A STUDY OF THIOL BASED BOUND ANTIOXIDANTS IN ACRYLONITRILE-BUTADIENE RUBBERS

by

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A thesis submitted for the degree of

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of the University of Aston in Birmingham

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THE UNIVERSITY OF ASTON IN BIRMINGHAM

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SUMMARY

Thiol containing antioxidants, 3,5-di-tertiary-butyl-4-hydroxybenzyl mercaptan (BHBM), 4-anilinophenylthioglycollamide (PAPT) and 4-anilinophenylthiopropionamide (PPPT) have been successfully bound to acrylonitrile-butadiene rubber (NBR) by a free radical process in the latex and during processing.

Under optimum conditions, latex masterbatches and solid masterbatches of the bound thiol antioxidants were prepared and were used as additives for unstabilised NBR latex and normal solid NBR. The concentrations of bound antioxidants have been estimated by infra-red spectrophotometry.

The effect of bound antioxidants on the behaviour of vulcanisates has been investigated using the Monsanto oscillating disc rheometer. PAPT and PPPT increased the rate of cure and cross-link density while BHBM reduced the latter.

Conventional oxygen absorption, oven ageing and stress relaxation measurements and in addition a cyclic oil/air test specifically designed for nitrile rubber, in which the mechanical properties were measured, have been used to evaluate the effectiveness of the bound antioxidants before and after extraction with an organic azeotrope. For comparison the effectiveness of commercially available copolymerised antioxidant, N-(4-anilinophenyl) methacrylamide and a high molecular weight partially polymerised antioxidant, 2,2,4-trimethyl-1,2-dihydroquinoline, were also investigated. The result showed that, although the bound antioxidants retained much of their activity after extraction, the antioxidants behaved differently in different tests. The performance of the thiol based bound antioxidants particularly PAPT, is better in the cyclic oil/air test.

Mechanistic studies showed that the antioxidant activity of thiolamides, PAPT and PPPT, involves synergistic chain breaking catalytic peroxide decomposition mechanisms.

KEY WORDS: ACRYLONITRILE-BUTADIENE RUBBER : BOUND ANTIOXIDANTS : MASTERBATCHES : AGEING : ANTIOXIDANT MECHANISMS

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CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

AO	ANTIOXIDANT
NBR	ACRYLONITRILE-BUTADIENE RUBBER
LM	LATEX MASTERBATCH
LML	LATEX MASTERBATCH LATEX DILUTED
LMCU	LATEX MASTERBATCH COAGULUM UNEXTRACTED
LMCE	LATEX MASTERBATCH COAGULUM EXTRACTED
MCM	MECHANOCHEMICAL MASTERBATCH
MCMU	MECHANOCHEMICAL MASTERBATCH UNEXTRACTED
MCME	MECHANOCHEMICAL MASTERBATCH EXTRACTED
TR	TORQUE RHEOMETER
TBH	TERTIARY-BUTYL HYDROPEROXIDE
DLP	DI-LAURYL PEROXIDE
TEPA	TETRA-ETHYLENE PENTAMINE
THF	TETRA-HYDROFURAN
TS	TENSILE STRENGTH
EB	ELONGATION AT BREAK
EX	EXTRACTED
UNEX	UNEXTRACTED

The abbreviation for antioxidants used is given in Table 4 (page 171).

CHAPTER ONE

INTRODUCTION

All polymers suffer thermo-oxidative degradation during fabrication into the form in which they are used, and thermal and photo-oxidation on subsequent exposure to uv light during outdoor use. This irreversible process in which the useful properties degenerate has been a serious limitation to the extensive application of polymers at the present time.

Although many polymers spend all or part of their service life in contact with oxygen, water, temperature, micro-organism and other atmospheric agents (eg gases), oxygen is by far the most important degradative agent. Both natural and synthetic polymers react with oxygen under extreme conditions, that is at combustion temperatures, and many oxidise extensively at much lower temperatures. Their reaction with oxygen accounts for the majority of polymer failures occurring during service conditions. Deterioration can be accelerated by foreign materials (impurities) such as catalyst residues from polymerisation.

Quite apart from the deterioration caused by external agents, it is well established that there are chemical modifications in the structures of degrading polymers. The manner in which the above mentioned environmental factors affect the structural composition of polymers leading to degeneration of useful properties and ultimately to failure of the polymer is determined by the chemical nature and basic constituents of the material. Typical examples of polymer deterioration are development of colour and reduction of optical clarity, embrittlement and cracking of rubber.

Since all polymers are inevitably exposed to oxygen and other agents that cause their deterioration in varying degrees under appropriate conditions, it is therefore essential to protect them against such damage that ultimately renders them useless. The development of antioxidants has helped to extend the life of polymers during service. The basic theory of stabilisation of polymers has developed extensively since its discovery and reaction mechanisms have been proposed in the literature to explain the deterioration processes occurring during fabrication and under service conditions.

1.1 General Mechanism of Polymer Degradation

The reaction of polyolefins and other hydrocarbon polymers with oxygen has been shown(1-3) to involve a free radical mechanism characterised by three distinct steps, viz initiation, propagation and termination. The process of oxidation may be represented as follows:

Initiation:

$$\text{Initiator} \longrightarrow R^{\cdot}$$

$$ROOH \longrightarrow RO^{\cdot} + {}^{\cdot}OH$$

$$2ROOH \longrightarrow ROO^{\cdot} + RO^{\cdot} + H_2O$$

Propagation:

$$R\cdot + O_2 \longrightarrow ROO^{\cdot}$$

$$ROO^{\cdot} + R\text{-}H \longrightarrow ROOH + R^{\cdot}$$

$$ROO^{\cdot} + C{=}C \longrightarrow ROO\text{-}C\text{-}C^{\cdot}$$

$$HO^{\cdot} + R\text{-}H \longrightarrow R^{\cdot} + H_2O$$

$$RO^{\cdot} + R\text{-}H \longrightarrow R^{\cdot} + ROH$$

$$RO^{\cdot} + C{=}C \longrightarrow RO\text{-}C\text{-}C^{\cdot}$$

Termination:

$$\left.\begin{array}{l} 2R^{\cdot} \\ ROO^{\cdot} + R^{\cdot} \\ 2ROO^{\cdot} \\ 2ROO^{\cdot} \end{array}\right\} \longrightarrow \text{Unreactive products}$$

The initiation step consists of the formation of a polymeric free radical by rather ill-defined reaction. Such reactions probably occur at sensitive irregularities in the polymer. The initiation process is of considerable complexity and its exact mode depends on whether it occurs photolytically or thermally.

However, it is generally accepted that the mechanisms of thermal and uv oxidation are initiated primarily by the formation and breakdown of hydroperoxide, but they differ in their breakdown products since most of the breakdown during thermal oxidation occurs via hydroperoxides whilst photolysis of carbonyl compounds is also involved in uv degradation.

Propagation is a two-step sequence which involves firstly a rapid combination of polymeric free radical with oxygen to give alkylperoxyl radical and secondly the abstraction of an allylic hydrogen by the alkylperoxyl radical to form hydroperoxide (ROOH). But if a double bond is present in the polymer chain the alkylperoxyl radical may add to the double bond. The hydroperoxide so formed can undergo thermal or photo-decomposition when subjected to temperature or uv radiation:

$$\mathrm{ROOH} \xrightarrow{h\nu} \mathrm{RO^{\cdot}} + {}^{\cdot}\mathrm{OH}$$

$$2\mathrm{ROOH} \xrightarrow{\Delta H} \mathrm{ROO^{\cdot}} + \mathrm{RO^{\cdot}} + \mathrm{H_2O}$$

The decomposition of the hydroperoxide indicates a further source of initiation of free radicals and thus rate of oxygen uptake is speeded up (autoxidation).

Transition metal ions can cause the degradation of polymers depending on their structures. Ions of metals such as chromium, copper, iron and cobalt can catalyse the decomposition of hydroperoxides, the mechanism by which the process occurs is represented by the following equation:

$$M^{n} + ROOH \longrightarrow M^{n+1} + {}^{-}OH + RO^{\cdot}$$
$$M^{n+1} + ROOH \longrightarrow M^{n} + H^{+} + ROO^{\cdot}$$

Where M is a transition metal species of more than one valence. In view of the above reactions, it is obvious that traces of the metals in the polymer will result in enhanced response to attack by oxygen. However, metal ions (eg Cu) can also behave as alkyl radical traps under oxygen deficient conditions.

Thermal effects are major factors in polymer degradation. Exposure to relatively high temperatures during processing and to more moderate temperatures during long-term ageing accounts for the failure of polymers. A primary environmental factor responsible for pyrolysis in vacuum or in an inert atmosphere is the absorption of thermal energy by polymers. However, thermal effects are most generally evident in the temperature dependence of other reactions that result in polymer deterioration. Reaction rates increase with temperature as defined by the activation energy of the particular process. Deterioration, however, usually occurs through a complexity of reactions so that the observed activation energy is that of the composite mechanism and not of individual reactions. Temperature dependence is observed in all types of polymer breakdowns but its effects have been studied most extensively in the autoxidation of polyolefins.

Autoxidation is the thermal oxidation that takes place between room temperature and about 150^{o}C and proceeds by a typical free radical chain mechanism. Most polymers undergo this reaction, although there is considerable variation in resistance to this type of degradation. The reaction is usually autocatalytic.

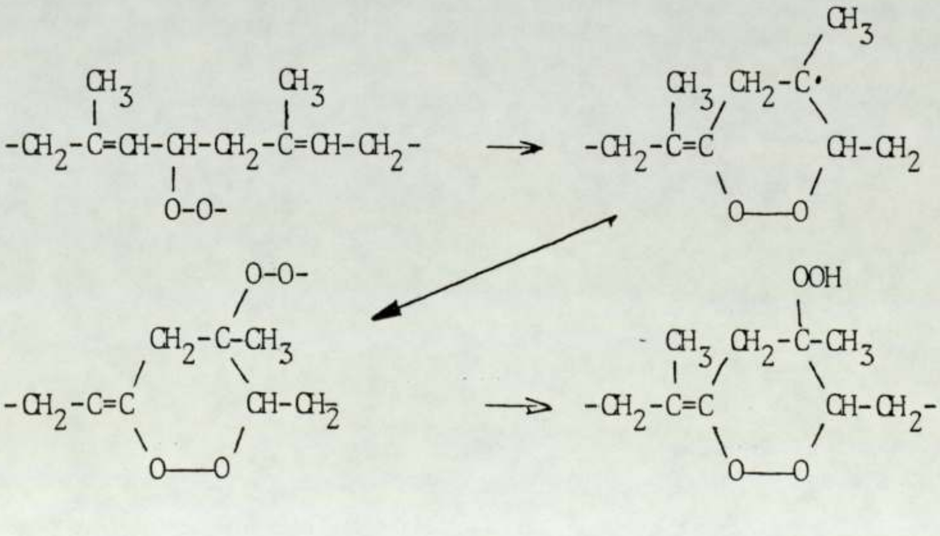
Although the reaction with oxygen is the more general phenomenon, thermal deterioration also occurs in the absence of oxygen or other chemical reactants. There are two basic mechanisms for thermal deterioration under non-oxidative conditions. Depending on the structure of the polymer and to a lesser extent on reaction conditions, deterioration can occur through elimination of low molecular weight volatile fragments leaving the backbone chain intact. Alternatively, chain scission can occur, either by random process or stepwise depolymerisation. Elimination of low molecular weight fragments usually takes place at a lower temperature and is restricted to a relatively small group of polymers. The structure of the polymers must be such that reactions are possible with activation energy lower than those required to break the bond along the main chain. Elimination of hydrogen chloride from poly(vinyl chloride) is a typical example of this reaction. As temperature is increased, all polymers eventually dissociate. Volatile products are formed and depending on the polymer structure, there may be varying proportions of carbonaceous residue.

Rupture of the backbone chain occurs by depolymerisation or by a random process, perhaps initiated at weak bonds in the chain. Both reactions can occur in a single polymer with relative rates depending on temperature.

1.2 Oxidation of Rubber

As previously discussed, the oxidation of simple hydrocarbon polymers involves the formation of hydroperoxides. Abundant evidence now exists indicating that the oxidation of rubber and other elastomers containing appreciable amounts of olefinic unsaturation proceeds in basically a similar manner.

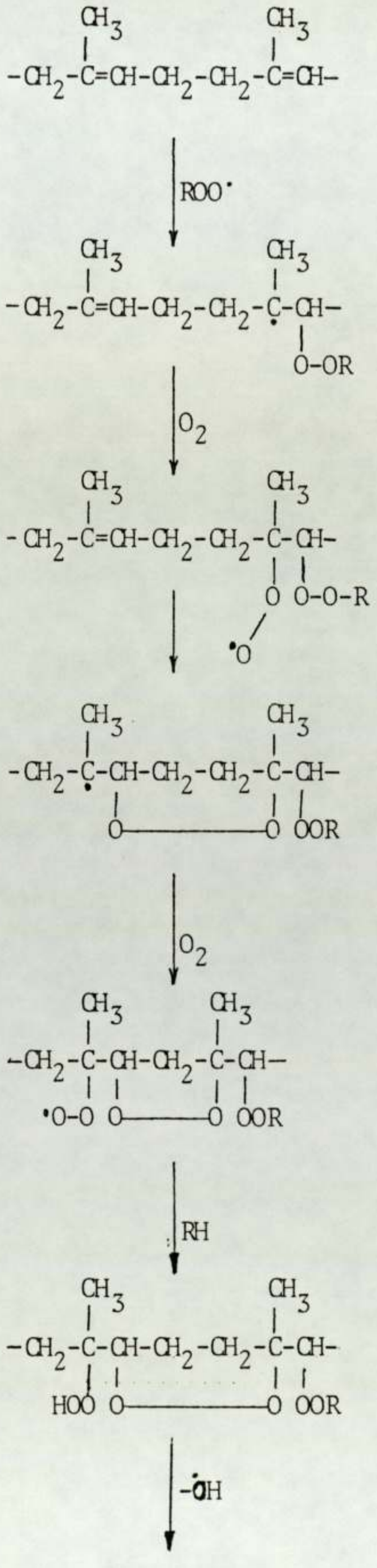
In polyisoprene, because of the spacing of neighbouring double bonds, cyclisation of the chain carrier occurs to the virtual exclusion of intermolecular α-methylenic hydrogen capture except in so far as this occurs after the incorporation of a second oxygen molecule into the cyclised unit.



This type of peroxide has been shown to be given by squalene(2) and dihydromyrcene(4).

As soon as the oxidation proceeds to a more advanced stage, the generalised oxidation scheme is accompanied by secondary reactions of the initially formed peroxides, leading to the appearance of various functional groups, such as carboxyl, ester, hydroxyl, carbonyl, and ethereal(5,6). These are the groups to be expected from the decomposition of hydroperoxide in the presence of polyisoprenic unsaturation. Only about half of the oxygen absorbed by natural rubber can be accounted for as hydroperoxide. This observation is explained by the occurrence of intramolecular radical addition reaction along the polymer chain.

Natural rubber loses practically all its useful elastomeric properties by the time only about 1% by weight of oxygen has been absorbed; there is also a decrease in the molecular weight of the polymer. Thus scission reaction must be part of the degradation process. These features are illustrated in the following scheme for the oxidative degradation of natural rubber(7).



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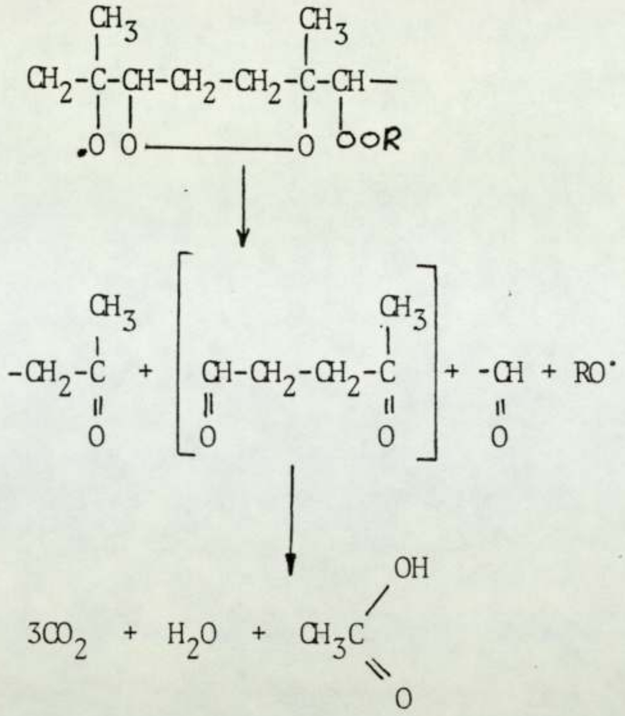


1.3 Antioxidants and Stabilisers

After many years of active work in the field of antioxidants, it was found that the most important classes are the secondary diarylamine and hindered phenols that function as a free radical chain stoppers. Comparison of some commercially important antioxidants$^{(8)}$ show that although the secondary diarylamine are still the most important class of protective agents, the phenolics offer a non-staining effect which makes them most desirable in the light-coloured articles. These two classes of antioxidant comprise most of the materials currently used as protective agents in the rubber industry.

An extensive study by Miksch and Obermeier$^{(9)}$ showed the effect of a variety of commercial antioxidants on the physical properties of vulcanisates on heat ageing, static and dynamic weathering, creep, ozone and colour.

The best of the amine antioxidants give more comprehensive protection to rubber goods than phenols, but they also cause more discolouration and staining.

The amines may be conveniently divided into the following groups:

- (I) secondary amines
    - (a) phenyl-naphthyl amines
    - (b) substituted diphenylamines
    - (c) para-phenylenediamines
- (II) keto-amine condensates,
- (III) aldehyde-amine condensates,
- (IV) Alkyl-aryl secondary amines, and
- (V) primary amines.

With the development of synthetic rubbers, interest in non-staining antioxidants increased enormously. Since the synthetic rubbers do not contain naturally occurring antioxidants, as does natural rubber, it is necessary to add a protective agent at the time of manufacture to preserve the rubber until it is compounded and cured. An example of such a protective agent is the simple phenol-3,5-di-tert-butyl-para-cresol (TBC). If the polymer is intended for use in light coloured goods, it is necessary that the stabiliser does not cause any discolouration of the rubber.

The phenolic antioxidants may be classified as follows:

(A) hindered phenols,
(B) hindered thiobisphenols,
(C) hindered bisphenols, and
(D) polyhydroxy phenols.

In view of the fact that hydroperoxides are the major cause of oxidation, it follows therefore that agents which promote the decomposition of hydroperoxides to form free radicals will bring about a more rapid oxidation of the polymer(10). Since for all practical purposes, materials which have degraded are valueless technologically, additives which either preserve the hydroperoxide or decompose it in a reaction which does not involve free radicals will act as effective antioxidants and stabilisers.

1.3.1 Antioxidant Mechanisms

Antioxidants may be classified according to their modes of action in protecting polymers, viz:

(a) Chain-breaking:
    (i) chain-breaking donor mechanism (CB-D)
    (ii) chain-breaking acceptor mechanism (CB-A)

(b) Preventive:
    (i) metal ion deactivating mechanism
    (ii) peroxide decomposing - stoichiometrical mechanism (PD-S)
    (iii) peroxide decomposing - catalytic mechanism (PD-C)

(c) UV stabilising (eg the use of screeners or absorbers - 2-hydroxybenzophenone, hydroxybentriazoles)

(d) Quenching (eg some nickel chelates)

1.3.2 Chain-breaking Mechanism

The kinetic chain-breaking mode of action can be summarised in the following scheme:

$$\begin{tikzcd}
R^{\cdot} + O_2 \arrow[r] \arrow[d, "(-e)"'] & ROO^{\cdot} \arrow[r, "(+e)"] & ROO^{-} \\
R^{+} & &
\end{tikzcd}$$

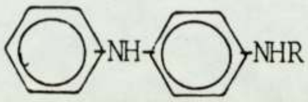
Chain-breaking
(donor mechanism, CB-D)

Chain-breaking
(acceptor mechanism, CB-A)

Radical chain-breaking antioxidants act by removing alkylperoxyl and alkyl radicals which are the important species normally involved in the chain propagation step, from the medium. The former may be achieved by use of single electron donors or compounds which after donating a labile hydrogen gives rise to a stable (non-propagating) radical. This mechanism is referred to as chain-breaking donor (CB-D).

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

The best known antioxidants in this respect are the hindered phenols - 3,5-di-tertiary-butyl-para-cresol (TBC) and 5-tertiary-butyl-xylol (TBX) and the aromatic amines:

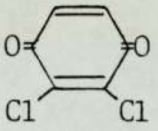


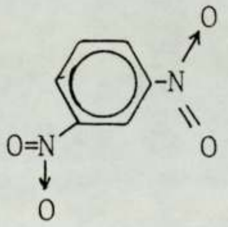
R = isopropyl = (IPPD)

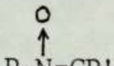
R = phenyl (DPPD)

The removal of alkyl radicals involves an electron acceptor (an oxidising agent) chain-breaking acceptor mechanism (CB-A). Among the variety of oxidising agents capable of removing alkyl radical from an autoxidising system are the quinones, nitro compounds, nitrones and a variety of stable radicals of which the phenoxyls and the nitroxyls have been most studied.

Oxidising agents:

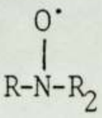




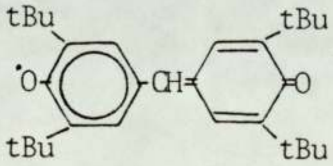


$R\text{-}\overset{\overset{O}{\uparrow}}{N}\text{=}CR'$

Stable radicals as alkyl traps:



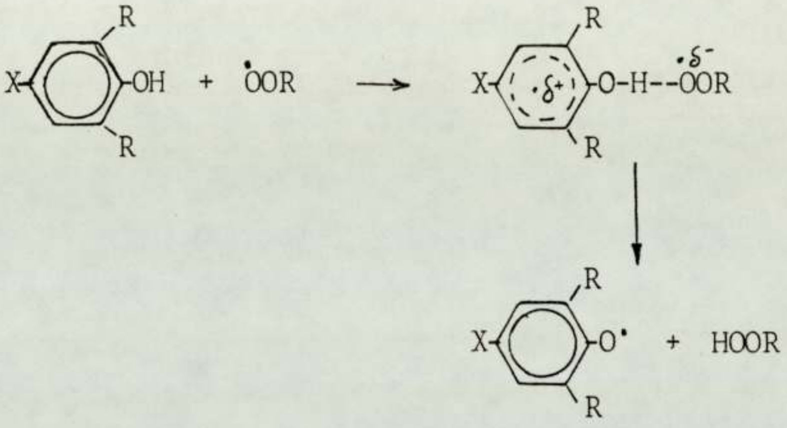
$R\text{-}\overset{\overset{O^{\bullet}}{|}}{N}\text{-}R_2$;



; $RS\text{=}O^{\bullet}$

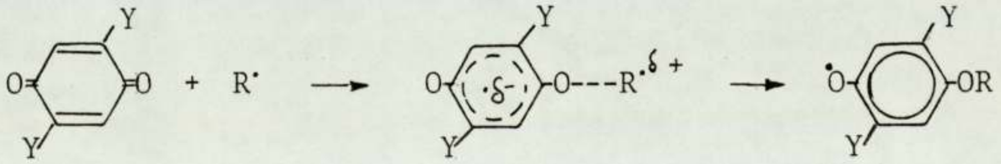
The consideration of the structures of the transition state, in the reaction of peroxyl radical with a phenol and also the reaction of alkyl radical with a quinone will explain the molecular requirements for an effective CB-D and CB-A respectively.

CB-D



In the chain-breaking donor mechanism, electron releasing and electron delocalising substituents (X,R) reduce the energy of the transition state and increase antioxidant activity(11). The products formed by further reaction of the initially formed phenoxyl radical are complex and they may have some activity (either positive or negative) in the autoxidation reaction(12).

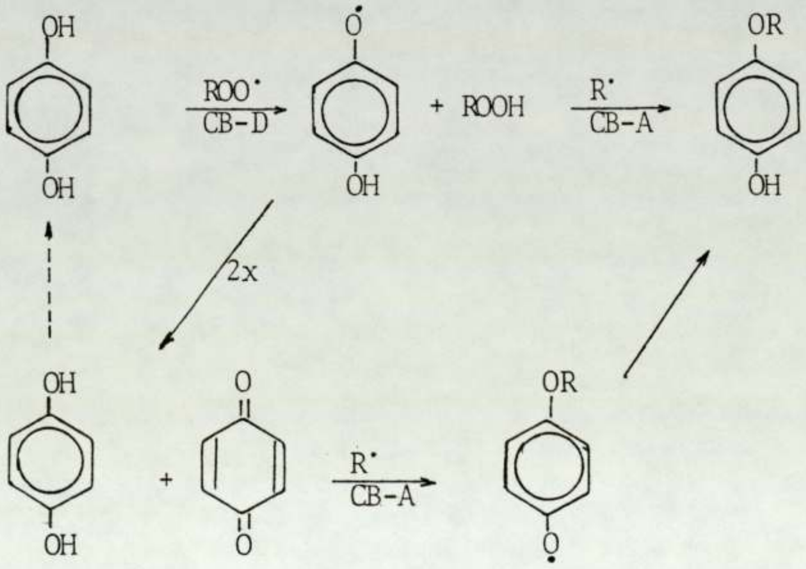
CB-A



In the reaction of alkyl radical and a quinone, a partial transfer of an electron to the aromatic bond, is involved in the transition state and this demands that substituents Y to be electron attracting and delocalising in order to increase antioxidant activity. The CB-A antioxidants listed above act in a similar way.

The majority of the chain-breaking donor (CB-D) antioxidants function most effectively when the alkylperoxyl radical is the major radical propagating species present in an autoxidising system whereas the CB-A type operates only in oxygen deficiency or at high initiation rates.

Antioxidants which exhibit both kinds of activity no doubt have advantage over those operating by a single mechanism because in many antioxidant processes both species are present to some degree. The best known example of antioxidants which involve both mechanisms is the simple hydroquinones which are converted to the corresponding benzoquinones by the CB-D mechanism.



Some chain-breaking antioxidants have the ability to alternate between the oxidised and the reduced states and hence exhibit regenerative behaviour under conditions where both alkyl and alkylperoxyl radicals are important. Such actions are observed when sulphoxides (eg dilauryl sulphinyl dipropionate) are used in the melt stabilisation of polypropylene(13), also the photo-stabilisation of paint films by copper ions(14) and there is recent evidence(11,12,15) that a regenerative process involving the nitroxyl radical is involved in the uv stabilisation of polyolefins by hindered piperidines.

The lack of activity of the reaction products derived from the hindered phenols and aromatic amines by their resonance stabilisation and or dimerisation with other species accounts for their antioxidant properties.

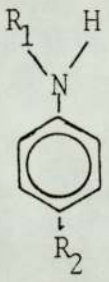
A number of experiments were carried out with phenolic compounds to find out the effect of substitution in the 2, 4 and 6 positions on the antioxidant activity of the phenols and the following conclusions emerged:

(1) Electron releasing groups (eg methyl, tert-butyl and ethoxy) reduce the energy of the transition state and tremendously increase the antioxidant activity. This has been shown to be true, although to a lesser extent, of similar substitution in the meta-position.

(2) Electron attracting groups (eg nitro, carboxy, halogen, etc) decrease the antioxidant efficiency.

(3) α-branched ortho-alkyl groups considerably increase antioxidant activity whereas groups in the para-position decrease the activity of the antioxidant.

In the case of the amines, the following observations have been made:



If an N-hydrogen is substituted by a methyl group ($R_1 = CH_3$) there is a minor effect on antioxidant activity but if substituted by a phenyl ($R_1 = C_6H_5$) the efficiency of the antioxidant is boosted. Furthermore, substitution on the aromatic ring has little effect. As in the case of the phenols, electron releasing substituents have powerful activating effects. The effectiveness of chain-breaking antioxidants depends very much on their rate of interaction with alkylperoxyl radical and also upon the stability of the resulting product (eg phenoxyl radical).

In order to understand the mechanism involved in the interaction a knowledge of the chemistry of phenols and amine oxidation(1,2,16) is necessary. If ($A^\cdot$) is taken to be the resulting phenoxyl radical in the interaction of an antioxidant, this radical can react further according to the following scheme:

$$
A^{\cdot} \; + \;
\begin{array}{l}
\left.\begin{array}{lll}
\text{(a)} & \xrightarrow{A^{\cdot}} & \text{A-A} \\
\text{(b)} & \xrightarrow{ROO^{\cdot}} & \text{AOOR}
\end{array}\right\} \text{Terminating steps} \\
\left.\begin{array}{lll}
\text{(c)} & \xrightarrow{O_2} & \text{AOO}^{\cdot} \xrightarrow{RH} \text{AOOH} + R^{\cdot} \\
\text{(d)} & \xrightarrow{R\text{-}H} & \text{AH} + R^{\cdot}
\end{array}\right\} \text{Transfer steps}
\end{array}
$$

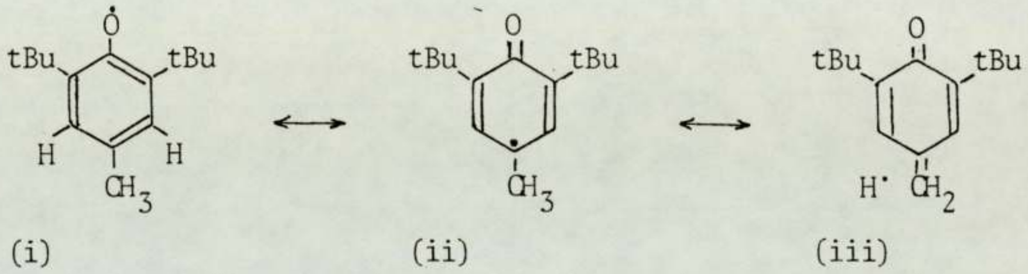
Reactions (a) and (b) are terminating steps and the radicals are being removed from the system. (c) and (d) on the other hand are chain transfer steps since they lead to continuation of chain. Substituents in the antioxidant affect its activity by:

(i) increasing or decreasing the rate of reaction of alkylperoxyl radical with phenol, and

(ii) changing the ratio of chain transfer to termination and to effect this, three factors have been found to be important.

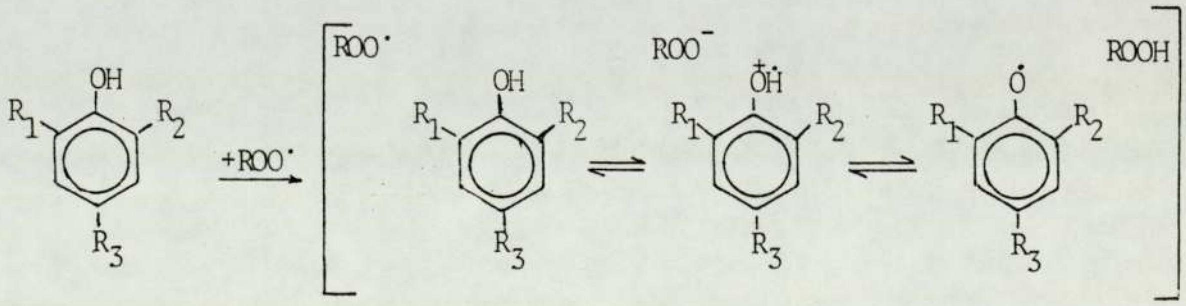
(A) Stability of aryloxyl radical

It has been shown that in the case of polycyclic phenols, antioxidant efficiency can roughly be correlated with the resonance energy of aryloxy radical as calculated by molecular orbital method. Using the esr technique to observe the electron distribution in phenoxyl radical of oxidised 2,6-di-tert-butyl-4-methyl-phenol, a well defined spectrum which can be interpreted in terms of a major interaction of the unpaired electron with three hydrogens and a minor interaction with two was given. The major interaction of the unpaired electron with three hydrogens accords with hyperconjugation (structure (ii)) in which the hydrogen atoms are equivalent and the minor interaction is due to the presence of a negative spin density in the meta-position of the benzene ring.



(B) <u>Ease of electron release from oxygen atom</u>

The alkylperoxy radical tends to gain electrons (electrophillic agent), with the formation of alkylperoxide anion (ROO$^-$). As a result, substituents in the phenol which favours the electron release increase the stability of the electron transfer component of the transition state.

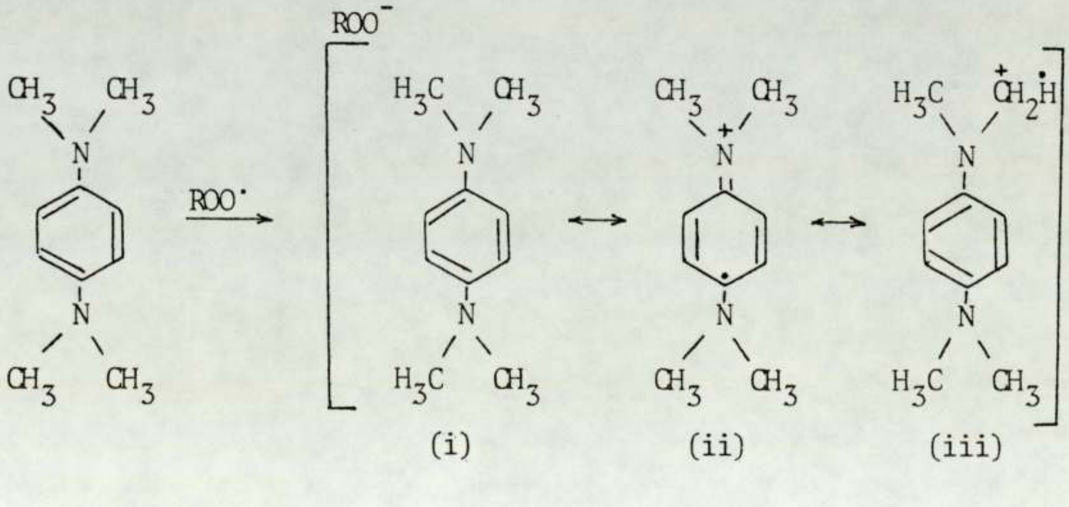


Electron attracting groups decrease the ease of oxidation and electron releasing groups powerfully increase it and the relationship between oxidation potentials and oxidation efficiency is linear.

(C) Steric stabilisation of aryloxy radical

The only stable phenoxy radicals are those which contain two bulky ortho substituents. Similarly, the reaction of the phenols from which they are derived is dependent upon the other substitution. Maximum antioxidant activity occurs at a high degree of substitution, and a minimum hydrogen bonding with the most highly substituted member of the series, 2,6-di-tert-butyl-p-cresol (TBC).

As regards the amine antioxidants, basically the same principles apply but electron transfer complexes are more important here than in the case of the phenols because completely alkylated p-phenylene diamine such as tetramethyl-p-phenylene diamine are effective antioxidants and the resultant radical ion can be identified as a product of oxidation under antioxidant conditions.



The resultant radical is stabilised by resonance contributions from structures (ii) and (iii). This can be shown by esr studies of the radical. The electronic effect of the substituents is similar to those in phenol and the steric hinderance of the nitrogen leads to increased activity. Substitution of the nigtrogen by phenyl or by secondary alkyl groups will give better results.

1.3.3 Preventive Antioxidants

The preventive mechanism is concerned with preventing the introduction of chain-initiating radicals into the system. As mentioned earlier, the most important source of free radicals is hydroperoxides and both metal ions and uv light are powerful catalysts for their decomposition. It therefore means that preventive mechanisms will involve deactivation of metal ion, the decomposition of peroxides to non-radical products and the absorption or screening of uv light.

1.3.3.1 Metal Ion Deactivation

It has been suggested that metal ions exert their pro-oxidant effect by forming unstable co-ordination complexes with alkyl hydroperoxides followed by electron transfer to give free radicals. The effectiveness of a metal ion as a redox catalyst depends on the ease of co-ordination and the redox potential of the metal involved. It follows then that metal catalysed reactions may be prevented by either strongly complexing the ion to its maximum co-ordination number and thereby inhibiting futher co-ordination with hydroperoxide (1,17) or alternatively, and in some cases additionally, by stabilising one valency state at the expense of the other.

The denticity of the chelating agent is the most important factor in the determination of the stability of metal complexes. It has been shown that, in the formation of the co-ordinate bond, the metal ion functions as a Lewis acid and the ligand as a Lewis base.

The result of the work of Calvin and Bailes (18) on the stability of copper chelates revealed that the strongest complexes are formed with strongly electron releasing groups (eg methoxy group) and the weakest with electron attracting groups (eg NO_2). Furthermore, it was found that the greater the number of chelate rings that can be formed per ligand, the greater the stability of the chelate. An equally important aspect of chelate effect is the size of the ring formed by co-ordination. In the case of calcium chelate of alkyldiamine-tetra-acetic acid, there is a maximum stability which corresponds to the formation of five rings. Generally it has been observed that:

(1) as the ring involving nitrogen becomes bigger, so the chelate formation constant decreases towards that of the monofunctional amino acid,

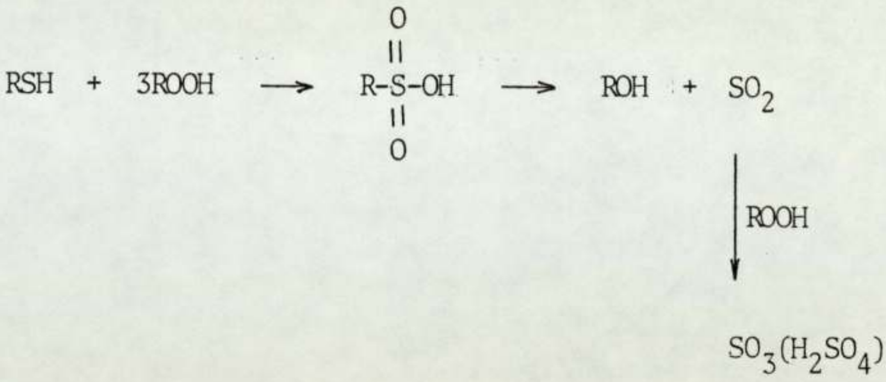
(2) the effect on metal deactivating efficiency of increasing the chelate ring from five to ten falls rapidly, and

(3) alkyl substitution can be disadvantageous when it hinders the approach of the chelating group to the metal ion and this results in a decrease of the metal deactivating efficiency.

1.3.3.2 Peroxide Decomposers

Bearing the hydroperoxide initiation mechanism in mind, it will be true to say that compounds which remove hydroperoxides in a process which does not involve free radical formation or protect hydroperoxides from decomposition should effectively inhibit oxidation.

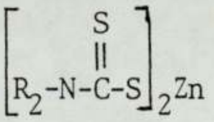
A number of workers(19-22) found that a variety of sulphur-containing compounds are effective peroxide decomposers. Bateman et al(23) found that many sulphides are auto-inhibiting. Some of the more effective inhibitors of autoxidation caused an initial rapid uptake of oxygen followed by auto-inhibition. In fact, it has been suggested that the sulphides themselves are not effective antioxidants but rather the sulphoxides and the thiolsulphinates derived from their stoichiometric reaction with the hydroperoxides(1,24). Denison(25-27) showed that antioxidant active sulphides were destroyed and were converted to sulphoxides and sulphones.



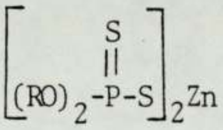
$$\mathrm{RSH} + 3\mathrm{ROOH} \longrightarrow \mathrm{R{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}OH} \longrightarrow \mathrm{ROH} + \mathrm{SO_2} \xrightarrow{\mathrm{ROOH}} \mathrm{SO_3(H_2SO_4)}$$

A number of disulphides and their derived oxygenated products are effective catalysts for the decomposition of cumene hydroperoxide and the product results from heterolytic breakdown, the main gaseous product being sulphur dioxide and sulphur trioxide and it has been proposed that this is the effective antioxidant.

Another important class of sulphur containing antioxidants is the group of metal complexes derived from dithiocarbamic acid and dithiophosphoric acid and related thiols such as mercaptobenzimidazole.

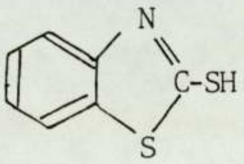


$$\left[\mathrm{R_2{-}N{-}\overset{\overset{S}{\|}}{C}{-}S}\right]_2\mathrm{Zn}$$

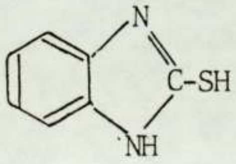


$$\left[\mathrm{(RO)_2{-}\overset{\overset{S}{\|}}{P}{-}S}\right]_2\mathrm{Zn}$$

Zinc dialkyl-dithiocarbamate, Zinc dialkyl-dithiophosphate

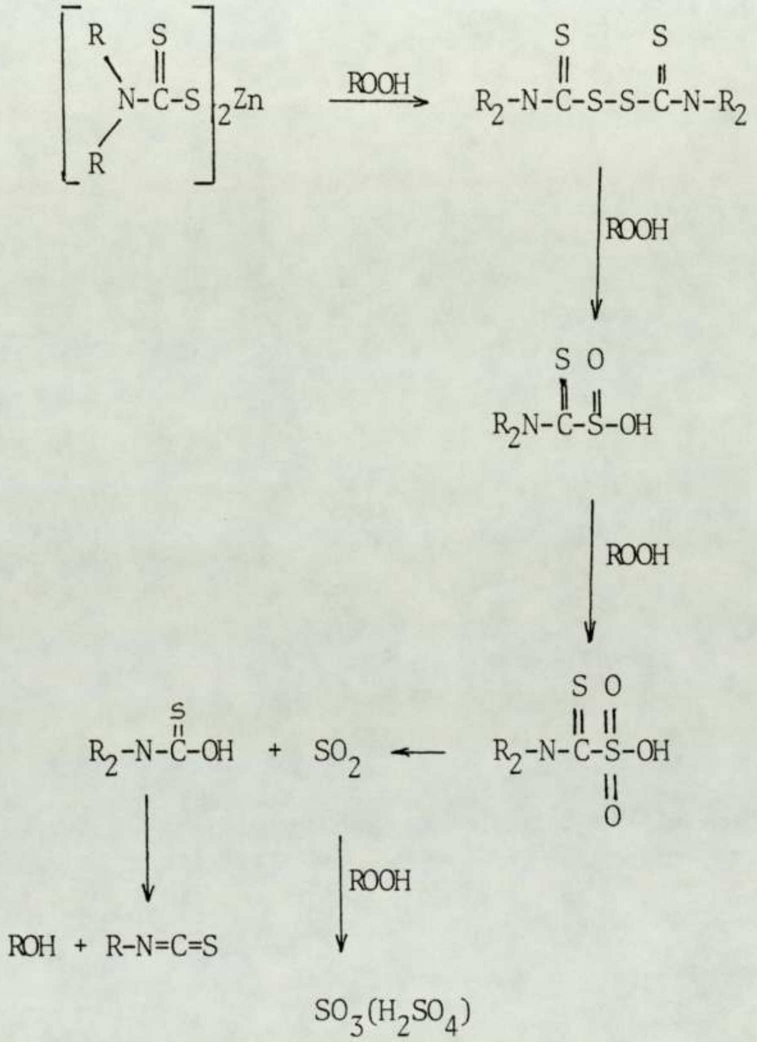


Mercaptobenzthiazole



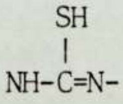
Mercaptobenzimidazole.

The activity of thiocarbamates both as antioxidants and catalysts for the decomposition of hydroperoxides shows that a free radical process is involved in the early stages (CB-D), later a catalytic non-radical (PD-C) decomposition of hydroperoxide by acid formed



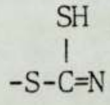
by oxidative breakdown of the sulphur complex. In the study of the mechanism of the process, isothiocyanate has been found as one of the products of oxidation(28,29).

Holdsworth and Scott(28) found that sulphur dioxide is one of the products of interactions of dithiocarbamates with cumene hydroperoxide. They suggested that this is due to the decomposition of the intermediate sulphonic acid and related sulphur dioxide generators have been found to be powerful catalysts for the decomposition of cumene hydroperoxide at temperatures above that which affects their decomposition to sulphur dioxide. Another important feature of the metal dialkyldithiocarbamates is that they exhibit a pro-oxidant activity during the early stages of oxidation. However, this is short lived. A possible explanation for this may be the ability of thiols containing the following structure to generate free radicals by redox reaction with



$\mathrm{NH{-}\overset{SH}{\overset{|}{C}}{=}N{-}}$

OR



$\mathrm{{-}S{-}\overset{SH}{\overset{|}{C}}{=}N}$

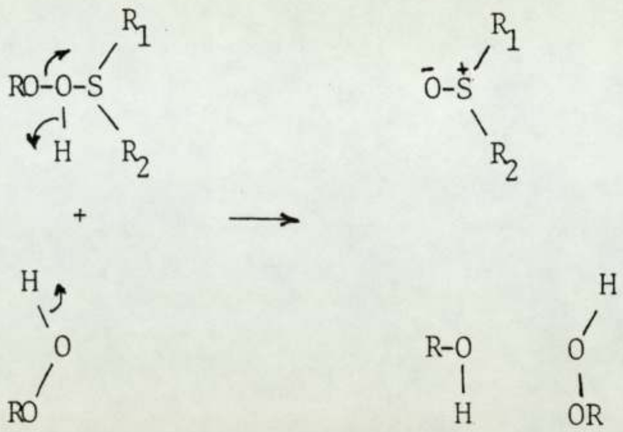
hydroperoxides(30). Aromatic thiols are well known transfer catalysts for oxidation and they are widely used in the reaction where there is need for reduction of activation energy of autoxidation chain reaction.

$$ROO^{\cdot} + ArSH \longrightarrow ROOH + Ar\text{-}S^{\cdot}$$

$$Ar\text{-}S^{\cdot} + R\text{-}H \longrightarrow Ar\text{-}SH + R^{\cdot}$$

$$R^{\cdot} + O_2 \longrightarrow ROO^{\cdot}$$

In the oxidation of monosulphides, the mechanism of reaction with hydroperoxide is by synchronous bond rearrangement.



When the reaction is carried out in a hydrogen bonding solvent such as acetic acid or if the sulphide contains a carbonyl group in the β-carbon atom, a hydrogen bonded complex is involved(31,32). Such a complex formation could of course show a profound effect on the ease of generation of sulphur dioxide.

Dibenzyl and dibenzoyl monosulphides are also pro-oxidants in both rubber(19) and in polypropylene(33) but in polypropylene they are autoretarding at elevated temperatures and are thus powerful antioxidants. The mode of reaction involves the formation of free radicals from benzylic sulphoxides on pyrolysis.

Recent studies by Armstrong, Plant and Scott(34,35) have thrown light into the mechanism of sulphur antioxidants, particularly the thiodipropionate esters.

$ROOCCH_2CH_2\text{-}S\text{-}CH_2CH_2COOR$

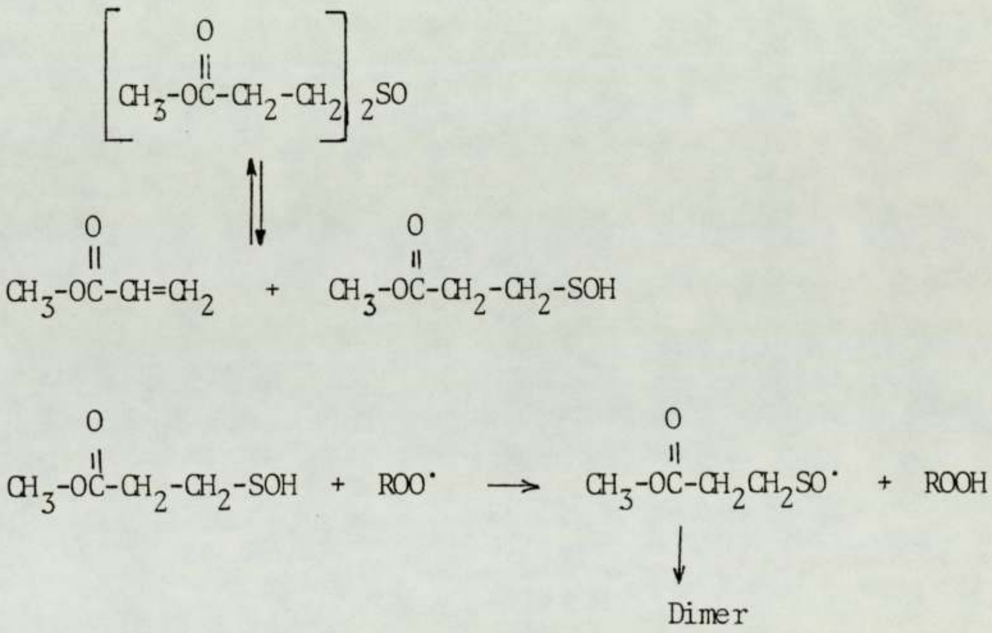
Three distinct mechanisms are proposed to account for the observed chemical reactions of the antioxidant behaviour:

(i) a radical trapping process involving the sulphenic acid formed by the breakdown of sulphoxide,

(ii) a radical generating reaction resulting from redox reaction between hydroperoxide and sulphenic acid, and

(iii) a Lewis acid catalysed destruction of hydroperoxide by a further oxidation product of the sulphonic acid.

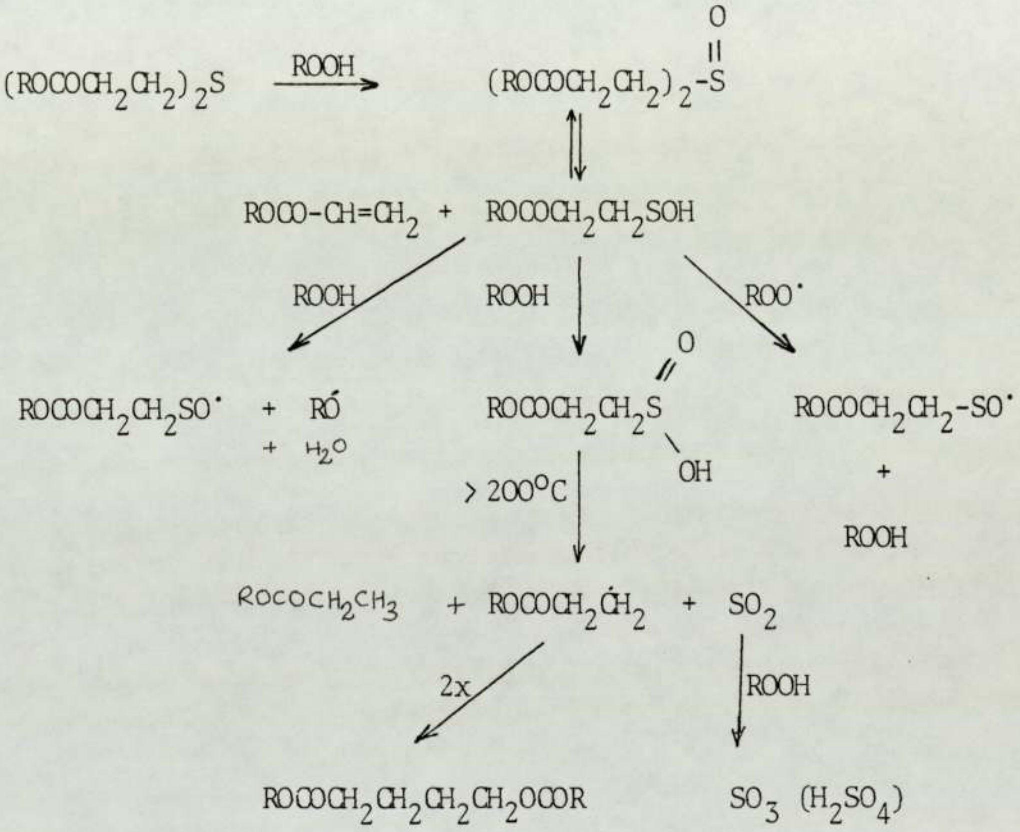
The first mechanism is accounted for by the following equation:



$$\left[CH_3-O\overset{\overset{O}{\|}}{C}-CH_2-CH_2\right]_2SO \rightleftharpoons CH_3-O\overset{\overset{O}{\|}}{C}-CH=CH_2 + CH_3-O\overset{\overset{O}{\|}}{C}-CH_2-CH_2-SOH$$

$$CH_3-O\overset{\overset{O}{\|}}{C}-CH_2-CH_2-SOH + ROO^{\cdot} \longrightarrow \underset{\underset{\text{Dimer}}{\downarrow}}{CH_3-O\overset{\overset{O}{\|}}{C}-CH_2CH_2SO^{\cdot}} + ROOH$$

The hydrogen of the sulphenic acid being labile, will be abstracted by the peroxy radical and in so doing will stop the kinetic chain. The sulphenic acid, therefore acts in a similar way to that of the phenolic and amine antioxidants, that is radical trapping process is involved. The presence of the initial pro-oxidant stage as demonstrated by most sulphide antioxidants is rationalised in terms of production of initiating free radical species. This means a bimolecular reaction of sulphenic acid with hydroperoxides to produce peroxyl and sulphenyl radicals.

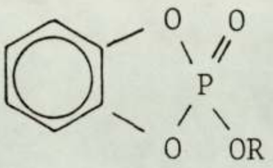


Phosphite Esters

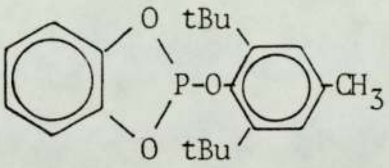
The behaviour of the phosphite esters is similar to that of the metal dialkyldithiocarbamates. Basic studies of the mechanism of the actions of the phosphite esters(1,22,36,37) have shown that trialkylphosphites react stoichiometrically with hydroperoxides to give phosphate ester and alcohol which are not reactive in subsequent oxidation reactions.

$$(RO)_3\text{-P} + ROOH \longrightarrow (RO)_3\text{-P=O} + ROH$$

Cyclic phosphites on the other hand give rise to a Lewis acid catalyst which in a closed system is capable of destroying hydroperoxide by ionic mechanism(36) (eg catechol phosphites and the derived phosphates).



R = H, aryl or transition metal ion



Aryl phosphites have become increasingly important in recent years as stabilisers for polyolefins because of the reactions of phosphine and phosphite with hydroperoxide as represented by the above equation.

1.3.4 Synergism

The phenomenon of synergism is the combination of two or more antioxidants, an effect which gives greater protection than the sum of the effects of the individual antioxidant used independently.

$$\text{EFFECT } (A + B) > \text{EFFECT } (\underline{A}) + \text{EFFECT } (\underline{B})$$

If the effect is merely additive, both antioxidants are probably acting by the same mechanism. True synergism implies that the two component antioxidants play different roles during inhibition(38). Thus selection of combinations which are likely to involve different modes of action will increase the probability of finding a greater than additive effect. The most commonly observed synergistic combinations includes (a) an effective radical chain stopper of hindered phenol or secondary arylamine type with peroxide decomposer of type organic sulphur or phosphorus compound. Various light absorbers, metal deactivators, peroxide decomposers and free radical chain breakers can be selected according to the demands by particular materials and conditions of use.

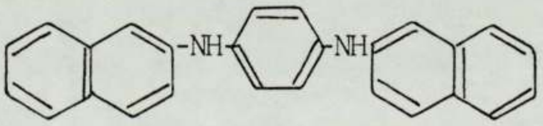
Inhibitor regeneration is another basis for synergism, the mechanism involves the donation of hydrogen from one inhibitor to the radical formed in the reaction of the other inhibitor with peroxy radical. The more efficient free radical chain stopper would be regenerated by this process from its oxidation products by a suitable hydrogen donor, which may be a relatively weak antioxidant when used in isolation. As discussed above, the antioxidants may act by the same or different mechanisms. the phenomenon may be explained by the following examples.

(a) The synergist regenerates the primary antioxidant and is itself destroyed. Ascorbic acid, amino acid and dialkyl phosphites(38-42) are typical examples of antioxidants that act in this way.

(b) In this mechanism, the second class protects the primary antioxidant (eg phenol and amine) by preventing the formation of free radicals in the system. The most technologically important synergist acts by this method. some illustrative examples are given below.

(1) Phenol-metal deactivator synergism

If phenolic antioxidants are used in combination with hydroxy dicarboxylic acids, amino acids, polya-lcohol (eg sorbitol) and other metal complexing agents, such as phosphoric acid, they show synergistic effects. Another class of auto-synergistic antioxidant which is particularly useful in rubber is the diaryl-p-phenylene diamine, eg di-β-naphthyl-p-phenylene diamine.



It is both chain breaking antioxidant and a metal complexing agent, the two functions are combined in one molecule.

(2) Phenol or amine - peroxide decomposer synergism

This type of synergism has recently assumed great importance in the stabilisation of polypropylene(43) (eg phenolic antioxidant and dilaurylthiopropionate).

1.3.5 Effect of Carbon Black on Arylamine and Phenolic Antioxidants

The influence of one antioxidant upon another when used in combination for protection of polymers against oxidation is of considerable importance, as is the interaction of inhibitors with other compounding ingredients.

Secondary arylamines or alkylated phenols which are effective stabilisers in most polymers, are appreciably less effective in the presence of carbon black, particularly in uv light, as compared to the clear polymer without carbon black(44). It has been suggested that this loss of antioxidant efficiency which occurs even though carbon black is itself a moderately effective inhibitor against thermal oxidation, may result from a catalytic effect of carbon surface on the direct oxidation of amine or phenol. Also Kuzminskii et al(45) attributed the accelerating effect of carbon black upon the rate of retarded antioxidant in the presence of amine antioxidants to absorption of the antioxidant on the carbon surface, making it less available as an inhibitor. The loss of inhibiting effect of the carbon black in the presence of antioxidants, together with the decrease in effectiveness of the antioxidants in the presence of carbon black clearly indicate antagonistic effects.

1.4 Nitrile Rubber

Nitrile rubber covers a broad range of materials based on the elastomeric copolymers of acrylonitrile and butadiene. It is used primarily when excellent swell resistance, combined with good resistance towards ageing, heat, wear, low temperature flexibility and thermo-oxidative stability are required.

The proportions of acrylonitrile and butadiene in the copolymer have a tremendous influence on these properties.

In many of its properties, nitrile rubber is superior to all other oil and solvent resistant elastomers (see Table 1.1)(46).

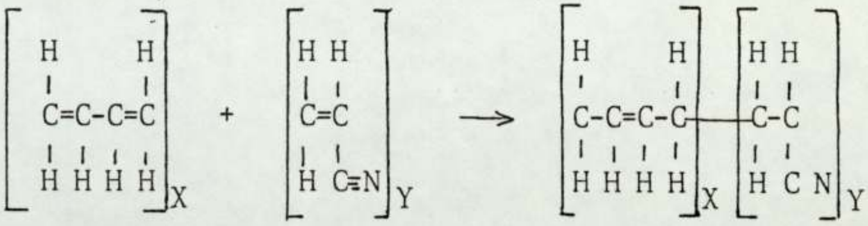
The use of nitrile rubber is rather restricted at both low and high ends of the temperature scale. Above 120°C for instance nitrile rubber hardens and its sealing efficiency falls. The desire to improve the heat resistance of nitrile has been experienced by manufacturers and users of this rubber because this limitation precludes it from many applications in the motor and aero industries.

The preparation of nitrile rubber is well described in the literature(39) and it involves essentially the copolymerisation of acrylonitrile and butadiene. Depending on the type of nitrile desired, the ratio of the monomers vary within wide limits. The commonly used nitrile rubbers contain 18-48%,

Table 1.1

Rubber	Useful Temperature Range (°C)		Resistance to solvent	Compression set	General Physical properties	Processibility
Nitrile	-50	120	G	G	G	G
Acrylic	-20	150	G	F-P	F	P
Silicone	-60	175	F	E	F-P	F
Fluorocarbon	-40	205	E	F	F	P

Key: E = Excellent, G = Good, F = Fair, P = Poor preferentially 26-40% acrylonitrile.



The butadiene acrylonitrile ratio in the nitrile rubber affects a number of important physical properties such as processibility, resilience, the oil resistance, thermal and thermo-oxidative behaviour of the rubber. The polarity of the rubber increases with increasing acrylonitrile content, giving rise to incompatibility with non-polar solvents (ie aliphatic hydrocarbons and paraffinic oils). This is shown in terms of improved swell resistance and decreased solubility. The resilience and low temperature flexibility of the vulcanisate decreases at the same time. As a consequence of increasing the polarity, the compatibility with polar plastics (eg PVC, phenoplasts) increases and the gas permeability of the vulcanisate increases with increasing acrylonitrile content.

Compounding

Nitrile rubber is usually vulcanised with sulphur, accelerators and zinc oxide. The amount of sulphur used in nitrile rubber is somewhat lower and the amount of accelerator somewhat higher than that used in natural rubber. This is because nitrile rubber is less reactive than natural rubber and also because sulphur is more soluble in natural rubber than it is in nitrile rubber. With large amounts of sulphur, nitrile rubber can be vulcanised to a hard rubber which, in addition to the oil resistance, has an excellent heat distortion resistance.

Accelerators of the benzothiazyl type which gives safe processing conditions have been found particularly useful. They can be activated with basic accelerators, thiuram disulphide or dithiocarbamates. Sulphenamide accelerators are often activated with thiuram monosulphide. Sulphur free vulcanisates can be prepared with organic peroxides and particularly with tetramethyl thiuram disulphide. Such vulcanisates have excellent hot air resistance. To improve the hot air resistance of thiuram or peroxide vulcanisates, 2-mercaptobenzimidazole and aldol-β-naphthylamine and their combinations have proved satisfactory.

In contrast to vulcanisates like that of natural rubber, or that of polychloroprene, relatively low mechanical properties are experienced with unfilled nitrile rubber or with inert fillers alone. However, with reinforcing blacks or light coloured reinforcing fillers, the tensile strength of nitrile rubber approaches that of natural rubber vulcanisates. From the point of view of ageing, the use of light coloured reinforcing fillers is advantageous. The swelling resistance of vulcanisates both in gasoline and oils decrease with increasing amount of fillers (corresponding to the decreasing content of rubber). All plasticisers influence the tensile strength of nitrile rubber and they can be used to regulate some of its properties.

1.4.1 Changes Occurring During Oxidation of NBR

A reduction of molecular weight due to oxidation or increase of molecular weight due to cross-linking takes place when a polymer is exposed to the atmosphere. Also it has been found that a trace of oxygen is capable of destroying the characteristic macromolecular structure of nitrile rubber(48).

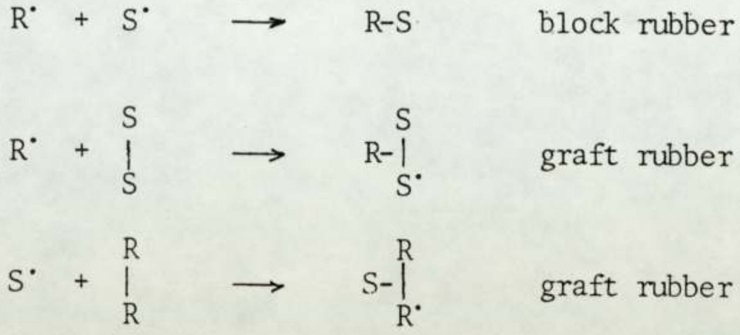
During compounding, processing and fabrication, free radicals are formed in the rubber. These attack the nitrile rubber causing the formation of rubber hydroperoxide leading to breakdown of the rubber chain. The necessary energy for the formation of free radicals during the compounding is supplied directly as mechanical energy(49). The molecules being ruptured by the shearing forces imposed during the deformation of bulk rubber. According to Kauzman and Eyring(50) C-C bonds of the polymer backbone break directly into free radicals.

$$\text{R-R} \xrightarrow[\text{energy}]{\text{mechanical}} 2\text{R}^{\cdot}$$

When mastication is carried out with another polymer in the absence of radical acceptors, one or both may rupture mechanically(51).

$$\text{R-R} \longrightarrow 2\text{R}^{\cdot}$$
$$\text{S-S} \longrightarrow 2\text{S}^{\cdot}$$

The radicals R˙ and S˙ may undergo further reactions as follows:



$$R^{\bullet} + S^{\bullet} \longrightarrow R\text{-}S \qquad \text{block rubber}$$

$$R^{\bullet} + \begin{array}{c} S \\ | \\ S \end{array} \longrightarrow R\text{-}\begin{array}{c} S \\ | \\ S^{\bullet} \end{array} \qquad \text{graft rubber}$$

$$S^{\bullet} + \begin{array}{c} R \\ | \\ R \end{array} \longrightarrow S\text{-}\begin{array}{c} R \\ | \\ R^{\bullet} \end{array} \qquad \text{graft rubber}$$

If the rubber is masticated in the absence of oxygen, the free radicals produced react by addition to the double bonds of the rubber structure. As a result, these free radicals are destroyed either by disproportionation or dimerisation.

In the presence of an efficient radical acceptor, on the other hand, there are two possibilities (a) if the addition product is another reactive free radical acceptor, thus when elastomers(49) are masticated in the presence of vinyl monomers such as methyl methacrylate, graft polymerisation and gel formation occurs(52).

During service at elevated temperatures, NBR-elastomers age by two major pathways either by a thermal process or by a thermo-oxidative process(48,53,54). Both processes can lead to either scission reactions and breakdown of the network or to cross-linking reactions with the accompanying hardening or embrittlement. Which of these two ways is determined by the amount of oxygen present in the system.

The thermal stability of the main chain is an inherent property of the polymer and is related to the bond strength. Thermal reactions of the cross-links are not uncommon, especially in sulphur vulcanised rubbers, and these manifest themselves as compression set and chemical creep. Thermo-oxidative reactions are responsible for most of the deterioration in the properties of NBR and other polymers.

Lee and Morrell(48) proved that oxygen is required in the hardening of nitrile rubber at elevated temperatures by ageing samples of nitrile rubber both in nitrogen and in air. Based on past work with other butadiene polymers, it was proposed that the most likely source of new cross-links during ageing of nitrile rubber is through the hydrocarbon backbone, as a step in the sequence of reactions constituting autoxidation. Also it is frequently suggested that the purely thermal reactions of nitrile groups and the intermolecular reaction of the nitrile groups are sources of new cross-links on ageing nitrile rubber but there is no concrete evidence to show that this is so.

In a TMTD/sulphur nitrile rubber vulcanisate, it has been found(48) that there is a reversible scission reaction at an oxidised form of the cross-link and it has been assumed to be sulphoxide. The speculative mechanism for this reaction is hypothesised through the recorded allylic shifts involving sulphoxides. It was also established that the hardening of nitrile rubber in TMTD/sulphur systems could be due to either main-chain modification or extra network material and that monosulphide cross-links are susceptible to oxidation(54). It seems very likely that a good heat resistant nitrile rubber will be obtained where the compound yields monosulphide cross-links and uncomplicated network structure, unreactive vulcanisation product and contains a highly effective antioxidant system.

In the literature a variety of heat resistant nitrile rubber formulations have been reported. Table 1.2 shows the important ones including ASTM standard formulation (D).

From the information given in Table 1.2 it seems that only formulation 'C'(47) is uncommon in the literature. This formulation is the so-called cadmium-magnesium cure system. Essentially, the system consists of five ingredients which are:

(i)	magnesium oxide	5.0 phr
(ii)	cadmium oxide	2.0 - 5.0 phr
(iii)	cadmium diethyldithiocarbamate	1.5 - 7.0 phr
(iv)	MBTS	0.5 - 2.5 phr
(v)	sulphur	0.0 - 0.1 phr

(i) Cadmium oxide performs the same function as zinc oxide, (ie it is a vulcanisation activator). In general, the lower the concentration level, the lower the compression set, the higher the level, the greater is the heat resistance.

Table 1.2 Nitrile rubber formulation table

	A	B	C	D
Nitrile rubber	100	100	100	100
Stearic acid	1.0	1.0	1.5	0.5
Zinc oxide	5.0	5.0	-	5.0
Cadmium oxide	-	-	5.0	-
Magnesium oxide	-	-	5.0	-
Tetramethyl thiuram disulphide (TMTD)		3.0		2.0
2-Mercaptobenzthiazole (MBT)	1.0	-	MBTS 1.0	-
Di-octyl phthalate (DOP)	-	-	-	5.0
Cadmium-di-ethyl-dithiocarbamate	-	-	2.5	-
N-tert-but-2-benzthiazole sulphenamide	-	-	-	1.0
Carbon black	-	-	65.0	60.0
Sulphur	1.5	0.2	0.5	0.5
Diphenyl guanidine (DPG)	0.25	-	-	-

(ii) Magnesium oxide appears to stabilise the compound by controlling the basicity. This affects the scorch and the rate of cure. Optimum heat resistance and stress-strain properties are obtained at a concentration of 5.0 phr.

(iii) Cadmium-di-ethyldithiocarbamate. Because of the greater activity Cd-DC is used specifically as an ultra-accelerator. It is unique in the sense that its inherent ability to provide stable cross-links such as monosulphides for the protection of unsaturated rubbers at elevated temperatures. When coupled with cadmium oxide, the two ingredients produce a variation of synergistic common ion effect. For most compounds, 2.5 phr cadmium diethyldithiocarbamate gives the best balance of properties. (The dithiocarbamates are also powerful antioxidants.)

(iv) MBTS. As booster, MBTS represents the best choice for scorch safety and heat resistance. MBT and Cd-DC show better heat resistance but are too scorchy.

(v) Sulphur. As in any other vulcanisation system, sulphur provides cross-links. Its level and presence has the greatest influence on vulcanisation. The proper level of elemental sulphur is critical when deciding how 'tight' to make the cure. Generally, high sulphur levels (0.5 - 1.0 phr) gives high modulus, lower compression set and lower volume changes in oil. Low sulphur levels

(0.0 - 0.5 phr) typically give better scorch safety and higher elongation and better ageing performance.

Studies have shown strong interactions between sulphur, MBTS and diethyldithiocarbamate. In the use of this system, specifically the nitrile elastomer to be compounded, must be stabilised with an aromatic amine such as di-octyl-di-phenylamine without which no cadmium-magnesium cured nitrile compound will give 145°C (300°F) heat resistance.

The main attraction of the magnesium-cadmium system is the heat resistance. This is however not limited to nitrile rubber only but it is an effective means of expanding heat resistance of styrene-butadiene elastomers.

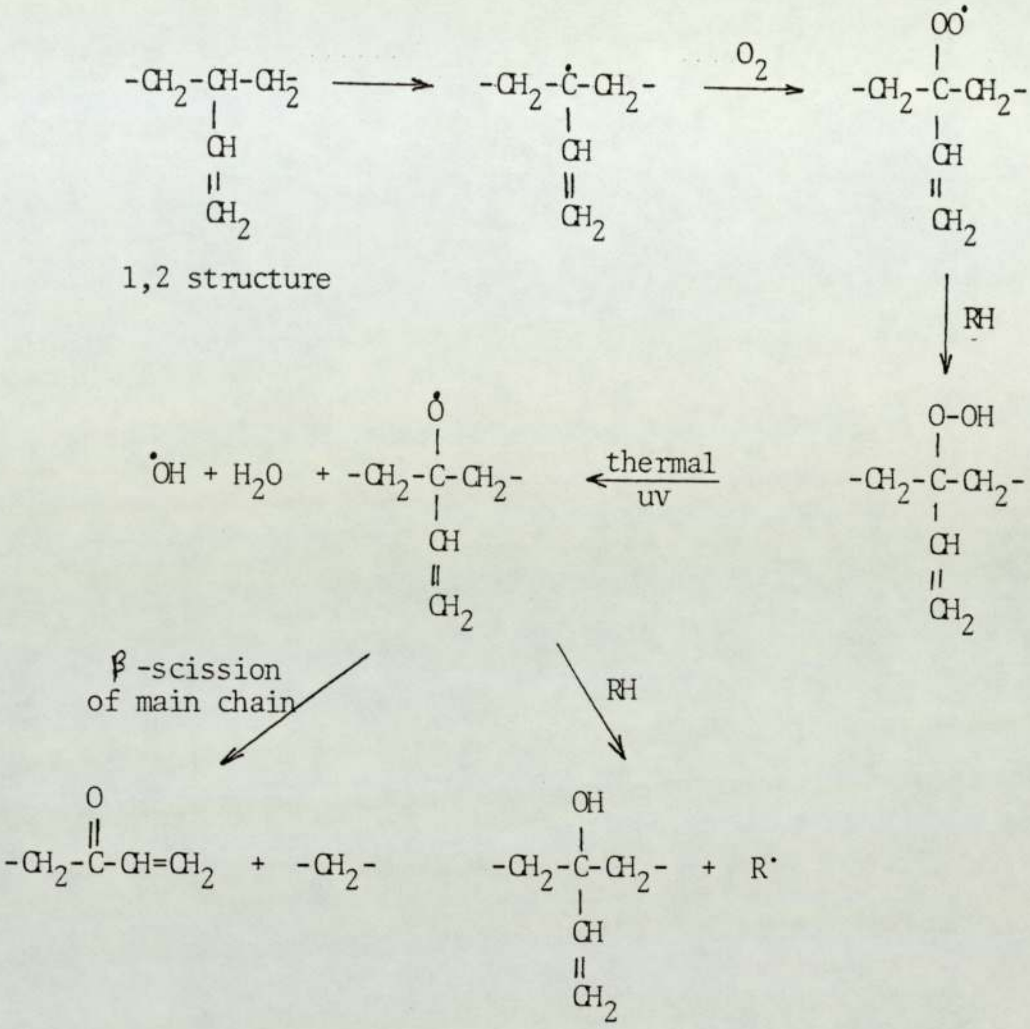
The good heat resistance of vulcanisates produced by the cadmium magnesium cure system is probably due to the presence of dithiocarbamates and MBT which are converted into antioxidant species. Both dithiocarbamates and MBT are very good thermal stabilisers, because of their ability to decompose hydroperoxide.

The primary disadvantage of the cadmium-magnesium cure system is vulcanisate bloom. But the quantity of blooms can be controlled by limiting the 'total' available sulphur. However, this bloom does not reflect a decrease in property retention. Although the cure system is known to provide a higher degree of heat resistance toxicity problems is a limiting factor to its widespread use.

1.4.2 Influence of Structure on Degradation

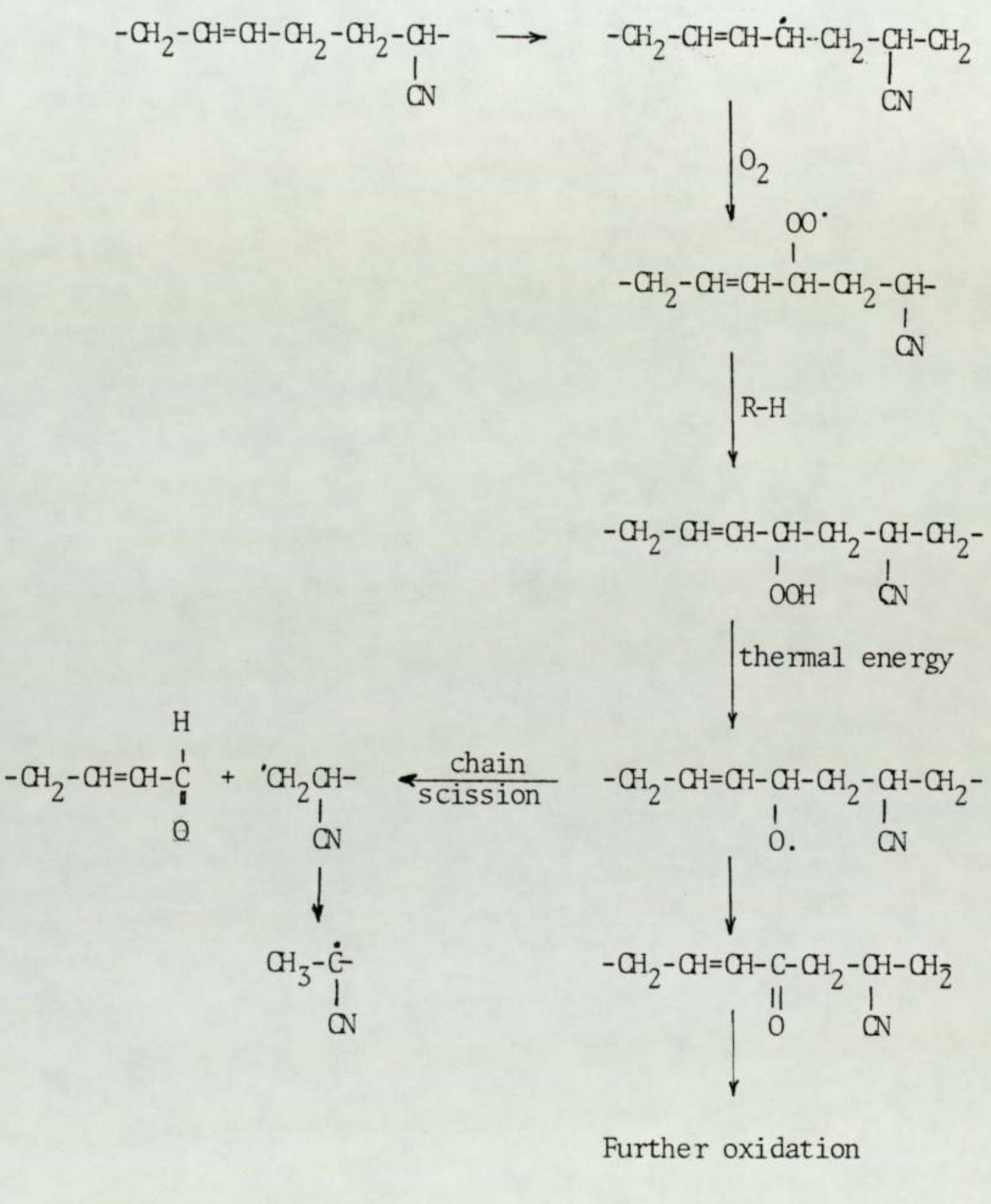
The structural units of unsaturation in the polybutadiene component of NBR are similar to pure polybutadiene (PBD), namely cis-1,4, trans-1,4 and 1,2-vinyl. Although present in small amounts, depending on the percentage of acrylonitrile content, the 1,2- structure plays an important role in the degradation of NBR.

According to Scott(55), 1,2-vinyl bonds are initially consumed rather than cis or trans unsaturated units during PBD photo-oxidation. Mayer(56) also observed a large decrease in thermal oxidative degradation (by oxygen absorption) with the first 20% saturation of PBD by the addition of methyl mercaptan and attributed this to faster saturation of vinyl double bonds in the system; thereby increasing the double bond dissociation energy of the tertiary C-H bond. Scott also found that the formation of hydroperoxide precedes the development of carbonyl or hydroxyls during photo-oxidation and concludes that hydroperoxides and not carbonyl are responsible for oxidative deterioration.



The alkoxy radicals derived from allylic methylenic sites as well as 1,2-vinyl units can give rise to carbonyl products, carboxylic acid, carbon monoxide, unsaturated ketones, etc. The formation of carbonyl during the breakdown of 1,2 units involves chain scission and hence reduction in molecular weight and its dispersion of the main chain is involved.

The oxidative degradation of nitrile rubber is to a little extent influenced by the nitrile group since experience of many polymers containing polybutadiene show polybutadiene residual double bonds (mainly 1,4-positioned) to be responsible for their deterioration. The following scheme shows the possible route by which nitrile rubber deteriorates.



1.4.3 Rubber Bound Antioxidants

If diene rubbers are to withstand attack by oxygen, they must be protected with additives. These compounds, known as antioxidants (the majority of which are phenols, amines) may sublime from thin-sectioned rubber goods at high temperatures or they may be dissolved out of the goods by solvents. Loss of antioxidant in either of these ways can be prevented by using antioxidants that are bound to the polymer.

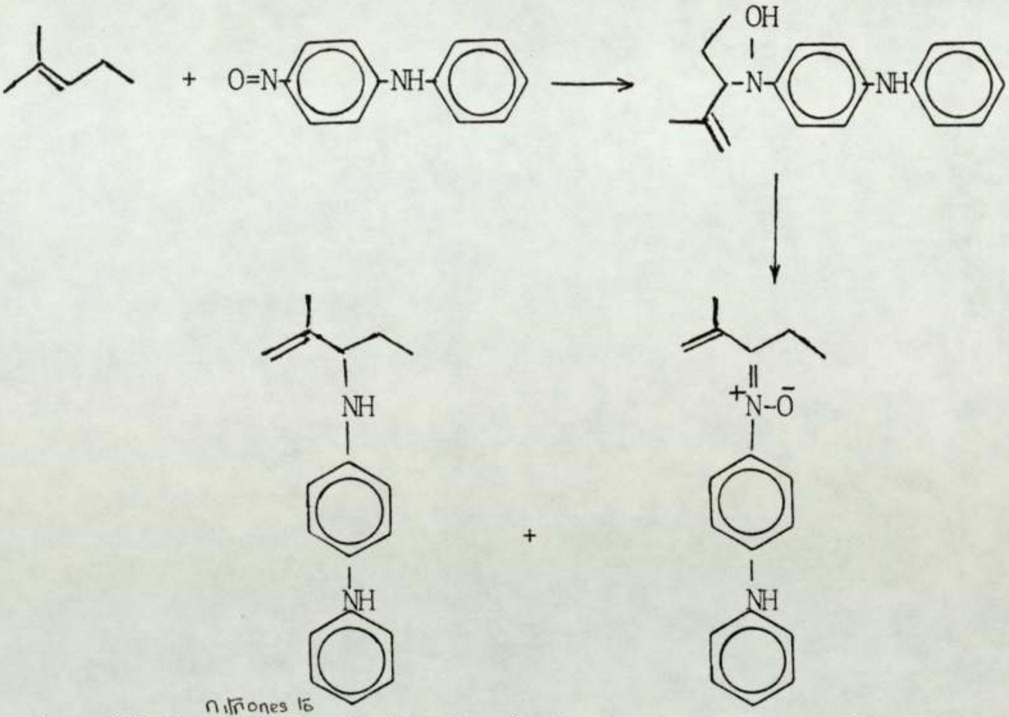
There are at present several approaches to overcoming the problems associated with loss of antioxidant by extraction or by volatilisation of rubber vulcanisates. One is by developing a 'network bound' antioxidant system and another is by incorporating polymeric, but unbound, antioxidants which have adequate resistance to volatilisation or extraction under service regime envisaged.

Recently Scott and co-workers(181) have shown that a variety of thiol-containing antioxidants can be reacted with rubber or rubber modified plastics in the latex form to give antioxidants which are bound chemically through the sulphur atom. The resulting modified polymers are consequently much more stable under conditions of high temperature performance and in applications where solvent or detergent leaching is important.

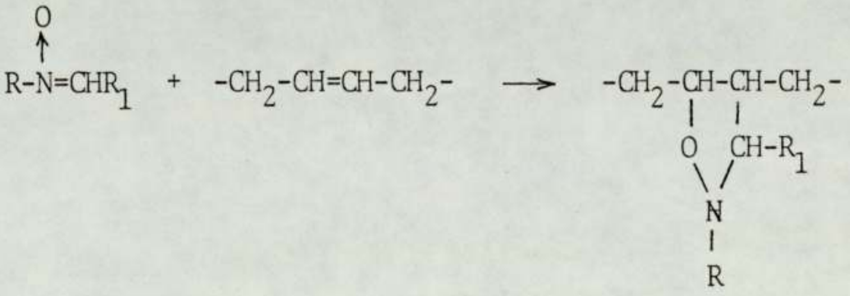
Early investigations were concerned with natural rubber latices due to the relative ineffectiveness of the present generation of commercial phenolic antioxidants in rubbers subjected to detergent extraction or dry cleaning (notably rubber gloves and latex threads). However, the process has been recently applied to the synthetic rubbers (notably SBR and NBR) and rubber modified plastics (ABS). In all these studies, a very consistent improvement has been found for the thiol-bound antioxidants over the best commercial materials available.

The effectiveness of bound antioxidants in rubber has been shown(57-60) in a formulation for nitrile rubber in the sequence ageing tests which proved damaging to the same rubber formulated with conventional antioxidants. The potential which exists for antioxidants which form part of the polymer structure has been demonstrated by Cain and co-workers(61). They successfully reacted antioxidants containing a rubber-reactive nitroso group with natural rubber, during vulcanisation, a rubber-bound antioxidant was obtained. After solvent extraction it was discovered that the activity of the rubber-bound antioxidant was relatively unaffected, whereas the conventional secondary alkyl amine diphenylamine antioxidant was lost almost immediately by extraction.

Model compounds have been used to ellucidate the mechanism of reaction of the nitroso compounds with natural rubber and the operating mechanism has been suggested to be as follows:



The 1,3-cyclo addition of nitrones to the double bonds in elastomers provides a general technique for introducing an antioxidant group into rubber molecule. This technique has been successfully applied to cis-polybutadiene and cis-polyisoprene during vulcanisation using a variety of curing systems$^{(62)}$.



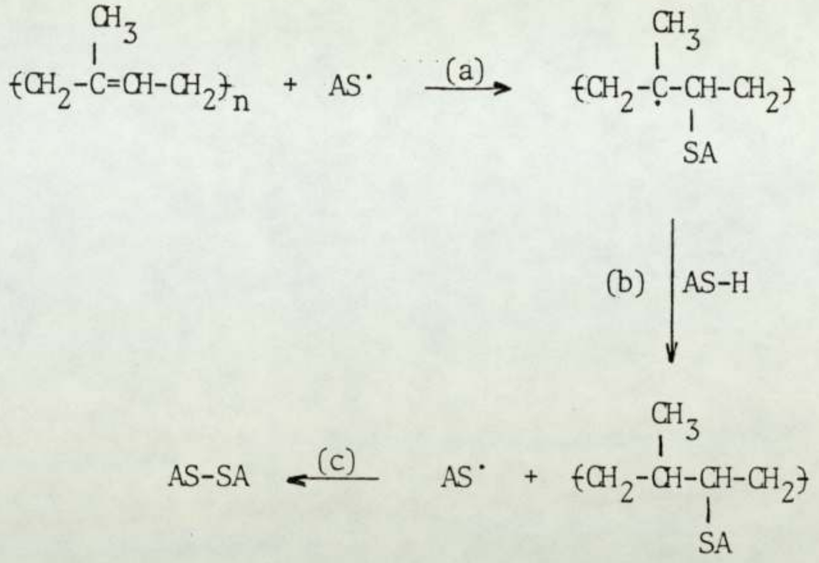
$$\mathrm{R{-}\overset{\overset{O}{\uparrow}}{N}{=}CHR_1 + {-}CH_2{-}CH{=}CH{-}CH_2{-} \longrightarrow {-}CH_2{-}\underset{\underset{O\diagdown N(R)\diagup}{|}}{CH}{-}\underset{\underset{CH{-}R_1}{|}}{CH}{-}CH_2{-}}$$

Through R and R_1 the antioxidant functions were introduced. The effectiveness of bound antioxidants was compared with commercial arylamine antioxidants both before and after extraction. It was found that 'network' bound antioxidants were as effective as the commercial amine antioxidant before extraction and retains its activity very much better after extraction.

A major disadvantage of the arylamine antioxidants is their tendency to discolour which limits their use to rubbers for such purposes where colouration is not a disadvantage. Hindered phenolic nitrones were found to react readily with rubber during vulcanisation to give rubbers with much lower levels of discolouration.

1.4.4 Bound Antioxidants in Latex Products

It is difficult to react simple phenols with a variety of rubbers to give a high yield of rubber bound antioxidants. Furthermore, the concentration achievable is also limited by side reactions and, although concentration of bound antioxidants in the region of 2-3% can be readily achieved, the process is less suitable for the operation of latex antioxidant masterbatches. It is, however, possible to react thiol-based antioxidants, eg 3,4-di-tert-butyl-4-hydroxybenzyl mercaptan to much higher levels (70-80%) than the corresponding alcohols (maximum 20%), since they undergo facile addition to the double bond in rubber in the presence of free radicals(63). The scheme below shows that the reaction involved is a radical chain process and is terminated by reaction of the radical (AS$^\cdot$) with other radicals in the system.



Scott (64) and co-workers have shown that the by-products are themselves powerful antioxidants and cause no significant interference with scorch time or subsequent vulcanisation reactions.

Latex cre-ps containing bound antioxidants based on thiols show a considerably improved colour retention after drying than unmodified cre-ps made from the same latex. This leads to the practically very important consequence that, where guaranteed cleanliness and non-toxicity are of paramount importance, for example in medical applications, thiol bound antioxidants not only give better colour products but the antioxidant system is completely safe since it cannot be leached from the rubber during use.

When used in applications where the loss of antioxidant by volatilisation or leaching may occur, latex products containing bound antioxidants show exceptional stability.

1.4.5 Bound Antioxidant Latex Masterbatch

The fact that thiol-based bound antioxidants can be used conveniently for the preparation of high concentration of latex masterbatch which can be used as additives for fully formulated or partially prevulcanised latices which are now in common use is of great advantage. Indeed, it is a convenient and cheap way of introducing bound antioxidants into rubbers. Provided that there is a considerable concentration (30% or more) of the original double bonds, co-vulcanisation of the thiol modified and conventional latices occurs readily.

It has been shown(63) that bound antioxidant masterbatches are very much superior to conventional antioxidants used at twice the concentration of bound antioxidants. In masterbatch form, the thiol based bound antioxidants are generally superior to the bound simple phenolics due to higher levels of reaction achieved. However, in spite of this, the durability of the latter is very much superior to the best conventional antioxidants used as additives.

1.4.6 Mechanism of Addition of Thiols

The mechanism of addition of the thiols to unsaturated polymers is a free radical type and the alkylthiyl or arylthiyl radicals being the resulting product of initiation which subsequently adds to the unsaturated substrates to form a carbon radical, the second stage being usually reversible.

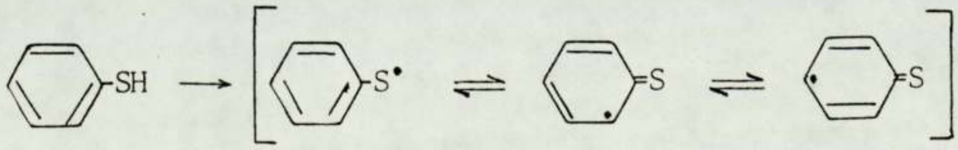
$$\mathrm{RSH} \longrightarrow \mathrm{RS^{\bullet}} + {}^{\bullet}\mathrm{H}$$

$$\mathrm{{>}C{=}C{<}} + \mathrm{RS^{\bullet}} \rightleftharpoons \mathrm{RS{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}^{\bullet}}$$

The carbon radical then reacts with thiol molecule to give the end product and the thiyl radical thus propagates the radical chain.

$$\mathrm{RS{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}^{\bullet}} + \mathrm{RSH} \longrightarrow \mathrm{RS{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}H} + \mathrm{RS^{\bullet}}$$

The addition of the thiyl radical and the hydrogen transfer are normally exothermic with the result that the overall reaction is fast and the kinetic chain length is a few hundred to a thousand(65). The hydrogen transfer is usually the determining step because the cleavage of an S-H bond is involved and the rate is strongly influenced by the structure of the to-be-added thiol. Hence aromatic thiols, which require lower energy to break the S-H bond by virtue of resonance stabilisation of the thiyl radical formed, are better transfer agents than the aliphatic thiols(66).



The rate of hydrogen transfer influences all the variables that depend on the life time of the intermediate carbon radical such as:

(a) the degree of reversibility of the primary reaction (carbon radical formation),

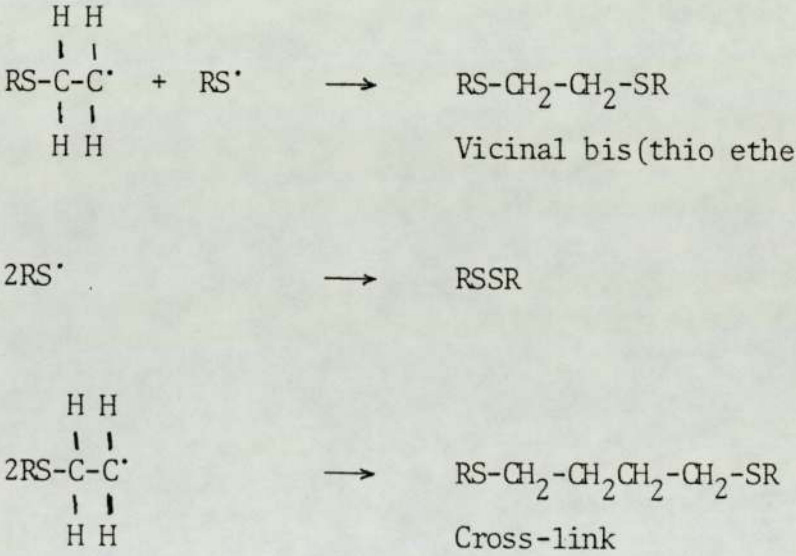
(b) the stereochemical course of the overall reaction,

(c) possible rearrangement of the intermediate carbon radical,

(d) the extent of telomerisation, and

(e) the chain termination.

The termination may yield various products(66).



$$RS\text{-}\overset{H}{\underset{H}{C}}\text{-}\overset{H}{\underset{H}{C}}^{\cdot} + RS^{\cdot} \longrightarrow RS\text{-}CH_2\text{-}CH_2\text{-}SR$$

Vicinal bis(thio ether)

$$2RS^{\cdot} \longrightarrow RSSR$$

$$2RS\text{-}\overset{H}{\underset{H}{C}}\text{-}\overset{H}{\underset{H}{C}}^{\cdot} \longrightarrow RS\text{-}CH_2\text{-}CH_2CH_2\text{-}CH_2\text{-}SR$$

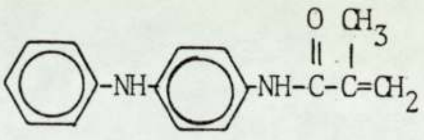
Cross-link

Simple thiol adduct with polymers in general follows the same reaction mechanism. Though the various polymers containing olefinic double bonds undoubtedly react with thiols under appropriate conditions.

1.4.7 Bound Antioxidants in Nitrile Rubber

At the present, the main use of nitrile rubber is in oil seals due to its resistance to lubricants. However, under prolonged exposure to high temperature and oils, the mechanical properties of the vulcanisates are destroyed rapidly due to the removal of low molecular weight antioxidants(53). Under these conditions bound antioxidants have proved to be very effective. Simple phenol ditertiary butyl-para-cresol (TBC) and 3,5-di-tert-butyl 4-hydroxybenzyl mercaptan (BHBM) are examples of antioxidants which have been successfully bound into nitrile rubbers(67). BHBM binds to much higher yields based on thiol and is consequently more effective under aggressive conditions encountered by most polymeric materials during service life.

Goodyear Chemical Division(68) developed a system in which the antioxidant is copolymerised with nitrile rubber. In this way, the antioxidant becomes part of the rubber molecule providing unique persistant performance in rubber parts exposed to extracting fuels and oils or to severe heat ageing. The basis of the bound antioxidant system is the monomeric amine antioxidant N-(4-anilinophenyl)methacrylamide (IV). The structure contains both an unsaturated polymerisation site through which it is tied into the rubber molecule and an active amine antioxidant group.



(IV)

This antioxidant like many other amines is staining and cannot be used in light coloured articles, besides the effectiveness is limited to formulations containing silica. Theoretically, it is expected that (IV) will not be as efficient as the (II) and (III) because these contain sulphur atoms within the antioxidant molecule. It is assumed that they will operate by two mechanisms chain breaking mechanism and peroxide decomposing mechanism, a mode of action with which sulphur containing antioxidants are identified, whereas the former can only act by chain-breaking mechanism. Also since the rate of oxidation is determined by hydroperoxide concentration, it is only logical to think that PAPT and PPPT should be more effective as an antioxidant.

1.5 Initiator System

In the attempt to graft polymerisable vinyl monomers on to natural rubber latex, successful polymerisation was reported(69) by using water soluble catalysts such as persulphate or organic hydroperoxide. In a similar undertaking, Le Bras and co-workers(70) observed the role of ammonia as polymerisation retardant but this was overcome by using different catalyst systems, namely a hydroperoxide activated by an activator, usually polyethylene-polyamine(71).

There are three main types of radical intermediates involved in the system of vinyl monomer and natural rubber latex copolymerisation:

(a) radicals derived from the initiator ($I^{\bullet}$),

(b) the polymer radical (Mn) from polymerisation of monomer, and

(c) those derived from the rubber molecule R-H.

The radical thus formed can either add to double bond in the rubber to produce rubber radicals,

$$I^{\bullet} + R\text{-}H \longrightarrow I\text{-}\dot{R}H$$
$$M\dot{n} + R\text{-}H \longrightarrow Mn\text{-}\dot{R}H$$

or it can abstract labile hydrogen atom from R-H:

$$I^{\bullet} + R\text{-}H \longrightarrow I\text{-}H + R^{\bullet}$$
$$Mn^{\bullet} + R\text{-}H \longrightarrow Mn\text{-}H + R^{\bullet}$$

The newly formed free radical centre on the rubber molecule may react with monomer radical or polymer radical. In the end a compound in which the vinyl polymer chains are chemically bound to rubber is produced.

Bacon and co-workers(72,73) successfully copolymerised common vinyl monomer with natural rubber latex using tertiary butyl hydroperoxide and tetra ethylenepentamine, the polymerisation was completed within a few hours at room temperature.

Another technique by Sekhar(74) was the use of catalyst formed in the rubber in situ; the latex was aerated by rotating a half-filled container for a few days and the product was found to be able to initiate polymerisation of a variety of monomers without the addition of hydroperoxide, but in the presence of a small amount of ferrous ion or polyamine activator. The reactive site was assumed to have been formed on the rubber molecules and probably being hydroperoxide in nature.

Redox Initiators

Redox systems comprise two or more substances whose mutual interactions produce free radicals which are able to initiate polymerisation. The fact implies that these combinations usually depend for their effectiveness upon interaction between a reducing agent and an oxidising agent. An important feature of this system is their stability in water and a fairly fast, steady liberation of radicals in the aqueous phase.

Redox initiators can be classified into the following categories:

(a) peroxide system/polyamine reducing agents,

(b) peroxydisulphate system with reducing agents such as thiols, hydroxylamine, hydrogen sulphide and salts of various oxy acids of sulphur and polyhydric phenols,

(c) redox-pair involving metal ions,

(d) electrochemical initiation, and

(e) miscellaneous redox systems.

Although the mode of action of all these systems is very well documented in the literature(75-79), the importance of the hydroperoxide-polyamine system used in the present work cannot be over emphasised. The presence of appreciable quantities of iron, which is contained in most of the above listed systems; in the eventual polymer is undesirable for at least two reasons:

(a) it may catalyse oxidative degradation of the rubber (polymer), and

(b) it may cause discolouration.

For these reasons, endeavours were made to find an alternative activation system for hydroperoxide which is nominally iron-free, and aliphatic amines were found to be the best.

Whitby et al(75) noted that many aliphatic and alicyclic amines are capable of decomposing organic peroxides vigorously and in consequence found that a large number of amines acted as activators for the emulsion polymerisation of styrene initiated by a peroxide catalyst. The polyalkylene polyamines were however observed to have a powerful activating effect in the emulsion polymerisation of styrene although only mild in the bulk polymerisation of this polymer. The polyethylene polyamines from diethylenetriamine to nonaethylene-decamine were investigated and the conclusion was that the effectiveness reaches a maximum in tetraethylene pentamine (TEPA) and pentaethylenehexamine, and then gradually decreases as the molecular size is further increased.

