STUDIES ON POLYMER BOUND ANTIOXIDANTS

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by

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March 1995

CERTIFICATE

This is to certify that this thesis entitled "**Studies on Polymer Bound Antioxidants**" is a report of the original work carried out by Ms.Shanti A.Avirah under my supervision and guidance in the Department of Polymer Science and Rubber Technology, Cochin University of Science and 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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DECLARATION

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

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Shanti A.Avirah

CONTENTS

ABBREVIATIONS

Polymers

NR	Natural Rubber
SBR	Styrene-butadiene rubber
BR	Polybutadiene rubber
IR	Polyisoprene rubber
NBR	Acrylonitrile-butadiene rubber
CR	Polychloroprene rubber
HTNR	Hydroxy terminated liquid natural rubber

Antioxidants

SP	Styrenated phenol
DA	Diphenylamine
PD	Paraphenylenediamine
CNSL	Cashew nut shell liquid
HTNR-SP	Styrenated phenol bound to HTNR
HTNR-Phenol	Phenol bound to HTNR
HTNR-DA	Diphenylamine bound to HTNR
HTNR-CL	Cardanol bound to HTNR
NR-DA	Diphenylamine bound to natural rubber during UV-irradiation
NR-PD	Paraphenylenediamine bound to natural rubber during UV-irradiation
NR-PDM	Paraphenylenediamine bound to natural rubber during aggressive mastication
Card-SB	Sulphur bridged cardanol

NR-DAM	Diphenylamine bound to natural rubber during aggressive mastication
Accinox DN	Phenyl-β-napthylamine
Vulkanox 4020	N(1,3-dimethyl butyl-N'-phenyl-p-phenylenediamine)
Vulkanox SP	Mixture of styrenated phenols
Vulkanox HS	(1,2-dihydro-2,2,4-trimethylquinoline, polymerised)
Pilflex-13	[N-1,3-dimethyl butyl)-N'-phenyl-p-phenylenediamine

Additives

An.$AlCl_3$	Anhydrous aluminium chloride
An.$ZnCl_2$	Anhydrous zinc chloride
HAF black	High abrasion furnace black
MBT	Mercaptobenzothiazole

Other abbreviations

RH	Polymer
C	Compatibility ratio
$t_{0.5}$	half time crystallisation of the mixture
$t^{\circ}_{0.5}$	half time crystallisation of pure polymer
$\bar{C}$	Compatibility of the stabiliser with the polymer
A'_{o}	Volatility of the pure stabiliser in a mixture
A	Volatility of the antioxidant

Ao	Constant depending on the character of the polymer and additive
E	Activation energy
R	Gas constant
T	Temperature
W	Gas flow
a & b	Constants
C_o	Initial concentration of the antioxidant
d	Thickness of the polymer sample
ΔG	Free energy of the system
ΔH	Enthalpy change of the system
ΔS	Entropy change of the system
ΔH_1	Heat of phase transition of the dissolving substance
ΔH_2	Heat of solvation
V_r	Volume fraction of rubber network
V_{r_o}	Value of V_r for filled vulcanizates
M_c	Number average molecular weight of rubber chains between crosslinks
χ	Polymer-solvent interaction parameter
V_s	Molar volume of solvent
ρ_r	Density of rubber
ρ_s	Density of solvent
ISNR	Indian standard natural rubber
ASTM	American Society for Testing and Materials

BS	British Standard
IR	Infrared spectroscopy
'H-NMR	Proton magnetic resonance spectroscopy
TGA	Thermogravimetric analysis
TLC	Thin layer chromatography
GPC	Gel permeation chromatography
ML(1+4), at 100°C	Mooney viscosity determined using large rotor after a dwell time of one minute and rotor run of four minutes at 100°C
$\bar{M}_v$	Viscosity average molecular weight
$\bar{M}_w$	Weight average molecular weight
Nm	Newton meter
v/v	Volume / volume
phr	Parts per hundred
ppm	Parts per million
mol	mole
UV	Ultraviolet
rpm	Revolutions per minute

Chapter 1

INTRODUCTION

Rubber has such remarkable and desirable properties that it is used in many engineering applications like bearings, springs and seals in addition to bulk products like tyres, tubes, beltings, hoses etc. Load can be safely supported and misalignments accommodated by its ready elastic deformability, shock and vibrations can be isolated by exploiting its energy absorbing properties and spring characteristics and the deformability and resilience of rubber can be used to advantage in the provision of efficient seals.

The base rubbers are classified into two broad groups, natural and synthetic. Synthetic rubbers are further classified into two categories namely, the general purpose types like styrene-butadiene rubber (SBR), polybutadiene rubber (BR), polyisoprene rubber (IR) which are intended for the manufacture of tyres and general mechanical products and the special purpose types like acrylonitrile-butadiene rubber (NBR), polychloroprene rubber (CR) etc. which have special properties and are in consequence intended for specialised applications.

Natural and synthetic polymers deteriorate on ageing in varying degrees as a result of the combination of a number of factors such as heat, light, oxygen and ozone. Thermal and light initiated oxidation in polymers proceed by a free radical chain mechanism involving the formation of hydroperoxides, which can be summarised as below.

Initiation

$$\underset{\text{(Polymer)}}{RH} \xrightarrow{\text{under oxidative conditions}} \dot{R} + \dot{H} \tag{1}$$

$$R^{\bullet} + O_2 \longrightarrow ROO^{\bullet} \tag{2}$$

Propagation

$$RO\dot{O} + RH \longrightarrow ROOH + R^{\bullet} \tag{3}$$

$$ROOH \longrightarrow R\dot{O} + \dot{O}H \tag{4}$$

$$ROOH + RH \longrightarrow R\dot{O} + R^{\bullet} + H_2O \tag{5}$$

Termination

$$RO\dot{O} + R\dot{O} \longrightarrow \text{Inert Products} \tag{6}$$

Impurities such as a low concentration of certain transition metal ions can greatly accelerate initiation through reduction and oxidation of hydroperoxides.

$$M^{+} + ROOH \longrightarrow M^{++} + RO^{\bullet} + OH^{-}$$

$$M^{++} + ROOH \longrightarrow M^{+} + ROO^{\bullet} + H^{+}$$

The external manifestations of these reactions are changes in physico-chemical properties and include decrease in strength and elongation at break, change in resistivity and colour etc. Thus the degradative processes impair the useful properties of polymers. Oxidative degradation of polymers can be retarded by appropriate antioxidants[1-7].

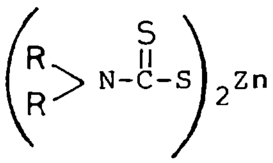
Two main classes of antioxidants are (1) initiation inhibitors and (2) propagation inhibitors.

1. Initiation inhibitors

Initiation inhibitors inhibit the initiation step in thermal auto-oxidation. There are two important types of initiation inhibitors.

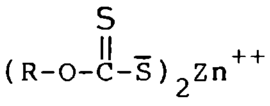
(a) Peroxide decomposers

Peroxide decomposers decompose hydroperoxides through polar reactions, thereby inhibiting initiation. This class includes metal salts of certain dithioacids such as zinc dithiocarbamates (I), xanthates (II), di-tert-butyl sulphide (III), tert-butyl thio sulphoxylic acid (IV)$^{8-10}$ etc.



$\left(R_2N\text{-}\overset{\displaystyle S}{\overset{\|}{C}}\text{-}S\right)_2Zn$

(I)



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

(II)

$(H_3C)_3C\text{-}S\text{-}C(CH_3)_3$

(III)

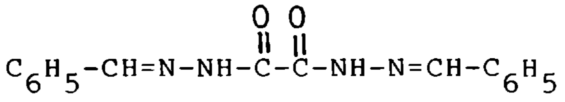
$(CH_3)_3CSSOH$

(IV)

(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

(V), ethylenediamine tetra acetic acid (VI), N,N'-di-β-naphthyl-p-phenylenediamine (VII), 2,2'-methylene-bis(4-methyl-6-tert-butyl phenol) (VIII)[11-12].

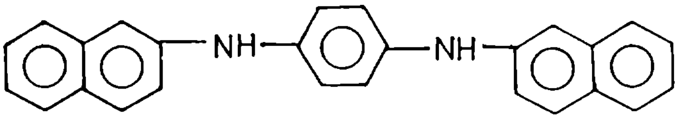


$$C_6H_5\text{-}CH{=}N\text{-}NH\text{-}\overset{\overset{O}{\|}}{C}\text{-}\overset{\overset{O}{\|}}{C}\text{-}NH\text{-}N{=}CH\text{-}C_6H_5$$

(V)

$$(HOOCH_2C)_2N\text{-}CH_2\text{-}CH_2\text{-}N(CH_2COOH)_2$$

(VI)



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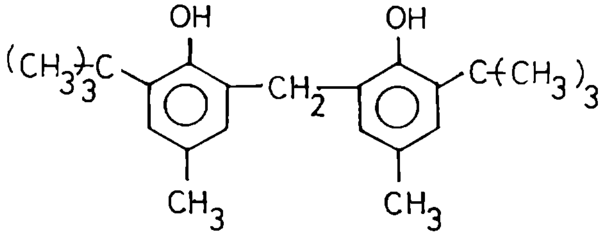


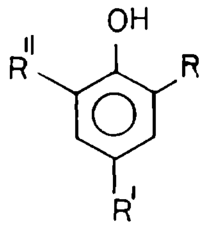
(VIII)

2. Propagation inhibitors

Propagation inhibitors interrupt the propagation step and hence markedly reduce the rate of oxidation. The mechanism of inhibition involves hydrogen transfer to the peroxy radical in a rate controlling step[13-14].

$$AH + R\dot{O}_2 \longrightarrow \dot{A} + ROOH \qquad (7)$$

where AH is the antioxidant. The most important commercial antioxidants that function this way are hindered phenols (IX), substituted diphenylamines (X), substituted para-phenylenediamines (XI), phenyl napthylamines (XII), and ketone-amine condensation products (XIII) eg.



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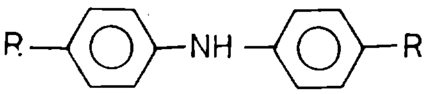
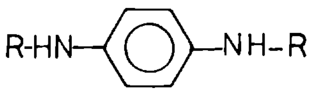
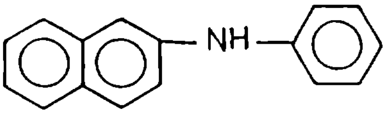


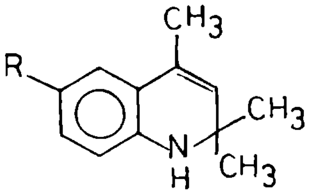
(X)



(XI)



(XII)



(XIII)

The geometry of reaction (7) is influenced by the steric environment of the reaction site of the antioxidant (OH or NH)[15]. From a sterically hindered InH, '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[16]. Depending on the nature of the initial InH, the radical In$^{\bullet}$ may be either a phenoxyl or an amino radical. Transformation products of phenoxy or amino radical are summarised by Pospíšil[17].

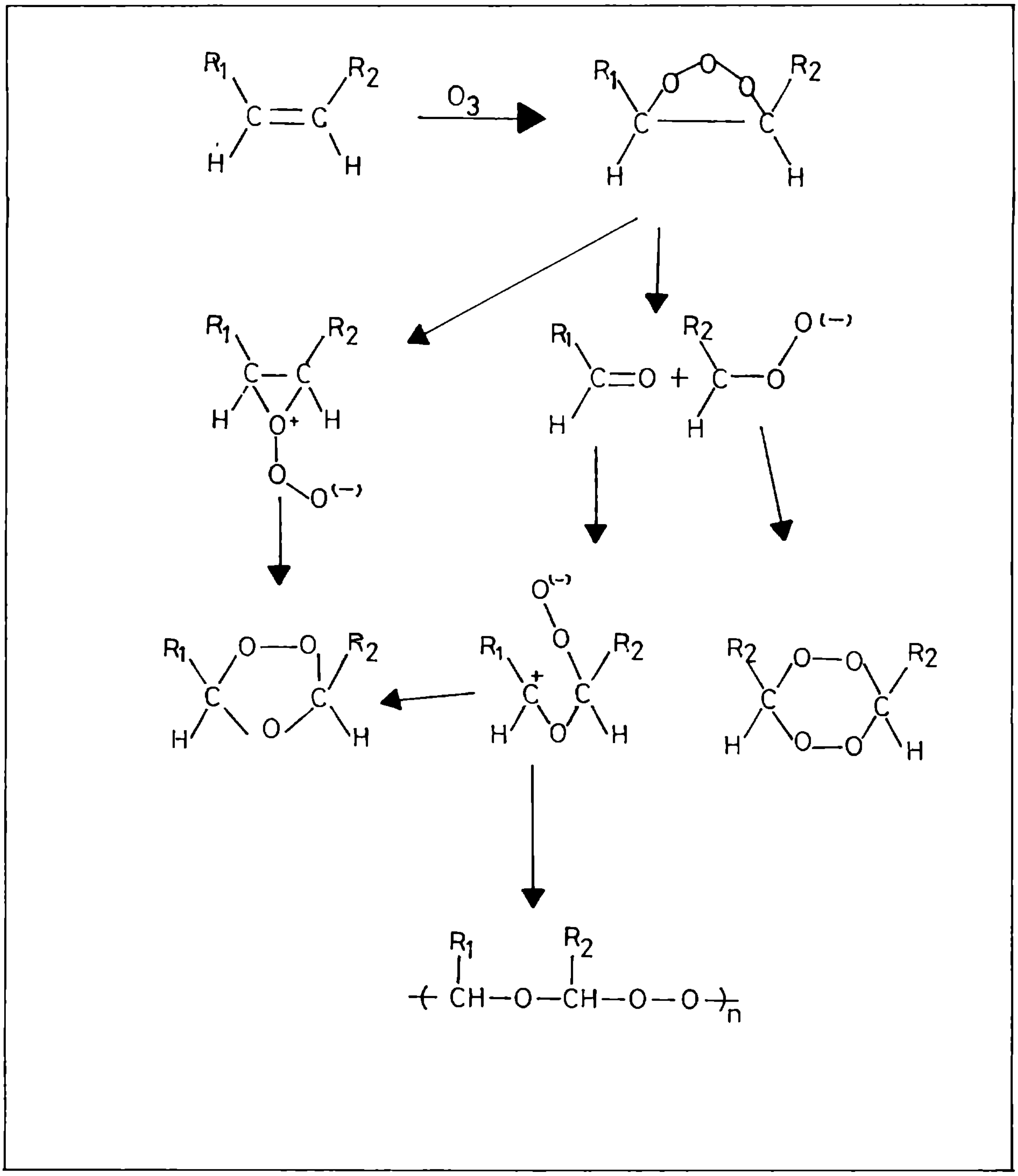
Degradation by ozone

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

Ozonation may be interpreted as shown in scheme 1.1[18-20].

Inhibitors

Two broad groups of additives are used commercially to inhibit ozonolysis of unsaturated elastomers. One group includes relatively unreactive film forming waxes while the other group react with ozone, ie., antiozonants. Wax protection alone is inadequate for products, such as tyres that flex in service causing film to break. In general the most effective class of antiozonants are N-N'-disubstituted



Scheme 1.1

p-phenylenediamines, and continue to enjoy widespread growth, especially for tyre applications[18].

Essentially three theories of antiozonant action have been developed.

(1) The antiozonant blooms to the surface of the rubber compound and reacts preferentially with the incident ozone.

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

(3) The antiozonant reacts with intermediates formed in the ozonation of rubber preventing chain scission or recombining severed rubber chains[19-21].

Antiozonant efficiency should therefore be dependent on the rate of diffusion of fresh antiozonant to the surface, rate of reaction of antiozonant with O_3 and the initial concentration of the antiozonant in the rubber phase[22]. Products of the ozonation of aromatic amines and diamines include oximes, hydroxylamines, nitroso and nitro compounds[23-26].

The combined effect of oxygen, ozone and heat on rubber vulcanizate and the action of inhibitors can be schematically represented (Scheme 1.2).

Service requirements placed on many finished rubber products demand improved polymer stabilisation. The effectiveness of antioxidants depends on two factors.

(a) Intrinsic activity of the antioxidant

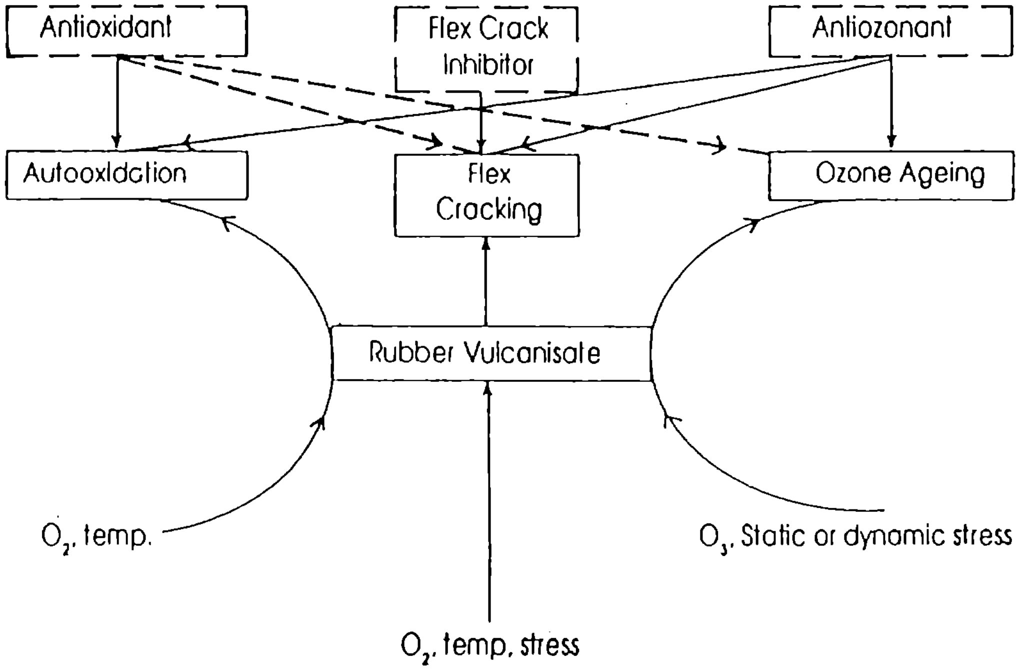
This is the fundamental ability of the antioxidant and its transformation products to interfere with and retard the radical chain oxidation process, which in turn depend on the chemical structure of the antioxidant.

(b) Permanence of the antioxidant in the polymer

The concentration of the antioxidant in a polymer decreases during long term use as a consequence of two processes (1) chemical loss of antioxidant; (2) physical loss of antioxidant from the polymers[27-31].

Chemical loss of antioxidant as a result of their mechanism of stabilisation is summarised by Vink[32].

MECHANISM OF DEGRADATION :
ROLE OF ANTIOXIDANTS AND ANTIOZONANTS



Diagrammatic Representation of the Mechanism of Rubber Degradation

Scheme 1.2

Physical loss of antioxidant mainly depends on (a) distribution of antioxidants in polymers, (b) compatibility of antioxidants in polymers (c) volatility of antioxidants, (d) extractability of antioxidants from polymers and (e) diffusion of antioxidants in polymers.

(a) Distribution of antioxidants in polymers

The distribution of antioxidants is uniform in amorphous polymers where the antioxidant forms micro-heterogeneous phases uniformly dispersed in a polymer according to their compatibility with the polymers.[33] In semi-crystalline polymers, the distribution of antioxidant is not uniform owing to the presence of crystalline and amorphous phases. Low molecular weight compounds are concentrated in the amorphous phase, especially at the boundaries of spherulites and in the defective spot of spherulites[34]. Ambrovič and Mikovič have similarly concluded from the changes in melting point of polypropylene on repeated remelting that pyrocatechol additives are found only in the amorphous phase of the polymer[35]. N.C.Billingham et al. observed the rejection of antioxidants into the amorphous regions on the boundaries of spherulites during the growth of the spherulites with the aid of X-ray fluorescence mapping in a scanning electron microscope and ultraviolet and fluorescence spectroscopy, depending upon the compound investigated[36-39]. They also ascertained that the distribution of antioxidants in spherulite polymers depend on the conditions of crystallisation and on the total amount of the atactic polymer concentrated at the boundaries of spherulites. Such distribution of antioxidants in polymers appears to be advantageous because the amorphous portion of most polymers, especially polyolefins, is the region most sensitive to degradation. The non-uniform distribution of antioxidant raises its concentration in the amorphous phase, thus protecting the polymer more effectively against degradation.

(b) Compatibility of antioxidants

One of the factors which affect the effectiveness and permanence of antioxidants in polymers is compatibility, which represents the total effects which are involved in the polymer-additive interaction. If the polymers are modified by antioxidants, a physical mixture characterised by a certain degree of homogeneity or heterogeneity arises. The degree to which this occurs depends mainly on the magnitude of cohesion and adhesion forces between the components and their bulk or surface interactions. Measurement of changes in solubility parameters, changes in surface tension of antioxidants, and free surface energy have been used for investigating the compatibility of antioxidants[40-42]. The rate of isothermal crystallisation of a polymer and the influence of 2-hydroxy-4-alkoxy benzophenones on the course of this crystallisation were studied by Marcinčin and Cicchetti et al.[43-45]. The effect of diluent on isothermal crystallisation can be regarded as a measure of the compatibility of a polymer with an additive, the relationship can be represented as

$$C = \frac{t_{0.5}}{t^{\circ}_{0.5}}$$

where

$t_{0.5}$ - half time of crystallisation of the mixture

$t^{\circ}_{0.5}$ - half time of crystallisation of pure polymer

and C - compatibility ratio

If $C > 1$, the additive is considered to be compatible with the polymer.

Another interesting method of evaluating the compatibility is the volatility of the pure substance and their mixtures with the polymer[46-47]. The equation that may be used is,

$$\bar{C} \approx \frac{A_o'}{A_p}$$

where

$\bar{C}$ - compatibility of the stabiliser with the polymer

A_o' and A_p - volatilities of the pure stabiliser and in a mixture

According to the equation, in the case of two substances with equal escaping tendency from a polymer, the substance with higher volatility in the pure state is more compatible.

Compatibility is characteristic of a particular polymer-antioxidant system. By comparing the volatility of different kinds of antioxidants in the pure state and in a mixture with polyethylene, Temchin et al. found some effects due to the influence of the structure of the stabilisers on their compatibility with the polymer[48,49]. The compatibility of antioxidants containing the same functional group with polyethylene increases with the length and number of alkyl substituents, degree of branching of the alkyls and the uniformity of the alkyl distribution in the molecule. The introduction of polar groups as well as the replacement of aliphatic substituents by aromatic ones reduces the compatibility[50]. The presence of polar groups in an antioxidant leads to stronger interactions between a polymer with polar functional groups thus raising the compatibility and permanence of the antioxidant in a polymer.

Volatility of antioxidants

Volatility is a manifestation of thermal motion of molecules on the surface of a sample. Assuming a uniform distribution of the antioxidant in the bulk of the polymer, the evaporation of the antioxidant from the surface layer results in the formation of a concentration gradient which is the driving force for diffusion in the polymer. So there are two processes causing the loss of antioxidant from the polymer viz. diffusion of the antioxidant from the bulk of the polymer and its evaporation from the surface.

Several methods are described in the literature to determine the volatility of antioxidants[48-51]. Luston et al. and Minuora et al. performed thermogravimetric analysis[52-53]. Hawkins et al. and Blumberg et al regarded the decrease in stability as a manifestation of the volatility of antioxidants in polymers[54-55]. The stability of polymers was evaluated by induction periods in oven-ageing tests and sealed tube tests. Angert et al. and Temchin et al. found that the rate of evaporation of antioxidants from rubber or polyethylene is inversely proportional to the thickness of the sample and directly proportional to the surface area[56,46]. Evaporation of antioxidants from polymers is a thermally activated process which is governed by Arrhenius equation[46,56-58]. The physical aspects of antioxidant evaporation from polymers have been summarised by Angert et al.[56]. The following equation may be used

$$A = A_o \exp(E/RT)(\frac{W}{b}+W)(1 + aC_o)\frac{1}{d}$$

where,

A - volatility of the antioxidant

A_o - constant depending on the character of the polymer and additive

E - activation energy
R - gas constant
T - temperature
W - Gas flow
a&b - constants
C_o - initial concentration of the antioxidant and
d - the thickness of the polymer sample.

The influence of the structure, molecular weight and other properties of the antioxidant on its volatility has been the subject matter of several papers[54,55,58-60]. An increase in molecular weight results in an increase in intermolecular forces which brings about a decrease in volatility of antioxidants in polymers. Attempts to eject a phenolic antioxidant of low volatility from a polymer failed even when high vacuum was applied[61]. The formation of intermolecular hydrogen bonds leads to an increase in intermolecular attraction forces which results in a decrease in volatility[62]. The branching of substituents enhances the volatility of derivatives of 2-hydroxy benzophenone and 2,6-di-tert-butyl phenol while the replacement of alkyls in these derivatives by cycloalkyls or aralkyls results in a volatility decrease[59,62-64].

The volatility of the antioxidant from the polymer depends on the characteristics of the polymer also. As the volatility is governed by the diffusion of antioxidant in polymer, this phenomenon is to be expected. Angert et al. found that the rate of evaporation of phenyl-2-napthylamine from polymers decreased in the series polyethylene > fluorinated rubber > polybutadiene > butadiene-styrene rubber > butadiene-acrylonitrile rubber. This sequence is in agreement with the solubility of phenyl-2-napthylamine in these polymers and also the polarity of these polymers which results in increased intermolecular forces[58].

Extractability of antioxidants

This plays a part wherever the polymer particles come in contact with water or organic solvents. Water extraction of the antioxidants is clearly a problem in rubber such as latex threads which are in regular contact with hot water and hot detergent solution[65,66] Extraction of the antioxidant from nitrile rubber based polymers used in the fabrication of seals, belts, cables and hoses, which are in contact with hot lubricating oil is a serious problem[67]. Leachability decreases with increasing molecular weights of antioxidants. Another factor which influences the extractability is the relation between the interactions of antioxidants, extraction medium and polymer. For non-polar polymers the extractability of polar antioxidants with polar solvents must be faster than the extractability of non-polar antioxidants.

Dissolution of an antioxidant in an extraction medium takes place if the free energy of the system, decreases ie., ΔG in the equation

$$\Delta G = \Delta H - T \Delta S$$

has a negative value. As the entropy change accompanying dissolution is always positive, the solubility depends on heat of solution ΔH. The heat of solution may be divided into two terms,

$$\Delta H = \Delta H_1 + \Delta H_2$$

where ΔH_1 is the heat of the phase transition of the dissolving substance and ΔH_2 the heat of solvation. Since ΔH_2 is always a negative value, the heat of solution depends on ΔH_1. For solid substance ΔH_1 is always positive because heat energy must be expended for disruption in the crystal lattice[68]. Considering the extraction of antioxidants from polymers, ΔH_1 corresponds to the antioxidant-polymer or antioxidant-antioxidant interactions while ΔH_2 is related to the antioxidant-solvent interaction. In the case of non-polar polymers,for extraction with non-polar solvents, the heat of solvation is higher than ΔH_1, and the antioxidants are readily washed out of polymers. When a polar solvent is used for extraction, the extractability depends on the relative magnitude of the interaction forces between the antioxidant and the solvent and the antioxidant and polymer. For polar polymers, the interactions between an antioxidant and the polymer will be more intense owing to the presence of functional groups in the antioxidant molecule. In some cases the polymer-antioxidant interactions may be so strong that in washing with non-polar solvent, $\Delta H_1 > \Delta H_2$. In this case, the antioxidant is not extracted from polymer provided the entropy change is not too high.

Extraction of the antioxidant is faster than evaporation because it does not necessitate the presence of energy rich molecules and depends only on the interactions between the antioxidant and the solvent. The extraction of the antioxidant from the surface of polymer gives rise to the formation of a concentration gradient between the interior of the polymer and the surface which results in diffusion.

When a polymer is in contact with solvents, the diffusion of the solvent molecules into the polymer must also be considered and it is characterised by a high solvent concentration gradient in the interface. Since solvent molecules are usually smaller than antioxidant molecules, the diffusion rate of the solvent must be greater than that of the antioxidant.

Decrease in physical properties after extraction and ageing of polymers was taken as the measure of extractability by Horvath et al.[69].

Diffusion of antioxidants in polymers

The diffusion of an antioxidant in a polymer does not itself produce any loss of antioxidant from the polymer. But the diffusion processes play an important role in the evaporation and leaching of antioxidants from polymers. Several methods for determining the diffusion coefficients in polymers are described[45,70,71]. Bair et al. developed a thermogravimetric method for the determination of diffusion coefficients[72]. The diffusion coefficient is inversely proportional to the solubility of the substance in a polymer. Owing to the low solubility in many polymers, antioxidants diffuse to the surface which may be regarded as a manifestation of incompatibility and migration ability of the additives in polymers. Diffusion in polymers decreases when they contain polar and methyl groups. Methyl groups, impair the flexibility of the chain, which results in lower diffusion coefficients and greater activation energy for diffusion. For a series of butadiene-acrylonitrile copolymers, the diffusivity decreases with increasing content of acrylonitrile[73]. Unsaturation in the back bone of polymers also contributes to the increase in the coefficient of diffusion. Another factor which affects diffusion is the presence of crosslinks. It was found by Barner et al. that diffusion was slower in crosslinked natural rubber than it was in a non-crosslinked sample[74-75].

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

(1) to produce antioxidant of high molecular weight; (2) to chemically attach the antioxidant to a polymer, thereby guaranteeing its persistance in the final product ie., Polymer Bound Antioxidants.

Polymer bound antioxidants

Cain et al. have shown that the mobility of the antioxidant is not essential for heat ageing or oxidative ageing, but will become essential for protection against ozone attack or dynamic fatigue[76]. One of the more exciting and at times ingenious areas of research during the past decade has been the preparation of polymer-bound antioxidant systems.

Several polymerisable amine and phenolic antioxidants are discussed in the literature[77-88]. For example, butadiene and acrylonitrile, butadiene and styrene were terpolymerised with N-(4-anilino phenyl) methacrylamide.[89-90] Bader reported alkenyl-substituted phenols by Friedal-Craft's alkylation reaction of the phenol with a suitable diene.[91-93] Smutny produced excellent yields of ortho and para [1-(2,7-octadienyl)] phenols by reaction of 1,3,7 octatriene with phenol in presence of palladium, platinum or ruthenium catalyst.[94]

Interesting technique for introducing α,β-unsaturation, into phenolic monomer was described by Steinburg by direct alkylation of phenolic antioxidant with various acetylene dicarboxylates[95-96].

The most versatile method of polymer modification is the direct introduction of an antioxidant function by the reaction of a conventional polymer with a suitably reactive adduct. Several methods are discussed in the literature[97-111]. Gregory prepared polymer bound phenolic antioxidants by alkylation of various alkylated phenols by a variety of polydiene rubbers[112-114] Minuora et al. prepared a series of hydroxy terminated polybutadiene (HTPB) bound amine antioxidants by direct Friedel-Craft's alkylation reaction of arylamines by HTPB[5]. Scott et al. have demonstrated that simple hindered phenols which contain a methyl group in the ortho and para position can react with natural rubber in presence of an oxidising free radical to yield polymer bound antioxidants[115-117]. Mohamed et al. and Egbase described the preparation of polymer bound antioxidants by direct hot melt mixing of chlorine containing polymers and a commercial antioxidant[118,119].

Objects and scope of the present work

The primary aim of this work has been to prepare efficient and cost effective polymer bound antioxidants by direct attachment of conventional antioxidants to a modified polymer. Due to the importance and easy availability of natural rubber in Kerala, it is proposed to make use of low molecular weight natural rubber as the polymer substrate for binding the antioxidant in most cases. The molecular weight of such low molecular weight natural rubber can be easily manipulated by varying the time of mastication, UV-irradiation etc. Further, the bound antioxidant may also get vulcanized during the vulcanization of the elastomer to which it is added, making the antioxidant non-volatile and non extractable. Several methods are proposed to be investigated for attaching the antioxidant to the low molecular weight natural rubber such as modified Friedel-Craft's alkylation reaction, binding during UV-irradiation, binding during aggressive mastication etc. The efficiency of such rubber bound antioxidants is proposed to be compared with that of conventional antioxidants in terms of volatility, extractability in solvents, ageing resistance etc. Naturally occuring antioxidants such as cardanol, are also proposed to be modified by binding them to low molecular weight natural rubber. 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 applications.

This thesis is divided into following chapters.

Chapter 1: Introduction

Chapter 2: Experimental techniques

Chapter 3: Preparation of HTNR based bound antioxidants and their use in NR and SBR

Part I: Preparation and characterisation of hydroxy terminated natural rubber (HTNR) bound antioxidants and their use in filled natural rubber/latex compounds

Part II: Application of HTNR bound diphenylamine in styrene-butadiene rubber

Part III: Preparation and characterisation of HTNR bound cardanol antioxidant and sulphur bridged cardanol and their use in filled natural rubber vulcanizates

Chapter 4: Binding of antioxidants to liquid natural rubber by UV-irradiation and their use in NR and NBR

Part I: Preparation and characterisation of natural rubber bound diphenylamine and its use in natural rubber filled vulcanizates

Part II: Preparation and characterisation of natural rubber bound paraphenylenediamine and its use in filled NBR vulcanizates

Part III: Studies on natural rubber bound paraphenylene diamine antioxidant in filled NR vulcanizates

Chapter 5: Binding of antioxidants to masticated natural rubber and their use in NR and SBR

Part I: Preparation and characterisation of natural rubber bound diphenylamine/paraphenylenediamine during mastication and their use in filled NR compounds

Part II: Application of natural rubber bound paraphenylenediamine antioxidant in styrene-butadiene rubber

Chapter 6: Summary and Conclusions.

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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.

MATERIALS USED

1. Elastomers

(1) Natural rubber (NR)

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

Mooney viscosity [ML(1+4), at 100°C]	82.00
Other Parameters	Limit
Dirt content, % by mass, Max.	0.05
Volatile matter, % by mass, Max.	1.00
Nitrogen, % by mass, Max.	0.70
Ash, % by mass, Max.	0.60
Initial plasticity, P_o, Min.	30.00
Plasticity retention index (PRI) Min.	60.00

(2) Acrylonitrile-butadiene rubber (NBR)

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

(3) 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.

4. Natural rubber latex

Natural rubber latex (centrifuged) was obtained from Rubber Research Institute of India, Kottayam and had the following specifications:

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

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

(5) Hydroxy terminated liquid natural rubber (HTNR)

Hydroxy terminated liquid natural rubber (HTNR) was prepared in the laboratory by the sunlight irradiation of a mixture of natural rubber solution and hydrogen peroxide using tetrahydrofuran as the homogenizer.[1] It had a molecular weight ($\bar{M}_w$) of 2800 and hydroxyl value of 26.04 mg of KOH/g.

2. Antioxidants

(1) Accinox DN

Accinox DN (phenyl-β-napthylamine) was obtained from ICI Ltd., India. The sample had a specific gravity of 1.10.

(2) Vulkanox 4020

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

(3) Vulkanox SP

Commercial phenolic type antioxidant vulkanox SP

(Mixture of styrenated phenols) was obtained from Bayer India Ltd. It had a density of 1.08 g/cc.

(4) Vulkanox HS

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

(5) Pilflex-13

Commercial antioxidant pilflex-13 [N-(1,3-Dimethyl butyl)-N'-phenyl-p-phenylenediamine], was obtained from Polyolefin Industries Ltd., India. The sample had a specific gravity in the range 0.986-1.00

(6) Phenol

Phenol was supplied by S.D.Fine Chemicals, India. It had a melting point of 41°C and a specific gravity of 1.071.

(7) Diphenylamine

Diphenylamine was supplied by BDH Laboratories India Ltd. and had a melting point of 54°C and a specific gravity of 1.16.

(8) Paraphenylenediamine

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

(9) Cardanol

Cardanol was obtained by vacuum distillation of cashew nut shell liquid (CNSL) at 3-4 mm Hg, and had the following specifications:

Colour - pale yellow, specific gravity at 29°C - 0.9320, hydroxyl number (mg of KOH/g) — 185-200, iodine value g/100 g of resin - 237.

3. Catalysts

(1) Anhydrous zinc chloride (An.$ZnCl_2$)

Anhydrous zinc chloride was obtained from Ranbaxy Laboratories. It had a melting point of 290°C and a specific gravity of 2.097.

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

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

4. Compounding Additives

(1) Zinc oxide

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

(2) Stearic acid

Stearic acid used in the study was supplied by Godrej Soaps (Pvt.) Ltd., Bombay 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.

(3) Mercaptobenzothiazole (MBT)

Mercaptobenzothiazole having the following specifications was supplied by Bayer Chemicals, Bombay: specific gravity - 1.45-1.52; melting point - 160-180°C.

(4) Dibenzthiazyl disulphide (MBTS)

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

(5) Tetramethyl thiuram disulphide (TMTD)

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

(6) Zinc diethyl dithiocarbamate (ZDC)

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

(7) Zinc salt of mercaptobenzothiazole (ZMBT)

Zinc salt of mercaptobenzothiazole was supplied by Polyolefins Industries Ltd., Bombay. Its melting point was 178°C and specific gravity 1.65.

(8) Benzthiazyl 2-sulphenmorpholide (MOR)

Benzthiazyl 2-suphenmorpholide (MOR) was supplied by ICI Ltd., India. It had a specific gravity of 1.34.

(9) High abrasion furnace black (HAF, N 330)

High abrasion furnace black (HAF) was supplied by M/s.Carbon and Chemicals (India) Ltd., Kochi. It had the following specifications: Iodine adsorption 80 mg/g, DBP absorption 105 cm^3/100 g, mean particle diameter 32 nm.

(10) 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.

(11) Sulphur

Sulphur was supplied by Standard Chemical Company (Pvt.) Ltd., Madras, and had the following specifications: Specific gravity 2.05, acidity 0.01% max., ash 0.01% max., solubility in CS_2 - 98% max.

(12) Dispersol-F

Dispersol-F (sodium salt of a disulphonic acid) used was buff coloured powder supplied by ICI Ltd., India.

5. Other Additives

Benzoyl peroxide, potassium iodide, starch, sodium thiosulphate, potassium dichromate, potassium permanganate, sodium carbonate, m-cresol, ninhydrin, acetic anhydride,, sodium nitrite, potassium hydroxide, fused calcium chloride, used were of analytical grade. Dioctyl phthalate used was of commercial grade.

6. Solvents

O-xylene, toluene, benzene, ethyl acetate, methanol, acetone, iodine monochloride, dimethyl formamide were of analytical grade.

EXPERIMENTAL METHODS

1. Characterisation Methods

a) Infrared spectroscopy (IR)

IR spectra were taken on Beckmann and Perkin-Elmer Model 377 IR spectrometer using thin film prepared from 10% solutions of the samples.

b) Proton magnetic resonance spectroscopy ('H-NMR)

The 'H-NMR measurements were carried out using a Hitachi Perkin Elmer R-243 (60 Mhz) model and the spectra were measured at 20°C using a 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 (1090) TG-DSC standard model at a heating rate of 10°C per minute.

d) Thin layer chromatography

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) Molecular weight determination

(1) Using gel permeation chromatograph (GPC)

Molecular weights of the samples were determined by gel permeation chromatograph (Waters Associates, Model 6000) employing a differential refractometer R-401, using toluene as the elutent and comparing the molecular weights to polystyrene standards.

(2) Using Sc̈hott Gerate AVS 400 Capillary Viscometer and Ubbelohde Viscometer

Intrinsic viscosities of the samples were measured using a Sc̈hott gerate capillary viscometer and also with Ubbelohde viscometer. Molecular weights of the samples were calculated by substituting intrinsic viscosities in Mark-Houwink-Sakurada equation, taking the value 'K' as (5.02x10^{-2}ml/g) and 'a' as (.667) for natural rubber[2].

f) Free sulphur estimation

Free sulphur in the crosslinked product was determined according to ASTM D297-72A.

The principle of this method is based on the reaction of free sulphur with sodium sulphite to give sodium thiosulphate which is finally titrated against standard iodine solution.

$$S + Na_2SO_3 \longrightarrow Na_2S_2O_3$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$$

2g of the sample was digested gently with 100 ml of aqueous sodium sulphite solution (5g/litre) for 16h, in presence of 5 ml of sodium stearate suspension in water (1g/litre) to assist wetting and approximately 1g of paraffin wax to avoid aerial oxidation. 100 ml of strontium chloride (5g/litre) solution was added to precipitate fatty acids and 10 ml of cadmium acetate solution (30g/litre) to remove accelerators. The precipitate was separated by filtration. It was then washed twice with 75 ml portions of cadmium acetate solution (1.2g/litre). To the filtrate 10 ml 40% formaldehyde solution was added with vigorous stirring and subsequently it was acidified with glacial acetic acid (10 ml). The solution was cooled below 10°C by adding enough crushed ice and titrated with 0.05N iodine solution using starch as indicator.

A blank run was taken without sample and the free sulphur content was calculated using the following equation:

$$\text{Free sulphur \%} = \frac{(x-y) \times N \times 0.032 \times 100}{w}$$

where x is the volume of iodine solution required for the titration of the sample in cc, y the volume of iodine solution required for the titration of the blank in cc, N the normality of iodine solution and w the weight of sample taken.

g) Determination of iodine value[2]

0.2g of sample was dissolved in 25 ml chloroform in a 500 ml conical flask. 20 ml of 0.1N solution of iodine monochloride in glacial acetic acid was added. It was then 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, taking the same volumes of chloroform and Wigs reagent. Iodine value was calculated as

$$\text{Iodine value} = \frac{(V_1 - V_2) \times 12.69 \times n}{m}$$

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 polymer sample in g.

h) Determination of hydroxyl value

Determination of aliphatic-OH group

This procedure is based on the acetylation of OH group with acetic anhydride in pyridine solution. The excess anhydride is decomposed with water and the resulting acetic acid, which is formed both in the hydrolysis and in the acetylation process, is titrated with a standard alkali solution, using phenolphthalein as indicator.[2]

2 g of polymer sample was weighed in 250 ml quickfit conical flask and 20 ml of the acetylating mixture

(acetic anhydride in pyridine) was added, and the mixture was refluxed for an hour. When the dissolution was complete, 25 ml benzene was added, with vigorous shaking. 100 ml water was added and titrated with 0.5N potassium hydroxide, using phenolphthalein as indicator.

Hydroxyl number, in mg of KOH per g of sample was determined using the formula

$$\text{Hydroxyl number} = 56.1\ (V_1 - V_2)n/m$$

where V_1 and V_2 - the volume (ml) of 0.5N potassium hydroxide used for titration of the sample and the blank respectively; n - normality of potassium hydroxide; and m - weight of polymer sample in g.

2. Determination of aliphatic -OH group in presence of phenolic -OH group

When alcoholic hydroxyl groups were determined separately in presence of phenolic -OH groups, phthaloylation was used instead of acetylation using the following procedure.[2]

2 g of polymer sample was weighed into a 500 ml quickfit conical flask and 100 ml of 1N phthalic anhydride solution in anhydrous pyridine was added and the mixture was refluxed for 1h. After cooling the reaction mixture was titrated against 1N aqueous potassium hydroxide using phenolphthalein as indicator. The hydroxyl value was calculated using the above formula.

i) Determination of chemical crosslink density

The concentration of chemical crosslinks was estimated from the equilibrium swelling data as follows.

Samples of approximately 1 cm diameter, 0.20 cm thickness were punched out from the central portion of the vulcanizate, accurately weighed and allowed to swell in solvent (toluene). 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 (V_r) in the swollen network was then calculated by the method reported by Ellis and Welding from the following equation.[3]

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

where,

T - weight of the test specimen

D - Deswollen weight of the test specimen

F - Weight fraction of insoluble components

A_o - Weight of the absorbed solvent corrected for the swelling increment

ρ_r - Density of rubber

and 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_s Toluene - 0.886 g/cm^3

In the case of the vulcanizates containing HAF black, the value of V_r obtained as above, was converted into V_{r_o}, by means of the following equation which was derived by Porter[4]

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

where z - weight fraction of filler.

The crosslink density $\frac{1}{2Mc}$ was determined from V_{r_o} using the Flory-Rehner equation[5,6],

$$\frac{1}{2Mc} = \frac{-\left[(\ln(1-V_{r_o})) + V_{r_o} + \chi_o V_{r_o}^2\right]}{2 \rho_r V_s (V_{r_o})^{1/3}}$$

where,

V_s - molar volume of solvent

V_s(toluene) - 106.2 cc/mol and

and χ_o - parameter characteristic of interaction between rubber and solvent. Values of parameter χ_o taken for calculations were the following.[7,8]

For NR - toluene - 0.42

SBR - toluene - 0.32

2. Mixing and homogenization using mixing mill

Mixing and homogenization of elastomers and compounding ingredients were done on a laboratory size (15x33 cm) two roll mill at a friction ratio of 1:1.25. The elastomer was given one pass through the nip (0.002x100)". Then it was given 2 passes through the nip of (0.002x10)" and allowed to band at the nip of (0.002x55)". 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 D 3182 (1982) in the order activators fillers, accelerators and curing agents. Before the addition of accelerators and sulphur the batch was thoroughly cooled.

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

3. Determination of Cure Characteristics

The cure characteristics of the elastomers were determined using a Goettfert elastograph model 67.85. It is a microprocessor controlled rotorless cure meter with a quick temperature control mechanism and well defined homogeneous temperature distribution in the die or test chamber. 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. A typical elastograph cure curve is shown in Fig.2.1 and the following data can be taken from the torque time curve.

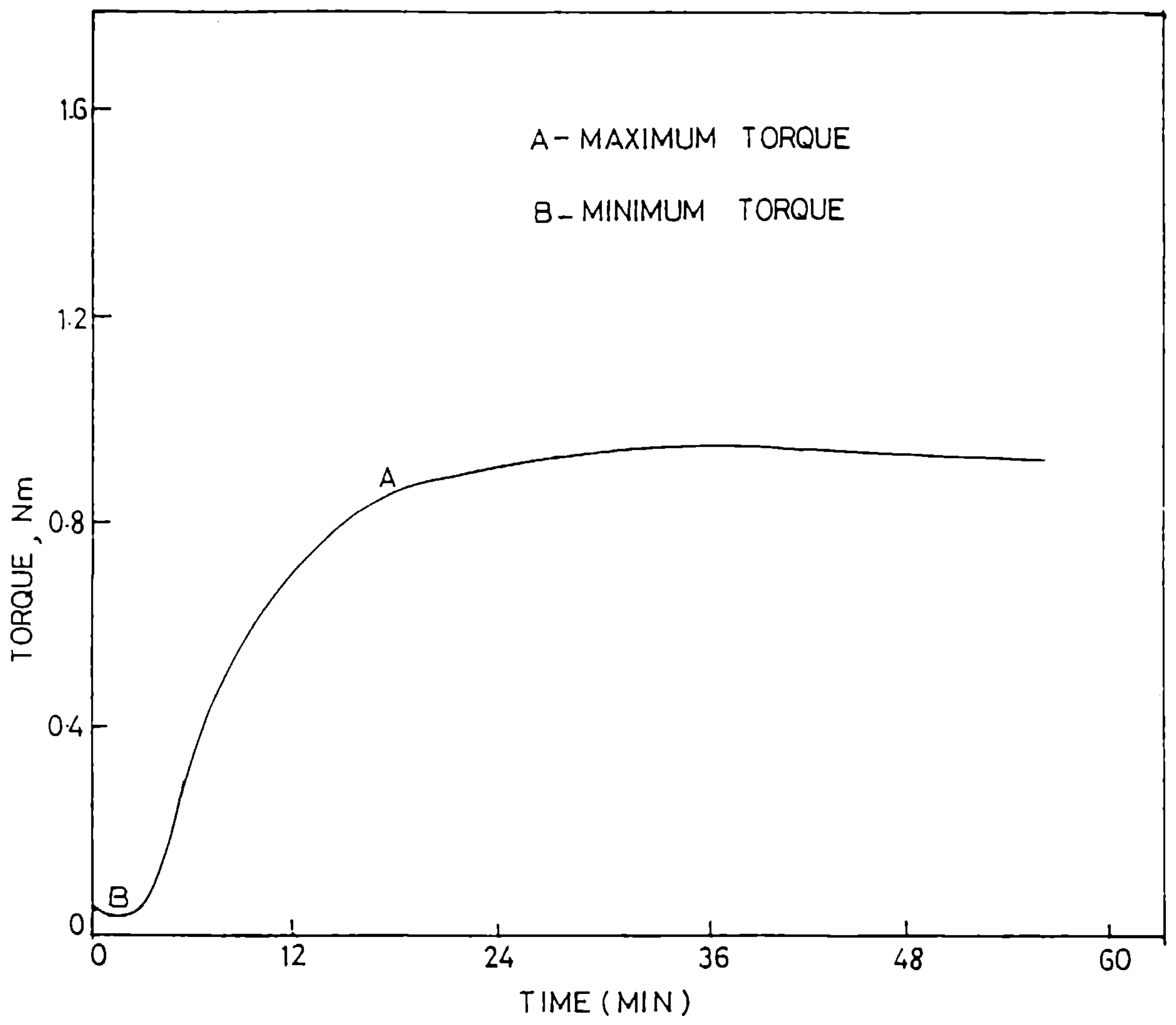

Fig.2.1: A typical cure curve of a rubber compound from Elastograph

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

(ii) Maximum torque: This is the torque recorded after the curing of the mix is completed.

(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.

(v) Cure rate: Cure rate was determined from the following equation

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

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

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

4. Moulding of Test Specimens

a) Casting of latex based test specimens

The compounds were cast on a specially designed glass plate in the form of sheets and cured in an electrically heated laboratory oven at 125°C for 20 minutes.

b) Moulding of dry rubber based test specimens

The test specimens were prepared in standard moulds by compression moulding on a single day light, electrically heated press having 30x30 cm platens at a pressure of 120 kg/cm^2 on the mould. The rubber compounds were vulcanized 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.

5. Physical Test Methods

a) Tensile stress-strain behaviour

Tensile properties of elastomers were determined according to ASTM D 412 (1980) using dumbell specimens on a

Zwick universal testing machine model 1445. All the tests were carried out at 28±2°C. Samples were punched out from compression moulded sheets using a dumbell 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 grip 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 (1981) 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 a 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 (1981). The tests were performed on a mechanically unstressed sample of 300 mm diameter and minimum 6 mm 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 (6.25 mm 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.

$$\text{Compression set } \% = \frac{t_o - t_1}{t_o - t_s} \times 100$$

where t_o 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 (1982) (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 prerun 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 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 Δm - mass loss, ρ - density of the sample and v - abrasion loss.

f) Rebound resilience

Dunlop tripsometer (BS 903, Part 22, 1950) was used to measure rebound resilience. The sample was held in position by applying vacuum. It was conditioned by striking the indentor six times. The temperature of the specimen holder and the sample was kept constant at 30°C. Rebound resilience was calculated as follows:

$$\text{Rebound resilience } \% = \frac{(1 - \cos\theta_2) \times 100}{(1 - \cos\theta_1)}$$

where θ_1 and θ_2 are the initial and final rebound angles respectively, θ_1 was 45° in all cases.

g) Heat build-up

The Goodrich flexometer conforming to ASTM D 623-67 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 constant at 50°C. The stroke was adjusted to 4.45 mm and load of 10.9 kg. The sample was preconditioned to the oven temperature for 20 minutes. The heat developed was sensed by thermocouple and relayed to a digital temperature indicator. The temperature rise ((ΔT)°C) at the end of 20 minutes was taken as heat build-up.

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) Ageing studies

Dumbell samples for evaluation of physical properties were prepared and kept in an air oven at predetermined 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.

k) Density

The densities of the samples were estimated 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,

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

1) Solvent extraction studies

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

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Chapter 3

PREPARATION OF HTNR BASED BOUND ANTIOXIDANTS AND THEIR USE IN NR AND SBR

The developments in product design and improvements in compounding have increased service life for dry rubber as well as latex products. However, most of the conventional antioxidants, mainly amine type and phenolic type, suffer from fairly high volatility and extractability in water or other fluids. Water extraction of antioxidant is a serious problem with rubber articles such as latex threads which are in regular contact with hot water or hot detergent solution[1,2]. One method of alleviating this problem is to attach the antioxidant chemically to the polymer. Alkylation was suggested as an efficient method for the production of polymer bound antioxidants[3-5].

In the search for alternate feed stocks for the production of polymers, certain organic biomonomers possibly stand a good chance for potential utilisation[6]. Among these biomonomers, unsaturated hydrocarbon phenols appear to possess very interesting structural features for the synthesis of speciality polymers[7]. According to Tyman, there are a variety of such phenols present in a number of species available in many parts of the world[8]. Unsaturated hydrocarbon phenols with a C_{15} side chain at the meta position are abundantly available in the plant species Anacardium occidentale L, the nuts of which are famous for their nutritious and high protein value[9]. The liquid, commonly known as cashew nut shell liquid (CNSL) obtained from the outer shell of the nuts, as a byproduct of the cashew industry consists of mainly mono and dihydric phenols[10]. Vacuum distillation of CNSL yields pure cardanol. Cardanol is a versatile material used in diverse applications, such as friction materials, surface coatings, laminating resins and antioxidants[11-16].

This chapter describes alkylation of phenol, styrenated phenol, cardanol and diphenylamine, using hydroxy terminated liquid natural rubber (HTNR) by modified Friedel-Craft's alkylation reaction. Sulphur grafting is an efficient method for the production of macromolecular antiageing compounds[17]. Preparation of high molecular weight cardanol by sulphur bridging is also described in this chapter.

I. PREPARATION AND CHARACTERISATION OF HYDROXY TERMINATED LIQUID NATURAL RUBBER (HTNR) BOUND PHENOLIC/AMINE ANTIOXIDANTS AND THEIR USE IN FILLED LATEX/DRY RUBBER COMPOUNDS

This part describes the alkylation of phenol, styrenated phenol and diphenylamine using hydroxy terminated liquid natural rubber (HTNR) and their use in natural rubber vulcanizates. The HTNR part gets attached to natural rubber during sulphur vulcanization and the antioxidants become non volatile and non extractable. The efficiency and permanence of these bound antioxidants were compared with conventional antioxidants in dry rubber/latex vulcanizates.

Experimental

The antioxidants were alkylated using modified Friedel-Craft's alkylation reaction. 150 g of HTNR (0.1 mol OH), .224 mol of antioxidant (phenol, styrenated phenol or diphenylamine), .448 mol of catalyst (anhydrous zinc 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 on a hot plate with magnetic stirring for 16h at 145°C. There was no appreciable degradation of the polymer during this prolonged exposure to high temperature as seen by molecular weight measurements, probably since the atmosphere inside the set-up was not aerobic. 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 rubber bound antioxidant. The unreacted phenol or diphenylamine was removed by repeated reprecipitation using a toluene-methanol (1:1 v/v) mixture, and the product was dried in a vacuum oven. The rubber bound antioxidant was obtained in the form of a viscous liquid.

Analysis of the rubber bound antioxidants

Analysis of the rubber bound antioxidants was carried out using thin layer chromatography (TLC), hydroxyl value, gel permeation chromatography (GPC), infrared spectroscopy (IR), proton magnetic resonance spectroscopy ('H-NMR) and thermogravimetric analysis.

TLC was carried out using silica gel as the adsorbent. A mixed solvent of benzene and ethyl acetate (4:1 v/v) was used as the developing solvent for all the samples while Br_2 and KI solution were used as the colour developing agents for phenolic type antioxidants, ninhydrin for the amine type and iodine for HTNR[18,19].

Molecular weights of the rubber bound antioxidants were measured by a gel permeation chromatograph (Waters Associates, Model 6000) employing a differential refractometer R-401. The concentration of the bound antioxidants for maximum retention in properties, after ageing was optimised by varying the amount of antioxidants in a standard formulation from 1 to 7 phr. (Table 3.1 A&B, 3.2.A). The compounds employed for testing rubber bound antioxidants are shown in Tables 3.1 and 3.2. The latex compounds were cast on a glass plate in the form of sheets and cured in an electrically heated laboratory oven at 125°C for 20 minutes. Dumbell-shaped tensile test pieces were punched out of these sheets. The tensile properties of the vulcanizates were evaluated on a Zwick universal testing machine model 1445 using a crosshead speed of 500 mm/min. as per ASTM D 412-80. The ageing resistance of the vulcanizates was studied by ageing the vulcanizates for 12, 24, 36 and 48h at 70 and 100°C and then measuring the retention in tensile properties. The extractability of the rubber bound phenolic antioxidants

Table 3.1

Formulations for testing rubber bound phenolic antioxidants

	X	A	B	C
*Natural rubber latex	167	167	167	167
10% Potassium hydroxide	0.5	0.5	0.5	0.5
50% Zinc oxide	1.0	1.0	1.0	1.0
50% Zinc diethyl dithiocarbamate	1.5	1.5	1.5	1.5
50% Zinc salt of mercaptobenzothiazole	0.5	0.5	0.5	0.5
50% Sulphur	3.0	3.0	3.0	3.0
30% China clay	66	66	66	66
50% Vulkanox SP	--	--	--	2.0
50% HTNR-phenol	--	--	3.00	--
50% HTNR-SP	--	3.0	--	--

* 60% centrifuged latex.

Table 3.2

Formulations for testing rubber bound amine antioxidants

	X	A	B
Natural rubber (phr)	100	100	100
Zinc oxide	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0
Mercaptobenzothiazole	0.6	0.6	0.6
Sulphur	2.5	2.5	2.5
Carbon black (HAF N 330)	40.0	40.0	40.0
Aromatic oil	5.0	5.0	5.0
Accinox DN	--	--	1.0
HTNR-DA	--	5.0	--

was studied by keeping the samples in a warm detergent solution (50°C) for 1, 2 and 3 days and then measuring the retention in tensile properties. The rubber bound diphenylamine antioxidant was tried in a dry rubber compound as per the formulation given in Table 3.2. The optimum cure times and scorch times of the compounds were determined on a Goettfert Elastograph model 67.85 as per ASTM D 1646 (1981). Rubber compounds were moulded in an electrically heated laboratory hydraulic press at 150°C upto their respective optimum cure times. Dumbell shaped tensile test pieces were punched out of these sheets along the mill grain direction. The tensile properties of the vulcanizates were evaluated as before. The ageing resistance of the vulcanizates was studied from the retention in tensile properties after air oven ageing at 70 and 100°C for 12, 24, 36 and 48h.

Results and Discussion

Fig 3.1 shows the TLC of phenol, styrenated phenol (SP), diphenylamine (DA), HTNR, phenol bound to HTNR (HTNR-phenol), styrenated phenol bound to HTNR (HTNR-SP) and diphenylamine bound to HTNR (HTNR-DA). HTNR was not coloured by Br_2 and KI or ninhydrin, but the HTNR-SP and HTNR-phenol were coloured by Br_2 and KI solution and HTNR-

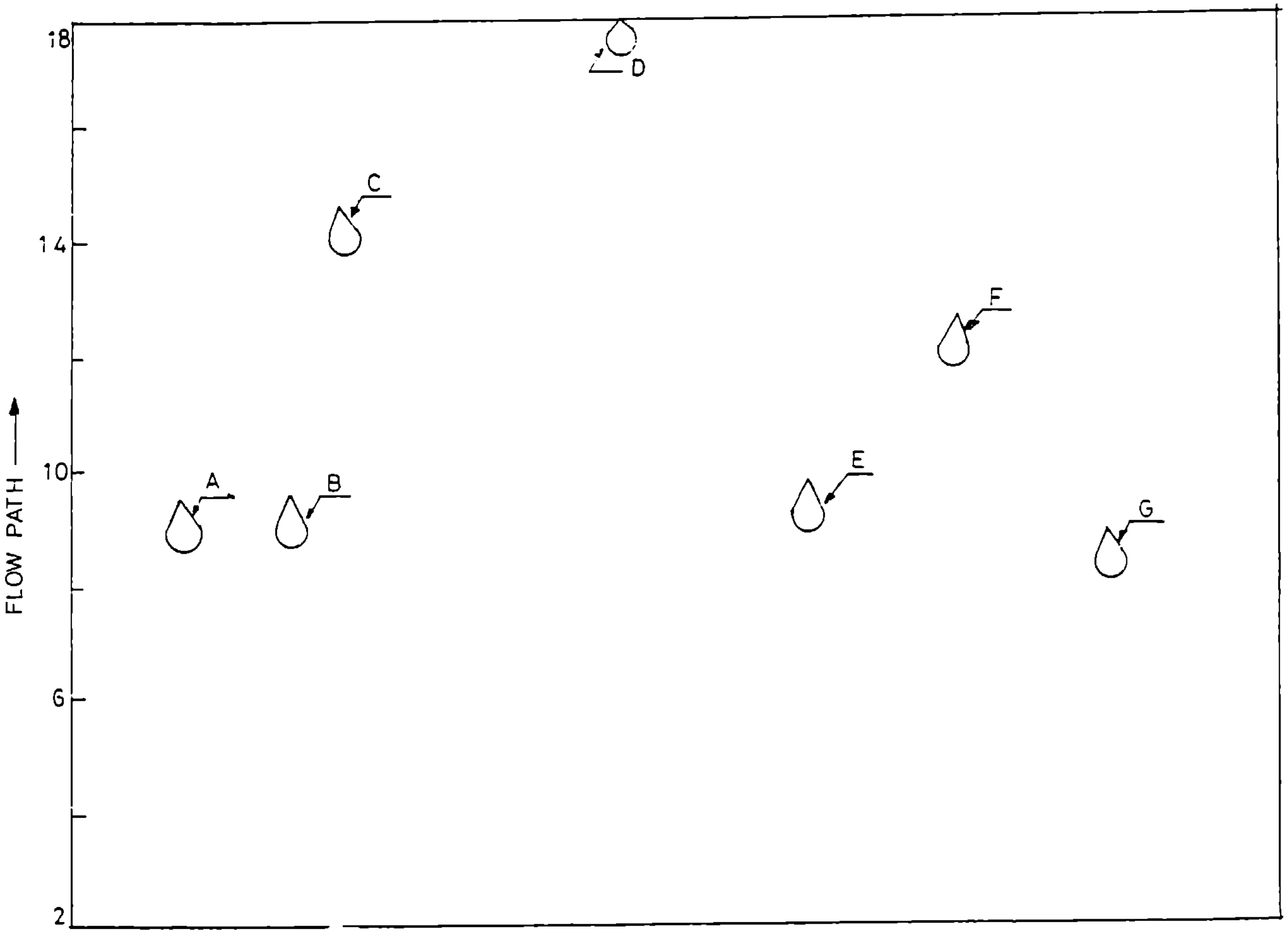

Fig.3.1: TLC of compounds (A) HTNR, (B) HTNR-DA, (C) DA, (D) Phenol, (E) HTNR-Phenol, (F) SP, (G) HTNR-SP

DA was coloured by ninhydrin. The R_F values of the HTNR-SP, HTNR-phenol and HTNR-DA are found to be different from those of SP, phenol and DA respectively. The R_F values of rubber bound antioxidants were found to be almost equal to that of HTNR. This indicates the chemical linking of SP, phenol and DA to HTNR.

Fig.3.2 shows the gel permeation chromatograms of the rubber bound antioxidants. The molecular weights of the rubber bound antioxidants HTNR-phenol ($\bar{M}_w$ - 2990), HTNR-SP ($\bar{M}_w$ - 3000) and HTNR-DA ($\bar{M}_w$ - 2996) obtained from GPC are very close to that of HTNR ($\bar{M}_w$ - 2800). This indicates that linking takes place at one of the positions of the phenol, SP and one of the para positions of diphenylamine.

Hydroxyl values of the bound antioxidants in mg of KOH/g of HTNR-SP (10.45), HTNR-phenol (12.68), HTNR-DA (10.01), are lower than that of HTNR (26.03). This confirms the alkylation of SP, phenol and DA by HTNR.

