SYNTHESIS, CHARACTERISATION AND USES OF POLYMER- BOUND ANTIOXIDANTS

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MARCH 2002

Certificate

This is to certify that this thesis entitled ***"Synthesis, Characterisation and Uses of Polymer-bound Antioxidants"*** *is a report of the original work carried out by Smt.Sulekha P.B. under my supervision and guidance in the Department of Polymer Science and Rubber Technology. No part of the work reported in this thesis has been presented for any other degree from any other institution.*

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20th March 2002

DECLARATION

I hereby declare that the thesis entitled ***"Synthesis, Characterisation and Uses of Polymer-bound Antioxidants"*** *is the original work carried out by me under the supervision of Dr. Rani Joseph, Professor, Department of Polymer Science and Rubber Technology, Kochi 682 022, and no part of this thesis has been presented for any other degree from any other institution.*

Sulekha

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20th March 2002

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PREFACE

We have entered the 21st century, rather the new millennium, with tremendous growth prospects in rubber industry. Vast internal market, rapid industrialisation, improved living standard of the masses and the availability of all types of raw materials from within the country and the emergence of IT revolution etc have paved the way for the phenomenal growth of the rubber industry. With this growth the need for longer service life of rubber goods has become a challenge. A new class of antioxidants namely polymer -bound antioxidants have shown great potential in this regard. This thesis is about the synthesis, characterisation and uses of novel polymer -bound antioxidants.

This thesis is divided into eight chapters as follows:

Chapter 1 presents a review of the literature in this field and the scope of the present investigation.

Chapter 2 deals with the materials used and the experimental procedures adopted for the study.

Chapter 3 is divided into four parts. Part I is concerned with the preparation and characterisation of polyisobutylene-bound paraphenylene diamine antioxidant. Part II deals with the preparation and characterisation of chlorinated paraffin-wax bound paraphenylene diamine antioxidant. Part III covers the preparation and characterisation of polyethylene glycol -bound paraphenylene diamine antioxidant. Part IV includes the preparation and characterisation of polyisobutylene-bound diphenylamine antioxidant.

Chapter 4 is divided into two parts. Part I deals with the efficiency of polyisobutylene-bound paraphenylene diamine and chlorinated paraffin wax-bound paraphenylene diamine antioxidants in NR, NR modified bitumen, SBR, IIR and NBR. Part II deals with the use of polyisobutylene-bound diphenylamine and polyethylene glycol-bound paraphenylenediamine antioxidants in NR.The accelerated ageing studies of these vulcanizates are also discussed in each part.

Chapter 5 is divided into two parts. Part I includes the preparation, characterisation and application of polyisobutylene -bound phenol in NR. Part II deals with the preparation, characterisation and application of 4-octadecyl phenol in NR.

Chapter 6 includes the ozone and flex crack resistance of NR, SBR, IIR and NBR vulcanizates and NR/BR and NR/SBR blends containing polymer -bound antioxidants in comparison with those with and without conventional antioxidant.

Chapter 7 deals with the effect of polyisobutylene-bound paraphenylene diamine and chlorinated paraffin wax -bound paraphenylene diamine antioxidants in NR/BR and NR/SBR blends in comparison with corresponding blends with and without antioxidant.

Summary and conclusions of the present investigation is described in the last chapter, **Chapter 8**.

At the end of each chapter a list of references has been given. A list of abbreviations used in this thesis is also cited.

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Chapter 1

INTRODUCTION

The technological performance of various types of rubber depends on their ability to withstand the effects of the service environment. The development of rubber for many modern uses would not have been possible without the discovery of chemicals to prevent their degradation during service.

The deterioration in the useful properties of rubber products with time is a serious problem involving the oxidation of polymers by the oxygen of the atmosphere.[1] Natural and synthetic polymers deteriorate on ageing in varying degrees as a result of the combination of a number of factors like heat, light, oxygen and ozone. The irreversible nature of the oxidative processes to which industrial polymers are subjected during high temperature processing and under aggressive conditions during service has intensified the search for improved stabilising systems. This has resulted in the development of antioxidants, antifatigue agents, melt stabilisers, uv-stabilisers and fire retardants.

1.1 Antioxidants - Historical Background

Natural rubber latex contains a small percentage of non-rubbery materials, which function as antioxidants. These materials effectively protect the rubber during coagulation and storage, but they are destroyed during the processing and curing operations.[2] Thus, it is not surprising that the earliest manufacturers of rubber products who knew nothing of oxidation, were plagued by the problem of deterioration. Hofman in 1861 was credited with being first to discover the oxygen absorption involved in this degradation, and the first patent, concerned with the use of phenol and cresol as antioxidants was issued by Murphy in 1870.[3]

Until about 1910 the materials chosen to reduce this oxidative degradation were natural products, such as coal tar resins, coumarone resins, paraffin, creosote and inorganic and organic reducing agents. The stability of the rubber product was not greatly improved when these additives were used.

The first antioxidants made their appearance in 1924 and slowly gained acceptance. Within a few years, their true value in rubber industry became apparent and the resulting search for new antioxidants led to the patenting of hundreds of materials. The first two widely used antioxidants were the reaction product of aniline and acetaldehyde and aldol naphthylamine. Hydroquinone and pyrogallol were patented in1901,[4] resorcinol and 2- naphthol in 1920,[5] 1- naphthol and aldehyde condensation products in1922,[6] and mercaptobenzimidazole in 1931.[7] In 1957, a new way to manufacture 2,6-di-*tert*-butylphenol in high yield and purity was discovered.[8] The attachment of methylene bridged groups to the *para* position of this phenol by condensation reactions with formaldehyde and acrylates led to the discovery and commercialisation of a number of new antioxidants. Currently, bound antioxidants are being developed to give maximum resistance to losses by extraction and volatilisation.

1.2 General Aspects of Polymer Degradation and Stabilisation

All hydrocarbons are vulnerable to deterioration caused by heat, light and oxygen. These polymers vary widely in their susceptibility to oxidative degradation. It is well-known that the relationship between polymer structure and ease of oxidation depends primarily on the relative C-H bond dissociation energies of the various polymers. Polymers with C-H bonds of low dissociation energies are more readily oxidised than polymers with higher C-H bond dissociation energies. Consequently, branching and unsaturation lower bond energies and increase the polymer's susceptibility to oxidation.[9] The amount of unsaturation present in a polymer is also important. The rubber with low olefinic content, such as EPDM(ethylene propylene diene terpolymer), is more resistant to oxidation than the highly unsaturated rubbers, such as SBR (styrene - butadiene rubber) and NR (natural rubber).[10]

The chemical structure of the polymer not only determines the rate of oxidation but also the physical changes that can occur during oxidation. Hardening of the polymer occurs when oxidative crosslinking pre-dominates in the degradation process. Most rubbers, such as SBR, NBR (nitrile-butadiene rubber) and BR (cis-polybutadiene) harden during oxidation, while rubbers derived from isoprene, such as NR, IR (cis-polyisoprene) and IIR(isobutylene isoprene rubber), soften on oxidation due to chain scission.[11] It is not surprising, then, that an antioxidant which affords excellent protection in one rubber is not the most effective stabiliser for another.

A broad distinction is generally made between materials, which can protect raw synthetic rubber, and those, which protect vulcanised rubber products. Synthetic rubbers are very susceptible to oxidation and must be protected with an antioxidant immediately after they are formed by polymerisation in order to prevent oxidative degradation during the high temperature drying step and during the subsequent storage.

Tyres account for the largest volume of antioxidants used each year,[12] they are primarily the amine staining antioxidants. A wide variety of light coloured vulcanised products are protected with non-staining antioxidants.

1.2.1 Mechanism of polymer oxidation

Oxidation of polymers can lead to chain scission, crosslinking or formation of oxygen containing functional groups in the polymer or its degradation products. In order to understand the antioxidant inhibition mechanisms, a brief outline of the oxidation process is given below.[13,14]

Initiation

$$RH + O_2 \longrightarrow R^{\cdot} + HO_2^{\cdot} \qquad (1)$$

$$AH + O_2 \longrightarrow A^{\cdot} + HO_2^{\cdot} \qquad (2)$$

$$R^{\cdot} + O_2 \longrightarrow ROO^{\cdot} \qquad (3)$$

Propagation

$$\mathrm{ROO^{\cdot} + RH \longrightarrow ROOH + R^{\cdot}} \qquad (4)$$

$$\mathrm{ROOH \longrightarrow RO^{\cdot} + OH^{\cdot}} \qquad (5)$$

$$\mathrm{ROOH + RH \longrightarrow RO^{\cdot} + R^{\cdot} + H_2O} \qquad (6)$$

$$\mathrm{2ROOH \longrightarrow RO^{\cdot} + ROO^{\cdot} + H_2O} \qquad (7)$$

Chain transfer

$$\mathrm{ROO^{\cdot} + AH \longrightarrow ROOH + A^{\cdot}} \qquad (8)$$

$$\mathrm{A^{\cdot} + RH \longrightarrow AH + R^{\cdot}} \qquad (9)$$

Termination

$$\mathrm{ROO^{\cdot} + RO^{\cdot}} \longrightarrow \text{stable products} \qquad (10)$$

$$\mathrm{ROO^{\cdot} + 2A^{\cdot}} \longrightarrow \text{stable products} \qquad (11)$$

$$\mathrm{A^{\cdot} + ROO^{\cdot}} \longrightarrow \text{stable products} \qquad (12)$$

Scheme1

RH = polymer molecule or portion thereof, AH = antioxidant, $A^{\cdot}$ =antioxidant radical, $RO_2^{\cdot}$ = polymer peroxy radical, and ROOH = polymer peroxide.

1.2.2 Basic classification of antioxidants

Rubber antidegradants included in this classification are divided into six classes as shown below.[15] The classification in general is based on chemical structure and application on rubber.

a) Class 1. p-Phenylene diamines (PPDs) - This group of additives represents the primary materials used in tyres and other mechanical goods to impart ozone protection. These additives are also used as antioxidants and antiflex agents in a number of applications but are considered to be strongly staining and thus limited to black rubber applications. They can also be used as raw polymer stabilisers.

b) Class 2. Trimethyl-diquinolines (TMQs) - These materials are primarily used to protect rubber articles from degradation by atmospheric oxygen at higher temperatures. They are moderately staining.

c) Class 3. Phenolics - Phenolic antidegradants represent a group of nonstaining and non discoloring additives used primarily in light colored mechanical goods and tyres. They can also be employed as raw polymer stabilisers. In general they are weaker antioxidants than amine types.

d) Class 4. Alkylated diphenylamines (DPAs) - This class of additives generally represents substituted amine antioxidants and it is used as raw polymer stabiliser in vulcanizate applications. These additives are moderately discoloring and staining.

e) Class 5. Aromatic phosphites - These are phosphorus containing fully non-staining, non-discoloring additives used as stabilzers for synthetic elastomers in 'white rubber' applications. They also have applications as peroxide decomposers and radical traps in polymer systems.

f) Class 6. Diphenylamine - ketone condensates - This group of additives is used primarily in carbon black loaded compounds to protect them against oxygen and heat deterioration.

1.2.3 Classification of antioxidants based on their mode of action

Two main groups of antioxidants are distinguished according to their mode of action: primary or chain breaking, and secondary or preventive antioxidants.

Chain breaking antioxidants

Chain breaking antioxidants interfere with the chain propagation steps of polymer oxidation. These antioxidants can terminate the kinetic chain by,

a) ***Free radical traps*** which interact with chain propagating $RO_2^{\cdot}$ radicals to form inactive products. Quinones and conjugated molecules (e.g. anthracene) can function as free radical traps.

b) ***Electron donors*** give electron to peroxy radical and thus stabilising the system.

c) ***Hydrogen donors*** are the most commonly used chain terminating antioxidants. Inhibitors of the aromatic amine (InH) type interfere with oxidative chain propagation by competing with the polymer for peroxy radicals:

$$InH + RO_2^{\cdot} \longrightarrow In^{\cdot} + ROOH \qquad (13)$$

Preventive antioxidants

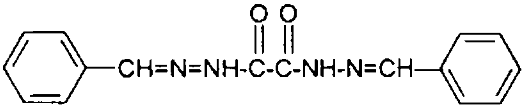
a) Light absorbers

Processes operative in environmental ageing of hydrocarbon polymers include transformations induced by light. Commonly used photostabilisers are hydroxybenzophenone derivatives, substituted benzotriazole derivatives, metal complexes of different ligands and different metals etc.

The oxidation mechanism developed by Bolland [13] to explain the thermal oxidation of rubber has been applied successfully to thermal oxidation of other substrates and also to photo-oxidation.

b) Metal deactivators

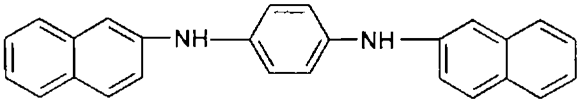
They are strong metal ion complexing agents that inhibit catalysed initiation. The most effective groups are polydentate chelating agents capable of forming very stable chelates in which all the co-ordination sites are occupied. Examples are oxalyl bis- benzylidene hydrazide (I), ethylene diamine tetra acetic acid(II), N,N^1-di--naphthyl-p-phenylene(III), $2,2^1$methylene-bis (4-methyl-6-tert-butylphenol) (IV).[15-16]



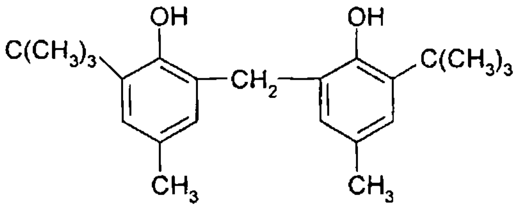
(I)

$$(HOOCH_2)_2N - CH_2 - CH_2 - N(CH_2COOH)_2$$

(II)



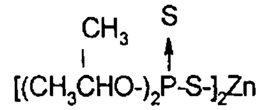
(III)



(IV)

c) Peroxide decomposers

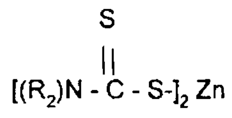
Peroxide decomposers have proved to be very important in rubber. The main requirement of compounds falling into this class is that they should substantially reduce hydroperoxides to alcohols without substantial formation of free radicals. Several organic sulphur compounds, including zinc dialkyl dithiophosphates (V) were found to decompose hydroperoxides and the mechanism of inhibition by the latter has been reviewed.[17]



$[(CH_3\overset{CH_3}{\overset{|}{C}}HO-)_2\overset{S}{\overset{\uparrow}{P}}-S-]_2Zn$

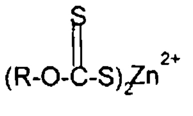
(V)

Compounds containing an imino group have also been found to be effective antioxidants. In certain cases peroxide decomposers decompose hydroperoxides through polar reactions, thereby inhibiting initiation. This class includes metallic salts of certain dithioacids such as zinc dithiocarbamates (VI), xanthates(VII), di-tert - butyl sulphide (VIII), tert-butyl thio sulphoxylic acid(IX).[18-20] etc.



$[(R_2)N-\overset{S}{\overset{\|}{C}}-S-]_2Zn$

(VI)



$(R-O-\overset{S}{\overset{\|}{C}}-S)_2Zn^{2+}$

(VII)

$(CH_3)_3C$ k S k $C(CH_3)_3$

(VIII)

$(CH_3)_3CSSOH$

(IX)

1.2.4 Important characteristics of antioxidants

There are a number of properties that antioxidants must possess besides good antioxidant activity if they are to be widely used in rubber applications. They should be inexpensive and should not interfere with the cure characteristics of the rubber. They should be non - toxic, non-fugitive, handy, compatible with the rubber and for certain applications, non-discolouring and non-staining.

Service requirements placed on finished rubber products demand improved polymer stabilization. The effectiveness of antioxidant depends on two factors.1) intrinsic activity of the antioxidant and 2) permanence of the antioxidant in the polymer.

1) Intrinsic activity of the antioxidant

This is the fundamental ability of the antioxidant and its transformation products to interfere with and retard the radical chain oxidation process, which in turn depend on the chemical structure of the antioxidant.

2) Permanence of the antioxidant in the polymer

The concentration of the antioxidant in a polymer decreases during long term use as a consequence of the following processes: (1) chemical loss of antioxidant and (2) physical loss of antioxidant from the polymers.[21, 22]

Chemical loss of antioxidant as a result of their mechanism of stabilization is summarised by Vink.[23] Physical loss of antioxidant mainly depends on (a) distribution of antioxidants in polymers, (b) compatibility of antioxidants in polymers, (c) volatility of antioxidants, (d) diffusion of antioxidants in polymers and (e) extractability of antioxidants from polymers.

(a) Distribution of antioxidants in polymers

In general, it may be assumed that the distribution of antioxidants is uniform in amorphous polymers where the antioxidants form micro heterogeneous phases uniformly dispersed in a polymer according to their compatibility with the polymer.[24] In semicrystalline polymers, the distribution of antioxidants is not uniform owing to the presence of crystalline and amorphous phases. The distribution of several types of low molecular weight compounds in different polymers was investigated by Billingham et al.[25] They also ascertained that the distribution of stabilisers in spherulitic polymers depended on the conditions of crystallisation and on the total amount of the atactic polymer concentrated at the boundaries of spherulites.

Irrespective of the problems of solubility and migration of the antioxidants, such distribution of antioxidants in polymers appears to be advantageous because the amorphous portion of most of the polymers is the region most sensitive to degradation. The uneven distribution of an antioxidant raises the concentration in the amorphous phase thus protecting it more effectively against degradation.

(b) Compatibility of antioxidants in polymers

One of the factors which affect the effectiveness and permanence of antioxidants in polymers is compatibility, which represents the totality of effects which are involved in the polymer additive interaction. If polymers are modified by antioxidants, a physical mixture characterised by certain degree of homogeneity or heterogeneity arises. The degree to which this occurs depends mainly on the cohesion and adhesion forces between the components and their bulk or surface interactions.

The theory of solutions of macromolecular substances[26] is most frequently applied to mixtures of polymers with low molecular weight substances or to polymer —polymer mixtures. This theory predicts that the compatibility of components in mixing may be approximately estimated from the squared difference of the values of solubility parameters of the components $(\Delta\delta)^2$. The solubility parameter δ represents the density of cohesion energy and is numerically equal to the potential energy of a unit volume of a material,

$$\delta = \frac{E}{V} = \frac{N_0 v}{V} \qquad \text{..............(14)}$$

where E is the potential energy, V is molar volume, N_0 is the Avogadro number and v is the potential energy of one molecule. The greatest difference between the solubility parameters of the polymer (δ_p) and the second component (δ_a) defines the critical value:

$$(\Delta\delta)_{max} = (\delta_p - \delta_a)_{max} \qquad \text{..............(15)}$$

If the experimental or calculated value of $(\Delta\delta)^2$ is less than the critical value $(\Delta\delta)^2_{max}$, the components are able to form a homogeneous mixture. If the value $(\Delta\delta)^2$ exceeds the maximum value, the formation of a heterogeneous mixture is to be expected.[27]

c) *Volatility of antioxidants*

One of the causes of the physical loss of stabilisers in polymers is their volatility which in turn is a manifestation of thermal motion of molecules on the surface of a sample. It is related to the heat of evaporation of antioxidant in the sense of the Clausius Clapeyron equation (16) and dependent on the interactions in the polymer - stabiliser system.

$$d \ln p / dT = \Delta H / RT^2 \qquad \text{..............(16)}$$

The solubility of an additive in a polymer is a thermodynamic equilibrium property of the additive polymer combination and the diffusion coefficient is a kinetic parameter defined for closely controlled conditions. In contrast, the rate of evaporation of an additive is a kinetic quantity which is sensitive to the conditions of measurement. Spacht et al.[28] measured the vapour pressures of a series of phenolic and amine antioxidants by a direct manometric measurement at temperatures above the melting points. Angert et al.[29] showed that the loss of amine antioxidant from a thick rubber sample follows the first order kinetics and concluded that the rate constant is related to the volatility of the pure additive. These authors showed that the presence of carbon black or chalk as fillers significantly reduces the loss rate although they did not interpret this result. The introduction of an amine or hydroxy group into the para position of diphenylamine reduces the volatility almost by an order of magnitude, the formation of intermolecular hydrogen bonds leads to an increase in intermolecular attraction forces and thus lead to volatility.[30]

(d) Diffusion of antioxidants in polymer

The diffusion of antioxidant in polymer does not itself produce any loss of antioxidant from the polymer. The diffusion processes play an important role in the evaporation and leaching of antioxidants from polymers. The diffusion of gases, solvents and hydrocarbons in rubber has been extensively studied.[31-33]The nature of the polymer and the size of the diffusant appear to be the main factors that govern the rate of diffusion.

In most cases, the method employed for diffusion coefficient determination is a radio isotope labelling technique[34]. The attempt to correlate the antioxidant diffusivity to rubber crosslink densities was done by N. C. Billingham et al.[31] Carlsson et al.[33] believe that the optimum stabilisation may be achieved by using a very low concentration of the antioxidant in the bulk of the polymer but a higher concentration in the surface layer. Nevertheless, evaporation of the low molecular weight antioxidants washing with water or organic solvents and mechanical abrasive wear of the surface layers in long term use results in an overall decrease in stabiliser content in the polymer and hence a decrease in its resistance to degradation.

(e) Extractability of antioxidants from polymers

Another factor causing the physical loss of antioxidants in polymers is extraction. This plays a part wherever the polymer articles come into contact with water or organic solvents. The extraction reduces the antioxidants in the polymers especially in the surface layers which are the most sensitive to degradation during ageing. The extractability can be estimated. (1) by determining the stabiliser concentration in the polymer after extraction,[34] (2) according to the content of antioxidant in the extraction medium[35-36] and (3) by comparing the stability of non-extracted and extracted samples.[37]

Cain et al.[38] have observed that diethylaniline bound to rubber, although less effective than its low molecular weight analogue, N-phenyl-N'-isopropyl-p-phenylene diamine becomes more effective with water at 100°C and its antioxidant activity does not decrease.

Leachability decreases with increasing molecular weight of the stabiliser. Another factor which influences extractability is the relation among the interactions of stabiliser, extraction medium and polymer.

Accelerated solvent extraction of antioxidants in linear low density polyethylene was studied by M. Waldeback et al.[39] A method for quantitative supercritical fluid extraction of Ethanox 330 antioxidant from high-density polyethylene was studied by A M Pinto et al.[40]

As a result of the above processes, the decrease in concentration of the antioxidants in polymers affects the resistance to degradation. Basically there are two approaches in increasing the persistence of an antioxidant:

(1) to produce antioxidant of high molecular weight.

(2) to chemically attach the antioxidant to a polymer, thereby guaranteeing its persistence in the final product i.e. polymer-bound antioxidants.

1.2.5 Mechanism of antioxidant action

Oxidation inhibition processes have been classified into two main types: kinetic chain-breaking processes and initiation prevention mechanisms. The first type embraces the traditional rubber antioxidants, the aromatic amines and phenols, and the second includes the hydroperoxide decomposers, the transition metal deactivators and u.v. stabilisers acting by the light absorption mechanism.

Chain-Breaking (CB) mechanism

This was the first antioxidant mechanism to be investigated in detail.[41] The free radical oxidation chain reaction indicates two ways in which the chain might be interrupted. These may be summarised in scheme 2.

Scheme.2

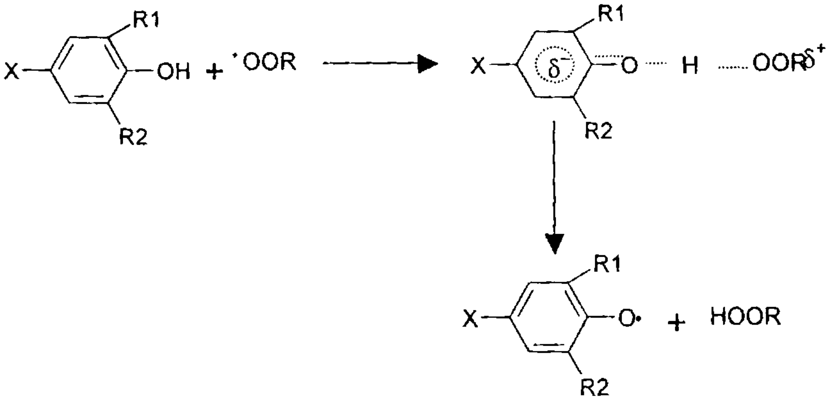
Chain-Breaking Donor Mechanism (CB-D)

Chain breaking antioxidants act according to the following general reaction.

$$AH + RO_2^{\cdot} \longrightarrow A^{\cdot} + ROOH$$

where AH is the antioxidant. The chain breaking antioxidants are frequently called as primary antioxidants. The geometry of the reaction is influenced by the steric environment of the reaction site of the antioxidant (OH or NH).[42-44] From a sterically hindered 'AH', H is transferred in a direction perpendicular to the plane of the aromatic ring. If at least one ortho substituent is not very bulky, the process is most likely a coplanar one, a longer life may be assumed for the resulting transition state.[45-46] Depending on the nature of the AH, the radical A$^\cdot$ may be either phenoxyl or amino radical. Transformation products of phenoxy and amino radical are summarised by Pospisil.[47]

Both amine type and phenolic type antioxidants can donate hydrogen to an alkylperoxy radical. The effects of substituent groups in the aromatic rings is to reduce the energy of the transition state (II) which involves electron delocalisation in the aromatic ring (scheme3).

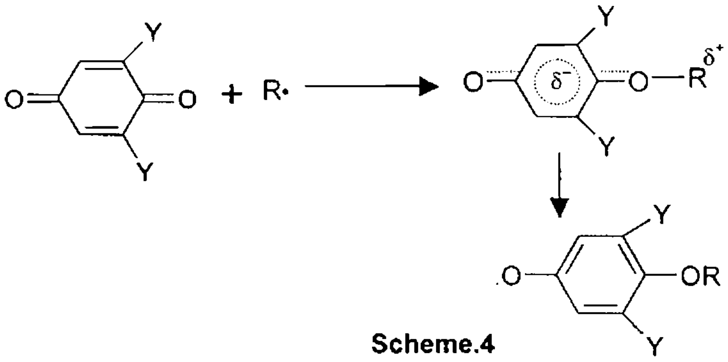


Scheme. 3

The products formed by further reaction of the initially formed phenoxyl radical are complex and may have either antioxidant or pro-oxidant activity.[48]

Chain - Breaking (Acceptor) Mechanism (CB- A)

Macro-alkyl radicals, unlike alkylperoxyl radicals, are not powerful oxidising agents, but they are themselves readily oxidised by electron acceptors. A variety of oxidising agents are capable of removing alkyl radicals from an auto-oxidising system and if they are able to do this in competition with alkylperoxyl radicals, they have antioxidant activity.[49] In general, the molecular requirements for a CB-A antioxidants are the same as for polymerisation inhibitors. This class includes quinones, nitro compounds and stable free radicals of which nitroxyls[50] and phenoxyls[51] have been most studied.



Scheme.4

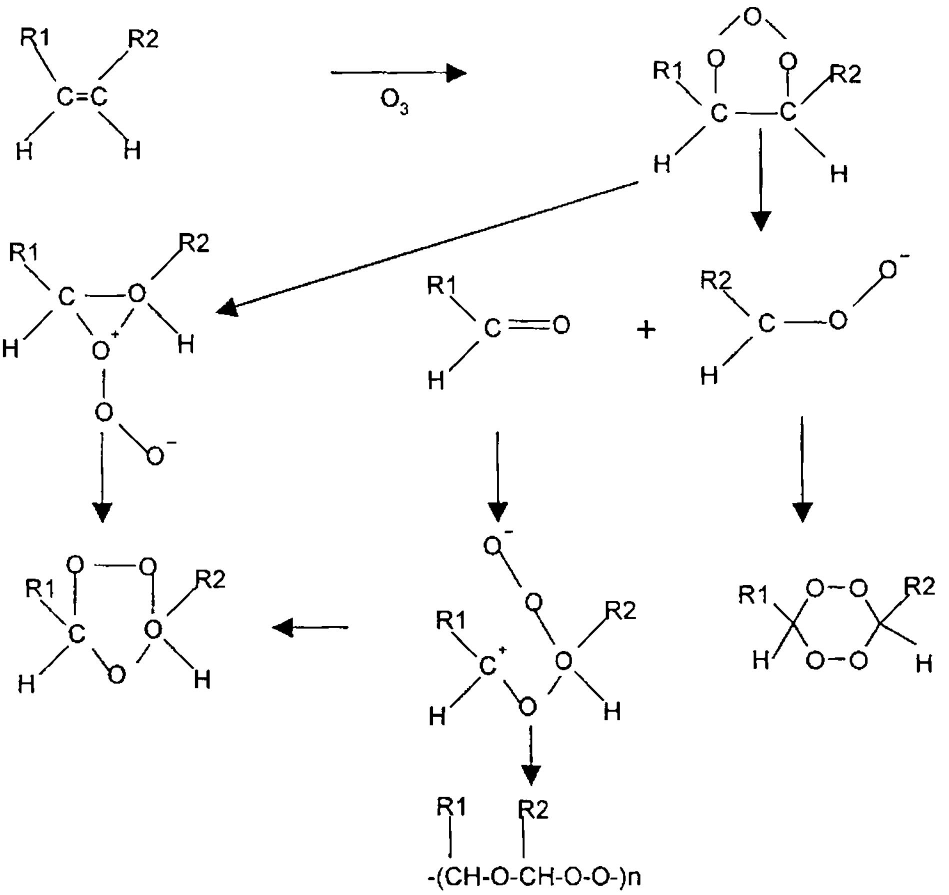
1.3 Polymer Degradation Caused by Ozone

Ozone, a degradant of vulcanized rubber, occurs naturally and is formed in the earth's stratophere by the action of sun's ultraviolet light on atmospheric oxygen. Even though ozone is only present in the atmosphere at concentrations normally in the range 0-7pphm[52] it can severely attack non-resistant rubbers when these are in strain. The interaction of rubber with ozone during the process of fatigue is the most destructive and dangerous mode of ageing. Ozone directly destroys the surface of rubber. The use of antiozonants is an effective means of protecting stressed rubber against surface cracking.

1.3.1 The mechanism of ozone attack on elastomers

The unsaturation in diene based elastomers accounts for their high sensitivity to ozone attack. Ozone causes cracking of stressed or flexed vulcanized rubber as a result of chain scission and formation of polymeric peroxide.

Ozonation may be interpreted as shown in scheme 5.[53-55]



Scheme. 5

1.3.2 Theories of antiozonant action

The process of ozone ageing of vulcanizates is extremely complicated and no simple model approach to the explanation of protection against O_3 attack can explain all the important factors involved. The simplest mechanism involves diffusion of antiozonant into the rubber surface and preferential reaction with O_3.[56-59] The rubber matrix therefore remains protected until all the antiozonant in the rubber is depleted.

Essentially three theories of antiozonant action have been developed:

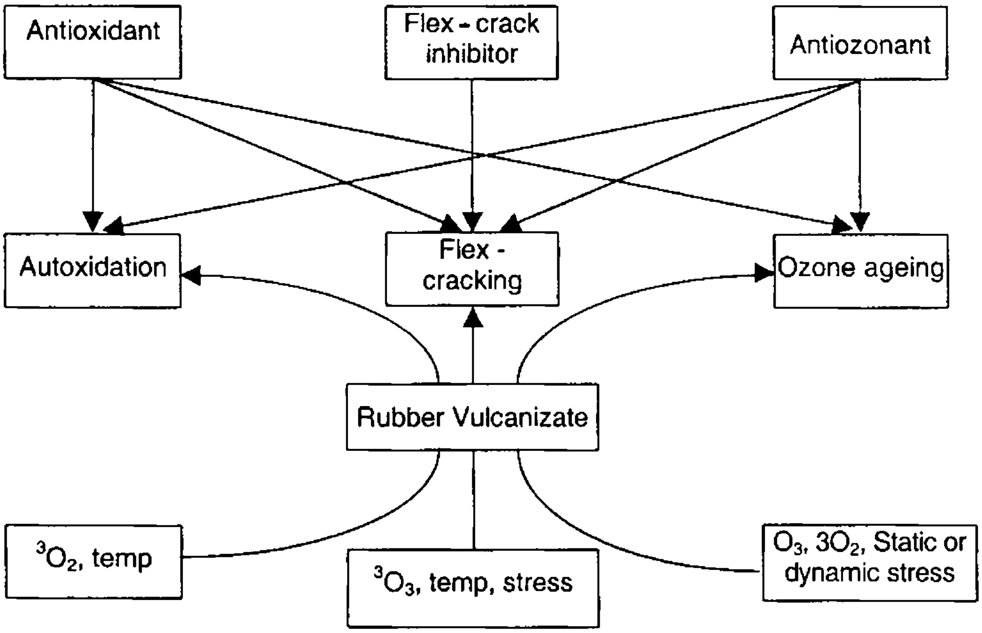
(1) The antiozonant blooms to the surface and preferentially reacts with the ozone so that the rubber is not attacked until the antiozonant is exhausted and reacts preferentially with the incident ozone (Ozone scavenging).

(2) The antiozonant blooms to the surface of the rubber and forms a protective film on the surface.

(3) The antiozonant reacts with the intermediates formed in the ozonation of rubber preventing chain scission or rubber chain relinking.

The antiozonant efficiency is dependent on the rate of reaction of antiozonant with O_3, on the initial antiozonant concentration in the rubber surface and on the rate of diffusion of fresh antiozonant on the outer surface. The antiozonant effect was found to increase with the initial surface concentration of antiozonant[60] and the reaction rate was reported to be related to antiozonant efficiency.[61]

The schematic representation (scheme.6) of involvement of antioxidants in different aspects of rubber degradation mechanism is given below:



Scheme. 6

1.4 Use of Antioxidants in Elastomer Blends

Owing to economic and technical uncertainties associated with synthesizing polymeric materials, the utilization of polymer blends to achieve a desired combination of properties has obvious attraction. Blending of two or more rubbers is carried out for improvement in technical properties, better processing and to lower compound cost.

Many products in rubber industry are based on blends in all or part of their construction. Tyres are typical examples of products in large-scale volume production. The introduction of cis- 1,4 - polybutadiene [butadiene rubber (BR)] during the late 1950s is probably the single most important development relating to the use of elastomer blends in tyres. Blends of NR with BR has enabled significantly improved tread wear and groove cracking resistance without reduction in resilience.[62] Better oil extension and higher black loadings are additional benefits made possible by the development of BR, along with less dependence on the availability of NR.

Evstratov et al[63] evaluated the tread wear performance of NR/BR and NR/SBR blends under different road conditions. Under test conditions with considerable breaking and turning, the wear advantage of treads containing BR was found to increase. Milner and Windibank[64] showed that the state of degradation of NR is reduced in blends with BR. Corish[65]reviewed different aspects of elastomer blends. A. K. Bhowmick and S. K. De[66] studied the effects of curing temperature and curing system on structure property relations of NR/BR, NR/SBR and NR/SBR/BR blends.

Rubber blends used in industrial products have a complex and multifunctional nature. Vulcanizate properties can be optimised by proper selection of rubber types, including viscosity considerations and by control of the distribution of insoluble and soluble compounding ingredients, the latter with particular emphasis on achieving good 'infra'- and, 'inter'-phase crosslinking.[67]

Even though elastomer blends have been in use for several decades, a clear understanding of their rheological and physical properties in relation to the properties of constituents and morphology is still limited.[68] Physical properties of cured polymer blends are generally inferior to those predicted from the properties of the component polymers. This behaviour is especially seen in the cured blends of dissimilar polymers having large differences in polarity and unsaturation. In polymer blends of similar polarity and unsaturation, the cured blends exhibit additive properties and so-called covulcanized state is realized.[69]

A major cause for the inferior properties exhibited by the cured elastomer blends is that its constituents are incompatible on the molecular scale and exist in the form of separate phases.[70] It is found that the mechanical properties of elastomers depend very strongly on crosslinks density.[71] Practical information regarding processing and vulcanization of NR/SBR blends was reported by Springer.[72] Mastication of NR[73] is necessary prior to blending with SBR. Shundo[74]has compared the use of roll mill and Banbury mixer for the preparation of NR/SBR blends and found that mill mixing furnishes more uniform compounds.

1.5 Polymer-Bound Antioxidants

The antioxidant action depends mainly on three factors. The first is the intrinsic activity of the antioxidant itself. This is the fundamental ability of the antioxidant or its transformation products to interfere with and retard the radical chain oxidation process. The second factor is the compatibility or solubility of the antioxidant in the polymer matrix. Polarity changes will result in aggregation of the stabiliser, insolubility in the matrix, spewing or blooming of the material, or preferential absorption on the filler. All these factors result in the stabiliser not being present uniformly in the polymer.

The third factor is the volatility or fugitive nature of the antioxidant. Losses due to extraction or volatility immediately affect the ultimate performance of the final product. Of the three factors, the third factor is the most important, since it affects the antioxidant's persistence directly. Basically, there are two approaches for increasing the persistence of an antioxidant. One is to produce antioxidants of high molecular weight and therefore, of low volatility or extractability. The other is to chemically bind the antioxidant to the polymer i.e. polymer-bound antioxidant, thereby guaranteeing its persistence in the final product.

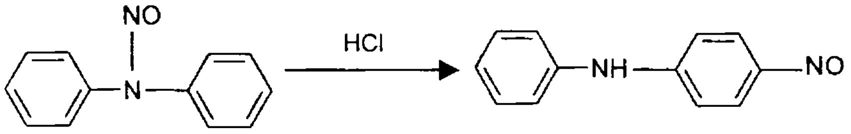
One of the more exciting areas of research during the past decade was the preparation of polymer-bound antioxidant systems. The advantages of bound antioxidants in oil and fuel resistant nitrile rubber have been well documented.[75]

Considerable effort has been expended in the preparation and utilisation of phenolic antioxidants which have pendant unsaturated groups. The utility of such a system was demonstrated by Davy and Williams,[76] who co-vulcanised 2-allyl - 4 - alkoxy - phenols into natural and synthetic rubber recipes. Excellent nonstaining and anti-flex properties were claimed for the vulcanizates.

The preparation of nitrile rubber containing copolymerized N- (4-anilinophenyl) methacrylamide was reported by Meyer and coworkers.[77] Several polymerisable amine and phenolic antioxidants were discussed in the literature.[78-86]

Most versatile method of polymer modification is the direct introduction of an antioxidant function by the reaction of a conventional polymer with a suitable reactive adduct. The advantages of such modification are numerous. These include a multiplicity of polymer choices, a choice on ultimate level of stabiliser loading and the introduction of the stabiliser in a separate step from the production process. An existing commercial polymer is modified inexpensively by a chemical reaction with a polymer reactive antioxidant.

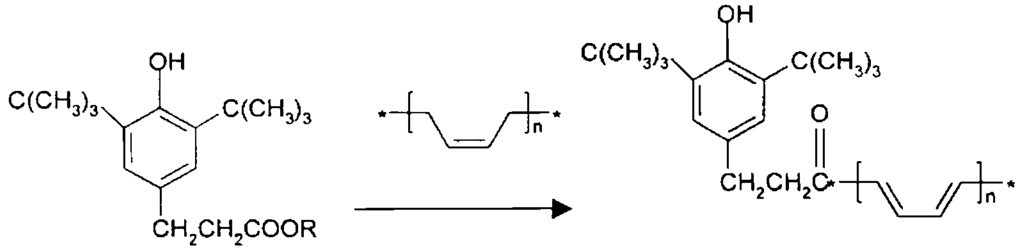
Cain and co workers[87] found that "ene" addition of nitroso phenols or aniline derivatives produce polymer-bound stabilisers. A commercial preparation of *p*-nitrosodiphenylamine by hydrochloric acid catalysed rearrangement of the N-nitrosodiphenylamine was described by Levy and Seif[88] (Scheme.7).



Scheme.7

The preparation of polymer-bound antioxidants by 1,3 - Saltman first described cycloaddition reaction and Auerbach.[89] They prepared a series of compounds related in structure to 1-(3,5-di-t-butyl-4-hydroxophenyl)-N-phenyl-nitrone. This material was found to add readily to unsaturated polymers to provide a bound antioxidant.

One novel process for introducing bound antioxidants was described by Farrar[90] Living polymers, produced by lithium-catalysed polymerisation of diene monomers were reacted with a variety of commercial antioxidants, which contained ester functionality. Presumably, the polymer behaves as a normal alkyl lithium reagent, which adds to the carbonyl function. Neutralisation produces the bound antioxidants as a ketone (scheme. 8).



Scheme.8

Although synergism between sulphur compounds such as thiodipropionates and chain breaking antioxidants is well- known and reasonably well understood in polyolefin and in certain non vulcanized rubbers, the synergistic effect is generally not noted in vulcanised rubber.[91-92] Shelton has attributed this lack of synergism as possibly being due to a masking effect from the presence of other sulphur compounds present in the vulcanizate such as crosslinks and vulcanization fragments.[93] Other explanations centre on antagonism between the synergist and the curative system, other antioxidants or fillers. This antagonism leads to synergist destruction, trapping, or absorption.

An additional example of a system which binds into the polymer during cure was described by Dhami.[94] This material is 2-mercapto-3-allyl-3,4 dihydroquinazoline-4-one. Oxidation-resistant polymers were produced, but no explanation was given as to its method of attachment.

Gregory prepared polymer-bound phenolic antioxidants by alkylation of various alkylated phenols by a variety of polydiene rubbers.[95-96] M. S. Al-Mehadawe et al described the preparation of polymer-bound antioxidants by direct hot melt mixing of chlorine containing polymers and a commercial antioxidant.[97]

Scott et al have demonstrated that simple hindered phenols which contain a methyl group in the ortho or para position can react with natural rubber in the presence of oxidising free radicals to yield polymer-bound antioxidants.[98] Antioxidants like styrenated phenol, diphenylamine etc bound to hydroxy terminated liquid natural rubber by modified Friedel Craft's reaction were also found to be effective in improving ageing resistance.[99] Natural rubber bound diphenylamine antioxidants were reported by Avirah and Joseph.[100] Synthesis of new polymeric antioxidants were reported in recent literature.[101-103]

1.6 Scope and Objectives of the Present Work

Even though polymer-bound antioxidants are advantageous in maintaining their permanence in rubber, they have a serious disadvantage of low mobility especially when they are network-bound[104]. Since such bound antioxidant cannot bloom to the surface readily ozone attack cannot be effectively controlled. Most of the polymer-bound antioxidants reported in literature have an unsaturated backbone. So during the process of vulcanisation their backbone gets attached to the main chain through sulphur cross-linking and they lose their mobility still further.[106] The primary aim of this work has been to overcome this defect by preparing polymer-bound antioxidants with saturated backbone. The work envisages the preparation of both amine and phenolic type of antioxidants. The efficiency of such polymer-bound antioxidants is compared with that of conventional antioxidants in terms of volatility, extractability in solvents, ageing resistance etc. The study is undertaken with the intention of generating a class of bound antioxidants, which can be used in elastomers for aggressive and long-term application.

One of the potential areas where the novel polymer-bound antioxidants can be used is in the rubberisation of roads. The use of NR in road tarring will reduce the maintenance cost of roads and ensure a "smooth ride", and would lead to better highways with longer life. Further more natural rubber sector has been facing the problem of low prices over the last five years primarily due to low demand in domestic and global markets. Thus rubberisation of roads will lead to increased consumption of NR and it will be a great help to rubber plantation sector. One of the main disadvantages of using natural rubber in bitumen modification is that it cannot withstand the high temperature during mixing and hence it is susceptible to degradation. Most of the conventional antioxidants are volatile and are not effective in protecting rubber under such adverse conditions. The use of the novel polymer-bound antioxidant is one proposed to be evaluated in a typical application such as bitumen modification.