As a result of extensive investigations, Whitby and his co-workers came to the conclusion that two structural requirements must be fulfilled if successful activation is to occur.

(1) The amine must contain, within the molecule, amino groups of different degrees of substitution, in particular, it appears that the amino group must be either primary and secondary or primary and tertiary. As an example, to illustrate this conclusion, it was found that ethylene diamine is a very weak activator, its symetrical N,N-dialkyl substitution derivative ($RHN-CH_2-CH_2-NHR$) have no activating power but its N-mono alkyl substitution derivatives ($H_2N-CH_2CH_2-NHR$) are effective activators.

(2) The amino groups must be separated by not more than two carbon atoms. Thus tri(β-ethylamino)amine ($N(CH_2CH_2NH_2)_3$) with two carbon atoms between the nitrogen atom was observed to activate whereas tri(γ-aminopropyl)amine ($(H_2NCH_2CH_2CH_2)_3N$) with three did not.

Spolsky and Williams (76) confirmed that tetraethylenepentamine can be used as sole activator for cumene hydroperoxide but do not agree with Whitby's contention that the ability of a polyamine to activate is associated with the presence of primary and secondary amino groups. They suggested instead that the effectiveness is nearly proportional to the amine content of the polyethylenepolyamine and that primary and secondary amines are equivalent in their ability to activate.

Many other workers(77-79) have investigated the effectiveness of the hydroperoxide-polyethenepolyamine system. It appears that little is known regarding the precise chemistry of the system. It is, howevever, plausible to write a radical generating reaction as follows:

$$\mathrm{ROOH} + \mathrm{R'NH_2} \longrightarrow \mathrm{RO^{\cdot}} + \mathrm{R'NH^{\cdot}} + \mathrm{H_2O}$$

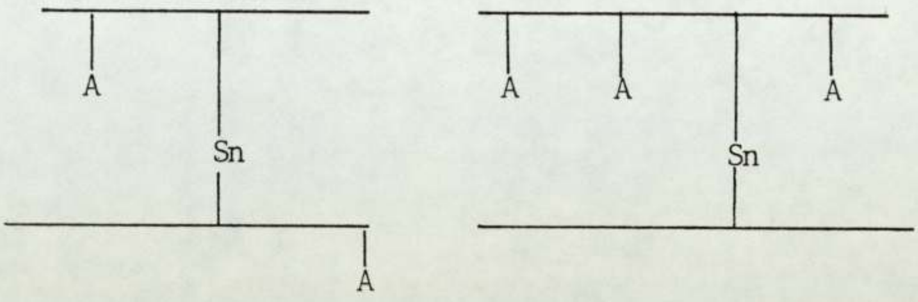
There is also doubt as to whether in practice, hydroperoxide-polyamine systems are truly iron-free for it had been claimed that the rigorous purification of the components from all traces of iron results in a reduction in the effectiveness of the combination. It may be that, in practice, it is minute traces of an iron-polyamine complex which interacts with hydroperoxide and this explains the sensitivity of the system to changes of pH; for the cause could then be variable hydrolysis of the iron-polyamine complex.

Another view is that the formation of a salt between the amine and hydroperoxide components may provide the initial pathway for the reaction. It is possible to envisage the formation of species such as $ROO^- \; RNH_3^+$. If $R'NH_3^+$ has complexed within it minute traces of iron, such salt formation would inevitably bring the iron into close proximity with the hydroperoxide entity, thereby enabling the iron to exert its catalytic effect at an effective concentration which is considerably higher than the prevailing in the system as a whole. The formation of salt would certainly explain why the behaviour of hydroperoxide amine pair in ionising media such as water can differ markedly from their behaviour in a non-polar media.

1.6 Aim and Scope of Project

It has been shown(19,67,80) that thiol-containing antioxidants can be successfully reacted with natural rubber(19,80), styrene-butadiene rubber(80), acrylonitrile-butadiene(67) and acrylonitrile-butadiene-styrene copolymers(80) to give polymer adducts which function as bound antioxidants. An important application of this technology is the formation of 'masterbatch' latex concentrates of bound thiols which can be used as additives for unstabilised latices of the same polymer(67,80) with consequent economic advantages.

In the case of rubbers, this kind of process relies on the co-vulcanisation of the modified latices with normal latices and the antioxidant is much less evenly distributed than it is in the latex formed by normal procedure. This is illustrated schematically in the following diagram:



Normal process Masterbatch process

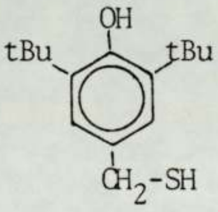
A consequence of uneven antioxidant (A) distribution in the second case could be less effective protection of the polymer since existing evidence suggests that an even dispersion of additive in the polymer leads to maximum effectiveness.

The latex masterbatch technique can be applied in two ways. The first is to mix the latex concentrate with normal (untreated) latex and then proceed normally and the second is to coagulate the masterbatch and use the dry rubber as normal compounding ingredient. The former offers economic advantages since it eliminates a stage in the process but the latter is more versatile since it is much easier to store a solid rubber masterbatch than latex. Besides, evidence suggests that a synergistic mixture of different bound antioxidants made separately do not readily mix in the latex form and hence the synergistic effect is eliminated(80). But on severe mixing, the mixture does mix.

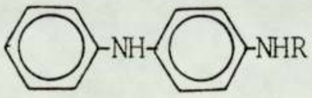
In view of the above discussed facts, the present work is aimed at investigating the effectiveness of bound thiol antioxidants in nitrile rubbers. Comparing three techniques, (a) normal adduct, (b) latex masterbatch and (c) solid masterbatch. Nitrile rubbers are representative of the class of vulcanised elastomers in which bound antioxidants are of technological importance.

Also the purpose of the project is to obtain scientific evidence on the importance of antioxidant/stabiliser distribution in the polymer and to obtain information which will be of practical value in using polymer bound antioxidants.

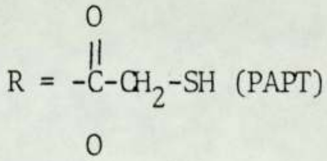
A comparative study of thiol-based phenolic antioxidant BHBM (I) and thiol-based amine antioxidants (II) and (III) will be carried out using the methods of Amarapathy(81), Fernando(80), Kularatne(67) and Fernando(19).



(BHBM, I)

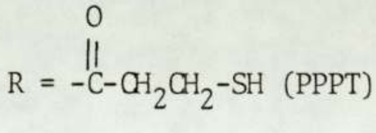


(II)



$R = -\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-SH$ (PAPT)

(III)



$R = -\overset{\overset{\displaystyle O}{\|}}{C}-CH_2CH_2-SH$ (PPPT)

CHAPTER TWO

EXPERIMENTAL

2.1 General Experimental Techniques

2.1.1 Materials: Sources and Purification Methods

The purification of the reagents used in the present work were modifications of the methods described by Weissberger(82). The literature values are quoted from the 'Handbook of Chemistry and Physics'(83) or the 'Dictionary of Organic Compounds'.

(a) Nitrile rubber latex

(Elaprim D/3360/225) experimental grade stabilised with 0.1% of antioxidant BHT (based on the dry rubber content) was supplied by Montedison Chemical Company Limited with the following characteristics:

35.3% solid content
34.4% bonded acrylonitrile content
70 ppm residual acrylonitrile and pH = 10.4

The pH was always reduced to neutral in all reactions.

(b) Solid Nitrile Rubbers

(i) The commercial grade nitrile rubber type Krynac 800 NS with 34.5% acrylonitrile content was supplied by Polysar Limited.

(ii) Chemigum. This is a polymerisation stabilised nitrile rubber, grade HR-665 lot 441-813180/11 with 32% acrylonitrile content. It was supplied by Goodyear Chemicals, Rubber Division, Limited.

(c) 2,6-Di-tertiary-butyl-phenol

This was obtained from Aldrich Chemical Company Limited at 99 + % purity and was used without further purification in the synthesis of antioxidants.

(d) Thioglycollic Acid and β-Mercaptopropionic Acid

These were used as supplied by Aldrich Chemical Company Limited without further purification.

(e) Para-aminodiphenylamine

This was supplied by Sigma Chemicals and used without further purification.

(f) Hexane

Hexane was used in the crystallisation of amine antioxidants. The technical grade was fractionally distilled at 69°C before use (ex Aldrich Chemicals).

(g) Dispersol LN

This was obtained from Imperial Chemical Industries Limited.

(h) Acetone

Analytical reagent grade (Fisons Limited) was used without further purification.

(i) Acetophenone

Acetophenone (ex BDH) was fractionally distilled and the fraction that boiled at 202°C was collected (Bpt 202°C/760 mm).

(j) Chlorobenzene

Chlorobenzene was dried over phosphorus pentoxide and fractionally distilled. (Bpt 132°C/760 mm)(83).

(k) Chloroform

Analytical reagent grade (Fisons Limited) was used without further purification.

(l) Cumene Hydroperoxide

Cumene hydroperoxide (ex Koch Light) was purified via the sodium slat according to the method of Kharasch(85). It was fractionally distilled under reduced pressure and the fraction that boiled at 51-52°C/0.02 mm was collected. Iodometric titration(86) gave values of purity of 99-100% (Bpt 60°C/0.2 mm)(87).

(m) Tertiarybutyl hydroperoxide

Tertiarybutyl hydroperoxide (ex Koch Light) was purified via the sodium salt as (l) above. It was then fractionally distilled and the fraction boiling at 60°C/12 mm was collected.

(n) α-Methyl Styrene

α-Methyl styrene (ex BDH) was distilled and the fraction boiling at 165°C was collected (Bpt 167-170°C(84)).

(o) Phenol

Phenol (ex Fisons Limited) was distilled and the fraction boiling at 182°C collected, Mpt 33-34°C (Mpt 35-37°C(84)).

(p) Reagents for Hydroperoxide Determination

Analytical reagent grade (Fisons Limited) benzene, methanol and ferrous ammonium sulphate were used. 1,10-phenanthroline hydrate (BDH) was used as indicator without further purification.

(q) Cumyl Alcohol

This was distilled and the fraction that boiled at 202°C was collected. It was then recrystallised from 60-80 petroleum ether, Mpt 33-34°C (Mpt 35-37°C(82)).

2.1.2 Bound Antioxidant Masterbatch Formation

The technique used by Kularatne was to react BHBM with nitrile rubber after removing free monomers. More recently it has been reported(88) that some thiols can be reacted with solid rubber on the mill in the absence of vulcanising ingredients and that the higher the concentration of the thiol in the rubber, the higher the level of binding. This is because during the binding reaction there are two competing reactions (i) radical reaction between the thiol and the peroxide and (ii) ionic reaction between the thiol and the peroxide. There is evidence to suggest(35,89-91) that at high thiol to peroxide concentration ratios the radical reaction dominates whereas at high peroxide concentration to thiol concentration ratio the ionic reaction pathway is favoured. It is also known that the success of the grafting reaction depends very much on the extent of free radical reaction. Hence after a period of time the ionic reactions may predominate over the free radical process and hence inhibiting further grafting.

2.1.3 Latex Procedure

In the case of hydrolysable thiols, the problem of hydrolysis may be avoided by working at neutral pH. In this present work, this has been made possible by the use of a non-ionic dispersant (Dispersol LN) or emulsifier (Vulcastab LS).

Using BHBM, PAPT and PPPT attempts were made to produce masterbatches of the following concentrations:

4×10^{-3} $\quad$ 4×10^{-2}
8×10^{-2} $\quad$ 1.2×10^{-1} $\quad$ moles antioxidant/
1.6×10^{-1} $\quad$ 2×10^{-1} $\quad$ 100 g (DRC) NBR latex

All masterbatches were divided into two parts and examined in two ways.

(A) All were reduced to three concentrations 1, 4 and 8×10^{-3} moles per 100 g of rubber by addition of latex masterbatches to untreated latex. They were then coagulated, washed with distilled water and dried under vacuum at room temperature. The dried rubber was then vulcanised with the standard system used in nitrile rubber. Films were cast on glass plates and the unvulcanised films were examined in oxygen absorption before and after extraction and the concentration of the antioxidants in each sample was estimated by the ir technique (see section 2.1.5).

(B) All were coagulated and divided into two parts:

(i) One part of the coagulum was added to solid NBR as normal additive to give concentrations 1, 4 8×10^{-3} moles/100 g rubber.

(ii) The other part was extracted similar to film extraction described in section 4.4.3 under Chapter Four and added to NBR by normal compounding to give the same adduct rubber concentration as in (i) above.

The concentration of the antioxidant was again measured by the ir technique.

2.1.4 Solid Rubber Procedure

The effect of the following parameters was investigated.

(a) Pre-milling time (before the addition of thiol) and variation of formed peroxide concentration with milling time.

(b) Effect of added peroxide on the concentration of thiol bound in the rubber.

The evaluations of the solid rubber containing bound antioxidants were carried out as for latex masterbatch technique.

2.1.5 Estimation of Bound Antioxidant Concentration

The estimation of the bound antioxidant concentration was by infra-red absorption spectrometry. The spectra were recorded using a Perkin Elmer ir spectrophotometer, model 599. The samples used were transparent and of thickness 0.003 ± 0.0005 inch. A peak at 2240 cm^{-1} characteristic of the acrylonitrile butadiene rubber (ie due to C≡N stretching vibration) was used as a reference band to minimise errors due to vibration in sample thickness. This band, whose intensity was directly proportional to film thickness, was found to remain unchanged after film extraction.

Evaluation of bound phenolic antioxidant was found by measuring absorbance at 3640 cm^{-1} due to O-H stretching of non-hydrogen bonded phenolic hydroxyl group. The strong aromatic absorption at 1590 cm^{-1} was used to determine the amount of bound thiol amine antioxidants. Typical spectra are shown in Figs 2.1 and 2.2.

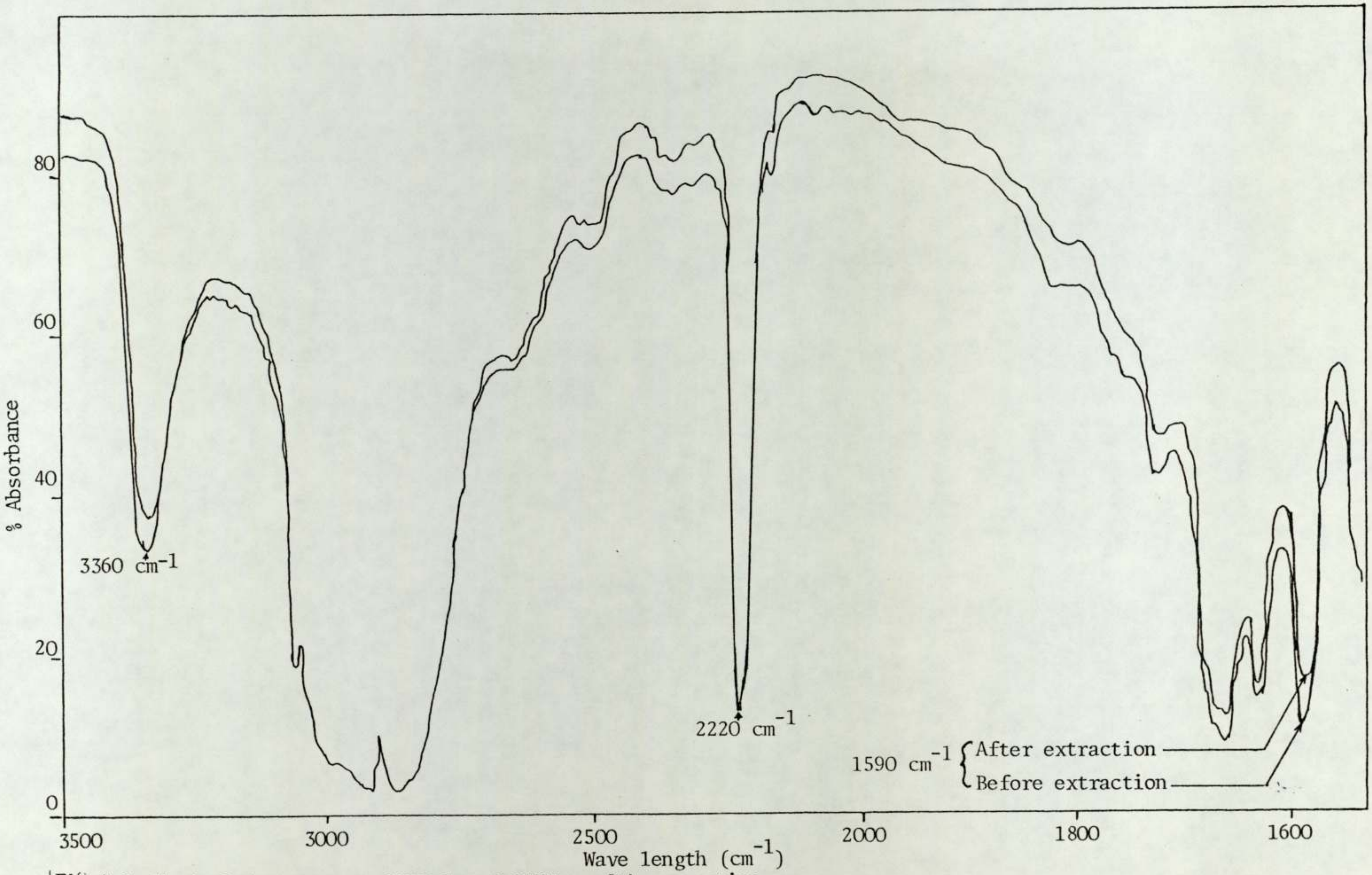


Fig 2.1 Typical ir spectra of NBR bound PAPT grafting reaction

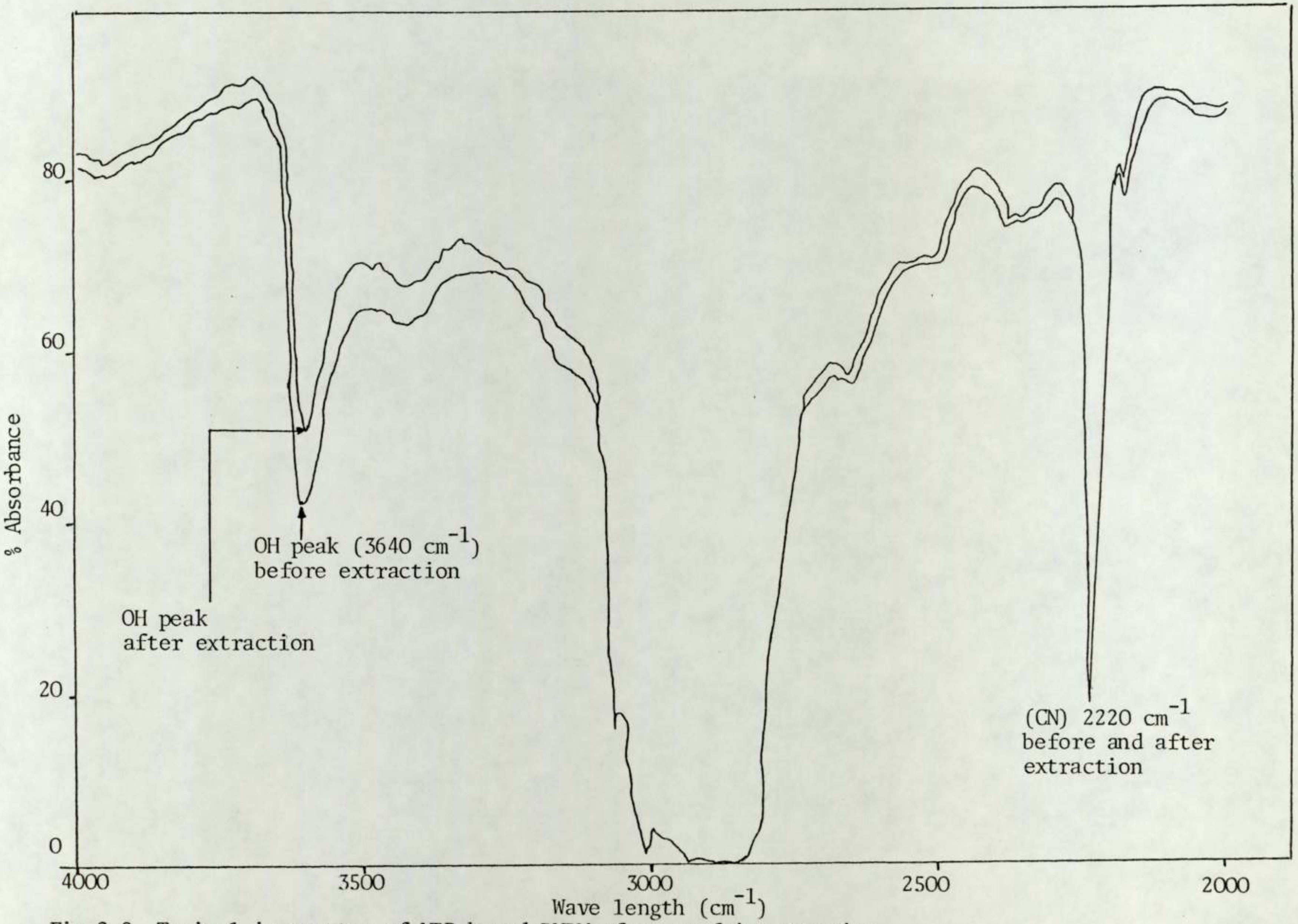


Fig 2.2 Typical ir spectra of NBR bound BHBM after grafting reaction

The base line technique(92) was used to calculate the optical density or absorbance due to various functional groups. This was done by drawing a vertical line through the analytical wavelength until it intersected the base line which has been drawn tangential to the adjacent absorption maxima or shoulder. This was similarly repeated for the reference peak. Before the commencement of any spectral measurement, the spectrophotometer was adjusted to read 100% transmittance at 2800 cm^{-1} and this was known as the background line.

In all quantitative analysis, the following combined form of Beer Lambert equation was used(93).

$$A = \log_{10} {}^{I_o}/_{I} = Ecl$$

where A = absorbance or optical density

I_o = intensity of radiation effectively entering the sample

I = intensity of radiation energy emerging from the sample

E = extinction coefficient expressed in litres $moles^{-1}$ cm^{-1}

c = concentration of absorbing group present in sample, mole/litre

l = path length of the radiation within the sample in cm

Hence for the hindered phenols the

$$\text{Hydroxyl Index} = \frac{A(3640\ \text{cm}^{-1})}{A(2240\ \text{cm}^{-1})} = \frac{A(\text{OH})}{A(\text{CN})}$$

and for aromatic amines, the

$$\text{Aromatic Absorption Index} = \frac{A(1590\ \text{cm}^{-1})}{A(2240\ \text{cm}^{-1})}$$

Calibration Curves

288 mls (100 g DRC) of 35% NBR latex was mixed with known quantities of the antioxidant. From this mixture films were cast on glass plates as described in Chapter Three. After drying, samples of equal thickness $3 \times 10^{-3} \pm 0.005$ in were selected and the ir spectrum of the films were taken. Samples were prepared with varying concentrations of antioxidant, 0.4, 4, 8, 12, 16 and 20 $\times 10^{-2}$ moles antioxidant/100 g (DRC) rubber.

The intensities of the phenolic -OH at 3640cm^{-1} and of the aromatic (amine) absorption at 1590 cm^{-1} were proportional to the concentration of the antioxidant added and were measured as a function of peak area.

The concentration of the phenolic antioxidant was interpreted as the ratio of peak area of phenolic -OH at 3640 cm^{-1} to the peak area of the reference peak at 2240 cm^{-1} and the concentration of the amine antioxidants was interpreted as the ratio of the peak area of the absorbance at 1590 cm^{-1} to that of the reference peak.

Curves of the peak ratios versus concentration of antioxidants added were plotted (see Figs 2.3 and 2.4). These curves were used in estimating the concentration of bound antioxidant.

2.1.6 The Effect of Uneven Distribution of Antioxidant

The mobility of a chemical compound has been assumed to be one of the prerequisites for such compounds to take part in chemical reactions. In view of the above statement, antioxidants which are physically blended into the polymers possess this mobility (within a limited range) and function well unless they are removed by volatilisation or leaching out. However, when antioxidant molecules become part of the polymer molecule (bound antioxidant) their ability to move is in a way restricted and this may lead to the assumption of a reduced antioxidant efficiency. But evidence to date shows the reverse to be true since antioxidant is not lost from the system.

When the masterbatch technique is used only a small proportion of the rubber chains contain the attached antioxidant molecule and the major proportion of the rubber chains will have no antioxidant bound on to them. Depending on the degree of binding in the masterbatch, the ratio of the antioxidant containing rubber chain to no-antioxidant containing chains will vary in a

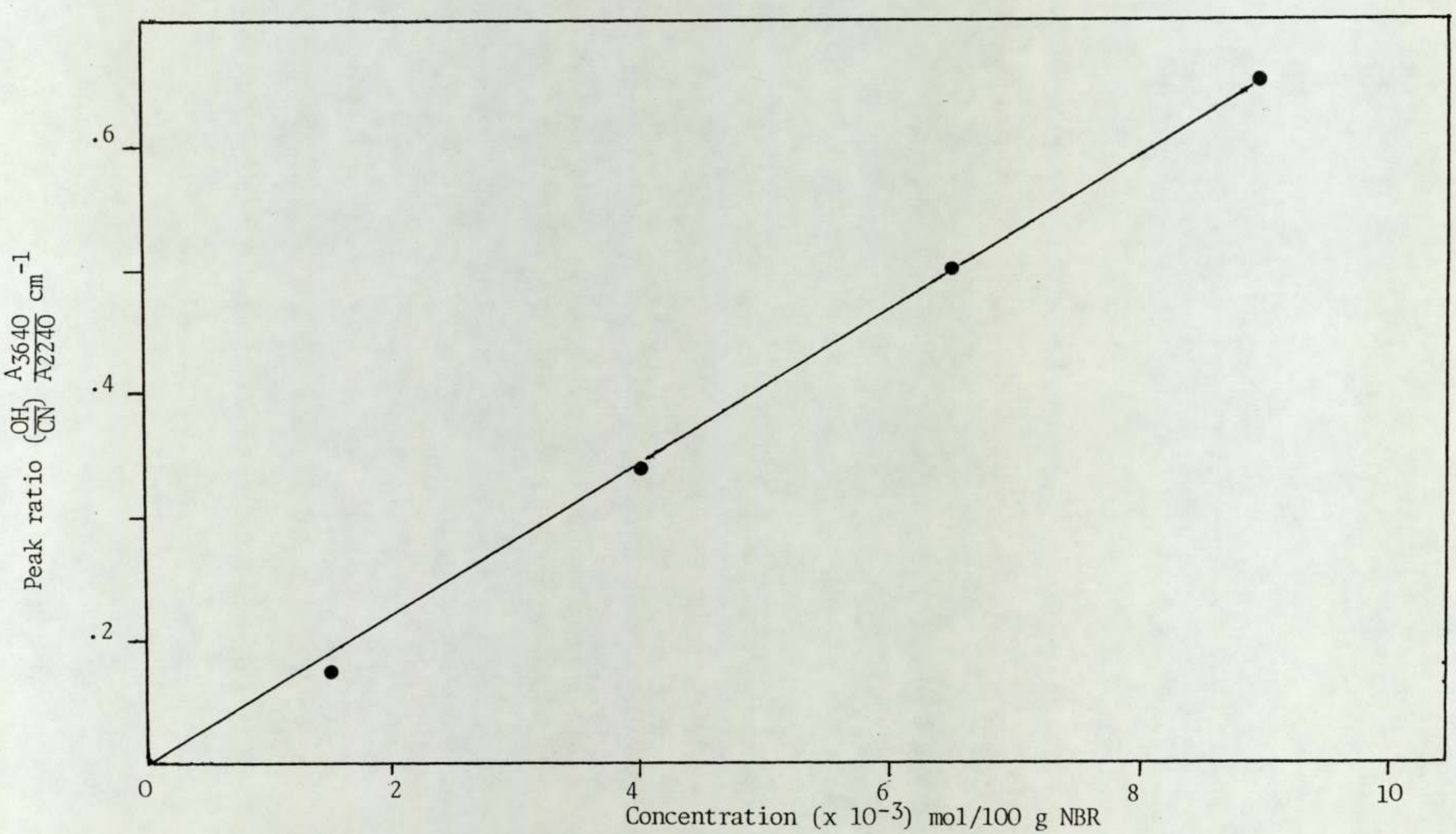


Fig 2.3 BHBM calibration curve

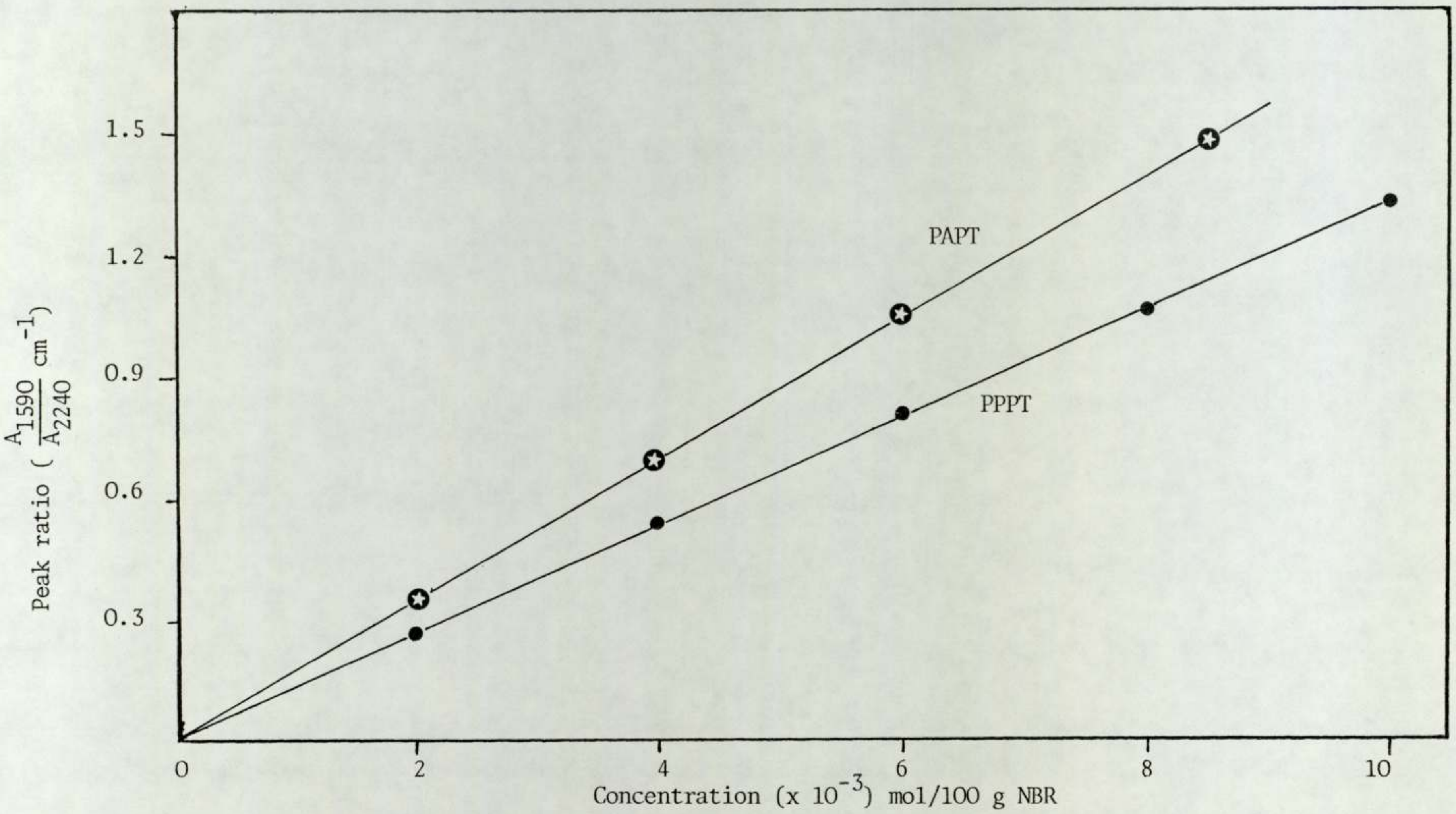


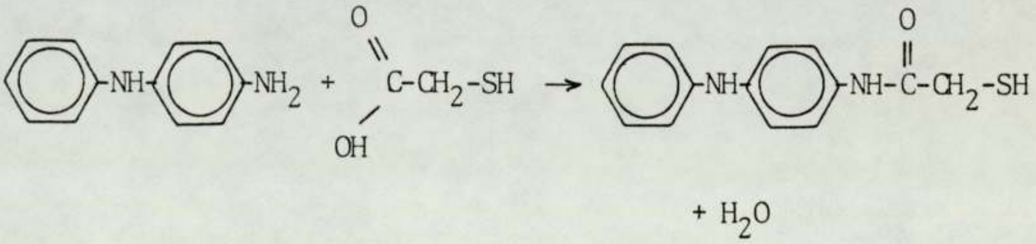
Fig 2.4 Thiolamide calibration curve

given vulcanisate.

If, for example, rubber samples are produced by (a) addition of a given amount of antioxidant into the whole rubber and (b) by diluting a masterbatch containing a certain amount of bound antioxidant to contain the equivalent molar concentration of antioxidant, the distribution of bound antioxidant groupings in the samples will be different, and this may lead to differences in ageing characteristics of the two samples. And in fact, Fernando(19) found that in ABS there is a slight decrease in antioxidant efficiency when samples are prepared by the masterbatch technique by comparison with samples prepared by physical addition and although he attributed this to the mobility of antioxidant molecules, the contribution made by by-products formed in side reactions must not be ignored.

2.2 Synthesis of Antioxidants

2.2.1 Preparation of 4-Anilinophenyl-thioglycolamide (PAPT)



The method employed in the preparation of this antioxidant was the one described by Weinstein(94); according to the above scheme. The compound was obtained by amidation of para-aminodiphenylamine with thioglycolic acid in refluxing xylene.

A mixture of 18.4 g (0.1 mole) of para-aminodiphenylamine, 9.2 g (0.1 mole) of thioglycollic acid and 150 cm^3 of technical grade xylene was heated to reflux (about 140°C in a 500 cm^3 flask under nitrogen gas for about 10 hours. The pot residue was then diluted with n-hexane, allowed to cool to room temperature and left overnight. A crystalline product was obtained and by recrystallising this product from toluene, a pure white crystalline product which melted at 135-136°C was obtained. The yield was 69%. The product readily oxidised during recrystallisation to a constant melting mixture of thiol and disulphide and in view of this, recrystallisation of the compound must be carried out in an atmosphere of nitrogen.

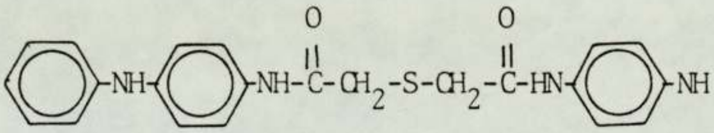
			Sulphur %	
	Yield	Mpt °C	Cal'd	Found
Experimental Values	69%	135-136	12.4	12.46
Literature Values (94)	69-77%	135.5-136.5	12.4	12.3

Ir data:	Aromatic ring	880 cm^{-1}
	Secondary NH-	3450 cm^{-1}
	Secondary amide carbonyl	1650 cm^{-1}
	S-H group	2561 cm^{-1}
	$-CH_2-$ alkyl	1440-1460 cm^{-1}
	Amide -NH-	3340 cm^{-1}

Nmr data:	Aromatic protons	2.96 τ	(singlet)
	S-H protons	3.0-40 τ	(singlet)
	Secondary NH- protons	3.5-60 τ	(singlet)
	Methylenic proton	6.3 τ	(doublet)

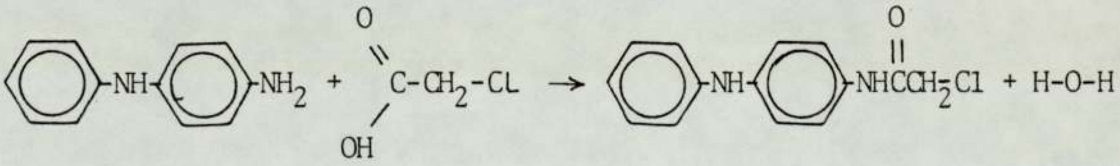
Mass spectrum: Peak appeared at 258.

2.2.2 Preparation of Bis-(4-anilinophenylglycolamide)-monosulphide



STEP ONE

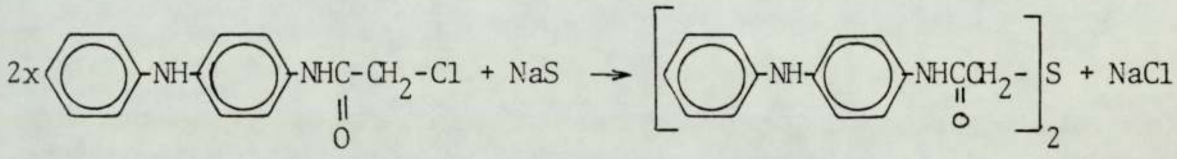
2.2.2.1 Preparation of 4-Anilinophenylmonochloro-acetamide



0.5 moles (9.2 g) of p-aminodiphenylamine was carefully weighed into a 500 ml two-necked round-bottomed flask containing 300 ml of dry xylene. The mixture was stirred until the amine dissolved. Then 0.54 moles (51.03 g) of monochloroacetic acid in 100 ml of dry xylene was added to the mixture. The flask was then connected to a Dean and Stark apparatus fitted with reflux condenser. The mixture was refluxed until an equivalent amount of water was collected. The reaction mixture was allowed to cool down to room temperature and washed with 5% solution of sodium bicarbonate to remove the unreacted acid, after dilution with n-hexane. The slightly yellowish crystalline product was recrystallised from toluene to give a white crystalline product which melted at 114-115°C. The yield was 59.5%.

STEP TWO

2.2.2.2 Reaction of 4-Anilinophenylmonochloroacetamide with Sodium Sulphide



A solution of 0.054 mole of dry sodium sulphide in 20 ml of distilled water was poured into a 500 ml two-necked round-bottomed flask, which was immersed in a cold water bath. Then a solution of 2.6 g (0.01 mole) of 4-anilinophenylmonochloroacetamide in 150 ml of ethanol was dropped into the sodium sulphide solution from a dropping funnel. The reaction mixture was stirred magnetically throughout the addition and the temperature was maintained at 25°C. When the addition of the chloride was completed, the reaction mixture was stirred further for another 24 hours. The crystals formed were separated by filtration, dried and recrystallised from toluene to give a white crystalline solid (Mpt 188°C). The yield was 55%. The product was identified by elemental analysis and quantitative chemical tests.

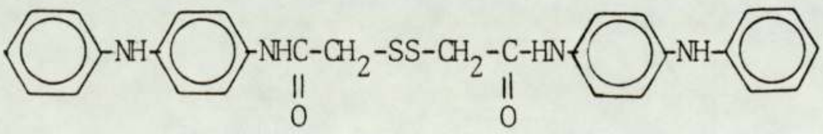
			Sulphur	
	Yield	Mpt	Cal'd	Found
Experimental values	55%	188°C	8.26	8.1
Literature values	-	-	-	-

Ir data:	Free N-H stretch	3520 cm^{-1}
	C=O stretch	1640 cm^{-1}
	C-N stretch	1548 cm^{-1}
	Ph-N stretch	1191 cm^{-1}
	Aromatic ring	1590 cm^{-1}
	CH- stretch	1398 cm^{-1}

Nmr:	Secondary N-H- protons	8.6 τ (quadruplet)
	Aromatic protons	2.60 τ (closed sextet)
	Methylene protons	7.1 τ (triplet)

Mass spectrometry gave a mass number of 482.

2.2.1.3 Preparation of Bis-(4-anilinophenyl-thioglycolamide)



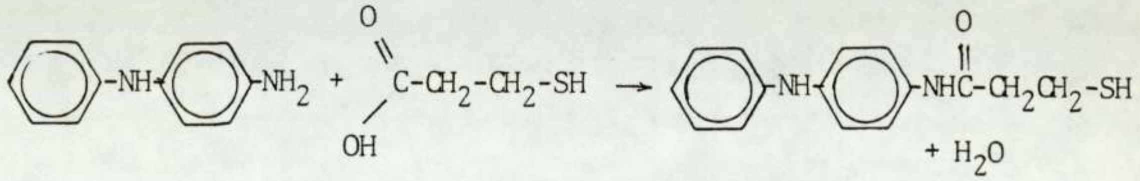
2 g of 4-anilinophenylthioglycolamide was dissolved in 150 ml of methanol in a 500 ml conical flask. Gently with a magnetic stirrer, a solution of 0.48 g (0.0038 mole) of iodine (in 20 ml methanol) was slowly added from a dropping funnel. When the addition of iodine was completed, the reaction mixture was diluted with distilled water and the solid was filtered. The grey solid product was recrystallised from methanol and vacuum dried. Mp 157^{o}C. The thiol titration showed no mercaptan was present. The yield was 82%.

Ir data:	Free N-H stretch	3525 cm^{-1}
	C-N stretch	1548 cm^{-1}
	Aromatic ring	1590 cm^{-1}
	C=O stretch	1640 cm^{-1}
	Ph-N stretch	1191 cm^{-1}
	CH- stretch	1398 cm^{-1}

Nmr data:	Secondary NH protons	8.71 τ (quadruplet)
	Aromatic protons	2.60 τ (closed sextet)
	Methylenic protons	7.2 τ (multiplet)

Mass spectrometry gave a peak at 514.

2.2.4 Preparation of 4-anilinophenylthiopropionamide (PPPT)



4-Anilinophenylthiopropionamide was prepared according to the above scheme.

This compound was obtained in a yield of about 53% by a similar amidation of p-aminodiphenylamine with β-mercaptopropionic acid, in refluxing xylene.

A mixture of 18.4 g (0.1 mole) of para-aminodiphenylamine, 10.6 g (0.1 mole) of β-mercaptopropionic acid and 150 cm^3 of technical grade xylene was heated to reflux in a 500 ml three-necked flask under nitrogen gas over a period of 10 hours. A crystalline product was obtained from the pot residue by diluting it with 160 cm^3 of n-hexane and allowing it to cool overnight.

The product was recrystallised from toluene. A purer product in the form of silvery white plates which have a melting point Mpt 98^{o}C was obtained.

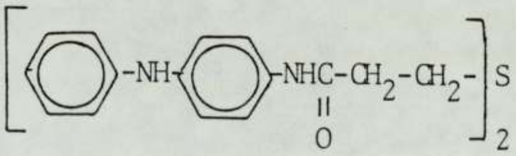
			Sulphur %	
	Yield	Mpt.	Cal'd	found
Experimental values	83.8%	98^{o}C	11.8	10.01
Literature values	95.6%	98^{o}C	11.8	11.8

Ir data:	S-H group	2515 cm^{-1}
	Secondary NH group	3360 cm^{-1}
	Amide -NH-	3240 cm^{-1}
	Amide carbonyl	1650 cm^{-1}
	Alkyl $-CH_2-$	1440 cm^{-1}
	Benzene ring	1590 cm^{-1}

Nmr data:	Secondary amide NH protons	8.5 τ (singlet)
	Aromatic protons	6.7-7.6 τ (multiplet)
	Methylenic protons	3.2 τ (doublet)
	S-H protons	1.8-2.2 τ (triplet)

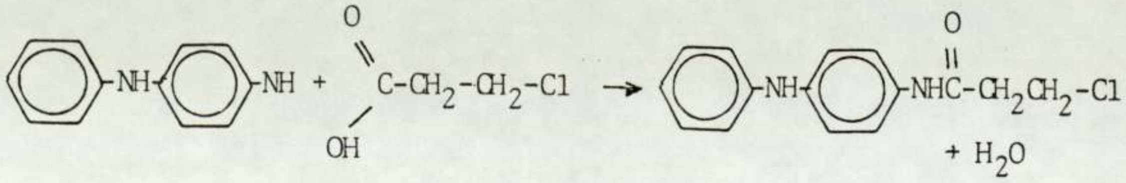
Mass spectrum yielded a peak at 272.

2.2.5 Preparation of Bis-(4-anilinophenylpropionamide)-monosulphide



STEP ONE

2.2.5.1 Preparation of 4-anilinophenyl monochloro propionamide



0.5 mol (9.2 g) of para-aminodiphenylamine was carefully weighed into a 500 ml two-necked round bottomed flask containing 300 ml of dry xylene. The mixture was stirred until the amine dissolved. Then 0.54 mole (58.05 g) of monochloropropionic acid in 120 ml of dry xylene was added to the mixture. The flask was then fitted with a Dean and Stark apparatus with reflux condenser. The mixture was refluxed until the equivalent amount of water was collected. The reaction product was allowed to cool down to room temperature, washed with 5% solution of sodium-bicarbonate to remove unreacted acid - after being diluted with n-hexane. The solid product was recrystallised from toluene to give a white crystalline product. Mpt = 167°C and the yield was 49%.

STEP TWO

2.2.5.2 Reaction of 4-Anilinophenylmonochloropropionamide with Sodium Sulphide

A solution of 0.05 mole of sodium sulphide in 20 ml of distilled water was poured into a 500 ml two-necked round bottomed flask, which was immersed in a cold water bath. Then a solution of 2.75 g (0.01 mol) of 4-anilinophenylmonochloropropionamide in 150 ml of ethanol was added drop-by-drop from a dropping funnel into the solution of sodium sulphide. The reaction mixture was stirred magnetically throughout the reaction and the temperature was maintained at 25°C. When the addition of the chloride was completed, the reaction mixture was stirred for a further 24 hours.

The crystals formed were separated by filtration. It was dried and recrystallised from aqueous acetic acid to give a purple-grey crystal. Mpt 212-214°C, the yield was 69.4%.

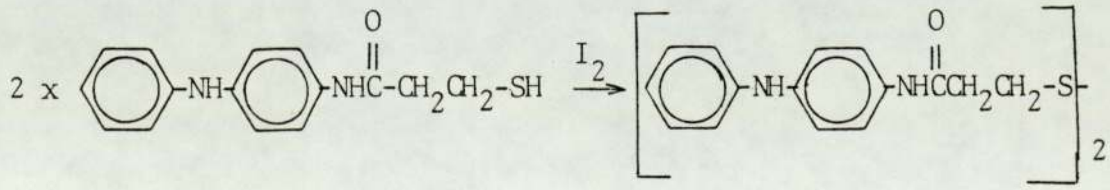
			Sulphur %	
	Yield	Mpt	Cal'd	Found
Experimental values	69.4%	212-214°C	6.27	5.78
Literature values(94)	-	212-214°C	6.27	6.22

Ir data:	Free N-H stretch	3500 cm^{-1}
	N-H deformation	1620 cm^{-1}
	C-N stretch	1280 cm^{-1}
	Aromatic ring	1590 cm^{-1}
	Carbonyl stretch	1650 cm^{-1}

Nmr data:	Secondary NH- proton	9 τ (quadruplet)
	Aromatic protons	3.2 τ (closed sextet)
	Methylenic protons	7-8 τ (triplet)

Mass spectrometry yielded a mass number of 510.

2.2.6 Preparation of Bis(4-anilinophenyl-thio-propionamide)



By heating a mixture of 27.2 g (0.10 mole) of 4-anilinophenylthiopropionamide and 50 g of iodine in 100 ml of methanol in a 250 ml conical flask for 5 hours in an oil bath, the product formed was cooled, the methanol was decanted to one third its original volume. The dark green solid was poured into 190 cm^3 hot toluene and the so-obtained solution was trilurated with 160 cm^3 n-hexane. A yellowish-green cyrstalline solid, Mpt 232-233^{o}C, was obtained by recrystallising the filtrate from hot toluene.

The mercaptan titration showed no thiol was present. The yield was 57%.

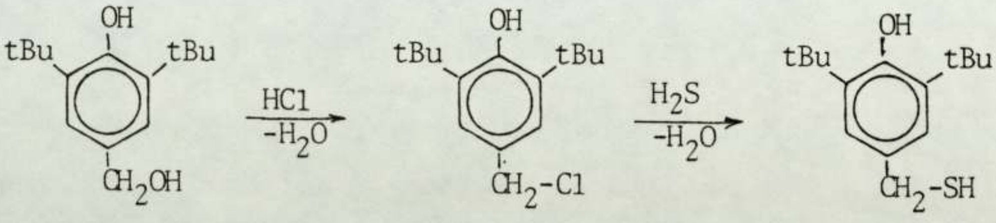
Ir data:	Free N-H stretch	3520 cm^{-1}
	N-H deformation	1620 cm^{-1}
	C-N stretch	1280 cm^{-1}
	Aromatic ring	1585 cm^{-1}
	C=O stretch	1620 cm^{-1}
	Ph-N stretch	1191 cm^{-1}

Nmr data:	Secondary N-H protons	8.7-9 τ (quadruplet)
	Aromatic protons	2.60 τ (closed sextet)
	Methylenic protons	7.08 τ (triplet)

Mass spectrometry yielded a mass number of 537, 542.

2.2.7 Synthesis of 3,5-di-tertiary-butyl-4-hydroxybenzyl mercaptan (BHBM)

3,5-Di-tertiary-butyl-4-hydroxybenzyl mercaptan was prepared according to the following scheme:



STEP ONE

2.2.7.1 Preparation of 3,5-di-tert-butyl-4-hydroxybenzyl alcohol

2,6-Di-tert-butyl phenol was used as obtained from Aldrich Chemical Company Limited without further purification. The method employed in the preparation was the one described by Butler$^{(95)}$.

53.3 mls of a 7.5% solution of paraformaldehyde in tertiary-butyl alcohol (0.140 mol formaldehyde), 50 ml of a 500 g/l solution of 2,6-di-tert-butyl phenol in anhydrous tertiary-butyl alcohol (0.128 mol 2,6-di-tert-butyl phenol) and 14 ml of freshly prepared 50 g/l solution of potassium tertiarybutyl butoxide in anhydrous tertiary butyl alcohol (0.006 mol potassium tertiary butyl butoxide) were mixed at 20°C and stirred under nitrogen (white spot grade) for about 50 minutes.

The reaction mixture was then poured into an excess of ice water, two layers were then formed. The upper oily organic layer promptly solidified. The recovered solids were freed of water, rewashed, stirred with hexane then filtered and washed with more n-hexane and then air dried. The resulting product was white crystalline solids which melted at 137°C. (95)

Ir data:	Free phenolic OH	3580 cm^{-1}
	Hydrogen bonded OH	3500 cm^{-1}

Nmr data:	Aromatic protons	2.9 τ (singlet)
	Phenolic protons	4.9 τ (singlet)
	Methylenic protons	5.5 τ (singlet)
	Tertiarybutyl protons	8.6 τ (singlet)

STEP TWO

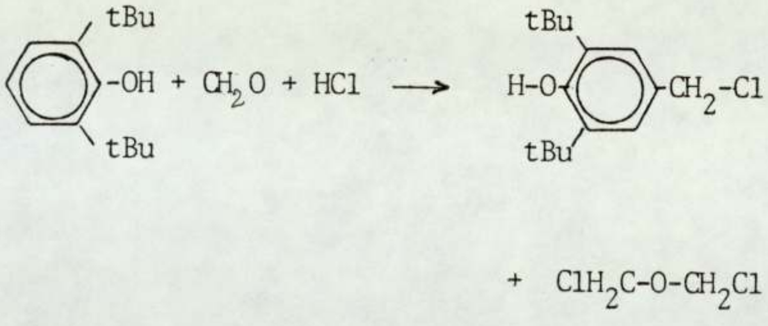
2.2.7.2 Preparation of 3,5-di-tert-butyl-4-hydroxybenzyl chloride

2 mols of 3,5-di-tert-butyl-4-hydroxybenzyl alcohol was stirred at room temperature in 500 g of toluene (slurry). 600 g of 30% HCl was added and the mixture stirred at 25°C for 3 hours. During this time, this went into solution. Reaction was completed by warming the mixture to 45°C when two layers separated. After separating the toluene layer, water was removed in vacuum and the toluene solution of the chloride was used directly for the preparation of BHBM in Step Three.

Alternatively, 206.0 g of 2,6-di-tert-butyl phenol is poured into a one litre three necked flask. To this, 120 g of paraformaldehyde is added. 500 mls of 36% hydrochloric acid was added and stirred vigorously with fast electric motor. Dry hydrogen chloride gas is then passed into the mixture for seven hours and keeping the escape gas to a minimum. The mixture was then allowed to stand for 20 hours, after which hydrogen chloride gas is again passed in for another 2 hours. An orange-coloured oily layer then separated and this was repeatedly washed with distilled water. Ether and benzene were then added to it and again it was washed with 2% sodium bicarbonate solution and distilled water to remove any unreacted hydrogen chloride gas.

The ether phase was then dried over anhydrous magnesium sulphate, filtered and the solvent evaporated. The residue, a thick oily liquid, was distilled under reduced pressure to collect the fraction that boiled at 128-132^{o}C (0.5 mm Hg).

NOTE: The latter (alternative) method of preparing 3,5-di-tert-butyl-4-hydroxybenzyl chloride described by Shell International Chemical(96) is not preferred to the former because the by-product (bis-chloromethyl) ether from the latter route is carcinogenic.



Carcinogenic

STEP THREE

2.2.7.3 Reaction of 3,5-Di-tert-butyl-4-hydroxybenzyl chloride with Hydrogen Sulphide Gas (96)

5.8 g of magnesium hydroxide powder was poured into a 500 ml round bottomed flask and 200 mls of N,N-dimethyl-formamide was added to it. The mixture was stirred and hydrogen sulphide gas was passed into it for 30 minutes. A deep blue colour developed.

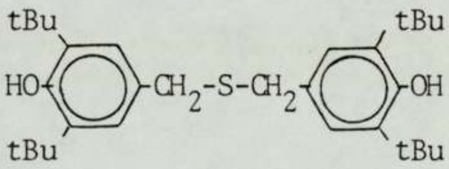
22.5 g of the toluen solution of the 3,5-di-tert-butyl-4-hydroxybenzyl chloride from Step Two was added to the mixture over a period of about 20 minutes. The addition was controlled so that a white colour remained throughout the period (not yellow).

After ninety minutes the mixture was added to ice cold water. The organic layer that formed was extracted with ether and dried over anhydrous magnesium sulphate. This was left overnight after which it was solvent evaporated. The residue was vacuum distilled and the fraction that boiled at 128°C (1.0-1.5 mm Hg) was collected. Yield was 56%, Mpt 28°C. (94,95,96)

Ir data:	Free phenolic OH	3640 cm^{-1}
	Tertiarybutyl group	1393 cm^{-1}
	Benzene ring	1580 cm^{-1}
	-SH group	2561 cm^{-1}

Nmr data:	Aromatic protons	2.96 τ (singlet)
	Hydroxyl protons	4.98 τ (singlet)
	Methylene protons	6.3 τ (doublet)
	Tertiarybutyl protons	8.54 τ (singlet)

2.2.8 Preparation of Bis-(3,5-di-tertiary-butyl-4-hydroxybenzyl) Monosulphide

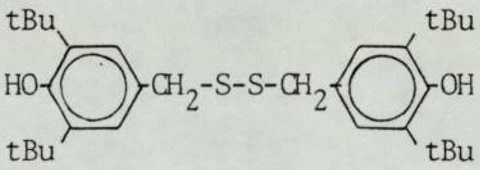


The starting material, 3,5-di-tertiarybutyl-4-hydroxybenzyl chloride was prepared as described in section 2.2.7.2. In a reaction vessel equipped with a heater, thermometer, water cooled condenser and a stirrer, a mixture of 19.2 g of sodium sulphide was dissolved in 15.0 ml of water, 120 ml of isopropyl alcohol, and 50 g of 3,5-di-tert-butyl-4-hydroxybenzyl chloride was refluxed for a period of two hours. The mixture was allowed to stand for 48 hours, solids were filtered, washed with water and dried. The product was recrystallised with iso-octane and methanol and yellow product was obtained. Mpt 142°C (literature value Mpt 142°C)(96,97).

Ir data:	Phenolic OH	3640 cm^{-1}
Nmr data:	Tert-butyl protons	8.6 τ (singlet)
	Phenolic protons	5.0 τ (singlet)
	Aromatic protons	2.9 τ (singlet)
	Methylenic protons	6.4 τ (singlet)

Mass spectrometry gave peaks at 469 and 510.

2.2.9 Synthesis of Bis-(3,5-di-tert-butyl-4-hydroxybenzyl) Disulphide



The preparation of benzyl mercaptan was discussed earlier.

A mixture of 25.3 g of 3,5-di-tert-butyl-4;hydroxybenzyl mercaptan, 100 ml of benzene and 25 ml of water was shaken vigorously in a round bottomed flask and a solution of 25.4 g of iodine, 100 mls of benzene and 25 mls of ethanol was slowly added from a dropping funnel. When the colour of the solution turned slightly brown, addition of iodine was stopped, and the organic layer was separated, dried over magnesium sulphate and was then concentrated. The solid obtained was recrystallised with benzene and petroleum ether and light crystals of Mpt 168^{O}C were obtained (literature value Mpt 168^{O}C(96,97)).

Ir data:	Phenolic OH	3620 cm^{-1}
Nmr data:	Tert-butyl protons	8.6 τ (singelt)
	Phenolic protons	5.0 τ (singlet)
	Aromatic protons	2.93 τ (singlet)
	Methylenic protons	6.4 τ (singlet)

Mass spectrum

Peak appeared at 502, 251, 219

Mass spectrometry yielded a mass number of 502.

2.2.10 Preparation of Dispersions

The dispersions were prepared in Szegvari attritor under a nitrogen atmosphere. The solid antioxidant was ground and sieved through 2 00 mesh size sieve. The required amount of powdered antioxidant and the equivalent amount of the dispersant were carefully weighed and poured into the container. Distilled water was added just to cover the surface of the glass balls contained in the attritor cylinder. The balls were attrited at constant speed for 10 hours. The temperature of the container was kept low by passing streams of cold water through the outlet. The dispersion was always used fresh to avoid oxidation during storage.

2.2.11 Preparation of Emulsions

The emulsions were prepared in two ways:

(i) by the addition of liquid antioxidants into water containing an emulsifying agent, and

(ii) by preparing soap in water.

PROCEDURE

(i) The required amount of the liquid antioxidant was added to 30 ml of distilled water containing the corresponding amount of the emulsifying agent (Vulcastab LS) in a 500 ml conical flask. This was vigorously shaken in a flask shaker for 24 hours under nitrogen gas.

(ii) The liquid antioxidant was added to the solution prepared by dissolving a known weight of lauric acid and a known weight of pot-assium hydroxide in distilled water. The container was shaken vigorously for 24 hours under a nitrogen atmosphere. The emulsions were always used fresh.

2.3 Formation of Masterbatch

The thiol bound antioxidant systems are potentially useful for the preparation of concentrated latex masterbatches. In as much as there is an appreciable amount of the original unsaturations present in such concentrations, co-vulcanision of the modified and the untreated rubber should occur readily by the addition of a relatively low concentration of masterbatch to unmodified latices.

2.3.1 Reaction of BHBM with Nitrile Rubber Latex

All reactions were carried out with 35% nitrile rubber latex elaprim D3360/225 which was supplied by Montedison.

Firstly, the latex was stripped of residual monomer by suction for 5 hours at 30-40°C. The optimum reaction parameters such as reaction time and reaction temperature were found to be in good agreement with that given by Kularatne(67) but the optimum initiator concentration was slightly different. The ratio of the thiol to hydroperoxide concentration was found to be 1 mole of thiol to 0.5 mole of the tertiarybutyl hydroperoxide. It was found necessary to use an activator in this experiment, tetraethylene pentamine (TEPA) and the amount needed was based on the volume of peroxide used. The ratio of the peroxide to activator (10% solution), was 1 : 1 by volume.

PROCEDURE

The grafting reaction was carried out in a five-necked reaction flask under nitrogen gas. A series of experiments were was carried out using 288 mls of NBR latex each time, increasing the concentration of BHBM and the concentration of tertiarybutyl hydroperoxide and the amount of TEPA (10% TEPA in water).

The emulsion of BHBM was swollen into the NBR latex at reaction temperature (60^{o}C) for about 2 hours and then the TBH/TEPA were added separately in aliquots over a period of 4 hours after which the reaction was allowed to proceed for a further 3 hours. At the end of the reaction, films were cast on glass plates, dried and were then extracted with n-hexane for about 24 hours, which was found to be sufficient to remove the unreacted BHBM and the other by-products too. The amount of BHBM bound was estimated by ir technique as described in section 2.1.5.

With this method, masterbatches of the following concentrations 4×10^{-3}, 4×10^{-2}, 8×10^{-2}, 1.2×10^{-1}, 1.6×10^{-1} and 2×10^{-1} mols of BHBM per 100 g of NBR (DRS) were prepared and evaluated.

The following data were established:

Swelling time	2-3 hours
Reaction temperature	$60^{\circ}C$
Reaction time	7 hours
Initiator concentration	(BHBM/TBH) = $^{1}/_{0.5}$ (mol : mol) (TBH/TEPA) (solution) = 1 : 1 v/v

2.3.2 Reaction of 4-Anilinophenylthioglycolamide (PAPT) with NBR Latex

The NBR latex used in this experiment was the same as in the previous experiment and the residual monomer was similarly removed by suction for 5 hours at 30-$40^{\circ}C$.

The reaction parameters such as reaction time, swelling time, reaction temperature and initiator concentration were investigated. During the experiment only the parameter under investigation was being varied while others were kept constant. For the determination of reaction time, for example, 288 mls of 35% NBR latex was ball-milled with the freshly prepared dispersion of PAPT for about 9 hours (preferably left overnight) under nitrogen gas in the Szagvari attritor. The glass balls are separated from the latex-PAPT dispersion mixture, pouring the latex-PAPT dispersion mixture into the reaction vessel. Stirring is continued under nitrogen gas throughout the reaction. When the reaction temperature is attained (2 hours), the initiator, TBH, and activator, TEPA, were added portionwise (4 increments) over a period of 3 hours. The temperature was maintained at $70^{\circ}C$ and the reaction was allowed to proceed for 6 hours after the last addition had been made. Samples were taken out at known intervals. Films were cast on glass plates, dried and were then extracted with methanol for 24 hours. The amount of PAPT bound was estimated by the ir technique (see section 2.1.5).

If TEPA was added, it made no difference, and whether or not TEPA was added, the latex remained coloured after the reaction.

The following data were established:

Swelling time	8-10 hours
Reaction time	9 hours
Reaction temperature	$70^{\circ}C$
Initiator concentration	PAPT TBH = 1 : 0.3 molar ratio

With the above data, masterbatches of the same concentration of antioxidant as in the previous section were prepared and examined.

2.3.3 The Reaction of 4-Anilinophenyl thiopropionamide (PPPT) with NBR Latex

The procedure of this experiment is exactly the same as described for the reaction of PAPT with NBR latex.

It was found that PPPT is very much less reactive towards NBR latex and the degree of binding was very low compared with the level achieved with PAPT (compare Tables 2.14 - 2.16).

2.3.4 Determination of the Optimum Reaction Conditions for Grafting in the Latex Phase

The experiments described below were carried out using 288mls of 34.5% (100 g DRC) of nitrile rubber latex which was stripped of free monomer by suction at 30-40°C for 5 hours.

The initiator system used was the redox pair, tertiarybutyl hydroperoxide (TBH) and tetraethylene pentamine (TEPA). The antioxidants were BHBM, PAPT and PPPT. The parameters under investigation were swelling time, reaction temperature, reaction time and the effect of initiator concentration.

The experiments were carried out in a five necked round bottomed reaction flask, immersed in a thermostatically controlled water bath. The antioxidant dispersions/emulsion was always added to the latex first and the initiator system was added separately in portions over a period of three hours. The pH of the reaction was kept about neutral to avoid hydrolysis. At the end of each reaction, the latex was coagulated and films were cast on glass plates by the method described in Chapter Four, section 4.3 and the amount of antioxidant bound estimated as described in section 2.1.5.

2.3.5 Effect of Swelling Time

288 mls (100 g DRC) of stripped nitrile rubber latex was mixed with an emulsion of BHBM but ball milled with a dispersion of the thiol amides as described in section 2.2.10. This was done for various known lengths of time and the reaction was then initiated by adding TBH and TEPA. After the reaction, the latex was coagulated, washed, dried and films were cast on glass plates and the amount of antioxidant bound was estimated. This is illustrated in Tables 2.1 - 2.3.

2.3.6 Determination of Optimum Reaction Temperature

To find out the most favourable reaction temperature, a set of experiments were carried out as described previously. The swelling times were for BHBM, 2 hrs; PAPT, 10 hrs and PPPT 8 hrs. The selected temperatures were 25, 30, 40, 50, 60 and 70^{o}C. The water bath was maintained at the required temperature ($\pm$ 2^{o}C). The reaction was allowed to proceed for 12 hours. At the end of the reaction the latex was coagulated, washed with distilled water, dried and films were cast on glass plates. The amount of bound antioxidant was estimated and the results are shown in Tables 2.4 - 2.6.

2.3.7 Determination of Optimum Reaction Time

A set of experiments was carried out with the antioxidants (BHBM, PAPT and PPPT) at 60^{o}C for a known length of time. The preswelling time for the antioxidants was 2, 10 and 8 hours respectively. Samples of the reaction mixture were withdrawn every hour, the samples were coagulated, washed, dried and films were cast so as to evaluate the amount of antioxidant bound at various stages of the reaction period. Results are given in Tables 2.11 - 2.13.

2.3.8 The Effect of Initiator Concentration

In another set of reactions, the concentrations of the antioxidants were kept constant and the concentration of the initiator was varied. The reaction temperature was kept constant at 60^{o}C. The swelling times were as described in the previous experiments. As in the previous experiments, the latex was coagulated at the end of the reaction. The coagulum was washed, dried and films were cast and the level of binding was estimated using the ir photo spectrometer. The results are given in Tables 2.7 - 2.9.

2.3.9 The Effect of Omitting TEPA

In order to determine the effect of TEPA on the grafting reaction, the above reaction was repeated but without TEPA. It was found that the level of binding fell sharply in the case of BHBM but the omission of TEPA from the system did not affect the reaction of the thiol amide. See Table 2.10.

Table 2.1 Effect of swelling time for BHBM

Swelling time mins	Conc of BHBM added mol/100 g	Conc of BHBM bound mol/100 g	Conc of TBH mol/100 g	BHBM Bound %
-	0.01	-	0.004	
30	0.01	4.49×10^{-3}	0.004	45
60	0.01	5.62×10^{-3}	0.004	56
90	0.01	5.95×10^{-3}	0.004	60
120	0.01	5.95×10^{-3}	0.004	60
180	0.01	6.15×10^{-3}	0.004	62

Table 2.2 Effect of swelling on on reaction of PAPT

Swelling time hrs	Conc of PAPT added mol/100 g	Conc of TBH mol/100 g rubber	Conc of PAPT bound mol/100 g	PAPT Bound %
0	0.01	0.003	0	0
½	0.01	0.003	0	0
1	0.01	0.003	1.08×10^{-3}	13
5	0.01	0.003	2.9×10^{-3}	19
6	0.01	0.003	2.33×10^{-3}	25
12	0.01	0.003	4.53×10^{-3}	45
19	0.01	0.003	4.64×10^{-3}	46

Table 2.3 Effect of swelling time on reaction of PPPT

Swelling time hrs	Conc of PPPT added mol/100g Rub	Conc of TBH mol/100g rubber	Conc of PPPT bound mol/100g Rub	PPPT Bound %
0	0.01	0.003	0	0
½	0.01	0.003	0	0
1	0.01	0.003	2.94×10^{-4}	3
5	0.01	0.003	8.08×10^{-4}	9
6	0.01	0.003	2.2×10^{-3}	25
12	0.01	0.003	2.2×10^{-3}	25
19	0.01	0.003	2.46×10^{-3}	26

Table 2.4 Determination of the optimum reaction temperature for BHBM reaction (with NBR latex). Reaction time, 8 hrs

Temperature oC	Conc of BHBM added mol/100g Rub	Conc of TBH mol/100g DRC	Conc of BHBM bound mol/100g Rub	BHBM Bound %
25	0.01	0.0045	0	0
30	0.01	0.0045	1.86×10^{-3}	19
40	0.01	0.0045	2.0×10^{-3}	26
50	0.01	0.0045	3.85×10^{-3}	39
60	0.01	0.0045	5.79×10^{-3}	58.5
70	0.01	0.0045	6.75×10^{-3}	70

<u>Table 2.5</u> Determination of the optimum reaction temperature for the reaction of PAPT with NBR latex

Temperature ^{o}C	Conc of PAPT added mol/100g rub	Conc of TBH mol/100g rubber	Conc of TEPA vol/100g rubber	Conc of PAPT bound g/100g	PAPT Bound %
	0.01	0.0028	0.5 mls		-
25	0.01	0.0028	0.5 mls	0	0
30	0.01	0.0028	0.5 mls	0	0
40	0.01	0.0028	0.5 mls	2.7×10^{-4}	3
50	0.01	0.0028	0.5 mls	1.5×10^{-3}	15
60	0.01	0.0028	0.5 mls	2.4×10^{-3}	24
70	0.01	0.0028	0.5 mls	2.83×10^{-3}	28

<u>Table 2.6</u> Determination of the optimum reaction temperature for the reaction of PPPT with NBR latex

Temperature ^{o}C	Conc of PPPT added mol/100g rub	Conc of TBH mol/100g rubber	Conc of TEPA vol/100g rubber	Conc of PPPT bound mol/100g rub	PPPT Bound %
	0.01	0.0045	0.5 mls	-	-
25	0.01	0.0045	0.5 mls	-	-
30	0.01	0.0045	0.5 mls	-	-
40	0.01	0.0045	0.5 mls	4.89×10^{-4}	5
50	0.01	0.0045	0.5 mls	1.08×10^{-3}	11
60	0.01	0.0045	0.5 mls	2.16×10^{-3}	22
70	0.01	0.0045	0.5 mls	2.65×10^{-3}	28

Table 2.7 Determination of the optimum initiator concentration in the reaction of BHBM with NBR latex

Conc of TBH mol/100 g rubber	Conc of TEPA mol/100 g rubber	Conc of BHBM bound mol/100 g	% BHBM bound
0.0025	0.67	1.39×10^{-3}	14
0.005	1.3	2.2×10^{-3}	22
0.0075	2.0	3.57×10^{-3}	36
0.01	2.7	5.55×10^{-3}	57.8
0.0125	3.3	5.96×10^{-3}	60
0.025	6.7	4.16×10^{-3}	42

Reaction temperature: 60°C Reaction time: 7 hours

Table 2.8 Determination of optimum initiator concentration for the reaction of PAPT with NBR latex

Conc of TBH mol/100 g rubber	Conc of TEPA mol/100 g	Conc of PAPT bound mol/100 g rub	% PAPT bound
0.0025	0.225	-	-
0.005	0.45	-	-
0.0075	0.675	7.75×10^{-4}	8
0.01	0.9	2.0×10^{-3}	20
0.0125	0.9	2.9×10^{-3}	29
0.015	0.9	2.9×10^{-3}	29
0.025	0.9	2.9×10^{-3}	29

Reaction temperature: 70°C Reaction time: 8 hrs Added PAPT conc 0.01 mol/100g NBR (DRC)

Table 2.9 Determination of optimum initiator concentration for the reaction of PPPT with NBR latex

Reaction temp, 70^{o}C; Reaction time, 8 hrs; Concentration of added PPPT, 0.01 mol/100 g NBR (DRC)

Conc of TBH mol/100 g rubber	Conc of TEPA mls/100 g rubber	Conc of PPPT bound mol/100 g	% PPPT bound
0.0025	0.225	1.84×10^{-4}	2
0.005	0.45	7.72×10^{-4}	8
0.0075	0.67	1.29×10^{-3}	13
0.01	0.9	1.99×10^{-3}	20
0.0125	0.9	1.69×10^{-3}	17

Table 2.10 The effect of omission of TEPA

BHBM concentration, 0.01 mol/100 g DRC (0.01 mol); Reaction temperature, 60^{o}C; Reaction time, 7 hrs; preswelling time, 2 hrs

Conc of TBH mol/100 g NBR	Conc of BHBM bound mol/100 g NBR	% BHBM bound
0.0025	3.96×10^{-4}	4
0.005	9.9×10^{-4}	10
0.0075	1.78×10^{-3}	18
0.01	2.5×10^{-3}	26
0.125	4.16×10^{-3}	42
0.025	4.56×10^{-3}	46

Table 2.11 Determination of optimum reaction time for the reaction of BHBM with NBR latex

Concentration of BHBM, 0.01 mol/100 g NBR (DRC); Reaction temperature, 60^{o}C; concentration of TBH, 0.005 mol; preswelling time, 2 hrs

Time hrs	BHBM bound mol/100 g NBR	% BHBM bound
0	0	0
3	2.66×10^{-3}	27
5	4.44×10^{-3}	45
7	5.75×10^{-3}	58
8	5.75×10^{-3}	58
9	5.79×10^{-3}	58.3
19	5.87×10^{-3}	59

Table 2.12 Determination of optimum reaction time for the reaction of PAPT with NBR latex

Concentration of PAPT, 0.01 mol/100 g NBR; Reaction temperature, 70^{o}C; Concentration of TBH, 0.0028 mole; preswelling time, lo hrs

Reaction time hrs	Conc of PAPT Bound mol/100 g NBR	% PAPT bound
0	0.0	0
3	7.75×10^{-4}	9
5	1.71×10^{-3}	17
6	1.94×10^{-3}	21
7	2.59×10^{-3}	26
8	2.83×10^{-3}	28
9	2.87×10^{-3}	28.5
21	2.79×10^{-3}	27

Table 2.13 Determination of optimum reaction time for the reaction of PPPT with NBR latex

Conc of PPPT, 0.01 mol/100 g NBR; Conc of TBH, 0.0028 mol/100 g NBR; Reaction temperature, 70°C; Preswelling time, 10 hrs

Reaction time hrs	Conc of PPPT Bound mol/100 g NBR	% PPPT Bound
0	-	-
3	-	-
5	7.72×10^{-4}	8
6	1.58×10^{-3}	16
7	1.69×10^{-3}	17
8	1.98×10^{-3}	20
9	2.28×10^{-3}	23

Table 2.14 Effect of increasing antioxidant concentration

BHBM conc g/100 g DRC	Initiator conc mol/100 g DRC	TEPA conc volume	Reaction time hrs	Reaction temp °C	% BHBM bound
1	0.004	3 mls	6	60	37
10	0.04	3 mls	6	60	58
20	0.08	5 mls	6	60	60
30	0.12	8 mls	6	60	63
40	0.16	1.2 mls	6	60	62
50	0.20	1.6 mls	6	60	62

Table 2.15

PAPT conc g/100 g DRC	Initiator conc mol/100 g DRC	TEPA conc ml	Reaction time hrs	Reaction temp ^{o}C	% PAPT bound
1	0.003	-	9	70	Nil
5	0.007	-	9	70	13
10	0.03	-	9	70	38-40
20	0.058	-	9	70	49-52
30	0.089	-	9	70	*32

Table 2.16

PPPT conc g/100 g DRC	Iniciator conc mol/100 g DRC	TEPA conc ml	Reaction time hrs	Reaction temp ^{o}C	% PPPT bound
1	0.003	-	9	70	Nil
5	0.007	-	9	70	8
10	0.03	-	9	70	26
20	0.06	-	9	70	32
30	0.092	-	9	70	*

* precoagulation of latex

2.3.10 Determination of the Most Efficient Initiator

A set of experiments was carried out with 288 mls (100 g DRC) of NBR latex. The latex was stripped by suction to remove residual monomer. A dispersion/emulsion containing 10 g of antioxidant in water was swollen into the latex. The radical generator was added in 4 portions over a period of 2 hours and the reaction allowed to proceed under a nitrogen blanket for a further 5 hours. The reaction temperature was kept constant at 65°C. After the reaction, the latex was coagulated, washed, dried and films were cast on glass plates. The films were then extracted and the amount of antioxidant bound was estimated by the ir technique. The results are shown in Table 2.17.

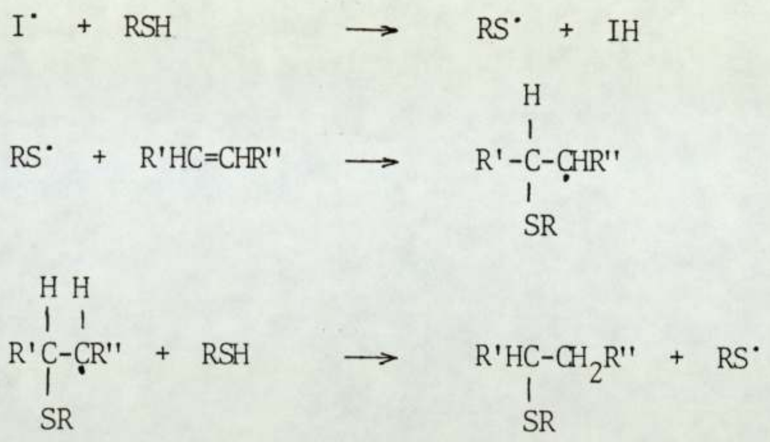
2.4 Results and Discussion

The well documented mechanism of addition of thiols to polymers containing unsaturation (free radical mechanism) has been employed in the grafting reaction to produce a polymer network to which the antioxidant has become bound via a sulphur link. The formation of a thiyl radical by the action of initiator (TBH/TEPA) on the thiol is the initiation step. This thiyl radical then adds to the double bond of the polymer chain forming adduct radical which in turn propagates the chain by abstracting a hydrogen atom from a molecule of the mercaptan yielding a saturated product and a new thiyl radical.

Table 2.17 Determination of best initiator system

Type of initiator	Initiator conc moles/100g^{-1} NBR	% Antioxidant bound
(a) Tertiarybutyl hydroperoxide/tetraethylene pentamine (10% solution in water) (TBH/TEPA)	0.03	56
(b) Azo-bis-isobutyronitrile (AZBN)	0.03	12.8
(c) 4,4'-Azo-bis(4-cyano valeric acid (AZBV/NaCO$_3$)	0.03	17
(d) Hydrogen peroxide/sodium tungstate*	*	9
(e) Potassium persulphate/ferrous sulphate	0.03	-

* 2 mls of (30%) H_2O_2/0.2 g sodium tungstate per 100 g NBR (DRC)



$$I^{\cdot} + RSH \longrightarrow RS^{\cdot} + IH$$

$$RS^{\cdot} + R'HC{=}CHR'' \longrightarrow R'\text{-}\underset{SR}{\overset{H}{C}}\text{-}\dot{C}HR''$$

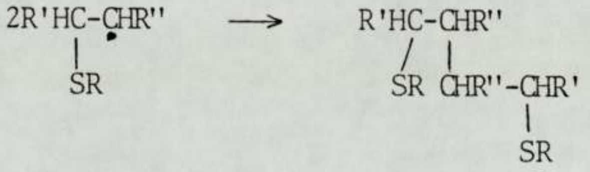
$$R'\underset{SR}{\overset{H}{C}}\text{-}\overset{H}{\dot{C}}R'' + RSH \longrightarrow R'\underset{SR}{HC}\text{-}CH_2R'' + RS^{\cdot}$$

where I˙ is the initiator and RSH the thiol.

However, as the concentration of the radical produced is increased, termination of the reaction can occur in any one or more of the following ways leading to the formation of by-products as reflected in the degree of adduct formation.

(a) $2RS^{\cdot} \longrightarrow RSSR$

(b)

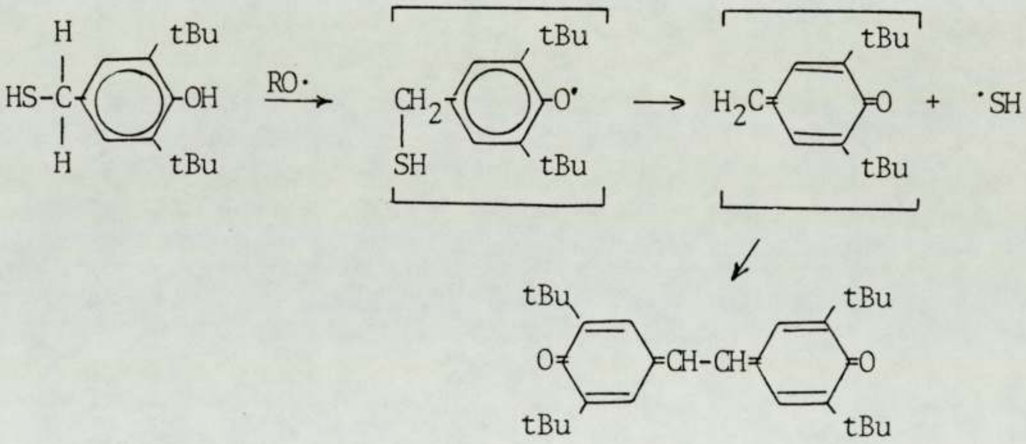


$$2R'\underset{SR}{HC}\text{-}\dot{C}HR'' \longrightarrow R'\underset{SR}{HC}\text{-}\underset{CHR''\text{-}\underset{SR}{CHR'}}{CHR''}$$

The formation of disulphide and other unbound by-products is undesirable however good antioxidants they may be because they will be lost under extraction conditions.

The results of the experiments to establish the reaction parameter for the reaction of BHBM, PAPT and PPPT are summarised in Tables 2.1 - 2.17 and Figs 2.1 and 2.2. From the calibration curves, it is obvious that less than 100% adduct formation of the antioxidants occurred during the grafting reactions.

After the reaction of BHBM with NBR latex only about 58-65% of the total amount of BHBM charged at the start of the reaction became bound to the rubber. This fact coupled with the formation of yellow-ish brown coloured extractable by-products clearly show that side reactions also occurred during the process of grafting. Cooray(97) observed a decay of initial peroxide concentration when PVC is processed with BHBM, this probably indicates the formation of radicals and these radical species may initiate the decomposition of BHBM in the following way:



The thiyl radical produced from BHBM by the redox reactions with TBH may also dimerise to react with quinone methide intermediates and recombination of the two thiyl radicals can enhance the formation of mono- and disulphide respectively(67). The formation of the mono- and disulphide of BHBM whose breakdown products (Lewis acids) could destroy peroxides(91) may be responsible for the limited binding level achieved by destroying the TBH and therfore inhibiting the grafting reaction. Although it has been found(67) that the sulphides are powerful antioxidants in their own right and there may be temptation to accept their formation to contribute to protecting the rubber during its service life (this will be discussed in detail under Chapter Five.) It must, however, be pointed out that they will quickly be lost under extraction conditions or leached out from the vulcanisate since they are not bound and will therefore not contribute to the protection of the rubber during service life.

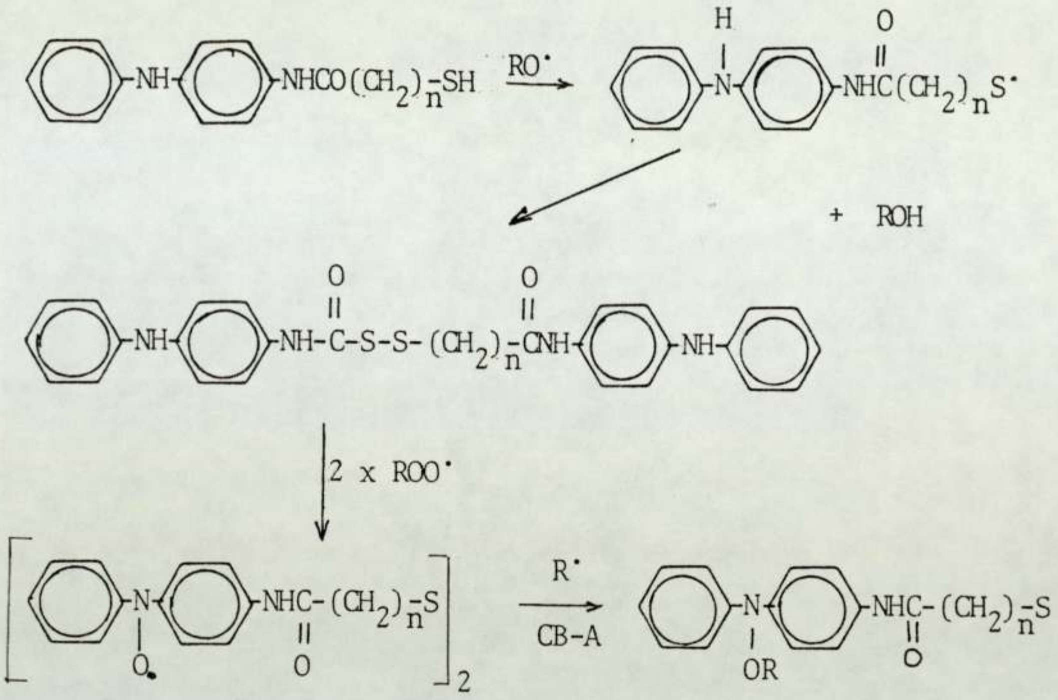
Other important information emerging from the reaction of BHBM with NBR latex are the need to allow the antioxidant molecules to penetrate into the molecules of the rubber and by this reaction will be within the rubber rather than at the surface. Much as initiator was found to be necessary for the reaction, its concentration was found to be limited. At above a molar ratio of [BHBM] : [TBH] of 1 : 0.5, it appeared too many radicals were being generated and that mainly by-products resulted as evidenced by the level of binding. Below this ratio, it looked as though not enough radicals were produced to initiate the reaction. The effect of increasing the reaction temperature was that binding increased with increase in temperature and reached the highest (70%) at 70°C. Although the experiment was not done beyond this temperature, because of coagulation problems, but it is hard to believe that increased binding will be achieved at a higher temperature since at 70°C degradation of the polymer was observed (presence of carbonyl group, measured by ir spectroscopy, peak at 1720 cm^{-1}) and since degraded polymer is undesirable, reaction at higher temperatures would not be of benefit. Also interesting was the result obtained when TEPA was excluded from the system. The binding achieved, even though low, is an indication of a possible redox reaction betwen the thiol (BHBM) and the hydroperoxide (TBH) but the low level of binding showed that there were not enough radicals being produced. Had there been higher binding, the exclusion of TEPA would have been preferred because a product with improved colour would result. The reaction time was found to be between 6-7 hours. A prolonged reaction (beyond 8 hours) will probably bring about the thermal decomposition of polymer and not further binding.

The reaction of the thiol amides with NBR latex is very similar to that of the BHBM but the formation of by-products becomes a dominant problem and PAPT was never bound beyond 52% while PPPT bound to only 29%.

In attempting to prepare masterbatchs of the concentrations 1, 5, 10, 20, 30 and 40 g of antioxidant (PAPT and PPPT) it became clear that at concentrations below 5 g/100 g no binding was achieved, and at concentrations above 20 g, coagulation of the rubber made the reaction impossible. This is not surprising because Meyer and co-workers(98) reported that some precoagulation was always found in latices when the acrylamide of p-aminodiphenylamine was reacted as a monomer.

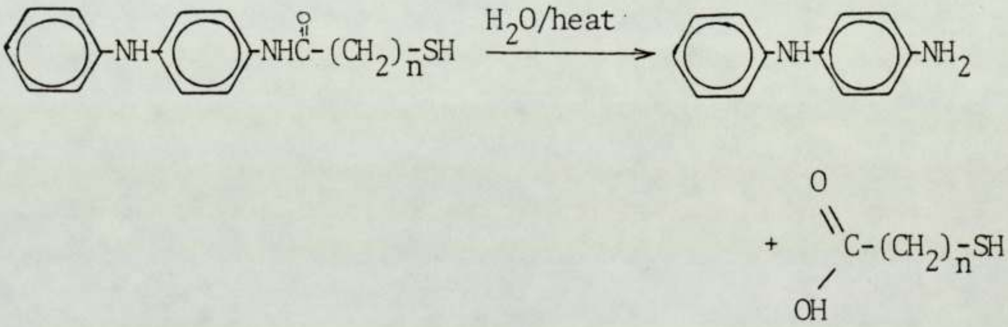
During swelling, the use of a mechanical stirrer resulted in the separation of the latex from the dispersion when allowed to stand for a few minutes. Ball milling was used to ensure effective penetration of the molecules of the antioxidants into the rubber. The reaction temperature was 70°C but for the same reason as mentioned for the reaction of BHBM with NBR latex, the temperature was not increased beyond 70°C. The reaction time was found to be 8 hours unlike the reaction of BHBM, the thiol amide required less peroxide, the optimum ratio of thiol concentration to concentration of TBH was 1 : 0.3 and TEPA was not required, indicating a redox reaction between the thiolamide and the peroxide.

Apart from the formation of by-products such as mono and disulphides, possible inhibition of the grafting reaction of the thiolamide by nitroxyl radicals cannot be overlooked. If the hydrogen atom of the NH- group is abstracted, rather than the H- atom from the S-H group, there is no doubt that initiation process will be interupted.



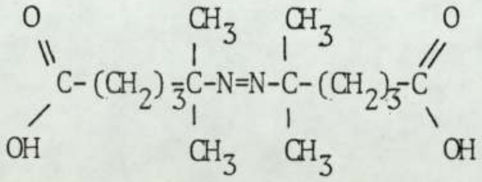
If the problem is viewed from the point of view of the melting points of the antioxidants (eg PAPT, Mpt = 135°C) and the reaction temperature 70°C, it will be correct to say that effective penetration by the molecules of the antioxidant into rubber may not be achieved during swelling and during subsequent reaction because there was only solid to solid contact between the two reactants. Whereas above their melting temperatures, the liquid antioxidant will swell into the rubber more quickly. Because of the high melting point, it might be expected that at the reaction temperature (70°C) only agg-lomerates of the antioxidant crystals are present in the reaction medium and as a result, only interfacial reaction leading to predominant formation of by-products occurred as evidenced by the intense yellowish-green coloured reaction product (probably disulphide and its oxidised derivatives). An attempt to swell more of the antioxidant into the rubber latex by first dissolving the antioxidant in an appropriate solvent and then swelling the solution of the antioxidant into the latex, failed because all the solvents for the thiolamides caused coagulation of the NBR latex.

It was reported(99) that hydrolysis may be responsible for lower binding levels because under heat and water, the starting materials (p-aminodiphenylamine and thioglycollic acid) may be regenerated.



This is very unlikely if the pH of the reaction is restricted to near neutral. The colour of the reaction product in this experiment (yellowish-green) further confirmed that hydrolysis did not occur because if the starting material was produced, the reaction product would have been more intensely coloured (the colour of p-aminodiphenylamine is dark gray).

The possibility that TBH abstracts the hydrogen atom from the amine group (-NH- group) rather than from the -SH group (by the tertiarybutyoxyl radical) prompted the use of other initiators such as azo-bis-isobutyronitrile (AZBN) and valeric acid (AZBV).



$$\mathrm{HO(O{=})C-(CH_2)_3-C(CH_3)_2-N{=}N-C(CH_3)_2-(CH_2)_3-C({=}O)OH}$$

The result of this experiment is shown in Table 2.17 and the redox system (TBH/TEPA) is shown to be the best initiator combination.

The ineffectiveness of other initiators is probably due to the fact that they may not be reacting with the rubber molecule but rather remaining in the water, for example, the water soluble 4,4'-azo-bis(4-cyano-valeric acid) system forms free radicals by itself, but it is negatively charged in nature. This may act as a repulsive barrier towards the latex since the latter is also negatively charged. Also the influence of the acid group on the pH of the reaction mixture must not be overlooked. Although acid will tend to cause coagulation, no such problem was encountered. Impurities in the latex may also contribute to the reaction observed.

2.5 Conclusion

The experiments showed that both BHBM and PAPT can be bound to NBR latex to a reasonable level, 60 and 52% respectively, but PPPT can only be bound to about 30%. BHBM reacted with NBR latex at all concentrations (1 - 50%) to produce masterbatches whereas the reaction of the thiolamides is limited to concentrations between 5 and 20%. All antioxidants showed increasing binding with increasing antioxidant concentration, but prolonged reaction time leads to a decrease. Another important factor that emerges was that the thiolamides can be reacted with the latex in the absence of TEPA whereas exclusion of this activator in the reaction of BHBM resulted in reduced binding which probably means that the redox reaction between the thiol amide and the hydroperoxide is higher than that which occurs between BHBM and TBH. A further proof of this is the fact that the amines required less peroxide (TBH) to initiate the binding reaction than that required in BHBM.

The higher level of binding achieved with BHBM is probably due to greater solubility and hence efficient penetration into the rubber molecule, and the reaction temperature well above the melting point of BHBM (33^{O}C). All these physical properties do not favour the thiolamides. Table 2.18 shows the requirements for the grafting reactions.

Table 2.18 The preferred reaction conditions for the grafting of BHBM, PAPT and PPPT to NBR latex

	BHBM	PAPT	PPPT
Swelling time (hrs)	2-3	8-10	8-10
Reaction time (hrs)	7	9	9
Reaction temperature (^{o}C)	55-60	70	70
Initiator concentration (molar ratio, RSH / TBH)	1:0.5	1:0.3	1:0.3
TEPA concentration (volume ratio, TBH / TEPA)	1:1	-	-

CHAPTER THREE

MECHANOCHEMICAL BINDING OF BHBM, PAPT AND PPPT TO NBR

3.1 Introduction

As has been pointed out in Chapter One, free radicals are produced in rubbers during processing, compounding and fabrication. The energy needed is supplied by shearing force (mechanochemical energy)(101) imposed during the deformation of the bulk rubber and it is this that is mainly responsible for the rupture of the rubber molecule.

$$R\text{-}R \xrightarrow[\text{(mechanical energy)}]{\text{Shear}} R^{\cdot} + R^{\cdot}$$

There is evidence that mechanochemically induced macroalkyl radicals can lead to peroxidation of the rubber. Under processing conditions, according to the originally postulated free radical mechanism of the degradation of polymer, postulated by Bolland(2,102).

$$R^{\cdot} + O_2 \longrightarrow ROO^{\cdot}$$

It has also been shown that when rubber is masticated with another polymer in the absence of oxygen, the free radicals so produced react by addition to the double bonds of the rubber structure. Furthermore if natural rubber or a similar polymer(49) such as polystyrene, polymethyl methacrylate or polyvinyl chloride are masticated with vinyl monomers such as methyl methacrylate, graft polymerisation occurs.

The underlying principle of the mechanochemical binding of the thiol based bound antioxidants into NBR is based on the formation of macroalkyl radicals during the mastication of NBR in the RAPRA torque rheometer with the exclusion of oxygen.

$$\mathrm{R\text{-}R} \xrightarrow{\text{Shear}} \mathrm{R}^{\cdot} + \mathrm{R}^{\cdot} \qquad (\mathrm{R} = \text{alkyl radical}$$

$$\mathrm{R'SH} + \mathrm{R}^{\cdot} \longrightarrow \mathrm{RS}^{\cdot} + \mathrm{RH} \qquad \text{from polymer})$$

Although some alkylperoxyl radicals are formed due to traces of oxygen in the polymer and in the mixing chamber, the formation of alkyl radicals predominates and grafting is by addition of the thiyl radicals to the double bonds.

3.2 Apparatus

This experiment was carried out in the prototype RAPRA torque rheometer(103,104). This is essentially a small mixing chamber with mixing screws contra-rotating at different speeds. It has good temperature control and a continuous read-out is provided of both the reaction temperature and the mixing torque. The chamber may be operated either open to the atmosphere or closed by a pneumatic ram.

The use of the RAPRA torque rheometer is advantageous because of its ease of operation and at the same time, simulates conditions encountered in actual commercial processing of polymers in industry. The rheometer has a volume capacity of 39.0 cc but in the present work 30.0 g of nitrile rubber was used to afford an effective mixing. After the processing operation, the rubber antioxidant adduct was discharged into cold water (quenched). Quenching was necessary to prevent further oxidation of the rubber on exposure to the atmosphere.

In this experiment, the commercial grade of nitrile rubber, type Krynac 800 NS supplied by Polysar Limited, was used.

3.3 Determination of Optimum Reaction Conditions for the Mechanochemical Binding of BHBM, PAPT and PPPT

It was essential that the optimum conditions for antioxidant adduct formation be determined before the evaluation of the products of the above mentioned phenol and thiolamides to NBR was carried out in detail. The parameters involved are (a) reaction temperature and (b) duration of the adduct process. In a preliminary experiment, it was found that the best result is achieved when the RAPRA torque rheometer is operated with a closed chamber and at high speed (70 mins^{-1}) and at a temperature of 55^{o}C.

3.3.1 Determination of Optimum Temperature

30 g of NBR solid rubber was sliced into small pieces and introduced into the mixing chamber of the RAPRA torque rheometer, followed by the addition of the antioxidant (10% of antioxidant based on weight of NBR) and the mixing chamber was closed with the aid of the pneumatic ram. The antioxidant and the rubber were sheared for 20 minutes at different temperatures (25, 30, 40, 50, 55, 60, 70, 80, 90, 100 and 120°C). At the end of each reaction, the extent of binding was estimated by dissolving a known weight (1.5 g) of the modified rubber in 30 mls of chloroform. The rubber solution was then spread on a glass plate to cast a film. The film so obtained was extracted with methanol for 24 hours to remove any unbound antioxidant. The extracted film was dried in a vacuum oven and the degree of binding was determined by the ir technique. The results are shown in Table 3.1.

Some samples were redissolved in THF (to give a concentration of 3×10^{-3} moles of antioxidant/l of THF) and were analysed by GPC. Details of this method are described in Chapter Five, section 5.5.

3.3.2 Determination of Optimum Reaction Time

A set of experiments were carried out at 55°C using 30 g of NBR solid rubber and the concentration of the antioxidant was 10% based

Table 3.1 Determination of optimum reaction temperature at 20 minutes processing

Temperature ^{o}C	Reaction time min	Antioxidant conc %	BHBM Bound %	PAPT Bound %	PPPT Bound %
25	20	10	-	8.5	-
30	20	10	28	26	3
40	20	10	47	46.8	10
50	20	10	47	71	30
55	20	10	20	80	28
60	20	10	10.5	43	23
70	20	10	10	35	9
80	20	10	10	29	2
90	20	10	9	16	-
100	20	10	Broadened peak	12	-
120	20	10	Broadened peak	12	-

Table 3.2 Determination of optimum reaction time at 50^{o}C

Reaction time min	Reaction temperature ^{o}C	Antioxidant conc %	BHBM Bound %	PAPT Bound %	PPPT Bound %
3	50	10	-		-
5	50	10	-	32	-
7	50	10	-	37	-
10	50	10	4.5	43	2
15	50	10	19	54	24
20	50	10	46	71	32
25	50	10	47	74	32.5
30	50	10	47.3	70	31.9
35	50	10	46	68	28
45	50	10	22	65	28
60	50	10	19	52	22
120	50	10	19	48	22

on the weight of the rubber. After closing the mixing chamber, the reactions were allowed to proceed for different lengths of time. After the reaction had ended, samples were dissolved in chloroform and films were cast on glass plates and the extent of binding estimated as described in section 2.1.5 under Chapter Two. Results are shown in Table 3.2.

3.3.3 Formation of Solid Masterbatch

Having obtained information on optimum reaction temperature and optimum reaction time, from the preliminary experiments, the results were used to prepare masterbatches of the following concentrations, 4×10^{-3}, 4×10^{-2}, 8×10^{-2}, 1.2×10^{-1}, 1.6×10^{-1} and 2×10^{-1} moles of antioxidant per 100 g of nitrile rubber. (1, 10, 20, 30, 40 and 50 g/100 g rubber). The reaction time of NBR with BHBM, PAPT and PPPT was 20 minutes but the reaction temperature varied from 40/45°C for BHBM, 55°C for PAPT and 50°C for PPPT.