Figs.3.3-3.5 are the IR spectra of HTNR, HTNR-SP and HTNR-phenol. IR spectrum of HTNR shows peaks at 3600-3400 cm^{-1} corresponding to OH stretching, 3000 cm^{-1} corresponding to aliphatic CH, 1665-1600 cm^{-1} (OH bending),

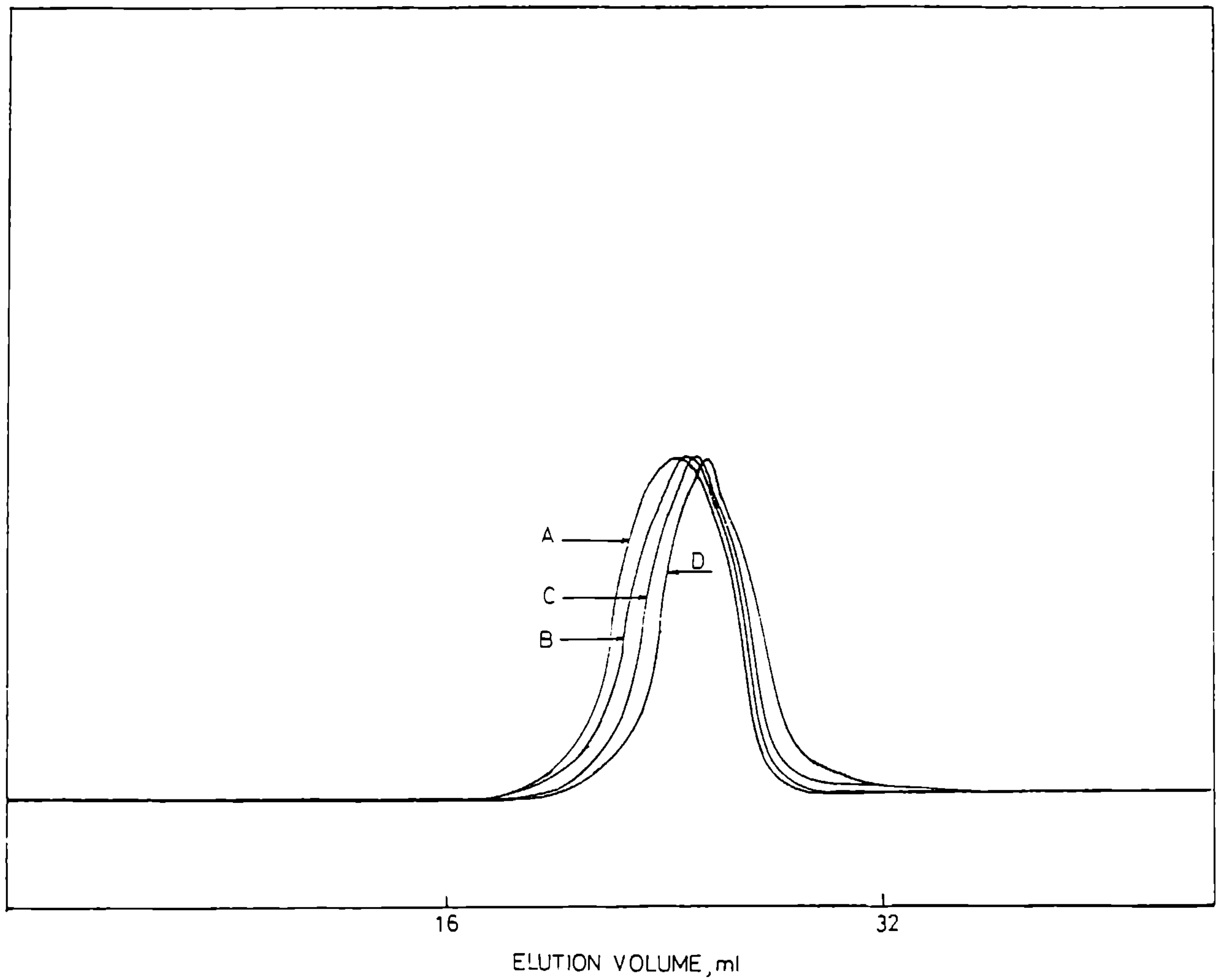

Fig.3.2: GPC traces of (A) HTNR-SP, (B) HTNR-DA, (C) HTNR-Phenol, (D) HTNR

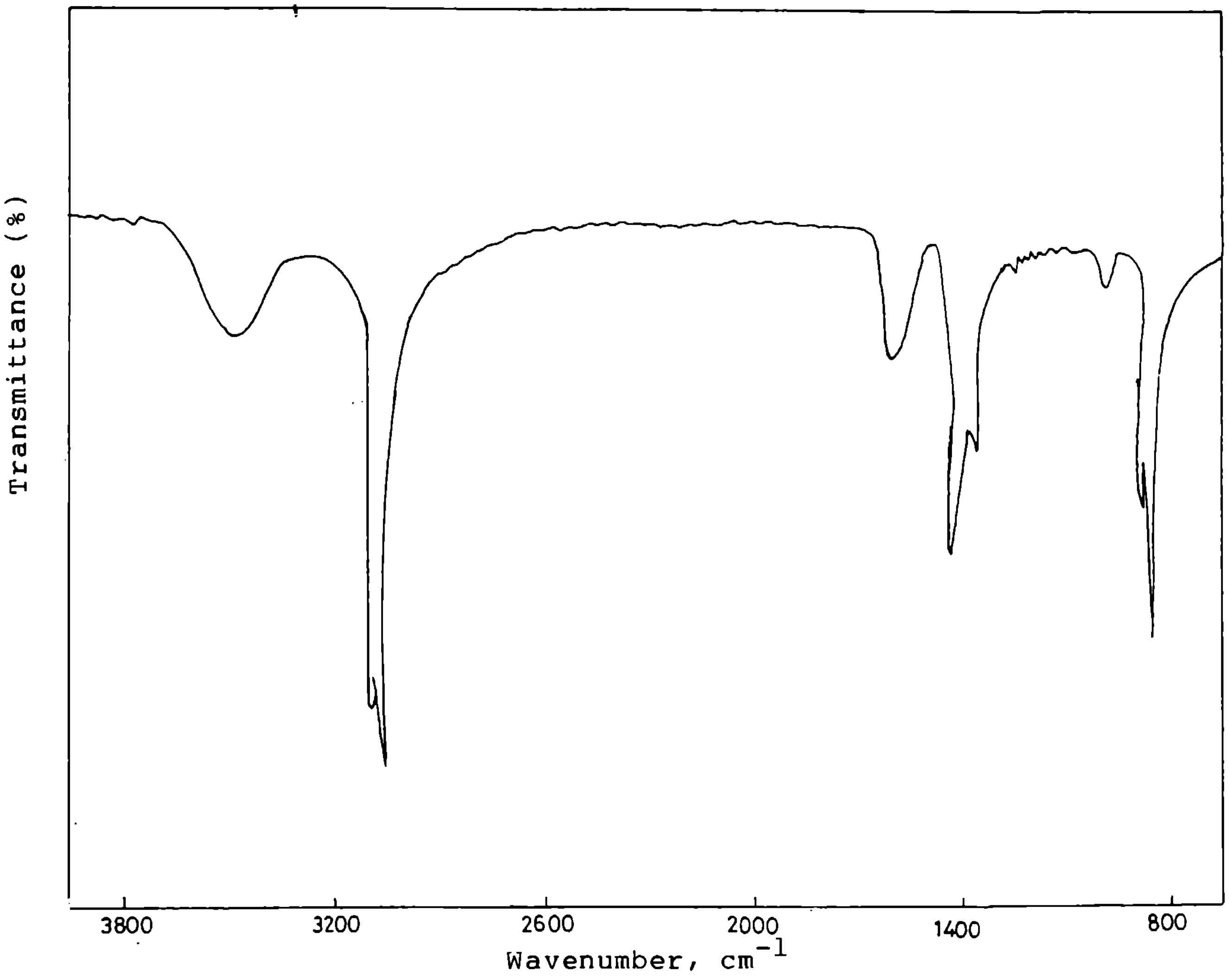

Fig.3.3: IR spectrum of HTNR

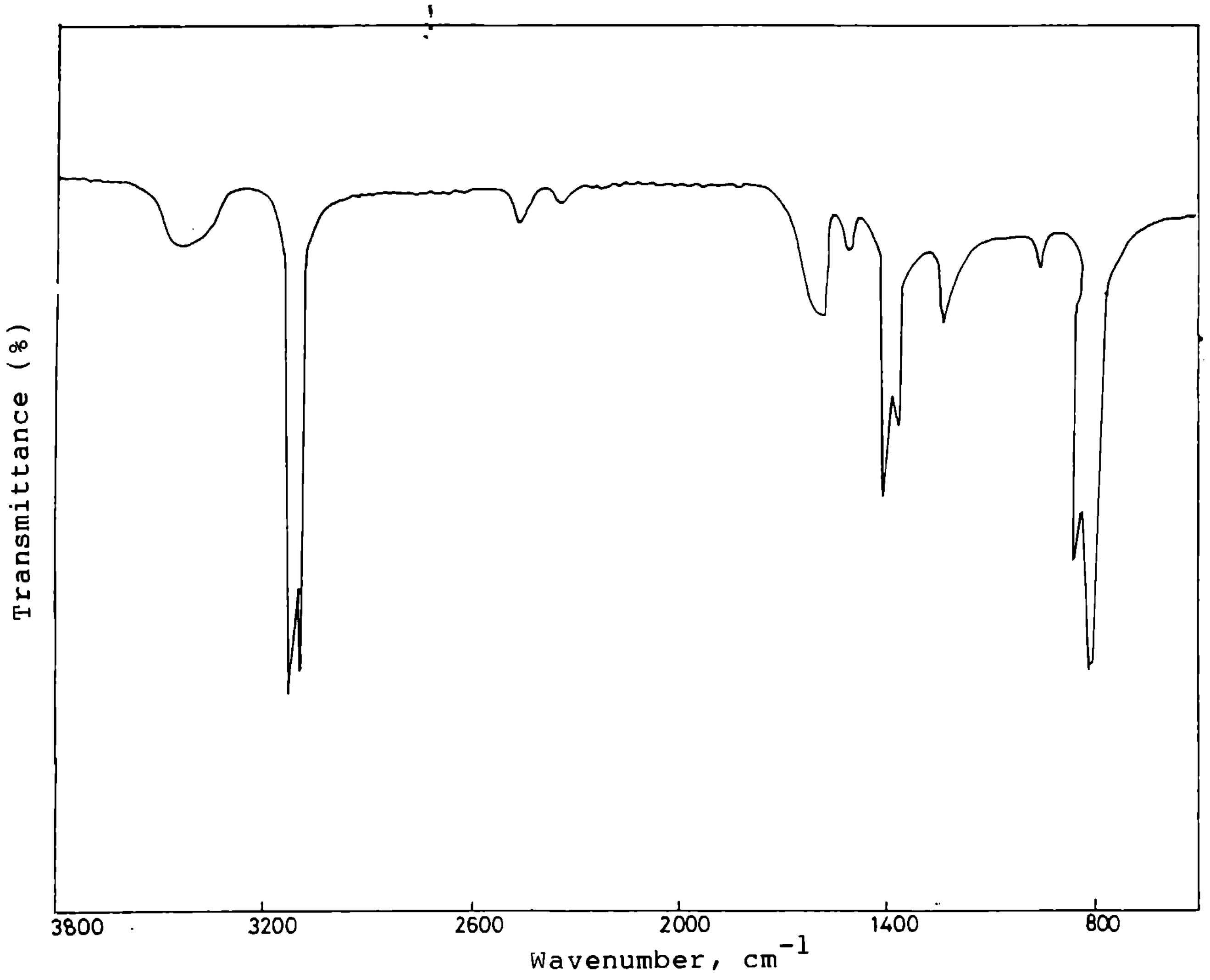

Fig.3.4: IR spectrum of HTNR-SP

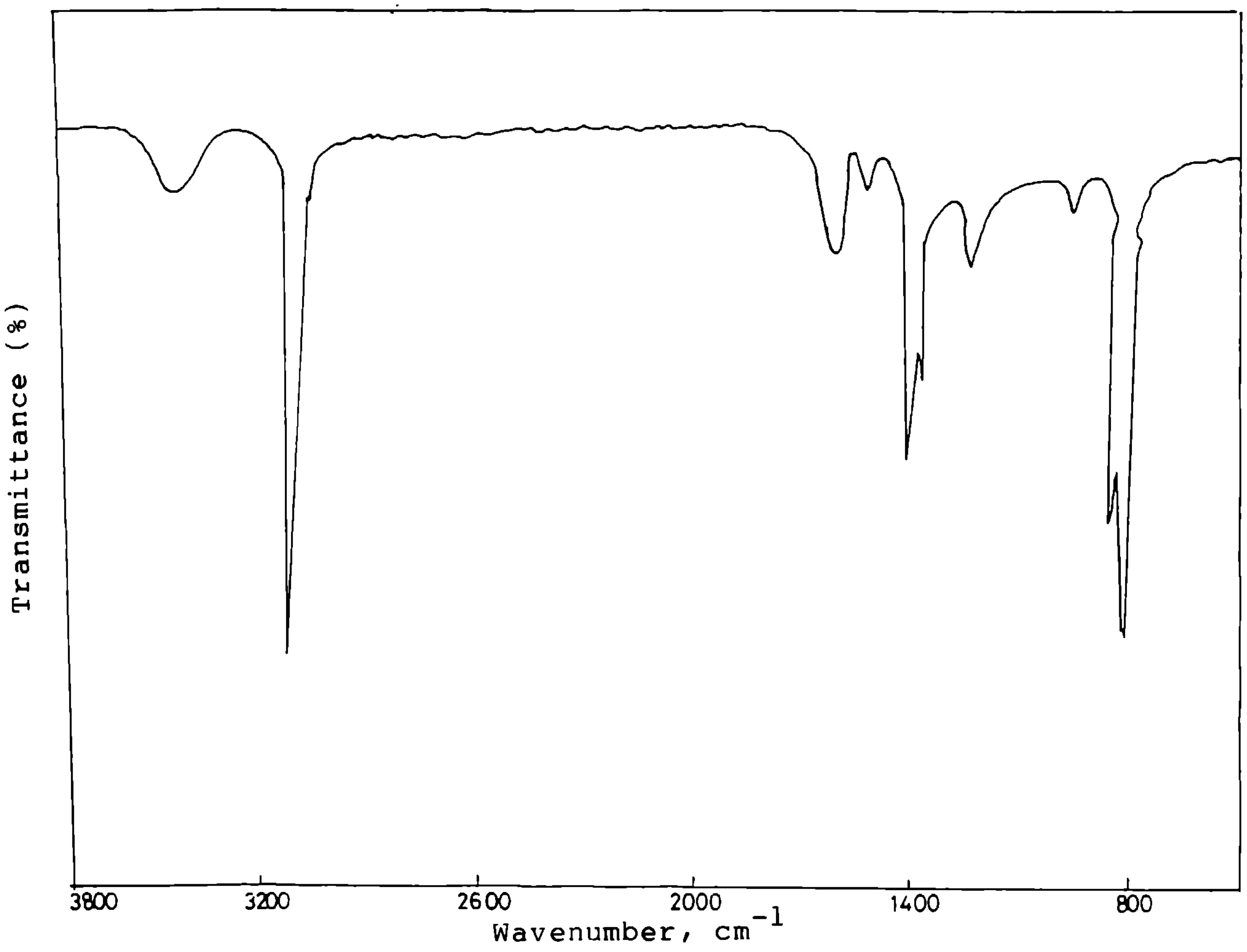

Fig.3.5: IR spectrum of HTNR-Phenol

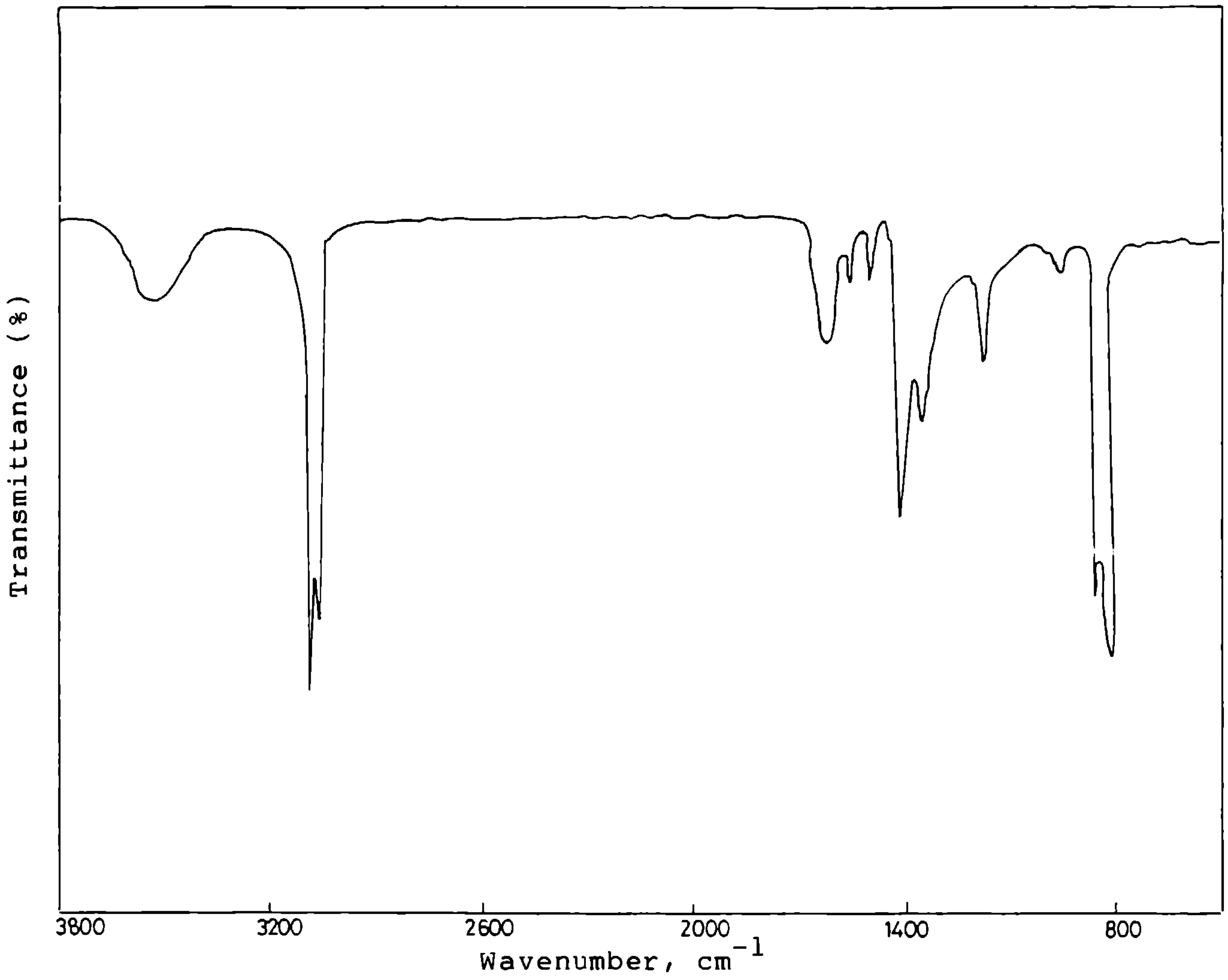

Fig.3.6: IR spectrum of HTNR-DA

1445 cm^{-1} ($-CH_3$ and C-O stretching) and 835 cm^{-1} due to $-C(CH_3) = CH$. The IR spectra of HTNR-SP and HTNR-phenol show additional peaks at 1500 cm^{-1} due to the presence of aromatic ring and 1400 cm^{-1} due to the presence of phenolic groups. This again confirms the alkylation of SP and phenol by HTNR. The IR spectrum of HTNR-DA (Fig.3.6) shows significant peaks at 1550 cm^{-1} (N-H bending) and at 1350 cm^{-1} (C-N vibration)^{20}.

Fig.3.7 shows the 'H-NMR spectrum of HTNR. There are peaks at $\delta = 5.1$ ($\mathrm{C{=}\underset{\diagdown\,H}{C}\diagup}$), $\delta = 1.2$ ($-CH_2$) and $\delta = 1.65$ ppm ($-CH_3$); the signal due to allylic hydroxy protons in the 'H-NMR spectrum is masked by the multiplet at $\delta = 5.1$ ppm of the $\mathrm{{>}C{=}\underset{H}{C}{<}}$. Figs. 3.8 and 3.9 show the 'H-NMR spectra of HTNR-SP and HTNR-phenol respectively, which show additional peaks at δ - 6.8 and δ - 7.1 ppm corresponding to the aromatic -OH group in polymeric association and aromatic ring respectively. Fig.3.10 shows the 'H-NMR spectrum of HTNR-DA, which shows additional peaks at $\delta = 1.12$ and $\delta = 7.1$ ppm corresponding to amino group and aromatic ring present in diphenylamine^{20}.

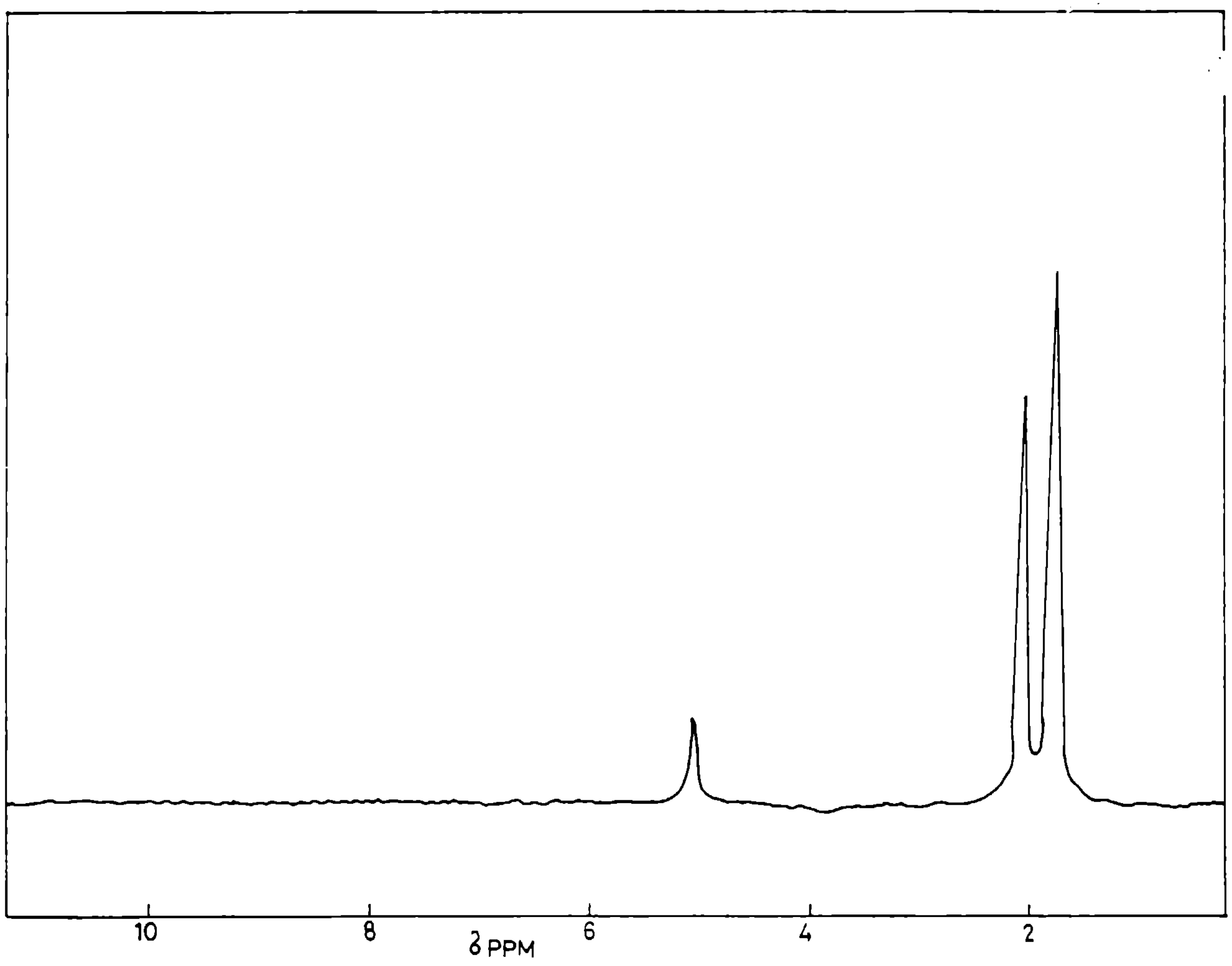

Fig.3.7: 'H-NMR spectrum of HTNR

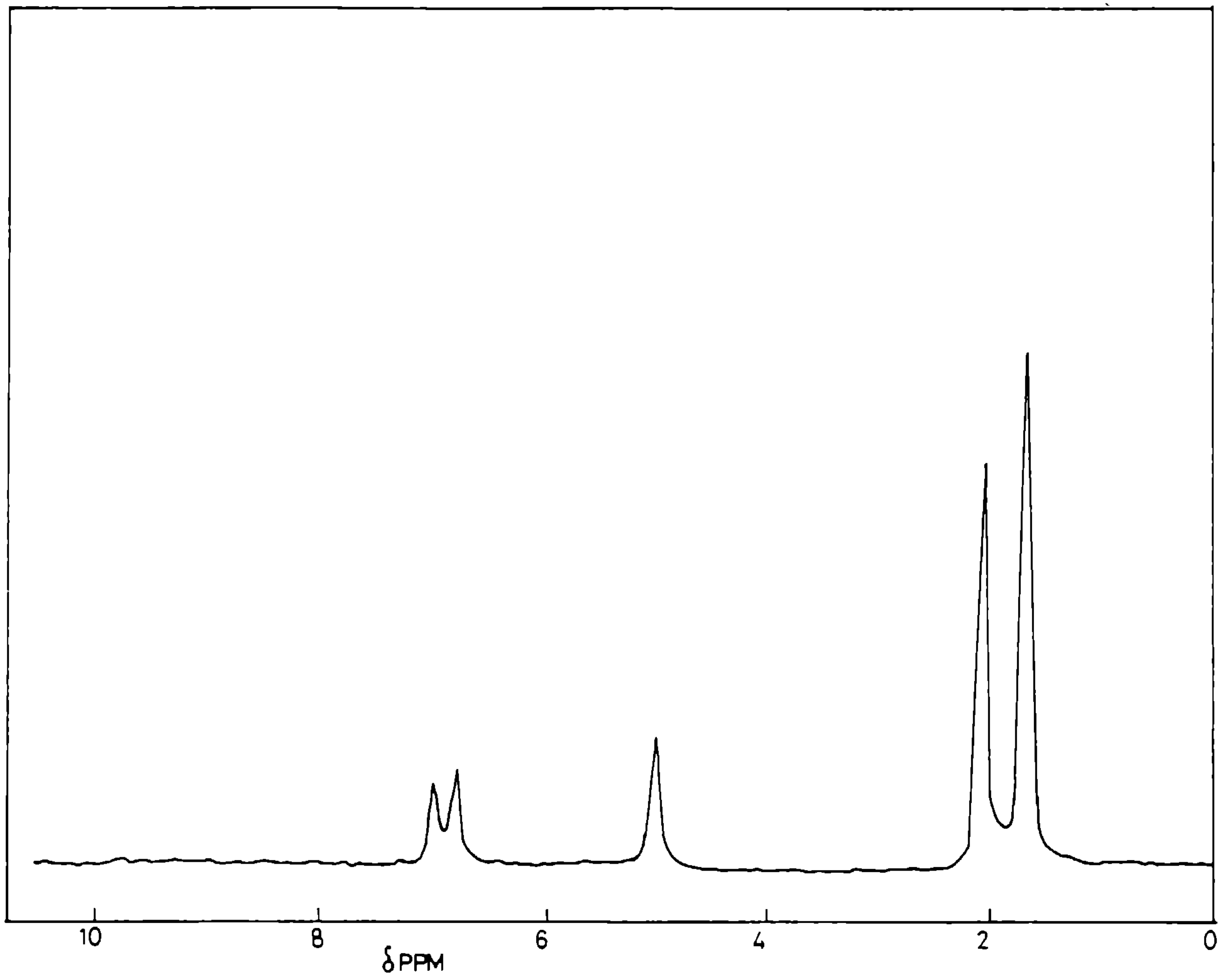

Fig.3.8: 'H-NMR spectrum of HTNR-SP

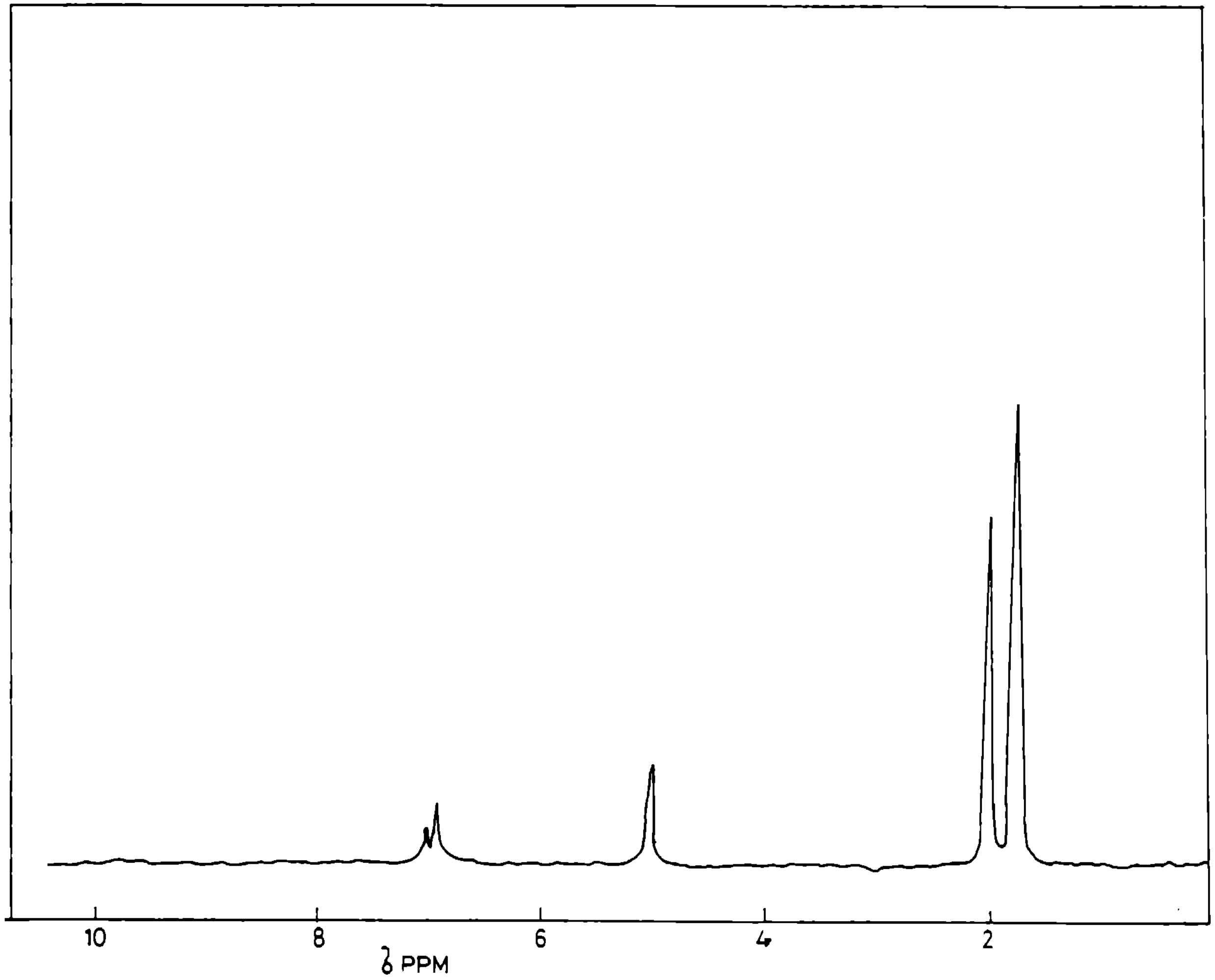

Fig.3.9: 'H-NMR spectrum of HTNR-Phenol

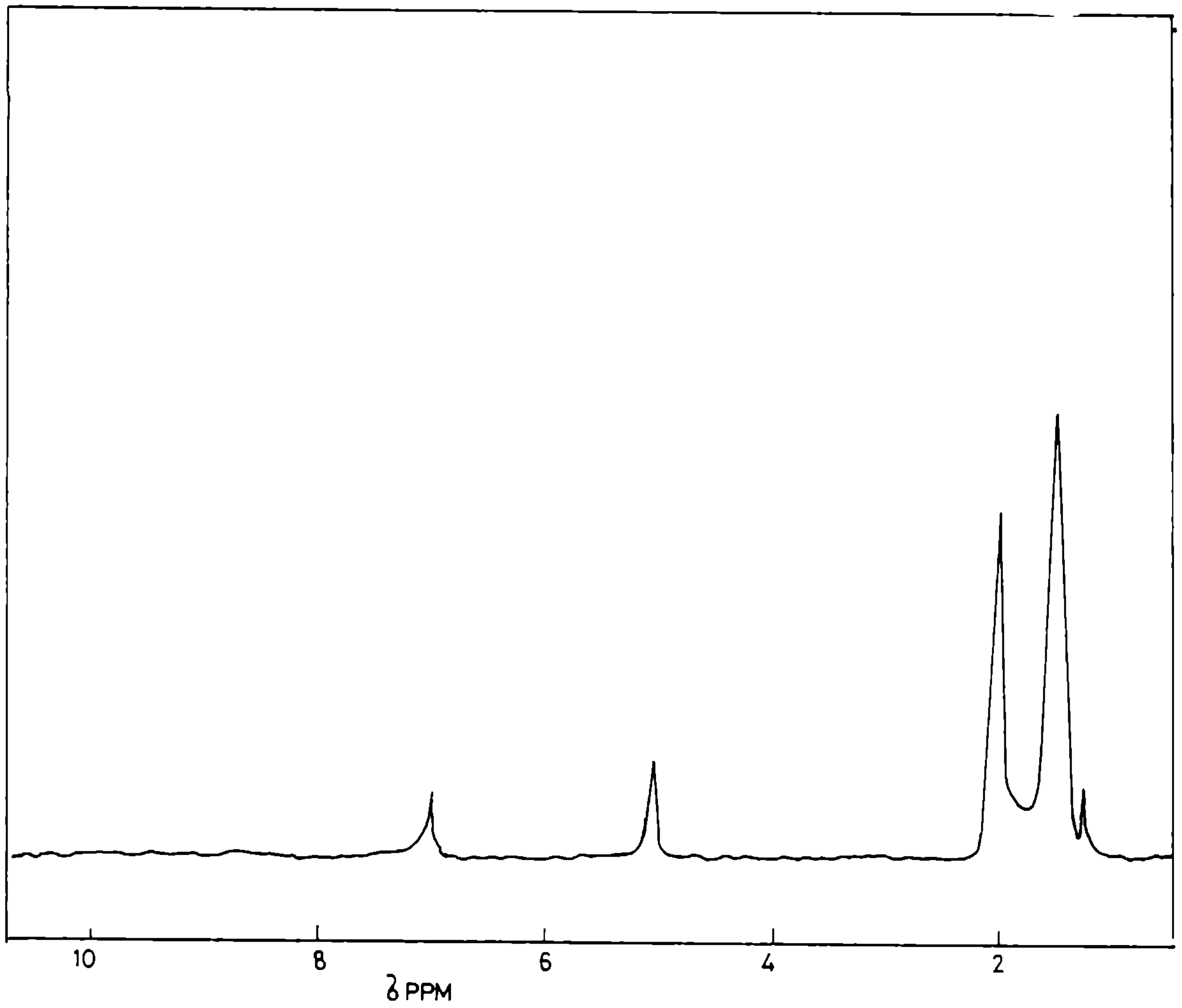

Fig.3.10: 'H-NMR spectrum of HTNR-DA.

Fig.3.11 shows the thermograms of HTNR-SP, HTNR-phenol, HTNR-DA, SP, phenol and diphenylamine. The low molecular weight conventional anti-ageing compounds volatalise easily while the HTNR bound antioxidants are much less volatile.

Fig.3.12 shows the variation in tensile strength after ageing with concentration of antioxidants. The tensile strength retention increases with the amount of chemically bound phenolic antioxidants, reaches a maximum, and then levels off. Similar trend is observed in the case of bound diphenylamine antioxidant. The higher amount of bound antioxidant, in comparison to conventional antioxidant, may be due to lower amount of effective antioxidant moeity in the rubber-bound product.

Fig.3.13 shows the tensile strength of the vulcanizates of the compounds shown in Table 3.1 before and after ageing. All the vulcanizates show fairly good resistance to ageing at 70°C, but only bound antioxidants show good ageing resistance when the ageing temperature was increased to 100°C, which shows the superiority of HTNR bound antioxidants over conventional antioxidant.

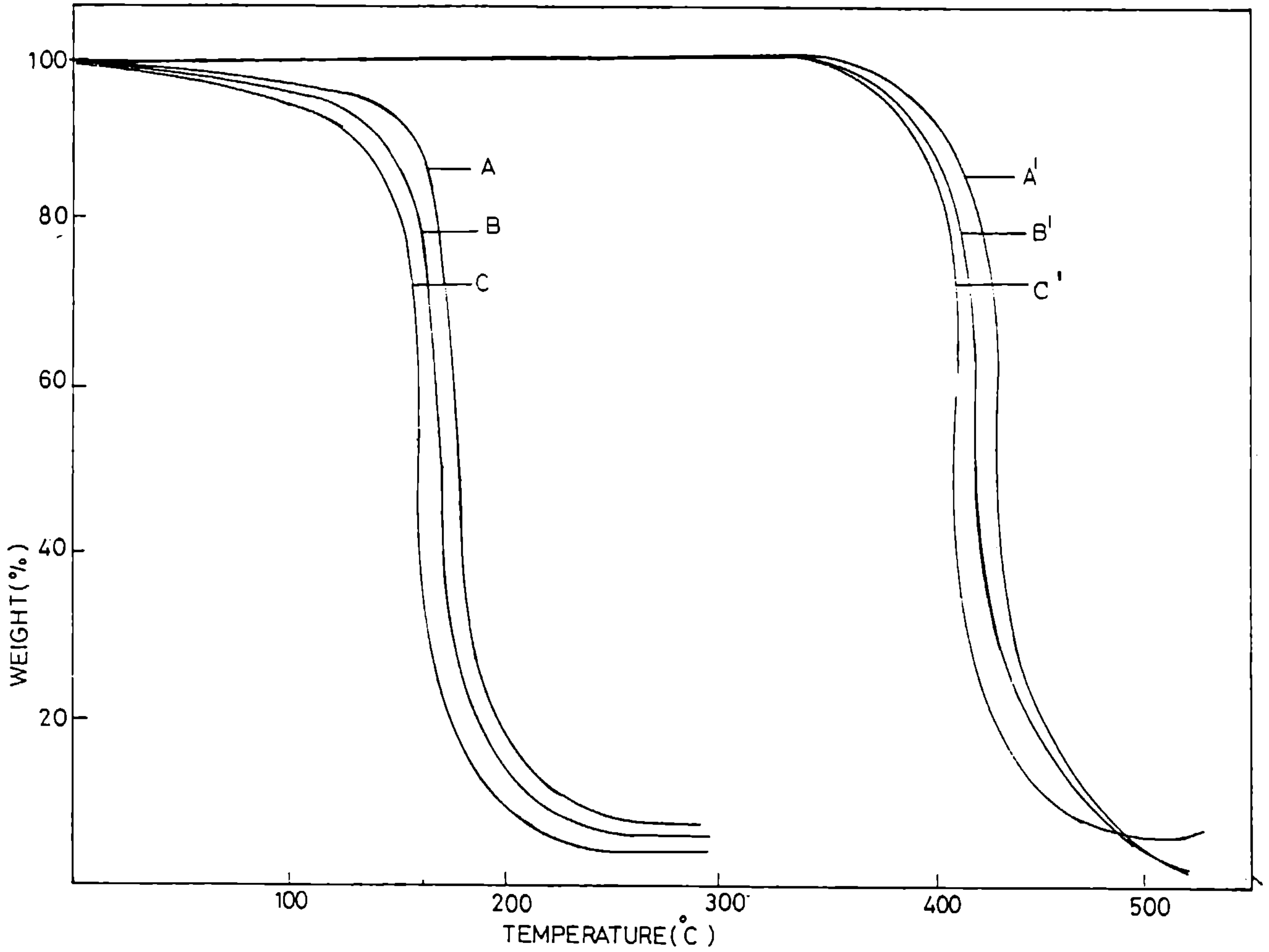

Fig.3.11: Thermograms of the antioxidants; (A) SP, (B) DA, (C) Phenol, (A') HTNR-SP, (B') HTNR-DA, (C') HTNR-Phenol

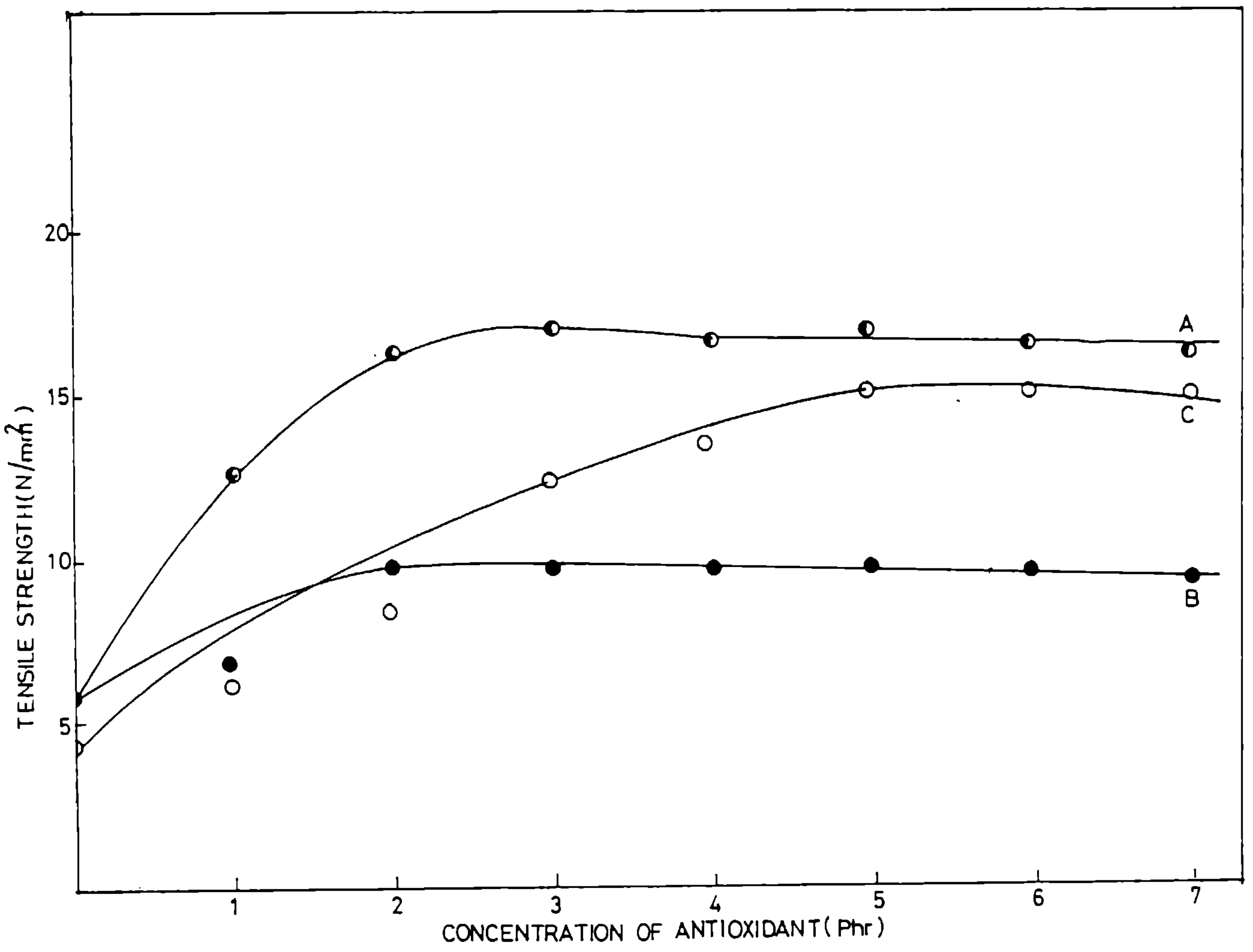

Fig.3.12: Variation in tensile strength after ageing with concentration of the antioxidants; (A) HTNR-SP, (B) HTNR-Phenol (C) HTNR-DA

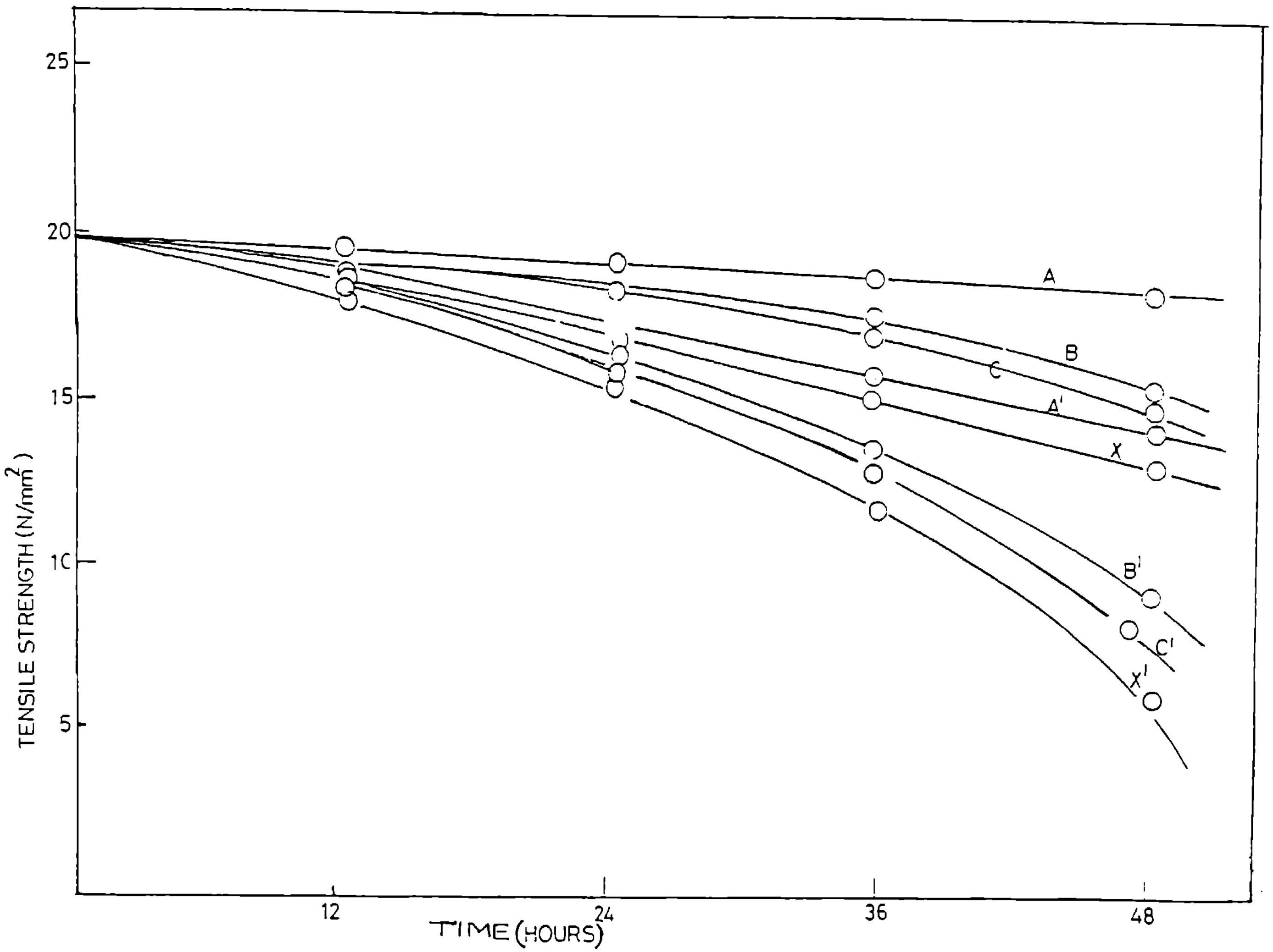

Fig.3.13: Variation in tensile strength of the vulcanizates before and after ageing at 70°C, (A) HTNR-SP, (B) HTNR-Phenol, (C) SP, (X) Without antioxidant; A', B', C' and X' are the corresponding vulcanizates after ageing at 100°C

Fig.3.14 shows the change in elongation at break of the above vulcanizates before and after ageing, which again confirms the superiority of the rubber bound antioxidants. The vulcanizates containing bound antioxidants show superior ageing resistance when temperature is increased to 100°C. This further confirms the low volatility of rubber bound antioxidants.

Figs.3.15 and 3.16 show the variation in tensile strength and elongation at break of the vulcanizates after extracting the samples in warm detergent solution for 1,2 and 3 days respectively. The retention of the properties by the vulcanizates containing bound antioxidants is probably due to their resistance to extraction by warm detergent solution.

Fig.3.17 shows the cure curves of the compounds shown in Table 3.2. Cure time and scorch time were increased by the addition of HTNR-DA. This is probably due to the co-crosslinking of HTNR-DA to NR.

Fig.3.18 shows the variation in tensile strength of the above vulcanizates before and after ageing. All the

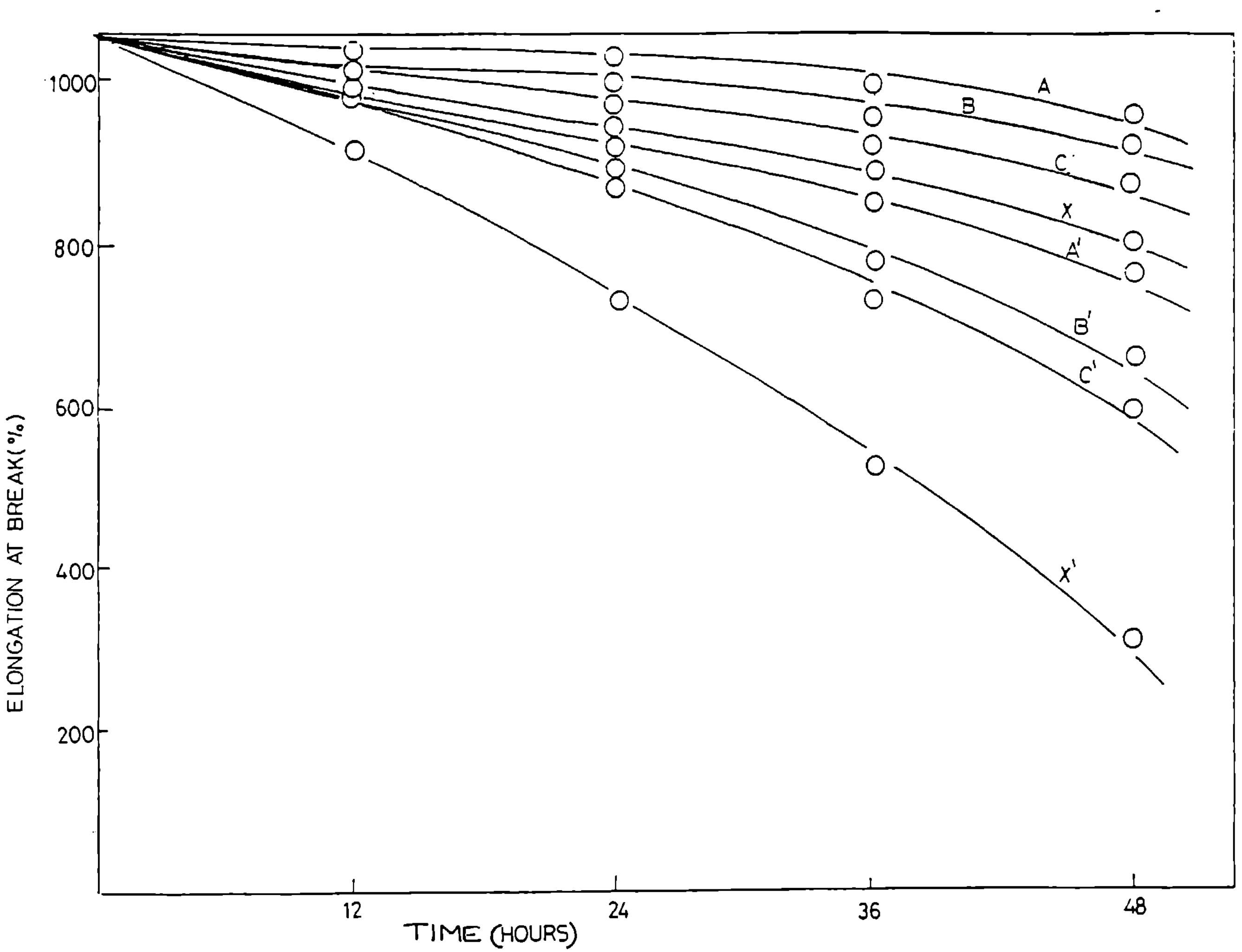

Fig.3.14: Variation in elongation at break of the vulcanizates before and after ageing at 70°C; (A) HTNR-SP, (B) HTNR-Phenol, (C) SP, (X) Without antioxidant; A', B', C' and X' are the corresponding vulcanizates after ageing at 100°C.

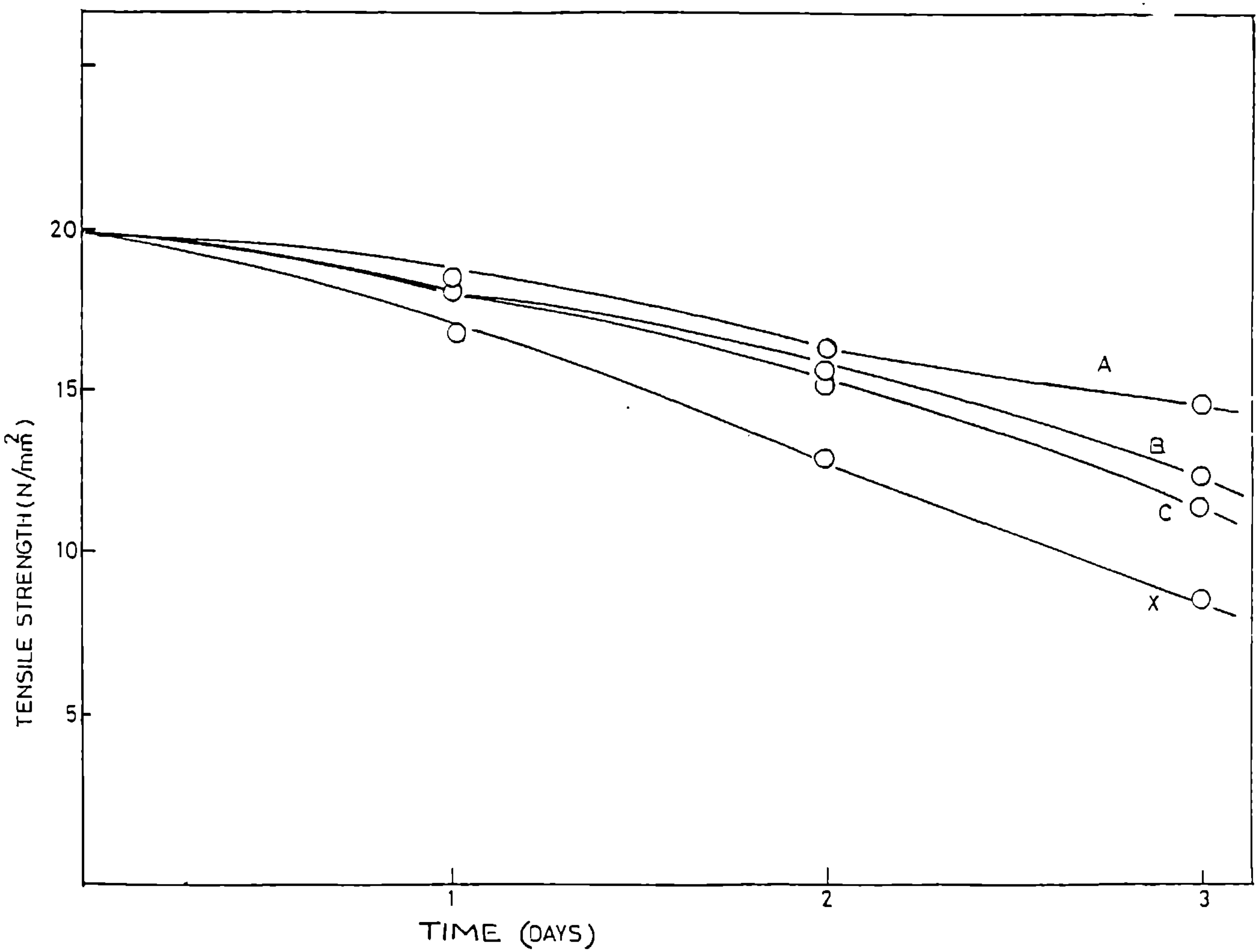

Fig.3.15: Variation in tensile strength of the vulcanizates before and after extraction with a detergent solution; (A) HTNR-SP, (B) HTNR-Phenol, (C) SP, (X) Without antioxidant.

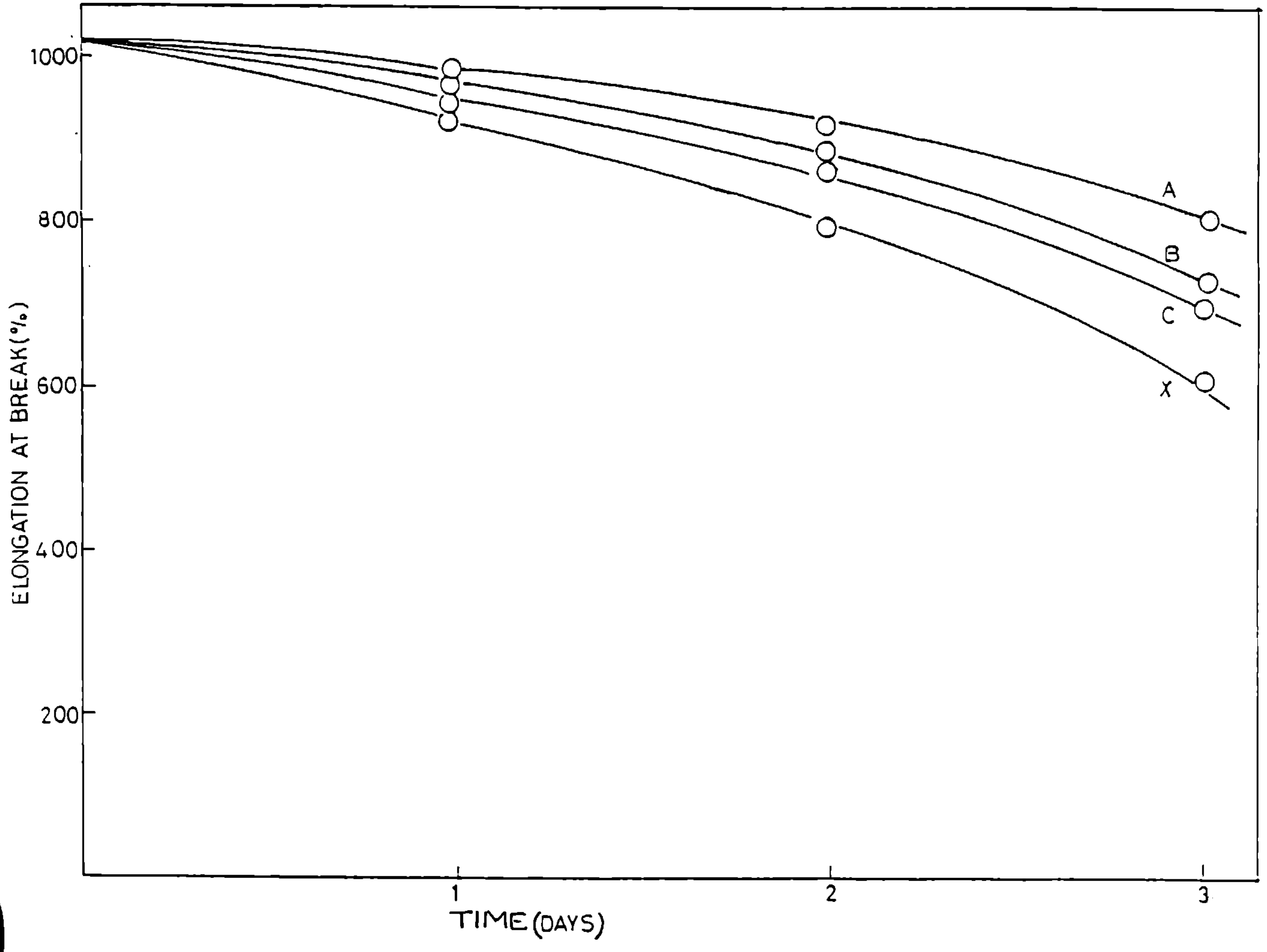

Fig.3.16: Variation in elongation at break of the vulcanizates before and after extraction with a detergent solution; (A) HTNR-SP, (B) HTNR-Phenol, (C) SP, (X) Without antioxidant.

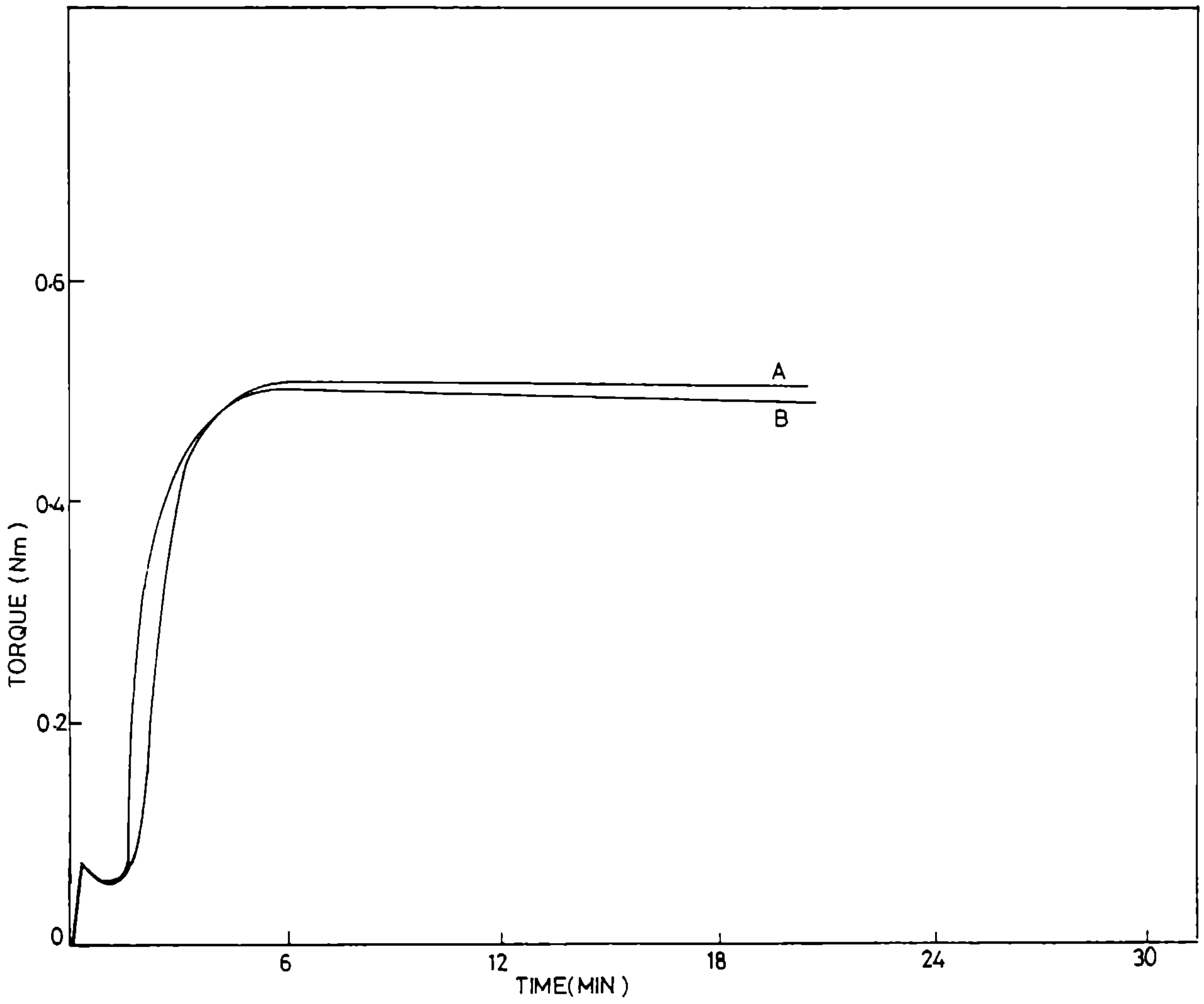

Fig.3.17: Cure curves of the compounds; (A) HTNR-DA, (B) accinox DN

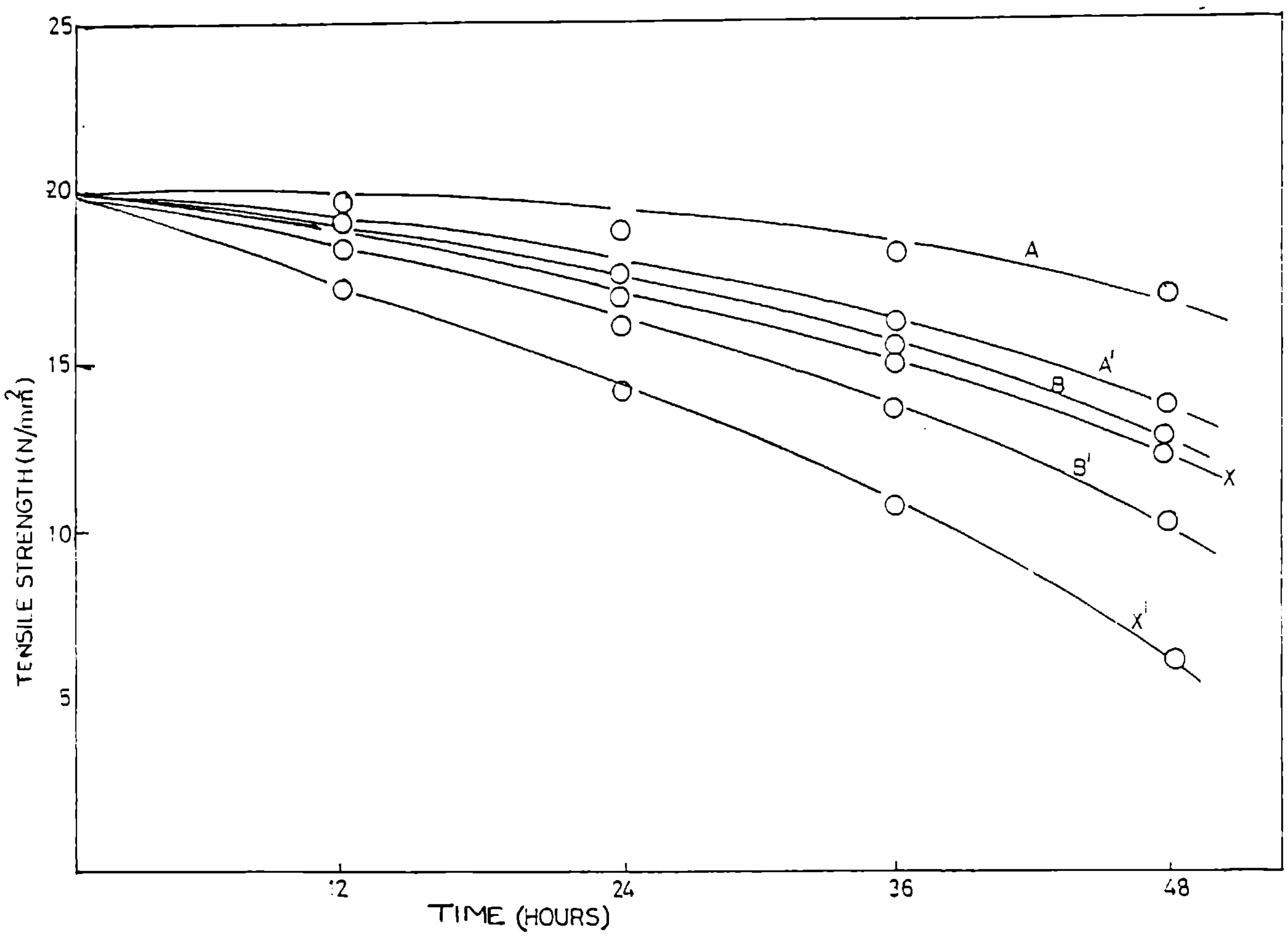

Fig.3.18: Variation in tensile strength of the vulcanizates before and after ageing at 70°C; (A) HTNR-DA, (B) accinox DN, (X) Without antioxidant; A', B' and X' are the corresponding vulcanizates after ageing at 100°C

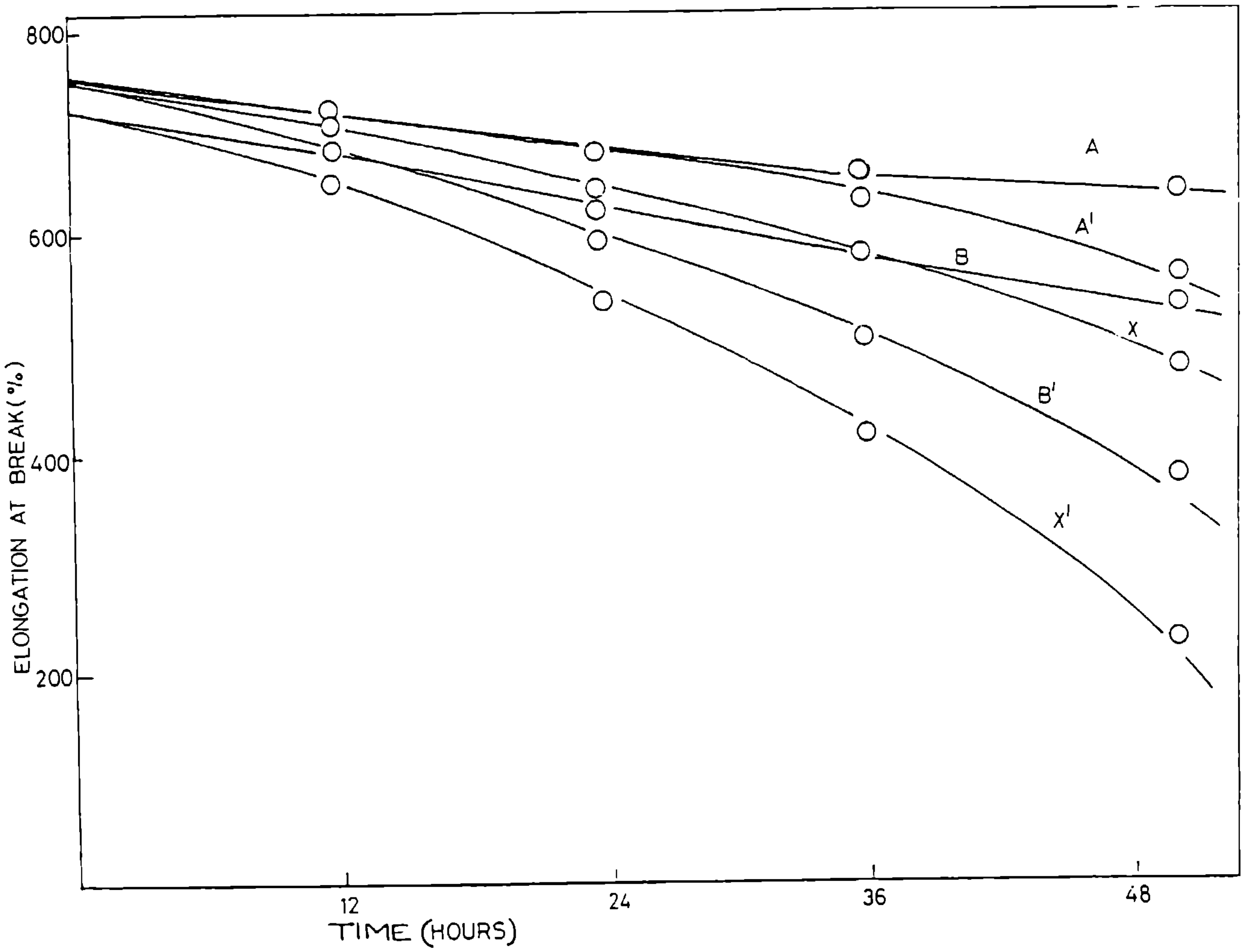

Fig.3.19: Variation in elongation at break of the vulcanizates before and after ageing at 70°C; (A) HTNR-DA, (B) accinox DN, (X) Without antioxidant; A', B', and X' are the corresponding vulcanizates after ageing at 100°C.

vulcanizates show fairly good ageing resistance at 70°C. But only the vulcanizates containing bound antioxidant, HTNR-DA show superior ageing resistance, when the ageing temperature was raised to 100°C.

