhesive are required to have a shelf life of about three months, which means that ultra accelerators cannot be used in them. Consequently the curing of the assembly takes about 2 to 3hs. However, the dough being in the liquid state, an ultra accelerator can be added to it just before use as it has to be vulcanized by the heat conducted through the tread and casing which may reduce the total curing time. This reduction in retreading time may reduce heat aging of the tread. The effect of this novel technique is also proposed to be investigated in this study.

Experimental

Natural rubber (NR) used for the study was ISNR-5 (Indian Standard Natural Rubber-5), ML (1 +4) 100°C- 82. The compounding ingredients viz., resins, zinc oxide, stearic acid, accelerator, antioxidants, HAF black and sulphur were commercial grade. The latex reclaim was prepared from the waste latex examination gloves supplied by M/s A.V.Thomas Rubber Company, CEPZ, Kakkanad, Cochin by the process developed in our laboratory[11].

Tire pieces and precured tread pieces used as adherends for bonding studies were cut from buffed tire and precured tread sheets. Both tire pieces and tread pieces were of the dimensions 120x25x10 mm.

The adhesives were prepared using formulations given in Table 3.21. The rubber was first masticated on a laboratory-mixing mill for 5min, followed by the addition of other compounding ingredients. After compounding the cure time of the matured compounds were determined using a Goettfert Elastograph model 67.85 according to ASTM D - 1648 (1981).

Table 3.21 Formulation of adhesives used for bonding

Ingredients	Adhesive		
	1	2	3
Natural rubber	100	—	50
Latex reclaim	—	100	50
Renacit-7	0.2	0.2	0.2
Zinc oxide	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0
HAF black	40.0	40.0	40.0
Pine tar	8.0	8.0	8.0
Wood rosin	2.0	2.0	2.0
MOR	0.8	0.8	0.8
TMTM	0.7	0.7	0.7
Vulkanox HS	1.0	1.0	1.0
Insoluble sulphur	2.5	2.5	2.5
*T_{10}, min	4.4	1.4	1.5
*T_{90}, min	8.8	4.8	5.8
Maximum torque, (Nm)	0.553	0.777	0.601

*Cure characteristics

The bonding characteristics were evaluated by determining the peel strength with a universal testing machine, model Zwick 1445 at a speed of 50mm/min. The samples for peel strength determination were prepared by placing adhesives of different thickness (25mm wide x 80mm long) between the adherend pieces and curing at a pressure of 20psi, in an autoclave.

The optimum thickness of the adhesive for bonding was determined using adhesive 1, by measuring the peel strength obtained for different thickness varying from 0.5 to 1.80 mm.

In adhesives 2 and 3 NR was replaced fully or partially by reclaimed latex waste. A 12% solution of adhesive 1, in solvent naphtha was used as dough A and dough A was modified by adding an ultra accelerator to form dough B. A comparative evaluation of adhesives 1, 2 and 3 in the presence of dough A and B were made by determining the respective bond strengths for a bonding time of 60 to 120min at intervals of 5min. To determine whether the cure time can be reduced by changing the dough, dough A was replaced by dough B. The effect of such reduction in bonding time on the abrasion resistance of the tread was also investigated.

Results and Discussion

The scorch time (T_{10}min) and cure time (T_{90}min) of the adhesives 1, 2 and 3 of the adhesives used for bonding are shown in Table 3.21.

The adhesive 3 based on 50/50 combination of NR and reclaim is found to cure faster than the one containing natural rubber alone. The adhesive 2 based on latex reclaim alone does not require a secondary accelerator. This may be due to the presence of crosslink precursors and/or unreacted curatives in the latex reclaim[12]. This is particularly so because of fast curing accelerators like ZDC (Zinc Diethyl dithiocarbomate), ZMBT (Zinc salt of mercaptobenzthiozole), TMTD (Tetra methyl thiourea disulphide) are used in latex compounding.

Figure 3.21 shows the variation of peel strength with thickness of the adhesive cured at a pressure of 20psi, in an autoclave.

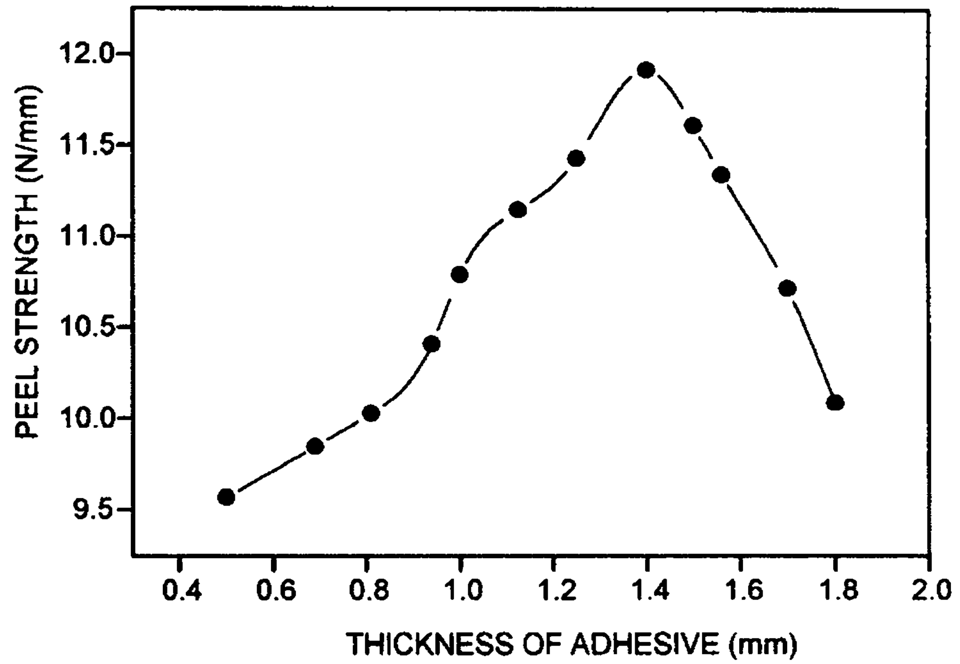


Fig. 3.21 Variation of peel strength with thickness of the adhesive cured at a pressure of 20psi in an autoclave.

The peel strength increases when the adhesive thickness is increased from 0.5 to 1.40mm and then decreases with further increase in thickness. This shows that there is an optimum thickness for adhesive to provide good bonding. Further increase in adhesive thickness results in poor bonding probably due to the under cure of the thick adhesive layer.

Figure 3.22 shows the variation of peel strength of samples with bonding time for adhesive 1 in the presence of dough A and B. The peel strength is found to be high with dough B. This may be due to the faster curing rate in the presence of dough B which contains an ultra accelerator. The peel strength increases with the increase in bonding time, reaches a maximum value and then decreases. The maximum peel strength is attained at 110min when dough A is used while the maximum strength is attained at 100min for dough B, which contains an ultra accelerator. The same trend in the peel strength variation with bonding time is found for adhesive 2 and 3 in the presence of dough A and B as shown in figures 3.23 and 3.24.

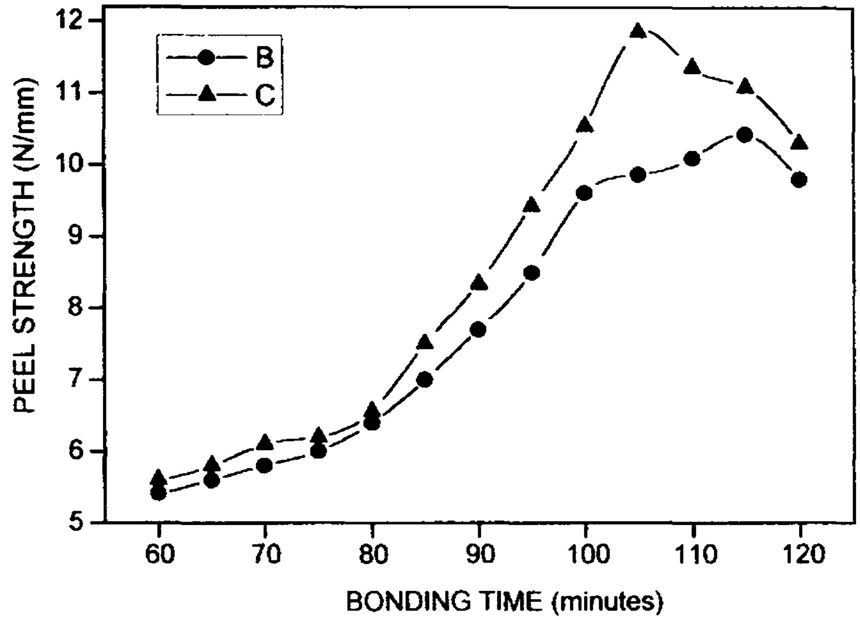


Fig. 3.22 Variation of peel strength with bonding time for adhesive 1.
(B) - Dough A; (C) -Dough B.

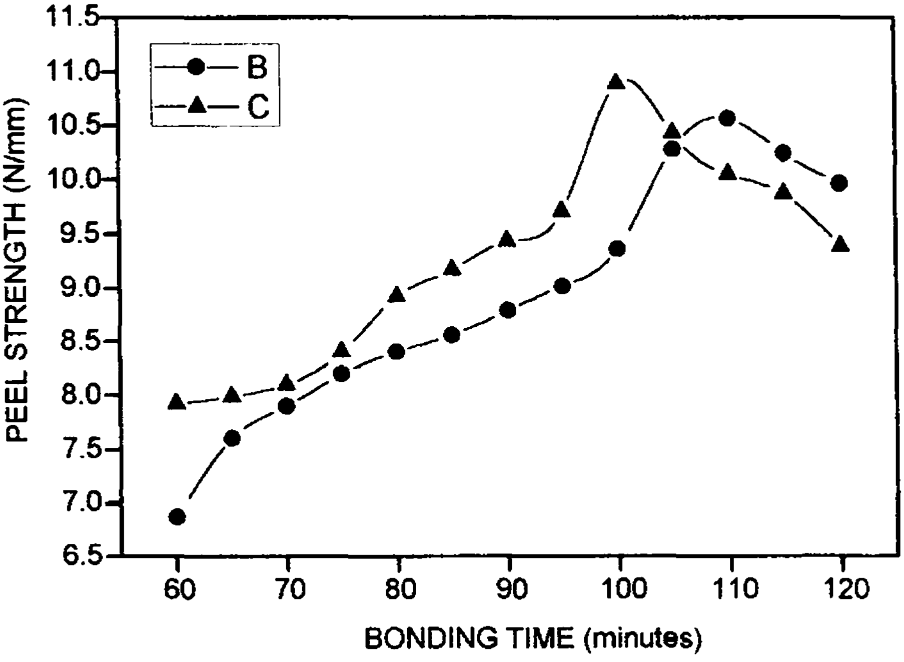


Fig. 3.23 Variation of peel strength with bonding time for adhesive 2.
(B) - Dough A; (C) - Dough B.

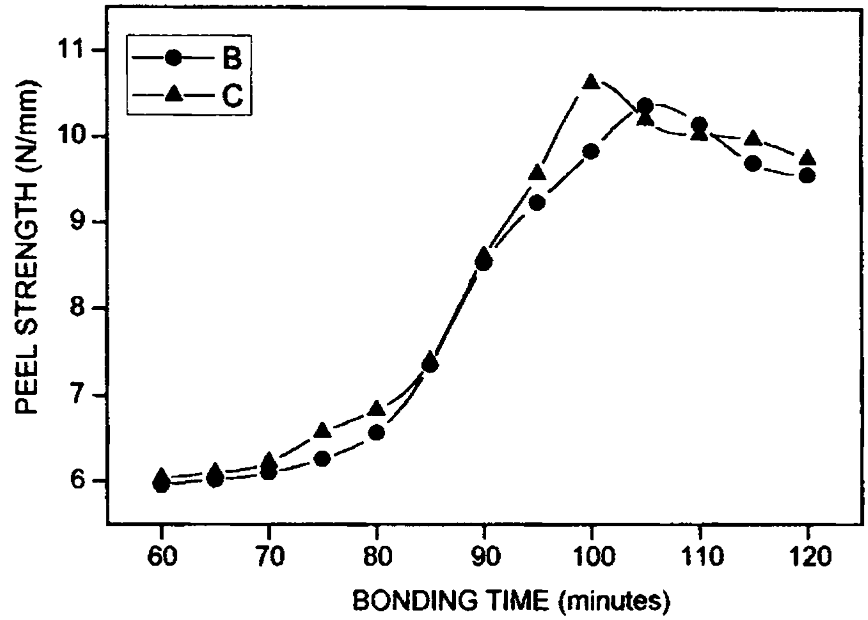


Fig. 3.24 Variation of peel strength with bonding time for adhesive 3.

(B) - Dough A; (C) - Dough B.

The reduction in bonding time will also help to reduce the degradation of the bonded tread. Figure 3.25 shows the variation of abrasion loss of the bonded treads with bonding time. The abrasion resistance is found to decrease as the bonding time is increased from 60 to 120min. This shows that lower bonding time can give increased mileage.

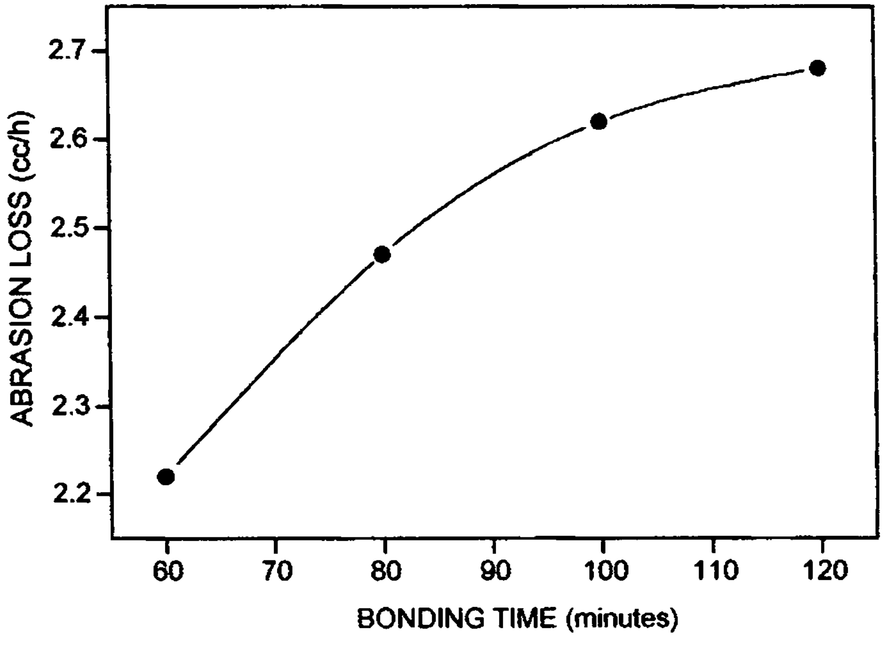


Fig. 3.25 Variation of abrasion loss of the bonded treads with bonding time.

Conclusions

1) Natural rubber can be replaced by latex reclaim partially or wholly in the cushion compounds for precured retreading process.

2) Modifying the dough with an ultra accelerator just before its use is a promising technique for reducing the cure time and hence increasing the tread life.

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Chapter IV

Part I

STUDIES ON ADHESIVES BASED ON DIFFERENT ELASTOMERS FOR BONDING VULCANIZATES OF CR WITH CR, CR WITH NR AND NBR WITH NR

Rubber surfaces experience varying degrees of adhesion when brought into contact. The physical forces of adhesion are generally thought to arise from two main sources: one electrostatic and the other van der Waals type short-range attraction. Adhesion may also be promoted by interdiffusion or chemical reaction at the interface. Considering the electrostatic source, surface change may be generated by contact of vulcanized rubber with different substrates such as gloves, sheet and plastic, and it has been suggested by Davies that electrostatic attraction may contribute significantly to the adhesion and hence friction. Studies have been conducted to understand the self-adhesion behavior of the elastomers and many theories have been proposed[1-3]. The dependence of the tackiness on the contact time and pressure had been explained in terms of the diffusion of the two adhering components into each other. But once the elastomer is vulcanized, the diffusion phenomenon of the macromolecules ceases and the tackiness disappears. For the bonding of vulcanized elastomers to each other the diffusion phenomena is expected to contribute little. Hence, in the fabrication of complex shaped products and in repairing rubber articles where the adhesion of vulcanized elastomers to themselves is vital, adhesives are essential.

Contact duration or dwell time can markedly influence the level of rubber adhesion and friction[4-7] and it is commonly observed that an increase in dwell time improves adhesion. In an attempt[7] to find physical reasons for the dwell effect, an optical study under a low power microscope was made of the contact area between smooth glass and smooth surfaced rubber. This study showed that surface bloom from free compounding ingredients appeared to be strongly linked with the dwell effect for the particular materials examined.

In this part of the study we propose to investigate the adhesion between different vulcanizates using CR, NR and NBR based adhesives. The effect of temperature and bonding time on the peel strength and the effect of adding chlorinated natural rubber in the adhesive dough are proposed to be investigated. The aging behaviour of the bonded pieces is also proposed to be investigated.

Experimental

The polymers used were chloroprene (CR), ML (1+4) 100°C - 45, nitrile rubber (NBR), ML (1+4) 100°C- 45 and natural rubber (NR), ISNR-5, ML (1+4) 100°C-82. The compounding ingredients viz. zinc oxide, stearic acid, magnesium oxide, resin, antioxidants, accelerator, HAF black and sulphur were of commercial grade.

CR, NBR and NR were mixed with other compounding ingredients according to the formulation given in Table 4.11, as per ASTM D 3182 (1982). The cure time (T_{90} min) and scorch time (T_{10} min) of the compounds were determined using a Goettfert Elastograph Model 67.85 according to ASTM D-1648 (1981).

Table 4.11 Formulation of CR, NBR and NR sheets for bonding

Ingredients	CR	NBR	NR
CR	100	—	—
NBR	—	100	—
NR	—	—	100
Zinc oxide	5.0	4.0	5.0
Stearic acid	—	1.5	2.0
Magnesium oxide	4.0	—	—
HAF black	40	20	40
Aromatic oil	—	—	5.0
DOP	5.0	—	—
MBTS	—	—	0.6
TMTD	—	—	0.2
TMTM	—	0.5	—
MOR	—	1.0	—
NA22	0.5	—	—
PF resin	—	10	—
Vulkanox HS	—	1.0	1.0
Sulphur	—	1.5	2.5
*T_{10}min	1.0	3.6	1.9
*T_{90}min	15.8	13.7	3.6
Maximum Torque, Nm	0 .466	0.262	0.494

* Cure characteristics

The CR and NBR based compounds were moulded at 160°C and the NR based compound was moulded at 150°C upto their optimum cure times. The rubber pieces to be used as the adherends for bonding studies (120x25x2mm) were cut from the moulded sheets.

The adhesives used in the study were compounded on a laboratory two-roll mixing mill and the doughs of the required concentration were prepared in the different solvents/ solvent mixtures.

The bonding characteristics were evaluated by determining the peel strength on a universal testing machine model Zwick 1445 at a speed of 50mm/min. The samples for peel strength determination were prepared by placing solid adhesive strip of optimum thickness, 1.35mm (25mm widex80mm long) between the adherend pieces.

The effect of temperature on the bonding of the vulcanized pieces of CR-CR was studied using a solid adhesive strip based on CR and two solutions, dough A and B (formulations shown in Table 4.12). Dough A and dough B are both CR based and are 25% solutions in a 1:1 solvent mixture of toluene and MEK. Dough A also contains chlorinated natural rubber (CNR). The CR based adhesive strip and dough A were applied on the adherend strip using three methods. In the first method the dough was applied on the adherend strip and the solid adhesive strip of optimum thickness was placed between the adherends. In the second method, the solid adhesive was also prepared as a 25% dough in the solvent mixture and applied on one of the adherend pieces. In the third method, the solid adhesive strip in the form of dough was applied on both the adherend strips. These studies were repeated by replacing dough A by dough B using the same solid adhesive strip. The samples were bonded at temperatures ranging from 40°C to 80°C at 10° intervals in an air oven.

Table 4.12 Formulation of CR based adhesive strip and doughs

Ingredients	CR adhesive strip	Dough A (25%)	Dough B (25%)
CR	100	13.40	14.97
Zinc oxide	5.0	0.7	0.75
Magnesium oxide	4.4	0.9	0.6
CNR	—	6.70	—
NA22	0.5	—	0.15
Thiocarbanilide	0.5	—	0.15
PF resin	—	3.35	1.5
CI resin	5.0	—	1.5
Wood rosin	—	—	2.39
HAF black	30	—	3.0
DOP	3.0	—	—
Toluene (ml)	—	50	50
MEK (ml)	—	50	50
Water (ml)	—	0.03	—

After optimizing the bonding temperature, the optimum bonding time at the optimum bonding temperature was determined for the same adherends using the solid CR based adhesive strip together with dough A or dough B. The time of bonding at the optimum temperature was varied from 75 to 120 minutes at intervals of 15 minutes.

In order to study the shelf life of the adhesive the above samples bonded at the optimum temperature and time of bonding were aged for a period of eight weeks by dipping in seawater and tap water at room temperature (28±2°C) and then the peel strength of the samples were determined at intervals of 7 days.

The bonding of CR-NR and NBR-NR were also investigated using CR, NR and NBR based adhesive and dough. Dough C is based on NR and dough D based on NBR. Dough C and D were used as 25% solution in a 1:1 solvent mixture of toluene and MEK. The effect of roughening the surface of the adherends before bonding was also investigated. The surface roughening was done by abrading with a carborundum paper. The bonding studies were carried out in an air oven at 130°C. The formulation of NR and NBR based adhesives and doughs are shown in Table 4.13.

Table 4.13 Formulation of NR, NBR adhesive and dough

Ingredients	NR adhesive strip	Dough C (25%)	NBR adhesive strip	Dough D (25%)
NR	100	15.4	-	-
NBR	-	-	100	16.72
Renacit-7	0.2	0.03	-	-
Zinc oxide	5.0	0.77	4.0	0.67
Stearic acid	2.0	0.30	1.5	0.25
HAF black	40	6.17	20	3.40
Pine tar	8.0	1.23	-	-
Wood rosin	2.0	0.30	-	-
PF resin	-	-	20	3.40
MOR	0.8	0.12	1.0	0.17
TMTM	0.7	0.11	0.5	0.083
Vulkanox HS	1.0	0.15	1.0	0.17
Insoluble sulphur	2.5	0.39	1.5	0.25
MEK	-	50	-	50
Toluene (ml)	-	50	-	50

Results and Discussion

Table 4.11 shows the scorch time and cure time of the CR, NR and NBR based compounds used for preparing the adherend strips.

Figure 4.11 shows the effect of temperature on the bonding of CR-CR using the CR based solid adhesive strip and dough A (as shown in Table 4.12). The curves B, C and D show the peel strength obtained for method I, Method II and method III of applying the dough and adhesive. It is found that as the temperature increases the bonding improves as seen from the increase in the peel Strength. The maximum peel strength is attained at 70°C, further increase in temperature showing a reduction in peel strength. Maximum bonding is obtained when the adhesive is used in the form of a solid strip, with dough A being applied on each of the adherend surface (curve B). When the adhesive strip is used in solution form and applied on one of the adherend pieces, there is a decrease in the peel strength. The peel strength is found to decrease

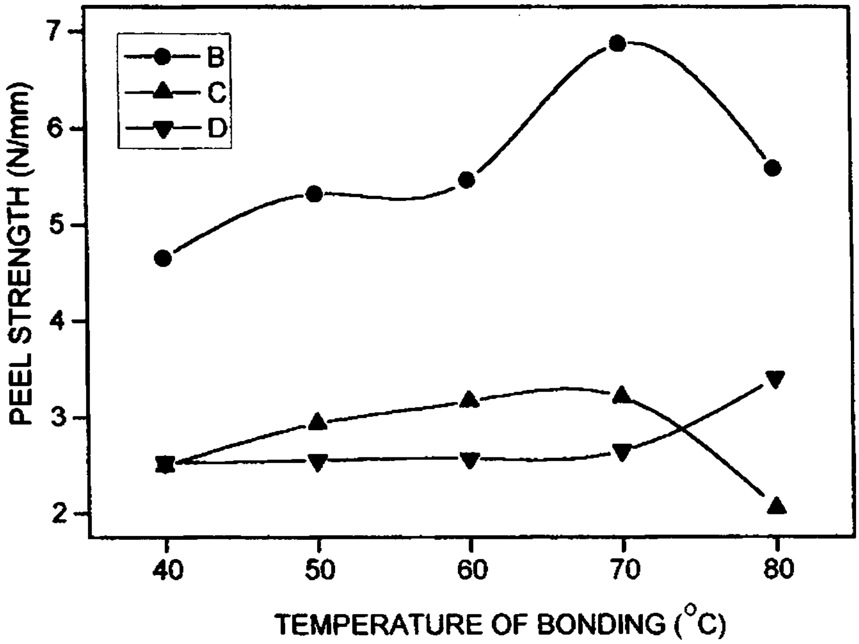

Fig. 4.11 Variation of peel strength with bonding temperature for CR-CR adherends using CR based adhesive strip and dough A. B- Method I; C- Method II; D- Method-III

further when the solid adhesive in the solution form is applied on both the adherend surface in addition to dough A.

Figure 4.12 shows the variation of peel strength with bonding time at the optimum bonding temperature (70°C). The peel strength is found to increase as the bonding time increases, reach a maximum value and thereafter decrease as the time of bonding is further increased. The optimum time of bonding is found to be 105min. At low contact temperatures the contact time has no effect on the joint strength, probably because of the incompatibility of the system which does not imparts substantial interdiffusion within a short contact time[8,9]. As the contact temperature increases the joints fail at the interface at short contact times and cohesively at long contact times. As the contact temperature increases both the degree of wetting and interdiffusion improve leading to the formation of a strong interface.