After each reaction, the rubber was dissolved in chloroform and films were cast on glass plates, the films were methanol extracted and the amount of antioxidant bound was determined by the ir method as described in section 2.1.5 under Chapter Two. The results are shown in Tables 3.3 - 3.5.

Table 3.3 Formation of (NBR-BHBM) masterbatch

BHBM	Maximum torque Nm	Reaction time min	Reaction temperature °C	Masterbatch conc g/100 NBR	% BHBM bound
	40	20	40	1	28
	40	20	40	10	47
	40	20	40	20	42
	40	20	40	30	42
	40	20	40	40	36*
	40	20	40	50	28*

* Surface lubrication between rubber and mixing rotor prevented effective shearing, hence less torque was recorded

Table 3.4 Formation of NBR-PAPT masterbatch

PAPT	Maximum torque Nm	Reaction time min	Reaction temperature ^{o}C	Masterbatch conc g/100 g NBR	% PAPT bound
	47	20	55	1	28
	47	20	55	10	75
	47	20	55	20	80
	47	20	55	30	75
	47	20	55	40	57**
	47	20	55	50	52**

** At these concentrations, the antioxidant appeared to be only partially soluble in the rubber. The rubbery properties seemed reduced and the antioxidant acted as a filler

Table 3.5 Formation of NBR-PPPT masterbatch

PPPT	Maximum torque Nm	Reaction time min	Reaction temperature °C	Masterbatch conc g/100 g NBR	% PPPT bound
	47	20	50	1	28
	47	20	50	10	36
	47	20	50	20	43
	47	20	50	30	40
	47	20	50	40	39
	47	20	50	50	30

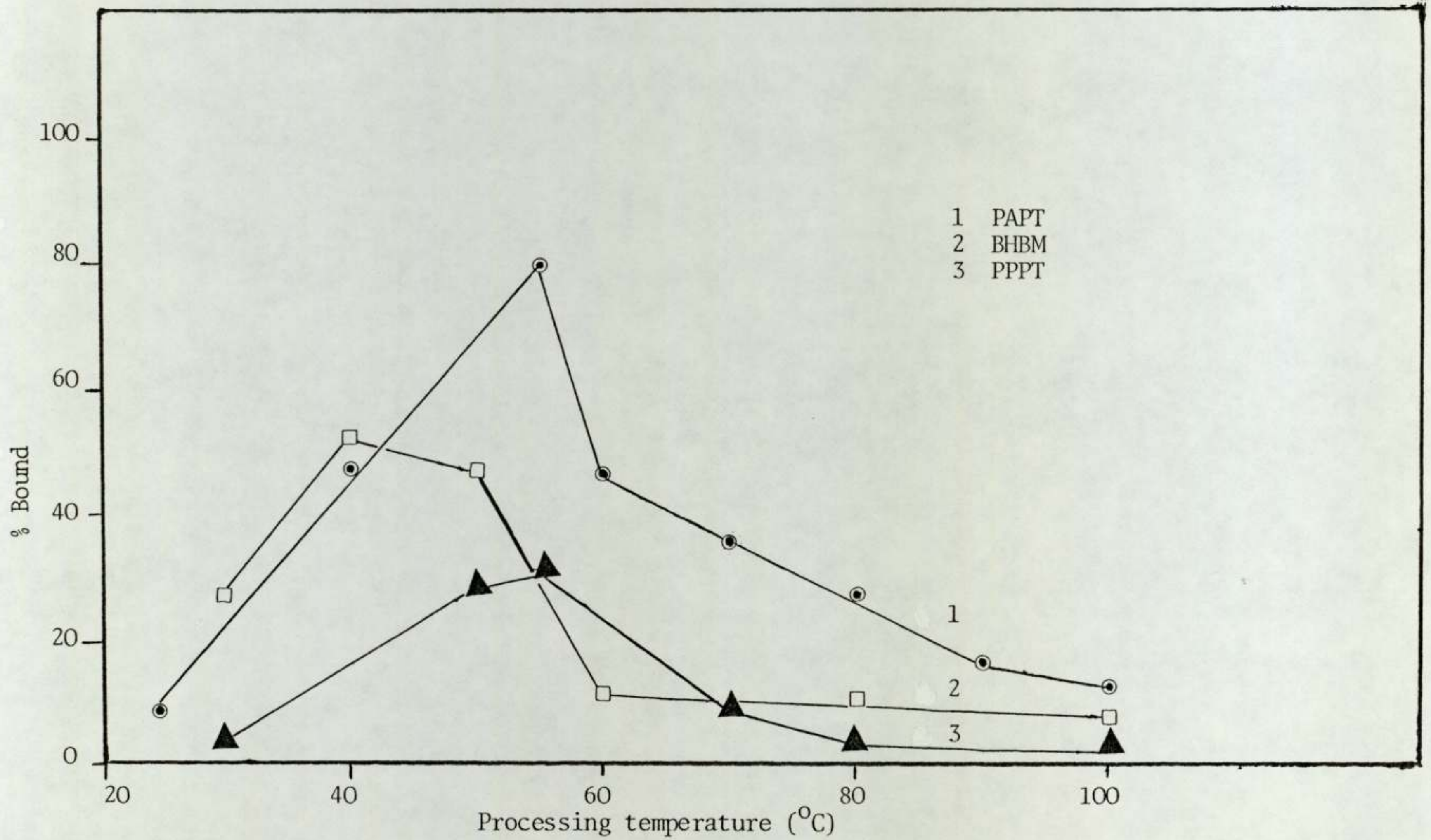


Fig 3.1 Percentage antioxidant bound against processing temperature at 20 mins processing time and conc = 20 g antioxidant/100 g NBR

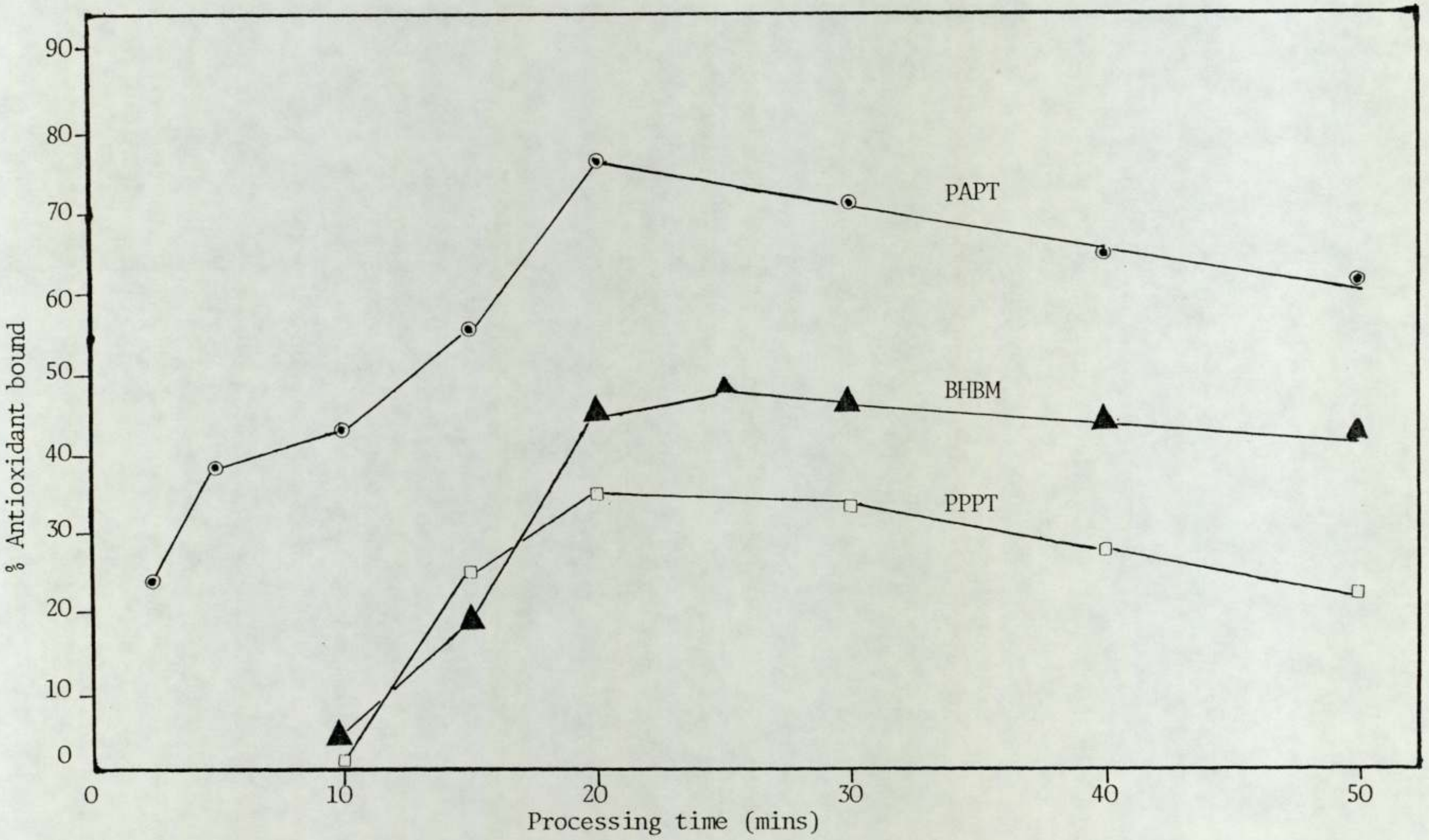


Fig 3.2 Curve of % antioxidant bound against processing time at 55°C

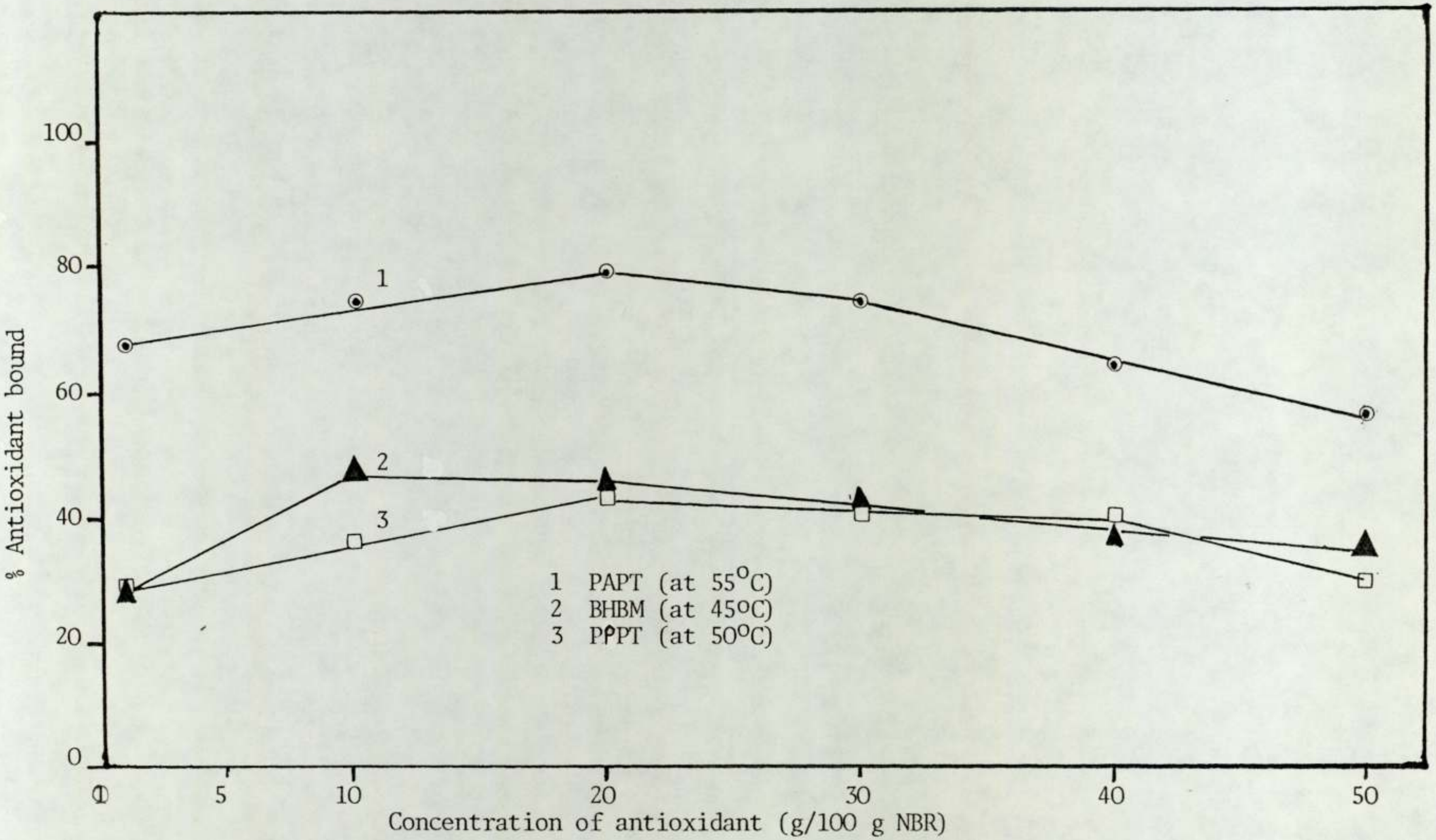


Fig 3.3 Effect of increasing concentration of antioxidant on percentage bound (processing time 20 mins)

3.4 Measurement of Torque Against Processing Time

The determination of torque against the processing time in the RAPRA torque rheometer was carried out on nitrile rubber (K800 supplied by Polysar Limited). The experiment was done both in the absence and in the presence of antioxidants (PAPT, PPPT and BHBM). The effect of each antioxidant on the torque during processing was carefully followed.

In all cases, there was a sharp rise in torque (when the rubber was introduced at the beginning of processing into the chamber) and when the processing chamber was closed by the pneumatic ram there was a further rise in the torque, this was followed by a rapid fall in torque to reach a minimum after about 3 - 4 minutes, due to breaking of the polymer chains leading to a reduction of the molecular weight. After about 5 minutes the torque remained almost constant. It was found that the time taken for NBR to go through all these stages was influenced by the antioxidant with which it was being processed (see Fig 3.4).

In a closed chamber, PAPT and PPPT did not seem to have a significant effect on the initialshearing force (47 Nm) but with time, the sample containing PPPT fell to a lower torque (27 Nm) compared with the control sample and sample containing PAPT dropping to 29 Nm after 20 minutes. The sample containing BHBM had a lower initial torque (40 Nm) an indication of its lubricating effect (Fig 3.4, curves 4 and 7) which became more pronounced with increase in concentration, and after 20 minutes, the shearing force had fallen to 22 Nm. However, when the antioxidants were individually premilled with NBR on a laboratory two-roll mill for 6 minutes each at room temperature, this was followed by processing in the torque rheometer (closed mixer). All samples showed considerable reduction in their initial shearing force (Fig 3.4, curves 5 to 7) and within 5 minutes the torque of all samples fell to below 25 Nm and after 20 minutes, the shearing force in all samples fell to below 23 Nm. This showed that premilling the samples was a disadvantage because high initial torque (viscosity) is required for the production of alkyl radicals in the system. The low binding of the BHBM is thus probably due to lubrication which prevented higher torque in the sample.

Although boundary lubrication of the metal surface by BHBM and PPPT lead to a reduction of frictional force, thus reduction of viscosity, internal plasticisation of the rubber molecule is also possible. Because these antioxidants are liquids at the processing temperature (55^{o}C) and do not volatilise out of the chamber, they quickly solvate the polymer. Usually the balance of polarity of plasticiser molecule relative to the parent polymer determines the mutual solubility and since both the antioxidants and NBR are polar, the compatibility may have brought about the ability of the antioxidant molecules to cause slippage within the rubber molecule. Therefore, a displacement of the glass/rubber transition temperature. Since this displacement is towards a lower temperature, this inevitably reduces

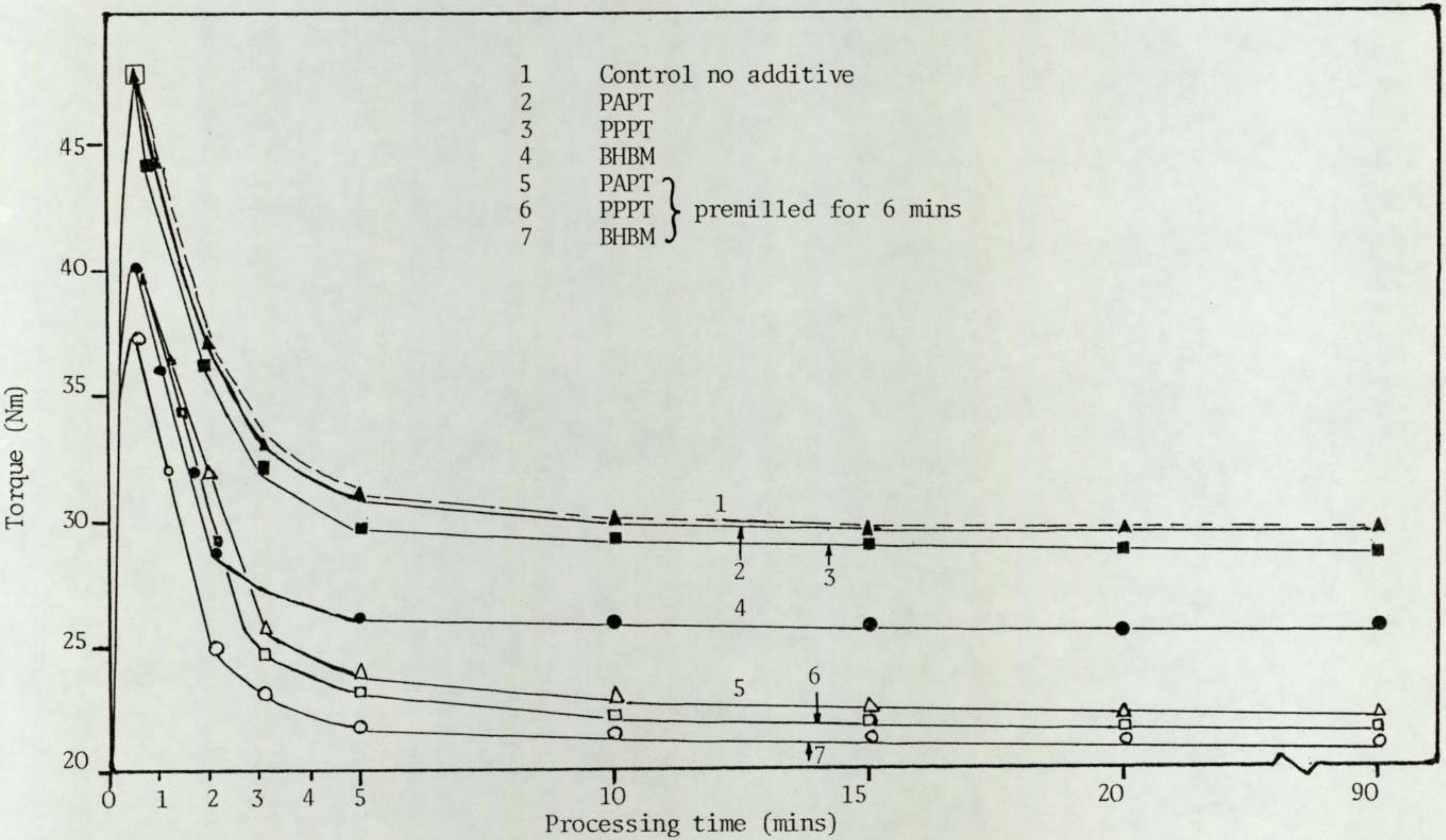


Fig 3.4 Torque -vs- time curve at 55^{O}C (closed chamber)

the rigidity of the polymeric composition by several orders of magnitude. Therefore, a reduction of the necessary torque to rupture the bulk rubber molecule, a direct consequence of this is that fewer alkyl radicals will be produced and hence the rate of initiation of grafting is very much slower than it ought to be.

3.5 Attempted Binding on the Two-Roll Mill

The binding of the thiol based bound antioxidants I, II and III to NBR in the RAPRA torque rheometer was achieved through the production of a significant concentration of alkyl radicals (closed chamber) which in turn initiated the binding. It is universally accepted that alkyl radicals are produced in a similar manner during the milling process. The concept of alkyl

$$\text{R-R} \quad \xrightarrow[\text{(shear)}]{\text{milling}} \quad \text{R}^{\cdot} + \text{R}^{\cdot}$$

radical production prompted the attempt to bind the antioxidants on the laboratory two-roll mill.

PROCEDURE

100 g of NBR was premilled for about 3 minutes, followed by the addition of the antioxidants and milling of the mixture of NBR and antioxidants was continued for a further 15 minutes. Samples were taken after 4, 6, 8, 10, 12 and 15 minutes. The samples were dissolved in chloroform and from the rubber solution films

were cast on glass plates. The films were extracted and dried in a vacuum oven and the amount of antioxidant bound was estimated by the ir method. In none of the samples did the antioxidant bind.

The result of this experiment showed that abundance of oxygen had an adverse effect on the reaction. The measurement of hydroperoxide formed in samples produced during this experiment showed that extensive oxidation had occurred (Fig 3.5, curves 1 and 2).

$$R^{\cdot} + O_2 \longrightarrow ROO^{\cdot}$$

$$R'SH + ROO^{\cdot} \longrightarrow ROOH + R'S^{\cdot} \xrightarrow{x2} R'SSR'$$

$$R'S^{\cdot} + ROO^{\cdot} \longrightarrow R'S\text{-}OOR \qquad \text{(unstable products)}$$

The reaction occurring during milling is complex but it appeared that the antioxidant reacted with alkylperoxy radical and the resulting thiyl radical is further oxidised to unstable products. The breakdown products of which will be discussed later in Chapter Five. It is the above mentioned reactions of the thiol antioxidants in the presence of oxygen that prevented the binding reaction.

3.6 Effect of Premilling Antioxidants with NBR Before Processing in the Torque Rheometer

Although a higher binding level (80%) was achieved when PAPT was processed in a closed chamber, the loss of the remaining 20% is presumed to be due to the formation of by products in the termination step as a result of bad antioxidant dispersion. It was then thought that a much better antioxidant distribution might achieve 100% binding. A better distribution was effected by premilling the antioxidant with nitrile rubber for a predetermined period (6 minutes) before the rubber is introduced into the mixing chamber of the RAPRA torque rheometer.

PROCEDURE

In this experiment, three concentrations (2, 10 and 20 g antioxidant/100 g NBR) were used. The rubber was sheared for one minute followed by the addition of antioxidants and milling was continued for 6 minutes. The mixture (NBR/antioxidant) was then introduced into the mixing chamber of the torque rheometer and was processed for 20 minutes at 55°C in a closed condition. At the end of the reaction, the samples were dissolved in chloroform and processed in the usual way and the degree of binding was estimated. The results are shown in Table 3.6, experiment number 2.

3.7 Effect of Preshearing NBR Before the Addition of Antioxidants

The object of this experiment is to show whether peroxides preformed in the polymer were responsible for the binding.

In this experiment, 30 g of nitrile rubber was presheared in the torque rheometer until the torque (shearing force) was constant (6 minutes), then the antioxidant was added and reacted with the nitrile rubber for 20 minutes with the mixing chamber closed. The temperature of the chamber was maintained at 55°C.

At the end of the reaction period, the amount of antioxidant bound to the rubber was estimated using the ir technique. The result is given in Table 3.6, experiment number 3.

Unlike the previous experiment, section 3.6, the result showed that some antioxidant became bound to the polymer. This is an indication that some alkyl radicals were produced but like the result in section 3.6, alkoxyl and alkylperoxy radical formation predominated. And because of this, the rate of formation of by products was faster than the rate of addition of the antioxidant to the nitrile rubber.

3.8 Mechanochemical/Peroxide Initiated Adduct Formation

This experiment was carried out both on the mill and in the torque rheometer. It is designed to find out whether the addition peroxides leads to an increase in the level of binding. Since the binding in the latex reaction required the addition of a small amount of hydroperoxide (TBH) for initiation and it has been suggested by Diamond Shamrock Limited(105) that addition of dilauryl peroxide is necessary to achieve optimal binding of

PAPT to NBR.

Three antioxidants were used in this experiment (BHBM, PAPT and PPPT) at 2, 10 and 20 g of antioxidant per 100 g of nitrile rubber. Two types of peroxides were used, dilauryl peroxide (DLP) and tertiarybutyl hydroperoxide (TBH). The concentration of peroxides was fixed at 1 phr after preliminary experiments to determine the effect of peroxide concentration. Particular attention was given to the sequence of operation and antioxidant to nitrile rubber, the effect of premilling the peroxide with NBR, the effect of premilling antioxidant with NBR, the effect of preshearing peroxide with NBR, the effect of preshearing antioxidant with NBR and the effect of reprocessing on binding level.

3.8.1 Effect of the Sequence of Addition of Peroxide and Antioxidants

A series of experiments was carried out in which peroxides (TBH and DLP in separate experiments) were added to nitrile rubber before the antioxidant on the two roll mill and in another series of experiments, the antioxidants were incorporated into the rubber prior to the addition of the peroxide. And the rubber was tested for the degree of binding as described in the previous experiments. The results are given in Table 3.6 (numbers 4 and 5).

3.8.2 Effect of Premilling NBR with Antioxidants in the Presence of Peroxide on Subsequent Processing in the Torque Rheometer

In this experiment, nitrile rubber was premilled with antioxidant for 6 minutes, followed by the addition of peroxide and was milled for a further 4 minutes. Then the rubber mixture was introduced into the torque rheometer where it was processed for another 20 minutes in a closed chamber. The level of binding of antioxidants was estimated in the usual way. The results are given in Table 3.6 (experiment numbers 6 and 7).

3.8.3 Effect of Preshearing NBR with Peroxide Before the Addition of Antioxidants

30 g of NBR was introduced into the torque rheometer and was immediately followed by the addition of 1% of peroxide. The mixture was sheared for 3 minutes (in a closed chamber and the temperature was kept at $55^{\circ}C$). This was followed by the addition of antioxidants and the process was continued for 20 minutes. Then the degree of binding was measured using the ir technique. See Table 3.6 (experiment numbers 8 and 9).

3.8.4 The Effect of Preshearing NBR with Antioxidants Before the Addition of Peroxide

In this experiment, 30 g of NBR was presheared with antioxidant in the torque rheometer at $55^{\circ}C$ (open mixer) until the shearing force was constant (6 minutes). Then the peroxide was added and the reaction was allowed to proceed for 20 minutes in a closed chamber and the temperature was maintained at 55°C. The reaction adduct rubber was dissolved in chloroform and the extent of binding was measured after the cast film had been extracted with methanol. The results are given in Table 3.6 (experiment numbers 10 and 11).

3.8.5 Effect of Reprocessing With and Without the Addition of Peroxide

For this experiment, the Goodyear nitrile rubber grade N612 was used and only PAPT masterbatch was involved.

Nitrile rubber grade N612 was reacted with PAPT in the Banbury mixer at 110°C to give masterbatch concentrations of 2 and 30 g per 100 g of NBR respectively. After analysis of binding, only 9 and 14% was bound to the rubber. These samples were reprocessed both in the absence of dilauryl peroxide and in the presence of 1 phr of dilauryl peroxide. The results are given in Table 3.6 (experiment number 14).

3.9 Attempted Binding of PAPT into NBR in the Banbury Mixer

In the rubber industries, compounding and processing of rubber is carried out mainly on a two-roll mill and in the Banbury mixer, because of the ease of operation and larger capacity of

Table 3.6 Effect of various processing conditions on the yield of bound antioxidants in NBR at 55°C

Processing conditions	Masterbatch concentration								
	PAPT			PPPT			BHBM		
	2	10	20	2	10	20	2	10	20
1 NBR + AO, open mill (3-10 min)	0	0	6	0	0	0	0	0	0
2 NBR + AO, open mill; 6 min, TR 20 min	4								
3 NBR presheared, open TR, to constant torque; 6 min, AO 20 min closed TR	8	9	10	0	0	0	0	0	0
4 NBR + DLP, open mill, 4 min; AO open mill, 6 min	41	46	47	7	12	15	*	*	8
5 NBR + TBH, open mill, 4 min; AO open mill, 6 min	32	40	53	9	13	14	3	6	6
6 NBR + AO, open mill, 6 min; DLP open mill, 4 min; open TR 20 min	42	48	58	0	5	12	10	8	8

Table 3.6 Continued

7	NBR + AO, open mill, 6 min, TBH open mill, 4 min, TR 20 min	45	47	44	5	5	8	10	9	10
8	NBR + DLP, open TR, 3 min; AO, closed TR 20 min	33	38	49	0	0	*	0	**	**
9	NBR + TBH, open TR, 3 min; AO, closed TR 20 min	28	32	36	0	0	*	*	**	**
10	NBR + AO, open TR, 5 min; DLP, closed TR 20 min	23	20	26	0	10	11	27	22	22
11	NBR + AO, open TR, 5 min; TBH, closed TR 20 min	18	23	30	0	8	12	20	19	29
12	NBR + AO + DLP together, closed TR 20 min	30	35	37	-	-	-	-	-	-
13	NBR + AO + TBH together, closed TR 20 min	27	36	38	-	-	-	-	-	-
14	NBR + PAPT (product from Banbury initial binding 10%) + 1% DLP	19	-	29						
15	Original process described in (NBR + AO, 20 min, TR 55°C)	60	68	78						

* = too small to estimate; ** = ir peak broadened; TBH = tert-butyl hydroperoxide; DLP = dilauryl peroxide;

TR = torque rheometer

the Banbury mixer compared with that of the prototype RAPRA torque rheometer. To simulate the industrial operation, an attempt was made to bind PAPT with NBR in the Banbury mixer. Success using this procedure would no doubt encourage the industrial production of the adduct rubber on a much larger scale because of the ease of operation. The procedure is very similar to that used in the experiment in the RAPRA torque rheometer.

The Banbury mixer has a capacity of about 1.2 litres and has three speeds (20, 40 and 60 rpm). The chamber can be operated either open to the atmosphere or sealed by a pneumatic activated ram, and the chamber is water cooled.

In the experiment, the nitrile rubber, type Chemigum 615 and 612, produced by Goodyear Rubber Chemicals Limited and supplied by Diamond Shamrock Euorpe Limited (DSE) was used in this experiment.

PROCEDURE

1100 g of the nitrile rubber was charged into the mixing chamber at room temperature followed by the addition of 23 g of PAPT. Within five minutes of mixing, the temperature rose to 90^{o}C. The water cooling system did not efficiently dissipate the heat that developed as a result of the high shearing force. Without closing the chamber, the mixing was continued for a period of about 30 minutes during which time the temperature rose to 110°C and when the ram was lowered, the temperature shot up to 145°C.

Under these uncontrollable conditions, masterbatches of 2 and 30% PAPT-NBR adduct were produced. After the reaction, the chloroform solution of the rubber samples was examined by the ir technique for the extent of binding. The results are given in Table 3.7.

3.10 Measurement of Peroxide in Processed Nitrile Rubber

The concentrations of peroxide in processed polymers are very low and as such, not many methods of peroxide detection are sensitive enough to measure the low concentration found in the processed polymer. The method of ferrous ion oxidation, adapted from Bocek(106,107) which is capable of measuring 10^{-6} moles in polymers of convenient size, was used in the following experimental procedure.

PROCEDURE

0.5 g of processed NBR was swollen in 75 ml of deaerated methanol for about 12 hours in a conical flask fitted with a rubber seal. 1 ml of deaerated 0.004 M phosphoric acid in deaerated methanol was then added, followed by 2 ml of deaerated solution of 0.005 M ammonium ferrous sulphate in methanol. After allowing to stand in the dark for 4 hours, 1 ml of a 0.5% solution of 1,10-phenantroline in deaerated AR-benzene was added. The

Table 3.7 Degree of binding in Banbury mixer

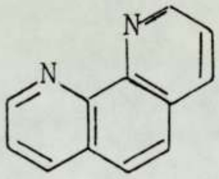
Reaction time min	Masterbatch concentration, g/100 g NBR		
	2	2	30
	Rubber grade		
	N612	N615	
	% PAPT bound		
3	Nil	Nil	Nil
5	1	Nil	4.5
10	2	3	9
15	9	6	12
20	18	7	12.9
25	26	7	14
30	27	9	14

reaction mixture was allowed to stand for 15 minutes after swirling. Then 5 ml of the reaction mixture, free of NBR, was carefully withdrawn and examined by measuring its absorption in the visible region (510 nm) against the blank reference using a Perkin Elmer model 137 uv visible spectrophotometer.

The difference between the absorbance of blank reference sample and that of the sample under examination gave the amount of divalent iron that had been oxidised by the peroxide in the processed polymer. The variation in the quantity of oxidised ferrous ion enabled a peroxide concentration-processing time curve using a calibration curve.

$$\mathrm{ROOH} + \mathrm{Fe}^{2+} + 2\mathrm{H}^{+} \longrightarrow 2\mathrm{Fe}^{3+} + \mathrm{ROH} + \mathrm{H_2O}$$

$2\mathrm{Fe}^{3+}$ +



→ coloured complex
(reddish brown)

The standard ferrous sulphate solution was made up by dissolving 1.9608 g of ferrous ammonium sulphate in methanol and adding 4 drops of concentrated sulphuric acid and making up to 100 ml with methanol, and 10 ml of this solution was made up to 1 litre using methanol. It is essential to add 4 drops of concentrated H_2SO_4 because in its absence the solution became oxidised very

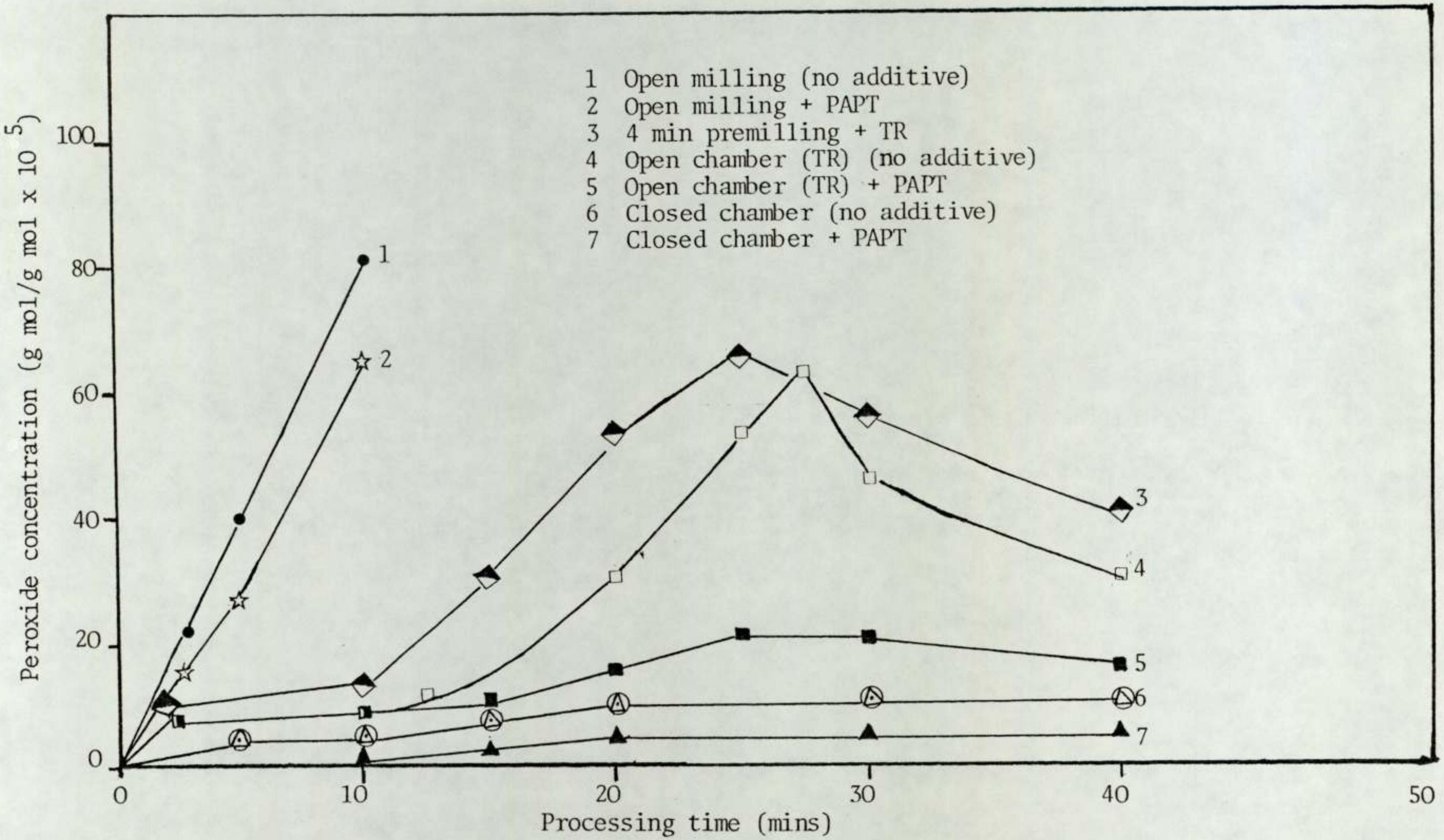


Fig 3.5 Measurement of peroxide concentration during processing of NBR in the RAPRA torque rheometer (TR) at 55°C

quickly.

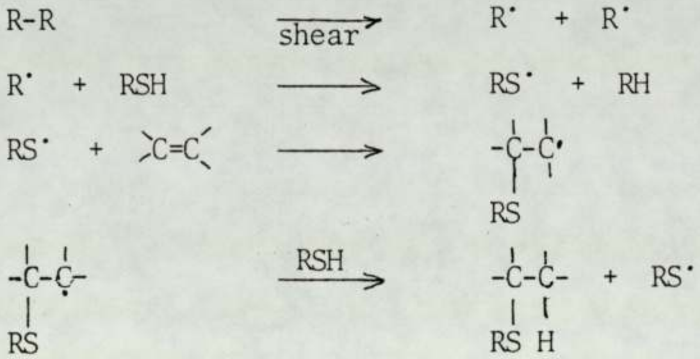
The addition or withdrawal from the reaction conical flask was by the use of a syringe. This was to prevent contamination of the solution by oxygen. In order to guard against the light sensitivity of the complex, the conical flask in which the reaction was taking place was wrapped first with aluminium foil and then with a fairly thick carbon coated paper.

3.11 Result and Discussion

The level of binding achieved, through the use of the mechanochemical technique (using the RAPRA torque rheometer) was estimated in the usual way and the results of the experiments are shown in Tables 3.1 - 3.5 and Figs 3.1 - 3.3.

The results clearly show that the temperature of the reaction plays a major role in determining the extent to which the binding occurs, irrespective of the type of antioxidant. All the antioxidants showed a maximum binding at a particular temperature. (BHBM at 40°C, PAPT at 55°C and PPPT at 48/50°C.) At room temperature, BHBM and PPPT were not bound, whereas about 9% of PAPT was bound. At 40°C, 47% BHBM and at 55°C, 75-80% PAPT and at 50°C about 30% PPPT were bound to NBR in separate experiments. As the temperature was increased, the level of binding fell (Fig 3.1) and above 80°C, no PPPT was bound, the hydroxyl peak due to BHBM became so broadened such that it was difficult to distinguish the OH peak of rubber oxidation products and at the same temperature range, the binding level of PAPT was reduced to only 12% (Table 3.1).

Table 3.2 and Fig 3.2 show the effect of processing time on the level of binding. It was found that a processing time of 20 minutes was adequate for the binding reaction. Varying the reaction time showed that the binding level increased steadily (curve a) to a maximum (74%) in 20 minutes and then fell to only 65% after 45 minutes. The most significant changes occurred in the first 5 minutes when the binding rose very sharply. The rate then slowed down and the binding appeared to reach a maximum after 20 minutes. This behaviour is probably due to the fact that high torque (shear) at the start of the reaction produced a substantial concentration of alkyl radicals which quickly reacted with the thiol antioxidant and so initiated binding.



$$R\text{-}R \xrightarrow{\text{shear}} R^{\cdot} + R^{\cdot}$$

$$R^{\cdot} + RSH \longrightarrow RS^{\cdot} + RH$$

$$RS^{\cdot} + {>}C{=}C{<} \longrightarrow -\underset{RS}{\overset{|}{\underset{|}{C}}}-\overset{|}{\underset{|}{C}}^{\cdot}$$

$$-\underset{RS}{\overset{|}{\underset{|}{C}}}-\overset{|}{\dot{C}}- \xrightarrow{RSH} -\underset{RS}{\overset{|}{\underset{|}{C}}}-\underset{H}{\overset{|}{\underset{|}{C}}}- + RS^{\cdot}$$

In the initial stages, alkyl radicals seem to be the sole source of initiation but after 5 minutes, the fall in viscosity as a result of molecular rupture (see Fig 3.4) is probably responsible for the slowing down in the rate of binding, because with the fall in viscosity, less alkyl radicals are being produced. It is also to be appreciated that there will always be some small amount of oxygen in the rubber, also in the mixing chamber of the torque rheometer, the formation of a small amount of alkyloxyl radicals is therefore expected and this radical may be the source of initiation in the time 15-20 minutes. Also the slowing down of the amount bound after 5 minutes may be attributed to the consumption of the antioxidant in destroying the hydroperoxide formed from the small amount of oxygen present in the processing chamber. The reversions observed in the pattern of the curve may be explained in terms of oxidation of both bound and unbound antioxidant and the subsequent cleavage of the (-S-C-) links. The levelling of the curve later on, probably marks the onset of the activity of the antioxidant species (SO_2, SO_3, H_2SO_4) derived from the oxidation products of the antioxidants and at this later stage, the concentration of the antioxidant is almost constant.

The trend was the same for PPPT and BHBM, except that the bindings were much less than that achieved with PAPT.

Fig 3.3 and Tables 3.3 - 3.5 show the effect of increasing concentration of antioxidant on the level of binding. A reasonable NBR antioxidant adduct was achieved up to a concentration of 30 g of antioxidant per 100 g of NBR. Above this concentration BHBM rendered the rubber less viscous and it soon became apparent that surface lubrication between the rubber and the mixing rotor and chamber wall prevented effective shearing. But at higher concentrations (40, 50 g) the reaction of PAPT with NBR presented a different problem entirely. The antioxidant was only partially absorbed in the rubber and the rubbery nature of the elastomer seemed reduced and the antioxidant acted as a filler. PPPT, a very similar compound to PAPT, did not bind to as high a level as did PAPT. Based on its structure (in which the sulphur atom is attached to a carbon atom which is β- to a carbonyl group and the carbon atom β- to the sulphur (α to carbonyl) bears more than one hydrogen atom), PPPT is assumed to be a much more reactive compound than PAPT but its reactivity towards NBR is somewhat low and this cannot be explained.

Although PAPT was successfully bound to NBR in the RAPRA torque rheometer, attempted scale up of the torque rheometer process using the Banbury mixer on the industrial scale failed to give as high a binding level as was achieved with torque rheometer. The highest level of binding achieved in the Banbury mixer was 27% (Table 3.7). This result is not at all surprising since it was difficult to control the experimental conditions, (section 3.9). Notwithstanding the fact that the mixer was water cooled, the heat developed during the process was not effectively dissipated and because of the problem of heat build-up, the chamber was not tighly closed. As has been pointed out in previous sections, the presence of oxygen adversely affects the binding reaction, hence the low binding level.

Table 3.6 summarises conditions examined and the results of the experiments in which the mechanochemical - peroxide initiated adduct formation was evaluated. The failure to bind any of the antioxidants on an open mill alone clearly demonstrates the ineffectiveness of the procedure. However, when the same sample was reprocessed in the closed torque rheometer, some binding occurred. (PAPT 13%, BHBM 6% but PPPT did not bind.)

It was also observed that none of the treatments with air and optionally peroxides is as effective as the anaerobic torque rheometer procedure in which air is excluded. It was found that the effect of air (and peroxide) always leads to a rapid decrease in applied torque and hence to a lowering of bound antioxidant yields. In all cases, the extent of binding increases with masterbatch concentration. It doesn't seem to make a great deal of difference whether the antioxidant is added before or after prior mastication with peroxide.

It is assumed that reduction of the molecular weight of the rubber during milling operation leads to extensive oxidation of the rubber since milling was done in an oxygen rich atmosphere. However, where the first stage is carried out in the presence of air, subsequent treatment with peroxide in a closed mixer considerably improves the binding (cf experiment numbers 3 and

6 of Table 3.6). The best result obtained was using the open mill (experiment number 6, Table 3.6).

When the procedure is carried out in a closed mixer, the addition of peroxides has no advantage, and there is evidence that when antioxidants and peroxides are added together, interactions not involving the rubber reduce the yield substantially and caused discolouration of the rubber.

The general conclusions that have emerged from this experiment are that an initial high NBR viscosity is an essential requirement for a high level of binding of the thiol based bound antioxidant (PAPT) to NBR by the mechanochemical procedure. This can be achieved by excluding oxygen and peroxide which lead to a rapid reduction in applied torque during mechanical treatment. If reaction is not achieved by the mechanochemical procedure, due to a rapid reduction in viscosity, it can be achieved in the case of PAPT by subsequent, more prolonged peroxide treatment, in a closed mixer. However, in no case did this process give as high a level of binding as the mechanochemical procedure. The mechanochemical anaerobic procedure and the post-peroxide treatment procedure both gave higher yields, the higher is the concentration of PAPT in the rubber.

The higher bound antioxidant yield (80%) achieved with PAPT in the mechanochemical procedure, compared with the lower yield by the latex procedure, can be explained in terms of the use of peroxide in the latex procedure. The peroxide probably initiates rapid formation of side reaction whose oxidation products (Lewis acids and nitroxyl radicals have been found to be one of the by-products of the interaction between hydroperoxide and the thiol amides, section 5.6, Chapter Five) could be responsible for the inhibition of the grafting reaction. The reaction in the torque rheometer on the other hand employs the macroalkyl radicals produced by shearing forces and before by-products begin to form, a higher proportion of the antioxidant had been bound. Although oxidation takes place in the latter part of the reaction, appreciable amounts of the antioxidant are still bound to the rubber. The effect of the peroxide will be discussed in more detail in Chapter Five.

As regards the level of BHBM bound, the reason for the low binding can only be due to the ineffective shearing of the antioxidant-NBR mixture whereas in the latex procedure, the solubility of the antioxidant influenced to greater extent the yield realised during the reaction.

The yield of PPPT bound with the mechanochemical procedure is about the same as in the latex procedure. The reactivity of this antioxidant will be discussed in greater depth in the mechanistic chapter (Five).

CHAPTER FOUR

THE ASSESSMENT OF AGEING CHARACTERISTICS OF NBR VULCANISATES

4.1 Introduction

The evaluation of antioxidants for use in elastomers and in other polymers is complicated by many factors. The best antioxidant for one polymer is often ineffective in others and a good antioxidant for the stabilisation of plastics may be of little value in a vulcanisate. The problem of solubility and volatilisation limits the use of some inhibitors at higher temperatures, the effect of metal impurities which often vary in concentration in different samples can completely obscure the important differences in antioxidant activity.

Since under atmospheric conditions, measurement of the rate of deterioration is normally too slow for the practical selection of antioxidants, accelerated technological tests are employed. These generally involve the use of abnormal conditions to accelerate oxidation. The major problem associated with this type of measurement is that of knowing whether the rate of deterioration under accelerated tests correlates with that under normal service conditions.

The factors which can be considered to be potentially important in the determination of the effectiveness of antioxidants in a polymer are:

(i) The inherent antioxidant activity as measured by the induction period in a closed system (eg in the oxygen absorption test).

(ii) The rate of loss of antioxidant (volatilisation and leaching) from the polymer under service conditions.

(iii) The mobility of antioxidant within the polymer and the ability to migrate to the point of attack by oxygen.

There is evidence that both inherent antioxidant activity and the rate of loss of antioxidant from a system are of primary importance, and together with mobility are very important when the surface area of the polymer is large or the temperature is high. The evidence suggests that in rubbers, bound antioxidants are potentially very important technologically, since they are part of the rubber molecule and cannot be lost physically. The evidence also suggests that in rubbers, the mobility of the antioxidant does not seem to be very significant, up to quite high molecular weight (1000) provided the antioxidant is efficient. The choice of suitable tests for antioxidant activity of the rubber bound antioxidants is therefore very important.

In this work, the effectiveness of bound and unbound antioxidants containing the same functional groups has have been assessed by measuring the change in the physical properties of the vulcanisates. The technological tests used to measure the stability of the modified nitrile rubber vulcanisates at high temperatures (150^oC) are:

(a) Oven ageing (hot air)

(b) Stress relaxation

(c) Cyclic oil/air ageing

and in addition, oxygen absorption tests were carried out because the latter gives information about the chemistry of the stabilisation. The technological tests used include tensile strength, hardness, modulus and elongation at break and the results before and after ageing are discussed in sections 4.6.2, 4.7.1, 4.8.1 and 4.9.2.

4.2 Experimental Procedure

4.2.1 Preparation of Rubber Vulcanisates

COMPOUNDING

The vulcanisates were prepared from antioxidant bound nitrile rubber. All masterbatches obtained by the procedures described in sections 2.3 and 3.3.3 were divided into two parts and each was examined in the following ways:

(A) All were reduced to three concentrations, 1, 4, and 8×10^{-3} moles of antioxidant per 100 g of rubber (DR) by addition of latex masterbatch to untreated latex. The latices were then coagulated and the dried rubber was compounded and vulcanised with the standard system used in nitrile rubber and was compression moulded into films.

(B) All were coagulated and divided into two parts. (i) One part was added to solid NBR as a normal additive to give concentrations 1, 4 and 8 x 10^{-3} moles antioxidant per 100 g of NBR and (ii) the other part was extracted with n-hexane/methanol to remove unbound antioxidant and by-products and was then added to solid NBR to give the same adduct rubber concentration in normal nitrile rubber.

The compounding ingredients were mixed with dry rubber on a 12 inch water cooled laboratory two roll mill. A friction ratio of 1:1 was employed. The rubber was premilled for 2 minutes and the ingredients were added separately and milled with the rubber for 1 minute each and the total compounding was 7 minutes. In all the formulations, sulphur was added after all other ingredients had been incorporated. Samples were prepared according to the formulations given in Table 4.1.

Formulation A contains masterbatch NBR prepared by grafting bound antioxidants BHBM, PAPT and PPPT onto nitrile rubber according to the procedure described in sections 2.3 and 3.3.3. As a control, sample formulation D was used, formulated by the standard compounding procedure as described in the ASTMS

FLOW DIAGRAM OF SAMPLE PREPARATION AND CODE NAME

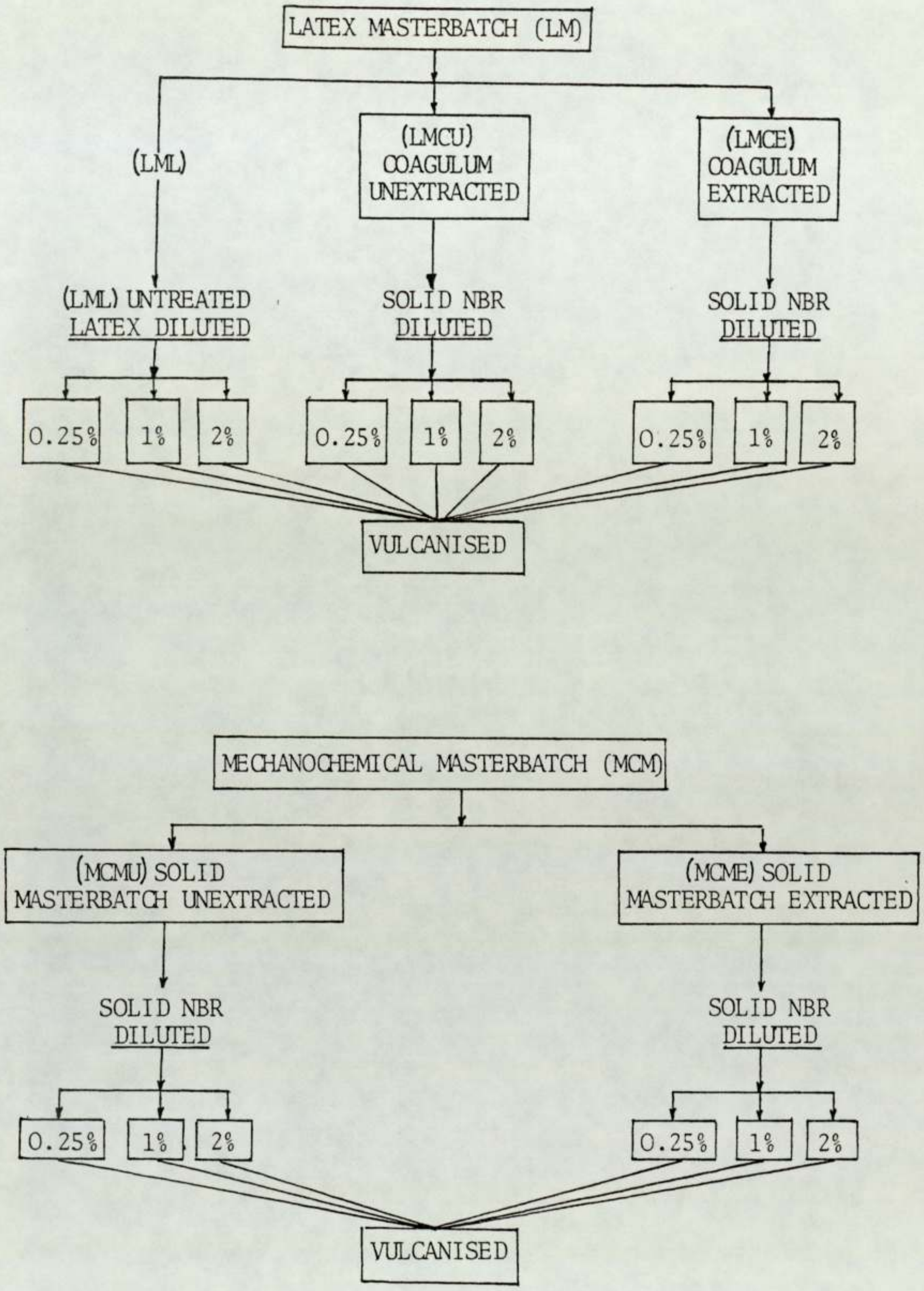


Fig 4

Table 4. List of antioxidants used, their chemical name, structure and code name

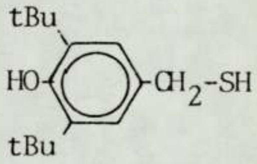
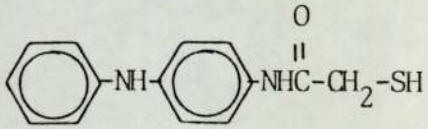
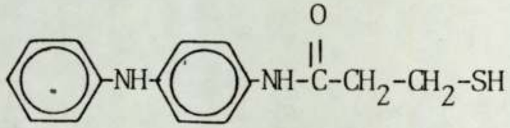
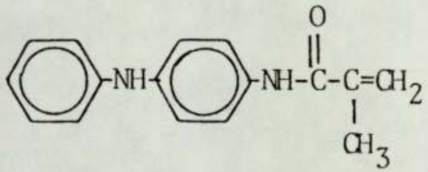
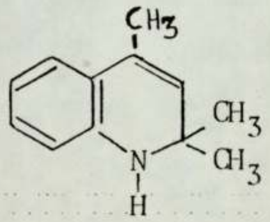
Chemical Name	Structure	Code Name
3,5-di-tert-butyl-4-hydroxybenzyl mercaptan		BHBM
N-(4-anilinophenyl)-thioglycollamide		PAPT
N-(4-anilinophenyl)thiopropionamide		PPPT
N-(4-anilinophenyl)methacrylamide		Chemigum
Polymerisable trimethyl hydroquinoline		Flectol-H

Table 4.1 Compound formulations

	Control Samples			
	A	B	C*	D
	Bound AO stabilised NBR	ASTM standard	Copolym stabilised Chemigum	No Additive
NBR masterbatch (+AO)	100	-	-	-
Commercial NBR	-	100	-	100
Chemigum - NBR	-	-	100	-
Zinc Oxide	5.0	5.0	5.0	5.0
Stearic Acid	0.5	0.5	0.5	0.5
Flectol H[a]	-	2.0	-	-
TMTD (Thiurad)[b]	2.0	2.0	2.0	2.0
Santocure NS[c]	1.0	1.0	1.0	1.0
Di-octyl phthalate	5.0	5.0	5.0	5.0
Carbon black	60.0	60.0	60.0	60.0
Sulphur	0.5	0.5	0.5	0.5

a Polymerisable trimethyl dihydroquinoline (see Table 4)

b Tetramethyl thiuram disulphide

c N-tertiary-butyl-benzothiazole-2-sulphenamide

* Copolymerisation stabilised NBR containing monomeric antioxidat N-(4-anilinophenyl)methacrylate (Table 4)

procedure(108). A second control containing Flectol H as antioxidant (formulation B) and for comparison a commercially available copolymerised antioxidant, N-(4-anilinophenyl) methacrylamide in NBR (formulation C).

4.2.2 Vulcanisation of Compounds

Vulcanisates were prepared in a fully positive stainless steel mould of cavity dimensions 13.5 x 13.5 x 0.018 cm so as to produce a vulcanisate sheet of thickness 0.018 - 0.023 cm. A sample of compound (10 g) was milled into a thin sheet and placed in the mould cavity. The mould was assembled and placed between the platens of a steam heated press; the temperature of which had previously been raised to the required cure temperature. A pressure of 1400 kg/cm^2 was applied to produce the required sheet thickness.

At the end of the cure time (15 minutes) the mould was removed and the sample taken out and quenched in cold water. The vulcanised sheet was dried and stored in vacuum desiccator in the dark.

4.3 Preparation of Rubber Films

In the preparation of rubber film, two techniques were used:

(i) By casting from solution

(ii) By casting directly from latex.

(i) Solution Technique

About 10 mls of the modified latex was coagulated using 100 mls of a 0.25% solution of calcium chloride (in water). The coagulum was washed thoroughly with distilled water. It was then hand pressed between polyethylene film to squeeze out the water. The coagulum was then dried in a vacuum oven at 40°C overnight to constant weight. The dried coagulum was dissolved in chloroform (1 g dried rubber in 20 mls chloroform). Using this rubber solution, films were cast on glass plates. The films when perfectly dry, were carefully removed from the glass and mounted on an infra-red 'specacard' (cardboard). This method was employed for all solid masterbatches.

(ii) Latex Technique

This was perhaps the most straight forward technique and the most accurate, since there was no danger of the antioxidant being thermally destroyed as might be the case in the compression moulding method or any loss of antioxidant during coagulation and washing or solvent interaction with the antioxidant during the process of redissolving the coagulum in chloroform.

In this method about 10 mls of the modified NBR latex was spread on glass plates over an area of 32 cm^2, and allowed to dry in a desiccator in an atmosphere of nitrogen gas. The film was carefully removed from the glass and mounted on an infra-red 'specacard'.

This method was used in plotting all the calibration curves.

4.4 Extraction

4.4.1 Extraction of Vulcanisates

In order to remove unbound antioxidants, unconsumed accelerator and accelerator fragments, vulcanisates were extracted with an azeotropic solvent consisting of 1,1,1-trichloroethane (60 mls), acetone (110 mls) and methanol (42 mls). Extraction was done in subdued light and in an atmosphere of nitrogen gas in a soxhlet extractor for 48 hours, at a temperature of about $50^{o}C$. The extracted vulcanisates were dried under vacuum at ambient temperature to constant weight and stored between aluminium foils in a vacuum desiccator in the dark until required.

4.4.2 Extraction of Rubber Films

Rubber films prepared as described in section 4.3 were extracted by methanol, when the antioxidant to be removed was a thiolamide and by n-hexane when the film contained BHBM. This involved subjecting the films (3×10^{-3} inch thickness) to continuous contact with a regulated stream of the appropriate solvent in an atmosphere of nitrogen gas in the soxhlet extractor. It was found that an 8 hour period of hot extraction was sufficient to completely remove all unbound antioxidants and by products of the grafting reaction. However, in this present work an extraction time of 24 hours was used to ensure complete removal of unbound antioxidant fragments.

4.5 Effect of BHBM and Thiolamide on the Curing Characteristics of NBR

To ensure that differences in the ageing behaviour of vulcanisates obtained using the same rubber and the same cure system was due to the antioxidants incorporated therein and not due to differences in their state of cure, it is essential to determine the effect of the thiol containing bound antioxidants on the vulcanisation of the nitrile rubber. The effect of the antioxidants on the curing characteristics of the nitrile rubber was investigated using the Monsanto Oscillating Disc Rheometer. The curve obtained from a Monsanto rheometer provides information regarding the curing characteristics of the rubber stock.

The Monsanto oscillating disc rheometer (model 100) used in this investigation, consisted of a biconical disc rotor, embedded in a cylindrical cavity in which the specimen is placed. The cavity and the specimen are maintained at a temperature of $\pm$ 0.5^{o}C by electric heaters regulated by thermistor controllers while the dies which form the cavity are held together by a force of 50 psi exerted by means of a ram operated by compressed air. The cavity is made up of two halves which open and close pneumatically. A motor driven eccentric oscillates the shaft of the bicononical disc sinusoidally. On the arm of the eccentric are mounted strain gauges which measure the force required to oscillate the disc. The torque applied to the disc and the resistance of the rubber to deformation cause a voltage, proportional to the stiffness of the rubber to be developed across the strain gauge. The resulting signal (imbalance in the strain gauge bridge circuit) is recorded directly on a potentiometric flat-bed recorder. In a typical Monsanto rheograph for a nitrile rubber stock, there is an initial drop in torque due to the decrease in the viscosity of the rubber as its temperature rises, this is followed by an induction period after which the torque increases steadily as curing proceeds. After a certain period of time, the torque reaches a maximum. In some cases, this maximum can further increase or decrease as an indication of secondary vulcanisation or a reversion respectively. Reversion can be caused by the breaking down of cross-links. A typical rheometer trace obtained with a Monsanto oscillating disc rheometer is shown in Fig 4.1.

It is thus possible to obtain a quantitative figure for the time to the onset of vulcanisation (induction period) based on an arbitrary number of units of torque above the minimum value, and for the rate of cure as assessed from the slope of the curve. However, a more accurate kinetic interpretation of the curve has been provided by Coran(109,110). The interpretation directly relates to the rate of change of cross-link density with time to the torque exerted by the oscillating rotor. If it is assumed that the cross-link formation is a first order reaction after the end of the induction period t_i, the rate of formation of cross-links is inversely proportional to the cross-link density. Since at full cure, the rate of formation of cross-links is zero, then

$$\frac{dv}{dt} = K\,(V_\infty - V_t) \qquad \ldots(a)$$

where K is the overall first order rate constant, V_∞ is the maximum cross-link density and V_t is the cross-link density at any time t. Thus on integration,

$$\int_{Vo}^{V_t} \frac{dv}{V_\infty - V_t} = K \int_{t_i}^{t} dt$$

hence

$$\ln \Big[V_\infty - V_t \Big]_{V_o}^{V_t} = K\Big[t\Big]_{t_i}^{t}$$

and

$$\ln \frac{V_\infty - V_t}{V_\infty} = K\,(t - t_i) \qquad \ldots(b)$$

Equation (b) thus describes the relationship between the cross link density and time in terms of the first order rate constant K. However, since torque developed (R) is a direct measure of cross-link density, equation (b) can be rewritten as:

$$\ln \frac{R_{max} - R_t}{R_{max}} = K\ (t - t_i)$$

or $$\log_{10} (R_{max} - R_t) = \log_{10} R_{max} + \frac{K}{2.303}\ (t - t_i)$$

Hence a plot of $\log_{10} (R_{max} - R_t)$ against time would have a slope of K/2.303 and an induction period of t_i, the time necessary for the reaction to become first order. A typical first order rate plot is shown in Fig 4.2.

The vulcanising system is therefore characterised by three parameters. (a) The overall first order rate constant K, (b) the maximum torque developed from R_{max}, which is a measure of cross-link density and (c) the induction period t_i which is a measure of time for formation of an active sulphurating species and the reaction of this with the hydrocarbon to form a rubber bound intermediate, the precursor to cross-link formation.

In the case of TMTD sulphurless vulcanisation system, the first order rate plot shows two rates, an initial rate (a) due to the primary mode of vulcanisation and a secondary rate (b) due to vulcanisation by ZDMC (111).

With regard to peroxide vulcanisation, which is a free radical reaction not involving the formation of rubber bound intermediates, t_i is a direct measure of the time for peroxide to undergo

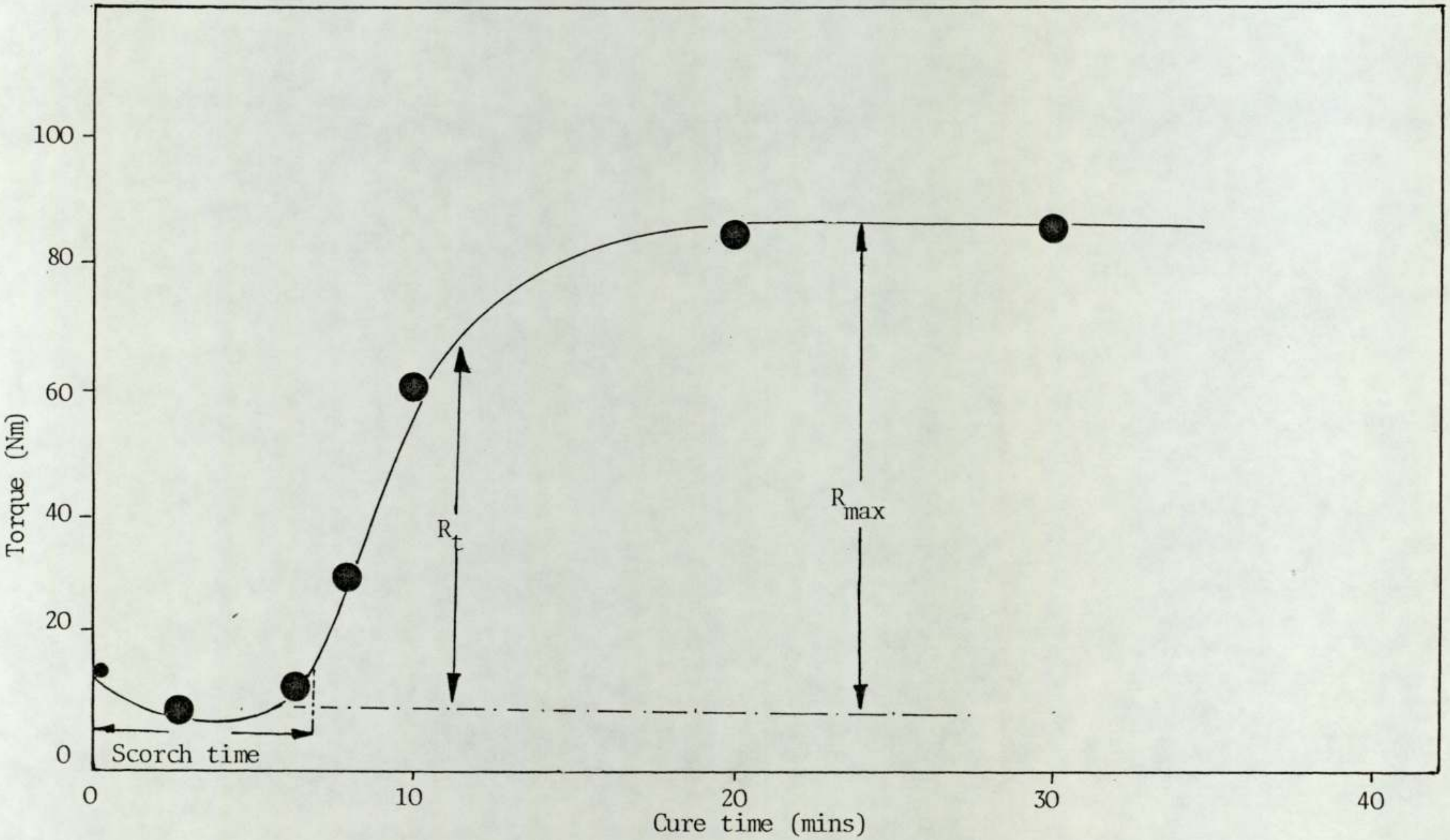


Fig 4.1 A typical Monsanto rheograph for vulcanisation of rubber

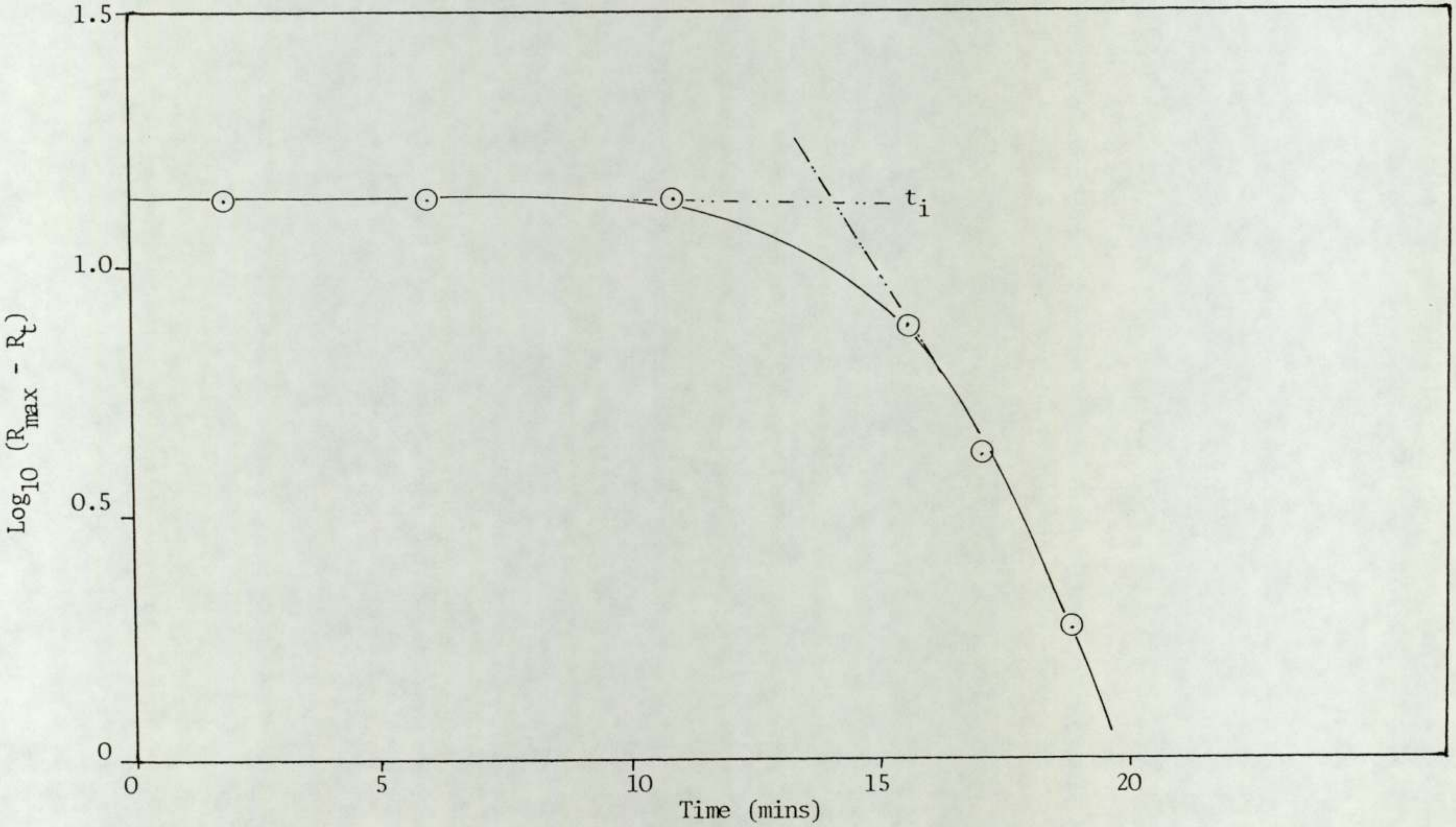


Fig 4.2 A typical curve of a plot of Log$_{10}$ (R$_{max}$ - R$_t$)

homolysis and to abstract labile hydrogens from the main chain. Since peroxide vulcanisation is normally performed at temperatures at which homolysis of peroxide is very rapid, and hydrogen abstraction is efficient, t_i is for most practical purposes zero.

4.5.1 Effect of Antioxidants on TMTD - Low Sulphur Cure of Nitrile Rubber

Vulcanisates produced by tetramethylthiuram disulphide (TMTD) cure system have been shown to consist mainly of mono and disulphide cross-links at optimum cure, and the major extra network material is ZDMC, which acts as a secondary accelerator(111,112) and also accounts for the good ageing resistance of such vulcanisates. However, antioxidants added during the compounding of the rubber may have some effect on the curing pattern of the rubber. Such effects are discussed in this section.

The effect of thiol-containing bound antioxidants (BHBM, PAPT and PPPT), high molecular weight antioxidant, Flectol H, at equimolar concentrations (8×10^{-3} mol/100 g DRC) on the cure of NBR with TMTD/low sulphur cure system at 168°C are compared in Figs 4.3 - 4.5 and Tables 4.2 and 4.3 with the commercially available copolymerisation produced bound amine antioxidant nitrile rubber (Chemigum 665 produced by Goodyear Co Ltd, the exact concentration of the antioxidant in Chemigum is not known, but it has been estimated to be about 2 - 3 phr). The effect of BHBM, PAPT and PPPT at different concentrations on various cure parameters are

Table 4.2 Effect of antioxidants on the cure of NBR with TMTD/S system at 168^{o}C

Antioxidant	Conc mol/100g NBR	ti (min)	K (min^{-1})	R_{max}	100% (min)
No additive	0	3	0.198	60	15
BHBM	0.008	4.3	0.227	57	15
PAPT	0.008	2.5	0.099	71	15
PPPT	0.008	2.5	0.106	70	15
Chemigum	0.008	3	0.158	60	15
Flectol H	0.008	3.5	0.201	58	15

Table 4.3 Effect of varying antioxidant concentration on the cure of NBR with TMTD/S system at 168^{o}C

Antioxidant	Conc mol/100g^{-1} NBR	ti (min)	K (min^{-1})	R_{max}	100% cure time (min)
No additive					
BHBM	0.001	3.9	0.208	58	15
PAPT	0.001	2.7	0.186	68	15
PPPT	0.001	2.7	0.192	65	15
BHBM	0.004	4.1	0.214	57	15
PAPT	0.004	2.6	0.165	69	15
PPPT	0.004	2.7	0.173	67	15
BHBM	0.008	4.3	0.227	57	15
PAPT	0.008	2.5	0.099	71	15
PPPT	0.008	2.5	0.106	70	15

also compared.

The parameters which have been affected are level of cure, rate of cure and to a lesser extent, the 'scorch time'. Generally, the thiol amide antioxidants (PAPT and PPPT) have increased the level and rate of cure and reduced the scorch time whereas the phenolic antioxidants BHBM and Flectol H, have both decreased the level of cure compared to the control sample containing no additive, but the scorch times are not affected to a very significant extent. Surprising though, Chemigum which contains the same amine moiety as PAPT showed a similar cure characteristic to the control sample. The increase in the level of cure caused by the thiol amine bound antioxidant is not unexpected since they are basic, they tend to accelerate cure whereas the phneolic antioxidant being acidic will have a retarding effect on the cure rate (see Figs 4.3 - 4.5). It is also observed that PAPT has a more marked effect on the rate of cure than PPPT which contains a similar functional group. In contrast to the behaviour of the BHBM and Flectol H, the thiol amine and PAPT in particular show a much greater effect on the rate of cure of NBR, causing a fast cure, increase in cross-link density and a slight reduction in 'scorch time'. BHBM caused the greatest decrease in modulus. And it thus appears that the thiol amides act as vulcanisation accelerators in this cure system and modify the mechanism so as to produce a much higher cross-link density in the final vulcanisate but the BHBM and the polymerised 1,2-dihydro-2,2,4-trimethyl quinoline did the opposite and were

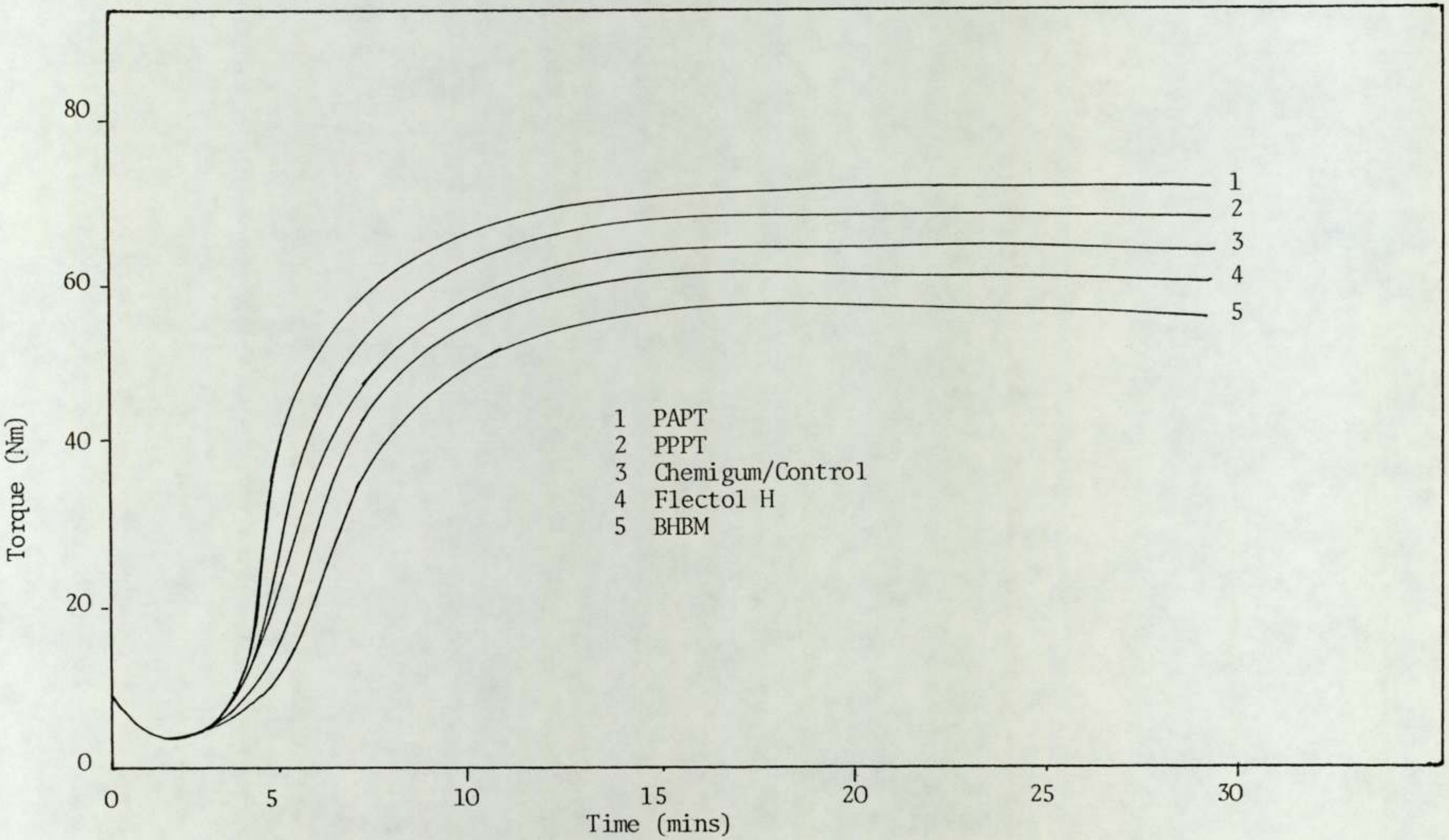


Fig 4.3 Effect of bound antioxidants (8×10^{-3} mol/100 g NBR) on curing characteristics of NBR (LM) TMTD/low-sulphur cure system at 168^{o}C

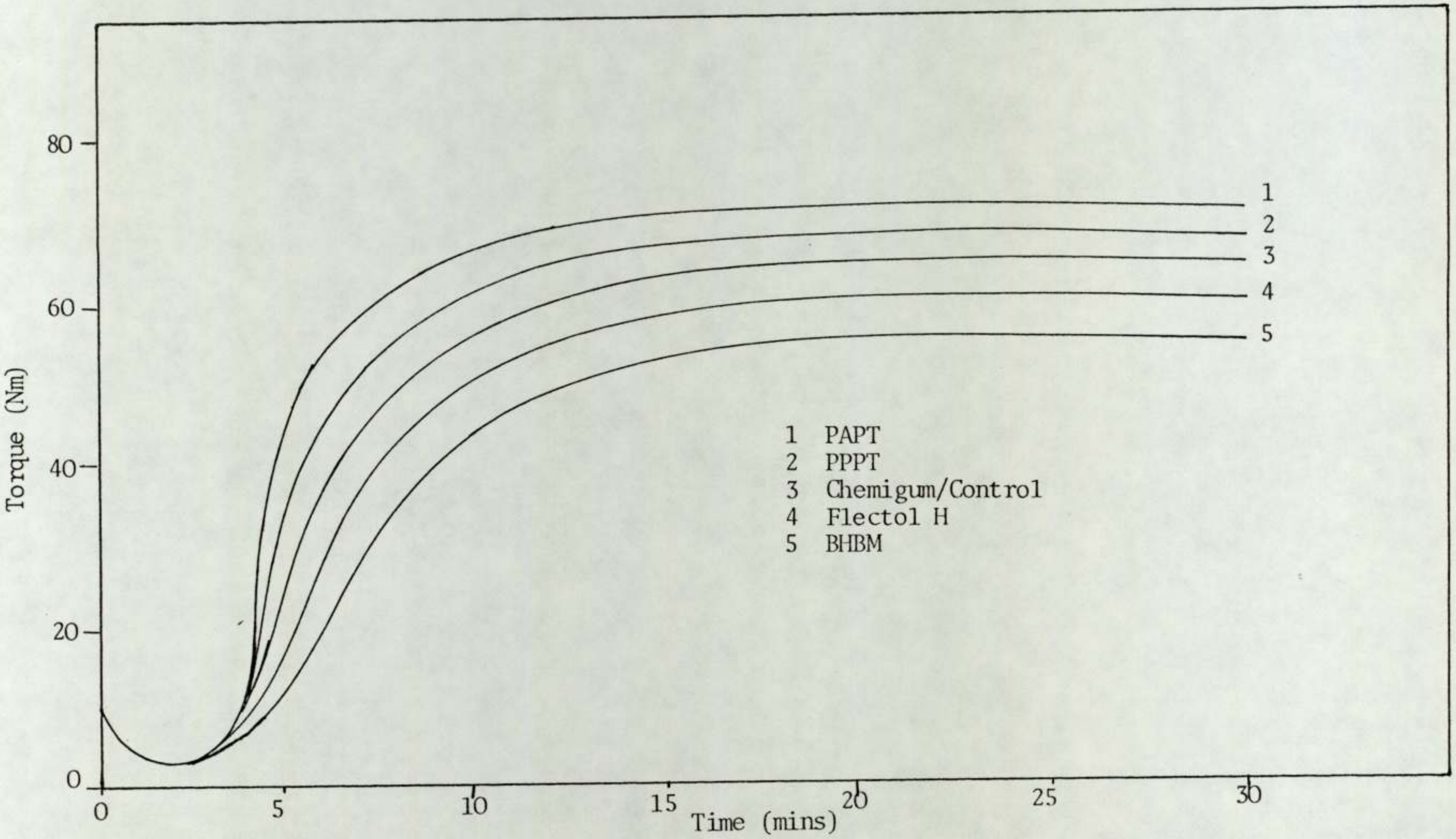


Fig 4.4 Effect of bound antioxidants (8×10^{-3} mol/100 g NBR) on the curing characteristics of NBR (MCM) TMTD/low sulphur cure system at 168°C

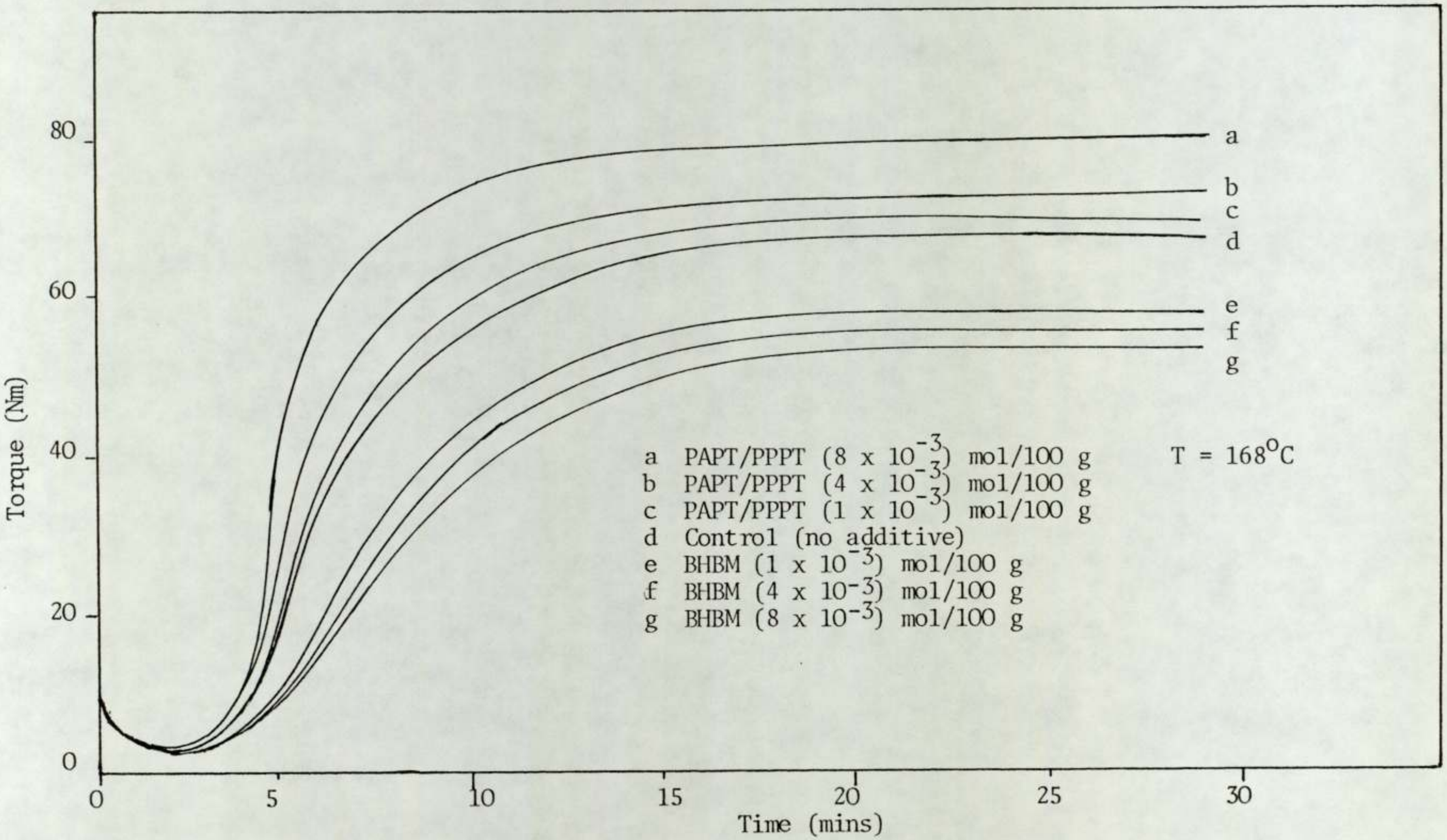


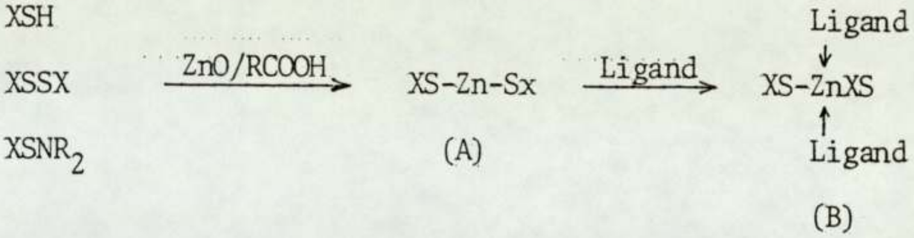
Fig 4.5 Effect of concentration of bound antioxidants on the curing characteristics of NBR at 168°C

probably least resistant to premature vulcanisation.

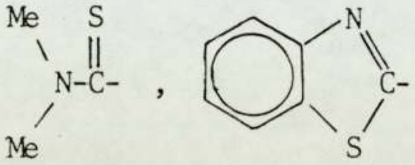
The effect of varying the concentrations of the antioxidants on the curing characteristics is shown in Fig 4.5 and Table 4.3. As the concentration of the thiol amide is increased, an increase in the cross-link density obtained occurs. BHBM on the other hand brings about a marginal further lowering of the cross-link density.

4.5.2 Discussion

Rubber technologists and chemists have given considerable attention to the mechanism of accelerated sulphur vulcanisation of diene elastomers and there appears to be different opinions as to the mechanism of this process. Some workers(113-117) proposed a free radical mechanism whilst the workers at MRPRA suggested that vulcanisation occurs through an ionic reaction(118,119). However, it is difficult to generalise since there is reason to believe that both free radical and ionic reactions are taking place simultaneously and, depending on the vulcanisation system, one or the other may predominate at different stages of the vulcanisation process(120-122). It has been widely accepted that the mechanism is predominantly ionic in nature as shown in the following scheme.

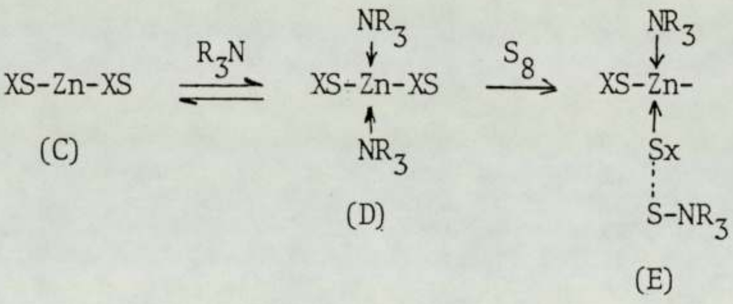


where: X =



etc

The reaction between the accelerator and activator with the findings of Krebs(123), in which zinc oxide is thought to take part in the formation of complexes and that complexes such as zinc dimethyldithiocarbamate (ZDMC) and zinc mercaptobenzthiazole (ZMBT) reacted with sulphur and amine as follows.

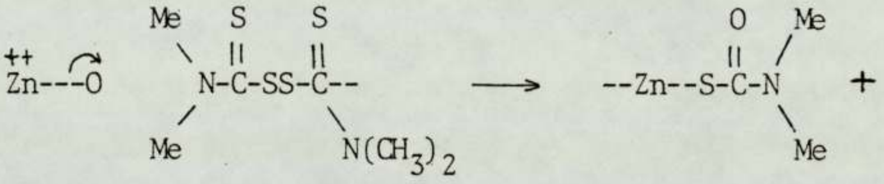


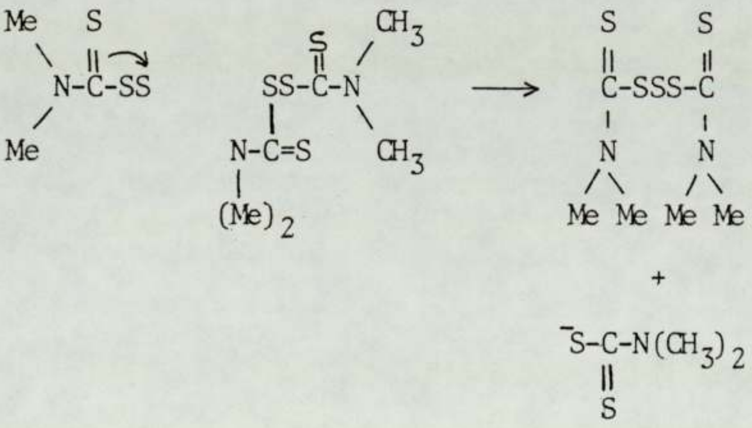
The reaction of the zinc accelerator complex with sulphur:

$$XSZnSX + S_8 \longrightarrow XSSxZnSxSX \quad (F)$$

There is no evidence to show that this step is involved in the mechanism. The persulphurated zinc salt (F) has not been isolated but it is thought by MRPRA workers to be formed in a series of equilibrium reaction which lies well on the side of the mercaptide complex (E) and free sulphur. Bateman$^{(118)}$ has advanced a mechanism for its formation and the complex itself is considered to be the active sulphurating agent.

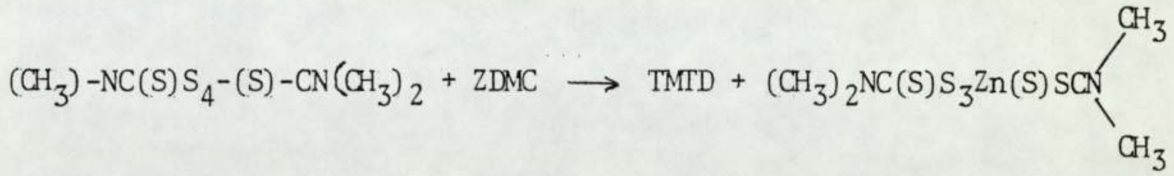
In the TMTD sulphurless vulcanising system, where there is initially no free sulphur, it is proposed that the complex (F) is formed by an interchange between thiuram polysulphides (TMTP) and ZDMC which are formed in an ionic reaction as follows.





The above reaction leads to the formal stoichiometry, nTMTD + $(n-1)\,ZnO = (CH_3)_2NC(S)SS_{n-1}SC(S)N(CH_3)_2 + \frac{1}{2}(n-1)\left[(CH_3)_2NC(S)O-\right]_2Zn + \frac{1}{2}(n-1)\left[(CH_3)_2-NC(S)S\right]_2Zn$.

The actual interchange reaction is:



$$(CH_3)\text{-}NC(S)S_4\text{-}(S)\text{-}CN(CH_3)_2 + ZDMC \longrightarrow TMTD + (CH_3)_2NC(S)S_3Zn(S)SCN\genfrac{}{}{0pt}{}{CH_3}{CH_3}$$

The mechanism involved in the TMTD alone and TMTD sulphur system is thought to be free radical since thiuram persulphenyl radicals were observed during the formation of TMTP as an intermediate of the thermal decomposition. Supporting evidence for thiuram and thiuram persulphenyl radicals was obtained from esr and in the presence of sulphur, cyclic carbon radicals $Me_2NC\,\cdot\,Sx$ were also detected. In the presence of zinc salts, a mixed ionic and free radical mechanism was postulated. The rapid ionic reaction as proposed by MRPRA, which yielded TMTP, was confirmed from Raman studies. Since these polysulphides are susceptible to cleavage at temperatures below that at which sulphide is cleaved, Coleman postulated the formation of thiuram persulphenyl radicals. Previous evidence has also shown these radicals to be reasonably stable(119). An overall reaction scheme was proposed as follows(124).

(i) $$\begin{array}{l} XSSX \\ XSSX + S_8 \end{array} \xrightarrow[145^{o}C]{\text{Free radical}} XS\cdot \;+\; XS_x\cdot$$

(ii) $$\begin{array}{l} XSSX + ZnO \\ XSSX + ZnO + S_8 \end{array} \xrightarrow[125^{o}C]{\text{Ionic}} XSxX \xrightarrow{\text{Thermolysis}} XS\cdot + XSx$$

(iii) $XSx\cdot(XS\cdot) + RH \rightleftharpoons R\cdot + XSxH(XSH) \xrightarrow{ZnO} ZDMC$

(iv) $R\cdot\ XSxX \longrightarrow RSyX + XS\cdot x{-}y$

(v) $R\cdot + XSx(XS\cdot) \longrightarrow RSxX(RSX)$

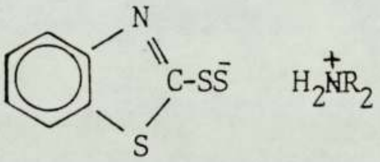
where $X = Me_2NC(S)-$

The free radical reaction leading to the formation of the rubber bound intermediate resembles that proposed by Bevilacqua(113), except that it allows for persulphurated rubber-bound intermediates necessary for the formation of polysulphide cross-links at a later stage of the reaction. It also resembles that proposed by MRPRA for homolysis of the zinc persulphurated complex, a mechanism later rejected(118). Although step (iii) is reversible, and is known to favour the thiyl radical, any R· formed would have the possibility of being trapped by reaction with TMTP (XSxS). This would be enhanced in the presence of zinc oxide since step (iii) would then favour the formation of R·. The mechanism is thus consistent with the results of Manik and Banerjee(120) and Shelton and McDonel(121). The results are also consistent with the findings of Wolfe(122) and Parks and co-workers(125) who showed that rubber bound intermediates were formed in the absence of zinc salts. In addition, there was no evidence from Raman studies for the zinc perthiomercaptide complex (vi), which was proposed by MRPRA to be the active sulphurating species, which leads to the formation of the rubber bound intermediate.

The above review of accelerated sulphur vulcanisation, much of which has been centred around the TMTD sulphurless vulcanising system, thus shows that the mechanism by which it is involved has still not be resolved and there are many conflicting views as to the formation of the rubber bound intermediate. However, irrespective of its mechanism of formation, it is now generally accepted as the precursor to the formation of cross-links.

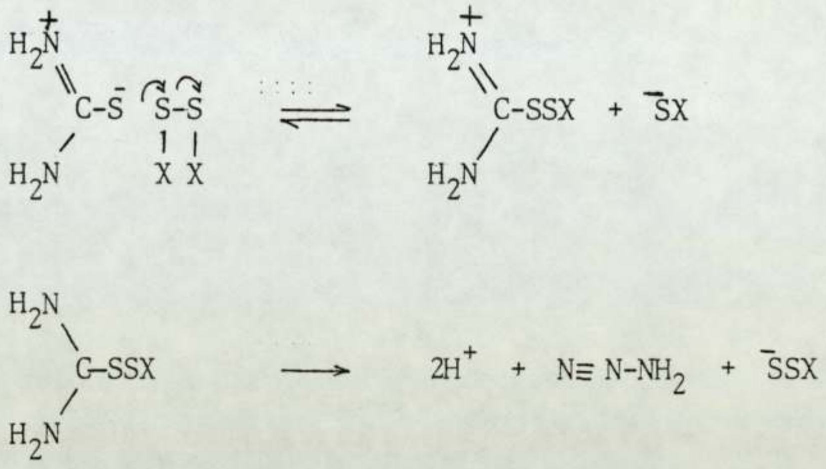
As mentioned earlier, the thiol amide bound antioxidants increase the level of cure in all cases whilst BHBM decreases it. The explanation for these differences in behaviour may lie in the fact that certain sulphur compounds are known to act as activators of premature vulcanisation as well as inhibitors of vulcanisation, a trend which is followed by BHBM. The ultimate torque R_{max} which is a direct measure of the cross-link density, decreased steadily but slowly as the concentration is increased; an indication of increased chemical interaction between the gumstock and the mercaptan. The thiol amides on the other hand, increased the rate of cure and produced a much higher cross-link density than the control sample.