Fig.3.19 shows the change in elongation at break of the vulcanizates before and after ageing. Here also, the bound antioxidant shows superior elongation at break after ageing at 100°C. This may be due to the low volatility of HTNR-DA compared to accinox DN.

Conclusions

1. Antioxidants can be bound to HTNR by modified Friedel-Craft's alkylation reaction in presence of anhydrous zinc chloride.

2. The rubber bound antioxidants have superior resistance to volatility and extractability compared to conventional antioxidant.

II. APPLICATION OF HTNR BOUND DIPHENYLAMINE IN STYRENE-BUTADIENE RUBBER

This part describes the application of HTNR bound diphenylamine (HTNR-DA) in styrene-butadiene rubber. The

HTNR part in bound antioxidant gets attached to styrene-butadiene rubber during sulphur vulcanization and the antioxidant becomes non-volatile and non-extractable. Efficiency and permanence of this bound antioxidant were compared with conventional antioxidants in filled SBR vulcanizates.

Experimental

HTNR-DA was prepared in the laboratory as per the procedure described in Part I of this chapter. HTNR-DA was tried in an SBR compound as per the formulation given in Table 3.3. The optimum cure times and scorch times of the compounds were determined on a Goettfert elastograph model 67.85 as per ASTM D 1646 (1981). Rubber compounds were moulded in an electrically heated laboratory hydraulic press at 150°C upto their optimum cure times. Tensile properties, tear resistance, hardness, abrasion resistance and compression set of the vulcanizates were evaluated as per standard procedure.

Retention in tensile properties and tear strength was evaluated after ageing the samples at 100°C for 24, 48 and 72h. Retention in compression set and abrasion resistance was evaluated after ageing the samples at 100°C

Table 3.3

Formulations for testing the antioxidants

Ingredients	A	B	C
Styrene-butadiene rubber (SBR 1502) (phr)	100	100	100
Zinc oxide	4.0	4.0	4.0
Stearic acid	2.0	2.0	2.0
Carbon black (HAF N 330)	45.0	45.0	45.0
Aromatic oil	3.0	6.5	6.5
Benzthiazyl 2-sulphen-morpholide (MOR)	1.0	1.0	1.0
Tetramethyl thiuram disulphide	0.4	0.4	0.4
HTNR-DA	5	--	--
Vulkanox 4020	--	1.0	--
Vulkanox HS	--	--	1.0
Sulphur	1.5	1.5	1.5

for 48h. Extractability of HTNR-DA from SBR vulcanizates was studied by keeping the samples in methanol and acetone for 48h at room temperature. Retention in tensile properties was studied after ageing the samples at 100°C for 48h.

Results and Discussion

Fig.3.20 shows the cure curves of the compounds shown in Table 3.3. Cure time and scorch time are found to be reduced by the addition of HTNR-DA. This may be due to the presence of faster curing natural rubber in HTNR-DA.

Fig.3.21 shows the tensile strength of the compounds shown in Table 3.3 before and after ageing. All the vulcanizates show fairly good resistance at 100°C for 24h. When the ageing time was increased to 48h, the vulcanizate containing HTNR-DA was found to be superior compared to that containing vulkanox HS, and comparable to that containing vulkanox 4020. After 72h ageing, although the vulcanizate containing HTNR-DA is superior to that containing vulkanox HS, it cannot compete with that containing the strong paraphenylenediamine type antioxidant, vulkanox 4020. This may be due to the lower antioxidant activity of secondary amino group present in the bound product.

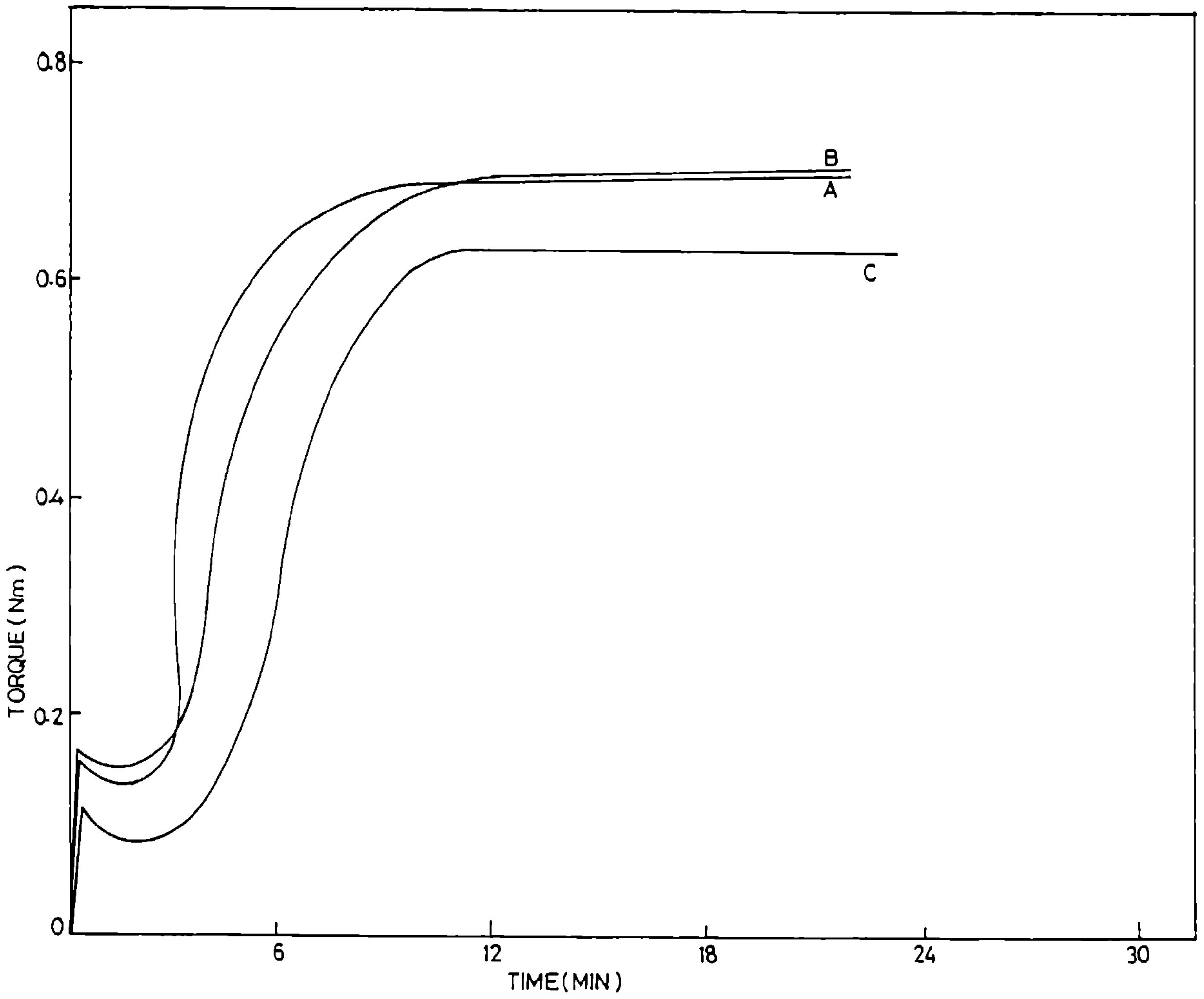

Fig.3.20: Cure curves of the compounds; (A) HTNR-DA, (B) vulkanox-4020, (C) vulkanox HS

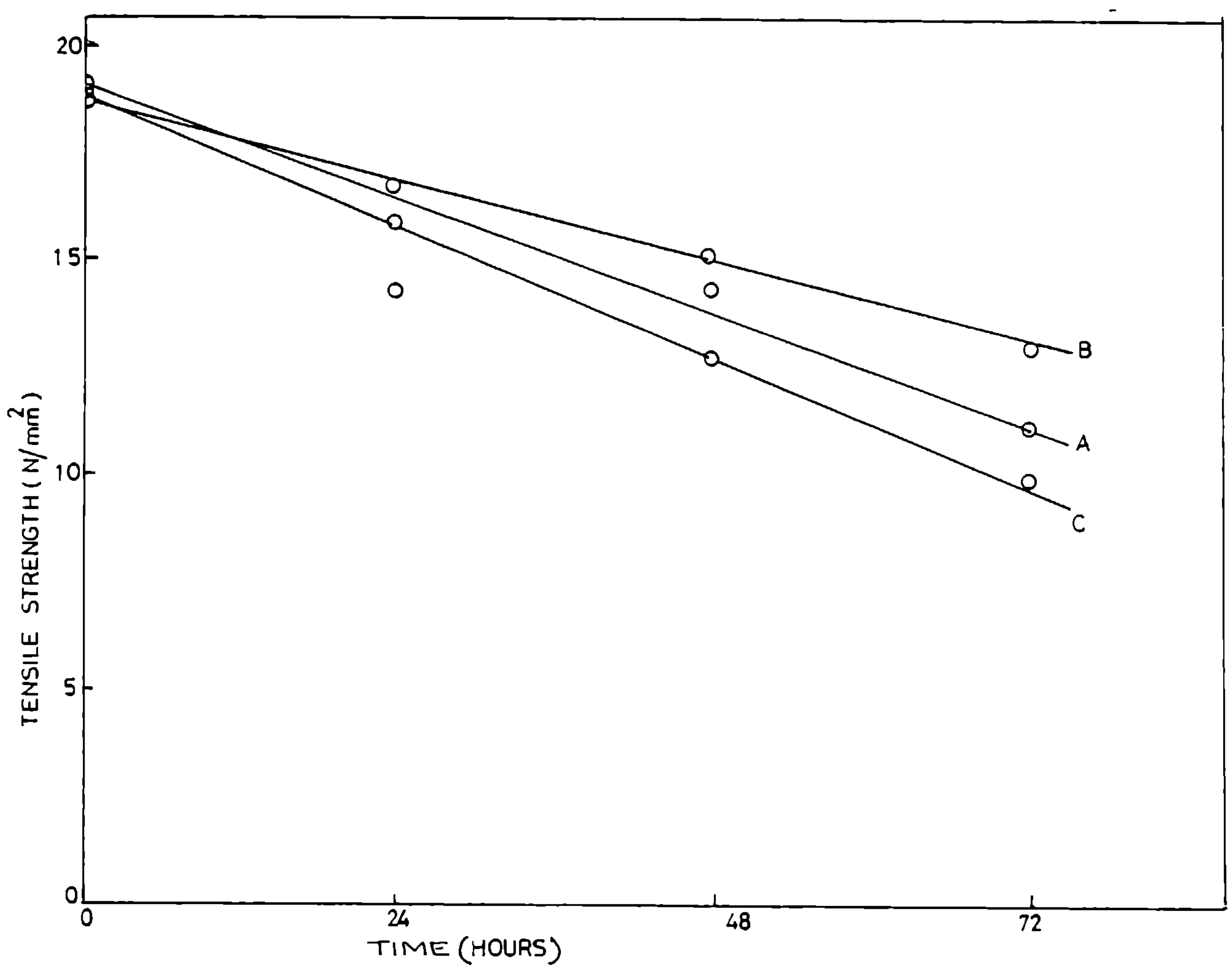

Fig.3.21: Variation in tensile strength of the vulcanizates before and after ageing at 100°C; (A) HTNR-DA, (B) vulkanox 4020, (C) vulkanox HS

Fig.3.22 shows the elongation at break of the vulcanizates before and after ageing. All the vulcanizates show fairly good retention in elongation at break after 24h ageing. Elongation at break of the vulcanizate containing HTNR-DA is superior to the vulcanizates containing vulkanox HS when ageing time was increased to 72h, but inferior to that containing vulkanox 4020. This may be due to the lower antioxidant activity of secondary amino group in HTNR-DA.

Fig.3.23 shows the modulus of the vulcanizates before and after ageing. The increase in modulus after ageing may be due to the increase in crosslink density as shown in Table 3.4. The increase in crosslink density may be due to the co-crosslinking of NR present in HTNR-DA.

Fig.3.24 shows the change in hardness of the vulcanizates before and after ageing. Hardness value of the vulcanizate containing HTNR-DA was found to be higher than that containing conventional antioxidants. This may be due to the lower amount of aromatic oil in the compound (Table 3.3).

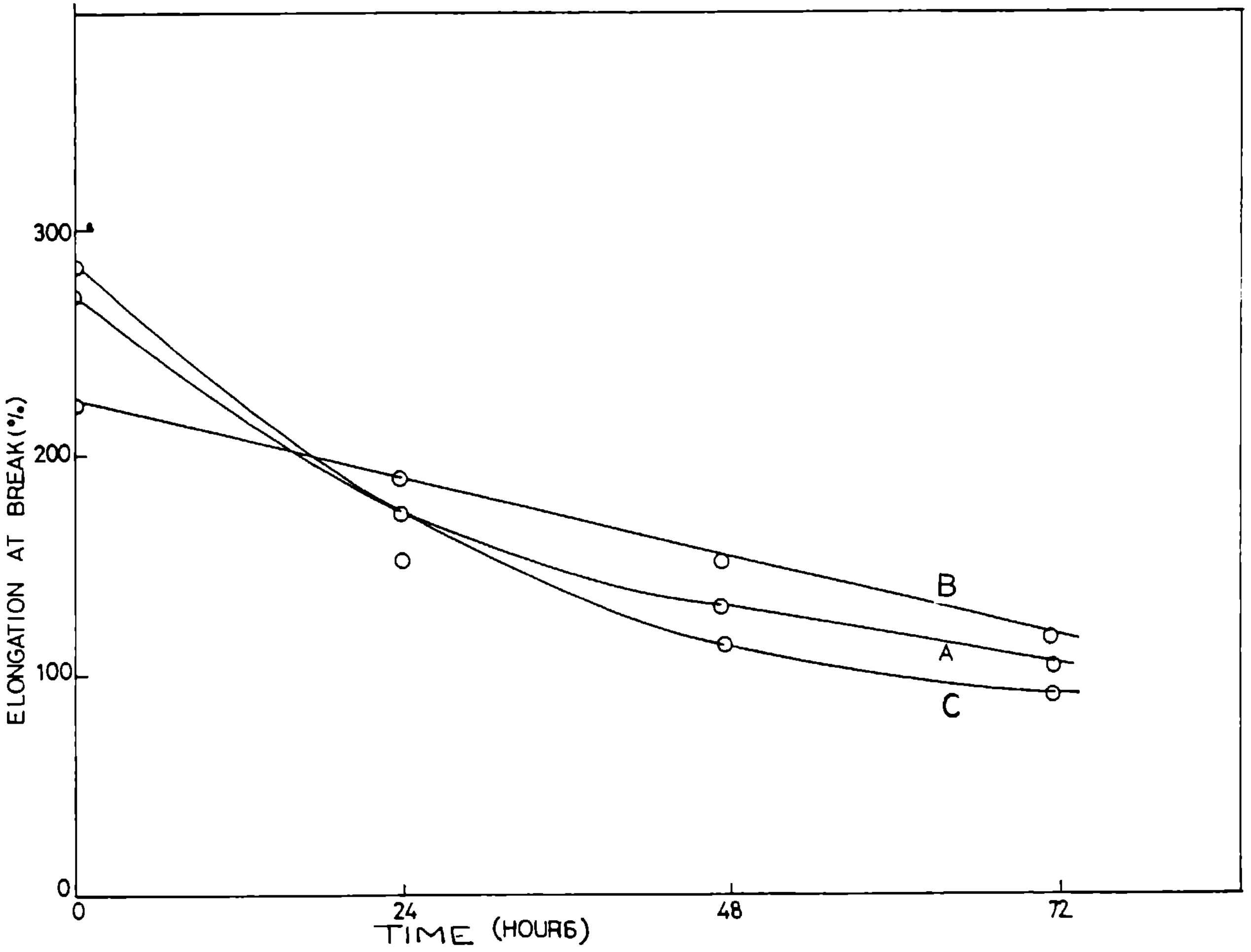

Fig.3.22: Variation in elongation at break of the vulcanizates before and after ageing at 100°C; (A) HTNR-DA, (B) vulkanox 4020, (C) vulkanox HS

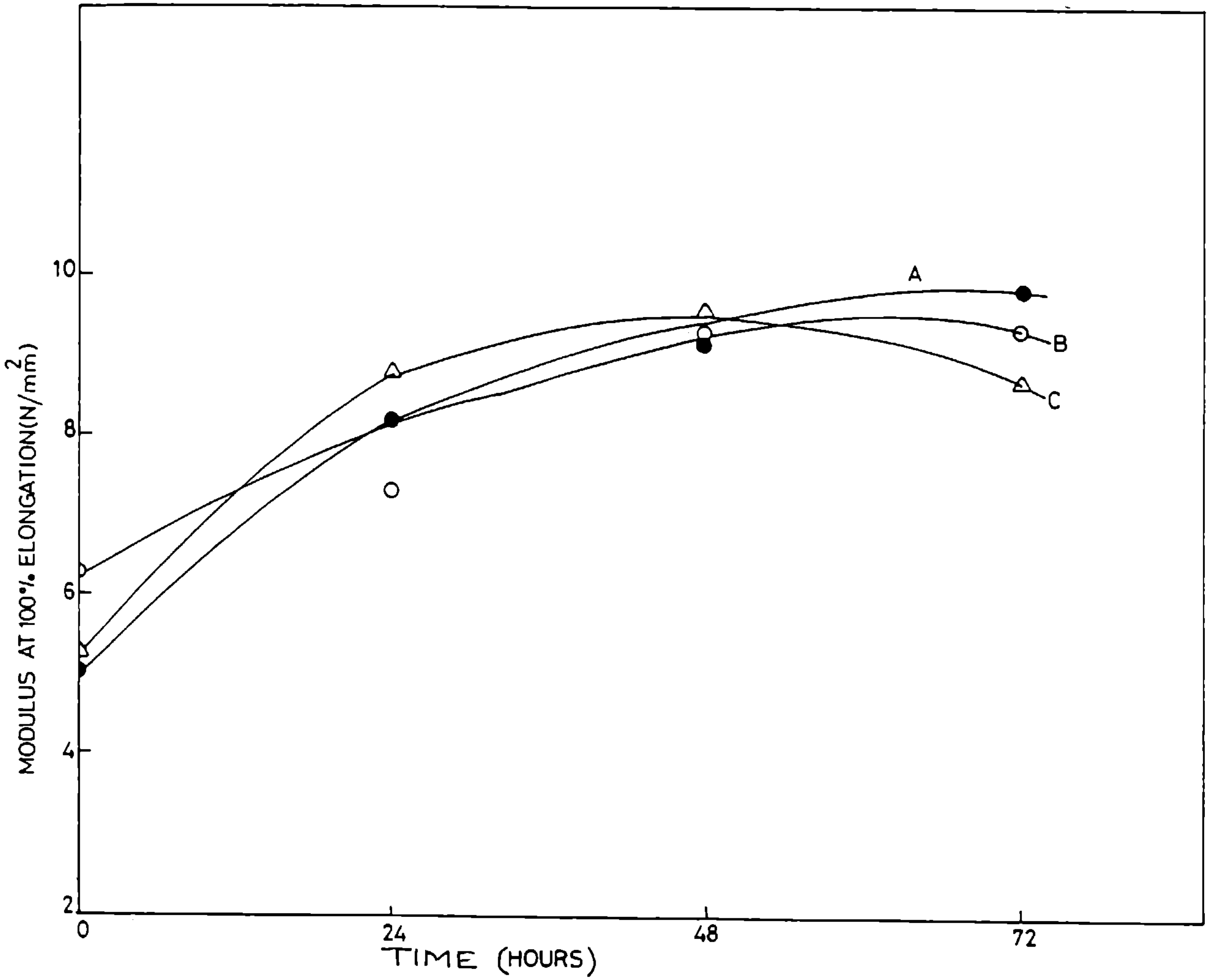

Fig.3.23: Variation in modulus of the vulcanizates before and after ageing at 100°C; (A) HTNR-DA, (B) vulkanox 4020, (C) vulkanox HS

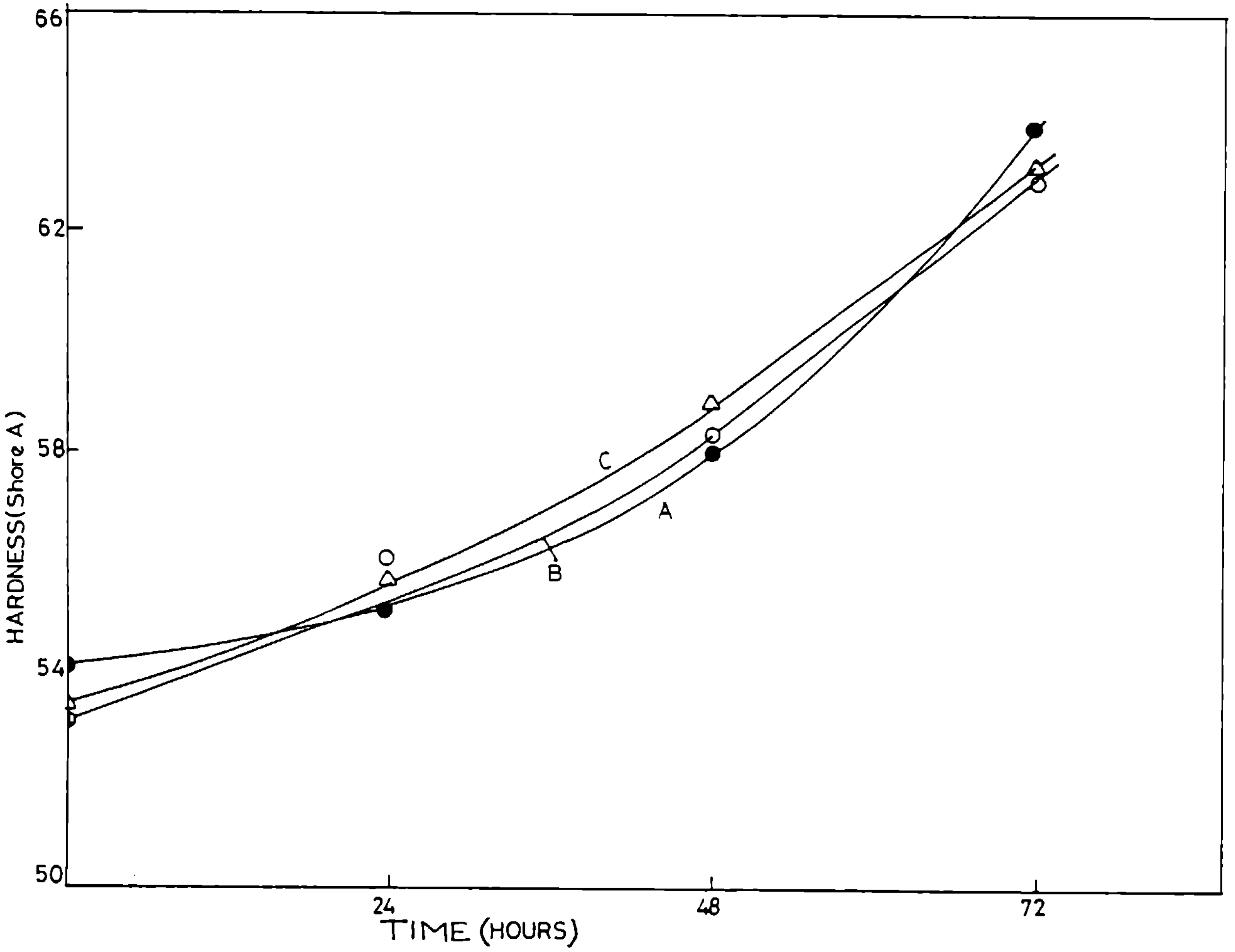

Fig.3.24: Variation in hardness of the vulcanizates before and after ageing at 100°C; (A) HTNR-DA, (B) vulkanox 4020, (C) vulkanox HS

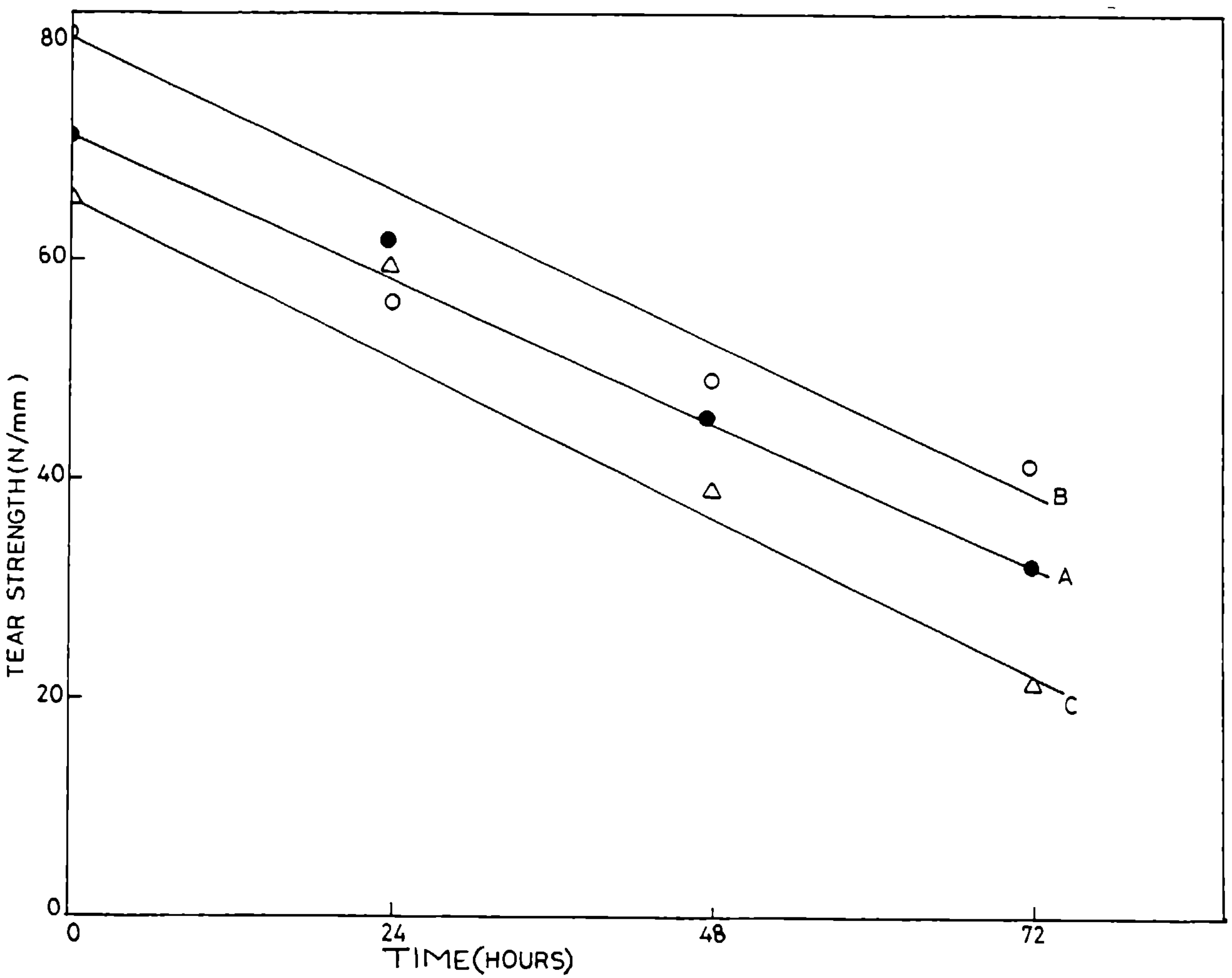

Fig.3.25: Variation in tear strength of the vulcanizates before and after ageing at 100°C: (A) HTNR-DA, (B) vulkanox 4020, (C) vulkanox HS

Table 3.4

Crosslink densities of the vulcanizates before and after ageing at 100°C

Time of ageing (h)	Crosslink density in g mole/cc A	 B	 C
0	$5.508x10^{-5}$	$4.067x10^{-5}$	$4.001x10^{-5}$
24	$4.018x10^{-4}$	$2.8991x10^{-4}$	$3.5854x10^{-4}$
48	$4.128x10^{-4}$	$3.081x10^{-4}$	$3.826x10^{-4}$
72	$5.837x10^{-4}$	$3.021x10^{-4}$	$3.781x10^{-4}$

Table 3.5

Properties before, and after extracting the samples in methanol and acetone (48h at 27°C) followed by ageing at 100°C for 48h

Property	Properties before extraction			Properties after extraction and ageing					
				Methanol			Acetone		
	A	B	C	A	B	C	A	B	C
Tensile strength (N/mm^2)	19.90	17.12	19.75	14.80	15.80	14.41	14.47	16.04	13.88
Elongation at break (%)	268.71	231.01	279.93	160.32	165.65	152.06	150.87	168.08	145.13
Modulus at 100% elongation (N/mm^2)	5.55	6.18	5.20	7.95	8.69	8.07	8.26	8.05	8.40
Hardness (Shore A)	54	53	53	48	47	47	47	46	46
Tear strength (N/mm)	71.11	81.60	65.00	50.35	43	41	51.75	53	44.70

Table 3.6

Properties of the vulcanizates before and after ageing at 100°C for 48h

	A	B	C
<u>Before Ageing</u>			
Abrasion resistance (Volume loss, cc/h)	3.72	3.75	3.77
Compression set (%)	30.97	28.87	29.87
<u>After Ageing</u>			
Abrasion resistance (Volume loss, cc/h)	4.20	4.05	4.25
Compression set (%)	15.71	14.25	17.18

Fig.3.25 shows the tear strength of the above vulcanizates before and after ageing. Retention in tear strength of the vulcanizate containing HTNR-DA after ageing is superior to that containing vulkanox HS but inferior to that containing vulkanox 4020.

Table 3.5 shows the retention in tensile properties, tear strength and hardness of vulcanizates before and after ageing, after extracting the samples in acetone and methanol for 48h. The vulcanizate containing HTNR-DA shows better retention in properties than the vulcanizate containing vulkanox HS and it is comparable to that containing vulkanox 4020.

Table 3.6 shows the abrasion resistance and compression set of the samples before and after ageing. These properties after ageing are comparable for all the vulcanizates. The decrease in compression set after ageing may be due to the increase in crosslink density as shown in Table 3.4.

Conclusions

1. The ageing resistance of SBR vulcanizate containing HTNR-DA is superior to that containing vulkanox HS, but inferior to that containing vulkanox 4020.

2. The amount of plasticiser required can be reduced by the addition of liquid rubber bound antioxidant.

III. PREPARATION AND CHARACTERISATION OF HTNR BOUND CARDANOL ANTIOXIDANT AND SULPHUR BRIDGED CARDANOL AND THEIR USE IN FILLED NATURAL RUBBER VULCANIZATES

India, being one of the major countries in the production and consumption of natural rubber, attempts to improve its properties using cardanol, another natural derivative, is very interesting. It has already been noted that natural rubber is highly prone to ageing by oxidation compared to synthetic rubbers like SBR, NBR etc.

Cardanol can undergo a series of reactions as any other phenolic derivative, although it suffers steric hindrance from bulky alkyl chain at the meta position. Here cardanol was modified by (a) Friedel-Craft's alkylation reaction using hydroxy terminated liquid natural rubber (HTNR) as the alkylating agent and anhydrous aluminium chloride as the catalyst, (b) by reacting with sulphur in presence of accelerators.

Experimental

(a) Alkylation reaction of cardanol

Cardanol was alkylated using modified Friedel-Craft's alkylation reaction. 150 g of HTNR (0.1 mol OH)

.224 mol cardanol, .448 mol of catalyst (anhydrous $AlCl_3$) and 60 ml 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 on a hot plate with magnetic stirring for 16h at 145°C. 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 was then poured into excess methanol with stirring to precipitate the liquid rubber. The unreacted cardanol was removed by repeated reprecipitation using a toluene-methanol (1:1 v/v) mixture, and the product was dried in vacuum oven. The rubber bound cardanol was obtained in the form of brown viscous liquid. Hereafter the product is referred to HTNR-CL.

(b) Sulphur bridging of cardanol

100 ml cardanol was introduced into a flat bottomed flask, fitted with a reflux condenser and thermometer. Ingredients as shown in Table 3.7 were added as dispersions in carbon tetrachloride. The mixture was heated on a hot plate with magnetic stirring for 8h at 110°C. Sulphur bridged cardanol was obtained in the form of dark viscous liquid. Hereafter the product is referred to Card-SB.

Table 3.7

Formulation for reacting cardanol with sulphur

Cardanol	100 g
Sulphur	2
Zinc oxide	0.5
Stearic acid	0.5
Tetramethyl thiuram disulphide	0.5
Zinc diethyl dithiocarbamate	1
Dispersol F	0.005

Analysis of the antioxidants HTNR-CL and Card-SB

Analysis of HTNR-CL and Card-SB was carried out by thin layer chromatography (TLC), infrared spectroscopy (IR), proton magnetic resonance spectroscopy ('H-NMR), thermogravimetric analysis (TGA), hydroxyl value, free sulphur estimation and iodine value.

TLC was carried out using silica gel as the adsorbent. Benzene, N-N'-dimethylformamide mixture (6:1, v/v) was used as the developing solvent for all samples, Br_2 and KI as detecting agent for antioxidants and iodine for HTNR[21,22]. Intrinsic viscosities of antioxidants were calculated by measuring relative viscosities using Sc̈hott Gerate AVS400 capillary viscometer.

Experimental technique

The antioxidants were tried in natural rubber as per the formulation given in Table 3.8. The optimum cure times and scorch times of the compounds were determined on a Goettfert elastograph model 67.85 as per ASTM standards. Rubber compounds were moulded in an electrically heated laboratory hydraulic press at 150°C upto their optimum cure times. Tensile properties, tear resistance, hardness, abrasion resistance and compression set of the vulcanizates were evaluated as per relevant ASTM standards.

Table 3.8

Formulations for testing the antioxidants

	A	B	C	D
Natural rubber (phr)	100	100	100	100
Zinc oxide	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0	2.0
Mercaptobenzothiazole	0.6	0.6	0.6	0.6
Tetramethyl thiuram disulphide	0.2	0.2	0.2	0.2
Carbon black (HAF N 330)	40.0	40.0	40.0	40.0
Aromatic oil	2.0	--	5.0	5.0
Vulkanox SP	--	--	1.0	--
Cardanol	--	--	--	1.0
Card-SB	--	2.5	--	--
HTNR-CL	5.0	--	--	--
Sulphur	2.5	2.5	2.5	2.5

The ageing resistance of the vulcanizates was studied after ageing at 100°C for 12, 24, 36 and 48h and compared with vulcanizate containing vulkanox SP. Extractability of the antioxidants was studied by keeping the samples in methanol and acetone for 48h, followed by ageing at 100°C.

Results and Discussion

Fig.3.26 shows the TLC of HTNR-CL, Card-SB, HTNR and cardanol. HTNR-CL and Card-SB were coloured by Br_2 and KI while HTNR not. R_F value of HTNR-CL is different from cardanol and it is close to HTNR. The difference in R_F values of Card-SB and cardanol indicate the molecular weight increase of Card-SB over cardanol.

Fig.3.27 shows the intrinsic viscosities of HTNR-CL, and HTNR. Intrinsic viscosity of HTNR-CL is close to that of HTNR. This indicates that linking is taking place only at one of the positions of aromatic ring of cardanol. The hydroxyl value of HTNR-CL (11.86 mg of KOH/g) is found to be lower than that of HTNR. This confirms the alkylation of cardanol with HTNR. Intrinsic viscosity of Card-SB (Fig.3.28) is about five times that of cardanol (Fig.3.29).

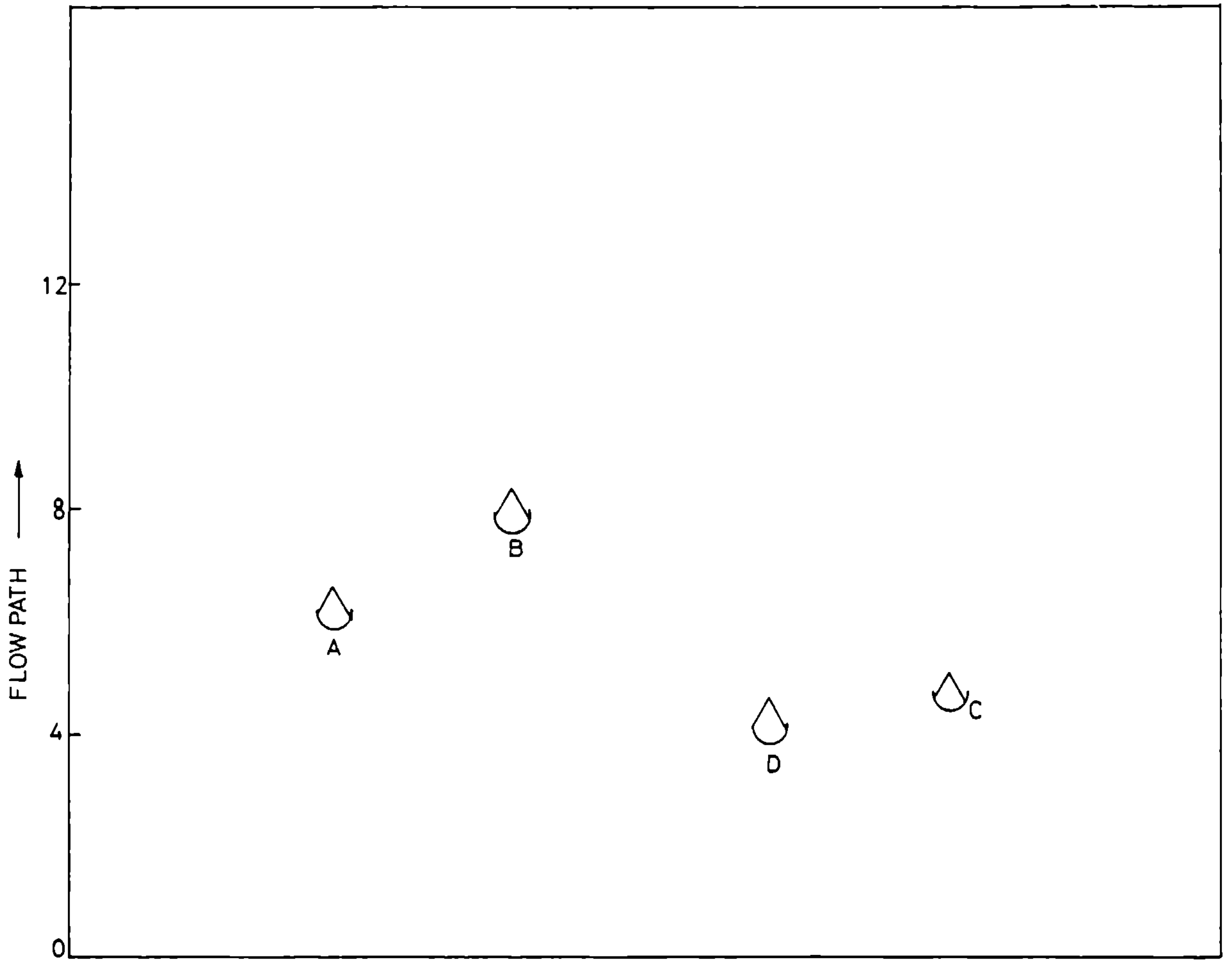

Fig.3.26: TLC of compounds; (A) Card-SB, (B) cardanol, (C) HTNR, (D) HTNR-CL

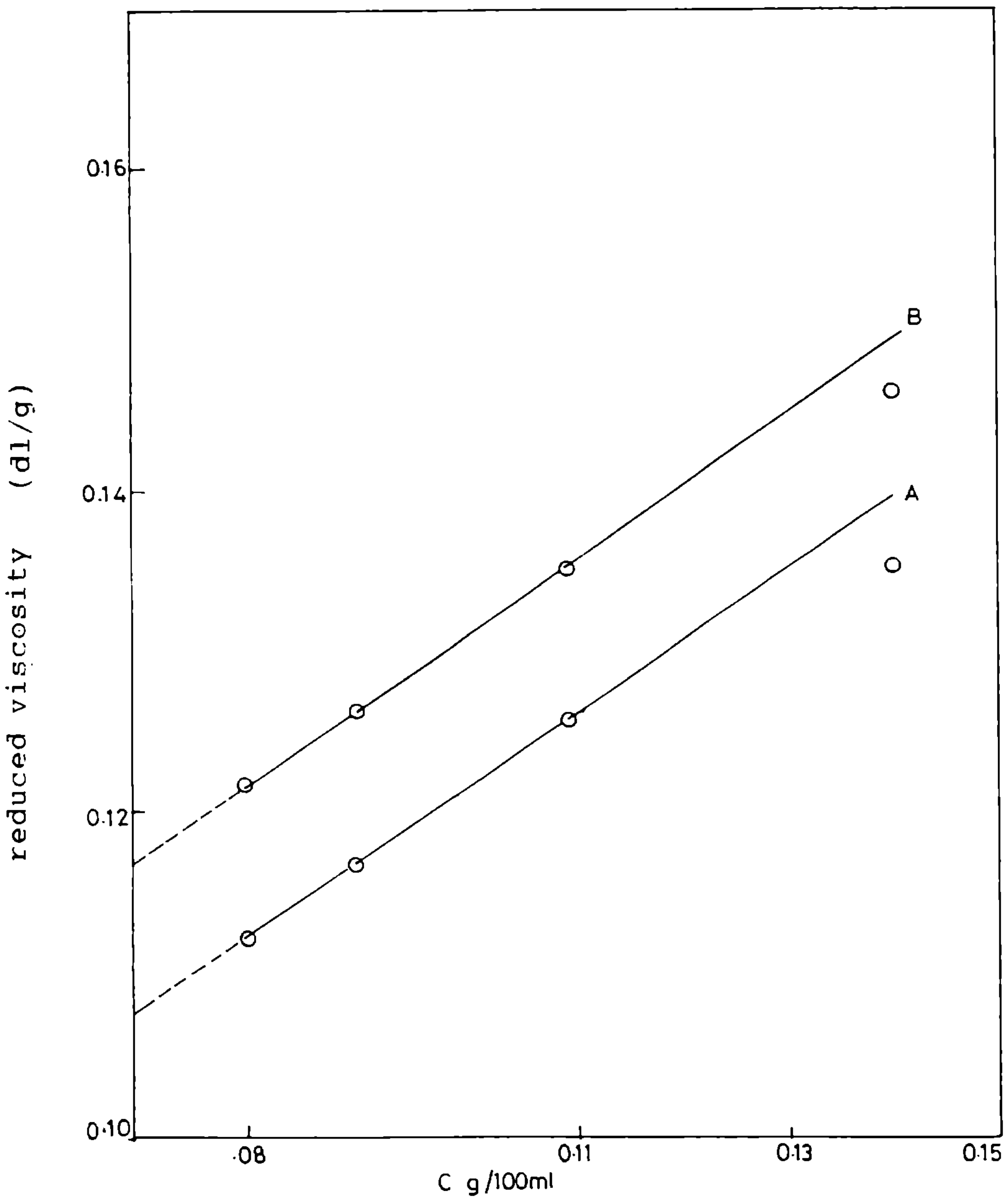

Fig.3.27: Reduced viscosity vs. concentration of compounds; (A) - HTNR, (B) - HTNR-CL.

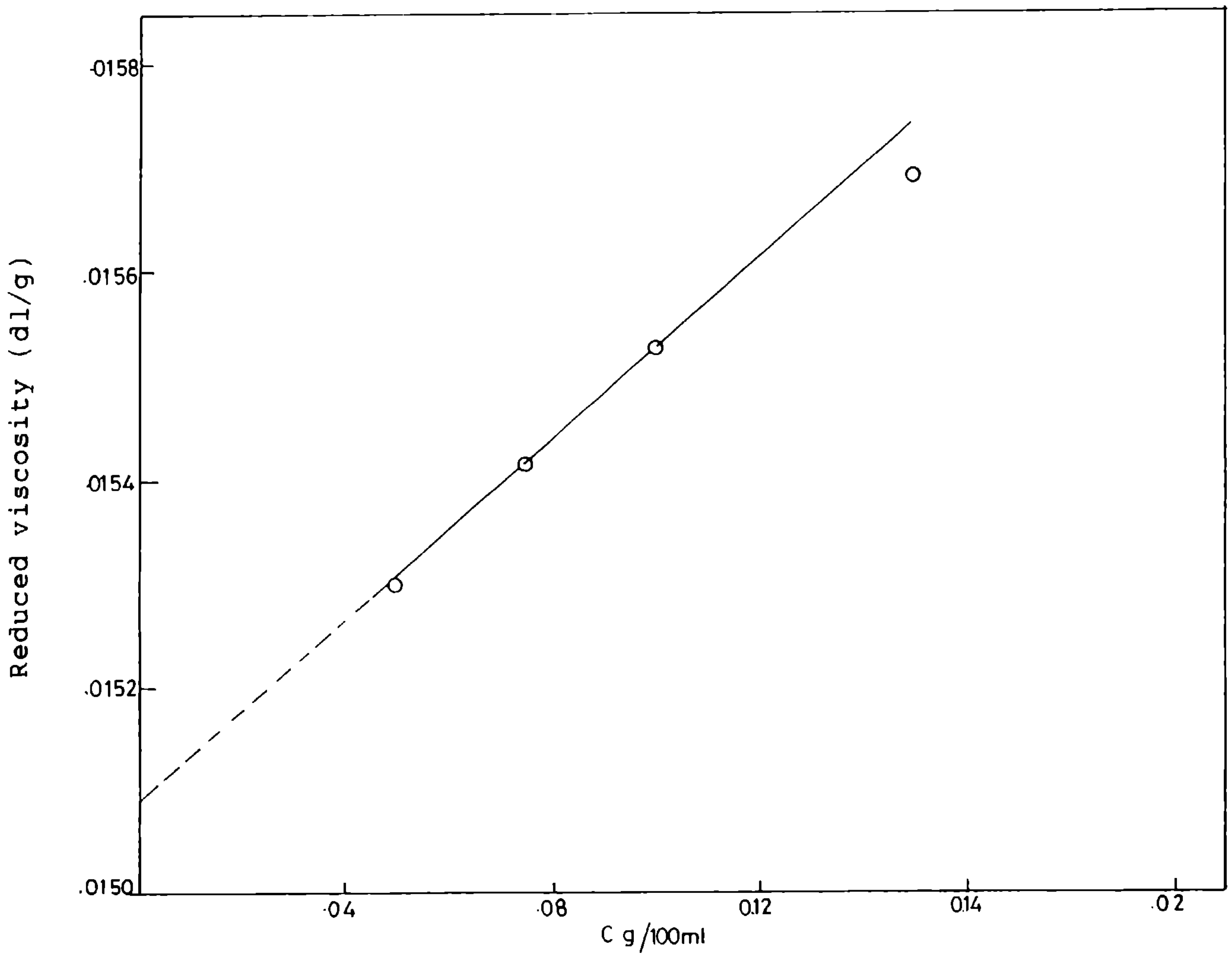

Fig.3.28 Reduced visocity vs. concentration of Card-SB.

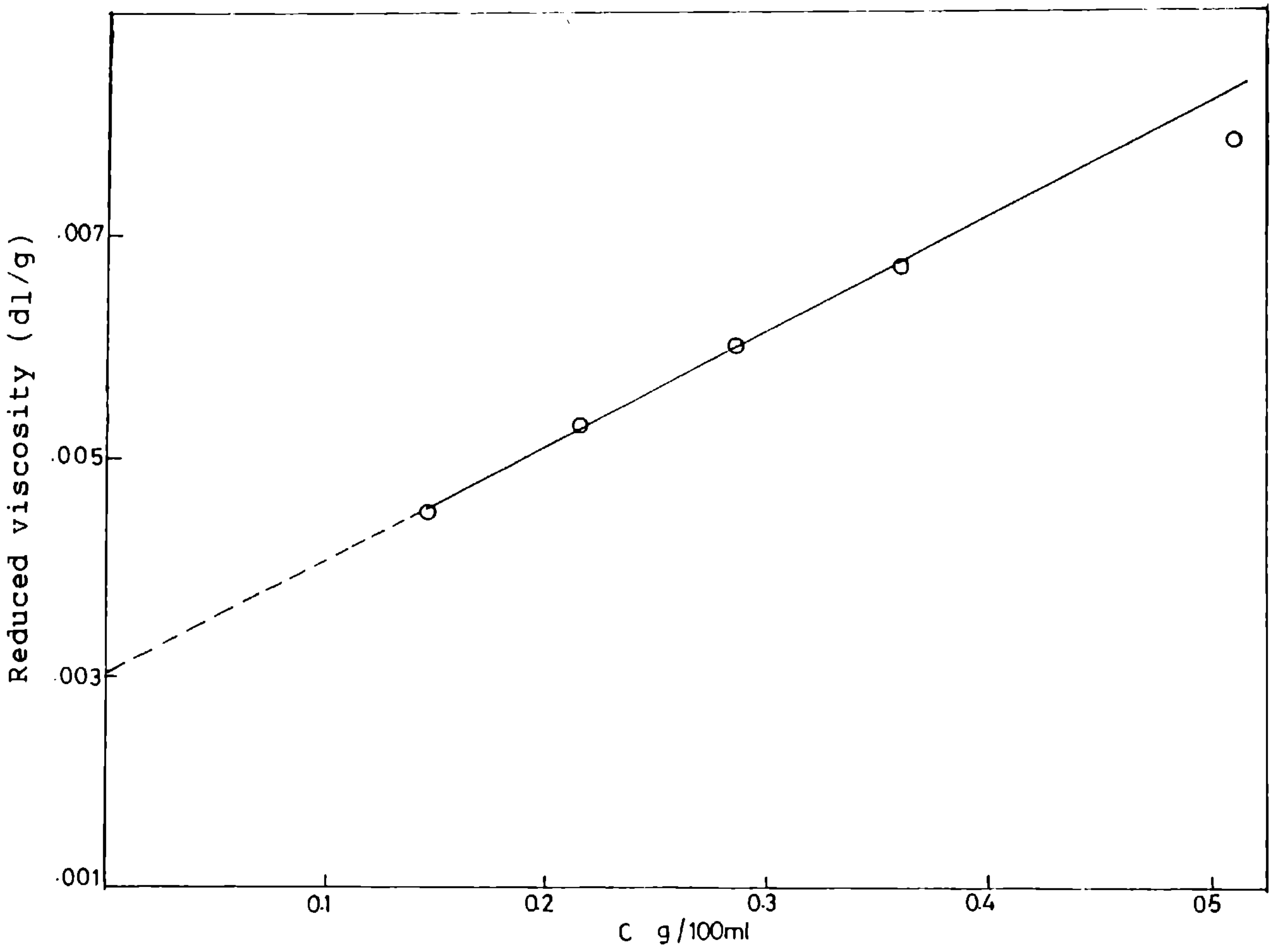

Fig.3.29: Reduced viscosity vs. concentration of cardanol.

This shows that a product which has molecular weight approximately five times that of cardanol is formed as a result of its reaction with sulphur in presence of accelerators.

Free sulphur content of Card-SB is very low (0.25%). Iodine value of Card-SB (185g/100g sample) is considerably less than that of cardanol (237g/100g of sample).

Figs.3.30 and 3.31 show IR spectra of cardanol and HTNR-CL. IR spectrum of cardanol shows the peaks at 3300 cm^{-1} (phenolic -OH), 630 cm^{-1} (vinyl), 690 cm^{-1} (CH_2-CH_2-CH_2-CH), 1450 cm^{-1} (CH_2 bending), 895-995 cm^{-1} (vinyl), 1600 cm^{-1} (aliphatic -CH), 3015 cm^{-1} (vinyl). IR spectrum of HTNR-CL shows peaks at 3400 cm^{-1} (-OH group), 1665 cm^{-1} ($>C=C<$), 1400 cm^{-1} and 830 cm^{-1} corresponding to $-CH_3$ and isoprene unit[20]. In short, the peaks due to cardanol are retained and some of them are merged with those of HTNR. Also the presence of isoprene unit (835 cm^{-1}) is clearly evidenced in HTNR-CL.

Fig.3.32 shows the IR spectrum of Card-SB. The peaks due to cardanol was retained in Card-SB, although the

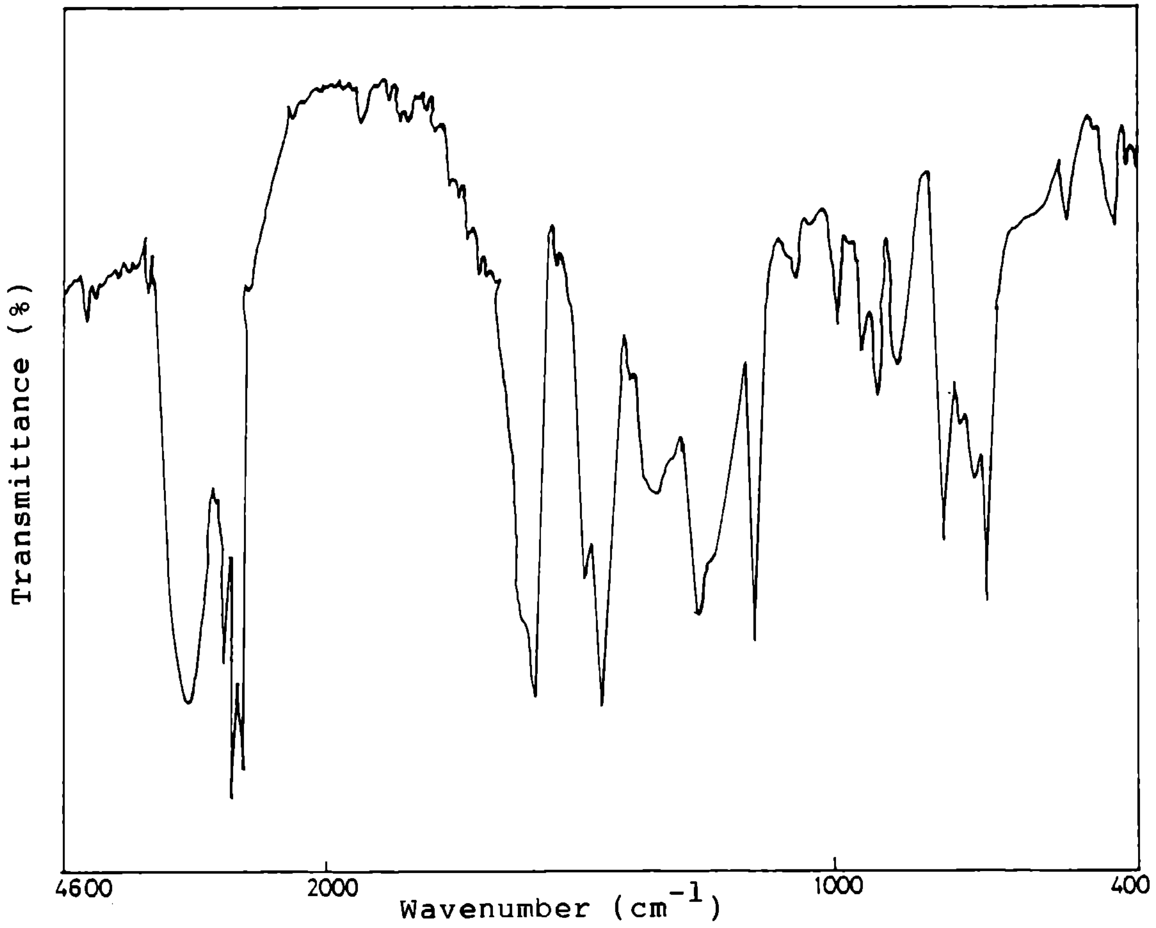

Fig.3.30: IR spectrum of cardanol

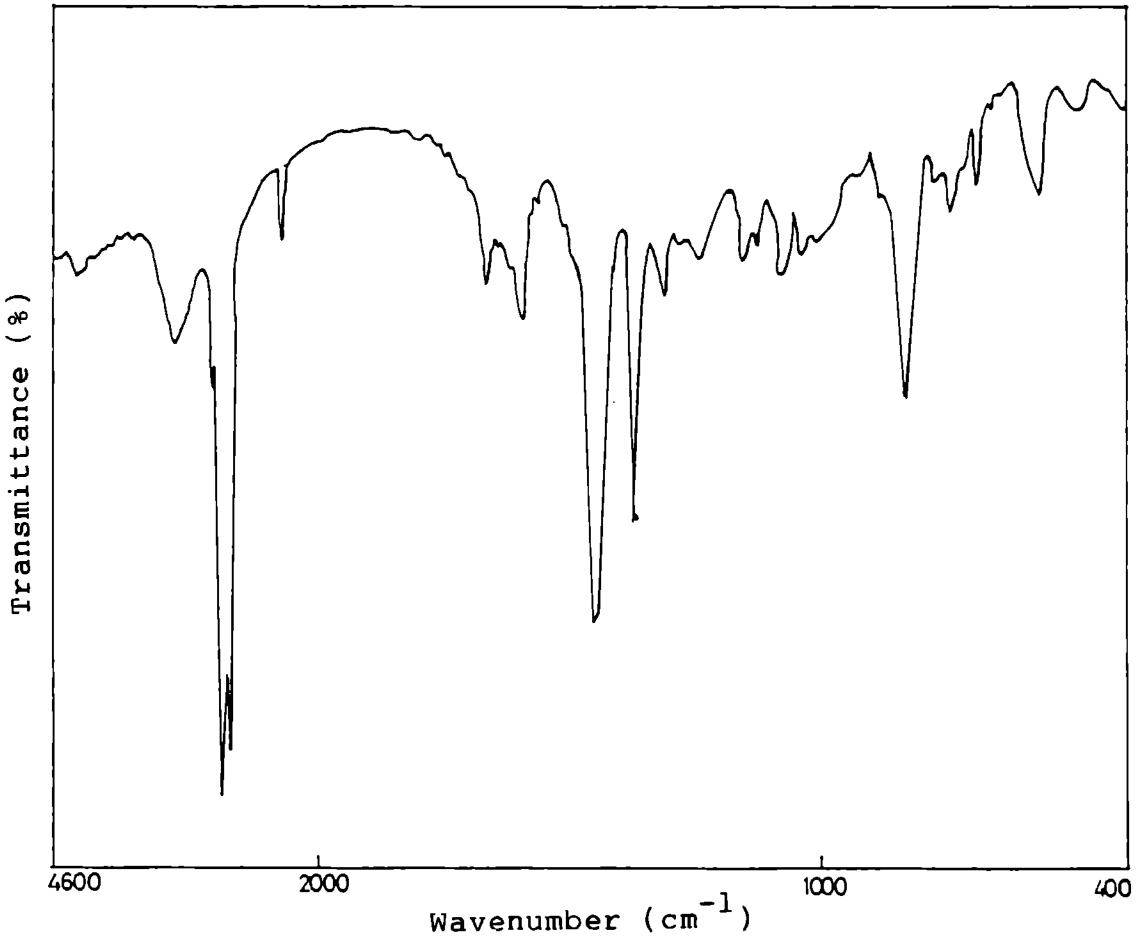

Fig.3.31: IR spectrum of HTNR-CL

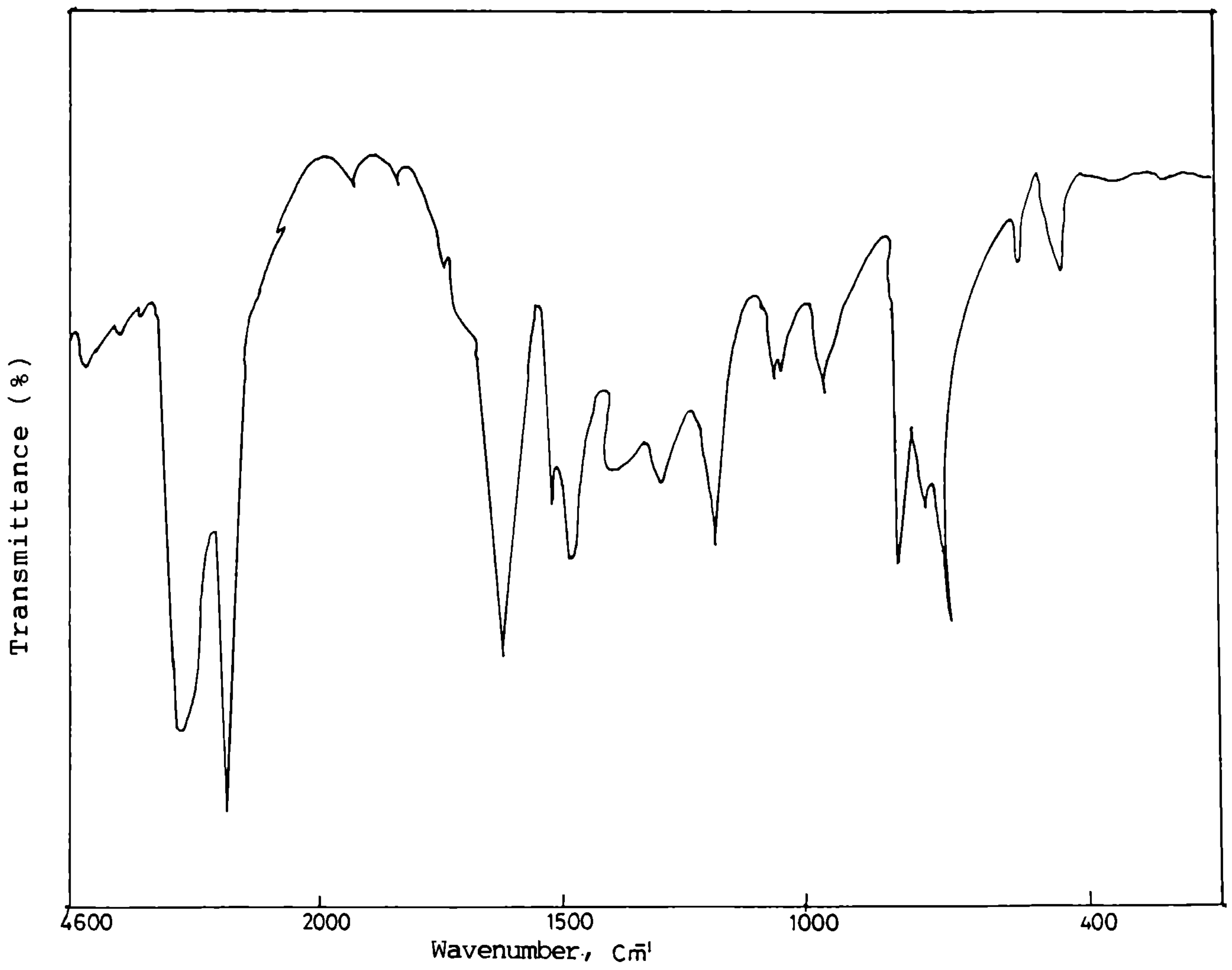

Fig.3.32: IR spectrum of Card-SB

vinyl peak intensities (1600, 895, 905 and 995 cm^{-1}) are considerably reduced. Phenolic -OH group in cardanol is retained in Card-SB.

Fig.3.33 shows 'H-NMR spectrum of HTNR-CL. This closely resembles that of HTNR (Fig.3.7). However additional peaks due to the aromatic (δ-6.6-7.5 ppm) protons of cardanol residue are visible. The signals of the aliphatic protons of cardanol residue are masked by the alkyl proton signals of HTNR.

Fig.3.35 shows 'H-NMR spectrum of Card-SB. It exhibits peaks at δ - 6.6-7.3 (aromatic), 5.4 and .8-2.8 ppm (aliphatic protons)[20]. Comparison of the 'H-NMR spectrum of Card-SB with that of cardanol (Fig.3.34) suggests the disappearance of the multiplet centred around δ= 5.2 ppm (vinylic-H). This may be taken to mean that the double bonds in the side chain of cardanol undergo modification. It is quite likely that disulphide bridges are formed between two or more cardanol units. (As described earlier, intrinsic viscosity measurements indicated the possibilities of a tetramer or pentamer formation, which is in accordance with this observation). It may be mentioned here that earlier crosslinking

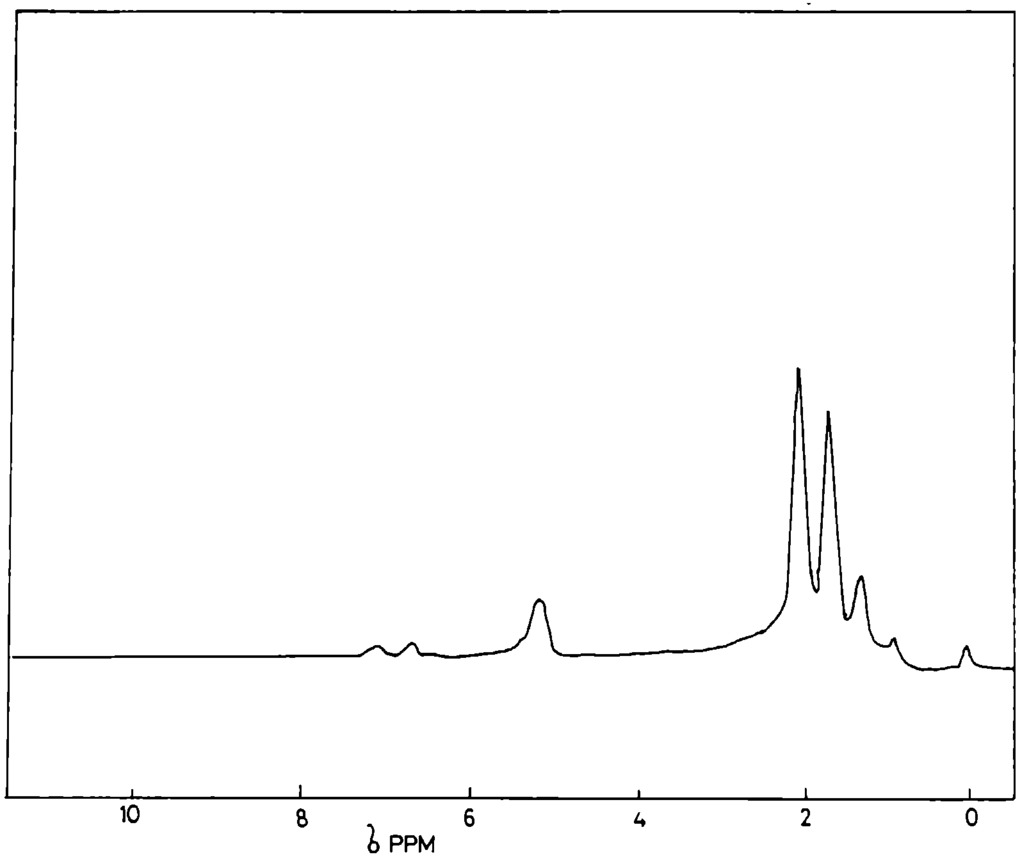

Fig.3.33: 'H-NMR spectrum of HTNR-CL

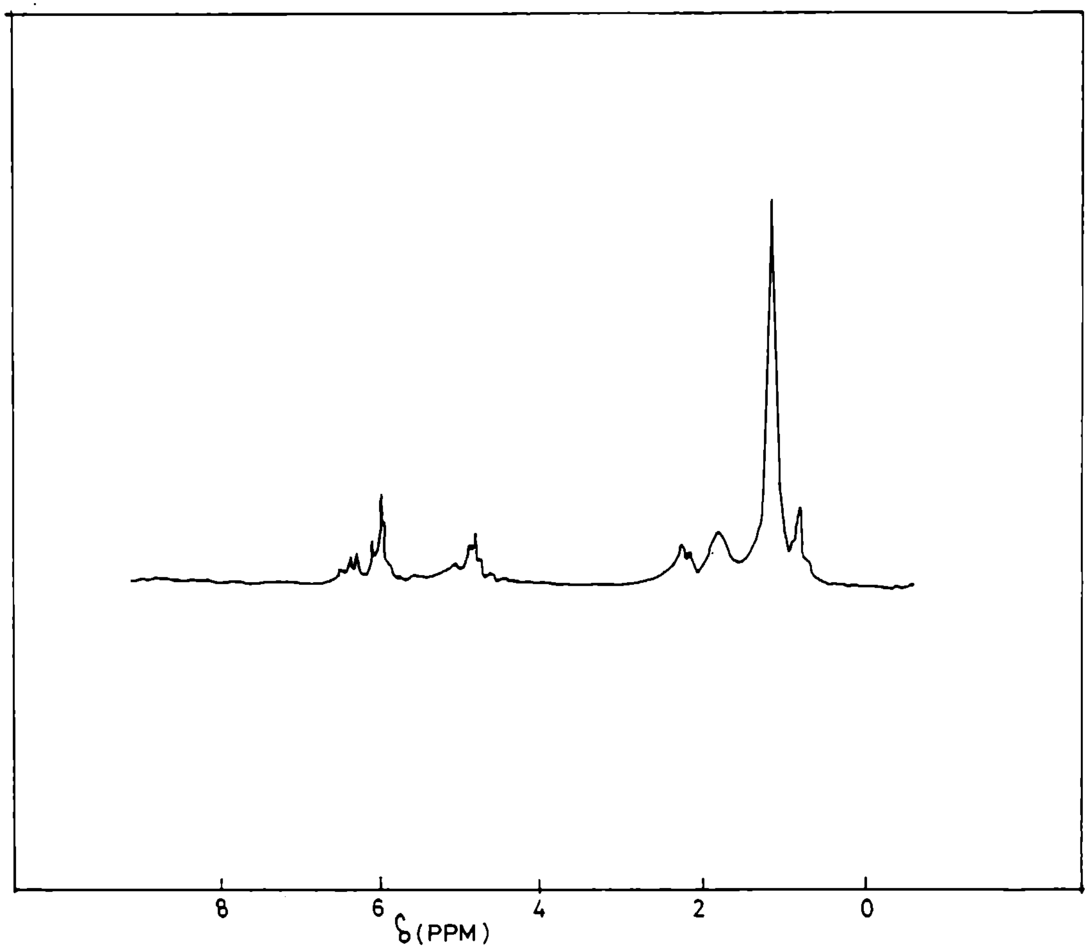

Fig.3.34: 'H-NMR spectrum of cardanol

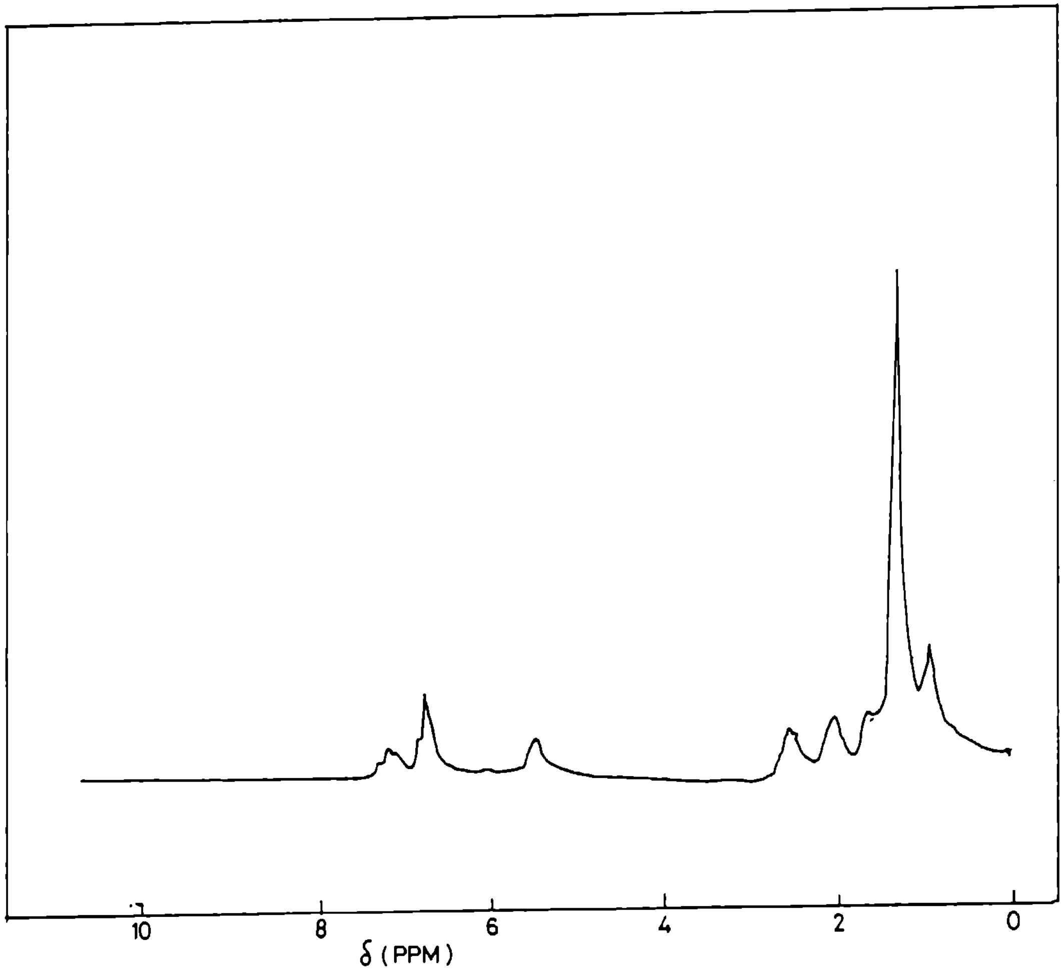

Fig.3.35: 'H-NMR spectrum of Card-SB

experiments conducted on the saturated analogue of cardanol resulted in the formation of diaryl sulphide bridges[14]. However those systems lack double bonds in the side chain and hence are likely to behave differently from cardanol. In cardanol the formation of disulphide linkages at the side chain may occur in preference to the benzene ring.