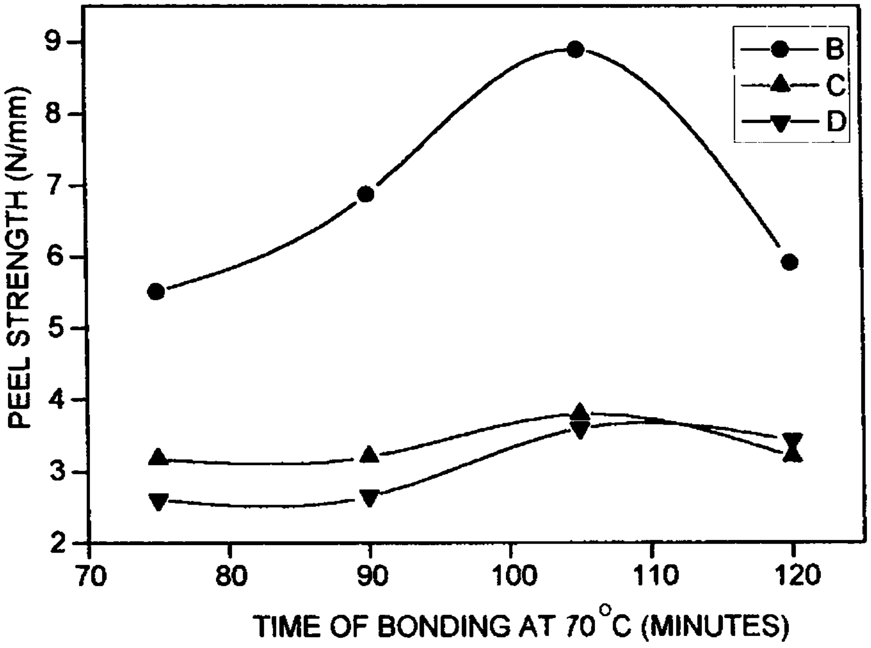

Fig. 4.12 Variation of peel strength with bonding time at optimum bonding temprature (70° C) for CR-CR adherends using CR based adhesive strip and dough A.B- Method I; C- Method II; D- Method-III

When dough A is replaced by dough B the results are more or less similar (figures 4.13 and 4.14). As in the case of dough A peel strength is again found to increase with increase in temperature, attain a maximum value and thereafter decrease with increase in temperature (figure 4.13). The optimum bonding temperature is again found to be 70°C.

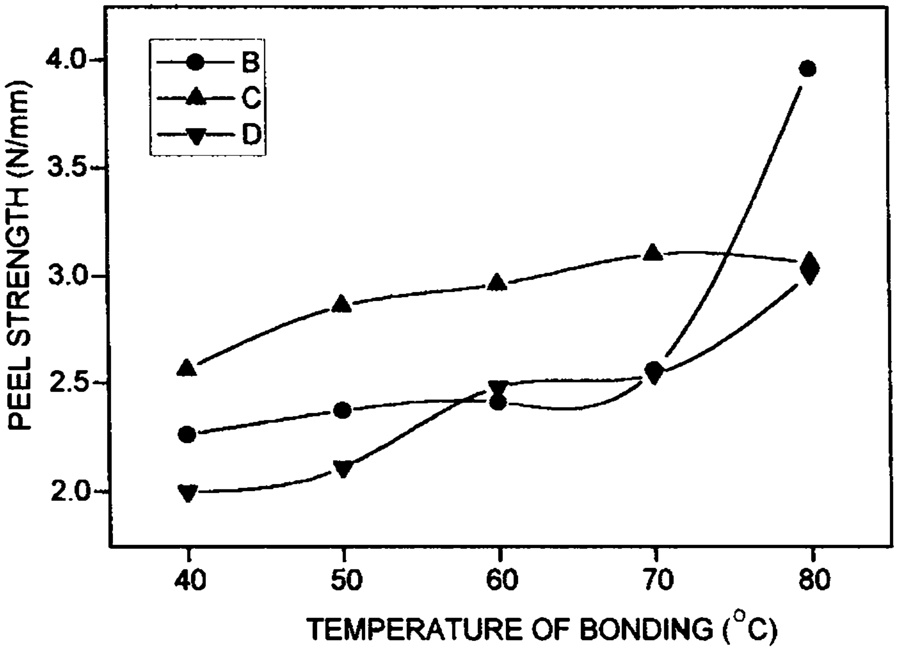

Fig. 4.13 Variation of peel strength with bonding temperature for CR-CR adherends using CR based adhesive strip and dough B. B- Method I; C- Method II; D- Method-III

Figure 4.14 shows the variation of peel strength with bonding time at the optimum bonding temperature of 70°C. The optimum bonding time at 70°C for dough B is found to be 120min. This shows that dough A cures faster than dough B and also has better bonding than dough B. This may be due to the presence of chlorinated rubber in the dough A.

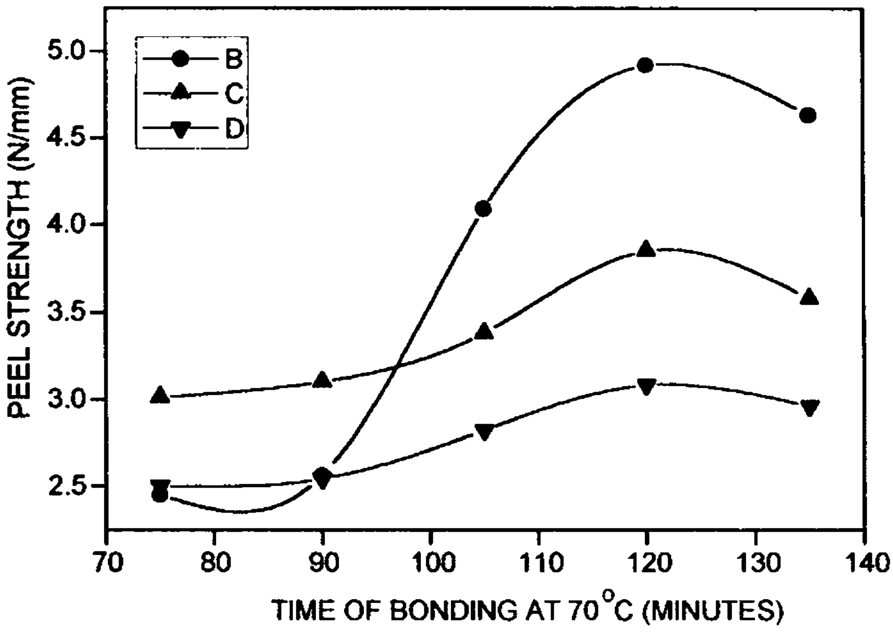

Fig. 4.14 Variation of peel strength with bonding time at optimum bonding temprature (70° C) for CR-CR adherends using CR based adhesive strip and dough B. B- Method I; C- Method II; D- Method-III

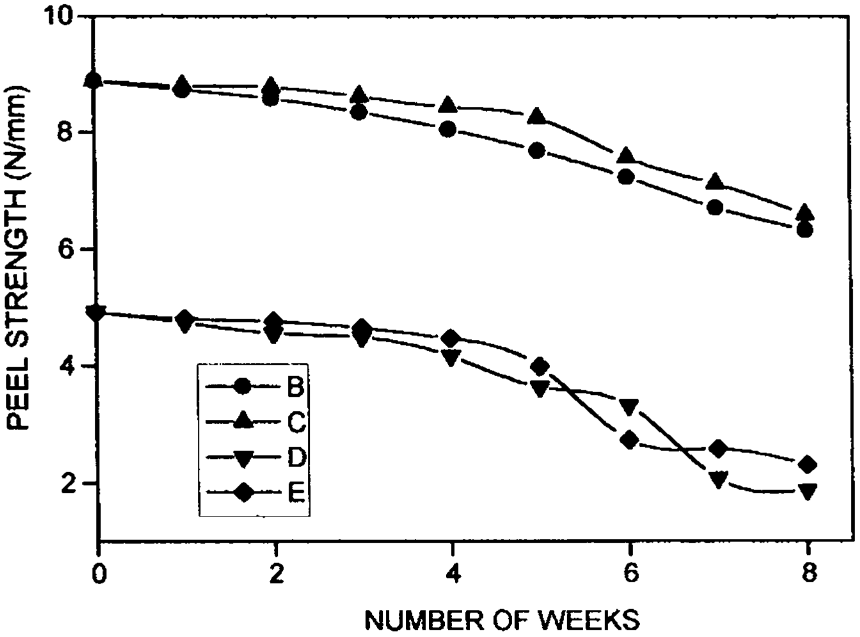

Fig. 4.15 Aging behaviour of the bonded samples of CR-CR at optimum conditions. B- Dough A in tap water; C- Dough A in sea water; D- Dough B in tap water; E- Dough B in sea water.

Figure 4.15 shows the aging behaviour of the bonded samples using dough A and B at the optimized conditions in seawater and tap water. The bond strength of pieces bonded by dough A retains their bond strength compared to the pieces bonded using dough B which may also be attributed due to the presence of the chlorinated rubber in the dough.

Table 4.14 shows the peel strength obtained for bonding vulcanized pieces of NR-CR and NR-NBR sheets (bonded to adhesive and dough as shown in Table 4.13) at 130°C in an air oven.

Table 4.14 Peel strength at 130°C without applying pressure

Adhesives	NR-CR	NR-NBR	NR*-NBR *
CR adhesive with Dough A	1.27	1.58	2.36
CR adhesive with Dough B	1.36	0.09	2.18
NR adhesive with Dough C	1.20	0.52	1.64
NBR adhesive with Dough D	0.11	0.14	2.40

* *Roughened surface*

Both NR-CR and NR-NBR show good bonding with CR based adhesive and dough A compared to dough B. However, NBR adhesive and dough D are not efficient. NR-CR gives better bonding than NR-NBR when NR adhesive and dough C are used. At high contact temperatures the molecules diffuse across the interface and interfacial crosslinks are formed. The formation of the chemical bonds has been proven by Infrared spectroscopy[10]. Such chemical interaction across the interface has been reported where each substrate contains a component which can diffuse to the interface and chemically interact thereby coupling the two adherends[11-13]. Once the interfacial chemical linkages are formed, the interface becomes stronger than the elastomer matrix which fails under the applied stress, with the interface remaining intact. Network formation across the interface by permanent entanglements[14] and interlinking covalent bonds[11] has been reported. Since both polymers contain polar groups, polar-polar interaction can also contribute towards increased adhesion.

Table 4.14 also shows the effect of roughening the surface of the adherends. It is found that there is an improvement in the bonding of NR-NBR on surface roughening. This may be due to the penetration of surface asperities and the increases in the real area of contact.

CONCLUSIONS

1) The CR based adhesive strip gives maximum bonding when used in the form of solid adhesive strip, in the presence of the dough applied on the adherend surface.
2) Chlorinated natural rubber when used in the CR based dough improves the bonding.
3) The dough containing chlorinated rubber has better aging properties.
4) The bonding between NR-NBR can be improved by surface roughening before bonding.

Part-II

DEVELOPMENT OF ROOM TEMPERATURE CURABLE ADHESIVES FOR BONDING VULCANIZATES OF CR WITH CR AND NR WITH NR

Most adhesive are applied in a wet or fluid condition so that the surfaces are easily wetted or permeated and the load bearing strength of the bond develops by drying or chemical setting action.

The most important solvents for preparing rubber elements are derived largely from petroleum and coal tar fractions, solvent naphtha and benzene being the most widely used. Others such as toluene, carbon disulphide, carbontetrachloride, trichloroethylene are also used in large quantities. When a rubber solution is prepared in any of these solvents a highly viscous solution capable of depositing tacky, adhesive films is formed.

Adhesives may be solvent or non-solvent types. The solvent whether water or an organic liquid, has a significant role in the development of adhesion, since its retention by the resin at the glue line may influence the setting and the subsequent ability of the adhesive to resist creep and cold flow. Further, the characteristics of the resin films formed on the evaporation of solvents have been shown to be dependent upon the nature of the solvent or solvent combination[15].

K.E. Simpson has reported[16] the use of natural rubber gum, aluminium silicate-filled and black-filled vulcanizates which have been tested for adhesion using a room-temperature vulcanizing natural rubber cement, a polychloroprene adhesive and surface chlorination followed by a polyurethane adhesive.

In this part of the study we propose to investigate the bonding between vulcanizates of CR-CR and NR-NR using different adhesive dough at room temperature, by applying pressure.

Experimental

The polymers used were two grades of chloroprene (CR), ML (1+4) 100°C-45 (Neoprene W and Neoprene AD) and natural rubber (NR), ISNR-5, ML (1+4) 100°C-82. The compounding ingredients viz., zinc oxide, stearic acid, magnesium oxide, resin, antioxidants, accelerator, HAF black and sulphur were of commercial grade.

CR and NR were mixed with other compounding ingredients according to the formulation given in Table 4.21, as per ASTM D 3182 (1982).

Table 4.21 Formulation of rubber compounds

Ingredients	CR	NR
CR	100	—
NR	—	100
Zinc oxide	5.0	5.0
Stearic acid	—	2.0
Magnesium oxide	4.0	—
HAF black	40	40
Aromatic oil	—	5.0
DOP	5.0	—
MBTS	—	0.6
TMTD	—	0.2
NA22	0.5	—
Vulkanox HS	—	1.0
Sulphur	—	2.5
*T_{10}min	1.0	1.9
*T_{90}min	15.8	3.6
Maximum Torque, Nm	0.466	0.494

*Cure characteristics

The cure time (T_{90} min) and scorch time (T_{10} min) of the compounds were determined using a Goettfert Elastograph Model 67.85 according to ASTM D 1648 (1981).

The CR based compounds were moulded at 160°C and the NR based compounds at 150°C upto the respective optimum cure time. The rubber pieces to be used as the adherends for bonding studies (120x25x2mm) were cut from the moulded sheets.

For preparing the adhesive, the rubber was first masticated on a laboratory-mixing mill for 5 minutes, followed by the addition of other compounding ingredients. After compounding, 25% solution of the adhesive dough was prepared in the solvent mixture.

The bond strength was evaluated by determining the peel strength using a universal testing machine at a speed of 50mm/min. The samples for peel strength determination were prepared by applying three coatings of the adhesive dough on the adherend strips giving an interval of 20 minutes for drying after each coating. The samples were bonded by applying a pressure of $1 kg/cm^2$.

The bonding of CR-CR and NR-NR were tried using different adhesives based on CR and NR. The formulation of the CR based adhesive (general grade and adhesive grade) and NR based adhesive are shown in Table 4.22. The adhesive dough was prepared in a 1:1 mixture of toluene and methylethylketone (MEK). All the three adhesive doughs contained chlorinated rubber.

The effect of modifying the CR (adhesive grade) based adhesive dough with NR was evaluated by varying the amount of NR from 10 to 40phr. The optimum amount of NR to be added in the dough to get maximum bonding was determined.

Table 4.23 shows the formulation of CR (adhesive grade) based adhesive in which an accelerator (thiocarbanilide) was added to study its effect on bonding. The adhesive dough was prepared by using different solvent mixtures. The solvent mixtures used were combination of MEK/benzene, MEK/toluene, MEK/toluene/hexane and toluene/acetone/ benzene.

In order to study the effect of resin content in the adhesive dough, the resin content was varied from 25 to 45phr and the optimum resin content was determined.

The effect of replacing MEK by benzene partially and wholly was evaluated by selecting the CR based adhesive dough containing NR and CR based adhesive containing chlorinated rubber. The formulations of the adhesives are given in Table 4.24.

For comparison, the bonding of CR-CR and NR-NR were done with four commercial samples. The efficiency of the adhesives doughs in textile to textile bonding was also compared with that of commercial samples.

Results and Discussion

Table 4.21 shows the cure time (T_{90} min) and scorch time (T_{10} min) of CR and NR based sheets used as the adherends.

Table 4.22 shows the peel strength obtained for CR (W and AD grade) and NR based adhesives used for bonding vulcanized pieces of CR-CR and NR-NR at room temperature by applying a pressure. The adhesive grade CR gives maximum bond strength for CR-CR bonding has expected. For NR-NR the two grades of CR based adhesive give almost comparable bonding. The NR based adhesive does not give appreciable bonding. This may be due to the incompatibility of the adhesive dough and the adherend pieces and the lower modulus of the adhesive dough. In the case of CR adhesive, the chlorinated rubber improves the strength significantly.

Table 4.22 Formulation of adhesives and the peel strength for bonding CR-CR and NR-NR

Ingredients	1	2	3
CR (adheisve grade)	—	100	—
CR (general grade)	100	—	—
NR	—	—	100
Zinc oxide	5.25	5.25	5.25
Magnesium oxide	6.75	6.75	6.75
CNR	50	50	50
PF resin	35	35	35
Water (ml)	0.25	0.25	0.25
MEK(ml)	50	50	50
Toluene(ml)	50	50	50
Peel Strength (N/mm), CR-CR sheets	2.16	3.45	1.12
Peel Strength (N/mm), NR-NR sheets	1.85	1.83	1.08

Figure 4.21 shows the variation of peel strength with NR content in the adhesive 2 of Table 4.22. As the NR content increases, the peel strength is found to increase and the

maximum peel strength is obtained at 30phr of NR in the dough. Further increase in the NR content reduces the bonding. The effect is more in the case of NR-NR bonding than CR-CR. This shows that for CR-CR bonding, addition of NR into CR dough is not very effective even though it enhances the NR-NR bonding. This may be due to the combined effect of "dry tack" of NR and adhesive nature of CR.

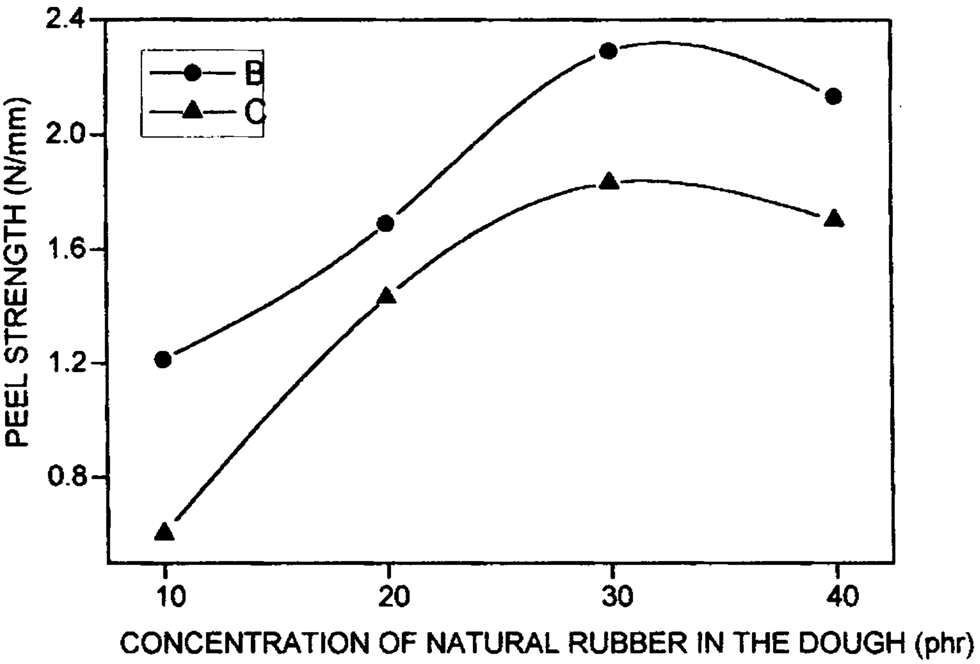

Fig. 4.21 Variation of peel strength with NR content in adhesive 2.
B- CR-CR; C- NR-NR.

Table 4.23 shows the effect of adding an accelerator and NR into the CR based adhesive dough in different solvent combinations. The NR-NR sheets do not give appreciable bonding and the values differ only marginally with different solvent combinations. For CR-CR bonding, a combination of toluene and MEK gives better bonding than other solvent combination.

Table 4.23 Effect of an accelerator on peel strength in CR based adhesive

Ingredients	8	9	10	11
CR (adheisve grade)	-	100	100	100
CR (general grade)	100	-	-	-
NR	10	10	10	10
Zinc oxide	5	5	5	5
Magnesium oxide	4	4	4	4
Thiocarbanilide	0.5	0.5	0.5	0.5
CI resin	5	5	5	5
PF resin	35	35	35	35
Wood rosin	5	5	5	5
Water	0.25	0.25	0.25	0.25
MEK	50	50	30	-
Toluene	-	50	45	50
Hexane	-	-	25	-
Acetone	-	-	-	25
Benzene	50	-	-	25
Peel Strength (N/mm), CR-CR sheets	1.87	2.36	1.09	1.10
Peel Strength (N/mm), NR-NR sheets	1.67	1.96	0.92	0.88

Table 4.24 shows the effect of replacement of MEK by benzene partially or wholly. It is found that replacing MEK by benzene does not affect the peel strength appreciably for CR-CR bonding. The dough containing NR gives better bonding than the dough containing chlorinated rubber.

Table4.24 Effect of different solvent mixtures on CR based adhesives

Ingredients	12	13	14	15
CR (adheisve grade)	100	100	100	100
NR	30	30	—	—
Zinc oxide	5.0	5.0	5.25	5.25
Magnesium oxide	4	4	6.75	6.75
CNR	—	—	50	50
PF resin	35	35	35	35
CI resin	5.0	5.0	—	—
Wood rosin	5.0	5.0	—	—
Water	0.25	0.25	0.25	0.25
MEK	25	—	25	—
Toluene	50	50	50	50
Benzene	25	50	25	50
Peel Strength (N/mm), CR-CR sheets	2.59	2.98	2.57	2.48

Figure 4.22 shows the variation of peel strength with PF resin content in the dough. The optimum resin content is found to be 35phr. Too low or too high resin content gives poor bonding, due to the low and high modulus of the adhesive film formed.

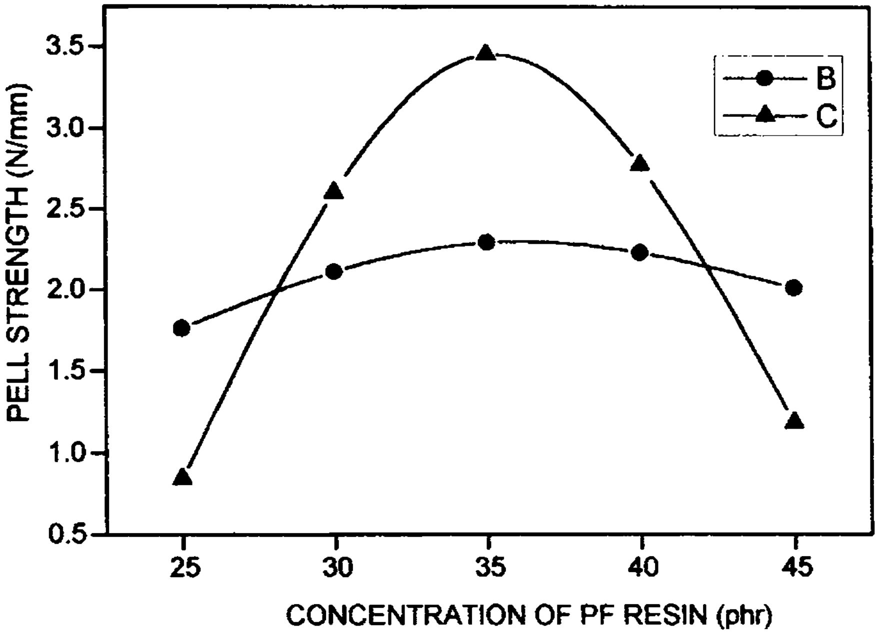

Fig. 4.22 Variation of peel strength with PF resin content in the dough

B- NR-NR; C- CR-CR.

Table 4.25 shows the peel strength of NR-NR and CR-CR sheets bonded using commercial samples at room temperature. The commercial samples do not give appreciable bonding compared to the adhesive prepared in the laboratory.

Table 4.25 Variation of peel strength for different commercial samples

Commercial samples	Peel strength (N/mm)	
	NR-NR	CR-CR
I	0.32	1.95
II	0.45	1.79
III	0.57	1.78
IV	0.22	1.59

Table 4.26 shows the peel strength obtained for textile bonding using adhesives prepared in the laboratory and the commercial samples. The laboratory samples give better bonding than the commercial samples.

Table 4.26 Comparison of peel strength for textile to textile with selected adhesives

Adhesive	Peel strength (N/mm)
Commercial sample I	3.94
Dough 2	4.18
Dough 6	3.45
Dough 12	2.17
Dough 13	3.06

Conclusions

1) NR-NR bonding can be improved by adding an optimum amount of NR in the CR (AD grade) based dough. The optimum amount is found to be about 30phr.
2) CR-CR bonding is affected by the choice of the solvent mixtures used. A solvent mixture of toluene and MEK is found to give good bonding for CR-CR while NR-NR bonding does not show much dependence on the solvent mixtures.
3) The MEK in the solvent mixture of MEK/toluene can be replaced by benzene partially or wholly without any appreciable change in the peel strength for CR-CR bonding.
4) While using the benzene/toluene mixture, the CR based dough containing NR gives better bonding than the dough containing chlorinated natural rubber.

5) The optimum amount of PF resin in CR based dough is found to be about 35phr.

6) The adhesive formulated in this study are found to give better bonding than the commercially available samples.

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Chapter V

Part I

STUDIES ON RUBBER TO NYLON TIRE CORD BONDING

Nylon fabric is widely used in tires and hence its bonding with rubber is very important since the load carrying capacity, the performance characteristics and durability of an automobile tire is determined by the textile reinforcement.

One of the major problems encountered during tire manufacture is the poor adhesion between the cords and the rubber. To overcome this drawback, adhesion-promoting systems, such as resorcinol-formaldehyde latex and polyisocyanates have been utilized to provide a coating on the cord surface to improve adhesion at the interface between the cord and rubber[1-7]. In general the layer of adhesive forms an intermediate between the cord and rubber and thus two interfaces, rubber/adhesive and adhesive/cord are introduced in place of one[3,8]. The improvement in the adhesion depends upon various conditions of dipping[2] and the rubber matrix used for bonding.