The resulting lower cross-link density observed in samples containing BHBM may be attributed to the influence of the radical trapping ability of the compound which may also influence the formation of the rubber bound intermediates but it must be appreciated that their formation does not inhibit this process otherwise there would not have been cross-linking at all. In the thiol amides, it appears an additional mechanism, which predominates, is responsible for the higher level of cure. It is known that nitroxyl radical may be formed, so also are thiyl radicals, both of which could have led to the reduction of cure level and may be interpreted as radical trapping behaviour. But the acceleration effect could be due to the ability of the para-aryl-amino diphenyl group to act as a reducing agent for the cleavage of the S-N bond of the accelerator and also the involvement of the amino group in the formation of the amino salt in the presence of liberated hydrogen sulphide and they may



also be involved in the formation of complex (F) which accelerates the formation of persulphurated zinc salt and the subsequent reactions of the salt with the rubber hydrocarbon. However, there is some doubts whether this is true since Chemigum did not behave similarly.

The result obtained with the thiolamide may be compared with the investigation of Duchacek(126) on the effect of thiourea on the kinetics of TMTD vulcanisation. He suggested an interchange between thiuram polysulphides and ZDMC and that the action of thiourea as an accelerator could be attributed to its ability to undergo an interchange reaction in a similar way to ZDMC, to give a second source of perthioanions:



where X = $(CH_3)_2$-N-C(=S)-

It was also postulated that the formation of rubber bound intermediates was by a free radical process in accordance with the theories of Bevilacqua(113) and Scheele(117). It is difficult to see how thiol amides and BHBM could participate in an interchange with thiuram polysulphides in a similar way to that postulated for ZDMC and thiourea, since the antioxidants were bound into the polymer chain through their sulphur atoms and the sulphur atom is no longer free to be donated. But it is possible that there is cleavage of the S-C link during vulcanisation or sulphur atoms of the unextracted unbound antioxidant reacted as outlined.

The role of the free thiol group (-SH) as a reducing agent cannot be over-emphasised. It is this reducing ability in the presence of an amine group that leads to the accelerating activity of the thiol amides (PAPT and PPPT) whereas the reduction in the cure level of the BHBM containing samples and that of Flectol H may be due to the formation of radicals derived from this compound during the curing process. These radicals may therefore act as free radical traps for the radicals produced by the vulcanising system as described by Coleman and co-workers(127).

In the case of BHBM thiyl radicals are mainly involved whereas both thiyl and nitroxyl radicals are produced in the case of PAPT and PPPT. And all these radicals are potentially capable of trapping radicals produced by the vulcanising system.

4.6 Oxygen Absorption Test

An important technique for studying antioxidants is the measurement of the rate of oxygen absorption by the polymer in their presence. Oxygen absorption is meaningful as a practical test only in so far as it can be related to changes in physical properties of the elastomer.

Shelton and co-workers(128) related the volume of oxygen absorbed to the tensile strength of SBR and NR. The correlation of changes in properties with the amount of oxygen absorbed at a given temperature were quite good, and it was found(129) that the modulus is much more sensitive than the tensile strength to the relative amounts of chain scission and cross-linking.

During the process of oxygen absorption by vulcanisates, two main factors control the rate of oxidation, viz:

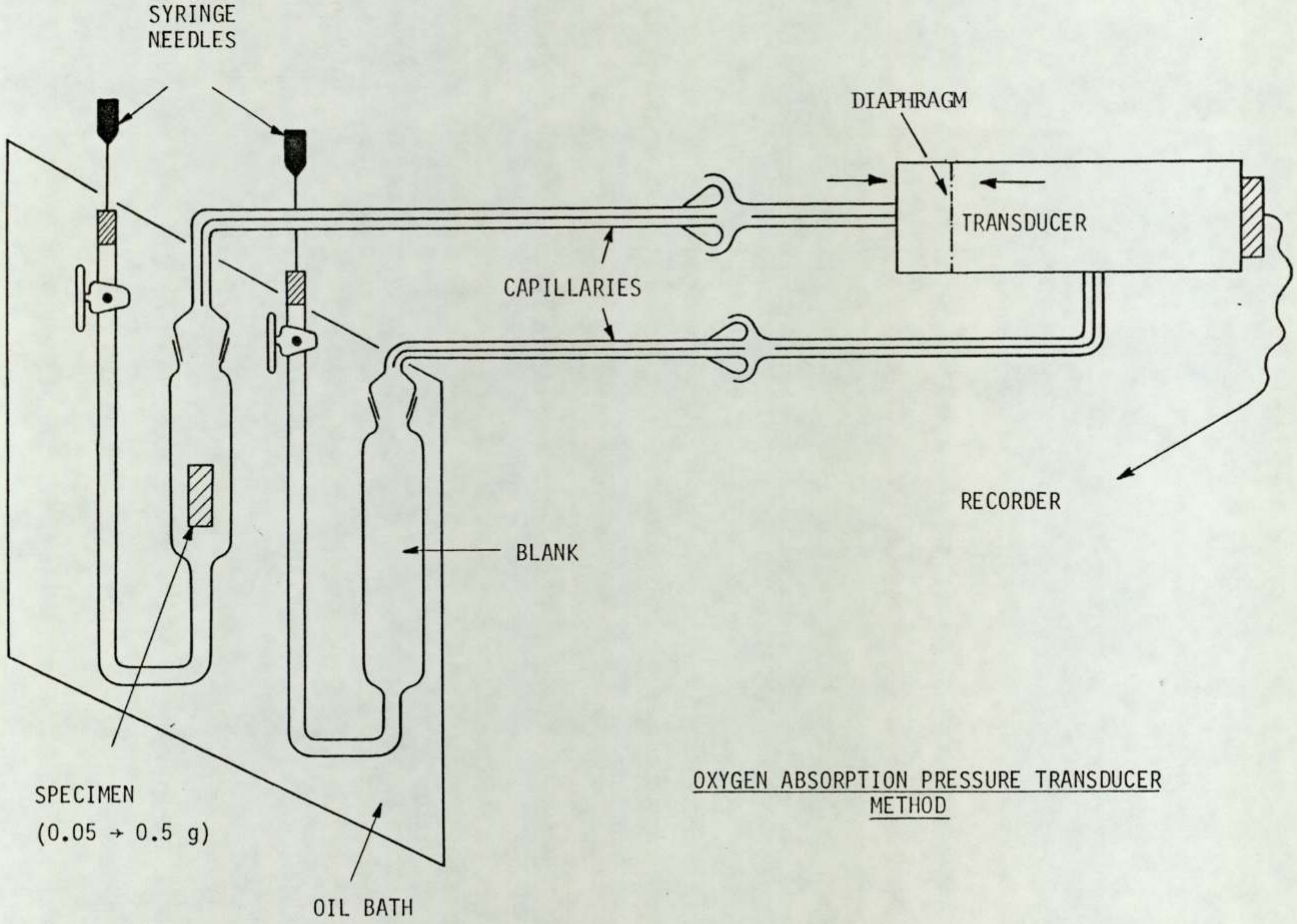
(i) the rate at which oxygen can diffuse into the sample,

(ii) the rate at which oxygen reacts with the vulcanisate.

Since the rate at which oxidation takes place at room temperature is slow, the chemical reaction becomes the rate controlling step but at higher temperatures, the rate of diffusion of oxygen into the sample may become rate determining, depending on the thickness of the vulcanisate. It is therefore very necessary to use samples in which diffusion control does not occur. Consequently, it is necessary to control the sample thickness, the temperature at which the reaction is taking place and the concentration of oxygen.

The various ways by which oxygen absorption can be measured and the different apparatus used are described in the literature(130-133). In the present work, the absorption of oxygen by vulcanisates was monitored continuously and automatically by means of a strain gauge type pressure transducer (Pye Ether Limited, Model UP3, 5 psi range). This was connected to an absorption vessel containing the sample and a ballast vessel of corresponding dimensions. The vessels were placed side by side in a thermostatted oil bath (150 ± 0.5°C) (see Fig 4.6A).

As oxygen was absorbed by the vulcanisate, a pressure difference



<u>OXYGEN ABSORPTION PRESSURE TRANSDUCER METHOD</u>

Fig 4.6A

developed between the two vessels, proportional to the output voltage of the transducer. The latter was recorded using a Perkin Elmer Model 165 recorder. The system was calibrated by withdrawing a known volume of oxygen and the corresponding deflection on the recorder recorded. Calibration checks were made at the end of each run.

4.6·1 Procedure

0.2 - 0.3 g of the vulcanisate was carefully weighed and the thickness of the sample was about 0.008 inch. The sample was placed on a glass clip as shown in Fig 4. so that oxygen was able to diffuse freely on to both surfaces. The glass clip and the content were carefully transferred into the absorption vessel and the apparatus assembled using a small amount of silicone grease to ensure that the apparatus was air tight. The absorption vessel was purged with oxygen and then placed in the thermostatted oil bath and connected to the transducer, to which the ballast vessel had already been attached. The vessels were left for about 5 minutes so that both temperature and pressure in both vessels could be equilibrated by venting both to the atmosphere through the luer needle attachments. The samples were then left to absorb oxygen. The maximum pressure change which was allowed to occur was of the order of 5% and hence it was assumed that this change would not affect the kinetics of the oxidation process.

4.6.2 Results and Discussion

4.6.2.1 Introduction

Oxygen absorption studies provide a useful means of evaluating the extent to which an antioxidant can protect a rubber vulcanisate and since this test is carried out in a closed system, factors such as antioxidant volatility which can reduce the effectiveness of the antioxidant below that which would be expected from the inherent antioxidant activity determined in liquid model systems, can be eliminated.

Although the mobility of antioxidant within the polymer and the ability to migrate to the point of oxygen attack have been assumed not to be significantly affected, however, such factors may be important in the case of rubber bound antioxidants, where mobility is restricted, but this has been shown to be unimportant with very efficient antioxidants such as bound p-phenylenediamine(134).

In the present work, the degree to which the vulcanisates were protected by the bound antioxidants was assessed by extracting unbound antioxidant as described in section 4.4.1 and examining the absorption of oxygen by such vulcanisates compared to an unextracted vulcanisate and to control samples (see Table 4.1). As earlier mentioned, all masterbatches were diluted to concentrations 1, 4 and 8 x 10^{-3} mol antioxidant per 100 g NBR before compounding and vulcanising.

4.6.2.2 Discussion

The results of the oxygen absorption test with vulcanisates prepared from latex masterbatches are shown in Figs 4.6 - 4.30 and the times to absorb 1% by weight of oxygen are given in Tables 4.4 - 4.6.

In all the masterbatches, the resistance of the antioxidants increased as the concentration increased (ie 0.25% < 1% < 2%). Although it was possible to bind BHBM at all masterbatch concentrations employed in this present work, PAPT could not be bound below a concentration of 5 g/100 g NBR (DRC) in the latex and above 30 g/100 g NBR (DRC). Precoagulation (latex coagulated during reaction) was a major problem and as a result the work on PAPT has been based on samples produced from the 10, 20 and 30% masterbatches. PPPT did not bind to any appreciable level.

From the test results, only the vulcanisates produced from the 2o% PAPT masterbatch gave a good level of activity in all tests. In the case of BHBM, the optimum lies between the 10% and the 20% masterbatch and for comparison with PAPT, the 20% masterbatches have been evaluated in some tests with both compounds.

The results that emerged from the oxygen absorption tests show that all the samples give induction periods of between 5 hours in the extracted samples to about 22 hours in the unextracted samples. It is also clear that the unextracted samples show more

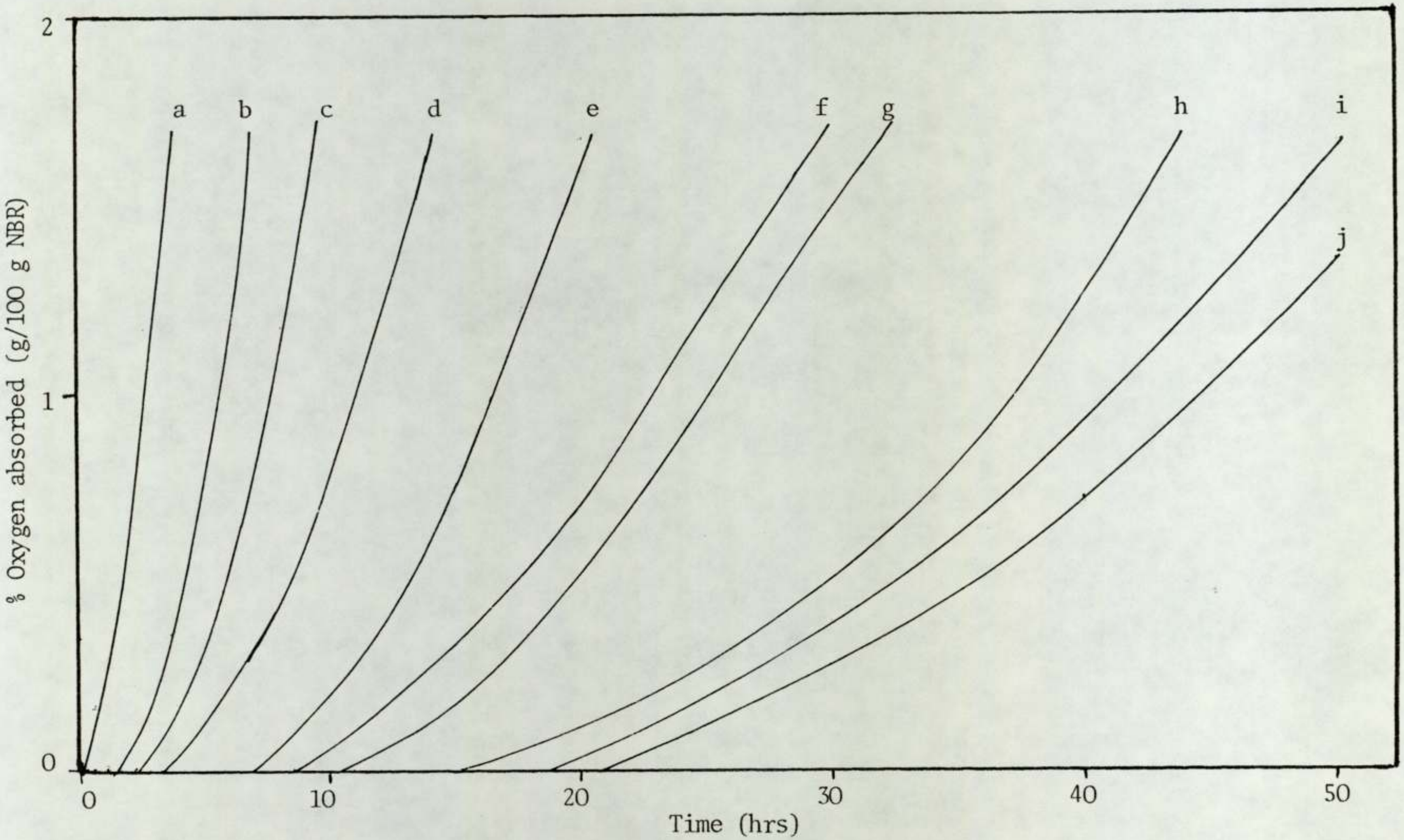


Fig 4.6 Oxygen absorption of latex diluted 1% BHBM LM at 150^{O}C. a - control(ex); b - control(unex); c - Flectol-H(ex); d - 0.25%(ex); e - 0.25%(unex); f ; 1%(ex); g - 1%(unex); h - Flectol H(unex); i - Chemigum(ex); j - Chemigum(unex)

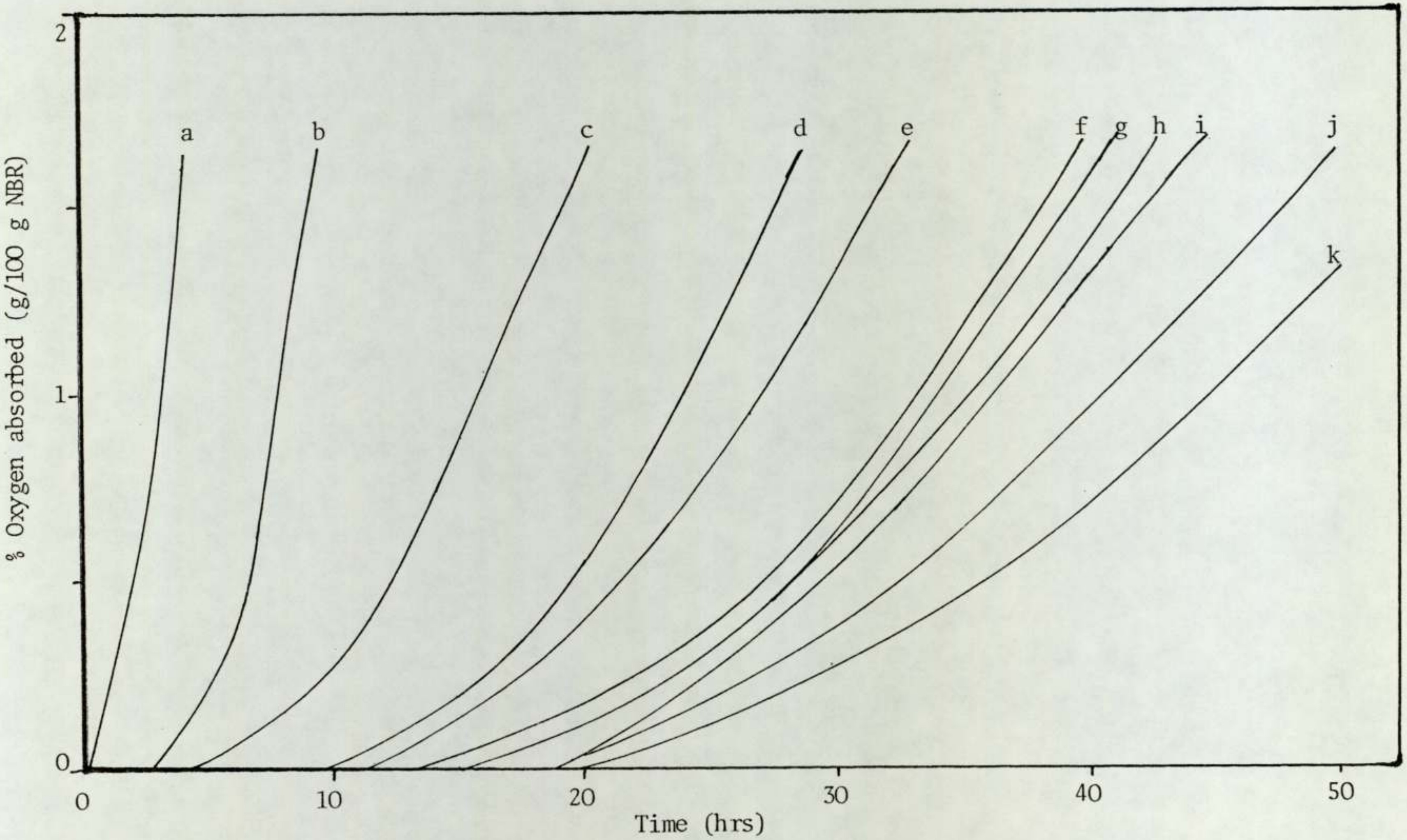


Fig 4.7 Oxygen absorption of latex diluted 10% BHBM LM at 150°C. a - control; b - Flectol h(ex); c - 0.25%(ex); d - 0.25%(unex); e - 1%(ex); f - 2%(ex); g - 1%(unex); h - Flectol H(unex); i - 2%(unex); j - Chemigum(unex); k - Chemigum(ex)

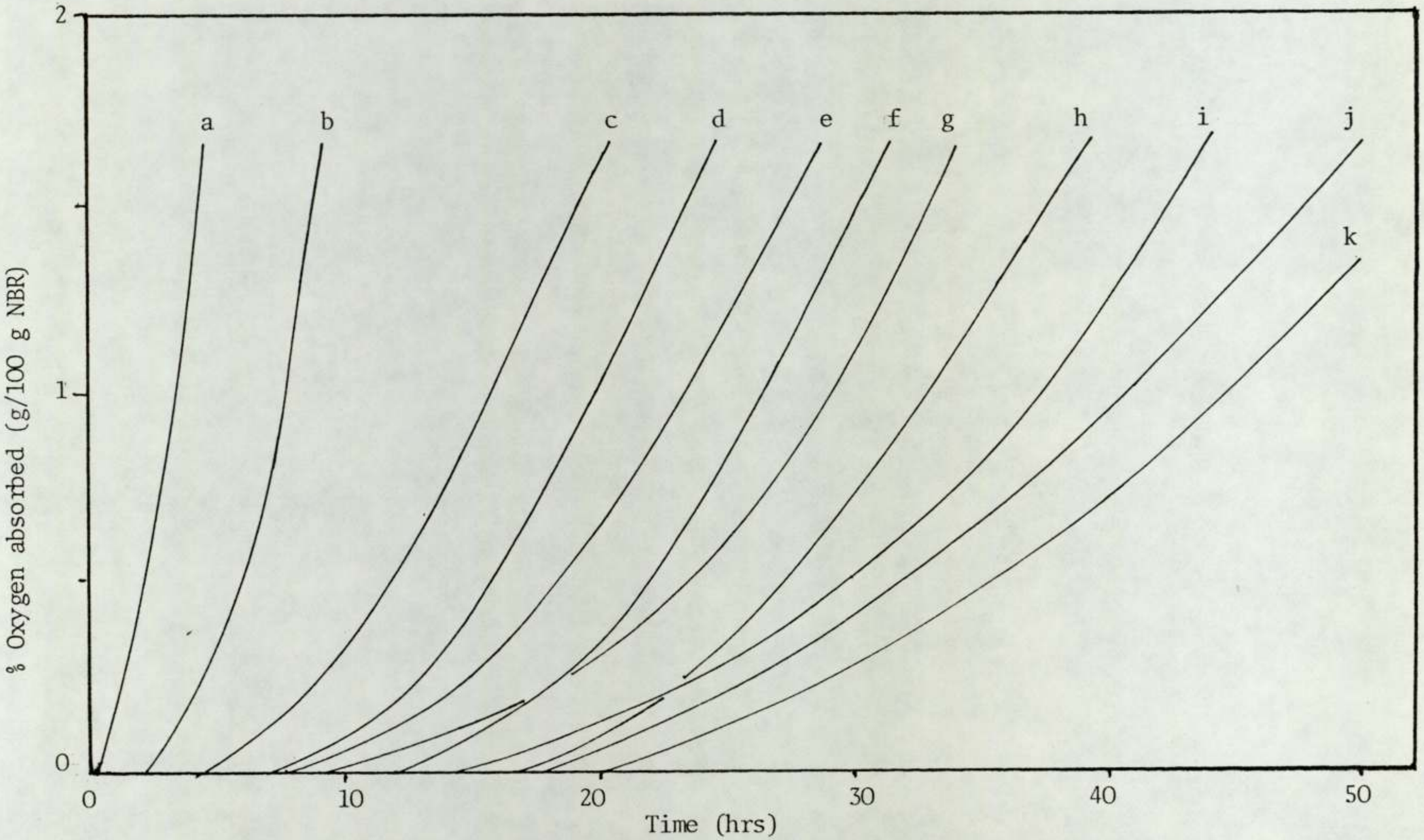


Fig 4.8 Oxygen absorption of latex diluted 20% BHBM LM at 150^{O}C. a - control; b - Flectol H(ex); c - 0.25%(ex); d - 0.25%(unex); e - 1%(ex); f - 1%(unex); g - 2%(ex); h - 2%(unex); i - Flectol H(unex); j - Chemigum(ex); k - Chemigum(unex)

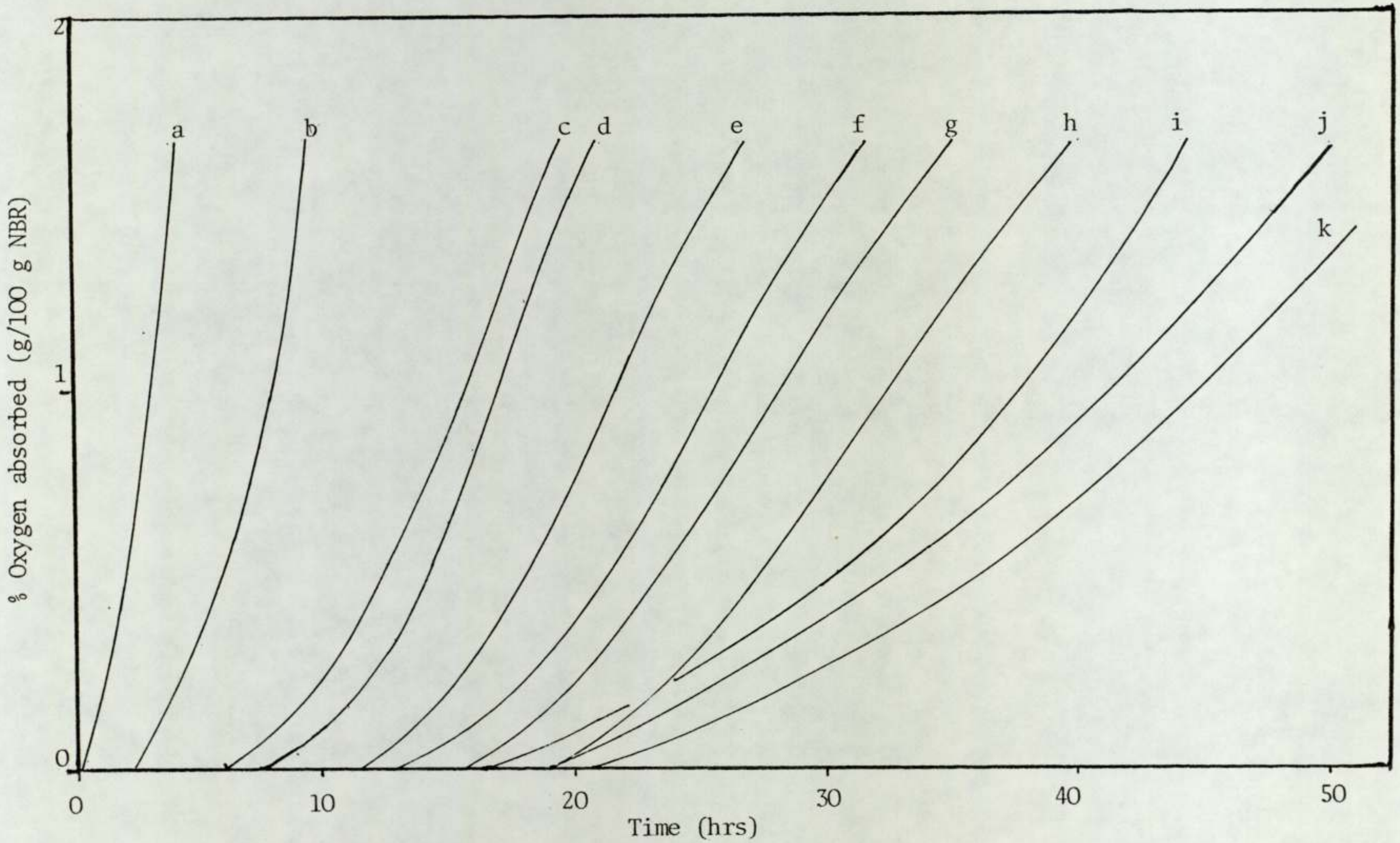


Fig 4.9 Oxygen absorption of latex diluted 30% BHBM LM at 150°C. a - control; b - Flectol H(ex); c - 0.25%(ex); d - 1%(ex); e - 0.25%(unex); f - 2%(ex); g - 1%(unex); h - 2%(unex); i - Flectol H(unex); j - Chemigum(ex); k - Chemigum(unex)

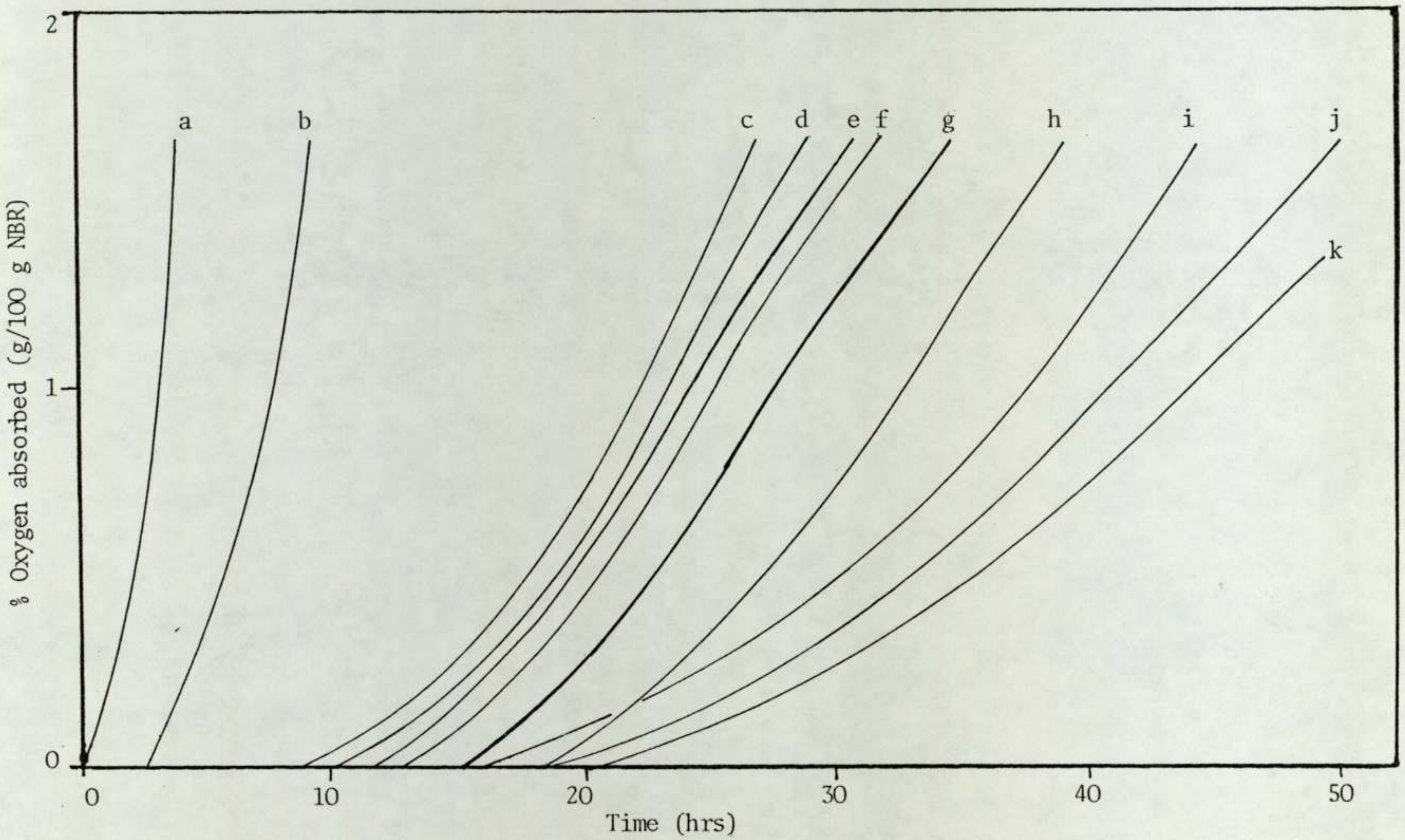


Fig 4.10 Oxygen absorption of latex diluted 40% BHBM LM at 150°C. a - control; b - Flectol H(ex); c - 0.25%(ex); d - 1%(ex); e - 0.25%(unex); f - 2%(ex); g - 1%(unex); h - 2%(unex); i - Flectol H(unex); j - Chemigum(ex); k - Chemigum(unex)

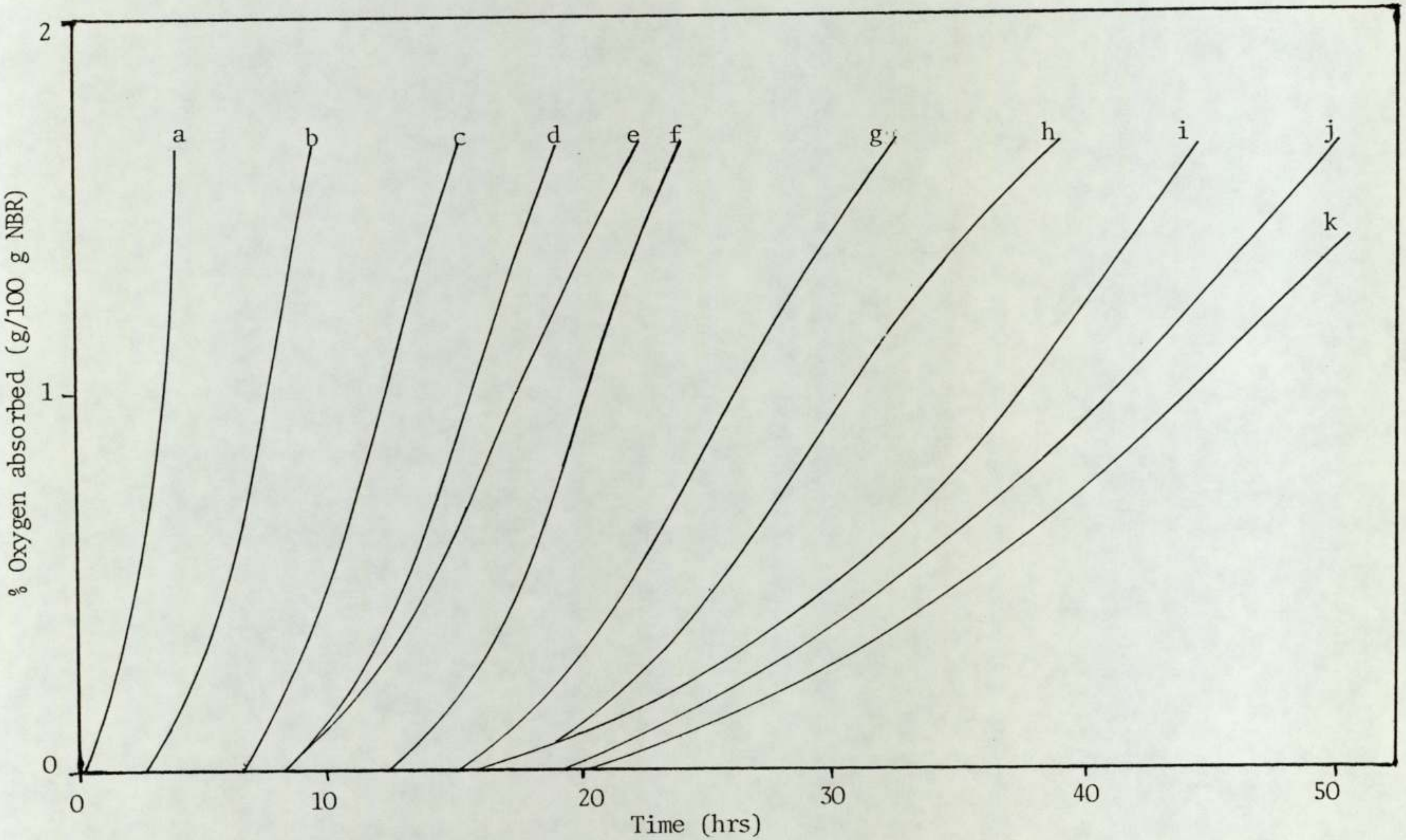


Fig 4.11 Oxygen absorption of latex diluted 50% BHBM LM at 150^{O}C. a - control; b - Flectol H(ex); c - 0.25%(ex); d - 0.25%(unex); e - 1%(ex); f - 2%(ex); g - 1%(unex); h - 2%(unex); i - Flectol H(unex); j - Chemigum(ex); k - Chemigum(unex)

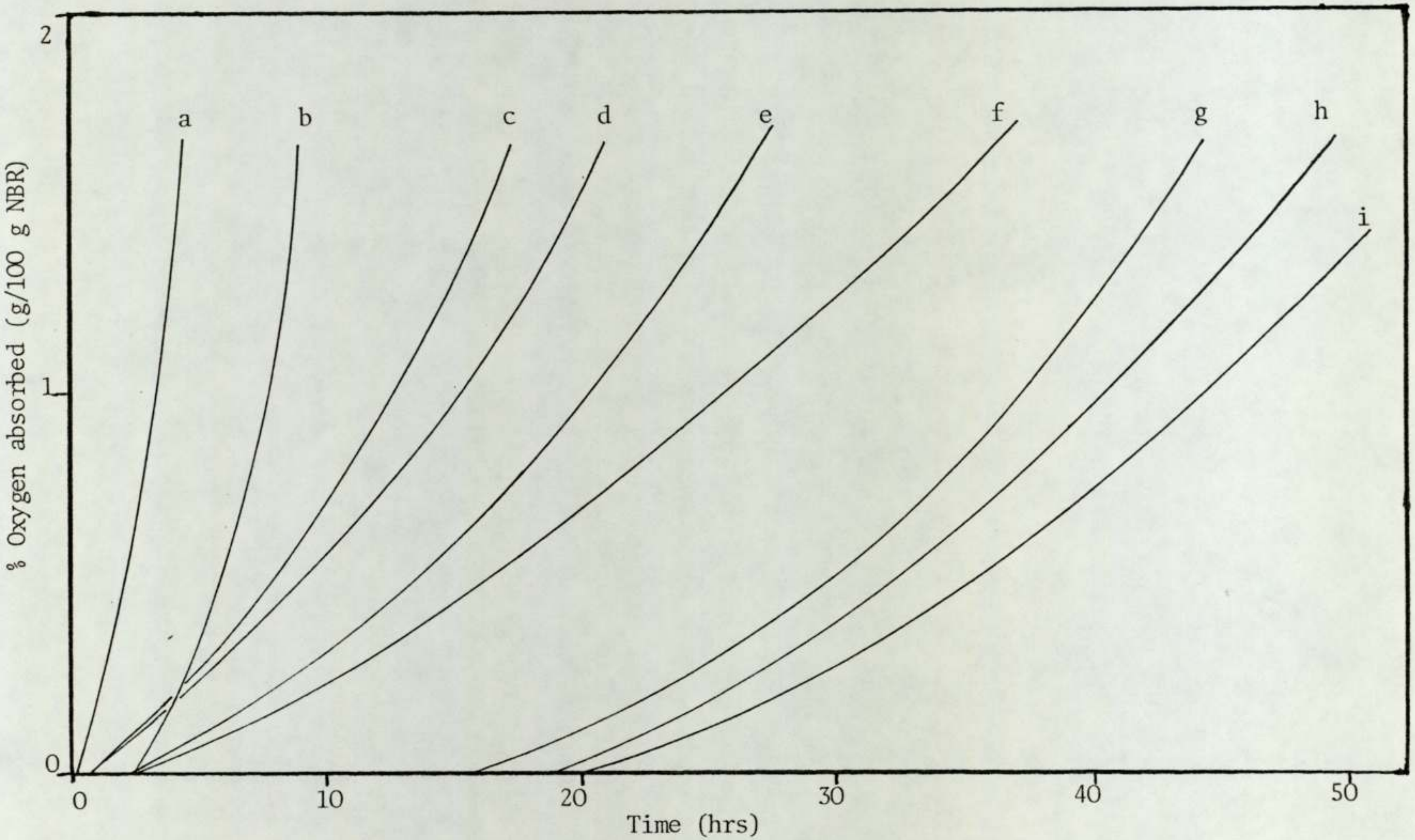


Fig 4.12 Oxygen absorption of rubber diluted 1% BHBM LMCU at 150°C. a - control; b - Flectol H(ex); c - 0.25%(ex); d - 0.25(unex); e - 1%(ex); f - 1%(unex); g - Flectol H(unex); h - Chemigum(ex); i - Chemigum(unex)

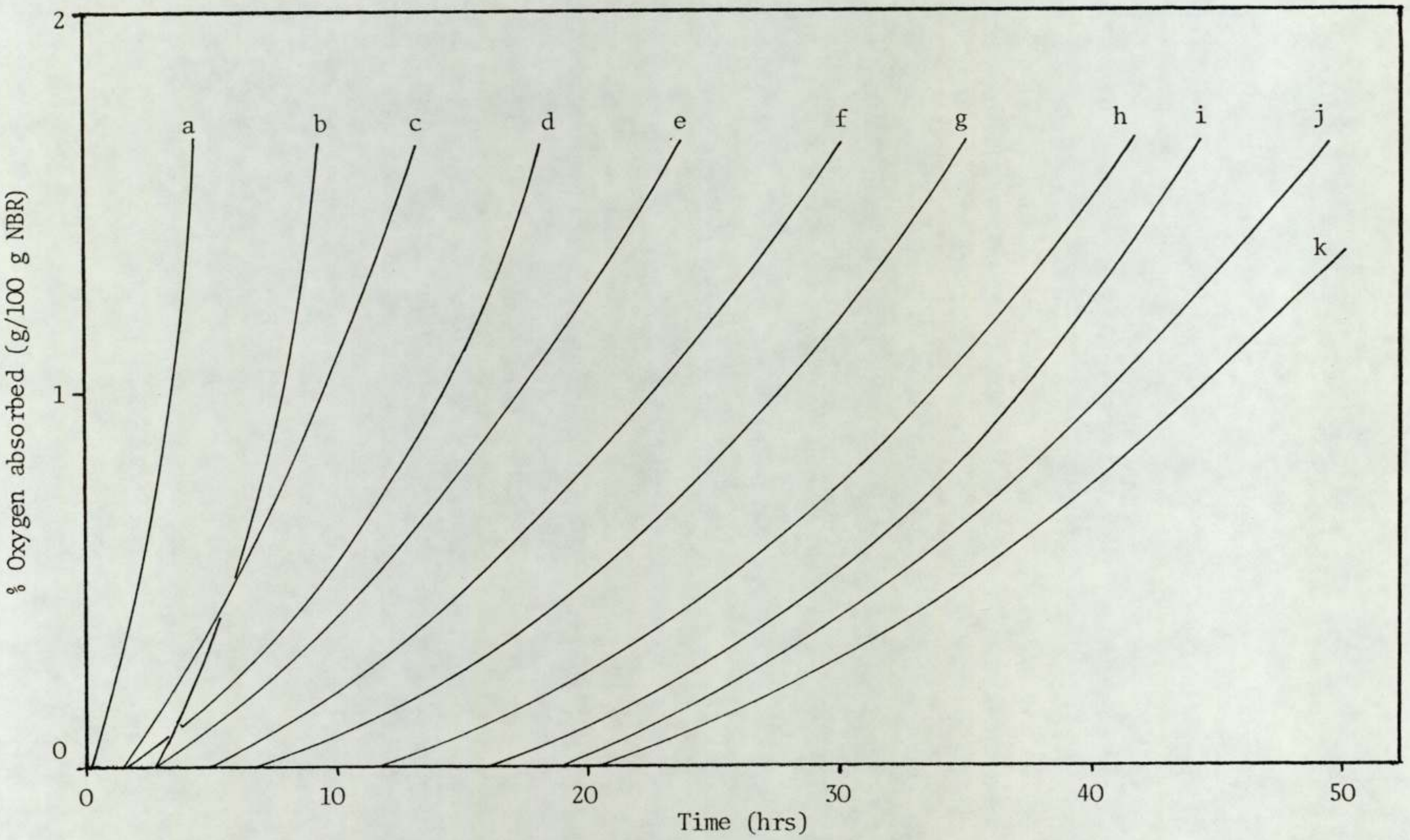


Fig 4.13 Oxygen absorption of rubber diluted 10% BHBM LMCU at 150°C. a - control; b - Flectol H(ex); c - 0.25%(ex); d - 0.25%(unex); e - 1%(ex); f - 2%(ex); g - 1%(unex); h - 2%(unex); i - Flectol H(unex); j - Chemigum(ex); k - Chemigum(unex)

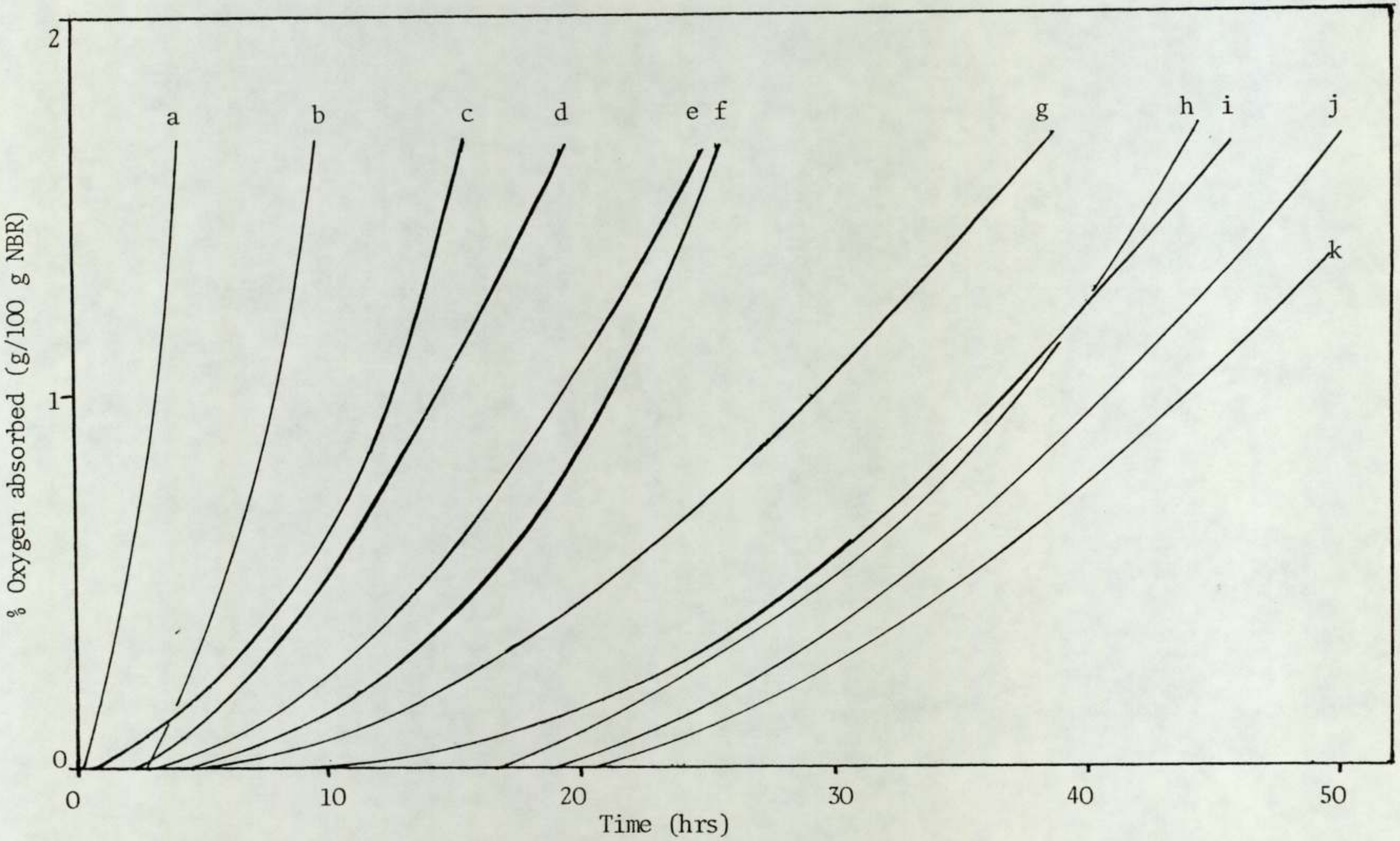


Fig 4.14 Oxygen absorption of rubber diluted 20% BHBM LMCU at 150^{o}C. a - control; b - Flectol H(ex); c - 0.25%(ex); d - 1%(ex); e - 0.25%(unex); f - 2%(ex); g - 1%(unex); h - Flectol H(unex); i - 2%(unex); j - Chemigum(ex); k - Chemigum(unex)

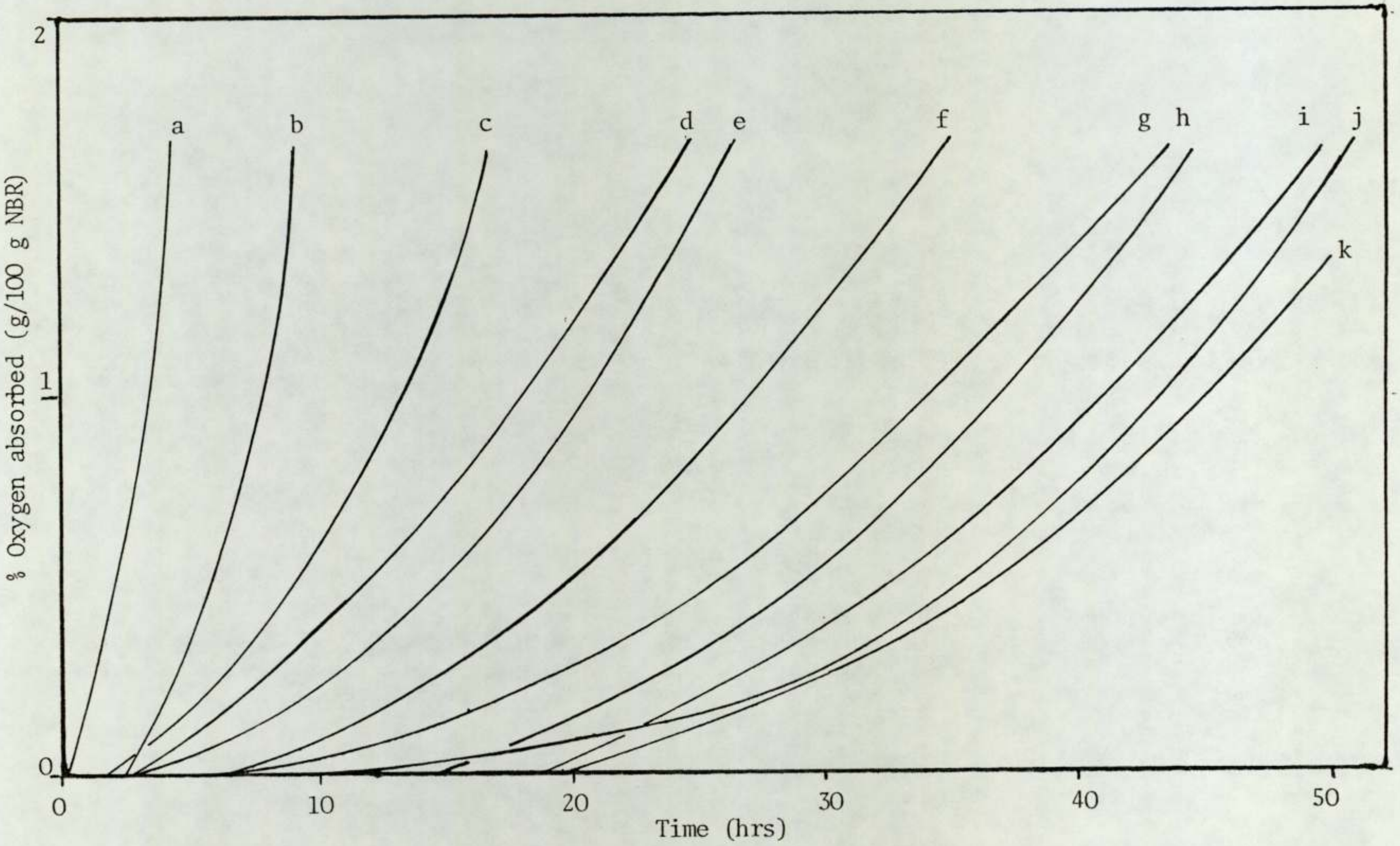


Fig 4.15 Oxygen absorption of rubber diluted 30% BHBM LMCU at 150^{O}C. a - control; b - Flectol H(ex); c - 0.25%(ex); d - 1%(ex); e - 0.25%(unex); f - 2%(ex); g - 1%(unex); h - Flectol H(unex); i - Chemigum(ex); j - 2%(unex); k - Chemigum(unex)

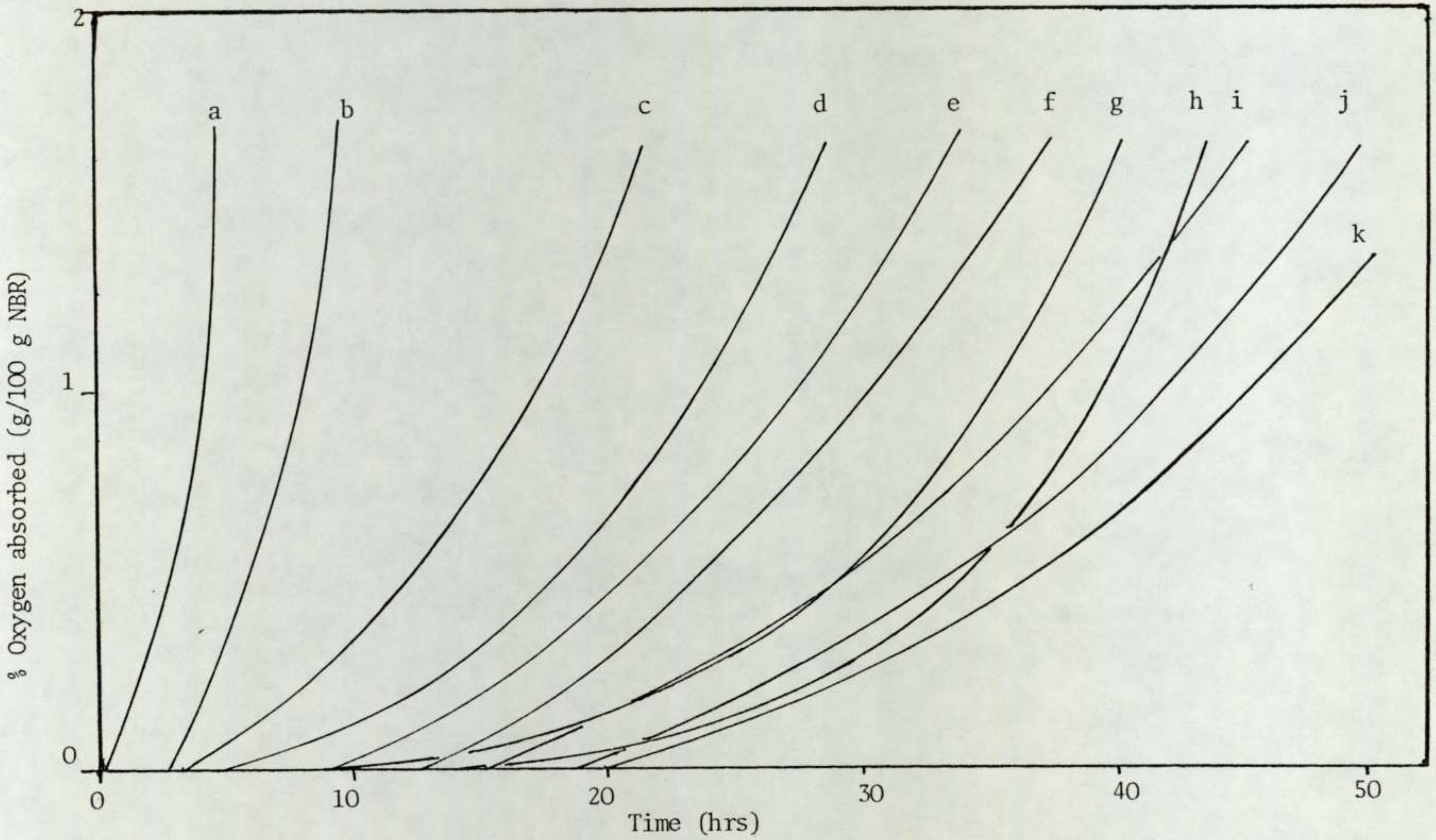


Fig 4.15A Oxygen absorption of rubber diluted 40% (50%) BHBM LMCU at 150^{o}C. a - control; b - Flectol H(ex); c - 0.25%(ex); d - 0.25%(unex); e - 1%(ex); f - 2%(ex); g - 1%(unex); h - 2%(unex); i - Flectol H(unex); j - Chemigum(ex); k - Chemigum(unex)

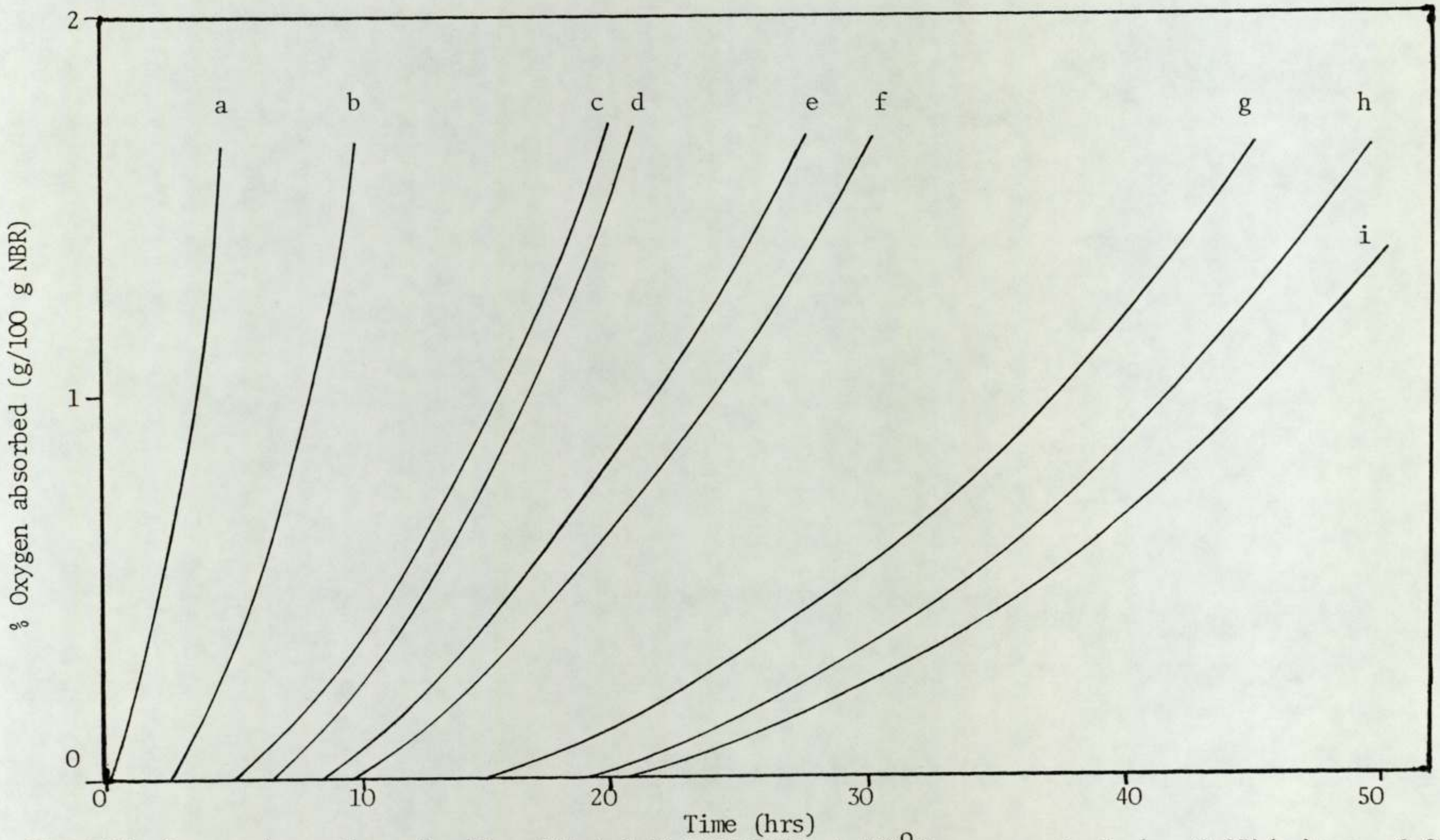


Fig 4.16 Oxygen absorption of rubber diluted 1% BHBM LMCE at 150^{o}C. a - control; b - 0.25%(ex); c - 0.25%(unex); d - Flectol H(ex); e - 1%(ex); f - 1%(unex); g - Flectol H(ex); h - Chemigum(ex); i - Chemigum(unex)

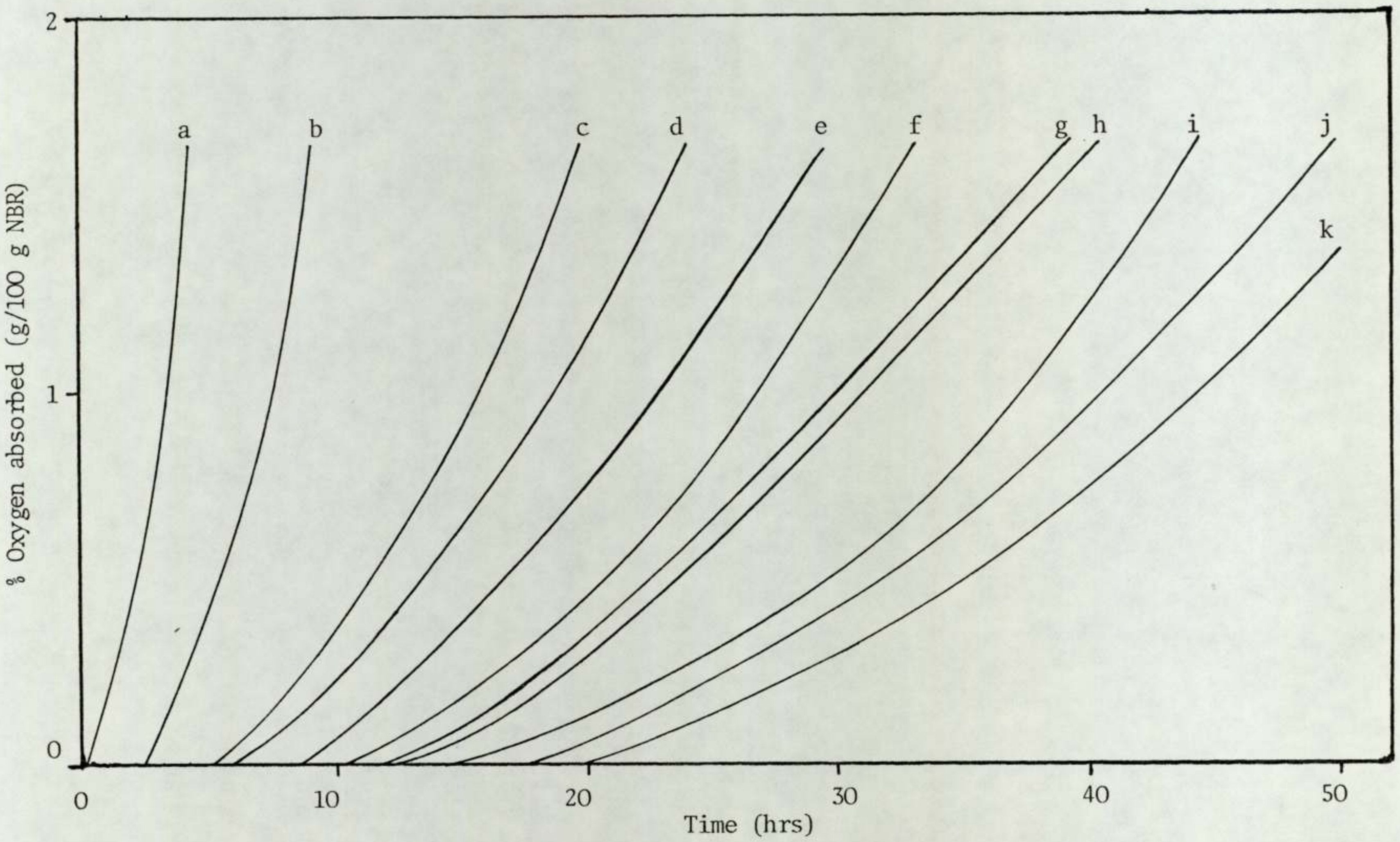


Fig 4.17 Oxygen absorption of rubber diluted 10% BHBM LMCE at 150°C. a - control; b - Flectol H(ex); c - 0.25%(ex); d - 0.25%(unex); e - 1%(ex); f - 1%(unex); g - 2%(ex); h - 2%(unex); i - Flectol H(unex); j - Chemigum(ex); k - Chemigum(unex)

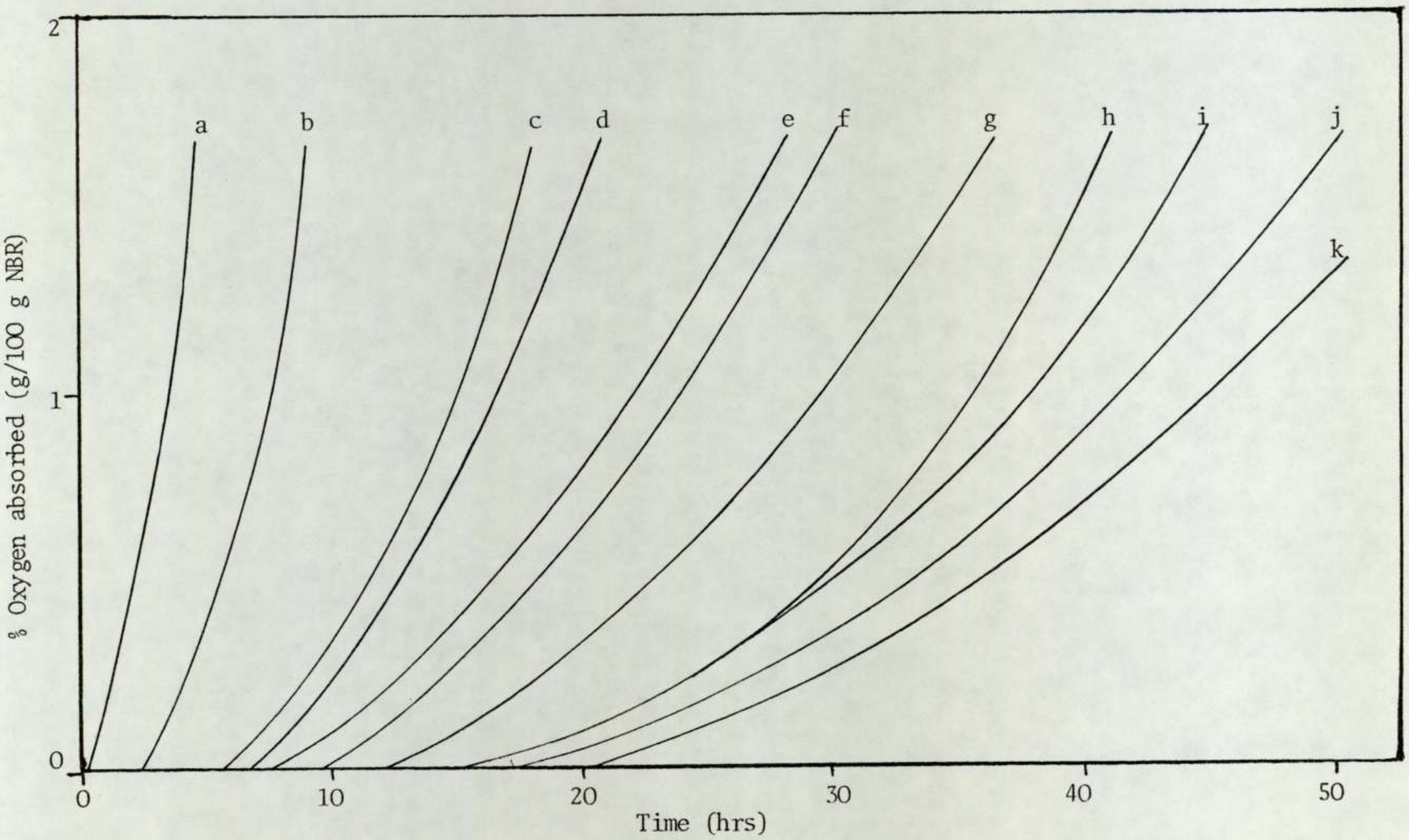


Fig 4.18 Oxygen absorption of rubber diluted 20% BHBM LMCE at 150^{o}C. a - control; b - Flectol H(ex); c - 0.25%(ex); d - 0.25%(unex); e - 1%(ex); f - 1%(unex); g - 2%(ex); h - 2%(unex); i Flectol H(unex); j - Chemigum(ex); k - Chemigum(unex)

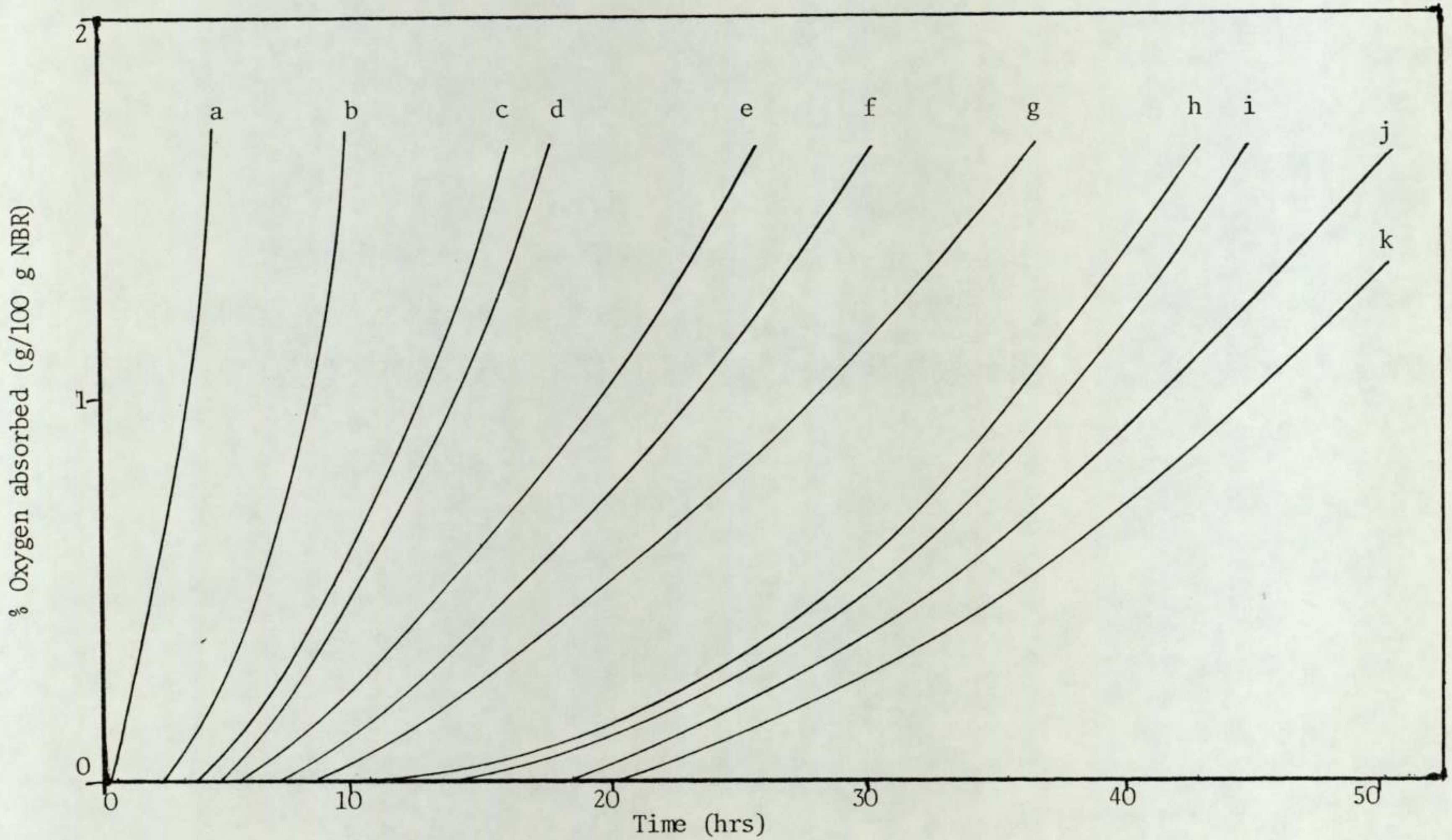


Fig 4.19 Oxygen absorption of rubber diluted 30% BHBM LMCE at 150^{o}C. a - control; b - Flectol H(ex); c - 0.25%(ex); d - 0.25%(unex); e - 1%(ex); f - 1%(unex); g - 2%(ex); h - 2%(unex); i - Flectol H(unex); j - Chemigum(ex); k - Chemigum(unex)

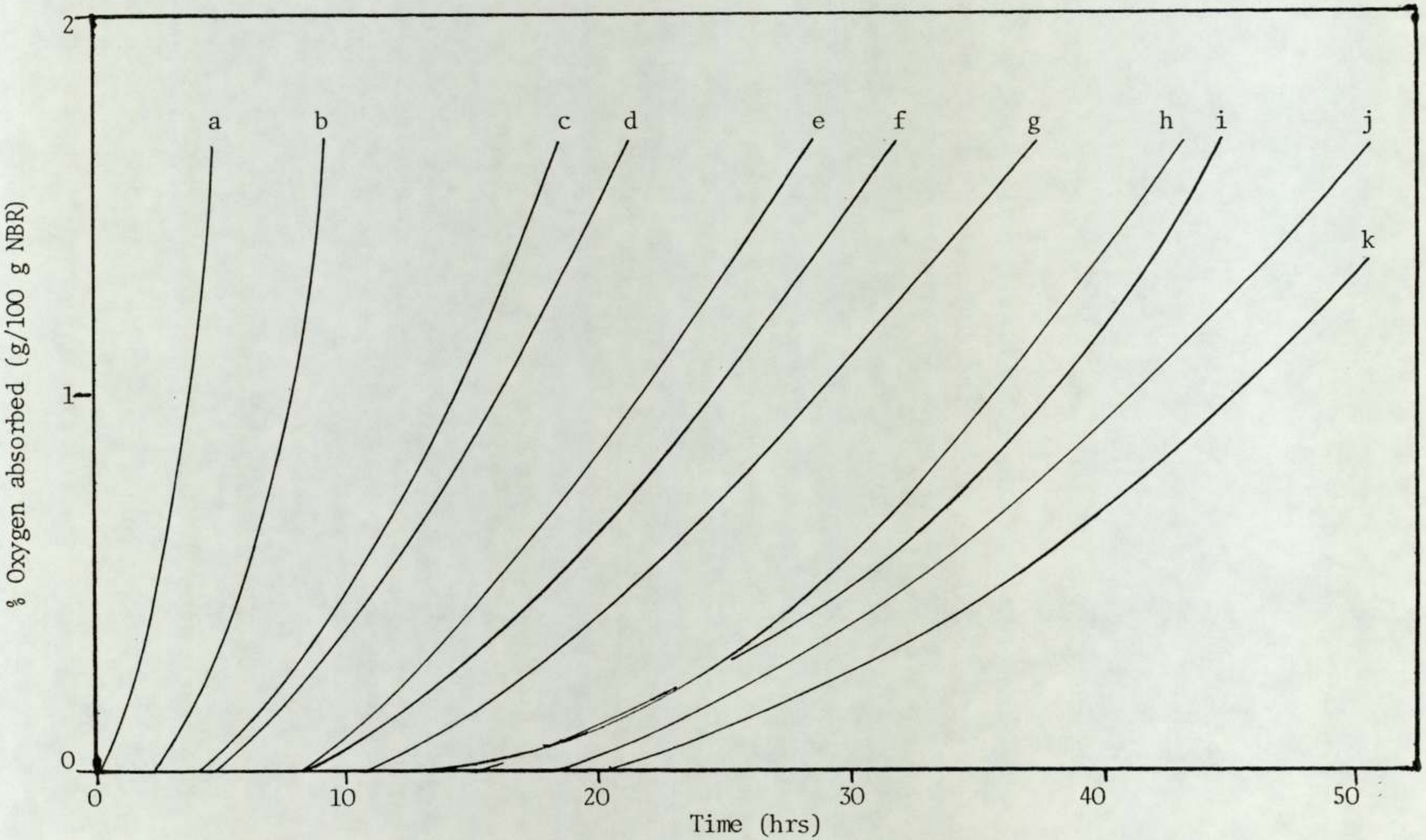


Fig 4.20 Oxygen absorption of rubber diluted 40% BHBM LMCE at 150^{o}C. a - control; b - Flectol H(ex) c - 0.25%(ex); d - 0.25%(unex); e - 1%(ex); f - 1%(unex); g - 2%(ex); h - Flectol H(unex); i - 2%(unex); j - Chemigum(ex); k - Chemigum(unex)

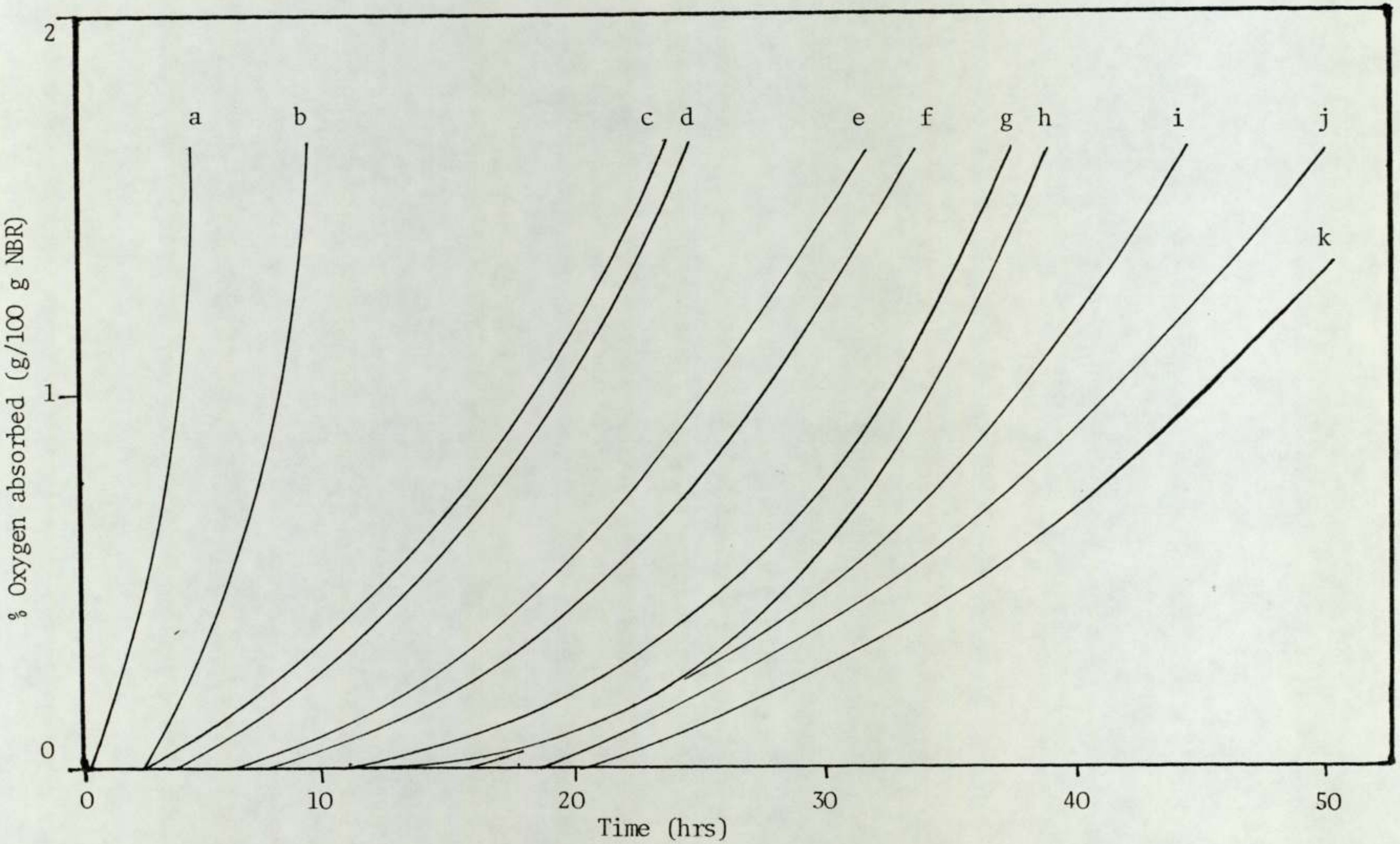


Fig 4.21 Oxygen absorption of rubber diluted 50% BHBM LMCE at 150^{O}C. a - control; b - Flectol H(ex); c - 0.25%(ex); d - 0.25%(unex); e - 1%(ex); f - 1%(unex); g 2%(ex); h - 2%(unex); i - Flectol H(unex); j - Chemgium(ex); k - Chemigum(unex)

resistance to oxygen than the extracted samples. After the induction period, all the samples containing thiol amide antioxidant show an autocatalytic oxygen absorption (Figs 4.22 - 4.30). The goodyear rubber Chemigum 665 behaved in a similar manner and the sample containing Flectol H was no exception to the rule. The samples from BHBM masterbatchs (LML) (Figs 4.6 - 4.11) show some autoretardation at long times. All show clear induction periods before extraction, all the samples prepared by latex dilution show autoretarding behaviour but after extraction they absorb oxygen in an autocatalytic fashion similar to samples prepared by solid dilution (see Figs 4.6 - 4.10). This behaviour probably indicates the formation of by-products and the extent to which they give protection to the rubber.

After extraction, all the samples lost about half of their antioxidant efficiency prior to extraction (see Tables 4.4 - 4.6). However, Chemigum is an exception, it retained about 86% of its efficiency and the difference between the extracted and unextracted may be due to the loss of extra network materials rather than the loss of antioxidant molecule.

It must be realised that BHBM is only about 60% bound and PAPT 52% bound (Tables 2.14 and 2.16) and the concentration of antioxidant in Chemigum is estimated to be about 2-3%. In the light of this, the difference between the extracted and unextracted samples containing BHBM and PAPT is in agreement with the amount of extracted unbound antioxidant and accelerator residues which could have contributed to the protection of the rubber.

It is important to know that all the samples, irrespective of the concentration of the antioxidants, offer protection to nitrile rubber as measured by comparing the test samples with the control. The time to absorb 1% oxygen by the control sample before and after extraction is 5 hours and 2 hours respectively (Table 4.4). After extraction, the sample containing Flectol H was comparable to the control whereas the bound antioxidants show considerable improvement over the control.

If the masterbatch coagulum is extracted before diluting with solid rubber and then vulcanised, the oxygen absorption of such vulcanisates (Figs 4.16 - 4.21) before and after extraction show only marginal difference showing that the difference to be due to extracted network materials from the vulcanisation system. If, however, the coagulum is not extracted before dilution and subsequently vulcanised, the marked difference is due to the combined effect of the extracted unbound antioxidant and the extra network materials presumably ZMDC (see Figs 4.16, 4.17, 4.28, 4.29 and 4.30).

The oxygen absorption curves of the samples prepared from solid masterbatch (MCM) (20%) by the mechanochemical procedure are shown in Figs 4.31 - 4.36 and the time for each sample to absorb 1% oxygen is given in Tables 4.7 and 4.8.

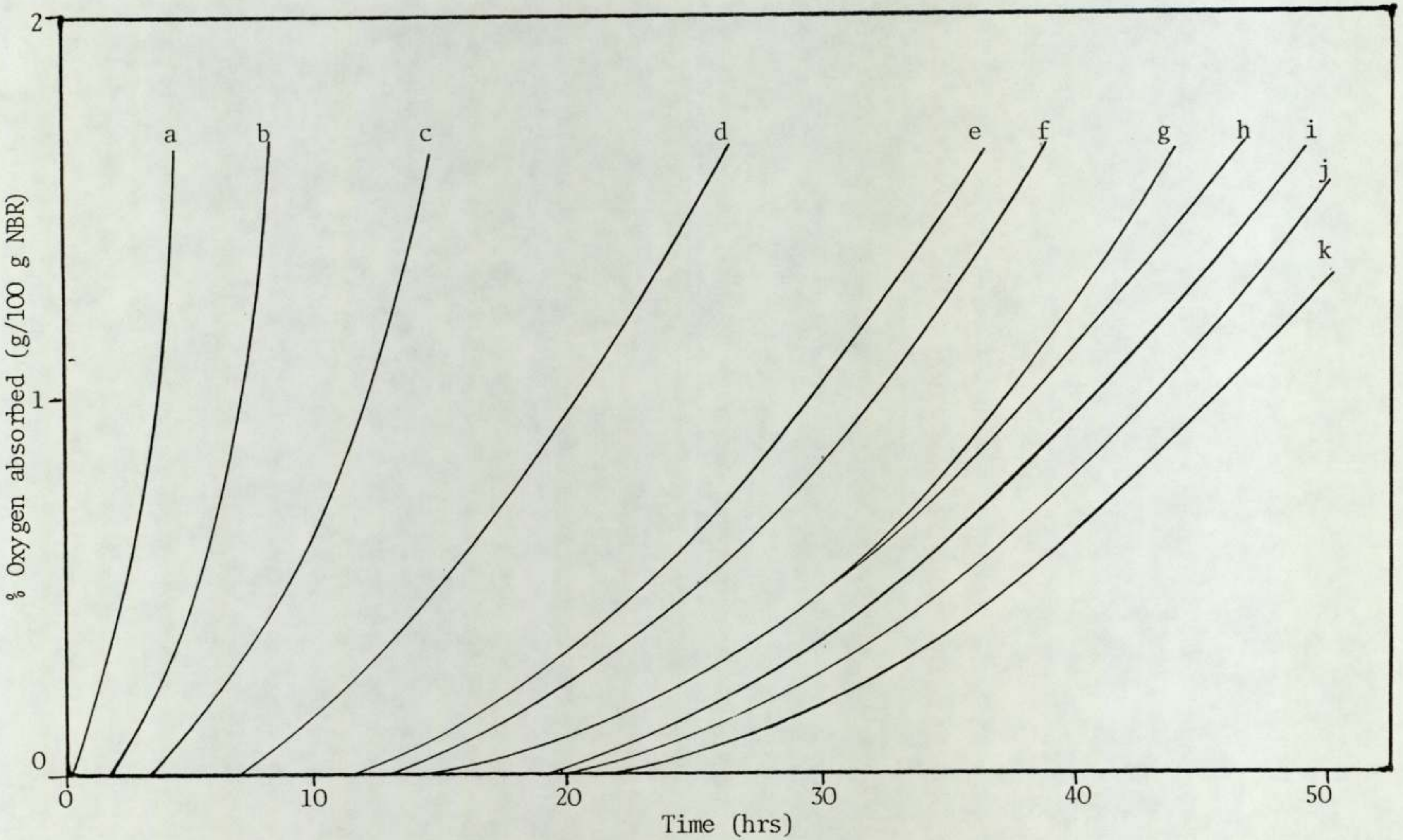


Fig 4.22 Oxygen absorption of latex diluted 10% PAPT LM at 150°C. a - control; b - Flectol H(ex); c - 0.25%(ex); d - 0.25%(unex); e - 1%(ex); f - 1%(unex); g - Flectol H(unex); h - 2%(ex); i - 2%(unex); j - Chemigum(ex); k - Chemigum(unex)

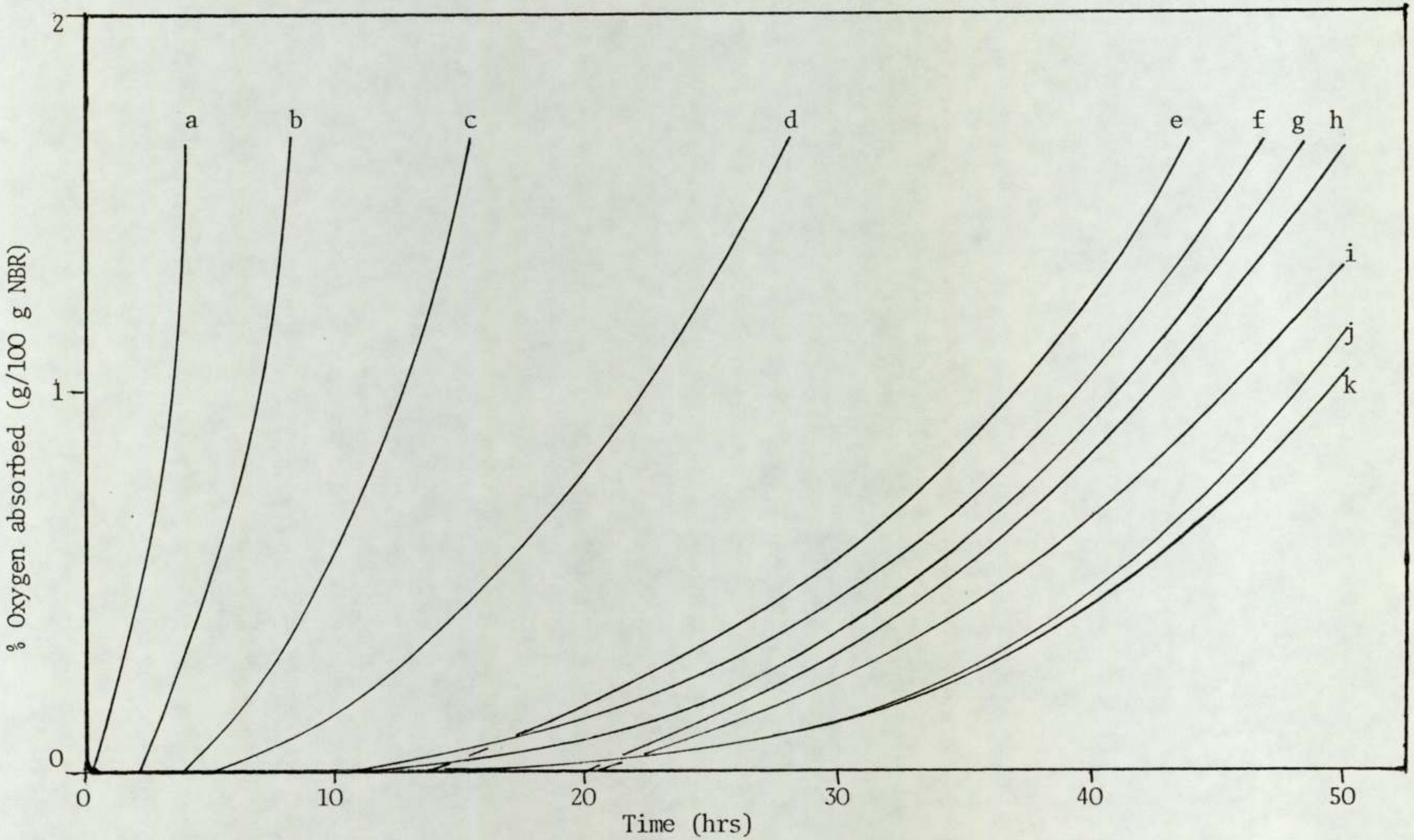


Fig 4.23 Oxygen absorption of latex diluted 20% PAPT LM at 150^{o}C. a control; b - Flectol H(ex); c - 0.25%(ex); d - 0.25%(unex); e - Flectol H(unex); f - 1%(ex); g - 1%(unex); h - Chemigum(ex); i - Chemigum(unex); j - 2%(ex); k - 2%(unex)

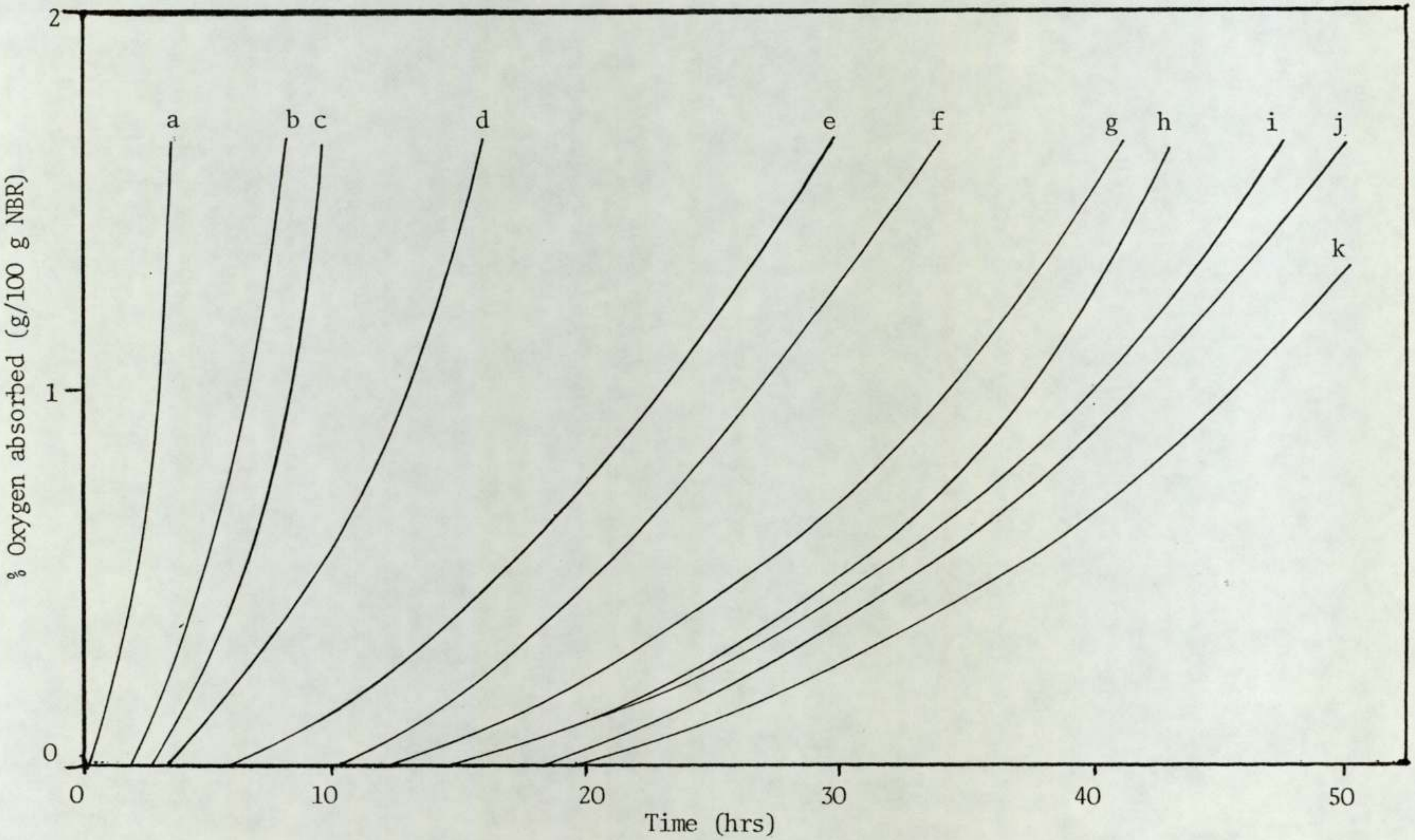


Fig 4.24 Oxygen absorption of latex diluted 30% PAPT LM at 150^{o}C. a - control; b - 0.25%(ex); c - Flectol H(ex); d - 0.25%(unex); e - 1%(ex); f - 1%(unex); g - Flectol H(unex); h - 2%(ex); i - 2%(unex); j - Chemigum(ex); k - Chemigum(unex)

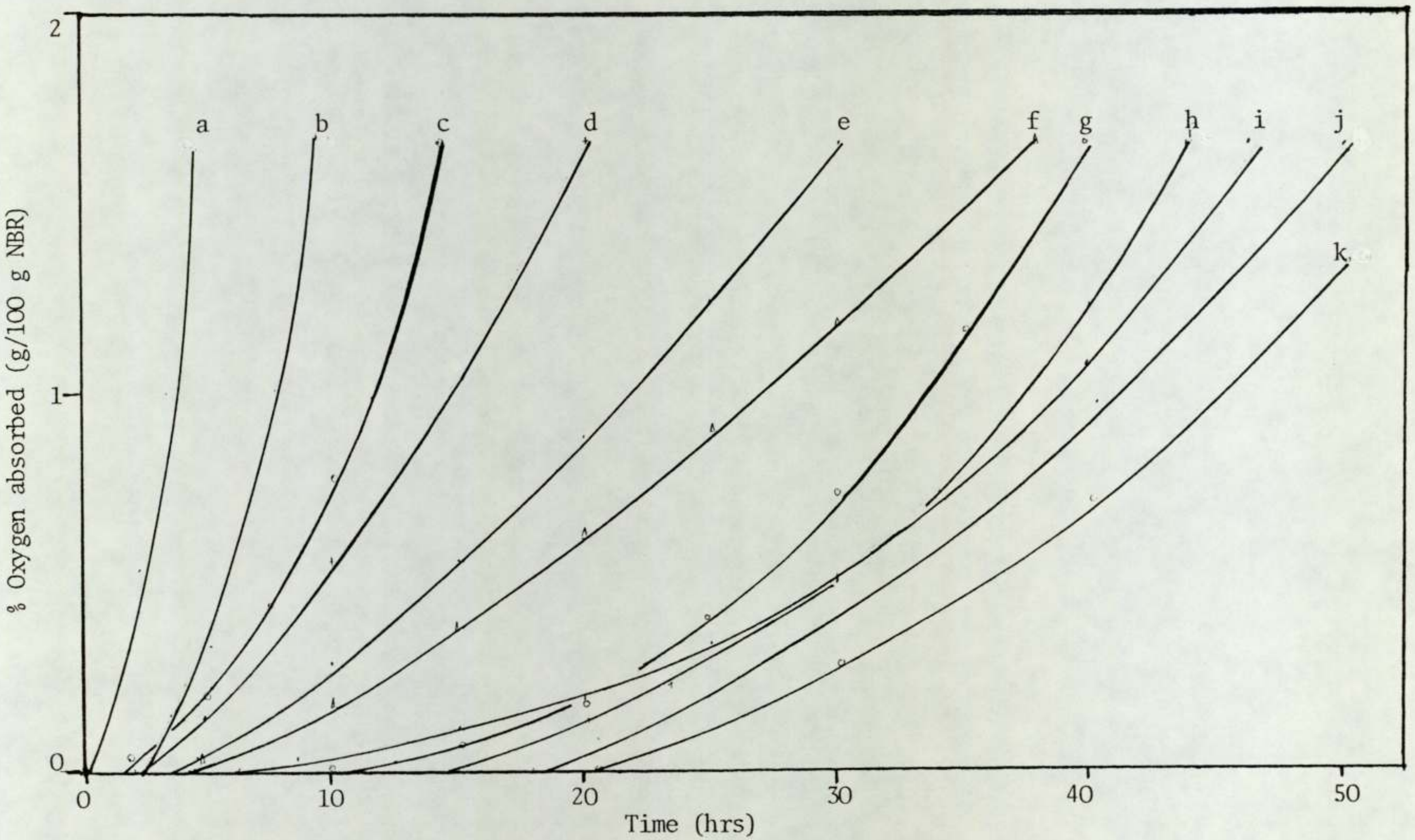


Fig 4.25 Oxygen absorption of rubber diluted 10% PAPT LMCU at 150^{o}C. a - control; b - Flectol H(ex); c - 0.25%(ex); d - 0.25%(unex); e - 1%(ex); f - 2%(ex); g - 1%(unex); h - Flectol H(unex); i - 2%(unex); j - Chemigum(ex); k - Chemigum(unex)

