BISPEROXYCARBAMATES AS CROSSLINKING AGENTS FOR NATURAL AND POLYISOPRENE RUBBERS

by

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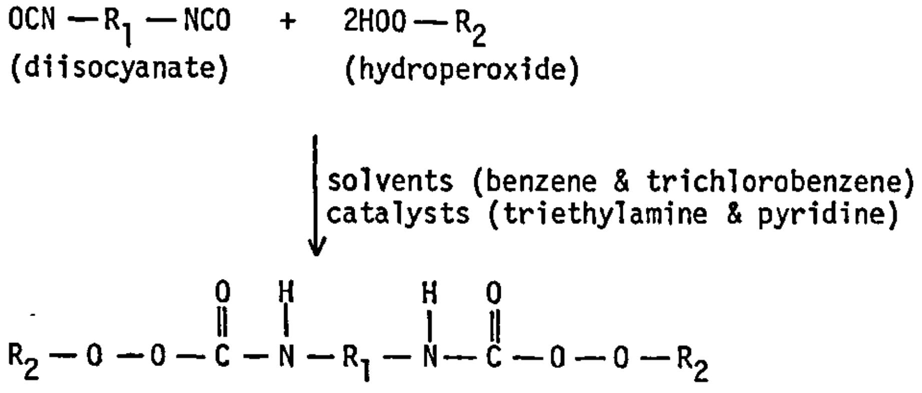
ABSTRACT

Most of the early studies using peroxycarbamates concerned their synthesis, decomposition and use as initiators in vinyl or diene polymerisation. The only attempt to use one as a crosslinking agent was reported in 1960 for a plastic. The author's research work is an attempt to prepare new bisperoxycarbamates and to evaluate them as crosslinking agents in natural rubber (DPNR) and polyisoprene rubber (Cariflex IR 305).

Bisperoxycarbamates were prepared by the method shown below:



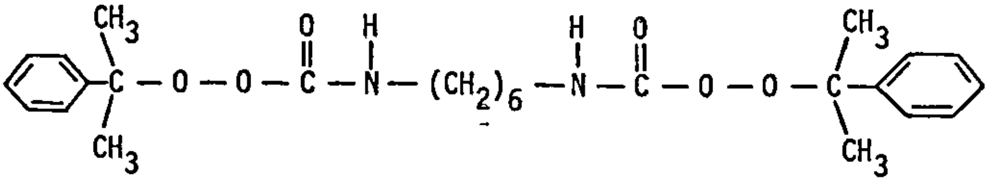
$$\underset{\text{(diisocyanate)}}{OCN-R_1-NCO} + \underset{\text{(hydroperoxide)}}{2HOO-R_2} \xrightarrow[\text{catalysts (triethylamine \& pyridine)}]{\text{solvents (benzene \& trichlorobenzene)}} R_2-O-O-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-R_1-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-O-O-R_2$$

(bisperoxycarbamate)

With a variation of the structures of R_1, it was found that the rates of reaction of the diisocyanates with a given hydroperoxide were dependent on the specific structures and steric effect of the diisocyanates. The order of reactivity was found to be aromatic diisocyanate > aliphatic diisocyanate > aliphatic/cyclic diisocyanate > cyclic diisocyanate.

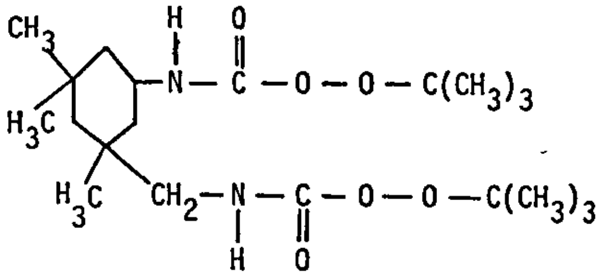
Seven bisperoxycarbamates were prepared and evaluated as crosslinking agents in the natural and polyisoprene rubbers. Their chemical structures were considered to be as follows:

I)



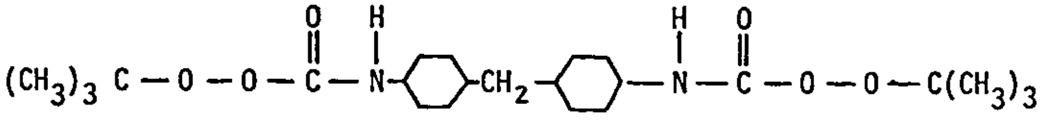
from aliphatic diisocyanate

II)