Fig.3.36 shows the TGA curves of cardanol, HTNR-CL and Card-SB. The low molecular weight cardanol, volatilise easily while HTNR-CL and Card-SB are found to be less volatile.

Fig.3.37 shows the cure curves of the compounds shown in Table 3.8. There is only a marginal change in the scorch and cure times for the compounds. This shows that addition of cardanol does not affect the vulcanization rate.

Fig.3.38 shows the tensile strength of the above vulcanizates before and after ageing at 100°C. All the vulcanizates show fairly good resistance to ageing after 12h. The vulcanizates containing HTNR-CL and Card-SB show good ageing resistance after 24 and 48h. Retention in tensile strength shown by the vulcanizates containing HTNR-

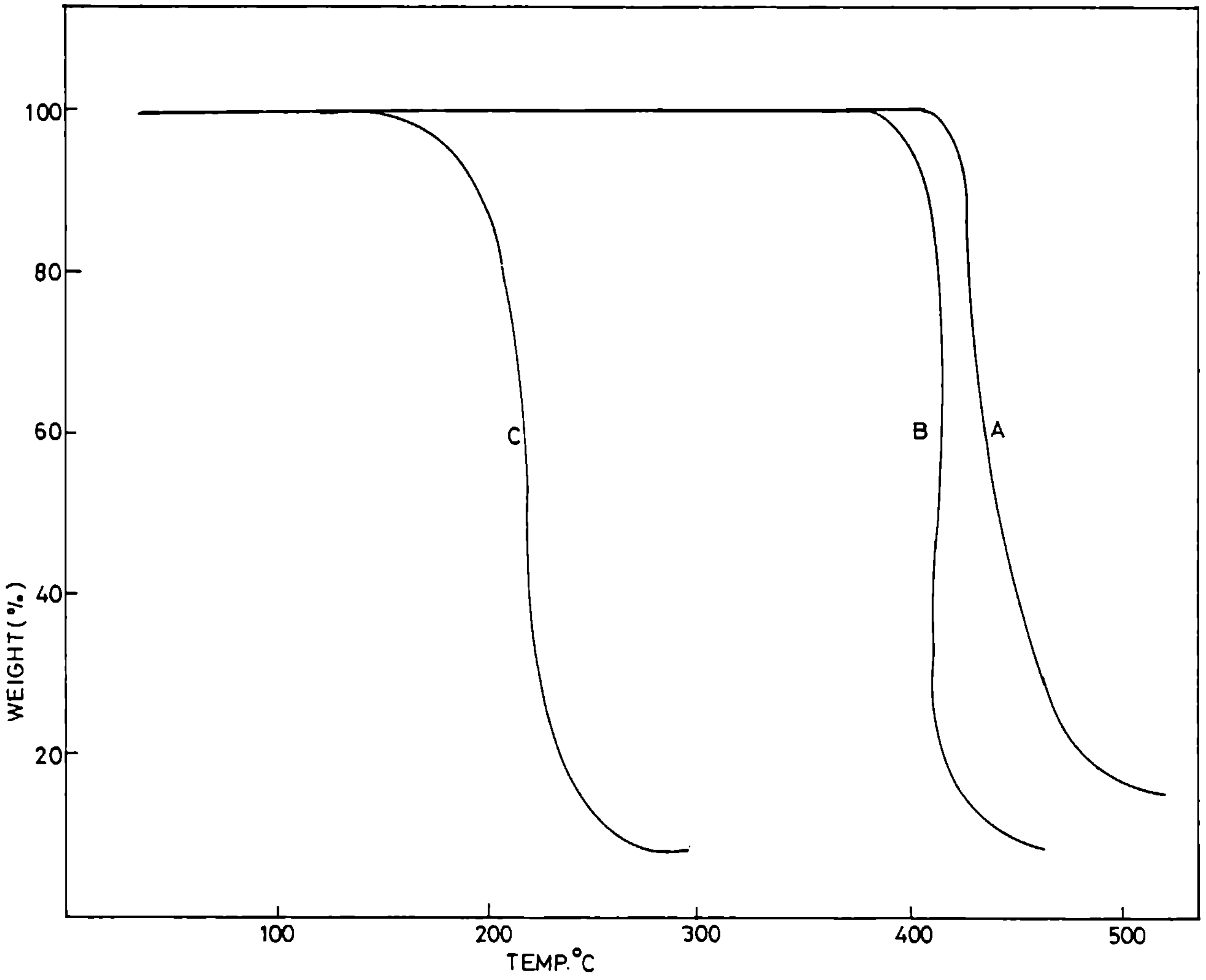

Fig.3.36: Thermograms of antioxidants; (A) HTNR-CL, (B) Card-SB, (C) cardanol

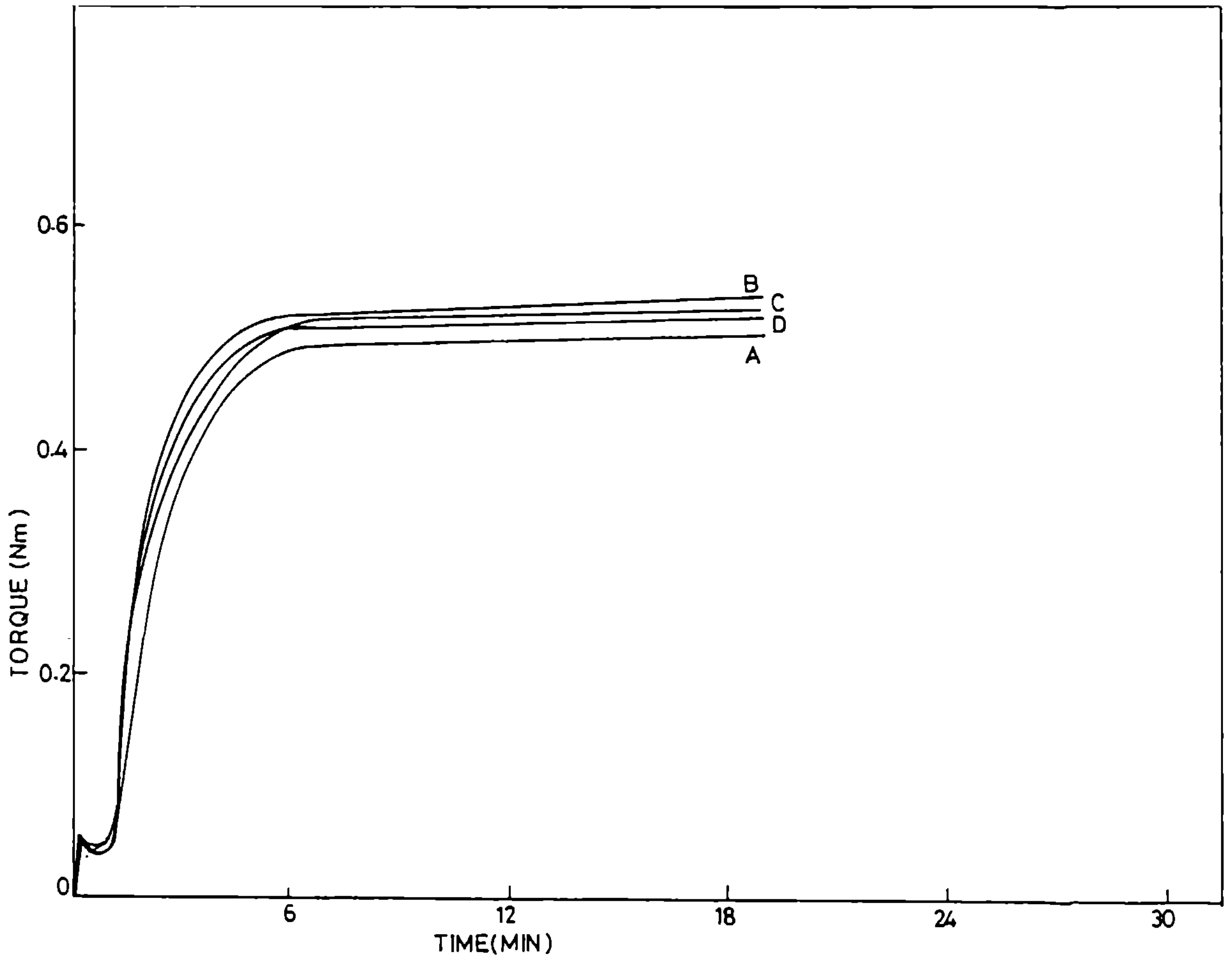

Fig.3.37: Cure curves of the compounds; (A) HTNR-CL, (B) Card-SB, (C) SP, (D) cardanol

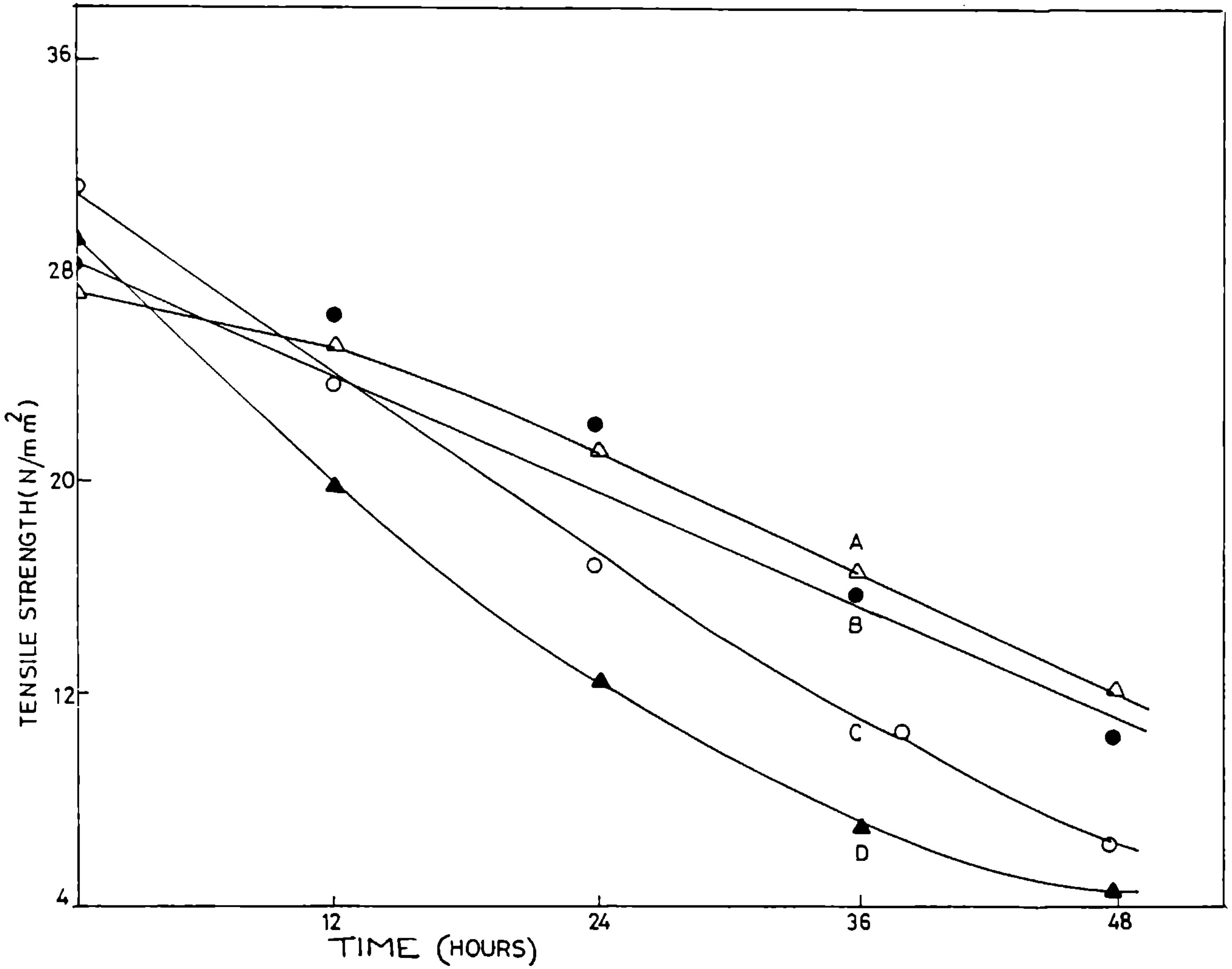

Fig.3.38: Variation in tensile strength of the vulcanizates before and after ageing at 100°C; (A) HTNR-CL, (B) Card-SB, (C) SP, (D) Cardanol.

CL and Card-SB confirms the superiority of HTNR-CL and Card-SB over vulkanox SP and pure cardanol.

Fig.3.39 shows the elongation at break of the vulcanizates before and after ageing. Elongation at break is improved by the addition of HTNR-CL and Card-SB. This shows that these products can act as good plasticisers in natural rubber. The retention in elongation at break after ageing shown by the vulcanizates containing Card-SB and HTNR-CL after 48h ageing, confirms the superiority of bound antioxidants over conventional antioxidant.

Fig.3.40 shows modulus at 100% elongation of the vulcanizates before and after ageing. The increase in modulus after ageing may be due to the increase in crosslink density as shown in Table 3.9. The increase in modulus shown by Card-SB and HTNR-CL after ageing may be due to the co-crosslinking of the bound antioxidants with NR.

Fig.3.41 shows the tear strength of the vulcanizates before and after ageing. Better retention in tear strength shown by vulcanizate containing Card-SB confirms the superiority of bound antioxidant. The

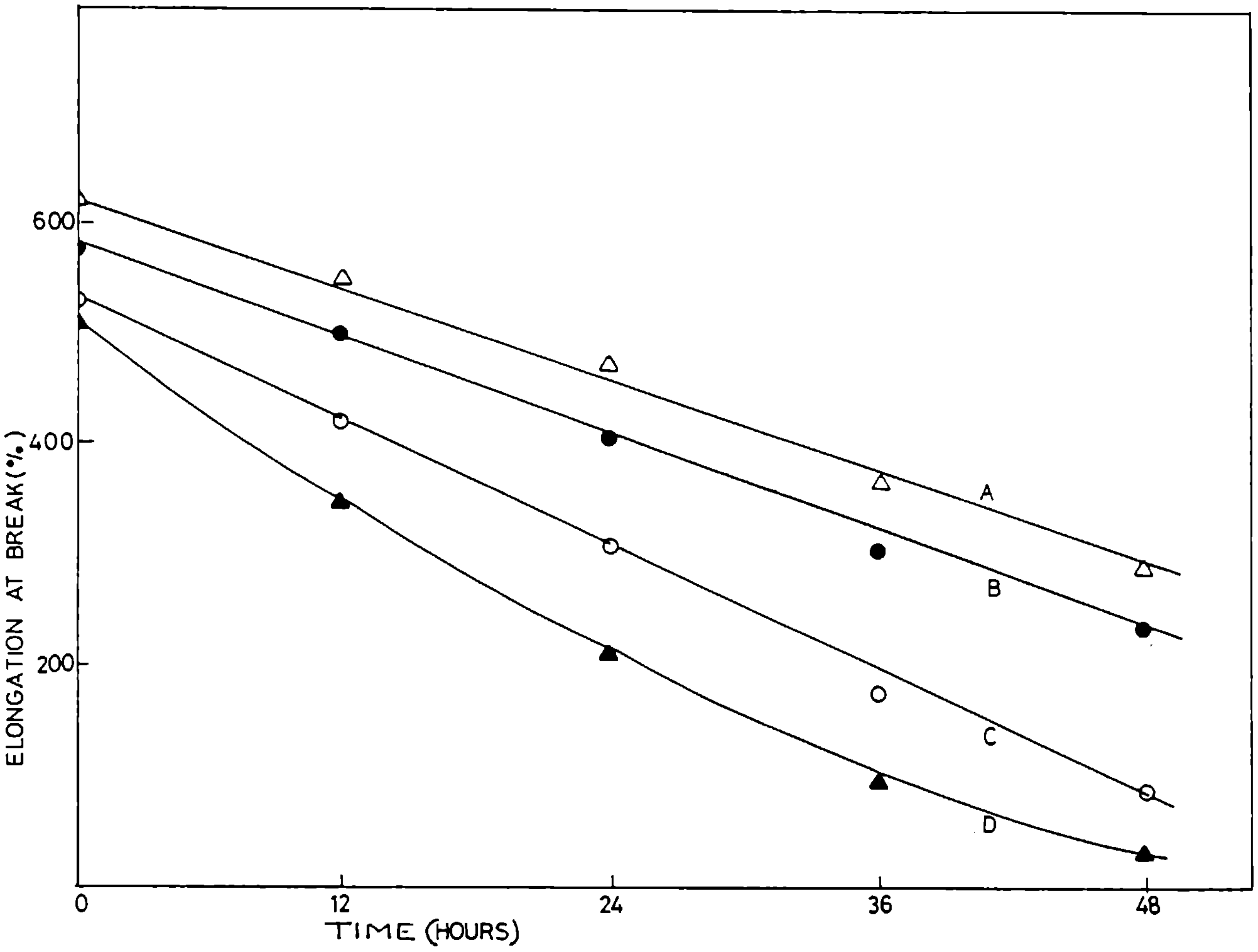

Fig.3.39: Variation in elongation at break of the vulcanizates before and after ageing at 100°C; (A) HTNR-CL, (B) Card-SB, (C) SP, (D) cardanol

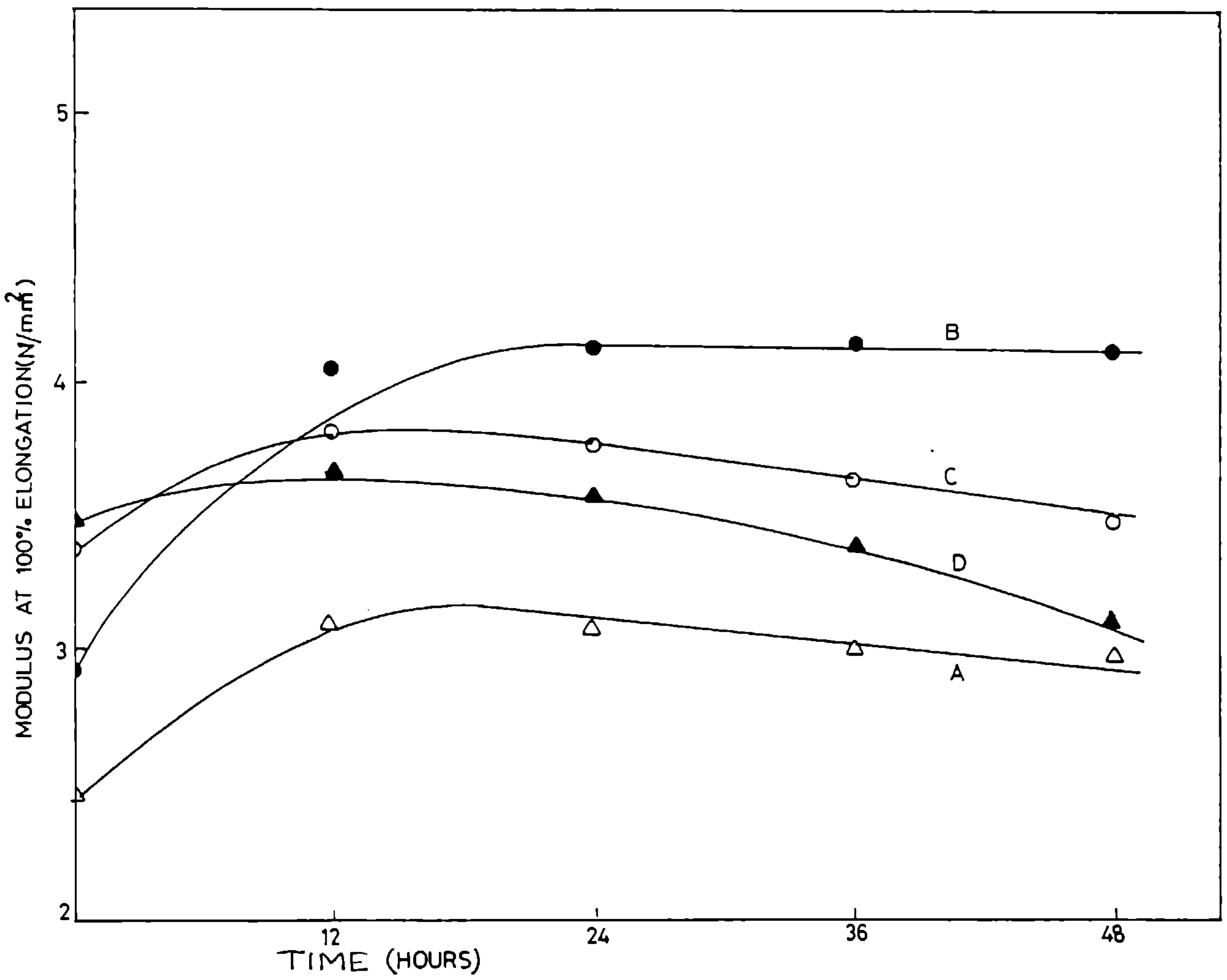

Fig.3.40: Variation in modulus (at 100% elongation) of the vulcanizates before and after ageing at 100°C; (A) HTNR-CL, (B) Card-SB, (C) SP, (D) cardanol

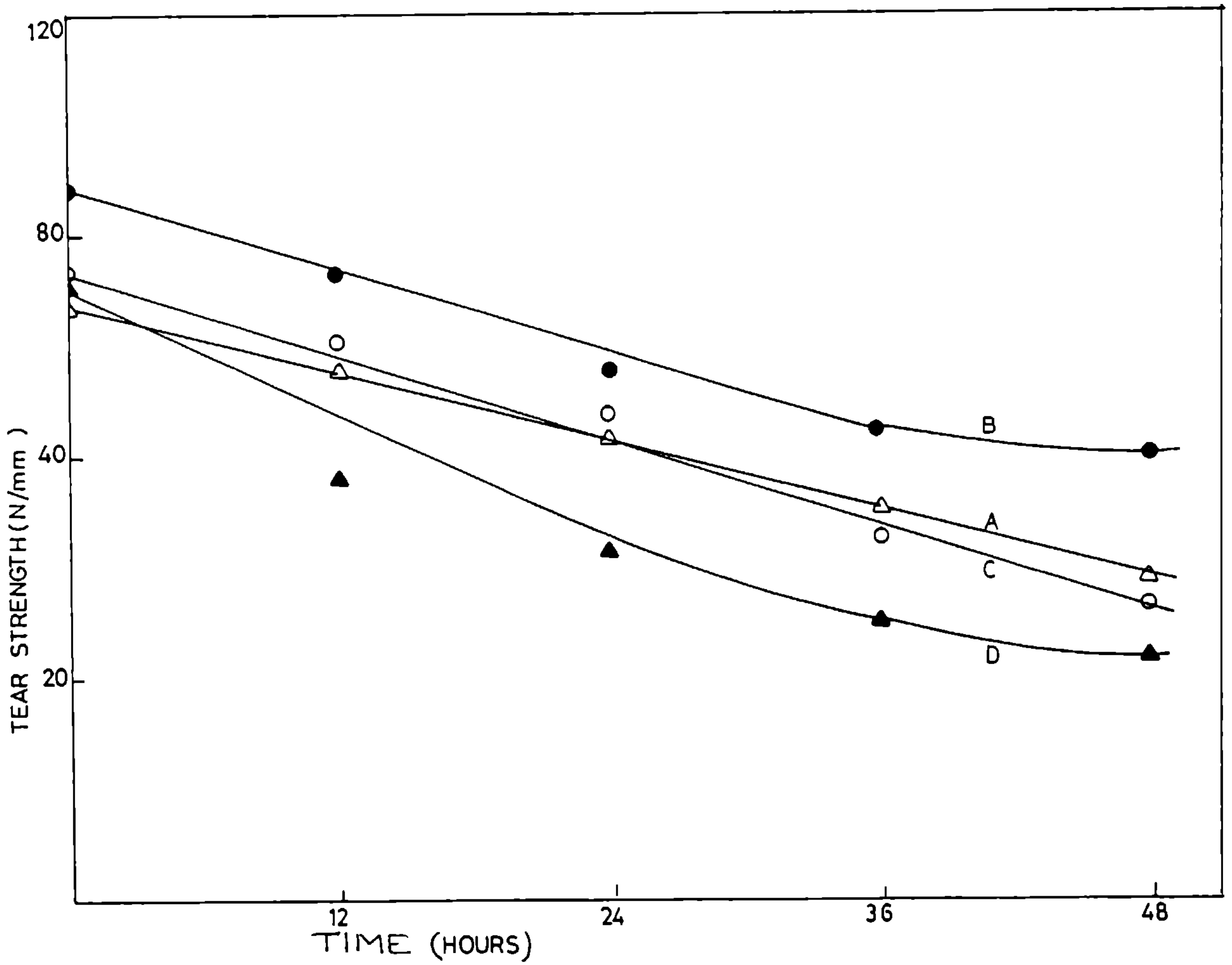

Fig.3.41: Variation in tear strength of the vulcanizates before and after ageing at 100°C; (A) HTNR-CL, (B) Card-SB, (C) SP, (D) cardanol

vulcanizate containing HTNR-CL shows equivalent retention in tear strength compared to vulcanizate containing vulkanox SP.

Fig.3.42 shows the change in hardness of the vulcanizates before and after ageing. The increase in hardness after ageing may be due to the post curing of vulcanizates during ageing, confirmed by the increase in crosslink density, as shown in Table 3.9.

Table 3.10 shows the retention in tensile properties, tear strength and hardness before and after ageing, after extracting the samples in acetone for 48h. The retention in properties shown by the vulcanizates containing HTNR-CL and Card-SB even after extraction and ageing may be due to lower extractability of bound antioxidants.

Table 3.11 shows the abrasion resistance and compression set of the samples before and after ageing. The retention in abrasion resistance shown by the vulcanizate containing Card-SB after ageing may be due to the lower volatility of the bound antioxidant. The decrease in compression set after ageing may be due to the increase in crosslink density, as shown in the Table 3.9.

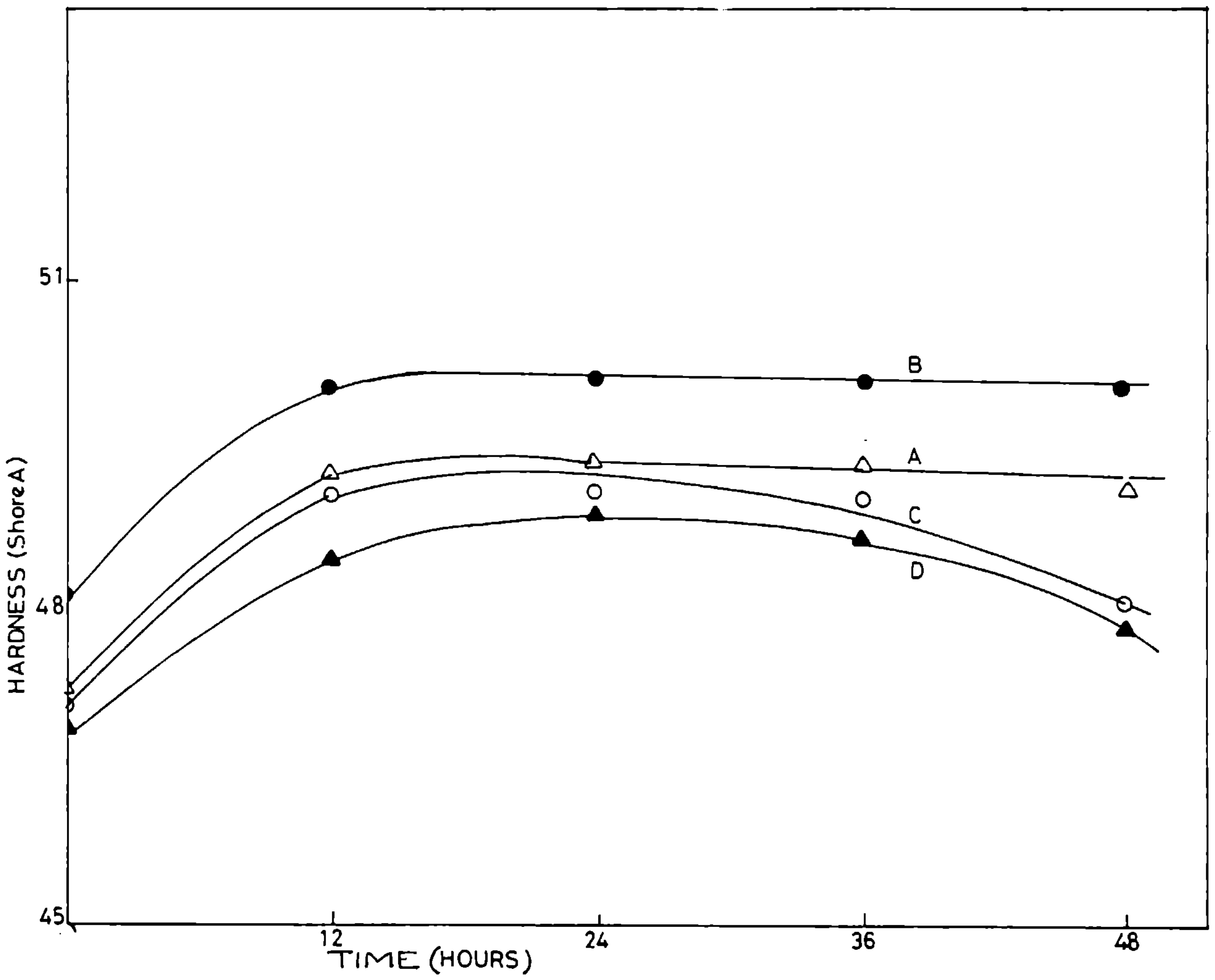

Fig.3.42: Variation in hardness of the vulcanizates before and after ageing at 100°C; (A) HTNR-CL, (B) Card-SB, (C) SP, (D) cardanol

Table 3.9

Crosslink densities of the vulcanizates before and after ageing at 100°C for 48h

Time of ageing (h)	Crosslink density in g mole/cc			
	A	B	C	D
0	4.621×10^{-5}	4.828×10^{-5}	4.94×10^{-5}	4.91×10^{-5}
24	4.42×10^{-4}	4.992×10^{-4}	1.990×10^{-4}	1.18×10^{-4}
48	6.0046×10^{-4}	7.98×10^{-4}	6.91×10^{-5}	5.01×10^{-5}

Table 3.10

Properties of the vulcanizates before and after extraction by acetone (48h and room temperature) followed by ageing at 100°C for 48h

	A	B	C	D
Properties before extraction				
Tensile strength (N/mm^2)	26.36	28.97	31.75	29.35
Elongation at break (%)	602.46	579.42	530.07	516.97
Modulus at 100% elongation (N/mm^2)	2.38	2.82	3.31	3.48
Hardness (Shore A)	47	48	47	47
Tear strength (N/mm)	54.36	87.42	73.02	71.35
Properties after extraction and ageing				
Tensile strength (N/mm^2)	9.52	9.08	5.34	4.47
Elongation at break (%)	212.42	187.36	142.18	142.68
Modulus at 100% elongation (N/mm^2)	4.15	4.57	3.54	3.08
Hardness (Shore A)	49	50	48	48
Tear strength (N/mm)	26.72	35.79	25	17.82

Table 3.11

Properties of the vulcanizates before and after ageing at 100°C for 48h

Properties	A	B	C	D
BEFORE AGEING				
Abrasion resistance (Volume loss, cc/h)	3.95	3.86	3.96	3.98
Compression set (%)	29.44	27.91	28.41	28.0
AFTER AGEING				
Abrasion loss (Volume loss, cc/h)	4.25	4.12	4.20	4.27
Compression set (%)	17.41	16.69	18.51	19.0

Conclusions

1. Cardanol can be chemically attached to HTNR by modified Friedel-Craft's alkylation reaction in presence of anhydrous $AlCl_3$.

2. High molecular weight, sulphur bridged cardanol can be prepared by heating cardanol with sulphur in presence of accelerators.

3. Bound cardanols can improve the ageing resistance of natural rubber vulcanizates.

4. Bound cardanols have superior resistance to volatility and extractability compared to conventional antioxidants.

5. The amount of plasticiser required for compounding can be reduced by the addition of bound cardanols.

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Chapter 4

BINDING OF ANTIOXIDANTS TO LIQUID NATURAL RUBBER BY UV IRRADIATION AND THEIR USE IN NR AND NBR

Developments in tyre design and improvements in compounding have resulted in high mileage performance and long service times on modern passenger car and truck tyres. The performance of a tyre is highly dependent on an effective antioxidant system when it is subjected to severe dynamic stressing and outdoor exposure. In the tyre industry aryl alkyl p-phenylenediamines 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.

Nitrile rubber based products are used as seals for use in contact with mineral oil based hydraulic fluids and require protective antioxidants in order to retain their elastomeric properties for a 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[1,2].

Polymer bound antioxidant can overcome these problems. Several preparative methods are described by Scott et al, and others[3-5]. In this chapter binding of diphenylamine and paraphenylenediamine to depolymerised natural rubber during UV irradiation and subsequent use of the products in filled rubber vulcanizates are described.

I. PREPARATION AND CHARACTERISATION OF NATURAL RUBBER BOUND DIPHENYLAMINE AND ITS USE IN NATURAL RUBBER FILLED VULCANIZATES

Experimental

a) Preparation of natural rubber bound diphenylamine antioxidant.

Natural rubber was masticated for 30 minutes at 50°C. 100 g of it was dissolved in one litre toluene and the solution was charged into a photochemical reactor, a glass vessel of 3L capacity fitted with a water condenser and mechanical stirrer. High pressure mercury vapour lamp in a quartz immersion well was placed in the solution. After 60h exposure, 25g diphenylamine dissolved in toluene was added slowly with stirring and irradiation was continued. Samples taken after 1,2,3,4,5,6,7,10,12 and 15h of exposure after adding diphenylamine were poured into excess of methanol with stirring, when liquid rubber precipitated. The unreacted diphenylamine was removed by repeated precipitation using a toluene-methylalcohol (1:1, v/v) mixture, and the product was dried in a vacuum oven. The rubber bound product was obtained in the form of a viscous liquid. Samples taken after different times of exposure were added in natural rubber compounds as per formulation given in Table 4.1(A). The optimum exposure time for preparing rubber bound antioxidant was determined by studying the retention in tensile strength after ageing the vulcanizates at 100°C for 48h. Maximum retention in tensile strength was obtained for vulcanizates containing the rubber bound samples produced by exposure for 6h and above. So time of exposure to UV light after the addition of diphenylamine was fixed as 6h. Hereafter the product is referred to NR-DA.

b) Analysis of the rubber bound antioxidant, NR-DA

Analysis of the bound antioxidant was carried out by thin layer chromatography (TLC), gel permeation chromatography (GPC), infrared spectroscopy (IR), proton magnetic resonance spectroscopy ('H-NMR) and thermogravimetric analysis. TLC was carried out using silica gel as the adsorbent. A mixed solvent benzene and ethylacetate (4:1, v/v) was used as the developing solvent for all samples while ninhydrin was used as the colour developing agent for NR-DA and diphenylamine and iodine for depolymerised NR[6]. Molecular weight of the NR-DA was measured by gel permeation chromatography.

The optimum concentration of the rubber bound antioxidant for getting maximum retention in properties after ageing was determined by varying the amount of NR-DA in a standard natural rubber compound (Table 4.1 (mix A)) from 1 to 8 phr.

NR-DA was added in NR as per the formulation given in Table 4.1. The amount of plasticiser can be reduced by the use of liquid rubber bound antioxidant as shown in Table 4.1. The optimum cure times and scorch times of the compounds were determined in a Goettfert Elastograph model 67.85 as per ASTM D 1646 (1981). Rubber compounds were moulded in an electrically heated laboratory hydraulic press at 150°C upto their optimum cure times. Dumbell shaped tensile test pieces were punched out of these compression moulded sheets along the mill grain direction.

Table 4.1

Formulations for testing the antioxidants

Sample	X	A	B
Natural rubber (phr)	100	100	100
Zinc oxide	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0
Mercaptobenzothiazole	0.6	0.6	0.6
Tetramethyl thiuram disulphide	0.2	0.2	0.2
Sulphur	2.5	2.5	2.5
Carbon black HAF (N 330)	40.0	40.0	40.0
Aromatic oil	5.0	3.0	5.0
Pilflex-13	--	--	1.0
NR-DA	--	5.0	--

The tensile properties and tear strength were measured as per relevant ASTM standards.

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

Results and Discussion

Fig.4.1 shows the variation in tensile strength after ageing at 100°C for 48h with exposure time after the addition of diphenylamine into the partially depolymerised natural rubber solution. The retention in properties increases first, reaches a maximum and levels off at an exposure time of 6h. This indicates that after an optimum time of exposure all the diphenylamine molecules get attached to the depolymerised NR.

Fig.4.2 shows the TLC of diphenylamine (DA), depolymerised NR (UV irradiated for an equivalent time) and

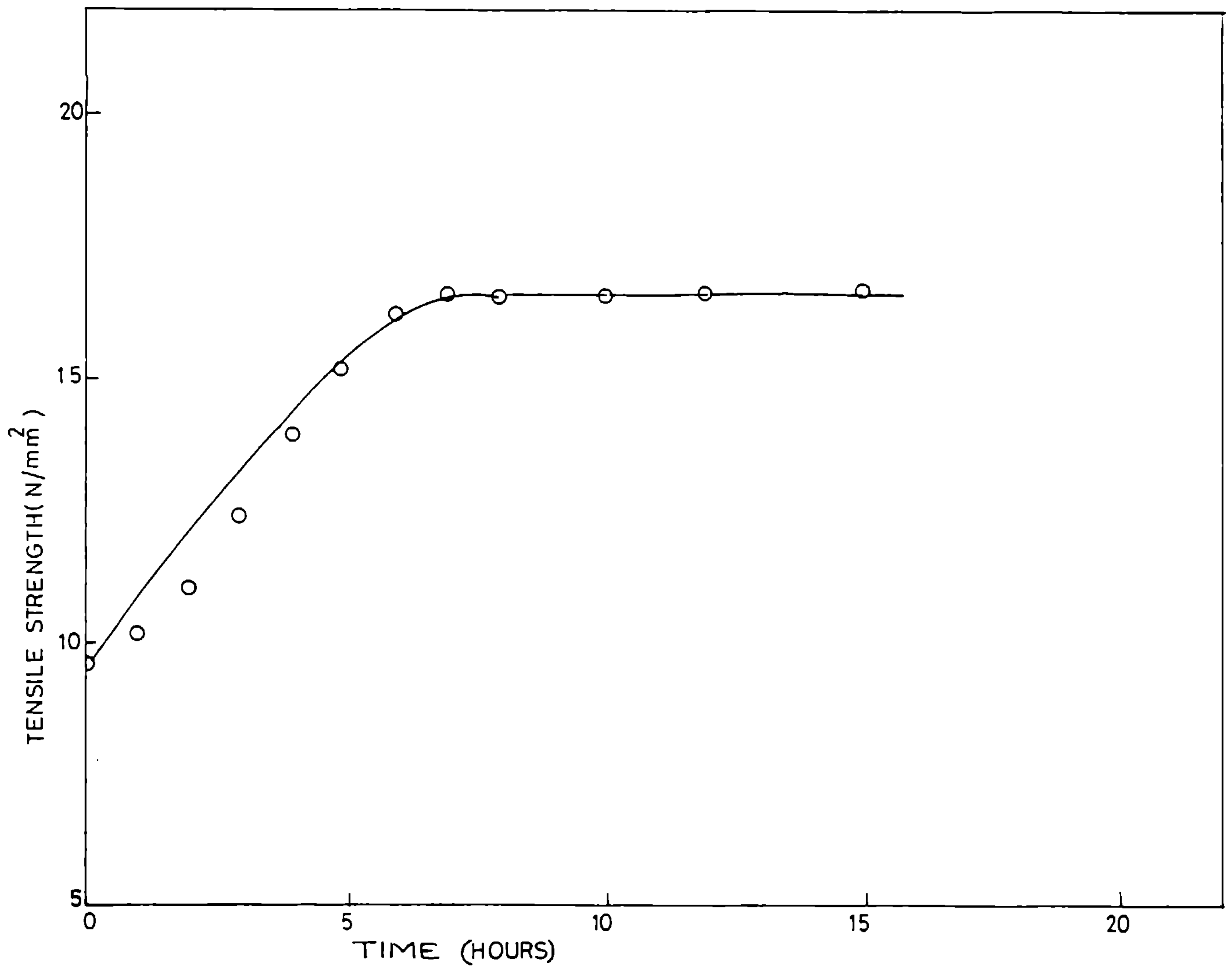


Fig.4.1: Variation in tensile strength after ageing with exposure time

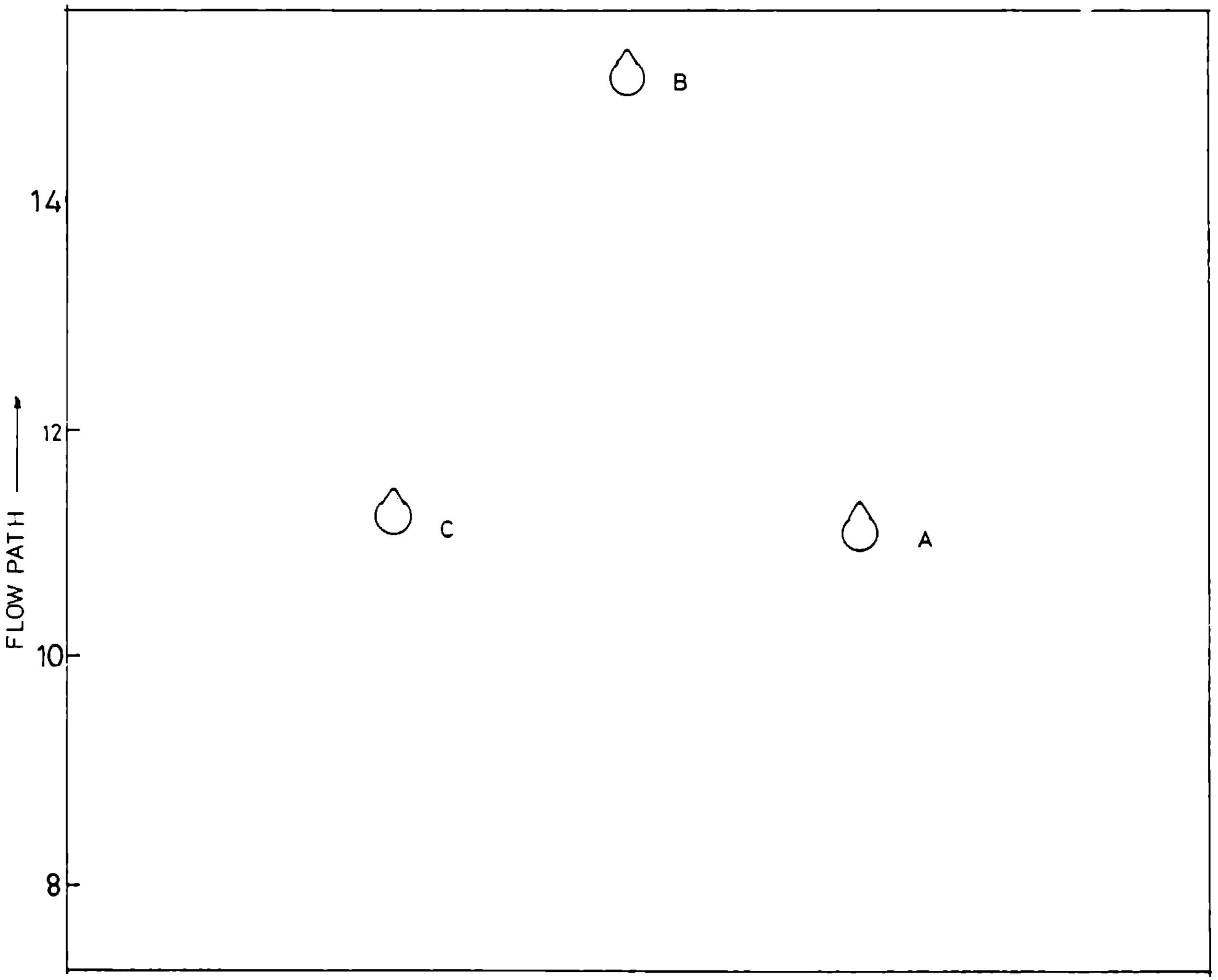
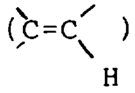


Fig.4.2: TLC of compounds; (A) NR-DA, (B) DA, (C) depolymerised NR

NR-DA. NR was not coloured by ninhydrin while NR-DA and DA were coloured. The R_F value of NR-DA was found to be almost equal to that of depolymerised NR. This also indicates that diphenylamine gets chemically attached to depolymerised natural rubber during UV irradiation.

Fig.4.3 shows the GPC traces of depolymerised NR and NR-DA. The molecular weight of NR-DA ($\bar{M}_w$ - 2300) is found to be very close to that of depolymerised NR ($\bar{M}_w$ - 2100). This shows that depolymerised NR gets chemically attached to one of the parapositions of diphenylamine.

Figs.4.4 and 4.5 show the IR spectra of depolymerised NR and NR-DA. The IR spectrum of depolymerised NR shows peaks at 3000 cm^{-1} corresponding to aliphatic C-H, 1665 cm^{-1} due to (C=C), 1400 cm^{-1} due to ($-CH_3$) and 835 cm^{-1} due to $-C(CH_3)=CH-$. IR spectrum of NR-DA shows additional peaks at 1500 cm^{-1} (N-H bending), 1350 cm^{-1} (C-N vibration) and 3400 cm^{-1} (N-H stretching). This confirms the chemical binding of diphenylamine to depolymerised NR during UV irradiation[7].

Fig.4.6 shows the 'H-NMR spectrum of depolymerised NR. There are peaks at $\delta = 5.1$  $(>C=C<_{H})$, $\delta = 1.5(-CH_2-)$ and

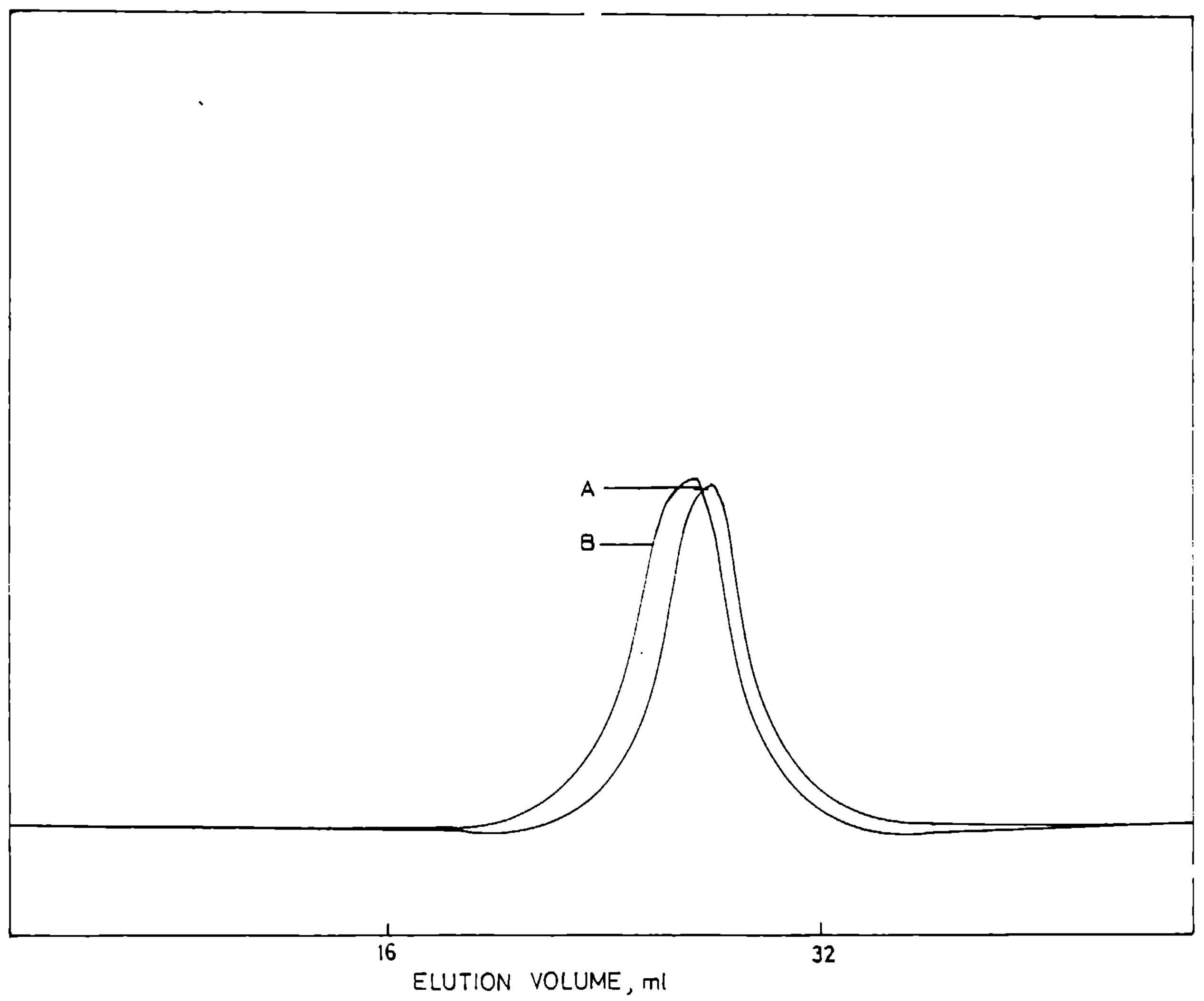


Fig.4.3: GPC traces of (A) depolymerised NR, (B) NR-DA

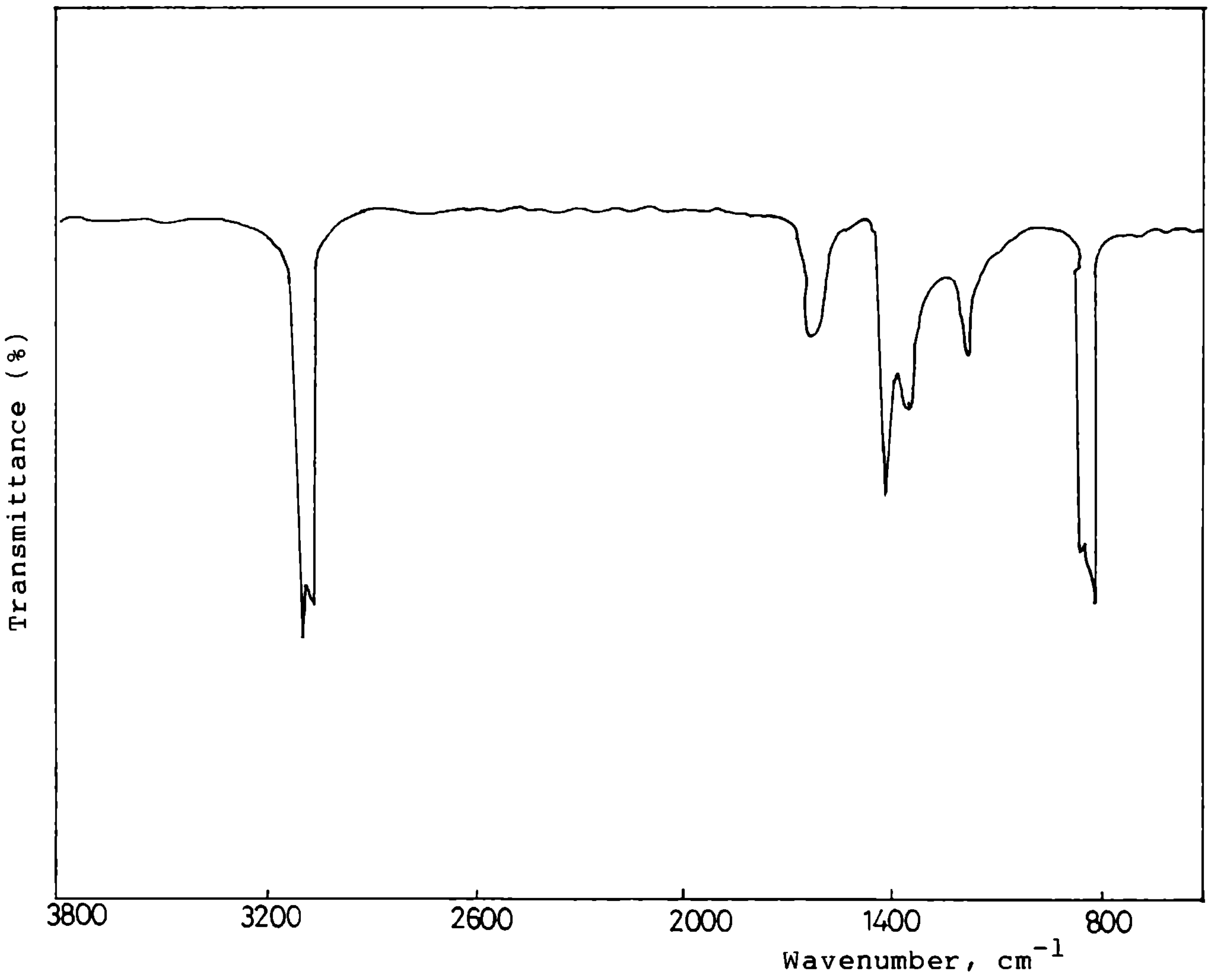


Fig.4.4: IR spectrum of depolymerised NR

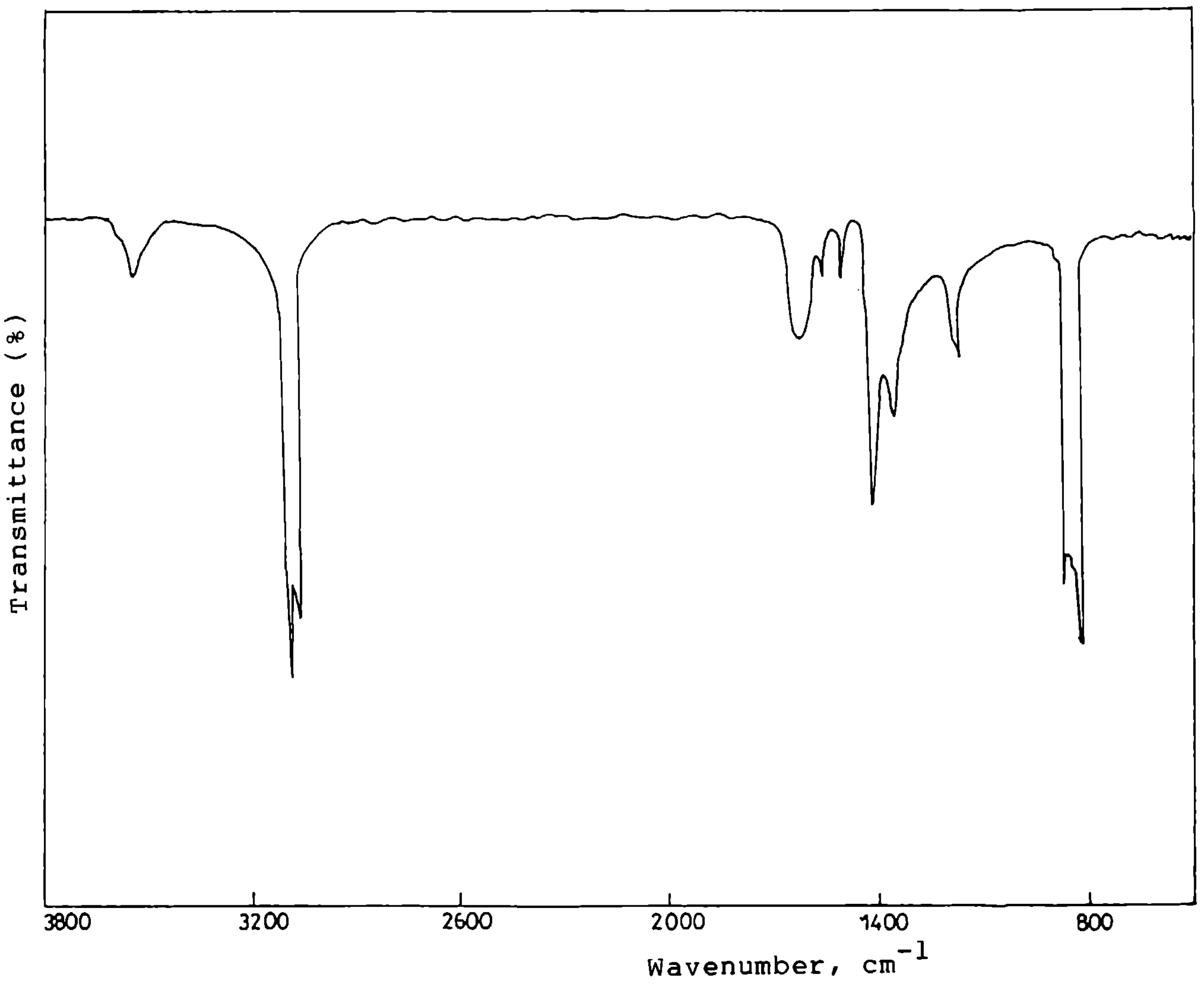


Fig.4.5: IR spectrum of NR-DA

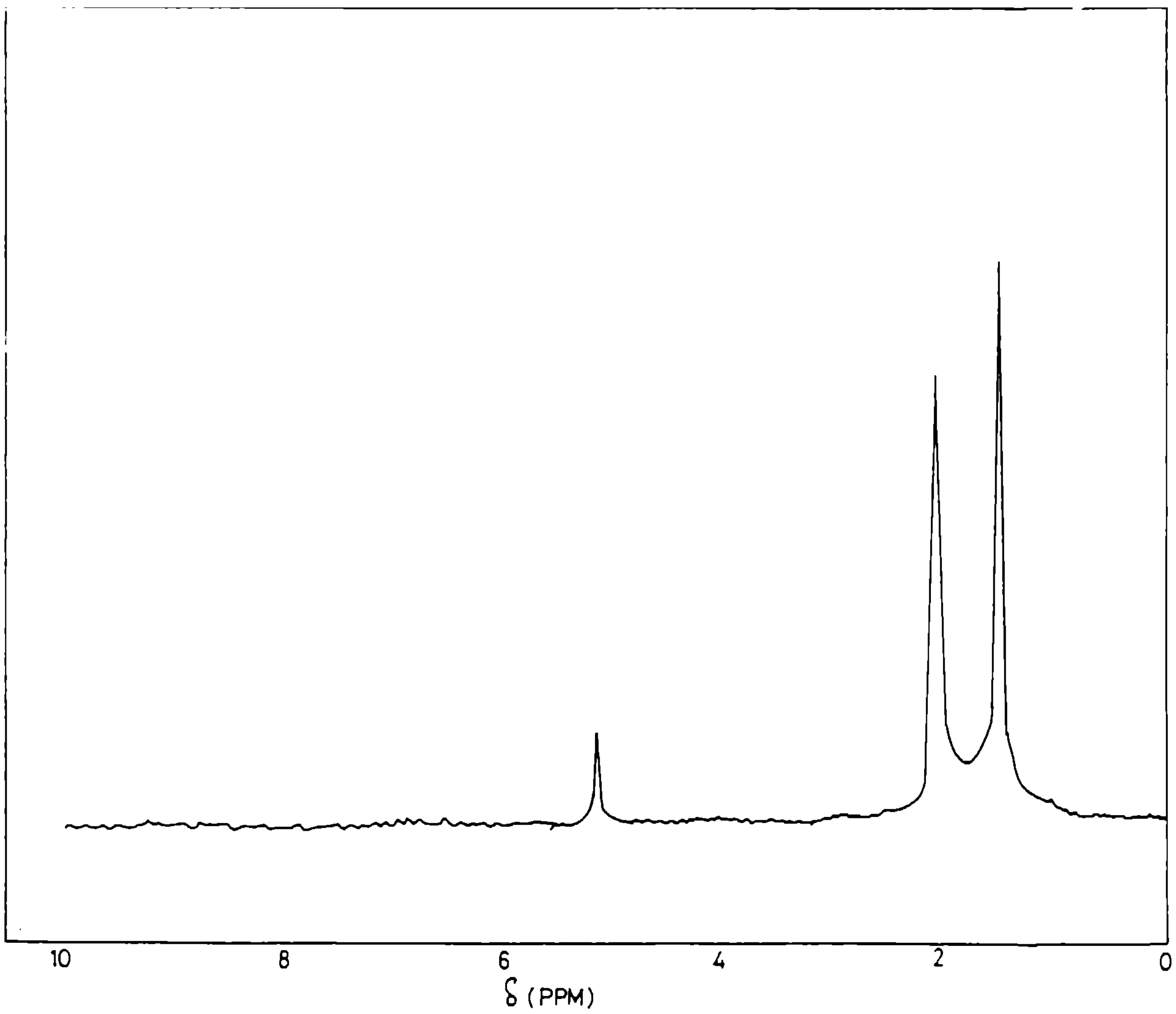


Fig.4.6: 'H-NMR spectrum of depolymerised NR

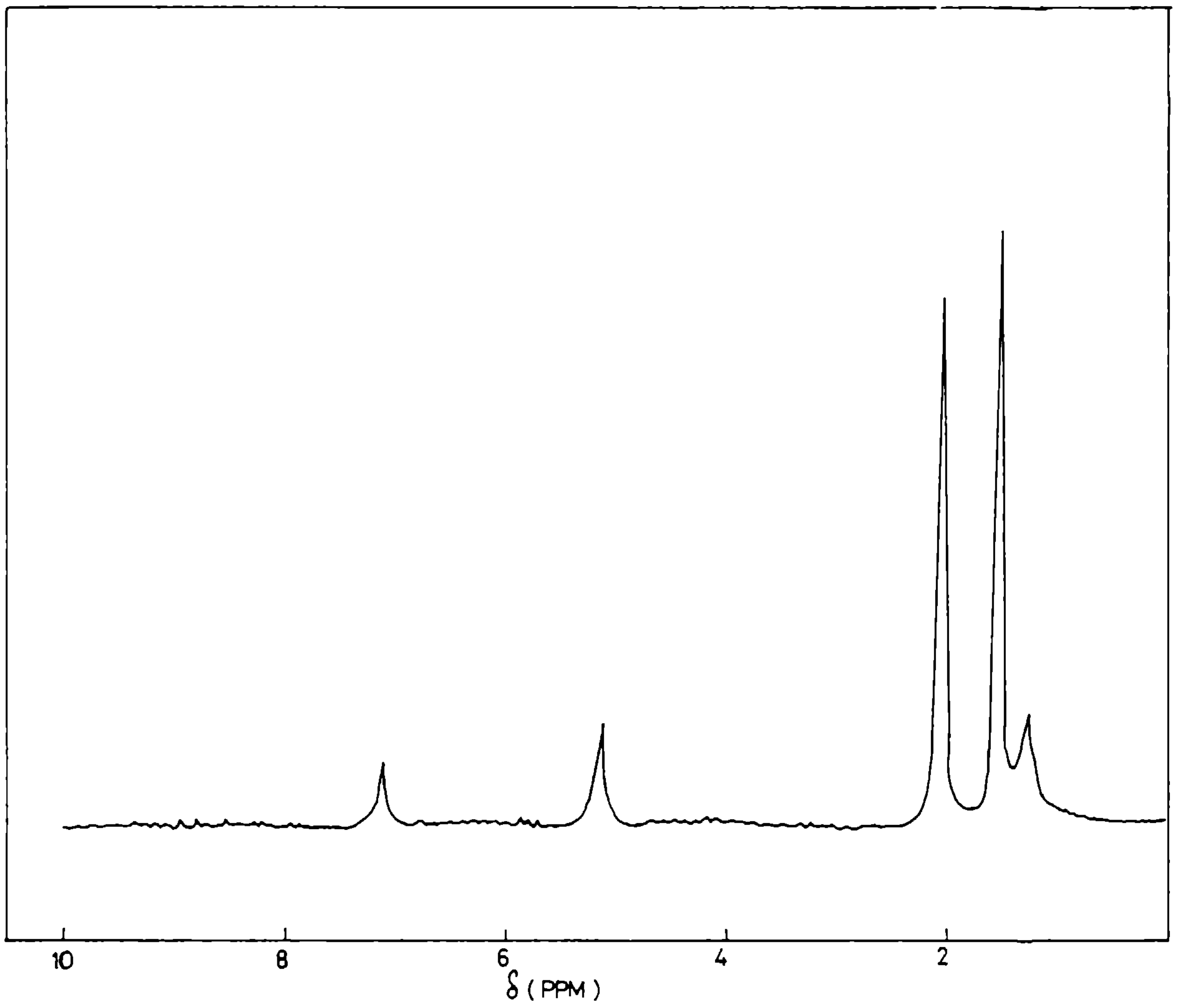
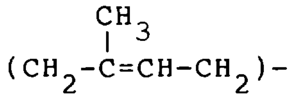
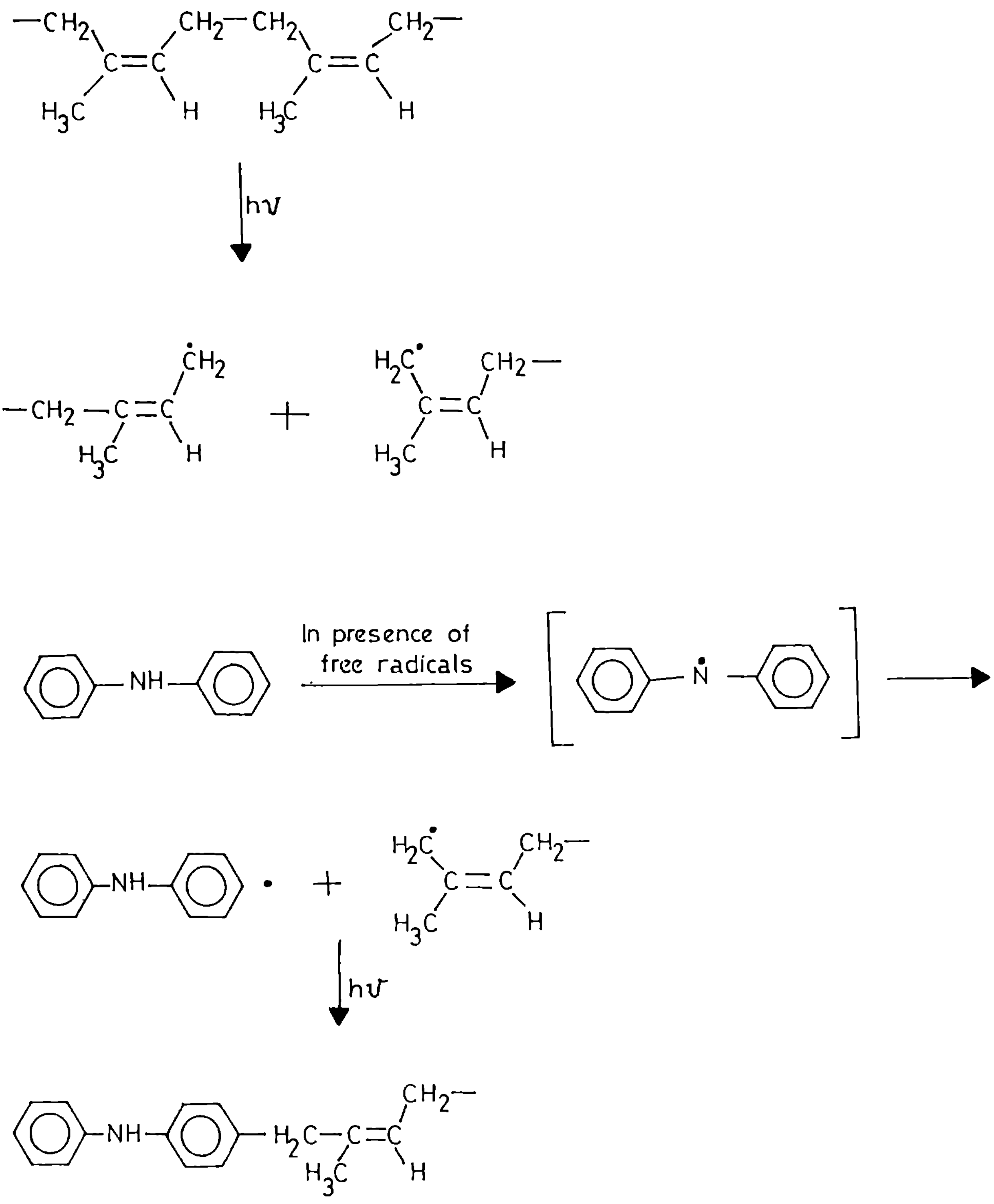


Fig.4.7: 'H-NMR spectrum of NR-DA

1.95 ppm ($-CH_3$). Fig.4.7 shows 'H-NMR spectrum of NR-DA, which has additional peaks at δ=1.2 and δ = 7.1 ppm corresponding to amino group and aromatic ring present in diphenylamine[7]. This again confirms the chemical binding of diphenylamine to depolymerised natural rubber.