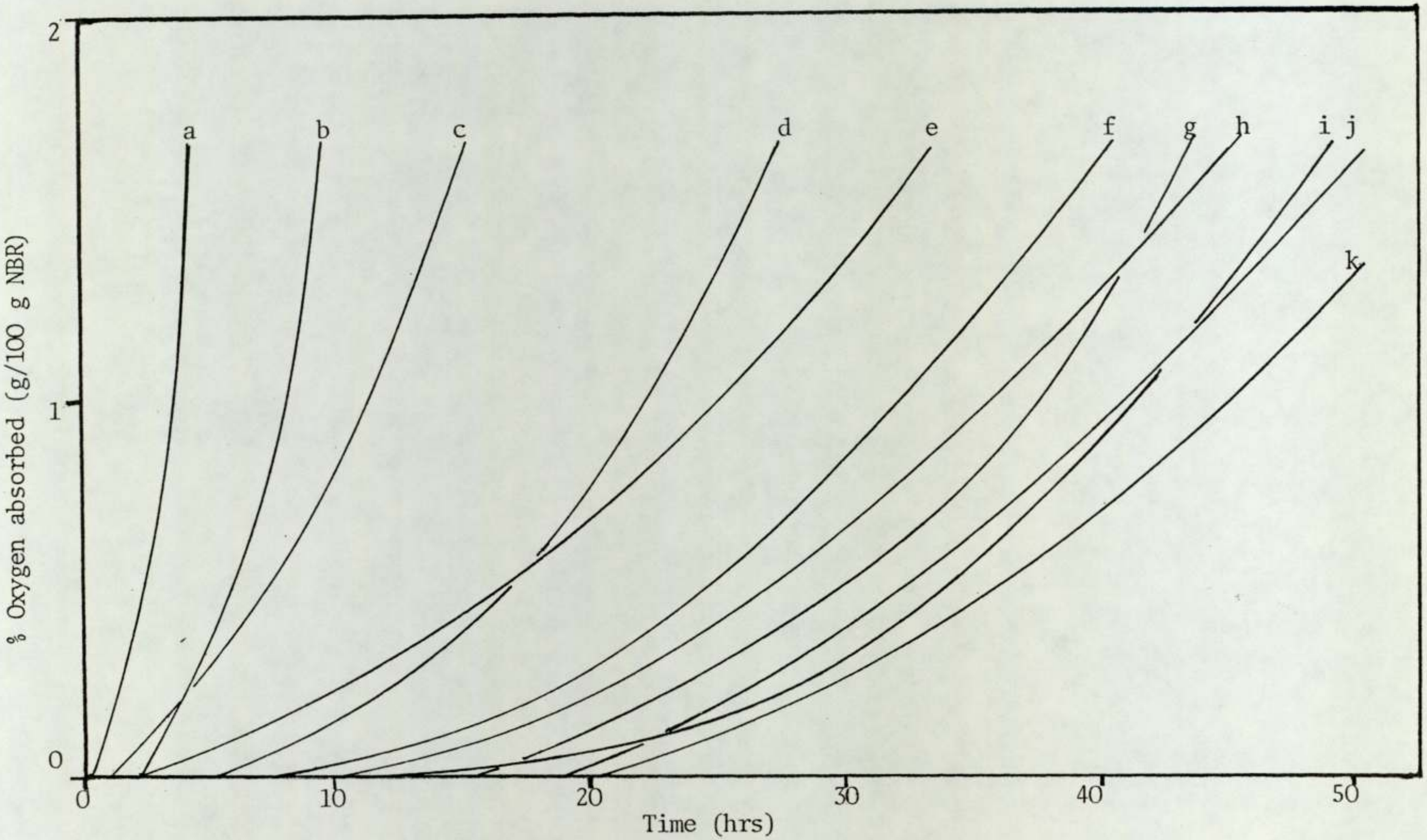


Fig 4.26 Oxygen absorption of rubber diluted 20% PAPT LMCU at 150°C. a - control; b - Flectol H(ex); c - 0.25%(ex); d - 0.25%(unex); e - 1%(ex); f - 1%(unex); g - Flectol H(unex); g - 2%(ex); i - 2%(unex); j - Chemigum(ex); k - Chemigum(unex)

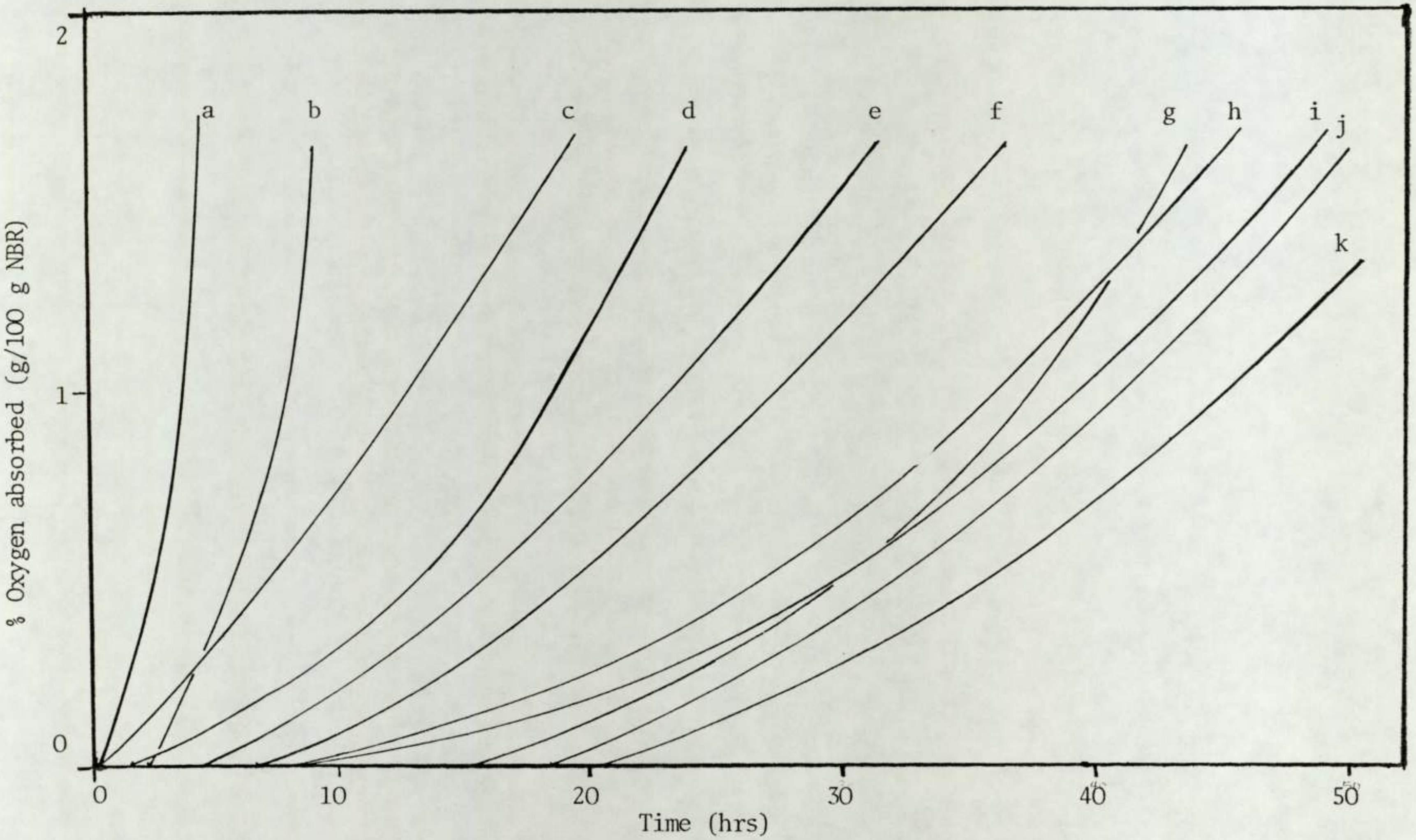


Fig 4.27 Oxygen absorption of rubber diluted 30% PAPT LMCU at 150^{O}C. a - control; b - Flectol H(ex); c - 0.25%(ex); d - 0.25%(unex); e - 1%(ex); f - 1%(unex); g - Flectol H(unex); h - 2%(ex); i - 2%(unex); j - Chemigum(unex); k - Chemigum(ex)

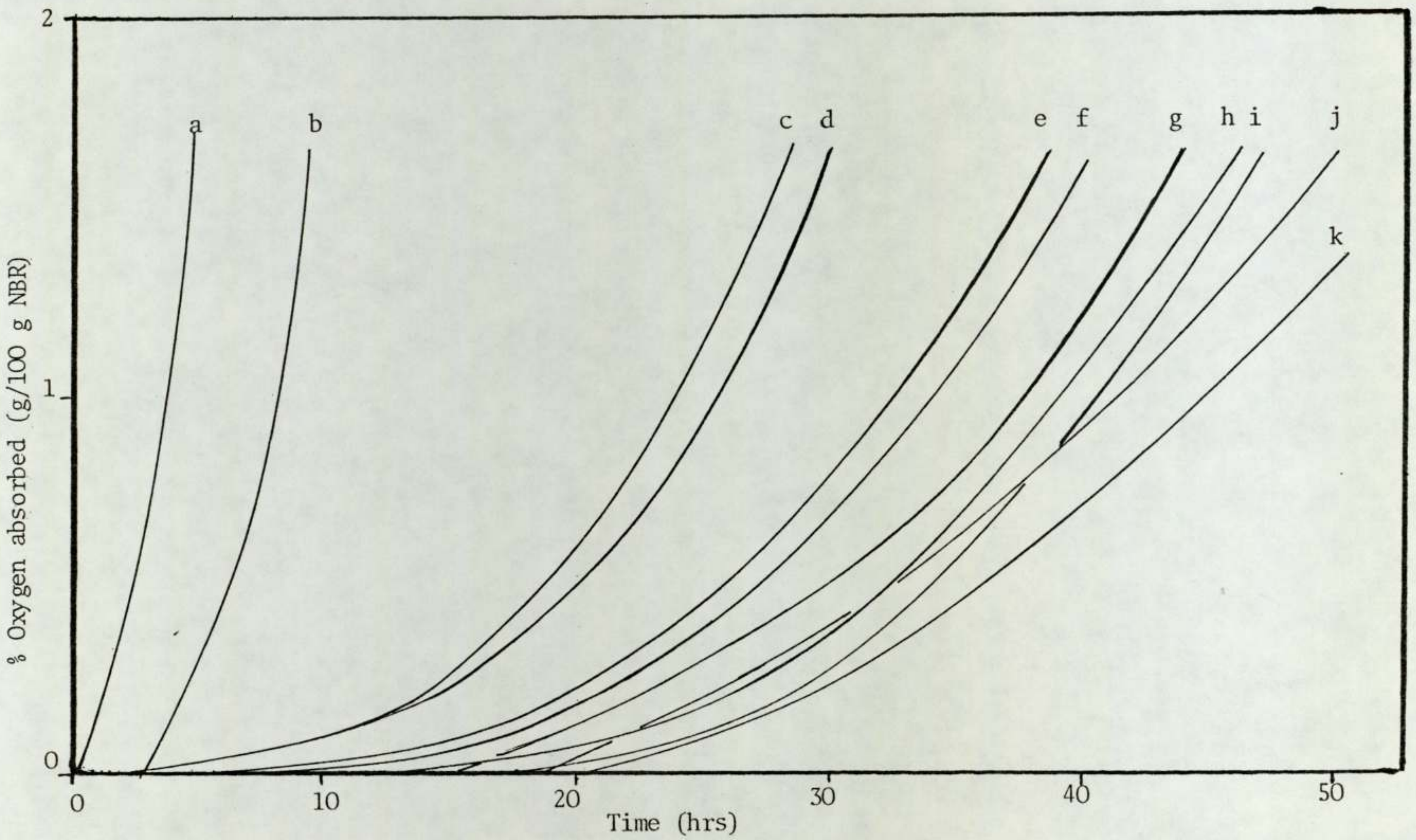


Fig 4.28 Oxygen absorption of rubber diluted 10% PAPT LMCE at 150^{o}C. a - control; b - Flectol H(ex); c - 0.25%(ex); d - 0.25%(unex); e - 1%(ex); f - 1%(unex); g - Flectol H(unex); h - 2%(ex); i - 2%(unex); j - Chemigum(ex); k - Chemigum(unex)

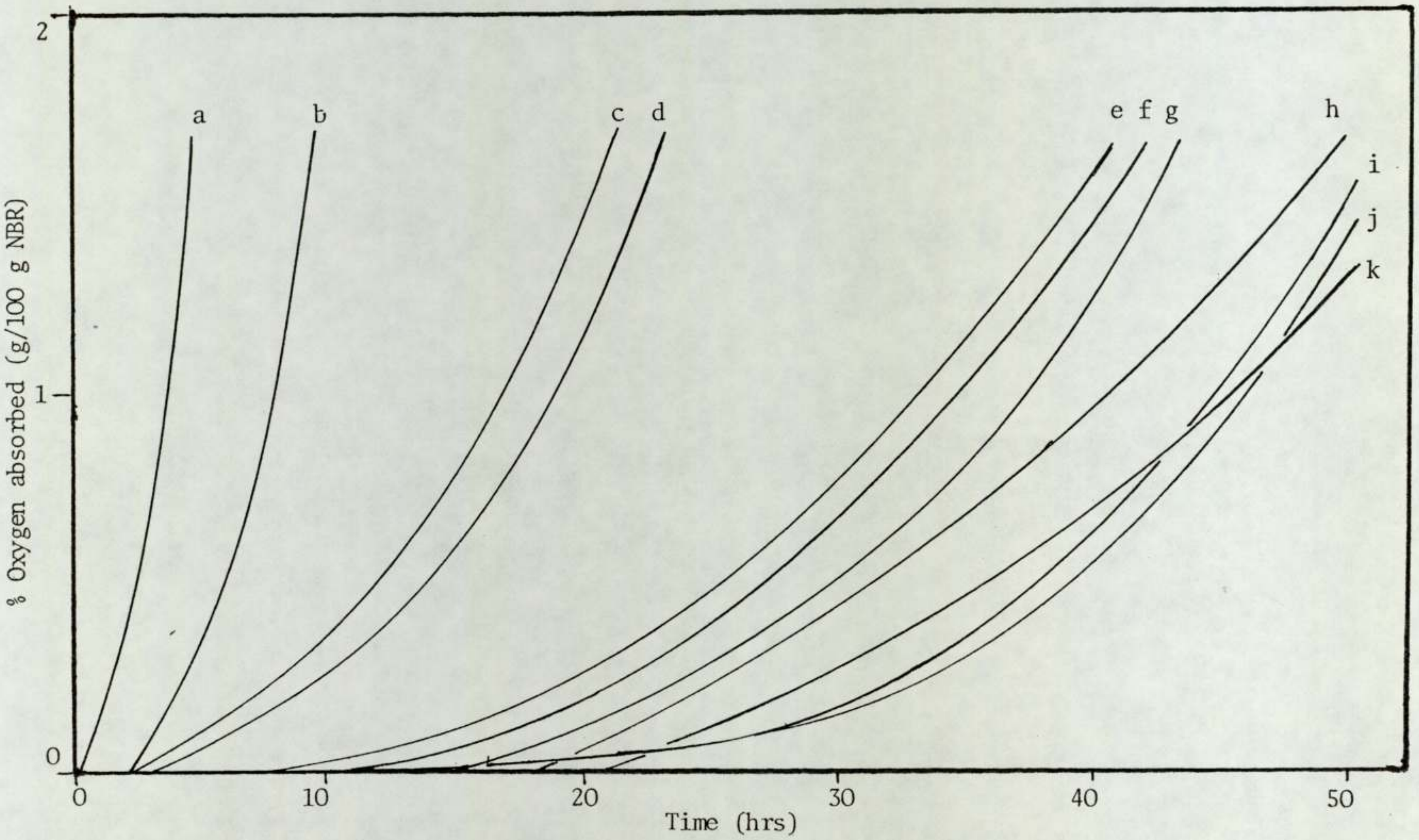


Fig 4.29 Oxygen absorption of rubber diluted 20% PAPT LMCE at 150^{o}C. a - control; b - Flectol H(ex); c - 0.25%(ex); d - 0.25%(unex); e - 1%(ex); f - 1%(unex); g - Flectol H(unex); h - Chemigum(ex); i - 2%(ex); j - 2%(unex); k - Chemigum(unex)

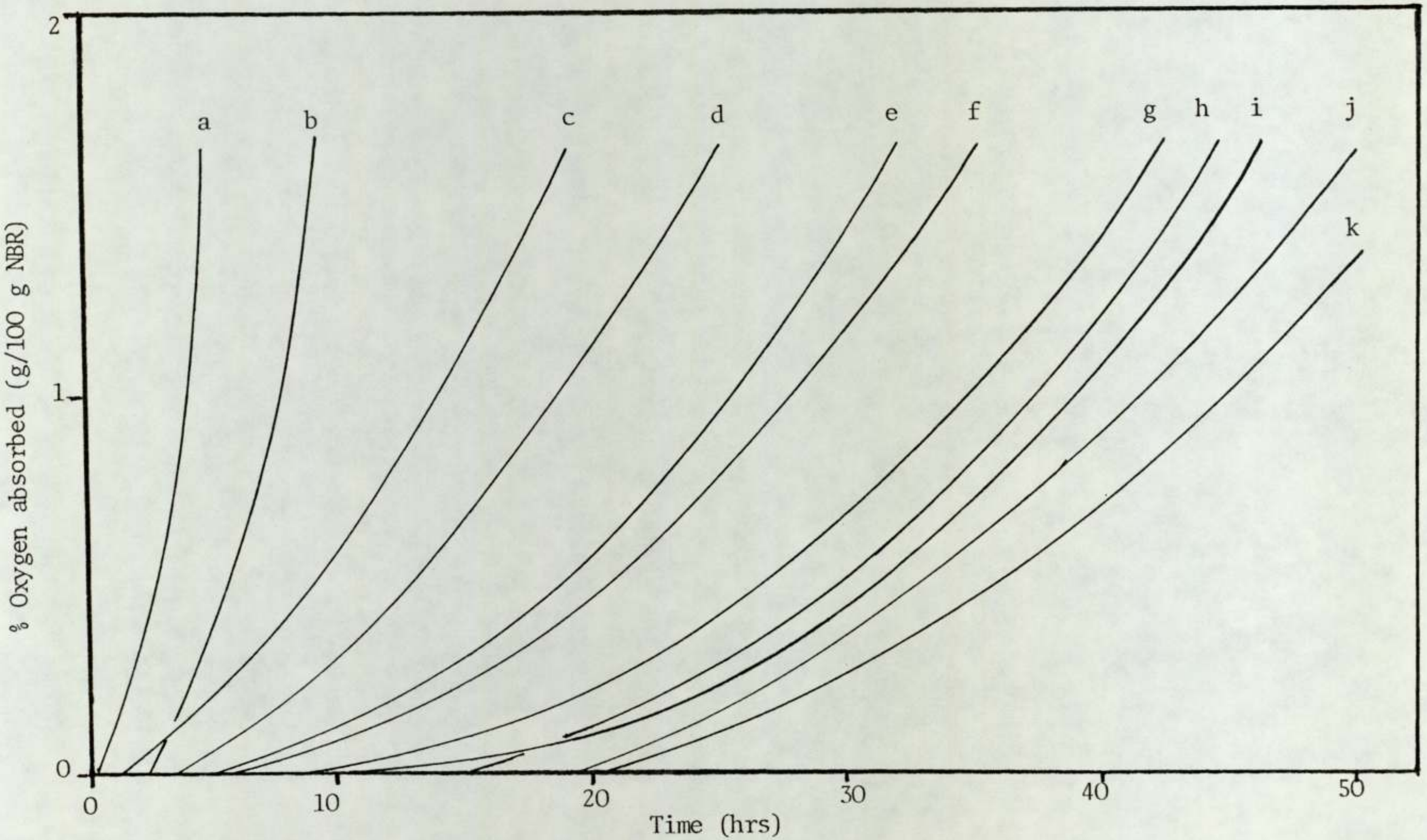


Fig 4.30 Oxygen absorption of rubber diluted 30% PAPT LMCE at 150°C. a - control; b - Flectol H(ex); c - 0.25%(ex); d - 0.25%(unex); e - 1%(ex); f - 1%(unex); g - Flectol H(unex); h - 2%(ext); i - 2%(unex); j - Chemigum(ex); k - Chemigum(unex)

Although PAPT was bound to about 75% in the torque rheometer (section 3.3.3), the oxygen absorption data showed that this level of binding has not improved the resistance of the rubber to oxidation, compared with the sample produced from the latex masterbatch where only 52% of PAPT was bound (Figs 4.22 and 4.35). In this case the dispersion of antioxidant in the rubber and the effectiveness of the byproducts probably play an important part since the use of hydroperoxide in the latex masterbatch could lead to the formation of byproduct which is not formed in the torque rheometer due to the absence of air and the formation of such byproduct may have influence on the stability of the rubber in subsequent tests.

As discussed (Chapter Three) it was not possible to bind BHBM and PPPT to a very high level in the torque rheometer and because of this, their poor behaviour as reflected by their oxygen absorption curves (Figs 4.31 - 4.36) is not surprising. Even at such low levels, they were able to protect the nitrile rubber to some degree when compared with the control.

The slowing down in the rate of oxidation of the antioxidants in the later stages particularly in the unextracted samples shows that binding probably occurs during vulcanisation, or post-vulcanisation during ageing, and also that more than one antioxidant mechanism is involved. (Synergistic behaviour between chain breaking activity and peroxide decomposing ability of the sulphur group of the antioxidant as well as that of ZDMC

Table 4.4 Oxygen absorption of vulcanisates from latex masterbatch (LM) after diluting to 0.25% antioxidants concentration

	Masterbatch concentration %					
	1	10	20	30	40	50
	Time to absorb 1% oxygen (hrs)					
0.25% BHBM sample (vulcanisate)						
LML (BHBM) unex	16	23.5	19.5	25	25	20
LML (BHBM) ex	11	15.5	15.5	14.5	22	12
LMCU (BHBM) unex	15	14	19.0	20.5	23	23.5
LMCU (BHBM) ex	12	9	12	13	17	17
LMCE (BHBM) unex	16	18.5	16	13.5	15.5	19
LMCE (BHBM) ex	15.5	15.15	14.5	12	14	18
0.25% PAPT sample (vulcanisate)						
LML (PAPT) unex		20	22	12½		
LML (PAPT) ex		11	12.5	7		
LMCU (PAPT) unex		14	22	18		
LMCU (PAPT) ex		11	11	13		
LMCE (PAPT) unex		24	15	18.5		
LMCE (PAPT) ex		23	13.5	13.5		
Control no antioxidant unex		5				
Control no antioxidant ex		2				
Flectol H unex		38				
Flectol H ex		6				
Chemigum unex		45				
Chemigum ex		40.5				

Table 4.5 Oxygen absorption of vulcanisates from latex masterbatch (LM) after diluting to 1% antioxidants concentration

	Masterbatch concentration %					
	Time to absorb 1% oxygen (hrs)					
	1	10	20	30	40	50
1% BHBM samples (vulcanisate)						
LML (BHBM) unex	25	33	26.5	28	27.5	26
LML (BHBM) ex	23	27	23	17	23	15
LMCU (BHBM) unex	25	27.5	29	34	35	35
LMCU (BHBM) ex	20	17	14.5	17.5	27	27
LMCE (BHBM) unex	24	26	23	23	24.5	27
LMCE (BHBM) ex	21.5	22	22	19	19	25
1% PAPT samples (vulcanisate)						
LML (PAPT) unex		32	41	26		
LML (PAPT) ex		29.5	38.5	23.5		
LMCU (PAPT) unex		26	31	27		
LMCU (PAPT) ex		22	25	23		
LMCE (PAPT) unex		33	34	27		
LMCE (PAPT) ex		32.5	33.5	35		
Control no antioxidant unex		5				
Control no antioxidant ex		2				
Flectol H unex		38				
Flectol H ex		6				
Chemigum unex		45				
Chemigum ex		40.5				

Table 4.6 Oxygen absorption of vulcanisates from latex masterbatch (LM) after diluting to 2% antioxidant concentration

	Masterbatch concentration %					
	Time to absorb 1% oxygen (hrs)					
	1	10	20	30	40	50
2% BHBM samples (vulcanisate)						
LML (BHBM) unex		36	33	32.5	32.5	30
LML (BHBM) ex		33	28.5	21	24.5	17.5
LMCU (BHBM) unex		33.5	37	43	39.5	39
LMCU (BHBM) ex		22.5	21.5	27	29.5	30
LMCE (BHBM) unex		31	35	36	36	33.5
LMCE (BHBM) ex		30	29	28	28.5	32
2% PAPT samples (vulcanisate)						
LML (PAPT) unex		43.5	49	40		
LML (PAPT) ex		38	48	34		
LMCU (PAPT) unex		39	41	39		
LMCU (PAPT) ex		33	35	36		
LMCE (PAPT) unex		40	45.5	38		
LMCE (PAPT) ex		39	44	35		
Chemigum unex		45				
Chemigum ex		40.5				
Flectol H unex		38				
Flectol H ex		6				
Control no antioxidant unex		5				
Control no antioxidant ex		2				

Table 4.7 Oxygen absorption of vulcanisates from unextracted 20% mechanochemical masterbatch (MCM) after dilution

Vulcanisate sample	% Antioxidant bound	Concentration of antioxidants after dilution					
		Time to absorb 1% oxygen (hrs)					
		Before vulcanisate extracted			After vulcanisate extracted		
		0.25%	1%	2%	0.25%	1%	2%
MCMU (BHBM)	47	30	19	22	18	15	19
MCMU (PAPT)	75	25	35	43	13	23	31
MCMU (PPPT)	32	13	15	12	4.5	8.5	10
Chemigum	*85	-	-	45	-	-	40
Flectol H	-	-	-	38	-	-	6
Control (no antioxidant)	-	-	-	5	-	-	2

* Chemigum appears to contain 2-3% before extraction

Table 4.8 Oxygen absorption of vulcanisates from extracted 20% mechanochemical masterbatch (MCM) after dilution

Vulcanisate sample	% Antioxidant bound	Concentration of antioxidants after dilution					
		Time to absorb 1% oxygen (hrs)					
		Before vulcanisate extraction			After vulcanisate extraction		
		0.25%	1%	2%	0.25%	1%	2%
MCME (BHBM)	47	21	21	23	18	26.5	26.5
MCME (PAPT)	75	25	26	37.5	14.5	22.5	30.0
MCME (PPPT)	32	11	11	15	4.5	5.5	9
Chemigum	*85	-	-	45	-	-	40
Flectol H	-	-	-	38	-	-	6
Control (no antioxidant)	-	-	-	5	-	-	2

* Chemigum appears to contain 2-3% before extraction

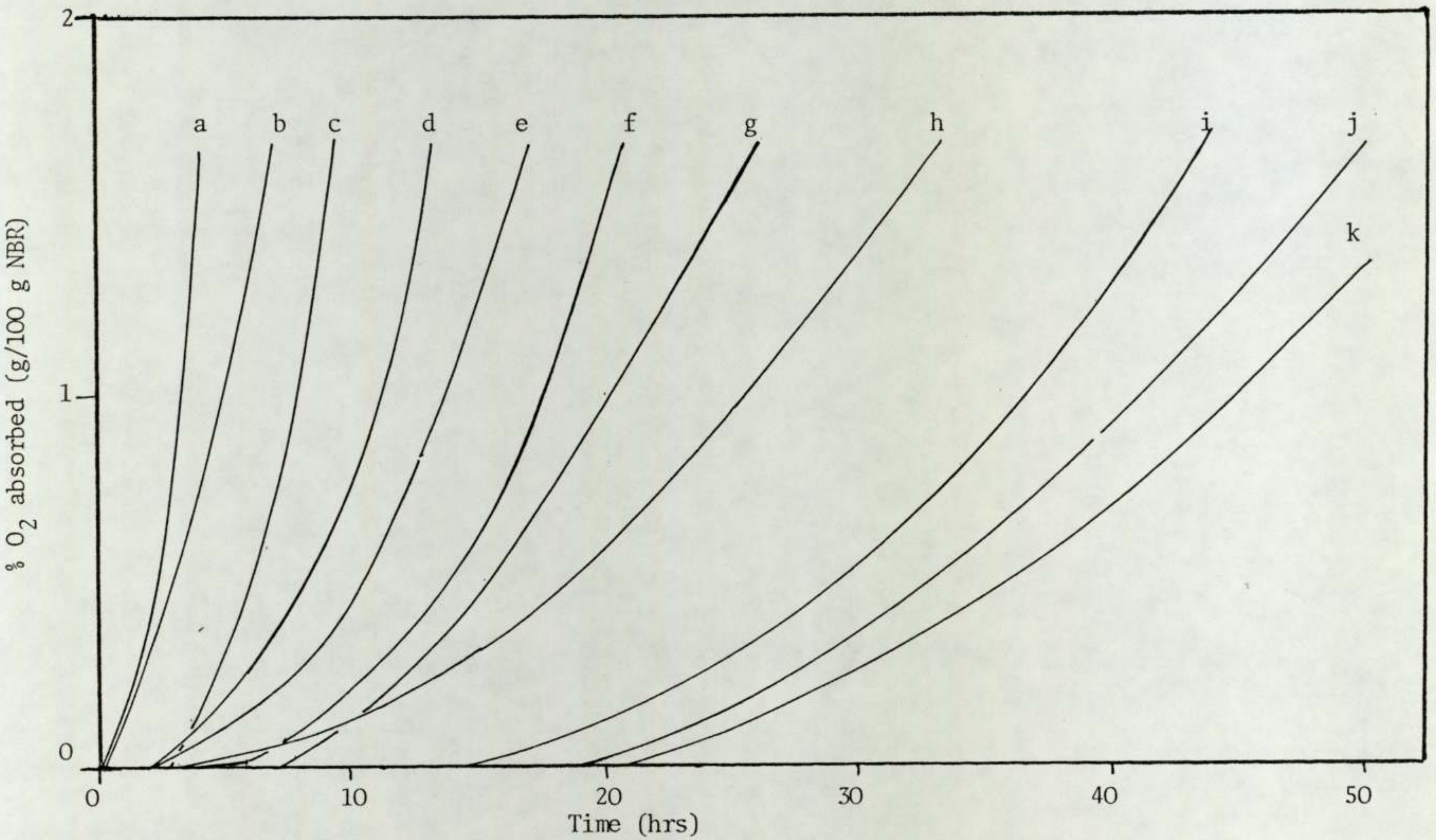


Fig 4.31 Oxygen absorption of 20% MCMU (reduced to 0.25%) vulcanisates at 150°C. a - control; b - PPPT(ex); c - Flectol H(ex); d - PPPT(unex); e - PAPT(ex); f - BHBM(ex); g - BHBM(unex); h - PAPT(unex); i ÷ Flectol H(unex); j - Chemigum(ex); k - Chemigum(unex)

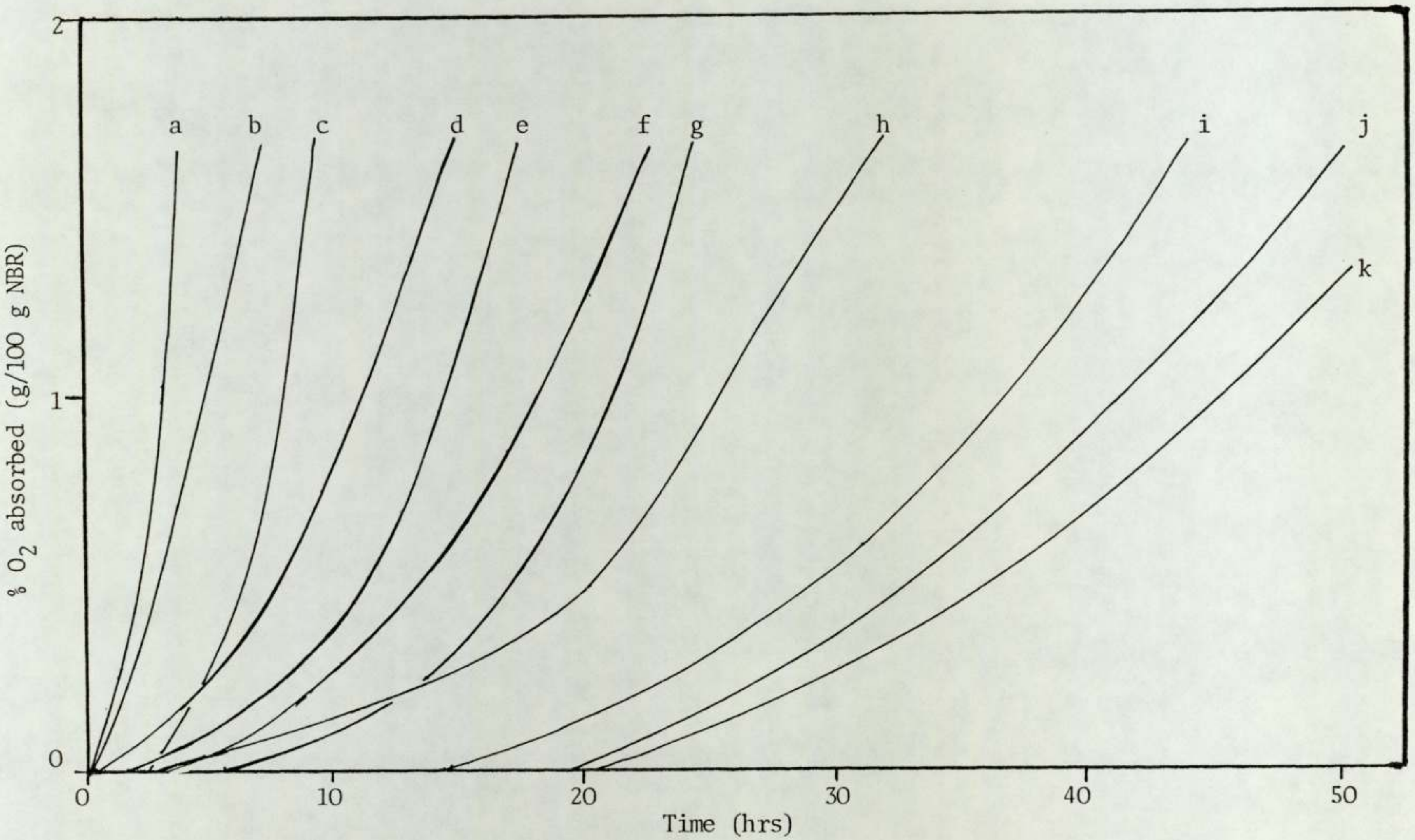


Fig 4.32 Oxygen absorption of 20% MCME (reduced to 0.25%) vulcanisates at 150°C. a - control; b - PPPT(ex); c - Flectol H(ex); d - PPPT(unex); e - PAPT(ex); f - BHBM(ex); g - BHBM(unex); h - PAPT(unex); i - Flectol H(unex); j - Chemigum(ex); k - Chemigum(unex)

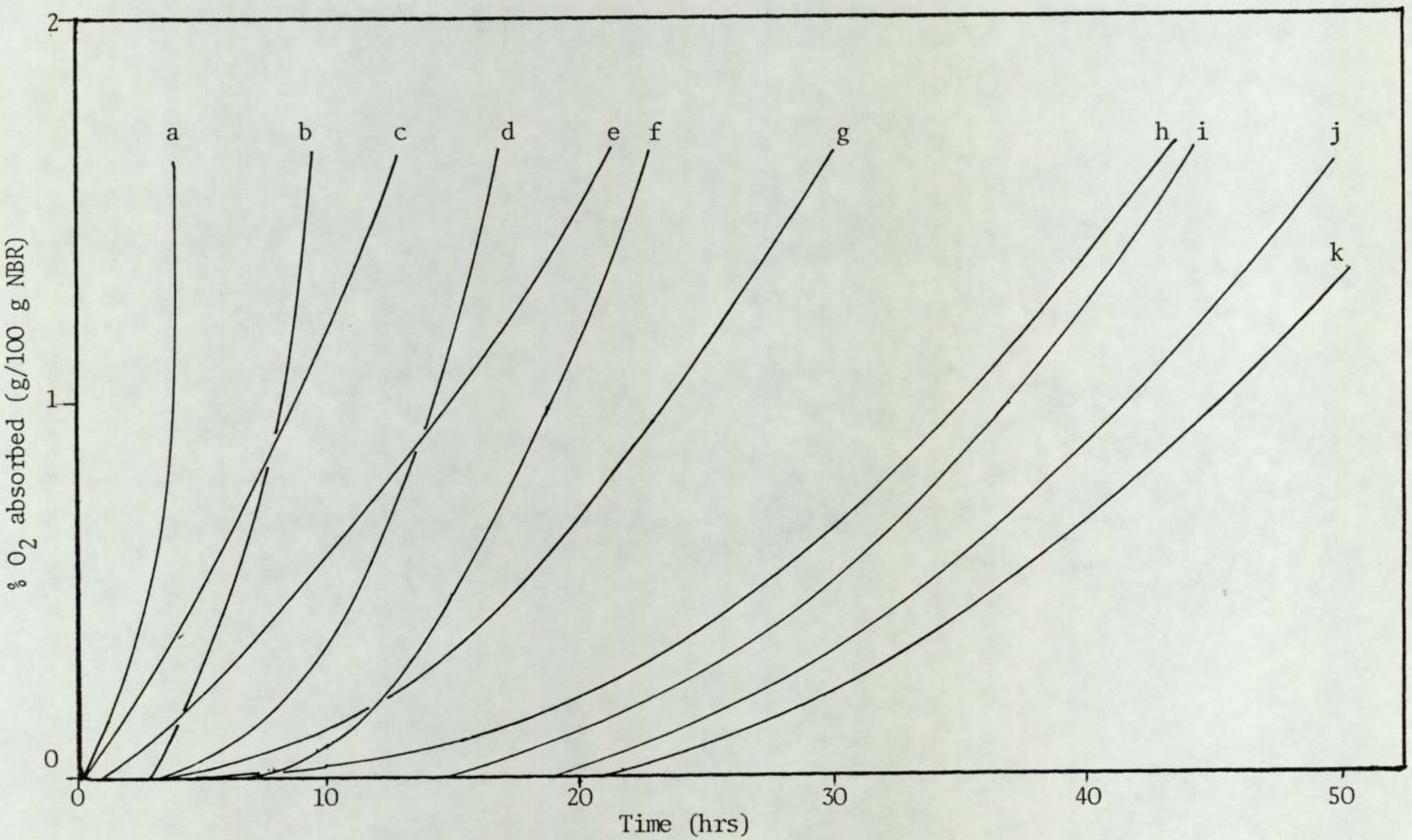


Fig 4.33 Oxygen absorption of 20% MCMU (reduced to 1%) vulcanisates at 150°C. a - control; b - Flectol H(ex); c - PPPT(ex); d - BHBM(ex); e - PPPT(unex); f - BHBM(unex); g - PAPT(ex); h - PAPT(unex); i - Flectol H(unex); j - Chemigum(ex); k - Chemigum(unex)

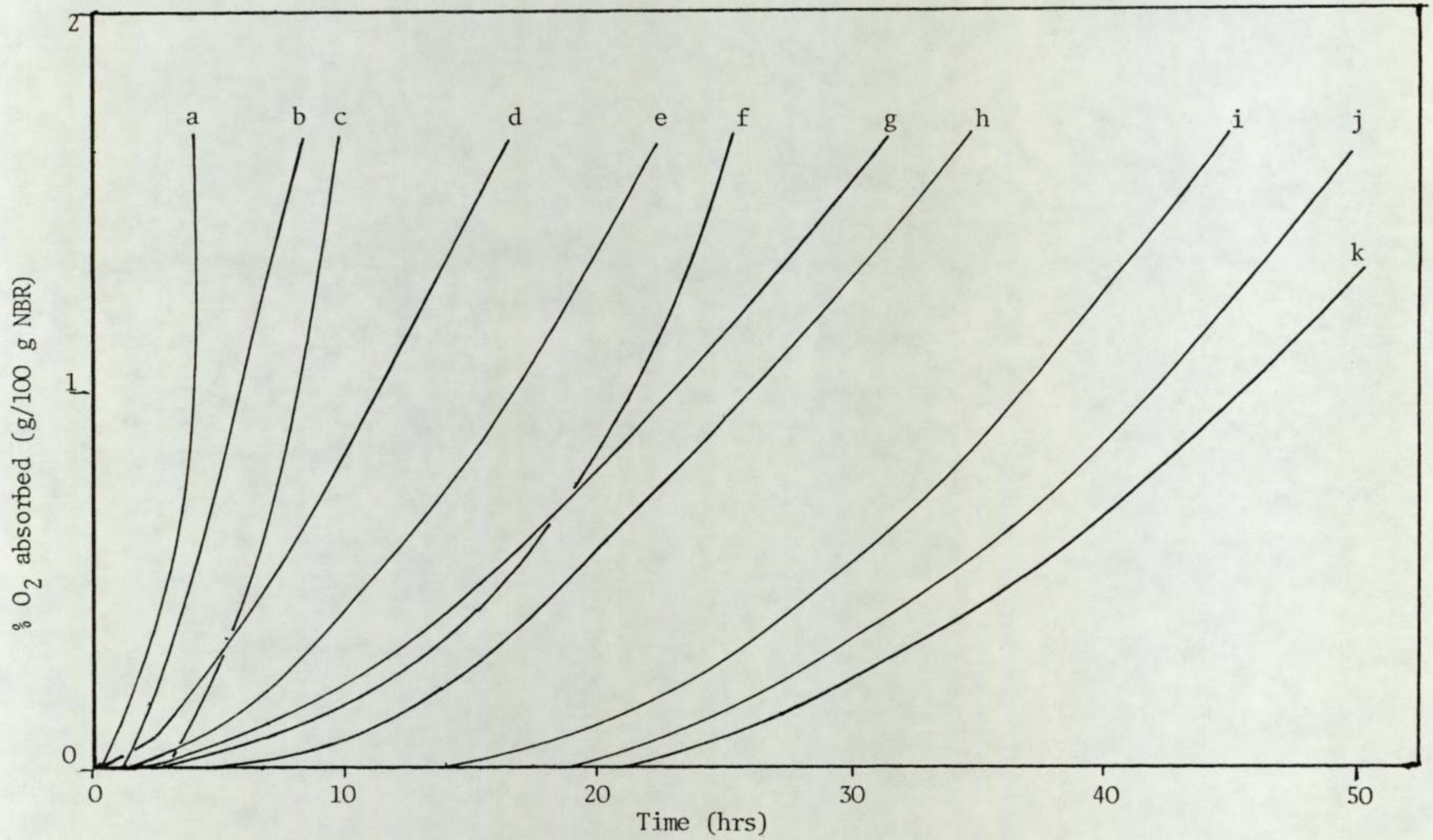


Fig 4.34 Oxygen absorption of 2.0% MCME (reduced to 1%) vulcanisates at 150^{o}C. a - control; b - PPPT(ex); c - Flectol H(ex); d - PPPT(unex); e - BHBM(ex); f - BHBM(unex); g - PAPT(ex); h - PAPT(unex); i - Flectol H(unex); j - Chemigum(ex); k - Chemigum(unex)

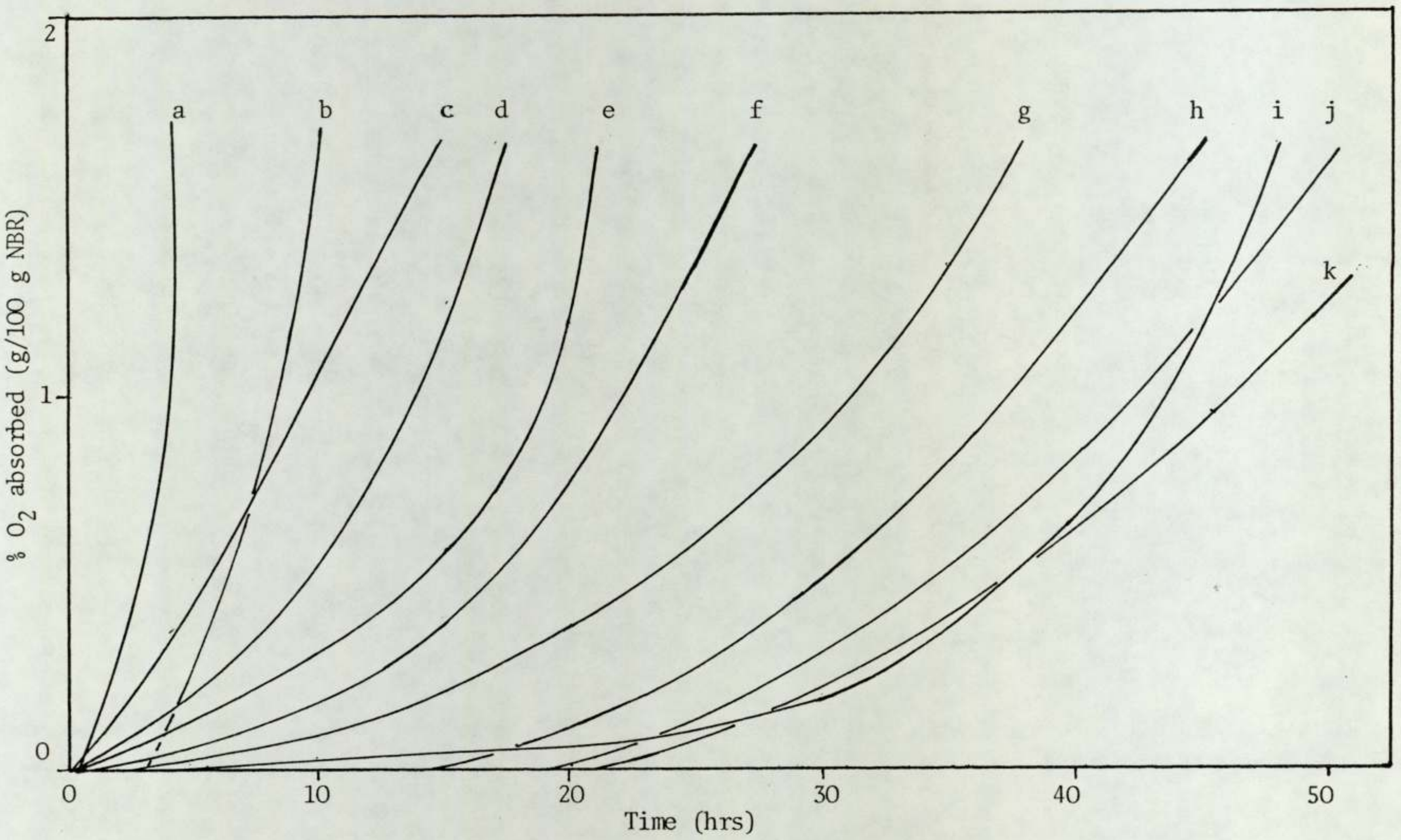


Fig 4.35 Oxygen absorption of 2.0% MCMU (reduced to 2%) vulcanisates at 150°C. a - control; b - Flectol H(ex); c - PPPT(ex); d - PPPT(unex); e - BHBM(ex); f - BHBM(unex); g - PAPT(ex); h - Flectol H(unex); i - PAPT(unex); j - Chemigum(ex); k - Chemigum(unex)

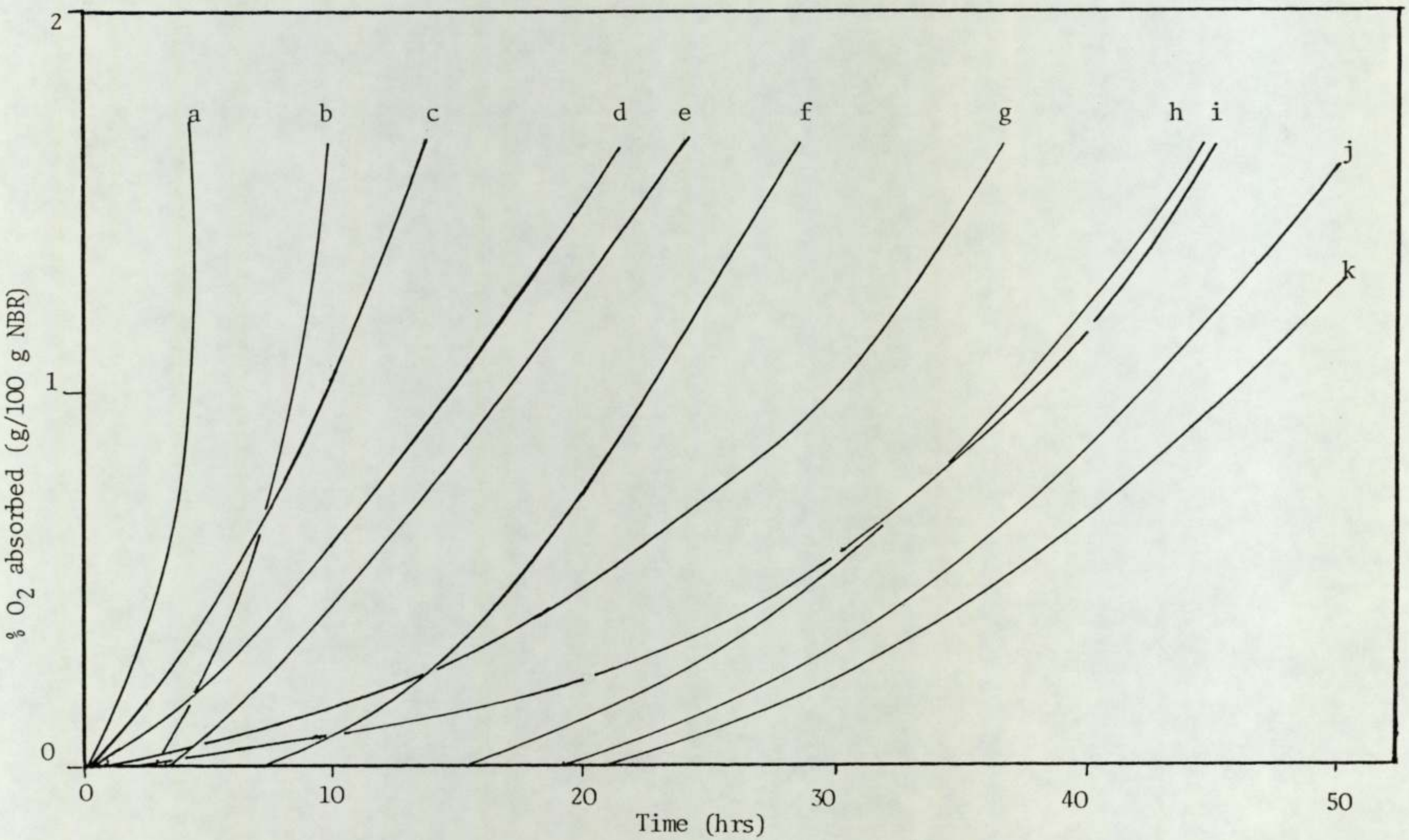


Fig 4.36 Oxygen absorption of 20% MCME (reduced to 1%) vulcanisates at 150°C. a - control; b - Flectol H(ex); c - PPPT(ex); d - PPPT(unex); e - BHBM(ex); f - BHBM(unex); g - PAPT(ex); h - Flectol H(unex); i - PAPT(unex); j - Chemigum(ex); k - Chemigum(unex)

formed during cure.)

The removal of unbound antioxidant fragments and ZDMC is thought to be responsible for the reduction in antioxidant efficiency. This may not necessarily be true because unbound antioxidant will only be present in the unextracted vulcanisate provided they are not consumed in the reaction with cure systems during vulcanisation. However, unbound antioxidant is likely to be present in the masterbatches where the antioxidants are less efficiently bound.

The times to absorb 1% oxygen (Tables 4.4 - 4.8) seem to be directly proportional to the concentration of antioxidant, but also show that for BHBM 10% masterbatch and for PAPT 20% masterbatches to show optimum properties.

4.7 Oxidative Stress Relaxation

Stress relaxation is an analytical procedure for measuring the effect of antioxidant in rubber vulcanisates. This method has been widely used in fundamental studies of the ageing of vulcanisates$^{(135)}$. Since the measurement is capable of being taken automatically without damage to the specimen, the method is attractive to the technologist. Since the extent of degradation can be determined and the test can also be used to determine the amount of cross-linking during ageing, it is also a useful scientific procedure. The method essentially follows the decay of stress by periodic measurement at a fixed strain, either continuous or intermittent.

In continuous stress relaxation, the sample is held extended throughout the experiment and the decay in stress at constant extension during ageing is measured and interpretted as degradation occurring in the network. In intermittent stress relaxation, the sample is stretched for a short period (2 minutes) for measurements to be made and is maintained in the unstretched condition for a longer period (28 minutes) and the process is repeated. Any new network will be formed within the specimen in the unstretched state and will contribute to the stress when the sample is extended. The difference in relaxation behaviour between the two methods is thus a measure of any cross-linking produced during the ageing process.

The interpretation of stress relaxation is based upon the kinetic theory of rubber-like elasticity according to which the stress of an elongated sample is given by(135):

$$f = SKt\ A_o \left[{}^{1}/lo - \left(\frac{lo}{L}\right)^2 \right]$$

where f = tension

S = number of chain per unit volume supporting stress

K = Boltzman's constant

t = temperature

$^{1}/lo$ = the ratio of stretched to unstretched length (extension ratio)

A_o = the unstrained cross-sectional area of specimen

Therefore if a sample of rubber can be maintained in extension at constant length and constant temperature (that is, keeping $^{l}/_{lo}$ constant) the value of stress f will be proportional to the number of stress supporting chains S.

$$^{f}/_{fo} = {}^{S}/_{So}$$

As chain scission occurs during thermal degradation of rubbers, the decay in stress is a direct measurement of degradation of the elastic network. The dependence of stress of a stretched rubber upon the time of application when held at a constant elongation and temperature provides valuable information about the material. Although stress relaxation employs simple apparatus, measurement of high degree of precision and reproducibility can be carried out. This method of accelerated ageing has been successfully used in the rubber industry to predict various reactions taking place during the thermal oxidation of vulcanisates.

In this work the continuous stress relaxation of vulcanisates was followed automatically using a Wallace Shawbury self recording age tester (Wallace Instruments Ltd) in conjunction with a six cell air ageing oven. The temperature in the cells was kept constant at 150°C by a thermostat. The samples were located between and clamped in two grips in such a way that they were enclosed inside the cells of the oven.

Samples were cut from vulcanised sheets using the MR-100 apparatus test cutter. Test samples were examined carefully for any nick and if such defects were found such samples were rejected. After clamping the instrument was zeroed for the weight of the specimen after which the lower specimen grip was tightened around the sample. The sample was extended, the instrument being used with a brass collar, so that the initial extension of the sample was a constant 50%. The instrument was then placed in the air ageing oven which was maintained at the ageing temperature (150°C). After allowing 5 minutes for expansion, the marker was adjusted to 100% stress and zero time on the chart. The specimen was then allowed to relax in stress. The instrument recorded stress as a function of time and the results being recorded as logarithm of the quotient of stress and initial stress (100%) against time.

4.7.1 Results and Discussion

For this test, 20% masterbatch was reduced to 0.25, 1 and 2% by diluting the latex masterbatch with untreated latex and solid rubber but where the masterbatch had been prepared by the mechanochemical procedure, the dilution was only by use of solid rubber.

The continuous stress relaxation of nitrile rubber TMTD low sulphur vulcanisate at 150°C are shown in Figs 4.37 - 4.42. In the absence of additive, the relaxation curve is autocatalytic but in the presence of antioxidants the shape of the curve is

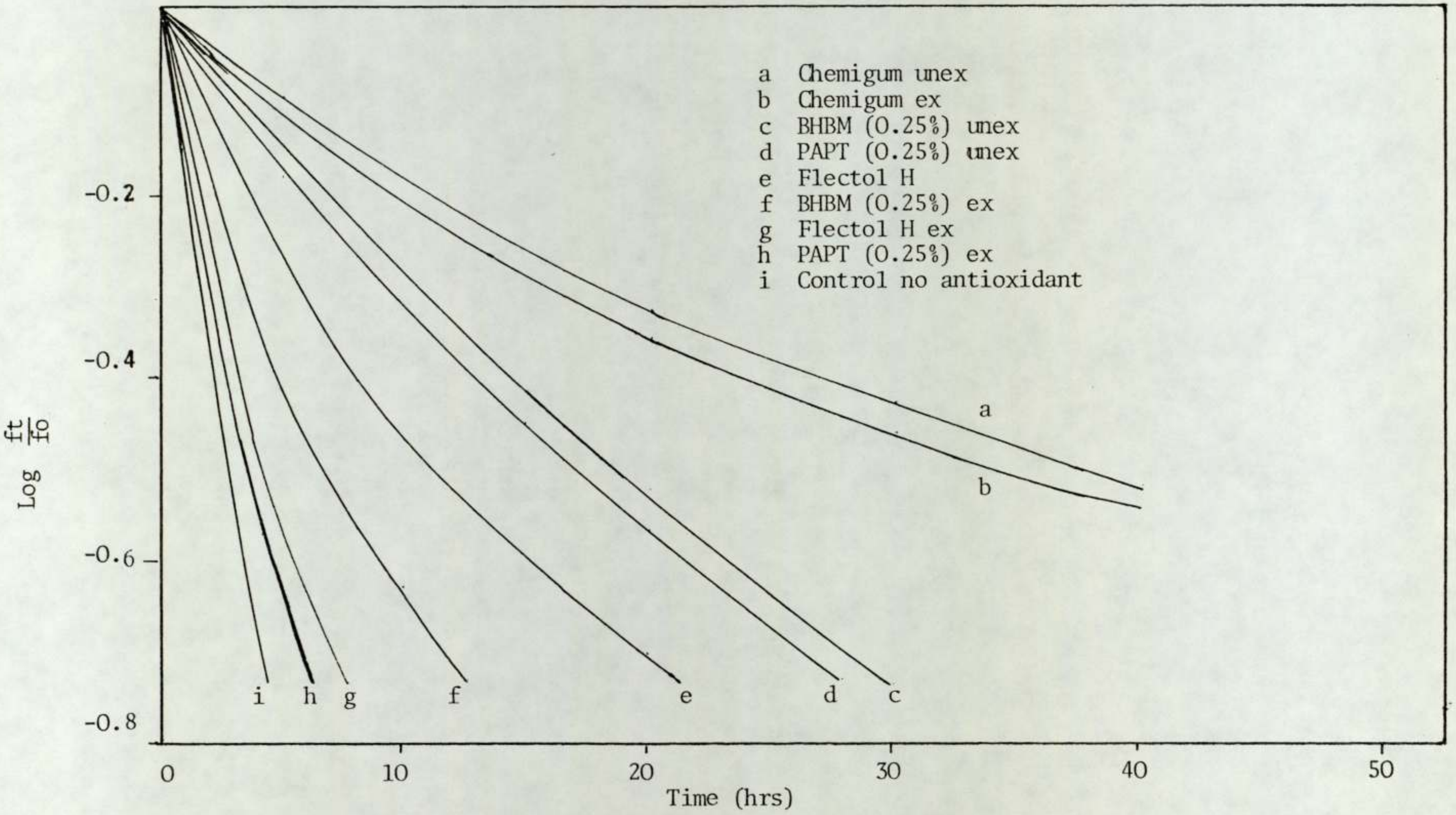


Fig 4.37 Continuous stress-relaxation of 20% bound antioxidant latex masterbatch (diluted to 0.25%) at 150^{O}C

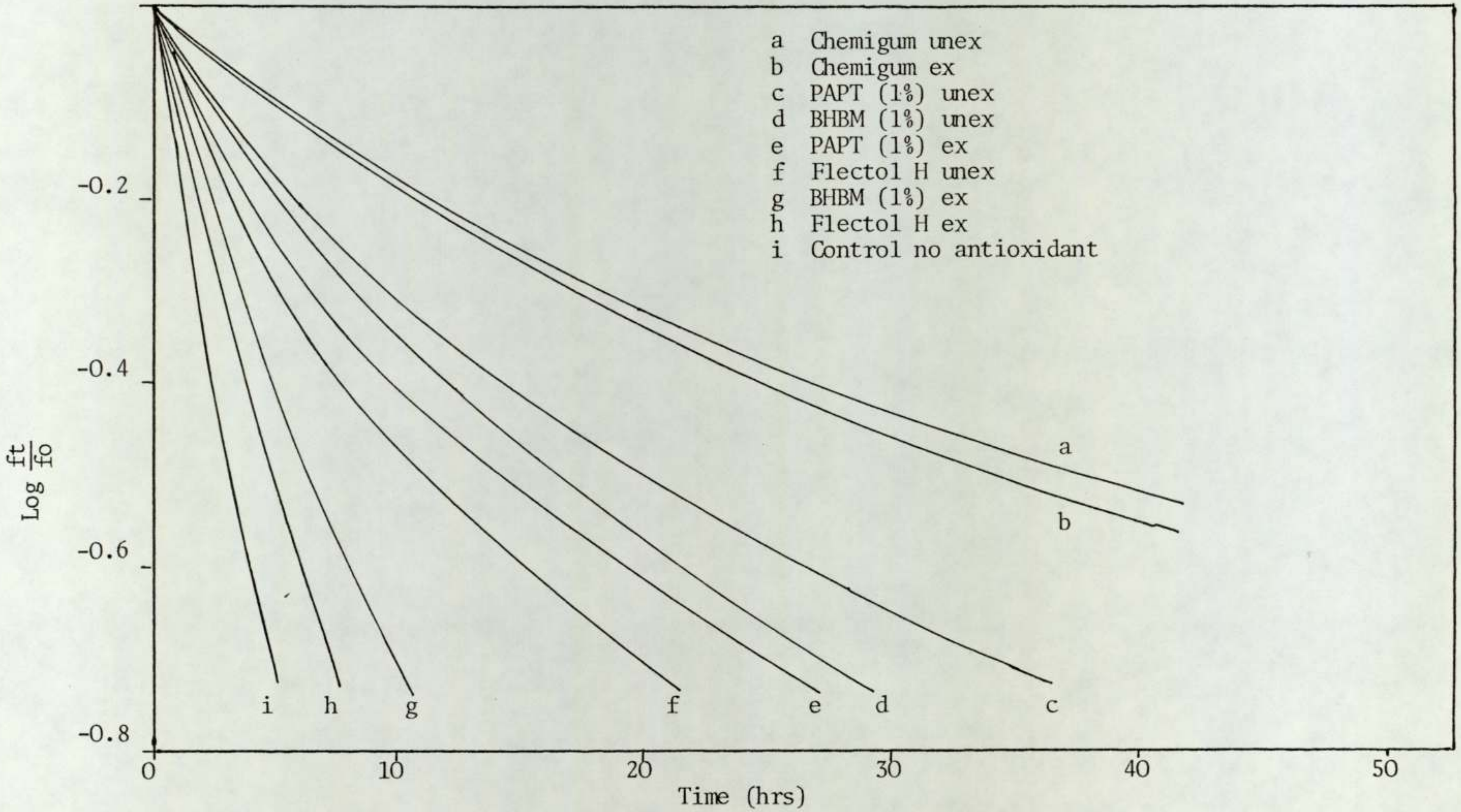


Fig 4.38 Continuous stress relaxation of 20% bound antioxidant latex masterbatch (diluted to 1%) at 150^{o}C

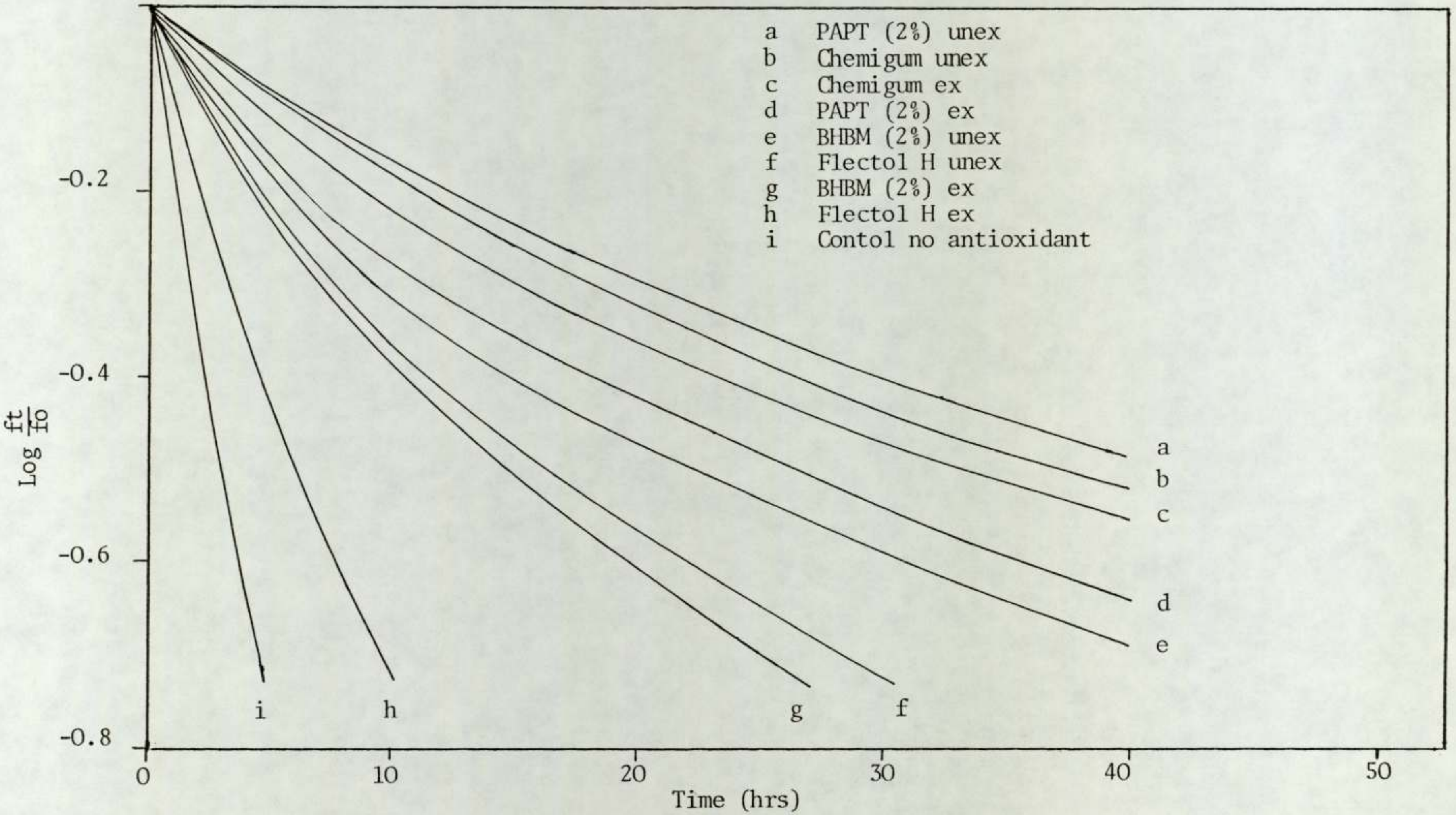


Fig 4.39 Continuous stress relaxation of 20% bound antioxidant latex masterbatch (diluted to 2%) at 150^{o}C

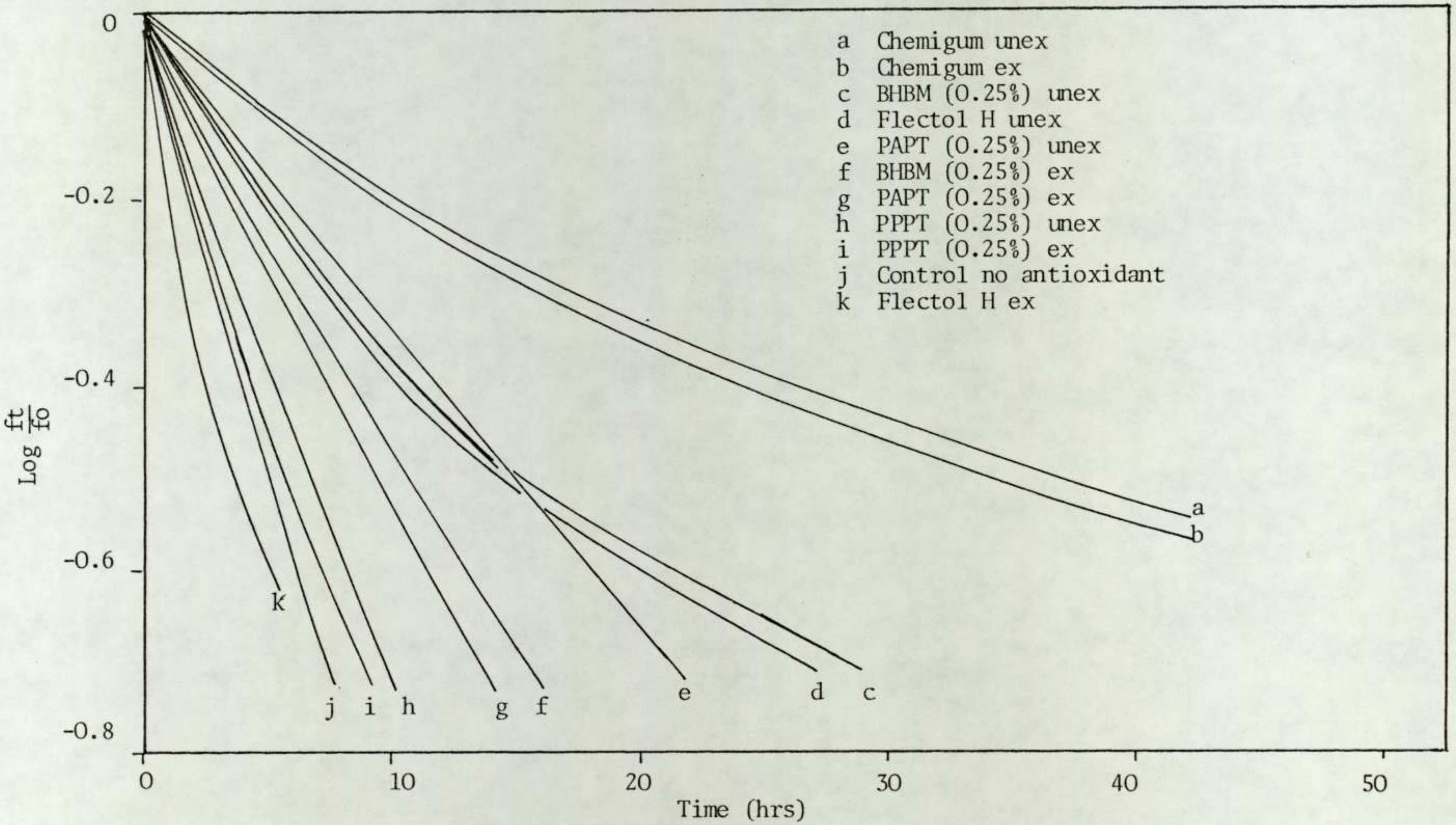


Fig 4.40 Continuous stress relaxation of 20% bound antioxidant MCM (diluted to 0.25%) at 150°C

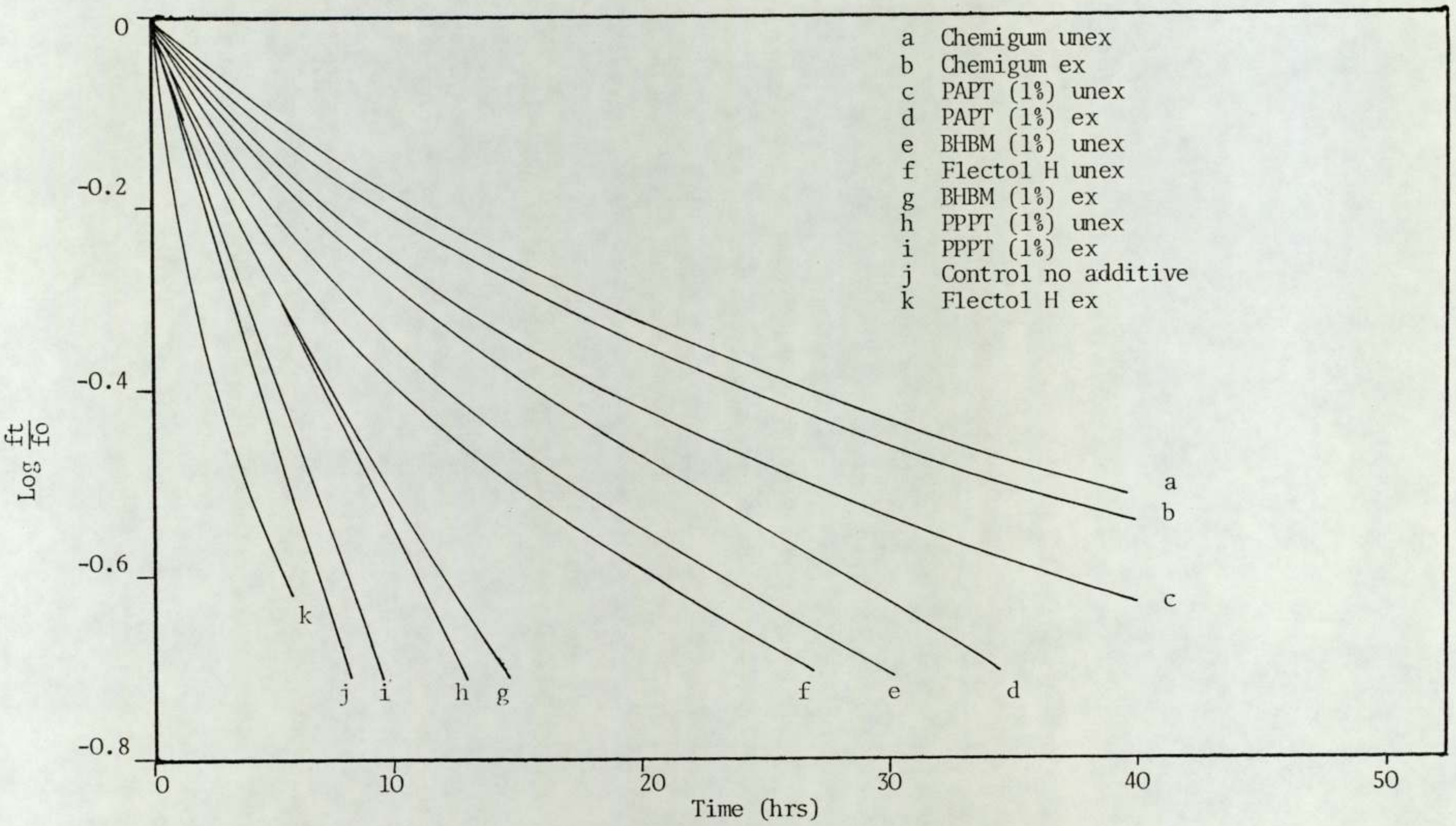


Fig 4.41 Continuous stress relaxation of 20% bound antioxidant MCM (diluted to 1%) at 150°C

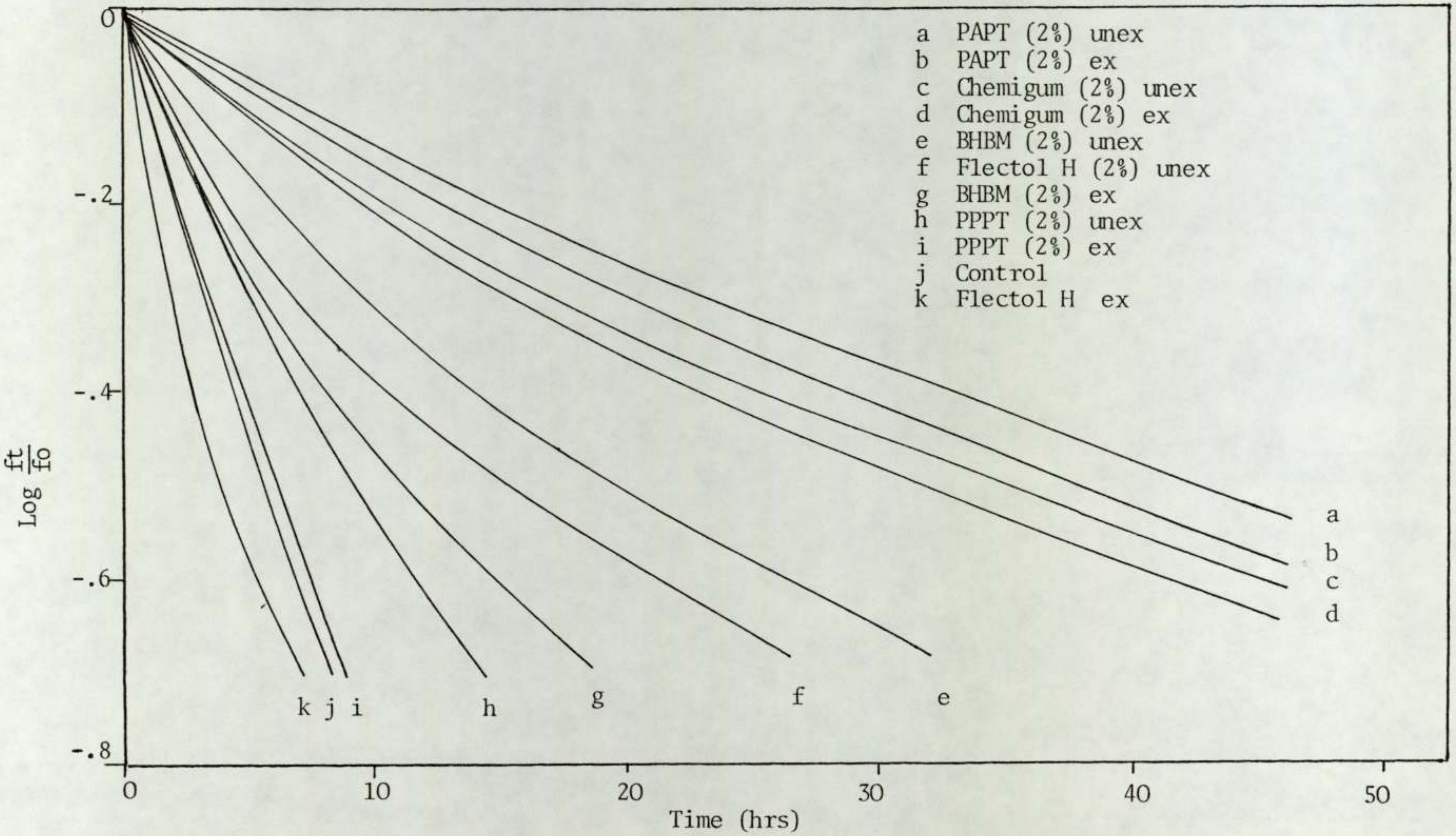


Fig 4.42 Continuous stress relaxation of 20% bound antioxidant MCM (diluted to 2%) at 150°C

autoretarding. Tables 4.9 and 4.10 show the time for the rubber to relax to 50% of the initial force.

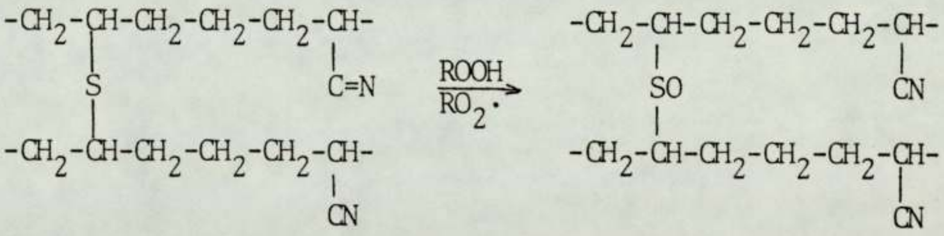
In none of the samples was an induction period observed and the antioxidant efficiency was very much dependent on the concentration. As the concentration is increased, so is the rate of retardation increased. It is observed that at low concentration (0.25%) in the samples produced from latex procedure, BHBM was much more effective than PAPT or Flectol-H before extraction but after extraction PAPT and Flectol-H were reduced to no more than the control (Fig 4.37). A comparison of Chemigum at this concentration is not possible since its concentration is much higher (2 - 3%). At the same concentration (0.25%) vulcanisates produced by the mechanochemical process (Fig 4.40) shows PAPT to be superior before extraction but after extraction BHBM was slightly better than both PPPT and Flectol H behaved very similarly to the control sample. The improved activity of PAPT is probably due to the higher binding level achieved in the torque rheometer.

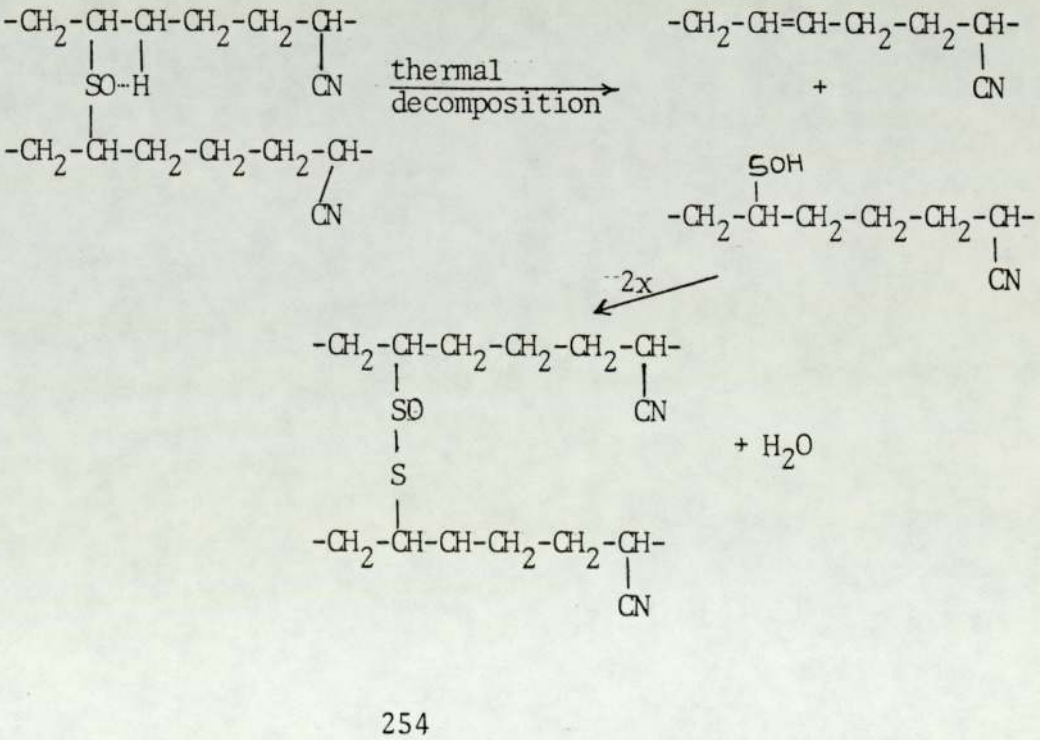
At a concentration of 1% (Fig 4.38), the vulcanisates produced by the latex procedure showed that PAPT was more effective than BHBM, Flectol-H and the control before extraction and after extraction. The same effect is observed with the vulcanisate produced through the mechanochemical procedure (Figs 4.40 - 4.42). At concentration 2% (Figs 4.42 and 4.39) it is clear that PAPT is more effective irrespective of the procedure involved in the masterbatch formation. In the unextracted samples, the order of activity is PAPT > Chemigum > BHBM > Flectol-H > control, but after extraction in the samples produced by the latex procedure, the order is Chemigum > PAPT > BHBM and control > Flectol-H. Whereas by the mechanochemical process the order after extraction is PAPT > Chemigum > BHBM > PPPT = control > Flectol-H. It is however observed that after 35 hours, PAPT dropped sharply below Chemigum.

The resistance shown by the control sample is probably due to the activity of ZDMC produced during cure.

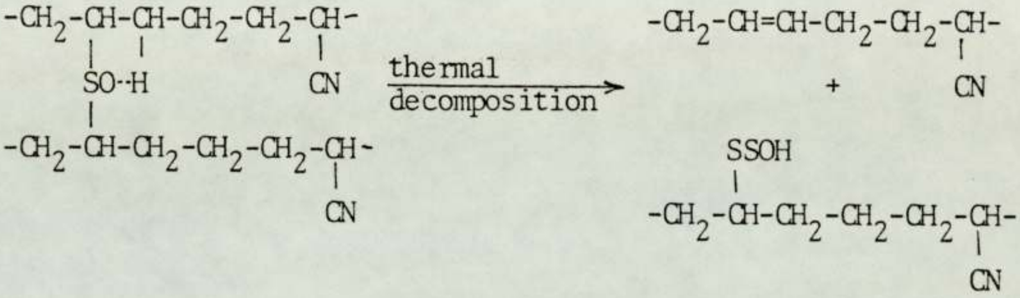
After the removal of unbound antioxidant, accelerator fragments and ZDMC, the antioxidant activity (at 0.25%) was greatly reduced. This is consistent with the oxygen absorption studies. At 2% the stability of the vulcanisates containing PAPT were retained to a high level after extraction and this is very similar to the behaviour of Chemigum whereas BHBM, Flectol H, PPPT lost most of their protective ability. The improved ageing provided by the antioxidants is due to the fact that they remain as part of the rubber molecule and in the unextracted samples the oxidation products of the antioxidants namely mono- and disulphides which were converted to antioxidant species, together with the presence of ZDMC contributed to the stability of the rubber.

As discussed earlier, the main network structure produced in these vulcanisates are mixtures of mono- and disulphide cross-links and the formation of pendant accelerator groups as main chain modification. Since hydroperoxides are inevitably formed in subsequent ageing of the vulcanisate, this implies that the reaction of hydroperoxide with the various sulphur compounds in the vulcanisate will produce sulphur oxidation products. Some of which will inhibit the oxidation of the vulcanisate and others may be pro-oxidant. It has been shown (136,137) that scission of cross-links occurs when sulphurated vulcanisates are oxidised and this may be represented as follows.





From the scission reaction, involving sulphur cross-links, sulphenic acid intermediate was formed and a new cross-link containing two sulphur atoms was formed because of the rearrangements a decrease in the cross-link density may be observed. The thiolsulphinate structure can react further and can undergo scission by a similar mechanism to give thiosulphoxylic acid.



The sulphenic acid (RSOH) and thiosulphoxylic acid (RSSOH) formed from the oxidised sulphur atom of the antioxidants and some from the sulphur cross-link would be expected to react with hydroperoxides to form the sulphinic (RSO_2H), sulphonic (RSO_3H) and probably the thiosulphuric ($RSSO_3H$) acids. All these acids have been shown to be powerful destroyers of hydroperoxides through the breakdown products (SO_2, SO_3, H_2SO_4). This will be discussed in more detail in Chapter Five. Since the sulphur cross-links and the pendant groups containing sulphur together with ZDMC are reservoirs of potential oxidised sulphur compounds which produce peroxide decomposing derivatives as needed during the oxidation process the stability of the rubber samples is not unexpected. It must be noted that the antioxidants (thiol based bound antioxidants)

Table 4.9 Stress relaxation of vulcanisate from 20% latex masterbatch (LM) NBR latex diluted

Vulcanisate Sample	% AO Bound	Concentration of antioxidants after dilution					
		Time for stress to decay to 50% (hrs)					
		Before extraction			After extraction		
		0.25%	1%	2%	0.25%	1%	2%
BHBM	60	12	15	17.5	4	4	11
PAPT	51	12	15	30	2	10	19
Chemigum	85*	-	-	25.5	-	-	25
Flectol H	-	-	-	11	-	-	3
Control (no antioxidant)	-	-	-	4	-	-	-

Table 4.10 Stress relaxation of vulcanisate from 20% mechanochemical masterbatch solid NBR diluted

Vulcanisate Sample	% AO Bound	Concentration of antioxidants after dilution					
		Time for stress to decay to 50% (hrs)					
		Before extraction			After extraction		
		0.25%	1%	2%	0.25%	1%	2%
BHBM	47	11	12	15	8	7.5	8
PAPT	75	12.5	19	34	7.5	16	30
PPPT	40	5.5	7.5	7	5	5	5
Chemigum	85*	-	-	25.5	-	-	25
Flectol H	-	-	-	11	-	-	3
Control (no antioxidant)	-	-	-	4	-	-	-

* Chemigum appears to contain 2-3% before extraction

in addition to their peroxide decomposing ability also function as chain breaking antioxidants. It is this dual function that enabled them to provide adequate protection to vulcanised nitrile rubber.

4.8 Thermal Oxidative Ageing of Vulcanisates

The thermal oxidative ageing of the vulcanisates was followed by ageing the vulcanisates individually in a six cell air ageing oven (Wallace Instruments Ltd) in a rapid stream of air.

The vulcanisates were aged individually to prevent migration of the antioxidant and thus preventing cross-contamination due to absorption of volatile degradation products and antioxidants between vulcanisates which is a serious limitation of conventional oven ageing tests in which samples are aged together.

The temperature (150°C) of the oven was kept constant by using thermostat control. The air flow was held constant such that 1 cu ft was renewed hourly, the flow was measured and adjusted by means of rotameter attached to the oven.

In order to follow the changes occurring in the vulcanisate, dumbell shaped test samples were hung from cardboard which in turn were hung with the aid of copper wire, so that oxygen was allowed to freely diffuse into both sides of the specimen. The copper wires were then suspended from the lid of each cell of the oven.

The extent of ageing was followed by withdrawing samples at regular intervals and they were subjected to selected physical property tests (hardness, modulus, tensile strength and elongation) which were also measured in the unaged vulcanisate.

It has been suggested(138,139) that the major factors which determine the behaviour of antioxidants in polymers under service conditions are the intrinsic antioxidant activity of the antioxidant determined by its structure. The microenvironment of the antioxidant in the polymer (eg compatibility and ease of migration) and the rate of loss of antioxidant from the elastomer (eg by volatilisation and extraction). The overall effect of these factors can be measured by studying the antioxidant behaviour in the form of a thin film in a rapid air stream. This kind of test tends to accentuate the effect of physical loss from the polymer which can be important under conditions of service and provides similar information to the stress relaxation test.

4.8.1 Result and Discussion

The vulcanisates have been prepared from 20% masterbatch reduced to the desired concentration (0.25. 1 and 2%). The results of the samples from latex procedure are shown in Figs 4.43 - 4.50 and show the behaviour of the samples at 2% level. Tables 4.11 and 4.12 gives the results obtained from the vulcanisate samples prepared via the mechanochemical procedure and Figs 4.51 - 4.54

show the behaviour of the vulcanisates containing 2% of the antioxidants. The antioxidants have been less consistent in their behaviour since different tests give different antioxidant behaviour.

At low concentration (0.25%) the improvement offered by the antioxidants is not significant and most of the samples were much like the control sample, particularly the thiolamide. Because the commercial antioxidants have been used at 2% level, much of the discussion and comparison in the work has been centred around the 2% samples.

In the hardness test, Fig 4.43, for latex masterbatch (LM) all antioxidants gave protection to the rubber and were much better than the control and both BHBM and PAPT hardened more slowly than Chemigum and Flectol-H. It is obvious that the LMCU-BHBM and LMCU-PAPT aged more slowly than LMCE-BHBM and LMCE-PAPT (Fig 4.43, curve B_3, B_2 and Fig 4.44, curves A_3, A_2). It is surprising that the sample which was diluted with untreated latex and containing BHBM (LML-BHBM) was worse than Flectol-H, whereas the corresponding sample containing PAPT (LML-PAPT) was better than Flectol-H and Chemigum after the sixth day but aged more quickly at the initial stage. It is to be observed that Chemigum always starts off slowly but accelerates in the later stages.

Figs 4.51 - 4.54 show the behaviour of the samples produced by the mechanochemical procedure (MCM). The order of antioxidant activity is MCMU-PAPT adduct, Chemigum, MCMU-BHBM adduct, MCME-PAPT adduct, MCME-BHBM adduct, Flectol-H and then the control. The improved behaviour of the PAPT is not unexpected since it is bound to a much higher level but the antioxidant activity does not reflect proportionality with concentration.

Figs 4.45 and 4.46 show the % increase in modulus (M_{100}) of the samples. From the latex procedure (LM) after 3 days the LMCE-(PAPT) was increased by about 30% and LMCE-BHBM by 35%. The LMCU-PAPT increased by 22% and LMCU-BHBM by 21% but a surprising result was observed for the latex diluted sample containing BHBM (LML) (Fig 4.45, curve B_1) but the corresponding PAPT latex dilution sample (Fig 4.46, curve A_1) increased by only 9% but after 6 days it had increased to 35%. The control was brittle, Flectol-H increased to about 95% after 3 days whilst Chemigum increased by 12% after 3 days and by 30% after 6 days and 49% after the eighth day. Table 4.11 shows the time for the vulcanisate to increase by 50% of the original moduli.

Fig 4.52 shows the % increase observed in the moduli of vulcanisates from the mechanochemically produced masterbatch. Table 4.12 shows the time for the samples to increase their moduli by 50% of the original unaged vulcanisate. Despite the higher binding achieved with PAPT, the rate of increase of the

Table 4.11 Retention of physical properties after oven ageing of LM vulcanisate at 150^{o}C

Samples	Ageing time (days)		
	Time to 50% modulus increase	Time to 50% TS decrease	Time to 50% EB decrease
LML (BHBM)	1.5	7	4
LMCU (BHBM)	6	8	7
LMCE (BHBM)	4	7	7.5
LML (PAPT)	7	8	4
LMCU (PAPT)	6.5	8	6
LMCE (PAPT)	5	7	7.5
Chemigum	8	7.5	7.5
Flectol H	1.5	4	2.5
Control (no antioxidant)	brittle	brittle	brittle

Table 4.12 Retention of physical properties after oven ageing of MCM vulcanisates at 150^{o}C

Samples	Ageing time (days)		
	Time to 50% modulus increase	Time to 50% TS decrease	Time to 50% EB decrease
MCMU (BHBM)	6	4.5	6
MCME (BHBM)	3.5	4	4.5
MCMU (PAPT)	7.5	6.5	8
MCME (PAPT)	5.5	6.0	6
Chemigum	8	7.5	7.5
Flectol H	1.5	4	2.5
Control (no antioxidant)	brittle	brittle	brittle

modulus was higher than that of Chemigum but slower than that of BHBM, Flectol-H and the control samples.

The measurement of retained tensile strength by the vulcanisates are shown in Figs 4.48 and 4.49 for the samples from latex masterbatch and Fig 4.53 for those from the mechanochemical procedure. After 6 days (from both procedures) vulcanisates retained more than 50% of their original tensile strength, except the control sample and Flectol-H which after 3 days retained only 19 and 40% of the original tensile strength. However, samples from the latex procedure showed only a marginal difference in behaviour but from the mechanochemical procedure the PAPT samples protected the rubber more effectively than the BHBM, Flectol-H but were not as good as the Chemigum (Fig 4.53). Flectol-H shows auto-inhibition after the third day whilst the MCME auto-accelerated after the sixth day.