R. Iyengar has reported[9] the nylon 6,6 adhesion to natural rubber. He has examined the adhesion of nylon 6,6 tire cords to natural rubber with particular emphasis on high curing temperatures and shorter cure cycles and the increasing use of faster curing NR as the sole elastomer in tire body stocks.

Other studies reported are the adhesion of nylon 6,6 to chloroprene rubber by N.A. Darwish[10]. The cords in this study were treated with conventional resorcinol formaldehyde-latex dipping solution. The effect of an adhesion promoter on the adhesion was also investigated.

A.N. Bibi [11] has carried out the chemical modifications of rubber (epoxidation) or nylon (chemical pre-treatment).

The effects of atmospheric pollutants at high temperature on the adhesion of RFL-coated tire cords to rubber was studied by R.E. Hartz [12]. The effects of oven pollutants at high temperatures on the adhesion of resorcinol–formaldehyde latex treated nylon and polyester cords to rubber were examined using a hot strip adhesion test. Ozone and ozone with UV light were found to be much greater degradants than other pollutants.

In this study we propose to make a systematic study of the resorcinol-formaldehyde (RF) resin preparation and its use as a bonding agent in RFL adhesive for rubber to nylon tire cord adhesion.

Experimental

The nylon cords used for dipping studies were 1680/2, 1260/2 and 840/2 supplied by SRF Ltd. Madras. The lattices used were vinyl pyridine terpolymer (VP) latex (Butadiene 70% - Styrene 15% - Vinyl pyridine 15%) and natural rubber (NR) latex (60% centrifuged latex). The elastomer used for bonding studies was natural rubber latex (NR), ISNR-5, ML (1+4) 100°C-82. The compounding ingredients viz., zinc oxide, stearic acid, HAF black, wood rosin, antioxidants, accelerators, sulphur, hexamethylenetetramine, resorcinol, paraformaldehyde and formaldehyde were of commercial grade. The resorcinol-formaldehyde (RF) resin used for the preparation of the RFL adhesive was prepared in the laboratory by two methods. In method I the ratio of the resorcinol to formaldehyde was 2:1 (RF resin-I) and in method II (commercial method) the ratio was 1: 2 (RF resin-II).

NR was mixed with other compounding ingredients according to the formulations given in Table 5.11, as per ASTM D 3182 (1982).

Table 5.11 Formulation of natural rubber compounds for bonding

Ingredients	1	2	3	4	5	6
Natural rubber	100	100	100	100	100	100
HAF black	40	40	40	40	40	40
ZnO	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
Wood Rosin	5	5	5	5	5	5
Vulkanox4020	0.75	0.75	0.75	0.75	0.75	0.75
Vulkanox HS	0.5	0.5	0.5	0.5	0.5	0.5
MOR	0.65	0.65	0.65	0.65	0.65	0.65
Hexamethylenetetramine	-	0.5	1.0	1.5	2.0	2.5
Sulphur	2.25	2.25	2.25	2.25	2.25	2.25
*T_{10} min	1.8	2.0	2.1	1.9	1.9	1.8
*T_{90} min	14.1	12.0	10.6	9.4	9.0	8.2

*Cure characteristics

The optimum cure time (T_{90} min) and scorch time (T_{10} min) of the compound, were determined using a Goettfert Elastograph model 67.85, according to ASTM D 1648 (1981). In compounds 2 to 6, the amount of hexamethylenetetramine was varied in increments of 0.5phr. In compounds 7 to 12, the amount of RF resin-I was varied by 0.2phr, keeping the amount of paraformaldehyde constant at 0.4phr as shown in Table 5.13.

Table 5.13 Formulation of natural rubber compounds for bonding

Ingredients	7	8	9	10	11	12
Natural rubber	100	100	100	100	100	100
HAF black	40	40	40	40	40	40
ZnO	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
Wood Rosin	5	5	5	5	5	5
Vulkanox 4020	0.75	0.75	0.75	0.75	0.75	0.75
Vulkanox HS	0.5	0.5	0.5	0.5	0.5	0.5
OR	0.65	0.65	0.65	0.65	0.65	0.65
Paraformaldehyde	0.4	0.4	0.4	0.4	0.4	0.4
RF resin-I	-	0.2	0.4	0.6	0.8	1.0
Sulphur	2.25	2.25	2.25	2.25	2.25	2.25
*T_{10} min	7.0	6.9	10.7	6.6	6.2	6.1
*T_{90} min	15.1	18.9	21.1	19.0	18.6	17.6

*Cure characteristics

The dipped cords were bonded with the rubber compounds and the pull through load was determined by the H- Adhesion test. The H- tests were designed to measure the force required to pull a cord in the direction of its axis from a strip of rubber in which the ends of the cords are embedded as per the ASTM D 2138 (1983).

RFL adhesives with varying amounts of RF resin were prepared using NR latex as well as VP latex. The RF resin-1 was dried and a 7.5 % solution of the dried resin was prepared in distilled water. RFL adhesives A, B, C, D and E contain 7, 8, 9, 10 and 11ml respectively (corresponding to 2.10, 2.31, 2.50, 2.67 and 2.84 % weight respectively) of the above RF resin-I solution mixed with 8ml NR latex and 10ml distilled water. The RFL adhesive based on RF resin-I was matured for a period of 20 hours. RFL adhesive F contains RF resin-II mixed with NR latex and distilled water. The RF resin-II based RFL adhesive was matured for a period of 4 hours. For the dipping, drying and curing of the cord, a dipping unit was designed and fabricated. The dipping unit consists of two drying zones and a curing zone. The temperature of each zone could be varied from 30 to 210°C. The length of each zone was 33.33cm. The cords were dipped dried, cured and wound on a pulley.

The 1680/2 nylon cord was dipped in RFL adhesives A, B, C, D, E and F. The effect of a formaldehyde donor, hexamethylenetetramine, in the rubber compound was studied by adding it in varying amounts from 0 to 2.5phr. The optimum resin-rubber ratio in NR latex and the amount of the hexamethylenetetramine in the rubber compound were determined.

The NR latex in the above RFL adhesives was replaced by VP latex to get RFL adhesives I, J, K, L, M and N respectively. A maturation time of 20 hours was given for adhesives I, J, K, L and M while a maturation time of 4 hours was given for adhesive N. The studies were repeated with 1680/2, 1260/2 and 840/2 nylon cords.

In order to study the effect of drying and curing temperature on bonding, the drying temperature was varied from 140 to 160°C and the curing temperature was varied from 180 to 200°C using the cord 1680/2.

The effect of donor concentration on bonding was also studied by adding a combination of paraformaldehyde and RF resin-I into the rubber compound (Table 5.13). The concentration of the paraformaldehyde in the compound was kept constant and the RF resin-I concentration was varied from 0 to 1phr. Also the concentration of paraformaldehyde was varied from 0 to 3phr in the RFL adhesive keeping the concentration of the RF resin-I constant.

The compounds 1-12 were compression moulded upto their respective optimum cure times at 150°C in a laboratory hydraulic press. The tensile strength of these vulcanizates were determined according to ASTM D 412 (1980) using dumbbell shaped specimens on a Zwick universal testing machine model 1445.

The effect of adding different resin combinations into the rubber compound was also studied. A combination of cashew nut shell liquid (CNSL) resin-wood rosin, phenol formaldehyde (PF) resin-wood rosin and RF resin-I/paraformaldehyde-wood rosin were used in the rubber compounds. Also the effect of replacing part of HAF black by silica in the rubber compound was studied. The formulations of the compounds bonded to nylon cord dipped in NR and VP latex are given in Table 5.14 and Table 5.15 respectively.

The pull through load of the bonded cords was measured after aging for a period of seven days at 30°C.

Table 5.14 Formulations of rubber compounds with different resin combinations

Ingredients	I	II	III	IV
Natural rubber	100	100	100	100
Zinc oxide	5	5	5	5
Stearic acid	2	2	2	2
HAF black	40	40	40	35
Silica	—	—	—	5
Aromatic oil	5	5	5	5
Wood rosin	2.5	2.5	5	5
CNSL resin	2.5	—	—	—
PF resin	—	2.5	—	—
RF resin-I	—	—	0.4	0.4
Vulkanox-HS	0.5	0.5	0.5	0.5
Vulkanox-4020	0.75	0.75	0.75	0.75
MOR	0.65	0.65	0.65	0.65
Hexamethylenetetramine	1.0	1.0	—	—
Parformaldehyde	—	—	0.4	0.4
Sulphur	2.25	2.25	2.25	2.25
*T_{10}min	4.1	3.8	4.8	5.3
*T_{90}min	11.8	12.5	14.2	14.4

*Cure characteristics

Table5.15 Formulations of rubber compounds with different resin combinations

Ingredients	I	II	III	IV
Natural rubber	100	100	100	100
Zinc oxide	5	5	5	5
Stearic acid	2	2	2	2
HAF black	40	40	40	35
Silica	—	—	—	5
Aromatic oil	5	5	5	5
Wood rosin	2.5	2.5	5	5
CNSL resin	2.5	—	—	—
PF resin	—	2.5	—	—
RF resin-I	—	—	0.4	0.4
Vulkanox-HS	0.5	0.5	0.5	0.5
Vulkanox-4020	0.75	0.75	0.75	0.75
MOR	0.65	0.65	0.65	0.65
Hexamethylenetetramine	1.5	1.5	—	—
Parformaldehyde	—	—	0.4	0.4
Sulphur	2.25	2.25	2.25	2.25
*T_{10}min	3.8	4.1	4.2	4.9
*T_{90}min	10.4	11.2	11.8	12.9

*Cure characteristics

The effect of resin-rubber ratio in the RFL adhesive (NR latex) on the pull through load is shown in figure 5.11.

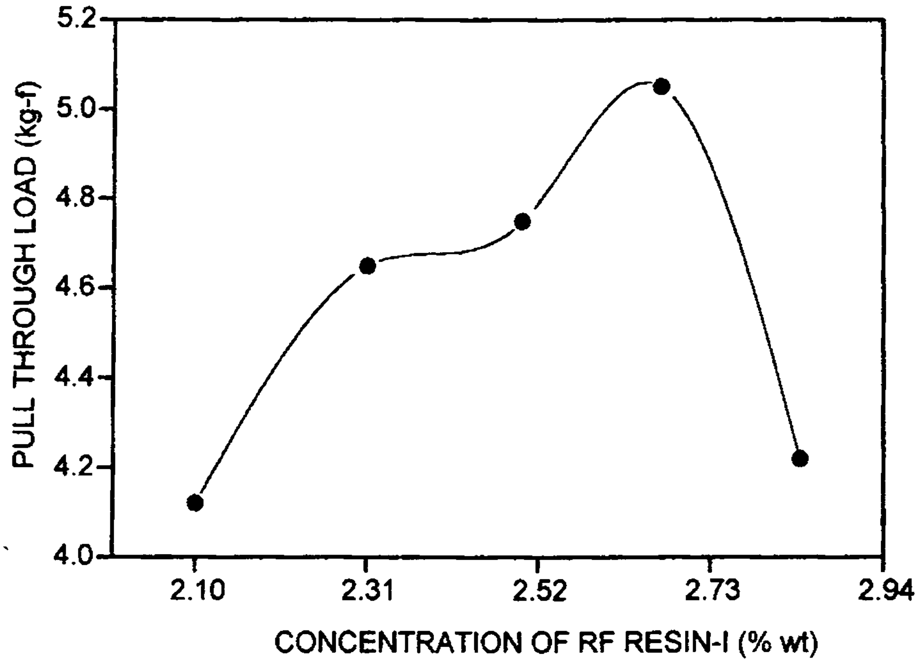

Fig. 5.11 Variation of pull through load with RF resin-I to rubber ratio in NR latex based RFL adhesive.

The RF resin-I shows better adhesion than RF resin -II. The pull through load is found to depend on the resin-rubber ratio, increases as the RF resin-I concentration in the RFL adhesive increases, reaches a maximum and then decreases. Thus the optimum resin-rubber ratio is found to be 5:4. The excess resin causes stiffness of the dipped cord resulting in high modulus of the cured RFL film[13].

When the NR latex is replaced by VP latex in the RFL adhesive, there is a significant increase in the pull through load and the optimum resin-rubber ratio is found to be 9:8, as shown in the figure 5.12. Thus it is found that the amount of RF resin-I required for VP latex is lower than that required for NR latex. This may be due to the exceptionally high stability and higher polarity of VP latex compared to NR latex and also the difference in the pH of the two lattices. Also the RF resin-I gives better adhesion than RF resin-II for both the NR and VP latex based RFL adhesive. The network structure of RFL resin may be getting modified widely with the resorcinol to formaldehyde ratio and the maturing time, which in turn effects the mechanical properties of RFL films prepared with various resorcinol to formaldehyde ratios.

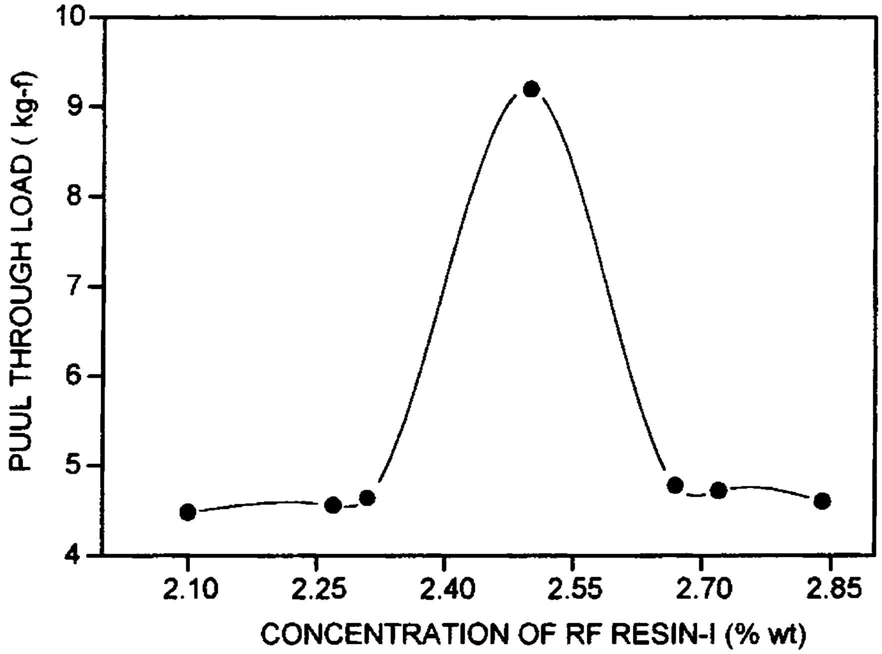

Fig. 5.12 Variation of pull through load with RF resin-I to rubber ratio in VP latex based RFL adhesive

Figure 5.13 shows the comparison of the optimum resin to rubber ratio in VP latex based RFL adhesives for the three cords dipped in it. The optimum resin-rubber ratio obtained for the 840/2 nylon cord is the same as that for the 1680/2 nylon cord. The ratio obtained for the 1260/2 nylon cord is lower than that for the other two cords. This ratio is found to be 1:1. This difference in the optimum resin-rubber ratio for the cords in the same latex may be due to the difference in the total surface area in contact with rubber.

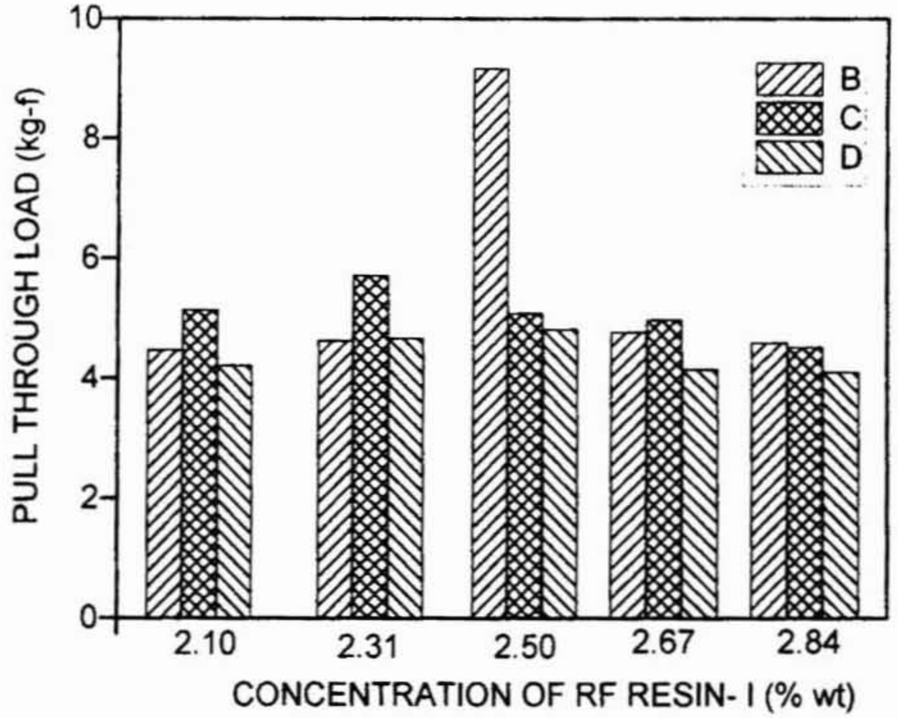

Fig. 5.13 Comparison of pull through load with resin rubber ratio for cords dipped in VP latex based RFL adhesive. B-1680/2, C-1260/2, D-840/2.

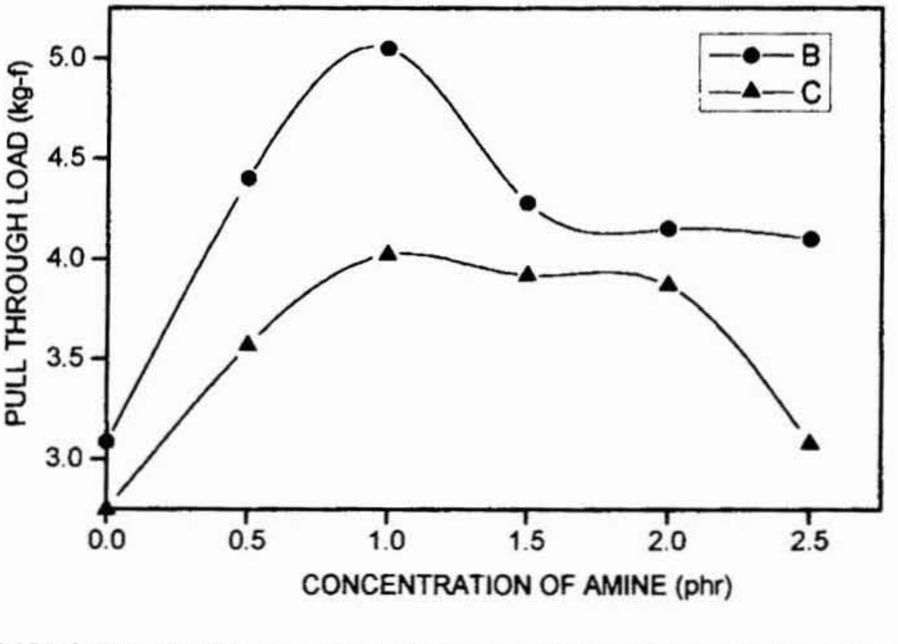

Fig. 5.14 Variation of pull through load with concentration of hexamethylenetetramine in the rubber compound. B - NR latex/ RF resin-I, C- NR latex/ RF resin-II.

Figures 5.14 and 5.15 show the effect of concentration of hexamethylenetetramine in the rubber compound on the pull through load for the nylon tire cord dipped in RFL adhesives prepared using RF resin-I and RF resin-II. The optimum amount is found to be 1phr as shown in figure 5.14, when NR latex based RFL adhesive is used. When VP latex is used, the optimum concentration is found to be 1.5phr as shown in figure 5.15.

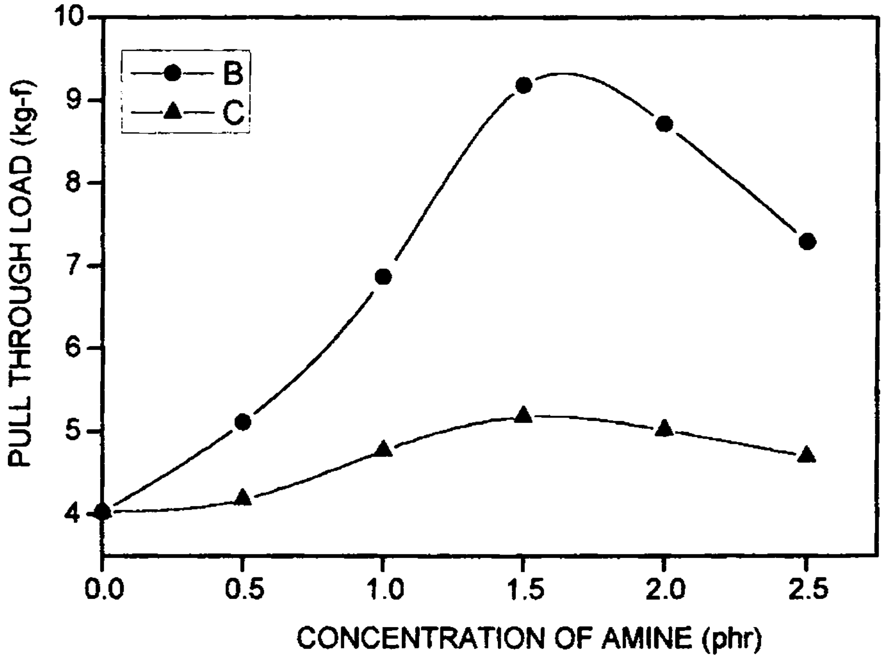

Fig. 5.15 Variation of pull through load with concentration of hexamethylenetetramine in the rubber compound. B - VP latex/ RF resin-I, C - VP latex/ RF resin-II.

The optimum concentration of the hexamethylenetetramine for the 840/2 cord and 1260/2 cord dipped in VP latex based RFL adhesive containing RF resin-I is found to be 2phr and 1phr respectively as shown in figure 5.16. This difference in the optimum amount may be due to the change of miscibility with the rubber compound, rigidity of the adhesive film and the contribution of covulcanization sites to adhesion[13-15].

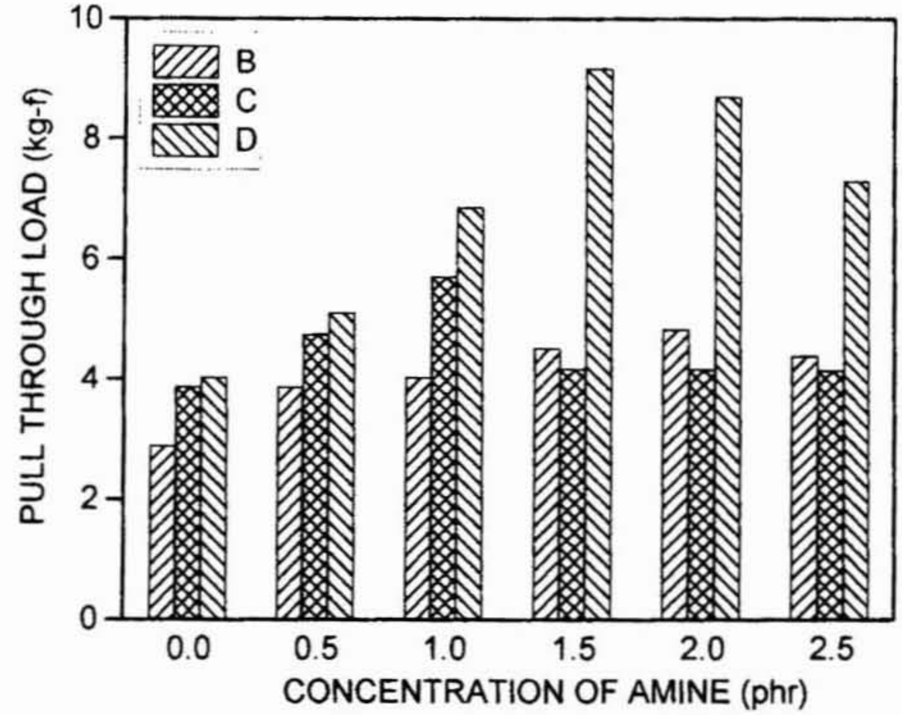

Fig. 5.16 Comparison of the pull through load with concentration of hexamethylenetetramine at optimum resin-rubber ratio. B-840/2, C-1260/2, D-1680/2.

Table 5.11 shows the scorch time and cure time of the rubber compounds varying in the concentration of hexamethylenetetramine used for bonding the dipped nylon cords. The scorch time and the cure time change only marginally with the increase in concentration of hexamethylenetetramine.

The tensile strength of the rubber compounds with the change in the concentration of hexamethylenetetramine is shown in figure 5.17. There is a slight increase in the tensile strength when the concentration of the hexamethylenetetramine is increased. This slight increase may not affect the pull through load of the dipped cord.

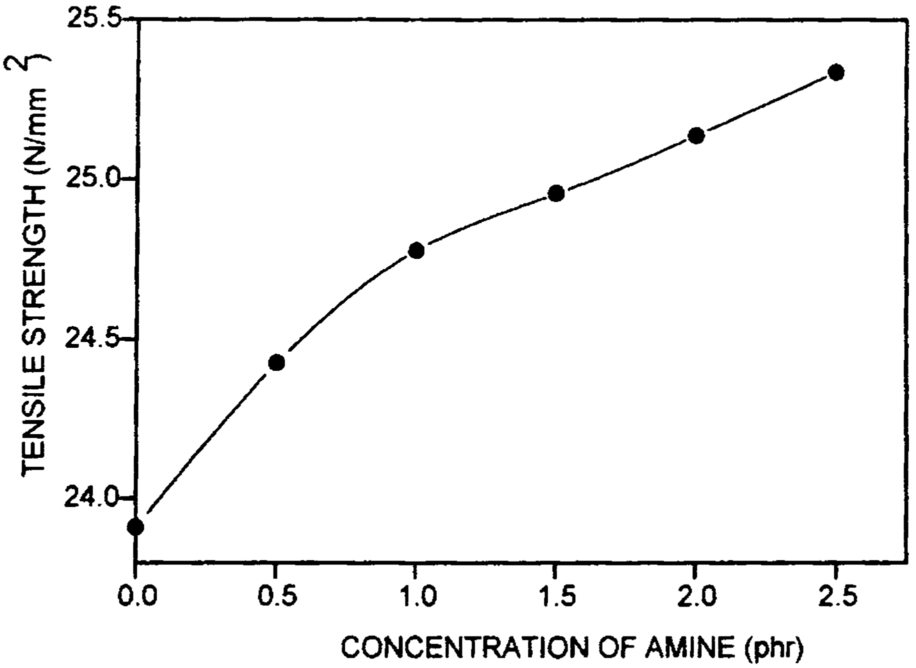

Fig. 5.17 Variation of tensile strength with concentration of hexamethylenetetramine in the rubber compound.