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

1. To prepare novel cost effective polymer-bound antioxidants with saturated backbone.
2. To characterise the prepared antioxidants using IR, ^{1}HNMR, VPO and TGA.
3. To study the effectiveness of these antioxidants in NR, SBR, NBR and IIR and to compare the volatility and extractability of these antioxidants with those of conventional antioxidants.
4. To evaluate the ozone ageing resistance of these antioxidants in comparison with conventional antioxidant.
5. To study the effectiveness of these antioxidants in rubber blends like NR/SBR and NR/BR.
6. To study the effect of novel polymer-bound antioxidant in NR modified bitumen for road rubberisation.

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Chapter 2

EXPERIMENTAL TECHNIQUES

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

2.1 Materials Used

2.1.1 Elastomers

a) Natural rubber (NR)

ISNR-5 was supplied by the Rubber Research Institute of India, Kottayam and had a Mooney viscosity [ML (1+4), at 100°C] of 82.

b) Acrylonitrile-butadiene rubber (NBR)

Acrylonitrile-butadiene rubber was obtained from Apar Polymers Ltd., India. Grade N553 with 33% acrylonitrile content and Mooney viscosity [ML (1+4), at 100°C] of 45.

c) Styrene-butadiene rubber (SBR)

Styrene-butadiene rubber (SBR, 1502) was obtained from Korea Kumho Co. Ltd. and had a Mooney viscosity [ML (1+4), at 100°C] of 45.

d) Isobutylene-isoprene rubber (IIR).

Isobutene - Isoprene rubber (IIR, Exon: 301) was supplied by polysar, Canada and had a Mooney viscosity [ML (1+4), at 100°C] of 50.

e) Chloroprene rubber (CR)

Chloroprene rubber (CR) was supplied by Distugil, Paris and had a Mooney viscosity [ML (1+4), at100°C] of 45.

f) Polybutadiene (BR)

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

g) Natural rubber latex

Natural rubber latex (centrifuged) was obtained from Rubber Research Institute of India, Kottayam conforming to the specifications of the Bureau of Indian Standards (BIS 5430 -1981).

2.1.2 Antioxidants

a) Pilflex-13

Commercial antioxidant pilflex-13 [N-(1,3-dimethyl butyl) N^1- phenyl-p-phenylenediamine], was obtained from Polyolefin Industries Ltd., India.

b) Accinox TQ

Polymerised 1,2 dihydro 2,2,4-trimethyl quinoline was supplied by ICI India Ltd. West Bengal, Melting point 78-90°C.

c) Vulkanox 4020

Vulkanox 4020 [N-(1,3-dimethyl butyl)-N^1- phenyl- p- phenylenediamine], was obtained from Bayer India Ltd.

d) Accinox DN

Phenyl- β-napthylamine was supplied by ICI India Ltd. West Bengal. It had a melting point of 105°C.

e) Vulkanox SP

Commercial phenolic type antioxidant vulkanox SP (Mixture of styrenated phenols) was obtained from Bayer India Ltd.

f) Phenol

S.D. Fine Chemicals, India, supplied phenol. It had a melting point of 41°C.

g) 2,6 di-t-butyl-4-methyl phenol

2,6 di-t-butyl-4-methyl phenol was supplied by BDH laboratories India Ltd.

h) Diphenylamine

Diphenylamine was supplied by BDH Laboratories India Ltd. The melting point of the sample was 54°C.

i) Paraphenylenediamine

Paraphenylenediamine used in the study was supplied by CDH Laboratories Ltd., India and a melting point of 141°C.

2.1.3 Catalysts

a) Anhydrous zinc chloride (An.ZnCl$_2$)

Anhydrous zinc chloride was obtained from Ranbaxy Laboratories. It had a melting point of 290°C.

b) Anhydrous aluminium chloride (An.$AlCl_3$)

Anhydrous aluminium chloride used was white powder obtained from Qualigens Fine Chemicals, India.

2.1.4 Fillers

a) High abrasion furnace black (HAF, N330)

High abrasion furnace black (HAF, N 330) used in these experiments was supplied by M/s. Philips Carbon, Kochi (India) Ltd. It had the following specifications:

DBP absorption	102 ± 5 cc/ 100g
Iodine number	82

b) Precipitated Silica

Precipitated silica used in this study was GSL-150 Grade obtained from Gujarat.

2.1.5 Compounding Additives

a) Zinc oxide

Zinc oxide (ZnO) was supplied by M/s. Meta Zinc Ltd. Mumbai. It had the following specifications: zinc oxide content - 98%, acidity-0.4% max., heat loss (2h at 100°C) - 0.5% max.

b) Stearic Acid

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

Melting point-50-69°C, acid number-185-210, iodine number-9.5 max., specific gravity 0.85 ± 0.01, ash - 0.1 % mass.

c) Mercaptobenzthiazole (MBT)

Mercaptobenzthiazole having the following specifications was supplied by Bayer Chemicals, Mumbai with melting point - 160-180°C.

d) Dibenzthiazyl Disulphide (MBTS)

Dibenzthiazyl disulphide was supplied by Bayer Chemicals, Mumbai. It had a melting point of 165°C.

e) Tetramethyl Thiuram Disulphide (TMTD)

Tetramethyl thiuram disulphide used was supplied by polyolefins industries Ltd., Mumbai. It had a melting point of 136°C.

f) Benzthiazyl 2- Sulphenmorpholide (MOZ)

Benzthiazyl 2- sulphenmorpholide (MOZ) was supplied by ICI Ltd., India.

g) 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.

h) Napthenic Oil

It was supplied by M/s.Hindustan Petroleum Ltd. India. It had the following specifications:

Viscosity gravity constant (VGC) - 0.85 - 0.9
Aniline point - 75°C

i) Paraffinic Oil

M/s. Hindustan Petroleum Ltd., India, supplied paraffinic oil. It had the following specifications:

Viscosity gravity constant (VGC) - 0.85
Aniline point - 96°C.

j) Dioctyl Phthalate (DOP)

Dioctyl Phthalate used was commercial grade supplied by Rubo - Synth Impex Pvt. Ltd., Mumbai. The viscosity of the sample was 60 mPa.s.

k) Sulphur

Sulphur was supplied by Standard Chemical Company (Pvt.) Ltd., Madras, and had the following specifications: acidity 0.01 % max., ash 0.01 % max., solubility in CS_2 - 98 % max.

l) PF resin

Phenol formaldehyde resin supplied by Bakelite Hylam. Hyderabad. The used grade was 6417 having the following specifications:

Softening point	88-102°C
Methylol group	14-16 %

2.1.6 Other Additives

a) Bitumen

Bitumen with penetration 80/100 was supplied by Cochin Refineries Ltd., Ambalamugal.

b) Chlorinated paraffin wax (CPW)

Chlorinated paraffin wax was supplied by KLJ Organic Ltd., Gujarat, India.

Sp. gravity	1.280
Chlorine content	51.5%
Viscosity	159 mPa.s

c) Polyethylene glycol - 600

Polyethylene glycol - 600 with molecular weight range 570-630 was supplied BDH Laboratories India Ltd.

Specific gravity	1.128
Viscosity	105 mPa.s

d) Polyisobutene (PIB-24)

Polyisobutylene(PIB) with molecular weight 934 was supplied by Cochin Refineries, Balmer Lawrie Ltd., Ambalamugal, Kerala.

Viscosity	248 mPa.s
Moecular weight	930

Sodium carbonate, sodium hydroxide, sodium thiocyanate, sodium thiosulphate, sodium peroxide, potassium carbonate, potassium chromate, potassium iodide, potassium dichromate, starch, silver nitrate, dil. nitric acid, ferric alum, fused calcium chloride, thionyl chloride used were analytical grade.

2.1.7 Solvents

Dioxan, toluene, carbon tetrachloride, methanol, tri ethyl amine, carbon disulphide acetone, iodine monochloride, aniline,2-butanone were of analytical grade.

2.2 Experimental Methods

2.2.1 Charaterisation methods

a) Infrared spectroscopy (IR)

IR spectra were taken on Perkin - Elmer Model 377 IR spectrometer.

b) Proton magnetic resonance spectroscopy (^1H NMR)

The ^{1}H-NMR measurements were carried out using a JEOL-JNM spectrometer and the spectra were measured at 20°C using 10 % solution in $CDCl_3$ with tetramethylsilane as the internal standard.

c) Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was carried out using Shimadzu and Du pont (1080) TG-DSC standard model at a heating rate of 10°C per minute.

d) Thin layer chromatography (TLC)

Thin layer chromatography was done using silica gel as the adsorbent (supplied by E.Merck). Eluent - detector system was selected according to the characteristics of the particular product.

e) Optical microscopic analysis

Carl Zeiss optical microscopic model Stemi 2000C with 2.5 magnification was used to take the photographs of the ozone cracked samples.

f) Vapour phase osmometry (VPO)

Molecular weights of the samples were determined by VPO method using Knauer Vapour Phase Osmometer. The principle is the Raoult's law i.e. the lowering of the vapour pressure of a solvent by a solute is proportional to the mole fraction of the solute.

g) Determination of Iodine Value

The iodine value[1] is determined as follows 0.2g of sample was dissolved in 25 ml of CCl_4 in an iodine flask. 20 ml of 0.1N solution of iodinemonochloride in glacial acetic acid was added. It was stoppered and allowed to stand in darkness for 30 minutes. After that 100 ml 10% potassium iodide solution was added. The resultant 2 phase solution was titrated against thiosulphate using starch as indicator. A blank was run separately. Iodine value was calculated as,

$$\text{Iodine value} = \frac{(v_1 - v_2)\ 12.69\ N}{m}$$

Where v_1 and v_2 - the volumes (ml) of 0.1N sodium thiosulphate used for titration of the sample and the blank respectively, N- normality of sodium thiosulphate and m- weight of the polymer sample in g.

h) Determination of chlorine content

A mixture of Na_2CO_3, K_2CO_3 and Na_2O_2 in the ratio 1: 1: 0.2 was prepared. About 5g of above mixture was used to cover the sample taken in a platinum crucible. Weight of the sample taken was in the range 0.1-0.3 g. The platinum crucible was kept in a muffle furnace at 900°C for 4h.

After 4h the crucible was taken out, cooled and placed in a beaker and 150ml water added. The contents were heated until the fusion mixture dissolves in water. Added conc. HNO_3 drop wise to neutralise the solution. Then added excess and boiled off. 35ml of $AgNO_3$ (0.1N)solution was added and the precipitate was filtered off. The filtrate was titrated with 0.1 N NaSCN. $AgNO_3$ was standardised with NaCl using K_2CrO_4 indicator. Similarly a blank was also done. Chlorine content was calculated using the following equation.

$$\text{Chlorine content} = \frac{(\text{Blank} - \text{sample volume})\ N \times 35.5 \times 100}{W \times 1000}$$

N - Normality of NaSCN

W - Weight of the sample.

i) Determination of chemical crosslink density

The chemical crosslinks was estimated from the equilibrium swelling data. Samples of approximately 1cm diameter, 0.20 cm thickness were punched out from the central portion of the vulcanizate, accurately weighed and allowed to swell in excess solvent. In the vulcanizates 'without antioxidant' swelling is done in the solvent containing 0.1% accinox DN. The swollen samples were taken out of the solvent after 24h and weighed. Samples were dried in vacuum oven and samples weighed again.

The volume fraction of rubber (Vr) in the swollen network was then calculated by the method reported by Ellis and Welding from the following equation.[2]

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

where,

T - weight of the specimen

D - Deswollen weight of the specimen

F - weight fraction of insoluble components

A_0 - weight of the absorbed solvent corrected for the swelling increment

ρ_r - density of rubber

ρ_s - density of solvent.

The value for ρ_r and ρ_s taken were,

ρ_r NR - 0.921 g/cm^3

ρ_r SBR - 0.94 g/cm^3

ρ_r NBR - 1.0118 g/cm^3

ρ_r IIR - 0.917 g/cm^3

ρ_r BR - 0.93 g/cm^3

ρ_s Toluene - 0.886 g/cm^3

ρ_s Methyl ethyl ketone - 0.804 g/cm^3

In the case of vulcanizates containing HAF black the value of V_r obtained as above, was converted into V_{ro}, by means of the following equation, which was derived by Porter.[3-7]

$$\frac{V_{ro}}{V_r} = 0.56 \times e^{-z} + 0.44$$

where z - weight fraction of filler.

The crosslink density $\frac{1}{2M_c}$ was determined from V_{ro} using the Flory - Rehner Equation[7,8]

$$\frac{1}{2M_c} = \frac{-\ln(1 - V_{ro}) + V_{ro} + \chi V^2_{ro}}{2\, \rho_r V_s (V_{ro})^{1/3}}$$

where,

V_s - molar volume of solvent

V_s (toluene) - 106.2 cc/mol

V_s (methyl ethyl ketone) - 89.5 cc/mol

and χ - parameter characteristic of interaction between rubber and solvent. Values of parameter χ taken for calculations were the following:

For NR - toluene - 0.39

SBR - toluene - 0.32

IIR - toluene - 0.56

BR - toluene - 0.34

NBR - Methyl ethyl ketone - 0.21

For NR/SBR and NR/SBR blends, χ was found to vary linearly with composition.[8] Hence average value of χ was taken for 70/30 blends of these polymers.

2.2.2 Mixing and homogenization using mixing mill

Mixing and homogenization of elastomers and compounding ingredients were done on a laboratory size (15 ×33 cm) two roll mill at a friction ratio of 1:1.25. The elastomer was given one pass through the nip (0.002 × 100)". Then it was given two passes through the nip (0.002×10)" and allowed to band at the nip of (0.002 × 55)". The temperature of the rolls was maintained at 70±5°C during mastication. After the nerve had disappeared, the compounding ingredients were added as per ASTM D 3184 (1980) and ASTM (1982) in the following order: activators, fillers, accelerators and curing agents. The batch was thoroughly cooled before the addition of accelerator and sulphur.

After complete mixing, the compound was homogenised by passing six times endwise through tight nip of 0.8mm and finally sheeted out at a nip gap of 3mm by passing the stock through the rolls four times folding it back on itself each time.

2.2.3 Determination of cure characteristics

The cure characteristics of the elastomers were determined using a Göttfert elastograph model 67.85. It is a microprocessor controlled rotorless cure meter with a quick temperature control mechanism and well defined homogeneous temperature distribution in the die or test chamber. In this instrument, a specimen of definite size is kept in the lower half of the cavity which is oscillated through a small deformation angle (±0.2). The frequency is 50 oscillations per minute. The torque is measured on the lower oscillating die half. Atypical elastograph cure curve is shown in Fig.2.1 and the following data can be taken from the torque time curve.

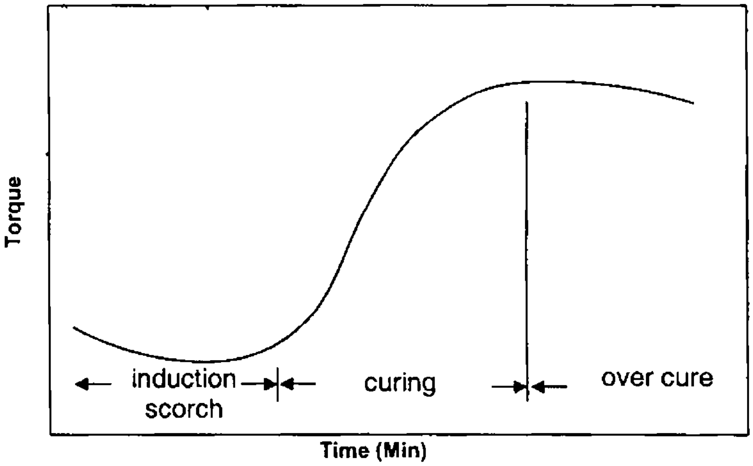

Fig.2.1

(i) Minimum torque: Torque shown by the mix at the test temperature before the onset of cure.

(ii) Maximum torque: This is the maximum torque recorded.

(iii) Scorch time (t_{10}) : This is the time taken for attaining 10%of the maximum torque.

(iv) Optimum cure time(t_{90}):This is the time taken for attaining 90% of the maximum torque.

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

2.2.4 Moulding of test specimens

The test specimens were prepared in standard moulds by compression moulding on a single day light, electrically heated press having 30×30 cm platens at a pressure of 200 kg/cm^2 on the mould. The rubber compounds were vulcanised up to their respective optimum cure times at 150°C unless otherwise specified. Mouldings were cooled quickly in water at the end of the curing cycle and stored in a cold and dark place for 24h and were used for subsequent physical tests. For samples having thickness more than 6 mm (compression set, abrasion resistance etc.) additional curing time based on the sample thickness was given to obtain satisfactory mouldings.

2.2.5 Physical test methods

a) Tensile stress-strain behaviour

Tensile properties of elastomers were determined according to ASTM D 412-98 using dumbbell specimens on a Zwick universal testing machine model 1445. All the tests were carried out at 28°C. 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, the upper of which was fixed. The rate of separation of the power actuated lower grip was fixed at 500 mm/min. for elastomeric specimens. The tensile strength, elongation at break and modulus were evaluated and printed out after each measurement by the microprocessor.

b) Tear resistance

This test was carried out as per ASTM D 624 -98 using unnicked 90° angled test pieces. The samples were cut from the compression moulded sheets parallel to the mill grain direction. The test was carried out on Zwick universal testing machine. The speed of extension was 500 mm/min and the test temperature 28 ± 2°C.

c) Hardness

The hardness (shore A) of the moulded samples was tested using Zwick 3115 hardness tester in accordance with ASTM D 2240-97. The tests were performed on a mechanically unstressed sample of 300mm diameter and minimum 6mm thickness. A load of 12.5N was applied and the readings were taken after 10 seconds of indentation after firm contact has been established with the specimens.

d) Compression set

The samples (6.25mm thick and 18 mm diameter) in duplicate, compressed to constant deflection (25%) were kept for 22h in air oven at 70°C. After the heating period, the samples were taken out, cooled at room temperature for half an hour and the final thickness was measured. The compression set was calculated as follows:

$$\text{Compression set } \% = \frac{(t_0 \; j \; t_1)}{(t_0 \; j \; t_s)} \times 100$$

where t_0 and t_1 are the initial and final thickness of the specimen respectively and t_s the thickness of the spacer bar used. The procedure used was ASTM D 395- 98 (method B).

e) Abrasion resistance

The abrasion resistance of the samples was tested using a DIN Abrader. Sample having a diameter of 12 ± 0.2 mm and a thickness of 16 to 20 mm, was kept on a rotating sample holder and 10N load was applied. Initially a pre run was given for the sample and its weight was taken. The weight after final run was also noted. The difference in weight is the weight loss of the test piece after its travel through 42 m in 132 seconds on a standard abrasive surface. It is expressed as volume loss(cc/h). The abrasion loss was calculated as follows:

$$V = \frac{\Delta m}{\rho}$$

where Δ m-mass loss, ρ-density of the sample and v- abrasion loss.

f) Heat build-up

The Goodrich flexometer conforming to ASTM D 623- 99(Method A) was used for measuring heat build-up. The test was carried out with the cylindrical sample of 2.5 cm in height and 1.9 cm in diameter. The oven temperature was kept at 50°C. The stroke was adjusted to 4.45mm and load 10.9kg. The sample was pre conditioned to the oven temperature for 20 minutes. The heat developed was sensed by thermocouple and relayed to a digital temperature indicator. The temperature rise (Δ T°C) at the end of 20 minutes was taken as heat build-up.

g) Resilience

The resilience was determined by vertical rebound conforming to ASTM D 2632-96 method. It is determined as the ratio of rebound height of a metal plunger of prescribed weight and shape which is allowed to fall on the rubber specimen. The test specimens of 12.5 ± 0.5 mm. thickness were molded. Level the instrument and raise the plunger to the top of the guide rod. Position the resilience scale so that its full weight rests upon the specimen. Lock it in this position and release the plunger making sure that it slides freely on its guide. Record the height after first three rebounds.

h) Flex resistance

The test is intended to compare the resistance of rubbers to the formation and growth of cracks and is recommended when flexing is encountered in service as in the case of a side wall. The apparatus used was a Wallace Demattia flexing machine as per ASTM D 430 - 57 T. Moulded test specimens with a circular groove, conditioned for 24 hours were tested in duplicate. The number of flexing cycles for crack initiation and for complete failure were noted on the counter. The test was conducted at ambient temperature.

i) Ozone resistance

Ozone ageing studies were conducted according to ASTM D 518 Method D in a Mast Model 700 - 1 ozone test chamber at 41°C. Ozone concentration in the chamber was adjusted to 50 parts per hundred million (pphm). Samples were placed in the chamber and the time for crack initiation and total failure were noted by checking the samples using a magnifying lens at regular intervals of 30 minutes.

j) Density

The densities of the samples were estimated by the method of displacement by the method of displacement of liquid (ASTM D 792). In this method the weight of the specimen in air was first noted and then the specimen was immersed in a liquid and its loss of weight in liquid was determined. The density is given by,

$$\text{Density} = \frac{\text{Weight of specimen in air}}{\text{Weight loss of specimen in liquid}} \times \text{Density of the liquid}$$

k) Solvent extraction studies

Dumbbell samples for evaluation of physical properties were prepared and kept in different solvents at pre determined temperatures for specified periods. Retention in physical properties was measured after ageing at predetermined time and temperature.

l) Ageing studies

Dumbbell samples for evaluation of physical properties were prepared and kept in an air oven at pre determined temperatures for specified periods. Retention in physical properties like tensile strength, elongation at break, modulus etc. was evaluated after conditioning the samples at room temperature for 24h according to the procedure given in ASTM D 573.

2.2.6 Determination of softening point (IP 58/82)

The softening point is the temperature at which the substance acquires a particular degree of softening under specified conditions of the test.

The material is heated to a temperature 75 to 100°C above its expected softening point. It is stirred until it is completely changed into fluid and is free from air bubbles and water and filtered through IS sieve 30. The rings, previously heated to a temperature approximately to that of the molten material, were kept on a metal plate coated with the mixture of equal parts of glycerine and dextrose. The ring was then filled with sufficient melt to give an excess above the level of the ring when cooled. After cooling for 30 minutes in air, the material is levelled in the ring by removing the excess with a warmed sharp knife.

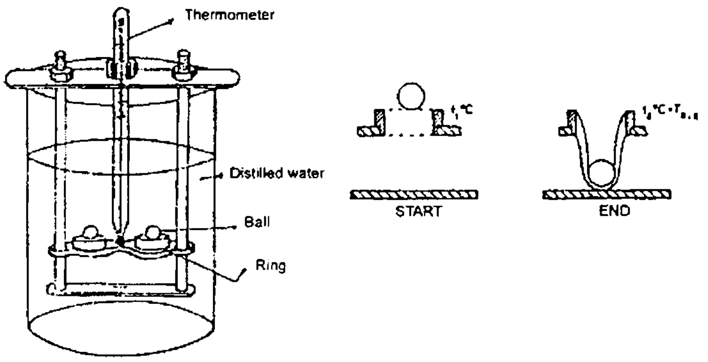

Fig.2.2

The apparatus is assembled with the rings, thermometer and ball guides in position. The bath was then filled with distilled water (for materials having softening point below 80°C) to a height of 50mm above the upper surface of the rings. The bath is then brought to a temperature of 5°C and maintained at that temperature for 15 minutes. Then the ball previously cooled to a temperature of 5°C is kept by means of forceps, in each ball guide. Now heat is applied to the liquid with stirring so that the temperature rises at a uniform rate of 5.0 ± 0.5°C per minute till the material softens and allows the ball to pass through the ring. For materials of softening point above 80°C glycerine is used in place of water in the bath and the starting temperature of the test is 35°C. For each ring and ball the temperature shown by the thermometer is recorded at the instant the sample surrounding the ball touches the bottom plate of the support. This temperature is reported as softening point.

2.2.7 Determination of penetration (IP 49/79)

The penetrometer of Precision Scientific Co. (USA) was used for the purpose. Penetration of a bituminous material is the distance in tenths of a millimetre that a standard needle will penetrate vertically into a sample of the material under standard conditions of temperature (25°C), load (100g) and time (5sec).

The penetration needle is a highly polished, cylindrical hard steel rod, coaxial, having the following shape, dimensions and tolerances as shown in the figure below:

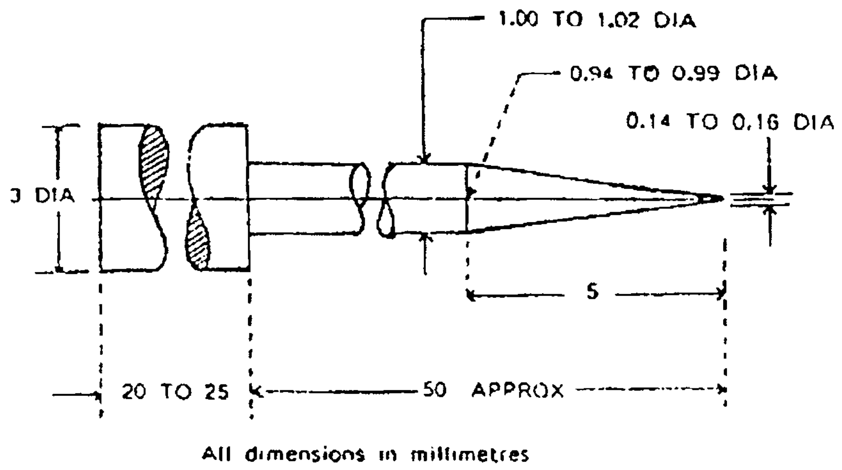

Fig.2.3

The needle is provided with a shank about 3mm in diameter into which it is fixed immovably. The taper shall be symmetrical and the point shall be 'blunted' by grinding to a truncated cone.

Preparation of sample

The material was softened to a pouring consistency between 75°C and 100°C above the approximate softening point and stirred thoroughly till it was homogeneous and was free from air bubbles and water. The melt was then poured into the container to a depth 10mm in excess of the excepted penetration. The sample was protected from dust and allowed to cool at a temperature between 15 to 30°C for 1 to 1.5 hours. It was then placed along with the transfer dish in the water bath at 25 ± 0.1°C and allowed to remain for another 1.5 hour. The sample was then placed on the base of the penetrometer and the needle point was kept in contact with the surface of the sample. The needle was then loaded with the weight required to make a total moving weight (i.e. the sum of the weights of the needle, carrier and superimposed weights) of 100 ± 0.25 g.

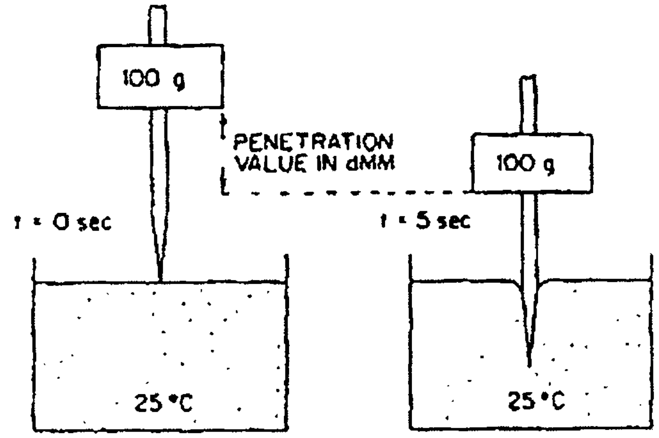

Fig.2.4

The pointer in the dial was brought to zero. Little water at 25°C was poured on the surface of the sample and released the needle for exactly five seconds. The distance in tenths of a millimetre vertically penetrated the sample is reported as the penetration. Two more determinations are made at points on the surface of the sample not less than 10mm apart and not less than 10mm from the side of the dish. The mean value of these three determinations is reported as penetration.

2.2.8 Determination of ductility (IP 32/55)

The ductility meter of Humboldt Manufacturing Company, (USA) was used for the purpose. The ductility of a bituminous material is t he distance in centimetres to which it will elongate before breaking when ends of a briquette specimen of the material of the specified form is pulled apart at a specified speed and at a specified temperature. The test was conducted at a temp of 27 ± 0.5°C and at a rate of pull of 50 ± 2.5 mm per minute. The bituminous material was heated to a temperature about 75 to 100°C above the approximate softening point, till it became thoroughly fluid. It was then filtered through IS : sieve 30 and then poured to the mould of the type (total length = 75mm,distance between the clips = 30 mm, width at mouth of clip = 20mm and width at minimum cross section = 10mm) as shown above.

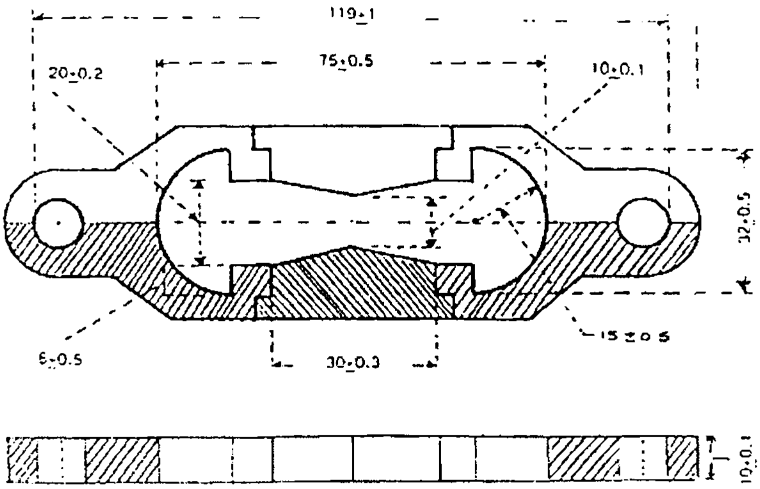

Fig.2.5

The mould was assembled on a brass plate and in order to prevent the material under test from sticking the surface of the plate as well as inferior surface of the sides of the mould were coated with the a mixture of equal parts of glycerine and dextrin. The material was poured as a thin stream back and forth from end to end of the mould until it was then allowed to cool at room temperature for 30 to 40 minutes and then placed in a water bath maintained at the specified temperature for 30 minutes. The excess bitumen was then cut off by means of a hot, straight-edged knife, so that the mould was just level full.

The brass plate and mould with briquette specimen was placed in the water bath at 27 ± 0.5°C for about 85 to 95 minutes. The briquette was then removed from the plate, the side pieces were detached and the rings at each end of the clips were attached to the pins in the testing machine. The two rings are then pulled apart horizontally at a uniform speed of 50 ±2.5 mm per minute until the specimen ruptures. The density of water in the bath was adjusted by the addition of sodium chloride so that the bituminous thread formed during the test does not touch the bottom of the bath at any time during the test. The distance is centimetres through which the standard briquette elongated before the bituminous thread formed breaks is reported as ductility.

2.2.9 Determination of flash point of bitumen (IP 34/85)

The flash point of a material is the lowest temperature at which the vapour of a substance momentarily takes fire in the form of a flash under the specified conditions of the test.

Pensky Martens Closed Method was used for the determination of the flash point of bitumen in this study. The flash cup was filled with the material to be tested upto the level indicated by the filling mark. The flash cup was then kept on the heater with the lid carrying the thermometer in position. The test flame was adjusted in such a way so that it is of the size of a bead of 4mm in diameter. The heating rate was adjusted in such a way so that it is of the size of a bead of 4mm in diameter. The heating rate was adjusted in such a way that the temperature recorded by the thermometer increases not less than 5°C and not more than 6°C per minute. The stirrer was turned at a rate of approximately 60 revolutions per minute. The test flame is applied at each temperature reading which is a multiple of 1°C up to 104°C. For the temperature range above 104°C the test flame is applied at each temperature reading which is a multiple of 3°C, the first application of the test flame being made at a temperature approximately 17°C below the actual flash point. The test flame is applied by operating the device controlling the shutter and test flame burner so that the test flame is lowered in 0.5°C seconds, left in its lowered position for one second and quickly raised to its high position. The stirring has to be discontinued during the application of the test flame. The duplicate results should not differ by more than 3°C of the mean.

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Chapter 3

PREPARATION AND CHARACTERISATION OF AMINE TYPE POLYMER-BOUND ANTIOXIDANTS

Introduction

Both natural and synthetic rubber requires effective antioxidants or protective agents in inhibiting oxidative degradation of rubber by atmospheric oxygen. The serious disadvantages of conventional antioxidants are their volatility and extractability in water and other solvents. The removal of antioxidants from the rubber during service has an adverse effect on the useful life of the products.[1] One method to overcome this problem is the use of polymer-bound antioxidants. There are two basic approaches to obtain polymeric antioxidants. One is to copolymerise various monomers having antioxidant moiety with elastomeric monomers and the other is by the direct combination of the conventional antioxidant with modified elastomers.[2,3] The large size of the resulting polymer-bound antioxidants makes them highly resistant to volatilisation and extraction.[4]

Polymerisable monomeric antioxidants were described by Tamura and coworkers.[5,6] The reaction of chloroprene (CR) w-type with amines producing polymer bound antioxidants were reported by Mohammed. S. Al-Mehadawe et al.[7] Scott et al have demonstrated that simple hindered phenols which contain a methyl group in the ortho or para position, can react with natural rubber in the presence of oxidising free-radicals to yield polymer-bound antioxidants.[8-10] Antioxidants like styrenated phenol, diphenylamine etc bound to hydroxy terminated liquid natural rubber by modified Friedel-Crafts reaction were also found to be effective in improving ageing resistance.[11] Natural rubber-bound diphenylamine antioxidants were reported by S. Avirah and R.Joseph.[12]

Polymer-bound antioxidants have many advantages but the main disadvantage is that the mobility of the network-bound antioxidants is restricted. Hence it does not bloom to the surface and ozone attack cannot be effectively controlled.[13] Most of the polymer-bound antioxidants reported have an unsaturated back bone. So during the process of vulcanisation their backbone gets attached to the main chain through sulphur crosslinking and it loses its mobility further.[14] Polymer-bound antioxidant with a saturated backbone may help to overcome this problem. This chapter describes the preparation of amine type polymer-bound antioxidants with saturated backbone.

PART I

3.1 Preparation and Characterisation of Polyisobutylene-Bound Paraphenylene Diamine

3.1.1Experimental

a) Materials

Polyisobutylene (PIB was supplied by Cochin Refineries Balmer Lawrie Ltd. Ambalamughal, Kerala, Paraphenylene diamine, methanol, carbon tetrachloride, ether, toluene, dioxan, triethylamine were of reagent grade supplied by E. Merck India was used.

b) Chlorination of polyisobutylene

Polyisobutylene (PIB) was dissolved in CCl_4 (50% solution) in a one litre flask fitted with a two hold cork carrying an inlet and outlet tube. Through the inlet tube, pure dry chlorine gas was passed and the outlet tube was connected to a jar containing sodium hydroxide in order to absorb the HCl gas evolved. The chlorine gas was passed for 5hrs. The resulting solution was poured into water at 80°C and excess chlorine and CCl_4 were removed. The chlorinated sample was dissolved in toluene and reprecipitated using methanol. The chlorinated polyisobutylene (PIB-Cl) was dried in a vacuum oven.

c) Binding of PIB-Cl with paraphenylene diamine

The chlorinated sample was dissolved in dioxan and mixed with paraphenylene diamine (PD) dissolved in dioxan in the ratio 2:1. The reaction mixture was made alkaline in order to neutralise the HCl evolved during the condensation reaction by adding triethylamine. The reaction mixture was taken in a two necked flask fitted with a water condenser and a thermometer. The mixture was heated at 100°C for 48hrs. Dioxan and triethylamine were distilled off and the mixture was washed with methanol a number of times in order to remove the unreacted PD. The resulting mixture was reprecipitated using a toluene-methanol (1:1 v/v) mixture and polyisobutylene-bound paraphenylene diamine (PIB-PD) was dried in vacuum oven.

3.1.2 Analysis of PIB-Cl and PIB-PD

Analysis of chlorinated polyisobutylene and polyisobutylene-bound para phenylene diamine was carried out using infrared spectroscopy (IR), proton magnetic resonance spectroscopy (^{1}HNMR),Vapour phase osmometry (VPO) and Thermogravimetric analysis (TGA).The chlorine content and iodine value were also determined.

The ^{1}HNMR spectra of the samples were recorded from a solution in CCl_4 using a JEOL-JNM spectrometer. IR spectra of the samples were taken on a Perkin-Elmer Model 377 IR spectrometer. Molecular weight was determined by using Knauer Vapour Phase Osmometer.

3.1.3 Results and Discussion

The Figs. 3.1, 3.2 and 3.3 show the IR spectra of PIB, PIB-Cl and PIB-PD. The IR Spectrum of PIB shows peaks at 2950cm^{-1} corresponding to aliphatic –CH stretching, at 1480 cm^{-1} due to –CH bending,1650 cm^{-1} corresponds to C=C. The IR spectrum of PIB-Cl (chlorinated PIB) shows a new peak at 780 cm^{-1} due to the presence of C-Cl stretching. The IR spectra of PIB-PD shows additional peaks at 3390 cm^{-1} due to NH stretching,1620cm^{-1}due to NH bending and 1500cm^{-1} due to aromatic ring present in PD. This confirms the chemical binding of PD to PIB[15].

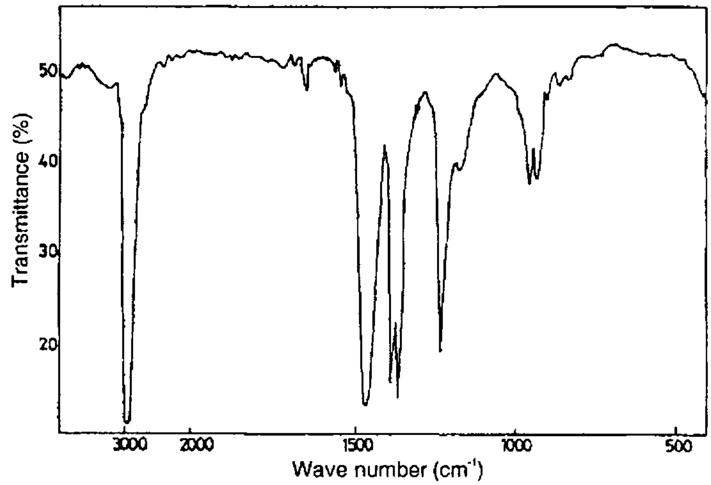


Fig.3.1 IR spectrum of PIB

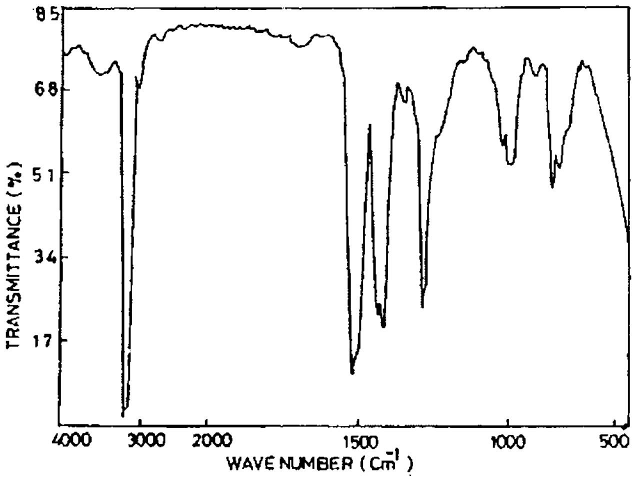


Fig.3.2 IR spectrum of PIB-Cl

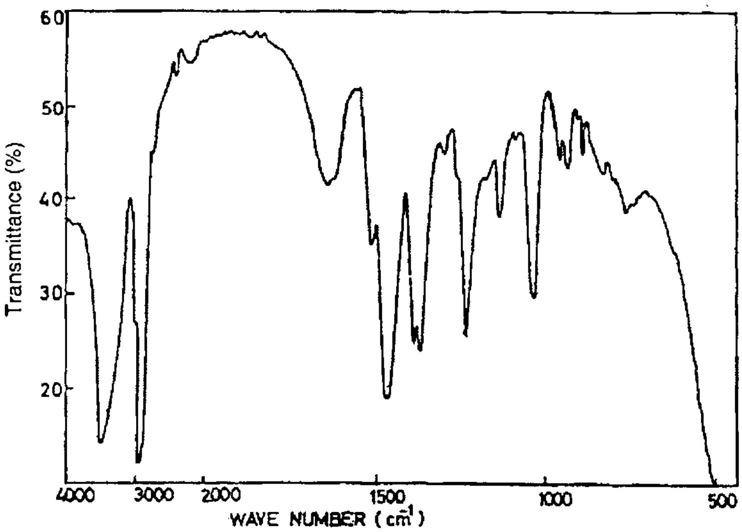


Fig.3.3 IR spectrum of PIB-PD

Figs. 3.4 and 3.5 show the ^1H NMR spectra of PIB and PIB-PD. There are peaks δ =1.22 ($-CH_2$) and δ=1.6 ppm ($-CH_3$).Fig. 5 shows additional peaks at δ=7.2 ppm and δ=3.5 ppm corresponding to aromatic ring and Ar-NH-R present in PIB-PD. This again confirms the chemical binding of PD to PIB.[14]

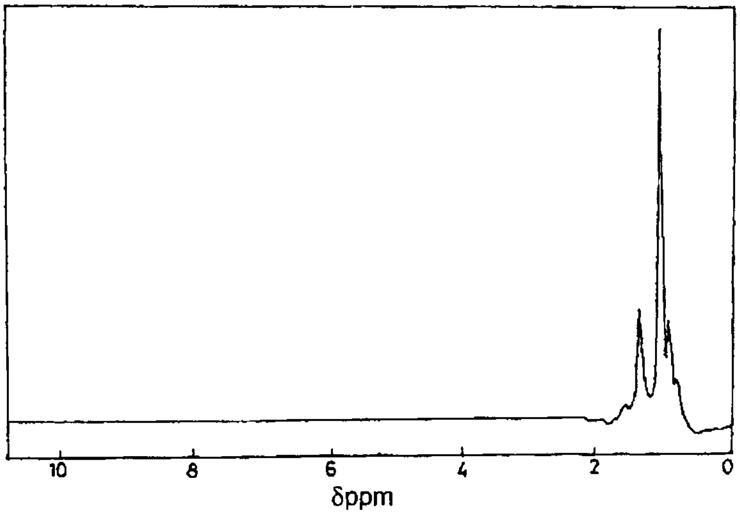


Fig.3.4 ^1H NMR spectra of PIB

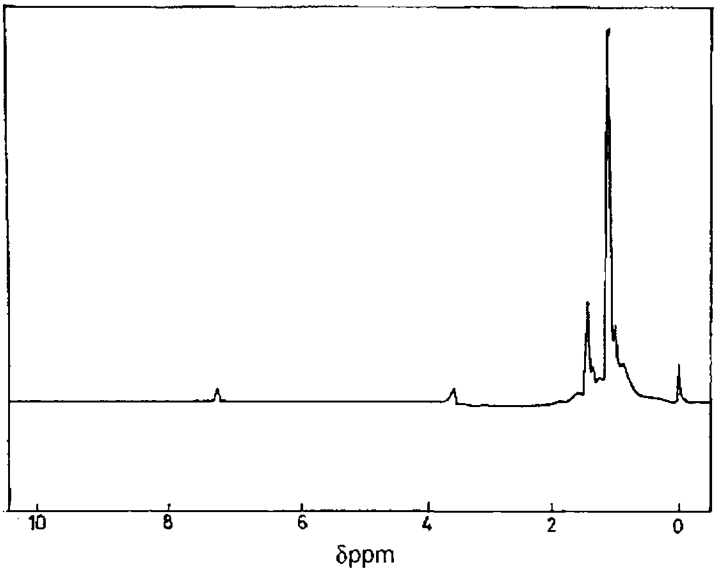


Fig.3.5 ^{1}H NMR spectra of PIB-PD

The molecular weight of the samples were determined by VPO. The molecular weights of PIB, PIB-Cl, PIB-PD and PD are 934,1005,2330 and 106 respectively. This shows that polyisobutylene is bound to para phenylene diamine at both the ends.