In the case of NR the σ— bond between α-methylenic groups which connect the isoprene units are not in the same plane with the double bonds. This is because there is a tendency of coiling up of the rubber segments due to its cis configuration. The steric hindrance caused by such an unbalanced structure with pendent methyl groups weakens the CH_2-CH_2 bond leading to its rupture under favourable conditions which are provided by thermal energy or radiation[8-10]. Further, the presence of isoprene unit  $(CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2)-$ was evidenced in the IR spectra of NR-DA (Fig.4.5, 835 cm^{-1}). Based on the complex transformations of aromatic secondary amine during ageing in presence of substituted hydrocarbon and from the mechanism of degradation of NR, a possible mechanism can be suggested for the attachment of diphenylamine to depolymerised NR[8,11-16] (Scheme 4.1).



Scheme 4.1

Fig.4.8 shows the thermograms of NR-DA and DA. The low molecular weight DA volatilises easily while rubber bound DA is less volatile.

Fig.4.9 shows the variation in tensile strength after ageing with concentration of NR-DA. The tensile strength retention is found to increase with the amount of chemically bound antioxidant, reach a maximum and then level 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.4.10 shows the cure curves of the compounds shown in Table 4.1. There is only a marginal variation in the optimum cure time and scorch time of the compounds. The compound containing NR-DA cures at a slightly lower rate compared to the other compounds. This may be due to the co-crosslinking of NR-DA with natural rubber.

Fig.4.11 shows the tensile strength of the vulcanizates, before and after ageing. All vulcanizates show fairly good resistance to ageing at 100°C for 24h but

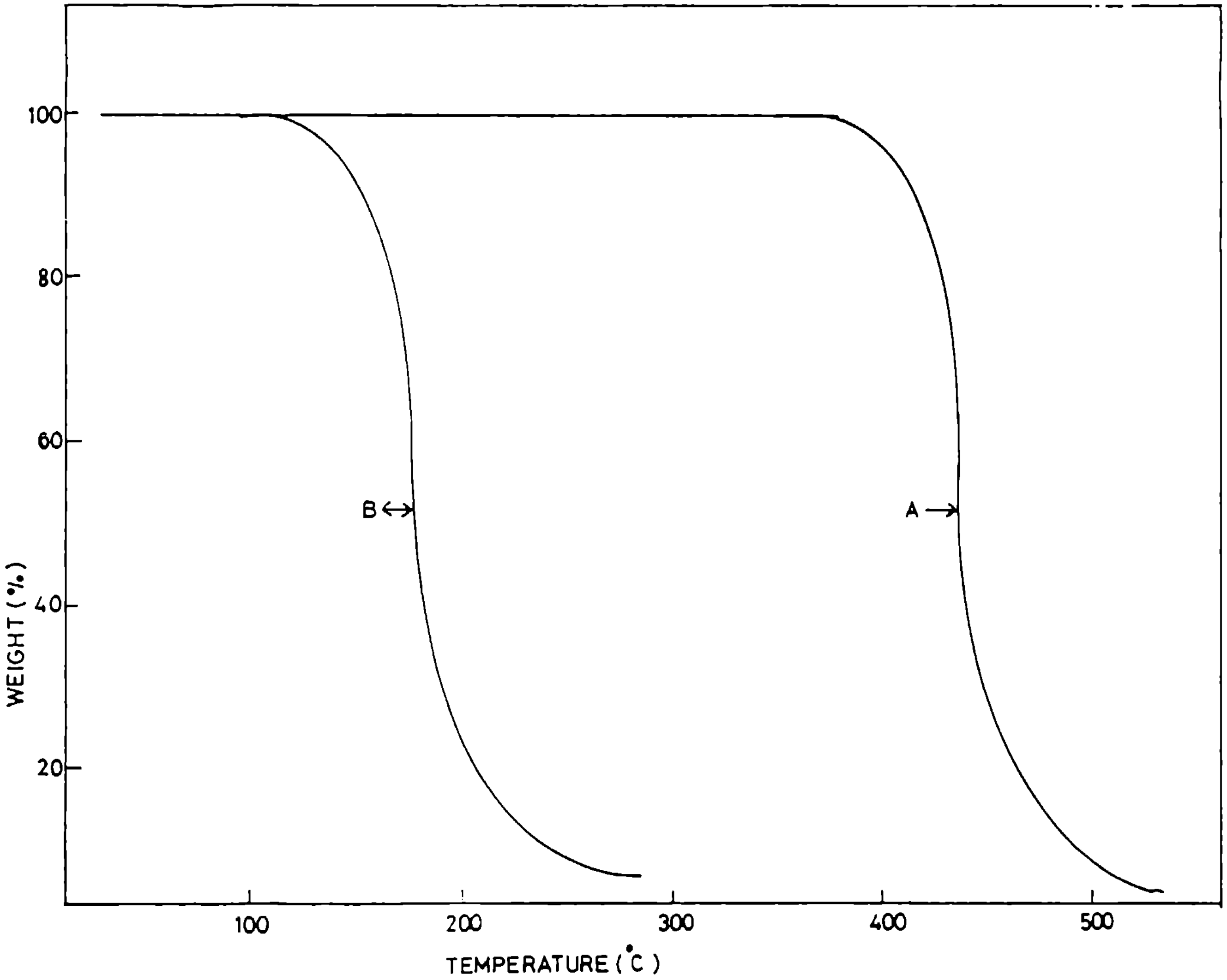


Fig.4.8: Thermograms of antioxidants; (A) NR-DA, (B) DA

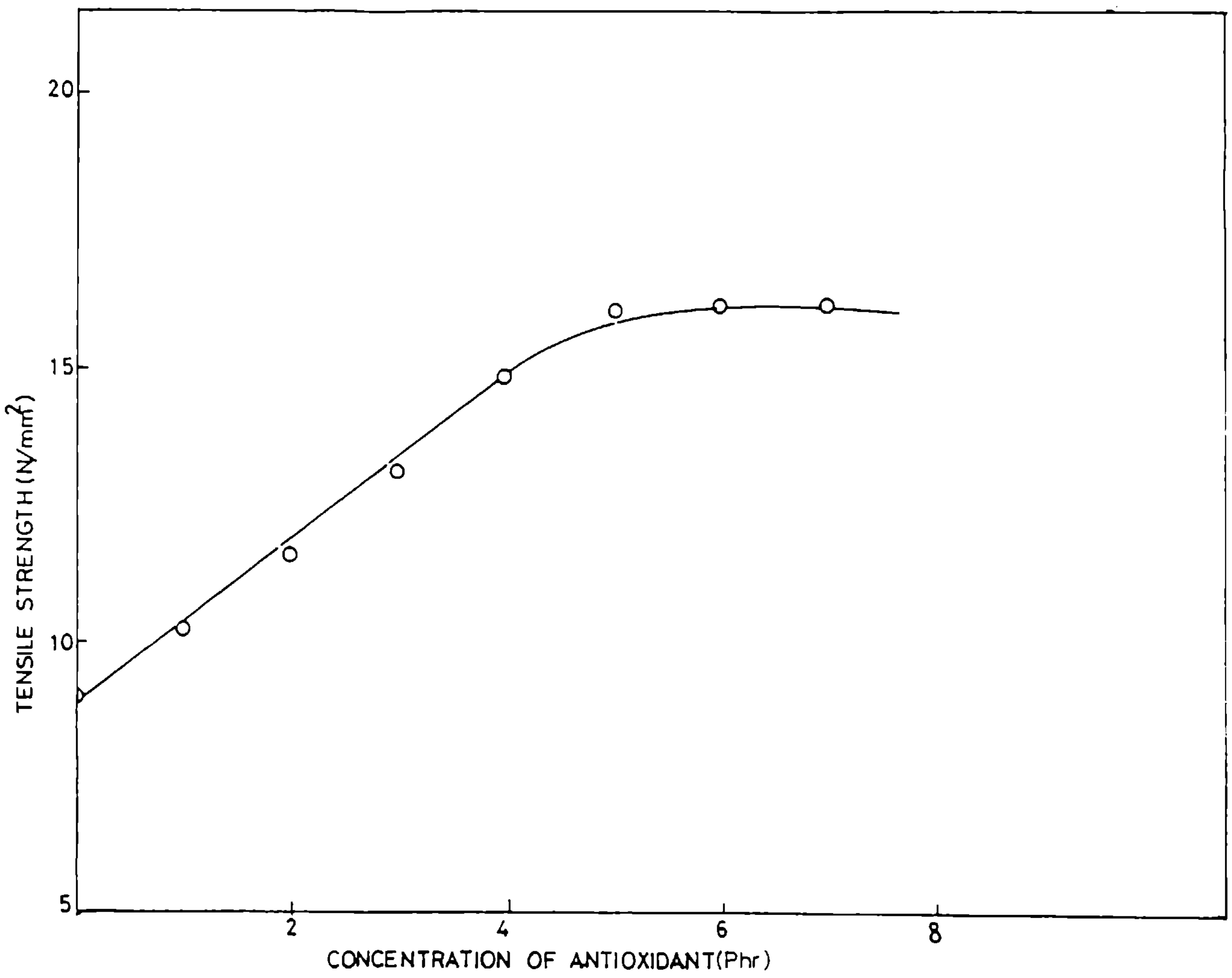


Fig.4.9: Variation in tensile strength after ageing with concentration of antioxidant

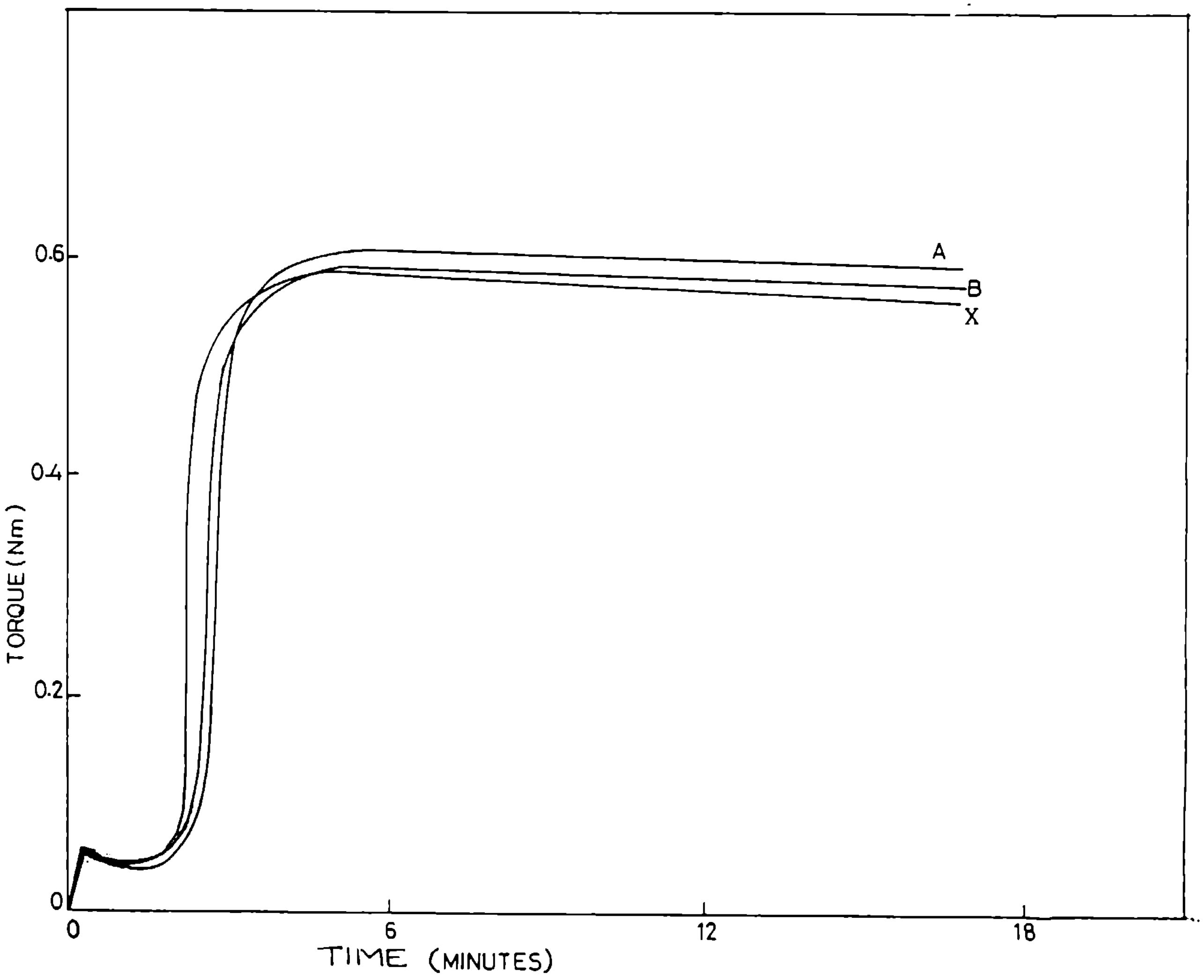


Fig.4.10: Cure curves of the compounds; (A) NR-DA, (B) pilflex-13, (X) without antioxidant

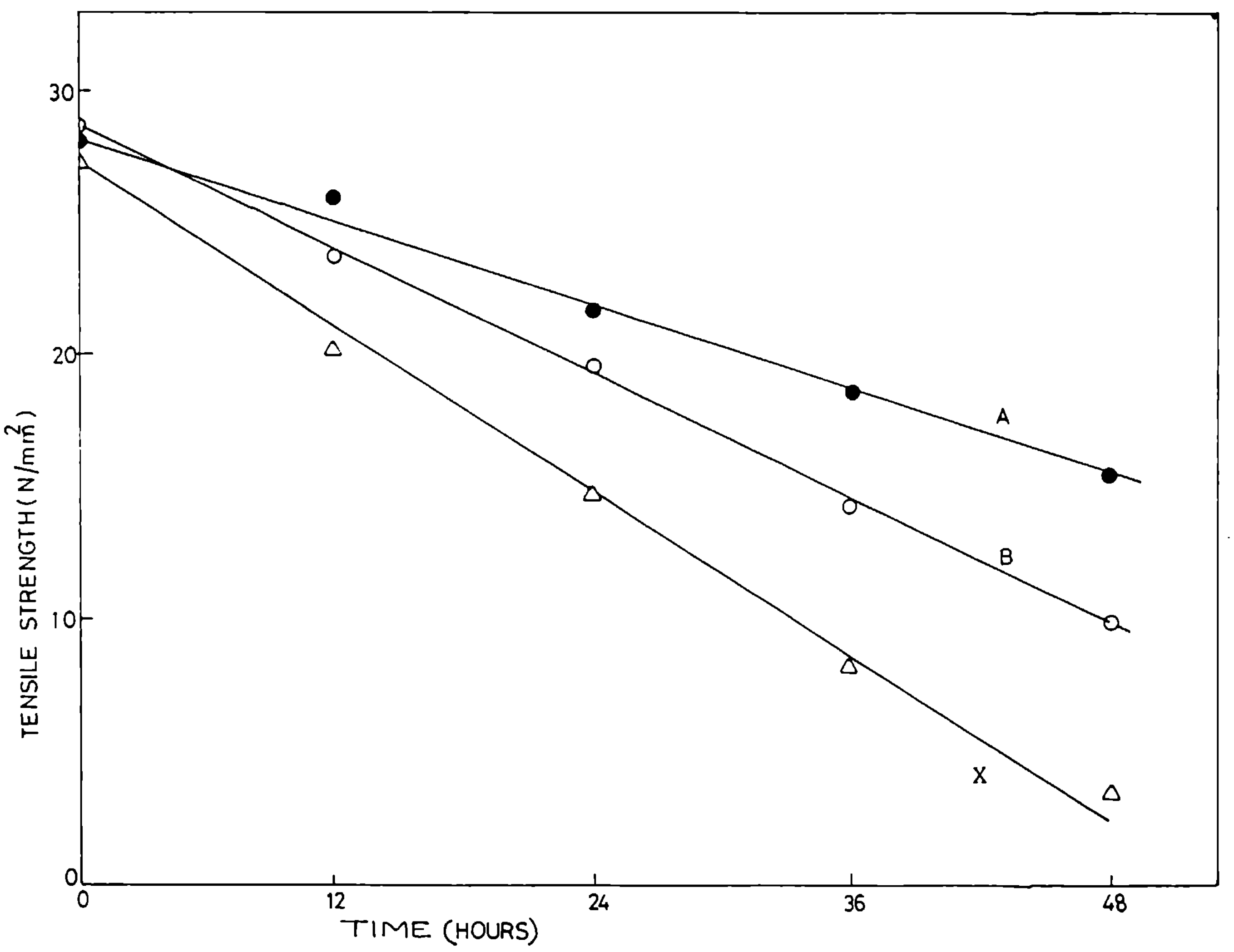


Fig.4.11: Variation in tensile strength of the vulcanizates before and after ageing at 100°C; (A) NR-DA, (B) pilflex-13, (X) without antioxidant

the compound containing NR-DA alone shows good ageing resistance when ageing time was increased to 48h, which shows the superiority of NR-DA over pilflex-13.

Figs.4.12 and 4.13 show the change in elongation at break and tear strength of the vulcanizates before and after ageing. The compound containing NR-DA shows better retention in elongation at break after ageing. This again shows that the bound antioxidant can improve the ageing resistance of NR compounds. Retention in tear strength by the compound containing NR-DA again confirms the superiority of the bound antioxidant.

Fig.4.14 shows the change in modulus of the vulcanizates before and after ageing. The increase in modulus after ageing may be due to the increase in total crosslink density due to the co-crosslinking of NR-DA with NR and the shortening of polysulphidic crosslinks.

Table 4.2 shows the variation in tensile strength, elongation at break, and modulus of the vulcanizates before and after ageing, after extracting the samples in acetone and methanol. The better retention in properties by the

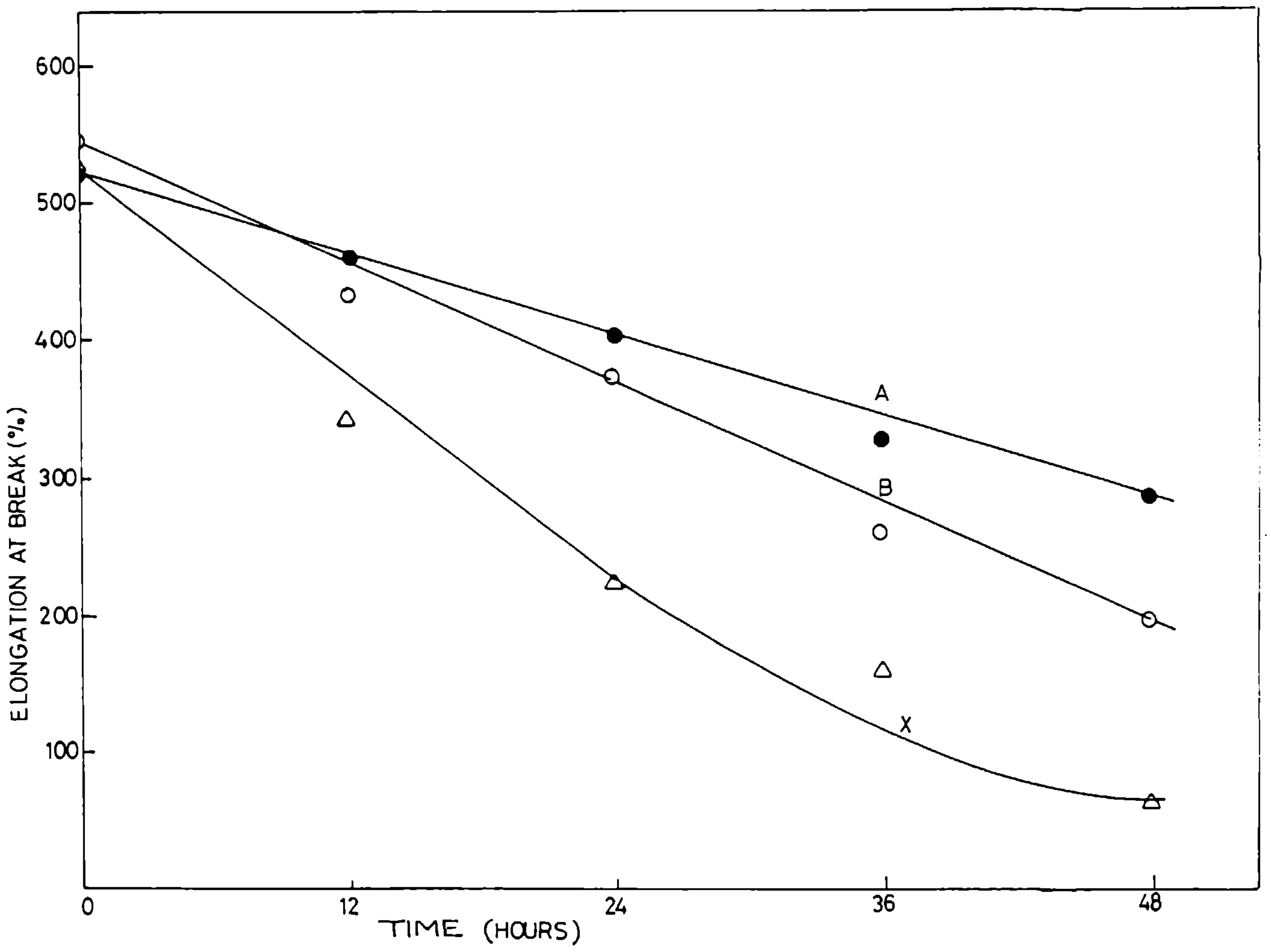


Fig.4.12: Variation in elongation at break of the vulcanizates before and after ageing at 100°C; (A) NR-DA, (B) pilflex-13, (X) without antioxidant

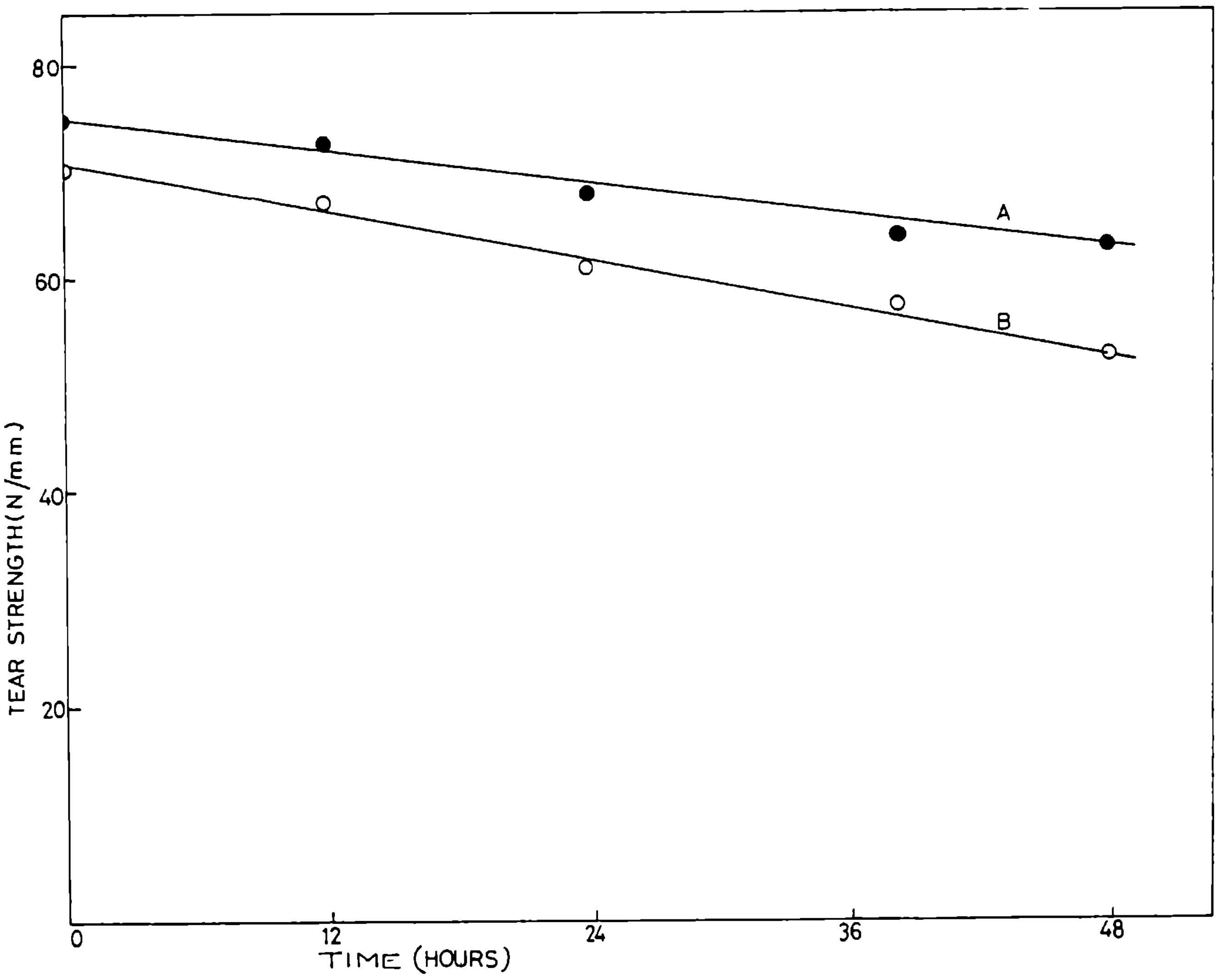


Fig.4.13: Variation in tear strength of the vulcanizates before and after ageing; (A) HTNR-DA, (B) pilflex-13

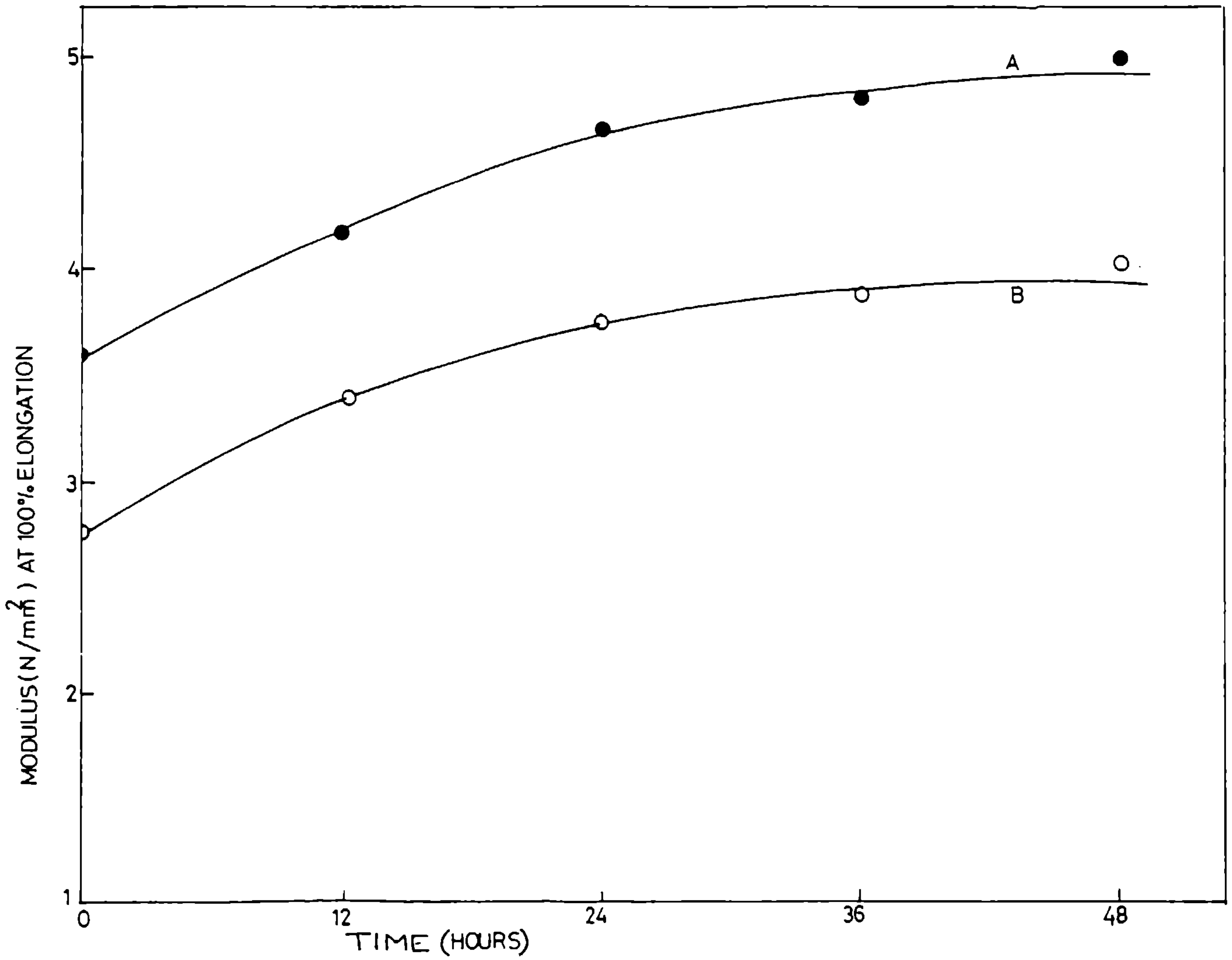


Fig.4.14: Variation in modulus of the vulcanizates before and after ageing; (A) HTNR-DA, (B) pilflex-13

Table 4.2: Properties before and after solvent extraction (48h at room temperature) followed by ageing at 100°C for 48 h

Properties	Properties before extraction		Properties after extraction followed by ageing at 100°C for 48h			
			Methanol		Acetone	
	A	B	A	B	A	B
Tensile strength (N/mm^2)	28.21	28.60	14.88	8.55	14.37	8.17
Elongation at break (%)	510.40	543.16	260.42	189.65	250.42	168.63
Modulus at 100% elongation (N/mm^2)	3.62	2.76	5.64	5.27	5.63	4.82

vulcanizate containing NR-DA is probably due to the lower extractability of the NR-DA by solvents.

Conclusions

1. Diphenylamine can be chemically attached to depolymerised natural rubber by photochemical reaction.

2. The rubber bound antioxidant has much superior resistance to volatility and extractability compared to conventional antioxidants.

3. The rubber bound antioxidant can improve the ageing resistance of natural rubber vulcanizate.

4. The rubber bound antioxidant can reduce the amount of plasticiser.

II. PREPARATION AND CHARACTERISATION OF NATURAL RUBBER BOUND PARAPHENYLENEDIAMINE ANTIOXIDANT AND ITS APPLICATION IN FILLED NBR VULCANIZATES

Experimental

a) Preparation of NR bound paraphenylenediamine

Natural rubber was masticated for 30 minutes at 50°C. 100 g of it was dissolved in one litre toluene and the solution was charged into a photochemical reactor, a glass vessel of 3 litre capacity fitted with water condenser and mechanical stirrer. High pressure mercury vapour lamp in a quartz immersion well was placed in the solution. After 60 h exposure to a part of depolymerised rubber solution, 25 g paraphenylenediamine dissolved in acetone was added slowly with stirring and irradiation was continued. Samples taken after 1,2,3,4,5,6,7,10,12 and 15h of exposure after adding paraphenylenediamine were poured into excess of methanol with stirring, when liquid rubber precipitated. The unreacted paraphenylenediamine was removed by repeated re-precipitation using a toluene-methyl alcohol (1:1 v/v) mixture, and the product was dried in a vacuum oven. The rubber bound antioxidant was obtained in the form of viscous liquid. Samples taken after different times of exposure were added in nitrile rubber compounds as per formulation given in Table 4.3(A). The optimum exposure time for preparing rubber bound antioxidant was determined by studying the retention in tensile strength after ageing the vulcanizates at 100°C for 48h. Maximum retention in tensile strength was obtained for vulcanizates containing the rubber bound samples produced by exposure for 6h and above. So, the time of UV irradiation after adding paraphenylenediamine was fixed as 6h. The bound antioxidant was prepared by irradiating depolymerised rubber with paraphenylenediamine for 6h. Hereafter the product is referred to NR-PD. Rest of the depolymerised rubber solution was irradiated continuously. Samples were taken after 1,2,3,4,5,6,7,10,12 and 15h of exposure, precipitated as above, and employed in nitrile rubber compounds as per the formulation given in Table 4.3(D).

Brookfield viscosities of the reaction mixture were measured at 0, 60 and 66h of irradiation using a Brookfield Synchro-lectric viscometer Model RVT.

b) Analysis of NR bound paraphenylenediamine (NR-PD)

Analysis of the bound antioxidant was carried out by thin layer chromatography (TLC), infrared spectroscopy (IR), proton magnetic resonance spectroscopy ('H-NMR) and thermogravimetric analysis (TGA). TLC was carried out using silica gel as the adsorbent, and mixed solvent, benzene and ethylacetate (4:2, v/v), was used as the developing solvent for all samples. Diazotisation using nitrous acid fumes was carried out to detect the antioxidants and iodine for depolymerised NR[17].

Molecular weight of the rubber bound antioxidant $\overline{M}_v$ was calculated using Mark-Houwink-Sakurada equation by measuring the intrinsic viscosity using an Ubbelohde viscometer and substituting the values K (5.02×10^{-2} ml/g) and a (.667) for natural rubber.

The optimum concentration of the rubber bound antioxidant for getting maximum retention in properties after ageing was determined by varying the amount of antioxidant in a standard formulation (Table 4.3(A)) from 1 to 10 phr. Paraphenylenediamine bound to NR and conventional antioxidants, vulkanox HS and vulkanox 4020 were added in NBR as per formulations given in Table 4.3. The optimum cure times and scorch times of the compounds were determined on a Goettfert Elastograph model 67.85 as per ASTM D-1646 (1981). Rubber compounds were moulded in an electrically heated laboratory hydraulic press at 150°C upto their optimum cure times. Dumbell shaped tensile test pieces were punched out of these compression moulded sheets along the mill grain direction. The tensile properties and tear resistance of the vulcanizates were evaluated on a Zwick Universal Testing machine model 1445 as per ASTM D 412 - 80 and ASTM D 624 - 81 respectively. Hardness, compression set, rebound resilience, flex resistance and abrasion resistance of the vulcanizates were evaluated as per relevant ASTM standards.

Table 4.3

Formulations for testing the antioxidants

Ingredients	X	A	B	C	D
Acrylonitrile-Butadiene Rubber (NBR) (phr)	100	100	100	100	100
Sulphur	1.5	1.5	1.5	1.5	1.5
Zinc oxide	4.0	4.0	4.0	4.0	4.0
Stearic acid	2.0	2.0	2.0	2.0	2.0
Carbon black (HAF, N 330)	40.0	40.0	40.0	40.0	40.0
Dioctyl phthalate	5.0	1.0	5.0	5.0	1.0
Dibenzthiazyl disulphide	1.0	1.0	1.0	1.0	1.0
Tetramethyl thiuram disulphide	0.5	0.5	0.5	0.5	0.5
Vulkanox 4020	-	-	1.0	-	-
Vulkanox HS	-	-	-	1.0	-
NR-PD	-	5.0	-	-	-
Depolymerised rubber	-	-	-	-	5

Efficiency and permanence of NR-PD were studied by evaluating the retention in tensile properties and tear strength after ageing the samples at 100°C for 12, 24, 36, 48 and 72h. Retention in compression set, heat build up, resilience, flex crack resistance and abrasion resistance was evaluated after ageing the samples at 100°C for 48h.

Oil resistance of the NR vulcanizates containing NR-PD was studied by keeping the samples in light oil, gear oil, transformer oil and engine oil at room temperature and also at 70°C for 24h. The retention in tensile properties, tear strength and hardness was evaluated. Solvent resistance of the bound antioxidant was studied in methanol and acetone by keeping the dumbell shaped test pieces, in methanol and acetone for 48h at room temperature. The retention in tensile properties of the samples after acetone and methanol extraction was evaluated after ageing the extracted samples at 100°C for 48h. Water extractability of the antioxidant was studied by keeping the samples in water at 70°C for 24h and also in boiling water for 10h. Retention in tensile properties, tear strength and hardness after water extraction was evaluated by ageing the samples at 100°C for

48 h. Swelling in oil of the vulcanizate containing NR-PD was studied by keeping a known weight of the sample in transformer oil and gear oil for 48 h at room temperature and then measuring the percentage increase in weight.

Results and Discussion

Fig.4.15 shows the variation in tensile strength after ageing at 100°C for 48h with exposure time after the addition of depolymerised natural rubber prepared in the presence and absence of paraphenylenediamine. The tensile strength retention is found to increase first, reach a maximum and then level off at an exposure time of 6h, on the addition of depolymerised natural rubber prepared in the presence of paraphenylenediamine. Also it shows that the ageing resistance of NBR vulcanizates is not influenced by the addition of depolymerised natural rubber.

Table 4.4 shows the Brookfield viscosities of the reaction mixture at 0, 60, and 66 h of exposure to uv irradiation. After 60 h exposure, Brookfield viscosity of the reaction mixture was considerably reduced. This shows that natural rubber was depolymerised considerably during uv irradiation. After the addition of paraphenylene diamine there is a slight increase in viscosity. This shows that after the addition of paraphenylenediamine, the

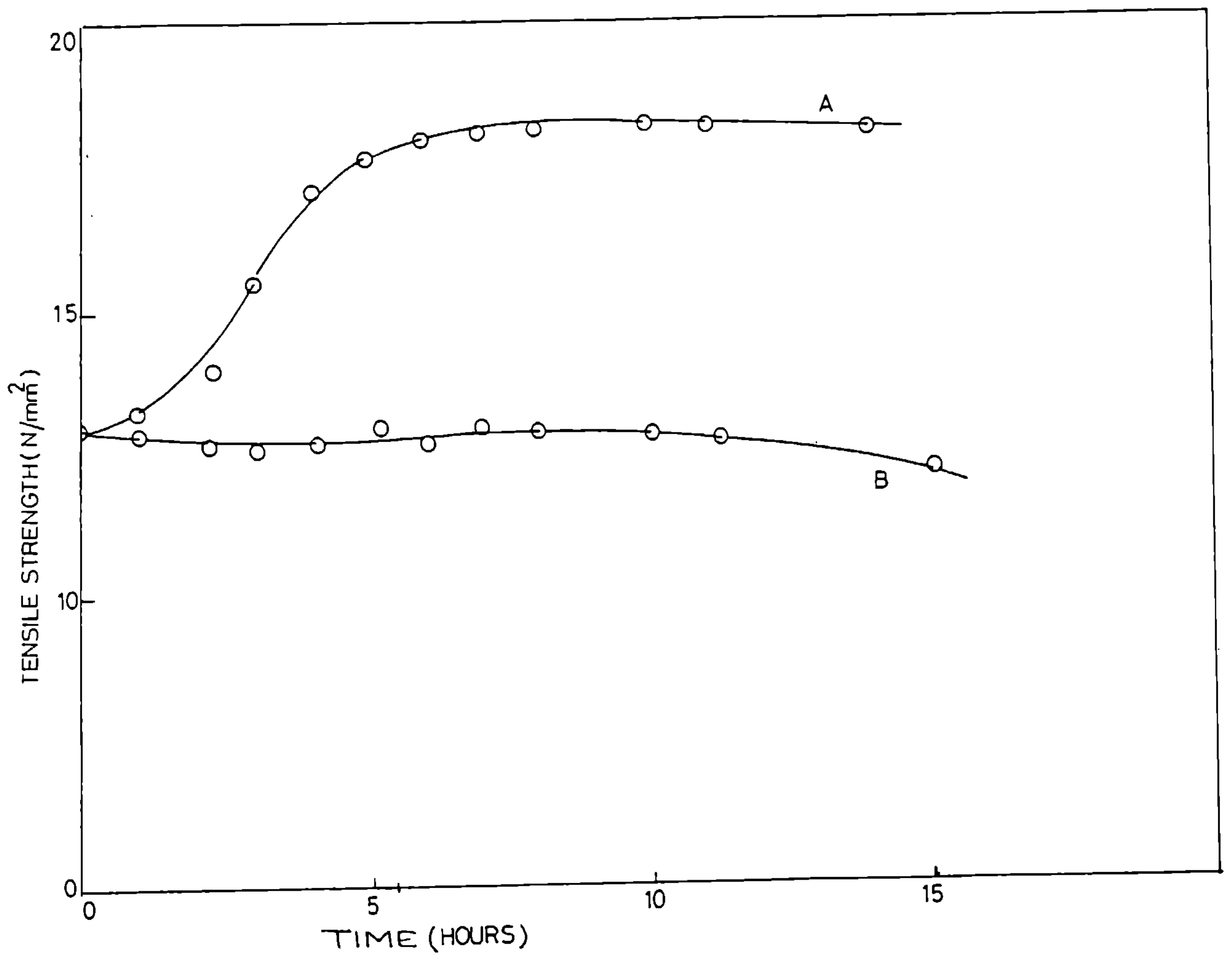


Fig.4.15: Variation in tensile strength after ageing with exposure time. A - NR-PD, B - Depolymerised NR.

Table 4.4

Brookfield viscosities of the reaction mixture of depolymerised natural rubber and paraphenylenediamine

Spindle speed (rpm)	Time of irradiation (h)					
	0		60		66	
	Brookfield viscosity (CPS) Spindle No.					
	I	II	I	II	I	II
10	225	50	18.5	3.5	20.5	4.5
20	230	52.5	20	4.5	25	5.0
50	Out of range	53	24	8.0	30	9.0
100		56.5	32	10	42.75	12.5

broken natural rubber chain, may be getting chemically attached to paraphenylenediamine.

Fig.4.16 shows the TLC of paraphenylenediamine, depolymerised NR (uv irradiated for an equivalent time) and NR-PD. Depolymerised NR was not coloured by nitrous acid/resorcinol system while NR-PD and paraphenylenediamine were coloured. The R_F value of NR-PD was found to be almost equal to that of depolymerised NR. This indicates that paraphenylenediamine gets chemically attached to depolymerised natural rubber during uv irradiation.

The viscosity average molecular weights of natural rubber and NR-PD were found to be 706496 and 2800 respectively. Figs.4.4 and 4.17 show the IR spectrum of depolymerised NR and NR-PD. IR spectrum of NR-PD shows additional peaks at 3400 cm^{-1} due to (N-H stretching primary) 3310 cm^{-1} (N-H stretching, secondary) 1590 cm^{-1} (N-H bending), 1350 cm^{-1} (C-N vibration) and 1500 cm^{-1} corresponding to aromatic ring in paraphenylenediamine.[7] This confirms the chemical binding of paraphenylenediamine to depolymerised natural rubber.

Figs.4.6 and 4.18 show the 'H-NMR spectrum of depolymerised NR and NR-PD. 'H-NMR of NR-PD shows additional peaks at

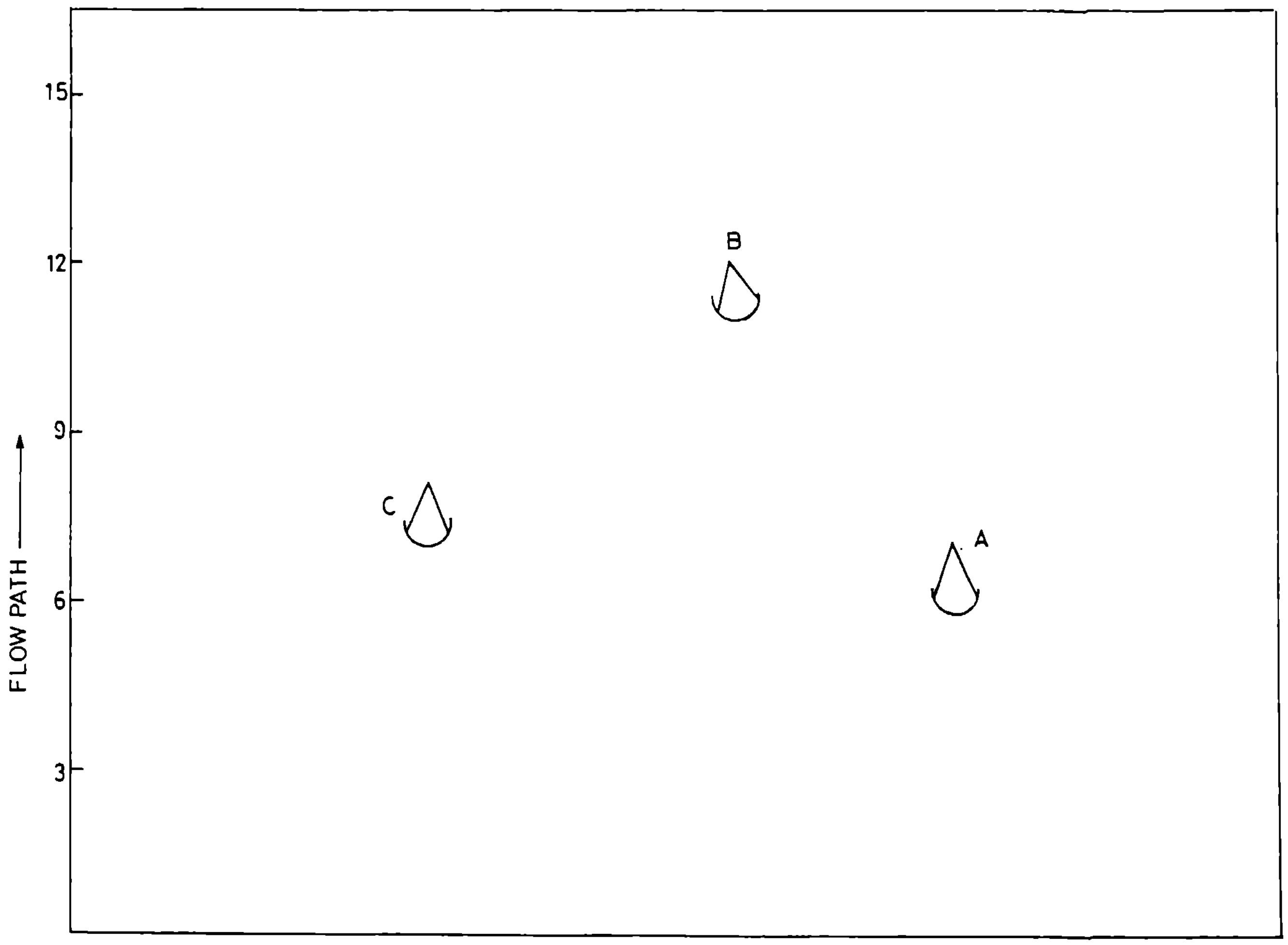


Fig.4.16: TLC of compounds; (A) NR-PD, (B) PD, (C) depolymerised NR

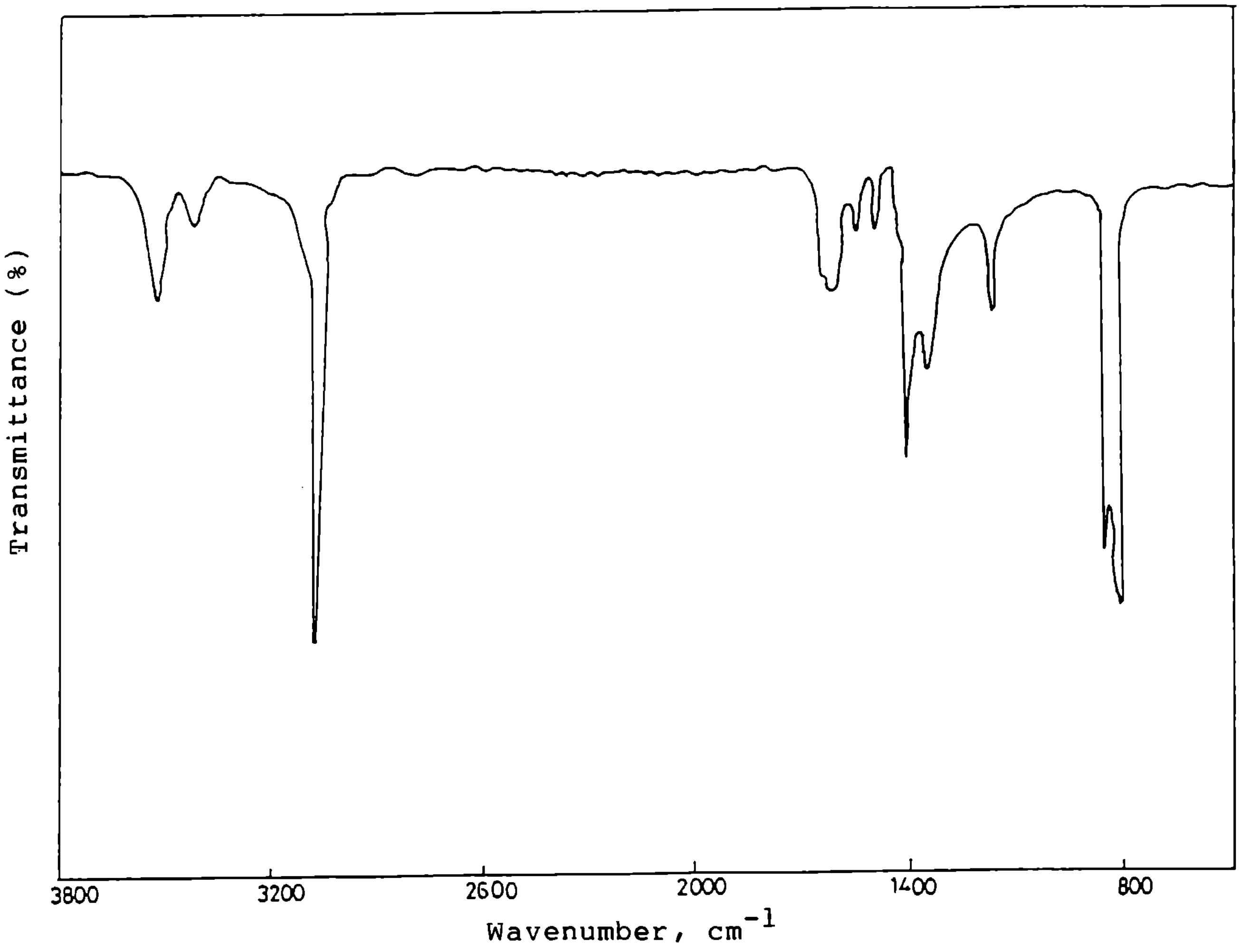


Fig.4.17 IR spectrum of NR-PD.

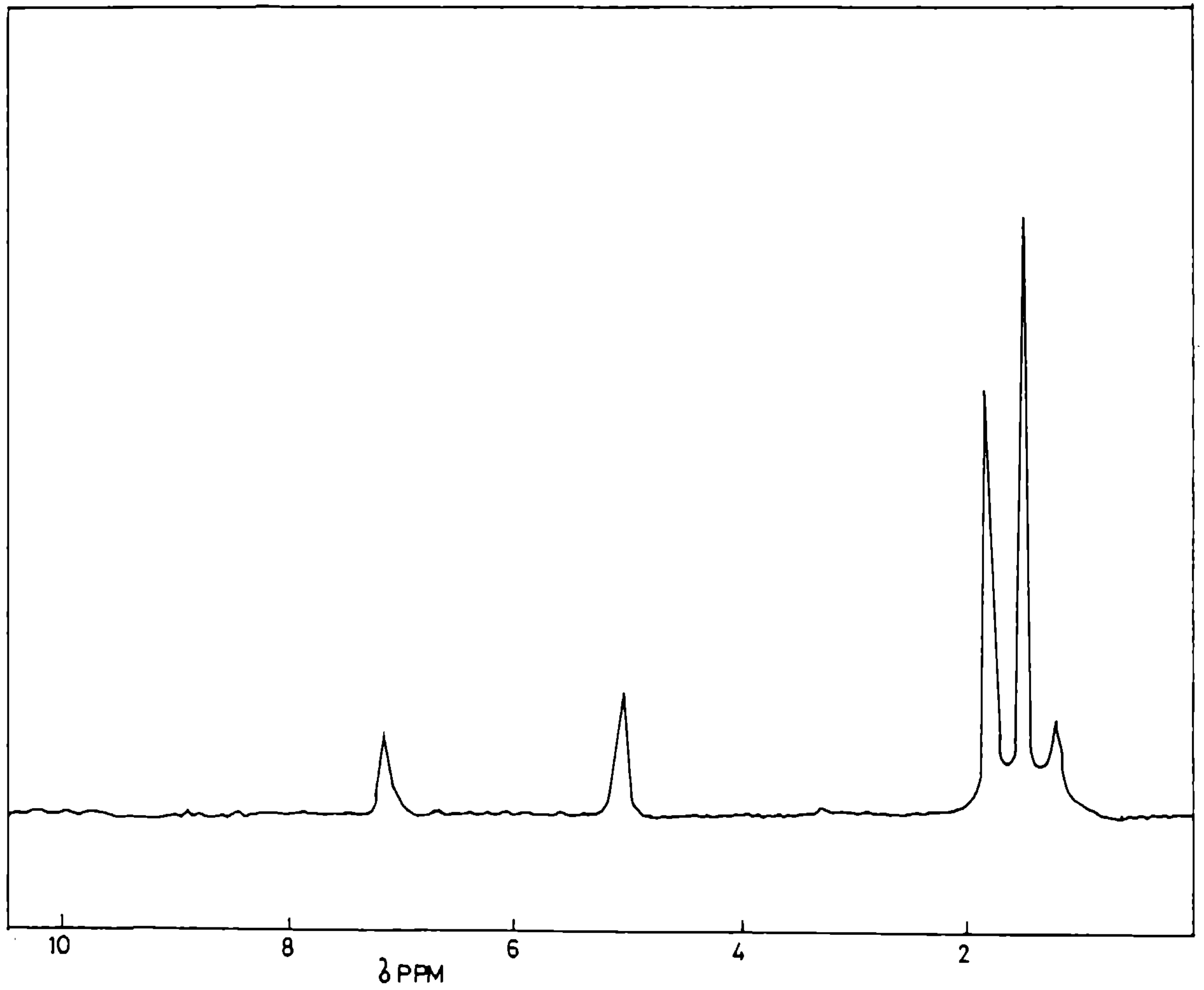


Fig.4.18: 'H-NMR spectrum of NR-PD

δ = 1.19 and δ = 7.1 ppm corresponding to amino group and aromatic ring present in paraphenylenediamine.

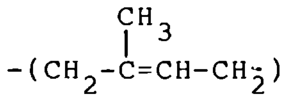
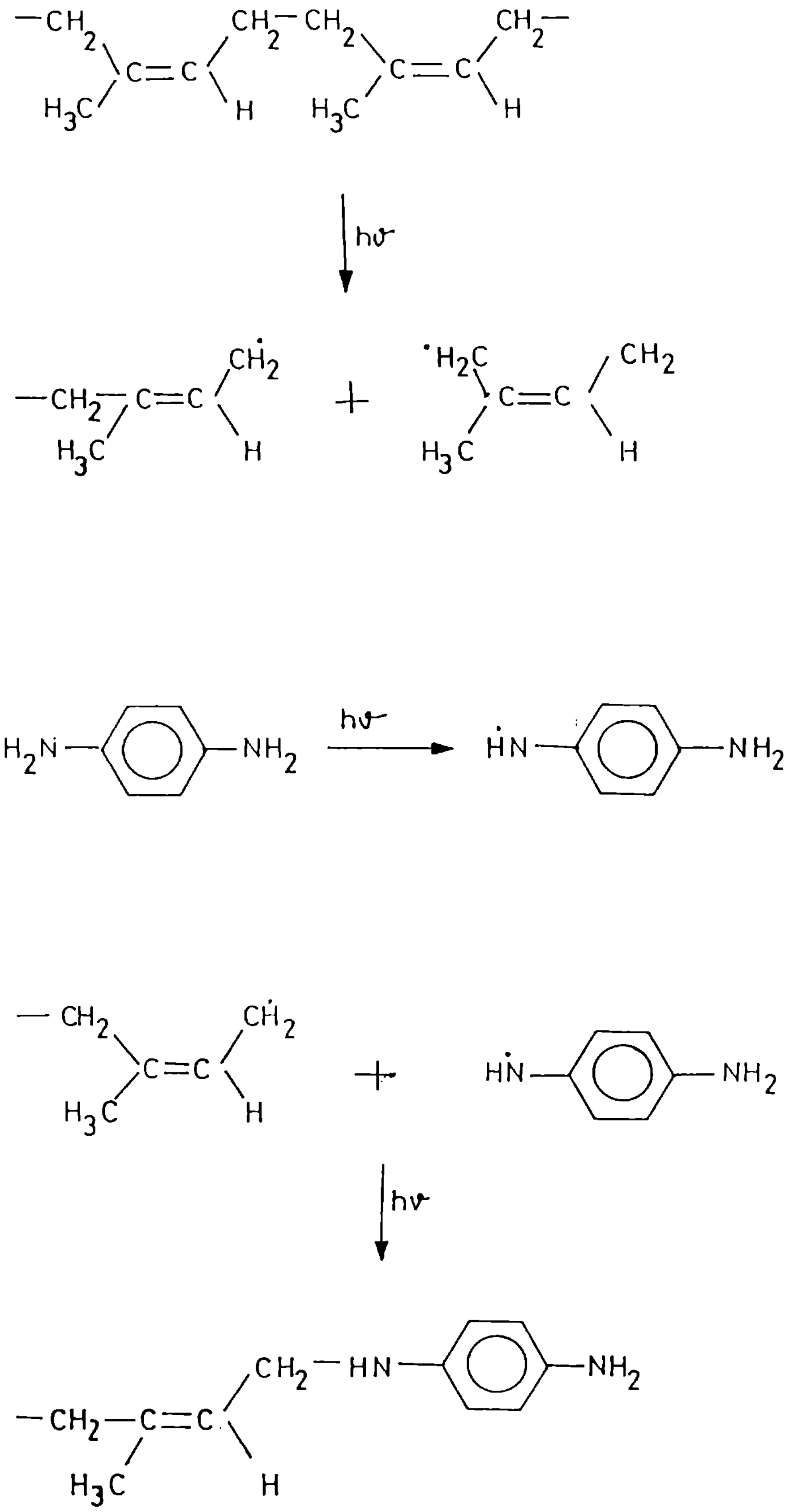
Free radical mechanism has been suggested for the photodegradation of NR.[8-10] The presence of  $-(CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2)$ group was evidenced from the absorption band of the isoprene unit in the IR spectra (Fig.4.17) at 835 cm^{-1} of NR-PD. Based on the photo-oxidation of paraphenylenediamine and from the mechanism of degradation of NR, a possible mechanism can be suggested for the attachment of paraphenylenediamine to depolymerised NR as shown in scheme 4.2[9,13-15,18].

Fig.4.19 shows the thermograms of paraphenylenediamine, vulkanox 4020 and NR-PD. Low molecular weight antioxidants volatilise easily while rubber bound paraphenylenediamine (NR-PD) is less volatile.

Fig.4.20 shows the variation in tensile strength after ageing with concentration of the bound antioxidant. The tensile strength retention increases with the amount of chemically bound antioxidant, reaches a maximum and then decreases. The decrease in tensile strength after an



Scheme 4.2

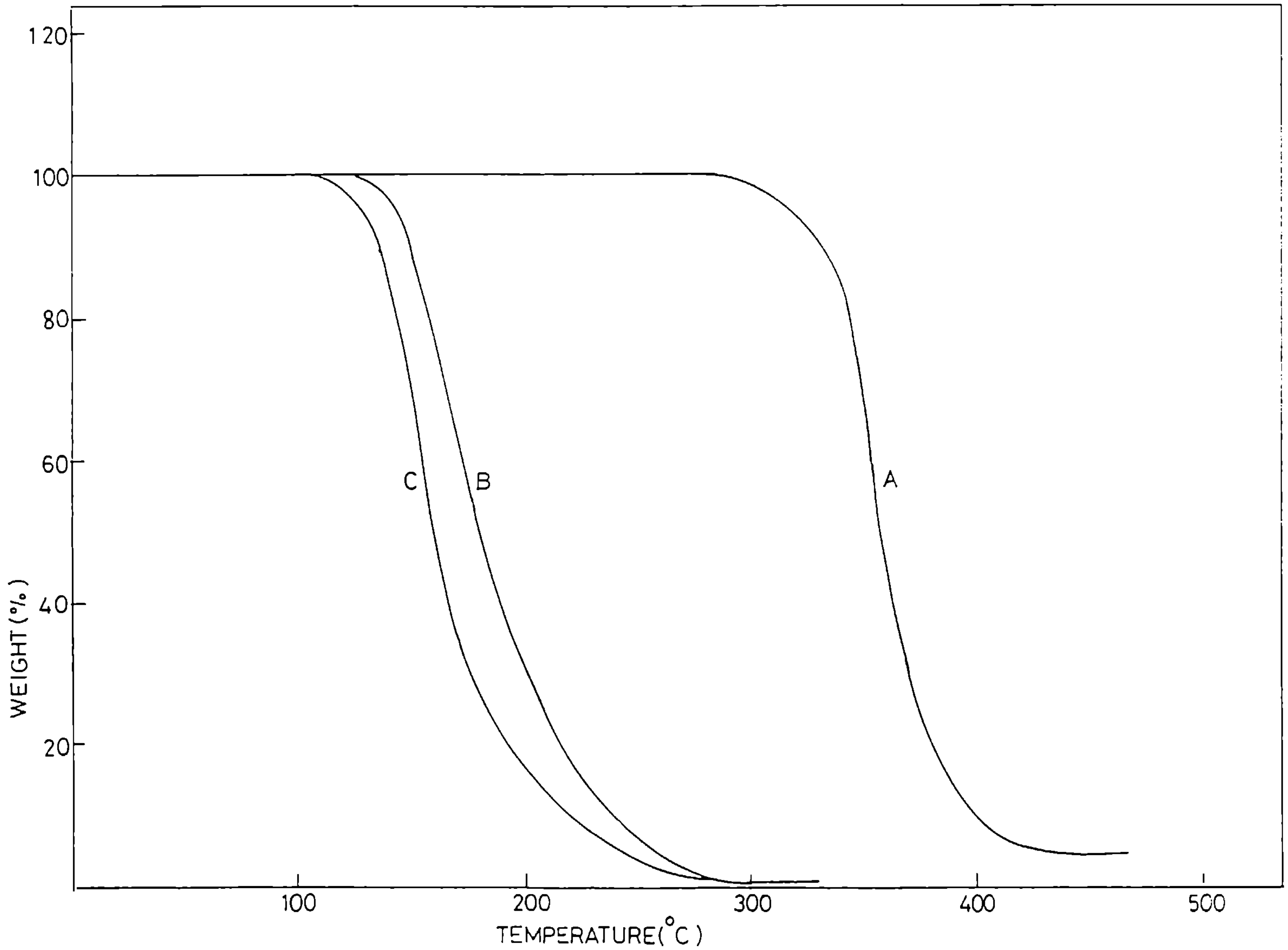


Fig.4.19 Thermograms of antioxidants. A - NR-PD, B - vulkanox 4020, C - PD.