Table 5.12 shows the variation in the pull through load with temperature of drying and curing of the nylon cord dipped in RFL adhesive.

Table 5.12 Variation of pull through load for nylon cord with drying and curing temperature

Drying Temperature °C	Curing Temperature °C	Pull through load (kg-f)
140	180	8.15
145	185	9.18
150	190	9.07
155	195	8.77
160	200	8.59

As the temperature increases the pull through load increases, reaches a maximum and then decreases. An optimum network structure is formed in the RFL adhesive coating up on adequate heat treatment resulting in strong interaction with the textile and rubber. Lower heat treatment causes the RFL coating to have lower crosslinking in the RFL adhesive resulting in inferior interaction with the textile. Strong treatment impairs compatibility with the rubber.

The effect of a donor into the RFL adhesive and the rubber compound is shown in figures 5.18 and 5.19. As the concentration of the donor paraformaldehyde, in the RFL adhesive increases the pull through load decreases. The highest value is obtained when the concentration of the paraformaldehyde is 1mole. Paraformaldehyde is soluble in cold water and slowly liberates formaldehyde. At higher concentrations of paraformaldehyde gelation takes place as the formaldehyde reacts with RF resin in the

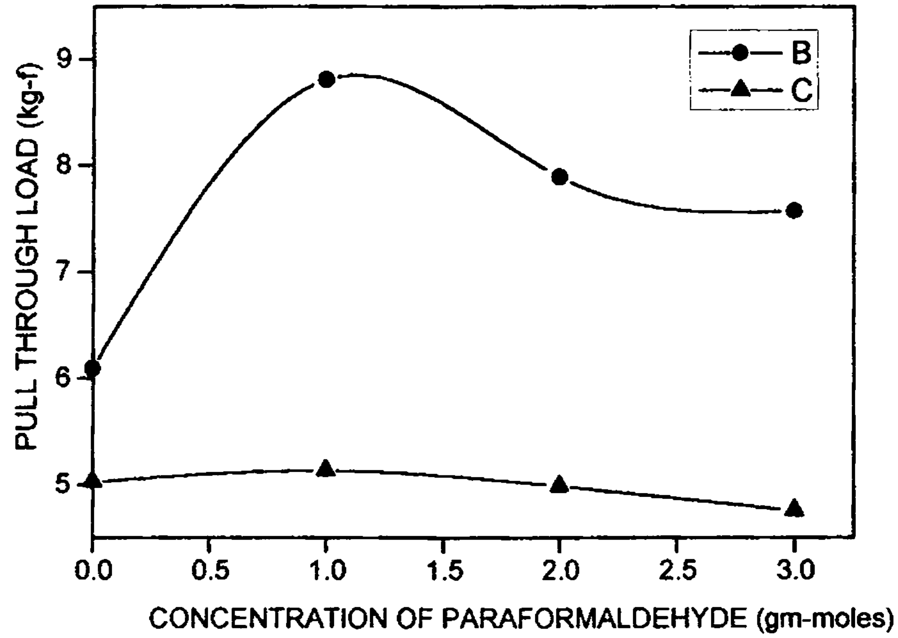

Fig. 5.18 Variation of pull through load with concentration of paraformaldehyde in the RFL adhesive. B- VP Latex; C- NR Latex.

RFL adhesive. It has been reported that in RF solutions containing two or more moles of formaldehyde per mole of resorcinol, sudden viscosity change occurs at a certain aging timeand ultimately the solution is gelled[16]. It is found that when the concentration of formaldehyde is decreased, the change in viscosity is depressed[15,17,18].

When RF resin-I and paraformaldehyde are added into the rubber compound the pull through load is found to increase with an increase in the RF resin concentration, reach a maximum and then decrease as shown in figure 5.19. The strength of adhesion is found to be maximum at 0.4phr of the RF resin-I when the amount of paraformaldehyde is kept constant (0.4phr). On heating, the paraformaldehyde releases the formaldehyde which reacts with the RF resin to form the methylol group which may react with the active hydrogen of the fiber. A possible ionic interaction or chemical reaction between the RF resin and the rubber compound might have also taken place[13,17,19,20].

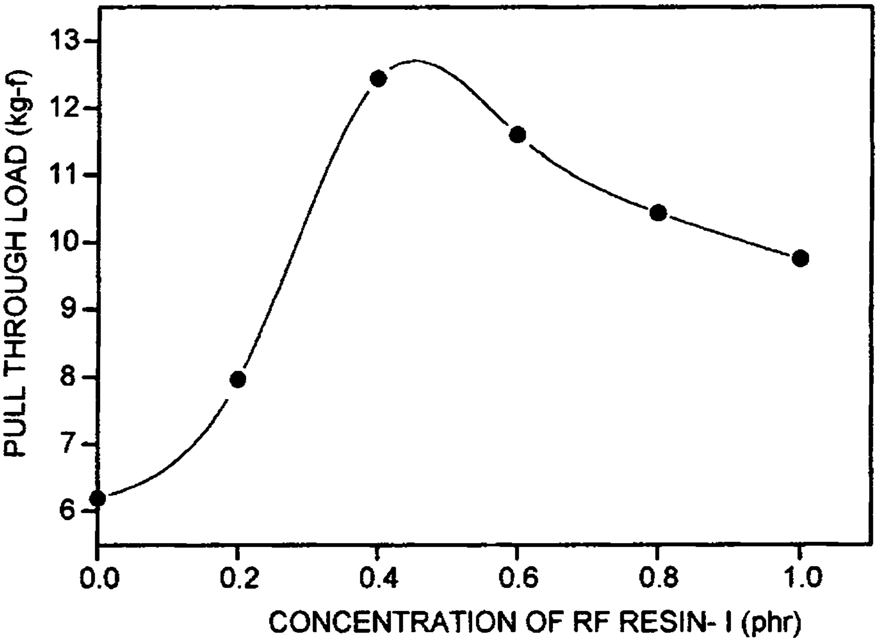

Fig. 5.19 Variation of pull through load with concentration of RF resin-I in the rubber compound.

The variation of tensile strength with the concentration of the RF resin-I is shown in figure 5.120. Their is a slight reduction in the tensile strength as the concentration of the RF resin-I increases which may not affect the pull through load of the RFL dipped cord.

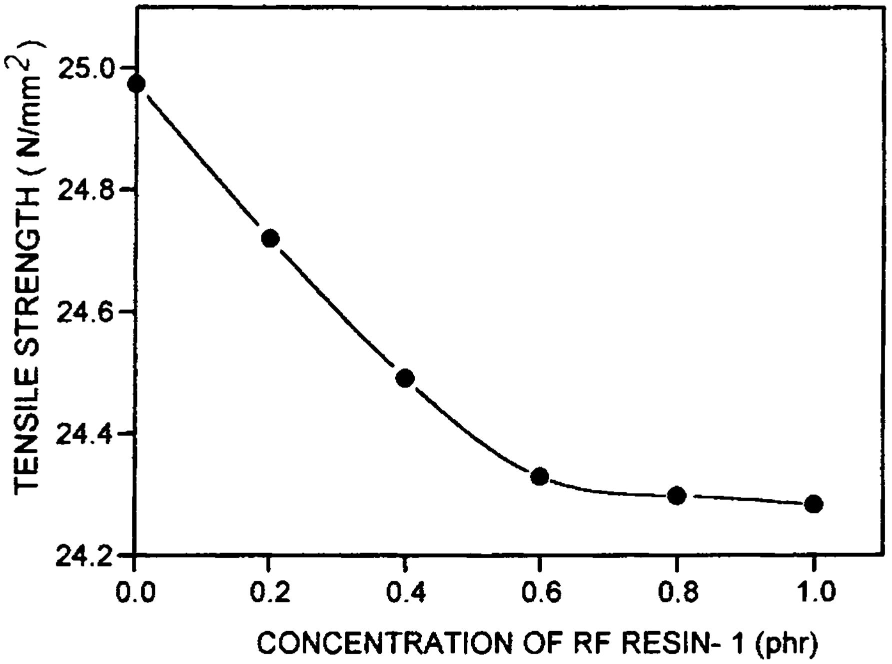

Fig. 5.120 Variation of tensile strength with concentration of RF resin-I in the rubber compound.

Table 5.13 shows the scorch time and cure time of compounds containing RFresin-I and paraformaldehyde. As the quantity of resin and paraformaldehyde increases, there is only a marginal change in both scorch time and cure time.

Table 5.14 shows the scorch time and cure time of the rubber compounds with different resin combinations bonded to the nylon cord dipped in NR latex based RFL adhesive.

Figure 5.121 shows the pull through load of the nylon tire cord dipped in NR latex based RFL adhesive prepared using RF resin-I or RF resin-II bonded to four rubber compounds with different resin combinations.

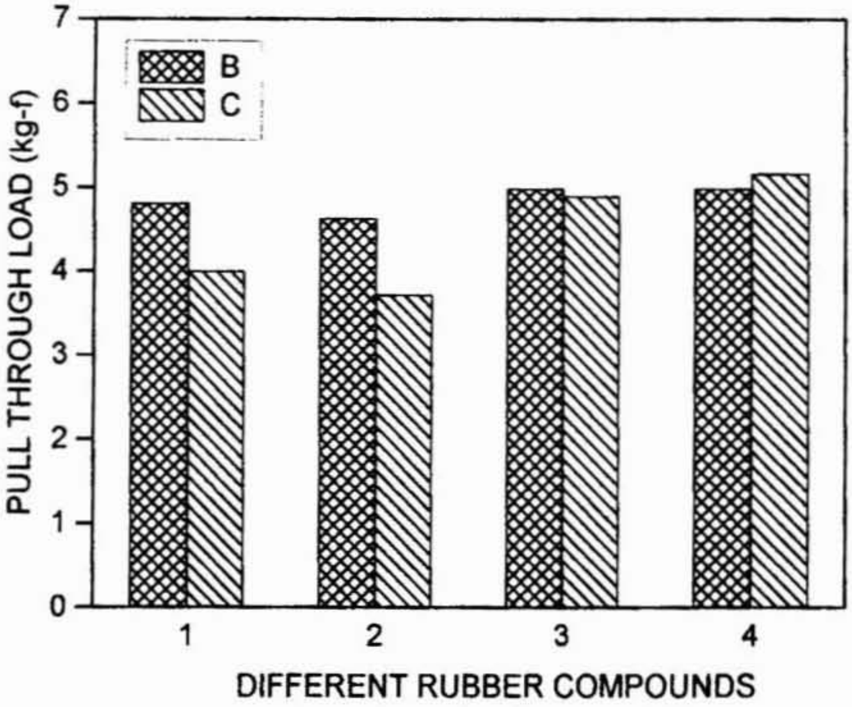

Fig. 5.121 Variation of pull through load with different rubber compounds for cord dipped in RFL adhesive. B- NR latex/ RF resin-I, C- NR latex/ RF resin-II.

The maximum pull through load is obtained for rubber compound containing RF resin-I/paraformaldehyde in combination with wood rosin (compound-III). The compound containing the CNSL resin-wood rosin combination (compound-I) shows slight reduction in the pull through load and further reduction with compound containing PF resin-wood rosin combination (compound II). When part of HAF black is replaced by silica in the compound containing RF resin-1, there is no change in the pull through load. When the nylon tire cord dipped in NR based RFL adhesive prepared using RF resin-II is bonded to the above compounds, the same pattern is obtained with rubber compounds (I, II and III).

But when part of HAF black is replaced by silica a marginal increase in the pull through load is obtained.

Table 5.15 shows the scorch time and cure time of the rubber compounds with different resin combinations bonded to the nylon cord dipped in VP latex based RFL adhesive.

Figure 5.123 shows the pull through load of the nylon tire cord dipped in VP latex based RFL adhesive prepared using RF resin-I and RF resin-II bonded to four rubber compound varying in different resin combinations.

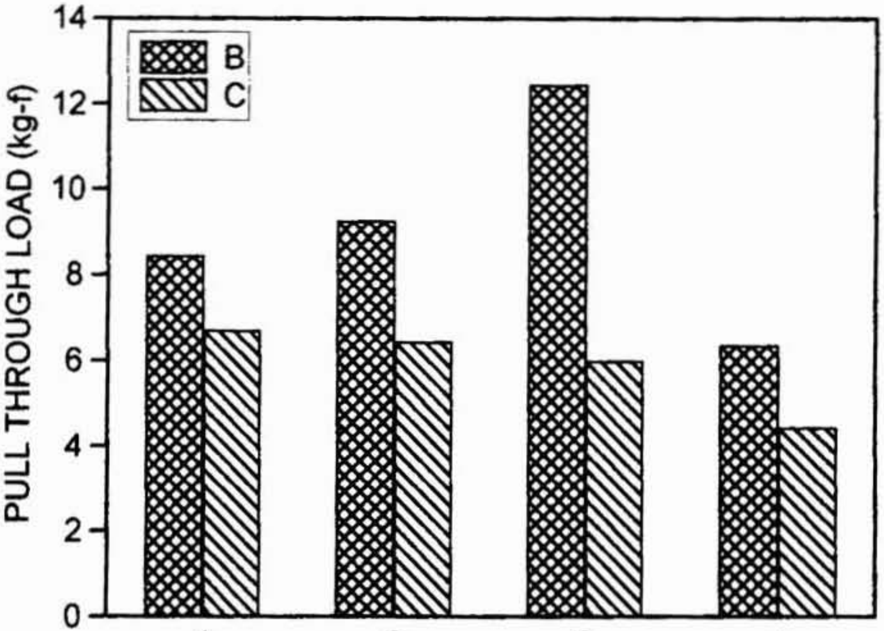

Fig. 5.123 Variation of pull through load with different rubber compounds for cord dipped in RFL adhesive. B-VP latex/ RF resin-I, C- VP latex/ RF resin-II.

The maximum pull through load is obtained when RF resin-I/paraformaldehyde resin is used in combination with wood rosin is used, and a reduction in pull through load is observed with the compound containing PF resin-wood rosin combination and a still further reduction with the compound containing CNSL resin-wood rosin combination. The bonding between nylon and RFL is due to hydrogen bonding between phenolic hydroxy groups in the RFL resin and the electronegative groups in the fibers[20]. Condensation reaction between methylol group of RF resin and active hydrogen in the fiber[17,13], dipole-dipole interaction[19], molecular entanglement[13].

As the molar ratio of the formaldehyde to resorcinol in the RF resin-I is 1:2, the monomethylolated resorcinol is found. This formaldehyde deficient species may react with the formaldehyde donor added into the rubber compound to form the dimethylolated structure, which in turn may react with the active sites on the fiber. The lower pull through load obtained in the case of the other two compounds may be due to the difference in the covulcanization sites to adhesion and change of miscibility with the rubber compound.

When the cords dipped in RFL adhesive based on RF resin-II is bonded to the above compounds the maximum pull through load is obtained for compound containing CNSL resin-wood rosin combination. The cord bonded to compound containing PF resin–wood rosin combination is found to have a lower pull through load. Compound containing RF resin-I/ paraformaldehyde in combination with wood rosin shows the lowest strength. But when RF resin-II which contains excess formaldehyde is used the addition of formaldehyde donor in the rubber compound does not produce any improvement in thepull through load. The CNSL resin in its resol form may react with the formaldehyde donor to give the methylolated structure. Here excessive condensation may not occur due to the steric hinderance of the bulky group since the contribution of the covulcanization sites to adhesion is limited.

When part of HAF black in the compound is replaced by silica and it is bonded to the nylon tire cords dipped in VP latex based RFL adhesive, containing on RF resin-I or RF resin-II a drastic decrease is found in the pull through load. Rubber compounds with polar silica filler usually show a very high level of adhesion if they have a very long scorch time. Since the compound containing silica and compound containing HAF black show only a marginal change in the scorch time, the expected increase in pull through load has not been obtained.

Table 5.16 shows the extent of decrease in the pull through load for the cord dipped in the aged RFL adhesive after storage of one week at 30°C. There is a reduction in the pull through load with aging which shows that there is a reduction in the activity of the RFL adhesive with storage[22].

Table5.16. Variation of pull through load for nylon tire cord dipped in RFL adhesive after a storage of one week at 30°C.

RFL Adhesive	Pull through load (kg-f)	
	Before aging	After aging
C**	9.18	5.182
F**	5.181	5.128
L*	5.05	4.91
N*	4.24	3.91

*Rubber compound used for bonding is compound (4) in Table 5.11

** Rubber compound used for bonding is compound (3) in Table 5.11

Conclusions

1) An optimum concentration of resin in the RFL adhesive is found to give maximum adhesion. The resin required is lower for VP latex based adhesive compared to NR latex.

2) RFL adhesive based on VP latex is found to have better rubber to nylon tire cord bonding compared to the one based on NR latex.

3) The optimum drying and curing temperature of the nylon cord is found to be 145°C and 185° C respectively.

4) Formaldehyde deficient resin in RFL adhesive gives good nylon tire cord to rubber bonding in presence of a formaldehyde donor in the rubber compound.

5) Rubber compound containing RF resin-I/paraformaldehyde combination gives good bonding for the cords dipped in RFL adhesive based on VP latex containing RF resin-I in the optimum resin rubber ratio.

6) Rubber compound containing CNSL resin gives good bonding for the cords dipped in RFL adhesive based on VP latex containing RF resin-II.

Part- II

STUDIES ON RUBBER TO RAYON TIRE CORD BONDING.

Natural polymers play an important role in the advancement of modern technology. Natural polymers are obtained from natural fibers such as jute, flax, cotton, silk, etc. Some are used for making carpet, carrier bags and decorative articles, while others are used in making beautiful apparel. Among the above fibers the present study deals with rayon fiber.

Looking back upon progress of tire cord adhesion, cotton was used with no adhesive treatment or rubber cement treatment. As loads, horsepowers and operating speeds of automobiles increased need grew for stronger and cooler running tires. Therefore rayon filament was introduced. Rayon has good mechanical properties, but lacks adhesion. Latex-Protein adhesives have been developed for bonding of rubber on rayon cord to improve adhesion. Casein is the most frequently recommended protein. A detailed study of the performance of latex-casein adhesives has been reported by Gardner and Williams[22] and Gillman and Thoman[23]. Later latex-casein has been replaced by resorcinol-formaldehyde latex dip solution. At present this adhesive is used extensively for rubber to rayon and nylon cords bonding.

In this study we propose a systematic study of the use of resorcinol-formaldehyde as a bonding agent for rubber to rayon tire cord bonding. The effect of concentration of resin, type of polymer, temperature of drying, curing etc., are proposed to be investigated.

Experimental

The rayon cord used for dipping studies was 1650/2, supplied by Century Rayons, Mumbai. The lattices used were vinyl pyridine terpolymer (VP latex) (Butadiene 70%, Styrene 15%, Vinyl pyridine 15%) and natural rubber latex (NR latex) (60% centrifuged latex). The elastomer used for bonding studies was natural rubber (NR), ISNR-5, ML (1+4) 100°C-82. The compounding ingredients viz., zinc oxide, stearic acid, HAF black, wood rosin, antioxidants, accelerators, sulphur, hexamethylenetetramine, paraformaldehyde, resorcinol and formaldehyde were commercial grade. The resorcinol-formaldehyde (RF) resin used for the preparation of the RFL adhesive was prepared in the laboratory by two methods. In method I the ratio of the resorcinol to formaldehyde was 2:1(RF resin-I) and in method II (commercial method) the ratio was 1: 2 (RF resin-II).

NR was mixed with other compounding ingredients according to the formulations given in Table 5.21, as per ASTM D 3182 (1982). The optimum cure time (T_{90} min) and scorch time (T_{10} min) of the compound were determined using a Goettfert Elastograph model 67.85, according to ASTM D 1648 (1981).

In compounds 2 to 6, the amount of hexamethylenetetramine was varied in increments of 0.5phr. In compounds 7 to 12, the amount of RF resin-I was varied by 0.05phr, keeping the amount of paraformaldehyde constant at 0.4phr as given in Table 5.23.

Table 5.21 Formulation of natural rubber compounds for bonding

Ingredients	1	2	3	4	5	6
Natural rubber	100	100	100	100	100	100
HAF black	40	40	40	40	40	40
ZnO	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
Wood Rosin	5	5	5	5	5	5
Vulkanox4020	0.75	0.75	0.75	0.75	0.75	0.75
Vulkanox HS	0.5	0.5	0.5	0.5	0.5	0.5
MOR	0.65	0.65	0.65	0.65	0.65	0.65
Hexamethylenetetramine	-	0.5	1.0	1.5	2.0	2.5
Sulphur	2.25	2.25	2.25	2.25	2.25	2.25
*T_{10} min	1.8	2.0	2.1	1.9	1.9	1.8
*T_{90} min	14.1	12.0	10.6	9.4	9.0	8.2

* Cure characteristics

Table 5.23 Formulation of natural rubber compounds for bonding

Ingredients	7	8	9	10	11	12
Natural rubber	100	100	100	100	100	100
HAF black	40	40	40	40	40	40
ZnO	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
Wood Rosin	5	5	5	5	5	5
Vulkanox 4020	0.75	0.75	0.75	0.75	0.75	0.75
Vulkanox HS	0.5	0.5	0.5	0.5	0.5	0.5
MOR	0.65	0.65	0.65	0.65	0.65	0.65
Paraformaldehyde	0.4	0.4	0.4	0.4	0.4	0.4
RF resin-I	-	0.25	0.30	0.35	0.40	0.45
Sulphur	2.25	2.25	2.25	2.25	2.25	2.25
*T_{10} min	7.0	7.1	7.9	8.5	10.7	8.7
*T_{90} min	15.1	19.2	19.9	20.6	21.1	20.8

* Cure characteristics

The dipped cords were bonded with the rubber compounds and the pull through load was determined by the H- Adhesion test. The H- tests were designed to measure the force required to pull a cord in the direction of its axis from a strip of rubber in which the ends of the cords are embedded as per the ASTM D 2138 (1983).

RFL adhesives with varying amounts of RF resin-I were prepared using NR latex as well as VP latex. The RF resin-1 was dried and a 7.5 % solution of the dried resin was prepared in distilled water. RFL adhesives A, B, C, D and E contain 7, 8, 9, 10 and 11ml respectively (corresponding to 2.10, 2.31, 2.50, 2.67 and 2.84 % weight respectively) of the above RF resin-1 solution mixed with 8ml NR latex and 10ml distilled water. The RFL adhesive based on RF resin-I was matured for a period of 20 hours. RFL adhesive F contains RF resin-II mixed with NR latex and distilled water. The RF resin-II based RFL adhesive was matured for a period of 4 hours.

For cord dipping, drying and curing, a dipping unit was designed and fabricated (details given in Chapter –II).

The 1650/2 rayon cord was dipped in different RFL adhesives A, B, C, D, E and F. The effect of a formaldehyde donor, hexamethylenetetramine, in the rubber compound was studied by varying its amount from 0 to 2.5phr. The optimum resin-rubber ratio in NR latex and the amount of the hexamethylenetetramine in the rubber compound were determined.

The NR latex in the above RFL adhesives was replaced by VP latex to get RFL adhesives I, J, K, L, M and N respectively. A maturation time of 20 hours was given for adhesives I, J, K, L and M and a maturation time of 4 hours was given for adhesive N. The studies were repeated with 1650/2 rayon cord.

In order to study the effect of drying and curing temperature on bonding, the drying temperature was varied from 140 to 160°C and the curing temperature from 180° to 200°C using the cord 1680/2.

The effect of donor concentration on bonding was also studied by adding a combination of paraformaldehyde and RF resin-I into the rubber compound. The concentration of the paraformaldehyde in the compound was kept constant (0.4phr) and the RF resin-I concentration was varied from 0.25 to 0.45phr (Table 5.23).

The effect of adding different resin combinations into the rubber compound was also studied. A combination of cashew nut shell liquid (CNSL) resin-wood rosin, phenol formaldehyde (PF) resin-wood rosin and RF resin-I/paraformaldehyde-wood rosin were used in the rubber compounds. Also the effect of replacement of part of HAF black by silica in the rubber compound was studied. The formulations of the compounds used for bonding the rayon cord dipped in NR and VP latex are given in Table 5.24 and 5.25 respectively.

The pull through load of the above RFL adhesives were measured after aging for a period of seven days at 30°C.