The results obtained by measuring the percentage elongation retained are shown in Figs 4.49, 4.50 and 4.54 and Tables 4.11 and 4.12 is the time for the elongation to decay to 50% of the original. The results are very similar to those obtained in the measurement of tensile strength. From Figs 4.48, 4.49 and 4.53 it is clear that the vulcanisate from LML lost their elongation with a steadily increasing rate but more slowly than the rate at which control sample and Flectol H lost the elongation. LMCU and LMCE decayed more slowly but Chemigum was better (see Figs 4.49 and 4.50). The samples from the mechanochemical process

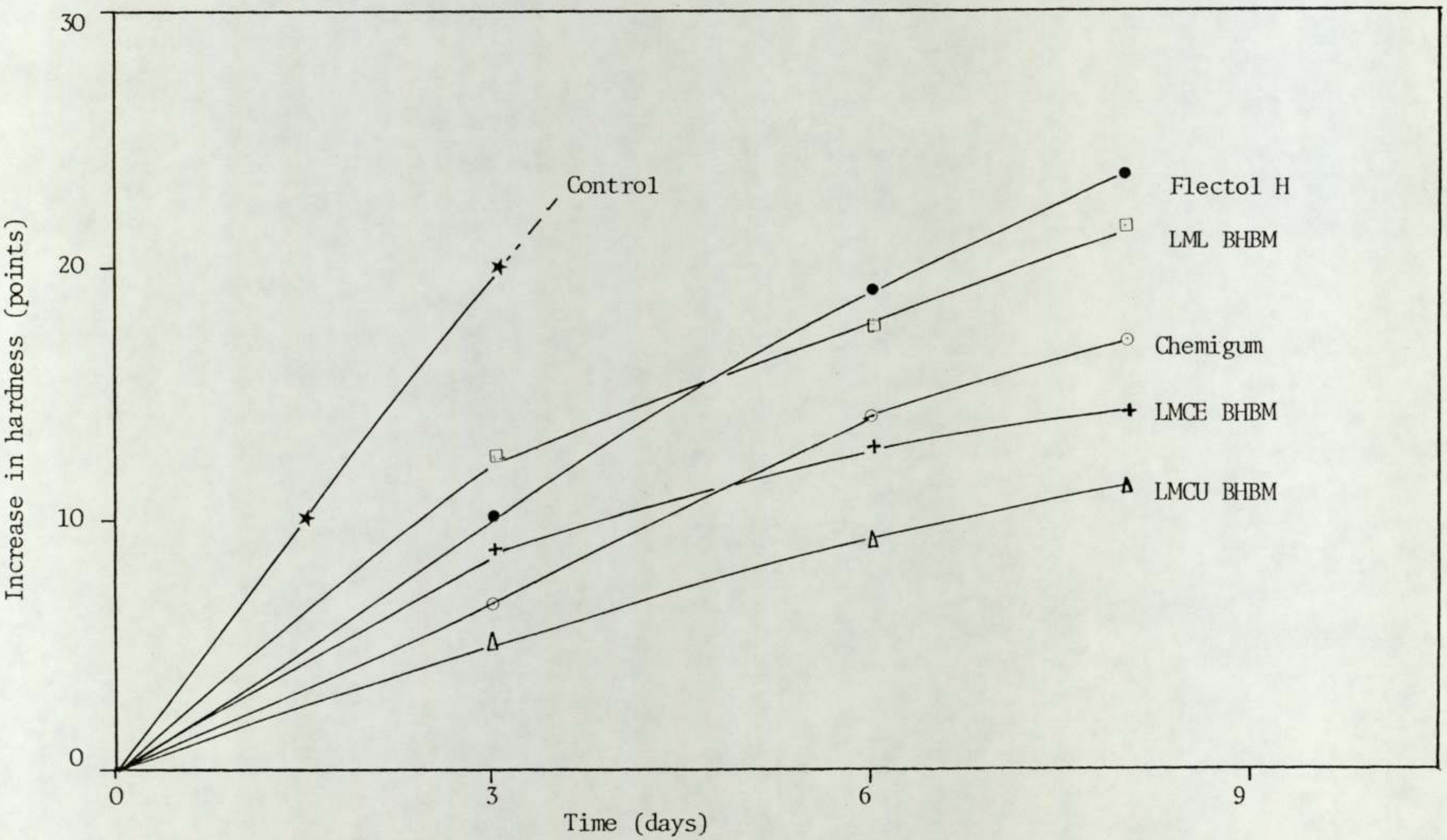


Fig 4.43 Effect on shore 'A' hardness of oven ageing of LM (bound BHBM) vulcanisates

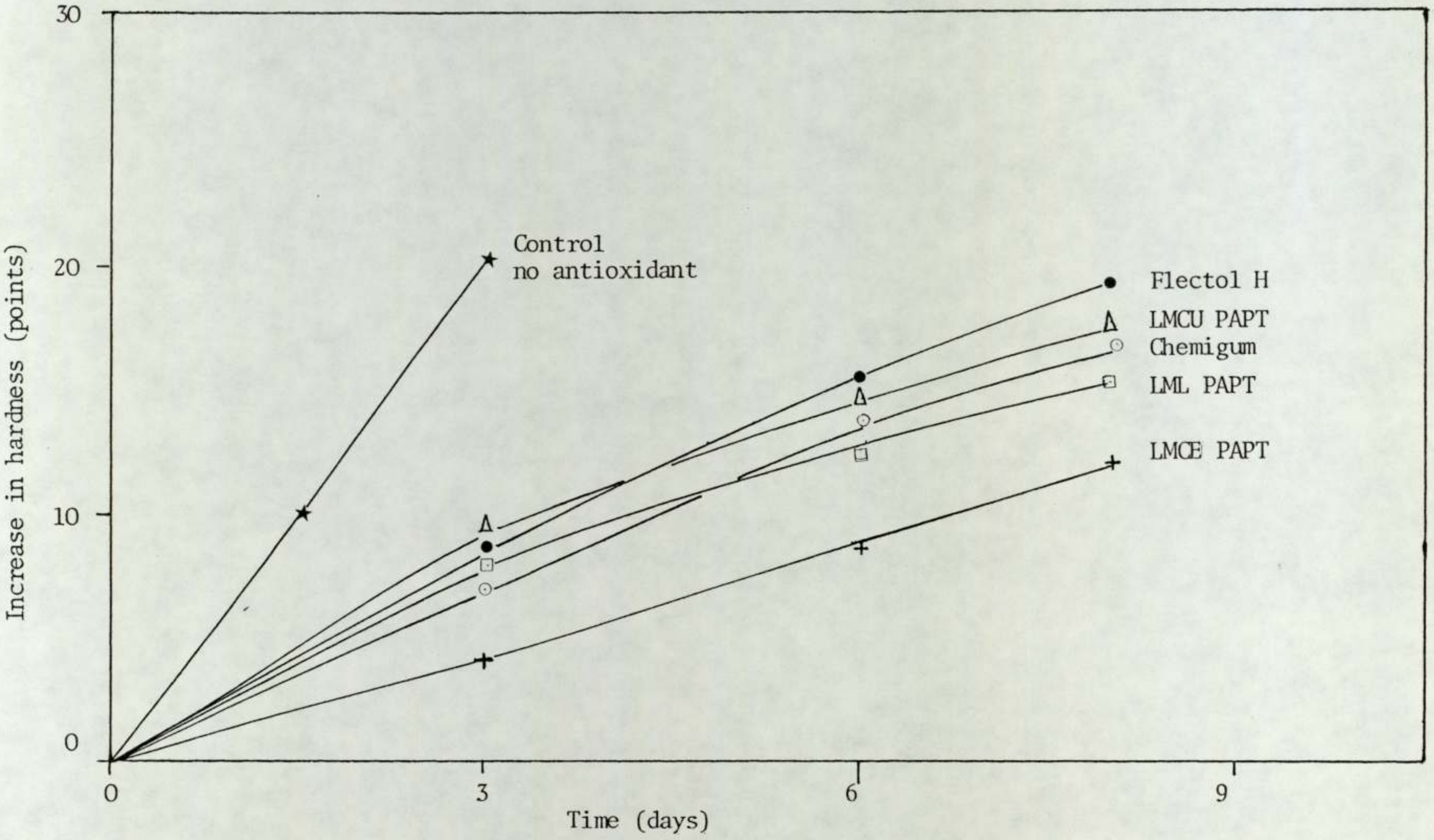


Fig 4.44 Effect on point shore 'A' hardness of oven ageing of LM (bound PAPT) vulcanisate at 150°C

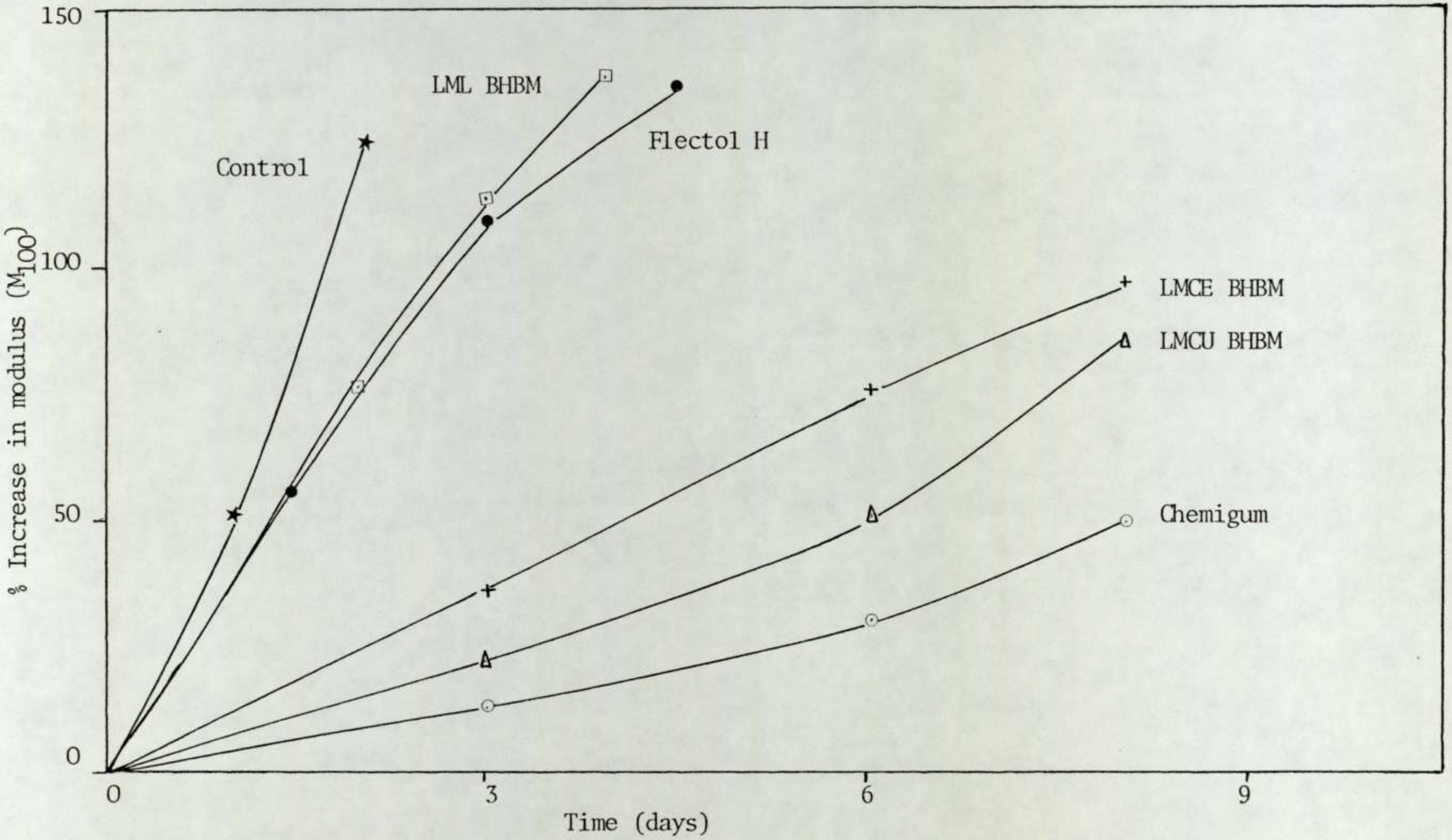


Fig 4.45 Effect on modulus of oven ageing of LM (bound BHBM) vulcanisate at 150°C

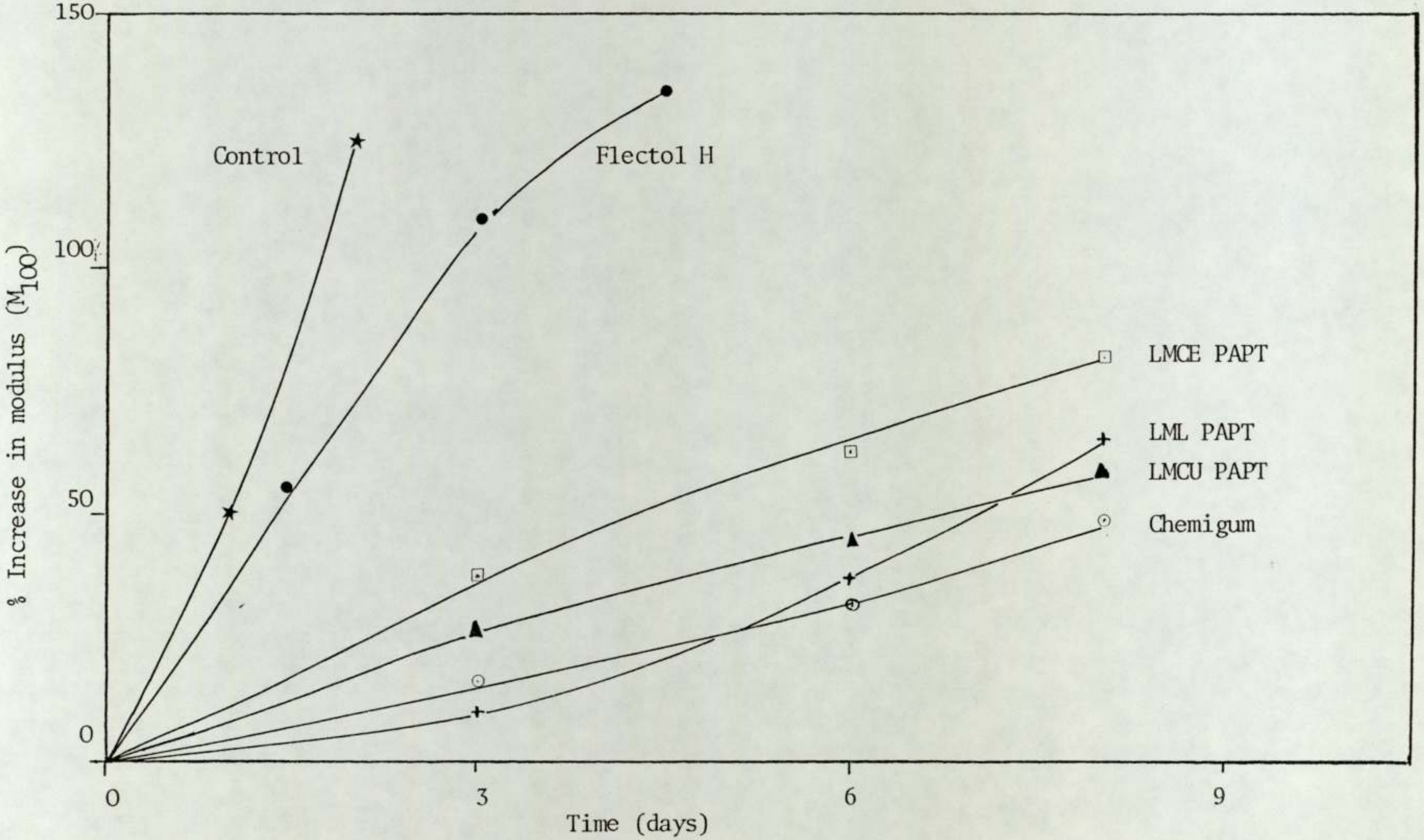


Fig 4.46 Effect on modulus of oven ageing of LM (bound PAPT) vulcanisate at 150°C

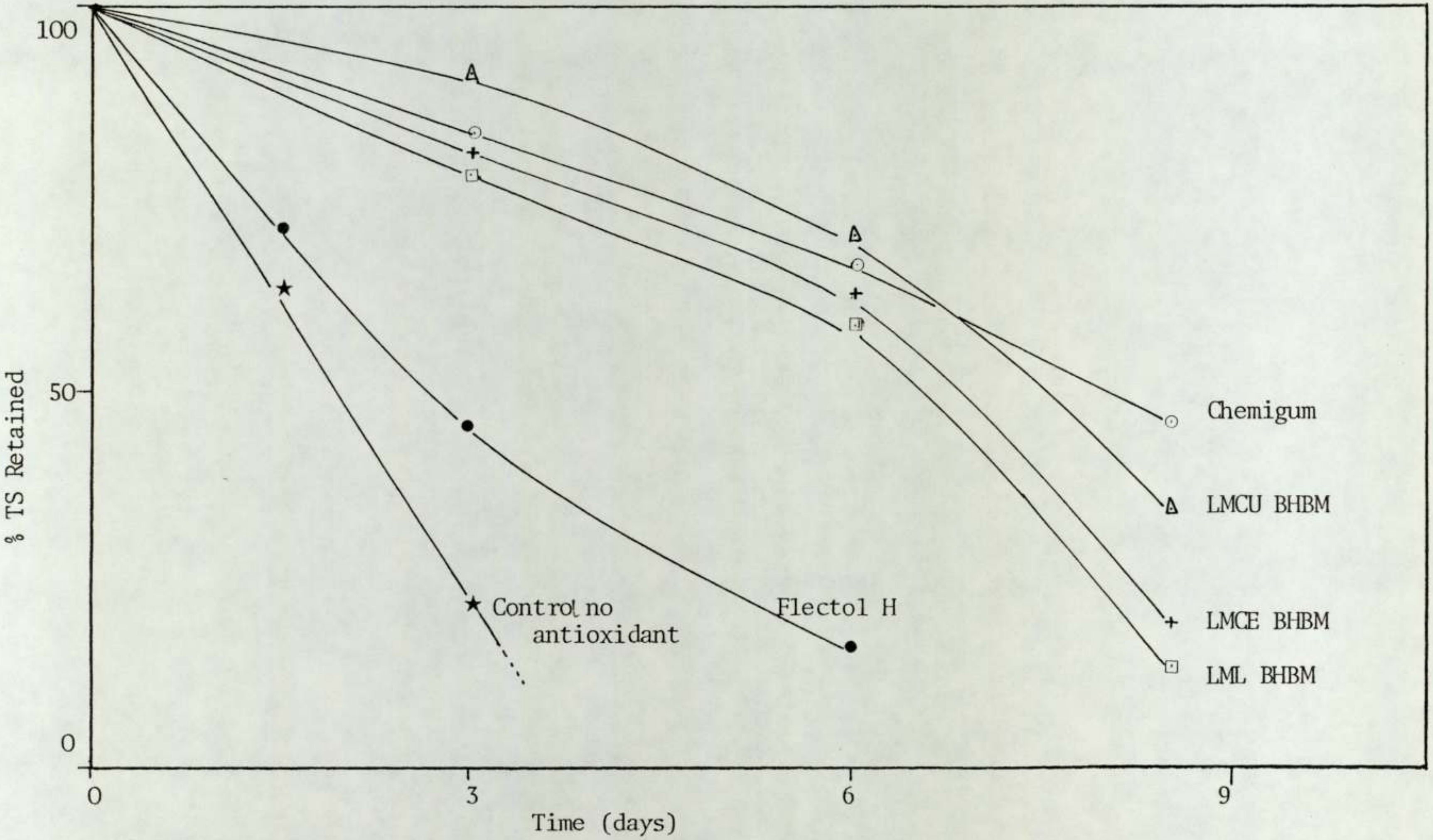


Fig 4.47 Effect on TS of oven ageing of LM (bound BHBM) vulcanisates at 150°C

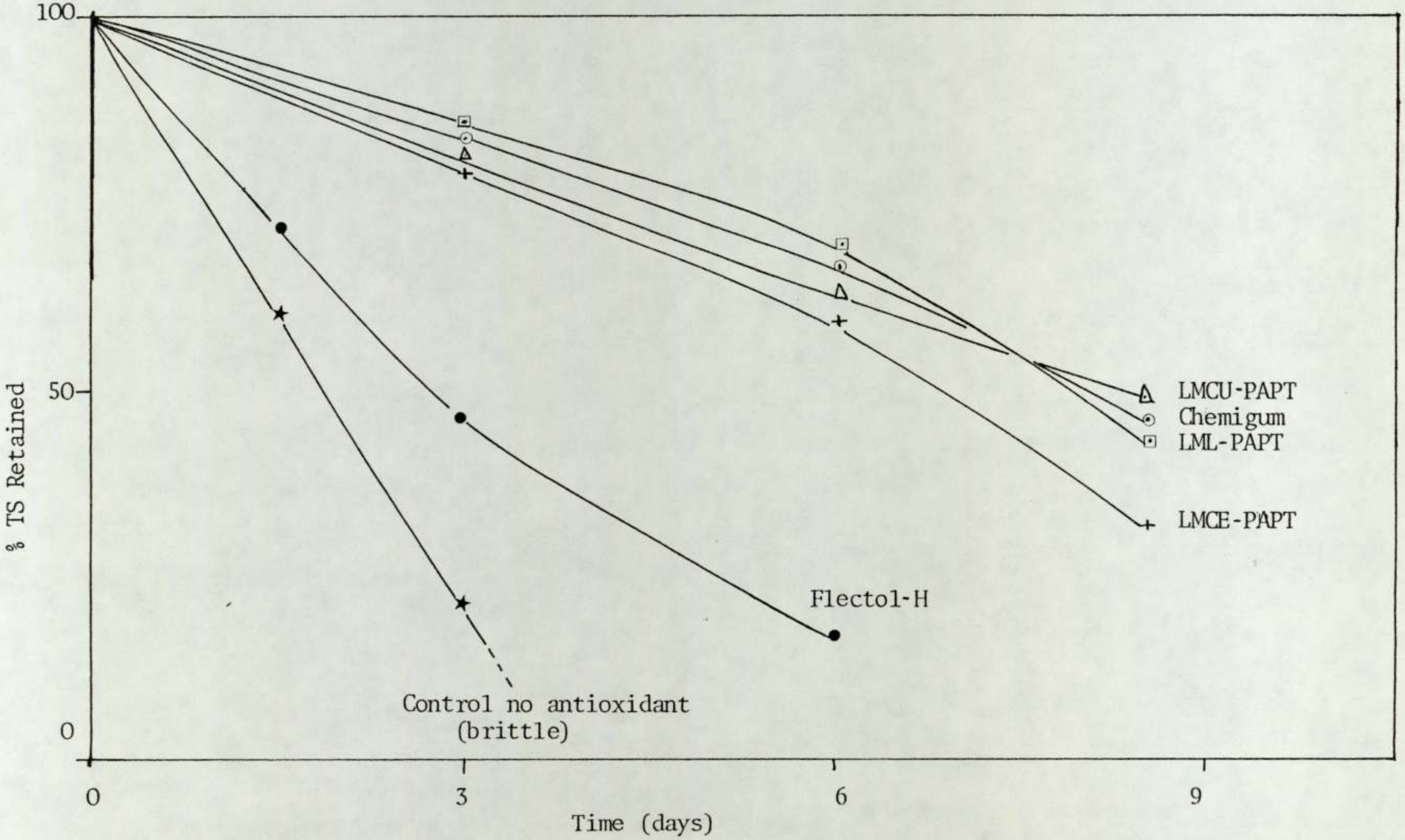


Fig 4.48 Effect on TS of oven ageing of LM (bound PAPT) vulcanisates at 150°C

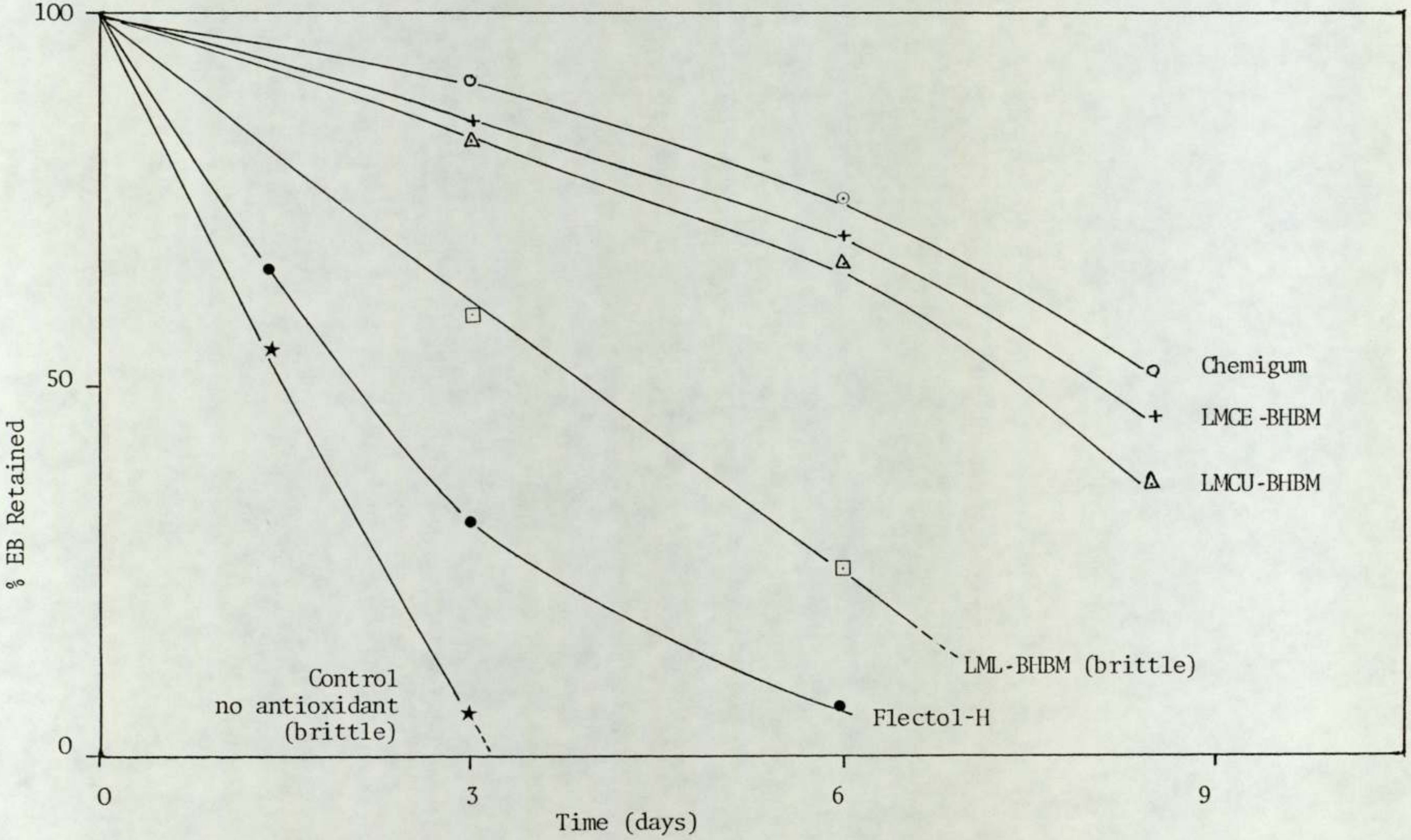


Fig 4.49 Effect of oven ageing on EB of LM (bound BHBM) vulcanisates at 150°C

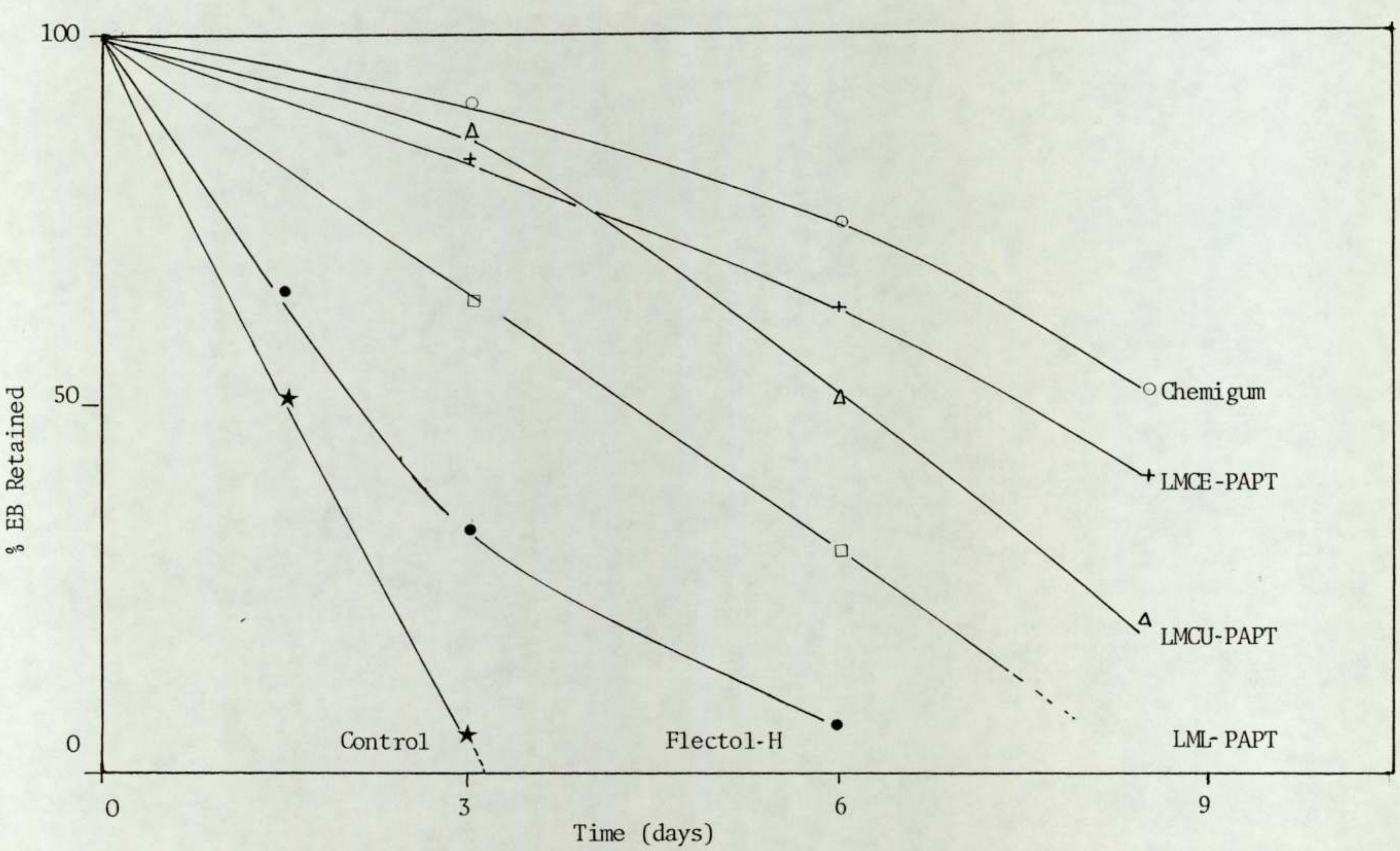


Fig 4.50 Effect on EB of oven ageing of LM (bound PAPT) vulcanisates at 150°C

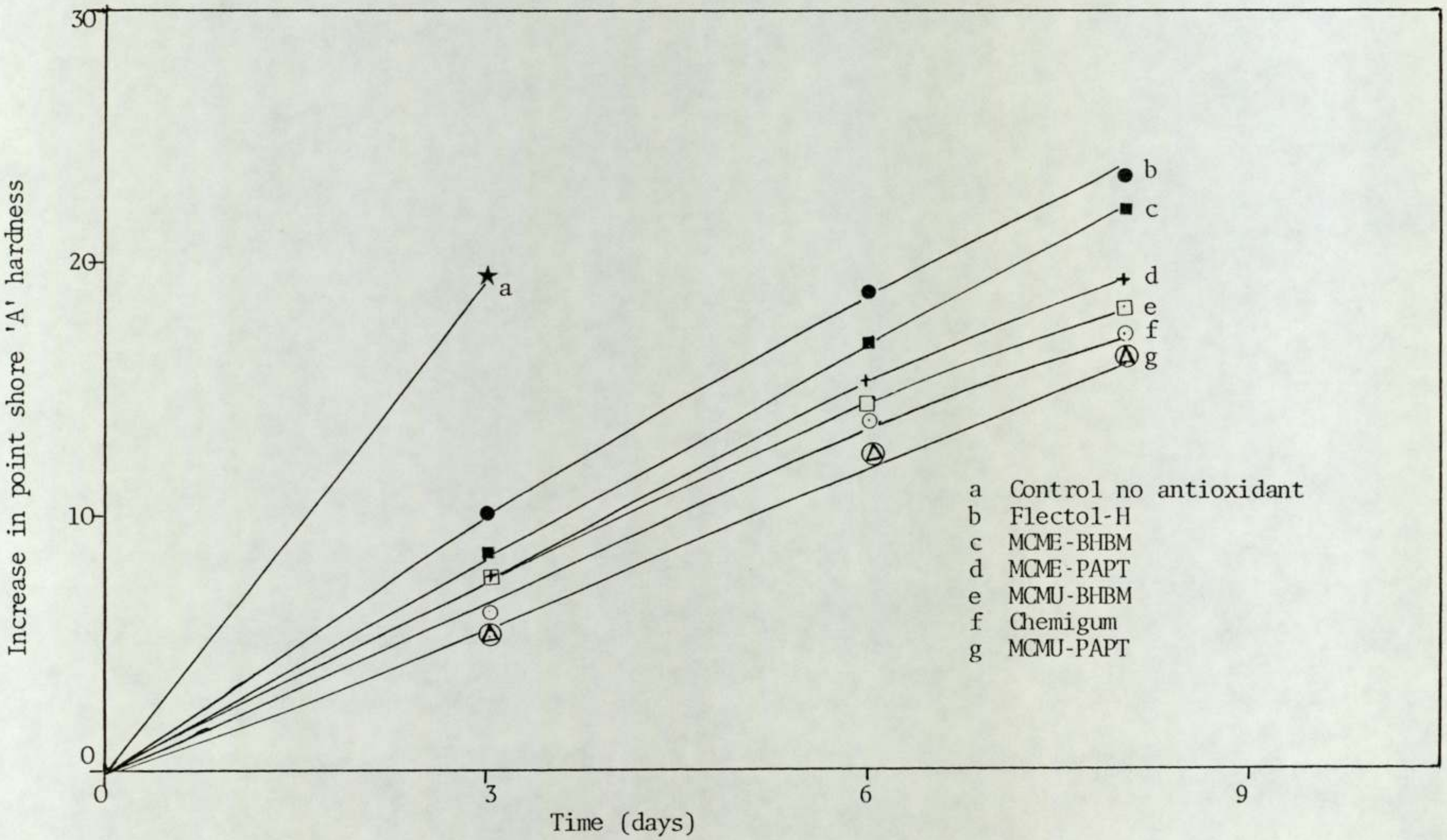


Fig 4.51 Effect on point shore 'A' hardness of oven ageing of MCM vulcanisates at 150^{o}C

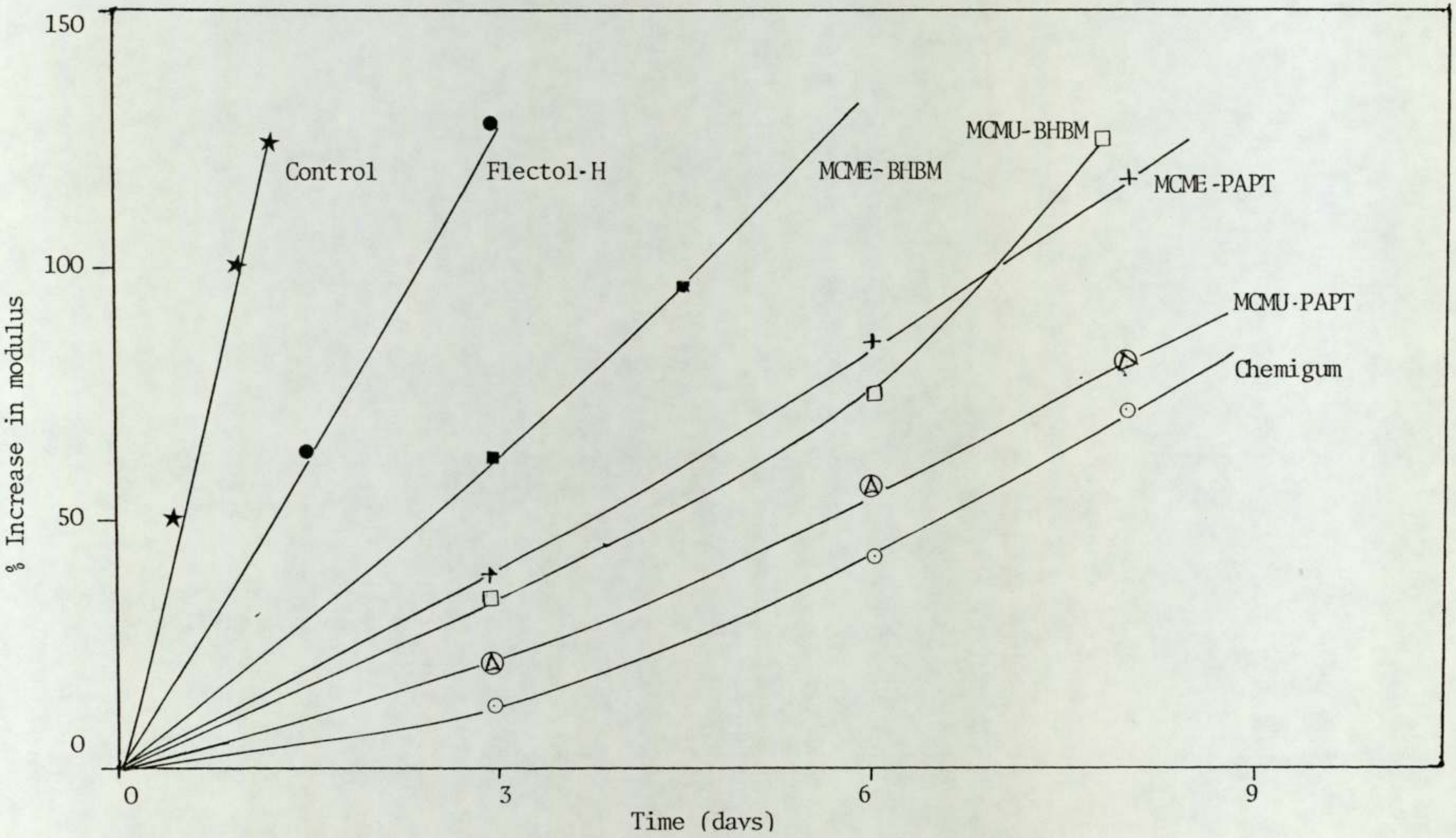


Fig 4.52 Effect on modulus of oven ageing of MCM vulcanisates at 150°C

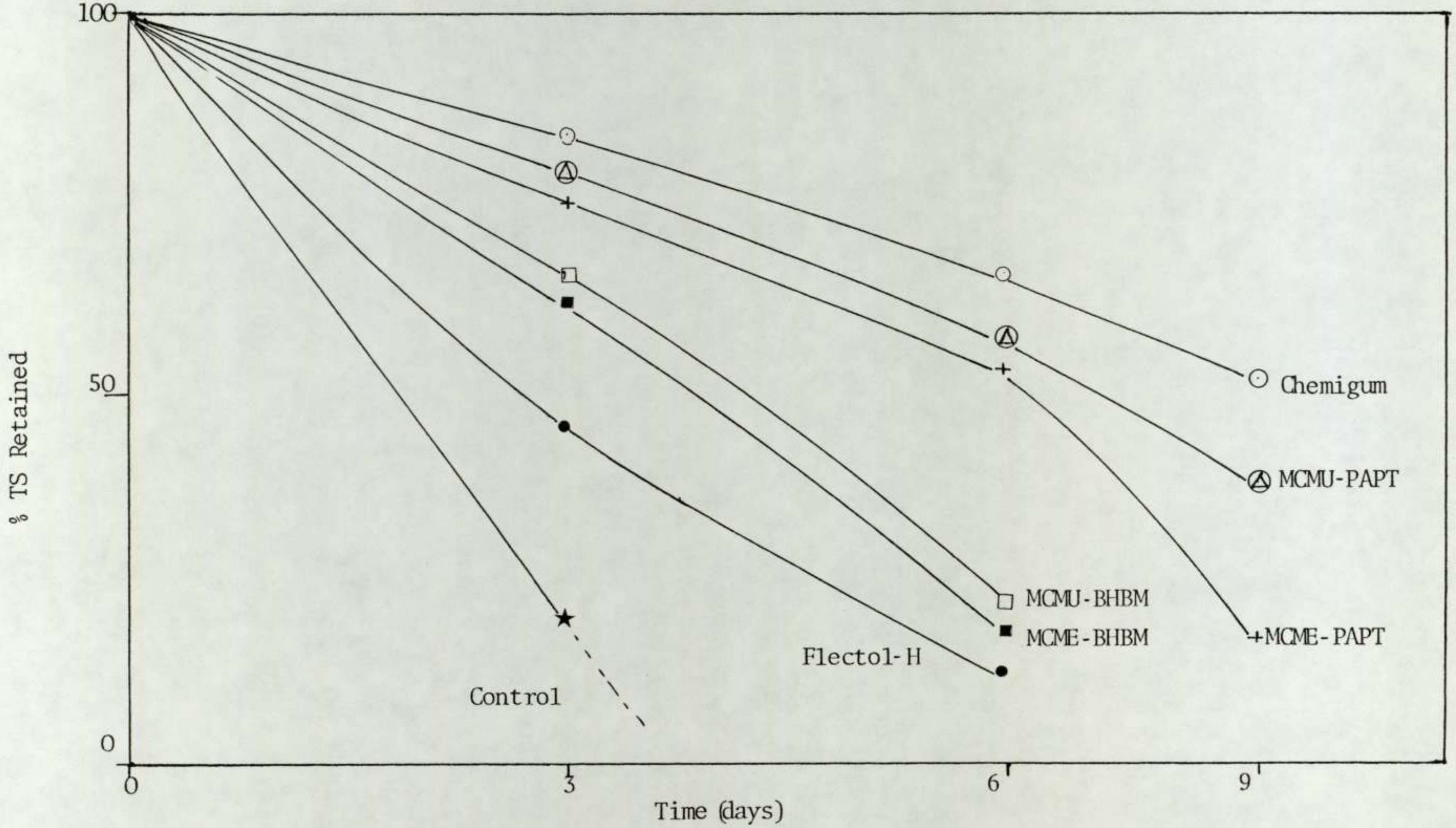


Fig 4.53 Effect on TS of oven ageing of MCM vulcanisates at 150°C

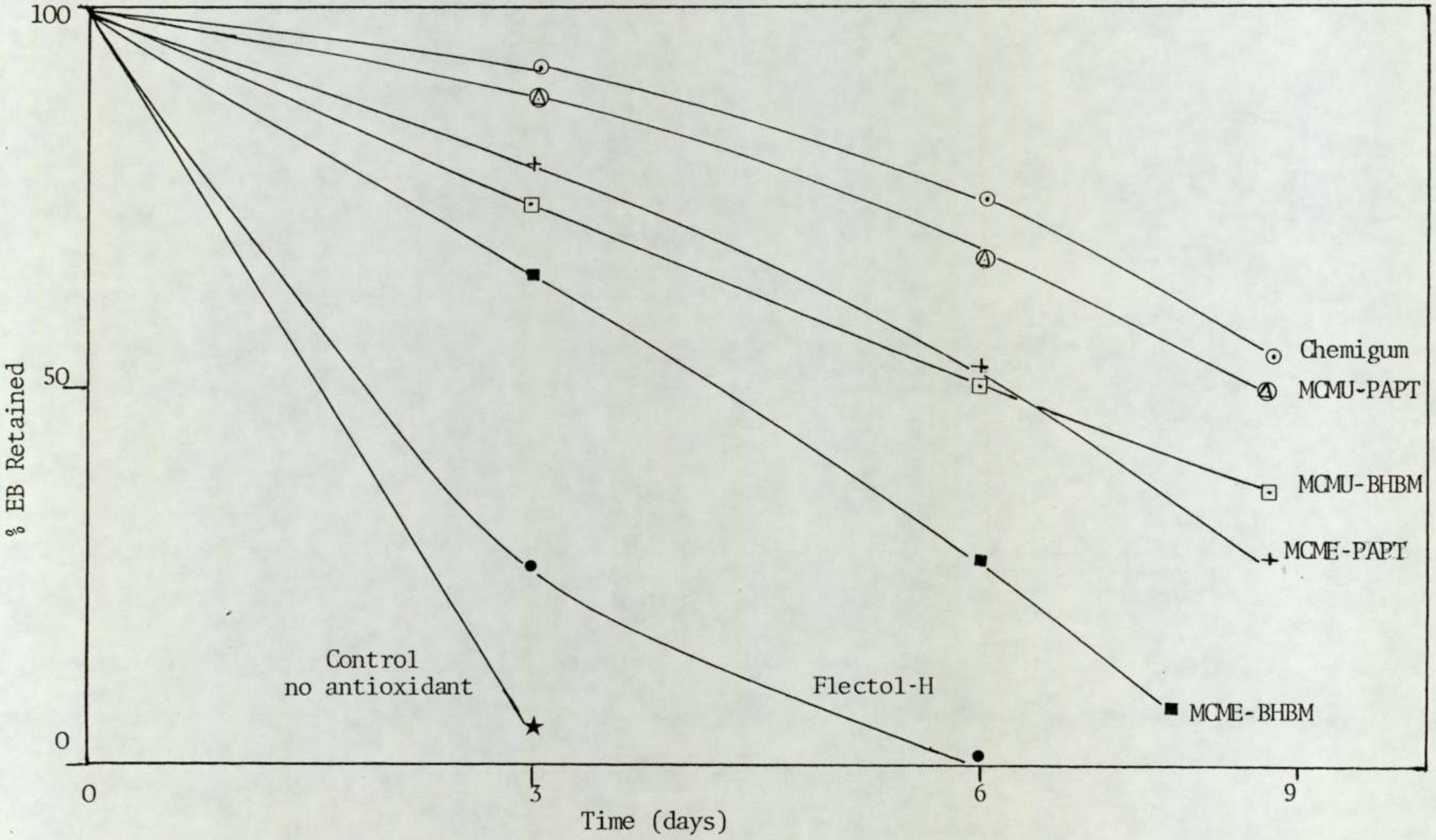


Fig 4.54 Effect on EB of oven ageing of MCM vulcanisates at 150°C

showed that the rate at which the elongation at break decreases in the MCMU-PAPT adduct is quite similar to that of Chemigum but after extraction, the rate increased. Despite the rate increase, the sample retained about 50% of its elongation after 6 days. Despite the low binding level of BHBM, the excellent thermal stability of this antioxidant is reflected in Fig 4.54 before extraction the EB decayed to 50% after 6 days and after extraction it still retained 25% of the original. The ineffectiveness of Flectol-H to offer adequate protection may lie in the fact that it is being lost from the system by volatilisation which does not occur in other samples since the antioxidants are bound and are part of the rubber molecule.

4.9 Effect of Liquids on Vulcanisates

This test is used to simulate conditions encountered by vulcanisates during severe service conditions (eg under bonnet rubber seals). It measures the ability of vulcanisates to withstand the effect of engine oils under definite conditions of temperature and time. The resulting deterioration is determined by noting the changes in physical properties of the vulcanisate before and after immersion in the test liquid.

In view of the wide variations often present in service conditions, this accelerated test may not give direct correlation with service performance (140). However, the method produces comparative data on which to base judgment as to expected service is

quality and its essentially useful in research and development.

The absorption of the test liquid by the vulcanisate causes the rubber to increase in volume and this is the phenomenon of swelling, a consequence of which is the deterioration in physical properties caused by the oxygen dissolved in the liquid. Although raw rubbers are completely soluble in certain liquids, vulcanised rubbers are virtually insoluble. Strong bonds such as chemical cross-links between rubber chains prevent rubber molecules from becoming completely surrounded by liquid and restrict the deformation of the rubber. The swelling of rubber by liquids is a diffusion process. As diffusion processes proceeds, the dimension of the rubber components will increase until the concentration of the liquid is uniform throughout the components and equilibrium swelling is achieved. The amount of a given liquid that will diffuse into the rubber before it reaches equilibrium depends upon the number of cross-links per unit volume of rubber. The greater the number of cross-links per unit volume, the shorter the average length of rubber chains between cross-links and the lower the degree of swelling. Apart from cross-linking restrictions on the equilibrium swelling, the degree of swelling depends also on the compatibility of the rubber and the liquid on molecular basis. It also depends on the amount and type of filler present in the rubber and the rate at which swelling proceeds depends upon the relative molecular size of the diffusing liquid molecule.

The choice of immersion time will depend upon the nature of the vulcanisate and the test temperature must be controlled. To obtain information on the rate of deterioration, it is necessary to make determinations after several immersion periods.

4.9.1 Cyclic Oil/Air Ageing of NBR Vulcanisates

For the purpose of this test, it is desirable to use liquid with which the vulcanisate will come into contact with during service. In this study, the test fluid used is the ASTM-oil number 3. The test method and apparatus were according to American Standard test method(140) (see Procedure) and as described by Dunn and co-workers(141). The cyclic alternating ageing of the vulcanisate in air and oil is very important because of the frequent exposure of automotive parts to both oil and air. The retained physical properties are measured after each such cycle.

PROCEDURE

Dumbell shaped samples were aged for 24 hours in ASTM oil number 3 according to ASTM-D-471. They were then wiped with an absorbent medium to remove excess oil and aged in a six-cell air oven (Wallace Instruments Ltd) at 150°C for 24 hours. This cycle was repeated several times. Samples were removed and tested at the end of each cycle (four samples each time, tested each time).

4.9.2 Results and Discussion

After ageing the increase in Shore 'A' hardness was measured by using the Shore durometer, with the frustoconical indentor readings being in arbitrary degrees, also the percentage increase in moduli, and percentage retention of tensile strength and elongation at break for various vulcanisates, after one to three cycles consisting of 24 hours in ASTM oil number 3, followed by a further 24 hours in air at 150^{O}C. The results are shown in Figs 4.55 - 4.66.

Fig 4.55 shows the increase in hardness. It is unexpected to find that LMCU-BHBM adduct showed a decrease in hardness after the first cycle (curve B) but after the second cycle, it increased by two points. The hardness of LMCE-BHBM adduct by contrast increased steadily. The latex diluted product (LML) started very slowly but later auto-accelerated, vulcanisates containing Flectol H and antioxidant N-(4-anilinophenyl)methacrylamide hardened so quickly that they were little better than the control but after the first cycle they autoretarded. Fig 4.56 shows the surprising superiority of LMCU-PAPT adduct. There was an induction period of more than one cycle after which it tended to increase autocatalytically, though at the end of the third cycle, it still had not increased more than nine points. The LMCE-PAPT adduct as well as the LML-PAPT adduct hardened at a similar rate which is higher than that of LMCU but far better than Chemigum, Flectol-H and the control.

The vulcanisates produced by the mechanochemical procedure behaved in a similar way (Fig 4.63); the unextracted vulcanisate showed the slowest increase in rate of hardening. The vulcanisates containing BHBM (MCM-BHBM) and bound to only 47% showed a higher rate.

The Flectol-H and Chemigum showed rates initially not much different from the control, but they autoretarded after the second cycle.

The measurement of the percentage increase in moduli is shown in Figs 4.57, 4.58 and 4.64. The results showed that the unextracted samples show a smaller increase to those of the extracted samples and the control. In Fig 4.57, the initial rate at which LML BHBM (curve B_1) hardened was slowest but auto-accelerated after the second cycle. The LMCU-BHBM adduct on the other hand gradually increased and after the second cycle it had increased by 44% of the original modulus. The modulus of the extracted coagulum (LMCE-BHBM) after an initial slow increase, auto-accelerated. The control sample was brittle after the first cycle, Flectol-H after the second cycle, while Chemigum autoretarded after the first cycle. Fig 4.58 shows that LMCU PAPT increased by only 50% after the third cycle. Although LMCE-PAPT adduct increased relatively more slowly than Flectol-H, by the third cycle it had increased by 100% (curve A_2). The LML-PAPT initially increased much more slowly than Chemigum but auto-accelerated after the second cycle.

The behaviour of the unextracted PAPT samples produced by the mechanochemical procedure (MCMU) (Fig 4.64) was extremely good. Even after the third cycle, the increase in modulus was below 40% whereas all other vulcanisates increased by 50% after the second cycle. After the first cycle, the antioxidant efficiency of both the bound antioxidants based on thiol was higher than in Chemigum or Flectol-H.

Figs 4.59, 4.60 and 4.65 compare the rate of decay of tensile strength after each cycle and Tables 4.13 and 4.14 show the time to decay to 50% of the original tensile strength. Fig 4.59 shows that the Flectol H containing sample, the LMCU-BHBM adduct and the LML vulcanisate lost 50% of the initial tensile strength while Chemigum lost 45% and the LMCE-BHBM lost 47% by the second cycle and the control sample auto-accelerated and was lost in the same time interval. PAPT latex procedure products on the other hand retained much of their tensile strength over this period (Fig 4.60). LMCU-PAPT retained about 77% after the second cycle and 55% after the third cycle. The LMCE-PAPT adduct initially showed autoretardation but after the first cycle auto-accelerated. The LML-PAPT lost its tensile strength linearly, 50% of the initial tensile strength was lost after the second cycle and 82% after the third cycle.

Fig 4.65, curve 1) shows the improvement offered by PAPT unextracted masterbatch from the mechanochemical process (MCMU-PAPT). Except for the control, Flectol-H and MCME-BHBM adduct which lost 75%, 68% and 62% respectively of the initial tensile strength after the second cycle, all other samples retained about 60% of the initial tensile strength after the second cycle. The improvement showed by MCMU-PAPT over the latex products (LML **and** LMCU-PAPT might be due to the high binding level in MCM products) (compare Figs 4.59, 4.60 and 4.65).

After cyclic oil/air ageing the retained EB was measured the results shown in Figs 4.61, 4.62 and 4.66. Fig 4.61 shows the decay of EB in samples containing BHBM from the latex procedure. The control, Flectol-H sample and LMCE-BHBM adducts auto-accelerated and decayed to less than 50% after the first cycle, while Chemigum and LMCU-BHBM adduct are very similar and retained about 70%. After the second cycle, Chemigum retained 45%, unextracted coagulum adduct retained 37% and the extracted 26% and at the end of the third cycle, they all retained less than 20% but surprisingly LML-BHBM adduct showed initial retardation, but otherwise similar.

Fig 4.62 shows the behaviour of samples containing PAPT. The latex dilution adduct again showed a lower rate of EB loss while LMCU-PAPT and LMCE-PAPT and Chemigum were very similar. However at the end of the third cycle, LMCU-PAPT adduct retained 32%, LMCE-PAPT adduct 27%, LML 21%, Chemigum 9%, Flectol-H and the control were unfit for test (brittle).

The results obtained from the vulcanisates from mechanochemical procedure are shown in Fig 4.66 again the superiority of MCMU PAPT adduct is clearly shown. The better stabilisation effect of PAPT in this sample than in the latex is definitely due to higher binding achieved by the mechanochemical binding procedure. The EB of Chemigum decreased more or less at a very steady rate, retaining 45% and 9% after second and third cycles respectively. The MCMU-BHBM adduct showed a linear rate of EB loss and decayed to nil after the third cycle. The EB loss of MCME-BHBM adduct is auto-accelerating but was much better than Flectol H and the control samples.

The result obtained with BHBM and PAPT reflected the extent of binding of the antioxidants. In the latex procedure, 60% of BHBM was bound while only about 49 - 52% of PAPT was bound (see Tables 2.14 and 2.15). Although it is generally accepted that better dispersion of antioxidant is achieved in the latex than on the mill, the undistinguished performance of the vulcanisates produced by the latex procedure in the cyclic oil/air test is perhaps an indication that the dispersion of antioxidant is not a major problem in this present work.

The improved performance of the MCM PAPT particularly in the cyclic oil/air test might be due to the post vulcanisation/post binding effect of unbound antioxidant during ageing. The rapid loss of the useful physical properties of the vulcanisates containing Flectol-H indicates that the antioxidant is lost at high temperature by volatilisation in the oven ageing test and by the combined effects of leaching and volatilisation during cyclic oil/air ageing and thus the advantage of bound antioxidant is shown.

It is known (Tables 3.3 and 3.4) that the level of binding achieved with PAPT by the mechanochemical procedure is high (75%) while only about 47% of BHBM could be bound by the same procedure. The observed difference in their performances could be attributed to the difference in the degree of binding and hence the availability of antioxidant to protect the vulcanisate under extractive conditions. It was also found that Chemigum which is a nitrile rubber copolymerised with amine N-(4-anilinophenyl)-methacrylamide was less effective in the cyclic oil/air test but is good in a dry atmosphere. This is probably an indication that the rubber could have been swelled by the oil under experimental conditions and the rubber network therefore damaged by the small amount of oxygen dissolved in the oil. Also a very slow leaching out of the damaged antioxidant fragment may be taking place. If however none of the above mentioned destructive processes occurred, then the better performance of the thiol based bound antioxidants PAPT could be due to their dual antioxidant function (chain breaking mechanism and peroxide decomposing activity).

The use of the thiol based bound antioxidants PAPT and BHBM, unextracted, permitted good retention of elongation at break. It seems likely that under high temperature conditions the oxidation of the unbound thiols and their oxidation products (Lewis acids) become very important and active antioxidant species. This is discussed in Chapter Five, section 5.7.

4.10 The Effect of Bound Antioxidants at the Same Concentration Reduced from Masterbatches

This experiment is to investigate the consequence of uneven antioxidant distribution in NBR, since it has been assumed in the past that this could lead to less effective protection of the polymer. It is thought that dispersion of the antioxidants in samples prepared by latex diluted masterbatches and those prepared by solid rubber diluted masterbatches accounts for the observed differences in the ageing behaviour of the samples.

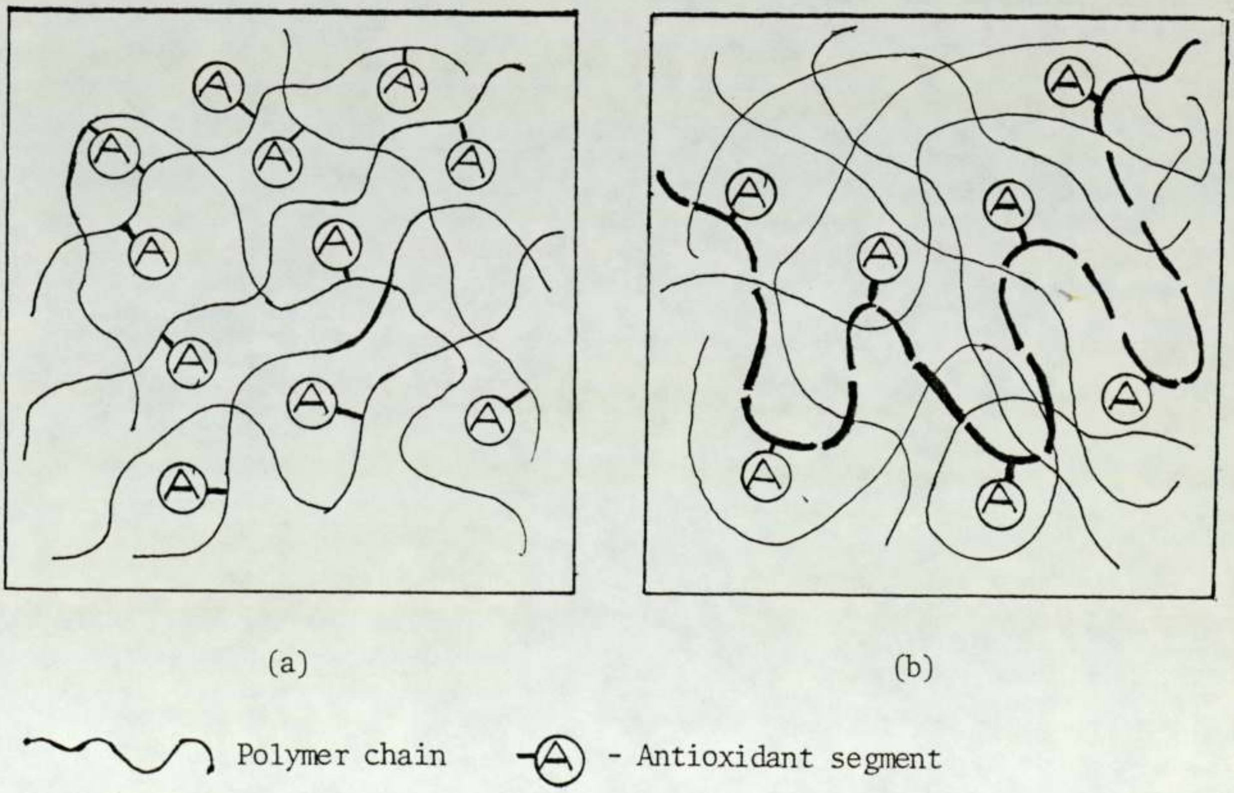


Table 4.13 Retention of physical properties after cyclic oil/air ageing of LM vulcanisate at 150°C

Samples	Time to 50% modulus increase	Time to 50% TS decrease	Time to 50% EB decrease
LML (BHBM)	> 2 cycles	≈ 2 cycles	2 cycles
LMCU (BHBM)	2 cycles	2 cycles	> 1 cycle
LMCE (BHBM)	> 1 cycle	> 2 cycles	1 cycle
LML (PAPT)	2 cycles	2 cycles	> 2 cycles
LMCU (PAPT)	3 cycles	> 3 cycles	≈ 2 cycles
LMCE (PAPT)	> 1 cycle	> 2 cycles	2 cycles
Chemigum	≈ 2 cycles	> 2 cycles	2 cycles
Flectol H	< 1 cycle	2 cycles	< 1 cycle
Control (no antioxidant)	< 1 cycle	Brittle	Brittle

Table 4.14 Retention of physical properties after cyclic oil/air ageing of MCM vulcanisate at 150°C

Samples	Time to 50% modulus increase	Time to 50% TS decrease	Time to 50% EB decrease
MCMU (BHBM)	2 cycles	2 cycles	> 1 cycle
MCME (BHBM)	≈ 1 cycle	> 1 cycle	> 1 cycle
MCMU (PAPT)	> 3 cycles	3 cycles	≈ 3 cycles
MCME (PAPT)	2 cycles	> 2 cycles	2 cycles
Chemigum	2 cycles	> 2 cycles	2 cycles
Flectol H	1 cycle	> 1 cycle	< 1 cycle
Control (no antioxidant	Hard	Nil	Nil

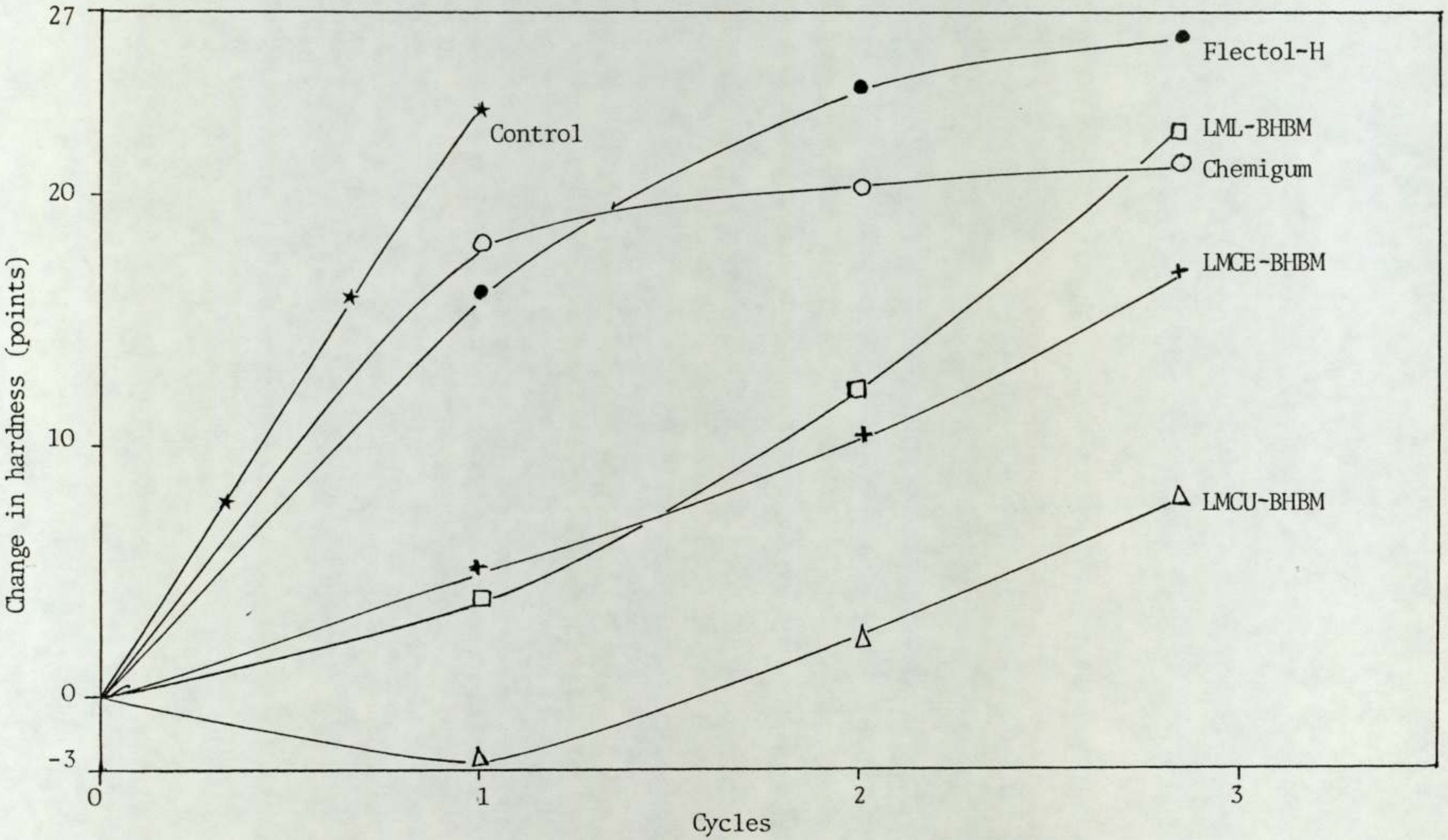


Fig 4.55 Effect on shore 'A' hardness of cyclic ageing of LM (bound BHBM) vulcanisates at 150^{O}C

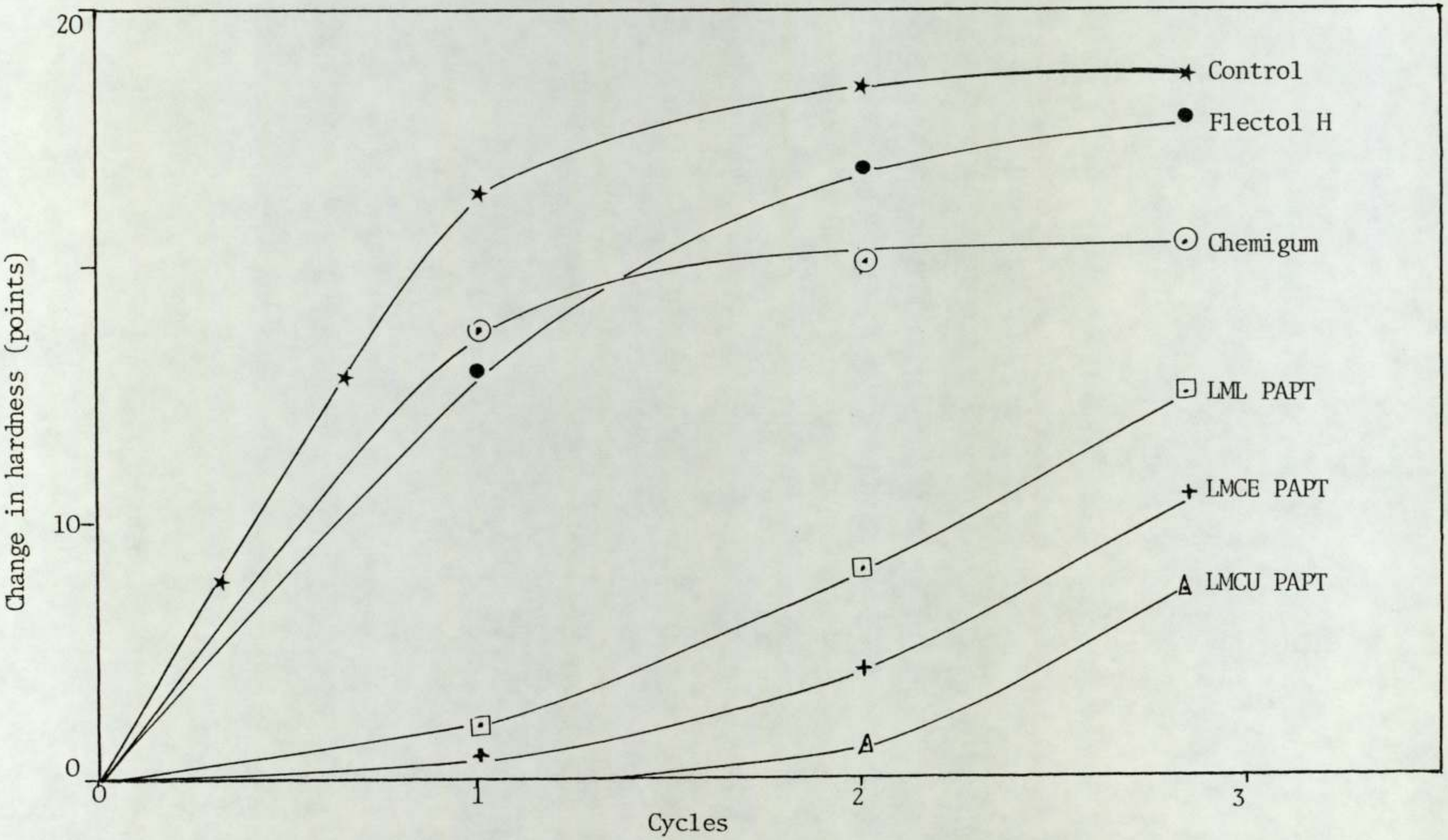


Fig 4.56 Effect on shore 'A' hardness of cyclic oil/air ageing of LM (bound PAPT) vulcanisates at 150°C

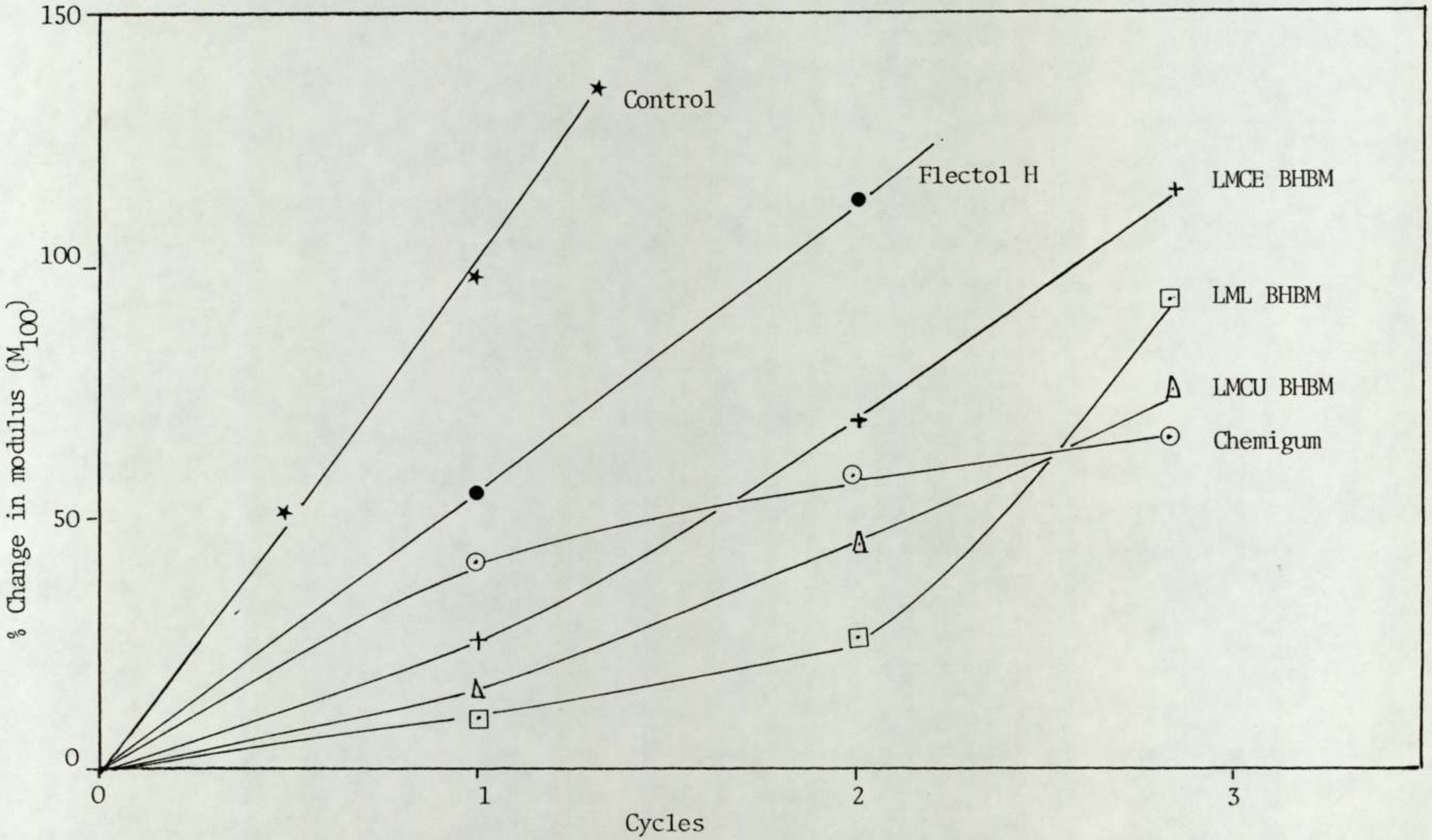


Fig 4.57 Effect of modulus of cyclic oil/air ageing of ML (bound BHBM) vulcanisates at 150°C

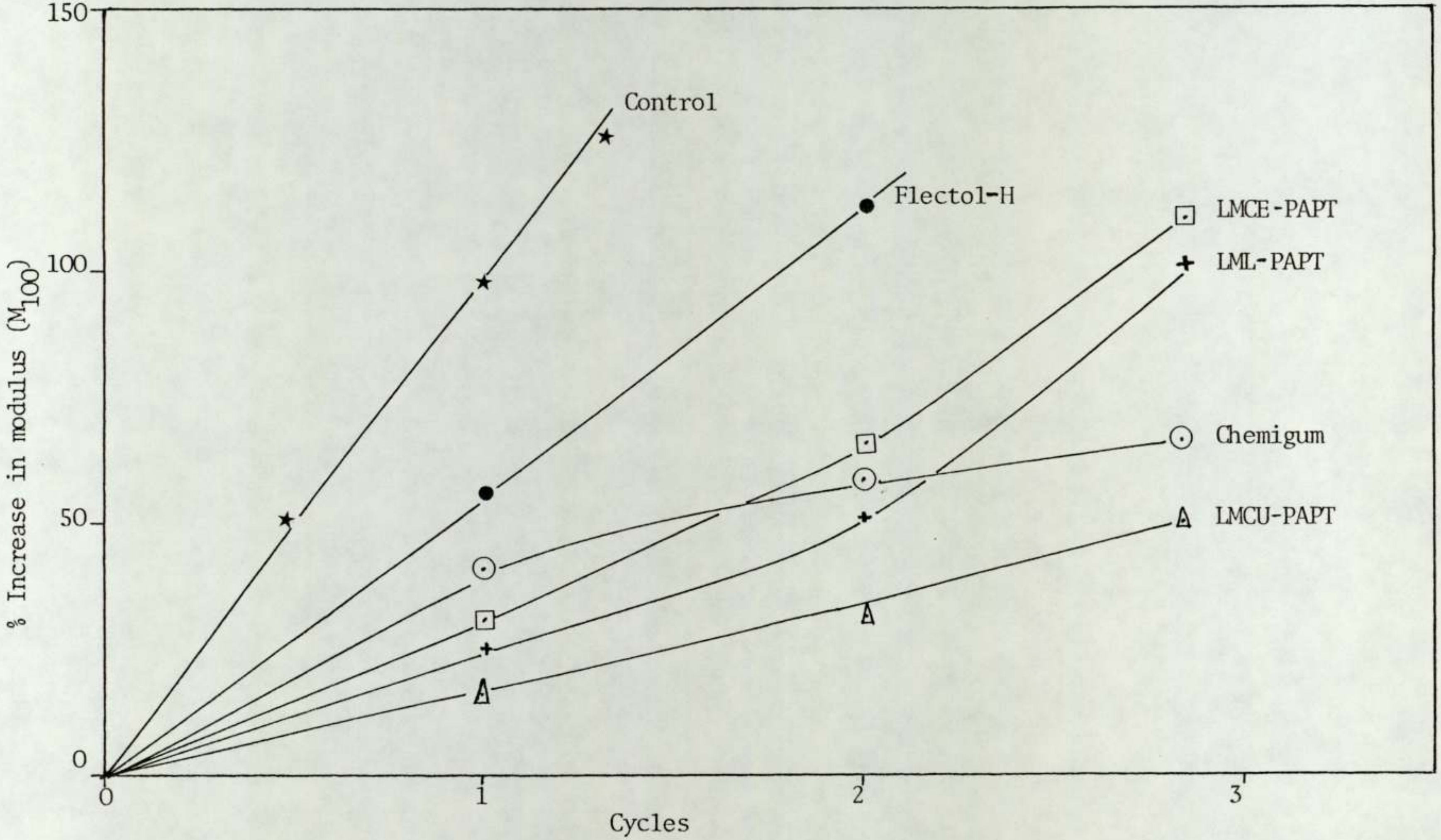


Fig 4.58 Effect on modulus of cyclic oil/air ageing of LM (bound BHBM) vulcanisates at 150°C

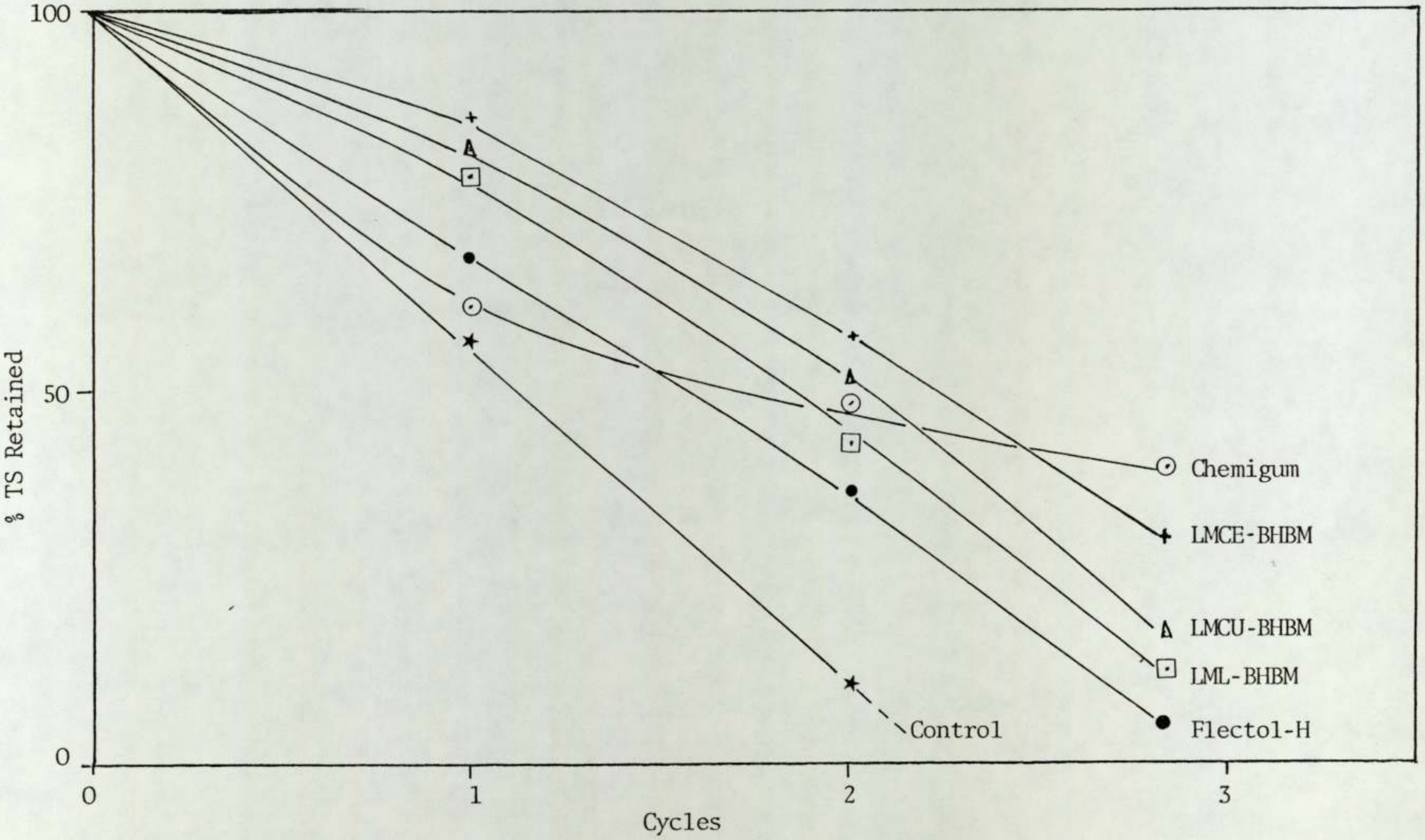


Fig 4.59 Effect of TS of cyclic oil/air ageing of LM (bound BHBM) vulcanisates at 150°C

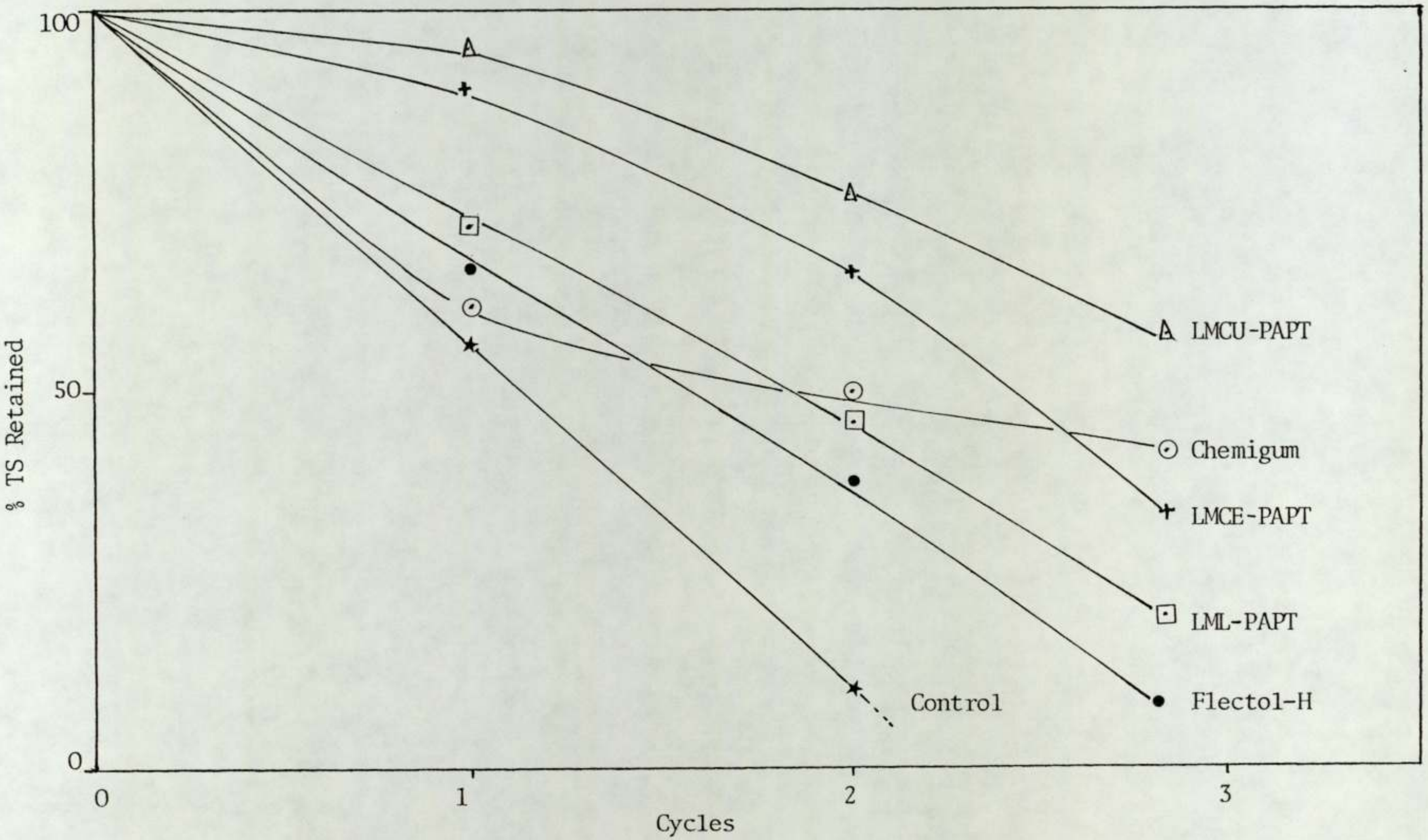


Fig 4.60 Effect on TS of cyclic oil/air ageing of LM (bound PAPT) vulcanisates at 150°C

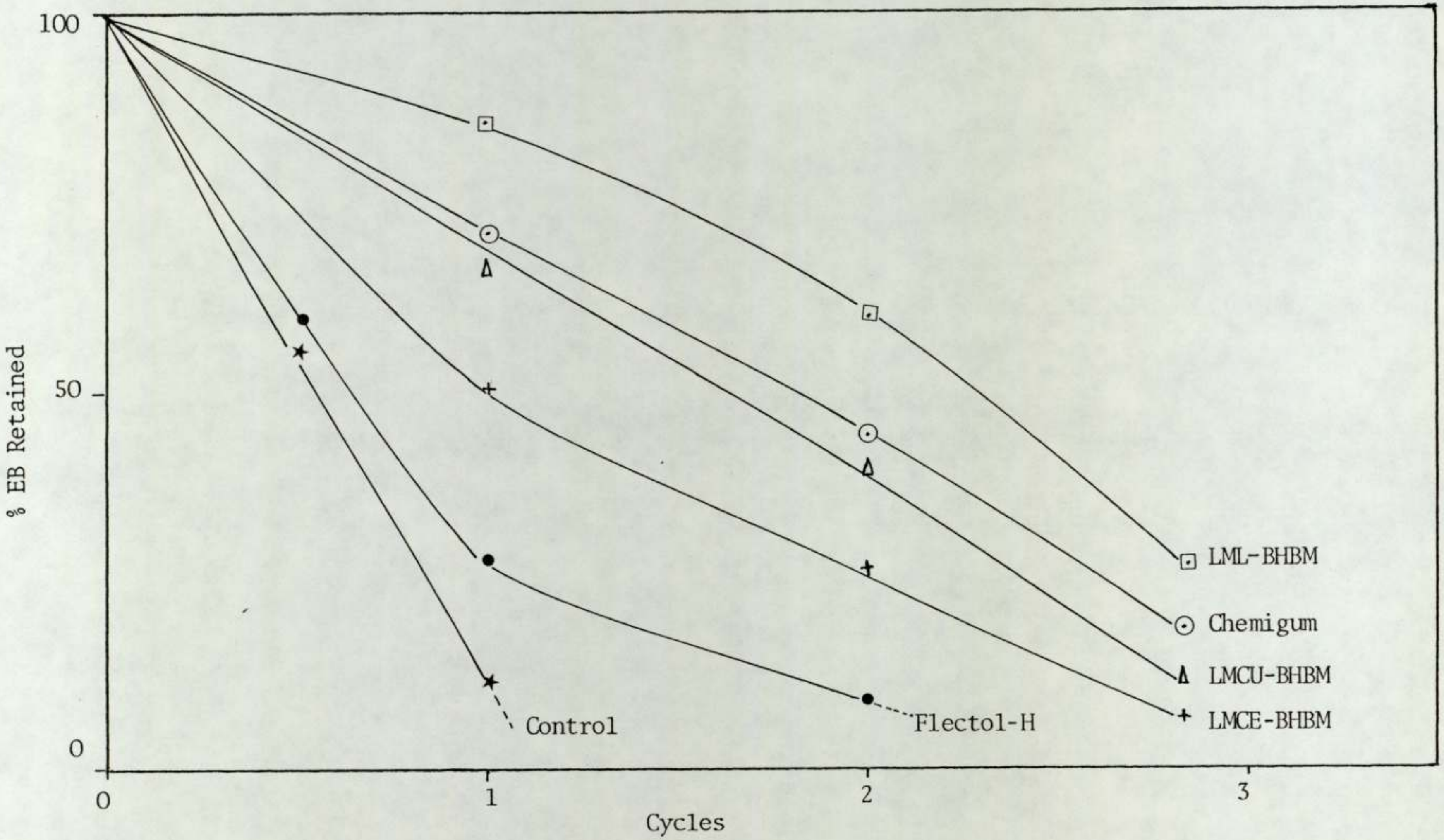


Fig 4.61 Effect of EB on cyclic oil/air ageing of LM (bound BHBM) vulcanisates at 150^{o}C

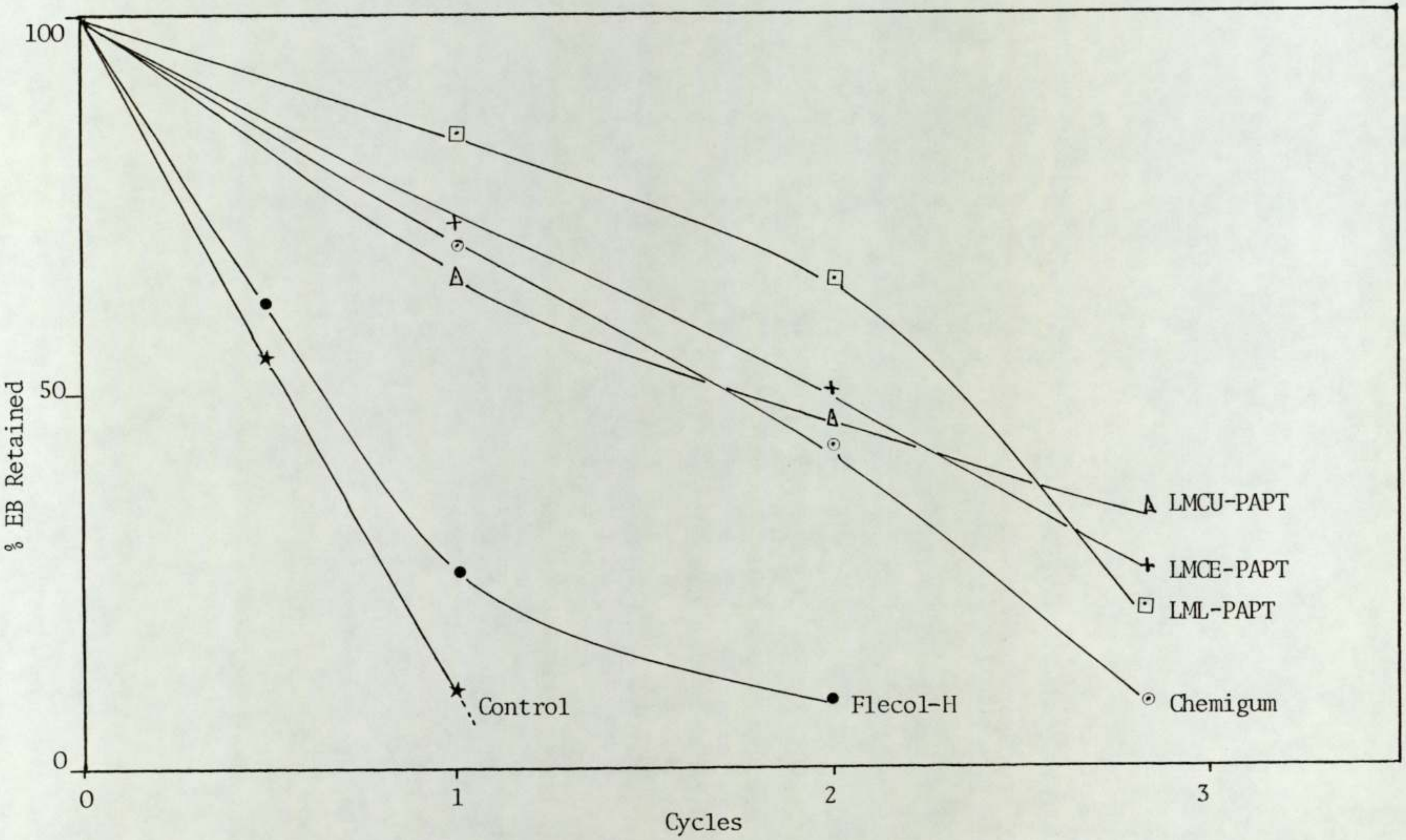


Fig 4.62 Effect on EB on cyclic oil/air ageing of LM (bound PAPT) vulcanisates at 150°C

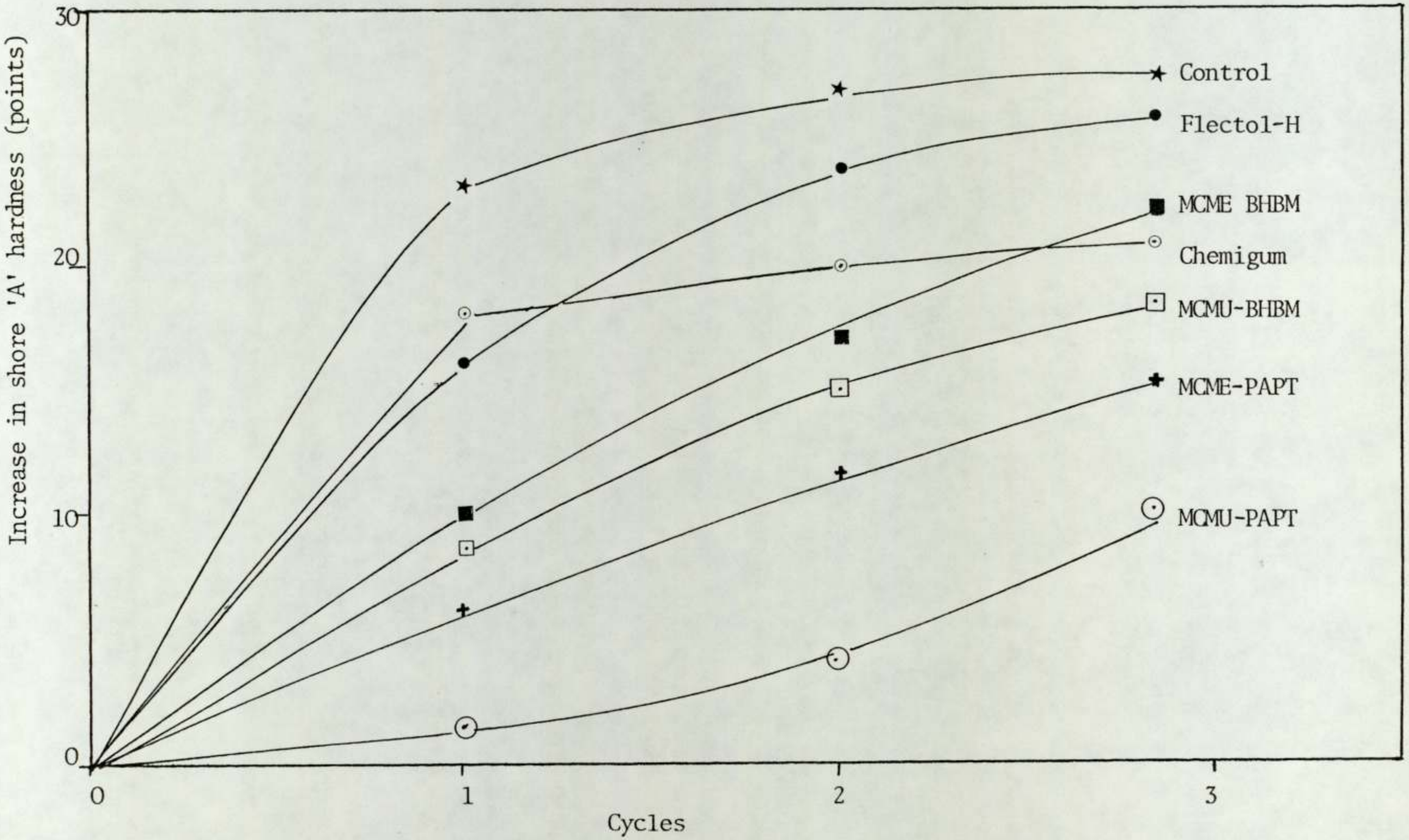


Fig 4.63 Effect on shore 'A' hardness of cyclic oil/air ageing of MCM vulcanisates at 150°C

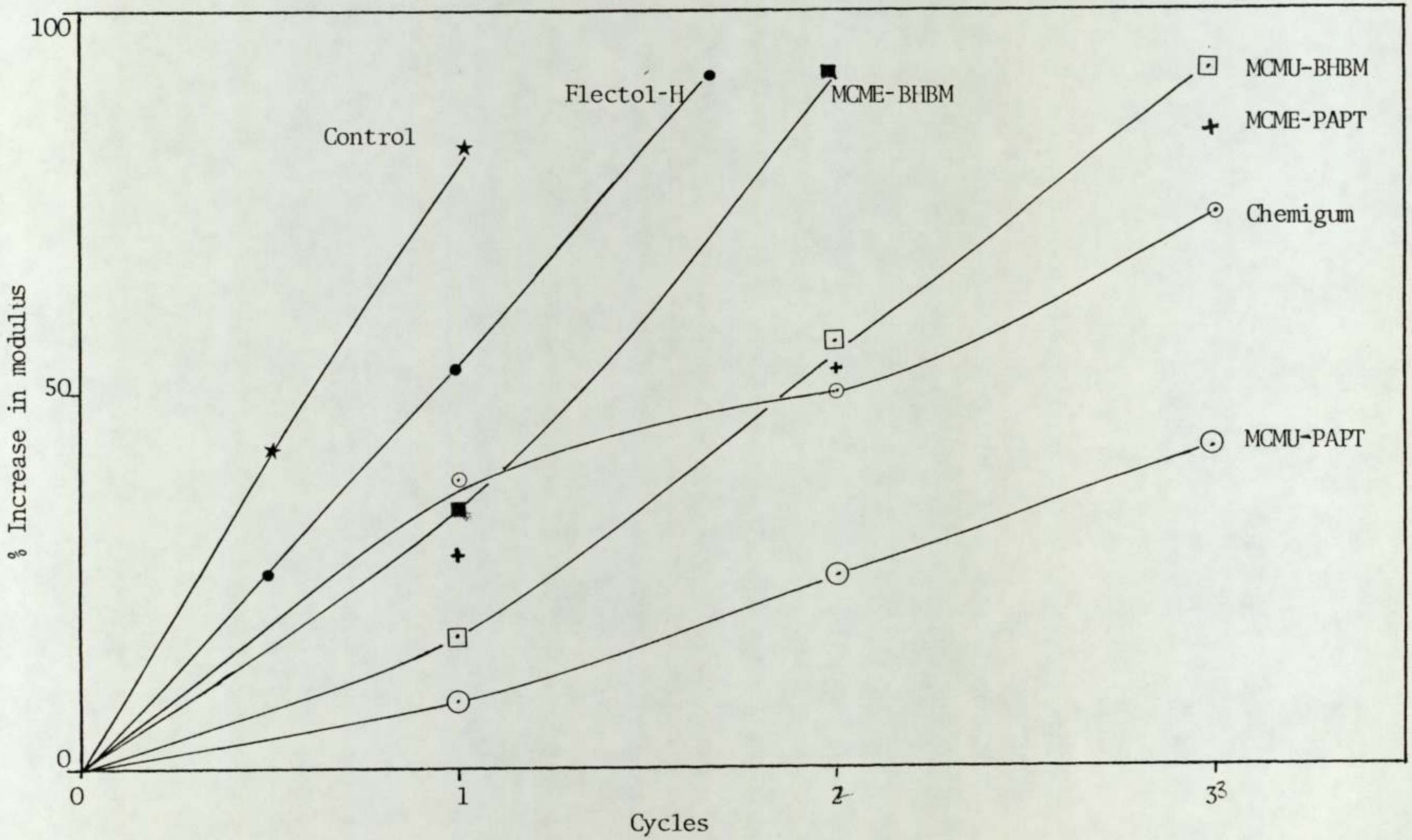


Fig 4.64 Effect on modulus of cyclic oil/air ageing of MCM vulcanisates at 150°C

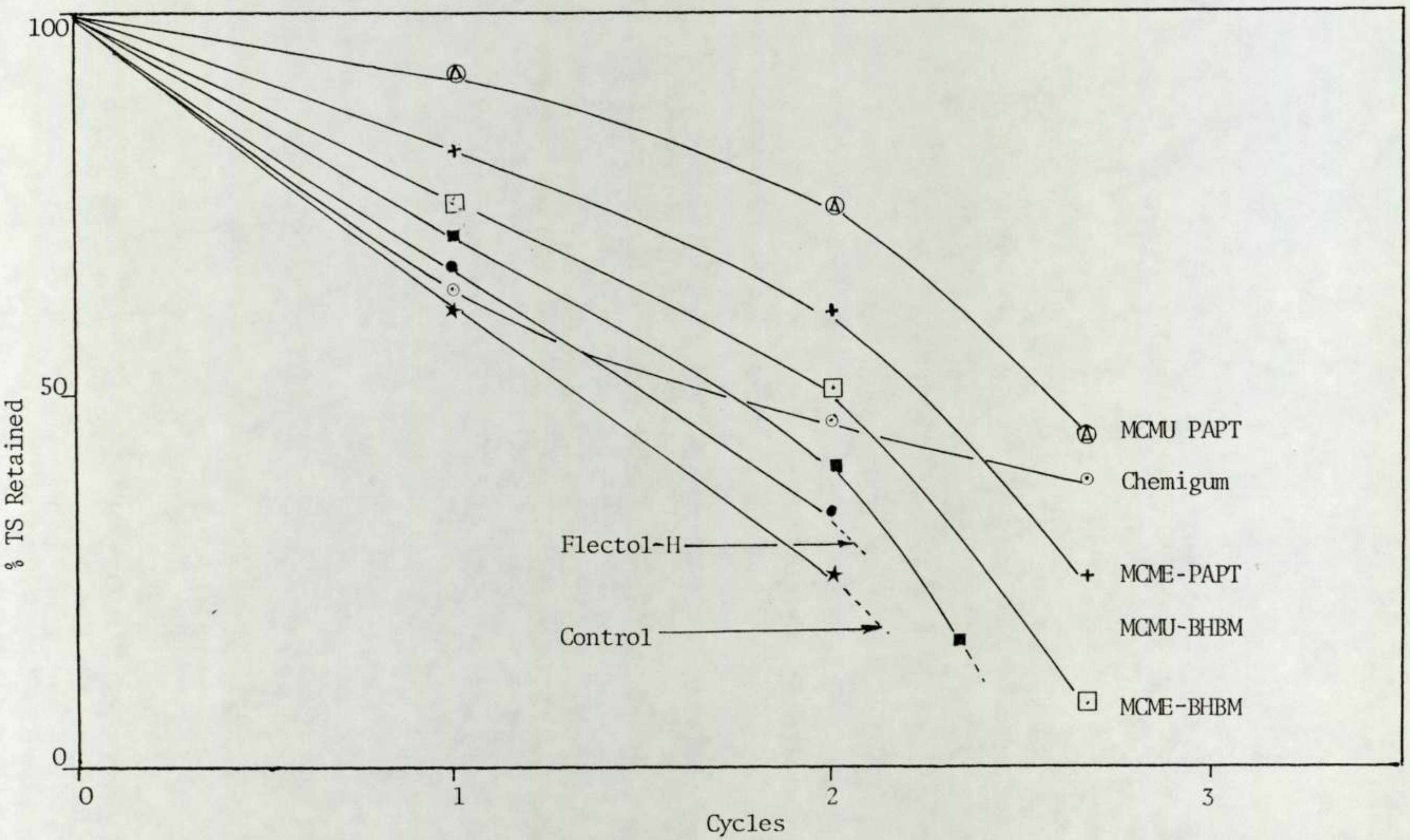


Fig 4.65 Effect on TS of cyclic oil/air ageing of MCM vulcanisates at 150°C

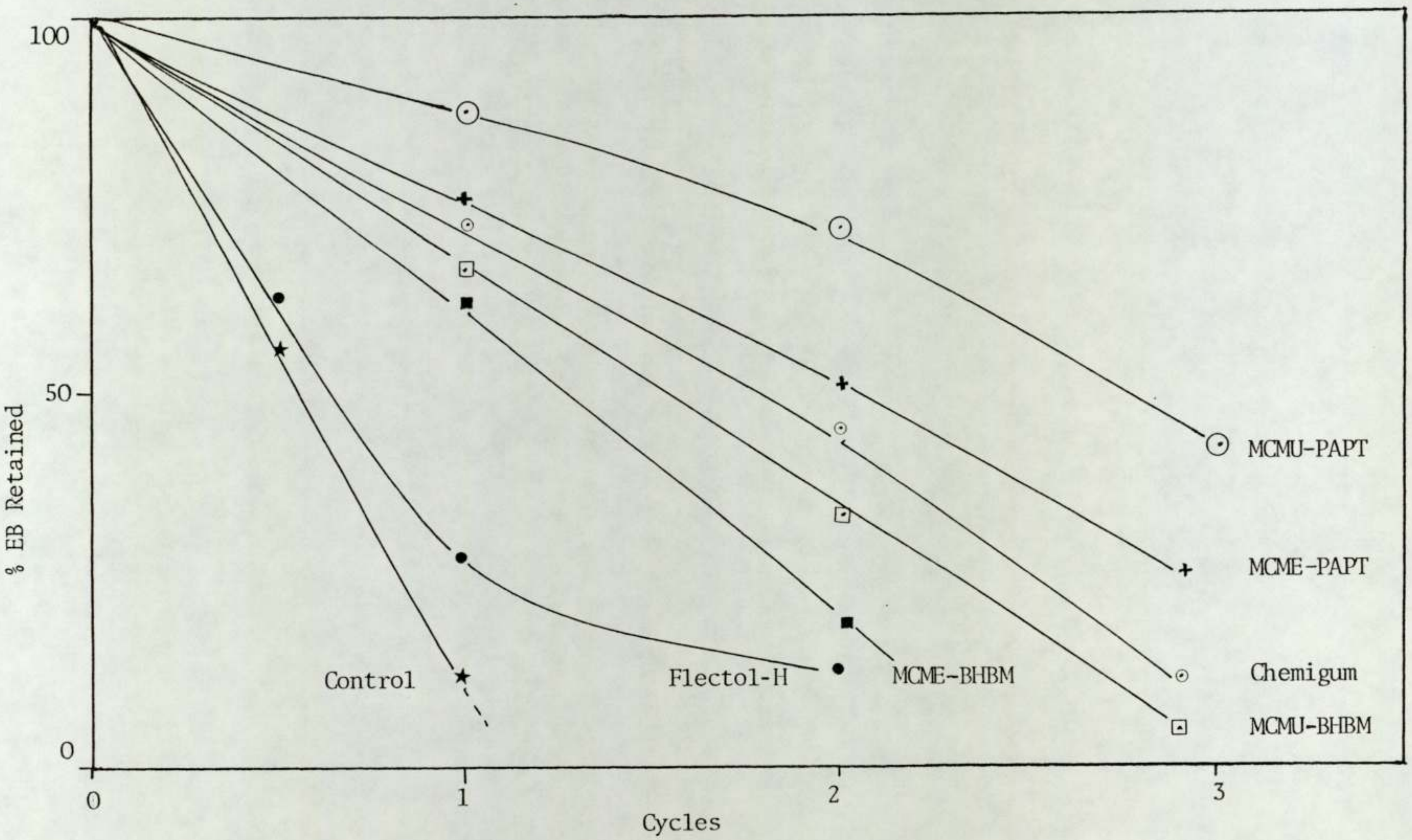


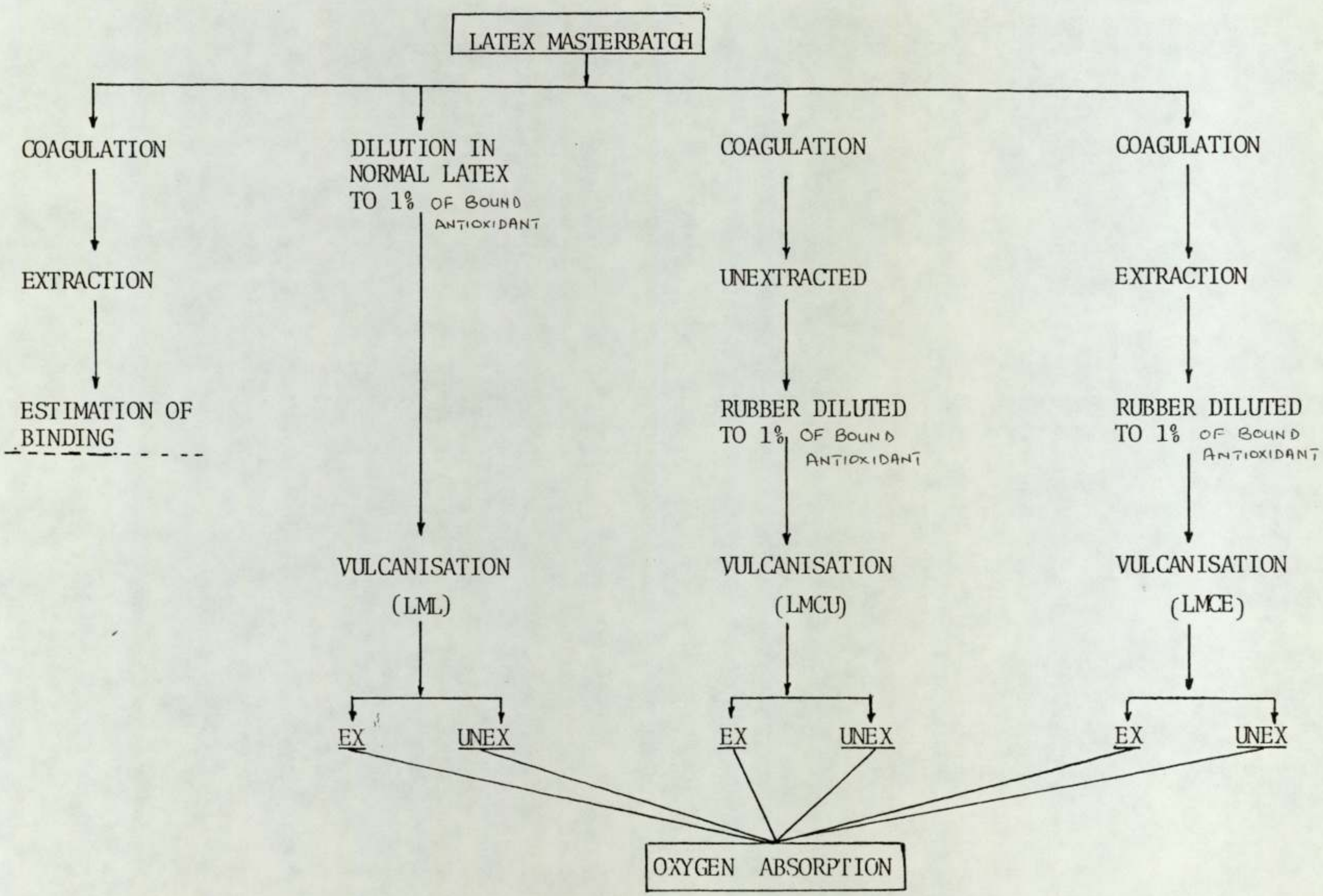
Fig 4.66 Effect on EB of cyclic oil/air ageing of MCM vulcanisates at 150°C

The above diagram illustrates the different distribution of the antioxidant functions in the samples: (a) addition of a given amount of antioxidant into the whole of the rubber, (b) diluted masterbatch containing the same overall amount of bound antioxidant.