The iodine value of PIB and PIB-Cl indicates that addition reaction has taken place at the double bonds. The chlorine content of the PIB-Cl is found to be 7.6%. This also confirms the addition of chlorine at the double bond.

Fig. 3.6 shows the thermograms of PD, PIB, and PIB-PD. The low molecular weight PD volatilises easily while polymer-bound PD is less volatile. This again confirms the chemical bonding of PD to PIB.

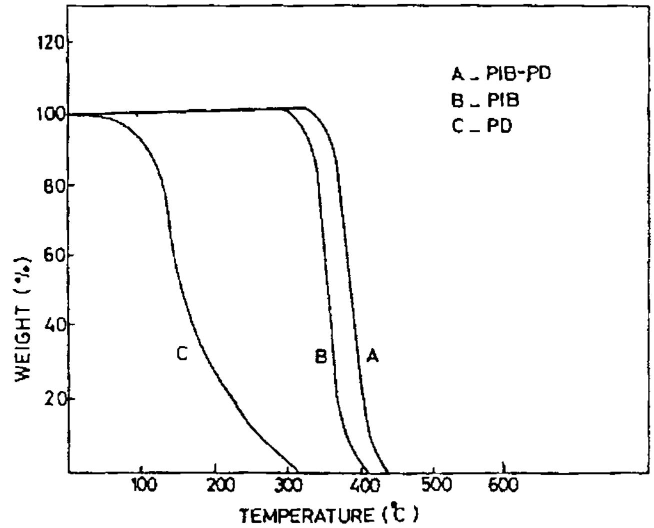
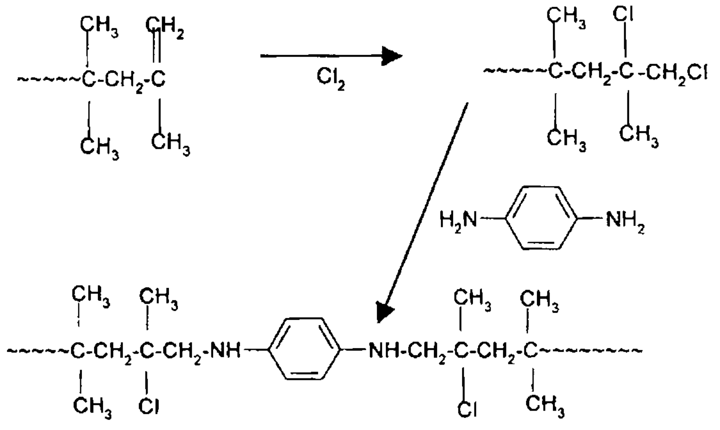


Fig. 3.6 TGA of PD, PIB, and PIB-PD

From the above data the chlorination and binding reaction between PIB and PD may be as shown below The polyisobutylene is chlorinated with pure dry chlorine and the chlorinated product is condensed with paraphenylene diamine.



Scheme 3.1

PART II

3.2 Preparation and Characterisation of Chlorinated Paraffin Wax-Bound Paraphenylene Diamine

3.2.1 Experimental

a) Materials

Chlorinated paraffin wax (CPW),dioxan, triethylamine, para-phenylene diamine (PD) were used.

b) Preparation of chlorinated paraffin wax bound PD

The chlorinated paraffin wax (CPW) and PD, were dissolved in dioxan, were mixed in the ratio1:1. The reaction mixture was made basic by adding triethylamine, to neutralise the HCl evolved during the condensation reaction. The reaction mixture was taken in a two necked flask fitted with a water condenser and a thermometer. The mixture was heated at 100°C for 14 h. Unreacted dioxan and triethylamine were distilled off and the mixture was washed with water a number of times to remove the unreacted PD. The resulting mixture was reprecipitated and dried in a vacuum oven.

3.2.2Characterisation of CPW-PD

Characterisation of chlorinated paraffin wax-bound para phenylene diamine were carried out using infrared spectroscopy (IR), proton magnetic resonance spectroscopy (^{1}HNMR),Vapour phase osmometry (VPO) and Thermogravimetric analysis (TGA).

3.2.3 Results and discussion

Figs. 3.7& 3.8 show the IR spectra of CPW and CPW-PD. The IR spectrum of CPW-PD shows additional peaks at 3400 cm^{-1} due to NH-stretching primary, at 3387 cm^{-1} due to NH-stretching secondary, at 1614.6 cm^{-1} due NH- bending, and 1500 cm^{-1}corresponding to aromatic ring in paraphenylene diamine.[25]

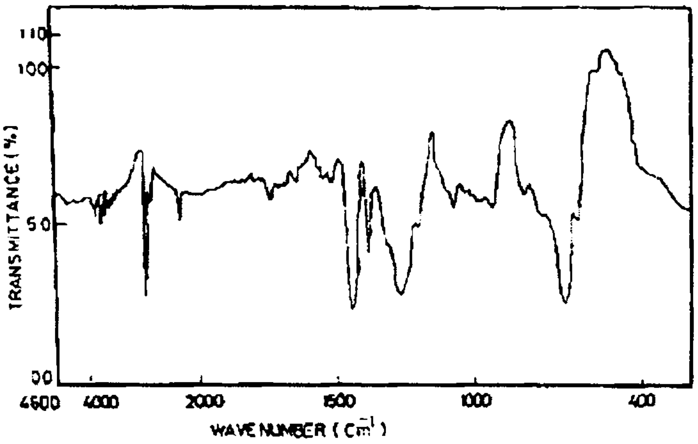


Fig. 3.7 IR spectrum of CPW

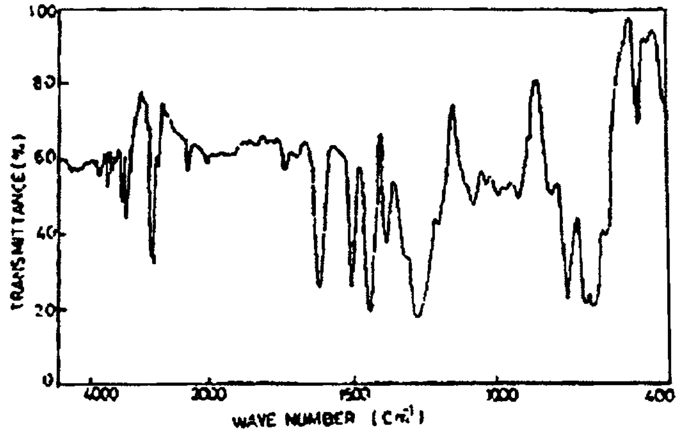


Fig. 3.8 IR spectrum of CPW-PD

Figs 3.9 & 3.10 show the ^1H NMR spectra of CPW and CPW-PD. ^1H NMR spectrum of CPW-PD shows additional peaks at 7.27 δ and 5.978 δ correspond to aromatic ring present in paraphenylene diamine. Note that the peak due to NH is masked by other peaks of the sample.

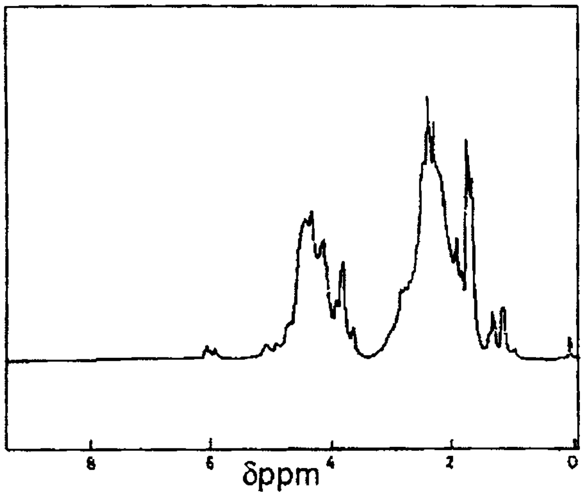


Fig.3.9 ^{1}H- NMR spectrum of CPW

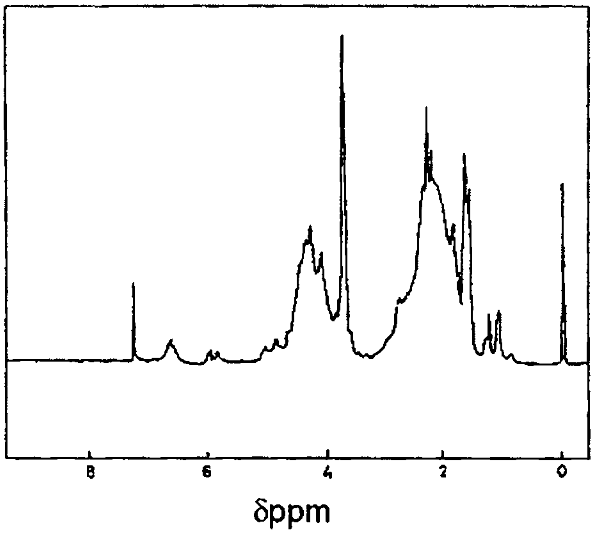
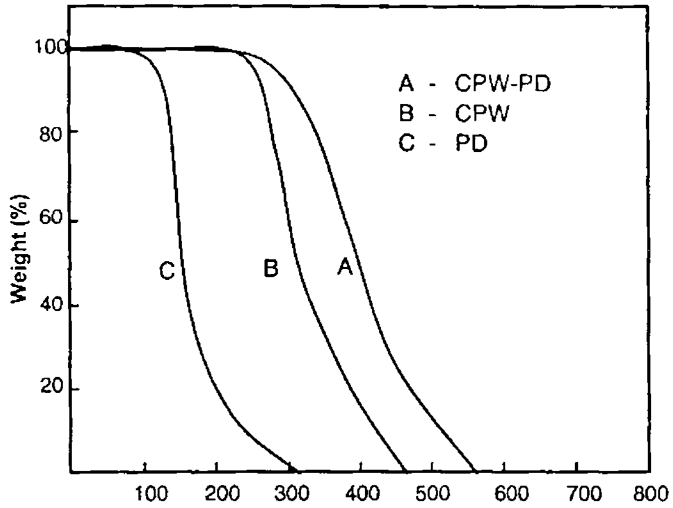


Fig.3.10 ^{1}H- NMR spectrum of CPW-PD

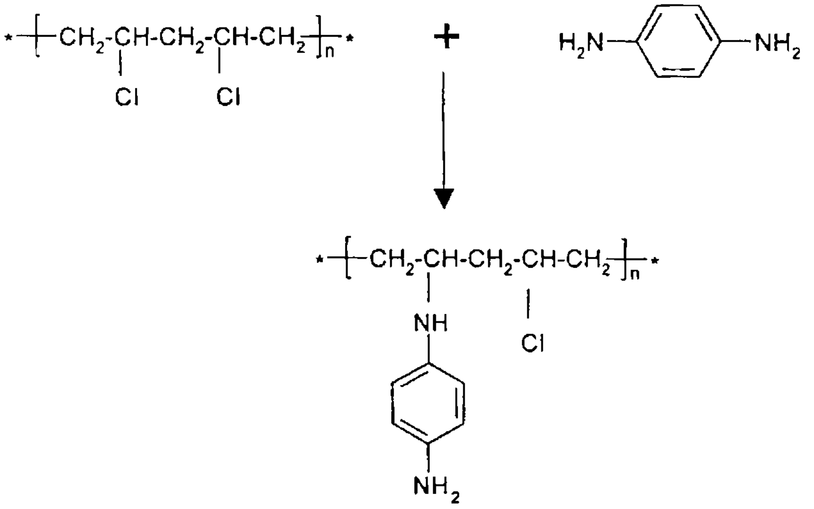
The Fig 3.11 shows the thermograms of PD, CPW and CPW- PD. The low molecular weight PD volatilises easily while rubber bound PD is less volatile. This again confirms the chemical binding of PD onto CPW.



Temperature °C

Fig. 3.11 TGA of PD, CPW and CPW-PD

The molecular weight of the samples were determined by VPO. The molecular weights of CPW, CPW-PD and PD were 530, 1050 and 110 respectively. This shows that chlorinated paraffin wax is bound to paraphenylene diamine. From the above data the condensation reaction of chlorinated paraffin wax and paraphenylene diamine may be represented as scheme 3.2.



Scheme 3.2

PART-III

3.3 Preparation and Characterisation of Polyethylene Glycol-Bound Paraphenylene Diamine

3.3.1Experimental

a) Materials

Polyethylene glycol (PEG) with molecular weight 600,methanol, thionyl chloride, ether, dioxan, triethylamine, para-phenylene diamine were used.

b) Chlorination of Polyethylene Glycol

0.1mol of polyethylene glycol was weighed and dissolved in dioxan and to it 0.1mol $SOCl_2$ was added drop wise with constant stirring by keeping the reaction mixture in an ice bath. It was then heated under reflux for 3hrs. The chlorinated polyethylene glycol(PEG-Cl) was separated.

c) Preparation of Polyethylene glycol bound paraphenylene diamine

The chlorinated polyethylene glycol was dissolved in dioxan and mixed with paraphenylene diamine (PD) dissolved in dioxan in the ratio 2:1. The reaction mixture was made alkaline in order to neutralise the HCl evolved during condensation reaction by adding triethylamine. The reaction mixture was taken in a two necked flask fitted with a water condenser and a thermometer. The mixture was heated at 100°C for 48h. Dioxan and triethylamine were distilled off and the mixture was washed with heptane number of times in order to remove the unreacted PD. The chlorinated polyethylene glycol(PEG-Cl) was separated and dried in a vacuum oven.

3.3.2 Analysis of PEG-Cl and PEG-PD

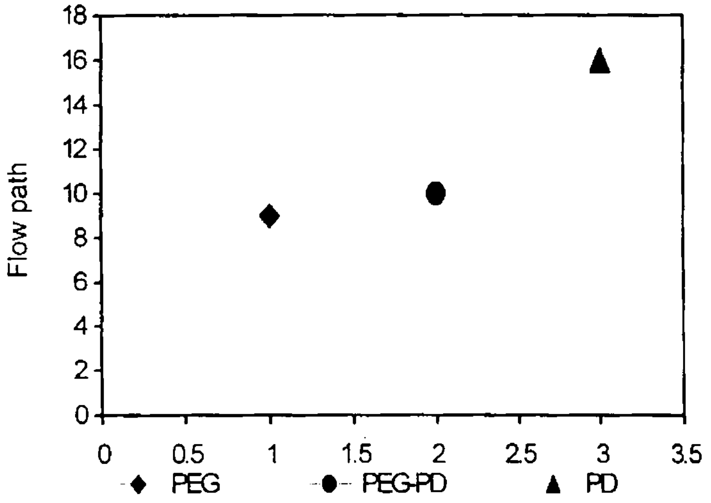
Analysis of polyethylene glycol-bound para phenylene diamine(PEG-Cl) was carried out using thin layer chromatography(TLC), infrared spectroscopy (IR), thermogravimetric analysis (TGA) and vapour phase osmometry (VPO).

3.3.3 Results and discussion

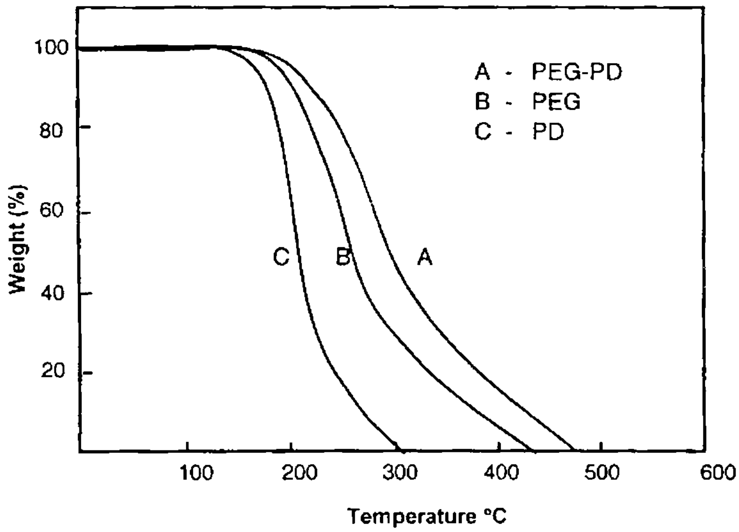
The Figs. 3.12 shows the Thin layer chromatography(TLC) of PEG, PEG-PD and PD. The R_f value of PEG-PD was found to be slightly lower than that of PEG. This indicates that paraphenylenediamine gets chemically attached to PEG to form PEG-PD.

Fig 3.13 shows the IR spectra of PEG-PD. The IR Spectra of PEG-PD shows peaks at 3400cm^{-1} and 2950 cm^{-1}corresponding to -NH stretching, at 1480 cm^{-1} due to -NH bending, 1650 cm^{-1} corresponds to aromatic ring. This confirms the chemical binding of PD on to PEG.[15]

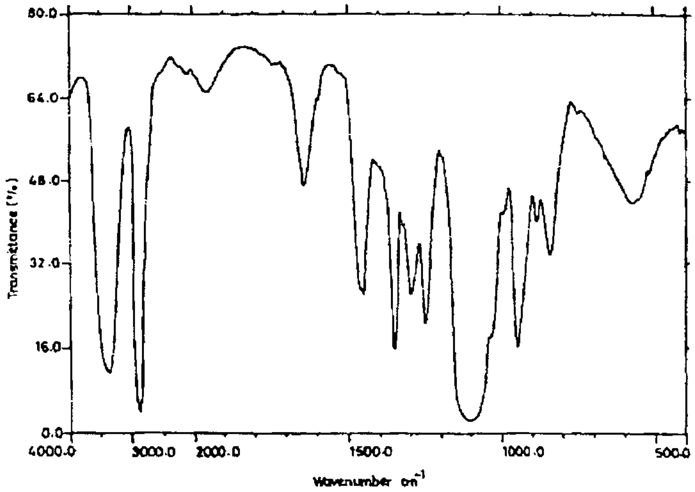
Fig. 3.14 shows the thermograms of PD, PEG and PEG-PD. The low molecular weight PD volatilises easily while polyethylene glycol bound PD is less volatile. This again confirms the chemical bonding of PD to PEG.



3.12 TLC of PEG, PEG-PD and PD

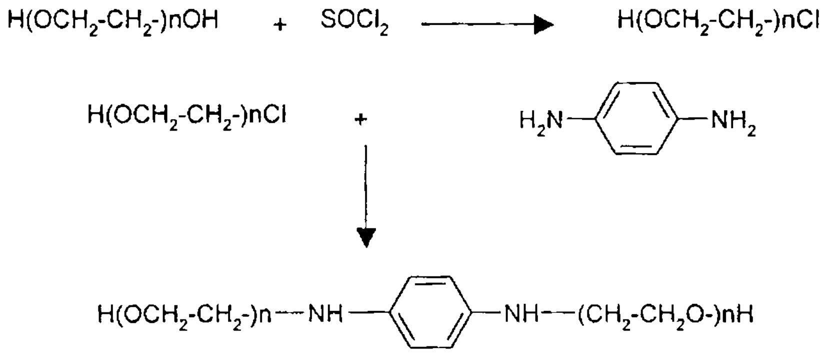


3.13 TGA of C-PD, B- PEG and A- PEG-PD



3.14 IR Spectrum of PEG-PD

The molecular weight of the samples were determined by VPO. The molecular weights of PEG, PEG-PD and PD were 590, 1250 and 110 respectively. This again confirms the binding of polyethylene glycol to paraphenylene diamine. From the above data the binding reaction of chlorinated polyethylene glycol and paraphenylene diamine may be represented as shown below. The PEG is chlorinated using thionyl chloride. The chlorinated polyethylene glycol is bound to paraphenylene diamine by the condensation reaction.



Scheme 3.3

PART IV

3.4 Preparation and Characterisation of Polyisobutylene-Bound Diphenylamine Antioxidant.

3.4.1 Experimental

a) Materials

Polyisobutylene, diphenylamine, methanol, carbon tetrachloride, ether, toluene, dioxan, triethylamine, anhydrous zinc chloride and sodium carbonate were used.

b) Preparation of Polyisobutylene-bound diphenylamine

The chlorinated polyisobutylene(PIB-Cl) was dissolved in dioxan and mixed with diphenylamine (DA) dissolved in dioxan in the ratio 1:2 and taken in a two necked flask fitted with a thermometer and a soxhlet extraction unit packed with fused $CaCl_2$. 0.5 mol of anhydrous zinc chloride was introduced into the flask. The reaction mixture was heated at 100°C on a hot plate with magnetic stirring for 24hrs. There was no appreciable degradation of the polymer during this prolonged exposure to high temperature as seen by molecular weight measurements, probably due to anaerobic atmosphere inside the set-up. When the reaction was complete, the reaction mixture was neutralised with sodium carbonate and washed several times with water to remove the catalyst. The contents of the vessel were then poured into excess methanol with stirring to precipitate the liquid polymer bound antioxidant. The unreacted DA was removed by repeated reprecipitation using a toluene-methanol (1:1 v/v) mixture and the product dried in a vacuum oven. The rubber bound antioxidant was obtained in the form of a brown viscous liquid.

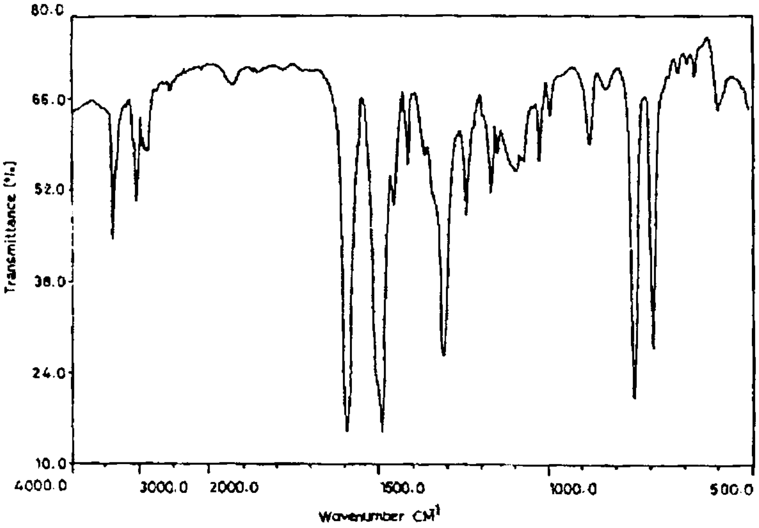
3.4.2Characterisation of PIB-DA

Characterisation polyisobutylene-bound diphenylamine were carried out using infrared spectroscopy (IR), thermogravimetric analysis (TGA) and vapour phase osmometry(VPO).

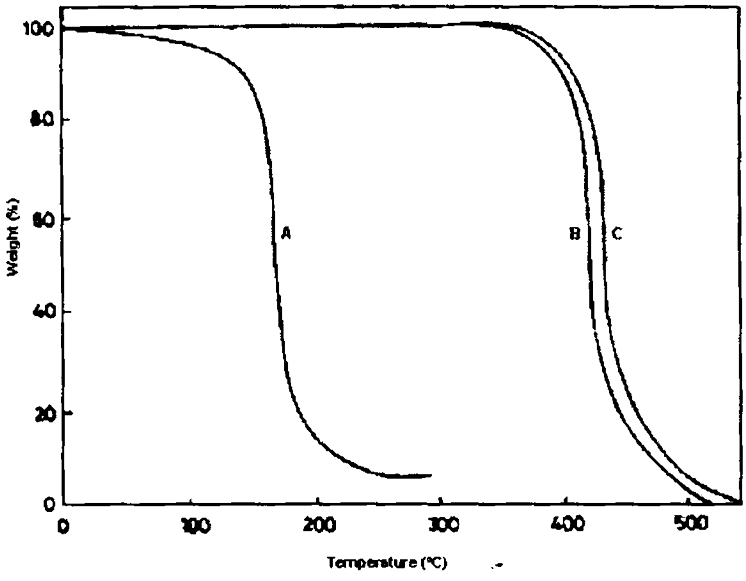
3.4.3 Results and discussion

Fig 3.15 shows the IR spectra of PIB-DA. The IR Spectra of PIB-DA shows peaks at 3497cm^{-1} corresponding to-NH stretching, at 1480 cm^{-1} due to -NH bending,1600 cm^{-1} corresponds to aromatic ring. This confirms the chemical binding of DA to PIB-DA.[15]

Fig. 3.16 shows the thermograms DA, PIB and PIB-DA. The low molecular weight DA volatilises easily while PIB-DA is less volatile. This again confirms the chemical bonding of DA to PIB.



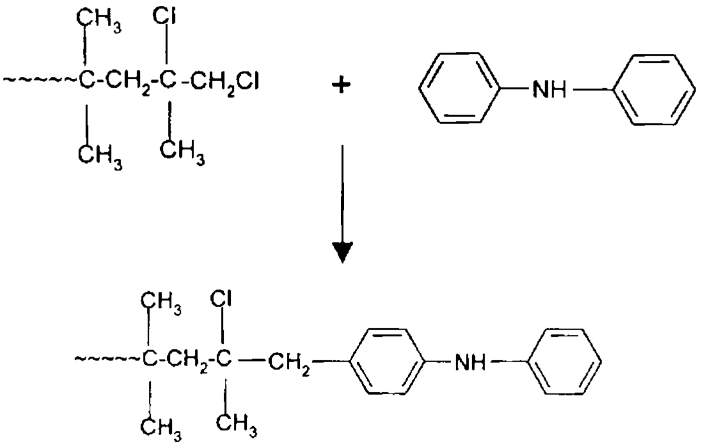
3.15 IR Spectrum of PIB-DA



3.16 TGA of A-DA, B- PIB, C- PIB-DA

The molecular weights of the samples were determined by VPO method. The molecular weights of DA, PIB-Cl and PIB-DA are 169,1005 and 1200 respectively. This confirms the binding of PIB-Cl to diphenylamine.

From the above data scheme of reaction can be summarised as follows:



Scheme 3.4

Conclusions

1. PIB can be chlorinated by passing dry chlorine through a solution of PIB in CCl_4.
2. p-phenylene diamine (PD)can be chemically attached to chlorinated PIB by condensation reaction.
3. PD can also be attached to chlorinated paraffin wax in a similar manner by condensation reaction.
4. Polyethylene gycol can be chlorinated using thionyl chloride and the chlorinated product was attached to PD.
5. Chlorinated polyisobutylene was bound to diphenylamine by modified Friedel Crafts reaction.

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Chapter 4

USE OF POLYMER-BOUND AMINE TYPE ANTIOXIDANTS IN NR, NR MODIFIED BITUMEN, SBR, NBR AND IIR

During recent years there has been an increasing demand from rubber products manufacturers for more efficient additives that can protect rubber against high temperatures, corrosive environment etc. Polymers are subjected to deterioration due to a variety of environmental factors, including light, mechanical stress, temperature and pollutants. To achieve the goal of enhanced polymer durability, one must understand the underlying failure mechanisms. The most common technological methods of assessing the strength of rubbers are by standard tests such as tensile strength and tear strength, which characterize the rupture resistance of polymer network.

In practice, rubber articles rarely fail in single loading. Most failures in rubber products occur under dynamic service conditions arising from the development of cracks. The growth of these cracks under repeated deformation can lead to catastropic failure. This process is known as fatigue. Examples include, groove cracking in tyres, tread and ply separation in tyres, and failure in torsion springs and motor mounts etc. These properties are strongly dependent upon the elastomer type, the microstructure, filler type and amount, antioxidant and cure system.[1-3]

Improvement in stabilising systems for rubbers must be based on up-to-date ideas concerning the role of physical and chemical factors in the failure of rubbers, the mechanism of the protective action of stabilisers and their effect on the formation of vulcanisation structures, mechanical properties, wear resistance and ozone resistance.[4-14]

Conventional antioxidants, especially in aggressive environment, may be rapidly depleted by volatility, migration, extraction and irreversible adsorption on fillers.[15-17] Due to the low molecular weight these antioxidants are highly volatile and are washed out by water during service of products.[18-20]

Since the discovery of vulcanized rubber, rubber chemists noted that unvulcanized rubber degraded rapidly when exposed to the elements, namely, oxygen, ultraviolet light, ozone etc. Protection of rubber articles from degradation is of primary concern to the rubber industry. Of the numerous classes of antioxidants available, the substituted p-phenylene diamines have found greatest acceptance in the rubber industry. These chemicals have limited solubility in rubber and typically show dramatic increase in protection of the elastomer against degradation. Increases in service life brought about by the introduction of radial tyres and improved rubber products have prompted the search for long lasting antioxidants. In the tyre industry aryl alkyl p-phenylene diamines alone or together with other antidegradants are preferred as they protect the tyres not only from oxidation but also from ozone cracking and mechanical fatigue. A serious drawback of all these antioxidants is their leachability and volatility.[21] One method for solving this problem is to attach the antioxidant chemically to the polymer. Alkylation was suggested as an efficient method for production of polymer-bound antioxidants.[22-23]

Polymer-bound antioxidants were synthesised to overcome serious disadvantages of conventional antioxidants: their disappearance from rubber vulcanizate during service due to volatility and extractability. This disappearance has been shown to have adverse effect on ageing.[24-25] Over the past several decades, numerous papers and reviews have appeared describing the benefits and various techniques of chemically incorporating antioxidants into polymeric substrates.[26-27]

On account of their low cost, availability and oil resistance, nitrile rubbers (acrylonitrile-butadiene rubbers) are still widely used as oil seals, O - rings, gaskets and, fuel and oil hoses. Nitrile rubber based products when in contact with mineral oil based hydraulic fluids require protective antioxidants in order to retain their elastomeric properties for useful period in service. But when they are subjected to continuous contact with hydraulic fluids at high temperature, the low molecular weight additives will be lost by extraction or volatilisation.[28-29] Butyl rubber (IIR) is mainly used in inner tubes of tyres, in curing bladders etc because of its high heat resistance. Curing bladders have to undergo the most severe operating conditions of all compounds. It is of great interest to study the effect of new amine type polymer-bound antioxidants in NR, SBR, NBR and IIR vulcanizates.

Rubberisation of roads is a topic of current interest. The use of NR in road tarring will reduce the maintenance cost of roads. It would lead to better highways with longer life. One of the main disadvantages of using natural rubber latex for road rubberisation is that due to high temperature of mixing it undergoes degradation. The efficiency of the novel polymer-bound amine type antioxidants in NR, NR modified bitumen, SBR, IIR and NBR is investigated in this chapter.

PART I

4.1 Use of Polyisobutylene-Bound Paraphenylene Diamine and Chlorinated Paraffin Wax-Bound Paraphenylene Diamine in NR, NR Modified Bitumen, SBR, NBR and IIR.

This part of the chapter describes the effect of newly prepared polymer-bound amine type antioxidants namely, polyisobutylene-bound paraphenylenediamine (PIB-PD) and chlorinated paraffin wax-bound paraphenylene diamine in filled vulcanizates of NR,SBR, NBR and IIR. The effect in NR modified bitumen is also studied.

4.1.1 Use of polyisobutylene-bound paraphenylene diamine and chlorinated paraffin wax-bound paraphenylene diamine antioxidants in NR

a) Experimental

The polymer-bound antioxidants prepared in the laboratory and conventional antioxidants were incorporated into standard NR based formulations (Tables 4.1

and 4.2) using two-roll laboratory mill as per ASTM D 3182-82. The compounded rubber was kept for 24 hrs maturation. The optimum cure time, T_{90} min (the time required to reach 90% of the maximum torque) and scorch time (the time required to reach 10% of the maximum torque) of the compounds were determined on a Göttfert Elastograph Model 67-85 according to ASTM D 1648 - 81.

Rubber compounds were moulded in an electrically heated laboratory hydraulic press at 150°C up to their optimum cure time. Dumbbell shaped tensile test pieces were punched out of these compression moulded sheets along the mill grain direction. The tensile strength of the vulcanizates were evaluated on a Zwick Universal Testing machine using a crosshead speed of 500mm/min according to ASTM D-412- 98, method A. Tear resistance of the vulcanizates was evaluated as per ASTM D-624-98 using un-nicked 90° angled test specimens.

The ageing resistance of the vulcanizates were studied by ageing for 12, 24,36 and 48 hrs at 100°C, then measuring the retention in tensile strength. The extractability of the bound antioxidants was studied by keeping the samples in methanol and acetone for 48hrs at room temperature. The retention in tensile strength was again evaluated after ageing the samples at 100°C for 12,24,36 and 48hrs.

The compression set of the samples was determined as per ASTM D-395-98, method B. The hardness (shore A) of the moulded samples was tested using a Zwick 3115 hardness tester in accordance with ASTM D 2240-97. Abrasion resistance was measured using a DIN abrader as per DIN 53516. Resilience of the samples was determined by vertical re-bound as per ASTM D 2632-96.The heat build up was measured using the Goodrich flexometer conforming to ASTM D 623-99(method A).Cross-link density ($1/2M_c$) was determined using equilibrium swelling method using toluene as solvent.

b) Results and Discussion

The Fig. 4.1 shows the cure curves of the compounds with and without antioxidants. The cure and scorch time were reduced by the addition of polyisobutylene-bound paraphenylene diamine (PIB-PD) and chlorinated paraffin wax -bound paradhenylene diamine (CPW-PD). This may be due to the presence of faster curing polymer-bound antioxidants.

Table 4.1. Formulations for testing PIB-PD antioxidant in NR.

Sample	A	B	C	D	E	F	G
Natural rubber	100	100	100	100	100	100	100
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
Carbon black (HAF, N330)	40.0	40.0	40.0	40.0	40.0	40.0	40.0
Mercaptobenzothiazole	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Tetramethylthiuramdisulphide	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Aromatic oil	-	5.0	5.0	3.0	1.0	-	-
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Pilflex 13	-	1.0	-	-	-	-	-
PIB- PD	6.0	-	-	2.0	4.0	8.0	10.0

The Fig 4.2 shows the variation in tensile strength after ageing at 100°C for 48hrs with the concentration of the antioxidants (Tables 4.1 and 4.2). The tensile strength retention increases with amount of chemically bound antioxidants, reaches a maximum and then levels off. The higher quantities of bound antioxidants are due to lower amount of effective antioxidant in the bound product.

Fig. 4.3 shows the tensile strength of the vulcanizates of compounds shown in Tables 4.1& 4.2 with time of ageing at 100°C. The deterioration in tensile strength of the vulcanizates with ageing may be principally due to main chain scission. All the vulcanizates show fairly good resistance to ageing at 100°C for 24hrs but only vulcanizates containing PIB-PD and CPW-PD show good retention in properties after 48hrs ageing. This shows the superiority of bound antioxidants to conventional antioxidant.

Fig. 4.4 shows the change in elongation at break of the vulcanizates with time of ageing. The compounds containing PIB-PD and CPW-PD show better retention in elongation at break after ageing. This again shows that bound antioxidants can improve the ageing resistance of the NR vulcanizates.

Table 4.2. Formulations for testing CPW-PD antioxidant in NR.

Sample	A_1	B_1	C_1	D_1	E_1	F_1	G_1
Natural rubber	100	100	100	100	100	100	100
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
Carbon black (HAF, N330)	40.0	40.0	40.0	40.0	40.0	40.0	40.0
Mercaptobenzothiazole	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Tetramethylthiuramdisulphide	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Aromatic oil	-	5.0	5.0	3.0	1.0	-	-
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Pilflex 13	-	1.0	-	-	-	-	-
CPW- PD	6.0	-	-	2.0	4.0	8.0	10.0

Fig. 4.5 shows the change in modulus of the vulcanizates with time of ageing at100°C. The increase in modulus after ageing may be due to the increase in total crosslink density.

Fig.4.6 shows the variation in tear strength with time of ageing at100°C for 48hrs. Only compounds containing PIB-PD and CPW-PD show good resistance when the ageing time is increased to 48hrs, which shows the superiority of bound antioxidants over conventional antioxidant.

Fig.4.7 shows the variation in tensile strength of the vulcanizates with time of ageing at 100°C after extracting the samples in methanol and acetone. The retention in properties by the vulcanizates containing bound antioxidants is probably due to the lower extractability of bound antioxidant by the solvents.

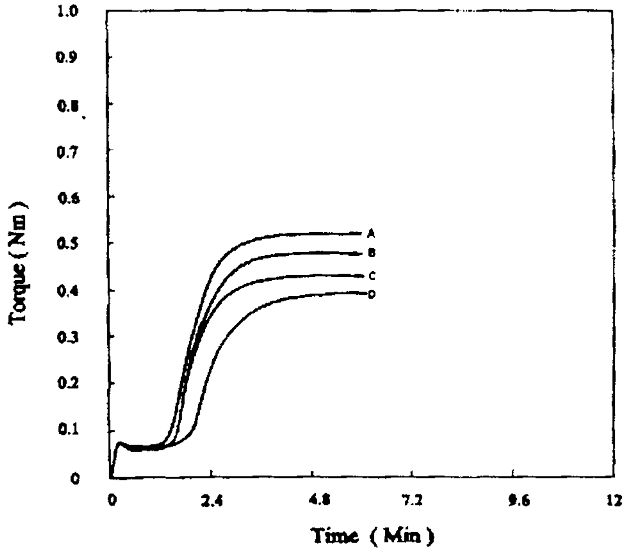


Fig. 4.1 Cure Curves of A-PIB-PD, B- CPW-PD C-pilflex 13, D-without antioxidant

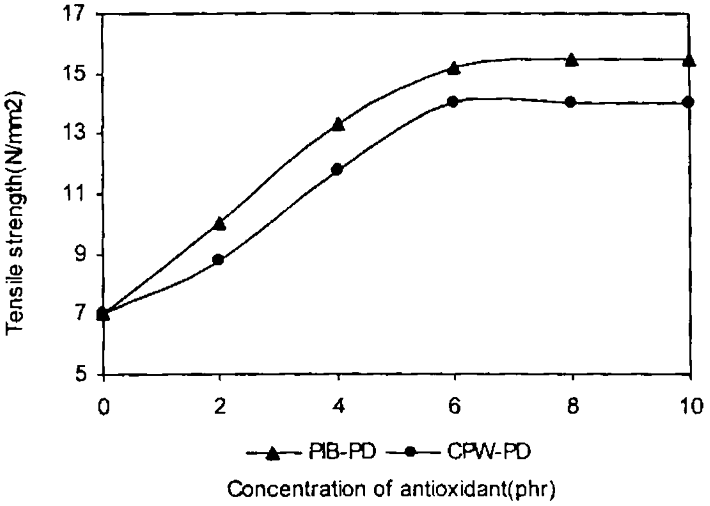


Fig.4.2 Variation in tensile strength with the amount of antioxidants after ageing at 100°C for 48hrs

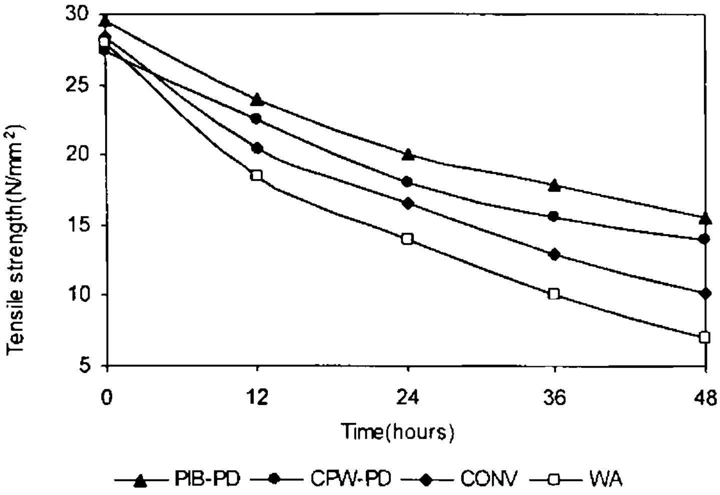


Fig.4.3 Variation in tensile strength of the NR vulcanizates with time of ageing at 100°C

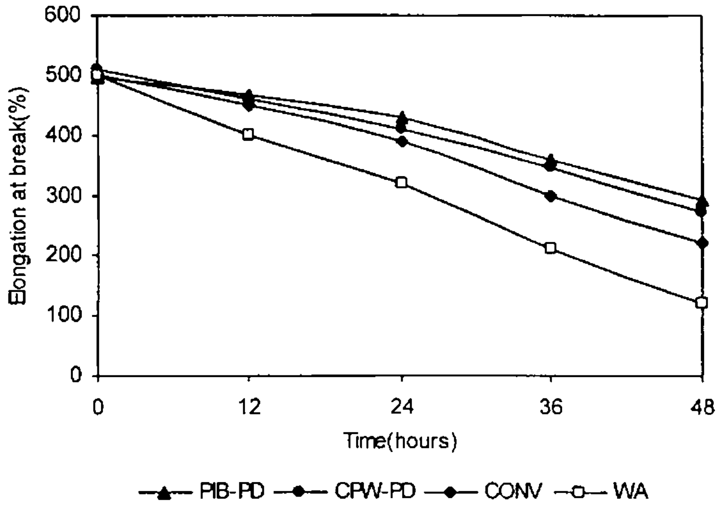


Fig.4.4 Variation in elongation at break of the NR vulcanizates with time of ageing at 100°C

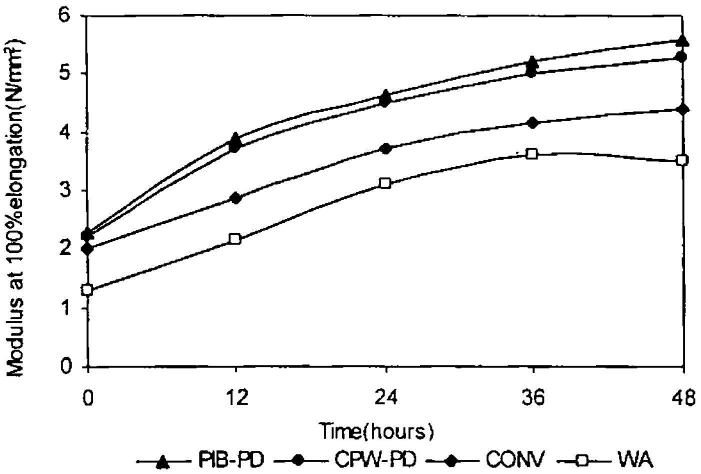
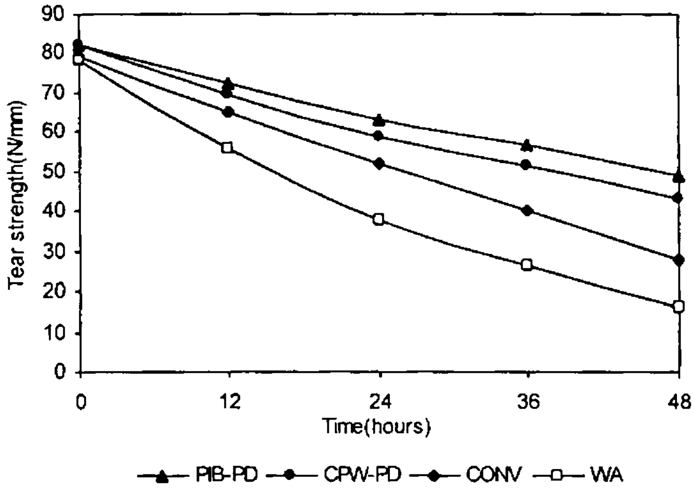


Fig.4.5. Variation in modulus of NR vulcanizates with time of ageing at 100°C



4.6 Variation in tear strength of NR vulcanizates with time of ageing at 100°C

Table 4.3 shows abrasion resistance, compression set, hardness, resilience, crosslink density and heat build up of the NR vulcanizates with and without antioxidants. The abrasion resistance and compression set of vulcanizates containing conventional and bound antioxidants are comparable as shown in Table 4.3. This shows that here properties are not affected by the addition of polymer-bound antioxidants.