Table 5.24 Formulations of rubber compounds with different resin combinations

Ingredients	I	II	III	IV
Natural rubber	100	100	100	100
Zinc oxide	5	5	5	5
Stearic acid	2	2	2	2
HAF black	40	40	40	35
Silica	-	-	-	5
Aromatic oil	5	5	5	5
Wood rosin	2.5	2.5	5	5
CNSL resin	2.5	-	-	-
PF resin	-	2.5	-	-
RF resin-I	-	-	0.4	0.4
Vulkanox-HS	0.5	0.5	0.5	0.5
Vulkanox-4020	0.75	0.75	0.75	0.75
MOR	0.65	0.65	0.65	0.65
Hexamethylenetetramine	0.5	0.5	-	-
Parformaldehyde	-	-	0.4	0.4
Sulphur	2.25	2.25	2.25	2.25
*T_{10}min	4.2	4.2	4.8	5.3
*T_{90}min	11.3	12.9	14.2	14.4

*Cure characteristics

Table 5.25 Formulations of rubber compounds with different resin combinations

Ingredients	I	II	III	IV
Natural rubber	100	100	100	100
Zinc oxide	5	5	5	5
Stearic acid	2	2	2	2
HAF black	40	40	40	35
Silica	-	-	-	5
Aromatic oil	5	5	5	5
Wood rosin	2.5	2.5	5	5
CNSL resin	2.5	-	-	-
PF resin	-	2.5	-	-
RF resin-I	-	-	0.4	0.4
Vulkanox-HS	0.5	0.5	0.5	0.5
Vulkanox-4020	0.75	0.75	0.75	0.75
MOR	0.65	0.65	0.65	0.65
Hexamethylenetetramine	1.0	1.0	-	-
Parformaldehyde	-	-	0.4	0.4
Sulphur	2.25	2.25	2.25	2.25
*T_{10} min	4.1	3.7	4.2	4.9
*T_{90} min	11.8	12.5	11.8	12.9

*Cure characteristics

RESULTS AND DISCUSSION

The variation in pull through load with the change in resin-rubber ratio in RFL adhesive based on NR and VP latex is shown in figure 5.21.

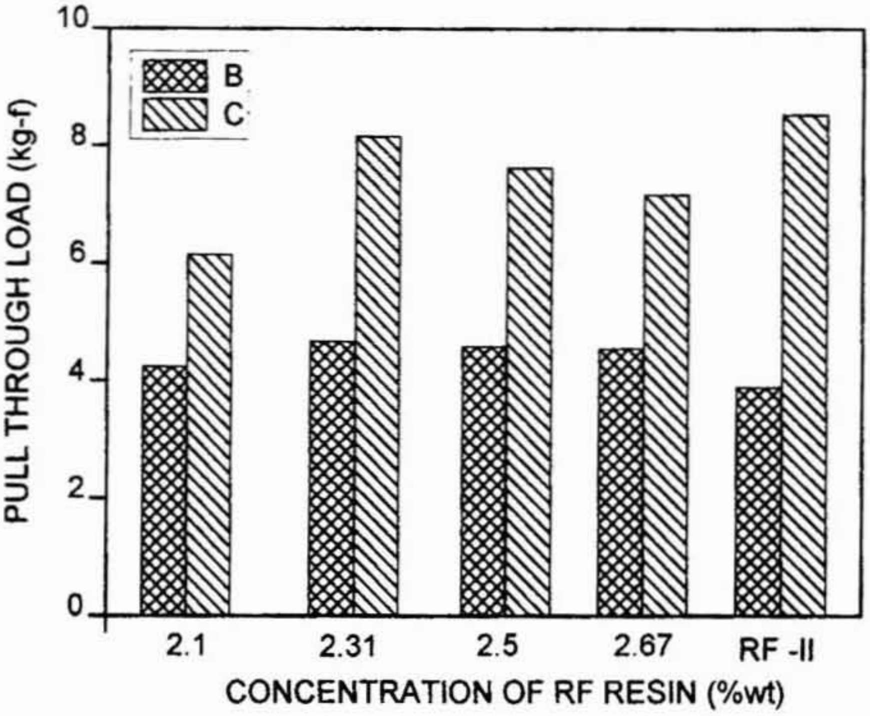

Fig. 5.21 Variation of pull through load with RF resin-rubber ratio in RFL adhesive for rayon cord.B- NR latex based, C- VP latex based.

For NR latex-based RFL adhesive, RF resin-I shows better adhesion than RF resin-II. The pull through load is dependent on the resin-rubber ratio in the RFL adhesive. The pull through load increases as the RF resin-I concentration in the RFL adhesive increases, reaches a maximum and then decreases. The optimum resin-rubber ratio is found to be 1:1. The excess resin causes stiffness of the dipped cord resulting in high modulus of the cured RFL film[13].

When the NR latex in the RFL adhesive is replaced by VP latex, RF resin-II shows slightly better bonding than RF resin-I. The pull through load is found to be high compared to the pull through load obtained for NR latex based RFL adhesive (in figure 5.21). The optimum resin-rubber ratio for RFL adhesive based on RF resin-I is again found to be 1:1. Thus the optimum resin-rubber ratio in VP latex and NR latex based RFL adhesive for rayon cord is found to be the same. This may be due to the exceptionally high stability and higher polarity of VP latex and also pH of the two lattices differs.

Comparing the pull through load obtained for RF resin-I and RF resin-II in NR and VP latex based RFL adhesives, the RF resin-I shows better adhesion than RF resin-II in NR latex and RF resin-II shows better adhesion than RF resin-I in VP latex. The network structure of RFL resin may be changing with the resorcinol to formaldehyde ratio and maturing time. This in turn affects the mechanical properties of RFL films prepared with various resorcinol formaldehyde ratios.

Figures 5.22 and 5.23 show the effect of concentration of hexamethylene tetramine in the rubber compound on the pull through load for rayon tire cord dipped in RFL adhesive prepared using RF resin-I and RF resin-II.

The optimum amount is found to be 0.5phr when NR latex is used in the RFL adhesive as shown in figure 5.22. When VP latex is used, the optimum concentration is found to be 1phr as shown in figure 5.23. This difference of the dependence of adhesion on the copolymer composition may be due to the change of miscibility with the rubber compound, rigidity of the adhesive film and contribution of the covulcanization sites to adhesion[13-15].

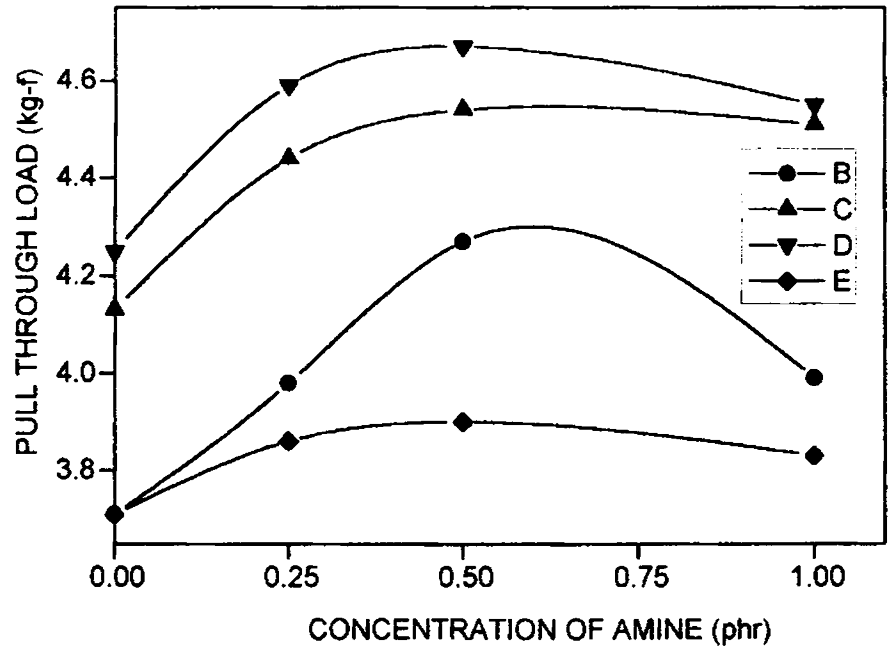

Fig. 5.22 Variation of pull through load with concentration of hexamethylenetetramine for rayon cord dipped in NR latex based RFL adhesive. B- 2.10, C- 2.31, D-2.50 (% wt RF resin-I); E- RF resin-II.

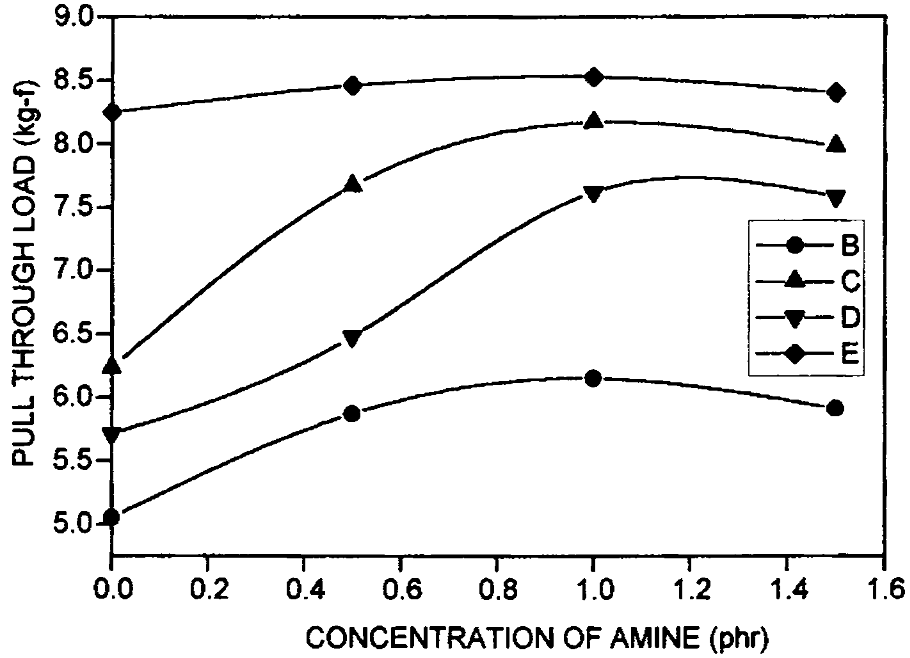

Fig. 5.23 Variation of pull through load with concentration of hexamethylenetetramine for rayon cord dipped in VP latex based RFL adhesive.
B- 2.10, C- 2.31, D-2.50 (% wt RF resin-I); E- RF resin-II.

Table 5.21 shows the scorch time and cure time of the rubber compounds varying in the concentration of hexamethylenetetramine used for bonding dipped rayon cords. The scorch time and the cure time are found vary only marginally with increase in concentration of hexamethylenetetamine.

Table 5.22 shows the variation in the pull through load with temperature of drying and curing of the rayon tire cord dipped in RFL adhesive. As the temperature increases the pull through load increases, reach a maximum and then decreases. This may be due to the highly crosslinked structure formed in the RFL adhesive at optimum heat treatment resulting in a strong interaction with the textile. Upon the heat treatment, if the temperature is low the RFL coating gives inferior tensile properties and there is a lack of interaction with the textile resulting in lower pull through load. Heat treatment at high temperature is found to impair compatibility with the rubber due to higher crosslinking in RFL adhesive.

Table 5.22 Variation of pull through load for rayon cord with drying and curing temperature

Drying Temperature ^{0}C	Curing Temperature ^{0}C	Pull through load (kg-f)
140	180	2.77
145	185	4.58
145	190	4.76
150	185	7.81
150	190	7.53
155	185	8.17
155	190	7.99
160	185	7.02
160	190	6.62

When RF resin-I and paraformaldehyde are added into the rubber compound the pull through load is found to increase with an increase in the RF resin concentration, reach a maximum and then decrease as shown in figure 5.24.

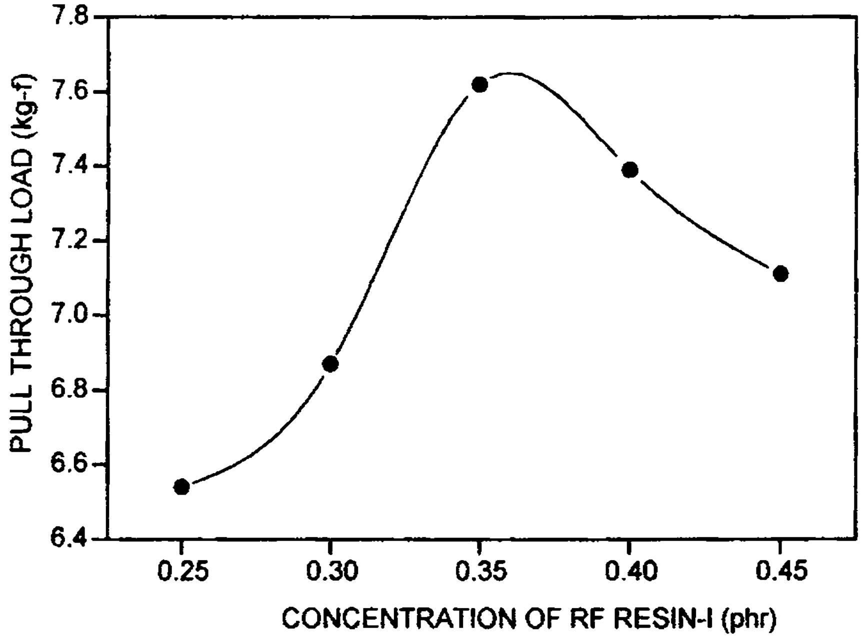

Fig. 5.24 Variation of pull through load for rayon cord with concentration of RF resin-I in the rubber compound.

The strength of adhesion is found to be maximum at 0.35phr of the RF resin-I when the amount of paraformaldehyde is kept constant (0.4phr). On heating, paraformaldehyde releases formaldehyde which reacts with the RF resin to form the methylol group which may react with the active hydrogen of the fiber. A possible ionic interaction or chemical reaction between the RF resin and the rubber compound may occur[13,17,19,20].

The scorch time and cure time of the compounds with different RF resin-I concentration used for bonding dipped rayon cord are given in Table 5.23

Figure 5.25 shows the pull through load of the rayon tire cord dipped in NR latex based RFL adhesive prepared using RF resin-I and RF resin-II bonded to four rubber compounds varying in different resin combinations.

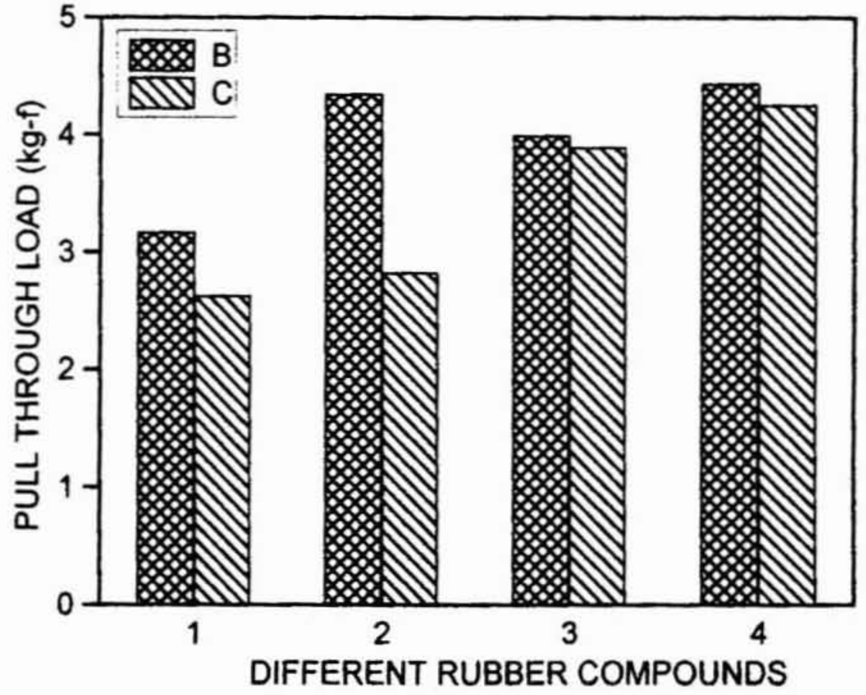

Fig. 5.25 Variation of pull through load with different rubber compounds for cord dipped in RFL adhesive. B- NR latex/ RF resin-I, C- NR latex/ RF resin-II.

When RF resin-I is used in the RFL adhesive the maximum pull through load is obtained for rubber compound containing PF resin in combination with wood rosin and RF resin-I in combination with wood rosin shows a marginal decrease. The compound containing CNSL resin-wood rosin combination shows a fall in pull through load. This may be due to the steric hindrance of the bulky groups of the CNSL resin. When part of HAF black is replaced by silica in the compound containing RF resin-I, there is an increase in pull through load. When the rayon tire cord dipped in RFL adhesive based on RF resin II is bonded to the four different compounds, the compound containing RF resin-I-wood rosin shows the maximum pull through load and this is found to show a better bonding when HAF black is replaced by silica. The compounds containing CNSL resin or PF resin in combination with wood rosin differs only marginally but is found to show a lower pull through load compared to that obtained for other compounds. This may be due to the lower polarity of the rayon cord and the natural rubber.

Table 5.24 shows the scorch time and cure time of the rubber compounds with different resin combinations bonded to the rayon cord dipped in NR latex based RFL adhesive.

Figure 5.26 shows the pull through load of the rayon tire cord dipped in VP latex based RFL adhesive prepared using RF resin-I and RF resin-II bonded to four rubber compounds varying in different resin combinations.

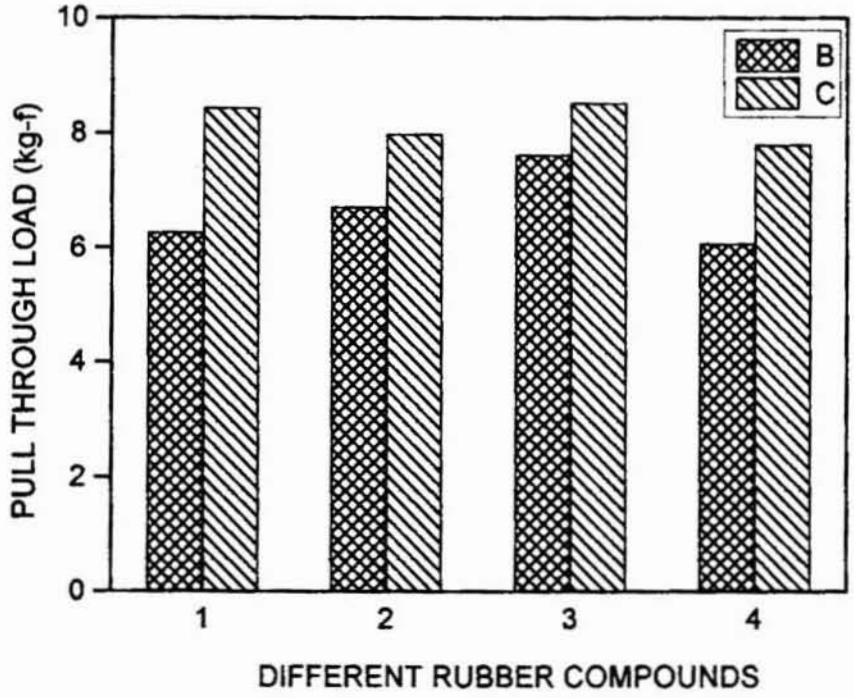

Fig. 5.26 Variation of pull through load with different rubber compounds for cord dipped in RFL adhesive. B- VP latex/ RF resin-I, C- VP latex/ RF resin-II.

The maximum pull through load is obtained when a RF resin-I/ parafomaldehyde in combination with wood rosin is used. The pull through load gets reduced for compound containing PF resin-wood rosin combination and further reduced for compound containing CNSL resin-wood rosin combination. When the cords were dipped in RFL based on RF resin-II is bonded to these four compounds again the maximum pull through load is obtained for compound containing RF resin-I/paraformalehyde-wood rosin combination, with a marginal decrease with compound containing CNSL resin–wood rosin combination and with a still further reduction in pull through load for compound containing PF resin-wood rosin combination. When a part of HAF black in the compound is replaced by silica and bonded to the tire cords dipped in VP latex based RFL adhesive based on either RF resin-I or RF resin-II, there is a lowering of the pull through load. This may be due to the change in miscibility with the rubber compound and contribution of the covulcanization sites to adhesion.

Table 5.25 shows the scorch time and cure time of the rubber compounds with different resin combinations bonded to the rayon cord dipped in NR latex based RFL adhesive.

Table 5.26 shows the decrease in pull through load after one week storage at 30°C, of the RFL adhesive. This is due to the loss in stability of the RFL adhesive because of the limited pot life of the RFL adhesive[21].

Table 5.26 Pull through load for rayon cord dipped in RFL adhesive after aging for a period of one week.

Latex	RF resin	Pull through load (kg-f)	
		Before aging	After aging
NR	RF resin-I	4.67	3.80
NR	RF resin-I	3.99	2.57
VP	RF resin-II	8.17	7.53
VP	RF resin-II	8.53	6.12

CONCLUSIONS

1) An optimum concentration of resin in the RFL adhesive is found to give maximum adhesion. The optimum resin-rubber ratio in both the lattices is found to be the same.

2) The optimum drying and curing temperature of the rayon cord is found to be 155°C and 185° C respectively.

3) Formaldehyde deficient resin in RFL adhesive gives good rayon cord to rubber bonding in presence of a formaldehyde donor in the rubber compound.

4) Rubber compound containing RF resin-I/paraformaldehyde combination gives good bonding for the cords dipped in RFL adhesive based on VP latex containing RF resin-I in the optimum resin rubber ratio.

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Chapter VI

Part I

STUDIES ON THE EFFECT OF REPLACEMENT OF RF RESIN IN THE RFL ADHESIVE PARTIALLY OR WHOLLY BY OTHER POTENTIAL AGENTS

Rubber to textile bonding is conventionally made by treating the fabric in resorcinol-formaldehyde (RF) latex dip solution. Rubber to textile adhesion can also be achieved by addition of bonding agents to the rubber compound, thus eliminating adhesive treatment of textile materials. Isocyanate derivatives have been used for this purpose[1], but more widely accepted bonding agents are combinations of resorcinol and formaldehyde donors[2], such as hexamethylenetetramine or paraformalydehyde. Many modifications of this method have been patented. For example, trimethylolnitromethane[3], trimethylolacetoaldehyde[4], or hexamethylol melamine[2] are used. Encapsulation of formaldehyde donors is also patented[5].

In this part of the study we propose to improve the bonding of rayon and nylon with rubber by modifying the dip solution. One of the objectives has been to replace the expensive RF resin partially or fully and the other to improve bonding. Modification of the rubber compound by potential agents is also proposed to be investigated.

Experimental

The nylon cord used for dipping studies was 1680/2, supplied by SRF Ltd. Madras and rayon cord used was 1650/2, supplied by Century Rayons, Mumbai. The lattices used were vinyl pyridine terpolymer (VP) latex (Butadiene 70% - Styrene 15% - Vinyl pyridine 15%) and natural rubber (NR) latex (60% drc). The elastomer used for bonding studies was natural rubber (NR) ISNR-5, ML (1+4) 100°C-82. The compounding ingredients viz., zinc oxide, stearic acid, HAF black, wood rosin, antioxidants, accelerators, sulphur, hexamethylenetetramine, resorcinol, paraformaldehyde and formaldehyde were of commercial grade. The resorcinol-formaldehyde (RF) resin used for the preparation of the RFL adhesive was prepared in the laboratory by two methods. In method I the ratio of the resorcinol to formaldehyde was 2:1(RF resin-I) and in method II (commercial method) the ratio was 1: 2 (RF resin-II).

NR was mixed with other compounding ingredients as per ASTM D 3182 (1982). The optimum cure time (T_{90} min) and scorch time (T_{10} min) of the compounds were determined using a Goettfert Elastograph model 67.85, according to ASTM D 1648 (1981).

Three potential agents were used to modify the dip solutions to replace resorcinol formaldehyde resin. The modifying agents used were polyvinyl alcohol (PVA) (10% solution), carboxymethyl cellulose (CMC) (1% solution) and polyethylene glycol (PEG) solution in distilled water to give dip solutions B, C and D. Different volumes of these solutions were mixed with NR latex or VP latex and 3 to 4 drops of ammonia were added as a stabilizer. The amount of the potential agent in the dip solution was optimized by bonding the cords dipped in these solutions to rubber compounds as shown in Table.6.11. The dip solutions were matured for a period of 30 min.

Table 6.11 Formulation of natural rubber compounds for bonding

Ingredients	1	2
Natural rubber	100	100
HAF black	40	40
Zinc Oxide	5	5
Stearic acid	2	2
Wood Rosin	5	5
Vulkanox4020	0.75	0.75
Vulkanox HS	0.5	0.5
MOR	0.65	0.65
Hexamethylenetetramine	1.0	1.5
Sulphur	2.25	2.25
*T_{10} min	2.1	1.9
*T_{90} min	10.6	9.4

Compound 1- for rayon cord
Compound 2- for nylon cord
*Cure characteristics

The 1680/2 nylon cord and 1650/2 rayon cords were dipped in the above three dip solutions containing the potential modifiers and were bonded to compounds whose formulations shown in Table 6.11. The amount of the modifiers in the dip solution was optimized and the efficiency of the modifying agents was investigated.

Table 6.12 and 6.14 show the formulation of the rubber compounds containing CNSL resin for bonding nylon and rayon cords respectively. The amount of wood rosin and CNSL resin was varied from 0 to 5phr.