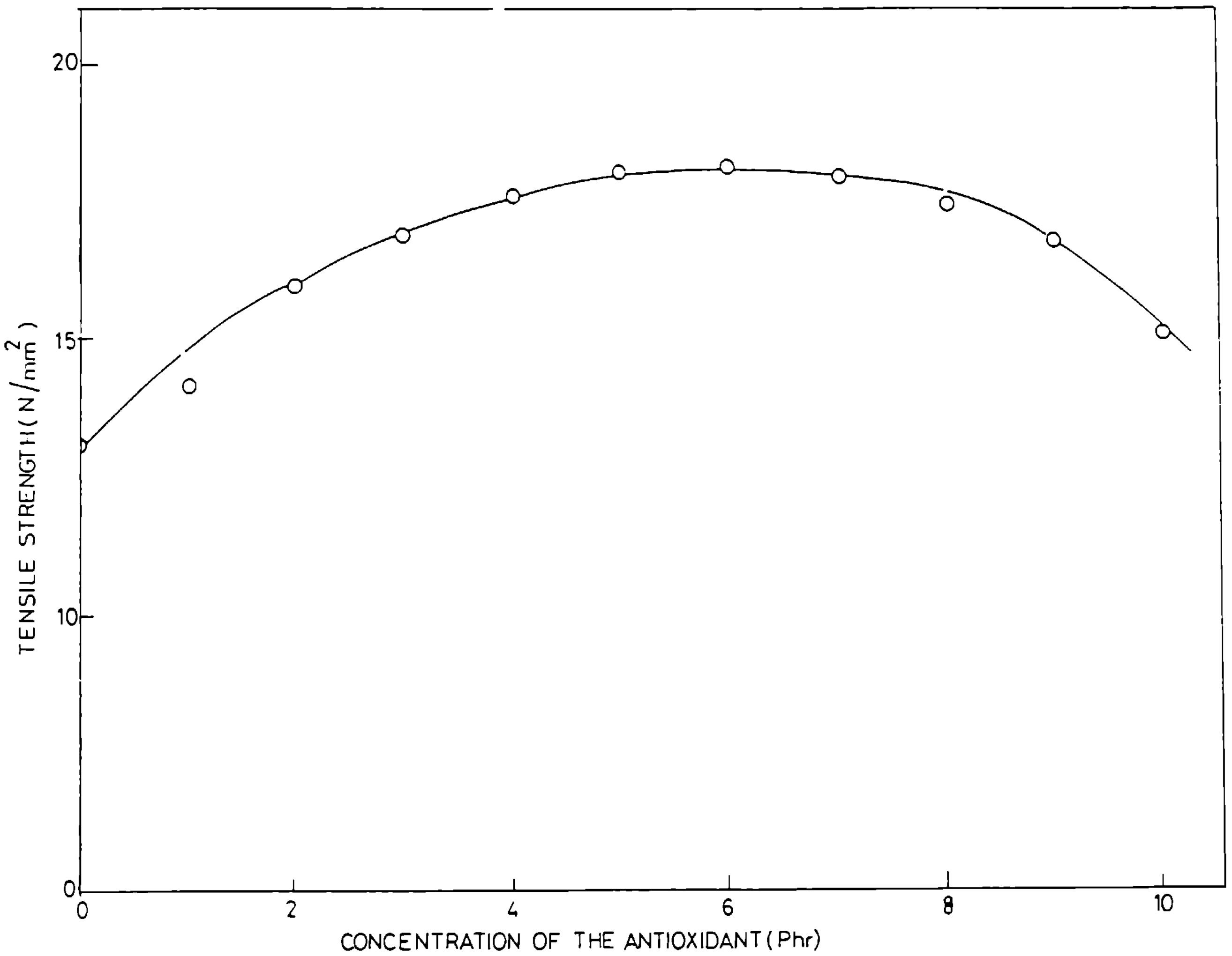


Fig.4.20: Variation in tensile strength after ageing with concentration of bound antioxidant

optimum level may be due to the incompatibility of bound antioxidant with NBR. The higher amount of bound antioxidant required may be due to lower amount of effective antioxidant in the bound product.

Fig.4.21 shows the cure curves of the compounds shown in Table 4.3. Scorch time and cure time of the compound containing NR-PD are found to be lower than those containing vulkanox HS and vulkanox 4020. This may be due to the presence of free amino group in NR-PD.[19]

Fig.4.22 shows the tensile strength of the above vulcanizates before and after ageing. All the vulcanizates show fairly good resistance to ageing at 100°C for 24h, but the compound containing NR-PD shows better ageing resistance, when ageing time was increased to 72h.

Figs.4.23 and 4.24 show the change in elongation at break and tear strength of the above vulcanizates before and after ageing. The vulcanizate containing the bound antioxidant shows lower elongation at break. This may be due to the lower amount of dioctylphthalate in the compound and the higher total crosslink density of the vulcanizate. The vulcanizate containing NR-PD shows better retention in

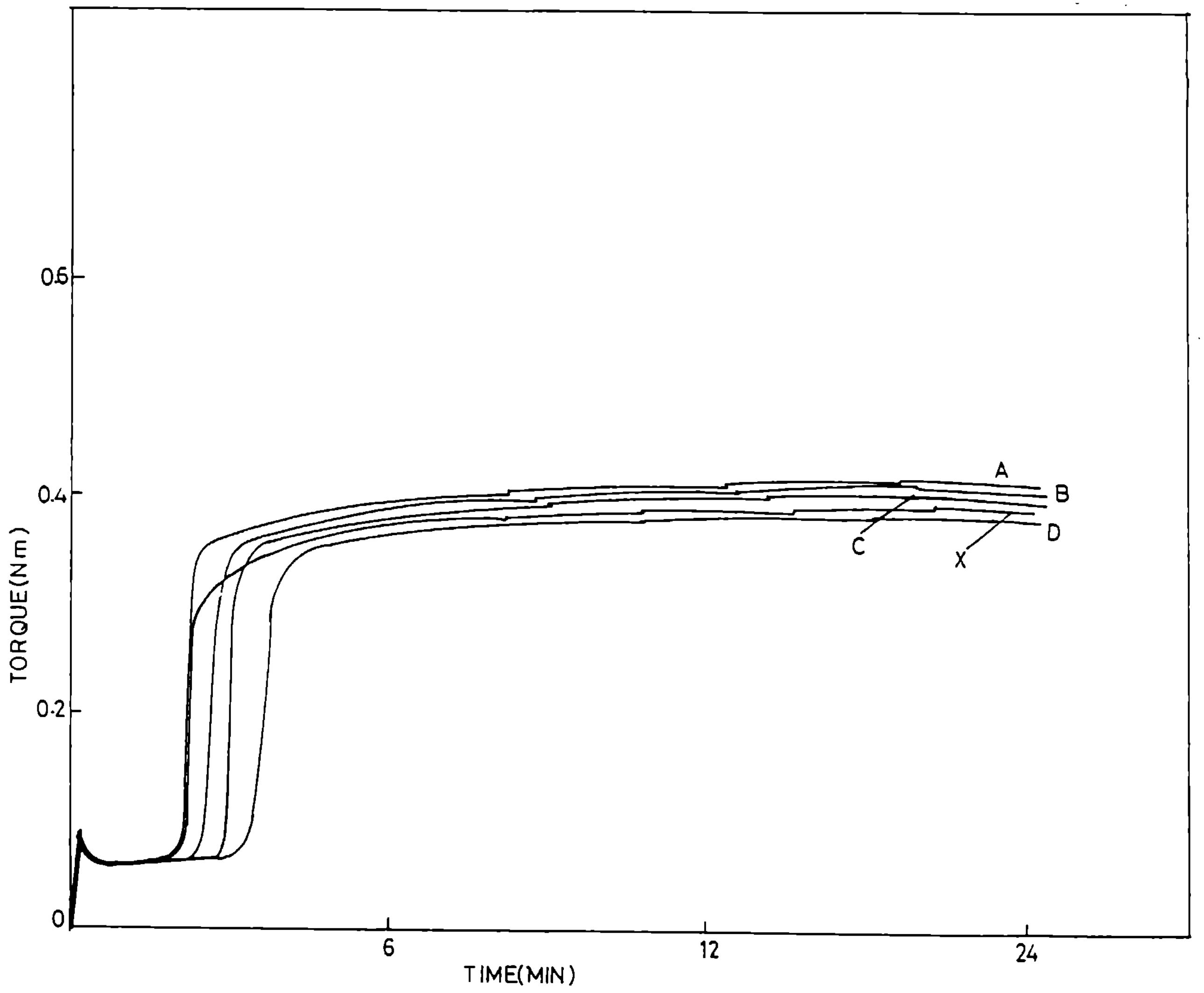


Fig.4.21: Cure curves of the compounds; (A) NR-PD, (B) vulkanox 4020, (C) vulkanox HS, (D) depolymerised rubber, (X) without antioxidant

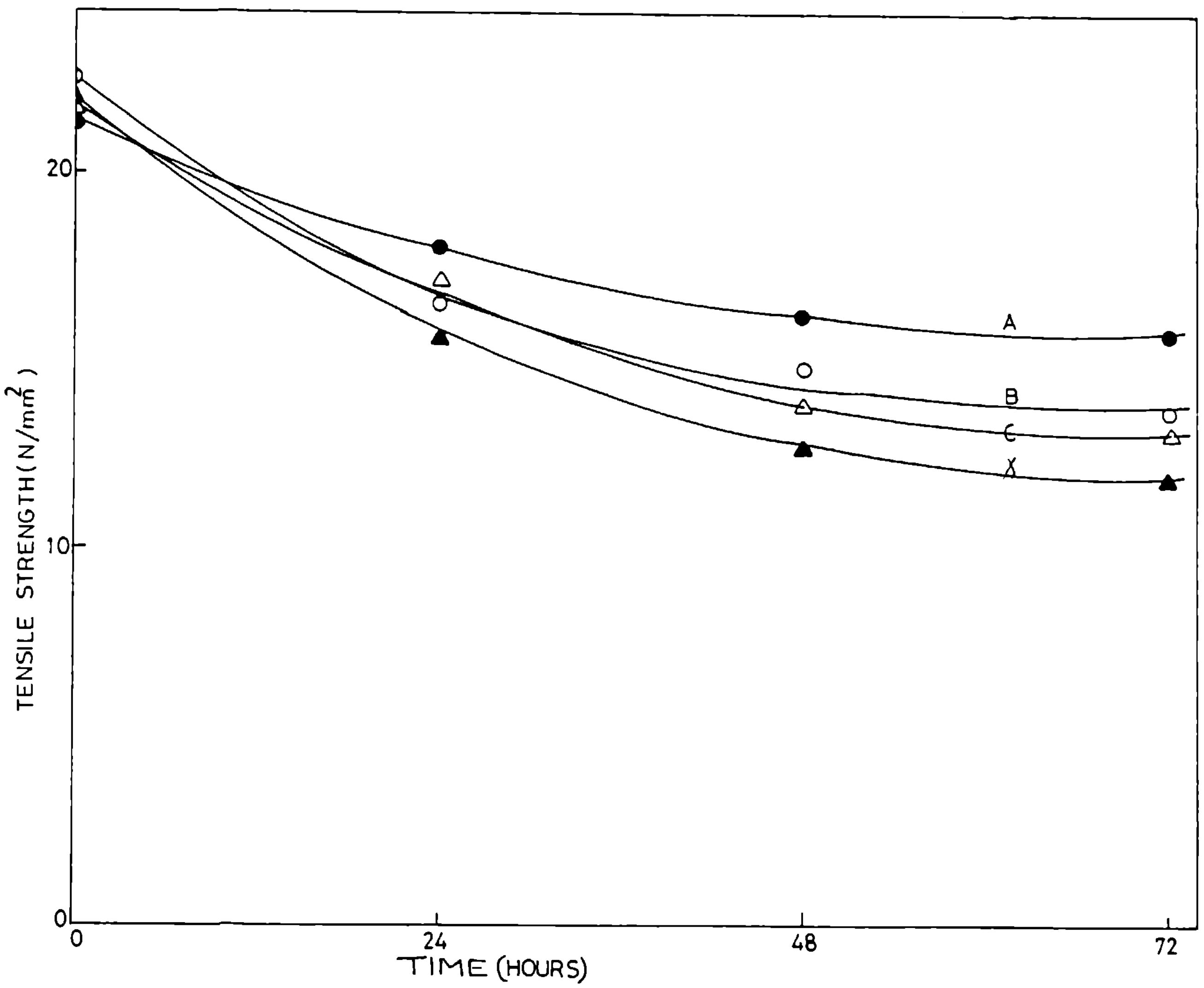


Fig.4.22: Variation in tensile strength of the vulcanizates before and after ageing at 100°C; (A) NR-PD, (B) vulkanox 4020, (C) vulkanox HS, (X) without antioxidant

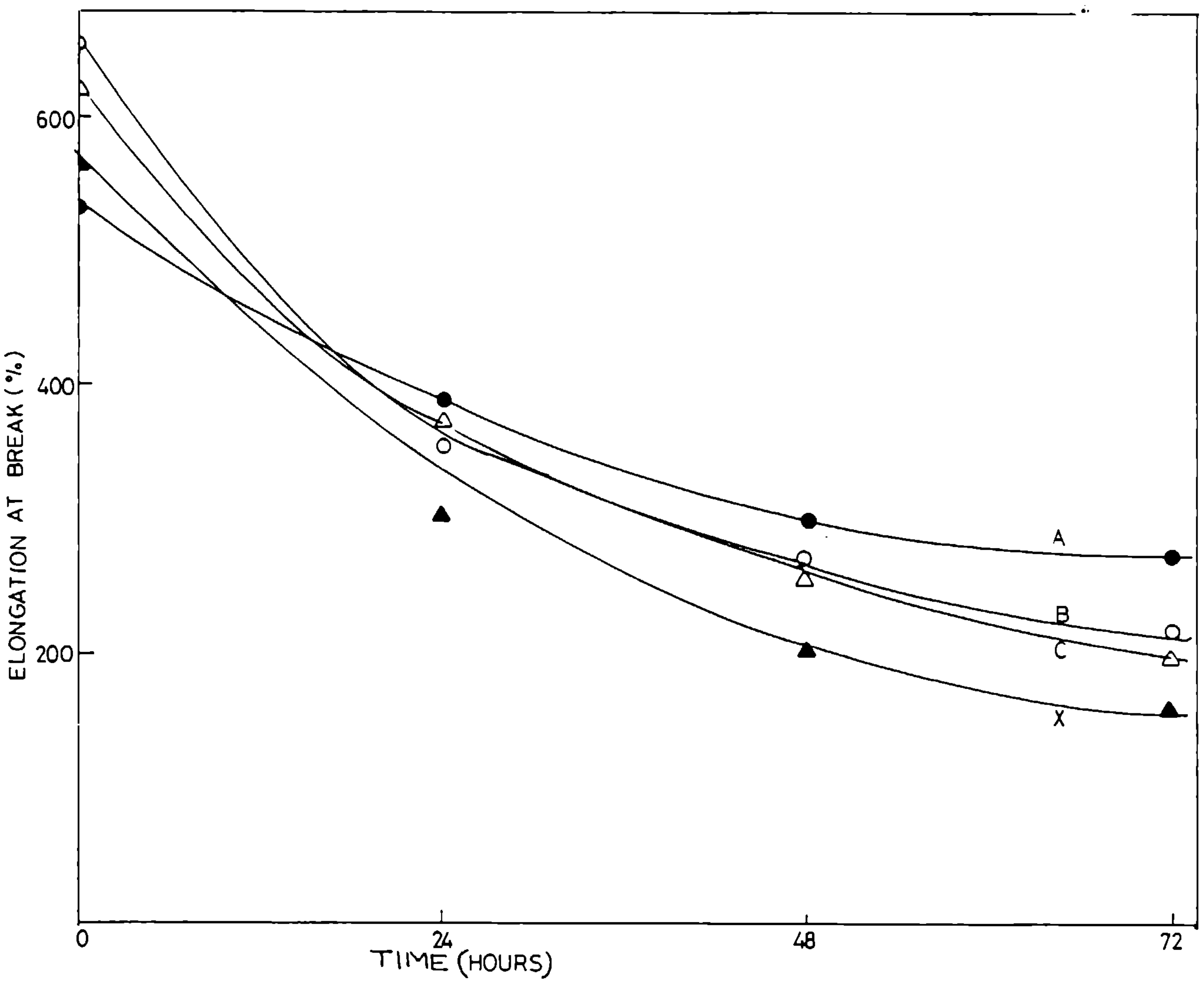


Fig.4.23: Variation in elongation at break of the vulcanizates before and after ageing at 100°C; (A) NR-PD, (B) vulkanox 4020, (C) vulkanox HS, (X) without antioxidant

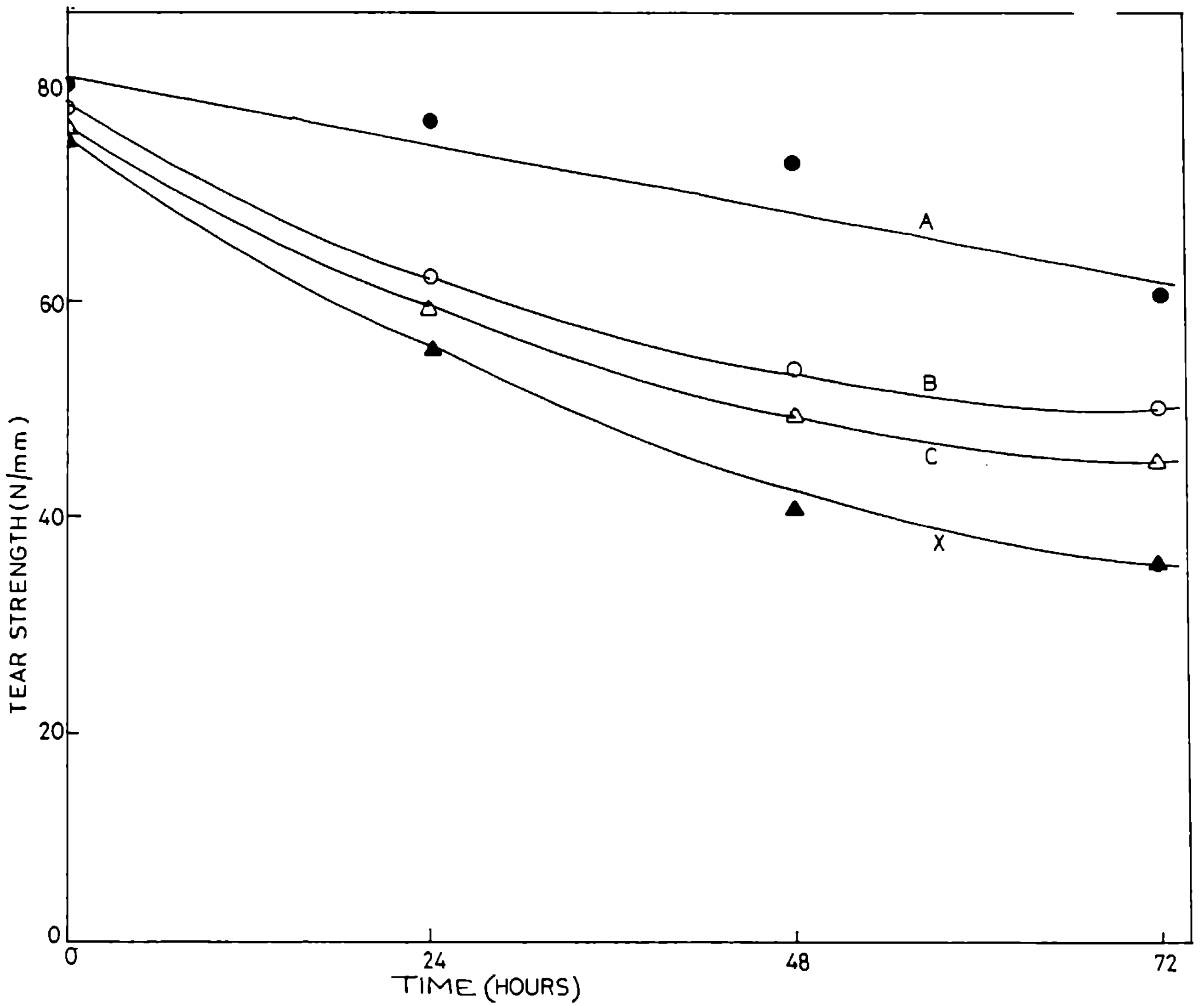


Fig.4.24: Variation in tear strength of the vulcanizates before and after ageing at 100°C; (A) NR-PD, (B) vulkanox 4020, (C) vulkanox HS, (X) without antioxidant

elongation at break after ageing. Retention in tear strength of the vulcanizate containing NR-PD again shows that the bound antioxidant can improve the ageing resistance of NBR vulcanizates.

Fig.4.25 shows the variation in modulus (at 100% elongation) of the vulcanizates before and after ageing. The increase in modulus may be attributed to the post curing of NBR[20].

Fig.4.26 shows the variation in hardness of the vulcanizates before and after ageing. There is a slight increase in hardness after ageing for all the vulcanizates. This also may be due to the post curing of NBR[20].

Table 4.5 shows the variation in tensile properties, hardness and tear strength of the vulcanizates of the compounds in Table 4.3 before and after extracting the samples in transformer oil, gear oil, light oil and engine oil at room temperature and also at 70°C. Tensile strength, elongation at break and modulus of the vulcanizates are comparable after room temperature oil extraction. Reduction of hardness values is observed in all the vulcanizates after extraction. This may be due to the

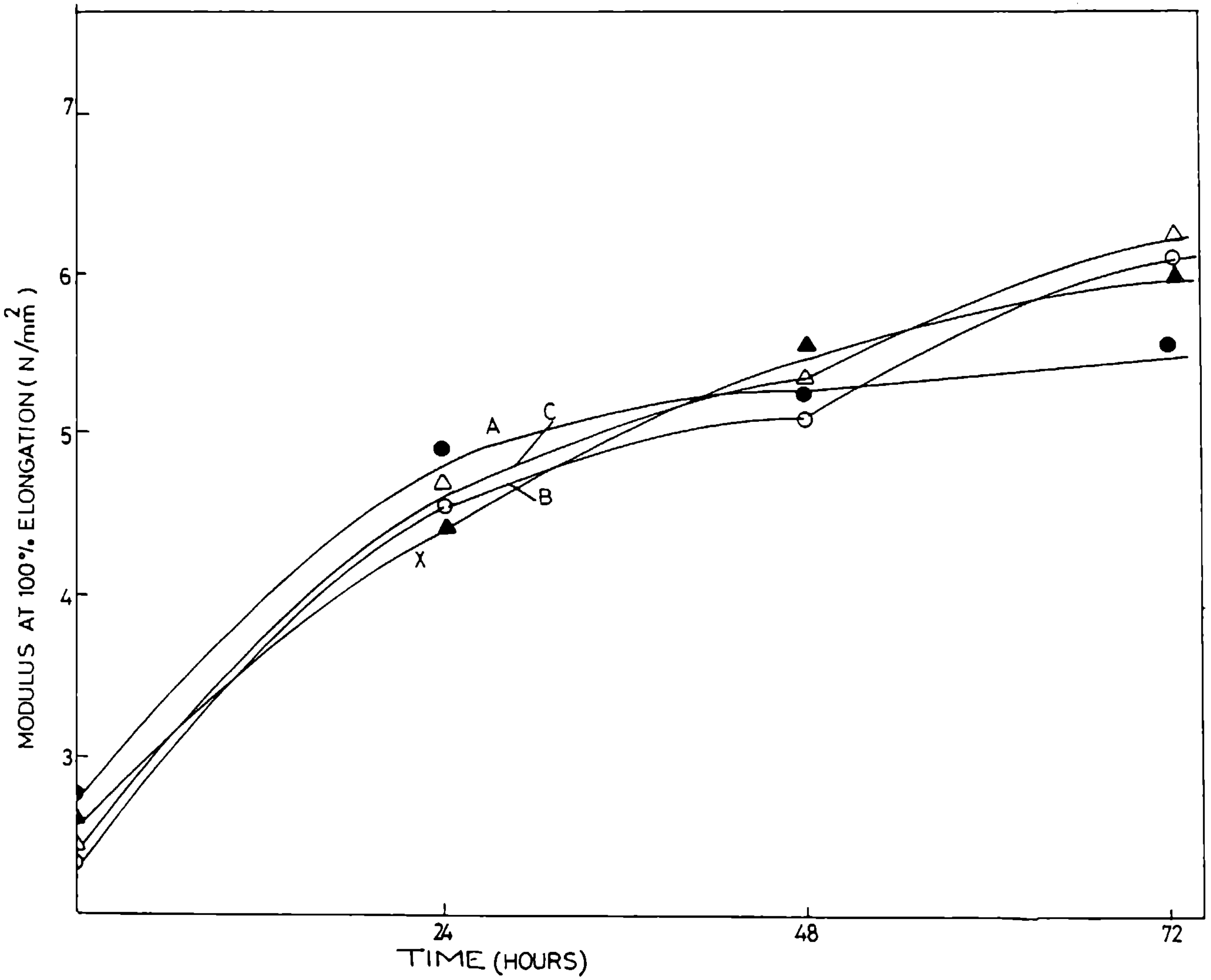


Fig.4.25: Variation in modulus of the vulcanizates before and after ageing at 100°C; (A) NR-PD, (B) vulkanox 4020, (C) vulkanox HS, (X) without antioxidant

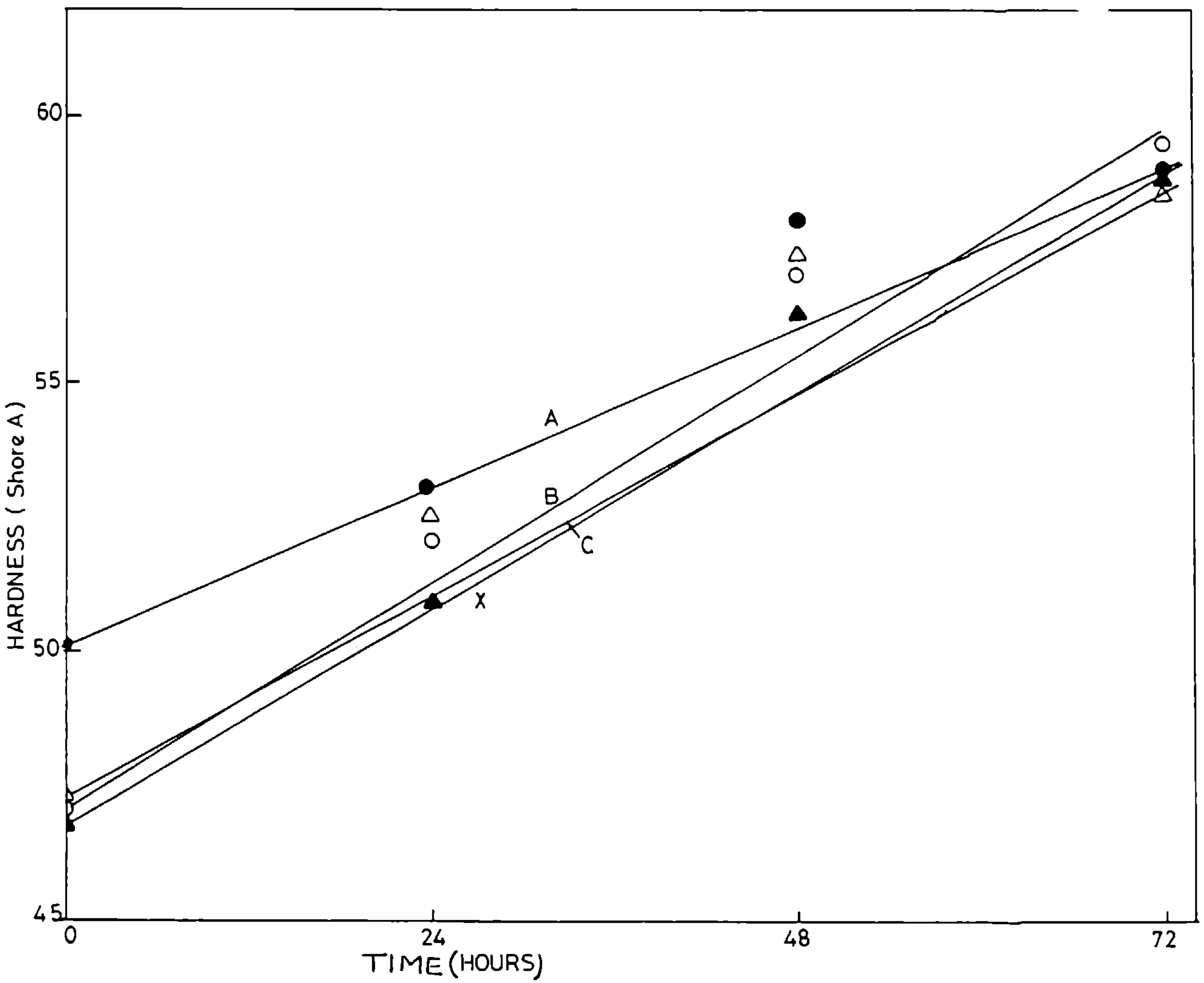


Fig.4.26: Variation in hardness of the vulcanizates before and after ageing at 100°C; (A) NR-PD, (B) vulkanox 4020, (C) vulkanox HS, (X) without antioxidant

Table 4.5

Properties before and after oil extraction at room temperature and 70°C

Property	Extraction		TYPE OF OIL							
	Time	Temp.	Light oil		Gear oil		Transformer oil		Engine oil	
			A	B	A	B	A	B	A	B
Tensile strength (N/mm^2)	0	27°C	21.23	22.59	21.23	22.29	21.23	22.59	21.23	22.59
Elongation at break (%)			535.43	699.03	535.43	699.03	535.43	699.03	535.43	699.03
Modulus at 200% elongation N/mm^2)			5.86	3.96	5.86	3.96	5.86	3.96	5.86	3.96
Tear strength (N/mm)			80.00	79.00	80.00	79.00	80.00	79.00	80.00	79.00
Hardness (Shore A)			50.00	47.00	50.00	47.00	50.00	47.00	50.00	47.00
Tensile strength (N/mm^2)	48h	27°C	20.18	22.43	21.12	22.20	20.18	17.79	21.10	21.27
Elongation at break (%)			506.76	660.52	525.16	656.30	511.17	675.53	517.12	641.76
Modulus at 200% elongation (N/mm^2)			6.27	4.49	6.50	4.32	6.29	3.84	6.46	4.51
Tear strength (N/mm)			61.98	58.12	60.74	59.11	51.02	40.80	61.50	48.42
Hardness (Shore A)			45.00	42.00	45.00	43.00	43.00	41.00	46.00	43.00
Tensile strength (N/mm^2)	24h	70°C	18.72	16.68	17.61	16.24	17.63	12.38	17.61	16.24
Elongation at break (%)			463.15	399.26	484.86	312.15	444.50	360.98	502.48	312.15
Modulus at 200% elongation (N/mm^2)			6.97	6.41	6.80	6.79	6.93	6.45	6.53	6.99
Tear strength (N/mm)			59.89	46.97	58.81	45.41	49.89	36.90	46.87	39.00
Hardness (Shore A)			46.00	43.00	47.000	44.00	44.00	42.00	47.00	44.00

diffusion of oil into the vulcanizate, causing dilution[21]. The tear strength retention after ageing is found to be superior for the vulcanizate containing NR-PD. This may be due to the lower extractability of NR-PD by oils. The retention in tensile properties and tear resistance of the vulcanizate containing NR-PD is more pronounced after oil extraction at 70°C. This shows that NR-PD is resistant to oil extraction even at 70°C.

Figs.4.27 and 4.28 show the variation in tensile strength and elongation at break of the vulcanizates before and after ageing, after extracting the samples in acetone and methanol. The retention in properties by the vulcanizate containing NR-PD is superior due to lower extractability of the bound antioxidant by acetone and methanol.

Table 4.6 shows the variation in tensile strength, elongation at break, hardness, modulus and tear strength of the vulcanizates before and after ageing, after extracting the samples in water at 70 and 100°C. More than 20% of the conventional antioxidant leached out during boiling water extraction. IR spectra of the dried water extract from vulcanizate containing vulkanox 4020 shows the peak at 3400

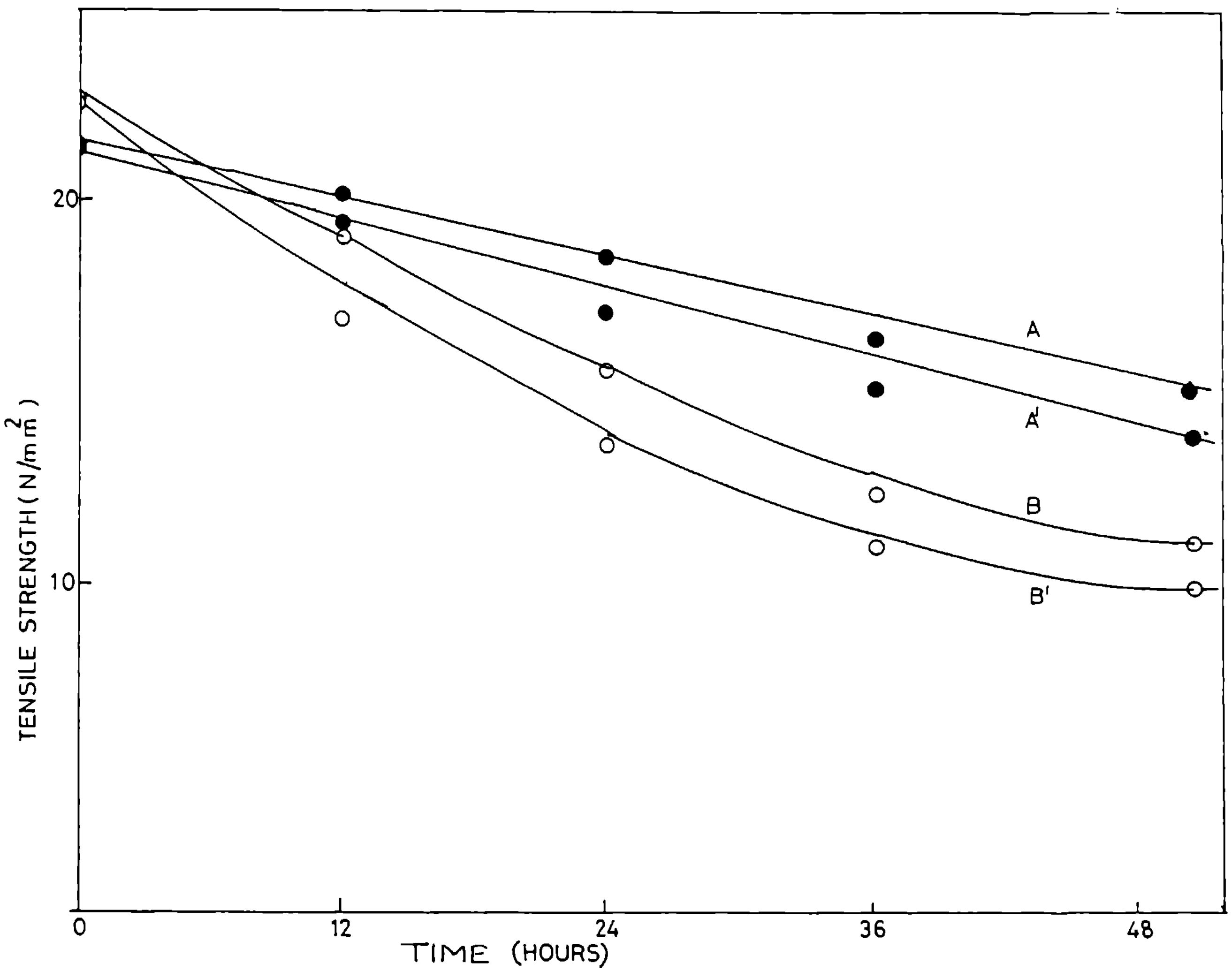


Fig.4.27: Variation in tensile strength of the vulcanizates before and after extraction in solvents followed by ageing at 100°C; (a) in methanol (A) NR-PD, (B) vulkanox 4020; (b) in acetone (A') NR-PD, (B') vulkanox 4020

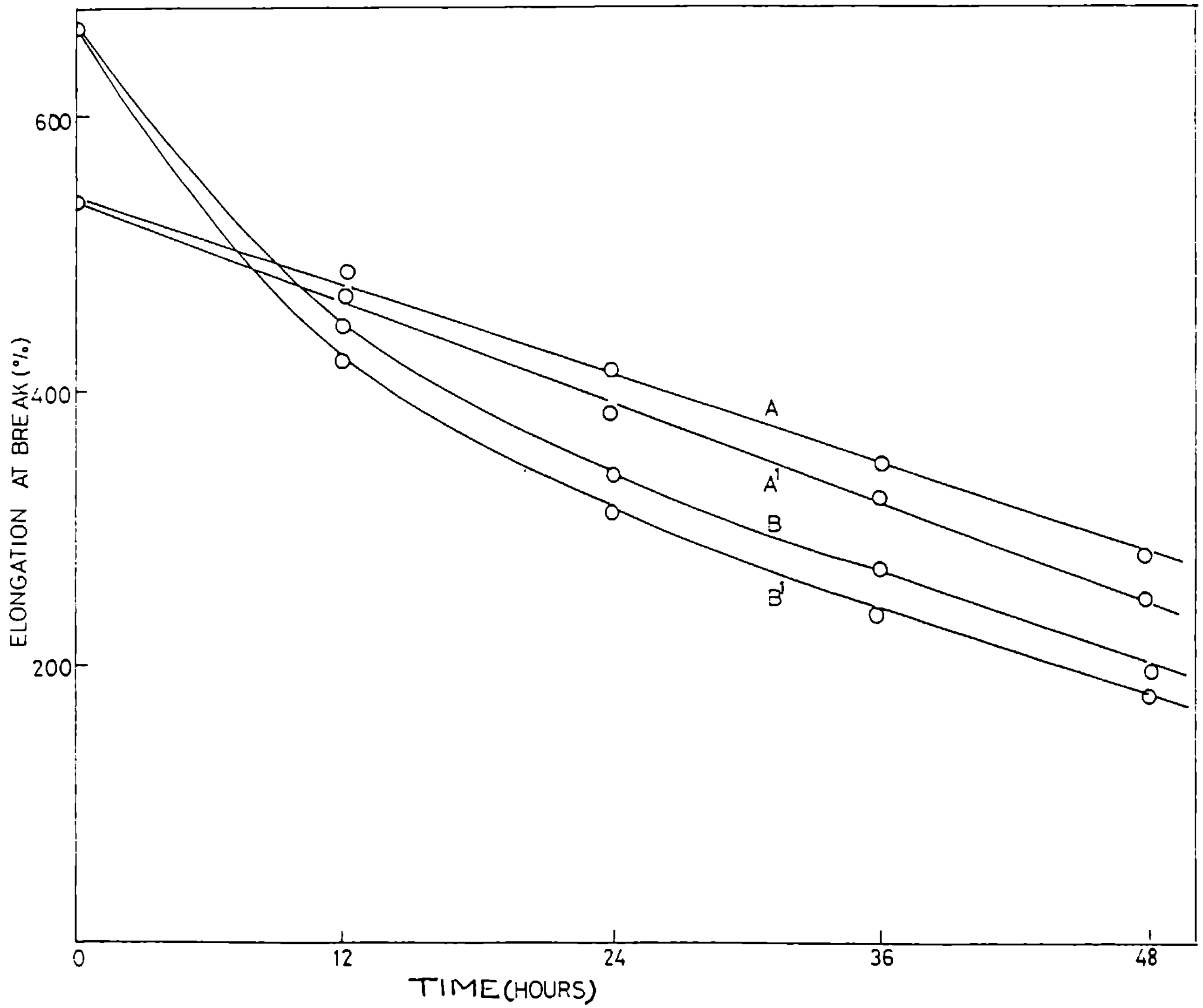


Fig.4.28: Variation in elongation at break of the vulcanizates before and after extraction in solvents followed by ageing at 100°C; (a) in methanol (A) NR-PD, (B) vulkanox 4020; (b) in acetone (A') NR-PD, (B') vulkanox 4020

Table 4.6

Properties before and after water extraction at 70 and 100°C followed by ageing at 100°C for 48h

Property	Extraction		A	B	C	X
	Time	Temp.				
Tensile strength (N/mm^2)	0	27°C	21.23	22.59	22.74	22.00
Elongation at break (%)			535.43	699.03	651.00	556.51
Modulus at 100% elongation (N/mm^2)			2.66	2.46	2.59	2.48
Tear strength (N/mm)			80.00	79.00	78.00	77.00
Hardness (Shore A)			50.00	47.00	47.00	47.00
Tensile strength (N/mm^2)	24h	70°C	19.57	15.84	14.79	13.11
Elongation at break (%)			286.50	248.46	214.14	211.47
Modulus at 100% elongation (N/mm^2)			5.66	5.07	5.01	5.02
Tear strength (N/mm)			69.41	52.12	45.84	40.84
Hardness (Shore A)			53.00	52.00	53.00	54.00
Tensile strength (N/mm^2)	10h	100°C	18.27	14.26	12.18	11.10
Elongation at break (%)			265.50	197.22	149.35	201.00
Modulus at 100% elongation (N/mm^2)			5.85	6.21	6.99	5.08
Tear strength (N/mm)			65.01	49.66	43.67	36.54
Hardness (Shore A)			55.00	54.00	54.00	55.00

cm^{-1}, corresponding to amino-group while NR-PD does not get extracted, in boiling water. The retention in properties after extraction and ageing of the vulcanizate containing NR-PD is superior to the vulcanizates containing vulkanox 4020 and vulkanox HS, obviously because NR-PD does not get extracted in boiling water.

Table 4.7 shows the percentage increase in weight of the vulcanizates of the compounds shown in Table 4.3(A) and (B) in transformer oil and gear oil. The lower increase in weight of the vulcanizate containing vulkanox 4020 in transformer oil may be due to the leaching of the antioxidant and plasticiser, while the compound containing NR-PD as antioxidant contains only lower amount of plasticiser. The percentage increase in weight of the vulcanizates in gear oil is more or less the same. This may be due to the lower extractability of the antioxidants and plasticiser in gear oil as evidenced by the mechanical property retention shown in Table 4.5.

Table 4.8 shows the variation in resilience, heat build up, flex crack resistance, abrasion resistance and compression set of the vulcanizates. Resilience and heat build up values of the NBR vulcanizate containing NR-PD are

Table 4.7

Percentage increase in weight of the vulcanizates in oils

Type of oil	A	B
Transformer oil	5.01%	4.81%
Gear oil	0.33%	0.37%

Table 4.8

Properties of the vulcanizates before and after ageing

Properties	A	B
Resilience (%)	59	48.61
Heat build up [(ΔT)°C]	23.0	25.6
Flex crack resistance (k cycles)	525.0	223.0
Compression set (%)	16.84	17.93
Abrasion resistance (Volume loss, cc/h)	2.813	2.791
<u>After ageing at 100°C for 48h</u>		
Resilience (%)	45.54	36.54
Heat build up [(ΔT)°C]	40.71	49.50
Flex crack resistance (k cycles)	390.72	120.75
Compression set (%)	15.94	14.83
Abrasion resistance (Volume loss, cc/h)	3.31	3.221

better than that containing vulkanox 4020. This may be due to the natural rubber part in the bound antioxidant. The better retention in properties after ageing by the vulcanizate containing NR-PD may be due to the lower volatility of NR-PD during ageing.

Conclusions

1. Paraphenylenediamine can be chemically attached to depolymerised natural rubber by photochemical reaction.

2. The rubber bound antioxidant (NR-PD) has much superior resistance to volatility and extractability compared to conventional antioxidants.

3. NR-PD can reduce heat build up, improve resilience and ageing resistance of the NBR vulcanizates.

4. Water and oil resistance of the NBR vulcanizates can be improved by the use of rubber bound antioxidant.

5. The rubber bound antioxidant can act as a polymeric plasticiser.

III. APPLICATION OF NATURAL RUBBER BOUND PARAPHENYLENEDIAMINE IN NATURAL RUBBER VULCANIZATES

Experimental

The optimum concentration of NR-PD for getting maximum retention in properties was determined by varying the amount of antioxidant in a standard formulation (Table 4.9(B)) from 1 to 8 phr.

NR-PD was added in NR as per formulation given in Table 4.9. The amount of plasticiser, can be reduced by the use of liquid rubber bound antioxidant as shown in Table 4.9. The optimum cure times and scorch times of the compounds were determined on a Goettfert Elastograph as per ASTM D 1646 (1981). Rubber compounds were moulded in an electrically heated laboratory hydraulic press at 150°C upto their optimum cure times. Dumbell shaped tensile test pieces were punched out of these compression moulded sheets along the mill grain direction. Tensile properties, tear resistance, hardness, compression set, resilience, heat build up, flex crack resistance and abrasion resistance of the samples were evaluated as per relevant ASTM standards.

Retention in tensile properties and tear strength was evaluated after ageing the samples at 100°C for 24, 48, 72, 96, 120 and 144h. Retention in abrasion

Table 4.9

Formulations for testing the antioxidants

Ingredients	A	B	C
Natural rubber (phr)	100	100	100
Zinc oxide	5	5	5
Stearic acid	2	2	2
Mercaptobenzothiazole	0.6	0.6	0.6
Tetramethyl thiuram disulphide	0.2	0.2	0.2
Sulphur	2.5	2.5	2.5
Carbon black	40	40	40
Aromatic oil	3	3	5
Vulkanox 4020	0.5	--	1
NR-PD	5	5	--

resistance, compression set, heat build up, resilience and flex crack resistance was evaluated after ageing the samples at 100°C for 48h. The extractability of bound antioxidant was studied by keeping the samples in methanol, acetone (48h at room temperature) and in boiling toluene for 10h. The retention in tensile properties was evaluated after ageing the samples at 100°C for 48h.

Results and Discussion

Fig.4.29 shows the variation in tensile strength after ageing with concentration of the antioxidant. The tensile strength retention increases with the amount of chemically bound antioxidant, reaches a maximum and then levels off. The higher quantities of bound antioxidant in comparison to conventional antioxidant may be due to lower amount of effective antioxidant in the bound product.

Fig.4.30 shows the cure curves of the compounds shown in Table 4.9. Scorch time and cure time are found to be slightly reduced by the addition of NR-PD. This may be due to the free amino group present in NR-PD.

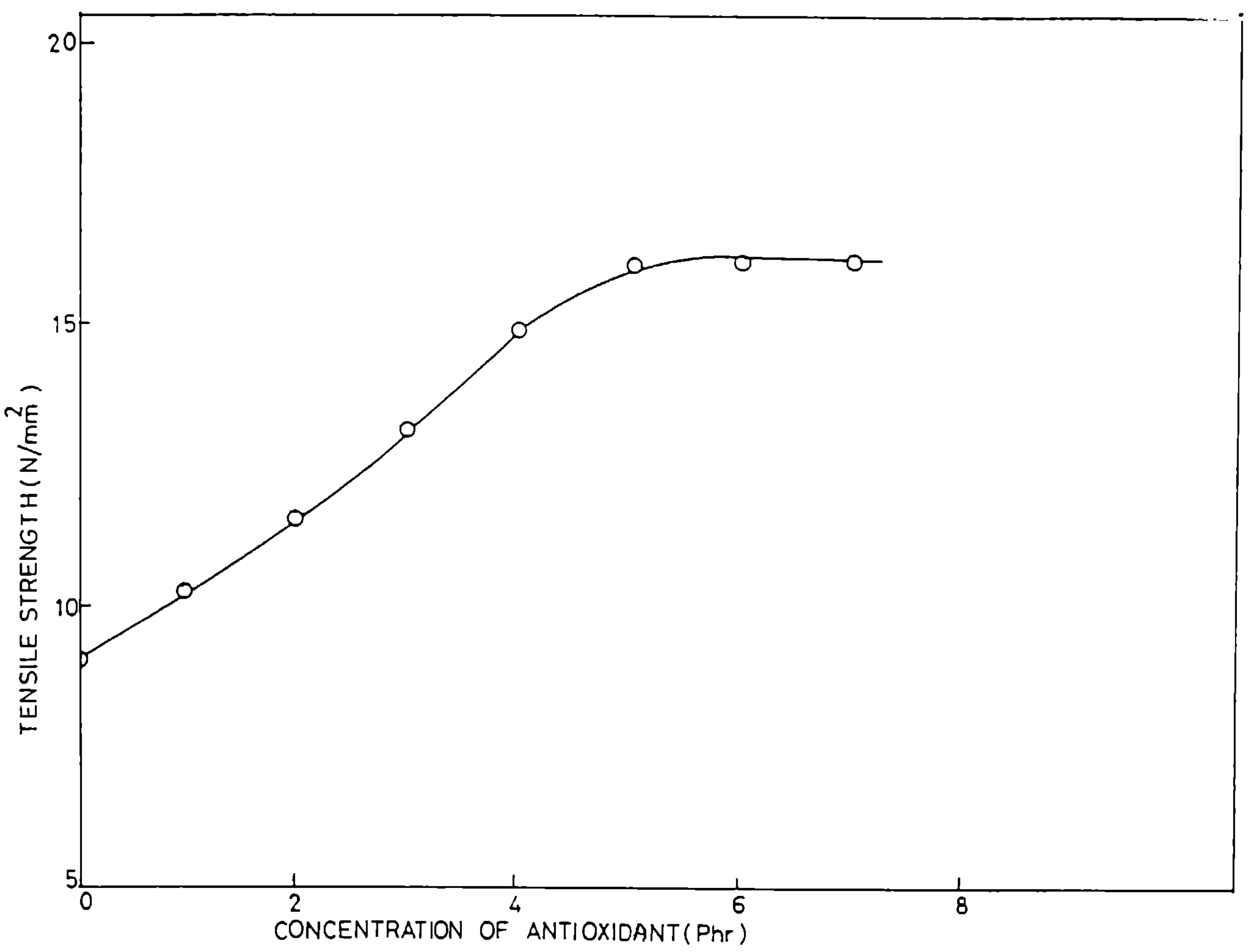


Fig.4.29: Variation in tensile strength after ageing with concentration of the antioxidant

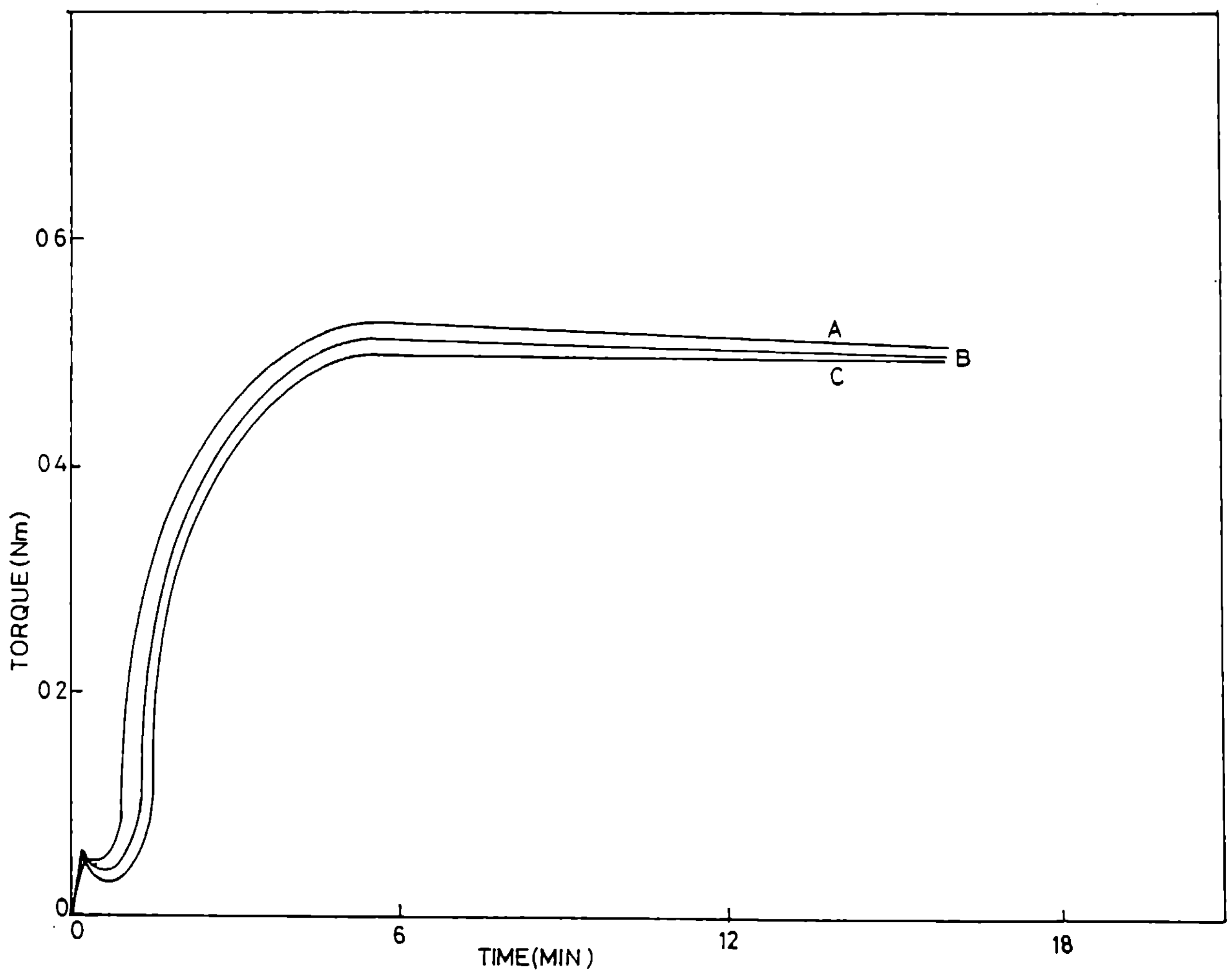


Fig.4.30: Cure curves of the compounds; (A) combination of NR-PD and vulkanox 4020, (B) NR-PD, (C) vulkanox 4020

Fig.4.31 shows the tensile strength of the vulcanizates before and after ageing. All the vulcanizates show fairly good resistance to ageing at 100°C for 24h. Vulcanizate containing NR-PD is found to be better than vulcanizate containing vulkanox 4020 when time of ageing is increased to 48h. The vulcanizate containing NR-PD and vulkanox 4020 has superior ageing resistance even after 144h. This shows that the combined antioxidant system is more effective against oxidative degradation in protecting the sample.

Figs.4.32 and 4.33 show the change in elongation at break and tear strength of the vulcanizates before and after ageing. The vulcanizate containing NR-PD has better retention in elongation at break after ageing, which confirms the superiority of the bound product. The combination of NR-PD and vulkanox 4020 is found to have better elongation at break after prolonged ageing for 144h. Retention in tear strength by the vulcanizates containing NR-PD shows that bound antioxidant can improve the ageing resistance of NR compounds. The combined antioxidant system shows superior retention in tear strength also.

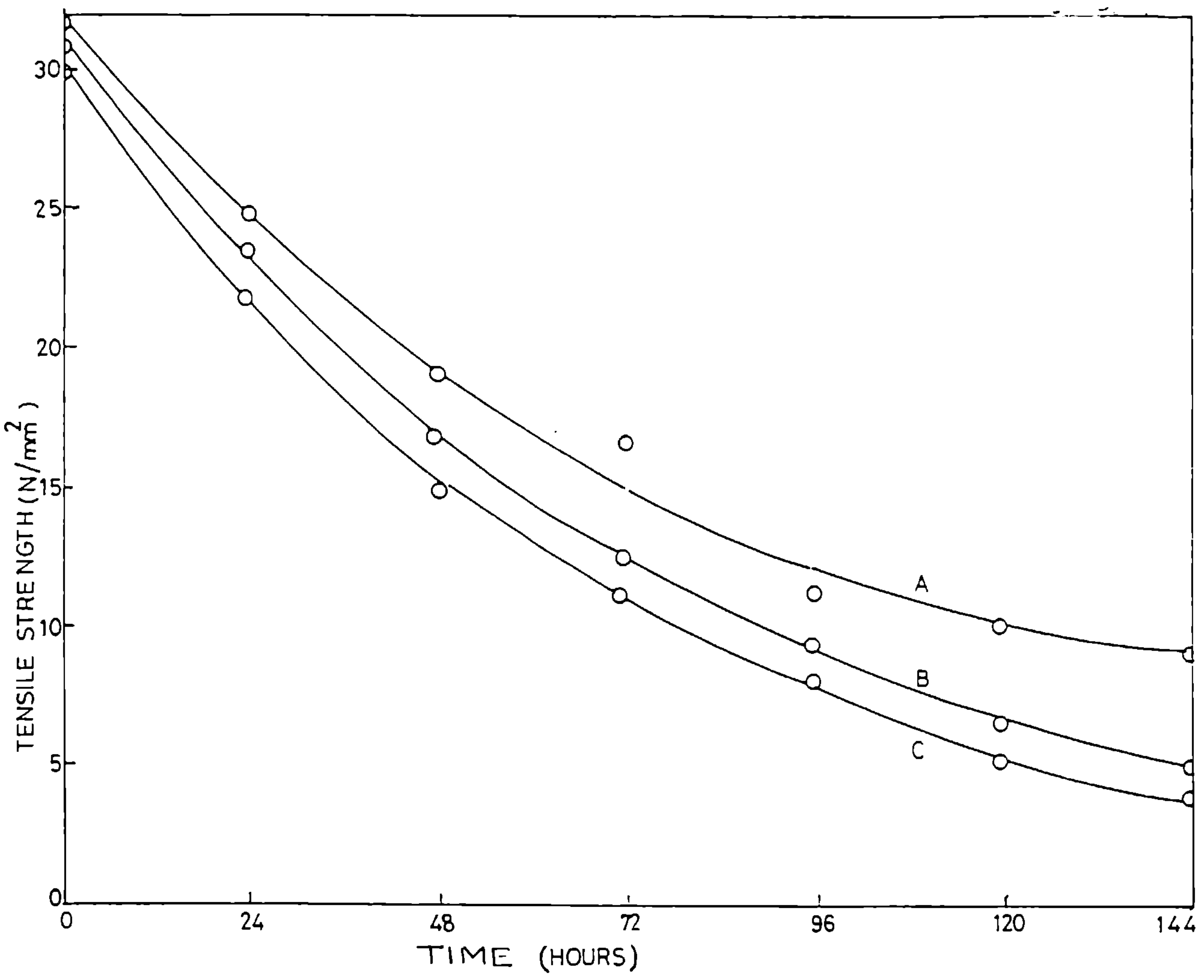


Fig.4.31: Variation in tensile strength of the vulcanizates before and after ageing at 100°C; (A) combination of NR-PD and vulkanox 4020, (B) NR-PD, (C) vulkanox 4020

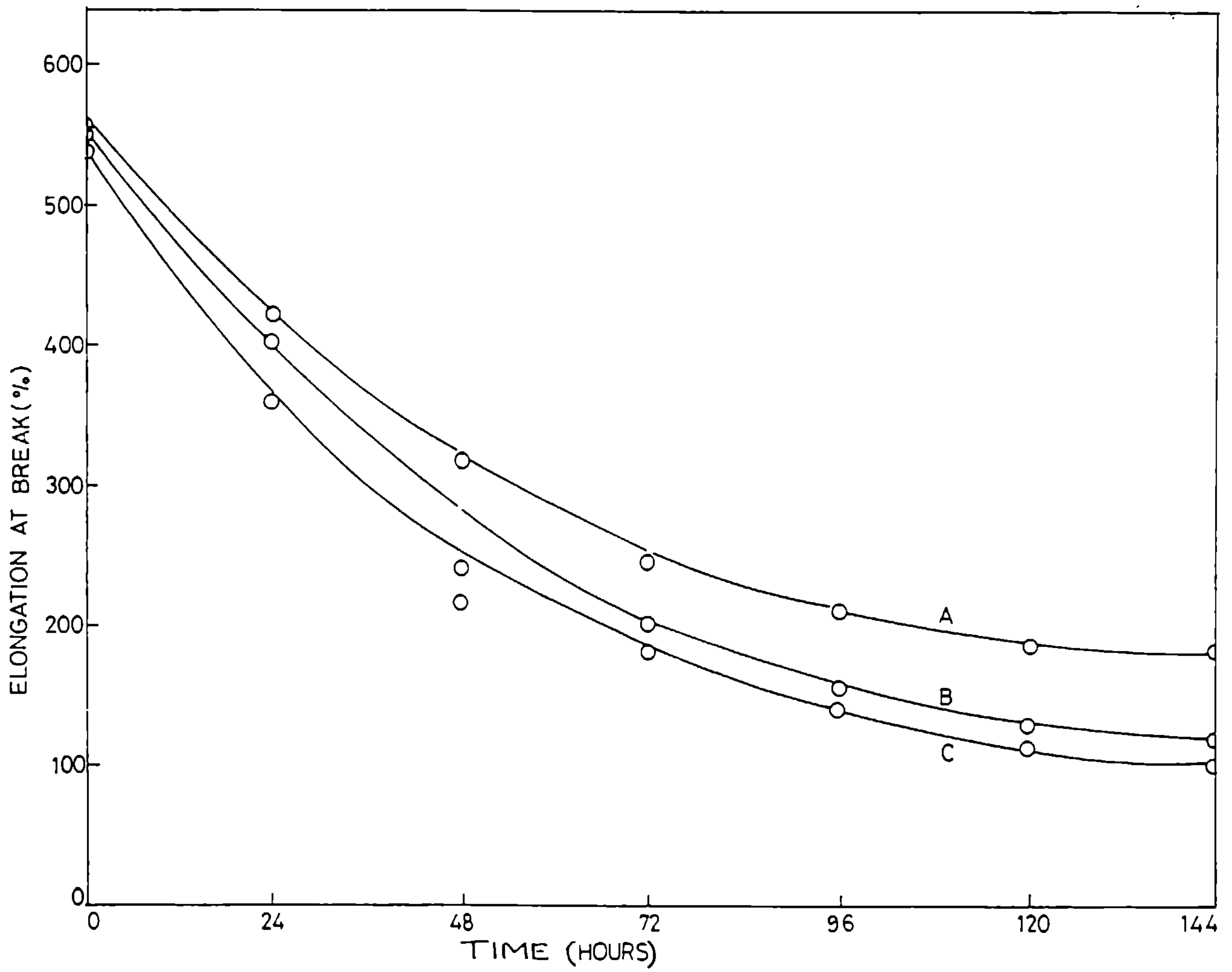


Fig.4.32: Variation of elongation at break of the vulcanizates before and after ageing at 100°C; (A) combination of NR-PD and vulkanox 4020, (B) NR-PD, (C) vulkanox 4020

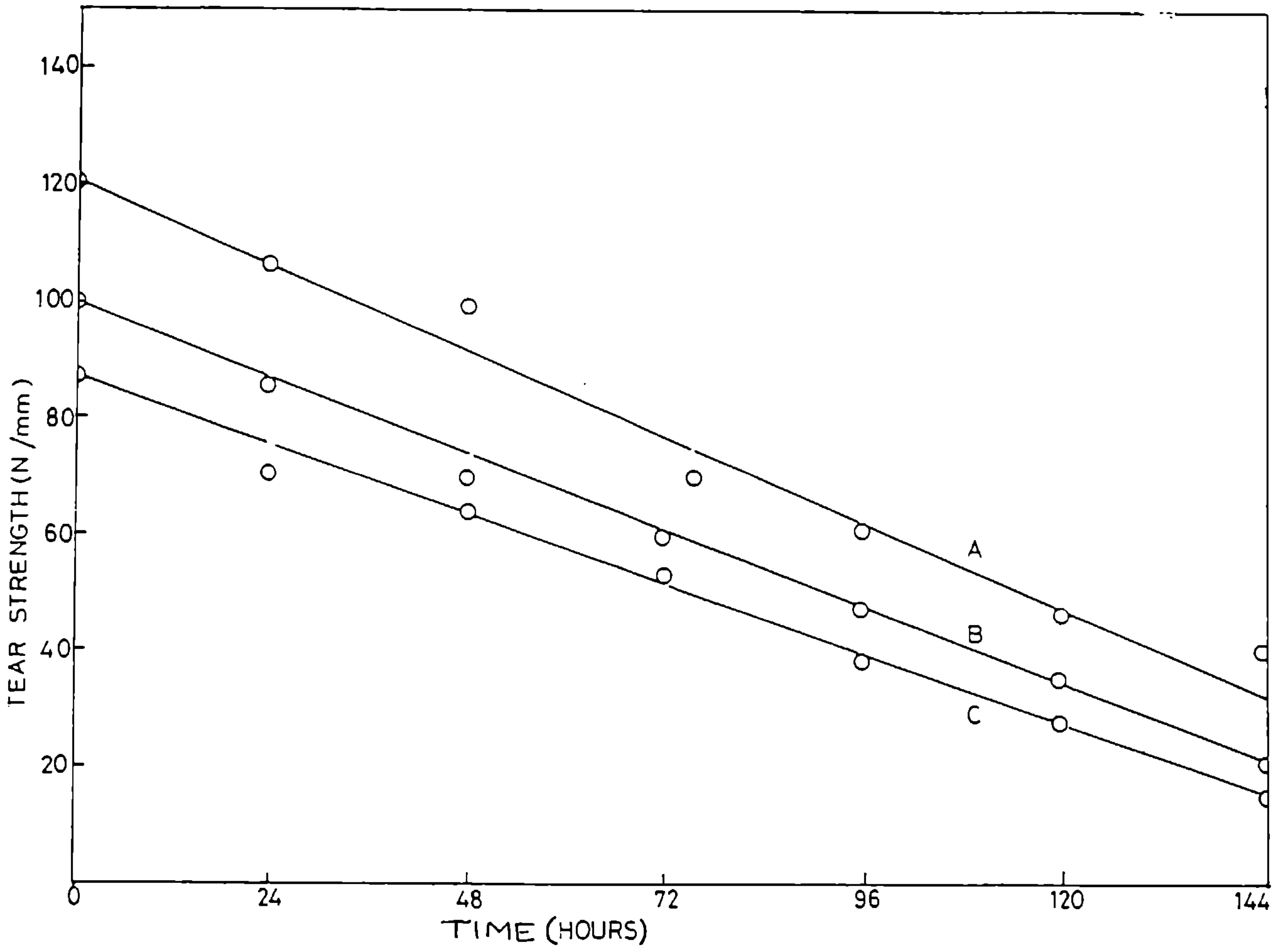


Fig.4.33: Variation in tear strength of the vulcanizates before and after ageing at 100°C; (A) combination of NR-PD and vulkanox 4020, (B) NR-PD, (C) vulkanox 4020

Fig.4.34 shows the change in modulus of the vulcanizates before and after ageing. The increase in modulus after 48h ageing may due to the increase in total crosslink density as shown in Table 4.10. (This increase may be due to the co-crosslinking of NR-PD with NR and shortening of polysulphidic linkages).

Fig.4.35 shows the change in hardness of the vulcanizates before and after ageing. Hardness of the vulcanizates containing NR-PD is found to be higher than that of the vulcanizate containing vulkanox 4020. This may be due to the lower amount of plasticiser in the vulcanizates containing NR-PD.

Table 4.11 shows the change in tensile strength, elongation at break, tear strength, hardness and modulus of the vulcanizates before and after ageing after extracting the samples in acetone, methanol and toluene. The superior retention in properties by the vulcanizates containing NR-PD may be due to the lower extractability of the bound product by the solvents. The retention in properties after extraction in toluene confirms the attachment of the rubber part in NR-PD to NR during sulphur vulcanization.