The heat build up values of vulcanizates containing conventional and bound antioxidants are almost same as shown in Table 4.3. This shows that the addition of PIB-PD and CPW-PD is not affecting the NR vulcanizate properties. The reduction in the amount of plasticizer also doesn't make any change in the heat build up values.

Table 4.4 shows the variation in tensile strength, tear strength, elongation at break and modulus of the vulcanizates after extracting the samples in acetone and methanol followed by ageing at100°C for 48 hrs. The retention in properties by the vulcanizates containing PIB-PD and CPW-PD is found to be superior. This is due to lower extractability of the bound antioxidants in acetone and methanol.

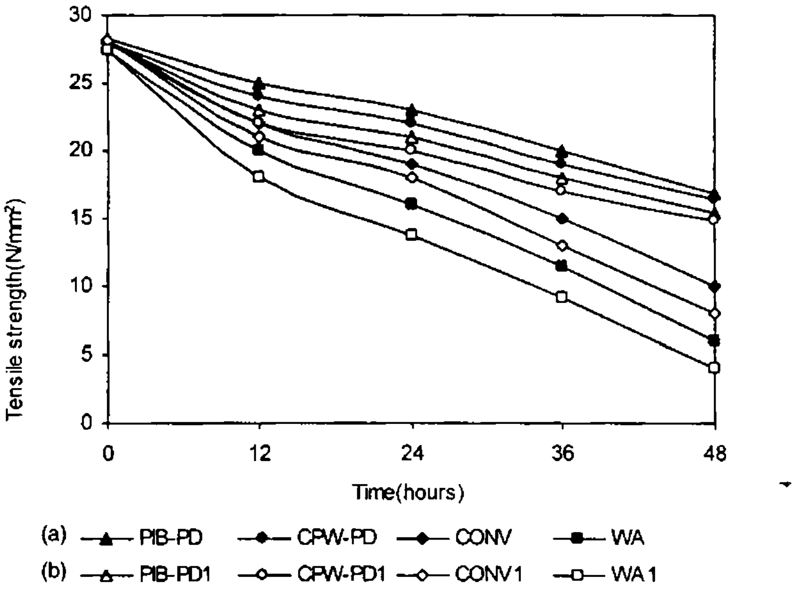


Fig.4.7 Variation in tensile strength of NR vulcanizates with time of ageing at 100°C, after extracting the samples (a) in methanol (b) in acetone

Table 4.3 Properties of NR vulcanizates

Properties	PIB-PD	CPW-PD	Pilflex-13	Without antioxidant
Abrasion resistance (Volume loss (cc/h)	3.5	3.5	3.6	3.7
Compression set (%)	16.8	17	17.7	18
Hardness (Shore A)	50	50	49	48
Resilience	65	65	63	62
Cross link density (g mol/cc) $\times 10^{-5}$	8.3	8.1	7.6	6.4
Heat build up (°C)	19	19	19.5	25

Table 4.4 Properties before and after extracting the NR samples (A-PIB-PD, B-CPW-PD C-pilflex13 and D-without antioxidant) in methanol and acetone (48hrs, 30°C) followed by ageing at 100°C for 48hrs

Properties	Properties before extraction				Properties after extraction and ageing for 48hrs							
					Methanol				Acetone			
	A	B	C	D	A	B	C	D	A	B	C	D
Tensile strength (N/mm^2)	27.5	27	27.2	28	15.1	14	10	6	14.6	14	8.2	5
Elongation at break (%)	444	450	464	475	282	285	205	140	280	282	180	150
Modulus at 200% elongation (N/mm^2)	8.3	8.2	8.1	8.0	9.9	8.7	9.5	-	8.6	8.6	-	-
Tear strength (N/mm)	83	82	79	70	50	48	30	20.5	49	46	25	16.5

Table 4.5 shows the variation in tensile strength; tear strength, elongation at break and modulus of the vulcanizates before and after extracting the samples in boiling water for 10hrs and in detergent for 3 days. The retention in properties by the vulcanizates containing PIB-PD and CPW-PD is found to be higher due to lower extractability of the bound antioxidant in boiling water and detergent.

Table 4.5 Properties before and after extracting the NR samples in boiling water for 10h and in detergent for three days.

Property	Properties before extraction				Properties after extracting							
					In boiling water for 10h				In detergent for three days			
	PIB-PD	CPW-PD	CONV.	WA	PIB-PD	CPW-PD	CONV.	WA	PIB-PD	CPW-PD	CONV.	WA
Tensile strength (N/mm^2)	27.5	27	27.2	28	22.7	22	20	14.5	27.4	27	23.2	18.5
Elongation at break (%)	444	450	464	505	382	365	315	280	437	434	380	250
Modulus at 200% elongation (N/mm^2)	8.2	8.2	8.1	8.0	8.9	8.7	8.5	8.6	8.6	8.6	8.3	7.5
Tear strength (N/mm)	82.2	82	79	70	69.2	67.2	50.3	40.5	79	75	65	56.5

Conclusions

1. The NR vulcanizates containing polyisobutylene-bound paraphenylene diamine and chlorinated paraffin-wax-bound paraphenylene diamine antioxidants have superior ageing resistance compared to that containing pilflex 13.
2. They impart superior resistance to volatility and extractability compared to conventional antioxidant.
3. The polymer-bound antioxidants can reduce the amount of plasticizer required for compounding.

4.1.2 Use of polyisobutylene-bound paraphenylenediamine type antioxidant in NR modified bitumen

Experimental

Materials

Natural rubber latex concentrate having the BIS 5430-81 specification, bitumen of 80/100 penetration, polyisobutylene-bound paraphenylenediamine (PIB-PD).

Preparation of NR modified bitumen

Bitumen was heated to a temperature of 150°C until it melts to a free flowing liquid. Then the correct quantity of rubber latex [2parts per hundred bitumen (pphb)] was sprayed slowly and uniformly over the surface of molten bitumen with constant stirring. Then the required quantity of antioxidant [6 parts per hundred rubber (pphr)] was added and stirring was continued using a high-speed stirrer, for a further period of 15 minutes. The total mixing time was kept as 1.5hrs.

The softening point of NR modified bitumen was determined by the ring and ball method according to IP 58/82. Water bath was used for heating as softening point was below 80°C. Penetration was determined as per IP 49/79. A penetrometer (Precision Scientific Co., USA) was used for the purpose. The experiment was conducted at 25°C for 5 seconds with a total moving weight of 100g. Ductility was determined as per IP 32/55 at 27°C and at a rate of pull of 50mm/min. A ductility meter (Humboldt manufacturing Co. USA) was used. Flash point was determined by the Pensky - Martens closed method as per IP 34/85, at a heating rate of 50°C/min and with a stirrer speed of 60rpm. Elastic recovery was determined as per IS 1208-78.

Results and Discussion

Table 4.6 shows the elastic recovery, softening point, penetration, flash point, specific gravity and ductility of NR modified bitumen with and without antioxidants.

No change in elastic recovery, flash point, specific gravity and ductility was observed for the control mix and antioxidant mix, but softening point is increased from 50 to 54. Penetration decreases from 62 to 42 due to addition of polymer-bound antioxidant. These two values show that bound antioxidant can improve the property of NR modified bitumen. This may be due to the retention of elastomeric properties of natural rubber present in it.

Fig. 4.8 shows the thermograms of bitumen-NR mix with and without PIB-PD. Slight increase in the temperature of decomposition is observed for compound containing bound antioxidant. This shows that the slight improvement in the degradation resistance of the mix is due to the polymer-bound antioxidant added.

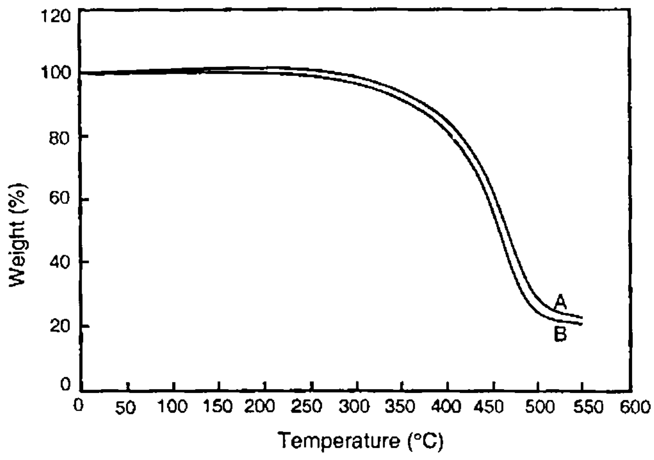


Fig.4.8 TGA of bitumen-NR mix; A- with PIB-PD and B- without antioxidant

Table 4.6 Data on heat treatment of NR modified bitumen

Sl.No	Properties	Control	Antioxidant
1	Elastic recovery	55	55
2	Penetration	62	42
3	Softening point	50	54
4	Specific gravity	1.036	1.036
5	Ductility	> 100	>100
6	Flash point	> 200	> 200

Fig.4.9 shows the weight loss with time at constant temperature (300°C) for bitumen- NR mix with and without antioxidant. Superior thermal stability is shown by compound containing PIB-PD. This confirms that it can reduce the degradation of NR in NR modified bitumen.

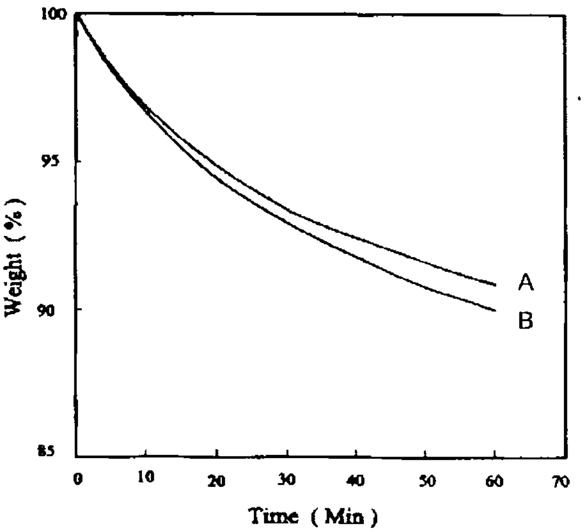


Fig.4.9 Weight loss with time at constant temperature (300°C)

Conclusions

1. The softening point is increased by the addition of PIB-PD to NR modified bitumen and hence the bleeding of bituminous road surfacing can be reduced.
2. Penetration point is decreased considerably, which signifies the increase in hardness of NR modified bitumen.
3. The degradation of NR in NR modified bitumen is reduced by the addition of PIB-PD

4.1.3 Use of polyisobutylene-bound paraphenylene diamine and chlorinated paraffin wax-bound paraphenylene diamine antioxidants in SBR

Experimental

The optimum concentration of antioxidants for getting maximum retention in properties was determined by varying the amount of antioxidant in a standard formulation from 1 to 10 phr (Tables 4.7 and 4.8). The optimum concentrations of polyisobutylene-bound paraphenylenediamine (PIB-PD) and chlorinated paraffin wax-bound paraphenylene diamine (CPW-PD) were determined.

PIB-PD and CPW-PD were added to SBR as per formulation given in Tables 4.7 and 4.8. The amount of plasticizer can be reduced by the use of liquid rubber - bound antioxidants.

Table 4.7 Formulations of SBR for testing PIB-PD antioxidant

Sample	A_2	B_2	C_2	D_2	E_2	F_2	G_2
Styrene butadiene rubber	100	100	100	100	100	100	100
Zinc oxide	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Carbon black (HAF, N330)	40.0	40.0	40.0	40.0	40.0	40.0	40.0
Dibenzthiazyldisulphide	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Tetramethylthiuramdisulphide	0.15	0. 15	0. 15	0. 15	0.15	0.15	0.15
Aromatic oil	–	5.0	5.0	3.0	1.0	–	–
Sulphur	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Vulkanox 4020	–	1.0	–	–	–	–	–
PIB- PD	8.0	–	–	2.0	4.0	6.0	10.0

The optimum cure time, T_{90} min (the time required to reach 90% of the maximum torque) and scorch time (the time required to reach 10% of the maximum torque) of the compounds were determined on a Göttfert Elastograph Model 67-85 according to ASTM D 1648-81.

Rubber compounds were moulded in an electrically heated laboratory hydraulic press at 150°C up to their optimum cure time. Dumbbell shaped tensile test pieces were punched out of these compression moulded sheets along the mill grain direction. The tensile strength of the vulcanizates was evaluated on a Zwick Universal Testing machine using a crosshead speed oL500mm/min according to ASTM D-412-98, method A. Tear resistance of the vulcanizates was evaluated as per ASTM D-624-98 using un-nicked 90° angled test specimens.

Table 4.8 Formulations of SBR for testing CPW-PD

Sample	A_3	B_3	C_3	D_3	E_3	F_3	G_3
Styrene butadiene rubber	100	100	100	100	100	100	100
Zinc oxide	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Carbon black (HAF, N330)	40.0	40.0	40.0	40.0	40.0	40.0	40.0
Dibenzthiazyldisulphide	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Tetramethylthiuramdisulphide	0.15	0. 15	0. 15	0. 15	0.15	0.15	0.15
Aromatic oil	-	5.0	5.0	3.0	1.0	-	-
Sulphur	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Vulkanox 4020	-	1.0	-	-	-	-	-
CPW-PD	8.0	-	-	2.0	4.0	6.0	10.0

The ageing resistance of the vulcanizates were studied by ageing for 24, 48 and 72hrs at 100°C, then measuring the retention in tensile strength. The extractability of the bound antioxidant was studied by keeping the samples in methanol and acetone for 48hrs at room temperature. The retention in tensile strength was again evaluated after ageing the samples at 100°C for 12,24,36 and 48hrs.

The compression set of the samples was determined as per ASTM D-395-98, method B. The hardness (shore A) of the moulded samples was tested using a Zwick 3115 hardness tester in accordance with ASTM D-2240. Abrasion resistance was measured using a DIN abrader as per DIN 53516. Resilience of the samples was determined by vertical re-bound as per ASTM D 2632-96. Crosslink density ($1/2M_c$) was determined using equilibrium swelling method-using toluene as solvent.

Results and Discussion

Fig. 4.10 shows the cure curves of the SBR compounds with and without antioxidants. Here also the cure time were reduced by the addition of PIB-PD and CPW-PD in comparison with compounds with the conventional antioxidant. This may be due to accelerating effect of liquid amine type antioxidants.

Fig.4.11 shows the variation in tensile strength with concentration of antioxidants after ageing the samples for 72hrs at 100°C. Ageing resistance of SBR vulcanizate were enhanced by the addition of PIB-PD and CPW-PD reaches a maximum and then levels off. The higher amount requirement of bound antioxidants compared to conventional antioxidant(Tables 4.7 and 4.8) may be due to a lower amount of effective antioxidant in the bound product.

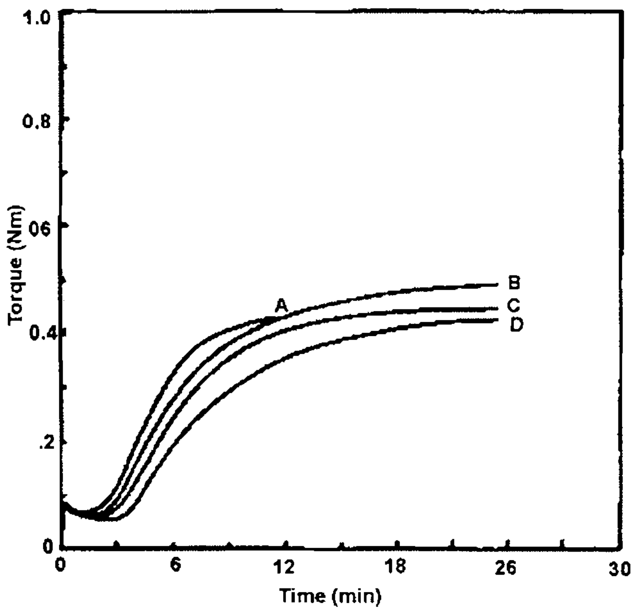


Fig.4.10 Cure curves of the SBR vulcanizates: (A) - PIB -PD, (B) - CPW-PD, (C)-vulkanox 4020 and (D) - without antioxidant.

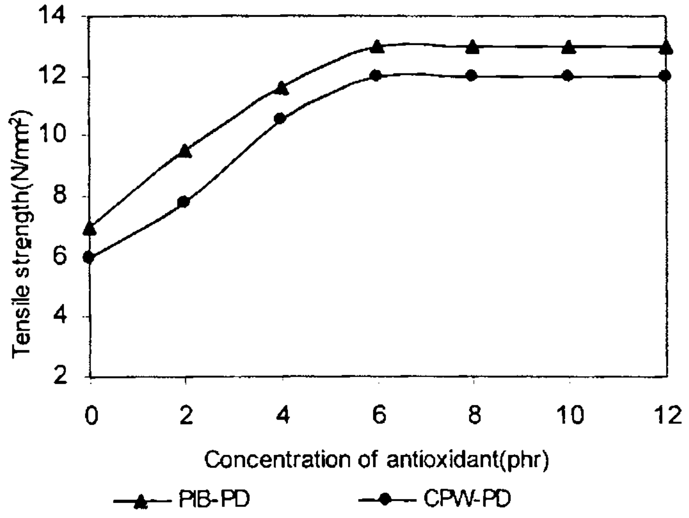


Fig.4.11 Variation in tensile strength retention with concentration of PIB-PD and CPW-PD after 72hrs ageing at 100°C

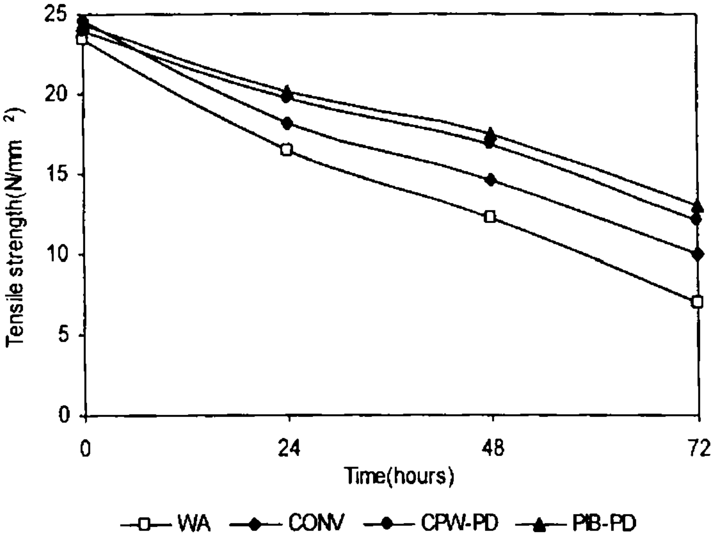


Fig.4.12 Variation in tensile strength of SBR vulcanizate with time of ageing at 100°C

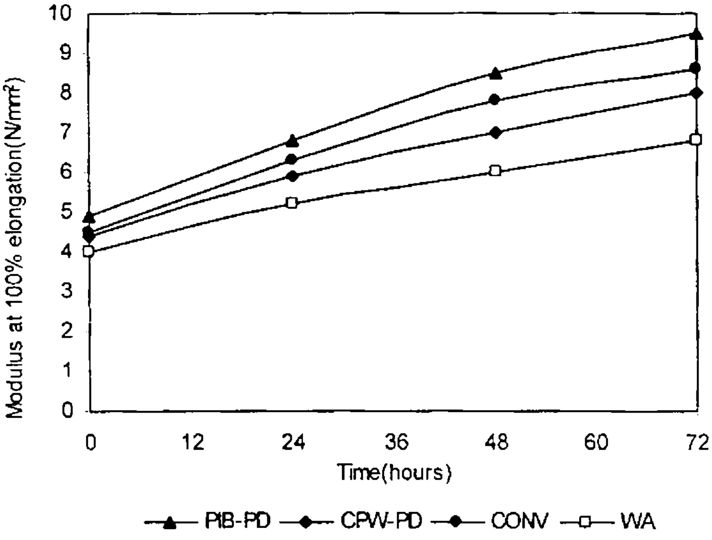


Fig.4.13 Variation in modulus of SBR vulcanizates with time of ageing at 100°C

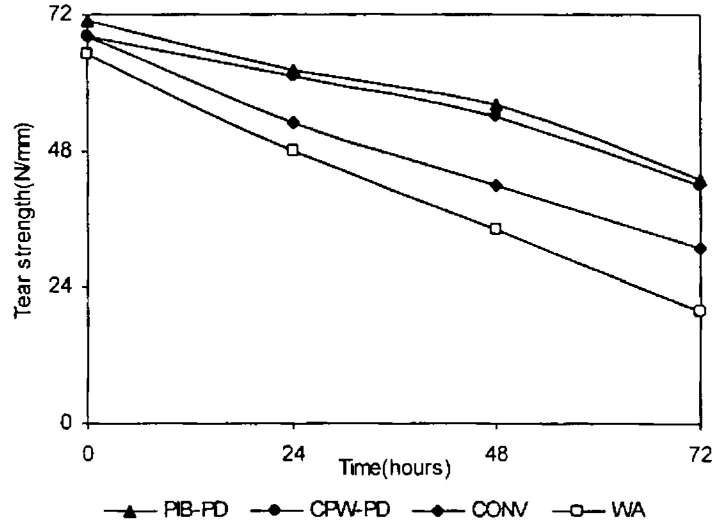


Fig. 4.14 Variation in tear strength of SBR vulcanizates with time of ageing at 100°C

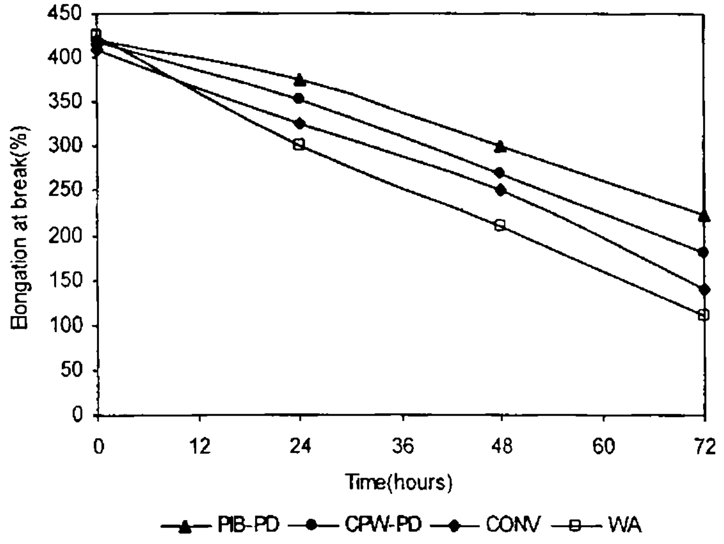


Fig. 4.15 Variation in elongation at break of SBR vulcanizates with time of ageing at 100°C

Fig. 4.12 shows the variation tensile strength of the vulcanizates with time of ageing at 100°C. The vulcanizates containing-bound antioxidants namely PIB-PD and CPW-PD show fairly good resistance to ageing at 100°C compared to those containing conventional and without antioxidant.

Fig. 4.13 shows the modulus of the vulcanizates time of ageing. The increase in modulus after ageing may be due to increase in cross-link density.

Fig. 4.14 shows the tear strength of the above vulcanizates time of ageing. Retention in tear strength of the vulcanizates containing PIB-PD and CPW-PD after ageing is superior to vulcanizate containing vulkanox 4020.

Fig. 4.15 shows the change in elongation at break of the vulcanizates time of ageing. The compounds containing PIB-PD and CPW-PD show better retention in elongation at break after ageing. This again shows that polymer-bound antioxidants can improve the ageing resistance of SBR.

Fig. 4.16 shows the variation in tensile strength of vulcanizates with time of ageing at 100°C after extracting the samples in acetone and methanol. The retention in properties is found to be better for the vulcanizates containing PIB-PD and CPW-PD compared to those without antioxidant and with conventional antioxidant. This may be due to lower extractability of the bound antioxidants by methanol and acetone. When we compare PIB-PD and CPW-PD, the former exhibits slightly better retention in properties. This may be due to its higher molecular weight compared to CPW-PD.

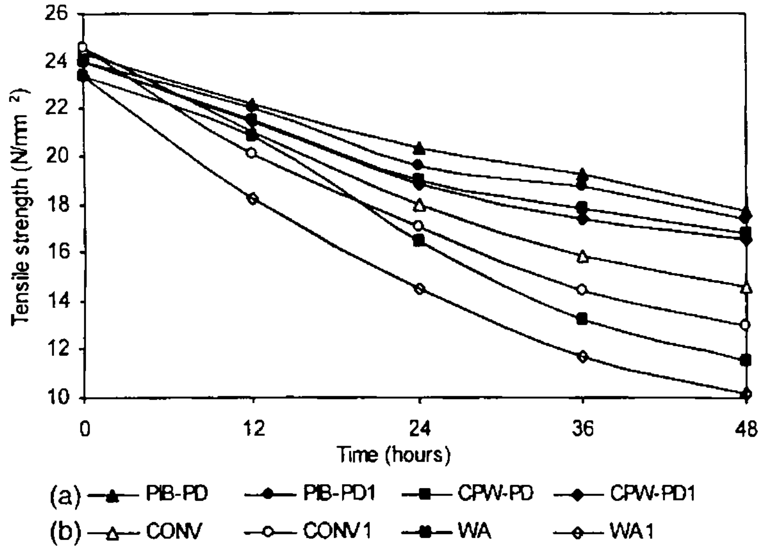


Fig. 4.16 variation in tensile strength of SBR vulcanizates with time of ageing, after extracting the samples in (a) acetone and (b) methanol.

Table 4.9 Properties of SBR vulcanizates

Properties	A (PIB-PD)	B (CPW-PD)	C (vulkanox4020)	D (without antioxidant)
Abrasion resistance (volume loss, cc/h)	2.9	3.0	3.1	3.1
Compression set (%)	28.8	28.6	28.9	29.9
Hardness (Shore A)	54	54	54	52
Resilience (%)	49	48	48	47
Crosslink density x 10^{-5} (g mol/cc)	7.34	7.12	6.66	4.95

Table 4.9 shows abrasion resistance, compression set, hardness, resilience and crosslink density of the vulcanizates. The abrasion resistance, crosslink density and compression set of vulcanizates containing conventional and bound antioxidants are almost same as shown in Table 4.9. This shows that here properties are not affected by the addition of polymer-bound antioxidant.

Table 4.10 Properties before and after extracting the SBR samples in methanol and acetone (48hrs, 30°C) followed by ageing at 100°C for 48hrs

Property	Properties before extraction				Properties after extraction and ageing for 48hrs							
					Methanol				Acetone			
	A	B	C	D	A	B	C	D	A	B	C	D
Tensile strength (N/mm^2)	24.3	24.6	23.4	24	17.7	16.8	14.6	11.5	17.4	16.5	13	10.2
Elongation at break (%)	420	418	400	424	282	26.7	250	265	264	225	220	250
Modulus at 100% elongation (N/mm^2)	4.9	4.5	4.4	4.0	8.5	7.8	7.0	6.0	8.2	7.6	6.4	5.1
Tear strength (N/mm)	71	69	68	65	55	52	40	30	53	49	35	22

Table 4.10 shows the variation in tensile strength, tear strength, elongation at break and modulus of the vulcanizates time of ageing at 100°C for 48hrs,after extracting the samples in acetone and methanol. The retention in properties by the vulcanizate containing PIB-PD is found to be high due to lower extractability of the bound antioxidant by the solvents.

Conclusions

1. The polymer-bound antioxidants can improve the ageing resistance of SBR vulcanizates.
2. The SBR vulcanizate containing polyisobutylene-bound paraphenylene diamine and chlorinated paraffin wax-bound antioxidants have much superior resistance to extractability in solvents compared to that containing conventional antioxidant.
3. The polymer-bound antioxidants can reduce the amount of plasticizer required for compounding.

4.1.4 Use of polyisobutylene-bound paraphenylene diamine and chlorinated paraffin wax-bound paraphenylene diamine antioxidants in NBR

Experimental

The optimum concentrations of PIB-PD and CPW-PD antioxidants in NBR for getting maximum retention in properties were determined by varying their amounts in the standard formulation from 1 to 10 phr as shown in Tables 4.11 and 4.12.

The formulations given in the Tables 4.11 and 4.12 show that the amount of plasticizer can be reduced by the use of liquid polymer-bound antioxidants. The optimum cure time, T_{90} min (the time required to reach 90% of the maximum torque) and scorch time (the time required to reach 10% of the maximum torque) of the compounds were determined on a Göttfert Elastograph Model 67.85 according to ASTM D 1648 (1981). Rubber compounds were moulded in an electrically heated laboratory hydraulic press at 150°C up to their optimum cure time. Tensile strength, tear strength, modulus, hardness, abrasion resistance, resilience and heat build up were found as per ASTM standards. Oil resistance of the NBR vulcanizates containing bound antioxidants was studied by keeping the samples in light oil, transformer oil and engine oil at room temp and also at 70°C for 24hrs.

Solvent resistance of bound antioxidants was studied in methanol and acetone by keeping the vulcanizates in methanol and acetone for 48hrs at room temperature. The retention in tensile strength of samples after methanol and acetone extraction was evaluated after ageing the extracted samples at 100°C for

12,24,36 and 48hrs. Water resistance of the samples was studied by keeping the samples in water at 70°C for 24hrs and also in boiling water for 10h. Retention in tensile strength, tear strength and hardness after water extraction was evaluated by ageing the samples at 100°C for 48hrs.

Table 4.11 Formulations for testing NBR with PIB-PD antioxidant

Sample	A_4	B_4	C_4	D_4	E_4	F_4	G_4
Acrylonitrile - butadiene rubber (NBR)	100	100	100	100	100	100	100
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Zinc oxide	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Carbon black (HAF, N330)	40	40	40	40	40	40	40
Dioctylphthalate (DOP)	-	5	5	3.0	1.0	-	-
Mercaptobenzothiazole (MBTS)	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Tetramethylthiuramdisulphide	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Vulkanox 4020	-	1.0	-	-	-	-	-
PIB PD	6.0	-	-	2.0	4.0	8.0	10.0

The heat build up was measured using the Goodrich flexometer conforming to ASTM D 623-99(method A).Cross link density ($1/2M_c$) was determined using equilibrium swelling method in 2-butanone.

Results and Discussion

Fig. 4.17 shows cure curves of the compounds given in Tables 4.11and 4.12. (A4, A_5, B_4, & C_4) Cure time and scorch time were reduced by the addition of PIB-PD and CPW-PD. This shows that PIB-PD and CPW-PD have got slight accelerating effect. This may be due to the basic nature of the antioxidants.

Fig.4.18 shows the variation in tensile strength with concentration of antioxidant after ageing the samples for 72hrs at 100°C. Ageing resistance of NBR vulcanizates was enhanced by the addition of PIB-PD and CPW-PD reaches a maximum and then levels off. The higher amount requirement of bound antioxidant compared to conventional antioxidant may be due to a lower amount of effective antioxidant in the bound product.

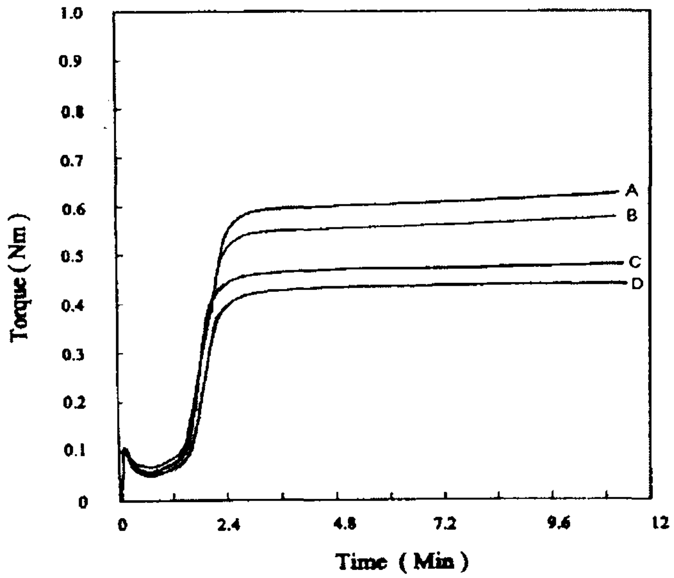


Fig.4.17 Cure cures of the compounds: (A) - PIB -PD, (B) - CPW-PD (C)-vulkanox 4020 and (D) - without antioxidant.

Fig.4.19 shows the tensile strength of the vulcanizates of compounds (Table 4.11 and 4.12) with time of ageing. All the vulcanizates show fairly good resistance to ageing at 100°C for 24hrs but only compounds containing PIB-PD and CPW-PD show good resistance when the ageing time is increased to 72hrs.which shows the superiority of bound antioxidants over conventional antioxidant.

Fig.4.20 shows the tear strength of the above vulcanizates with time of ageing. Retention in tear strength of the vulcanizates containing PIB-PD and CPW-PD after ageing is superior to vulcanizate containing vulkanox 4020.

Fig. 4.21 shows the modulus of the vulcanizates with time of ageing. The increase in modulus after ageing may be due to increase in crosslink density.

Fig. 4.22 shows the change in elongation at break of the vulcanizates with time of ageing. The compounds containing PIB-PD show better retention in elongation at break after ageing. This again shows that polymer-bound antioxidants can improve the ageing resistance of NBR vulcanizates also.

Table 4.12 Formulations for testing NBR with CPW-PD antioxidant

Sample	A_5	B_5	C_5	D_5	E_5	F_5	G_5
Acrylonitrile - butadiene rubber (NBR)	100	100	100	100	100	100	100
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Zinc oxide	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Carbon black (HAF, N330)	40	40	40	40	40	40	40
Dioctylphthalate (DOP)	-	5	5	3.0	1.0	-	-
Mercaptobenzothiazole (MBTS)	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Tetramethylthiuramdisulphide	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Vulkanox 4020	-	1.0	-	-	-	-	-
CPW- PD	6.0	-	-	2.0	4.0	8.0	10.0

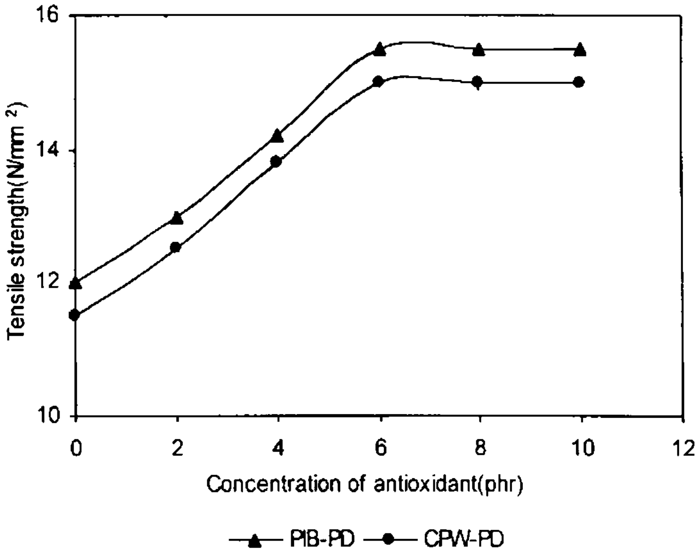


Fig.4.18 Tensile strength retention after ageing for 48hrs with the concentration of antioxidants after 72hrs ageing at 100° C

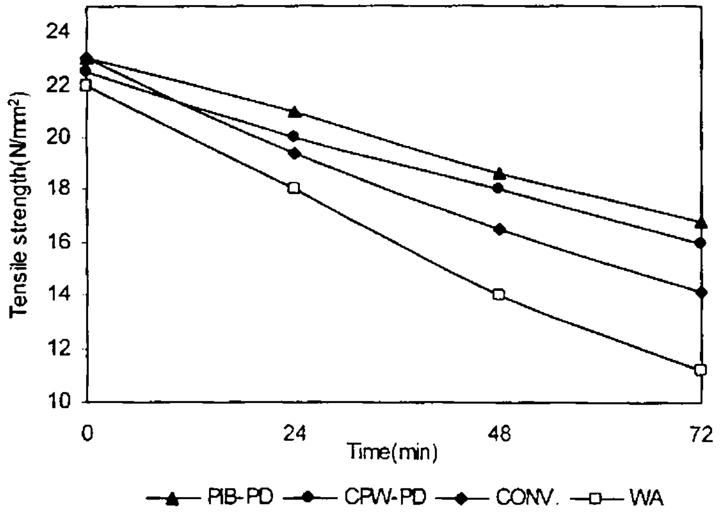


Fig.4.19 Variation in tensile strength of NBR vulcanizates with time of ageing at 100°C.

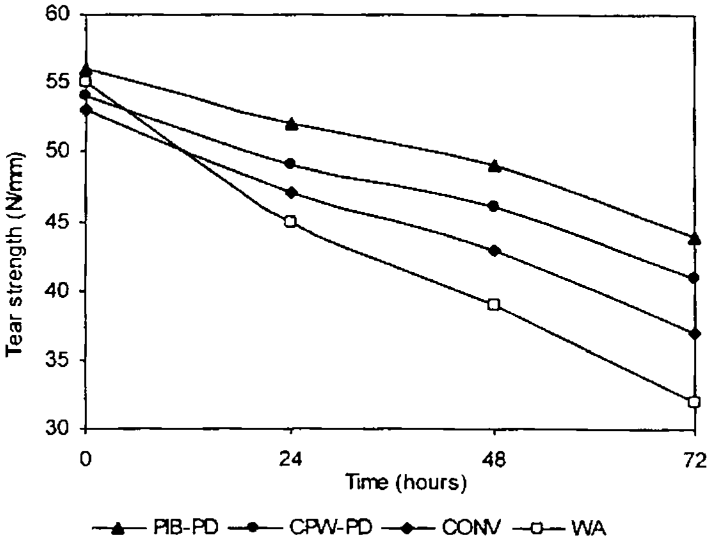


Fig.4.20 Variation in tear strength of NBR vulcanizates with time of ageing at 100°C.

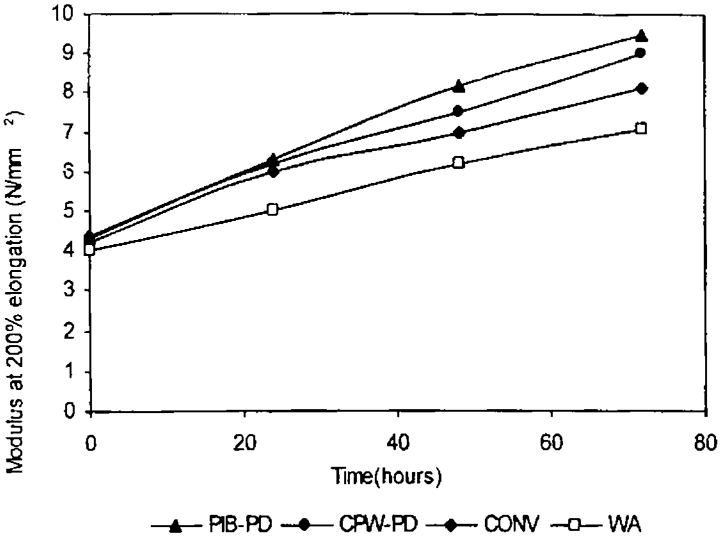


Fig.4.21.Variation in modulus of NBR vulcanizates with time of ageing at 100°C

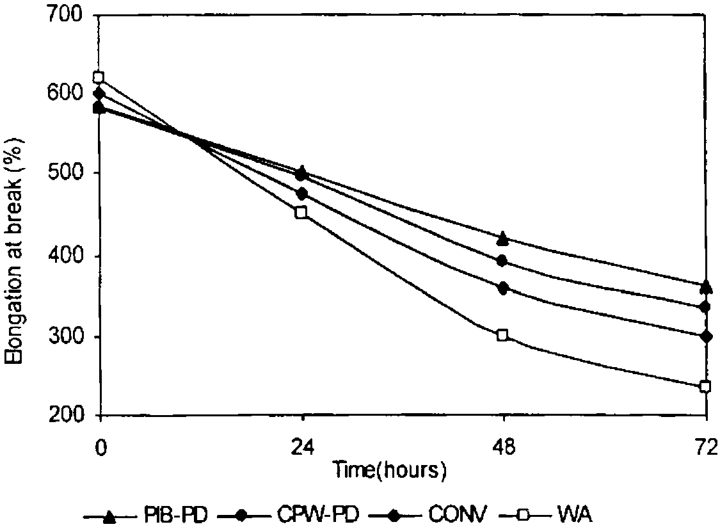


Fig.4.22 Variation in elongation at break of NBR vulcanizates with time of ageing at 100°C.

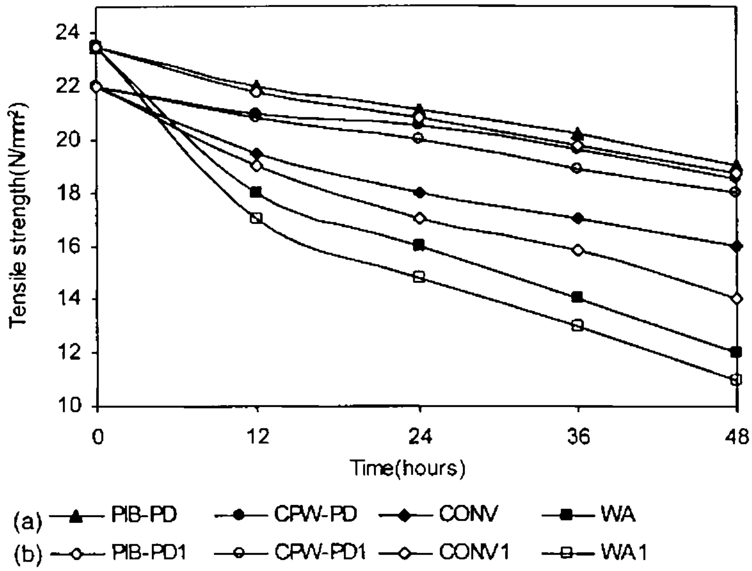


Fig.4.23 Variation in tensile strength of NBR vulcanizates before and after extraction in solvents followed by ageing at 100°C (a) in methanol and (b) in acetone

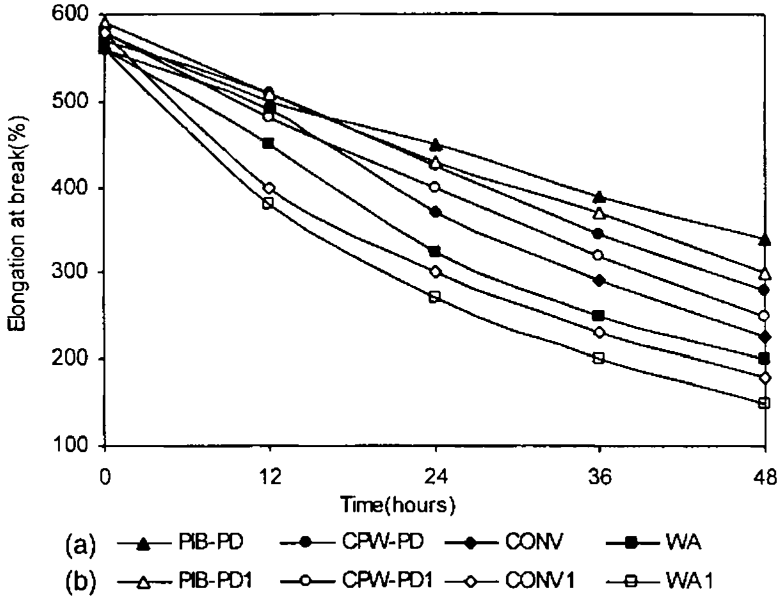


Fig.4.24 Variation in elongation at break of NBR vulcanizates before and after extraction in solvents followed by ageing at 100°C. (a) in methanol and (b) in acetone

Table 4.13 Properties of NBR vulcanizates.