EXPERIMENTAL PROCEDURE

Masterbatches of the antioxidants (BHBM and PAPT) were prepared as described under sections 2.3.1 and 2.3.2. In the case of BHBM it is possible to prepare masterbatches of concentrations 1, 10, 20, 30, 40 and 50 g/100 g NBR whereas those from PAPT were limited to 5, 10, 20 and 30 g/100 g NBR. By coagulating the masterbatch, extracting the coagulum and using ir technique to prepare a calibration curve it is possible to determine how much untreated latex (rubber) was needed to dilute the masterbatch such that 1 g of bound antioxidant was contained in 100 g of NBR before vulcanisation.

All masterbatches were then reduced to a concentration of 1 g of bound antioxidant/100 g NBR by the procedure described under section 2.1.3. The oxygen absorption characteristics of the vulcanisates at 150^{0}C, before and after extraction of the vulcanisates with an organic azeotrope, was studied according to the procedure described under section 4.6. The procedure is as illustrated schematically overleaf.


LATEX MASTERBATCH
COAGULATION
EXTRACTION
ESTIMATION OF BINDING
DILUTION IN NORMAL LATEX TO 1% OF BOUND ANTIOXIDANT
VULCANISATION
(LML)
EX
UNEX
COAGULATION
UNEXTRACTED
RUBBER DILUTED TO 1% OF BOUND ANTIOXIDANT
VULCANISATION
(LMCU)
EX
UNEX
COAGULATION
EXTRACTION
RUBBER DILUTED TO 1% OF BOUND ANTIOXIDANT
VULCANISATION
(LMCE)
EX
UNEX
OXYGEN ABSORPTION

RESULTS

Figs 4.67 - 4.72 show the behaviour of the bound antioxidants at the same concentrations reduced from different masterbatch concentrations.

The effect of bound PAPT latex diluted masterbatch (LML) is shown in Fig 4.67. All the samples were more resistant than the control sample and after the induction period they all absorbed oxygen autocatalytically. The sample reduced from 20% masterbatch (curves h and i) are most resistant to oxidation. It is surprising that the sample reduced from 30% masterbatch is not as good as that from 10% masterbatch even before extraction but it is by far better than the sample from 5% masterbatch.

Fig 4.68 compares the effectiveness of bound PAPT in samples prepared from solid rubber diluted, unextracted masterbatch coagulum (LMCU). The samples show similar pattern to the LML samples but unlike the LML the reduction of antioxidant activity after vulcanisate extraction is more pronounced in the LMCU samples. This is probably due to the loss of unbound antioxidant and ZDMC and also to the poor dispersion of the antioxidant in the LMCU.

Fig 4.69 shows that the antioxidant activity is substantially retained after extraction of vulcanisates prepared by solid rubber diluted extracted masterbatch coagulum (LMCE). The high retention of the antioxidant activity is most likely due to the fact that the unbound antioxidants have already been lost during the extraction of the coagulum, and after addition, the vulcanisate contained mainly bound antioxidant and since they have become part of the rubber molecule they are not substantially lost during vulcanisate extraction. It seems likely that the observed difference is only due to the loss of ZDMC which is not bound to the rubber. As in the case of LML and LMCU, the sample reduced from 30% masterbatch (Fig 4.69, curves d and e) is less efficient than those from 10 and 20% masterbatches.

Fig 4.70 compares the effectiveness of bound BHBM latex masterbatch (LML) reduced to 1 g BHBM/100 g NBR. Oxygen was absorbed autocatalytically. Before the extraction of the vulcanisate, there is not much difference between the samples but after extraction it is obvious that the sample from 30 and 50% masterbatches have their efficiency reduced but are still better than the control.

Fig 4.71 compares the effect of solid rubber diluted unextracted bound BHBM coagulum (LMCU). Before the extraction of the vulcanisate, the order of antioxidant activity is increased with increased antioxidant masterbatch concentration. This is indicative of increased binding with increased antioxidant concentration. (See Table below).

Masterbatch Concentration g AO/100 g NBR	% Antioxidant Bound PAPT	BHBM
1	-	57.2
5	38	-
10	47.6	60.5
20	52.2	61.0
30	47.1	61
40	-	59.5
50	-	59

However, after extraction of the vulcanisates the samples from 1% masterbatch show much better resistance to oxidation compared to those from 10, 20 and 30% masterbatches but were slightly inferior to the samples reduced from 40 and 50% masterbatches. The curves for the 1% masterbatch reflect the loss of antioxidant efficiency through dilution, which is prominent in other samples. Also it shows the advantage of uniform distribution of antioxidant functions during the grafting reaction.

Fig 4.72 shows the effect of extracting the coagulum before being diluted with solid rubber (LMCE). Curve g shows the behaviour of the sample reduced from 10 and 50% masterbatches. These offer good protection before extraction, after extraction, the 50% masterbatch retained most of its efficiency. Generally, the behaviour of the samples is in a way similar to those observed in the corresponding sample containing PAPT (Fig 4.69) but the

the behaviour of the sample reduced from 30% masterbatch is anormalous since the antioxidant activity is quickly lost after extraction.

DISCUSSION

As mentioned in section 2.1.6, when masterbatch technique is used only a small proportion of the rubber chains are containing all the attached antioxidant molecules. When the masterbatch is diluted further with untreated latex, or with unstabilised rubber, a major part of the resultant rubber mixture will have no bound antioxidant. It is therefore very important that the latex antioxidant concentrate be uniformly dispersed in the unstabilised latex to give interpenetrating molecule.

The result obtained from this experiment shows that the better dispersion achieved in the latex procedure (LML) (with PAPT in particular) accounted for the better ageing of such samples. The effect is not so clearly evident in the case of BHBM.

It is also obvious that when the coagulum of the masterbatches was extracted before vulcanisation, the difference in oxygen absorption of such vulcanisates before and after extraction is marginal and from this it is only logical to think that the bigger loss of antioxidant activity in LML and LMCU before and after extraction of vulcanisates are primarily due to loss of unbound antioxidant, and because the level of binding was low in some masterbatches the total unextractible antioxidant should be higher in LMCE and hence the effectiveness of the vulcanisates better; also the loss of ZDMC is a contributory factor to the reduced antioxidant efficiency of LML and LMCU and LMCE rather than debinding of the bound antioxidant.

From the behaviour of the undiluted 1% masterbatch (Figs 4.70 - 4.72) it is clear that there is not much advantage in the direct addition of antioxidant to latex method over the masterbatch. Although the latter leads to slightly reduced stability compared with the direct addition technique, the enormous advantages of using the masterbatch dilution technique in commercial applications can compensate the slight disadvantage.

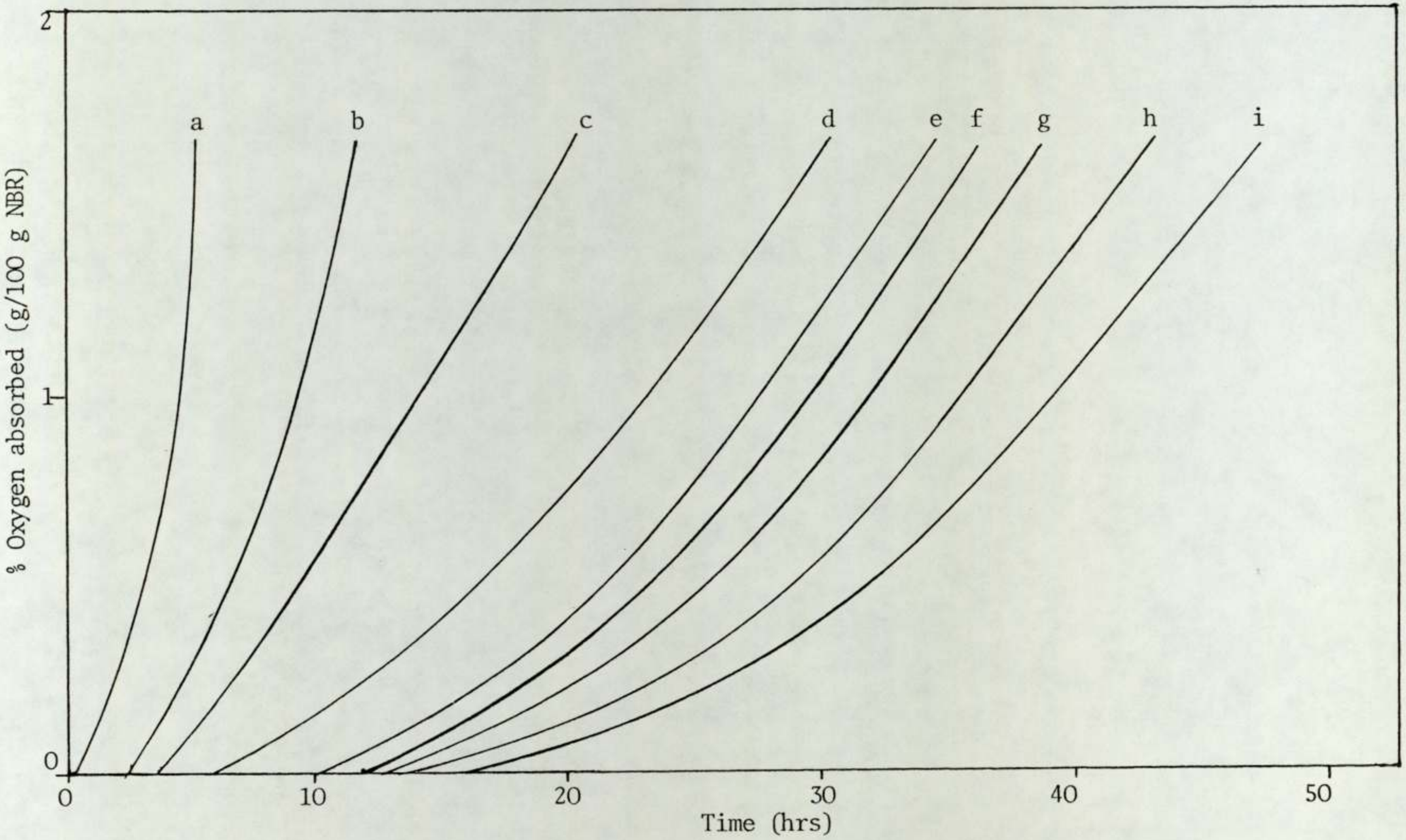


Fig 4.67 Effect of bound PAPT latex diluted (LML) from masterbatches to 1 g bound antioxidant/100 g NBR.
a - control; b - 1% ex (5% LM); c - 1% unex (5% LM); d - 1% ex (30% LM); e - 1% unex (30% LM);
f - 1% ex (10% LM); g - 1% unex (10% LM); h - 1% ex (20% LM); i - 1% unex (20% LM)

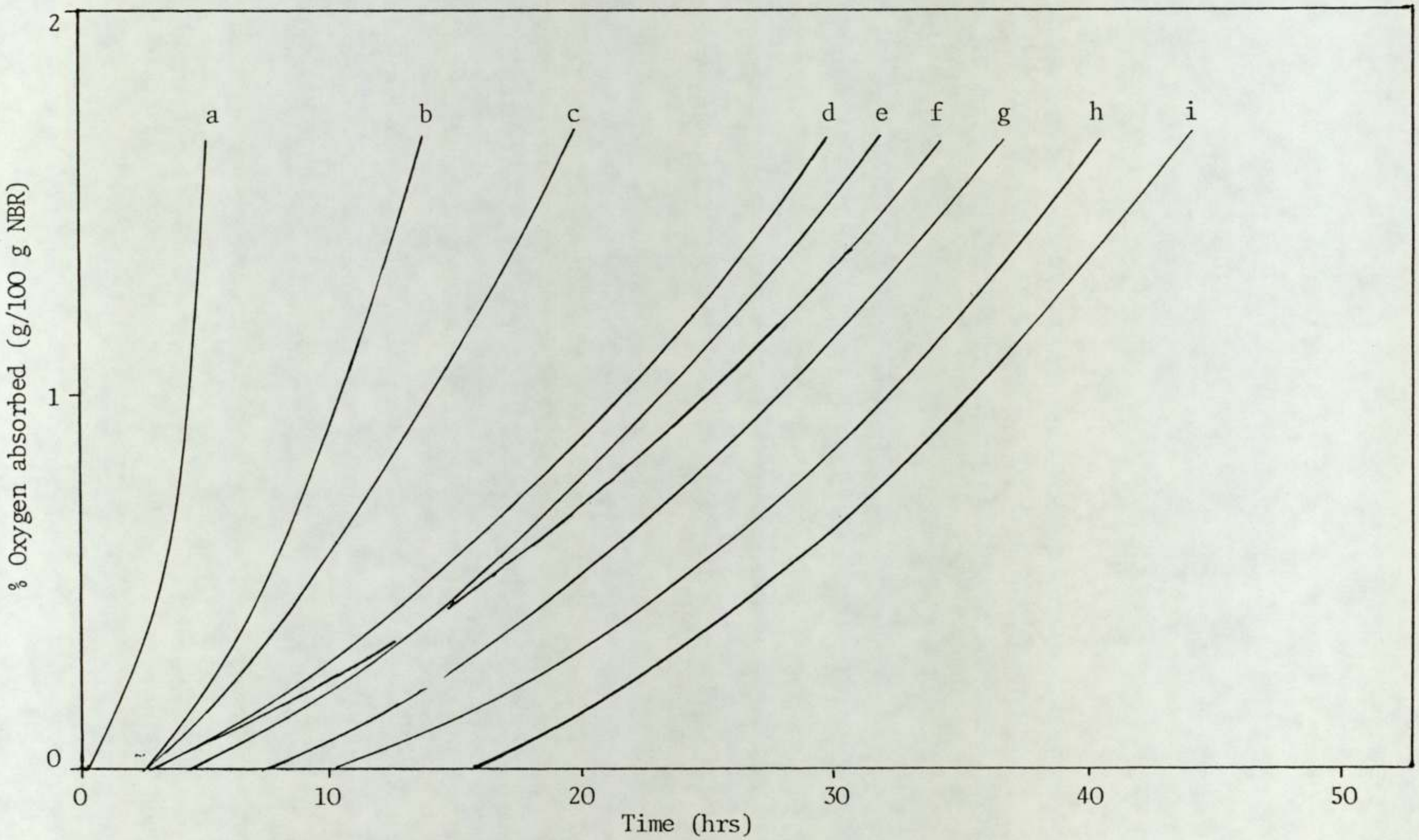


Fig 4.68 Effect of bound PAPT rubber dilute (LMCU) from masterbatches to 1 g bound antioxidant/100 g NBR.
a - control; b - 1% ex (5% LMCU); c - 1% unex (5% LMCU); d - 1% ex (10% LMCU); e - 1% ex (30% LMCU); f - 1% ex (20% LMCU); g - 1% unex (30% LMCU); h - 1% unex (10% LMCU); i - 1% unex (20% LMCU)

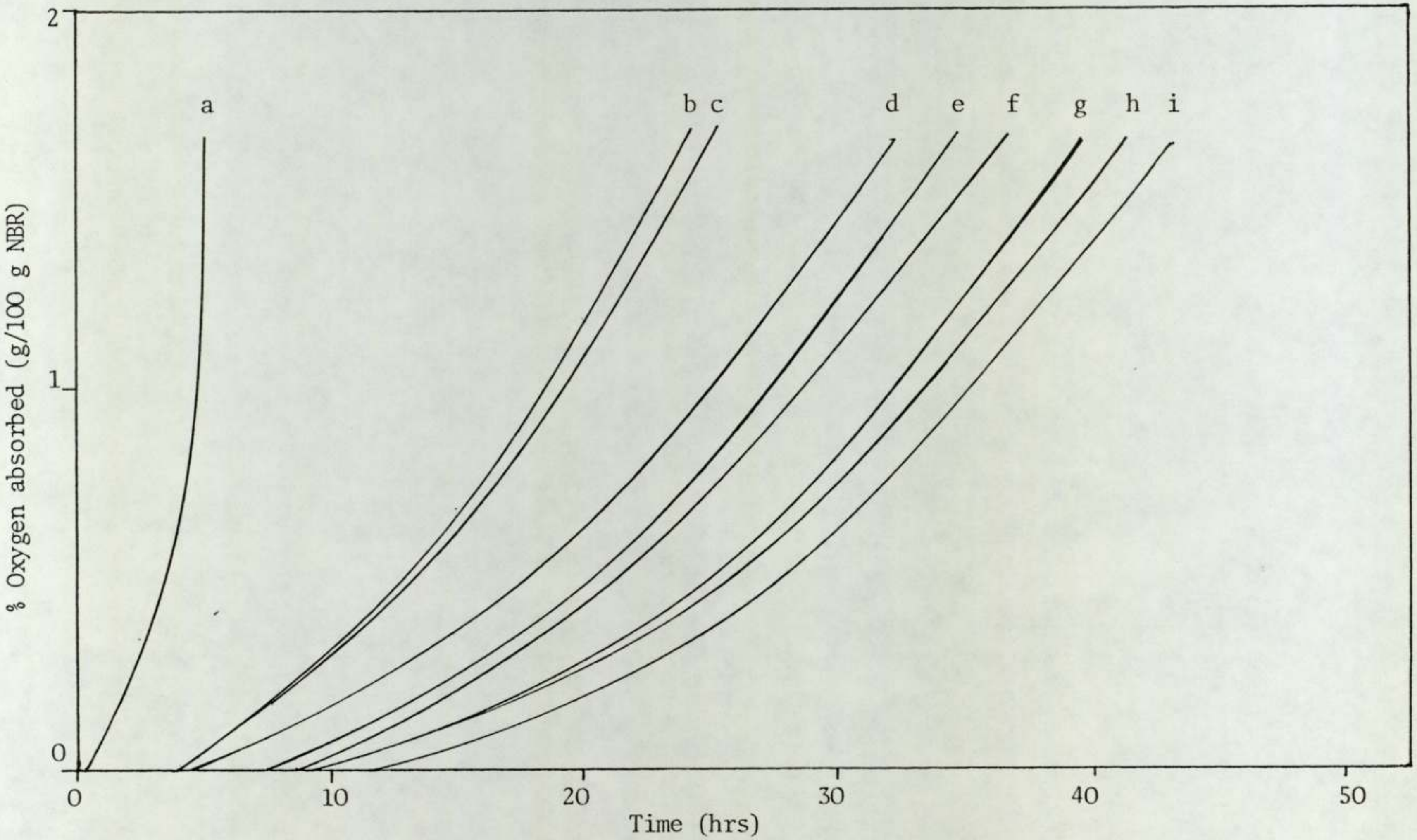


Fig 4.69 Effect of bound PAPT rubber diluted (LMCE) from masterbatches to 1 g bound antioxidant/100 g NBR.
a - control; b - 1% ex (5% LMCE); c - 1% unex (5% LMCE); d - 1% ex (30% LMCE); e - 1% unex (30% LMCE);
f - 1% ex (10% LMCE); g - 1% unex (10% LMCE); h - 1% ex (20% LMCE); i - 1% unex (20% LMCE)

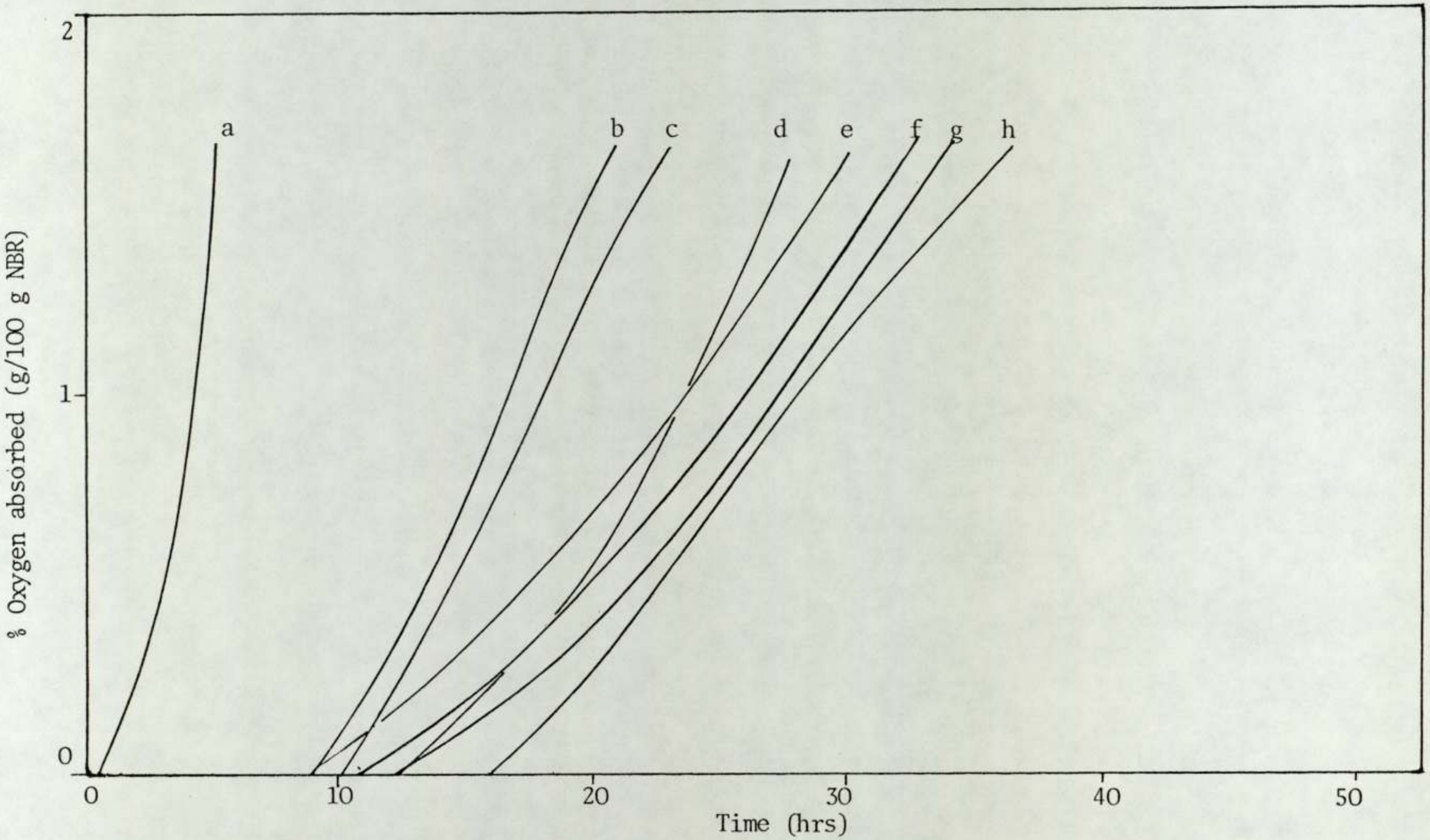


Fig 4.70 Effect of bound BHBM latex diluted (LM) from masterbatches to 1 g bound antioxidant/100 g NBR.
a - control; b - 1% ex (30% LM); c - 1% ex (50% LM); d - 1% ex (10% LM, 20% LM, 40% LM);
e - 1% ex (1% LM); f - 1% unex (1% LM, 20% LM, 50% LM); g - 1% unex (10% LM); h - 1% unex (30% LM, 40% LM)

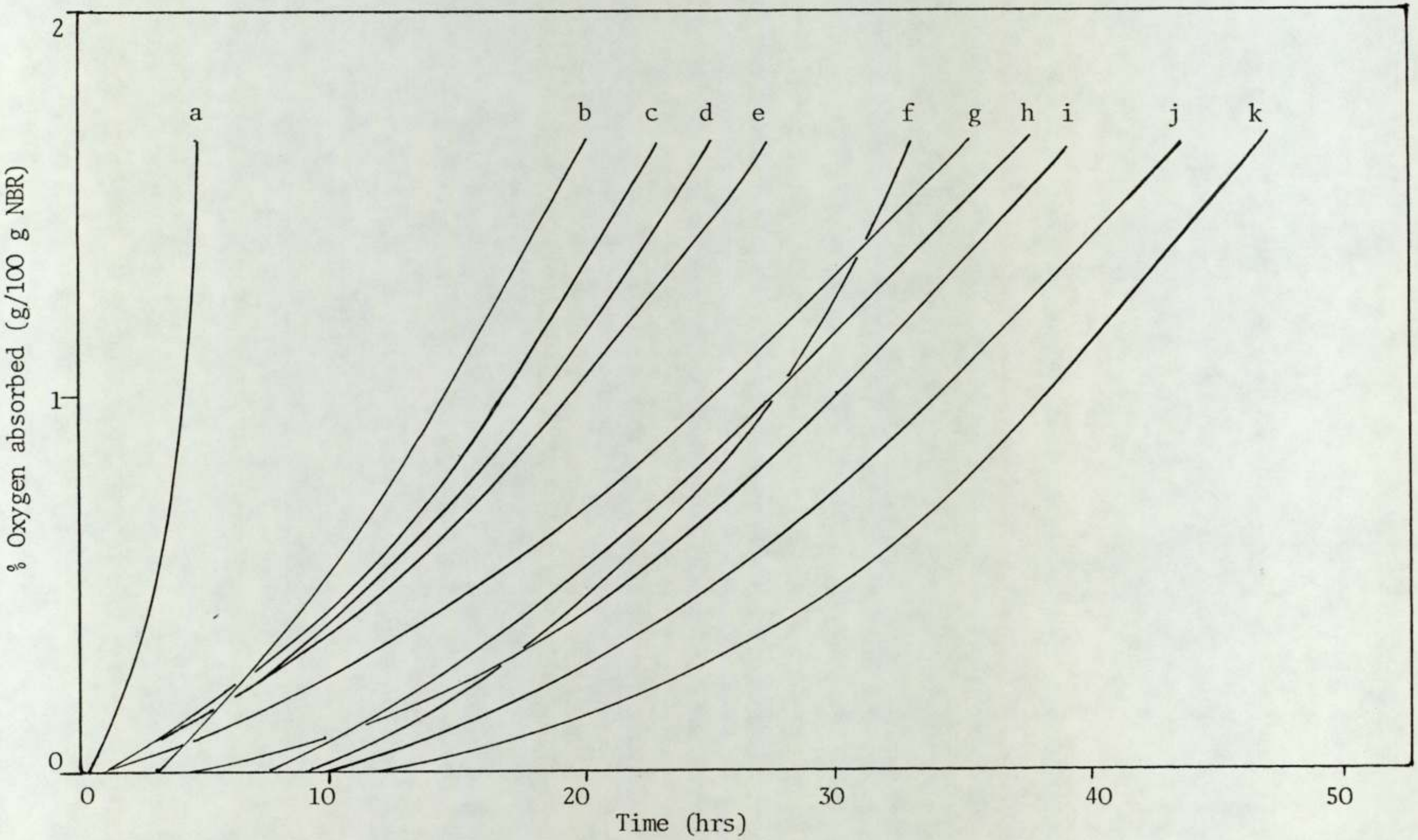


Fig 4.71 Effect of bound BHBM rubber diluted (LMCU) from masterbatches to 1 g bound antioxidant/100 g NBR.
a - control; b - 1% ex (20% LMCU); c - 1% ex (10% LMCU); d - 1% ex (30% LMCU); e - 1% ex (1% LMCU);
f - 1% ex (40, 50% LMCU); g - 1% unex (1% LMCU); h - 1% unex (10% LMCU); i - 1% unex (20% LMCU);
j - 1% unex (30% LMCU); k - 1% unex (40,50% LMCU)

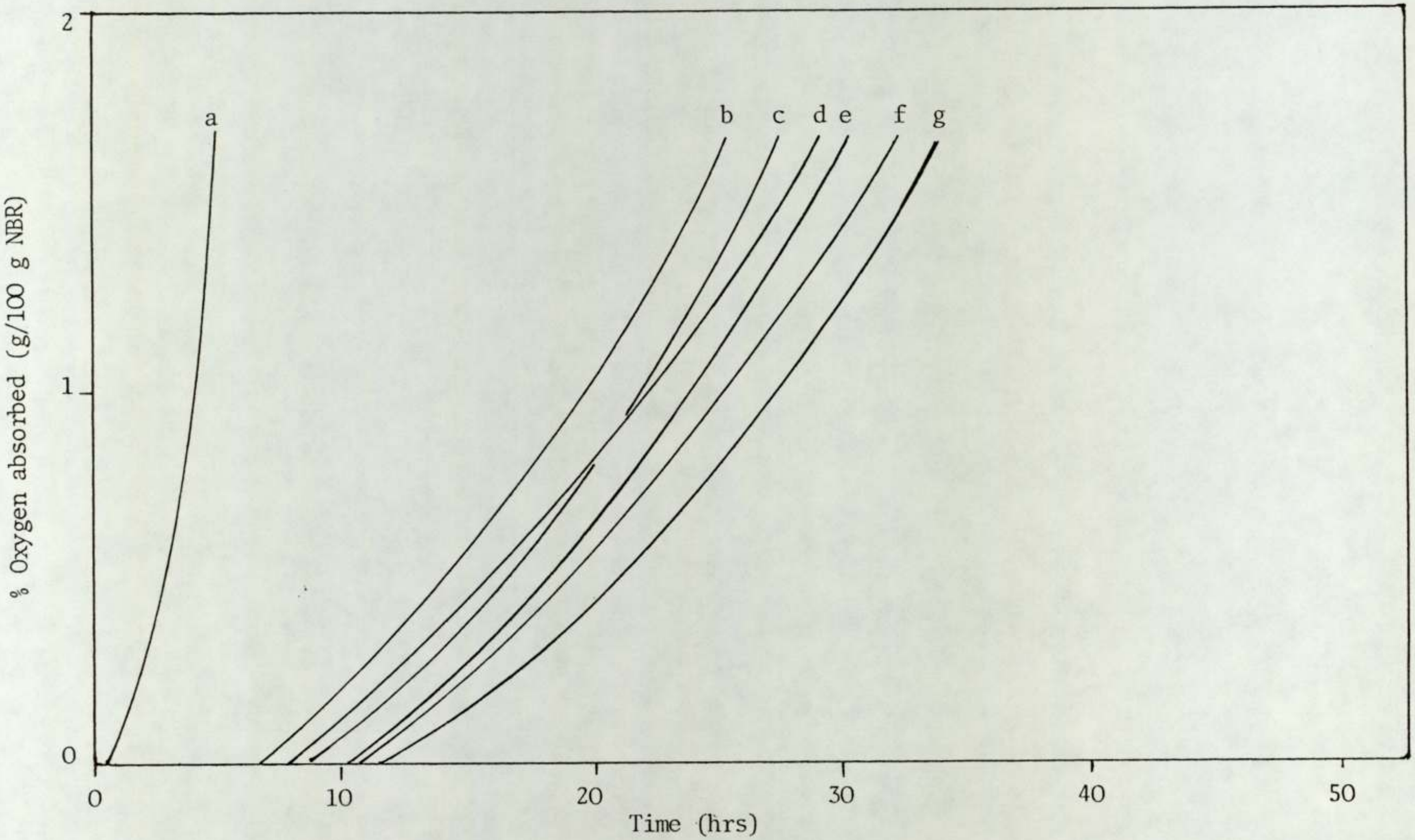


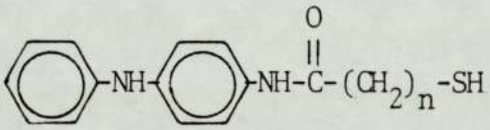
Fig 4.72 Effect of bound BHBM rubber diluted (LMCE) from masterbatches to 1 g bound antioxidant/100 g NBR. a - control; b - 1% ex (30% LMCE); c - 1% ex (1,20% LMCE); d - 1% ex (40% LMCE); e - 1% unex (1,20,30% LMCE); f - 1% unex (40% LMCE)/1% ex (50% LMCE); g - 1% unex (10,50% LMCE)

CHAPTER FIVE

INVESTIGATION OF THE REACTIONS OF PAPT AND PPPT IN THE PRESENCE OF HYDROPEROXIDES

5.1 Introduction

There is evidence that the amount of adduct formed in the reaction of thiol amides (II) and (III) with NBR is limited by the products formed in the adduct reaction.



n = 1, (II) PAPT

n = 2, (III) PPPT

Since this is also related to the mechanism of action of these bound antioxidants, the present work is intended to elucidate the products formed and how they function both as inhibitors of the adduct reaction and as antioxidants.

EXPERIMENTAL OUTLINE

The general techniques used are those described previously by Armstrong(142), Husbands(90) and Cooray(98) in their analogous studies of sulphur compounds. In the present work, the following aspects have been investigated:

(i) The reactions of hydroperoxides (CHP, TBH) in the presence of (II) and (III).

(ii) The products formed from the reaction of CHP and the thiol amides (II) and (III) since they give information on the mechanism.

(iii) An analytical investigation of the products formed from (II) and (III) using GLC, TLC and GPC methods.

(iv) A parallel investigation of the formation of nitroxyl radicals during the reaction by ESR.

5.2 The Thermal Decomposition of CHP and TBH in the Presence of PAPT and PPPT

The thiolamides (PAPT and PPPT) were reacted with cumene hydroperoxide (CHP) and tertiarybutyl hydroperoxide (TBH) in chlorobenzene in separate experiments under nitrogen, at 70°C. The concentration of the hydroperoxides (1×10^{-2} mol 1^{-1}) was constant in all the experiments whereas the concentration of the thiolamide was varied and ranged from 1×10^{-4} to 1×10^{-2} mol 1^{-1}.

The reaction products of the thiolamide with CHP at molar ratios (CHP : thiolamide) 1 : 10, 1 : 1, 10 : 1, 20 : 1, 40 : 1, 60 : 1, 80 : 1 and 100 : 1 after 10 hours at 70°C were quantitatively determined by the use of GLC, GPC and TLC.

PROCEDURE

In a 100 ml three necked reaction flask fitted with a condenser, chlorobenzene was introduced and allowed to equilibrate for 5 minutes to reaction temperature (70°C) in a suitable thermostatted oil bath (± 0.5°C). An amount of hydroperoxide was added and allowed a further 2 minutes to equilibrate under a steady stream of nitrogen which ensures purging of the mixture. Solutions of the additives in chlorobenzene were quickly added through a syringe and sampling of the reaction mixture was commenced after 3 minutes. The decomposition of hydroperoxides in the presence and absence of the additives was followed by chemical and infra-red analysis (see sections 5.2.1 and 5.2.2). An excellent correlation between the chemical and spectroscopic methods of hydroperoxide determination implies that the two methods may be used interchangably.

5.2.1 Chemical Method Determination of TBH and CHP

Sodium thiosulphate was prepared with freshly prepared distilled water, stabilised with a few drops of chloroform and stored in the dark. The strength of the thiosulphate was determined using a standard solution of potassium iodate.

PROCEDURE

To 25 ml of 10% acetic acid in isopropanol, 10 ml of 20% sodium iodide in isoprepanol was added, followed by 0.5 ml of the solution of reaction mixture of the thiolamide with the hydroperoxides. This was refluxed for 5 minutes and allowed to cool. Then 5 mls of distilled water was added and the liberated iodine was titrated against 0.01 N sodium thiosulphate solution.

5.2.2 Infra-Red Spectrophotometric Determination of TBH and CHP

The concentration of TBH in chlorobenzene solution was determined by monitoring the calibrated ir absorption at 3530 cm^{-1} in a Perkin Elmer Model 599 spectrophotometer using ordinate expansion technique(92).

The concentration of CHP in chlorobenzene solution was determined by following the calibrated ir absorption at 3520 cm^{-1} in a Perkin Elmer Model 599 spectrophotometer. Using the ordinate expansion technique, the peak height of the absorbance was measured.

5.2.3 Result

The results obtained from the thermal decomposition of tertiarybutyl hydroperoxide (TBH) and cumene hydroperoxide (CHP) both in the presence of PAPT and PPPT at different molar ratios [ROOH]:[RSH] are shown in Figs 5.1 - 5.4. Similar behaviour was observed with the two antioxidants. At molar ratios 40 and below, three distinct stages characterised the decomposition reaction:

(i) A rapid initial catalytic stage
(ii) An induction period
(iii) A slower zero order catalytic reaction

But at ratios of 60 and 100, the induction period disappeared. The induction period observed at lower molar ratios indicates the formation of more stable intermediate products which are precursors of the second stage catalyst (this will be discussed in detail later). A slight hydroperoxide decomposition was observed for the control with no thiol-antioxidant present. This is due to prolonged thermal (70°C) effect of the hydroperoxide.

The decomposition of the hydroperoxides was much faster in the presence of PPPT than in the presence of PAPT.

In this experiment, the decomposition of CHP and TBH in the presence of PAPT and PPPT characterised by the three stages listed above, gave a concentration - time profile similar to those observed by Burn et al(143) for the decomposition of CHP in the presence of zinc-di-isopropyldithiophosphate and by Howard(144) for the decomposition of TBH in the presence of cupric di-isopropyldithiophosphate.

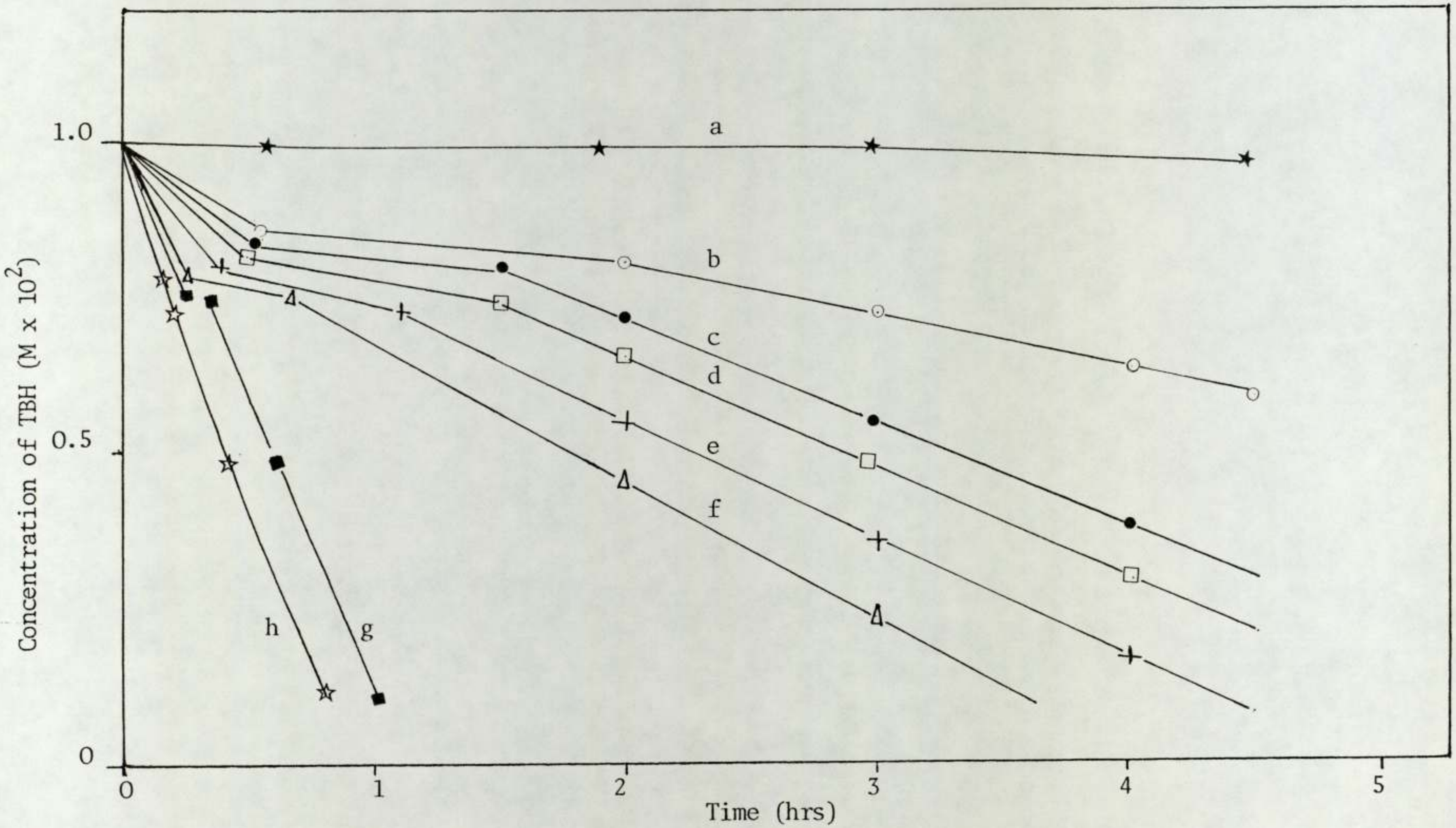


Fig 5.1 Decomposition of TBH (1 x 10^{-2} M) in chlorobenzene at 70°C in the presence of PAPT at the following molar ratios [TBH] / [PAPT] : a - control; b - 1:5; c - 1:1; d - 10:1; e - 20:1; f - 40:1; g - 60:1; h - 100:1

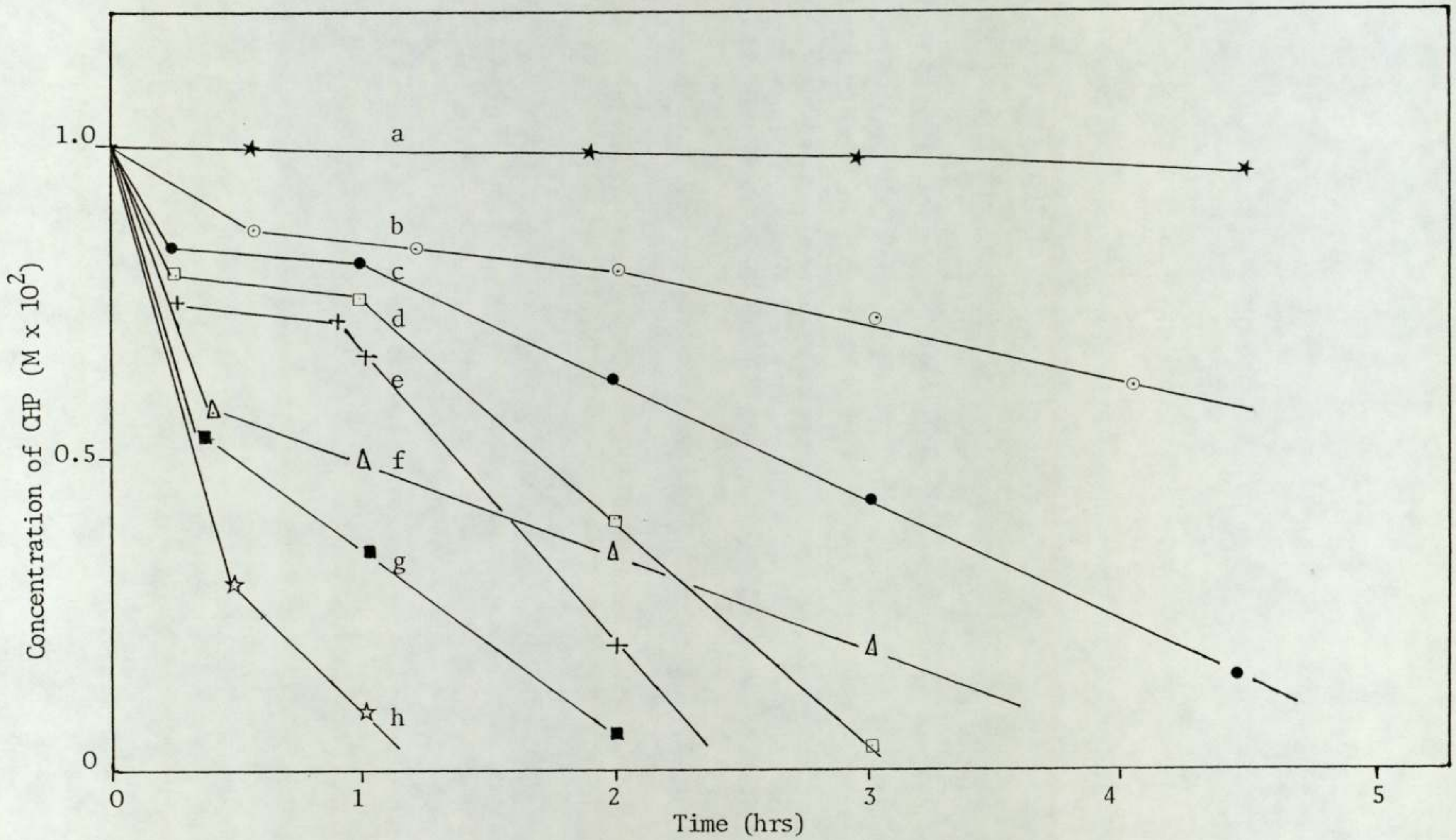


Fig 5.2 Decomposition of CHP (1 x 10^{-2} M) in chlorobenzene at 70°C in the presence of PAPT at the following molar ratios [CHP] / [PAPT] : a - control; b - 1:5; c - 1:1; d - 10:1; e - 20:1; f - 40:1; g - 60:1; h - 100:1

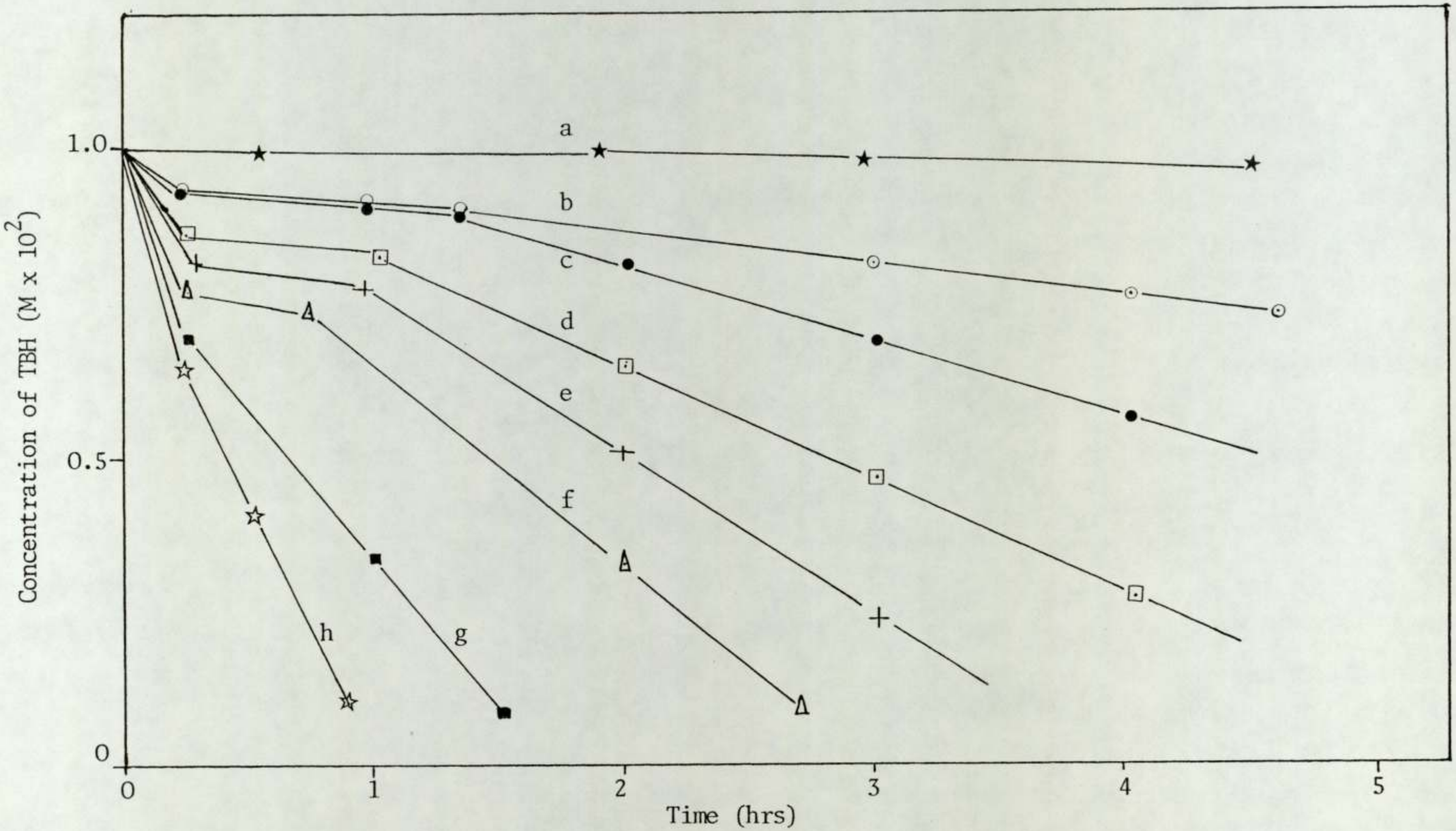


Fig 5.3 Decomposition of TBH (1×10^{-2} M) in chlorobenzene at 70°C in the presence of PPPT at the following molar ratios [TBH] / [PPPT]: a - control; b - 1:5; c - 1:1; d - 10:1; e - 20:1; f - 40:1; g - 60:1; h - 100:1

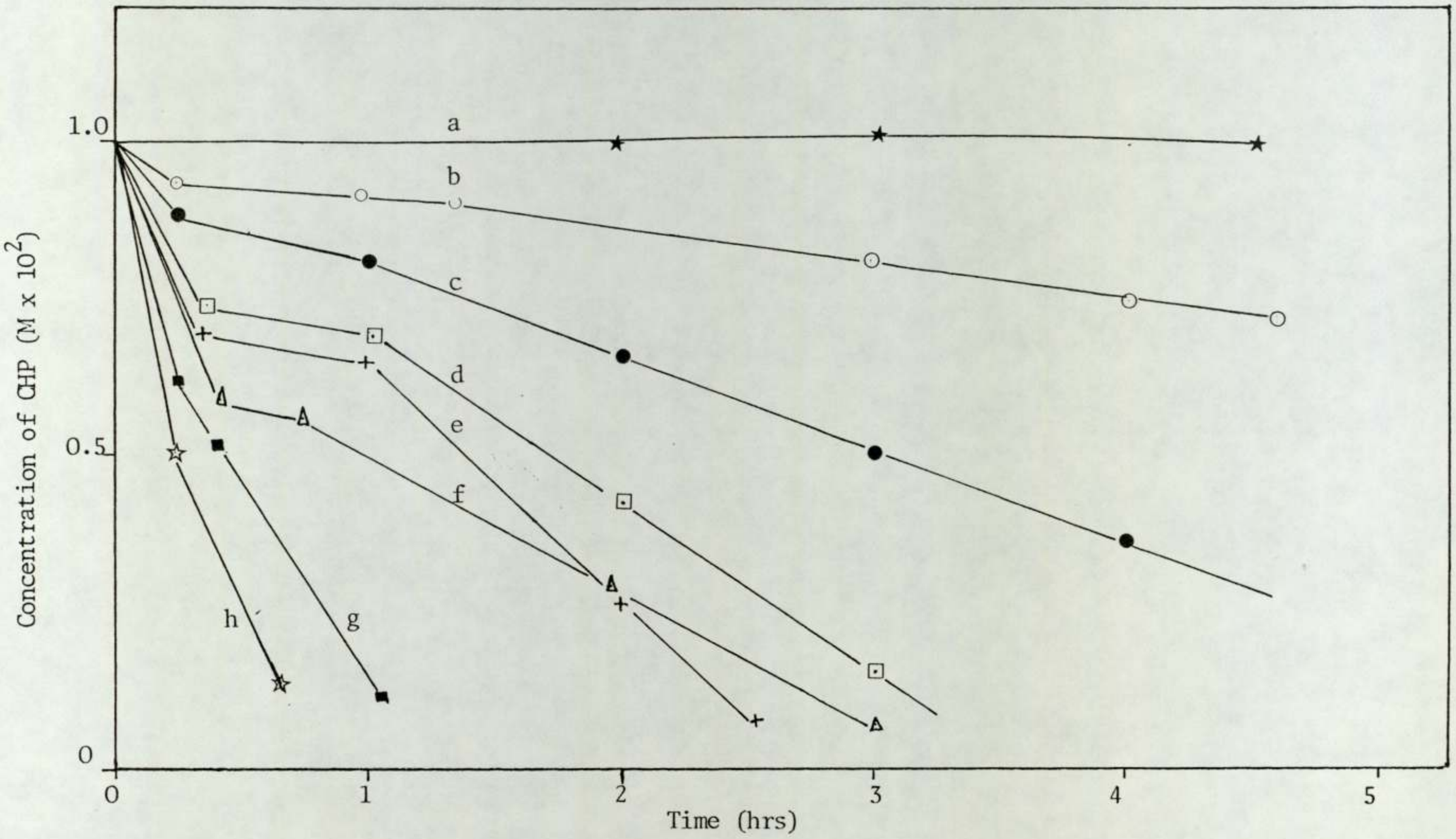


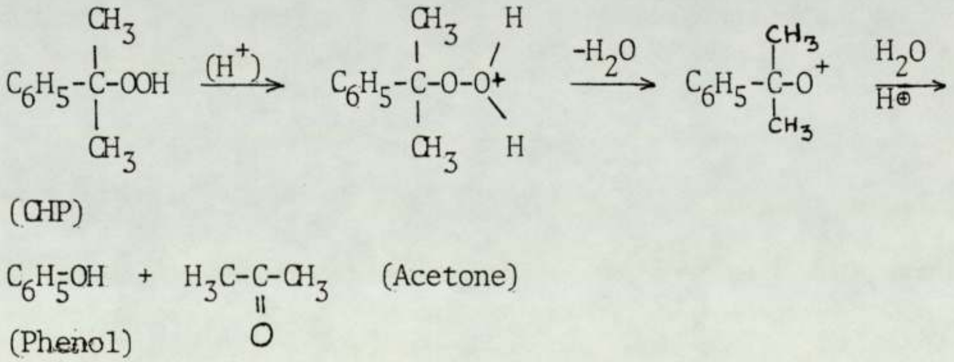
Fig 5.4 Decomposition of CHP (1 x 10^{-2} M) in chlorobenzene in the presence of PPPT at the following molar ratios [CHP] / [PPPT] : a - control; b - 1:5; c - 1:1; d - 10:1; e - 20:1; f - 40:1; g - 60:1; h - 100:1

5.3 Gas Liquid Chromatography

5.3.1 Introduction

The instrument used in the GLC analyses of the products formed during the reaction of PAPT (II) and PPPT (III) with cumene hydroperoxide (CHP) was the Perkin Elmer Model F30 which employed a high accuracy temperature programmer. The instrument has two detection facilities, hot wire or flame ionisation and the latter was employed in this work. The chromatograph was fitted with a 2 metre stainless steel column packed with 10% polyethyleneglycol adipate or Chromosorb W.

The decomposition products of cumene hydroperoxide are: phenol and acetone via an ionic decomposition pathway, whereas cumyl alcohol, acetophenone and α-methyl styrene are formed by a free radical decomposition process$^{(85)}$ through homolytic cleavage.



$$C_6H_5-\overset{CH_3}{\underset{CH_3}{C}}-OOH \xrightarrow{(H^+)} C_6H_5-\overset{CH_3}{\underset{CH_3}{C}}-O-\overset{+}{O}H_2 \xrightarrow{-H_2O} C_6H_5-\overset{CH_3}{\underset{CH_3}{C}}-O^+ \xrightarrow[H^{\oplus}]{H_2O}$$

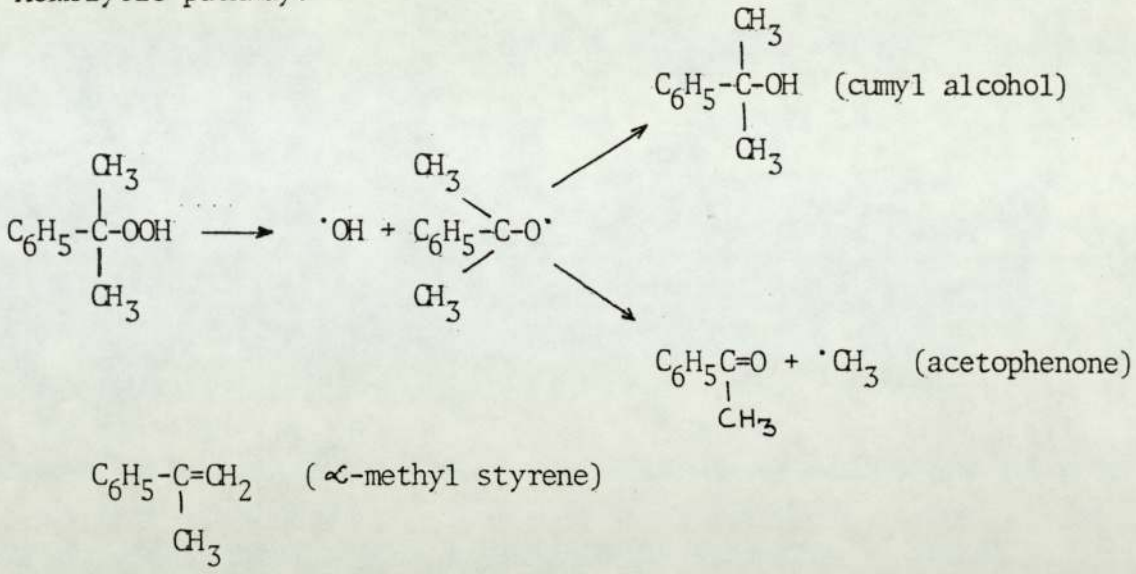
(CHP)

$$C_6H_5OH + H_3C-\underset{O}{\underset{\|}{C}}-CH_3$$

(Acetone)

(Phenol)

Homolytic pathway:



From the above information, the analysis of the reaction products of the thiolamides and CHP, it will be possible to predict the ex-act mode of action of the thiolamides as antioxidants. But before analysis, there is a need to calibrate the products from cumene hydroperoxide decomposition.

For the calibration of individual components, a series of solutions was made up in chlorobenzene containing varying amounts of the substance and a fixed amount of internal standard, iodobenzene, such that the ratio of the weight of the substance to the weight of the internal standard varied from zero to approximately 1.6.

The solutions were then analysed using an initial temperature of 85°C which was held for five minutes after which the temperature was programmed at 10°C per minute until a temperature of 180°C. The mobile phase was nitrogen carrier gas at a flow rate of 30 ml min^{-1}. The ratio of the peak height of the substance to the peak height of the internal standard was obtained from the chromatograph.

The relative amounts of the products in the reaction mixtures of cumene hydroperoxide with thiolamides (II) and (III) were then analysed. The detector was maintained at 200°C and one microlitre of the mixture was injected for analysis, after converting any residual CHP (quantitative titrimetrically) to cumyl alcohol by the addition of triphenyl phosphine in chlorobenzene. The calibrated chromatograph were then used to enable quantitative analyses of the products. The amount of cumyl alcohol derived from the reduction of unconverted CHP by triphenyl phosphine was estimated using suitably calibrated chromatograms.

5.3.2 Results

It is generally accepted that the products formed from the decomposition of CHP indicate the mechanisms of processes which are occurring during the decomposition reaction. As already discussed, the product expected from initial ionic process are phenol and acetone whereas the formation of acetophenone and α-methyl styrene is associated with homolytic cleavage of CHP and α-cumyl alcohol may be formed in both homolytic and by stoichiometric reduction of the hydroperoxide. Moreover, the formation of α-methyl styrene is also an indication of the liberation of an acid catalyst which is normally linked with the ionic catalytic decomposition products phenol and acetone$^{(145)}$.

The formation of these products at various molar ratios of [CHP]/[PAPT] is shown in Fig 5.5, and that of [CHP] / [PPPT] system is shown in Fig 5.6. It is clear that at [CHP] / [RSH] ratios of 1 : 5 and less, acetophenone is the major product formed. It is surprising that even at 1 : 10 ratio, phenol is present in an unusually high proportion (34%). At higher ratios, the ionic products predominate even though some radical products are present. Acetone was not detected both at low and higher ratios. A possible explanation is the probability of a condensation reaction between acetone and the thiolamide. Alternatively, the absence of acetone may be due to volatilisation since the reaction was carried out at a temperature above the boiling point of acetone.

It is quite clear from Figs 5.5 and 5.6 that the amounts of α-methyl styrene and α-cumyl alcohol were both low, presumably because of enhanced dehydration of alcohol by Lewis acid responsible for hydroperoxide decomposition. During the induction period, there was precipitation of insoluble fraction which after filtration was found to consist of the disulphides of the thiolamide and a so far unidentified greenish-brown high melting (168.5^{o}C) solid. At lower molar ratios of [CHP] / [PAPT] and less, there was no precipitate formed but the solution was turbid (greenish coloured).

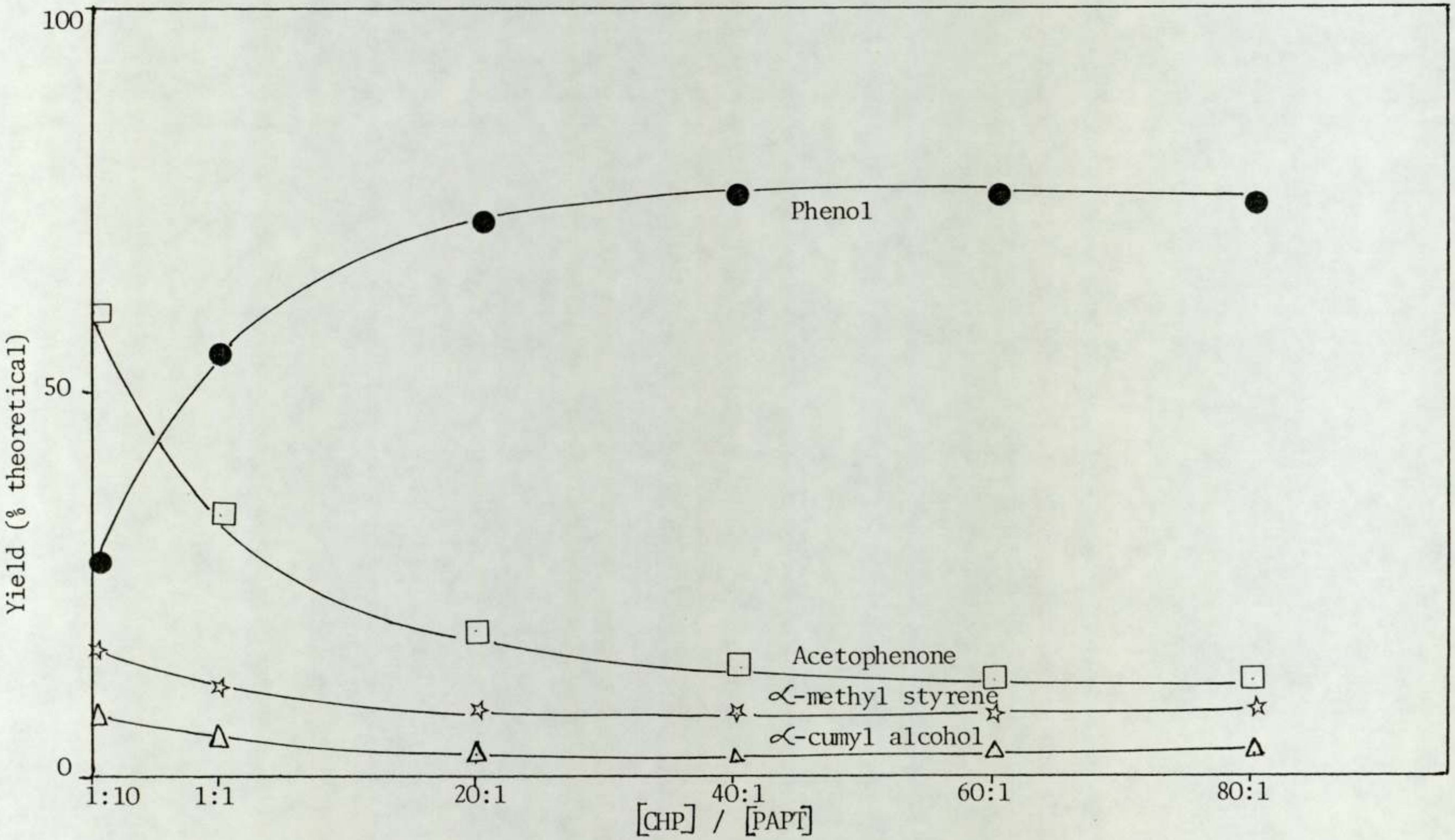


Fig 5.5 Product yields after complete reaction of CHP with PAPT at 70°C in chlorobenzene at various molar ratios [CHP] / [PAPT]

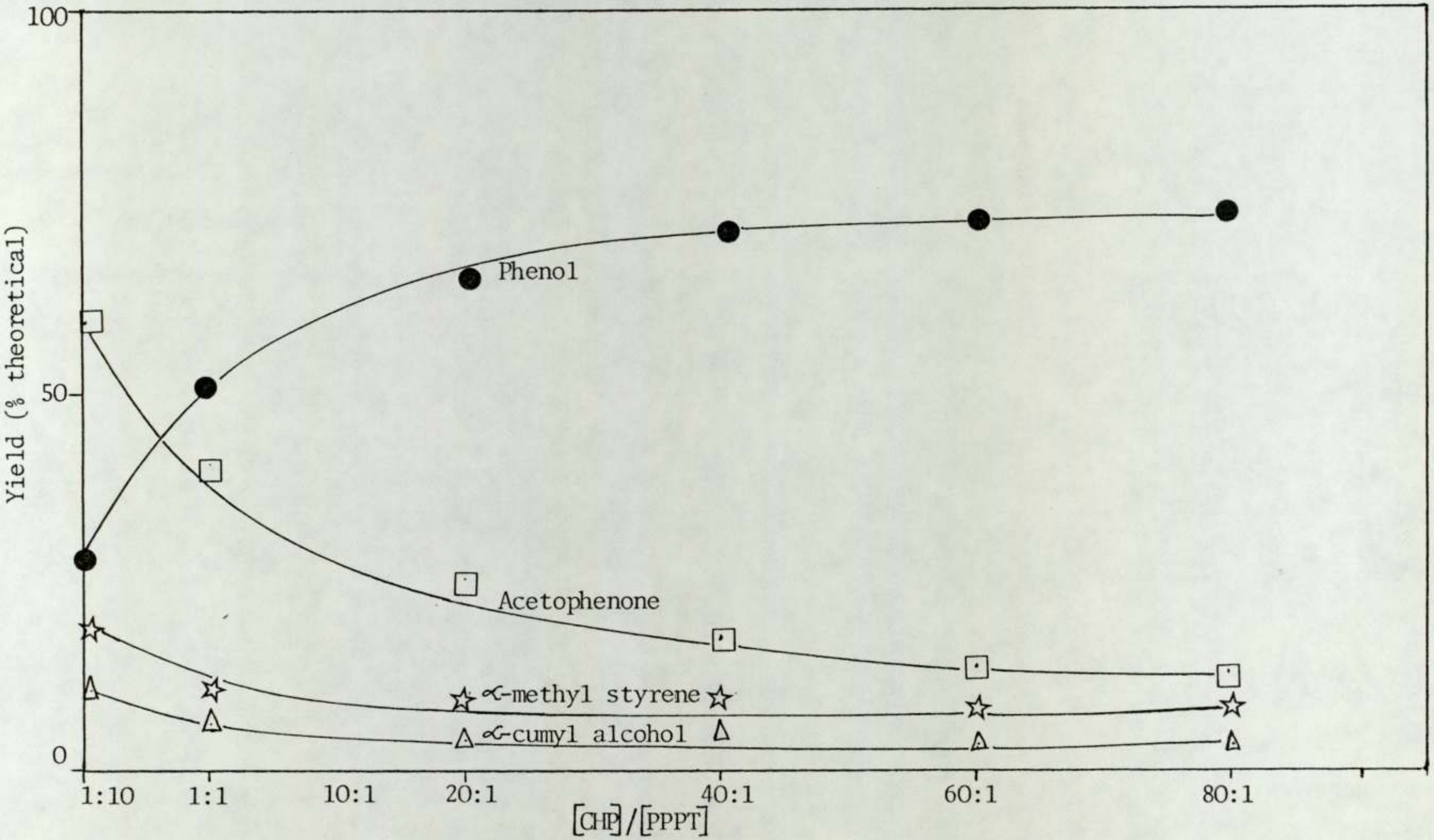


Fig 5.6 Product yields after complete reaction of CHP with PPPT at 70°C in chlorobenzene at various molar ratios [CHP] / [PPPT]

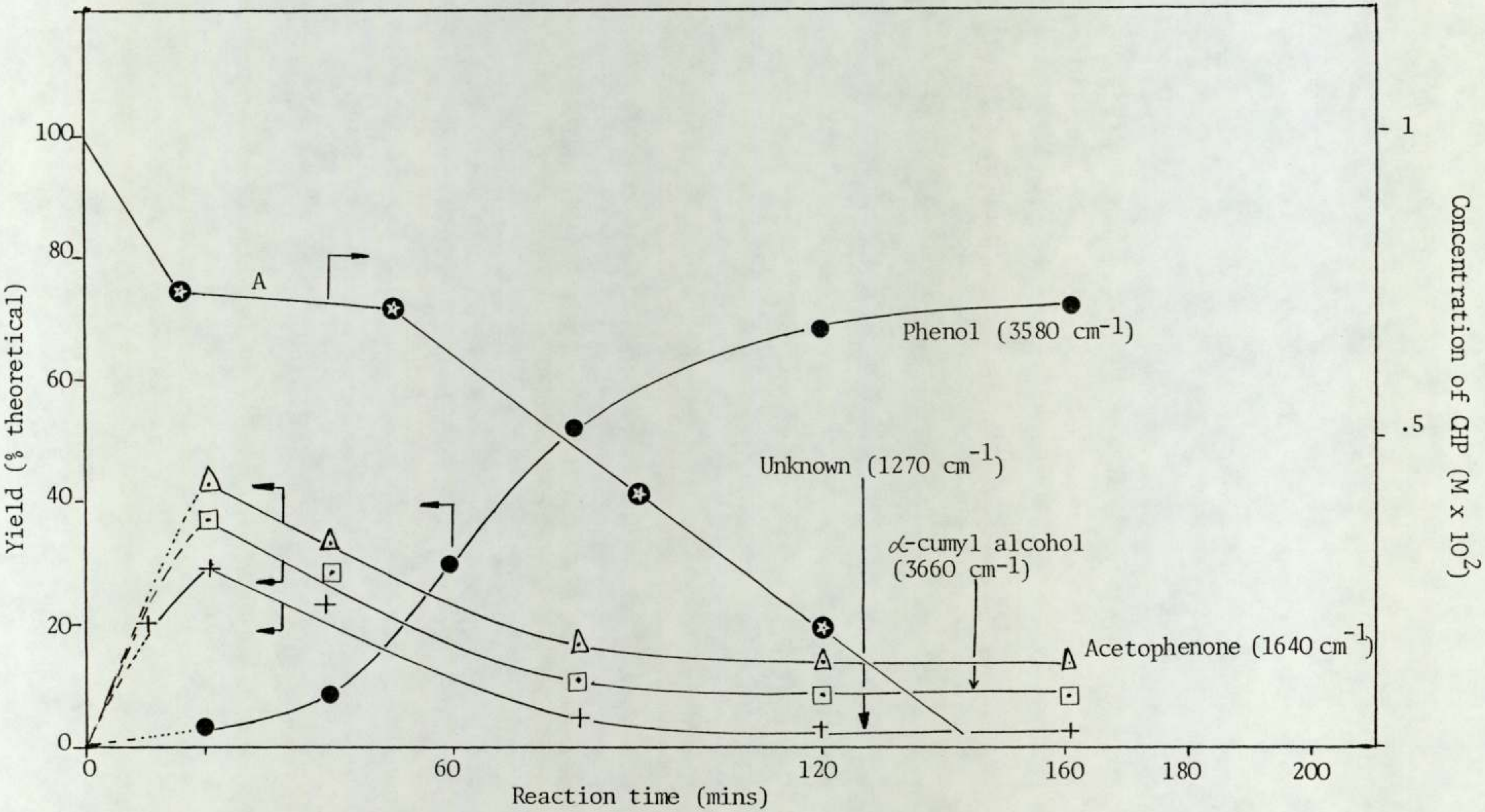


Fig 5.7 Kinetics of product formation during the reaction of CHP (1 x 10^{-2} mol/l) with PAPT (1 x 10^{-4} mol) in chlorobenzene at 70°C determined by infra-red spectrophotometry. The decomposition of CHP in the presence of PAPT (curve A) is also shown.

5.4 Identification of Reaction By-products by Method of Thin Layer Chromatography

Thin layer chromatography (TLC) was used to analyse all the extractable by-products formed during the process of grafting the additives to NBR latex, extracts of NBR vulcanisates and the decomposition products of the tertiarybutyl hydroperoxide (TBH) with thiolamides.

The cast films after the grafting reactions were methanol extracted and the vulcanisates were extracted with an azeotropic mixture of acetone, methanol and 1,1,1-trichloroethane. The extracts and the decomposition products of TBH in chlorobenzene solution were concentrated on a rotory evaporator to solid products. The analysis was carried out on 'polygram' plastic sheets with a layer of 0.25 mm silica gel.

2 μl of 1% solution of the concentrates in methanol was applied on to a 20 x 20 cm silica plate and the methanol allowed 3 minutes to evaporate after application. The chromatogram was developed by the ascending method, that is, by allowing the solvent mixture to move up an almost vertical plane by capillary action. The sides of the tank were lined with chromatographic papers so as to saturate the tank atmosphere as fully as possible. The solvent mixture for the phenolic (BHBM NBR reaction by product) extract analysis was a mixture of benzene, methanol and acetic acid (45 : 8 : 4 v/v) detection was done by drying the plate in

air before and after spraying with a 1% solution of phosphomolebdic acid in methanol followed by exposure to ammonia vapour. The extracts of the thiolamides were developed with a solvent mixture of n-butanol acetic acid and water (60 : 20 : 20 v/v). The plate was air dried. To observe the separated components a 1% solution of potassium persulphate containing 1 x 10^{-3} mol silver nitrate was used as locating agent.

The identification and characterisation of the different components was by Rf values. For the purpose of identification, the likely by products were prepared as described in Chapter Two.

$$\text{Rf value} = \frac{\text{Distance travelled by compound from origin}}{\text{Distance travelled by solvent front from origin}}$$

The different Rf values for compounds are shown in Tables 5.1 - 5.3.

5.4.1 RESULTS

The result of TLC analysis shown in Tables 5.1 and 5.2 indicates the formation of disulphides, monosuluphide derivatives of the parent thiol amides during the decomposition of hydroperoxide. In all cases, there are additional spots whose Rf values are 73 and 75 respectively and have light-green colour (in the case of PAPT), and 60, 57 with yellowish blue colour in the case of PPPT. These unknown spots are probably other oxidation species.

Table 5.1 TLC analysis of pure thiolamines (PAPT, PPPT) and of derived mono and disulphides

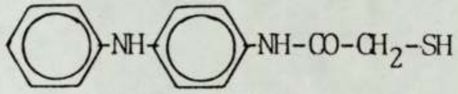
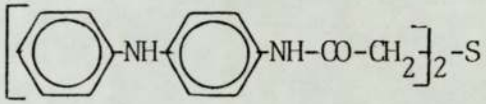
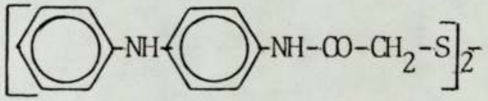
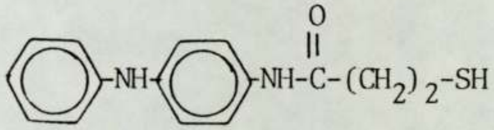
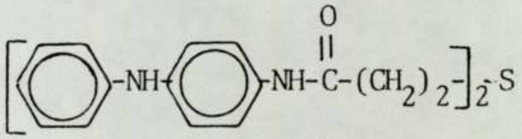
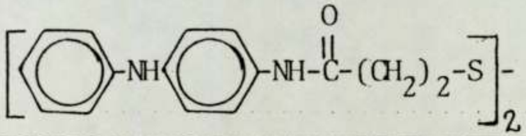
Compound		R_f value x 100
PAPT		89
Monosulphide		86
Disulphide		78
PPPT		76
Monosulphide		69
Disulphide		64

Table 5.2 TLC analysis of the reaction products of thiolamines and cumene hydroperoxide

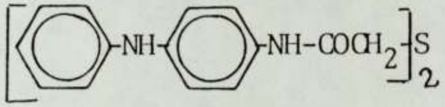
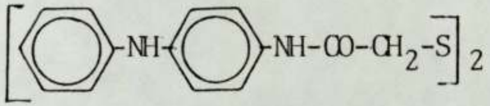
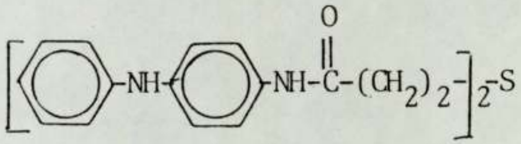
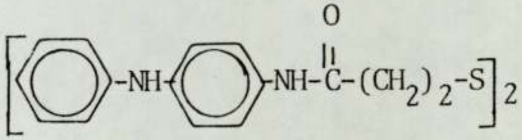
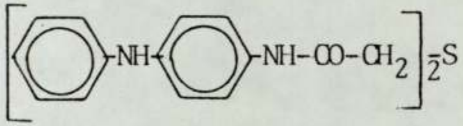
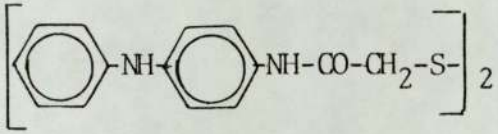
Identified compounds		R_f values	Colour
PAPT monosulphide		81	Brown
PAPT disulphide		77	Brown-green
Unknown		73,75	Light breen
PPPT monosulphide		68	Brown
PPPT disulphide		64	Brown
Unknown		60,57	Yellowish-blue

Table 5.3 TLC analysis of film extract

Identified compounds		R_f values	Colour
PAPT monosulphide		81	Brown
PAPT disulphide		77	Brown-green
Unknown		73,74	Light green

The results obtained from (TLC analysis of) BHBM film and vulcanisate extracts show spots corresponding to monosulphide (Rf = 82), disulphide (Rf = 91.5) and stilbenequinone (Rf = 90). The identification of compounds was based on the comparison of Rf values of spots with that of reference compounds.

Spots have been identified as being due to oxidation products of monosulphide or disulphide on the basis of identical Rf values with those of the pure compounds.

Table 5.3 gives the result of the analysis of extract, from the film cast after the latex grafting reaction, and it is obvious that apart from the formation of mono and disulphide, some unknown by products are still present which are also extractable and that their Rf values correspond to those of the unknown spots of the hydroperoxide decomposition products. It is also observed that spots having Rf values nearer to that of the pure compound (free thiol) were present. This suggests that not all the thiol become bound to nitrile rubber during the process of grafting.

Although the evidence is not conclusive but with the aid of theoretical consideration, it might be said that the thiolamides (II and III) are converted to the corresponding mono and disulphide (mainly the latter) during their reaction with hydroperoxides. Further evidence is considered in a later section (5.5) when the GPC method of analysis is considered. A similar result was obtained with the vulcanisate extract but no free thiol was identified in this case. This latter observation is important since this suggests that thiol is reacting further during vulcanisation.

5.5 Gel Permeation Chromatography

5.5.1 Introduction

Since the introduction of gel permeation chromatography as an analytical means to determine the molecular weight distribution (MWD) and average molecular weight (MW) the technique has become more sophisticated and the scope of application broadened. It has assumed a very important position in polymer chemistry, particularly in cellulose chemistry and technology where its unique ability to separate by molecular size can be exploited and put to beneficial use$^{(146)}$.

In principle, any soluble molecules can be separated by GPC, small molecules (MW $<$ 100) as well as large ones of several millions MW. The separation is usually carried out on columns that are tightly packed with a gel or some other porous material and completely filled with solvent. Usually the same solvent is used to dissolve the sample before it is introduced into the column and also for elution. The separation occurring in the gel column depends on the difference in the rate of migration of the polymer molecules through the micropores of the gel placed in the chromatograph columns. The smaller macromolecules diffuse through the gel pores to a greater depth and hence their flow time through the column is greater than that of the larger molecules which are excluded, the molecules of intermediate size can penetrate some of the larger pores.

5.5.2 Apparatus

Gel permeation chromatography was carried out at Diamond Shamrock Europe Limited, Research Centre. The instrument used was the Waters Associates Model 6000 gel permeation chromatograph equipped with styragel columns; fixed wavelength (254 nm) uv detector and differential refractometer detector. (The two detectors are connected in series.) The nominal porosity designation of the column is 50 Å with 5 μ particle size and the column is 60 cm long and was supplied by Polymer Laboratories Limited, Stretton.

The solvent employed was the HPLC grade THF (ex Rathburn Chemicals Limited). The flow rate of the mobile phase was 1 ml min^{-1} and the chart speed was 1 cm min^{-1} and the instrument operated at room temperature ($\pm$ 1^{o}C). It also is fitted with the Rheodyne 20 μ 1 loop injector.

5.5.3 GPC Analysis of Hydroperoxide Decomposition Products

PROCEDURE

Preparation of sample solution was by dissolving 60 mg of test solution (test compound) in 20 ml of tetrahydrofuran (ie 0.3%) and 15 μ 1 of chlorobenzene added to act as a reference for measurement of relative retensions.

20 μ l of the sample solution was injected through a loop injector into the column. The components (thiolamide, disulphide, monosulphide and other oxidation products) were identified by comparison of their relative retention (cm) with known standard materials (see Fig 5.10).

5.5.4 GPC Analysis of Bound Antioxidants

This method was applied to estimation of the level of binding by dissolving 60 mg of the modified NBR rubber in 20 ml tetrahydrofuran and the remainder of the procedure is exactly the same as described above.

The concentration of residual thiolamide, disulphide and monosulphide formed was determined by comparing peak heights measurement with standard solutions. The degree of binding was determined by measurement of the increase in uv absorbance (peak height) of the polymer.

5.5.5 GPC Calibration Curve

The calibration curve was constructed using the linear polystyrene calibration standards obtained from Polymer Laboratories Limited. The log of molecular weight against retention distance relative to chlorobenzene (see Figs 5.8 and 5.9).

$$\frac{\text{Retention of peak of interest}}{\text{Retention of peak of chlorobenzene}}$$

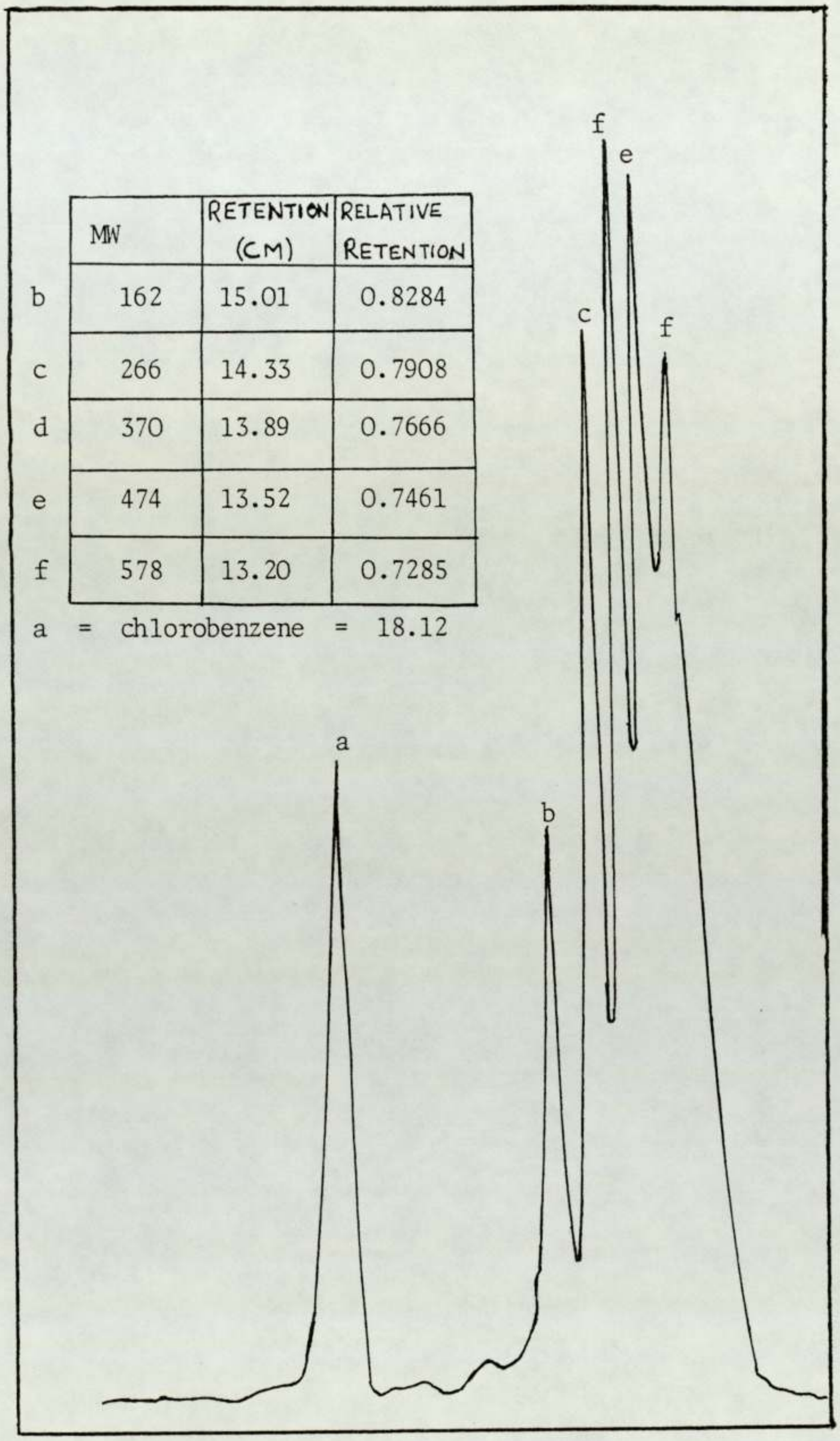
In the case of bound polymer (modified NBR) the calibration was carried out using polymers in which the degree of binding has previously been determined using the extraction / ir technique.

5.5.6 Results

Figs 5.10 and 5.11 show the relative amount of products formed during the decomposition of cumene hydroperoxide in the presence of PAPT. Since the decomposition products of cumene hydroperoxide did not absorb in the uv, they were not detected by the uv detector of the GPC. Only the oxidised products of PAPT could be detected.

The result showed that a relative high percentage of the reaction product consists of disulphide, followed by monosulphide. Two unidentified products with relative retentions of 0.844 and 0.6402 were formed (Fig 5.10, curves b and g). These products were not formed until after 30 minutes after the reaction had begun; also they were present in very small concentrations (Fig 5.11, curves d and e). It was also observed that the thiolamide PAPT was destroyed within 45 minutes of the commencement of the decomposition reaction.