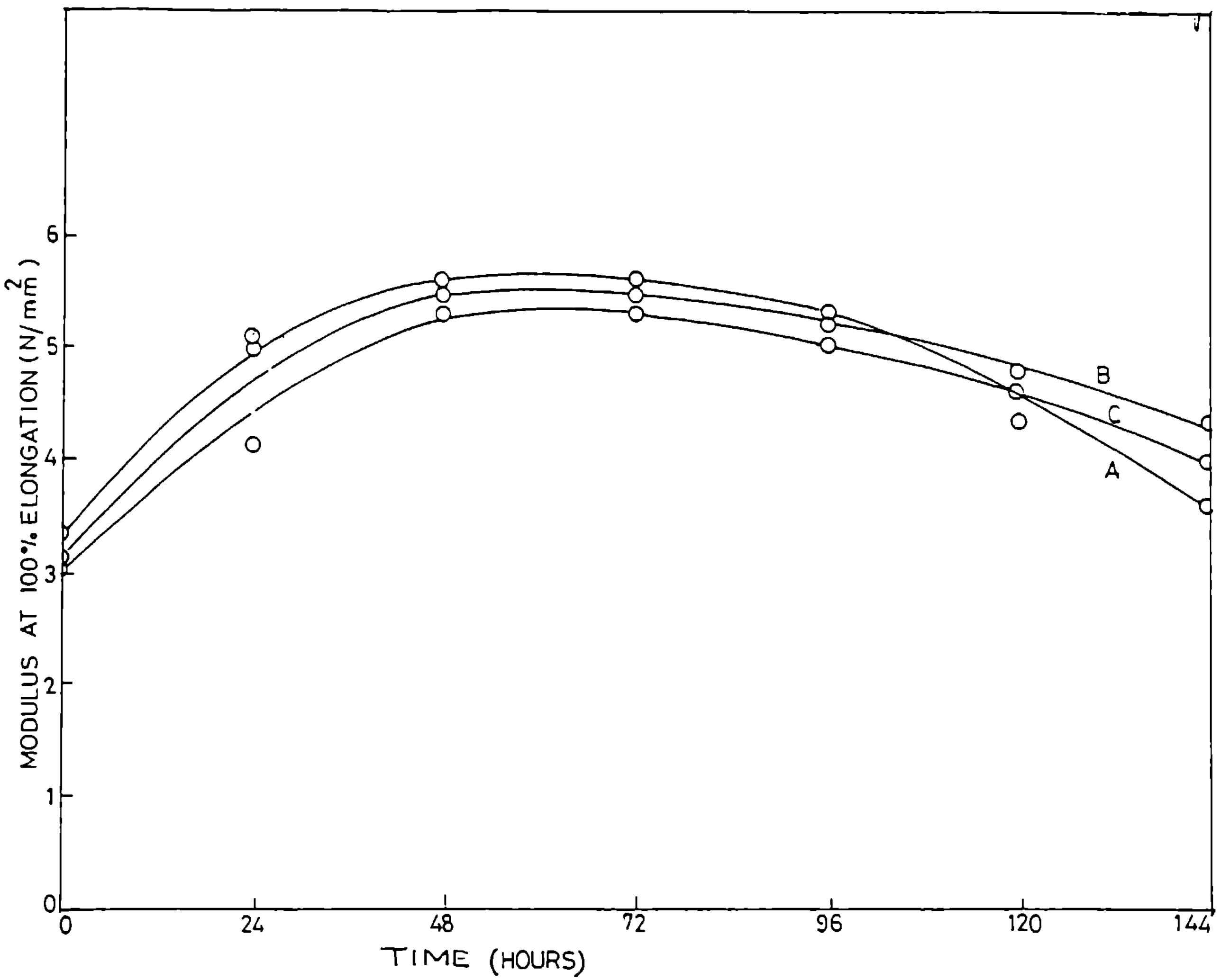


Fig.4.34: Variation in modulus of the vulcanizates before and after ageing at 100°C; (A) combination of NR-PD and vulkanox 4020, (B) NR-PD, (C) vulkanox 4020

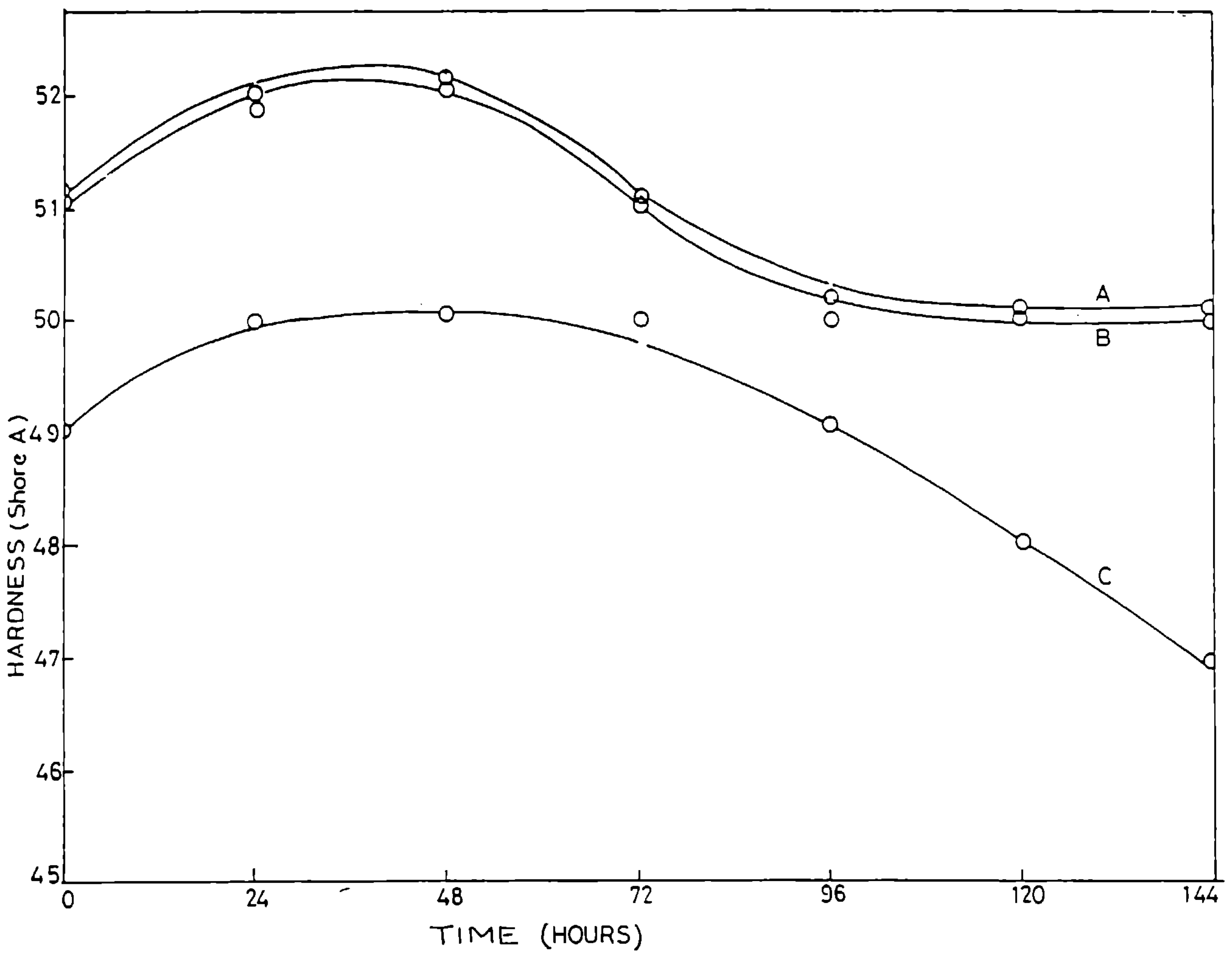


Fig.4.35: Variation in hardness of the vulcanizates before and after ageing at 100°C; (A) combination of NR-PD and vulkanox 4020, (B) NR-PD, (C) vulkanox 4020

Table 4.10

Crosslink densities of the vulcanizates before and after ageing at 100°C

Time of ageing (h)	Crosslink density in g mole/cc		
	A	B	C
0	5.628×10^{-5}	4.977×10^{-5}	4.0506×10^{-5}
24	4.4217×10^{-4}	1.2870×10^{-4}	3.2788×10^{-4}
48	6.2046×10^{-4}	1.9921×10^{-4}	1.1886×10^{-4}
72	2.5238×10^{-4}	2.0232×10^{-4}	3.4487×10^{-4}
96	2.253×10^{-4}	5.5719×10^{-5}	5.3132×10^{-5}
120	1.8006×10^{-4}	1.3903×10^{-5}	4.603×10^{-5}

Table 4.11

Properties before and after solvent extraction followed by ageing at 100°C 48h

(48h at room temperature in methanol and acetone, 10h in boiling toluene)

Property	Properties before extraction			Properties after extraction followed by ageing								
				Methanol			Acetone			Toluene		
	A	B	C	A	B	C	A	B	C	A	B	C
Tensile strength (N/mm^2)	31.98	30.16	29	16.39	12.89	8.89	14.09	11.97	7.21	14.07	12.97	7.04
Elongation at break (%)	544.43	554.08	538.09	311.43	220.84	187.85	308.05	212.34	162.89	282	194.98	188.52
Modulus at 200% elongation (N/mm^2)	7.50	7.10	6.80	9.91	10.72	--	9.48	10.26	--	7.51	--	--
Tear strength (N/mm)	121.32	112	80.40	53	30.81	27.74	50	31.82	20.78	42	39.97	20.97
Hardness (Shore A)	51	51	49	43	43	41	42	41	40	36	36	30

Table 4.12

Properties of the vulcanizates before and after ageing

Properties	A	B	C
Resilience (%)	67	62.34	62
Heat build up [(ΔT)°C]	18	19	19.3
Flex initiation (k cycles)	218.3	190.78	213.271
Flex crack resistance (k cycles)	399.718	371.615	381.840
Abrasion resistance (Volume loss, cc/h)	3.18	3.14	3.24
After ageing at 100°C, 48h			
Resilience (%)	49.74	46.02	37.40
Heat build up [(ΔT)°C]	39.4	37.4	43.9
Flex initiation (k cycles)	125.41	111.39	121.395
Flex crack resistance (k cycles)	199.931	133.7	154.625
Abrasion resistance (Volume loss, cc/h)	3.81	3.89	3.94

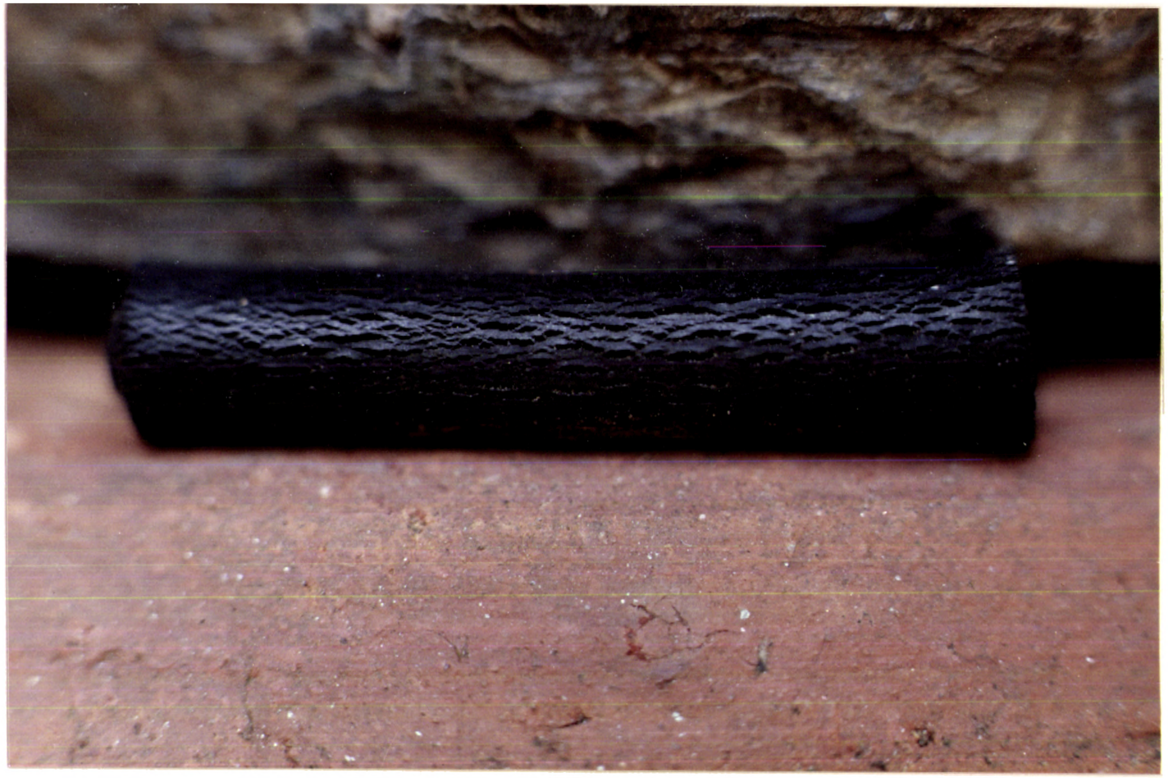


Fig.4.36: Photograph of ozone cracked vulcanizate containing NR-PD

Fig.4.37: Photograph of ozone cracked vulcanizate containing NR-PD and vulkanox 4020

Fig.4.38: Photograph of ozone cracked vulcanizate containing vulkanox 4020

Table 4.13

Ozone resistance of the samples

Sample	Crack initiation time hours	minutes
A	5	30
B	4	30
C	6	--

Table 4.12 shows the resilience, heat build up, flex crack resistance, abrasion resistance and compression set of the vulcanizates before and after ageing. The retention in properties shown by the vulcanizates containing NR-PD confirms the superiority of the bound antioxidant.

Figs.4.36 to 4.38 show the photographs of ozone cracked samples exposed to 8 h in an ozone chamber. The ozone resistance of the vulcanizate containing NR-PD is inferior to that of the vulcanizates containing vulkanox 4020 as shown in Table 4.13. This may be due to the immobility of NR-PD[22]. The vulcanizate containing combinations of the conventional antioxidant and bound antioxidant is found to have superior resistance to ozone cracking compared to that containing bound antioxidant, but inferior to that containing conventional antioxidant.

Conclusions

1. The rubber bound antioxidant NR-PD has better resistance to volatility and extractability compared to conventional antioxidant.

2. Ozone resistance of the vulcanizate containing bound antioxidant is inferior to that containing conventional antioxidant.

3. The combination of rubber bound antioxidant and conventional antioxidant can enhance the ageing resistance and ozone resistance of natural rubber vulcanizates.

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Chapter 5

BINDING OF ANTIOXIDANTS TO MASTICATED NATURAL RUBBER AND THEIR USE IN NR AND SBR

Binding of antioxidants to polymers during fabrication and processing was suggested as a promising method to enhance the ageing resistance of polymers[1-4]. In this chapter binding of diphenylamine and paraphenylenediamine to natural rubber during mastication is described.

I. BINDING OF DIPHENYLAMINE/PARAPHENYLENEDIAMINE TO NATURAL RUBBER DURING MASTICATION AND THE SUBSEQUENT USE OF THE PRODUCTS IN NR VULCANIZATES

a) Preparation of rubber bound antioxidants

100 g natural rubber was masticated for 15 minutes at 60°C in a two roll mill in the absence and in the presence of different additives like benzoyl peroxide, anhydrous aluminium chloride and mercaptobenzothiazole. The unreacted additives present in the masticated products was removed by repeated reprecipitation using toluene-methylalcohol mixture (1:1 v/v) and dilute sodium carbonate

solution and the products were dried in vacuum oven. The dried samples were dissolved in toluene and their intrinsic viscosities were determined using Schott Gerate AVS 400 capillary viscometer. Intrinsic viscosity is found to be lowest for the sample masticated in the presence of benzoyl peroxide. After 15 minutes of mastication of natural rubber in presence of benzoyl peroxide, 20 g diphenylamine/ paraphenylenediamine was added and mastication was continued for 25 minutes. The unreacted antioxidants and additives were removed as mentioned earlier. The rubber bound antioxidants were obtained in the form of semi solid masses.

The samples were taken at 5 minutes interval after the addition of paraphenylenediamine/diphenylamine to the masticated rubber containing benzoyl peroxide and reprecipitated using a mixture of toluene and methanol (1:1 v/v).

The dried samples were dissolved in toluene and their intrinsic viscosities were measured. The viscosity average molecular weights were calculated.

b) Analysis of the rubber bound antioxidants

Analysis of the bound antioxidants was carried out by thin layer chromatography (TLC), infrared spectroscopy (IR), proton magnetic resonance spectroscopy ('H-NMR) and thermogravimetric analysis (TGA).

TLC was carried out using silica gel as the adsorbent. A mixed solvent benzene and ethylacetate (4:1, v/v) was used as the developing solvent for all samples. Diazotisation using nitrous acid fumes was carried out to detect paraphenylenediamine and NR-PDM. Ninhydrin was used to detect diphenylamine and NR-DAM and iodine for NR[5,6].

Molecular weights of NR-PDM and NR-DAM were calculated using Mark-Houwink-Sakurada equation by measuring intrinsic viscosities using a Schott Gerate capillary viscometer and substituting the values K(5.02×10^{-2}ml/g) and a (.667) of natural rubber[7].

The optimum concentration of the rubber bound antioxidant for getting maximum retention in properties after ageing was determined by varying the amount of NR-PDM,NR-DAM in a standard formulation (Table 5.1 A&B) from 3 to 15 phr. NR-DAM and NR-PDM were added in NR as per formulation given in Table 5.1. The amount of plasticiser can be reduced by the use of semi-solid rubber bound antioxidant as shown in Table 5.1. The optimum cure times and scorch times of the compounds were determined on a Goettfert Elastograph model 67.85 as per ASTM D-1646-1981.

Rubber compounds were moulded in an electrically heated laboratory hydraulic press at 150°C upto their optimum cure times. Dumbell shaped tensile test pieces were punched out of these compression moulded sheets along the mill grain direction. The tensile properties and tear resistance were evaluated on a Zwick Universal Testing machine model 1445 as per ASTM D 412-80. Hardness, abrasion resistance, compression set, rebound resilience and flex crack resistance of the vulcanizates were evaluated as per relevant ASTM standards.

Retention in tensile properties and tear strength was evaluated after ageing the samples at 100°C for 12, 24, 36 and 48h. Retention in compression set, heat build

Table 5.1

Formulations for testing rubber bound antioxidants

Ingredients	A	B	C
Natural rubber (phr)	100	100	100
Zinc oxide	5	5	5
Stearic acid	2	2	2
Mercaptobenzothiazole	0.6	0.6	0.6
Tetramethyl thiuram disulphide	0.2	0.2	0.2
Sulphur	2.5	2.5	2.5
Carbon black HAF (N 330)	40	40	40
Aromatic oil	1	1	5
Vulkanox 4020	--	--	1
NR-PDM	10	--	--
NR-DAM	--	10	--

up, resilience, abrasion resistance and flex crack resistance was evaluated after ageing the samples at 100°C for 48h.

Extractability of the bound antioxidants NR-DAM and NR-PDM was studied by keeping the samples in methanol, acetone (48h, at 30°C) and in boiling toluene for 10h. The retention in tensile properties and tear strength was evaluated after ageing the extracted samples at 100°C for 48h. Extractability of the bound antioxidant in dilute acid and alkali was studied by keeping the samples in HCl (pH 1.02) and in NaOH (pH 9.86) for 48h at room temperature. The retention in tensile properties of the acid and alkali extracted samples was evaluated after ageing at 100°C for 12, 24, 36 and 48h.

Results and Discussion

Fig.5.1 shows the intrinsic viscosities of masticated natural rubber (after 15 minutes of mastication) in the absence of any additive and in the presence of benzoyl peroxide, anhydrous aluminium chloride, mercaptobenzothiazole. Intrinsic viscosity is found to be lowest for the mix containing benzoyl peroxide. This shows

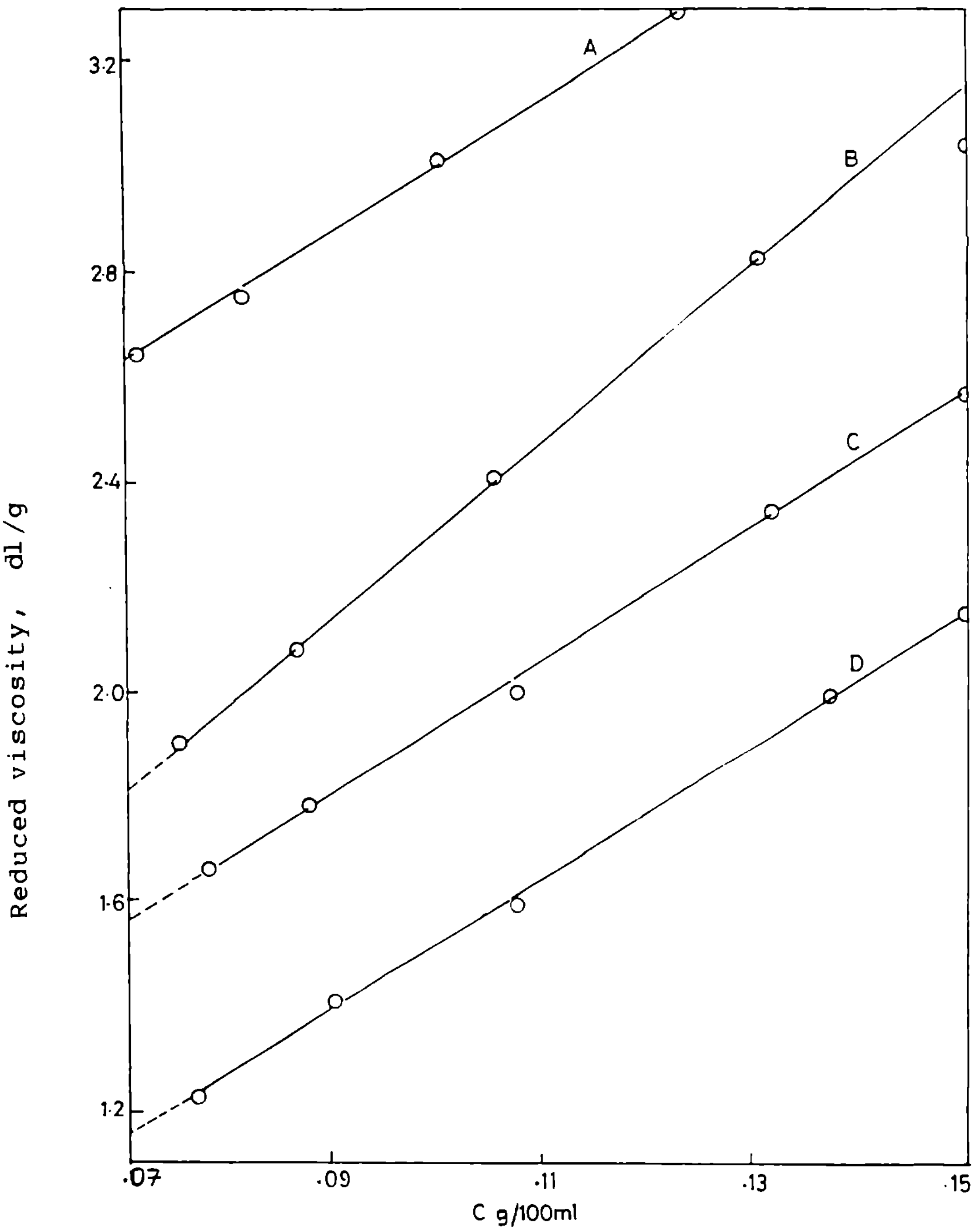


Fig.5.1 Reduced viscosity vs. concentration of NR masticated in the presence of different additives; (A) - without additive, (B) - MBT, (C) - An.$AlCl_3$, (D) - benzoylperoxide.

that the mechanical breakdown is faster in the presence of benzoyl peroxide.

Table 5.2 shows the intrinsic viscosities and viscosity average molecular weights of NR-PDM and NR-DAM during various stages of mastication. It is found that intrinsic viscosity is considerably reduced during mastication. So benzoyl peroxide is found to be effective in increasing the rate of mechano-chemical breakdown in natural rubber.

Fig.5.2 shows the TLC of paraphenylenediamine (PD), diphenylamine (DA), NR-PDM, NR-DAM and masticated rubber. NR was not coloured by nitrous acid fumes/ resorcinol system while NR-PDM and PD were coloured. NR-DAM and DA were coloured by ninhydrin while NR was not; masticated NR was coloured by iodine. The R_F values of masticated rubber and bound antioxidants were found to be almost equal. This indicates that diphenylamine and paraphenylenediamine get chemically attached to masticated rubber during prolonged mastication.

Figs.5.3 to 5.5 show the IR spectra of masticated NR, NR-PDM and NR-DAM. IR spectrum of masticated NR shows

Table 5.2

Intrinsic viscosities and viscosity average molecular weights of NR-PDM and NR-DAM during various stages of mastication

Time of mastication (min.)	Intrinsic viscosity		Viscosity average molecular weight ($\overline{M}_v$)	
	NR-PDM	NR-DAM	NR-PDM	NR-DAM
20	1.134	1.131	106539	98994
25	0.975	0.972	84949	84558
30	0.865	0.861	70995	70504
35	0.70	0.70	51694	51694
40	0.512	0.510	32347	32158

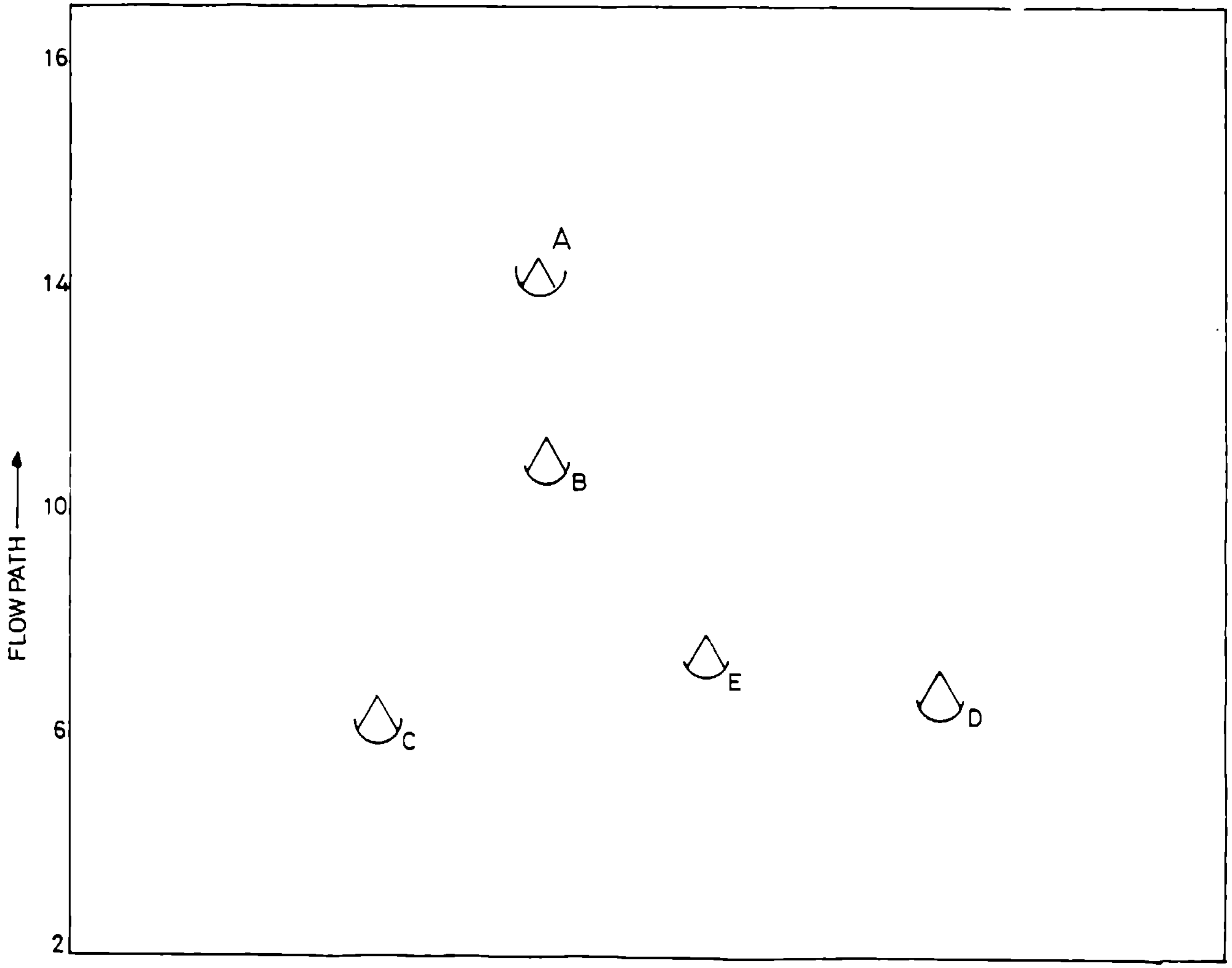


Fig.5.2: TLC of compounds, (A) DA, (B) PD, (C) NR-PDM, (D) NR-DAM, (E) Masticated NR.

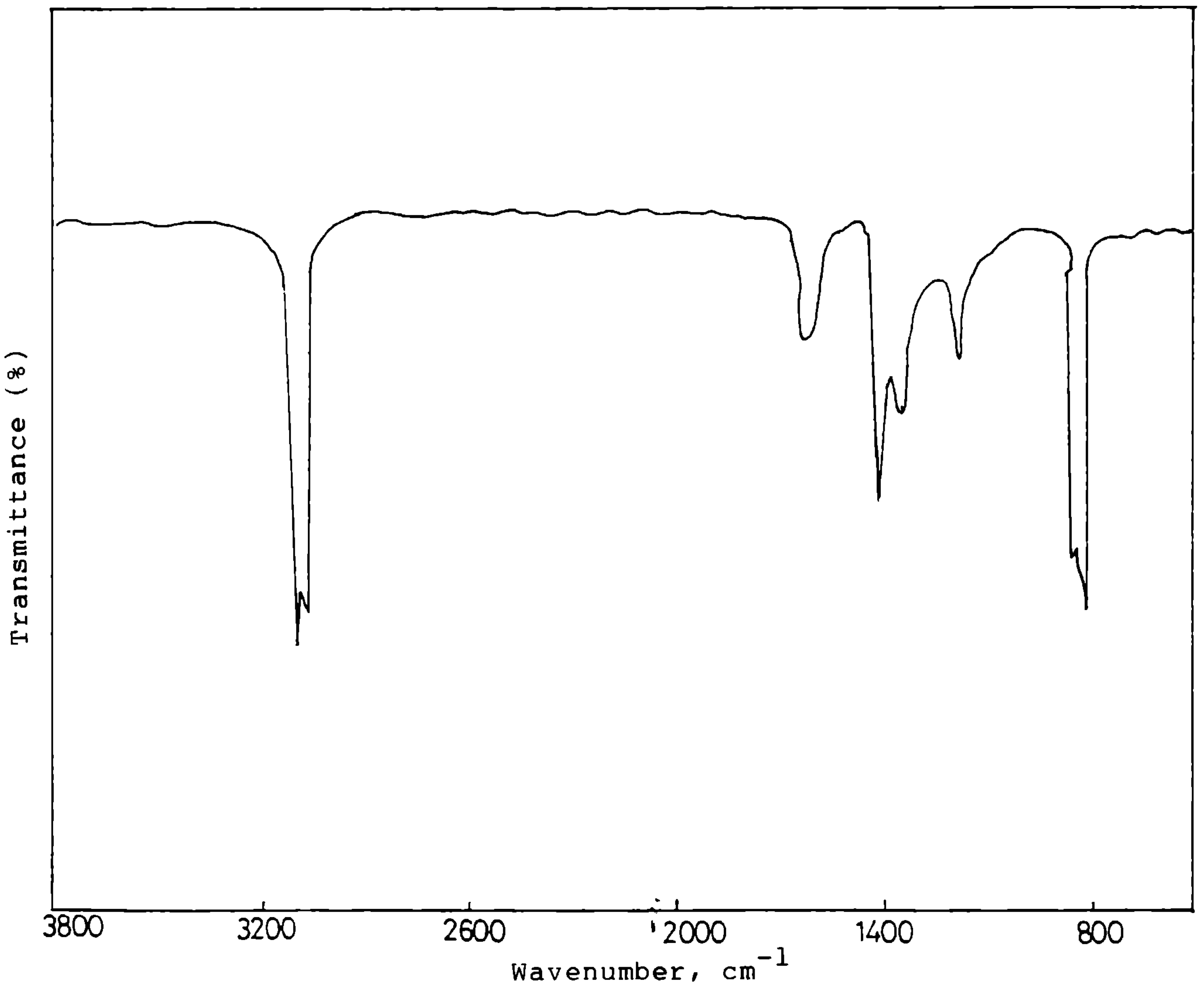


Fig.5.3: IR spectrum of masticated NR

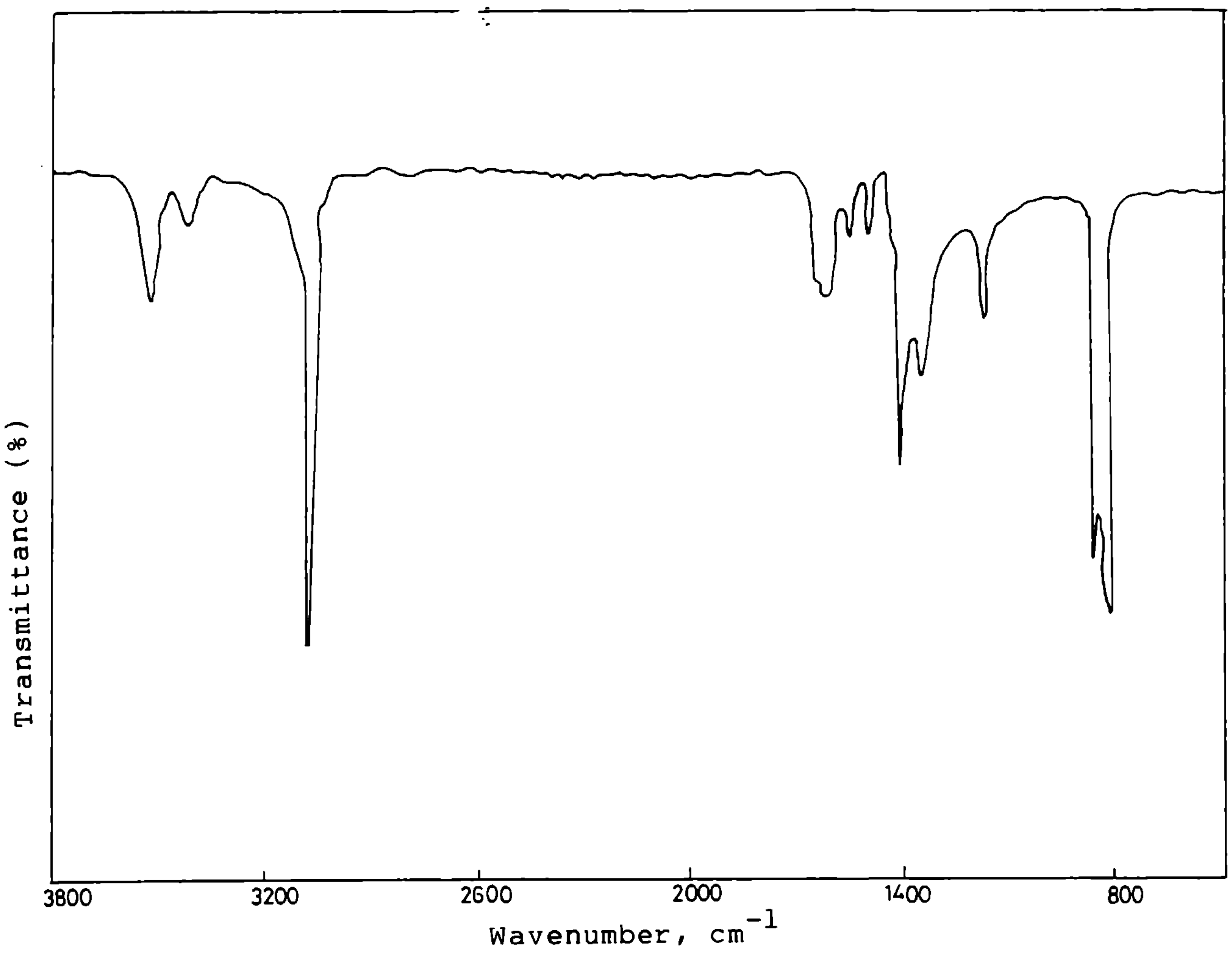


Fig.5.4: IR spectrum of NR-PDM

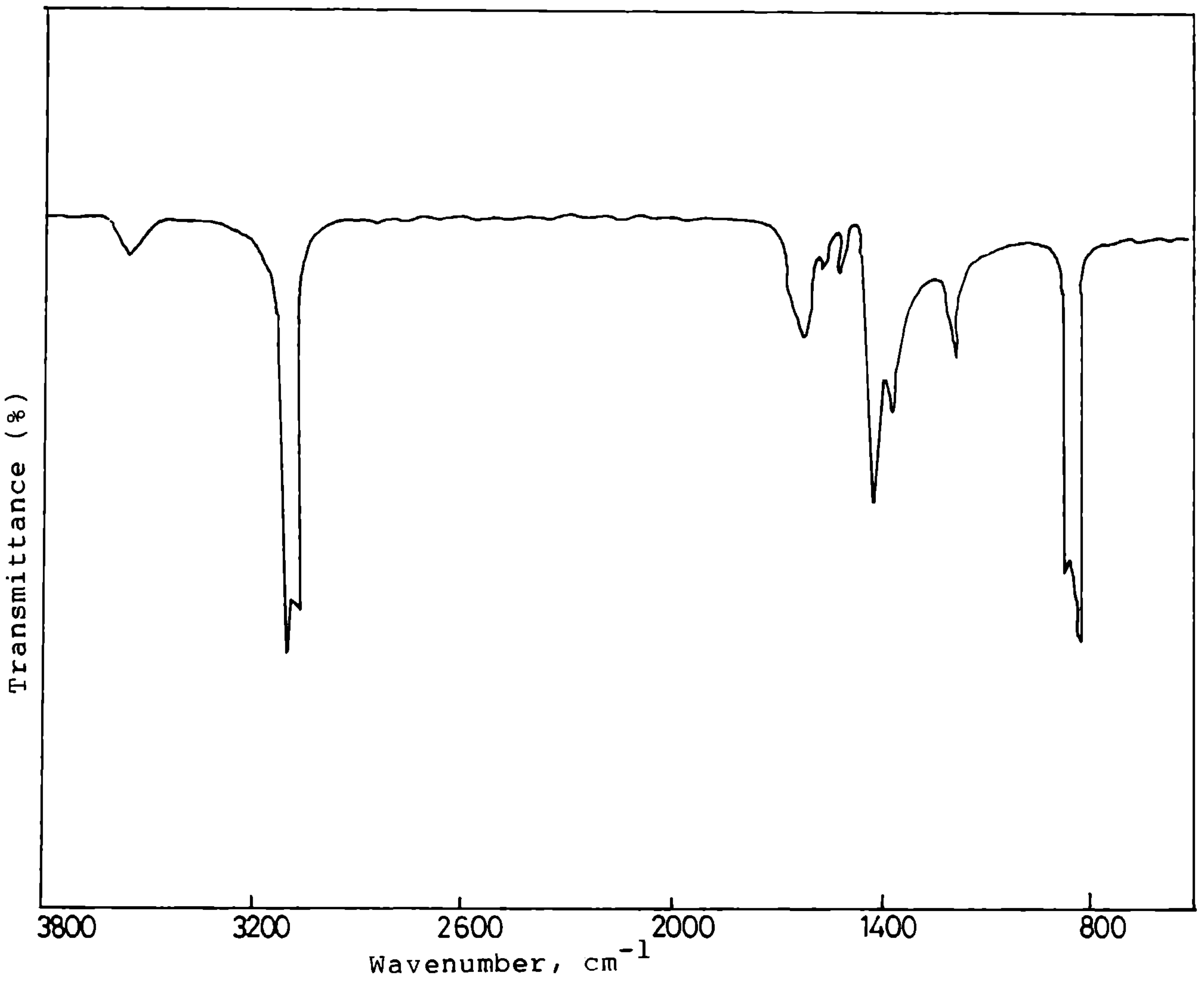


Fig.5.5: IR spectrum of NR-DAM

the peaks at 3000 cm^{-1} corresponding to aliphatic CH, 1665 cm^{-1} due to $>C=C<$,1400 cm^{-1} due to $-CH_3$ and 835 cm^{-1} due to $-C(CH_3)=CH-$. IR spectrum of NR-PDM shows additional peaks at 3500 cm^{-1} (N-H stretching, primary) 1590 cm^{-1} (N-H bending), 1350 cm^{-1} (C-N vibration) and 1500 cm^{-1} corresponding to aromatic ring in paraphenylenediamine. IR spectrum of NR-DAM shows peaks at 1500 cm^{-1} (aromatic ring), 1350 cm^{-1} (C-N vibration) and 3400 cm^{-1} (N-H stretching)[8]. This confirms the chemical binding of antioxidants to NR.

Fig.5.6 shows the 'H-NMR spectrum of masticated NR. There are peaks at δ =5.1 ($>C=C<_H$) , δ = 1.5 (CH_2) and δ = 1.65 (ppm) ($-CH_3$). Figs.5.7 and 5.8 show 'H-NMR spectra of NR-PDM and NR-DAM which show additional peaks at δ = 1.19 and δ = 7.1 ppm corresponding to amino group and aromatic ring present in bound antioxidants[8]. This again confirms the chemical binding of antioxidants to NR.

Free radical mechanism has been suggested for the mechanical breakdown during mastication in presence of chemical agents such as peroxides[9-14]. The steric hinderance caused by cis-configuration with pendent methyl

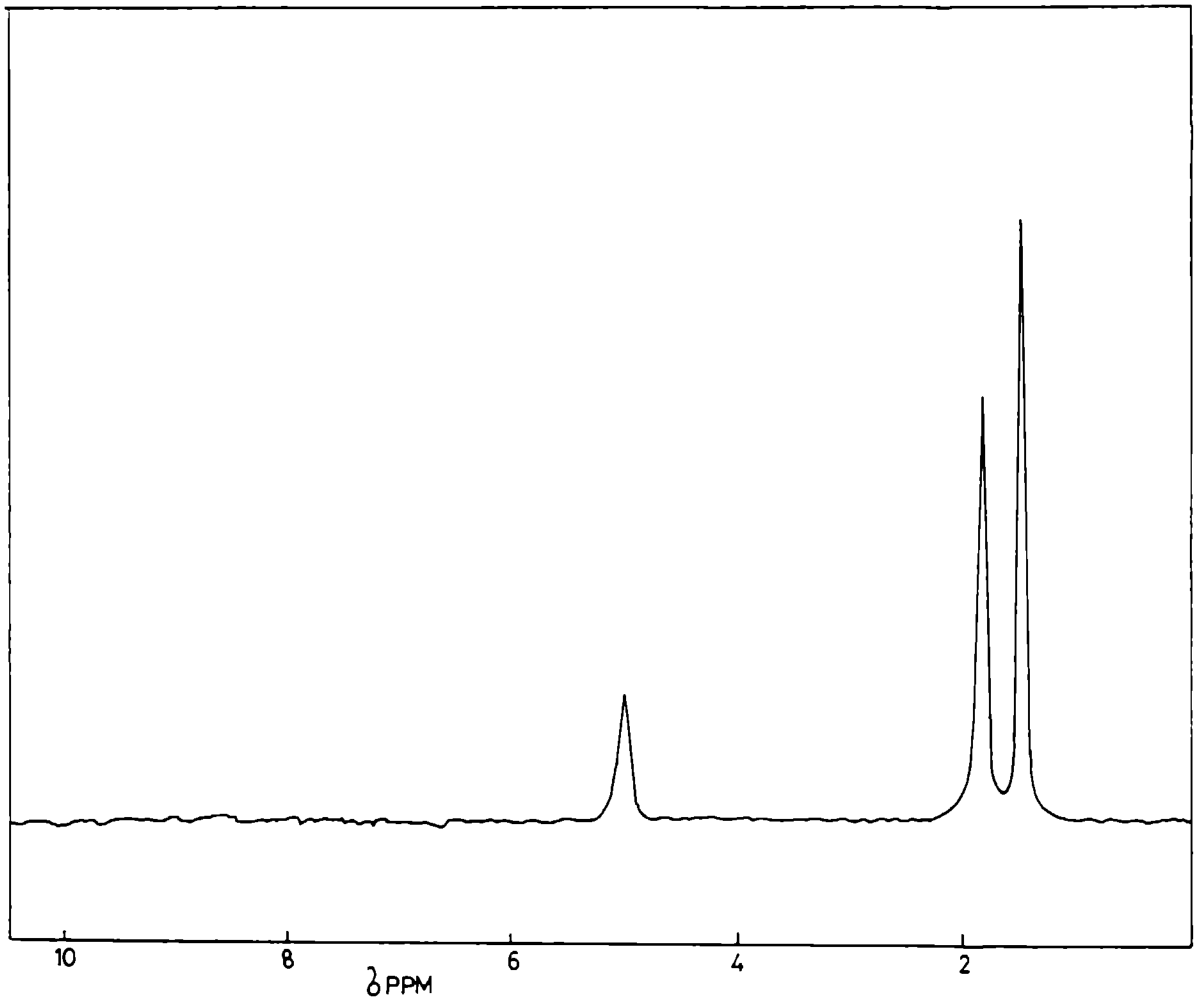


Fig.5.6: 'H-NMR spectrum of masticated NR

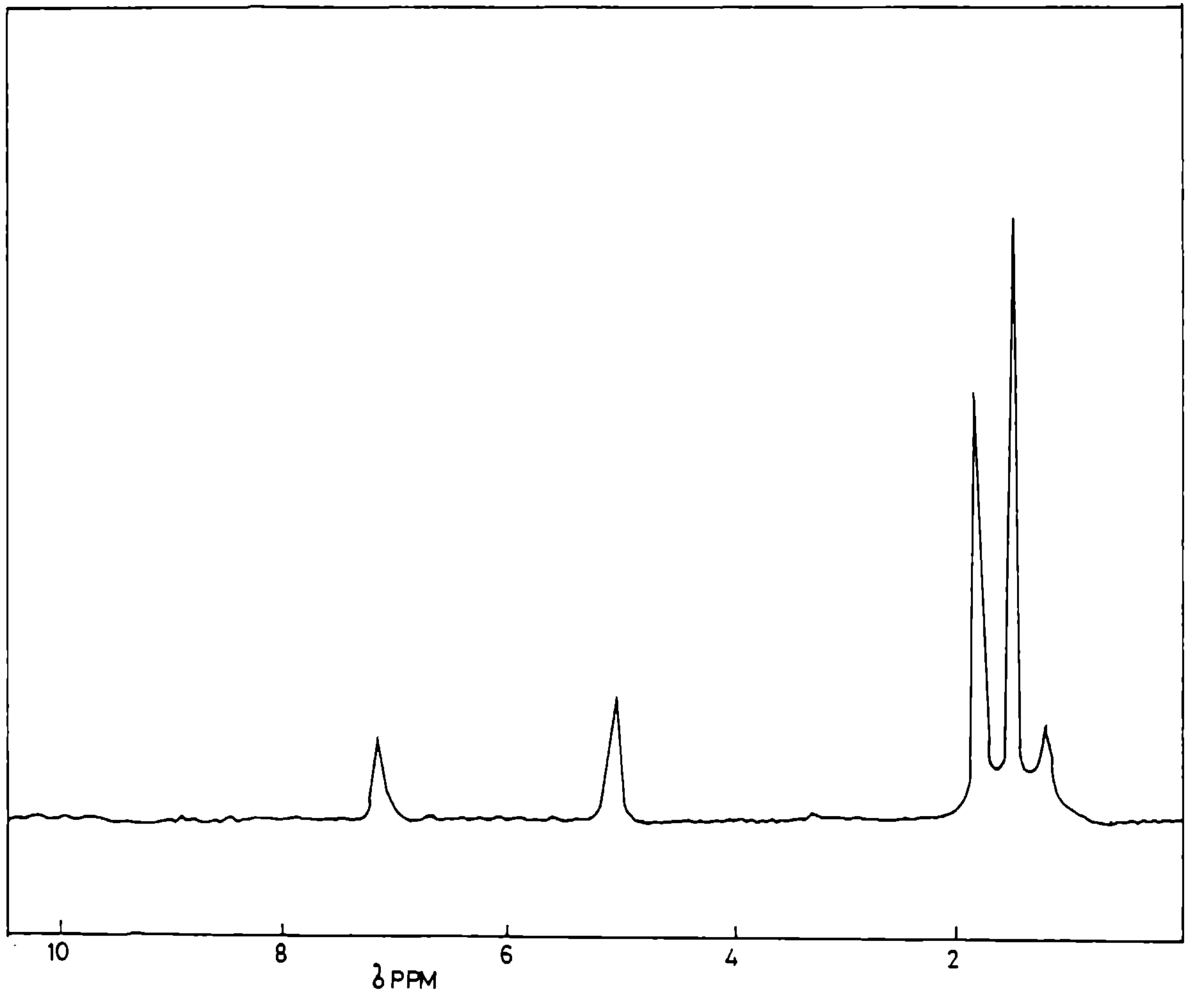


Fig.5.7: 'H-NMR spectrum of NR-PDM

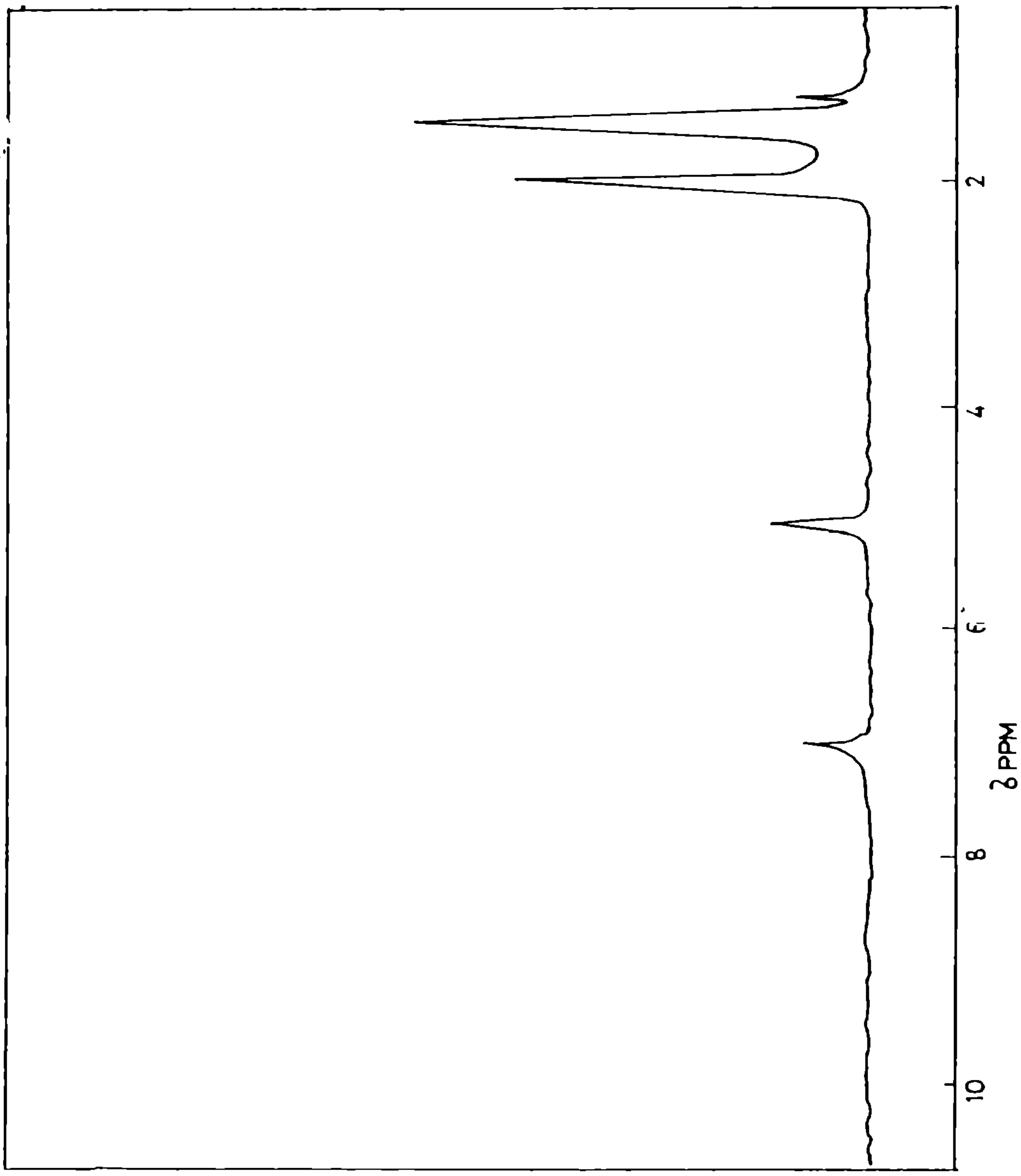


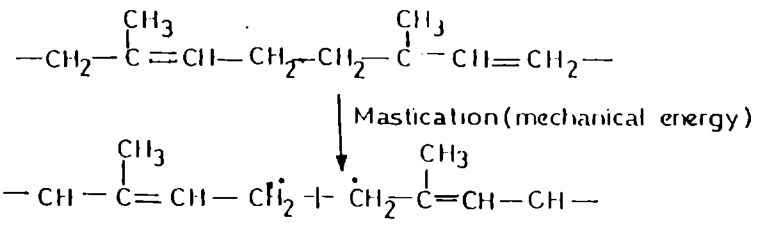
Fig.5.8 'H-NMR spectrum of NR-DAM

groups of natural rubber weakens the CH_2-CH_2 bond, leading to its rupture under favourable conditions. During mastication this bond undergoes cleavage. Based on the complex transformations of aromatic amines during ageing in presence of free radicals and from the mechanism of mastication of NR, a possible mechanism can be suggested for the attachment of paraphenylenediamine (Scheme 5.1) and diphenylamine (Scheme 5.2) to masticated NR[16-18].

Fig.5.9 shows the thermograms of PD, DA, NR-PDM and NR-DAM. The low molecular weight antioxidants volatilise easily while rubber bound antioxidants are less volatile.

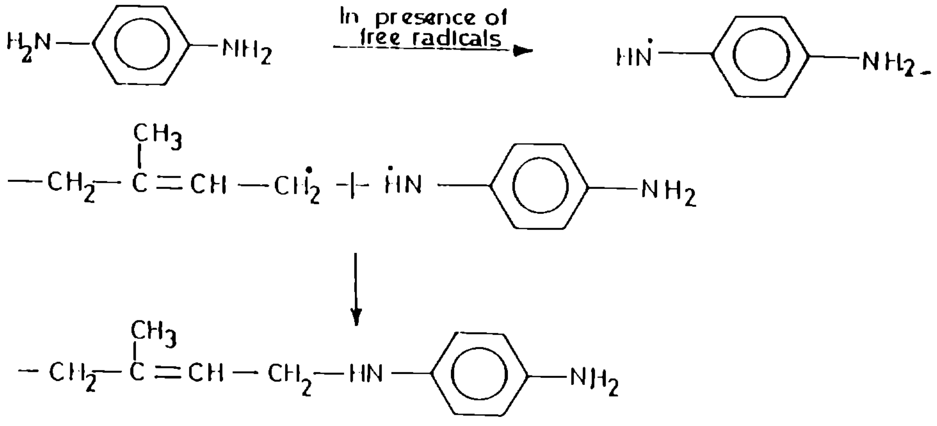
Fig.5.10 shows the variation in tensile strength after ageing with concentration of the antioxidant. The tensile strength retention increases with the amount of chemically bound antioxidant, reaches a maximum and then levels off. The higher requirements of bound antioxidant in comparison to conventional antioxidant may be due to lower amount of effective antioxidant in the rubber bound product.

Fig.5.11 shows the cure curves of the compounds shown in Table 5.1. Cure time and scorch time are reduced



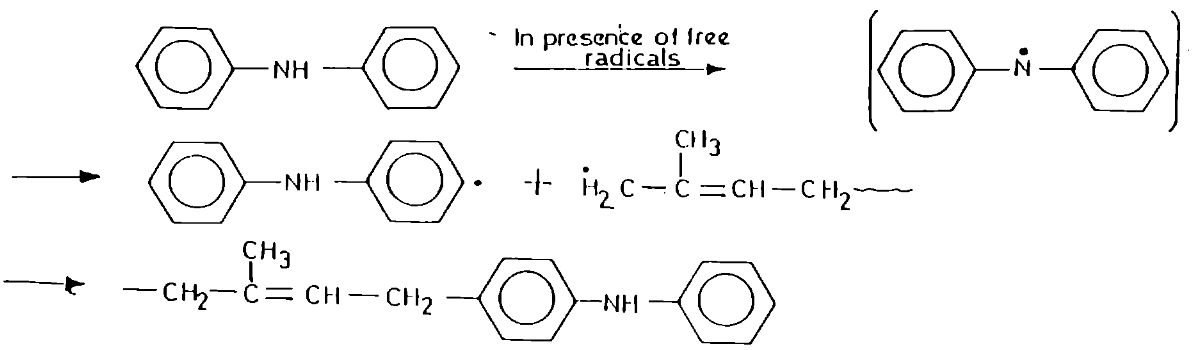
(Mechanical breakdown of NR during mastication)

No I



Scheme 5.1

No II



Scheme 5.2

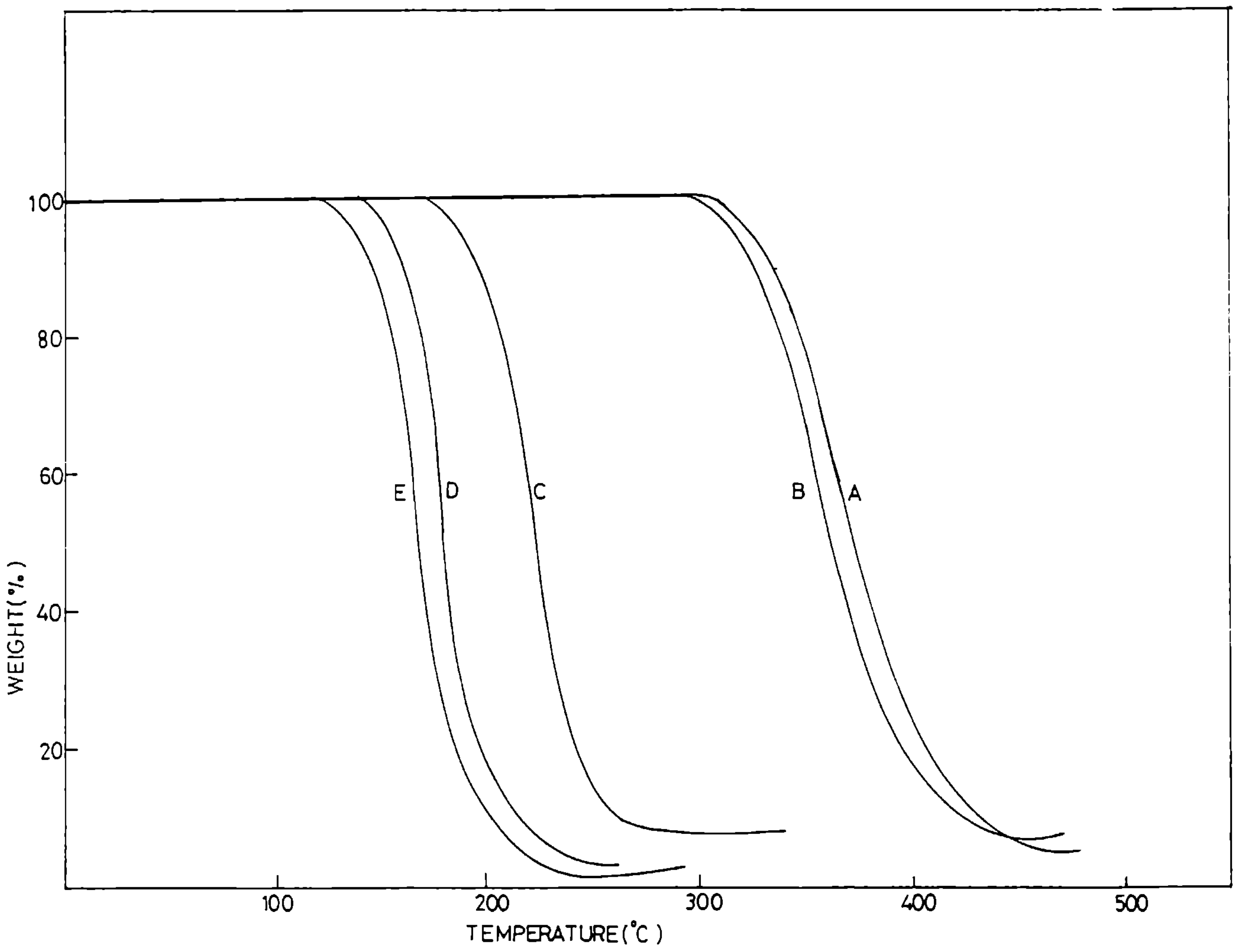


Fig.5.9: Thermograms of antioxidants
A - NR-PDM, B - NR-DAM, C - Vulkanox 4020,
D - diphenylamine, E - paraphenylenediamine.

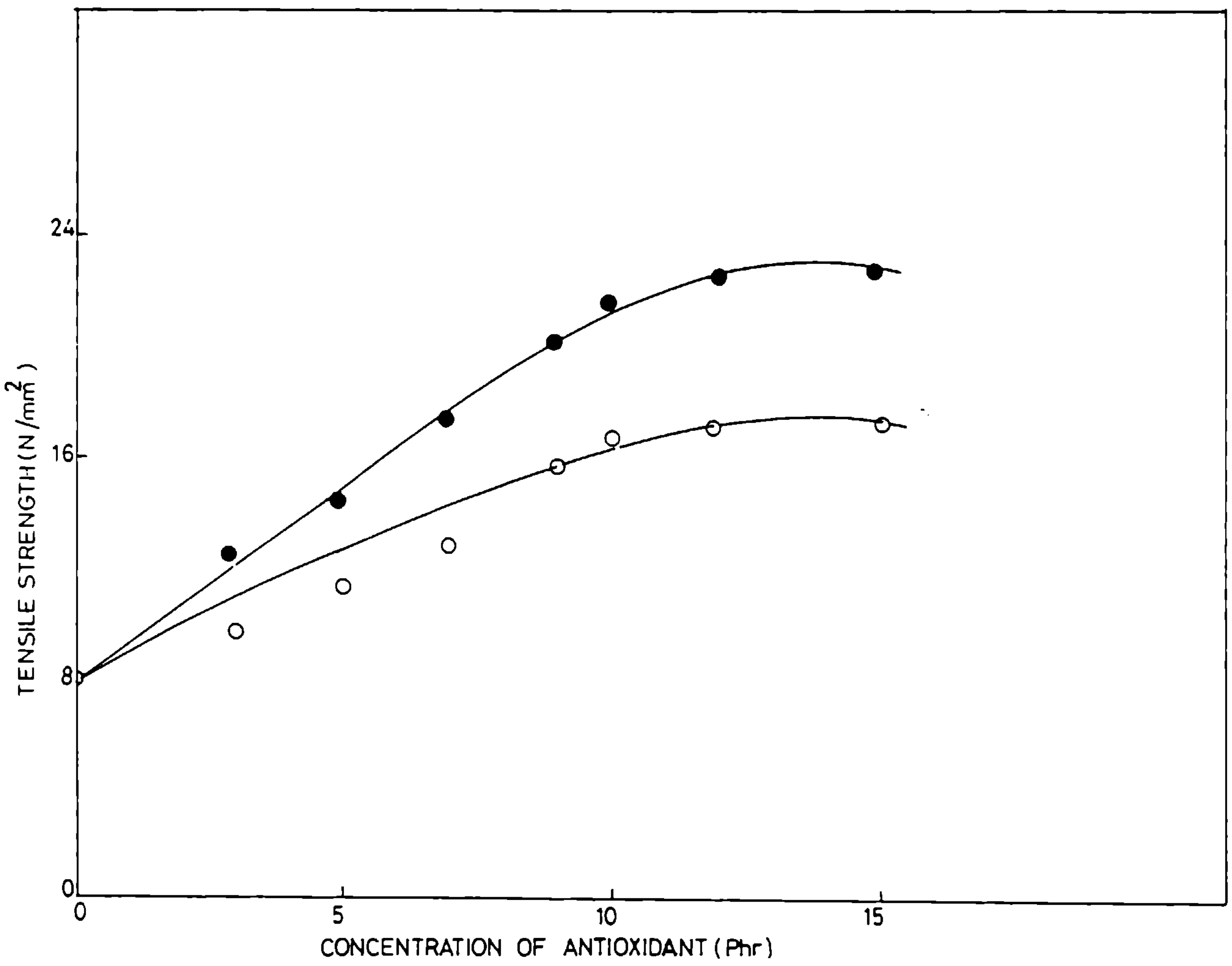


Fig.5.10: Variation in tensile strength after ageing with concentration of the antioxidant

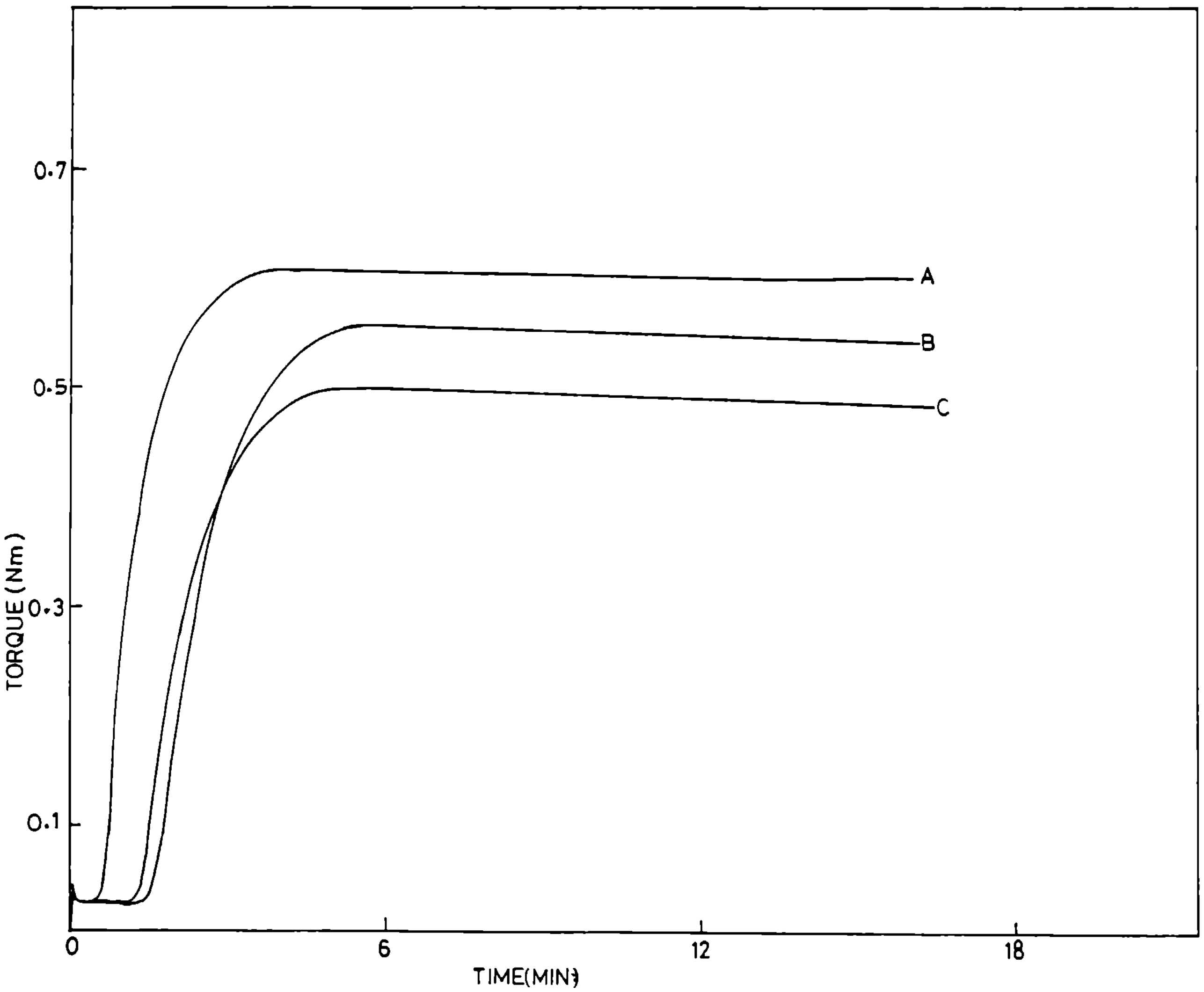


Fig.5.11: Cure curves of the compounds; (A) NR-PDM, (B) NR-DAM (C) vulkanox 4020

by the addition of NR-PDM. This may be due to the presence of free amino group in NR-PDM[19].

Fig.5.12 shows the tensile strength of the above vulcanizates before and after ageing. All the vulcanizates show fairly good resistance to ageing at 100°C for 24h, but the vulcanizates containing NR-PDM and NR-DAM show good ageing resistance when ageing time was increased to 48h, which shows the superiority of bound antioxidants over conventional antioxidants.

Figs.5.13 and 5.14 show the change in elongation at break and tear strength of the vulcanizates before and after ageing. The vulcanizates containing NR-PDM and NR-DAM show better retention in elongation at break and tear strength after ageing. This shows that bound antioxidants can improve the ageing resistance of NR compounds.

Fig.5.15 shows the variation in modulus of the vulcanizates, before and after ageing. The increase in modulus after 48 h ageing may be due to the increase in crosslink density as shown in Table 5.3. This may be partially due to the co-crosslinking of the chemically bound antioxidant with rubber and partially due to the shortening of polysulphidic linkages.