Properties	A (PIB-PD)	B (CPW-PD)	C (vulkanox 4020)	D (WA)
Abrasion resistance (volume loss, cc/h)	2.4	2.4	2.52	3.1
Compression set (%)	16.5	16.8	17	17.9
Hardness (Shore A)	66	66	65	62
Heat build up (°C)	23	23	24	26
Resilience (%)	49	49	48	47
Crosslink density × 10^{-4} (g mol/cc)	2.24	2.15	2.02	1.88

Table 4.14 Properties of samples after oil extraction at room temperature followed by ageing for 48hrs at 70°C.

Property	Properties before extraction				Properties after extraction and ageing for 48hrs at 70°C							
					Transformer oil				Engine oil			
	A	B	C	D	A	B	C	D	A	B	C	D
Tensile strength (N/mm^2)	22.3	22	21.4	22	18.5	18	16.6	14.3	18.9	18	16	14.2
Elongation at break (%)	550	570	580	595	437	542	462	385	508	510	482	350
Modulus at 100% elongation (N/mm^2)	2.8	2.6	2.4	2.2	4.97	7.2	4.31	4.03	4.99	6.9	4.5	4.12
Tear strength (N/mm)	69.5	67	68	67	57	42	49	41	58.2	38	43	38.5

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Table 4.15 Properties after water extraction at 70°C and 100°C followed by ageing at 100°C for 48hrs.

Property	Extraction		A (PIB-PD)	B CPW-PD	C (Conv)	D (without antioxidant)
	Time	Temp				
Tensile strength (N/mm^2)	0	27°C	22	22	21.4	22
Elongation at break (%)			550	570	580	595
Modulus at 100% elongation (N/mm^2)			2.8	2.6	2.4	2.2
Tear strength (N/mm)			69.5	67	68	67
Tensile strength (N/mm^2)	24h	70°C	19.2	18	16	14
Elongation at break (%)			410	480	425	400
Modulus at 100% elongation (N/mm^2)			5.6	5.5	5.42	5.12
Tear strength (N/mm)			55	53	49	39
Tensile strength (N/mm^2)	10h	100°C	18.3	17.1	14.5	10.8
Elongation at break (%)			382	261	305	218
Modulus at 100% elongation (N/mm^2)			5.92	6.24	5.6	5.22
Tear strength (N/mm)			56	52	50	40

Figs. 4.23 and 4.24 show the variation in tensile strength and elongation-at-break of the vulcanizates time of ageing, after extracting the samples in acetone and methanol. The retention in properties of vulcanizates containing PIB-PD and CPW-PD is probably due to the lower extractability of the bound antioxidant by the solvents.

Table 4.13 shows the variation in abrasion resistance, compression set, hardness, heat build up, resilience and crosslink density of the vulcanizates of the compounds shown in Tables.4.11 and 4.12.The abrasion resistance, compression set and crosslink densities of vulcanizates containing conventional and bound antioxidants are comparable. This shows that replacement of plasticizer by bound antioxidant doesn't make any change in the above-mentioned properties. While the heat build up values are decreased by the addition of bound antioxidants.

Table 4.14 shows the variation in tensile strength, elongation at break, modulus and tear strength of the vulcanizates (of the compounds shown in Table 4.11 and 4.12) before and after extracting the samples in transformer oil and engine oil at room temperature and 70°C. Retention in properties for vulcanizates containing bound antioxidants may be due to the lower extractability of PIB-PD and CPW-PD by oils.

Table 4.15 shows the variation in tensile strength, elongation at break, modulus and tear strength of the vulcanizates after keeping the samples in water at 70°C and 100°C followed by ageing at 100°C for 48 hrs. The retention in properties shown by the vulcanizates containing polymer-bound antioxidants is superior to those vulcanizates containing conventional antioxidant because PIB-PD does not get extracted in hot water or boiling water.

Conclusions

1. The polymer-bound antioxidant has much superior resistance to volatility compared to conventional antioxidant.
2. The polymer-bound antioxidant can improve the ageing resistance of NBR vulcanizates.
3. The polymer-bound antioxidant can reduce the amount of plasticizer required for compounding.
4. Water and oil resistance of the NBR vulcanizates could be improved by the use of polymer-bound product.

4.1.5 Use of Polyisobutylene-bound Paraphenylene Diamine and Chlorinated Paraffin Wax-bound Paraphenylene Diamine Antioxidants in IIR

Experimental

The optimum concentrations of PIB-PD and CPW-PD for getting maximum retention in properties was determined by varying the amount of antioxidant in a standard formulation from 1 to 10 phr for sulphur cured and resin cured butyl rubber compounds (Tables4.16 and 4.17). The optimum concentration of polyisobutylene -bound paraphenylenediamine (PIB-PD) was determined as 6phr. The optimum concentration of CPW-PD for sulphur cured and resin cured butyl rubber compounds was also determined in a similar manner and it was also found to be 6phr as in the above cases.

Table 4.16 Formulation of IIR (S-cure)

Sample	A	B	C	D	E	F	G	H
Isobutene -Isoprene rubber	100	100	100	100	100	100	100	100
Zinc oxide	5.0	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	2.0
Paraffinic oil	15	15	15	13	11	9.0	7.0	5.0
Carbon black (HAF, N330)	55	55	55	55	55	55	55	55
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Mercaptobenzothiazole (MBTS)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Tetramethylthiuramdisulphide	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
PIB-PD	6.0	-	-	-	2.0	4.0	8.0	10.0
Vukanox 4020	-	-	1.0	-	-	-	-	-
CPW-PD	-	6.0	-	-	-	-	-	-

Table 4.17 Formulation of IIR (resin cure)

Sample	A	B	C	D	E	F	G	H
Isobutene -Isoprene rubber	95	95	95	95	95	95	95	95
Neoprene	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Carbon black (HAF, N330)	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0
PF resin	10.8	10.8	10.8	10.8	10.8	10.8	10.8	10.8
Oleic acid	-	-	3.0	3.0	1.0	-	-	-
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Wax	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Paraffinic oil	-	-	4.0	4.0	2.0	1.0	-	-
Vulkanox 4020	-	-	1.0	-	-	-	-	-
PIB- PD	6.0	-	-	-	2.0	4.0	8.0	10.0
CPW-PD	-	6.0	-	-	-	-	-	-

PIB-PD and CPW-PD were added to IIR as per formulation given in Tables 4.16 and 4.17. The amount of plasticizer can be reduced by the use of liquid rubber -bound antioxidants.

The optimum cure time, T_{90} min (the time required to reach 90% of the maximum torque) and scorch time (the time required to reach 10% of the maximum torque) of the compounds were determined on a Göttfert Elastograph Model 67.85 according to ASTM D 1648-81.

IIR sulphur cure and IIR resin cure compounds were moulded in an electrically heated laboratory hydraulic press at 170°C and 190°C respectively up to their optimum cure time. Dumbbell shaped tensile test pieces were punched out of these compression moulded sheets along the mill grain direction. The tensile strength of the vulcanizates were evaluated on a Zwick Universal Testing machine using a crosshead speed of 500mm/min according to ASTM D-412-98, method A.

Tear resistance of the vulcanizates was evaluated as per ASTM D-624-86 using un-nicked 90° angled test specimens. Heat build up was measured as per ASTM D 623-99 method A.

The ageing resistance of the vulcanizates were studied by ageing for 24, 48 and 72hrs at 100°C for sulphur cured and at 130°C for resin cured samples. Then measuring the retention in tensile strength. The retention in tensile strength was evaluated after ageing the samples.

Steam ageing of resin cured samples was conducted in a specially designed pressure vessel at 381°F and 350psi pressure.

The compression set of the samples was determined as per ASTM D-395-98, method B. The hardness (shore A) of the moulded samples was tested using a Zwick 3115 hardness tester in accordance with ASTM D 2240-97.Abrasion resistance was measured using a DIN abrader as per DIN 53516.

Results and Discussion

Figs. 4.25 and 4.26 show cure curves of the butyl compounds in Table4.13 (A. B, C and D) and Table 4.14 (A, B, C and D). Cure time and scorch time were slightly reduced by the addition of PIB-PD and CPW-PD.

Fig. 4.27 shows the variation in tensile strength with concentration of antioxidant after ageing of IIR sulphur cured and resin cured samples, for 72hrs at 130°C. Ageing resistance of IIR vulcanizate were enhanced by the addition of PIB-PD reaches a maximum and levels off. The higher amount requirement of bound antioxidant compared to conventional antioxidant may be due to a lower amount of effective antioxidant in the bound product.

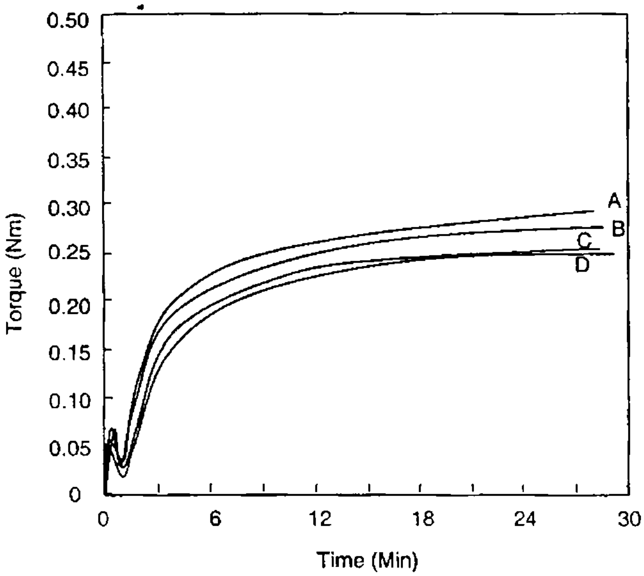

Fig. 4.25 Cure curves of IIR (S cure) compounds at 170°C (A) - PIB -PD, (B)- CPW-PD (C) -vulkanox 4020 and (D) - without antioxidant.

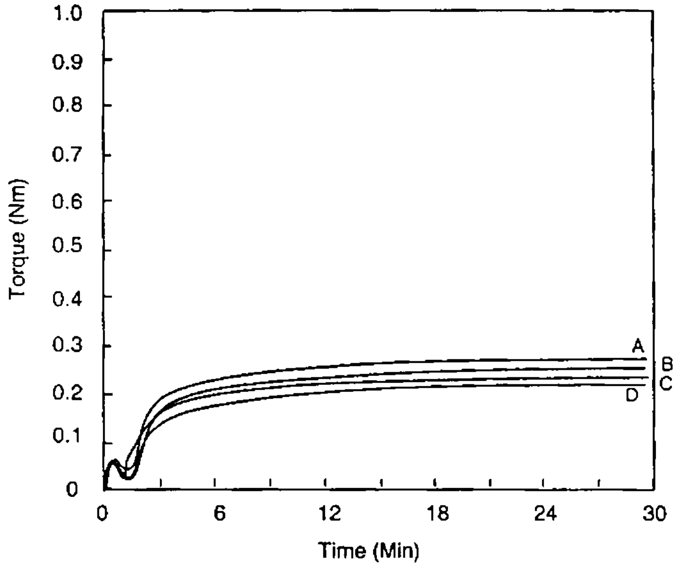

Fig.4.26 Cure curves of IIR (PF resin cure) compounds at 190°C: (A) - PIB -PD, (B)- CPW-PD (C) -vulkanox 4020 and (D) - without antioxidant.

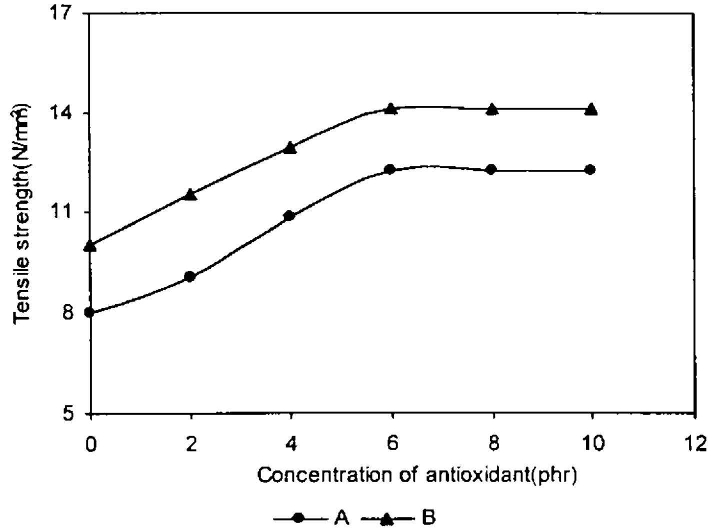

Fig. 4.27 Variation in tensile strength with concentration of PIB-PD: A- IIR (PF resin-cure) and B- IIR (S-cure)

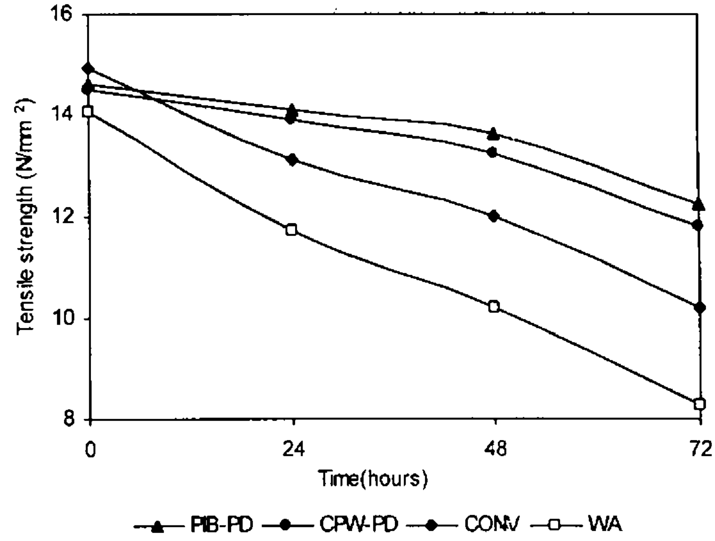

Fig.4.28 Variation in tensile strength of IIR Scure compounds with time of ageing at 100°C

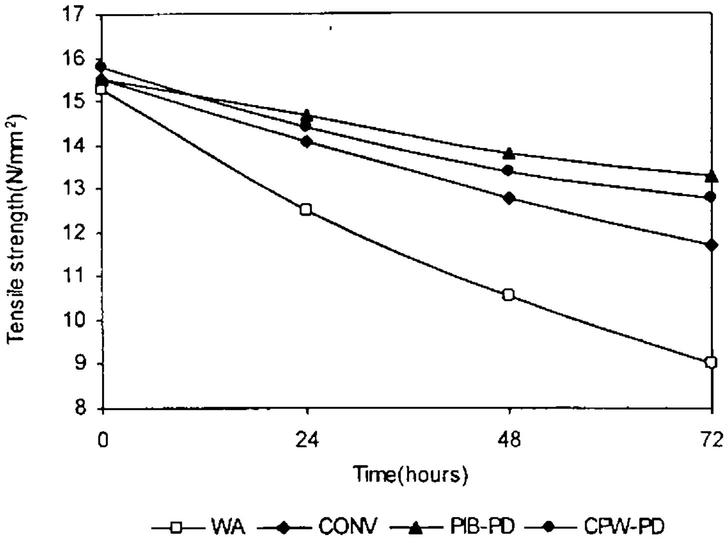

Fig.4.29 Variation in tensile strength in IIR resin cured compounds with time of ageing at130°C

Figs.4.28 and 4.29 show the tensile strength of s-cure and resin cure IIR compounds shown in Tables4.16 and 4.17 with time of ageing at 100°C and 130°C respectively. The retention in tensile strength is more pronounced for vulcanizates containing PIB-PD and CPW-PD when ageing time is increased to 72hrs.

Figs. 4.30 and 4.31 show the elongation at break of S-cure and resin cure IIR compounds with time of ageing. Retention in elongation at break of the vulcanizates containing PIB-PD and CPW-PD after ageing is superior to vulcanizate containing vulkanox 4020 for both cases.

Figs. 4.32 and 4.33 show the modulus of the vulcanizates with time of ageing. A slight increase in modulus is observed after ageing may be due to increase in crosslink density. Modulus of sulphur-cured compounds is slightly decreased when ageing is increased to 72hrs.

Figs. 4.34 and 4.35 show the variation in tear strength of IIR sulphur and resin cured vulcanizates with time of ageing at 100°C and 130°C respectively. The retention tear strength of the vulcanizates containing bound antioxidants after ageing for 72hrs is superior to those with conventional antioxidant and without antioxidant.

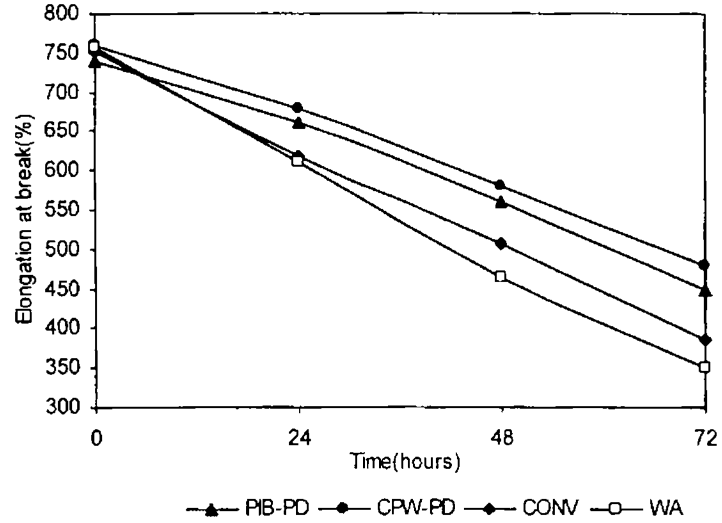

Fig.4.30 Variation of elongation at break of the IIR (S- cure) vulcanizates with time of ageing at 100°C

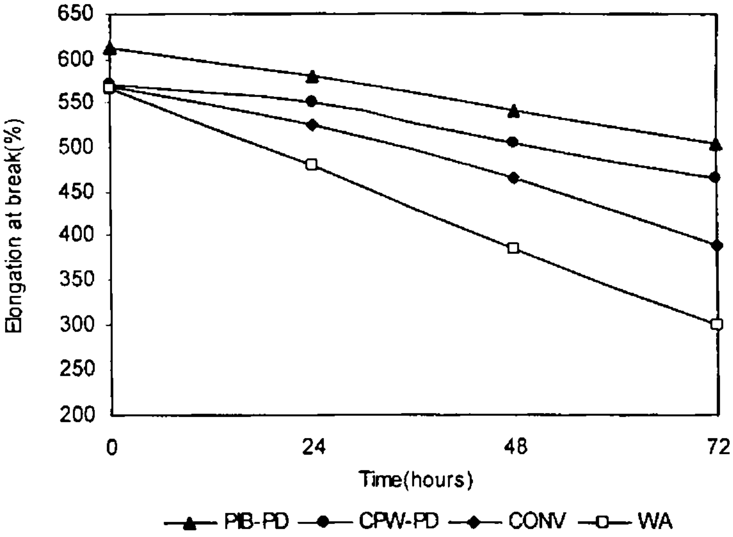

Fig.4.31 Variation of elongation at break of the IIR (resin cure) vulcanizates with time of ageing at 130°C

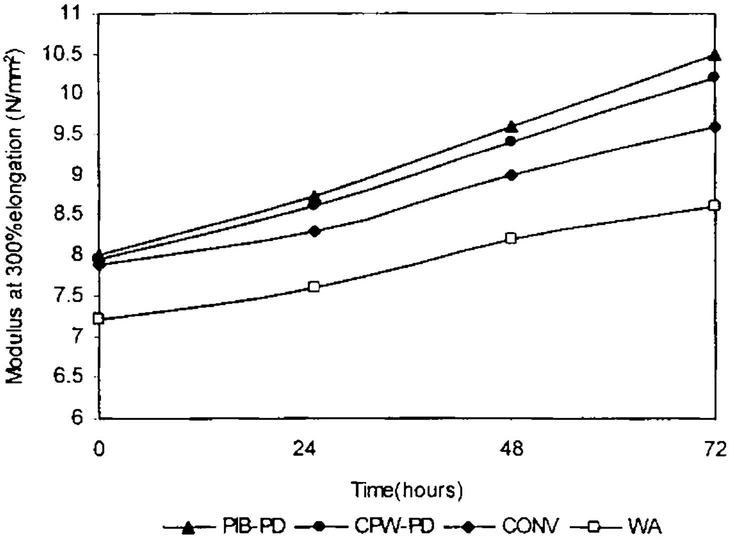

Fig.4.32 Variation of modulus of the IIR (resin- cure) vulcanizates with time of ageing at 130°C

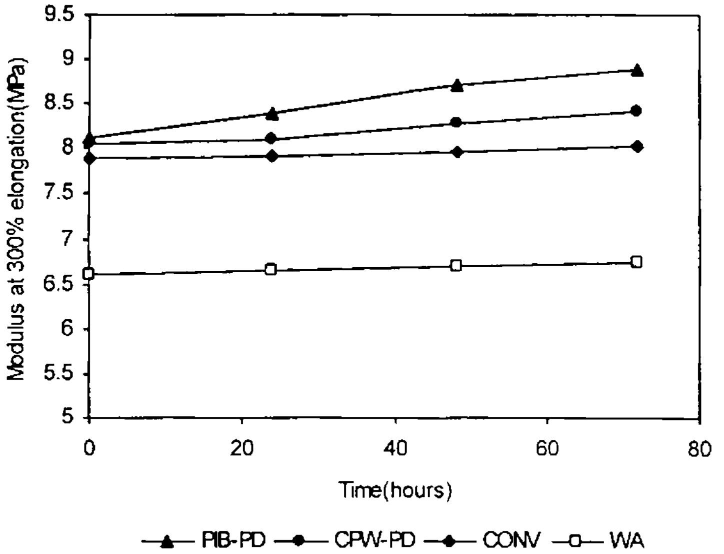

Fig.4.33 Variation of modulus of the IIR (S cure) vulcanizates with time of ageing at 100°C

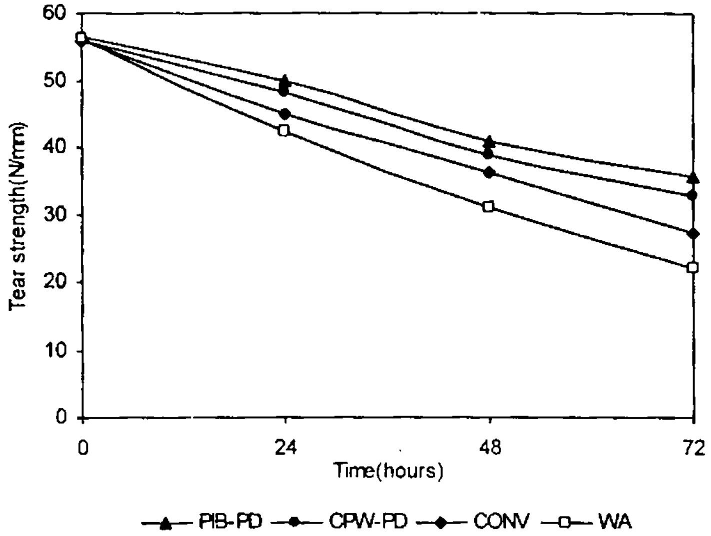

Fig.4.34 Variation of tear strength of the IIR (S cure) vulcanizates with time of ageing at 100°C

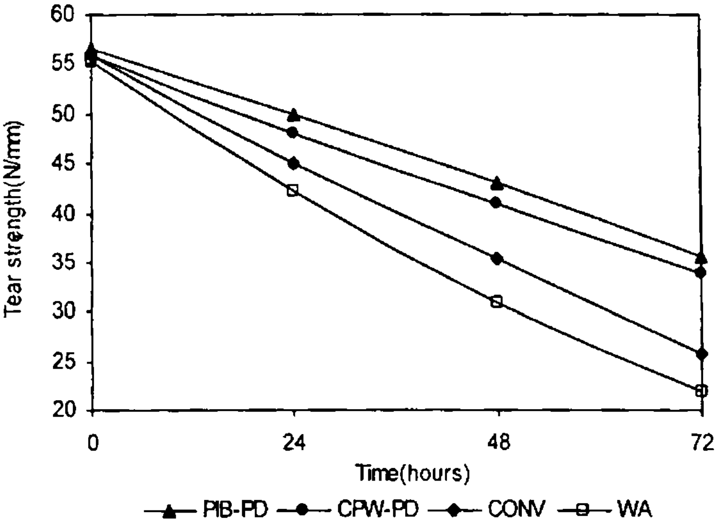

Fig. 4.35 Variation of tear strength of the IIR (resin cure) vulcanizates with time of ageing at 130°C

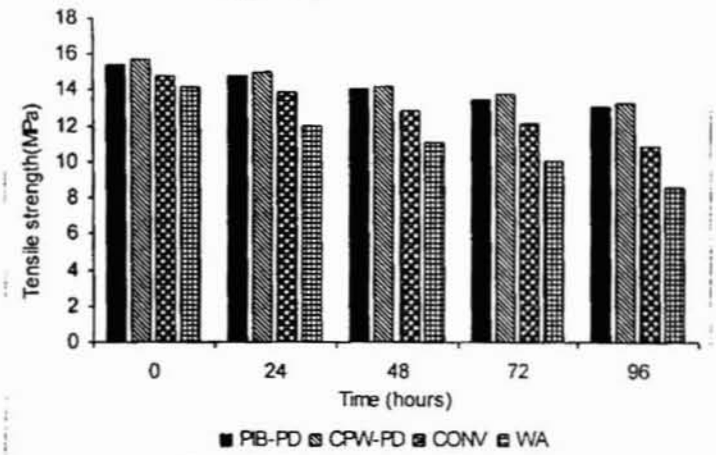

Fig. 4.36 Variation in tensile strength of the IIR (resin cure) vulcanizates with time of steam ageing at 380°F

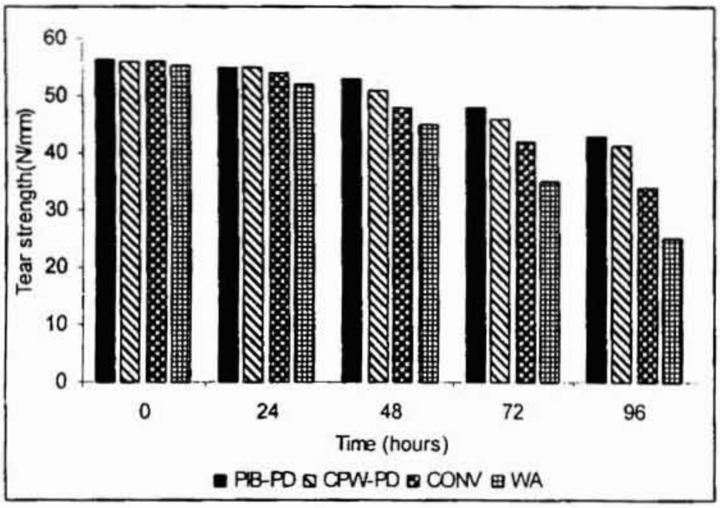

Fig. 4.37 Variation of tear strength of the IIR (resin cure) vulcanizates with time of steam ageing at 380°F

Figs. 4.36 and 4.37 show the variation in tensile strength and tear strength of IIR(resin cure) vulcanizates on steam ageing at 330°F and 185psi for 4 days. The vulcanizates containing bound antioxidants show superior retention in properties compared to those, with conventional antioxidant and without antioxidant.

Tables 4.18 and 4.19 show the variation in abrasion resistance, compression set, heat build up and hardness values of the IIR vulcanizates with and without antioxidants. The abrasion resistance compression set and hardness of the vulcanizates with bound antioxidants are comparable with that containing conventional antioxidants. But heat build up values of IIR vulcanizates(resin and S-cure) containing PIB-PD and CPW-PD are lower than that containing vulkanox 4020. This may be due to the higher plasticising effect of the bound antioxidants during ageing.

Table 4.18 Properties of IIR vulcanizates (resin- cure)

Properties	A (PIB-PD)	B (CPW-PD)	B (Vulkanox 4020)	C (without antioxidant)
Abrasion resistance (volume loss, cc/h)	3.1	3.1	3.137	3.5
Compression set (%)	32.2	31.5	30.5	29.7
Hardness	72	72	72	71.5
Heat build up	39	39	41	42

Table 4.19 Properties of IIR vulcanizates (S- cure)

Properties	A (PIB-PD)	B (CPW-PD)	C (Vulkanox 4020)	D (WA)
Abrasion resistance (volume loss, cc/h)	4.0	4.1	3.9	3.8
Compression set (%)	30.2	30.5	31.5	32.7
Hardness	65	64	64	64
Heat build up	29	30	31	32

Conclusions

1. The polymer-bound antioxidants can impart superior ageing resistance to IIR vulcanizates (S and resin cured).
2. Steam ageing resistance of IIR resin cured vulcanizates can be improved by the addition of PIB-PD and CPW-PD.
3. They can reduce the amount of plasticizer required for compounding.

PART II

4.2 Use of Polyisobutylene-Bound Diphenylamine and Polyethylene Glycol-Bound Paraphenylenediamine Antioxidants in NR

This part describes the application of polyethylene glycol-bound paraphenylenediamine (PEG-PD) and poyisobutylene-bound diphenylamine (PIB-DA) antioxidants in NR.

Experimental

Polyisobutylene-bound diphenylamine (PIB-DA), Polyethylene glycol -bound paraphenylenediamine (PEG-PD) and vulkanox 4020 were employed in NR as per formulation given in Table 4.20 and 4.21.The amount of plasticizer can be reduced by the use of liquid PEG-PD and PIB-DA. The optimum cure time and scorch time for the compounds were determined on a Göttfert Elastograph model 67.85 as per ASTM D 1646 –81. Rubber compounds were moulded in an electrically heated laboratory hydraulic press at 150°C up to their optimum cure time. Dumbbell shaped tensile test pieces were punched out of these compression-moulded sheets along the mill grain direction. The tensile strength and tear resistance were evaluated on a Zwick universal testing machine model 1445 as per ASTM standards. Hardness, abrasion resistance, heat build up and compression set of the vulcanizates were evaluated as per relevant ASTM standards.

Table 4.20 Formulations for testing PIB-DA antioxidant in NR

Sample	A	B	C	D	E	F	G
Natural rubber	100	100	100	100	100	100	100
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
Carbon black (HAF, N330)	40.0	40.0	40.0	40.0	40.0	40.0	40.0
Mercaptobenzothiazole	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Tetramethylthiuramdisulphide	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Aromatic oil	–	5.0	5.0	3.0	1.0	–	–
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Vulkanox 4020	–	1.0	–	–	–	–	–
PIB-DA	6.0	–	–	2.0	4.0	8.0	10.0

Retention in tensile strength and tear strength was evaluated after ageing the samples at 100°C for 12,24,36 and 48hrs.

Results and Discussion

Fig.4.38 shows the variation in tensile strength after ageing at100°C for 48 h with exposure time after the addition of PIB-DA and PEG-PD to NR vulcanizate. The retention in properties is found to increase with the amount of the bound antioxidant, reach a maximum and then levels off.

Table 4.21 Formulations for testing PEG-PD antioxidant in NR.

Sample	A	B	C	D	E	F	G
Natural rubber	100	100	100	100	100	100	100
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
Carbon black (HAF,N330)	40.0	40.0	40.0	40.0	40.0	40.0	40.0
Mercaptobenzothiazole	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Tetramethylthiuramdisulphide	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Aromatic oil	-	5.0	5.0	4.0	3.0	1.0	-
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Vulkanox 4020	-	1.0	-	-	-	-	-
PEG- PD	6.0	-	-	1.0	2.0	4.0	5.0

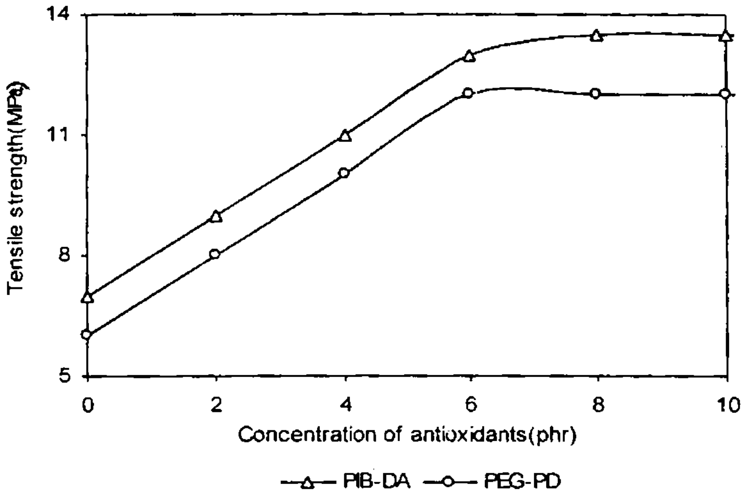

Fig4.38 Variation in tensile strength with the concentration of bound-antioxidants after ageing at 100°C for 48hrs.

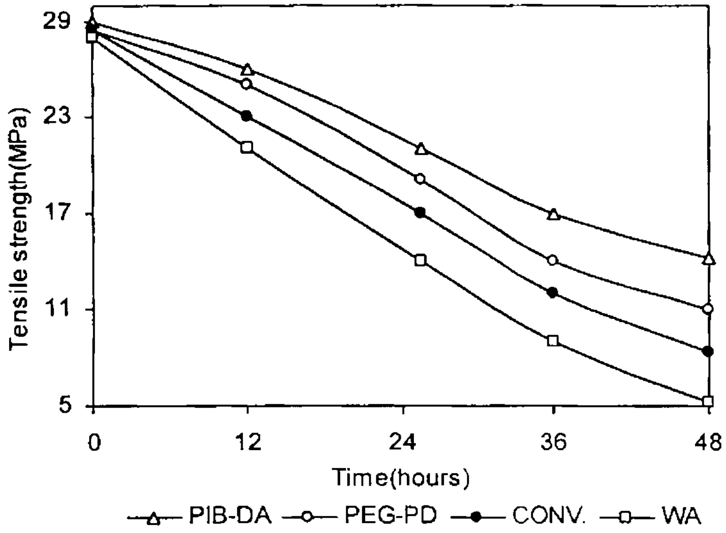

Fig.4.39 Variation in tensile strength of the NR vulcanizates with time of ageing at 100°C

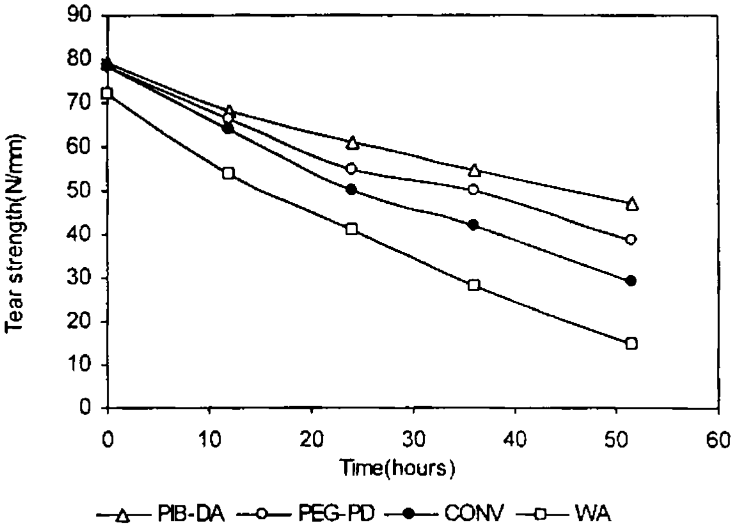

Fig.4.40 Variation in tear strength of the NR vulcanizates with time of ageing at 100°C

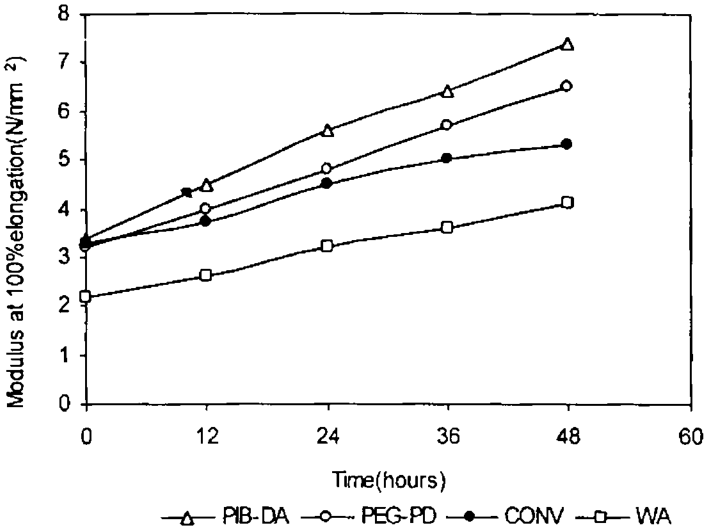

Fig. 4.41 Variation in modulus of the NR vulcanizates time of ageing at 100°C

Fig. 4.39 shows variation in the tensile strength of the vulcanizates of NR compounds shown in Table 4.20 & 4.21 with time of ageing. The vulcanizates containing PIB-DA and PEG-PD show good resistance when the ageing time is increased to 48hrs which shows the superiority of bound antioxidant over conventional antioxidant.

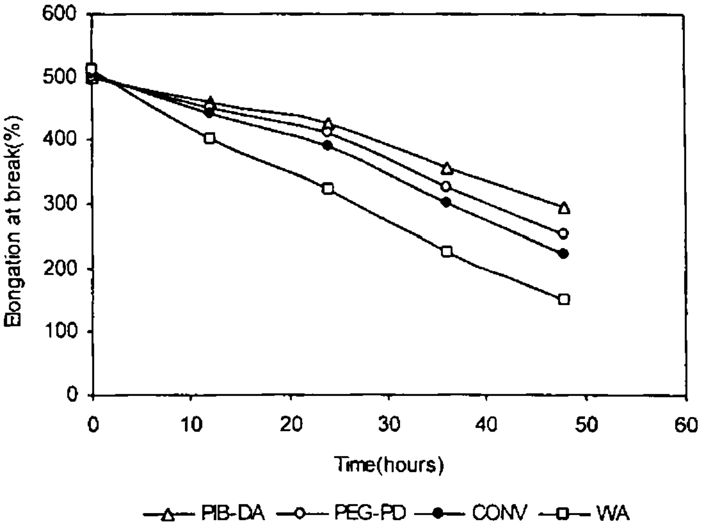

Fig. 4.42 Variation in elongation at break of the NR vulcanizates with time of ageing at 100°C

Fig. 4.40 shows the tear strength of the vulcanizates with time of ageing. The vulcanizates containing PIB-DA and PEG-PD show good resistance when the ageing time is increased to 48hrs which shows the superiority of bound antioxidants over conventional antioxidant.

Fig. 4.41 shows the change in modulus of the vulcanizates with ageing time. The increase in modulus after 48hrs ageing may be due to the increase in total crosslink density.

Fig. 4.42 shows the change in elongation at break of the vulcanizates ageing time. The compounds containing PIB-PD and PEG-PD shows better retention in elongation at break after ageing. This again shows that bound antioxidant can improve the ageing resistance of the NR vulcanizates.

Table 4.22 Properties of NR vulcanizates

Properties	A (PIB-DA)	B (PEG-PD)	C (Pilflex-13)	D (WA)
Abrasion resistance (volume loss, cc/h)	3.5	3.5	3.5	3.7
Compression set (%)	16.2	17.2	17.7	18
Hardness (Shore A)	49.5	49.5	49	47
Cross link density x 10^{-5} (g mol/cc)	7.98	7.92	7.66	6.45
Heat build up (°C)	19.8	19.8	21	24

Table 4.22 shows abrasion resistance, compression set, hardness, crosslink density and heat build up of the NR vulcanizates. The abrasion resistance and compression sets of vulcanizates containing conventional and bound antioxidant are comparable as shown in Table 4.22. This shows that these properties are not affected by the addition of polymer-bound antioxidants.

The heat build up values of vulcanizates containing bound antioxidant are slightly lower than that containing conventional antioxidant as shown in Table 4.22. This shows reduction may be due to the better plasticising effect of liquid bound antioxidants

Table 4.23 shows the variation in tensile strength, tear strength, elongation at break and modulus of the vulcanizates time of ageing at 100 °C for 48hrs,after extracting the samples in acetone and methanol. The retention in properties by the vulcanizates containing PIB-DA and PEG-PD is found to be high due to lower extractability of the bound antioxidants by acetone and methanol.

Table 4.23 Properties before and after extracting the NR samples in methanol and acetone (48hrs, 30°C) followed by ageing at 100 °C for 48hrs

Property	Properties before extraction				Properties after extraction and ageing for 48hrs							
					Methanol				Acetone			
	A	B	C	D	A	B	C	D	A	B	C	D
Tensile strength (N/mm^2)	27.5	27	27.2	28	13.9	13	10	7.5	13.5	13	8.2	5
Elongation at break (%)	498	444	464	475	285	280	205	160	282	280	180	150
Modulus at 100% elongation (N/mm^2)	3.7	3.5	2.98	2.24	5.26	5.2	5.14	4.86	5.2	5.1	4.9	4.7
Tear strength (N/mm)	81	80	79	70	49.4	48	30	19	47	45	25	15.5

Table 4.24 Properties before and after extracting the NR samples in boiling water for 10h and in detergent for three days.

Property	Properties before extraction				Properties after extracting							
					In boiling water for 10h				In detergent for three days			
	A	B	C	D	A	B	C	D	A	B	C	D
Tensile strength (N/mm^2)	27	27	27.2	28	21.7	20	18.5	14.5	26.4	25.4	23.2	18.5
Elongation at break (%)	498	444	464	475	362	355	300	280	487	420	380	300
Modulus at 100% elongation (N/mm^2)	3.7	3.5	2.98	2.24	8.7	8.5	8.2	8.6	3.8	3.6	3.3	3.5
Tear strength (N/mm)	81.2	80	79	70	67.2	65	52	40.5	78.9	76	65	56.5

Table.4.24 shows the variation in tensile strength, tear strength, elongation at break and modulus of the vulcanizates before and after extracting in boiling water for 10h and in detergent for 3days. The retention in properties by the vulcanizates containing PIB-DA and PEG-PD is found to be high due to lower extractability of the bound antioxidants in boiling water and detergent.

Conclusions

1. The PIB-DA and PEG-PD antioxidants have much superior resistance to volatility and extractability compared to conventional antioxidant.
2. The polymer-bound antioxidants can reduce the amount of plasticizer required for compounding.

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Chapter 5

PREPARATION, CHARACTERISATION AND USE OF NOVEL PHENOLIC TYPE ANTIOXIDANTS

Introduction

The trend towards the use of rubbers in aggressive atmosphere has led to a search for methods of producing non- extractable antioxidants. Phenol was one of the earlier materials used to retard the oxidation of rubber. Alkylated phenols were found to be more effective, less toxic and less volatile. Higher molecular weight non-staining antioxidants by alkylating phenols were reported.[1,2] A wide variety of substituted phenols have been synthesised and evaluated as antioxidants during last 70 years. The patent literature represents one of the best sources of information on the current direction of research in the area of polymer stabilisation. Two books deal exclusively with the United states patent literature on antioxidants during the period of 1972 to 1979.[3,4] For rubber applications, cost as well as low volatility and compatibility with the polymer are important and most of the research effort deals with the alkylation of phenols. Spacht[5] found that the reaction of p-cresol and dicyclopentadiene, when tertiary butylated in the ortho positions of the terminal phenol is an effective antioxidant. Goto[6] discovered that the three isomers of dicyclopentyl-p-cresol (2,6-, 2,5-, 3,5-) obtained by reacting cyclopentene with p-cresol, were as effective as BHT in retaining physical properties of NR vulcanizates when aged 3 days at 100°C. Scott and co-workers have demonstrated that simple hindered phenols which contain a methyl group in the ortho or para position, can react with natural rubber in the presence of oxidising free radicals to yield polymer-bound antioxidants.[7,8] De Jonge and Hope[9] described the development of a novel type of antioxidant based on 2,6 - diphenylphenol. These antioxidants display novel regenerative characteristics in the presence of thiodipropionate esters and lead to maintenance of the antioxidant concentration during processing and oxidation. Antioxidants like styrenated phenol bound to hydroxyl-terminated liquid natural rubber by modified Friedel-Crafts reaction were also found to be effective in improving ageing resistance.[10]

This chapter describes the chemical binding of phenol to polyisobutylene and stearic acid respectively. These bound-antioxidants were compared with conventional antioxidants like styrenated phenol and 2,6 di-t-butyl p-cresol in filled natural rubber.