Table 6.12 Formulation of natural rubber compounds for bonding nylon cord

Ingredients	1	2	3	4	5	6	7	8	9	10
Natural rubber	100	100	100	100	100	100	100	100	100	100
HAF black	40	40	40	40	40	40	40	40	40	40
ZnO	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2
CNSL resin	0	1.32	2.5	4	5	0	1.32	2.5	4	5
Wood Rosin	5	3.68	2.5	1	0	5	3.68	2.5	1	0
Hexamethylene-Tetramine	1.0	1.0	1.0	1.0	1.0	1.5	1.5	1.5	1.5	1.5
Vulkanox 4020	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Vulkanox HS	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
MOR	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65
Sulphur	2.25	2.25	2.25	2.25	2.25	2.25	2.25	2.25	2.25	2.25
*T_{10} min	3.6	3.9	4.1	3.5	3.1	3.7	3.8	3.8	3.3	2.4
*T_{90} min	11.5	11.6	11.8	10.7	10.5	10.9	10.6	10.4	9.8	9.2

Compounds 1-5 = for cords dipped in NR latex
Compounds 6-10 = for cords dipped in VP latex
*Cure characteristics

Table 6.14 Formulation of natural rubber compounds for bonding rayon cord

Ingredients	1	2	3	4	5	6	7	8	9	10
Natural rubber	100	100	100	100	100	100	100	100	100	100
HAF black	40	40	40	40	40	40	40	40	40	40
ZnO	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2
CNSL resin	0	1.32	2.5	4	5	0	1.32	2.5	4	5
Wood Rosin	5	3.68	2.5	1	0	5	3.68	2.5	1	0
Hexamethylenetetramine	0.5	0.5	0.5	0.5	0.5	1.0	1.0	1.0	1.0	1.0
Vulkanox 4020	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Vulkanox HS	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
MOR	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65
Sulphur	2.25	2.25	2.25	2.25	2.25	2.25	2.25	2.25	2.25	2.25
*T_{10} min	3.7	4.0	4.2	3.9	3.5	3.6	3.9	4.1	3.5	3.1
*T_{90} min	11.8	11.5	11.3	11.0	10.9	11.5	11.6	11.8	10.7	10.5

Compounds 1-5 = for cords dipped in NR latex
Compounds 6-10 = for cords dipped in VP latex
*Cure characteristics

Table. 6.13 and 6.15 show the formulation of the rubber compounds containing PF resin for bonding nylon and rayon cords respectively. The amount of wood rosin and PF resin was varied from 0 to 5phr.

Table 6.13 Formulation of natural rubber compounds for bonding nylon cord

Ingredients	1	2	3	4	5	6	7	8	9	10
Natural rubber	100	100	100	100	100	100	100	100	100	100
HAF black	40	40	40	40	40	40	40	40	40	40
Zinc Oxide	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2
PF resin	0	1.32	2.5	4	5	0	1.32	2.5	4	5
Wood Rosin	5	3.68	2.5	1	0	5	3.68	2.5	1	0
Hexamethylene-tetramine	1.0	1.0	1.0	1.0	1.0	1.5	1.5	1.5	1.5	1.5
Vulkanox 4020	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Vulkanox HS	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
MOR	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65
Sulphur	2.25	2.25	2.25	2.25	2.25	2.25	2.25	2.25	2.25	2.25
*T_{10} min	3.6	3.7	3.8	4.2	4.0	3.7	4.0	4.1	4.7	5.4
*T_{90} min	11.5	12.2	12.5	12.9	13.1	10.9	11.0	11.2	11.8	12.7

Compounds 1-5 = for cords dipped in NR latex
Compounds 6-10 = for cords dipped in VP latex
*Cure characteristics

Table 6.15 Formulation of natural rubber compounds for bonding rayon cord

Ingredients	1	2	3	4	5	6	7	8	9	10
Natural rubber	100	100	100	100	100	100	100	100	100	100
HAF black	40	40	40	40	40	40	40	40	40	40
Zinc Oxide	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2
PF resin	0	1.32	2.5	4	5	0	1.32	2.5	4	5
Wood Rosin	5	3.68	2.5	1	0	5	3.68	2.5	1	0
Hexamethylene-tetramine	0.5	0.5	0.5	0.5	0.5	1.0	1.0	1.0	1.0	1.0
Vulkanox 4020	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Vulkanox HS	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
MOR	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65
Sulphur	2.25	2.25	2.25	2.25	2.25	2.25	2.25	2.25	2.25	2.25
*T_{10} min	3.8	3.9	4.2	4.5	4.4	3.6	3.6	3.7	4.2	3.9
*T_{90} min	12.2	12.4	12.9	13.1	13.5	11.5	12.2	12.5	12.9	13.1

Compounds 1-5 = for cords dipped in NR latex
Compounds 6-10 = for cords dipped in VP latex.
*Cure characteristics

The dipped cords were bonded with the rubber compounds and the pull through load was determined by the H- Adhesion test. The H-tests were designed to measure the force required to pull a cord in the direction of its axis from a strip of rubber in which the ends of the cords were embedded as per the ASTM D 2138 (1983).

The effect of donor concentration on bonding was studied by adding a combination of RF resin-I and paraformaldehyde into the rubber compound. (Preparation of RF resin-I is given in Chapter-II of the thesis). The concentration of RF resin-I was varied from 0.2 to 1.2phr and the concentration of paraformaldehyde was kept constant (0.4phr). The formulations of the compounds are given in Table 6.16. Nylon and rayon cords dipped in VP latex based dip solutions containing polyvinyl alcohol (PVA) were bonded to rubber compounds.

Table 6.16 Formulation of natural rubber compounds for bonding

Ingredients	1	2	3	4	5	6
Natural rubber	100	100	100	100	100	100
HAF black	40	40	40	40	40	40
ZnO	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
Wood Rosin	5	5	5	5	5	5
Vulkanox 4020	0.75	0.75	0.75	0.75	0.75	0.75
Vulkanox HS	0.5	0.5	0.5	0.5	0.5	0.5
MOR	0.65	0.65	0.65	0.65	0.65	0.65
Paraformaldehyde	0.4	0.4	0.4	0.4	0.4	0.4
RF resin-I	0.2	0.4	0.6	0.8	1.0	1.2
Sulphur	2.25	2.25	2.25	2.25	2.25	2.25
*T_{10}min	6.9	10.7	6.6	6.2	6.1	5.9
*T_{90} min	18.9	21.1	19.0	18.6	17.6	16.4

*Cure characteristics

The above dip solution was modified by adding RF resin-I. RFL adhesives E, F, G, H, I and J containing 3, 4, 5, 6, 7 and 8ml respectively (1.07, 1.36, 1.63, 1.88, 2.10, 2.30 percentage weight of RF resin-I respectively) of the 7.5 % solution of RF resin-I with 8ml NR latex, 10ml distilled water and the optimum amount of PVA solution were prepared. The RFL adhesives were aged for 16h.

The NR latex in the above RFL adhesive was replaced by VP latex to get RFL adhesive K, L, M, N, P and Q. These RFL adhesives were also matured for a period of 16h.

The dipped cords were dried and cured at the optimum temperature of drying and curing (as described in Chapter-V of the thesis).

The cords dipped in the above RFL adhesives were bonded to four different rubber compounds. The nylon cords dipped in NR and VP latex based RFL adhesives were bonded to rubber compounds as formulated in Table 6.17. The rayon cords dipped in NR and VP latex based RFL adhesives were bonded to rubber compounds as per the formulation given in Table 6.18. Optimized combinations of CNSL resin/wood rosin, PF resin/wood rosin, RF resin-I/parafomaldehyde/wood rosin were used. A part of HAF black was replaced by silica in the compound containing RF resin-I/ parafomaldehyde/wood rosin.

Table 6.17 Formulations of rubber compounds with different resin combinations for nylon cord

Ingredients	I	II	III	IV	I'	II'	III'	IV'
Natural rubber	100	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2
HAF black	40	40	40	35	40	40	40	35
Silica	-	-	-	5	-	-	-	5
Aromatic oil	5	5	5	5	5	5	5	5
Wood rosin	2.5	1	5	5	2.5	1	5	5
CNSL resin	2.5	-	-	-	2.5	-	-	-
PF resin	-	4	-	-	-	4	-	-
RF resin-I	-	-	1.0	1.0	-	-	1.0	1.0
Vulkanox-HS	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Vulkanox-4020	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
MOR	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65
Hexamethylene tetramine	1.0	1.0	-	-	1.5	1.5	-	-
Parformaldehyde	-	-	0.4	0.4	-	-	0.4	0.4
Sulphur	2.25	2.25	2.25	2.25	2.25	2.25	2.25	2.25
*T_{90}min	11.8	12.9	14.4	14.3	10.4	11.8	12.9	13.0
*T_{10}min	4.1	4.2	5.3	8.6	3.8	4.7	4.9	5.4

*Cure characteristics

Table 6.18 Formulations of rubber compounds with different resin combinations for rayon cord

Ingredients	I	II	III	IV	I'	II'	III'	IV'
Natural rubber	100	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2
HAF black	40	40	40	35	40	40	40	35
Silica	-	-	-	5	-	-	-	5
Aromatic oil	5	5	5	5	5	5	5	5
Wood rosin	2.5	1	5	5	2.5	1	5	5
CNSL resin	2.5	-	-	-	2.5	-	-	-
PF resin	-	4	-	-	-	4	-	-
RF resin-I	-	-	0.8	0.8	-	-	0.8	0.8
Vulkanox-HS	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Vulkanox-4020	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
MOR	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65
Hexamethylene tetramine	0.5	0.5	-	-	1.0	1.0	-	-
Parformaldehyde	-	-	0.4	0.4	-	-	0.4	0.4
Sulphur	2.25	2.25	2.25	2.25	2.25	2.25	2.25	2.25
*T_{90}min	11.3	13.1	14.2	14.3	11.8	12.9	12.9	13
*T_{10}min	4.2	4.5	4.8	4.9	4.1	4.2	3.9	4.4

*Cure characteristics

Results and Discussion

Figures 6.11, 6.12 and 6.13 show the variation of pull through load with the concentration of the modifying agents in VP latex for nylon and rayon cords bonded to rubber compound whose formulation are shown in Table.6.11.

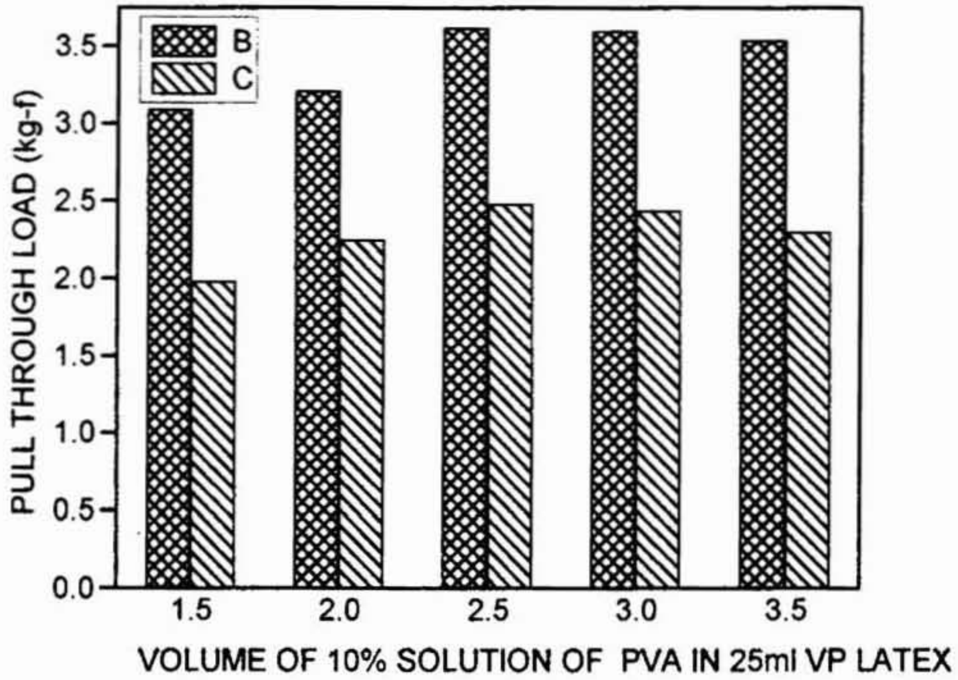

Fig.6.11 Variation of pull through load with concentration of PVA in VP latex. B- nylon cord ; C- rayon cord.

It is found that as the concentration of the modifying agent in the dip solution increases the pull through load increases and reaches a saturation with further increase in the concentration of the modifying agent. This saturation at high concentration may be due to the excessive stiffness of the cord, resulting in the high modulus of the cord. The optimum concentrations of PVA in the dip solution may be taken as 2.5ml in 25ml latex, 5ml of CMC in 25ml latex and 7ml PEG in 25 ml latex.

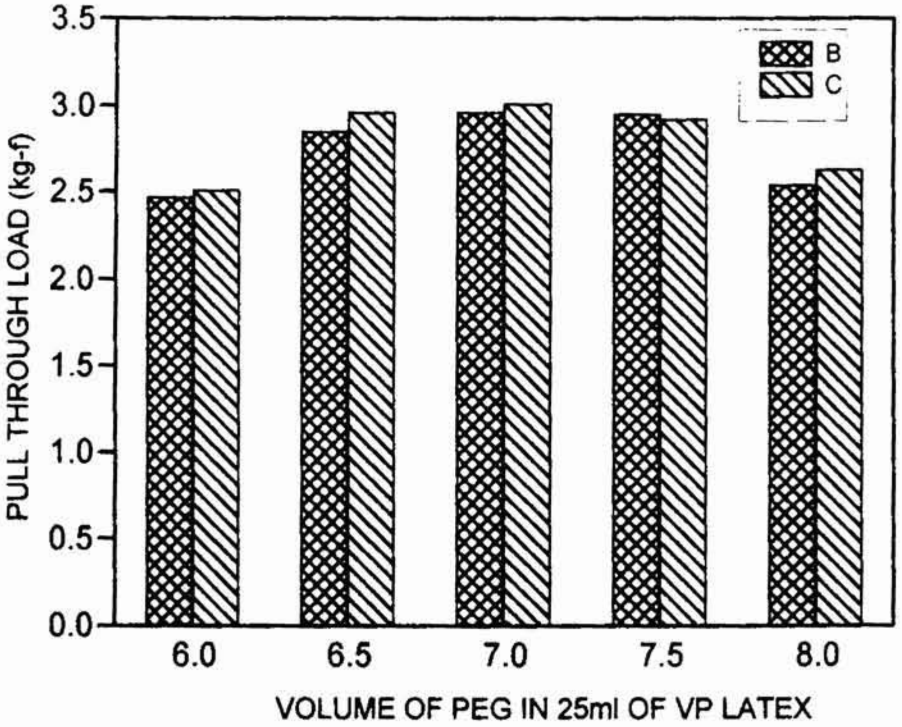

Fig.6.12 Variation of pull through load with concentration of PEG in VP latex. B- nylon cord ; C- rayon cord.

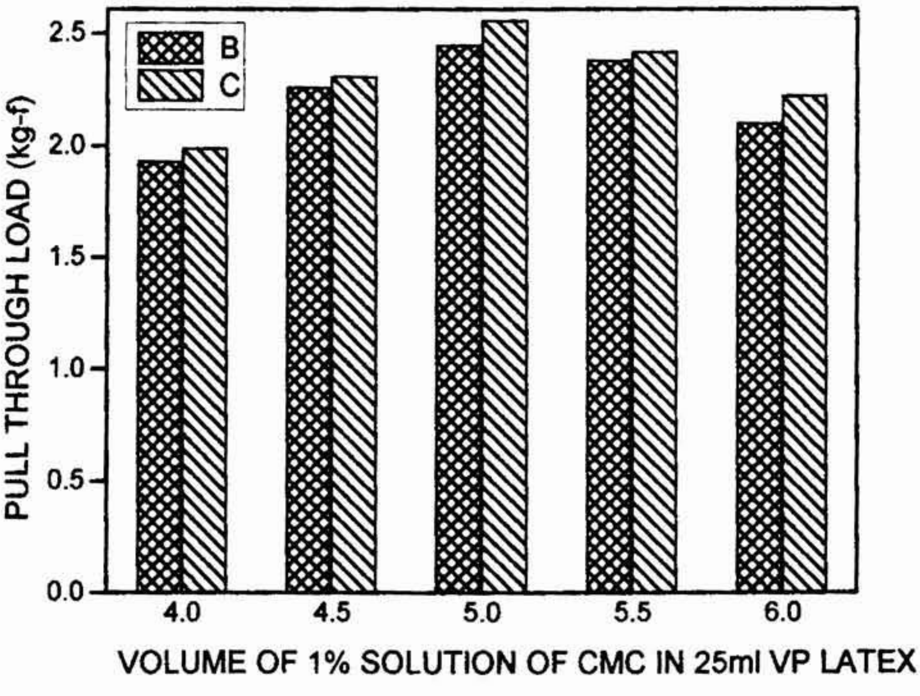

Fig.6.13 Variation of pull through load with concentration of CMC in VP latex. B- nylon cord ; C- rayon cord.

The scorch time and the cure time of the rubber compounds containing CNSL resin and PF resin used for bonding nylon cord dipped in NR and VP latex based dip solutions containing different modifiers are given in Table 6.12 and 6.13.

Figures 6.14 and 6.15 show the variation of pull through load with CNSL resin/ wood rosin ratio for nylon cord dipped in NR and VP latex based dip solutions containing the modifiers B, C and D. In figure 6.14 the pull through load is found to increase, reach a maximum value and then decrease. This is found to be common for all the three dip solutions. The value of the maximum pull through load obtained for the cords dipped in the three dip solutions differ only marginally. This shows that the choice of the modifying agent is not a crucial factor for bonding of nylon cord dipped in NR latex based dip solutions, but the ratio of the concentration of CNSL resin to wood rosin affects the bonding. The bonding is found to be low at high and very low concentration. The optimum bonding is obtained at resin ratios of 1:1 of CNSL resin to wood rosin.

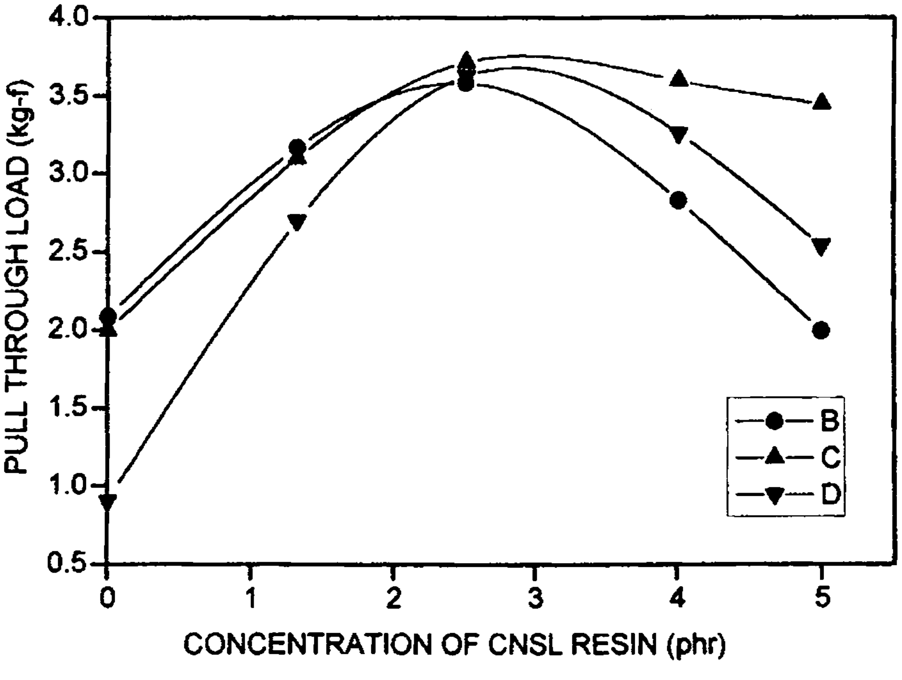

Fig.6.14 Variation of pull through load with CNSL resin/wood rosin ratio for nylon cord dipped in NR latex containing potential agent. B-PVA; C-CMC; D- PEG.

In figure 6.15 the pull through load is found to increase, reach a maximum for cord dipped in dip solution B, and then decrease. The maximum pull through load is obtained at the resin ratio 1:1. For cords dipped in dip solutions C and D, the pull through load is found to increase gradually as the concentration of CNSL resin increases.

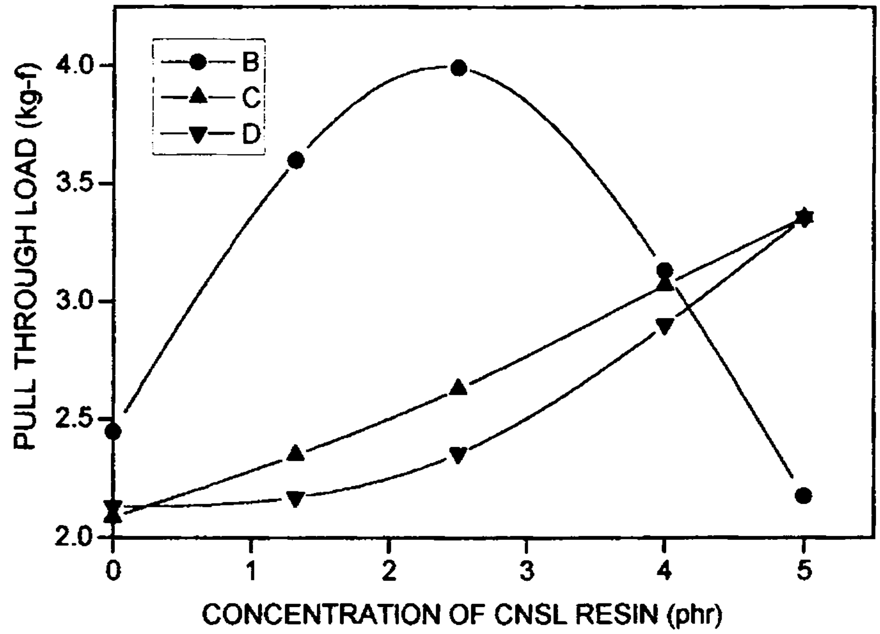

Fig.6.15 Variation of pull through load with CNSL resin/wood rosin ratio for nylon cord dipped in VP latex containing potential agent. B-PVA; C-CMC; D- PEG.

Figures 6.16 and 6.17 show the pull through load with different PF resin/wood rosin ratios for nylon cord dipped in NR and VP latex based dip solutions containing the modifiers. In figure 6.16, the cord dipped in solution C shows the lowest bonding and for cord dipped in solution B and D, the pull through load increases first reaches a maximum and then decreases. The optimum resin to wood rosin ratio is found to be 4:1

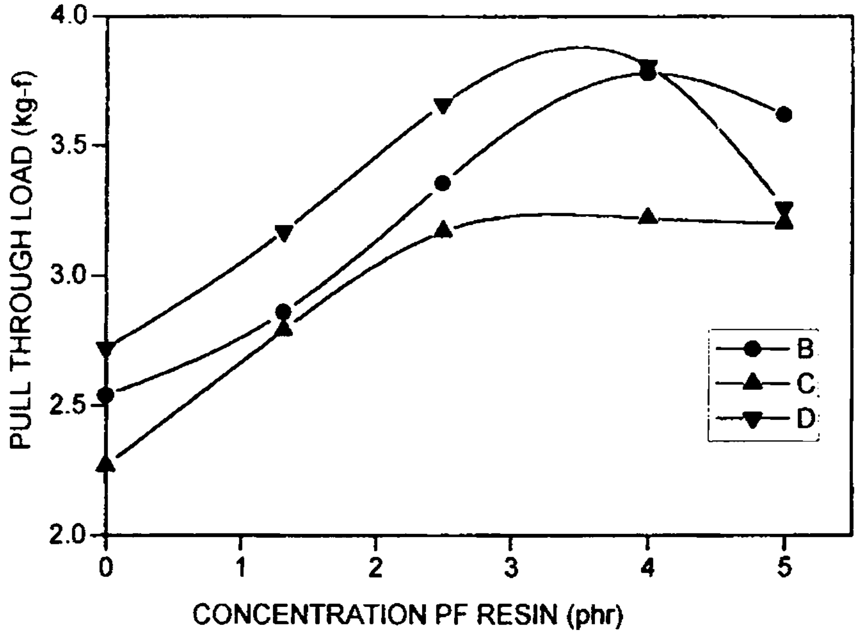

Fig.6.16 Variation of pull through load with PF resin/wood rosin ratio for nylon cord dipped in NR latex containing potential agent. B-PVA; C-CMC; D- PEG.

In figure 6.17, the pull through load is found to increase for cord dipped in solution B initially and as the ratio of concentration of the resin to wood rosin ratio increases the pull

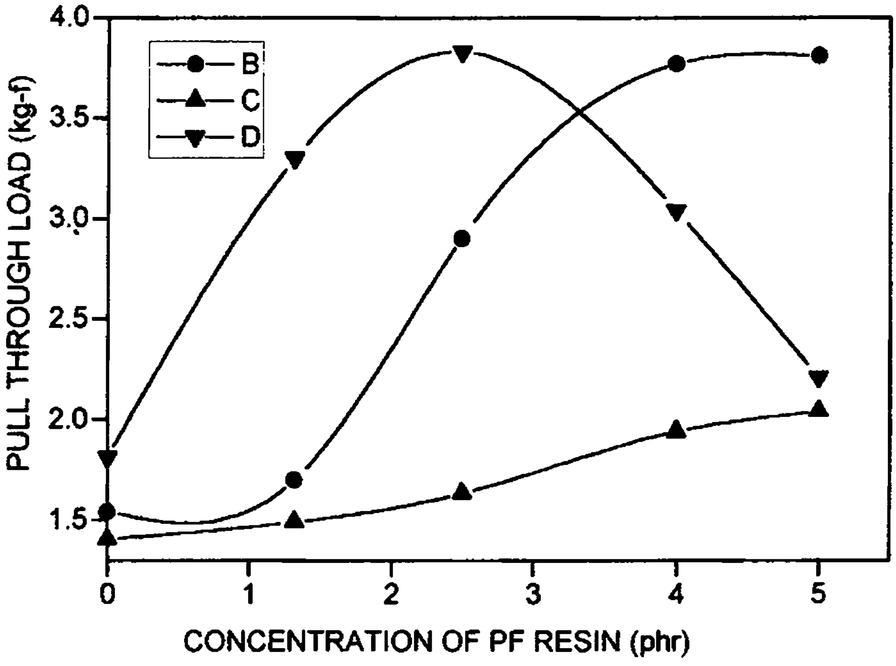

Fig.6.17 Variation of pull through load with PF resin/wood rosin ratio for nylon cord dipped in VP latex containing potential agent. B-PVA; C-CMC; D- PEG.

through load reaches a constant value. Considering the pull through load obtained for cord dipped in solution C, there is a gradual increase with the ratio of the resin-wood rosin but the bonding is found to be poor. For cord dipped in solution D, the pull through load increases first reaches a maximum and then decreases and the optimum ratio of resin to wood rosin for maximum pull through load is found to be 4:1 (for dip solution B).