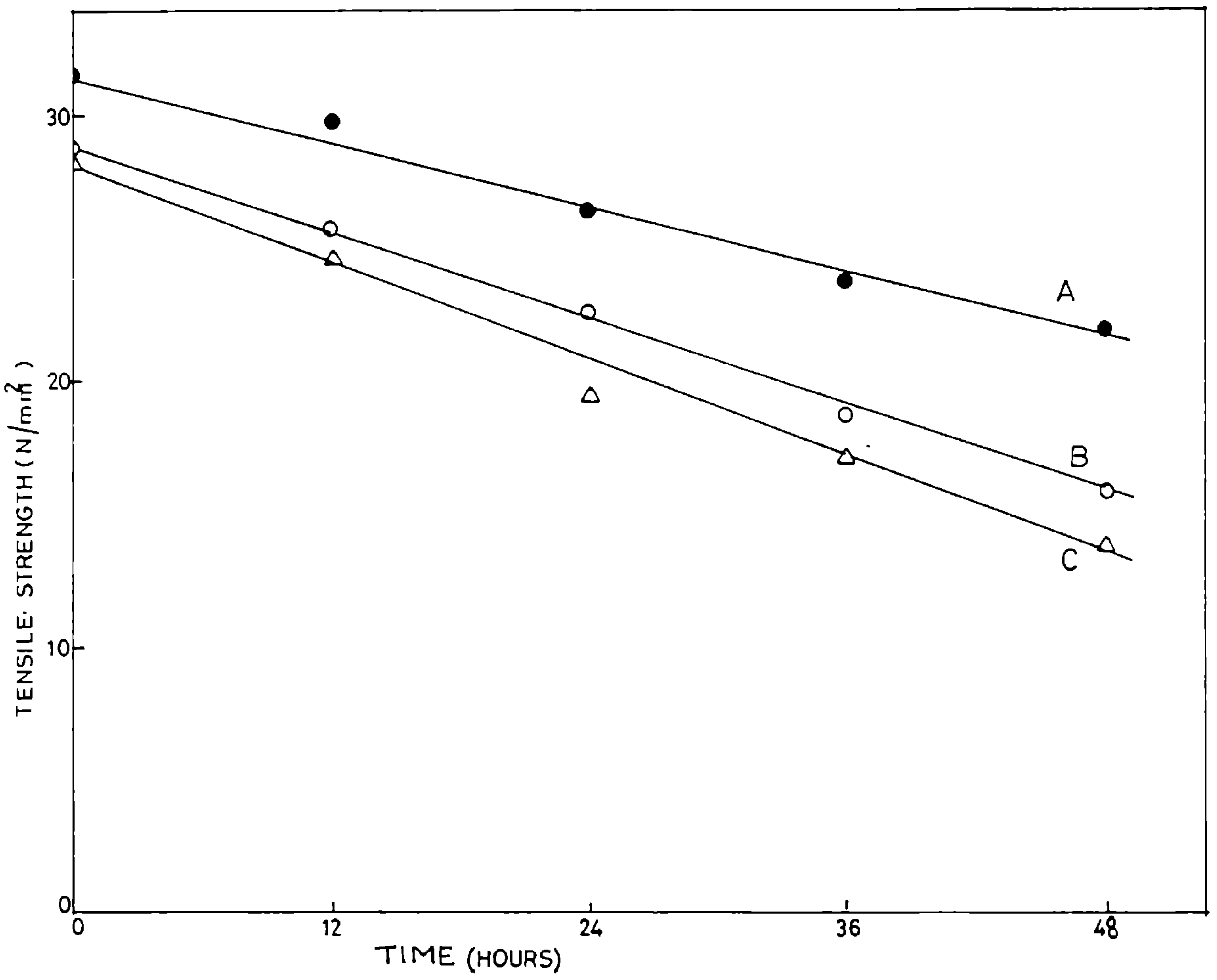


Fig.5.12: Variation in tensile strength of the vulcanizates before and after ageing at 100°C; (A) NR-PDM, (B) NR-DAM, (C) vulkanox 4020

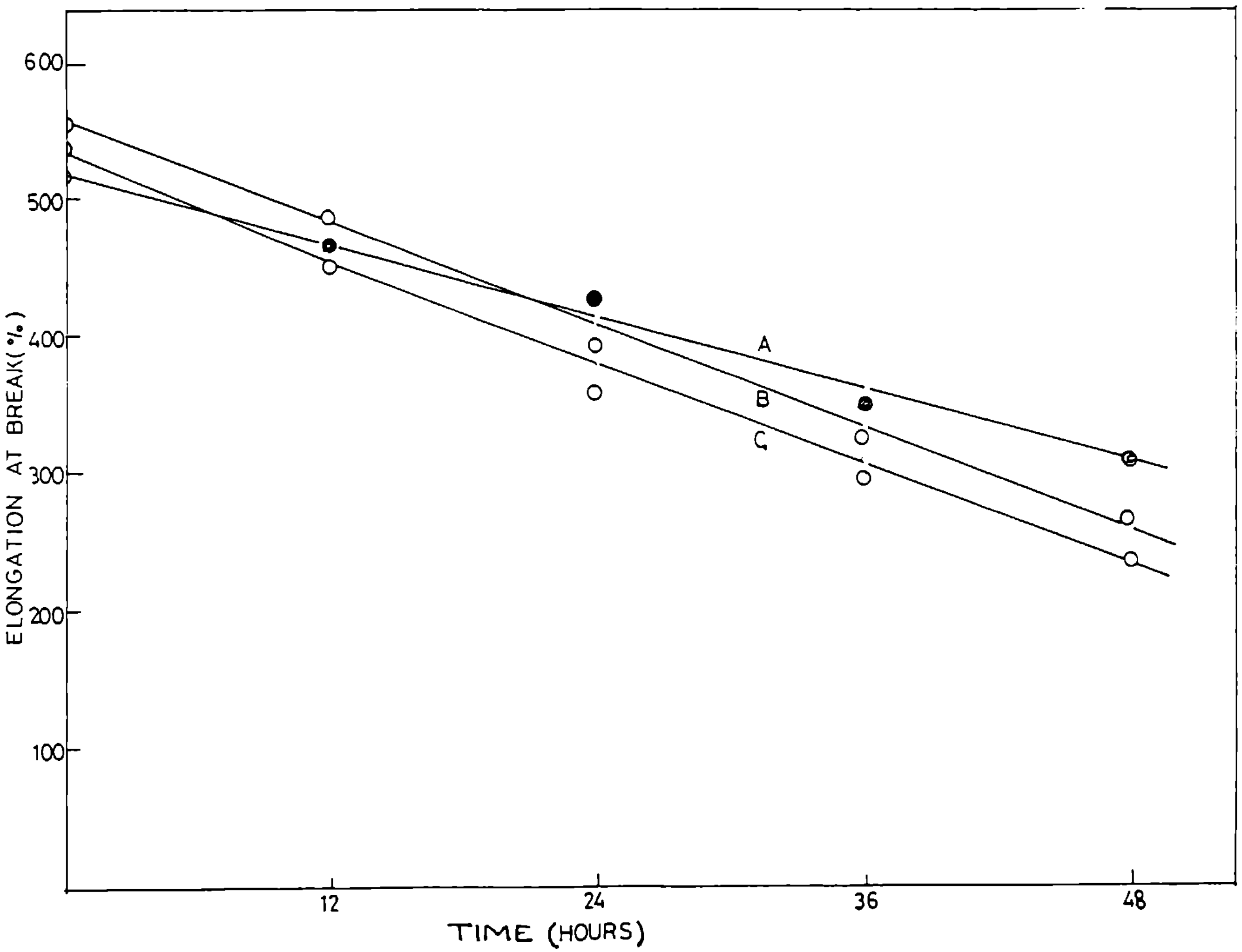


Fig.5.13: Variation in elongation at break of the vulcanizates before and after ageing at 100°C; (A) NR-PDM, (B) NR-DAM, (C) vulkanox 4020

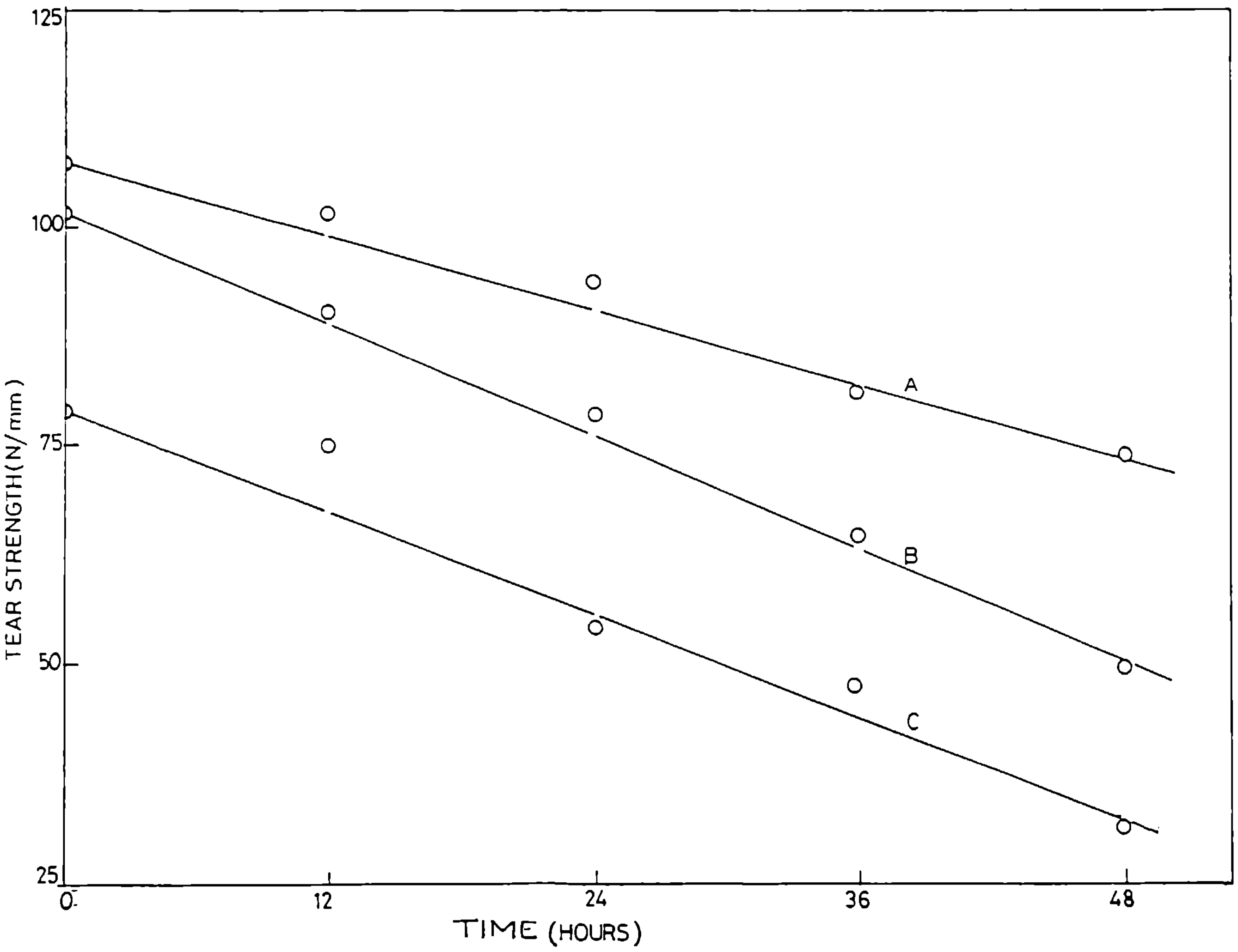


Fig.5.14: Variation in tear strength of the vulcanizates before and after ageing at 100°C; (A) NR-PDM, (B) NR-DAM, (C) vulkanox 4020

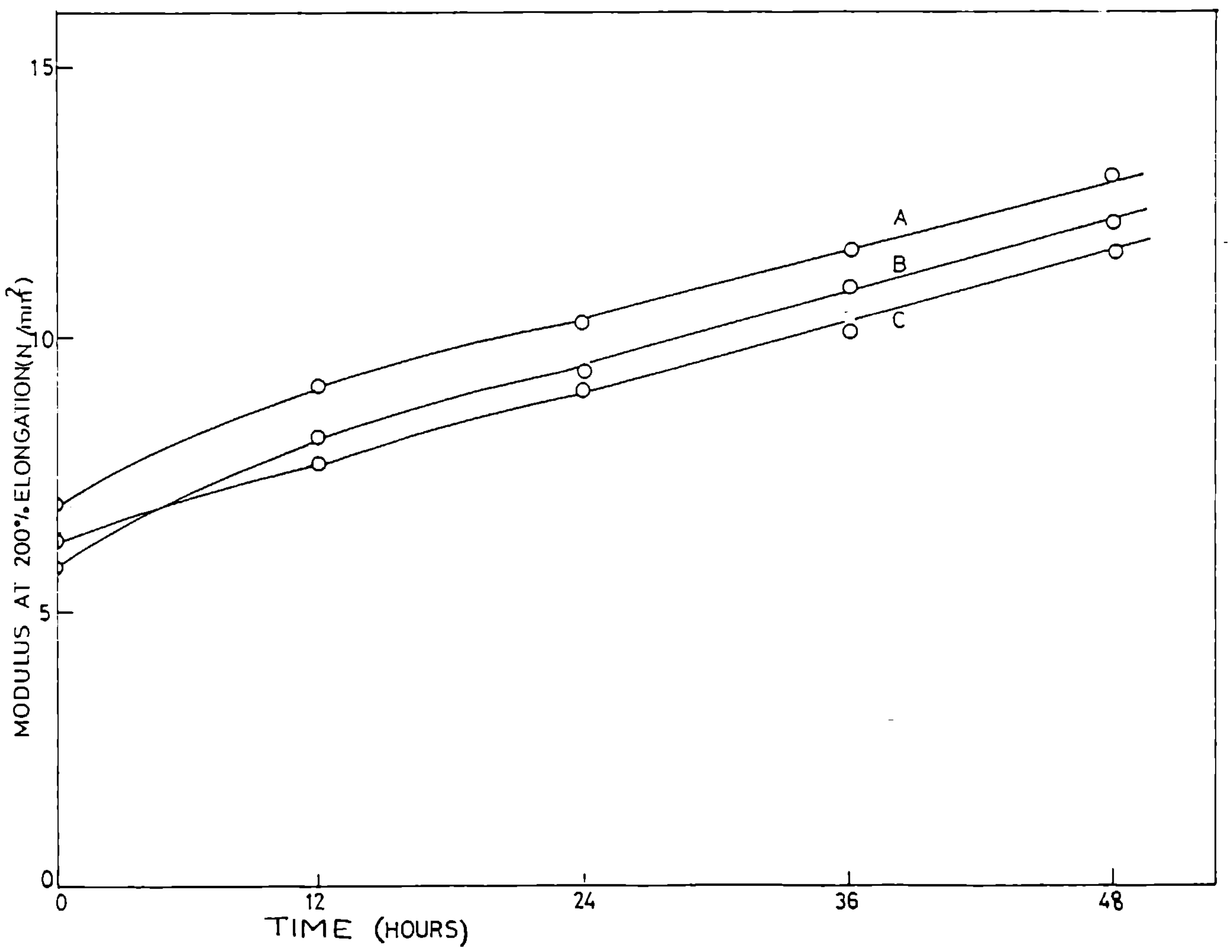


Fig.5.15: Variation in modulus of the vulcanizates before and after ageing at 100°C; (A) NR-PDM, (B) NR-DAM, (C) vulkanox 4020

Table 5.3

Crosslink densities of the vulcanizates before and after ageing at 100°C

Time of ageing (h)	Crosslink density in g mole/cc		
	A	B	C
0	5.639×10^{-5}	4.977×10^{-5}	4.05×10^{-5}
12	5.079×10^{-4}	4.509×10^{-4}	3.278×10^{-4}
24	6.437×10^{-4}	5.671×10^{-4}	3.248×10^{-4}
48	6.368×10^{-4}	5.779×10^{-4}	3.44×10^{-4}

Fig.5.16 shows the variation in hardness of the vulcanizates before and after ageing. Hardness values of the vulcanizates containing bound antioxidants are found to be higher than that containing conventional antioxidant. This may be due to the lower amount of plasticiser in the vulcanizates containing bound antioxidant.

Table 5.4 shows the variation in tensile properties, tear strength and hardness of the vulcanizates before and after ageing after extracting the samples in acetone, methanol and toluene. The retention in properties by the vulcanizates containing NR-PDM and NR-DAM are probably due to the lower extractability of the bound antioxidant by these solvents. The retention in properties after extraction in toluene confirms the chemical attachment of the rubber part in NR-PDM and NR-DAM to NR during sulphur vulcanization.

Figs.5.17 to 5.19 show the variation in tensile strength, elongation at break and modulus of the vulcanizates before and after ageing, after extraction in dilute HCl and dilute NaOH. The retention in properties shown by vulcanizate containing bound antioxidant shows its resistance to leaching in acidic and alkaline medium.

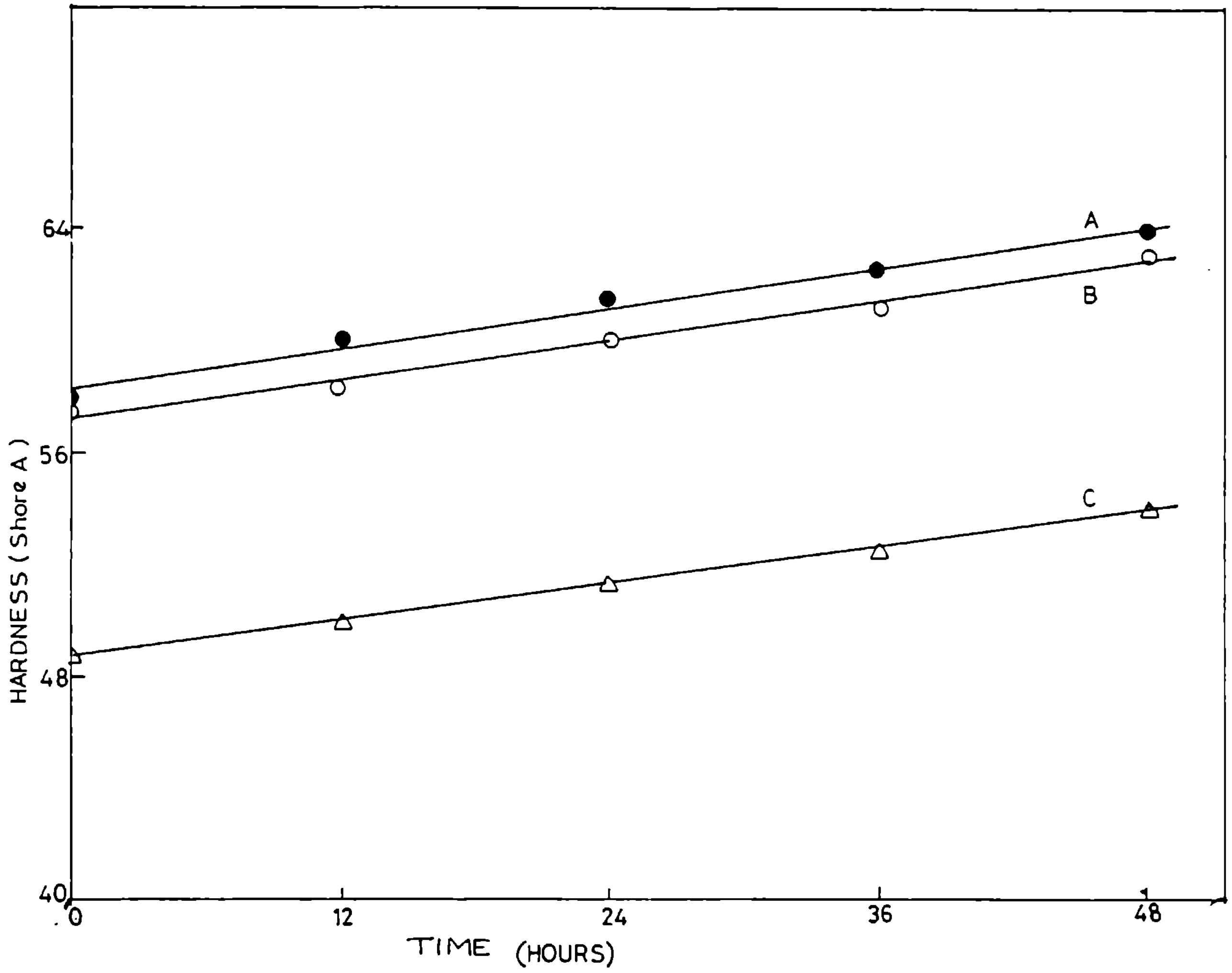


Fig.5.16: Variation in hardness of the vulcanizates before and after ageing at 100°C; (A) NR-PDM, (B) NR-DAM, (C) vulkanox 4020

Table 5.4

Properties before and after solvent extraction (48h at 27°C in methanol and acetone, 10h in boiling toluene followed by ageing at 100°C for 48h)

Properties	Properties before extraction			Properties after extraction followed by ageing at 100°C for 48h								
				Methanol			Acetone			Toluene		
	A	B	C	A	B	C	A	B	C	A	B	C
Tensile strength (N/mm^2)	30.75	29.41	28	20.48	16.06	8.89	18.55	14.37	7.21	18.20	16	7.04
Elongation at break (%)	511.47	561.17	536.66	306.96	312.30	187.85	294.72	322.13	162.89	257.37	193.42	188.52
Modulus at 200% elongation (N/mm^2)	7.12	5.71	6.58	10.93	9.88	00	9.96	9.45	00	12.67	00	00
Tear strength (N/mm)	115.60	102.71	80.40	52.85	47.71	27.74	50.84	45.64	20.78	39.97	30.80	20.97
Hardness (Shore A)	58	58	49	52	51	41	52	52	40	46	45	30

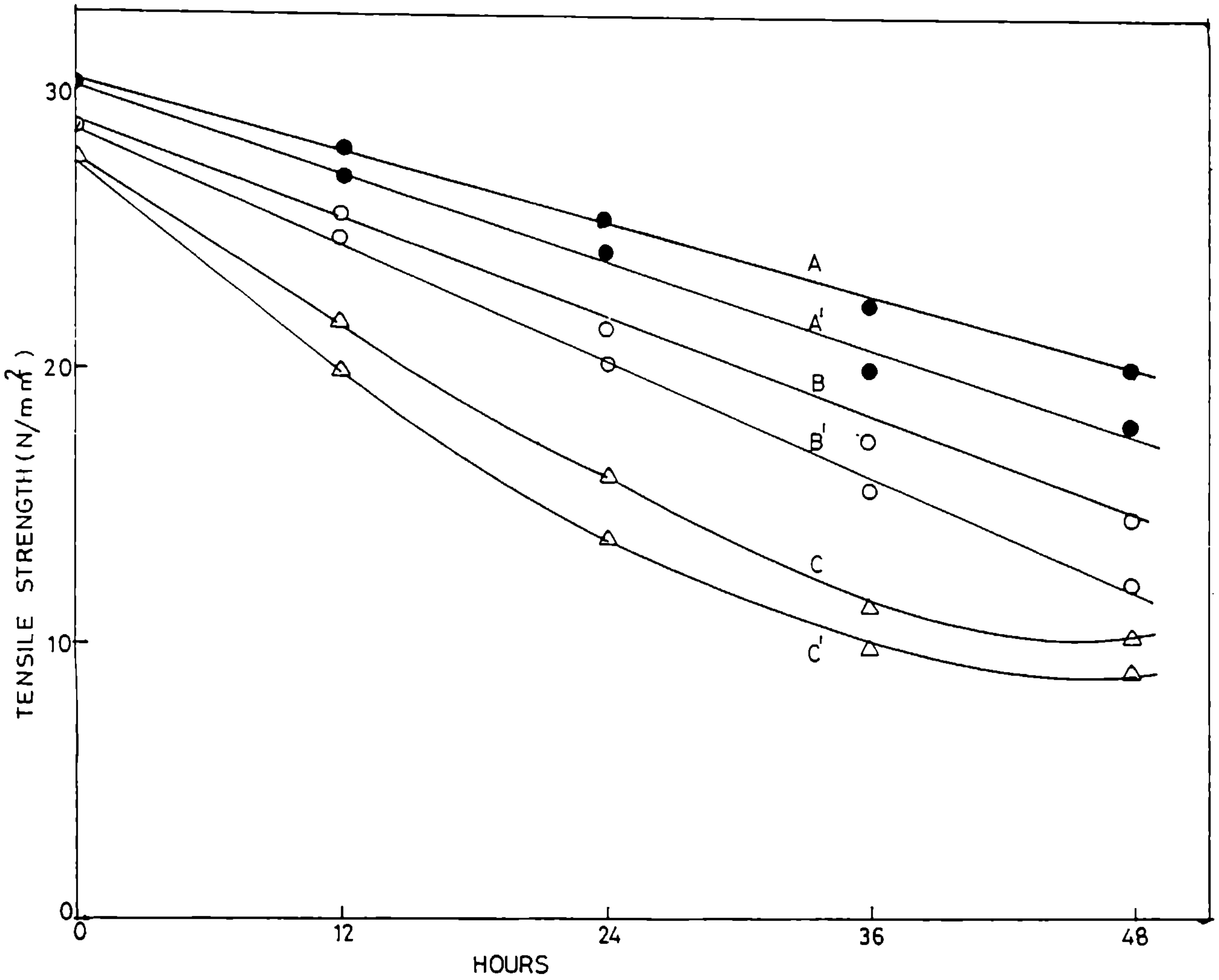


Fig.5.17 Variation in tensile strength of the vulcanizates before and after extraction in solvents followed by ageing at 100°C. (a) in dilute NaOH, A - NR-PDM, B - NR-DAM, C - Vulkanox 4020, (b) in dilute HCl, A' - NR-PDM, B' - NR-DAM, C' - Vulkanox 4020.

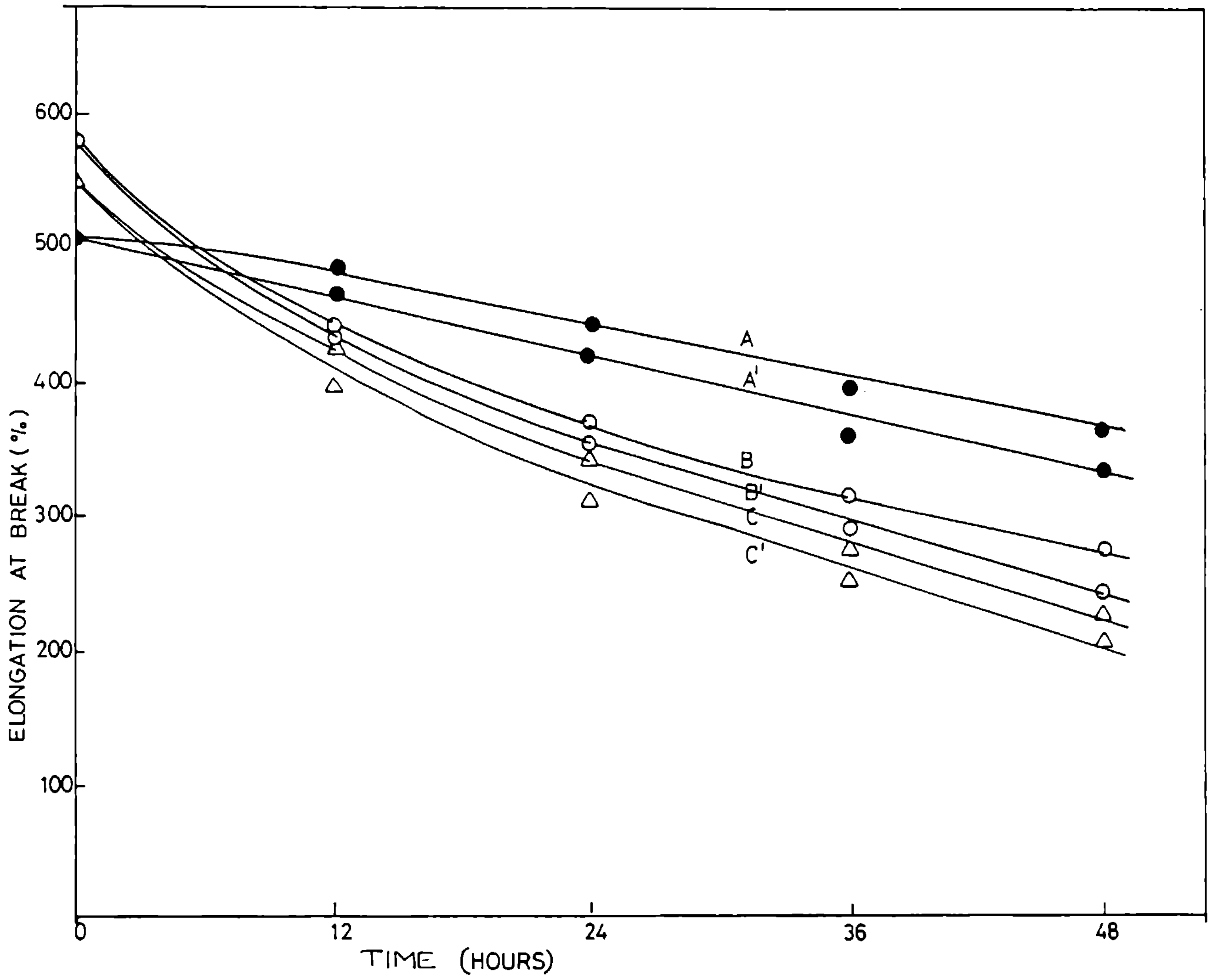


Fig.5.18 Variation in elongation at break of the vulcanizates before and after extraction in solvents followed by ageing at 100°C. (a) in dilute NaOH, A - NR-PDM, B - NR-DAM, C - Vulkanox 4020, (b) in dilute HCl, A' - NR-PDM, B' - NR-DAM, C' - Vulkanox 4020.

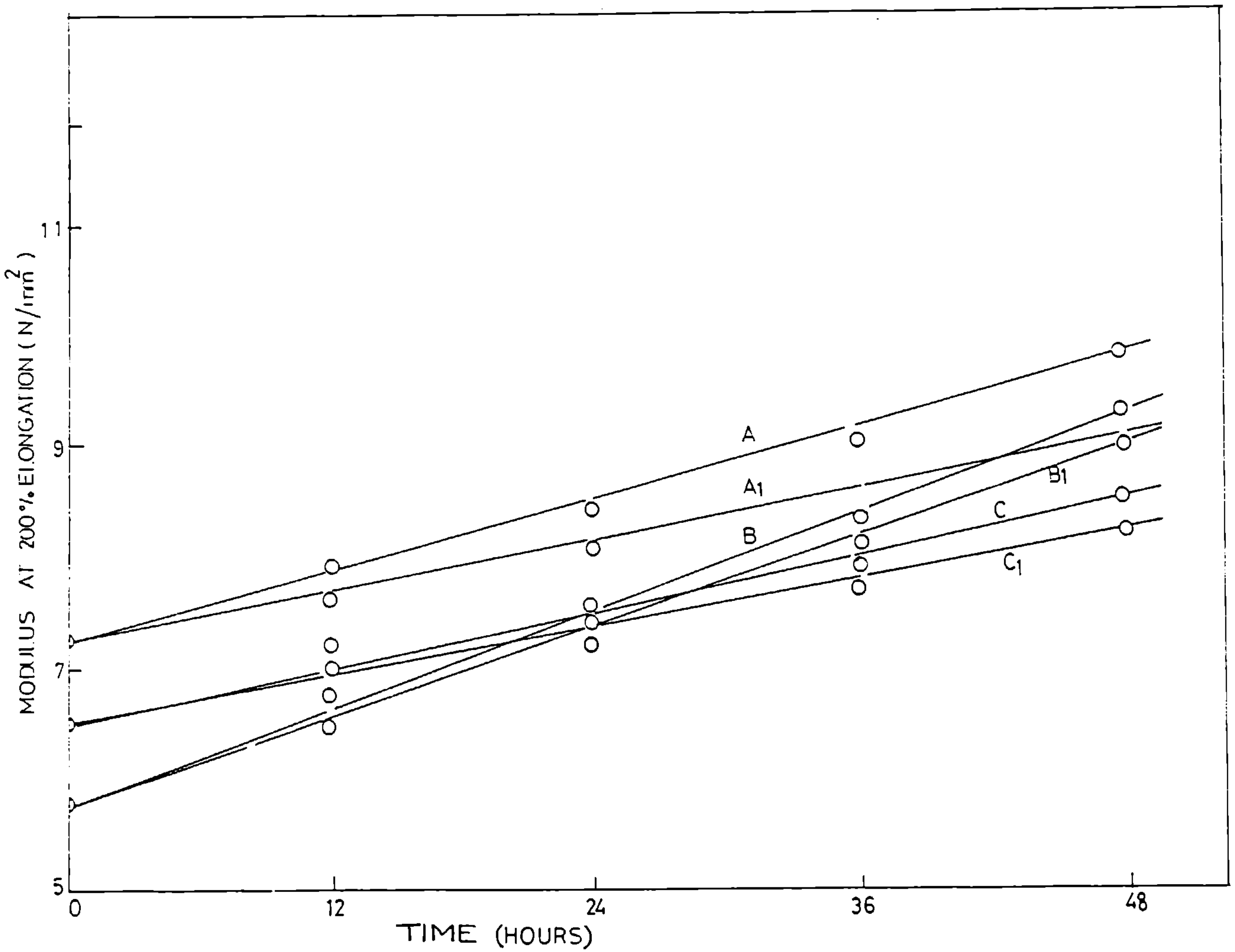


Fig.5.19 Variation in modulus of the vulcanizates before and after extraction in solvents followed by ageing at 100°C. (a) in dilute NaOH, A - NR-PDM, B - NR-DAM, C - Vulkanox 4020, (b) in dilute HCl, A' - NR-PDM, B' - NR-DAM, C' - Vulkanox 4020.

Table 5.5

Properties of vulcanizates (Table 5.1) before and after ageing

Properties	A	B	C
Properties before ageing			
Resilience (%)	61.34	61.55	62.00
Heat build up [(ΔT)°C]	20	21	19.3
Flex initiation resistance (k cycles)	437.111	289.79	213.271
Flex crack resistance (k cycles)	618.834	546.373	381.840
Compression set (%)	16.99	17.81	18.84
Abrasion resistance (Volume loss, cc/h)	3.71	3.20	3.24
Properties after ageing at 100°C for 48h			
Resilience (%)	51.43	49.02	46.02
Heat build up [(ΔT)°C]	40.1	42.5	43.9
Flex initiation resistance (k cycles)	290.73	190.73	121.395
Flex crack resistance (k cycles)	437.82	400.12	154.625
Compression set (%)	11.42	12.17	13.44
Abrasion resistance (Volume loss, cc/h)	3.89	3.91	3.94

Table 5.5 shows properties like resilience, heat build up, flex crack resistance, abrasion resistance and compression set of the vulcanizates before and after ageing. The retention in these properties for the vulcanizates containing NR-PDM and NR-DAM again confirms the superiority of the bound antioxidants.

Conclusions

1. Paraphenylenediamine and diphenylamine can be chemically attached to natural rubber during aggressive mastication in presence of a free radical generator like benzoyl peroxide.

2. The rubber bound antioxidants have much superior resistance to volatility and extractability compared to conventional antioxidant.

3. The rubber bound antioxidants can improve the ageing resistance of the natural rubber vulcanizates.

4. The rubber bound antioxidant can act as a polymeric plasticiser.

II. APPLICATION OF NATURAL RUBBER BOUND PARAPHENYLENEDIAMINE IN SBR VULCANIZATES

Experimental

NR-PDM and conventional antioxidants were employed in SBR as per formulation given in Table 5.6. The amount of plasticiser can be reduced by the use of semisolid NR-PDM as shown in Table 5.6. The optimum cure times and scorch times for the compounds were determined on a Goettfert Elastograph model 67.85 as per ASTM D 1646 (1981). Rubber compounds were moulded in an electrically heated laboratory hydraulic press at 150°C upto their optimum cure times. Dumbell shaped tensile test pieces were punched out of these compression moulded sheets along the mill grain direction. The tensile properties and tear resistance were evaluated on a Zwick universal testing machine model 1445 as per ASTM standards. Hardness, abrasion resistance and compression set of the vulcanizates were evaluated as per relevant ASTM standards.

Retention in tensile properties and tear strength was evaluated after ageing the samples at 100°C for 24, 48 and 72h. Retention in compression set, and abrasion resistance was evaluated after ageing the samples at 100°C

Table 5.6

Formulations for testing the antioxidants

Ingredients	A	B	C
Styrene-butadiene rubber (phr) (SBR 1502)	100	100	100
Zinc oxide	4	4	4
Stearic acid	2	2	2
Carbon black (HAF N330)	45	45	45
Aromatic oil	3	6.5	6.5
Benzthiazyl 2-sulphenmorpholide	1.0	1.0	1.0
Tetramethyl thiuram disulphide	0.4	0.4	0.4
Sulphur	2.0	2.0	2.0
NR-PDM	10.0	--	--
Vulkanox 4020	--	1	--
Vulkanox HS	--	--	1

for 48h. Extractability of NR-PDM from SBR vulcanizates was studied by keeping the samples in methanol and acetone for 48h at room temperature. Retention in tensile properties was studied after ageing these extracted samples at 100°C for 48h.

Results and Discussion

Fig.5.20 shows the cure curves of the compounds shown in Table 5.6. Cure time and scorch time were reduced by the addition of NR-PDM. This may be due to the accelerating effect of the free amino group present in NR-PDM[19].

Fig.5.21 shows tensile strength of the above vulcanizates before and after ageing. All the vulcanizates show good ageing resistance at 100°C for 24h, but the compound containing NR-PDM has better ageing resistance when ageing time was increased to 48h, which shows the superiority of bound antioxidant over conventional antioxidants.

Fig.5.22 shows elongation at break of the vulcanizates before and after ageing. Elongation at break

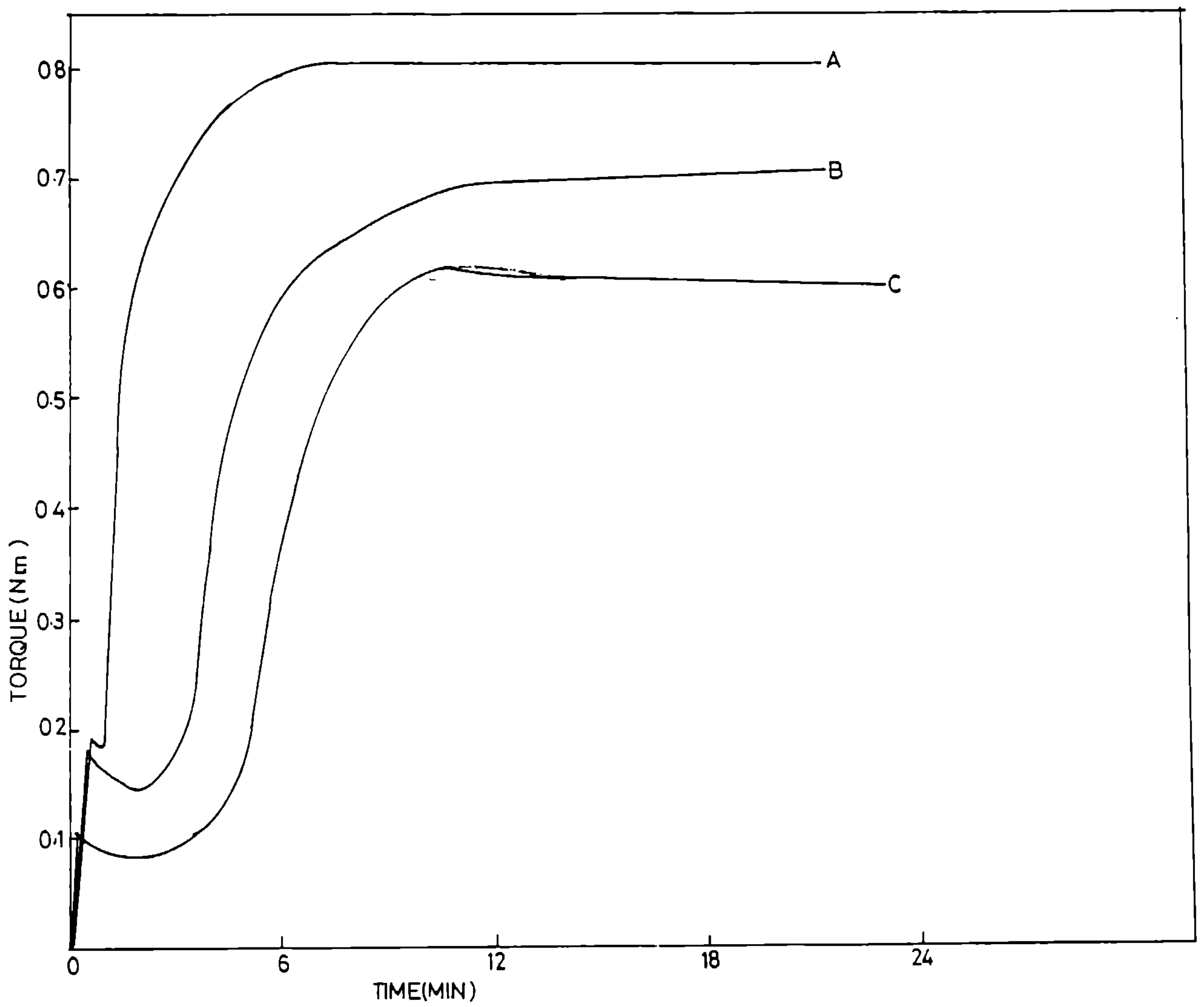


Fig.5.20: Cure curves of the compounds; (A) NR-PDM, (B) vulkanox 4020, (C) vulkanox HS

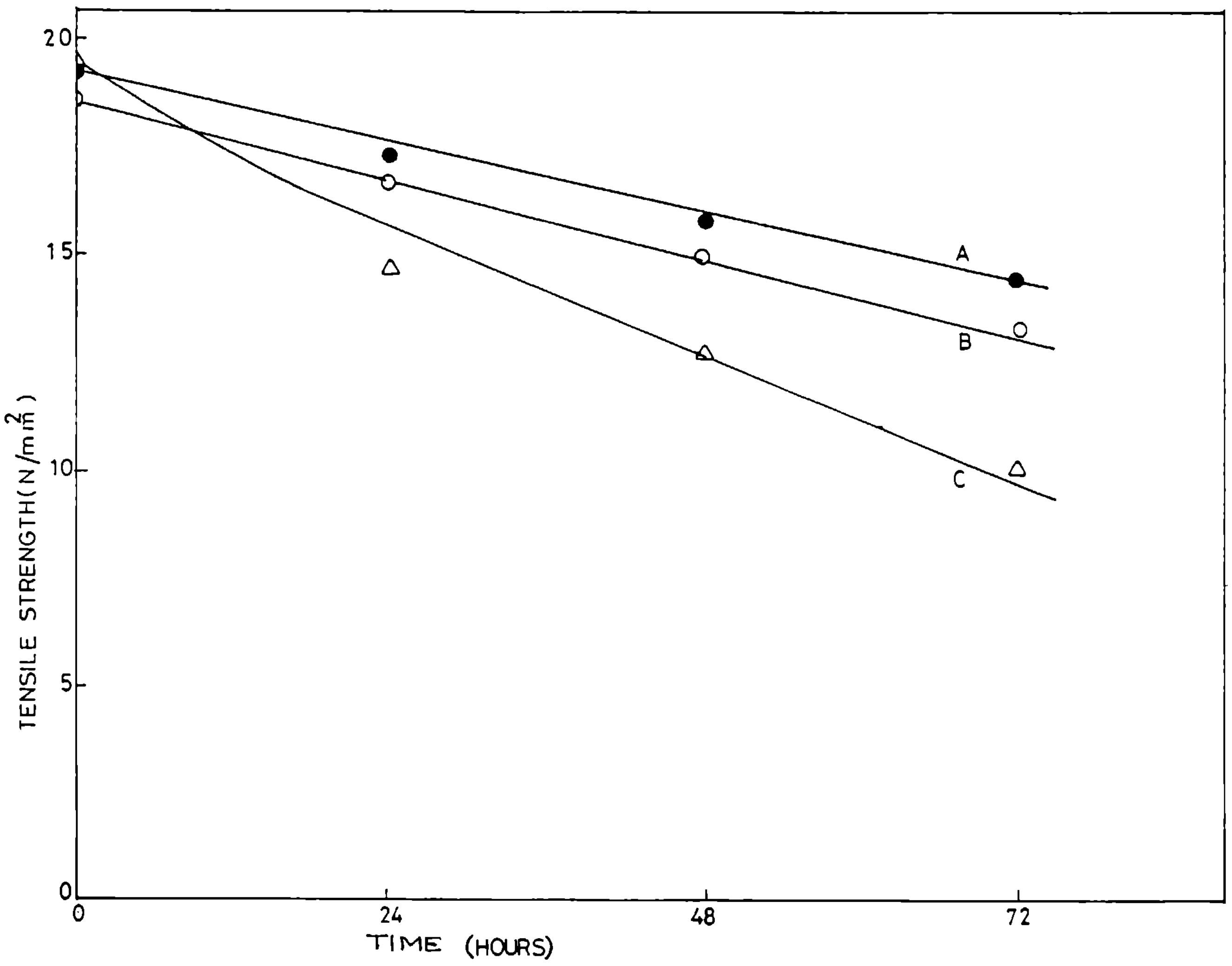


Fig.5.21: Variation in tensile strength of the vulcanizates before and after ageing at 100°C; (A) NR-PDM, (B) vulkanox 4020, (C) vulkanox HS

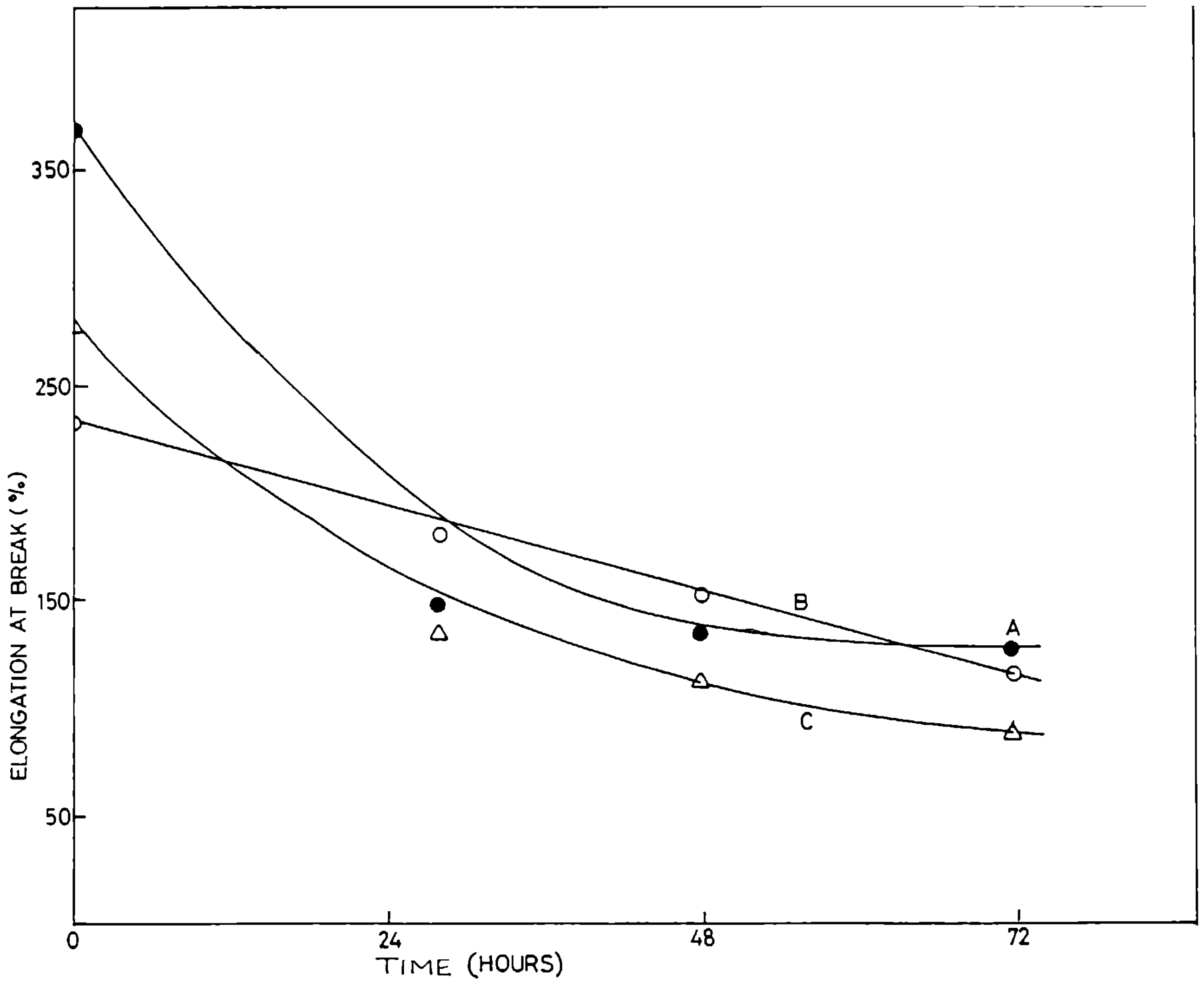


Fig.5.22: Variation in elongation at break of the vulcanizates before and after ageing at 100°C; (A) NR-PDM, (B) vulkanox 4020, (C) vulkanox HS

of the vulcanizate containing NR-PDM was found to be superior compared to the vulcanizates containing vulkanox 4020 or vulkanox HS. This may be due to the presence of NR counterpart in bound antioxidant. Retention in elongation at break after ageing of the vulcanizate containing NR-PDM is superior to the vulcanizate containing vulkanox HS and comparable to the vulcanizate containing vulkanox 4020.

Fig.5.23 shows the tear strength of the vulcanizates before and after ageing. Retention in tear strength of the vulcanizate containing NR-PDM is superior to that containing vulkanox HS and comparable to that containing vulkanox 4020. Fig.5.24 shows the modulus of the vulcanizates before and after ageing. Increase in modulus after ageing may be due to the increase in crosslink density, as shown in Table 5.7. Fig.5.25 shows hardness value of the vulcanizates before and after ageing. Hardness value of the vulcanizate containing NR-PDM is better than the vulcanizates containing conventional antioxidants. This may be due to the lower amount of plasticiser in the compound containing NR-PDM. The increase in hardness after ageing may be due to the increase in crosslink density as shown in Table 5.7.

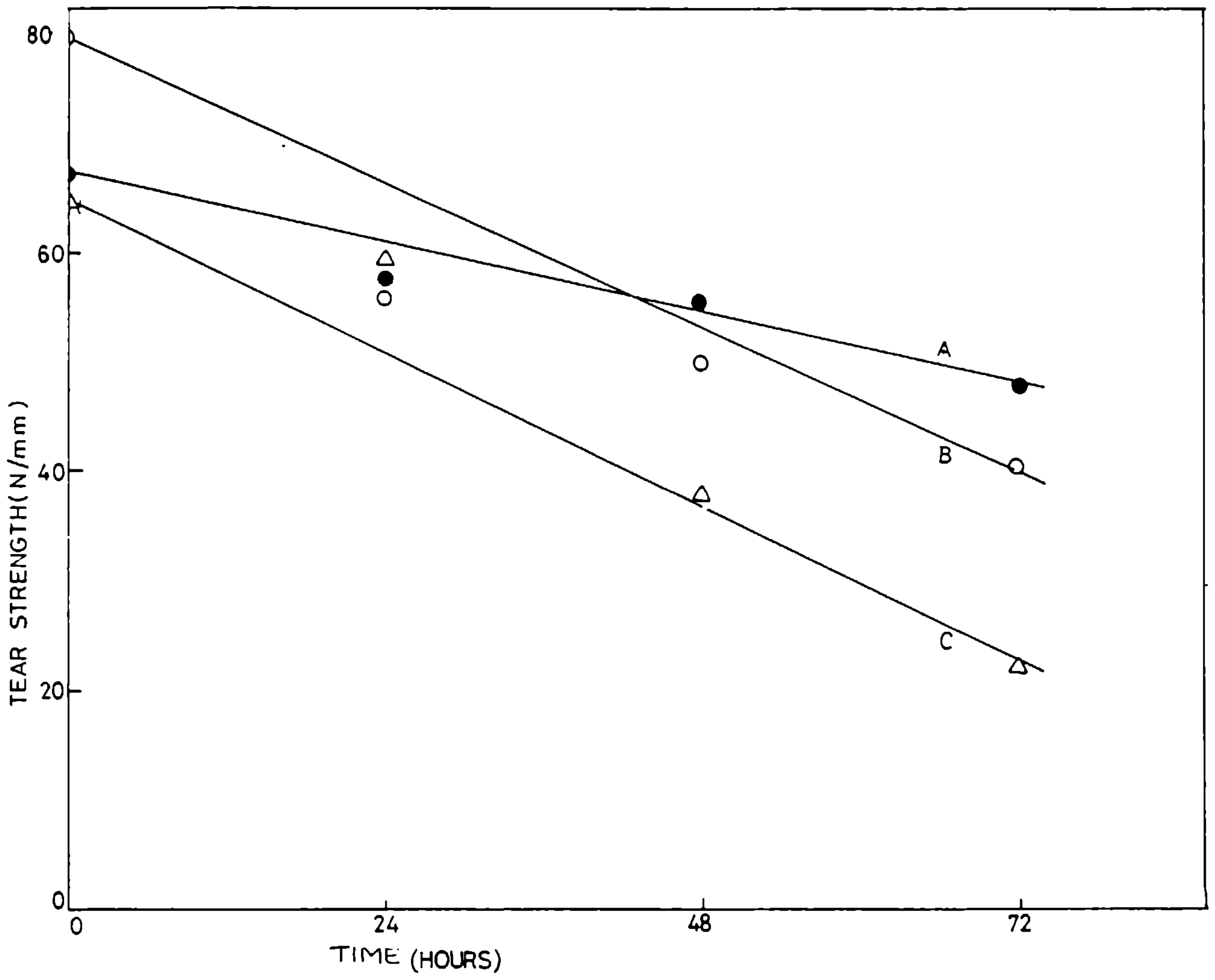


Fig.5.23: Variation in tear strength of the vulcanizates before and after ageing at 100°C; (A) NR-PDM, (B) vulkanox 4020, (C) vulkanox HS

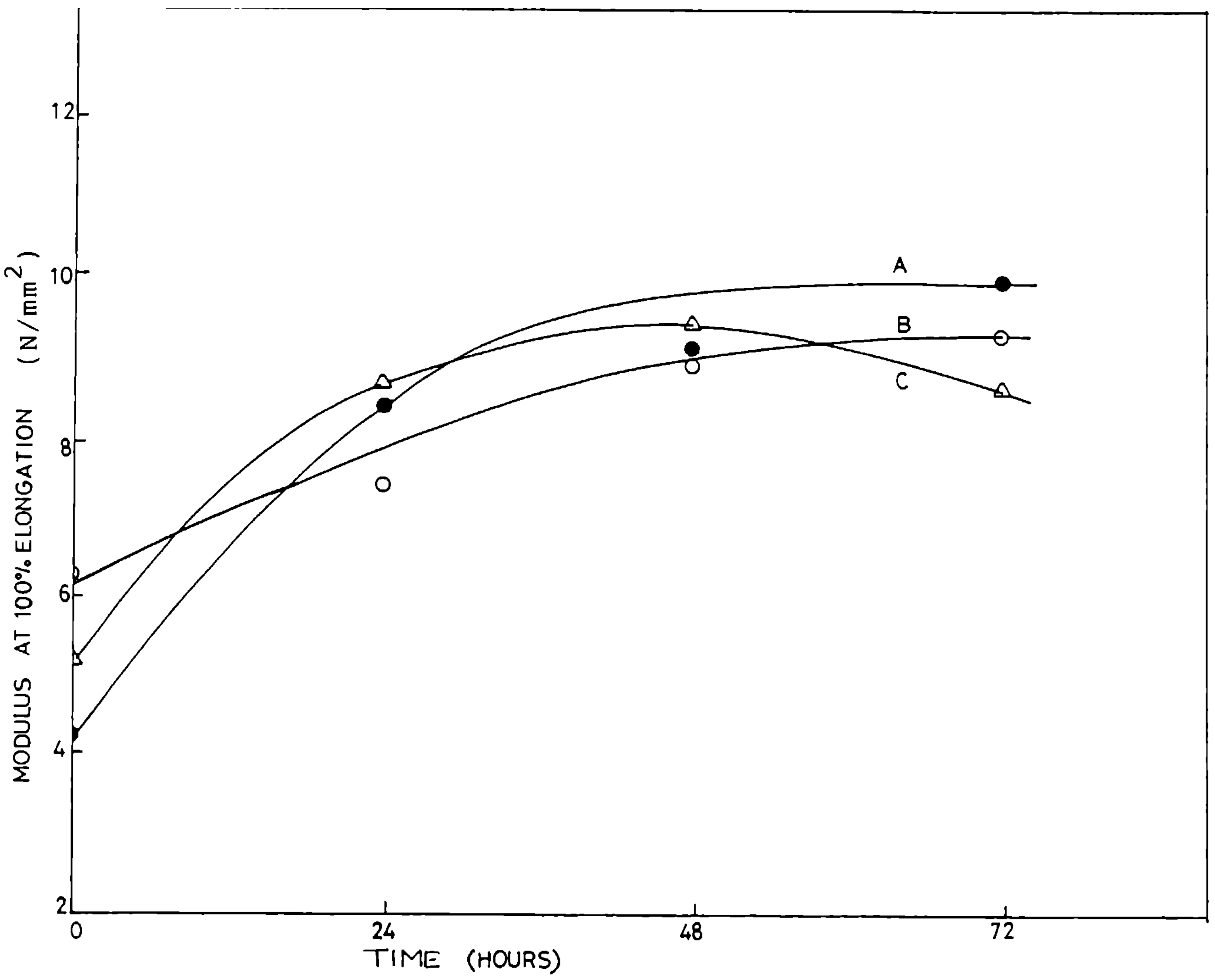


Fig.5.24: Variation in modulus of the vulcanizates before and after ageing at 100°C; (A) NR-PDM, (B) vulkanox 4020, (C) vulkanox HS

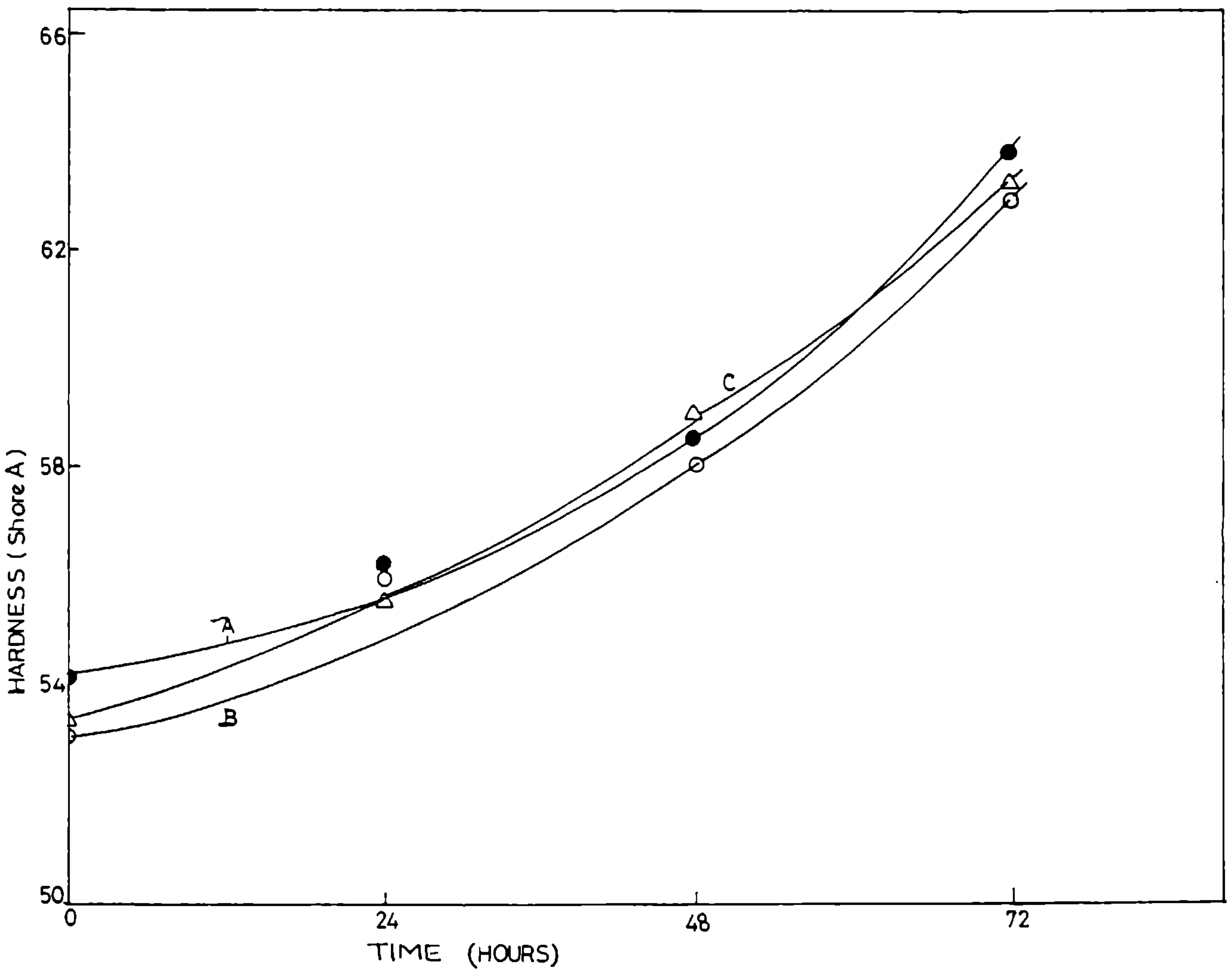


Fig.5.25: Variation in hardness of the vulcanizates before and after ageing at 100°C; (A) NR-PDM, (B) vulkanox 4020, (C) vulkanox HS

Table 5.7

Crosslink densities of the vulcanizates before and after ageing at 100°C

Time of ageing (h)	Crosslink density in g mole/cc		
	A	B	C
0	$5.602\text{x}10^{-5}$	$4.067\text{x}10^{-5}$	$4.001\text{x}10^{-5}$
24	$5.017\text{x}10^{-4}$	$2.8991\text{x}10^{-4}$	$3.5854\text{x}10^{-4}$
48	$5.628\text{x}10^{-4}$	$3.08\text{x}10^{-4}$	$3.826\text{x}10^{-4}$
72	$6.837\text{x}10^{-4}$	$3.021\text{x}10^{-4}$	$3.781\text{x}10^{-4}$

Table 5.8

Properties before, and after extracting the samples in methanol and acetone (48h, 27°C) followed by ageing at 100°C for 48h

Property	Properties before extraction			Properties after extraction and ageing					
				Methanol			Acetone		
	A	B	C	A	B	C	A	B	C
Tensile strength (N/mm^2)	18.15	17.12	19.75	15.21	15.80	14.41	14.27	16.04	13.88
Elongationat at break (%)	374.12	231.01	279.93	181.71	165.65	152.06	189.78	168.08	145.13
Modulus at 100% elongation (N/mm^2)	4.00	6.18	5.20	7.25	8.07	8.09	6.18	8.05	8.40
Tear strength (N/mm)	67.04	81.60	65.00	60	43	41	56.14	53	44.70
Hardness (Shore A)	54	53	53	49	47	47	48	46	46

Table 5.9

Properties of the vulcanizates before and after ageing at 100°C for 48h

Properties	A	B	C
Before ageing			
Abrasion resistance (Volume loss, cc/h)	3.61	3.75	3.77
Compression set (%)	28.71	28.87	29.87
After ageing			
Abrasion resistance (Volume loss, cc/h)	4.02	4.05	4.25
Compression set (%)	14.17	14.25	17.18

Table 5.8 shows tensile properties, tear strength and hardness of the vulcanizates before and after ageing after extracting the samples in methanol and acetone. The retention in these properties shown by the vulcanizate containing NR-PDM confirms the superiority of bound antioxidant over conventional antioxidants.

Table 5.9 shows the abrasion resistance and compression set of the vulcanizates before and after ageing. Retention in these properties is superior for the vulcanizate containing bound antioxidant.

Conclusions

1. Natural rubber bound paraphenylenediamine (NR-PDM) can improve the ageing resistance of SBR vulcanizates.

2. The semi solid NR-PDM can act as a polymeric plasticiser in SBR.

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Chapter 6

SUMMARY AND CONCLUSIONS

The primary objective of the present work has been to develop and utilise cost effective polymer bound antioxidants. Several novel methods have been suggested to prepare polymer-bound antioxidants. The bound antioxidants prepared were less volatile and less extractable than commercially available antioxidants and thus enhanced the service life of the elastomers concerned substantially.

The first method employed was modified Friedel-Craft's alkylation reaction. The alkylation was carried out on phenol, styrenated phenol, cardanol and diphenylamine using hydroxy terminated liquid natural rubber (HTNR) as the alkylating agent and anhydrous $ZnCl_2/AlCl_3$ as the catalyst. The products were characterised by TLC, hydroxyl value, 'H-NMR, IR, TGA and GPC. The products viz. HTNR bound phenol and styrenated phenol were tried in filled natural rubber latex compound. The vulcanizates were found to possess better resistance to ageing and solvent extraction, compared to vulcanizates containing conventional phenolic type antioxidant, as evidenced by the retention in mechanical properties. HTNR bound cardanol was tried in filled natural rubber compound. The vulcanizate was found to possess better resistance to ageing and solvent extraction compared to that containing cardanol and conventional phenolic type antioxidant, as seen from the retention in mechanical properties. HTNR bound diphenylamine was employed in filled natural rubber and styrene-butadiene rubber. The vulcanizates displayed better ageing resistance than vulcanizates containing some of the conventional antioxidants but was marginally inferior to the vulcanizate containing paraphenylenediamine antioxidant.

The second method investigated was sulphur bridging. In this method, when cardanol was heated with sulphur in presence of accelerators a high molecular weight sulphur bridged cardanol was formed. The product was characterised by TLC, hydroxyl value, free sulphur estimation, IR, 'H-NMR and TGA. Sulphur bridged cardanol was employed in filled natural rubber compound. The vulcanizate was found to possess better resistance to ageing and solvent extraction than the vulcanizate containing conventional phenolic type antioxidant as seen by the retention in mechanical properties after ageing.

Also the liquid product reduced the amount of plasticiser required for compounding.

The third method investigated was the chemical binding of amine type antioxidants to depolymerised natural rubber during UV irradiation. The amine type antioxidants employed were diphenylamine and paraphenylenediamine. The products were characterised by TLC, GPC, IR, ^{1}H-NMR and TGA. Natural rubber bound diphenylamine was tried in filled natural rubber compound. The vulcanizate was found to possess improved resistance to ageing and solvent extraction compared to vulcanizate containing conventional antioxidant. Natural rubber bound paraphenylenediamine was also employed in filled natural rubber and in acrylonitrile-butadiene rubber. The vulcanizates were found to possess better resistance to ageing and solvent extraction compared to those containing conventional antioxidants. But ozone resistance of the natural rubber vulcanizate containing bound antioxidant was found to be inferior to that containing conventional antioxidant. Combinations of conventional antioxidant and bound antioxidant gave excellent results. Further, water and oil resistance of NBR vulcanizates can be improved by the addition of natural rubber bound paraphenylenediamine antioxidant. It can improve resilience and reduce heat build up of NBR vulcanizates. Also, the depolymerised natural rubber bound amine type antioxidant can act as a polymeric plasticiser.

The fourth method investigated was the chemical binding of amine type antioxidants to natural rubber during aggressive mastication process. The amine type antioxidants employed were diphenylamine and paraphenylenediamine. The products were characterised by IR, ^{1}H-NMR, TLC and TGA. Natural rubber bound diphenylamine was employed in filled natural rubber compound. The vulcanizate was found to possess better resistance to ageing and solvent extraction, than the one containing conventional antioxidant as evidenced by the retention in mechanical properties after ageing. Natural rubber bound paraphenylenediamine antioxidant was also tried in filled natural rubber and styrene-butadiene rubber compounds. The vulcanizates were found to possess better resistance to ageing and solvent extraction than that containing conventional antioxidants. Also these semi solid rubber bound antioxidants can act as polymeric plasticiser.

Of the four successful methods described for preparing polymer bound antioxidants, the mastication stage binding of antioxidant seems to be the most promising since vulcanizates containing such antioxidants show the maximum resistance to ageing, even after extraction with solvents.

LIST OF PUBLICATIONS FROM THIS WORK

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