PART I

5.1 Preparation and Characterisation of Polyisobutylene-Bound Phenol and its use in NR Vulcanizates.

5.1.1Experimental

a) Materials used

Phenol, chlorinated polyisobutylene, anhydrous $AlCl_3$, o-xylene, fused calcium chloride and methanol.

b) Preparation of polyisobutylene-bound phenol

The chlorinated polyisobutylene (PIB-Cl) is prepared by the method described in chapter 3. The phenol was alkylated using modified Friedel-Crafts alkylation reaction. 0.1mol of PIB-Cl, 0.2 mol of phenol, 0.4 mol catalyst (anhydrous aluminium chloride and 60 mol of solvent (o-xylene) were introduced into a two-necked flask fitted with a thermometer and soxhlet extraction unit which was packed with fused $CaCl_2$. The reaction mixture was heated for 14h. When the reaction was complete, the reaction mixture was neutralized with sodium carbonate and washed several times with water to remove the catalyst. The contents of the vessel were poured into excess methanol with stirring to precipitate the liquid phenol-bound polyisobutylene (PIB-Ph). It was separated using a separating funnel, washed and dried in a vacuum oven. The polyisobutylene bound phenol was obtained in the form of a viscous liquid.

c) Analysis of bound antioxidant

Analysis of bound antioxidant was carried out by using infrared spectroscopy (IR), proton magnetic resonance spectroscopy (^{1}HNMR) and Thermo gravimetric analysis (TGA).

IR spectra of the samples were taken on a Perkin-Elmer Model 377 IR Spectrometer.

The ^{1}H-NMR spectra of the samples were recorded from a solution in CCl_4 using a JEOL-JNM spectrometer. TGA was carried out using a Dupont TG-DSC standard model in nitrogen atmosphere at a heating rate of 10°C/min. The optimum concentration of the rubber bound antioxidant for attaining maximum retention in properties was determined by varying the amount of the antioxidant in the mix from 1 to 10 phr

The polyisobutylene-bound phenol antioxidant was added in NR as per formulations given in table5.1.

The amount of the plasticiser can be reduced by the use of liquid polymer-bound antioxidant as shown in table 5.1. The optimum cure times (time to reach 90 % of the maximum torque) of compounds were determined on a Göttfert Elastograph, model 67.85, as per ASTM D-1646 (1981).

Table 5.1 Formulations for testing PIB-Ph antioxidant.

Sample	A	B	C	D	E	F	G	H	I
Natural rubber	100	100	100	100	100	100	100	100	100
Zinc oxide	5.0	5.0	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	2.0	2.0
Ethylene glycol	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Silica	40	40	40	40	40	40	40	40	40
Benzthiazyl 2-sulphenmorpholide	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Tetramethylthiuramdisulphide	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Naphthenic oil	-	5.0	5.0	5.0	3.0	1.0	-	-	-
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Styrenated phenol	-	1.0	-	-	-	-	-	-	-
2,6 di-t-butyl p-cresol	-	-	-	1.0	-	-	-	-	-
PIB- Ph	8.0	-	-	-	2.0	4.0	6.0	10.0	12.0

Rubber compounds were moulded in an electrically heated laboratory hydraulic press at 150°C up to their optimum cure time. Dumbbell shaped tensile test pieces were punched out of these compression moulded sheets along the mill grain direction. The tensile properties of the vulcanizates were evaluated on a Zwick Universal Testing machine using a cross head speed of 500mm /min according to ASTM D-412-80.Tear resistance of the vulcanizates was evaluated as per ASTM D-624-81 using un-nicked 90° angled test specimens. Retention in tensile and tear properties were evaluated after ageing the samples at 100°C for 12,24,36 and 48hrs. The compression set of the samples was determined as per ASTM D-395 method B (1982). The abrasion resistance of the samples was tested using DIN Abrader.

Results and discussion

Figs. 5.1 shows the IR spectra of polyisobutylene (PIB), polyisobutylene-bound phenol (PIB-Ph) respectively. The IR spectra of PIB shows peaks at 2950 cm^{-1} corresponding to aliphatic - CH stretching, at 1480 cm^{-1} due to - CH bending, 1650 cm^{-1} corresponds to C=C.

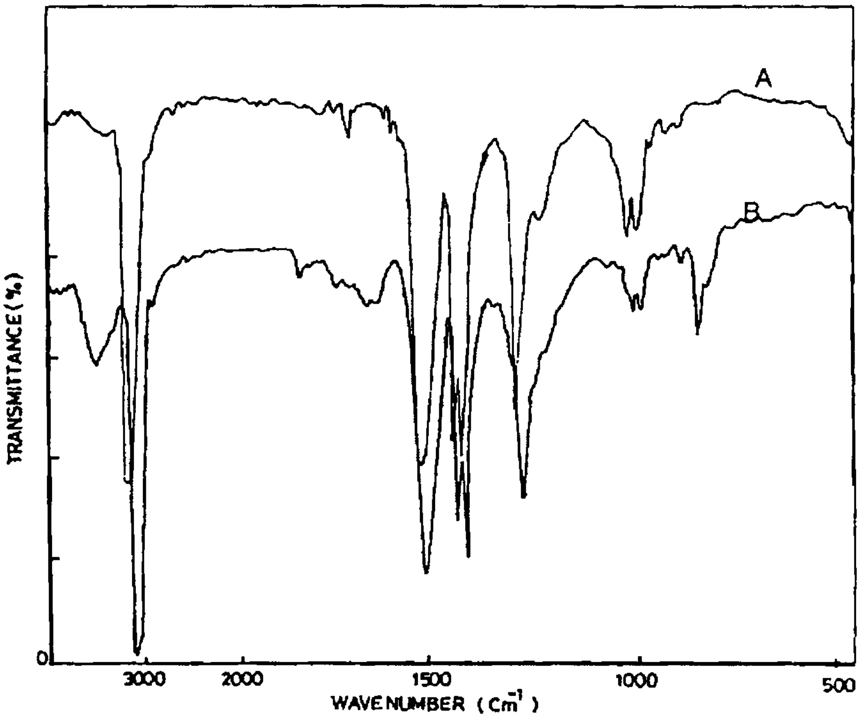


Fig.5.1 IR spectra of A-PIB & B- PIB-Ph

The IR spectra of PIB-Ph shows additional peaks at 3500cm^{-1} due to the presence of -OH stretching, 3000cm^{-1} corresponding to aliphatic -CH stretching,1600cm^{-1} corresponds to aromatic ring and 780cm^{-1}due to the presence of C-Cl stretching.[11] This confirms the chemical binding of phenol to polyisobutylene.

Fig.5.2 shows the ^{1}HNMR spectra of PIB and PIB- Ph respectively. PIB shows peaks at δ=1.22 ($-CH_2$) and δ=1.6 ppm ($-CH_3$) while PIB-Ph shows additional peaks at δ=7.2 and δ=6.8ppm corresponding to aromatic ring and -OH group in polymeric association respectively present in PIB-Ph. This again confirms the chemical binding of phenol to PIB.

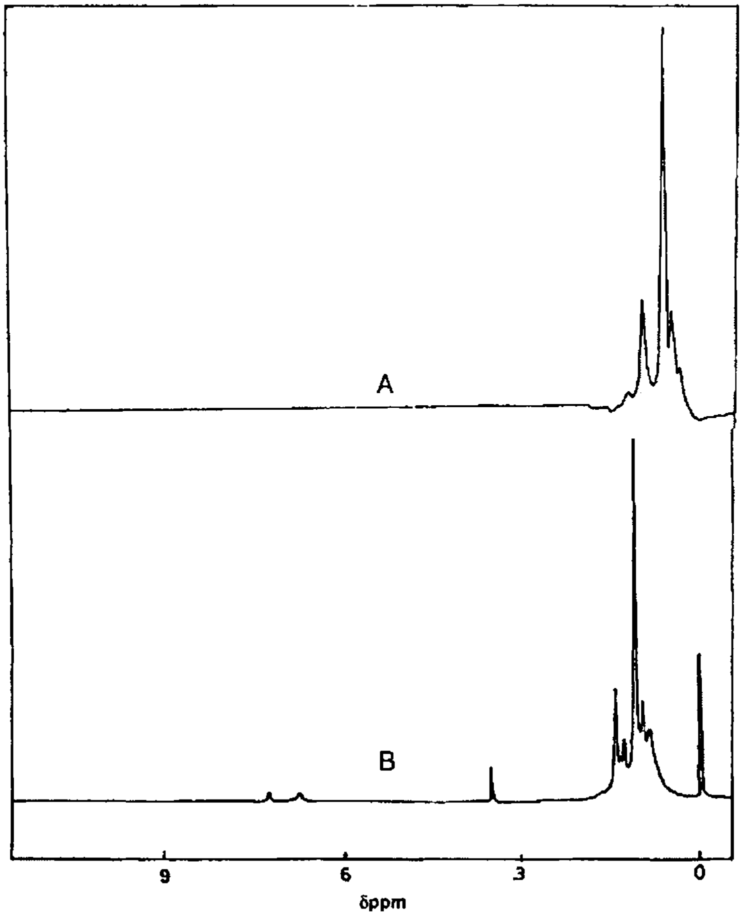


Fig.5.2 ^{1}HNMR spectra of A-PIB and B - PIB-Ph

Fig. 5.3 shows the thermograms of Phenol, PIB, and PIB-Ph. The low molecular weight phenol volatilises easily while polymer-bound phenols are less volatile. This again confirms the chemical bonding of phenol to PIB.

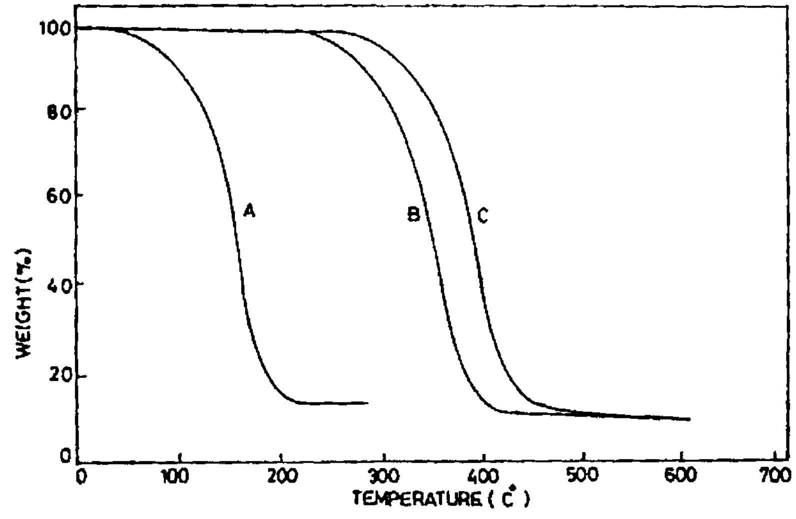
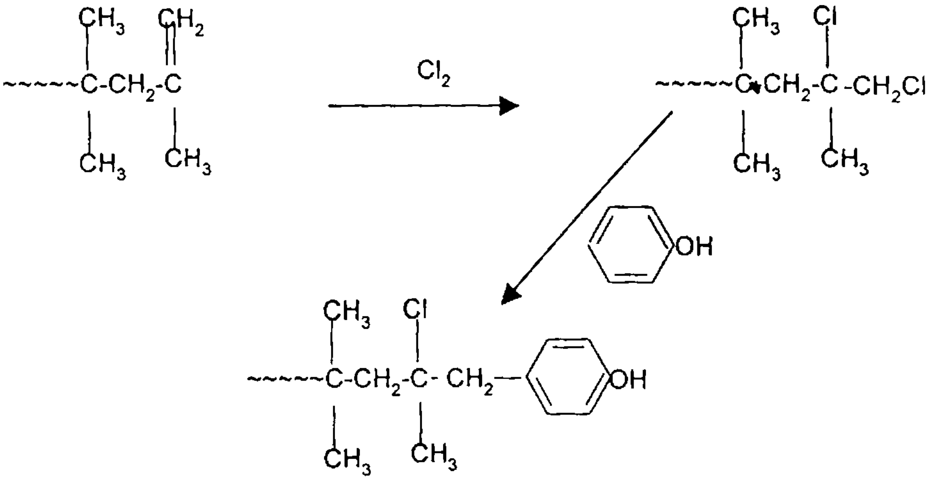


Fig.5.3 TGA of (A) Phenol, (B) PIB, (C) PIB-Ph

From the above data the binding of phenol and PIB may be represented as follows:



Scheme 5.1

The Fig.5.4 shows the variation in tensile strength with concentration of the compounds given in the Table5.1, after ageing at100°C for 48hrs. The retention in properties is found to increase with the amount of the bound antioxidant, reach a maximum and then levels off. The higher requirement of bound antioxidant in comparison to conventional antioxidant may be due to lower amount of effective antioxidant in the rubber bound product.

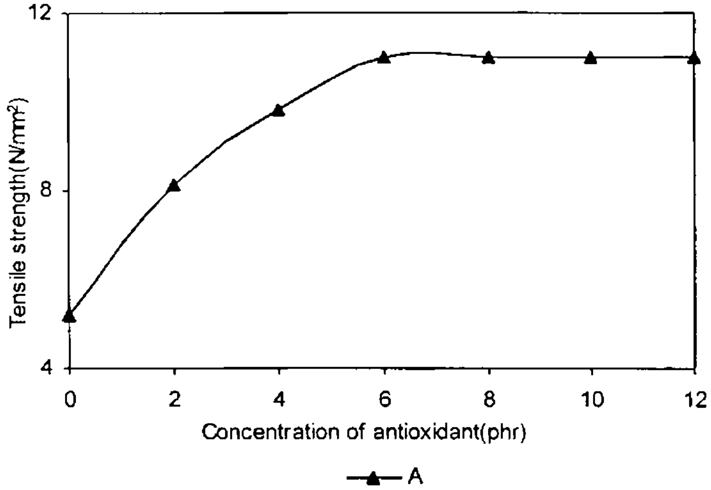


Fig. 5.4 Variation in tensile strength with the concentration of PIB- Ph after ageing at100°C for 48h.

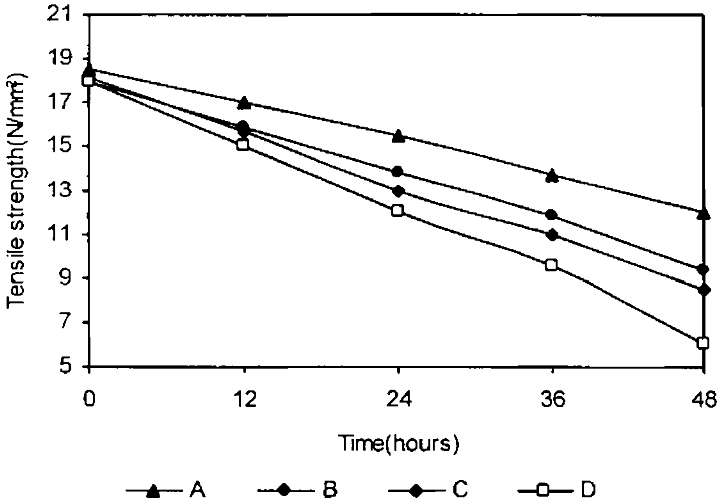


Fig. 5.5 Tensile strength Vs time of ageing at100°C, A- PIB-Ph, B- styrenated phenol C-2,6 di-t butyl p-cresol, D- without antioxidant.

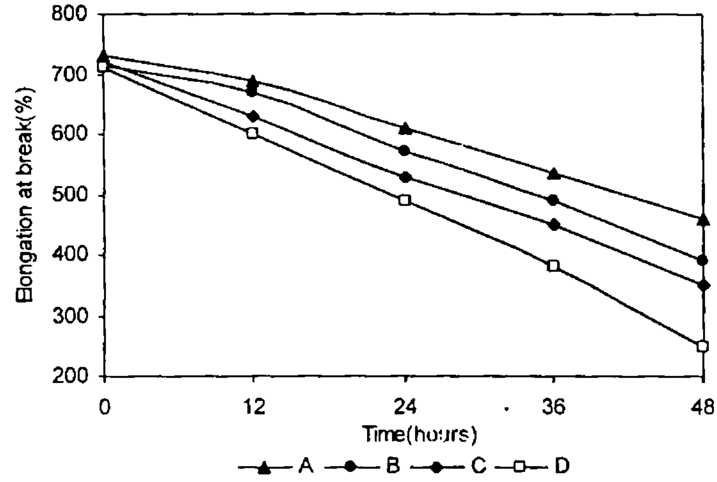


Fig. 5.6 Elongation at break of NR vulcanizates with time of ageing at 100°C, A- PIB-Ph, B- styrenated phenol C-2, 6 di-t butyl p-cresol, D- without antioxidant.

Fig. 5.5 shows the variation in tensile strength with ageing. All the vulcanizates show fairly good resistance to ageing at 100°C after 12hrs. The vulcanizates containing PIB-Ph show good resistance when the ageing time is increased to 48hrs. which shows the superiority of bound antioxidant over conventional antioxidant.

Fig. 5.6 shows the change in elongation at break of the vulcanizates time of ageing. The compound containing PIB-Ph shows better retention in elongation at break after ageing than compounds containing conventional antioxidants like styrenated phenol and 2,6 di-t-butyl p-cresol.

This again shows that bound antioxidant can improve the ageing resistance of NR compound.

Table 5.2 Properties of vulcanizates

Properties	A (PIB-Ph)	B (SP)	C (WA)
Abrasion resistance (volume loss, cc/h)	3.6	3.65	3.68
Compression set (%)	16.5	16.8	17.1

The table 5.2 shows the abrasion resistance and compression set of the vulcanizates containing PIB-Ph, SP and WA. The values show marginal decrease in comparison with the control mix.

PART II

5.2 Preparation and characterisation of 4-octadecyl phenol and its use in NR vulcanizates.

5.2.1 Experimental

a) Materials

Stearic acid, thionyl chloride, carbon disulphide, anhydrous aluminium chloride, zinc dust and concentrated HCl.

b) Preparation of alkylated phenol using stearic acid.

0.1mol of stearic acid (SA) was weighed and dissolved in CS_2 and to it 0.1mol $SOCl_2$ was added drop wise and the reaction mixture was cooled in an ice bath. The reaction mixture is then heated gently under reflux for 2h. The acid chloride formed was separated and used for conducting Friedel Craft's acylation. 0.1mol of phenol was dissolved in CS_2 and mixed with 0.1 mol of anhydrous aluminium chloride catalyst. It is cooled using an ice bath and acid chloride dissolved in CS_2 was added drop wise to the reaction mixture, swirling the mixture during addition. After addition is complete removed from the ice bath and allowed to stand at room temperature for 30 minutes. Swirl the reaction mixture frequently during this period. Then the reaction mixture was heated on a hot plate with magnetic stirring for 5h. When the action was complete, the acetylated phenol was separated and reduced using zinc dust and HCl. The phenol bound stearic acid (SA-Ph) was separated washed and dried.

5.2.2 Analysis of bound antioxidant

Analysis of bound antioxidant was carried out by using thin layer chromatography (TLC), infrared spectroscopy (IR) and Thermogravimetric analysis (TGA).

The optimum concentration of the 4-octadecyl phenol antioxidant for attaining maximum retention in properties was determined by varying the amount of the antioxidant in the mix from 1 to 10 phr. The antioxidant was added in NR as per formulations given in table5.3. The optimum cure times (time to reach 90 % of the maximum torque) of compounds were determined on a Göttfert Elastograph, model 67.85, as per ASTM D-1646 (1981).

5.2.3 Results and Discussion

The Fig.5.7 shows the TLC of phenol, stearic acid(SA) and phenol bound stearic acid (SA-Ph). The TLC plate was spotted with the sample and it was kept in iodine chamber for colour development. The Rf values of the phenol, styrenated phenol(SP) and phenol bound stearic acid (SA-Ph) indicate the chemical binding of phenol and stearic acid.

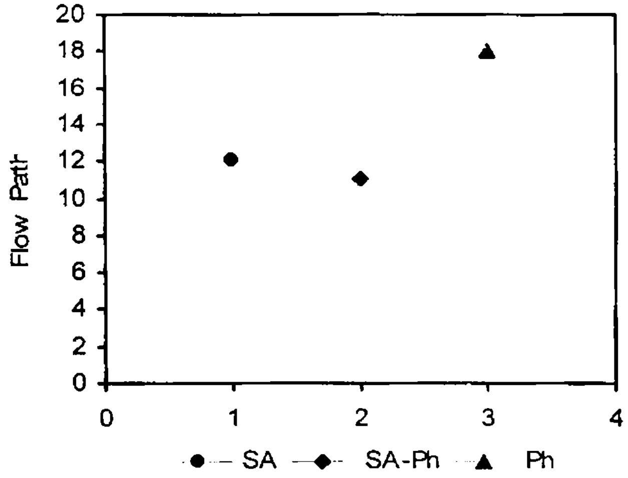


Fig.5.7 TLC of A- Phenol, B- Stearic acid C- SA-Ph

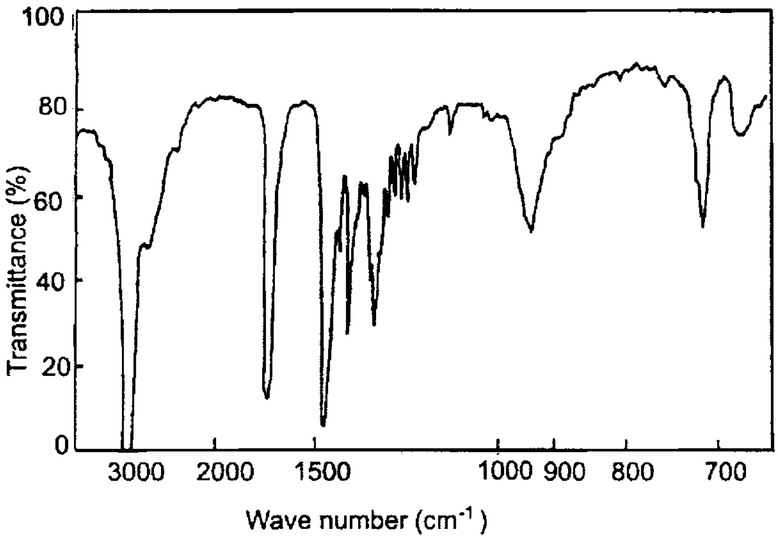


Fig.5.8 IR. spectrum of stearic acid

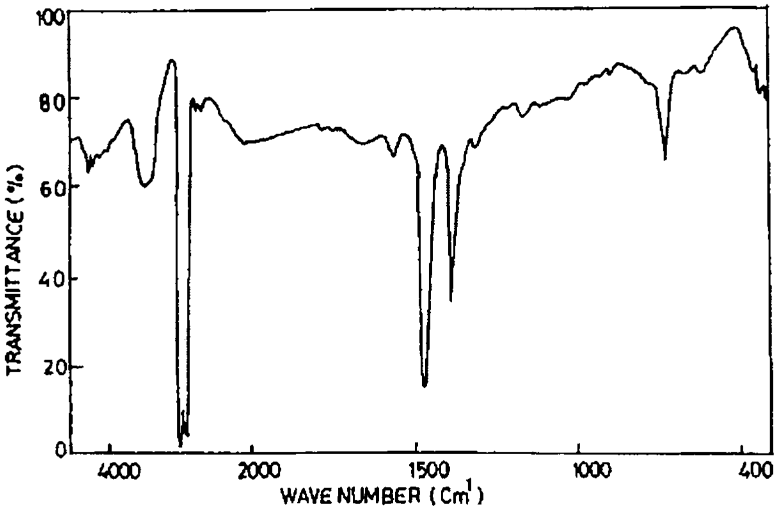


Fig.5.9 IR. spectrum of SAPh

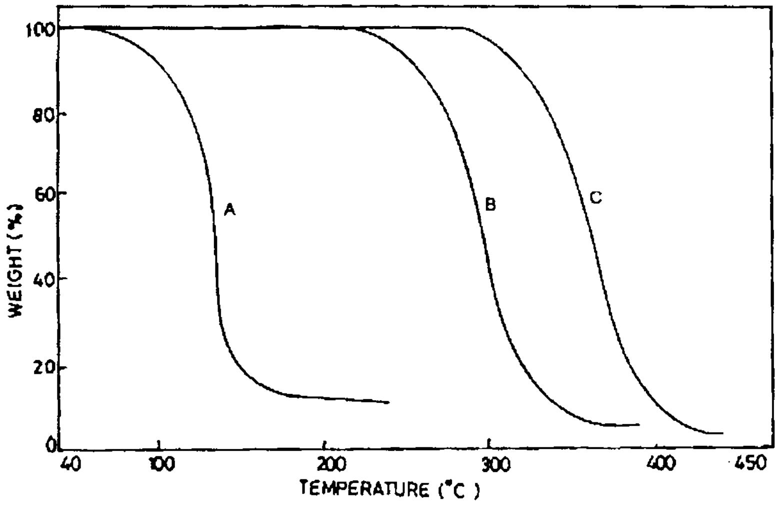
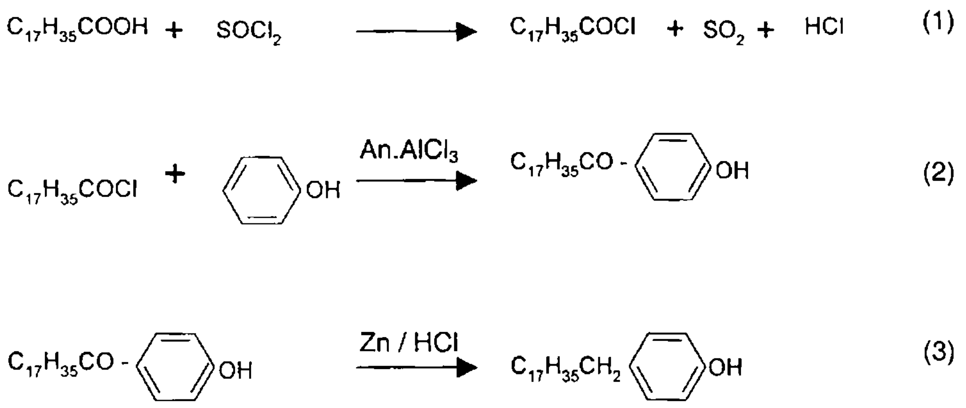


Fig.5.10 TGA of phenol, stearic acid and phenol bound stearic acid

The Fig. 5.8 & 5.9 shows the IR spectra SA and SA-Ph. The IR spectrum of stearic acid shows distinct peak of -C=O at 1709 cm^{-1}. IR Spectrum of SA-Ph shows peak at 3500 cm^{-1} due to -OH stretching, 3000 cm^{-1} corresponding to aliphatic -CH and peak at 1550 cm^{-1} due to the presence of aromatic ring. The disappearance of the peak at 1709 cm^{-1} confirms the absence of carbonyl group in the compound. This indicates the reduction of the carbonyl group. These data confirm the binding of phenol to stearic acid.

The Fig.5.10 shows the thermograms of phenol, stearic acid and phenol bound stearic acid. The higher TGA values of SA-Ph confirm the binding of phenol and stearic acid and the reduction of the carbonyl group.

Thus the formation of SA-Ph can be represented as follows:



Scheme 5.2

Table 5.3 Formulations for testing SA-Ph antioxidant.

Sample	A	B	C	D	E	F	G	H
Natural rubber	100	100	100	100	100	100	100	100
Zinc oxide	5.0	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	2.0
Ethylene glycol	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Silica	40	40	40	40	40	40	40	40
Benzthiazyl 2-sulphenmorpholide	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Tetramethylthiuramdisulphide	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Naphthenic oil	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Styrenated phenol	-	1.0	-	-	-	-	-	-
2,6 di-t-butyl p-cresol	-	-	-	1.0	-	-	-	-
SA- Ph	6.0	-	-	-	2.0	4.0	8.0	10.0

The Fig. 5.11 shows the variation in tensile strength after ageing at 100°C, for 48h after the addition of varying amounts of SA-Ph to NR vulcanizates. The retention in properties is found to increase with the amount of the bound antioxidant, reach a maximum and levels off. The higher requirement of bound antioxidant in comparison to conventional antioxidant may be due to lower amount of effective antioxidant in the bound product.

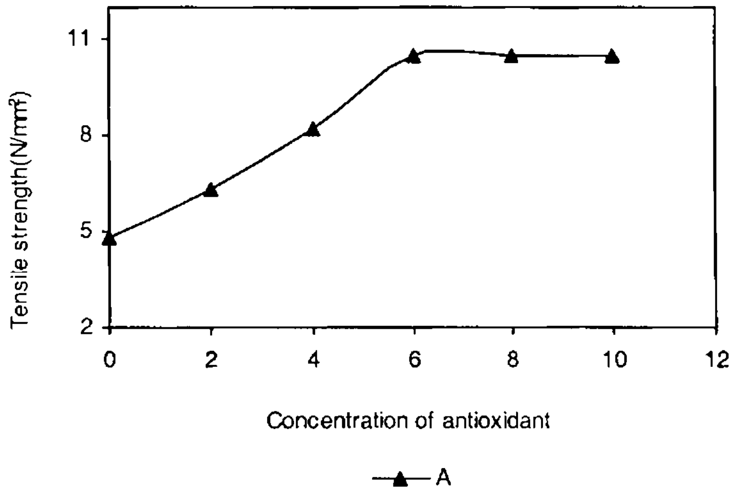


Fig. 5.11 Variation in tensile strength with the concentration of SA- Ph after ageing at100°C for 48h.

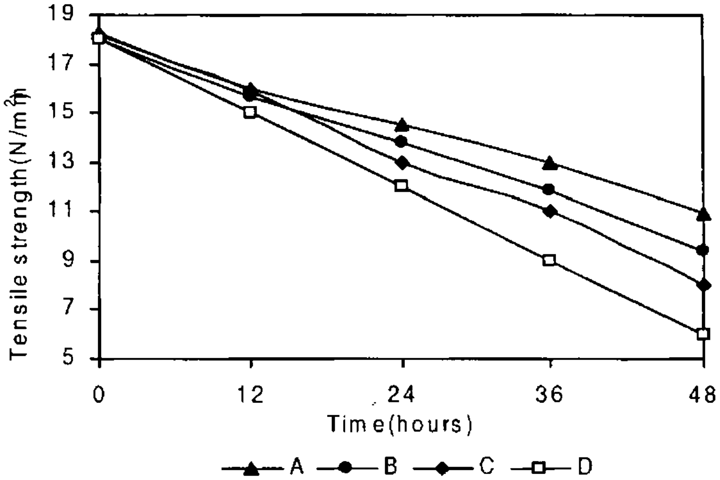


Fig. 5.12 Variation of tensile strength with ageing, A- SA-Ph, B- styrenated phenol C-2,6 di-t butyl p-cresol, D- without antioxidant.

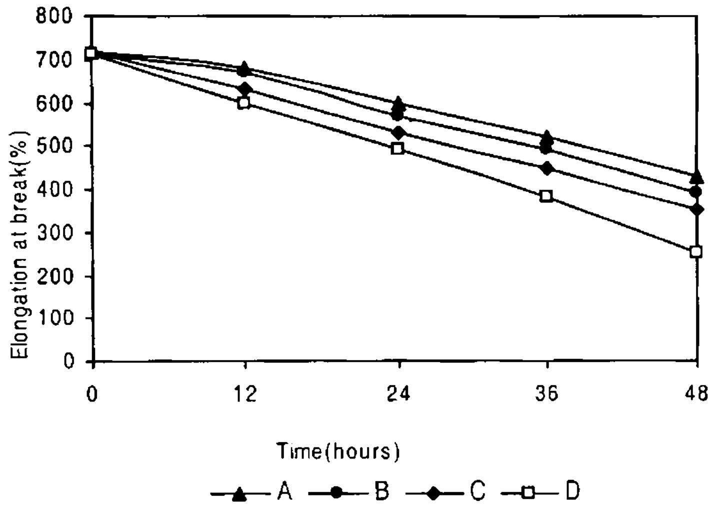


Fig. 5.12 Elongation at break of NR vulcanizates time of ageing A- PIB-Ph, B-styrenated phenol C-2,6 di-t butyl p-cresol, D- without antioxidant

Fig. 5.12 shows the tensile strength of the vulcanizates of compounds shown in Table 5.2 with time of ageing. All the vulcanizates show fairly good resistance to ageing at 100°C after 12h. The vulcanizates containing SA-Ph show good resistance when the ageing time is increased to 48h.which shows the superiority of bound antioxidant over conventional antioxidant.

Fig. 5.13 shows the change in elongation at break of the vulcanizates with time of ageing. The compound containing SA-Ph shows better retention in elongation at break after ageing while conventional antioxidants shows slightly less retention in elongation at break after ageing. This again shows that bound antioxidant can improve the ageing resistance of NR vulcanizate.

Table 5.4 Properties of vulcanizates.

Properties	A (SA-Ph)	B (SP)	C (WA)
Abrasion resistance (volume loss, cc/h)	3.63	3.65	3.68
Compression set (%)	16.7	16.8	17.1

The Table 5.4 shows that the abrasion resistance and compression set values of vulcanizates containing bound-antioxidant and conventional antioxidants are more or less same. So SA-Ph is comparable with conventional antioxidant.

Conclusions

1. Phenol was chemically attached to low molecular weight chlorinated polyisobutylene by Friedel Craft's alkylation reaction.
2. The bound antioxidant can improve the ageing resistance of NR vulcanizates. The liquid polyisobutylene-bound phenol can reduce the amount of plasticiser required for compounding.
3. Phenol was chemically attached to stearic acid by a series of reactions (halogenation, Friedel Crafts acylation and Clemmenson reduction).
4. 4-octadecyl phenol can also improve the ageing resistance of NR vulcanizates.

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Chapter 6

OZONE AND FLEX AGEING RESISTANCE OF NR, SBR, NBR AND IIR VULCANIZATES AND NR/BR AND NR/SBR BLENDS CONTAINING POLYMER-BOUND ANTIOXIDANTS

6.1 Introduction

Although ozone is present in the atmosphere at concentrations normally in the range 0-7pphm[1], it can severely attack non-resistant rubbers. The interaction of rubber with ozone is best noted when the rubber is stressed or stretched in use. A series of cracks develop, in time, perpendicular to the applied stress. Further exposure of these cracked surfaces to ozone cause the crack to become wider and deeper until the rubber fails.

The use of antiozonants is an effective means of protecting rubber against surface cracking. The general subject of protection of rubber against ozone attack has been reviewed by a number of authors.[2-4]

Several theories have appeared in the literature regarding the mechanism of antiozonant protection. The "scavenger" model states that the antiozonant blooms to the surface and preferentially reacts with ozone so that the rubber is not attacked until the antiozonant is exhausted.[4-5] The "protective film" theory is similar, except that the ozone-antiozonant reaction products form a film on the rubber surface that prevents ozone attack on the rubber.[6] A third "relinking" theory states that the antiozonant prevents scission of the ozonised rubber or recombines severed double bonds.[7]

The antiozonant effect was found to increase with the initial surface concentration of antiozonant and the reaction rate was reported to be related to antiozonant efficiency.[8-10]

During recent years there has been a gradually increasing demand from tyre manufacturers for chemical which will protect rubber compounds from attack by ozone and search for new and improved types of antiozonants is going on. In any classification of chemical protective agents for rubber, no clear distinction can be made between antioxidants and antiozonants. Some chemicals already known as antioxidants have been shown to possess antiozonant properties also. One of the main drawbacks of conventional antioxidant is its high volatility. This led to search of a new class of antioxidants having higher molecular weights i.e. polymer-bound antioxidants.

Polymer-bound antioxidants have many advantages but one of the main disadvantage is that the mobility of the antioxidant is restricted. Hence it does not bloom to the surface and ozone attack cannot be effectively controlled. Most of the polymer-bound antioxidants have unsaturated backbone, so during the process of vulcanisation their backbone gets attached to the main chain through sulphur crosslinking and it loses its mobility still further.[11] The synthesis of polymer-bound antioxidant adducts concentrates by a high shearing mixing procedure is outlined by G.Scott.[12]

The preparation and characterisation of new polymer-bound antioxidants with saturated backbone were reported in our earlier papers.[13-14] In this chapter we have evaluated the efficiency of these antioxidants in NR, SBR, IIR, NBR and in elastomer blends such as NR/SBR and NR/BR by comparing their flex resistance and ozone resistance with their counterpart containing conventional antioxidant and without antioxidant.

6.2 Experimental

The newly prepared antioxidants were added to NR, SBR, NBR, IIR and blends of NR/BR and NR/SBR as per formulations given in the Tables 6.1,6.2 and 6.3 The amount of plastciser can be reduced by the use of liquid polymer-bound antioxidants as shown in the Tables.6.1, 6.2 and 6.3. The optimum cure times (time to reach 90% of the maximum torque) of compounds were determined on a Göttfert Elastograph, model 67.85, as per ASTM D-1646 (1981).

NR, SBR, NBR NR/SBR and NR/BR mixes were moulded in an electrically heated laboratory hydraulic press at 150ºC up to their optimum cure time. While IIR (resin cure) and IIR (sulphur cure) mixes were moulded in an electrically heated laboratory hydraulic press at 190°C and 170°C respectively up to their optimum cure time.

Table 6.1 Formulation of test compounds

Sample	A	B	C	D	A_1	B1	C1	D1	A2	B2	C2	D2
NR	100	100	100	100	-	-	-	-	-	-	-	-
SBR	-	-	-	-	100	100	100	100	-	-	-	-
NBR	-	-	-	-	-	-	-	-	100	100	100	100
ZnO	5.0	5.0	5.0	5.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
HAF N330	40	40	40	40	40	40	40	40	40	40	40	40
MBTS	0.8	0.8	0.8	0.8	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
TMTD	0.2	0.2	0.2	0.2	0.15	0.15	0.15	0.15	0.5	0.5	0.5	0.5
Aromatic oil	5.0	5.0	-	-	5.0	5.0	-	-	-	-	-	-
DOP	-	-	-	-	-	-	-	-	5.0	5.0	-	-
Sulphur	2.5	2.5	2.5	2.5	2.0	2.0	2.0	2.0	1.5	1.5	1.5	1.5
Vulkanox 4020(C)	-	1.0	-	-	-	1.0	-	-	-	1.0	-	-
PIB-PD (S1)	-	-	8.0	-	-	-	8.0	-	-	-	8.0	-
CPW-PD (S2)	-	-	-	6.0	-	-	-	6.0	-	-	-	6.0

Table 6.2 Formulation of IIR compounds

Sample	A	B	C	D	A_1	B_1	C_1	D_1
IIR	95	95	95	95	100	100	100	100
Neoprene	5	5	5	5	-	-	-	-
HAF N330	60.0	60.0	60.0	60.0	55.0	55.0	55.0	55.0
ZnO	5.0	5.0	5.0	5.0	4.0	4.0	4.0	4.0
Stearic acid	1.0	1.0	1.0	1.0	2.0	2.0	2.0	2.0
Oleic acid	3.0	3.0	3.0	3.0	-	-	-	-
Wax	1.0	1.0	1.0	1.0	-	-	-	-
PF resin	10.8	10.8	10.8	10.8	-	-	-	-
Paraffinic oil	4.0	4.0	-	-	15	15	7.0	8.0
MBTS	-	-	-	-	1.0	1.0	1.0	1.0
TMTD	-	-	-	-	0.5	0.5	0.5	0.5
Sulphur	-	-	-	-	2.0	2.0	2.0	2.0
Vulkanox 4020(C)	-	1.0	-	-	-	1.0	-	-
PIB-PD (S1)	-	-	8.0	-	-	-	8.0	-
CPW-PD (S2)	-	-	-	6.0	-	-	-	6.0

Table 6.3 Formulation of NR/BR and NR/SBR blends

Sample	A4	B4	C4	D4	A5	B5	C5	D5
NR	70	70	70	70	70	70	70	70
BR	30	30	30	30	-	-	-	-
SBR	-	-	-	-	30	30	30	30
ZnO	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
Stearic acid	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
HAF N330	45	45	45	45	45	45	45	45
Aromatic oil	7.5	7.5	-	1.5	7.5	7.5	-	1.5
Accinox TQ(C)	-	1.0	-	-	-	1.0	-	-
MOR	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
TMTD	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Sulphur	2.1	2.1	2.1	2.1	2.2	2.2	2.2	2.2
PIB-PD (S1)	-	-	8.0	-	-	-	8.0	-
CPW-PD (S2)	-	-	-	6.0	-	-	-	6.0

Ozone ageing studies under static conditions were conducted according to ASTM D 518 Method D in a Mast Model 700-1 ozone test chamber at 41°C. Ozone concentration in the chamber was adjusted to 50 parts per hundred million (pphm).

The flex resistance was determined using Wallace Demattia flexing machine as per ASTM D 430 - 57 T. Moulded test specimens with a circular groove, conditioned for 24 hrs were tested in duplicate. The number of flexing cycles for crack initiation, crack growth and complete failure were noted on the counter. The test was conducted at ambient temperature.

Photographs were taken using optical microscope Carl Zeiss Stemi 2000 C with magnification 2.5.

6.3 Results and Discussion

The flex resistance of NR, SBR, NBR, IIR and elastomer blends of NR/BR and NR/SBR are given in Table6.4. The flex resistance is dependent on the network of the vulcanizate and the nature of the antidegradant present in the sample. The vulcanizates of NR, SBR, NBR and IIR containing novel polymer-bound antioxidants possess significantly better flex resistance compared to that containing conventional antioxidant even at pin hole crack formation level. Same trend is shown during medium crack growth and deep crack formation. NR/BR blends show superior flex crack resistance compared to NR/SBR blends as expected. Here also blends containing bound antioxidants show better performance. This improved performance is obviously due to the polymeric nature of the bound antioxidants.

Table 6.5 Flex resistance

Samples	Number of kilocycles for the development of															
	Pin holes				Small cracks				Medium cracks				Deep cracks			
	W	C	S1	S2	W	C	S1	S2	W	C	S1	S2	W	C	S1	S2
NR	35	40	50	55	40	60	80	90	66	82	100	102	80.7	104	181	185
SBR	150	180	220	240	180	235	290	295	230	270	325	330	260	300	350	360
NBR	55	75	100	105	85	99	124	136	100	152	163	170	113	183	194	196
IIR (S-cure)	58	65	75	68	75	82	85	87	78	88	90	94	82	92	100	110
IIR (resin cure)	465	509	748	800	512	589	785	980	582	685	813	1052	718	808	989	1200
NR/BR	200	310	351	378	422	462	421	428	462	500	555	560	500	550	600	620
NR/SBR	72	109	138	164	110	150	216	219	150	186	232	245	184	233	284	290

Table 6.5 shows the ozone resistance of NR, SBR, NBR, IIR and elastomer blends of NR/BR and NR/SBR. NR and SBR are easily vulnerable to ozone attack but the bound antioxidants are found to be capable of reducing the extent of cracking. The unsaturation in NR, SBR, NBR renders them susceptible to attack by ozone. The butyl rubber has high resistance to ozone degradation due to low level of unsaturation. IIR resin cured vulcanizates display better ageing resistance than sulphur cured ones. Here also the vulcanizates containing bound antioxidants have superior to resistance compared to one containing conventional antioxidants. NR/SBR blend is less susceptible to ozone attack compared to NR/BR.