The formation of the products was always accompanied with colour formation (brownish green). The result obtained from GPC method



	MW	RETENTION (CM)	RELATIVE RETENTION
b	162	15.01	0.8284
c	266	14.33	0.7908
d	370	13.89	0.7666
e	474	13.52	0.7461
f	578	13.20	0.7285

a = chlorobenzene = 18.12

Fig 5.8 Polystyrene GPC calibration chromatograph

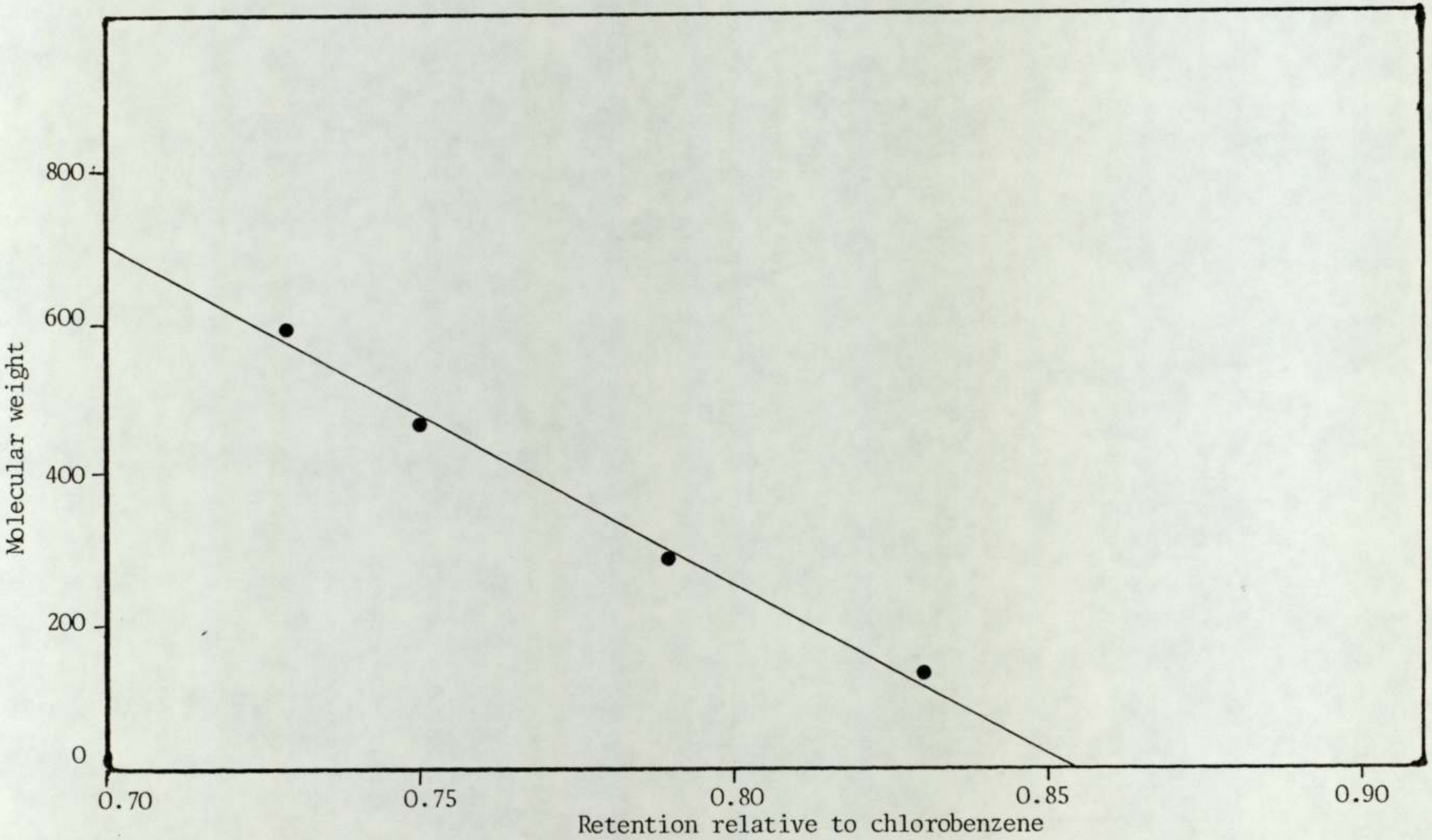
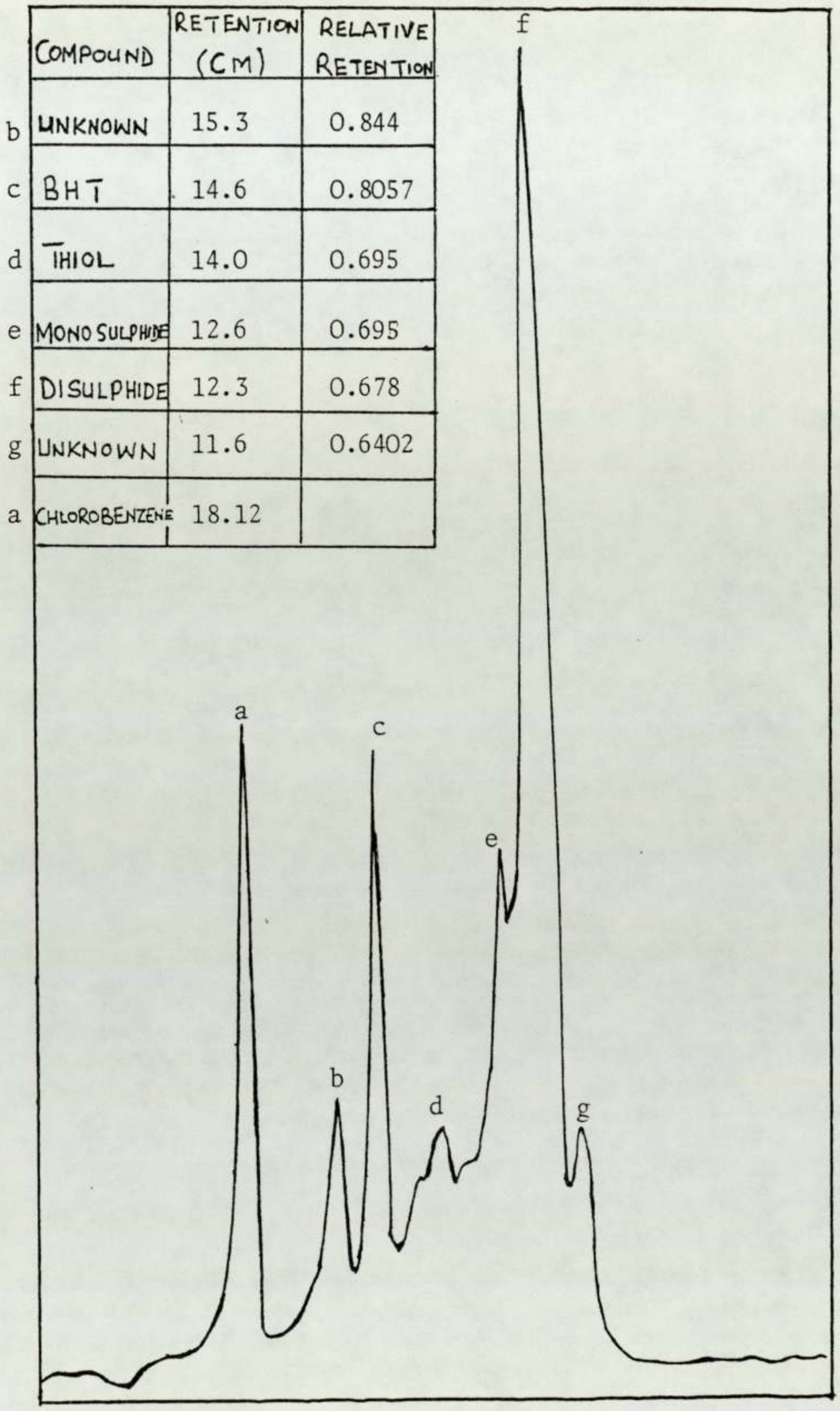


Fig 5.9 Polystyrene calibration curve for 50 Å GPC column



	COMPOUND	RETENTION (CM)	RELATIVE RETENTION
b	UNKNOWN	15.3	0.844
c	BHT	14.6	0.8057
d	THIOL	14.0	0.695
e	MONO SULPHIDE	12.6	0.695
f	DISULPHIDE	12.3	0.678
g	UNKNOWN	11.6	0.6402
a	CHLOROBENZENE	18.12	

Fig 5.10 Typical GPC chromatogram of decomposition of product of the reaction of CHP with PAPT at ratio 10:1

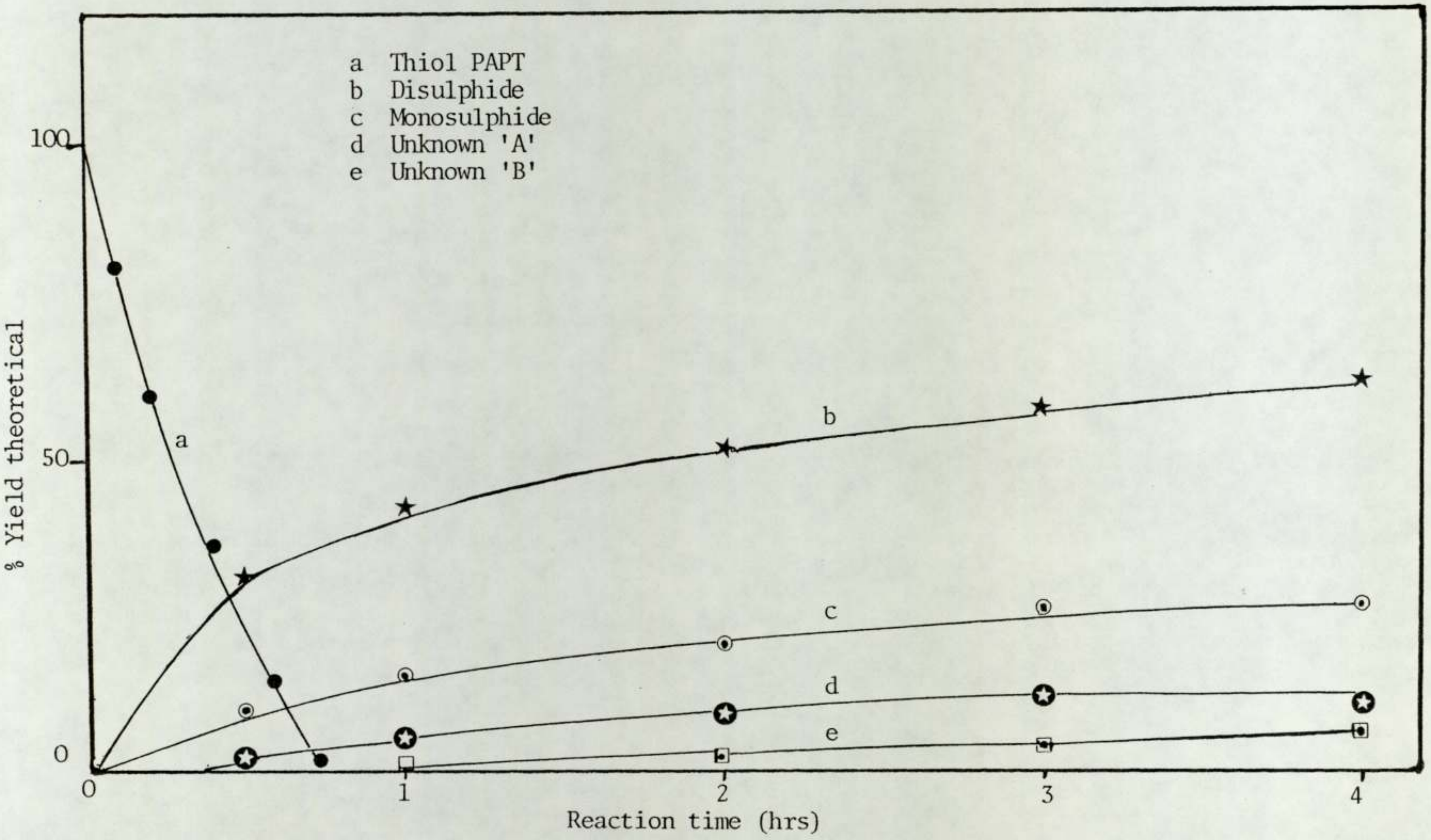
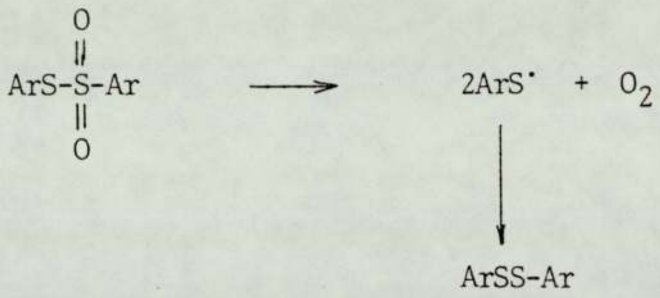


Fig 5.11 GPC analysis of reaction product of [CHP]/[PAPT] system at different reaction times

therefore confirms the formation of disulphide and monosulphide observed in the product separation by TLC (section 5.4). The infra-red spectra of the product of thermal decomposition of CHP in the presence of PAPT showed absorption at 1155 and 1340 cm^{-1}, characteristics for the thiolsulphonates which could be the unknown compound, but thiolsulphonates are known to be unstable since they probably breakdown to form disulphide and sulphur dioxide being evolved.



$$ArS\text{-}S(=O)_2\text{-}Ar \longrightarrow 2ArS^{\cdot} + O_2 \qquad 2ArS^{\cdot} \longrightarrow ArSS\text{-}Ar$$

The peak 'C' in Fig 5.9 is that due to the absorption of the stabiliser butylated hydroxyl toluene present in the THF used as solvent.

The results obtained from the GPC analysis on the grafted NBR showed that the thiol based antioxidants are bound to NBR but the inconsistency of the extent of binding (the GPC peaks actually being bigger than the theory for 100% grafting in some experiments and very low values in some) casts some doubt on the use of this method to analyse the modified nitrile rubber. It can only be assumed that the GPC provides a qualitative rather than quantitative measure of the bound antioxidant in the polymer (NBR).

5.6 Electron Spin Resonance Technique

5.6.1 Introduction

Electron spin resonance (ESR) spectroscopy is the observation of absorption of electromagnetic radiation caused by the magnetic dipole transitions between spin states of unpaired electrons in the magnetic field. The phenomenon was discovered by Zavoiskii(142) im 1945, and since then ESR has rapidly developed into a very powerful test for the study of free radicals.

The information obtainable from ESR spectra of free radicals is contained in

(i) The number and positions of the spectral lines
(ii) The line widths
(iii) The total absorption intensity

The analysis of the number and positions of the lines gives information about the chemical and steric structure of the radicals and provides insight into the odd electron distribution, the line width offers additional information on the structure as well as the kinetics of reversible radical reactions. The concentration of the radicals is determined from the absorption intensity.

The basic principles and details of the necessary analysis of ESR spectra have been described in the literature(148-151).

5.6.2 Theoretical Aspects

5.6.2.1 Resonance Condition

The electron has a non-classical, intrinsic angular momentum called spin. According to the principles of quantum mechanics, only one of the components of the spin in a given direction (z) can be measured accurately apart from its magnitude. The spin is characterised by the quantum number $S = \frac{1}{2}$, its component along the z-axis being characterised by the quantum number $M_S = \pm \frac{1}{2}$. The electron thus has two spin states differing in M_S.

The spin of the electron gives rise to a magnetic moment, μ_E, whose z-component μ_E^z can assume only two values corresponding to the spin quantum number $M_S = \pm \frac{1}{2}$. M_S and μ_E^z are related by equation:

$$\mu_E^z = M_S \cdot g_E \cdot \beta_E = \begin{cases} -(+\frac{1}{2}) g_E \beta_E & \text{for} \quad M_S = +\frac{1}{2} \\ \\ -(-\frac{1}{2}) g_E \beta_E & \text{for} \quad M_S = -\frac{1}{2} \end{cases} \qquad (5.1)$$

where μ_E is the Bohr magneton, a constant having the value of 9.2733×10^{-21} erg/gauss; g_E is a dimensionless number whose value for free electrons is 2.0023. The g_E value for electrons in atoms or molecules may be different. It is convenient to identify z-axis with the direction of applied magnetic field. The component μ_E^z of the magnetic moment is then responsible for the behaviour of the electron in the magnetic field.

In the absence of an external magnetic field, the two spin states which $M_S = +\frac{1}{2}$ and $M_S = -\frac{1}{2}$ are degenerate. When a magnetic field H is applied along the z-axis, it interacts with magnetic moment μ_E of the electron, and the spin states are no longer degenerate (Zeeman effect). The energy of interaction E is given by the formula:

$$E = -\mu_E^z . H = +(M_S g_E \; {}_E) . H \qquad (5.2)$$

and the energy difference between two spin states is:

$$E_2 - E_1 = g_E \beta_E H \qquad (5.3)$$

where E_1 and E_2 are energy levels of the spin states $M_S = -\frac{1}{2}$ and $M_S = +\frac{1}{2}$ respectively (Fig 5.12).

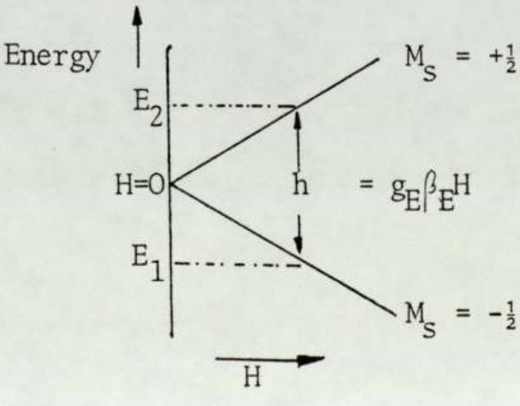


Fig 5.12 Splitting of the spin levels of an applied magnetic field of intensity H

Transition from one Zeeman level to the other (ie between E_1 and E_2), in which the electron changes its spin state, occurs when the system is exposed to an electromagnetic radiation with a resonance frequency ν. This frequency is determined by the resonance condition:

$$h\nu = g_E \beta_E H \tag{5.4}$$

where h is Plank's constant (6.624×10^{-27} erg sec); ν thus depends on H, and the proportionality constant between them γ_E amounts to 2.802 MHz gauss^{-1} when $g_E = 2.0023$.

$$\gamma_E = \frac{\nu}{H} = \frac{g_E \beta_E}{h} \tag{5.5}$$

To satisfy the resonance condition, one can vary ν and/or H. For technical reasons, the frequency ν is kept constant and the field strength H is varied to bring it to the value at which the resonance condition is fulfilled.

5.6.2.2 Relaxation Phenomenon

The resonance condition $h\nu = g\beta H$ implies that energy has been supplied to electron spins in a lower energy level and has transposed them to a higher energy level. These electron spins must eventually return to the lower state and the time they take to return is known as relaxation time.

Relaxation time comprise two terms, a dipolar spin-spin relaxation time T_2, which is determined by the amount of spin energy shared with other electrons or nuclei, and a spin-lattice relaxation time T_1, which is determined by the rate of sharing spin energy with thermal vibrations of the lattice. T_1 is defined as the time in which an initial excess of energy given to the spins will fall to 1/e or 0.368 of its value. T_1 and T_2 are related to   by:

$$\frac{1}{\tau} = \frac{1}{T_2} + \frac{1}{T_1} \tag{5.6}$$

where τ is defined by:

$$\tau = \pi g(\omega - \omega_0)_{max} \tag{5.7}$$

in which $g(\omega - \omega_0)$ is the line-shape function.

The magnitude of the spin-lattice relaxation time is controlled by spin-orbit coupling, but since this is a very small parameter in organic radicals, this mechanism does not usually contribute to the line-width of an ESR spectrum and T_1 is of the order of seconds. The major contribution to the line width of the ESR spectrum of an organic radical is the spin-spin relaxation time. This is the reduction of time spent in a particular spin state because of dipolar interations with surrounding magnetic particles whether these be electrons or magnetic nuclei.

5.6.2.3 g-Value

The g-value or spectroscopic splitting factor or Lande factor defined by the equation:

$$h\nu = g\beta H$$

is a proportionality constant, relating to the frequency and field at which resonance occurs. The g-value for free electron is 2.0023 which resonance occurs at X-band frequencies and with an applied field of some 3300 gauss. This is not generally the case for unpaired electrons in paramagnetic molecules since there may be a contribution to the magnetic moment arising from orbital angular momentum which will be observed as a deviation of the g-value from the free spin value (g_o), and resonance at a field different from 3300 gauss. The g-values of most organic free radicals are within 1% of the free electron value while those of hydrocarbon free radicals are within 0.1% of g_o. The deviation of the observed g from g_o has been interpreted as being due to spin orbit coupling; the spin orbit coupling parameters for most hetero atoms are greater than that of the carbon and this explains why those radicals with spin densities localised on, for example oxygen, nitrogen or sulphur atoms, have g-values which deviate from g_o more than those of carbon radicals. Since it is possible to measure g-values to very high precision, they can be used to give information about the orbital occupied by the unpaired electron and also to identify radicals.

5.6.3 The Electron Spin Resonance Spectrometer

5.6.3.1 A Description of the Instrument

The electron spin resonance spectrometer used in this work was a commercially available one, the 'JEOL PE 1' manufactured by Jeol Limited, Japan. This is an instrument using high frequency moduluation and phase sensitive detection. This is also known as homodyne detection and involves modulating the magnetic field at high frequency, usually 100 kHz, with an amplitude small compared with the line width and then sweeping slowly through the resonant condition.

A block diagram of the apparatus is given in Fig 5.13.

Energy is fed into the hybrid tee bridge from the klystron and is split equally between the side arms, one arm feeds energy to the resonant cavity, the other arm carries components which reflect back a resonance wave, adjustable in amplitude and phase. These two reflected waves are detected in the fourth arm of the tee. In the off-resonant condition, the reference wave is adjusted to give a reflection equal in amplitude and opposite in phase to the reflection from the sample and cavity, and therefore cancels, with zero power being transmitted to the crystal detector in the fourth arm. At resonance, an off-balance signal is detected.

A modulation coil is mounted inside the cavity. It modulates the

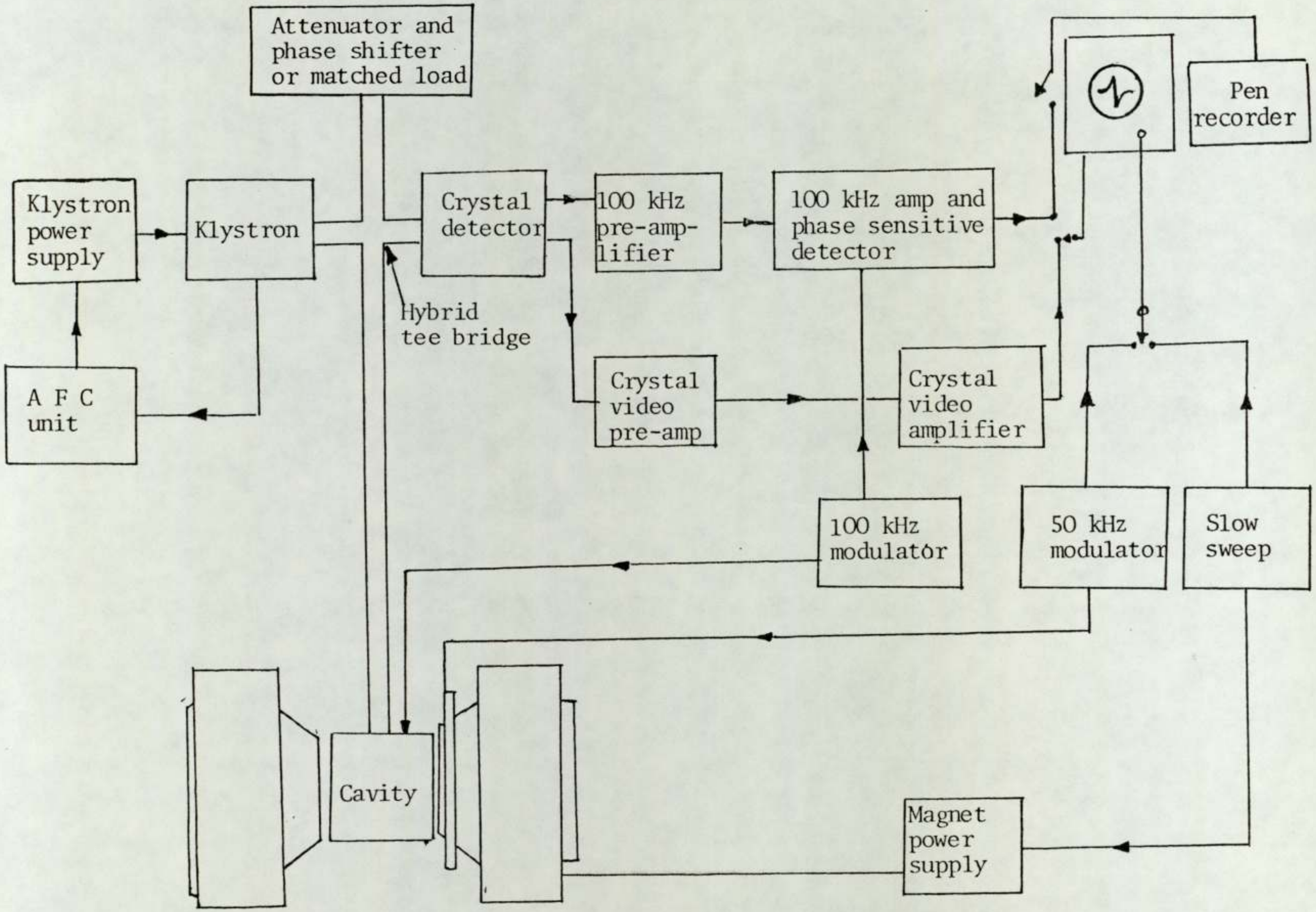


Fig 5.13 Block diagram of high frequency modulation spectrometer

steady magnetic field of the sample at the modulation frequency. Any absorption or dispersion due to resonance in the specimen changes the reflection coefficient unbalances the bridge. The crystal detects the resulting high frequency signal (100 kHz), which passes through a low noise pre-amplifier and a narrow band amplifier to a phase sensitive detector, which is also fed with a reference signal that is adjustable in phase relative to the modulation. The high frequency modulator supplies the modulation coils and also reference output for the phase sensitive detector.

Automatic frequency control is an incorporated feature of the machine, allowing the klystron frequency to be locked to the resonant frequency of the sample cavity.

The ESR signal may be displayed on a cathode-ray oscilloscope, or by a pen recorder.

All the work was carried out using X-band radiation, approximately 9400 MHz frequency, and the field intensity according to this frequency band is 3420 gauss.

5.6.3.2 Cavity

TE 011 mode (cylindrical) was used throughout this work. The magnetic and electric field configuration is shown in Fig 5.14. The maximum magnetic field is along the central verticle axis, and the sample should be positioned at the centre of the cavity.

In addition, the greater the sample quantity placed in the cavity, the greater the effective volume subject to the magnetic field, hence the stronger the signal.

5.6.3.3 Spectrometer Operation

The instrument was set up as instructed by the manufacturers. The frequency of the klystron and natural resonance frequency of the sample cavity were adjusted to be the same, and the klystron frequency was then locked to the sample cavity frequency by an AFC unit. Changes in sample cavity frequency were then followed by the klystron, the instrument remaining 'on tune' (assuming changes in the sample cavity frequency were small). This enabled the spectrometer to be used for several hours without retuning. Samples were often changed without necessitating more than very minor adjustment of the spectrometer, enabling comparisons between different samples to be carried out.

The absorption of microwave energy was detected using phase sensitive detection with a 100 kHz modulation current and the first derivative signal thus obtained displayed on an oscilloscope. The magnitude of the modulation current and thus the amplitude of the modulation field was made small enough to minimise lack of resolution by modulation current broadening and the scan speed and the amplitude set to display the signal. A permanent recording was made by a chart recorder.

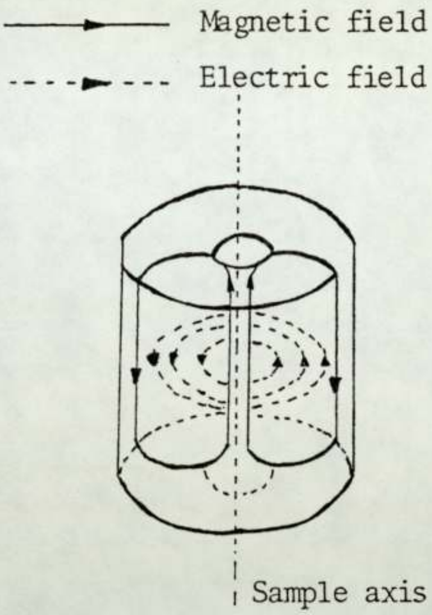


Fig 5.14 Cylindrical TE 011 resonant cavity and the electric and magnetic fields of the standing wave

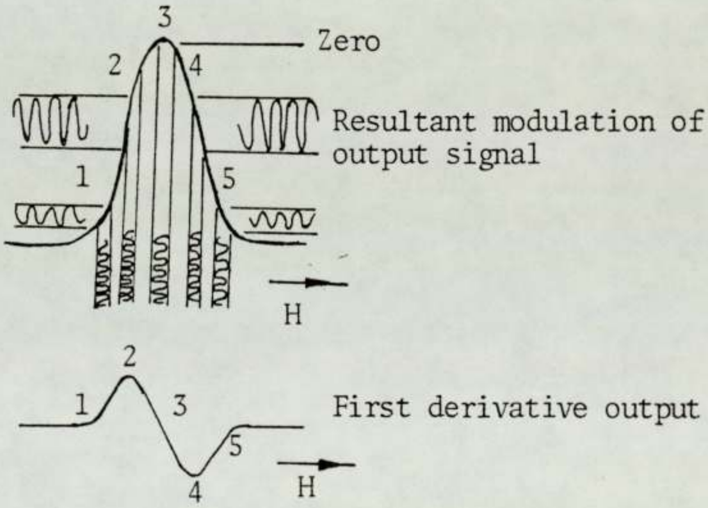


Fig 5.15 First derivative output, obtained when the amplitude of the high frequency modulation is small compared to the line width

5.6.3.4 Use of Derivative of Absorption

The amount of the supplied microwave power absorbed by the sample is only a small fraction, necessitating amplification of the signal. If the dc output from the microwave detector were amplified, it would be difficult to detect the small change in the dc level the absorption would make. If, instead, a small oscillating magnetic field is superimposed onto the large applied field, a process referred to as modulation of the applied field, this small field alternately adds to and abstracts from the large field, H_o.

As the resultant $H_o + H_{modulation}$ swings up and down, the dc output also increases and decreases. This therefore supplies an ac signal which may be amplified, and is not a small alteration of a large signal level but is zero when the sample is not absorbing microwave power. This process is illustrated diagramtically in Fig 5.15.

6.6.3.5 Measurement of g-values

The g-value or spectroscopic splitting constant of a paramagentic species is defined by the equation:

$$h\nu = g\beta H \qquad (5.8)$$

where h and β are known constants and it is usual for practical reasons to hold ν constant and sweep the magnetic field over the resonance positions. Thus,

$$gH = \frac{h\nu}{\beta} = \text{constant} \tag{5.9}$$

Thus, if the frequency ν and the magnetic field H are measured, g may be calculated. It was however, not possible to read the frequency accurately. The g-values were therefore calculated relative to a standard.

The standard chosen was Mn^{++} containing MgO which gives six lines ESR spectrum, the g-value of the fourth line counted from the low magnetic field side is $g_1 = 1.981$. In the JES-UCX-2 cavity resonantor, this value remains constant for cavity resonance frequencies between 9200 and 9400 MHz. Furthermore, the distance between the third and fourth lines is 86.9.

Assume that the following measured sample and ESR standard signals were recorded simultaneously and the data as shown in Fig 5.16 was obtained.

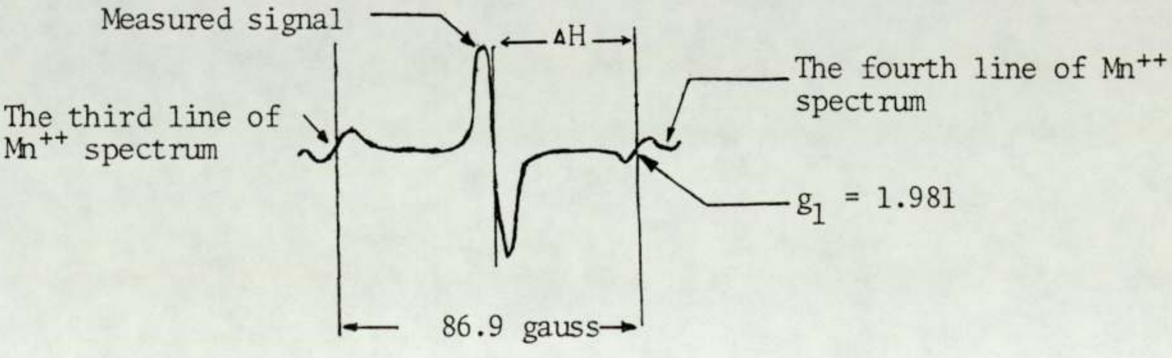


Fig 5.16

From the diagram:

$$g = \frac{g_1 H_1}{H_1 - \Delta H} \tag{5.10}$$

where g is the g-value of the unknown sample

g_1 is the g-value of the fourth line of Mn^{++} spectrum (1.981 at 9300 MHz)

H_1 is the value of the field at the fourth line of Mn^{++} spectrum

ΔH is the field deviation of the unknown peak and the fourth line of Mn^{++} spectrum.

Thus the g-value can be obtained easily without measuring the microwave frequency. In this case, if the measured sample spectrum appears in a magnetic field higher than that of the fourth line, it will be necessary to make ΔH negative.

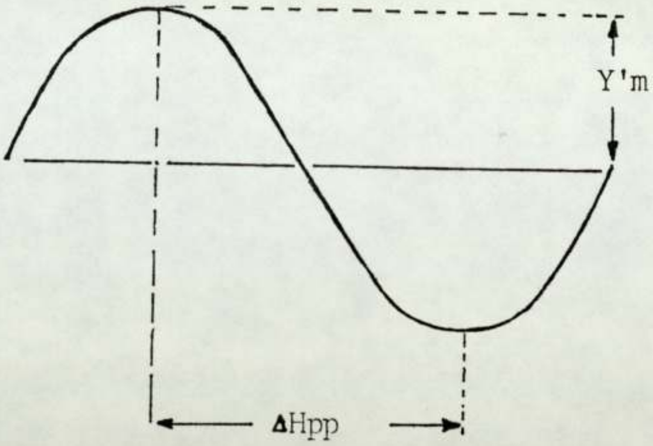
Using proportional calculation compared to the distance between the third and fourth lines of Mn^{++} spectrum, hyperfine splitting are easily determined from the recorded spectra.

5.6.4 ESR Study of the Formation of Nitroxyl Radicals During the Decomposition of TBH in the Presence of Thiolamide

The formation of nitroxyl radical during the grafting reaction of the thiolamide with NBR latex was thought to be one of the reasons for the failure to achieve a much higher level of binding in the latex reaction. In order to find out the possible participation of nitroxyl radicals in the reaction, an ESR study of the reaction products of TBH and PAPT in chlorobenzene solution was carried out.

The JEOL-PE spectrometer (section 5.6.3) was used to obtain electron spin resonance spectra (Fig 5.17). Solutions of the reaction products of TBH and PAPT in chlorobenzene (with different molar ratios of [TBH] : [PAPT]) were prepared in a melting tube and sealed on one end. This was placed into a quartz capillary tube. The tube was then immersed into the cavity of the spectrometer. The calibration of the instrument was by the use of MgO powder which contained thermally diffused Mn^{2+} ions as the marker. The ESR spectra is illustrated in Fig 5.17.

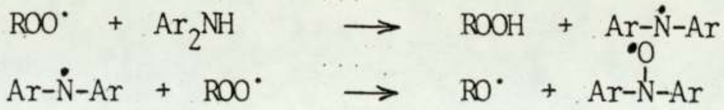
The concentration of the radicals in the sample solution was determined using a reference sample and the spectra of both samples were recorded simultaneously. To accomplish this, an accurately weighed amount of copper sulphate solution (0.1 M $CuSO_4$) contained in a capillary tube was fastened to the outer surface of the quartz tube inside which the probe sample is placed. The radical concentration was calculated from the recorded specta by comparing the ratio of the peak of the signal of the reference sample to that of the sample solution, as illustrated below.



$$\frac{Y'm\ (\Delta Hpp)^2\ \text{probe sample}}{Y'm\ (\Delta Hpp)^2\ \text{ref sample}} = \frac{\text{Concentration of radicals in probe sample}}{\text{Concentration of radicals in ref sample}}$$

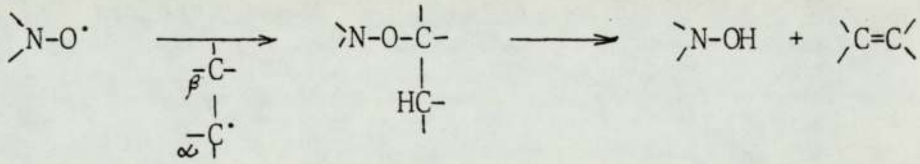
The ESR spectra of nitroxyl radicals are characterised by three lines each of which can be split by the protons of other groups attached to the nitrogen atom. The structure of the nitroxyl radical, the solvent as well as the crystallinity of the compound have a major influence on the magnitude of the coupling constant of the lines and the position of the spectra.

It is a known fact that the amines stop autoxidation process in a fashion similar to that of the phenols. Many workers(152,153) found that the rate determining inhibition process by the amines is connected with the abstraction of an amine hydrogen, and the formation of nitroxyl radicals(154-161) as shown below, made the inhibition of oxidation by the amines more complex than it is by the phenols.



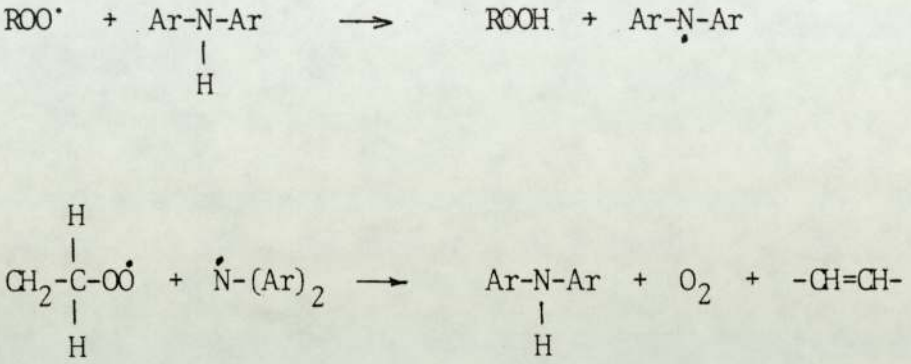
$$ROO^{\bullet} + Ar_2NH \longrightarrow ROOH + Ar\text{-}\dot{N}\text{-}Ar$$
$$Ar\text{-}\dot{N}\text{-}Ar + ROO^{\bullet} \longrightarrow RO^{\bullet} + Ar\text{-}\underset{}{\overset{\overset{\bullet}{O}}{N}}\text{-}Ar$$

Despite the ease of nitroxyl radical formation, it must be pointed out that both primary and tertiary amines do not form nitroxyl radicals and that of all the secondary amines, the diphenylamines are most efficiently converted to nitroxyl radicals. Murayama(166) reported the effectiveness of hindered amines as oxidation inhibitors and attributed their efficiency to the inability of the derived nitroxyl radical to propagate the kinetic chain because of steric hindrance, but it was able to react with in chain alkyl radical. The readiness of nitroxyl radicals to react with alkyl radical has been widely reported(162-165). Bolsmann and co-workers(165) further reported the catalytic inhibiting ability of a number of secondary amines and their related compounds such as nitroxyls and N,N-disubstituted hydroxylamines, they also found that diaryl nitroxyl radicals reacted with both alkyl and peroxy radicals as follows:



$$>N\text{-}OH + ROO^{\bullet} \longrightarrow >N\text{-}O^{\bullet} + ROOH$$

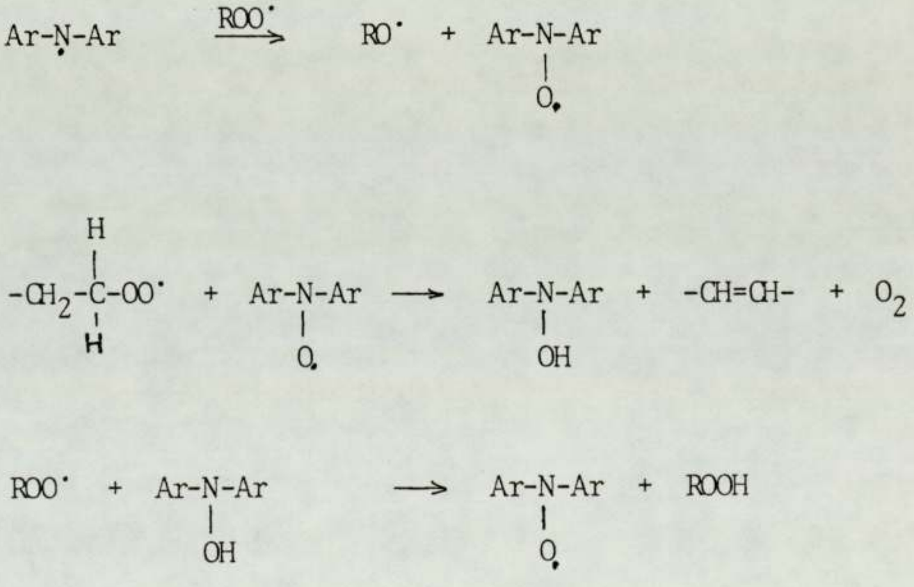
Different mechanisms have been proposed in the literature for the catalytic scavenging of radicals in an autoxidising hydrocarbon by secondary arylamines and their derived nitroxyl and hydroxylamines. Denisov and co-workers(167) advanced the following mechanisms:



$$\mathrm{ROO^{\cdot} + Ar\text{-}\underset{\substack{|\\ H}}{N}\text{-}Ar \longrightarrow ROOH + Ar\text{-}\underset{\bullet}{N}\text{-}Ar}$$

$$\mathrm{CH_2\text{-}\underset{\substack{|\\ H}}{\overset{\substack{H\\ |}}{C}}\text{-}O\dot{O} + \dot{N}\text{-}(Ar)_2 \longrightarrow Ar\text{-}\underset{\substack{|\\ H}}{N}\text{-}Ar + O_2 + \text{-}CH{=}CH\text{-}}$$

and alternatively to this:



$$\mathrm{Ar\text{-}\underset{\bullet}{N}\text{-}Ar \xrightarrow{ROO^{\cdot}} RO^{\cdot} + Ar\text{-}\underset{\substack{|\\ O^{\bullet}}}{N}\text{-}Ar}$$

$$\mathrm{\text{-}CH_2\text{-}\underset{\substack{|\\ H}}{\overset{\substack{H\\ |}}{C}}\text{-}OO^{\cdot} + Ar\text{-}\underset{\substack{|\\ O^{\bullet}}}{N}\text{-}Ar \longrightarrow Ar\text{-}\underset{\substack{|\\ OH}}{N}\text{-}Ar + \text{-}CH{=}CH\text{-} + O_2}$$

$$\mathrm{ROO^{\cdot} + Ar\text{-}\underset{\substack{|\\ OH}}{N}\text{-}Ar \longrightarrow Ar\text{-}\underset{\substack{|\\ O^{\bullet}}}{N}\text{-}Ar + ROOH}$$

Rozantsev(168) attributed the very long induction period observed in the radiation induced autoxidation of n-octane at 100°C to the presence of some bis-nitroxyl radicals and he suggested the inhibition reaction to be as follows:

$$\gt N\text{-}O^{\bullet} + R^{\bullet} \longrightarrow \gt N\text{-}O\text{-}R$$

$$\gt N\text{-}O\text{-}R \xrightarrow{ROO^{\bullet}/R^{\bullet}} \gt N\text{-}O^{\bullet} + \text{non-radical products}$$

In view of the discussed activity of the nitroxyl radicals, it seems very likely that its formation in this present work will inhibit the decomposition of hydroperoxide. More importantly, it would inhibit adduct formation by trapping alkyl radicals. But this activity would only be of secondary importance however since it would depend upon the rate of production of nitroxyl radicals from the thiolamide and also the formed nitroxyl radicals would still have to compete with oxygen for the alkyl and thiyl radicals in the system. If this activity is stoichiometric, as seem to be in this case, they would not exert their optimum effect until an advanced stage of the reaction, when they would be at a concentration similar to the initial concentration of the thiolamide. Thus, they could contribute to inhibition of oxidation in vulcanisates rather than in model compounds, where their full strength is not attained.

5.6.5 Results

The ESR study of the reaction product of PAPT with cumene hydroperoxide in chlorobenzene showed that nitroxyl radicals are formed. Fig 5.17 shows the ESR spectrum obtained while Fig 5.18 shows the concentration of nitroxyl radical at different times during the decomposition reaction.

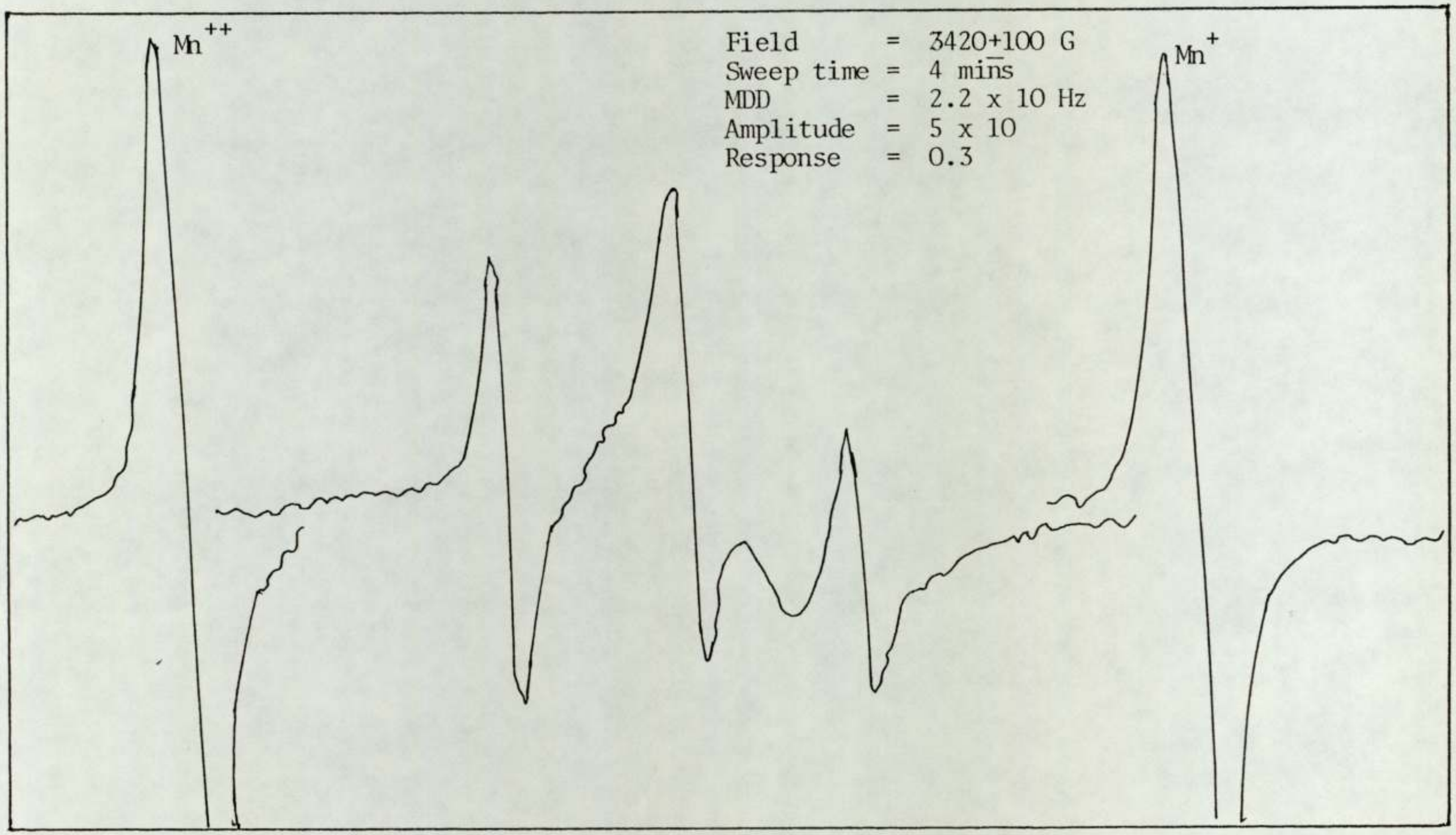


Fig 5.17 ESR spectrum of reaction product of [CHP]/[PAPT] 10 : 1 in chlorobenzene

The spectrum consists of a triplet for which the values of g-factor is 2.0077 and the splitting constant was found to be 10.1 G. These values imply that the recorded triplet corresponds to the nitroxyl radical whose g-values are generally within the range of 2.00 - 2.008 in the liquid state (160). The hyperfine coupling constant (10.1 G) of the triplet detected in this measurement fits in quite well within the range which Forrester and co-workers (163) reported for diaryl nitroxyls.

Fig 5.18 shows the formation of nitroxyl radical during decomposition of cumene hydroperoxide at various molar ratios [CHP] : [PAPT] at 70°C. Curve (e) shows that at a ratio of 1:1 nitroxyl radical was not formed up to 10 hours but when cumene hydroperoxide was added in excess and then heating was continued, nitroxyl radical was formed in an auto-accelerating manner. In curves (a), (b) and (c), nitroxyl radicals were not observed to any measurable level before 5 hours, but after 6 hours, the formation was auto-accelerating reaching a maximum concentration between 8 hours for curves (a) and (b) and 9 hours for curve (c). Then the concentration decayed. At a ratio [CHP] / [PAPT] = 10 : 1, formation of nitroxyl radical commenced after 6 hours. The concentration was very low and got to a maximum just after 8 hours and then remained constant (curve (d).

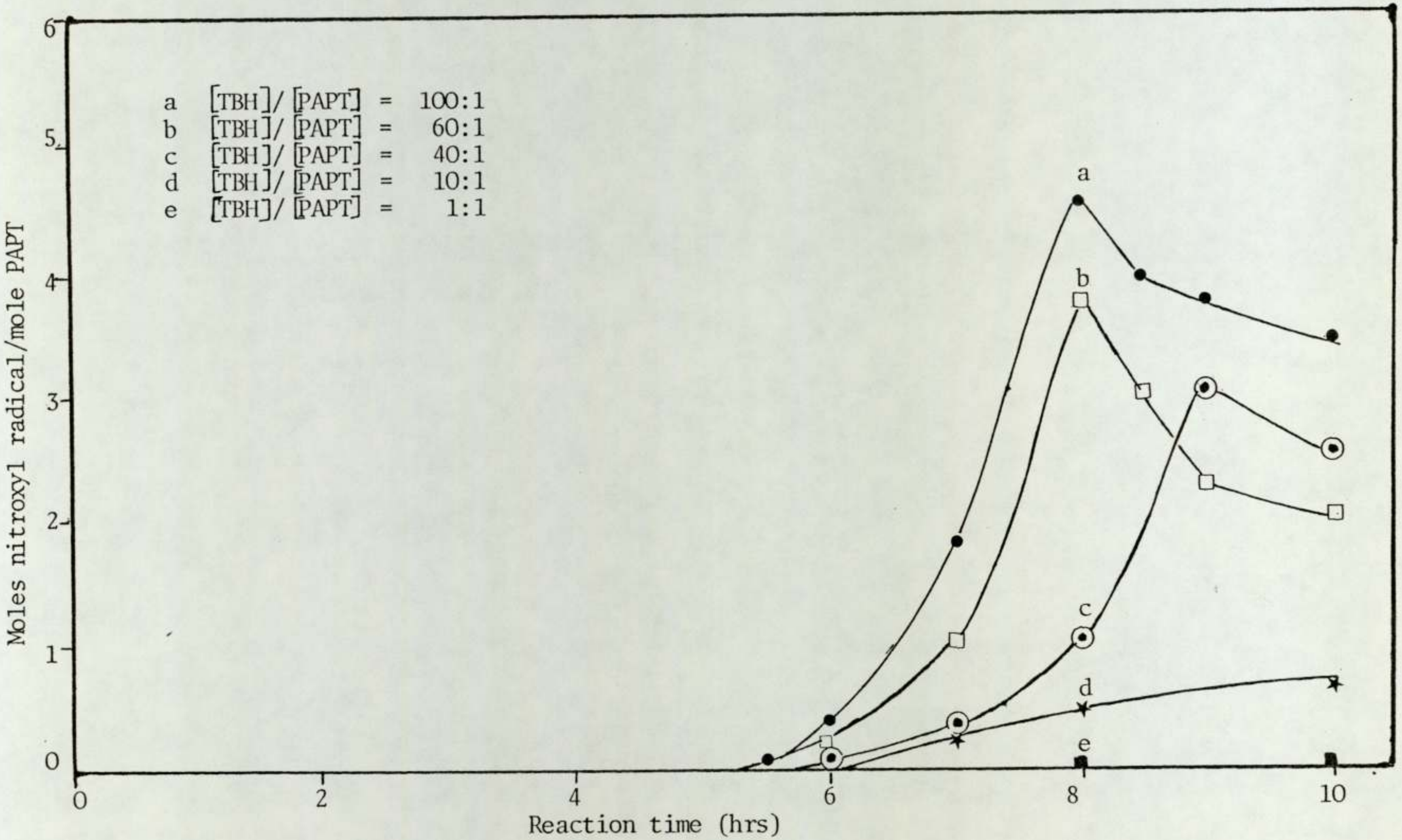


Fig 5.18 Measurement of nitroxyl radical concentration during the decomposition of TBH in the presence of PAPT at 70^{o}C by ESR

5.7 Discussion

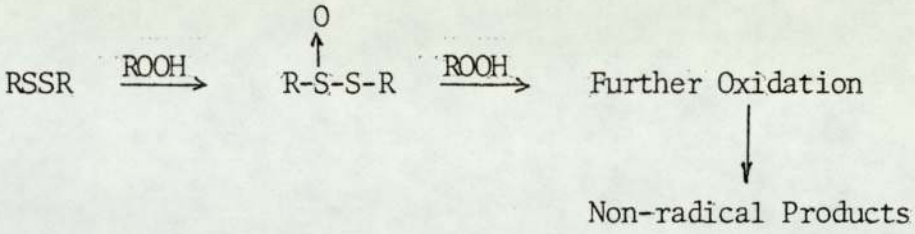
The analysis of the products of the decomposition of CHP in the presence of thiolamides (II and III) showed that more than one mechanism is involved in the catalytic decomposition process.

At low molar ratios of hydroperoxide to thiolamides, radical products predominate and at higher peroxide to thiolamide ratios, an ionic mechanism is favoured. The former leads to the formation of cumyloxy free radicals which would abstract hydrogen, when available, to form cumyl alcohol or undergo β-scission reactions to form acetophenone and methyl radicals. This stage probably explains the rapid initial drop in the concentration of hydroperoxide (Figs 5.1 - 5.4). Figs 5.5 and 5.6 show that the changeover from the radical process to the ionic process with increase in $[\mathrm{ROOH}]/[\mathrm{PAPT}]$ is rather gradual and Figs 5.1 - 5.4 show that at the lower ratios there is an induction period before the ionic stage commences. The induction period indicates that certain products are formed which inhibit the further decomposition of hydroperoxide and the production of free radical traps such as SO_2 and sulphinyl radicals which in addition to their peroxide decomposing function in autoxidising systems have been suggested to have radical trapping activity$^{(145,169)}$ and may be responsible for the induction period. Burn and co-workers$^{(143)}$ showed that the induction period observed in $\mathrm{Zn}\left[(\mathrm{RO})_2\mathrm{PS}_2\right]_2$-CHP system was lengthened by the addition of free radical traps such as 3,5-di-tertiary-butyl-4-hydroxy toluene (BHT) or α-naphthyl amine.

This observation therefore supports the suggestion that the intermediate products formed by the reaction of CHP and PAPT are radical traps and are responsible for the induction period.

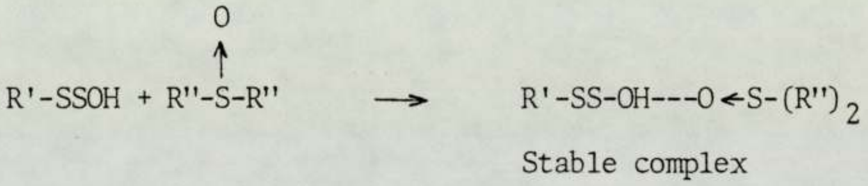
TLC analysis and GPC studies of the CHP decomposition product shows that the disulphides and monosulphides are formed when thiolamide is added to the system (sections 5.4 and 5.5) and it is known that one of the breakdown products of sulphide oxidation is sulphur dioxide. It follows therefore that sulphur dioxide can contribute to the inhibition of CHP during the induction period. The induction period could be the time during which the active catalyst for the CHP decomposition is being formed from the thiolamide. This is unlikely, however, since the induction period decreases with increasing initial CHP concentration. This suggests that the product(s) formed during the first stage are capable of inhibiting the formation of the catalyst.

Burn(170), Kennerly and Patterson(171) have shown that disulphides (and sulphides) are themselves unable to inhibit oxidation of substrates but rather the inhibition was attributed to products formed from them as peroxide accumulates in the substrate(89,169,172). It has been suggested(173,174) that the peroxides formed in the substrate at high temperatures oxidise the disulphides to thiosulphinates and that effective inhibition then results from peroxide decomposition by the thiosulphinate or subsequent reaction products.



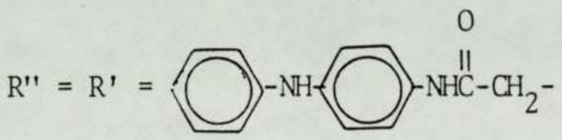
$$\mathrm{RSSR} \xrightarrow{\mathrm{ROOH}} \mathrm{R}-\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{S}}-\mathrm{S}-\mathrm{R} \xrightarrow{\mathrm{ROOH}} \text{Further Oxidation} \longrightarrow \text{Non-radical Products}$$

Shelton and co-workers(175) attributed a similar inhibition of hydroperoxide decomposition (observed in the present work) to the ability of produced sulphoxide to complex sulphoxylic acid (and other acids which may be formed from the systems). Such complexes are said to be stable and thus prevent catalysis of hydroperoxide decomposition. The possibility of the oxidised products of thiolamide forming a similar complex cannot be ruled out.

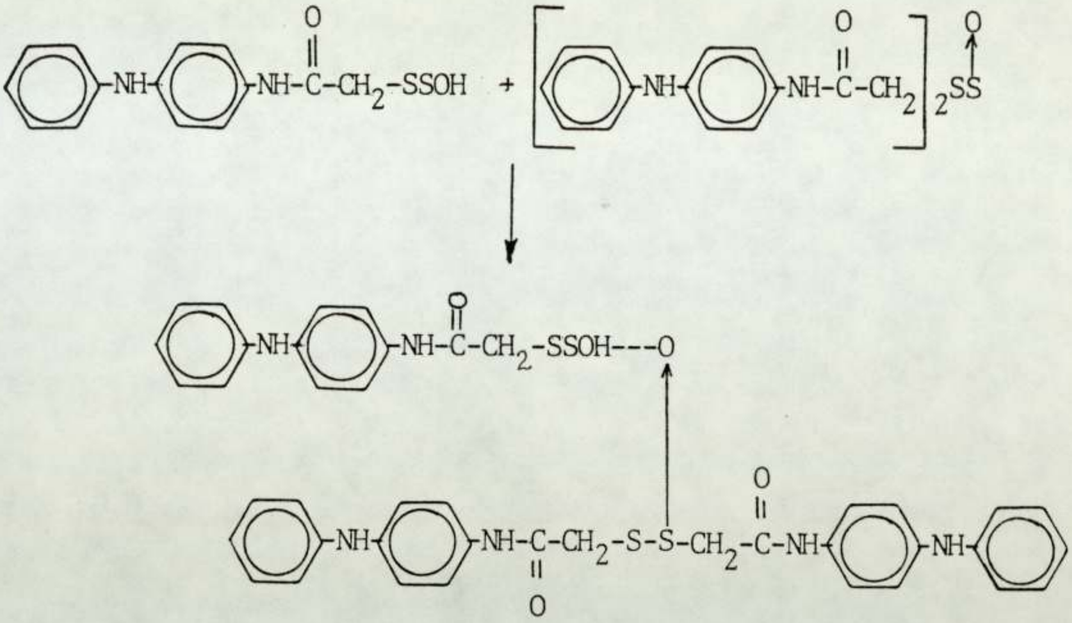


$$\mathrm{R'\text{-}SSOH} + \mathrm{R''}-\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{S}}-\mathrm{R''} \longrightarrow \mathrm{R'\text{-}SS\text{-}OH\text{---}O \leftarrow S\text{-}(R'')_2}$$

Stable complex



Also a similar complex of the sulphoxylic acid with the thiolsulphinate could account for the induction period observed before the onset of the catalytic decomposition of hydroperoxide.



It was suggested that when the concentration of the acid exceeds the complexing capacity of the remaining thiolsulphinate, the excess acid would decompose the hydroperoxide.

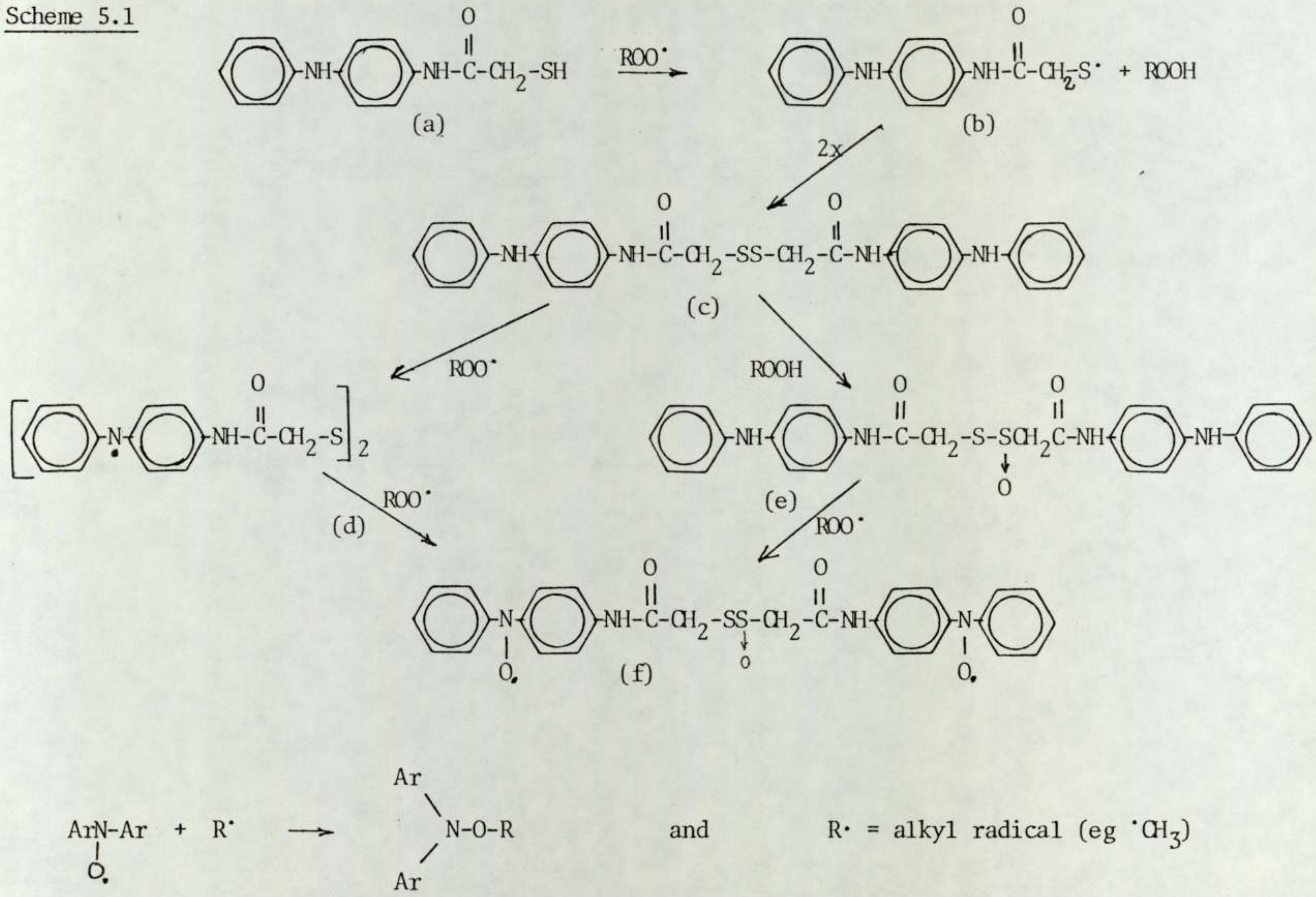
Since ESR studies of the product resulting from the decomposition of CHP in the presence of thiolamide showed that nitroxyl radicals are detected only at an advanced stage of the reaction (> 5 hours) (Fig 5.18), one would tend to eliminate the possible involvement of nitroxyl radical in the inhibition of the peroxide decomposition observed. It appears that the nitroxyl radical is formed when all the thiol group (-SH) has been oxidised. But if it is assumed that some small amount of nitroxyl radical (not detectable owing to its low concentration) could be formed, then the contribution of nitroxyl radicals as radical traps for cumyloxyl radical or methyl radical during the induction period cannot be over emphasised. It is well known that nitroxyl radicals react readily with alkyl radicals. The formation of nitroxyl radicals during the reaction of PAPT with CHP is shown in Scheme 5.1.

Reaction (d) is a probable source of nitroxyl radicals during the induction period while (e) will result in a medium where hydroperoxide is present in excess.

Scott and co-workers(28,89,91) have identified sulphur acids in the oxidation of nickel dithiocarbamates and also in the oxidation of mercaptobenzthiazole disulphide through the intermediate sulphinic and sulphonic acids. It seems likely that sulphur acids are formed and contribute to the decomposition of hydroperoxide in this present work.

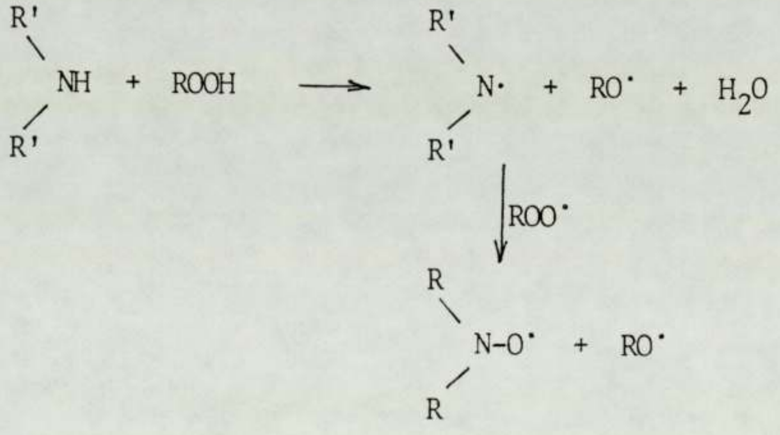
It is also clear that the products of the reaction affect the observed mechanism. The relative contribution of the free radical decreases with increasing concentration of hydroperoxide and it appears that competition between the radical generating and ionic peroxide decomposition is evident at around one to one molar ratio of hydroperoxide to thiolamide, and obviously the presence of reaction products increased the ionic process. From the result, it is obvious that the radicals produced at low $[ROOH]/[RSH]$ molar ratios are effective initiators and are doubtless responsible for the grafting process in the latex procedure. Unfortunately, the production of inhibitors (radical traps) during the delay period observed in the decomposition of hydroperoxide, probably accounts for lower binding level achieved in the latex procedure. The

Scheme 5.1



hydroperoxide decomposing activity of the decomposition products may be responsible for the better stability observed in the vulcanisate produced from latex masterbatch during oxygen absorption.

In Figs 5.5 and 5.6, the presence of a constant but low proportion of homolytic decomposition products at higher ratios indicates that the radical process makes a contribution at all ratios and this is in line with the fact that reducing agents based on sulphur (eg sulphenic acid, sulphur dioxide, sulphur trioxide, etc) are involved as precursors to the Lewis acid formation since it has been shown that these form an effective redox initiating system with hydroperoxide(145,169). The early stages of nitroxyl formation involves the following redox reaction between the amine and hydroperoxide:



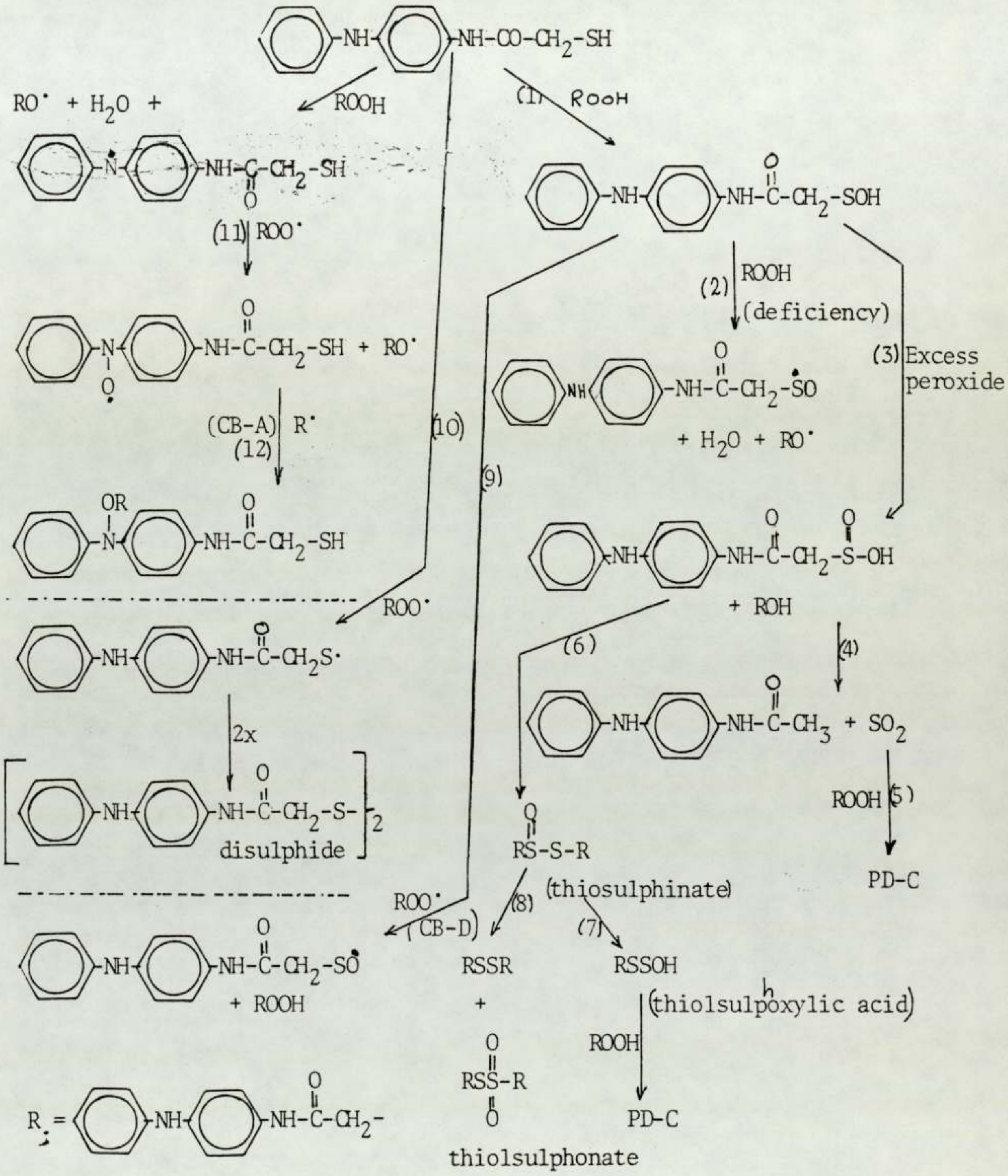
The intermediate redox reaction is likely to be the reason why a reducing agent (TEPA) is not necessary with thiolamide during the grafting process in the latex procedure (Chapter Two, sections 2.3.2 and 2.4).

Fig 5.7 shows the concentration - time profile of the formation of phenol, acetophenone and α-cumyl alcohol during the decomposition of CHP (1×10^{-2} M) in the presence of PAPT (1×10^{-4} M). It is quite clear from the curve that products could not be determined at times less than 10 minutes but the extrapolation of the curves to zero time was made. Acetophenone and α-cumyl alcohol are formed in the initial reaction while phenol is accumulated in the later stages though present in very low concentration at the start of the reaction. The unknown product which is formed during the initial reaction has been assumed to be one of the oxidation products of the disulphide formed during the decomposition reaction and it is probably the thiosulphinate. The unknown product decayed to almost zero after about 2 hours which is indicative of its possible involvement in the later reaction. Fig 5.11 shows that PAPT was lost auto-catalytically within 45 minutes, this observation suggests that the first stage reaction is primarily the reduction of CHP to α-cumyl alcohol with accompanying oxidation of PAPT to disulphide and other oxidation products. At the present time, it can only be concluded that the apparent kinetics for CHP decomposition in the presence of thiolamide are influenced by factors that are not immediately obvious.

The possible reactions of thiolamides with hydroperoxides are shown in Scheme 5.2. This includes reactions earlier discussed in this Chapter.

Reaction 1 involves a direct reaction of thiolamide with

Scheme 5.2 Possible reactions of thiolamine with hydroperoxides



hydroperoxide, leading to the production of sulphenic acid and most of the decomposition products are formed through this acid.

Reaction 2 involves the decomposition of sulphenic acid in a hydroperoxide deficient atmosphere, and it is most likely to occur at low [CHP]/[RSH] molar ratios and may be inhibitive.

Reaction 3 is the direct oxidation of the sulphenic acid to the sulphinic acid. This is in turn capable of destroying hydroperoxide catalytically through the oxidation of liberated sulphur dioxide in reaction 4.

In reaction 5 it is now known that it is not SO_2 which is the peroxide destroyer but its oxidation products which is SO_3 and in the presence of moisture this is converted into sulphuric acid. It has been shown(90) that the combination of the Lewis acids destroy peroxide powerfully.

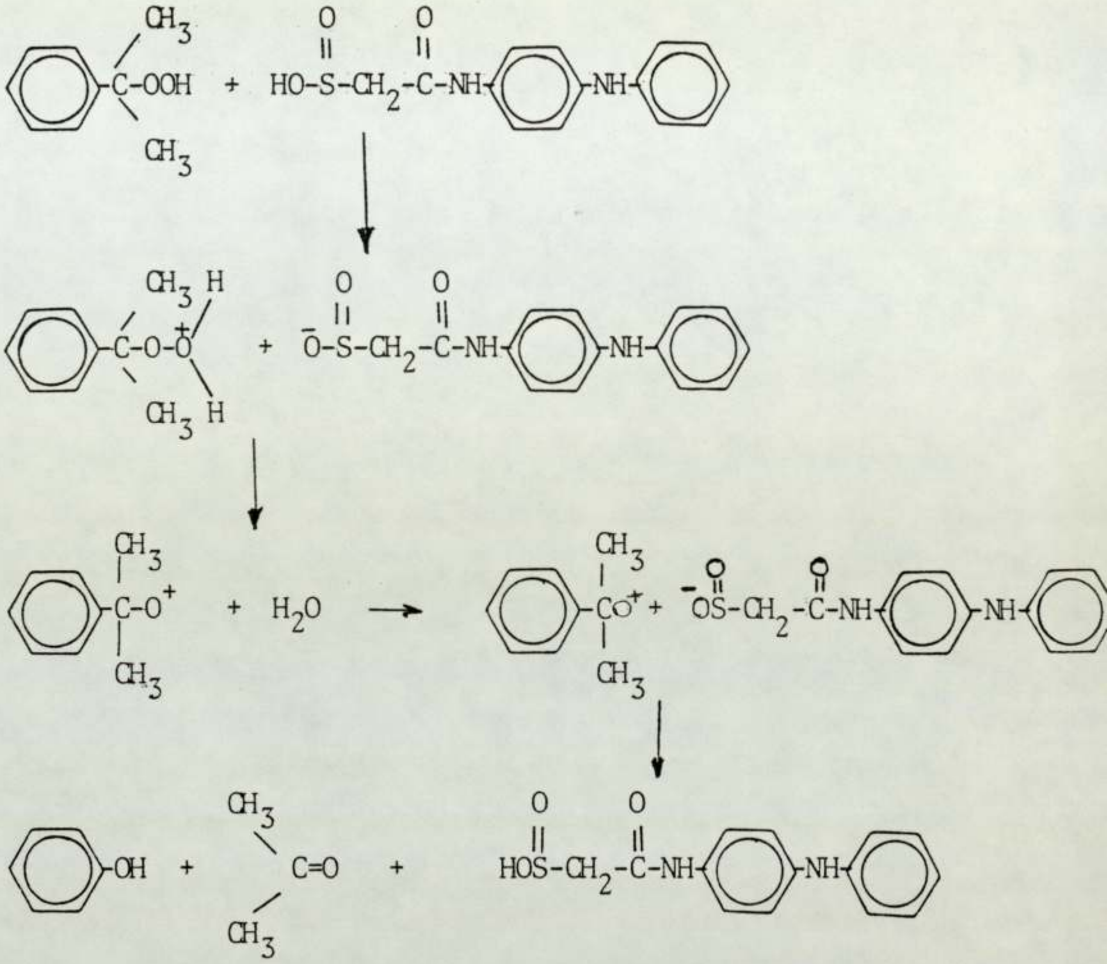
Reaction 6 which is a bimolecular production of thiolsulphinate with the elimination of water, the subsequent reaction of which leads to the formation of thiolsulphoxylic acid (reaction 7) by disproportion, and by the same process disulphide and thiolsulphonate are formed in reaction 8. All these products are potential catalytic peroxide decomposers through further oxidation.

Reaction 9 shows the chain breaking donor (CB-D) activity of the formed sulphenic acid but this reaction will be in competition with hydrogen abstraction from the parent amine.

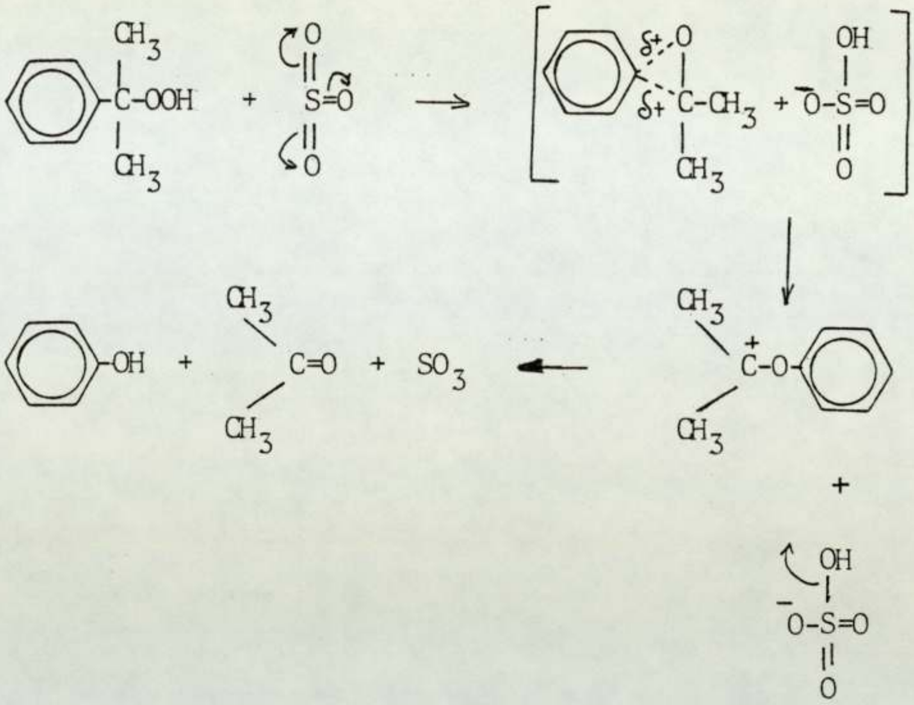
Reaction 10 is also involved in abstraction of H-atom, the derived thiyl radical may undergo bimolecular recombination to give disulphide which in the presence of hydroperoxide is oxidised to various sulphur acids already mentioned.

Reaction 11 which is the formation of nitroxyl radical (see Scheme 5.2) is very important in view of its readiness to react with alkyl radicals. Reaction 12 is a chain breaking acceptor mechanism. It is not clear whether the formation of nitroxyl radicals play any role during the decomposition of CHP since they were detected in the later stages of the reaction.

The above scheme and summary are based on the analysis of the product of CHP decomposition. Other unidentified products seen in TLC and GPC are indicative of other reactions which may or may not be very important. The previous works on sulphur compounds have also been taken into account. There is strong evidence to suggest that the ability of thiolamide antioxidants (PAPT and PPPT) to function as catalytic hydroperoxide decomposers is associated with their acidic properties. The decomposition of cumene hydroperoxide could follow the following scheme.



The activity of the sulphinic acid may be due to its ability to act as a Lewis acid or alternatively, it could be attributed to the ability to donate a proton. But since it is known that sulphur trioxide, one of the oxidation products of thiolamide, may be involved, then the mechanism may be as follows.



The sulphur atoms in SO_3 becomes the Lewis acid centre$^{(176)}$ by virtue of its electron deficiency. There is no evidence to say which of the two alternative mechanisms predominate but it is possible that both may operate at the same time. However, the sulphinic acid will be oxidised very readily to sulphonic like SO_2.

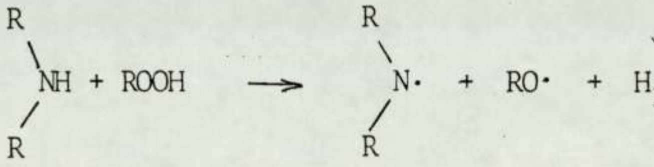
CHAPTER SIX

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

6.1 Conclusions

The result of the work carried out shows that 3,5-di-tertiary-butyl-4-hydroxylbenzyl mercaptan (BHBM), 4-anilinophenyl thioglycollamide (PAPT) and 4-anilinophenyl thiopropionamide (PPPT) can be chemically bound to nitrile rubber through the thiol group (-SH) by a free radical addition reaction. The reaction can be carried out both in the latex and in the solid phase.

In the latex, the grafting reaction normally required the use of a redox radical generating system such as tertiarybutyl hydroperoxide (TBH) and a polyamine activator, tetraethylene-pentamine (TEPA). However, it was found that the use of TEPA was not necessary in the reaction of PAPT and PPPT. This is an indication of possible redox reaction between the thiolamide and TBH, illustrated in the following scheme.

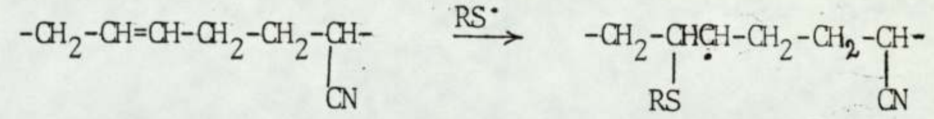


$$R_2NH + ROOH \longrightarrow R_2N\cdot + RO\cdot + H_2O$$

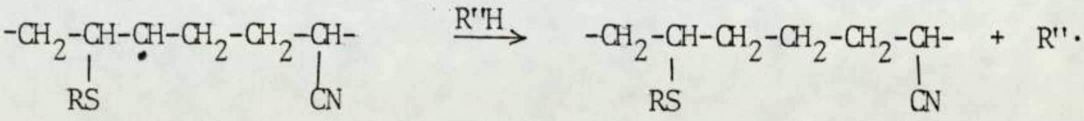
(initiation step involving amine)

The formation of adduct rubber may be represented as follows.

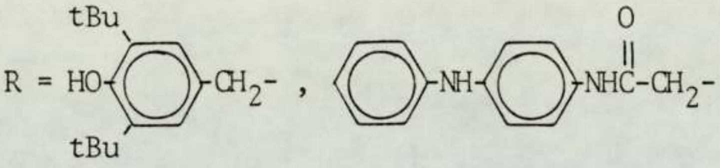
$$RSH + R'OOH \longrightarrow RS^{\cdot} + R'O^{\cdot} + H_2O$$



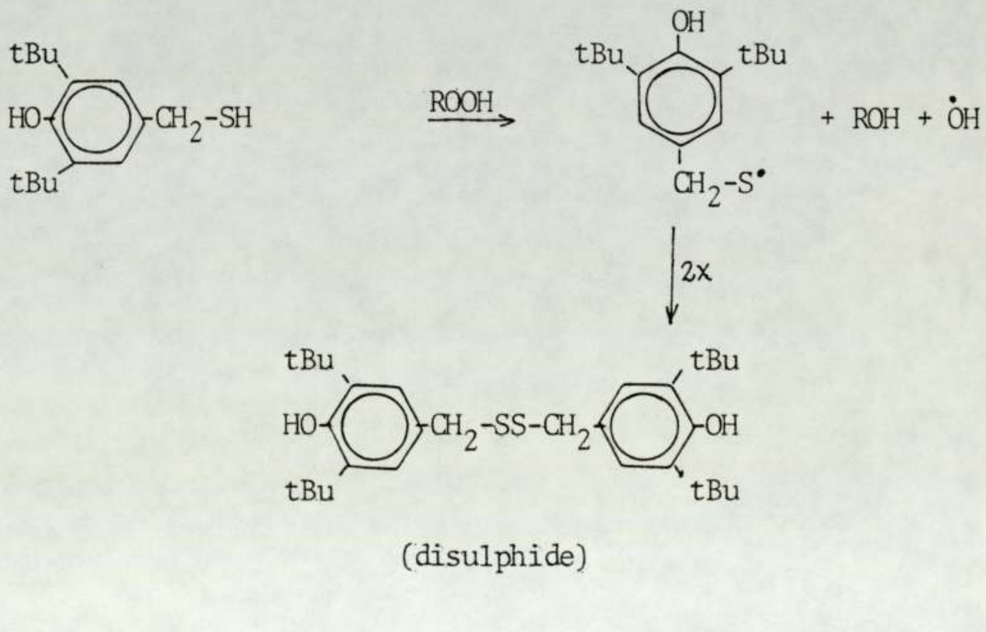
$$-CH_2-CH{=}CH-CH_2-CH_2-\underset{CN}{CH}- \xrightarrow{RS^{\cdot}} -CH_2-\underset{RS}{CH}\dot{C}H-CH_2-CH_2-\underset{CN}{CH}-$$



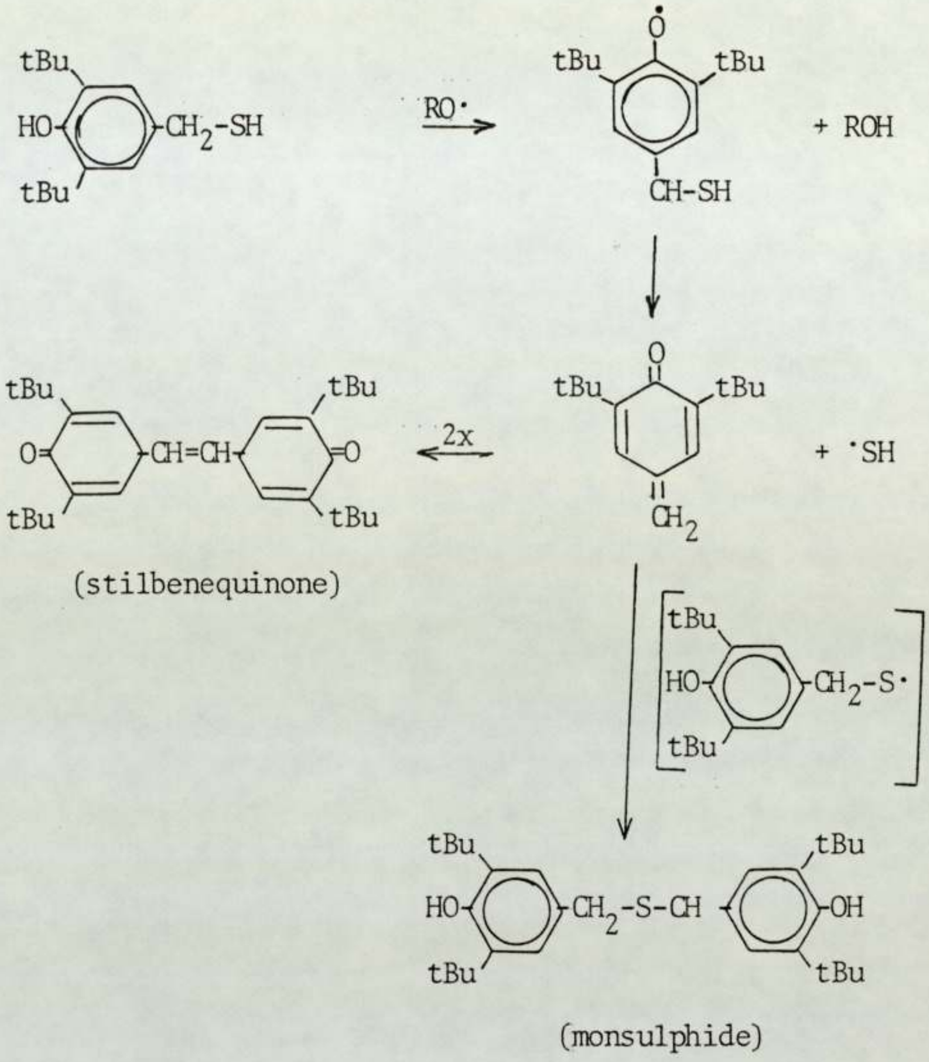
$$-CH_2-\underset{RS}{CH}-\dot{C}H-CH_2-CH_2-\underset{CN}{CH}- \xrightarrow{R''H} -CH_2-\underset{RS}{CH}-CH_2-CH_2-CH_2-\underset{CN}{CH}- + R''\cdot$$



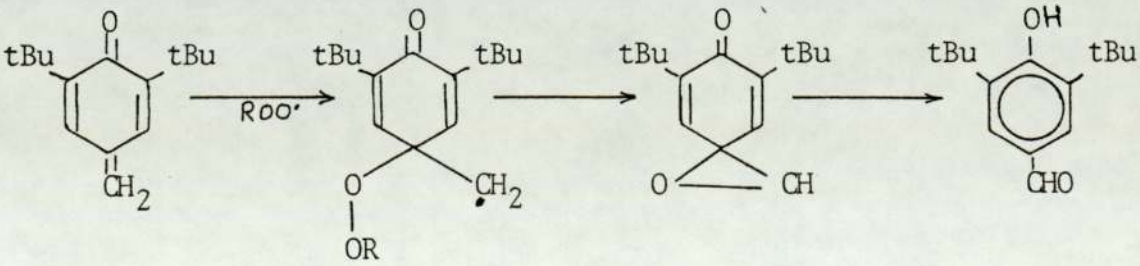
The formation of by-products limited the yield of antioxidant adduct. In the latex reaction, 60% of the original BHBM was found to be bound; 52% of PAPT and only 29% of PPPT. In the reaction of BHBM, the main by-products have been found to be disulphides, monosulphides and stilbenequinone.



(disulphide)



In view of the fact that thiols are oxidised to disulphides through thiyl radicals in the presence of a strong oxidising agent, such as a peroxide(177), Scott and co-workers(178) proposed the above reaction schemes. They also explain the formation of aldehyde through the quinone methide.



Since the intermediate thiol radical is more favoured than the phenoxyl radical, a high yield of bound BHBM resulted.

In the case of the thiolamide, disulphides and monosulphides are also formed and the mechanistic studies in Chapter Five suggest that nitroxyl radicals are involved and their possible inhibiting effect in the later stages of the reaction have already been discussed. (Chapter Five, section 5.6, Scheme 5.2, reaction 11).

The monosulphides and disulphides can undergo a further sequence of reaction in the presence of hydroperoxide.

The mechanochemical addition of the thiol-based bound antioxidants to NBR was initiated by macroalkyl radicals formed by the rupture of the polymer molecule by shearing. The presence of oxygen is disadvantageous in that the extent of binding is greatly reduced. Besides, the level of binding achieved is very much dependent on the initial viscosity of the NBR as well as the torque. There is a need for a balance between the viscosity and the solubility of the antioxidant in the rubber because if the antioxidant is too soluble, it will reduce the viscosity of the rubber so that no shearing will occur (eg BHBM). If on the other hand it is too insoluble, it will not be present in high enough concentration in the rubber to react. Also, like in the latex procedure, the formation of by-products such as mono-, disulphide, etc, limits the yield of adduct. Surprisingly, PAPT binds to a much higher level, 75%, than in the latex procedure. While the yield of both

BHBM and PPPT were reduced to 47 and 30% respectively. The reduction in binding is probably due to the plasticising effect of these antioxidants (BHBM and PPPT). The plasticising effect is due to the low melting point of the antioxidants (BHBM 28°C and PPPT 98°C) while PAPT melts at a relatively high temperature (135°C). Another contributory factor is the solubility of the antioxidants. In hydrocarbon solvents (eg acetonitrile, hexane and toluene) BHBM is very soluble in all, while PAPT and PPPT are only partially soluble in hexane and toluene. This implies that BHBM is too soluble in NBR to allow proper shearing.

The masterbatches of the latex and solid nitrile rubber produced by the mentioned procedures using BHBM and PAPT were diluted with untreated latex and solid rubber. The resultant rubbers were covulcanised to give vulcanisates which are more resistant to oxidation than the control and the commercial thermal antioxidant, Flectol-H, after extraction but the antioxidant activity of BHBM is somewhat lower than that of Chemigum. While that of PAPT is very much dependent on the test in question, but on the whole the activity of PAPT as an antioxidant compares very well with that of Chemigum at 'equimolar' concentration.

The effect of thiol-based bound antioxidants on the curing characteristics of nitrile rubber was investigated using the Monsanto oscillating disc rheometer. The thiolamides were observed to accelerate the rate of cure and increased the cross-link density and slightly decrease the scorch time. BHBM and

Flectol-H decrease cross-link density and slightly increase the scorch time, whereas Chemigum behaved very similarly to the control.

The reduction of the scorch time may be attributed to the amine functions incorporated therein and is a peculiar feature of the diphenylamines which are very active compounds and are known to reduce scorch safety particularly in a sulphenamide accelerated vulcanisation system. Although, quite a lot of work has been done to elucidate the mechanism of vulcanisation, the exact mechanism remains somewhat obscure. In the present work it appeared that the formation of nitroxyl radical may influence the vulcanisation reaction but it is very difficult to conclude this without further study.

The reduction in modulus of samples containing BHBM may be interpreted in terms of its activity as a free radical trap. Electron releasing groups in the aromatic ring of BHBM would, therefore, be expected to increase the trapping and cause greater modulus reduction. Contrary to this suggestion, other efficient radical traps, eg 3,5-di-tertiary-butyl para-cresol (TBC) do not show similar behaviour. Besides, thiuram persulphenyl radicals have been shown to be present in TMTD vulcanisation systems by several workers and would be expected to have some electrophilic character. However, it seems likely that the reduction of the modulus must be associated with the sulphur atom in BHBM but the mechanism is so far unknown. Although the same effects have been expected to occur in the sample containing thiolamides, the reaction of the amine with the active accelerator species could have eliminated the electrophilic character.

The antioxidant activity of the bound antioxidants was determined by oxygen absorption, stress relaxation, oven ageing and cyclic oil/air tests at 150^{o}C before and after extraction of the vulcanisates with azeotropic mixture, acetone, 1,1,1-trichloroethane and methanol (110 : 60 : 42 mls).

The oxygen absorption curves show distinct induction periods, followed by autocatalytic absorption but the rate of oxidation at any time being less than that of the control, indicating that antioxidant behaviour was still evident. In some of the samples, particularly those containing BHBM the curve tends to become autoretarding but only after more than 1% oxygen had been absorbed. After the removal of unbound antioxidant fragments and ZDMC the antioxidant activity is considerably reduced. This means therefore that the combined effect of bound antioxidants, unbound antioxidant and ZDMC give better protection to the vulcanisate. It was inferred from the mechanistic studies that the inhibition of oxidation by the thiol based bound antioxidant involved synergistic behaviour between the chain breaking activity and peroxide decomposition activity of the antioxidants. Also the formed ZDMC is known to be efficient peroxide decomposer. However, the samples prepared from the mechanochemical masterbatch are less efficient than those from latex masterbatch.

In the oven ageing test and the cyclic oil/air test, the change in hardness is a direct measure of cross-linking of the rubber molecule and the amount of oil that has been swelled into the network. In oven ageing test, the bound antioxidants retained much of their properties even after 6 days while the control and the sample containing Flectol-H were brittle after the third day. The coagulum adducts (extracted and unextracted) lost their physical properties much slowly than the corresponding latex adducts. The behaviour of the coagulum adducts were similar to that of Chemigum. On an individual antioxidant basis, PAPT gave better protection than BHBM or Flectol-H. Generally the rate of loss of physical properties of bound antioxidants is autoretarding at the start but later accelerated. The control and Flectol-H were autocatalytic all the way. This is not surprising since after extraction no Flectol-H remained in the vulcanisate.

In the cyclic oil/air test, the behaviour of the bound antioxidants were similar to that observed in the oven ageing test. But it is surprising that Chemigum is not very efficient in the cyclic oil/air test. This may be due to the fact that the oil that has swollen into the rubber molecule did cause damage through the dissolved oxygen. Alternatively, the superiority of the thiol-based bound antioxidants, particularly PAPT, may be an indication of post reaction of the unbound antioxidant fragments. At such a high temperature (150^{o}C) of the test oil, and in atmosphere of limited amount of oxygen, it seems that the further oxidation products of the mono or disulphides may be involved in the post binding process and a subsequent reinitiation of the unbound antioxidant is therefore made possible.

If this happens, the bound antioxidant fragments will give additional protection to the vulcanisate, hence improvement in ageing behaviour.

The result obtained from stress-relaxation showed that the relaxation curve of the control sample (no antioxidant) is autocatalytic but in the presence of bound antioxidants, the shape of the relaxation curves did not give induction period prior to the onset of relaxation. Initially the curves were linear, but later became autoretarding. Before extraction, the antioxidant effectiveness (at equal weight concentration of 2 g/100 g rubber) is in the order PAPT > Chemigum > BHBM > Flectol-H > control, but after extraction the positions of PAPT and Chemigum were reversed. After the removal of unbound antioxidants, accelerator fragments and ZDMC the antioxidant activity is considerably reduced as expected from oxygen absorption studies. The slightly greater antioxidant efficiency of PAPT may be due to its effective peroxide decomposing activity and in addition to this, in the samples prepared from mechanochemical masterbatch, the higher binding (75%) achieved through this process could be responsible. The lower degree of binding of the BHBM and PPPT would also reflect the lower activity shown in the test.

The results obtained from the technological tests (oven ageing, stress relaxation and cyclic oil/air tests) and oxygen absorption tests substantiated the need for the antioxidant to remain in the rubber during ageing. The chemically bound antioxidants (PAPT, BHBM and Chemigum) were more effective than conventionally added antioxidants (Flectol-H) after extraction and in the oil/air cyclic test. Also this result showed that the effectiveness of antioxidant increased with increasing antioxidant concentration.

Studies of the decomposition of cumene hydroperoxide (CHP) and tertiarybutyl hydroperoxide (TBH) in chlorobenzene at 70°C in the presence of PAPT and PPPT showed that the thiolamides decompose hydroperoxides catalytically. The product study confirmed that free radical mechanism operated at the early part of the reaction but in the later stages, ionic mechansim predominates. It was also observed that at molar ratio [ROOH]/[RSH] of 40 and less, there is always an induction period after about 10-20% of the peroxide had been decomposed. This induction period of about 2 hours in molar ratios [ROOH] / [RSH] of 1:1 decreases with increasing hydroperoxide concentration and disappeared at a ratio of 60 and above. During the course of the decomposition the thiolamides are themselves transformed. The TLC and GPC analyses showed that the major transformation products are disulphides and monosulphides. The further oxidative transformation of these sulphides are assumed to be connected with preventive mechanism of the antioxidation action which is characterised by the decomposition of peroxides. Many alkyl and aryl sulphides and disulphides have been shown to inhibit polymer oxidation. Aryl disulphides for example inhibit polyolefin oxidation(29,179). Studies at

MRPRA(180) have shown that thiolsulphinates which are formed by reaction of disulphides with hydroperoxides immediately inhibit the oxidation of squalene in contrast to the delayed stabilisation observed with corresponding sulphides. Scott and co-workers made a detailed investigation of the mechanism of action of sulphides with cumyl hydroperoxide. They used BHBM and its derived sulphides and analysed the specific features of the catalytic decomposition process. He then concluded that the catalytically active species is an organic acid compound probably SO_3 and according to Husbands this compound is the real catalyst of decomposition of hydroperoxide. In the light of these findings by these workers and the experimental results of the present work, it is only possible to make tentative conclusions regarding the mechanism of the antioxidant action of the thiolamides that the transformation products of the antioxidant accumulated in the vulcanisate play a specific role in the various stages of its ageing. In this complex process, compounds with initiation, retardation and/or antioxidant properties may be formed from the original antioxidant. These compounds take part in the integral stabilisation capacity of the antioxidant used during ageing and this fact explains the differences in properties of vulcanisate found under different conditions. The thiolamides in addition to their chain-breaking functions are (by virtue of the presence of sulphur groups in the molecule) also precursors of active species which catalytically decompose hydroperoxides.

'Masterbatch' NBR latex concentrates of bound thiol antioxidants

(BHBM) and PAPT) can be used as additives for unstabilised NBR latex and the solid masterbatch can also be used to achieve the desired level of stability in solid NBR with consequent economic advantages.

6.2 Suggestion for Further Work

Thiol based antioxidants (BHBM, PAPT and PPPT) have been bound to NBR latex and solid NBR rubber but the yields have been limited by the formation of by products in side reactions. It will be useful to investigate the way by which the side reactions could be eliminated or minimised to give a much higher adduct formation since higher binding will lead to increased antioxidant activity.

The experiment to find the effect of the bound antioxidant on the cure parameters of NBR showed that the thiolamide increased the rate of cure and the cross-link density compared with the control and since the ESR study of the decomposition products of CHP in the presence of thiolamide, showed nitroxyl radical to be present. It will be of practical use to find out to what extent does the nitroxyl radical influence the cure behaviour of NBR.

Mechanistic studies lead to the conclusion that transformation products of PAPT during the decomposition of CHP are inhibitors of decomposition and that one of the products may be thiosulphinate and some kind of radical trap. It would be therefore of practical interest to add known radical traps during the reaction to see if the assumption was correct. Besides, it may be useful to synthesise the thiolsulphinate derivative of PAPT and to see its effect on the decomposition of cumyl hydroperoxide and to investigate whether the NBR latex could be stabilised with the thiolsulphinate of PAPT.

A thorough investigation of the by products from latex masterbatch and from mechanochemical masterbatch may help to explain the differences in the performance of the vulcanisates produced by the procedures during ageing.

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