Thus comparing the effect of bonding on the concentration of CNSL resin/wood rosin and PF resin/wood rosin combinations in the rubber compound, it is found that a higher value of the ratio of the resin to wood rosin is required for nylon cord bonding, the cords dipped in solutions B and D showing comparable pull through load and the cord dipped in solution C showing poor bonding with nylon cord in both lattices.

The effect of bonding of rayon tire cord dipped in NR and VP latex based dip solutions containing modifiers B, C and D to four rubber compounds (formulation as given in Table 6.14 and 6.15) are shown in figures 6.18 to 6.112.

Figures 6.18 and 6.19 show the variation of pull through load with CNSL resin/ wood rosin ratio for rayon cord dipped in NR and VP latex based dip solutions respectively.

In figure 6.18 the pull through load for rayon cord dipped solution B and D is found to increase gradually, reach a maximum and then decrease. Cord dipped in solution C shows a decrease in pull through load as the concentration of the CNSL resin increases. The maximum pull through load for cord dipped in solution is obtained at a resin/wood rosin ratio of 1:1.

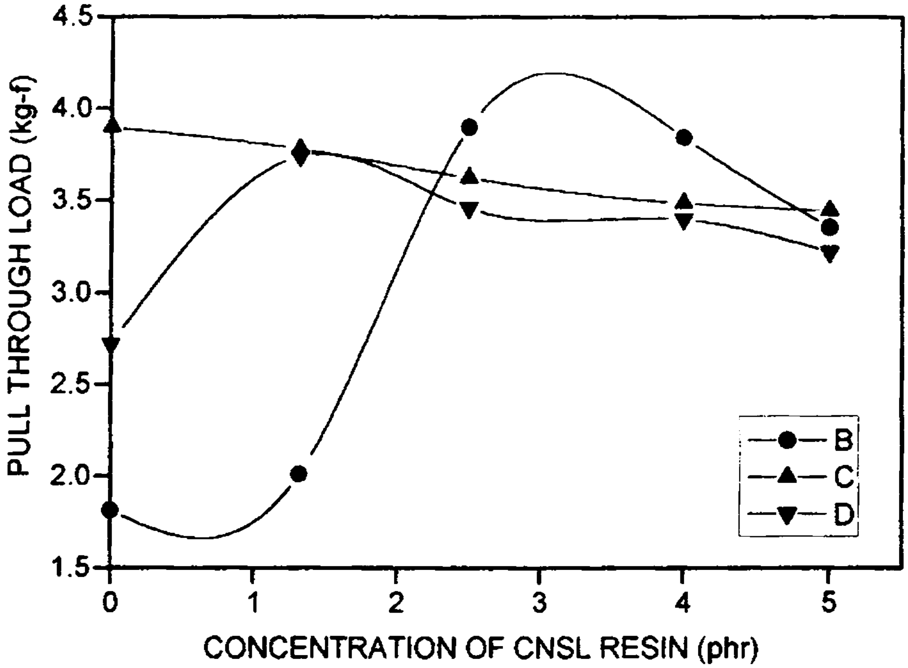

Fig.6.18 Variation of pull through load with CNSL resin/wood rosin ratio for rayon cord dipped in NR latex containing potential agent. B-PVA; C-CMC; D- PEG.

In figure 6.19 for cords dipped in solutions B and C the pull through load is found to increase with concentration of CNSL resin. The maximum pull through load in the two cases

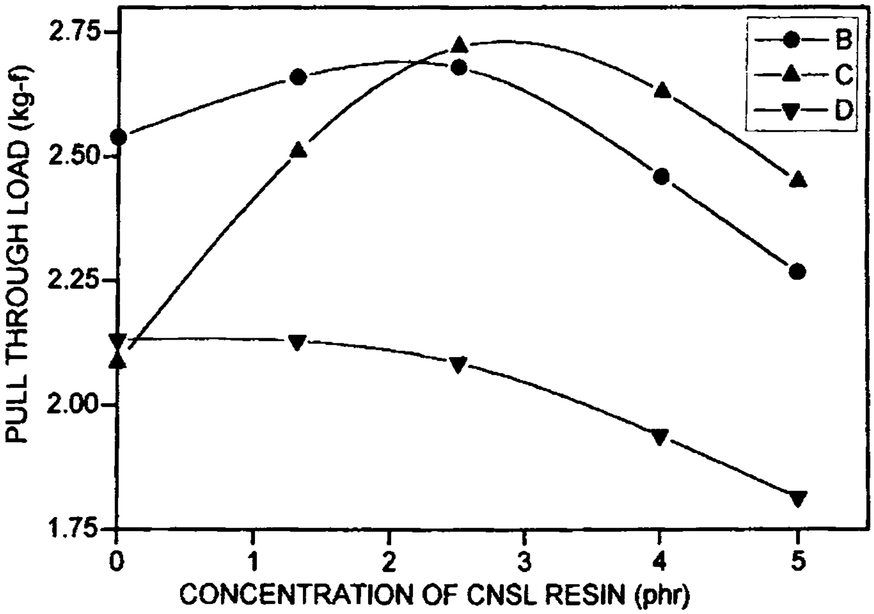

Fig.6.19 Variation of pull through load with CNSL resin/wood rosin ratio for rayon cord dipped in VP latex containing potential agent. B-PVA; C-CMC; D- PEG.

varies only marginally and the optimum resin to wood rosin ratio is found to be 1:1. For cord dipped in solution D, the pull through load is found to remain constant at low concentration of CNSL resin and at high concentrations the pull through load is found to decrease.

Figures 6.120 and 6.121 show the variation of pull through load with PF resin/ wood rosin ratio for rayon cord dipped in NR and VP latex based dip solutions respectively.

In figure 6.120 the rayon cord dipped in solution B shows an increase in pull through load as the concentration of PF resin increases and a slight decrease slightly at high concentrations, the optimum concentration of the resin to wood rosin ratio being 4:1. For cords dipped in solution C and D the pull through load steadily decreases with increase in concentration of wood rosin.

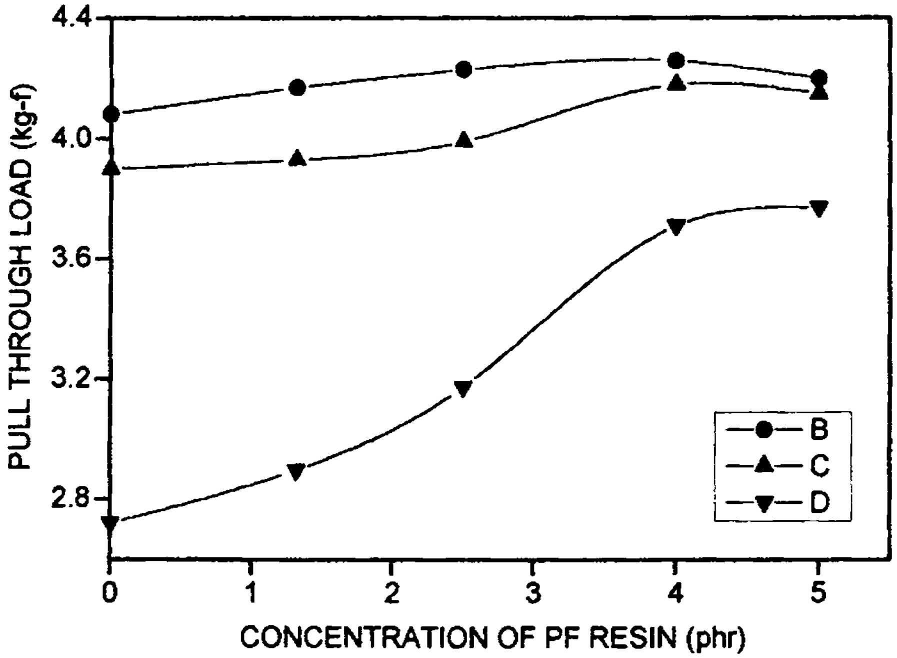

Fig.6.120 Variation of pull through load with PF resin/wood rosin ratio for rayon cord dipped in NR latex containing potential agent. B-PVA; C-CMC; D- PEG.

In figure 6.121, the cords dipped in all the three dip solutions behave similarly. The pull through load is found to increase, reach a maximum and then decrease. The maximum pull through load is obtained at a higher concentration of PF resin.

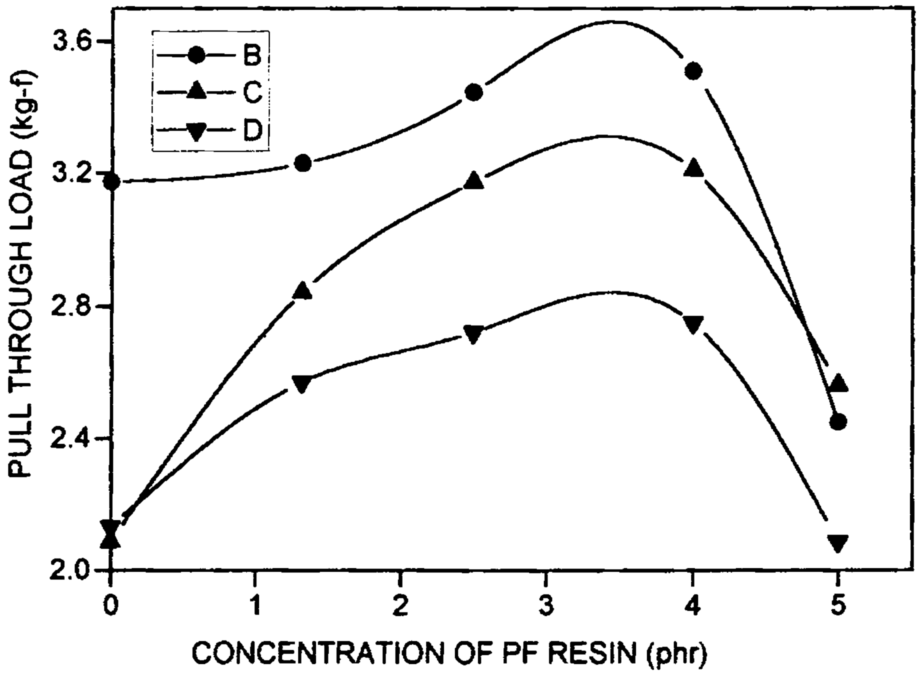

Fig.6.121 Variation of pull through load with PF resin/wood rosin ratio for rayon cord dipped in VP latex containing potential agent. B-PVA; C-CMC; D- PEG.

It is again found that a higher concentration of PF resin is required in the rubber compound for optimum bonding compared to that of CNSL resin. This difference may be due to the change of miscibility with the rubber compound, rigidity of the adhesive film and the contribution of covulcanization sites to adhesion[6-8].

Figure 6.122 shows the variation of pull through load with concentration of RF resin-I in the rubber compound for rayon and nylon cords dipped in VP latex based solution containing polyvinyl alcohol (PVA). For rayon cord the pull through load is found to increase, reach a maximum value and then decrease. The optimum concentration of the resin is found to be 0.8phr. But for nylon cord there is a gradual increase as the concentration of RF resin-I increases tending to a constant value at high concentration of RF resin-I. The optimum concentration is found to be about 1.0phr. This difference in the optimum concentration of RF resin for the two cords may be due to the difference in the polarity of the two cords. On heating the paraformaldehyde releases the formaldehyde which reacts with the RF resin to form the methylol group, which may react with the active hydrogen of the fiber. A possible ionic interaction or chemical reaction between the RF resin and the rubber compound might have also taken place[6,9,10,11]. The scorch time and the cure time of the rubber compounds used for bonding are given in Table 6.16.

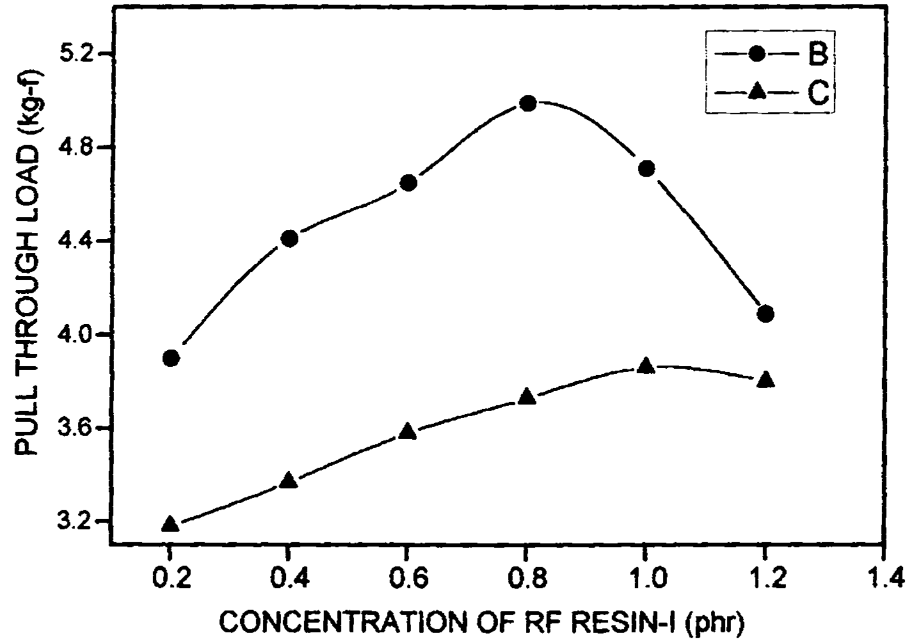

Fig.6.122 Variation of pull through load with concentration of RF resin-I in the rubber compound for cords dipped in VP latex containing PVA. B- nylon cord ; C- rayon cord.

Figures 6.123 to 6.130 show the effect of adding RF resin-I to the dip solution containing PVA based on NR and VP latex. Table 6.17 shows the cure time and scorch time of rubber compounds used for bonding nylon cords dipped in NR and VP latex based

RFL adhesives. Table 6.18 shows the cure time and scorch time of rubber compounds used for bonding rayon cords dipped in NR and VP latex based RFL adhesives.

Figures 6.123, 6.124, 6.125 and 6.126 show the variation of pull through load for nylon cord dipped in RFL adhesive bonded to four rubber compounds. The optimum resin to rubber ratio for cord dipped in NR latex based RFL adhesive with all the four compounds is 1:2. The compound containing RF resin-I gives the best bonding. The replacement of HAF black by silica does not affect the bonding or resin to rubber ratio. The optimum resin to rubber ratio for cord dipped in VP latex based RFL with the compounds is 5:8, except for compound containing RF resin-I showing an optimum ratio of 3:4. The compound containing PF resin gives the best bonding, though a higher resin to rubber ratio is required in VP latex. The replacement of HAF by silica reduces the bonding for nylon cord dipped

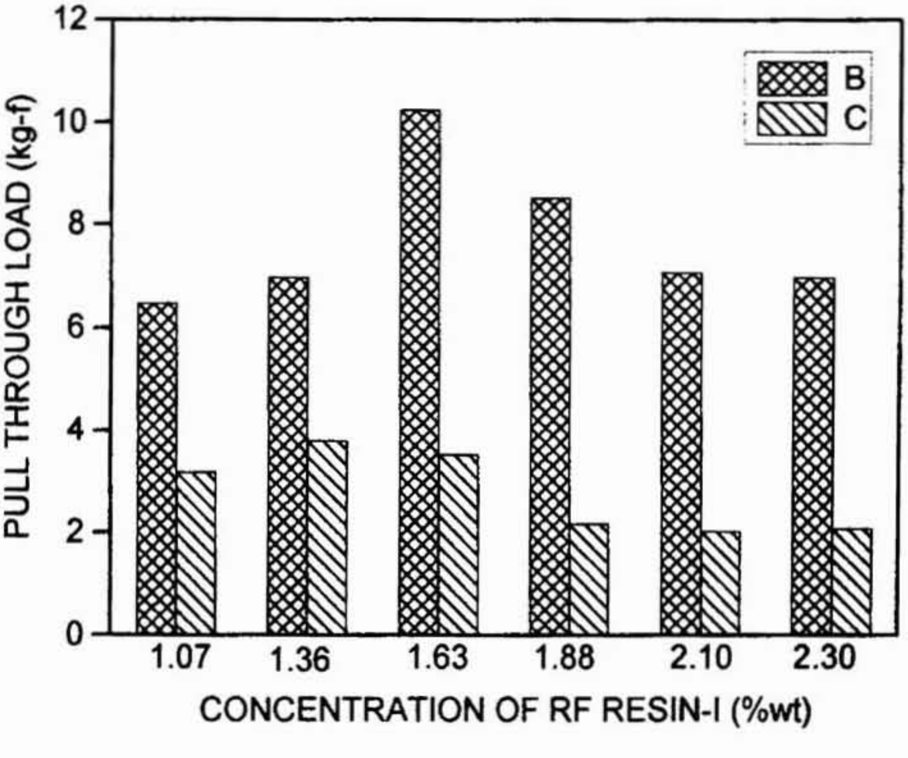

Fig. 6.123 Variation of pull through load for nylon cord dipped in RFL adhesive containing PVA bonded to compound containing CNSL resin. B- VP latex; C- NR latex.

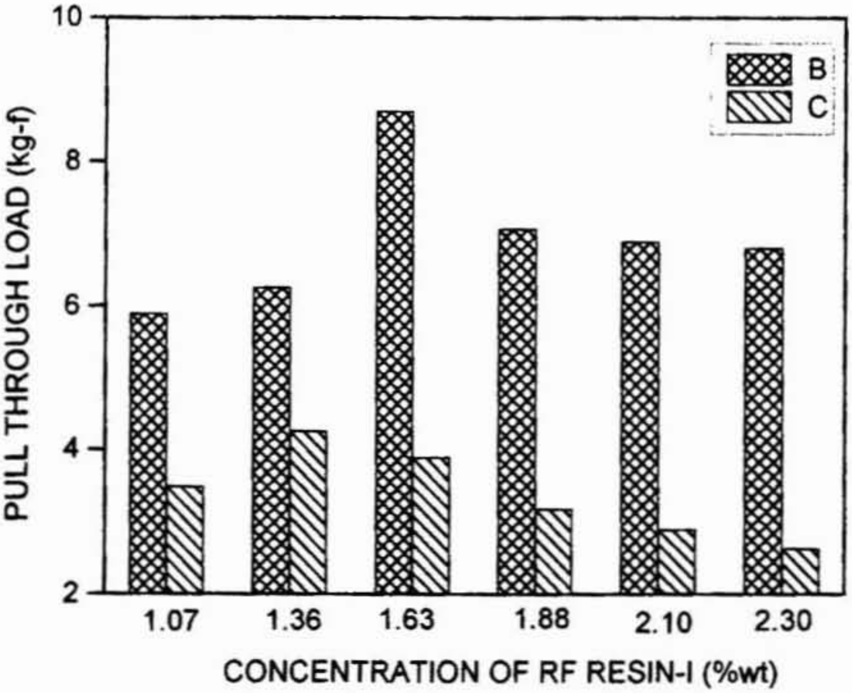

Fig. 6.124 Variation of pull through load for nylon cord dipped in RFL adhesive containing PVA bonded to compound containing PF resin. B- VP latex; C- NR latex.

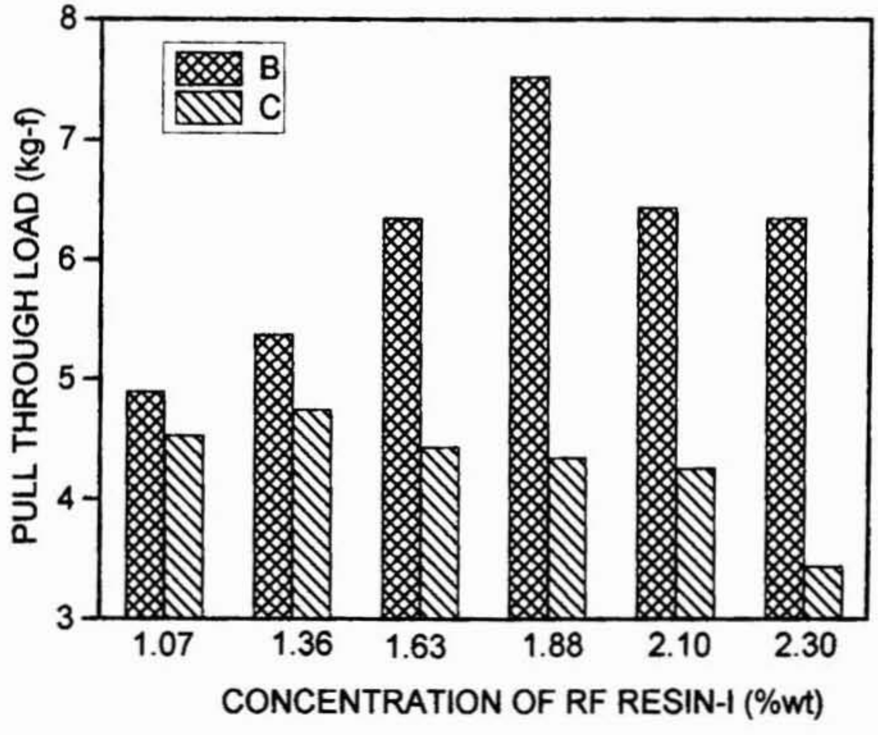

Fig. 6.125 Variation of pull through load for nylon cord dipped in RFL adhesive containing PVA bonded to compound containing RF resin-I. B- VP latex; C- NR latex.

in VP latex but does not affect the resin to rubber ratio (figure 6.126). It is suggested that the network structure of RFL resin gets modified widely with the resorcinol to formaldehyde ratio and the maturing time. This in turn affects the mechanical properties of RFL films prepared with various resorcinol to formaldehyde ratios.

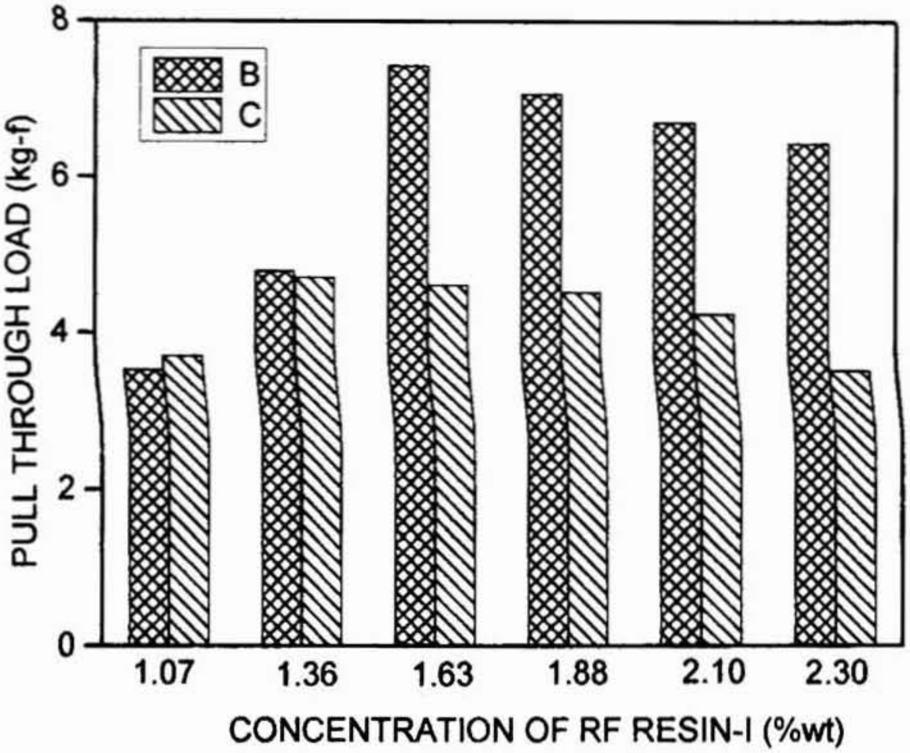

Fig. 6.126 Variation of pull through load for nylon cord dipped in RFL adhesive containing PVA bonded to compound containing RF resin-I and HAF partially replaced by silica. B- VP latex; C- NR latex.

Figures 6.127, 6.128, 6.129 and 6.130 show the variation of pull through load for rayon cord with resin to rubber ratio in the RFL adhesive bonded to four rubber compounds. The optimum resin to rubber ratio for cord dipped in NR latex based RFL adhesive bonded to PF resin based compound is 3:4, for all the other compounds, the optimum resin-rubber ratio being 1:2. The compound containing RF resin-I gives the best bonding. Replacement of HAF black by silica reduces the bonding, though there is no change in the resin to rubber ratio. When NR latex is replaced by VP latex this ratio becomes 7:8 for all compounds except compound containing RF resin-I, where a superior bonding is obtained at lower resin to rubber ratio (1:2). Replacement of HAF black by silica in the rubber compound increases the optimum resin to rubber ratio in the case of rayon cord in VP latex with no change in the pull through load.