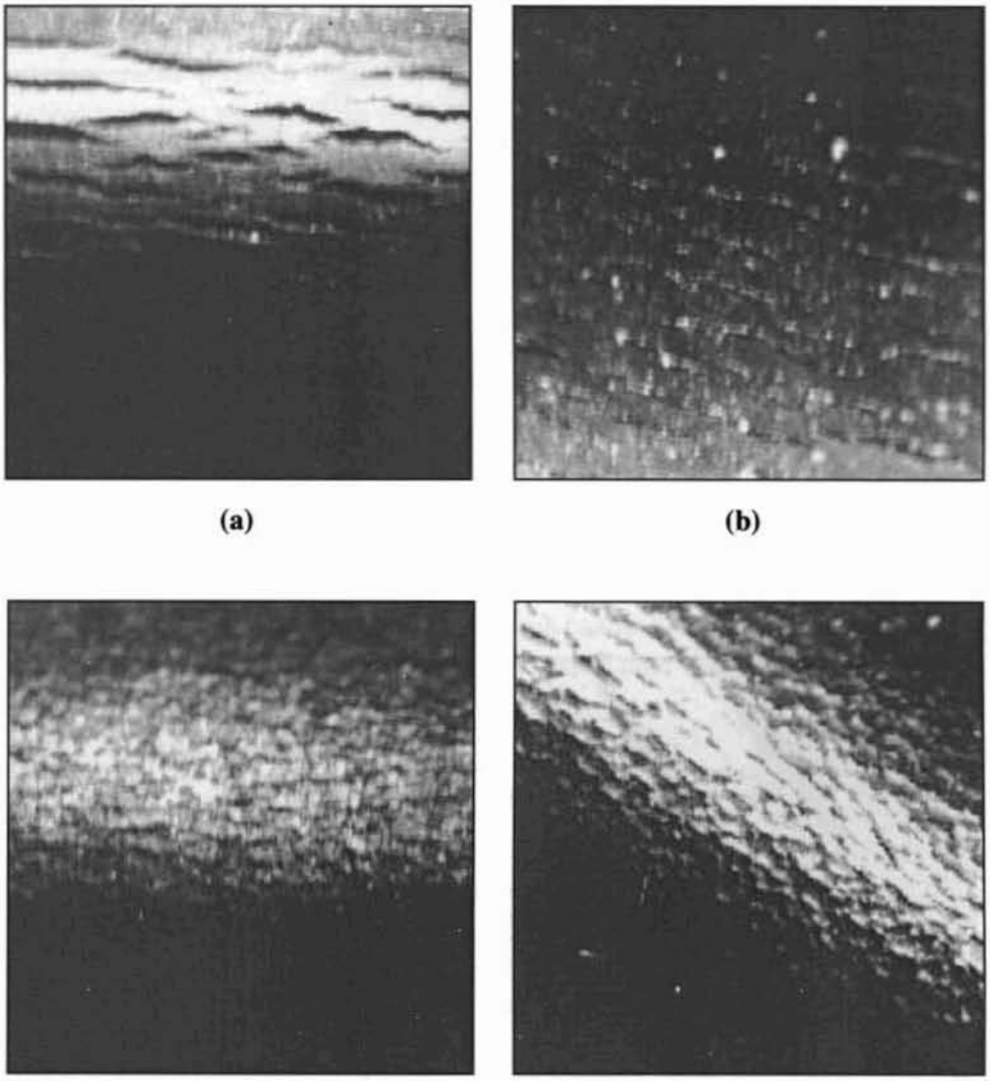
Table 6.6 Ozone resistance of the samples W-without antioxidant, C conventional antioxidant, PIB-PD and CPW-PD (bound antioxidants)

Samples	Crack initiation time (hrs)				Nature of ozone crack of samples after 19hrs in ozone chamber			
	W	C	PIB-PD	CPW-PD	W	C	PIB-PD	CPW-PD
NR	2	3	5	6	deep	deep	moderate	moderate
SBR	3	4	6	6.5	deep	deep	moderate	moderate
NBR	3	4	6	6.5	deep	deep	moderate	moderate
IIR (S-cure)	5	6	11	12	deep	deep	shallow	shallow
IIR (resin cure)	5	7	12	14	deep	moderate	shallow	shallow
NR/BR	3	4	7	8	deep	deep	moderate	moderate
NR/SBR	3.5	6	8	9	deep	deep	shallow	shallow

Figs.6.1 to 6.7 show the various optical photographs of ozone-cracked samples of NR, SBR, NBR, IIR (S-cure), IIR (resin cure), NR/SBR and NR/BR vulcanizates respectively. Figs. 6.1[A] (a)-(d) show the photographs of ozone cracked surface of NR vulcanizates on crack initiation. Figs. 6.1[B] (a')- (d') show the photographs of ozone-cracked surface of NR vulcanizates after 19hrs in an ozone chamber. Photographs clearly show that vulcanizates without antioxidants develop severe cracks[Figs.6.1[A](a) and 6.1[B] (a')]. Vulcanizates with conventional antioxidant show lesser cracks [Figs. 6.1[A](b) and 6.1[B] (b')], while least cracks are observed for samples containing bound antioxidants [Figs.6.1 [A] (c and d) and 6.1[B](c' and d')]. So it may be concluded that the ozone resistance of the vulcanizates containing bound antioxidants are superior to the vulcanizates containing conventional antioxidant.

Figs.6.2[A] (a)-(d) show the photographs of ozone-cracked surface of SBR vulcanizates on crack initiation. Figs. 6.2[B](a')- (d') show the photographs of ozone-cracked surface of SBR vulcanizates after 19hrs in an ozone chamber. Photographs clearly show that vulcanizates without antioxidants develop severe cracks [Figs. 6.2[A] (a) and 6.2[B] (a')]. Vulcanizates with conventional antioxidant shows lesser cracks [Figs.6.2 [A] (b) and 6.2[B] (b')], while least cracks are again observed for samples containing bound antioxidants [Figs.6.2 [A] (c and d) and 6.2[B] (c' and d')]. This further proves that the ozone resistance of the vulcanizates containing bound antioxidants are superior to the vulcanizate containing conventional antioxidant.

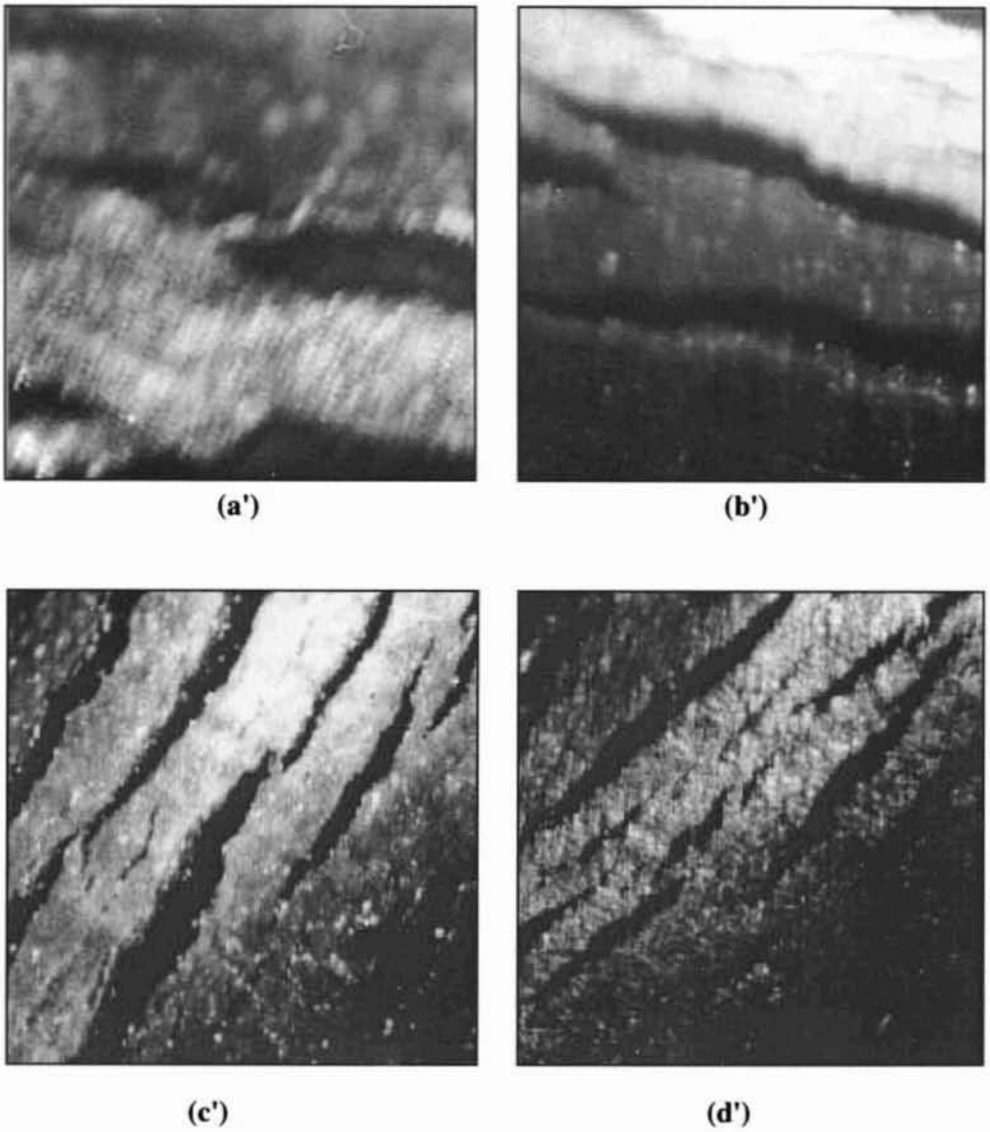
Figs.6.3[A] (a)-(d) show the micrographs of ozone-cracked surface of NBR vulcanizates on crack initiation. Figs.6.3[B](a')- (d') show the photographs of ozone-cracked surface of NBR vulcanizates after 19hrs in an ozone chamber. Photographs clearly show that vulcanizates without antioxidants develop severe cracks [Figs.6.3 [A] (a) and 6.3[B] (a')]. Vulcanizates with conventional antioxidant shows lesser cracks [Figs. 6.3[A](b) and [B](b')], while least cracks are observed for samples containing bound antioxidants [Figs.6.3[A](c and d) and 6.3[B](c' and d')]. The ozone resistance of the vulcanizates containing bound antioxidants are superior to the vulcanizates containing conventional antioxidant(Table.6.5) as in the previous case.



(a) (b)

(c) (d)

Figs.6.1 [A] ozone crack initiation of NR vulcanizates (a) without antioxidant, (b) with vulkanox 4020 (c) with PIB-PD (d) with CPW-PD



(a') (b')

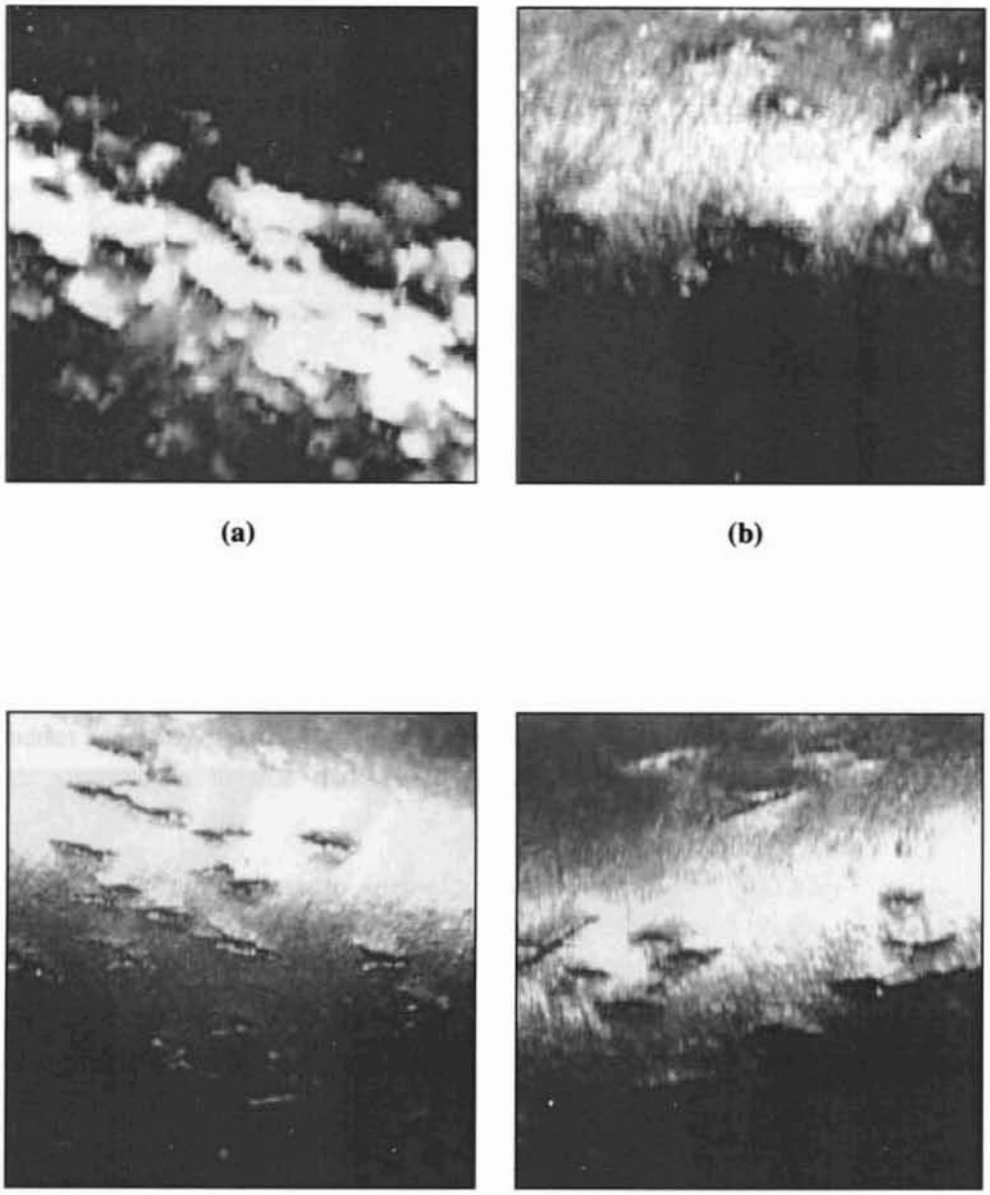
(c') (d')

Figs. 6.1 [B] ozone crack growth of NR after 19h (a') without antioxidant, (b') with vulkanox 4020 (c') with PIB-PD (d') with CPW-PD.

Figs. 6.4[A] (a)-(d) show the photographs of ozone-cracked surface of IIR (S-cured) vulcanizates on crack initiation. Figs.6.4[B] (a')- (d') show the photographs of ozone-cracked surface of IIR (S-cured) vulcanizates after 19hrs in an ozone chamber. Photographs clearly show that vulcanizates without antioxidants develop intense cracks [Figs.6.4 [A] (a) and 6.4[B] (a')]. Vulcanizates with conventional antioxidant show lesser cracks [Figs. 6.4 [A](b) and 6.4 [B] (b')], while least cracks are observed for samples containing bound antioxidants [Figs.6.4 [A] (c and d) and 6.4[B](c' and d')]. This again shows that the ozone resistance of the vulcanizates containing bound antioxidants are superior to the vulcanizates containing conventional antioxidant.

Figs 6.5[A] (a)-(d) show the photographs of ozone-cracked surface of IIR (resin cured) vulcanizates on crack initiation. Figs. 6.5 [B] (a')- (d') show the photographs of ozone-cracked surface of IIR vulcanizates after 19hrs in an ozone chamber. Photographs clearly show that vulcanizates without antioxidants develop severe cracks [Figs. 6.5[A] (a) and 6.5[B] (a')]. Vulcanizates with conventional antioxidant show lesser cracks [Figs.6.5 [A](b) and 6.5[B](b')], while least cracks are observed for samples containing bound antioxidants [Figs.6.5[A]. (c and d) and 6.5[B] (c' and d')]. The same trend is noticed as in the above cases. The resin-cured butyl rubber has superior inhibition against ozone cracking than sulphur cured ones as expected.

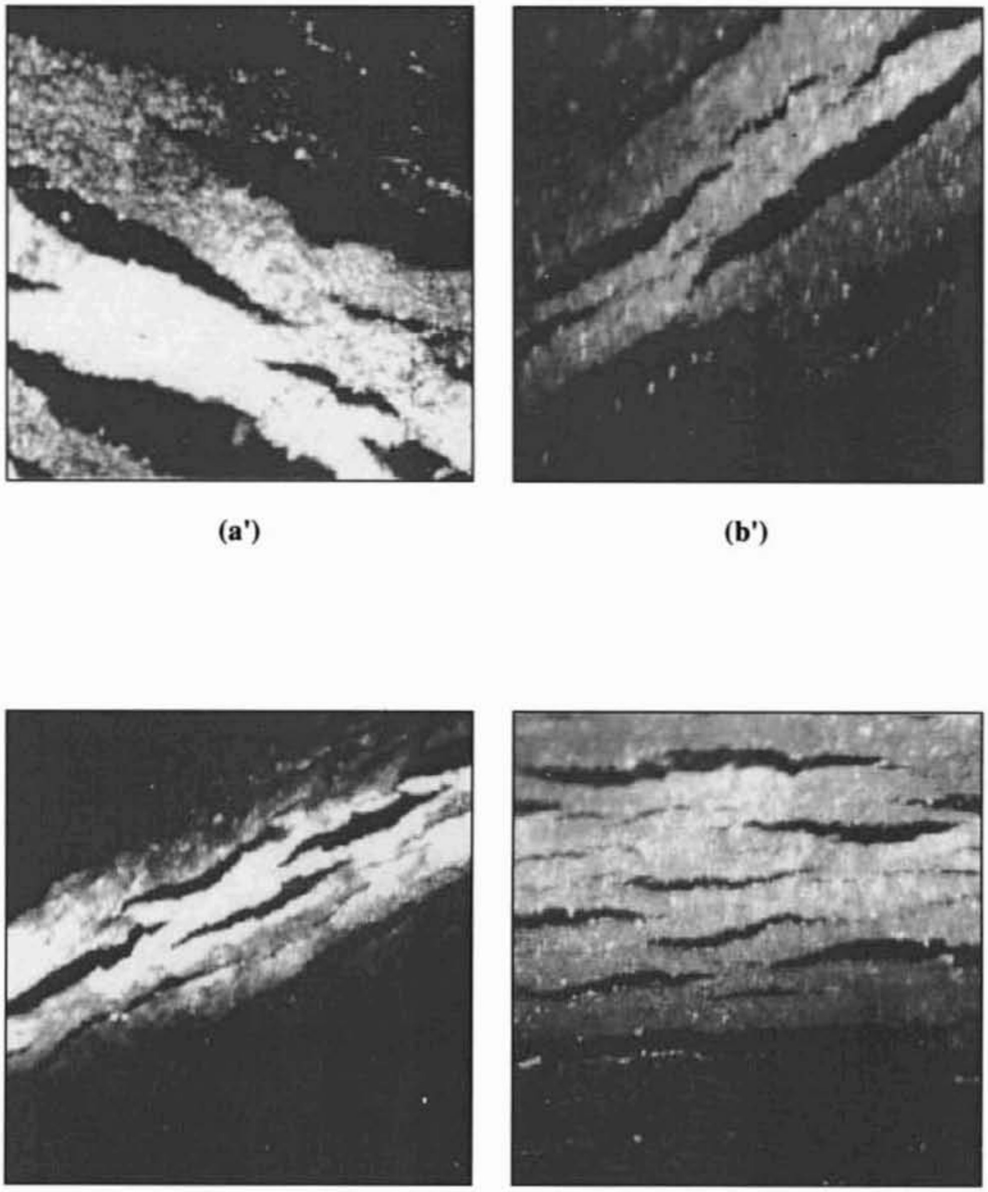
Figs.6.6[A] (a)-(d) show the photographs of ozone-cracked surface of NR/SBR blends on crack initiation. Figs. 6.6[B] (a')- (d') show the photographs of ozone-cracked surface of NR/SBR blends after 19hrs in an ozone chamber. Photographs clearly show that the blends without antioxidants develop deeper cracks [Fig 6.6[A] (a) and (a')] and the blends with conventional antioxidant show lesser cracks [Figs.6.6 [B](b) and (b')] whereas least cracks are observed for samples containing bound antioxidants [Figs.6.6 [A] (c and d) and 6.6[B] (c' and d')]. So improved ozone resistance of the blends containing bound antioxidants is elucidated. NR/SBR blends show excellent results, probably due to the nature of the blend as well as the efficiency of the antioxidant present in it.



(a) (b)

(c) (d)

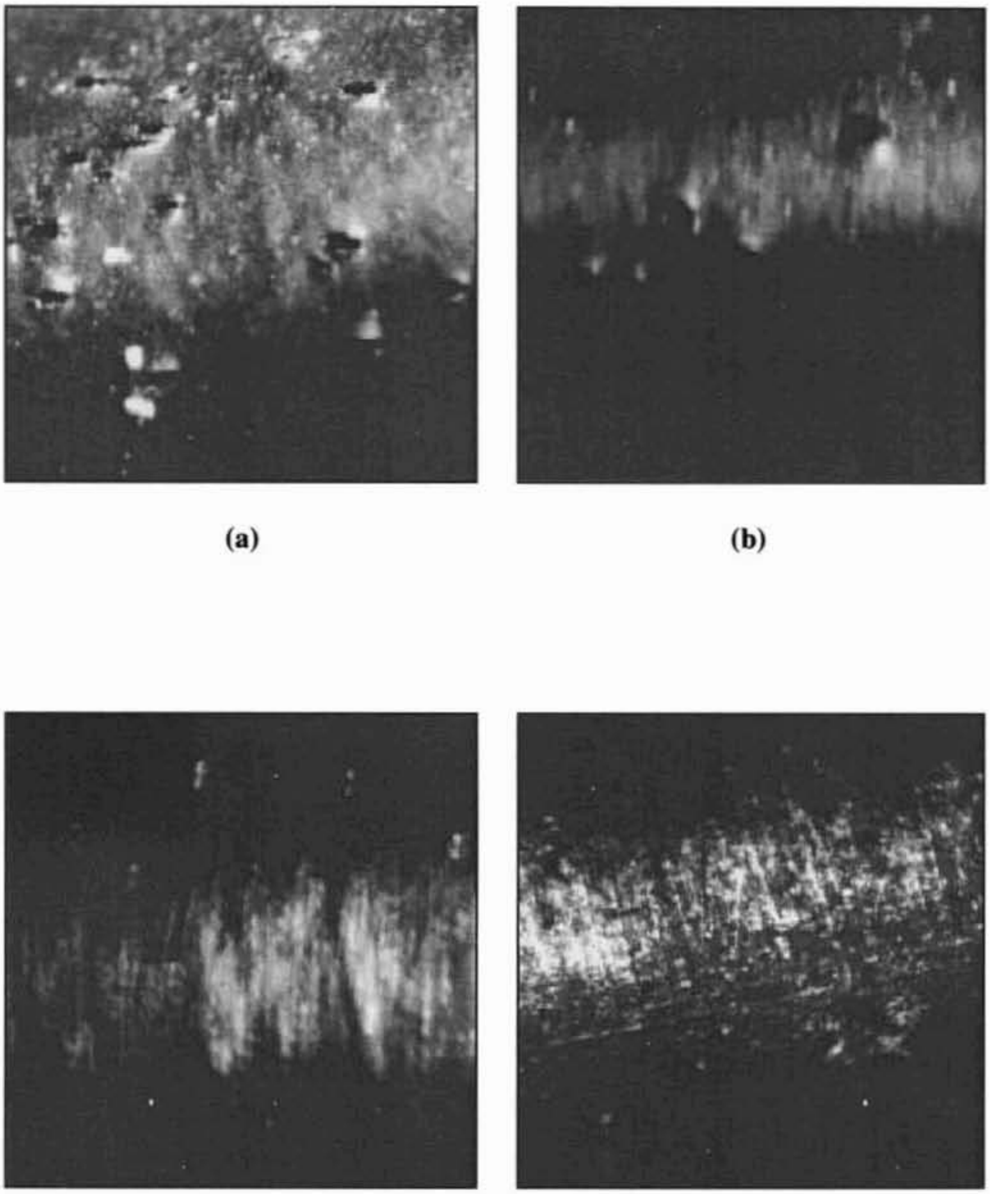
Figs. 6.2[A] ozone crack initiation of SBR vulcanizates (a) without antioxidant, (b) with vulkanox 4020 (c) with PIB-PD (d) with CPW-PD.



(a') (b')

(c') (d')

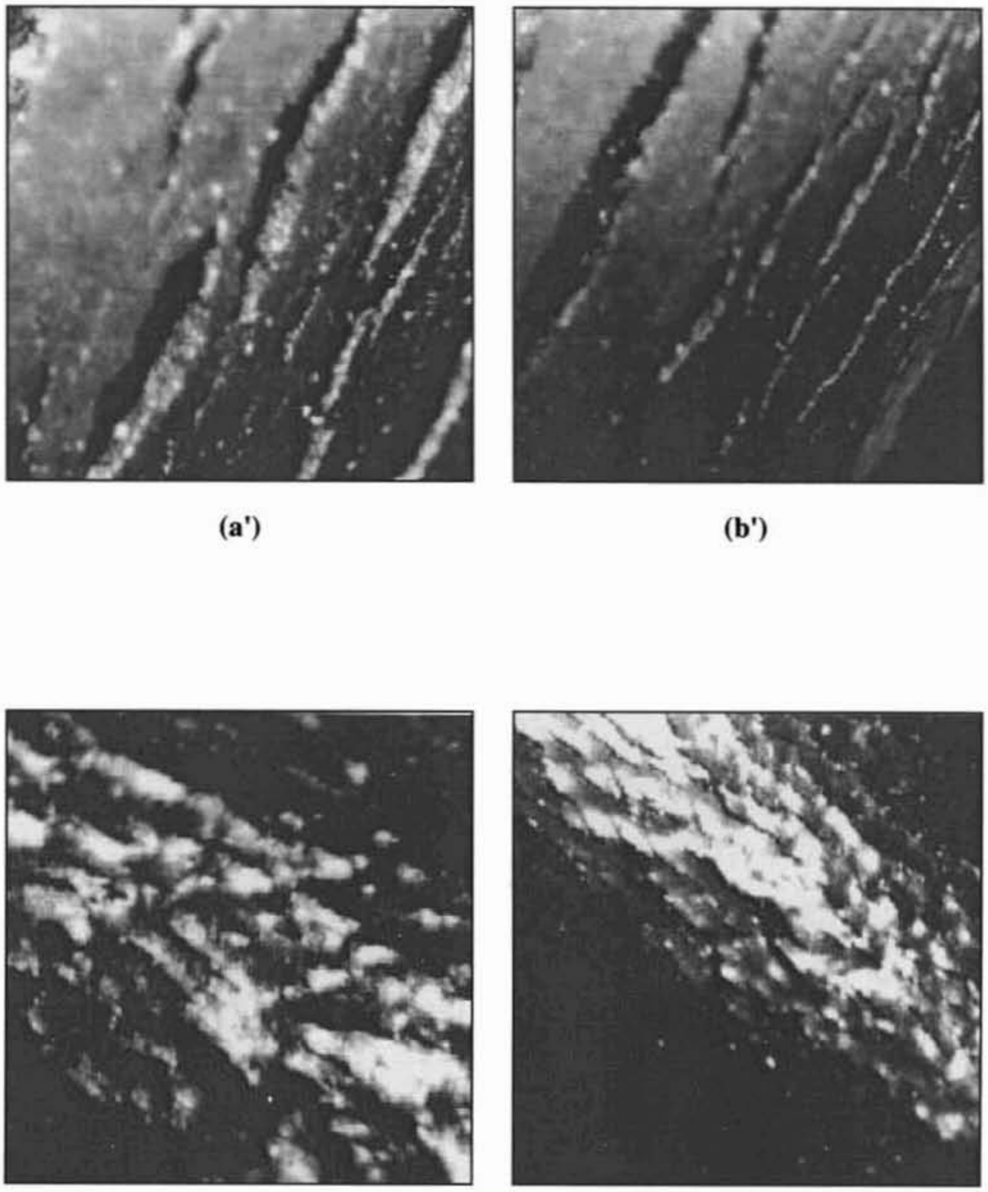
Figs. 6.2. [B] ozone crack growth of SBR after 19h (a') without antioxidant, (b') with vulkanox 4020 (c') with PIB-PD (d') with CPW-PD.



(a) (b)

(c) (d)

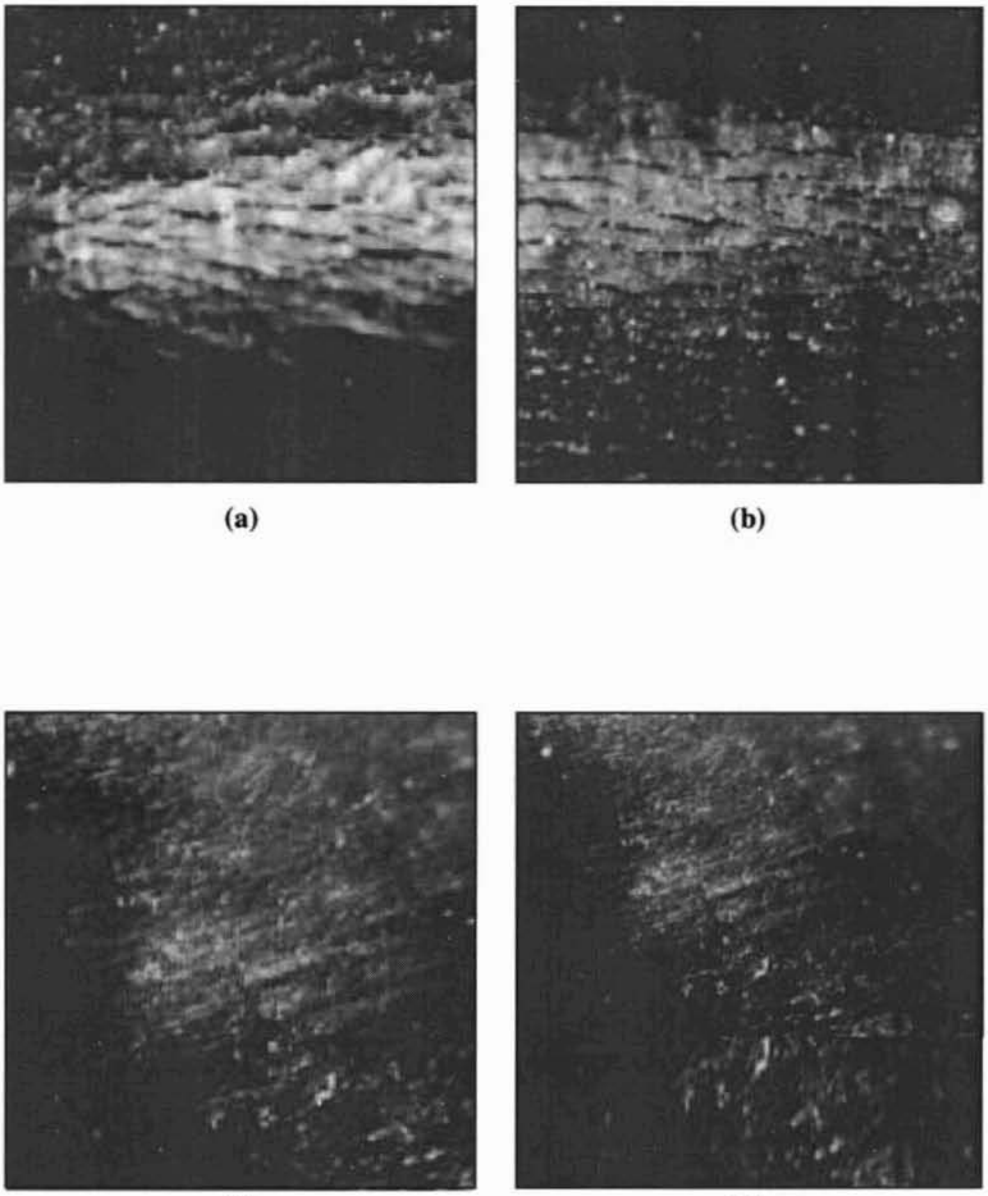
Figs. 6.3 [A] ozone crack initiation of NBR vulcanizates (a) without antioxidant, (b) vulkanox 4020 (c) with PIB-PD (d) with CPW-PD.



(a') (b')

(c') (d')

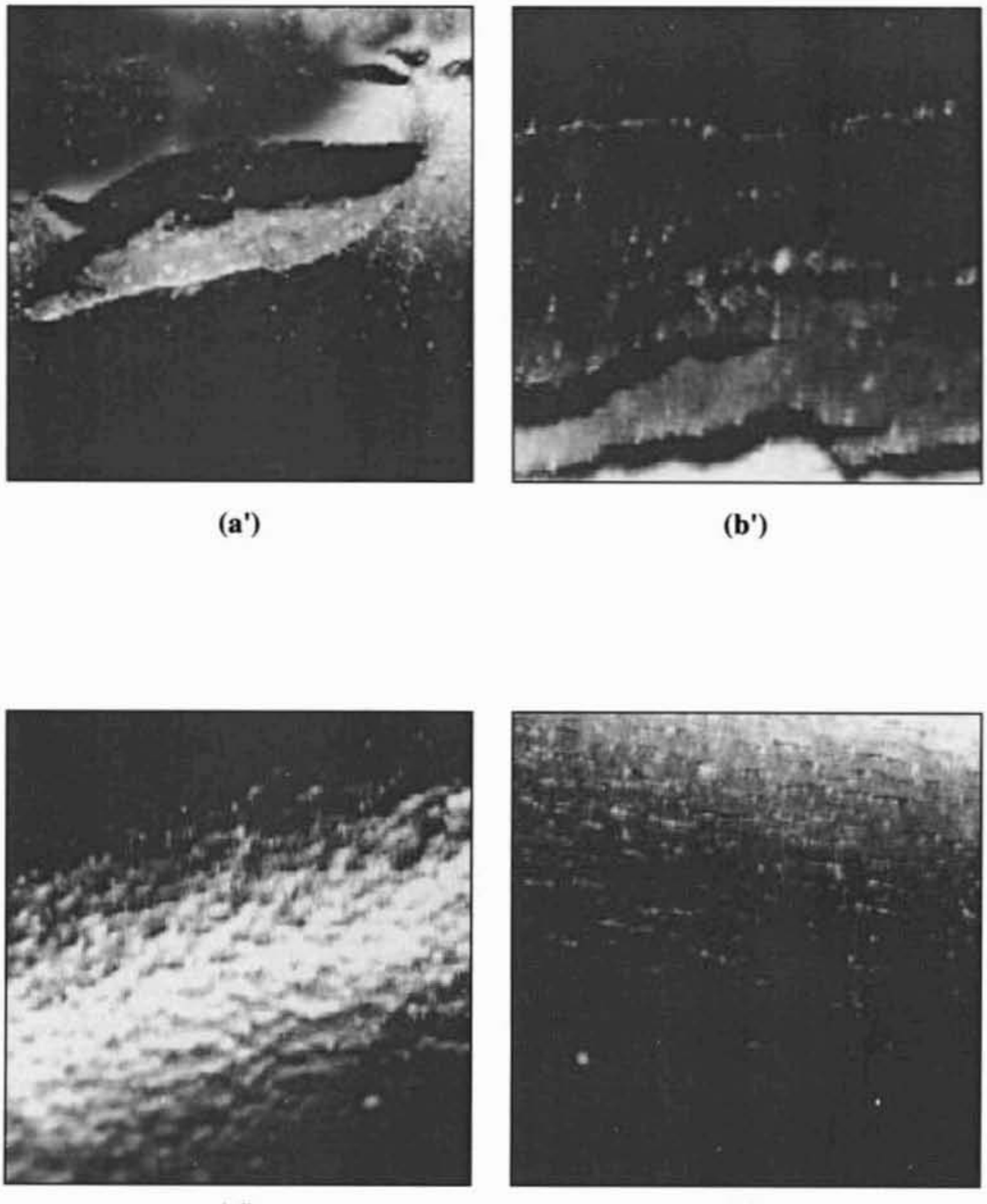
Figs. 6.3. [B] ozone crack growth of NBR after 19h (a') without antioxidant, (b') with vulkanox 4020 (c') with PIB-PD (d') with CPW-PD.



(a) (b)

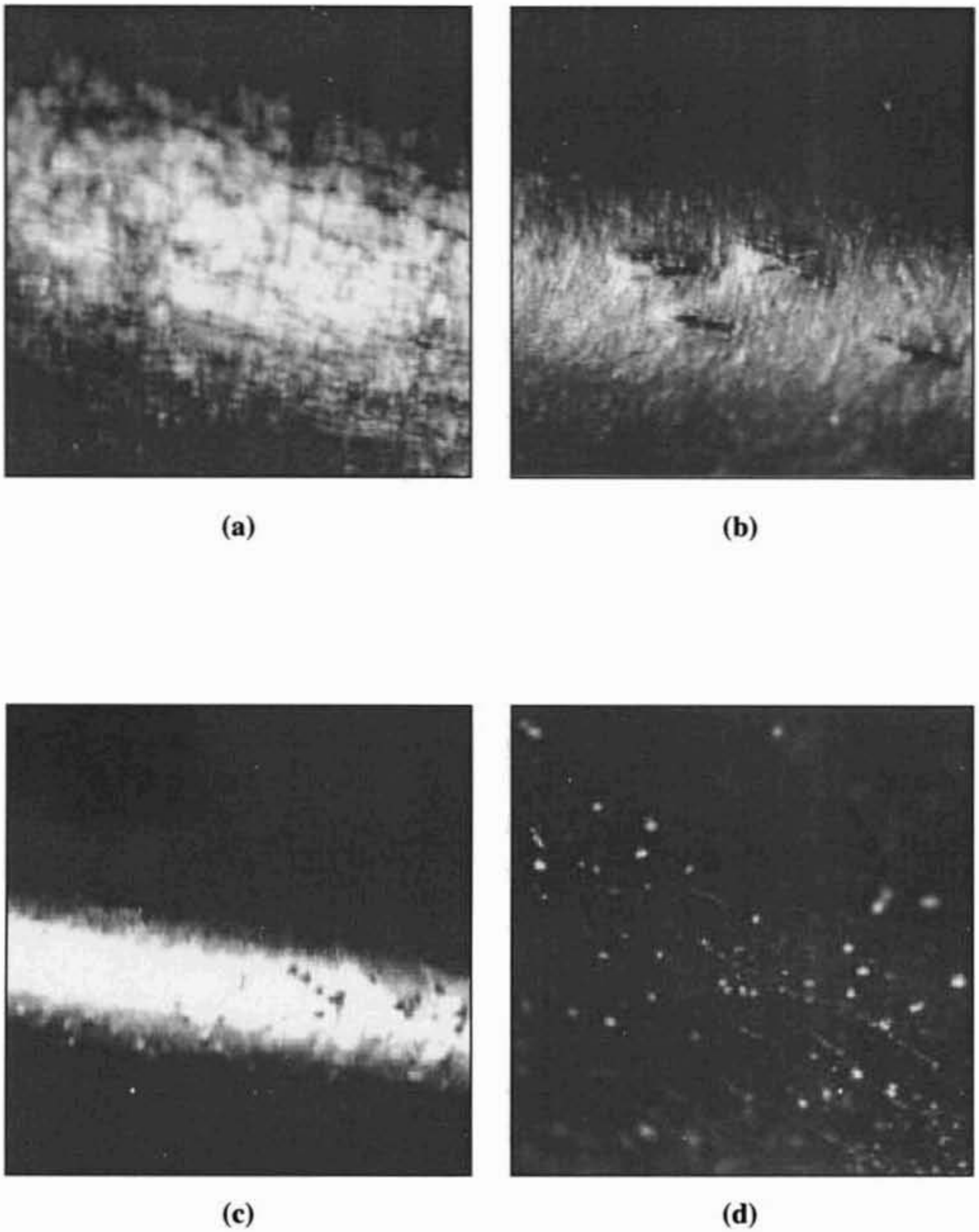
(c) (d)

Figs. 6.4 [A] ozone crack initiation of IIR (S-Cure) vulcanizates (a) without antioxidant, (b) with vulkanox 4020 (c) with PIB-PD (d) with CPW-PD.

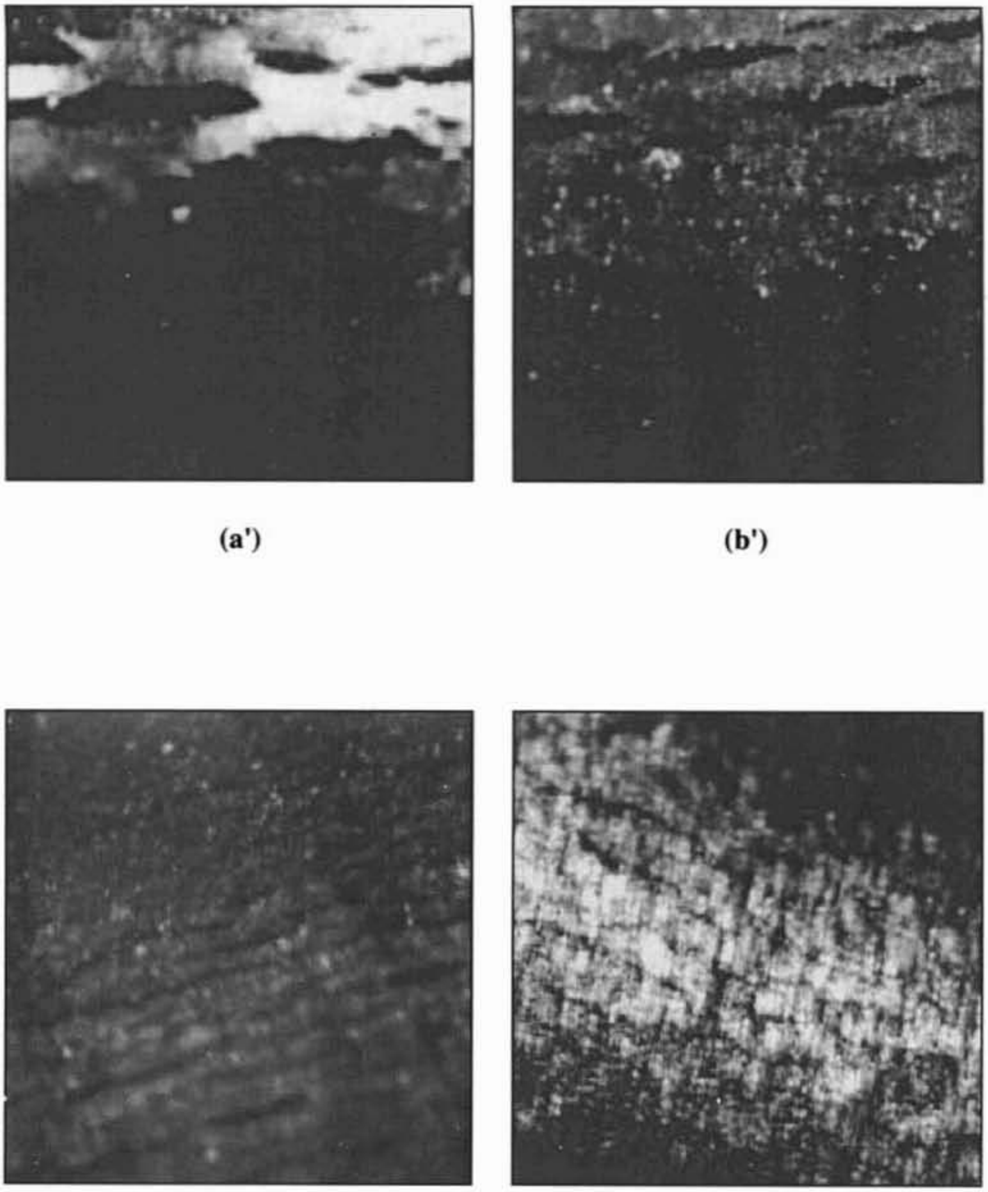


(a') (b') (c') (d')

Figs. 6.4. [B] ozone crack growth of IIR (S-Cure) after 19h (a') without antioxidant, (b') with vulkanox 4020 (c') with PIB-PD (d') with CPW-PD.



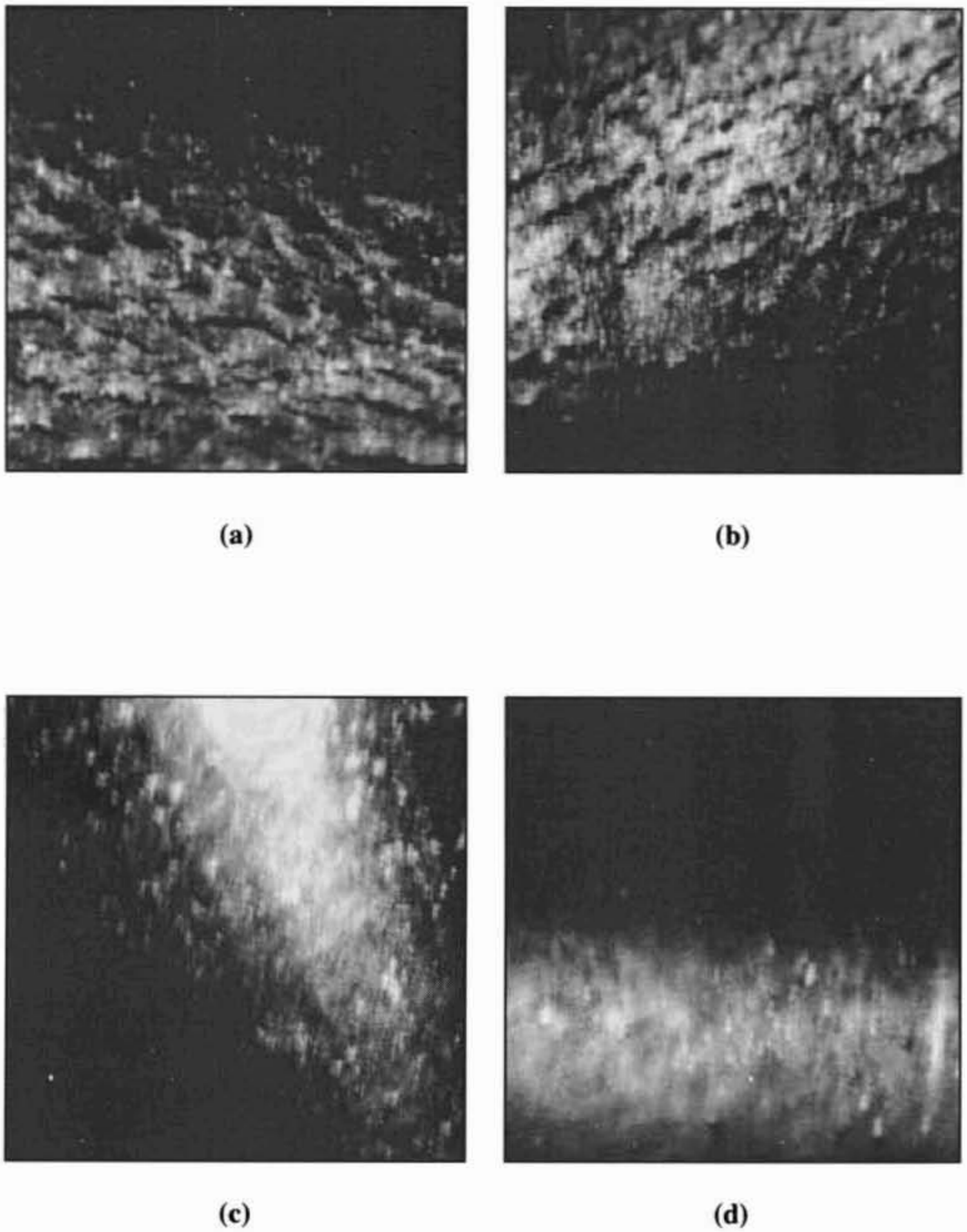
Figs. 6.5 [A] ozone crack initiation of IIR (resin cure) vulcanizates (a) without antioxidant, (b) with vulkanox 4020 (c) with PIB-PD (d) with CPW-PD.



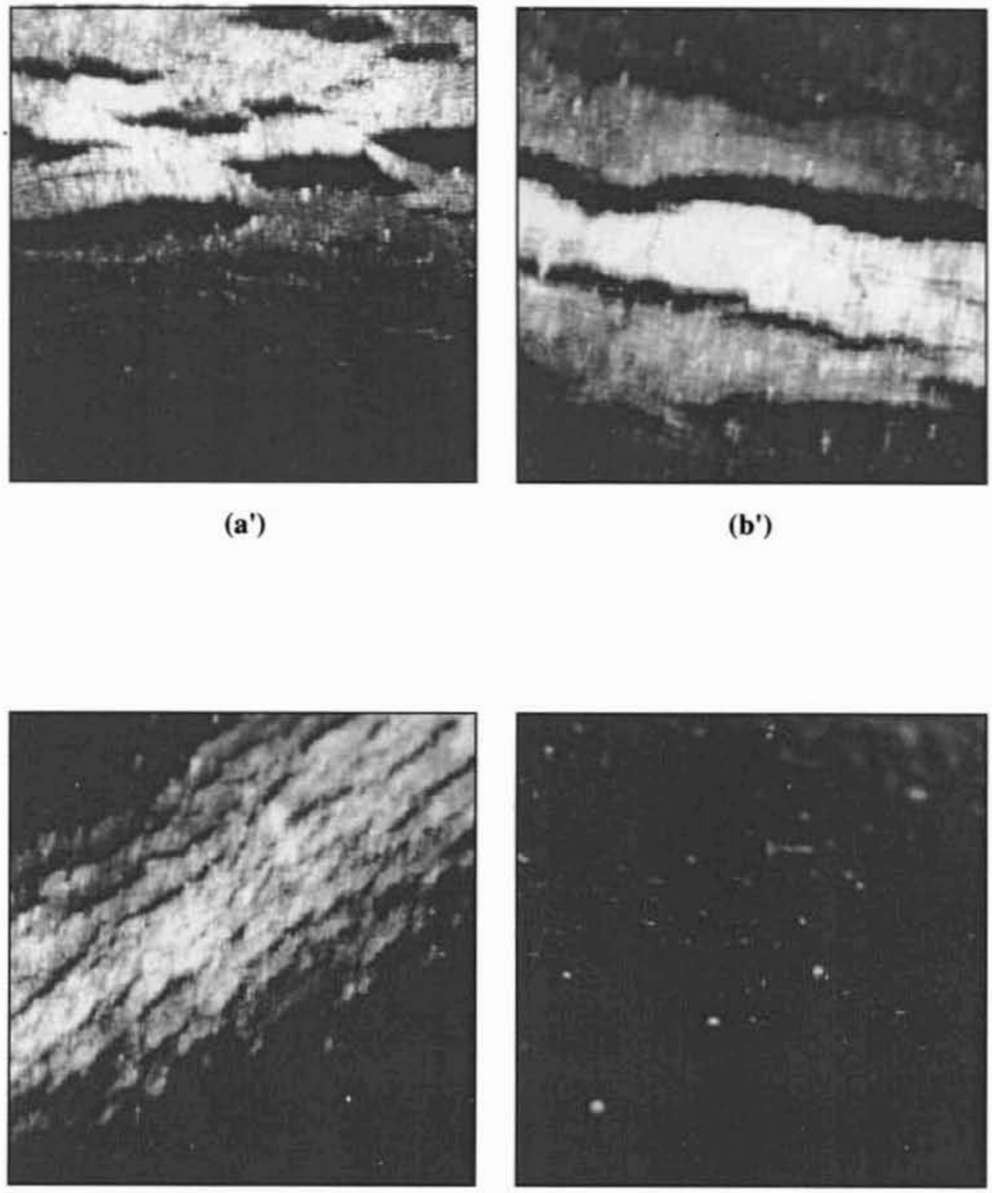
(a') (b')

(c') (d')

Figs. 6.5. [B] ozone crack growth of IIR (resin cure) after 19h (a') without antioxidant, (b') with vulkanox 4020 (c') with PIB-PD (d') with CPW-PD.


(a) (b) (c) (d)

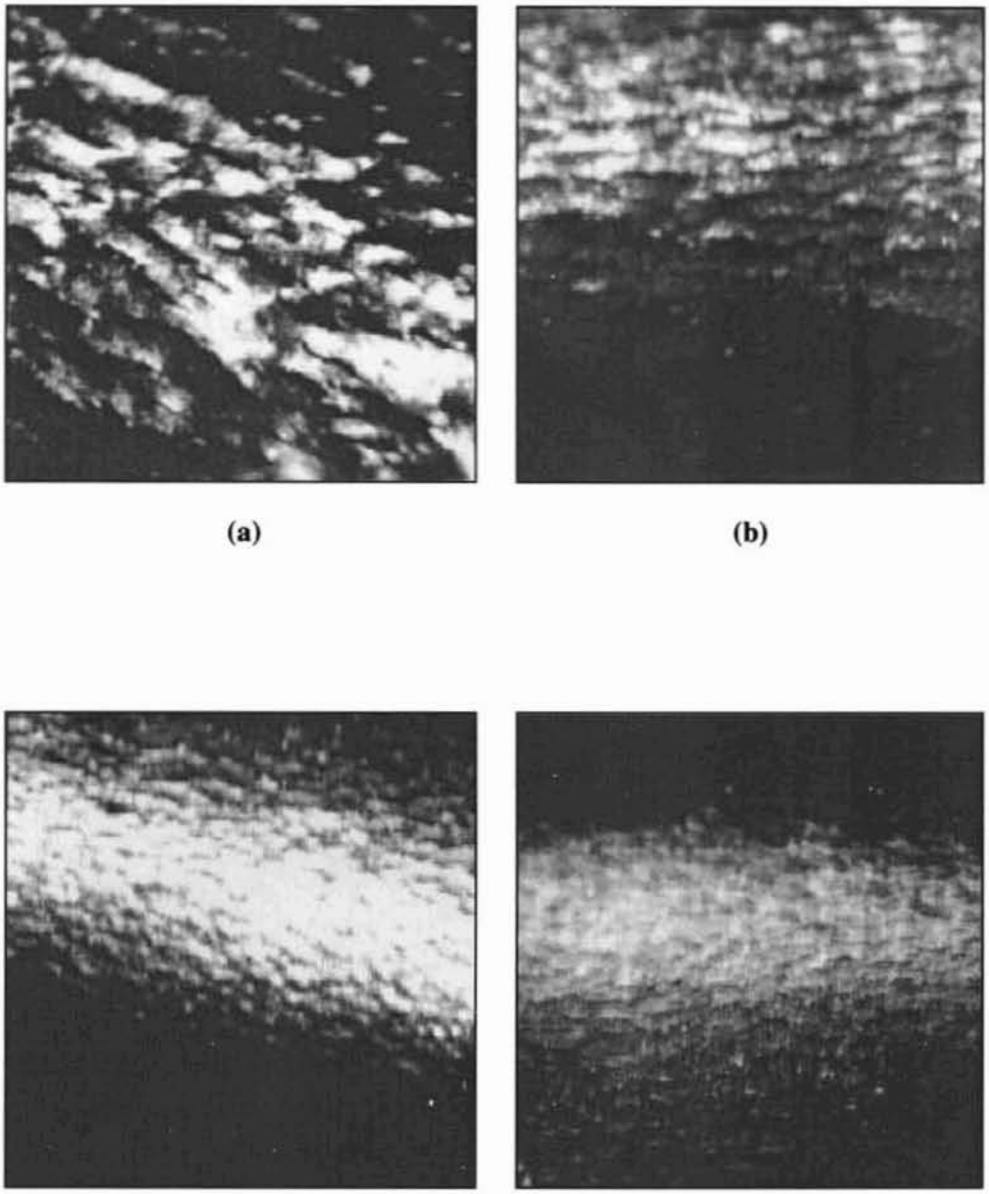
Figs. 6.6 [A] ozone crack initiation of NR/SBR blends (a) without antioxidant, (b) with vulkanox 4020 (c) with PIB-PD (d) with CPW-PD.



(a') (b')

(c') (d')

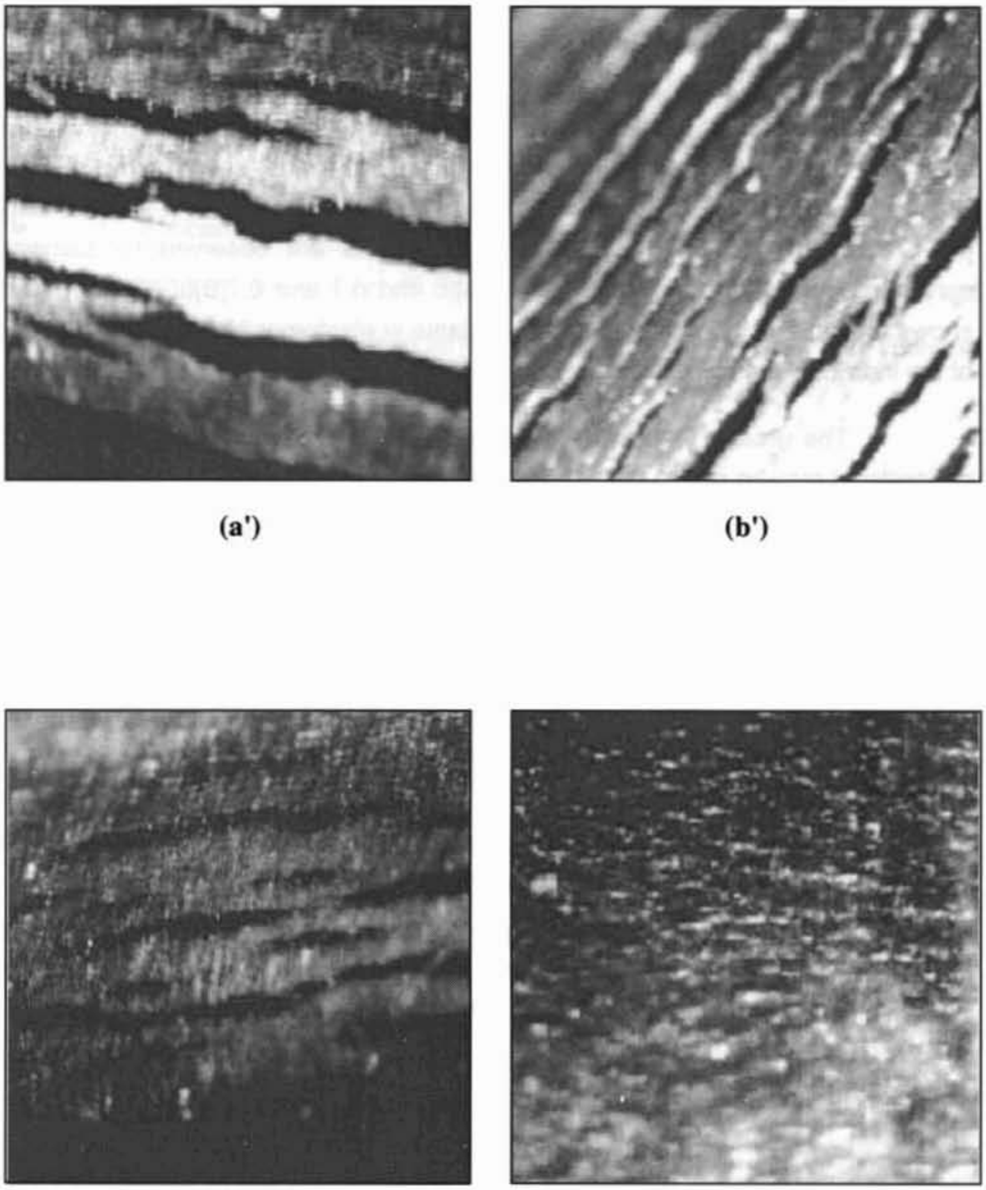
Figs. 6.6 [B] ozone crack growth of NR/SBR after 19h (a') without antioxidant, (b') with accinox TQ (c') with PIB-PD (d') with CPW-PD.



(a) (b)

(c) (d)

Figs. 6.7 [A] ozone crack initiation of NR/BR blends (a) without antioxidant, (b) with accinox TQ (c) with PIB-PD (d) with CPW-PD



(a') (b')

(c') (d')

Figs. 6.7 [B] ozone crack growth of NR/BR after 19h (a') without antioxidant, (b') with accinox TQ (c') with PIB-PD (d') with CPW-PD

Figs.6.7[A] (a)-(d) show the photographs of ozone-cracked surface of NR/BR blends on crack initiation. Figs 6.7[B]. (a')- (d') show the photographs of ozone-cracked surface of NR/BR blends after 19hrs in an ozone chamber. Photographs clearly shows that blends without antioxidants develop severe cracks Figs. 6.7[A](a) and 6.7[B] (a')], blends with conventional antioxidant show lesser cracks [Figs. 6.7[A](b) and 6.7[B](b')], while least cracks are observed for samples containing bound antioxidants [Figs.6.7 [A](c and d) and 6.7[B](c' and d')]. This shows the superiority of the bound antioxidants in elastomer blends as in the case of the individual elastomers.

The greater resistance to ozone ageing for polymers containing bound antioxidants may be due to their appreciably higher molecular weight, which makes them less volatile. The saturated backbone further prevents network formation, which helps blooming and acting as a good barrier for ozone attack. When the efficiency of bound antioxidants CPW-PD and PIB-PD were compared, it was observed that the former imparts higher resistance.. This may be due to its lower molecular weight, which helps blooming and formation of a protective film on the surface of the vulcanizate, preventing direct contact with the atmosphere.

Conclusions

- Ozone and flex resistance of the vulcanizates containing bound antioxidants are superior to those containing conventional antioxidants.
- It seems there is optimum molecular weight range for getting the maximum efficiency of the bound antioxidants as shown by the superior performance of chlorinated paraffin wax bound paraphenylenediamine.
- The bound antioxidant is found to be effective in elastomer blends of NR/SBR and NR/BR.

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Chapter 7

USE OF AMINE TYPE ANTIOXIDANTS IN NR/BR AND NR/SBR BLENDS

7.1 Introduction

Elastomer blends are of great importance to rubber industry. Almost all industrial rubber products are made of rubber blends. C. Michael Roland[1] reviewed the factors governing both morphology and behaviour of polymer blends. The largest use of elastomer blends is in the manufacture of tyres. For car tyre treads, SBR is preferred because of its good wet grip property but it has a penalty in heat build up performance. In large tyres, where heat build up must be minimised, NR or blends of NR with IR are used.

Compatibility is the fundamental property, deciding the practical utility of polymer blend.[2-4] If two elastomers in a blend are incompatible, it will exist in the form of two separate phases and the cured blend will show inferior properties.[5] The properties of miscible blends will follow relationships that are functions of composition and to some extend, the degree of interaction between the blend components.[6-7]

The introduction of cis- 1,4-polybutadiene(butadiene rubber or BR) during the late 1950's was an important development relating to use of elastomer blends in tyres. NR/BR blends has enabled significantly improved tread wear and groove cracking resistance without reduction in resilience.[8] Side walls of passenger tyres are made from a blend of equal proportions of NR and cis-1,4 polybutadiene rubber. Side wall must resist crack growth under severe service conditions, over wide range of temperature and after ageing for many years. Better oil extension and higher black loading are additional benefits, made possible by the addition of BR.[9] Corish reviewed different aspects of elastomer blends.[10] Glanville, Milner and Windibank[11] showed that the state of degradation of NR is reduced in blends with BR. Blow and Loo[12] studied the effects of curing temperature on technical properties of different blends consisting of NR, SBR and BR. Bhowmick and De[13] studied the effects of curing temperature and curing systems on the technical properties, polymer- filler interactions and network structures of NR/BR, NR/SBR and NR/BR/SBR blends.

Two industrially important blends were selected for detailed study in this investigation. The behaviour of the NR/BR and NR/SBR blends in many respects are found to be more or less similar to the behaviour of single elastomers. Even though NR phase takes a larger share of the curatives leaving SBR or BR slightly under crosslinked in conventional compounding, this does not affect the properties. One particular advantage of blending BR with NR is the effect of high curing temperatures on physical properties. This heat stability is conveyed by cis BR when blended with NR or SBR.[14] The addition of cis BR is said to decrease tensile strength and modulus of NR vulcanizates but to increase elasticity and abrasion resistance.[15] This chapter describes the use of new polymer-bound antioxidants namely polyisobutylene-bound paraphenylene diamine (PIB-PD) and chlorinated paraffin wax-bound paraphenylene diamine (CPW-PD) in NR/SBR and NR/BR blends in comparison with those containing conventional antioxidant.

7.2 Experimental

The chemically bound para-phenylene diamines were added in 70/30 NR/BR and NR/SBR blends as per formulations given in Table 7.1.

The amount of the plasticizer can be reduced by the use of liquid polymer-bound antioxidant as shown in Table 7.1. The optimum cure time of blends were determined on a Göttfert Elastograph, model 67.85, as per ASTM D-1646 (1981).

Table 7.1 Formulation of blends

Sample	A	B	C	D	A_1	B_1	C_1	D_1
Natural rubber	70	70	70	70	70	70	70	70
BR	30	30	30	30	-	-	-	-
SBR	-	-	-	-	30	30	30	30
Zinc oxide	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
Stearic acid	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Carbon black (HAF,N330)	45.0	45.0	45.0	45.0	45.0	45.0	45.0	45.0
Aromatic oil	-	1.5	7.5	7.5	-	1.5	-	-
MOR	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Tetramethylthiuramdisulphide	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Sulphur	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1
Accinox TQ	-	-	1.0	-	-	-	1.0	-
PIB PD	6.0	-	-	-	6.0	-	-	-
CPW-PD	-	6.0	-	-	-	6.0	-	-

Rubber compounds were moulded in an electrically heated laboratory hydraulic press at 150°C up to their optimum cure time. Dumbbell shaped tensile test pieces were punched out of these compression moulded sheets along the mill grain direction. The tensile properties of the vulcanizates were evaluated on a Zwick Universal Testing machine using a cross head speed of 500mm /min according to ASTM D-412-98,method A. Tear resistance of the vulcanizates was evaluated as per ASTM D 624-98. Retention in tensile and tear properties were evaluated after ageing the samples at 100°C for 12,24,36 and 48hrs. The compression set of the samples was determined as per ASTM D-395-98(method B). Shore A durometer was used to determine the hardness of the vulcanizates as per ASTM D 2240-97.

Crosslink density ($1/2M_c$) of the samples was determined by equilibrium swelling method using toluene as solvent. The swelling ratio was corrected for the non -network ingredients. The degree of crosslinking was calculated by using Flory Rehner equation.[16] For NR/SBR and NR/SBR blends, χ was found to vary linearly with composition.[17] Hence average value of χ was taken for 70/30 blends of these polymers.

7.3 Results and Discussion

Fig. 7.1 shows cure curves of the NR/BR blends (A, B, C, D in Table7.1). Cure time and scorch time are found to be reduced by the addition of PIB-PD and CPW-PD. This may be due the accelerating effect of the amino group present in the liquid bound antioxidants.

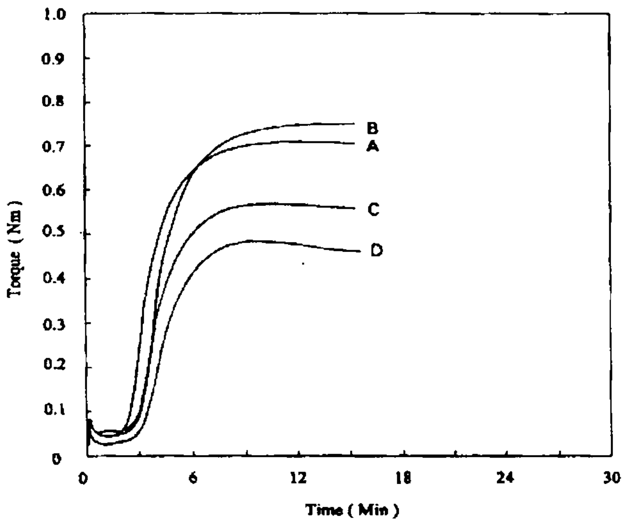

Fig. 7.1 Cure curves of NR/BR blends A-with PIB-PD, B-with CPW-PD, C- accinox TQ and D- without antioxidant

Fig. 7.2 shows the tensile strength of the NR/BR blends with time of ageing at 100°C. The NR/BR blends containing PIB-PD and CPW-PD show fairly good resistance to ageing at 100°C compared to those containing conventional and without antioxidant. This shows the bound antioxidants are efficient in polymer blends also.

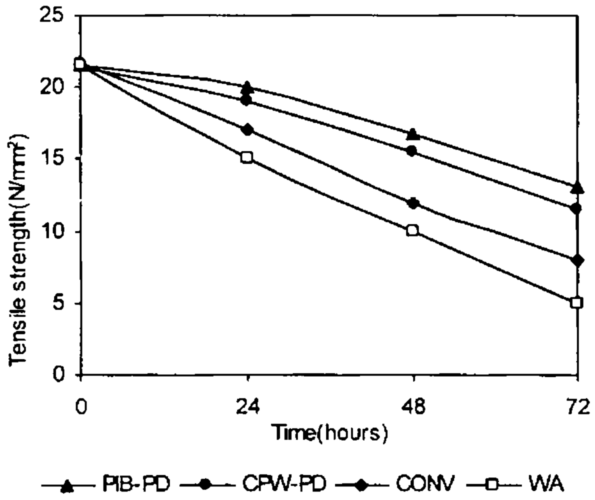

Fig.7.2 Variation in tensile strength of NR/BR blends with time of ageing at 100°C

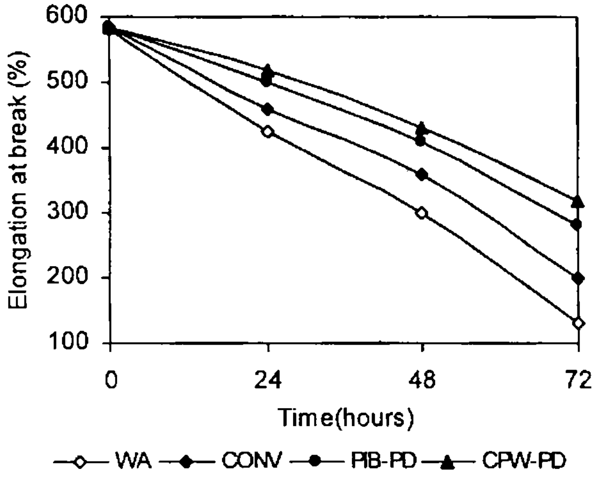

Fig.7.3 Change in elongation at break of NR/BR blends with time of ageing at 100°C

Fig. 7.3 shows the change in elongation at break of the NR/BR blends before and after ageing. The blends containing PIB-PD and CPW-PD show better retention in elongation at break after ageing for 72hrs at100°C. This again shows that polymer- bound antioxidants can improve the ageing resistance of blends.

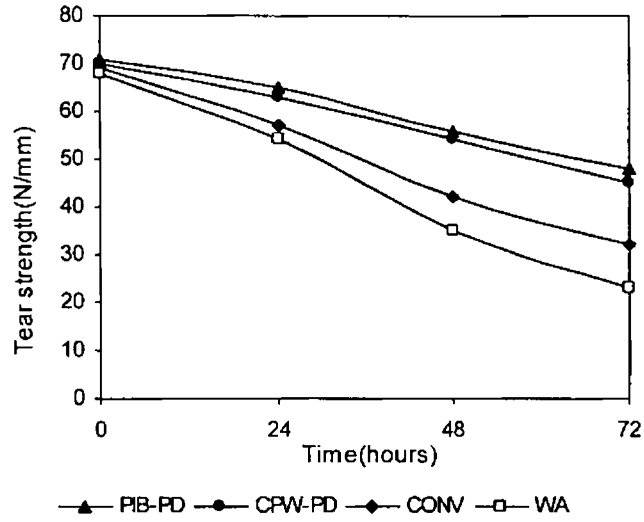

Fig.7.4 variation in tear strength of NR/BR blends with time of ageing at 100°C

Fig. 7.4 shows the tear strength of NR/BR blends before and after ageing. Retention in tear strength of the blends containing PIB-PD and CPW-PD after ageing are better than blends containing accinox TQ.

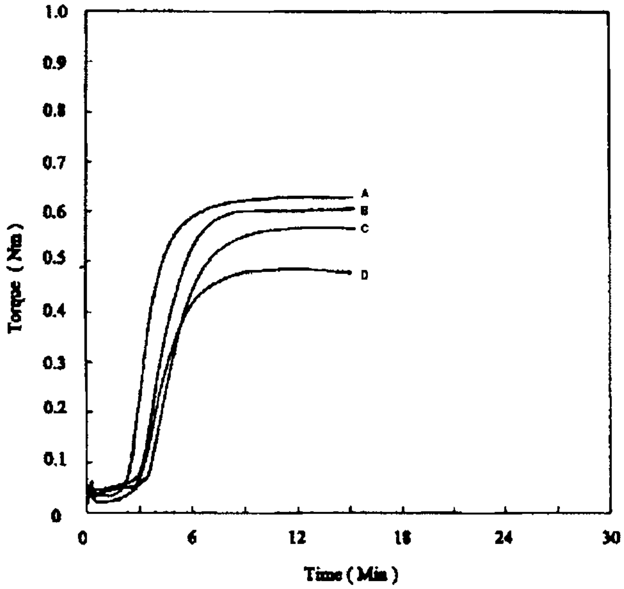

Fig.7.5 Cure curves of NR/SBR blends A_1-with PIB-PD, B_1-with CPW-PD, C_1- accinox TQ and D_1- without antioxidant

Fig. 7.5 shows cure curves of NR/SBR blends (A1, B1, C1, D1 in table7.1). Cure time and scorch time are found to be reduced by the addition of PIB-PD and CPW-PD.

Fig. 7.6 shows the tensile strength of the NR/SBR blends (A1, B1, C1, D1 in table.7.1) with time of ageing. The blends containing PIB-PD and CPW-PD show fairly good resistance to ageing at 100°C compared to those containing conventional and without antioxidant.

Fig. 7.7 shows the tear strength of the above blends time of ageing. Retention in tear strength of the blends containing PIB-PD and CPW-PD after ageing are better than blends containing accinox TQ.

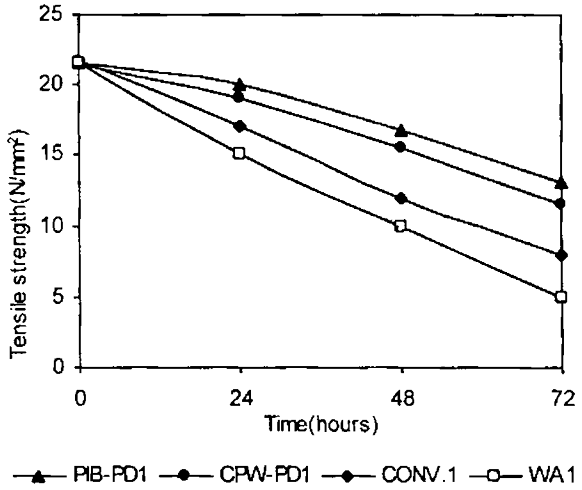

Fig.7.6 Variation in tensile strength of NR/SBR blends with time of ageing at 100°C

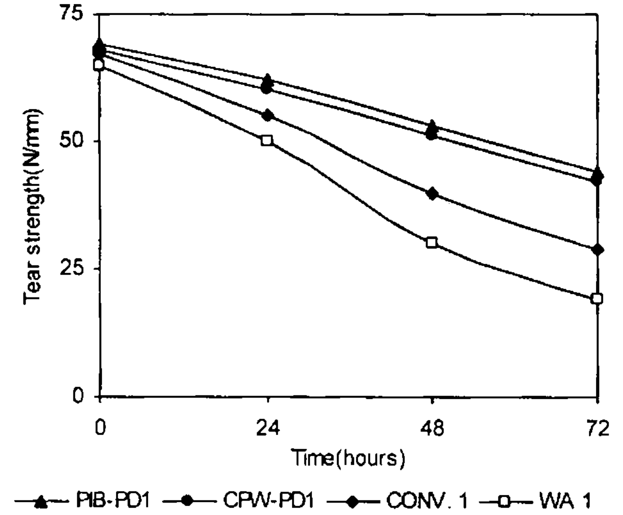

Fig.7.7 Tear strength Vs time of NR/SBR blends at 100°C

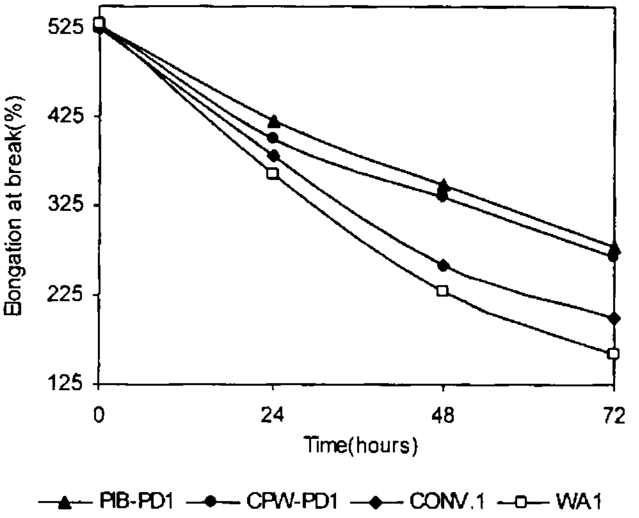

Fig.7.8 Elongation at break of NR/SBR blends Vs Time at 100°C

Fig.7.8 shows the elongation at break of NR/SBR blends with ageing at 100°C. Here also same trend is observed as in the NR/BR case.

Table 7.2 Properties of blends

Properties	A(PIB-PD)		B (CPW-PD)		C (Pilflex-13)		D(WA)	
	NR/BR	NR/SBR	NR/BR	NR/SBR	NR/BR	NR/SBR	NR/BR	NR/SBR
Abrasion resistance (volume loss, cc/h)	2.6	3.1	2.6	3.1	2.8	3.3	2.9	3.5
Compression set (%)	19.4	21	18.8	20.4	21.1	23	21.7	23.1
Hardness (Shore A)	74	60	73	59	72	54	70	53
Tear strength (N/mm)	70	69	69	64	68	63	67	62
Resilience (%)	58	50	59	51	57	48	58	48
Crosslink density × 10^{-5} (g mol/cc)	22.3	8.26	21.1	8	20.2	7.5	18.7	7

Table 7.2 shows the variation in abrasion resistance, compression set, hardness, resilience and crosslink density of NR/BR and NR/SBR blends with bound-antioxidant, accinox TQ and without antioxidant. The blends containing bound antioxidants show better properties than those containing conventional antioxidants. This may be due to low volatility of bound- antioxidants.

Conclusions

1. The blends containing polymer-bound antioxidants show much superior ageing resistance compared to the one containing conventional antioxidant.
2. The polymer-bound antioxidants can reduce the amount of plasticizer as in the previous cases.

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Chapter 8

SUMMARY AND CONCLUSIONS

The primary objective of the study is to develop novel and more effective polymer-bound antioxidants for protection of rubber from degradation than those employed conventionally. Phenolic and amine type antioxidants with saturated polymer backbones have been prepared and their efficiency is evaluated in elastomers, such as NR, SBR, NBR, IIR and elastomer blends like NR/BR and NR/SBR. The novel antioxidant, polyisobutylene-bound para phenylene diamine has been tried in a typical application such as bitumen modification where the conventional antioxidants are not effective. The study shows that the newly developed polymer-bound antioxidants scale up the performance of the elastomers significantly and that they can protect rubber in severe processing conditions. The contents of the various chapters in this thesis have been summarised below.

An introduction about antioxidants and the mechanism of antioxidant action are given in chapter 1. The various factors affecting the effectiveness of antioxidants and their functions are discussed in detail. A brief history of the development of various antioxidants and their classification is also given. The advantage of polymer-bound antioxidants over conventional ones is also highlighted. The principal objectives of the present study are also listed.

The specifications of all the materials used in the study and different experimental techniques used are given in chapter 2.

The synthesis and characterisation of four novel amine type polymer-bound antioxidants are given the chapter 3. The first one, polyisobutylene-bound paraphenylene diamine has been prepared by a two step process. The first step involves chlorinating of low molecular weight polyisobutylene with a terminal double bond using pure dry chlorine. The second step is the condensation of chlorinated product with paraphenylenediamine. The second antioxidant, chlorinated paraffin-wax-bound paraphenylene diamine has been prepared by condensation reaction between chlorinated paraffin-wax and p-phenylenediamine. The third bound antioxidant, polyisobutylene-bound diphenylamine has been prepared by the modified Friedel Craft's alkylation reaction between chlorinated polyisobutylene and diphenylamine. The fourth antioxidant polyethylene glycol bound paraphenylene diamine has been prepared by chlorinating polyethylene glycol using thionyl chloride and then condensing the chlorinated product with p-phenylene diamine. All these novel bound antioxidants have been characterised by ^{1}HNMR, TGA, IR, TLC and VPO.

The suitability of polymer-bound antioxidants in general purpose rubbers like NR and SBR, and special purpose rubbers like NBR and IIR is described in chapter 4. Since the amine type antioxidants namely polyisobutylene-bound paraphenylene diamine, chlorinated paraffin wax-bound paraphenylene diamine, polyisobutylene-bound diphenylamine and polyethylene glycol bound paraphenylene diamine are in the liquid form and have enough plasticizing action, aromatic oil is not needed for formulations involving these antioxidants. The vulcanizates are found to possess better resistance to ageing and solvent extraction compared with those that containing conventional antioxidants like vulkanox 4020 and pilflex13. The oil resistance of NBR vulcanizate is found to be superior to those containing conventional antioxidant like vulkanox 4020. The steam ageing resistance of IIR vulcanizates is also found to have improved by the addition of polymer-bound antioxidants. All vulcanizates containing the bound antioxidants show improved mechanical properties such as tensile strength, tear resistance, De Mattia flex resistance and rebound resilience. However compression set, abrasion resistance and heat build up values marginally decrease on the addition of the bound antioxidants.

One of the potential areas where the novel polymer-bound antioxidants can be used advantageously is in the rubberisation of roads. Polyisobutylene bound p-phenylene diamine has been tried in NR used for bitumen modification. The bound antioxidant is found to be significantly superior in this application requiring comparatively high resistance to oxidation.

The synthesis and characterisation of two novel phenolic type bound antioxidants are described in chapter 5. Polyisobutylene bound phenol has been prepared by modified Friedel Crafts alkylation reaction using chlorinated polyisobutylene and phenol. 4-octadecyl phenol has been prepared from stearic acid; it has been converted into acid chloride using thionyl chloride and then the acid chloride has been attached to phenol by Friedel Craft's acylation reaction. The carbonyl group has been reduced by Clemmenson reduction to get 4-octadecyl phenol. These bound-antioxidants are characterised by ^{1}HNMR, TGA, IR, TLC and VPO. The effect of these antioxidants on the vulcanizate properties of NR has been investigated. The properties of the vulcanizates containing phenol-bound antioxidants are found to be marginally superior to those with conventional antioxidants. The ageing resistance of the NR vulcanizates containing phenolic antioxidants are also superior to those containing conventional antioxidant.

The ozone ageing and flex resistance of vulcanizates of NR, SBR, NBR, IIR and elastomer blends like NR/BR and NR/SBR are described in chapter6.All the vulcanizates containing amine type polymer-bound antioxidants show excellent ozone ageing resistance and flex resistance in comparison with those containing conventional ones.

The application of amine type antioxidants like polyisobutylene-bound paraphenylenediamine and chlorinated paraffin-wax-bound paraphenylenediamine in elastomer blends like NR/BR and NR/SBR are described in chapter 7. The ageing studies are conducted as in the previous cases. The polymer-bound antioxidants are found to be more efficient than conventional antioxidant in these rubber blends also.

List Of Abbreviations and Symbols

A_0	weight of the absorbed solvent corrected for the swelling increment
AH	Antioxidant
An. $AlCl_3$	Anhydrous aluminium chloride
An. $ZnCl_2$	Anhydrous zinc chloride
ASTM	American Society for Testing and Materials
BR	Polybutadiene
BS	British Standards
CPW	Chlorinated paraffin wax
CPW-PD	Chlorinated paraffin wax-bound paraphenylene diamine
CR	Chloroprene rubber
D	Deswollen weight of the specimen
DA	Diphenylamine
DIN	Deutscher Normenausscchuss
DOP	Dioctyl Phthalate
E	Potential energy
F	weight fraction of insoluble components
HAF black	High abrasion furnace black
hrs	Hours
IIR	Isobutylene Isoprene rubber
IP	Institute of Petroleum
IR	Infrared spectroscopy
IS	Indian standard
ISNR	Indian standard natural rubber
M mol/Kg RH	Millimole per Kilogram of Rubber Hydrocarbon
MBT	Mercaptobenzothiazole
MBTS	Dibenzthiazyl disulphide
M_c	Number average molecular weight of rubber chains between crosslinks

Min	Minutes
ML(1+ 4) 100°C	Mooney viscosity determined using large rotor after a dwell time of 1 minute and rotor run of 4 minutes at 100^{0}C.
Mol	Mole
MOZ	Benzthiazyl 2-sulphenmorpholide
MPa	Mega Pascal
N	Normality
N/mm	Newton per millimetre
N_0	Avagardo number
NBR	Acrylonitrile-butadiene rubber
nm	Nano metre
Nm	Newton meter
NR	Natural rubber
PD	Para phenylene diamine
PEG	Polyethylene glycol
PEG-PD	Polyethylene glycol-bound para phenylene diamine
PF resin	Phenol formaldehyde resin
phr	Parts per hundred rubber
PIB	Polyisobutylene
PIB-DA	Polyisobutylene-bound diphenylamine
PIB-PD	Polyisobutylene-bound paraphenylene diamine
PIB-Ph	Polyisobutylene-bound phenol
pphb	parts per hundred bitumen
ppm	parts per million
R	Gas constant
RH	Polymer
rpm	Revolutions per minute
S	Sulphur
SA	Stearic acid
SA-Ph	4-octadecyl phenol

SBR	Styrene - butadiene rubber
T	Temperature in kelvin scale
t_0	initial thickness of the specimen
t_1	final thickness of the specimen
t_{10}	Scorch time
t_5	Induction time
t_{90}	Optimum cure time
TGA	Thermogravimetric analysis
TLC	Thin layer chromatography
T_m	Melting temperature
TMTD	Tetramethyl thiuram disulphide
t_s	thickness of spacer bar
V	molar volume
VPO	Vapour phase osmometry
V_r	Volume fraction of rubber
V_s	Molar volume of solvent
Vulkanox SP	a mixture of styrenated phenol
w/v	Weight/volume
w/w	Weight/weight
Z	Weight fraction of filler
χ	Polymer - solvent interaction parameter
ν	Potential energy of one molecule
δ	Solubility parameter
ΔH	Enthalpy change
δ_r	density of rubber
δ_s	density of solvent
ΔS_f	Entropy of fusion
^{1}H NMR	Proton magnetic resonance spectroscopy

List of Publications From The Work

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