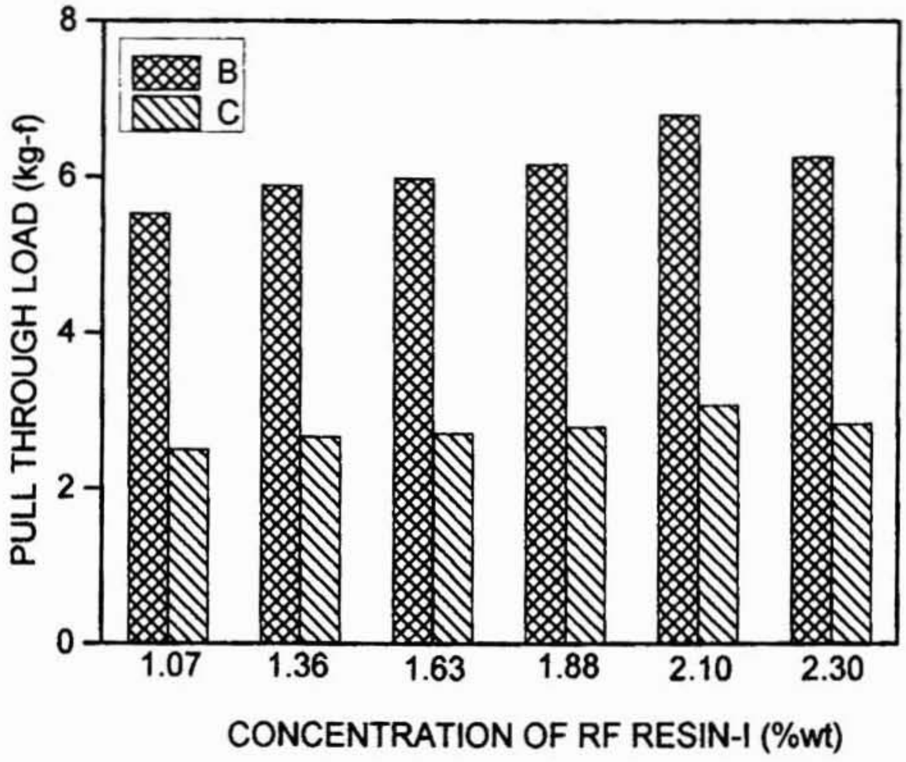

Fig. 6.127 Variation of pull through load for rayon cord dipped in RFL adhesive containing PVA bonded to compound containing CNSL resin. B- VP latex; C- NR latex.

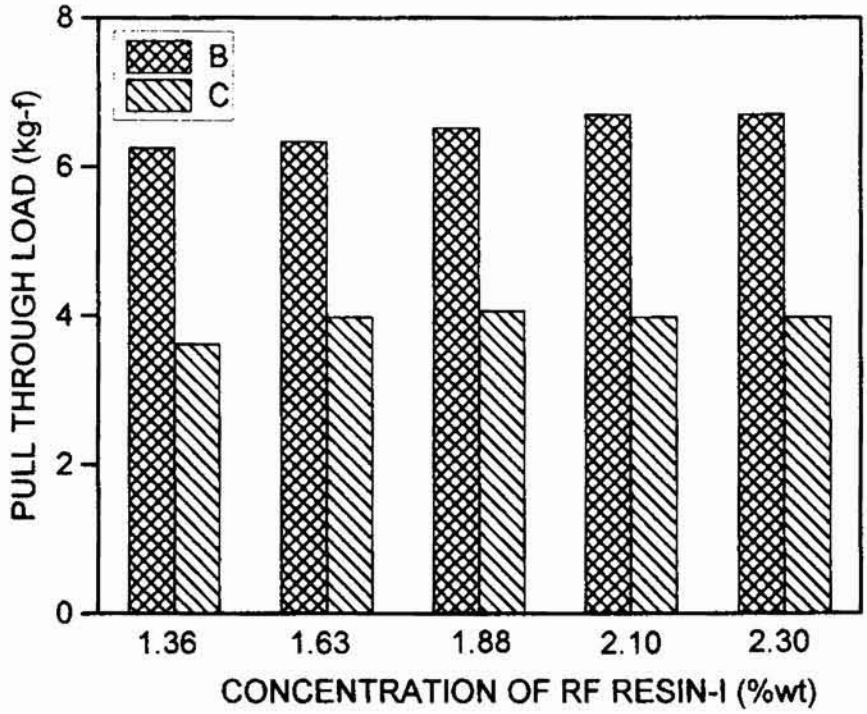

Fig. 6.128 Variation of pull through load for rayon cord dipped in RFL adhesive containing PVA bonded to compound containing PF resin. B- VP latex; C- NR latex.

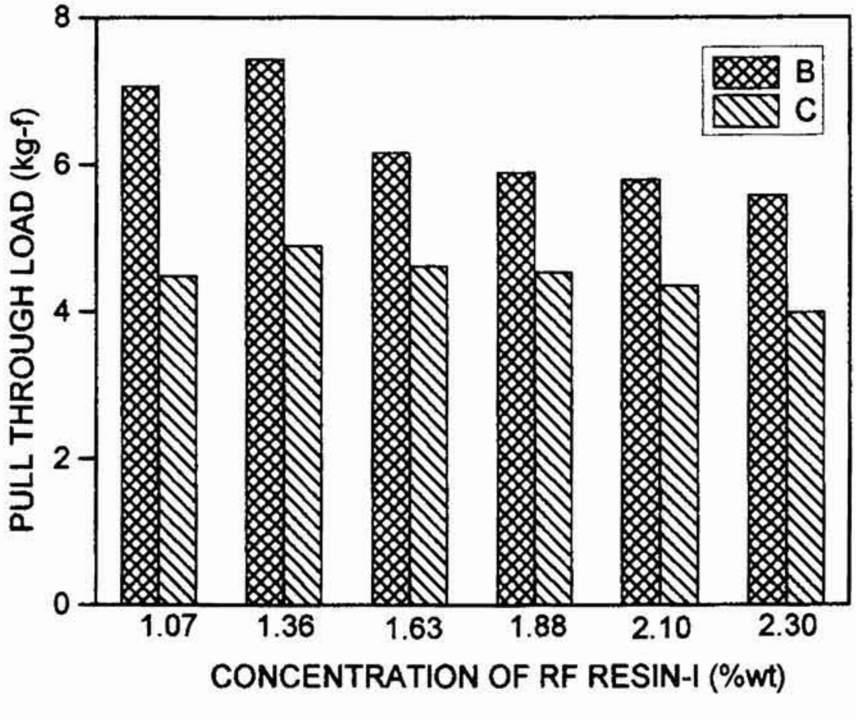

Fig. 6.129 Variation of pull through load for rayon cord dipped in RFL adhesive containing PVA bonded to compound containing RF resin-I. B- VP latex; C- NR latex.

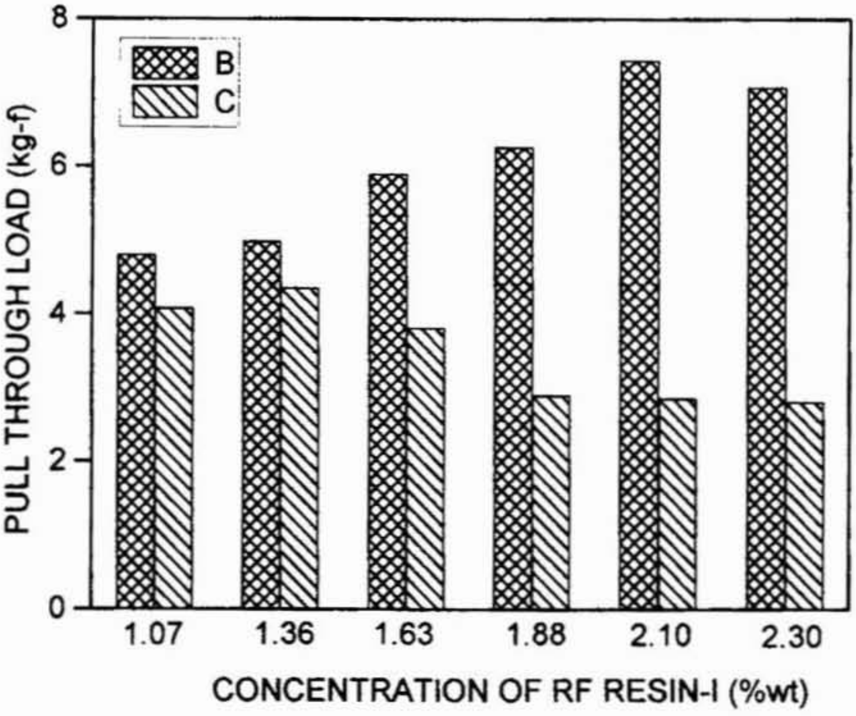

Fig. 6.130 Variation of pull through load for rayon cord dipped in RFL adhesive containing PVA bonded to compound containing RF resin-I and HAF partially replaced by silica. B- VP latex; C- NR latex.

CONCLUSIONS

1) The optimum ratio of the PF resin/wood rosin in the rubber compound to bond rayon and nylon cord dipped in latex containing modifier is about 4:1.
2) The optimum ratio of the CNSL resin/wood rosin in the rubber compound to bond rayon and nylon cord dipped in latex containing modifiers is about 1:1.
3) In the presence of the modifier the concentration of the RF resin- I required in the RFL is lower to get optimum bonding.
4) The replacement of HAF black partially by silica does not improve the bonding of the compound containing RF resin-I to rayon or nylon cord appreciably

Part –II

COMPARISON AND EVALUATION OF THE EFFICIENCY OF THE NOVEL ADHESIVES DEVELOPED WITH THAT OF COMMERCIAL ADHESIVES

Experimental

The efficiency of the novel adhesives developed is compared with that of commercial samples by comparing the pull through load. A typical rubber compound formulation used in the tire industry and the dipped nylon tire cord from the tire industry were used for the study. The nylon and rayon tire cords dipped in the laboratory were also bonded to the commercially available rubber compound and the pull through load was compared.

The nylon cords used for the study were 840/2, 1260/2 and 1680/2. These cords were dipped in a typical tire industry and also in the laboratory using RF resin-I and RF resin-II in the RFL adhesive (as given in Chapter-V, part-I). The dipped cords were bonded to the commercial rubber compound (1) and the rubber compound formulated for the present study (Compounds 2 and 3) are shown in the Table 6.21. The rayon cord used for the study was 1650/2. The cord was dipped in the RFL adhesives prepared in the laboratory using RF resin-I and RF resin-II (as given in Chapter-V, part-II).

In order to compare the bonding of untreated and latex dipped cords, 1680/2 nylon cord and the 1650/2 rayon cord were bonded to the compounds 2 and 3 respectively given in Table 6.21 and the pull through load was determined.

Table 6.21 Formulation of natural rubber compounds for bonding

Ingredients	1	2	3
Natural rubber	Commercial	100	100
HAF black	compound	40	40
ZnO		5	5
Stearic acid		2	2
Wood Rosin		5	5
Vulkanox 4020		0.75	0.75
Vulkanox HS		0.5	0.5
MOR		0.65	0.65
Paraformaldehyde		0.4	0.4
RF resin-I		0.4	0.35
Sulphur		2.25	2.25
*T_{10} min		10.7	8.5
*T_{90} min		21.1	20.6

Compound - 2 for nylon cord
Compound- 3 for rayon cord
*Cure Characteristics

Results and Discussion

Figure 6.21 shows the pull through load for nylon tire cord dipped in the tire industry bonded to the compounds 1 and 2 whose formulations are shown in Table.6.21. The 840/2 and 1260/2 nylon cords show lower bonding with compound 1. Unlike the 1680/2 cord which shows better bonding with the compound.

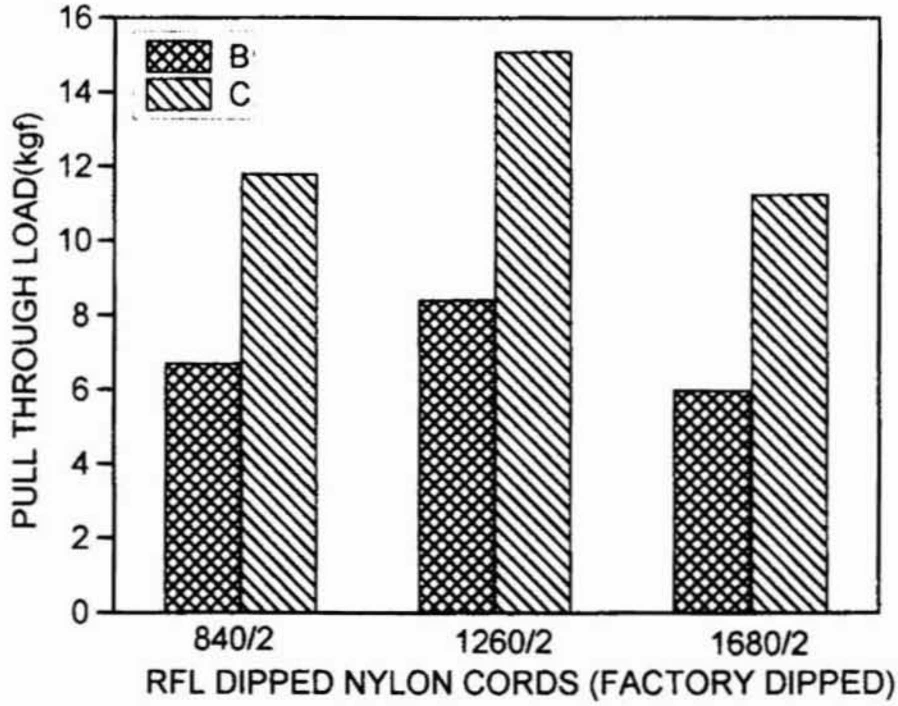

Fig. 6.21 Variation of pull through for RFL dipped nylon cords.
B- compound prepared in laboratory; C- Commercial compound.

Figures 6.22 and 6.23 show the pull through load obtained for rayon cord dipped in RFL adhesive based on NR and VP latex respectively, bonded to compounds 1and 3 whose

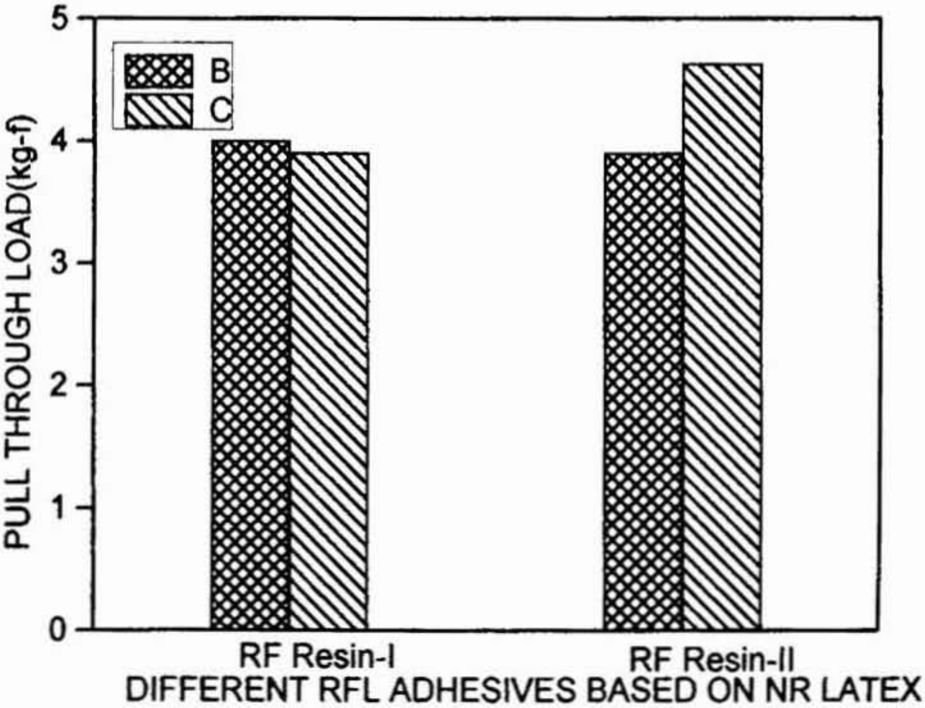

Fig. 6.22 Variation of pull through for RFL dipped rayon cords.
B- compound prepared in laboratory; C- Commercial compound.

formulations are given in Table 6.21. When the cord dipped in RFL based on RF resin-I is bonded to compounds 1 and 3, the pull through load varies only marginally as shown in figure 6.22. But when RF resin-I is replaced by RF resin-II, better bonding is obtained for compound 1. The cord dipped in RFL adhesive based on RF resin-I shows only marginal change in the pull through load with compounds 1and 3 as shown in figure 6.23. When RF resin-I is replaced by RF resin-II better bonding is obtained for compound 1.

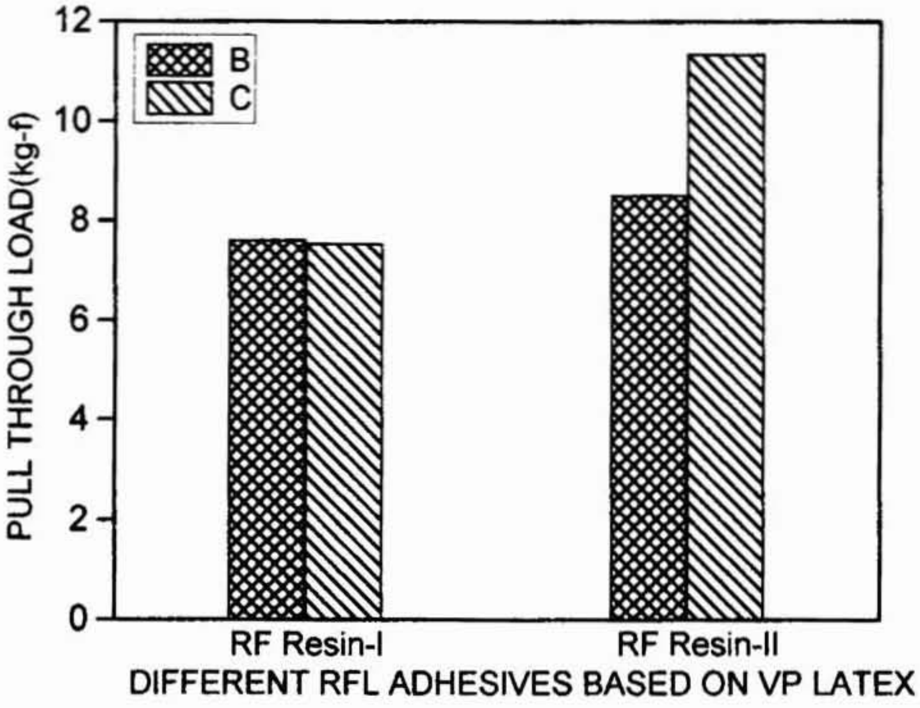

Fig. 6.23 Variation of pull through for RFL dipped rayon cords.
B- compound prepared in laboratory; C- Commercial compound.

Figures 6.24 and 6.25 show the pull through load obtained for nylon cord dipped in RFL adhesive based on NR and VP latex respectively, bonded to compounds 1 and 2 whose formulations are given in Table.6.21. When the cord is dipped in RFL based on RF resin-I and bonded to compounds 1 and 2, the pull through load for compound 2 is found to be higher than that for compound 1 as shown in figure 6.24. But when RF resin-I is replaced by RF resin-II, compound 1 gives better bonding.

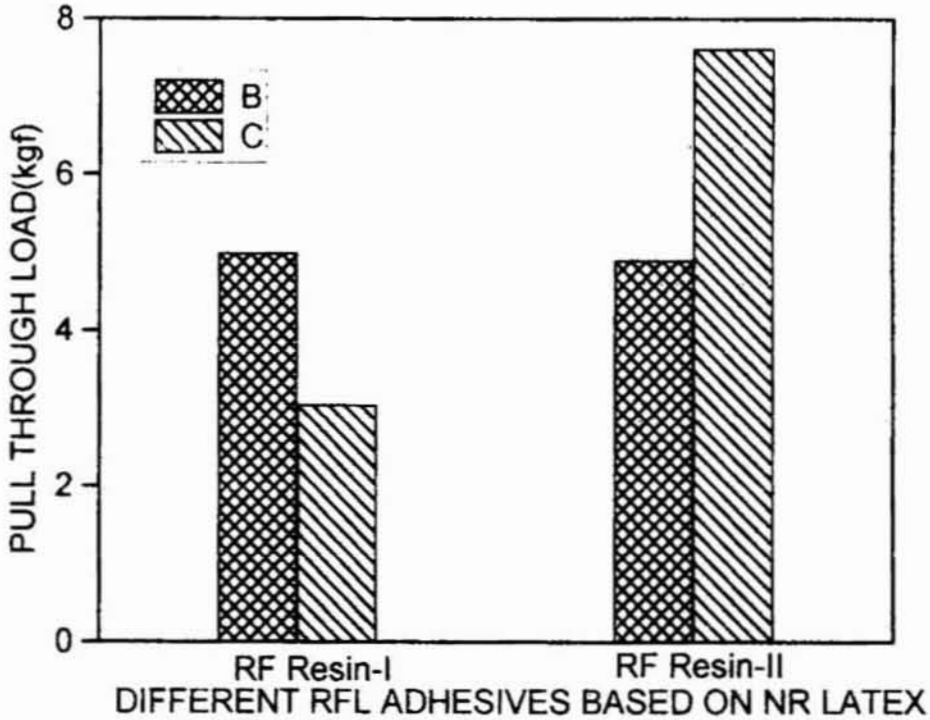

Fig. 6.24 Variation of pull through for RFL dipped nylon cords.
B- compound prepared in laboratory; C- Commercial compound.

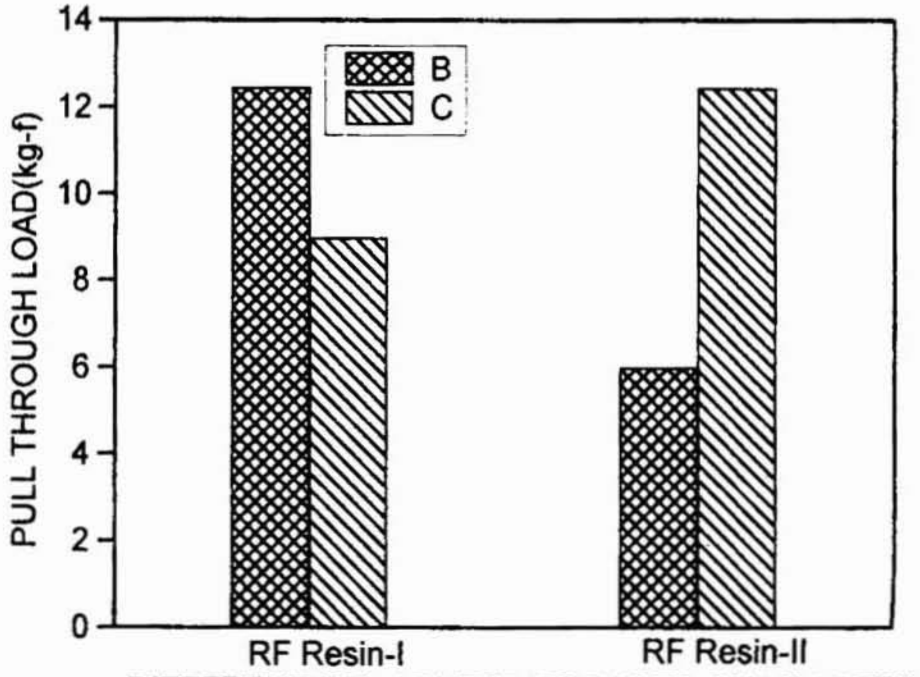

Fig. 6.25 Variation of pull through for RFL dipped nylon cords.
B- compound prepared in laboratory; C- Commercial compound.

In figure 6.25, the cord dipped in RFL adhesive based on RF resin-I is bonded to compounds 1 and 2, the pull through load obtained for compound 2 is appreciably higher than that for compound 1 and the pull through load so obtained is comparable with that obtained for the tire cord dipped in the tire industry and bonded to compound 1. When RF resin-I is replaced by RF resin-II better bonding is obtained for compound 1.

Table.6.22 shows the pull through load obtained for the untreated and latex treated tire cords bonded to compounds 2 and 3 as shown in Table 6.21. Both the cords show low bonding in the untreated condition. The nylon cord shows better bonding in VP latex and the rayon cord shows better bonding in NR latex.

Table.6.22 Pull through load for untreated and latex treated cords

Type of adhesive treatment	Nylon (kg-f)	Rayon (kg-f)
No treatment	1.53	1.73
NR latex alone	2.17	1.87
VP latex alone	2.22	2.13

CONCLUSIONS

1) The nylon cord dipped in RFL adhesive containing RF resin-I/VP latex bonded to the rubber compound prepared in the laboratory shows comparable bonding as the nylon cord dipped in the tire industry and bonded to the commercial compound.

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Chapter VII

SUMMARY AND CONCLUSIONS

The primary objective of this investigation has been to develop more efficient and low cost adhesives for bonding various elastomer combinations particularly NR to NR, NR/PB to NR/PB, CR to CR, NR to CR and NR to NBR.

A significant achievement of the investigation was the development of solventless and environment friendly solid adhesives for NR to NR and NR/PB to NR/PB particularly for precured retreading. Conventionally used adhesives in this area are mostly NR based adhesive strips in the presence of a dough. The study has shown that an ultra accelerator could be added to the dough just before applying it on the tire which can significantly bring down the retreading time resulting in prolonged tire service and lower energy consumption. Further latex reclaim has been used for the preparation of the solid strip which can reduce the cost considerably.

Another significant finding was that by making proper selection of the RF resin, the efficiency and shelf life of the RFL adhesive used for nylon and rayon tire cord dipping can be improved. In the conventionally used RFL adhesive, the resin once prepared has to be added to the latex within 30 minutes and the RFL has to be used after 4 hours maturation time maximum shelf life of the RFL dip solution being 72 hours. In this study a formaldehyde deficient resin was used and hence more flexibility was available for mixing with latex and maturing. It also has a much longer shelf life. In the method suggested in this study, formaldehyde donors were added only in the rubber compound to make up the formaldehyde deficiency in the RFL. The results of this investigation show that the pull through load by employing this method and the conventional method are comparable. This study has also shown that the amount of RF resin with RFL adhesive can be partially replaced by other modifying agents for cost reduction.

Another finding of this study was that cashew nut shell liquid (CNSL) resin can be employed for improving the bonding of dipped nylon and rayon cord with NR. Since CNSL resin cannot be added in the dip solution since it is not soluble in water, it was added in the rubber compound. The amount of wood rosin in the rubber compound can be reduced by using CNSL resin.

Another interesting result of the investigation was the use of CR based adhesive modified with chlorinated natural rubber for CR to CR bonding. Addition of chlorinated natural rubber was found to improve sea water resistance of CR based adhesive. In the bonding of a polar rubber like nitrile rubber or polychloroprene rubber to a non polar rubber like natural rubber, an adhesive based on polychloroprene rubber was found to be effective.

List of Publications

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