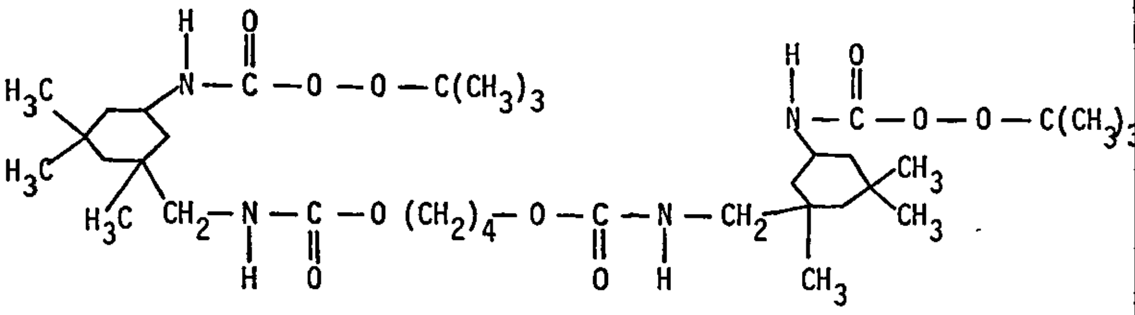
from aliphatic/cyclic diisocyanate

III)



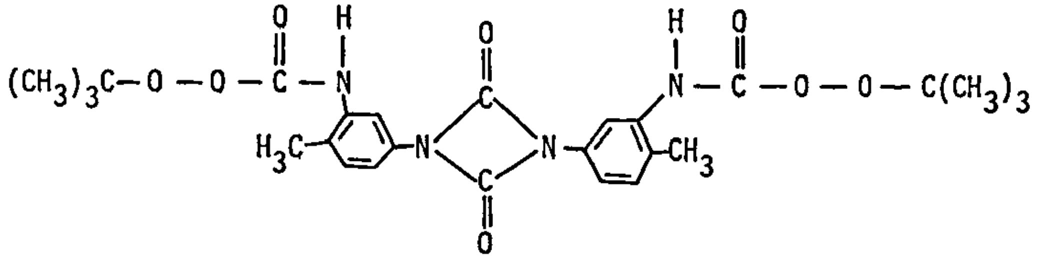
from cyclic diisocyanate

IV)



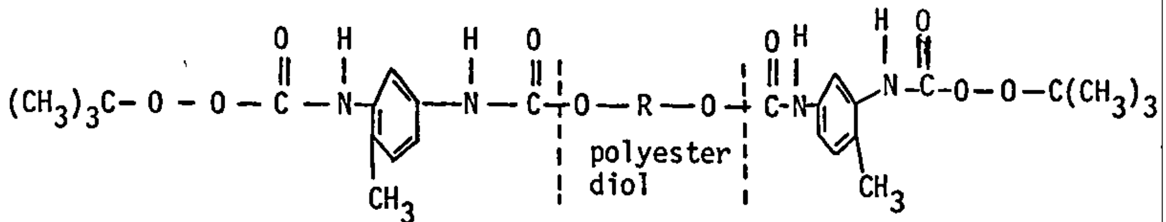
from prepolymer diisocyanate

V)



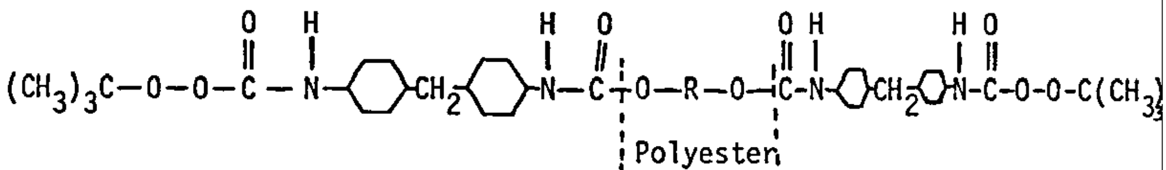
from aromatic diisocyanate

VI)



from prepolymer diisocyanate

VII)



from prepolymer diisocyanate

The relative effectiveness of the prepared bisperoxycarbamates as curing agents in the two rubbers was found to be dependent on the structures of the diisocyanate backbones investigated; cyclic > aliphatic/cyclic > aliphatic. The bisperoxycarbamates studied, based on the aromatic and prepolymer diisocyanate backbones, were found to be relatively ineffective crosslinking agents for natural and polyisoprene rubbers. However the three bisperoxycarbamates I-III were found to be effective crosslinking agents for rubbers, two of which were investigated in detail, DPNR and IR 305.

For a given molar concentration of bisperoxycarbamate, IR 305 was found to give a higher crosslink density than DPNR and this was considered due to the presence of vinyl structures in the polyisoprene macromolecules.

Of the three bisperoxycarbamates I-III, examined in detail in IR 305 and DPNR, the cyclic bisperoxycarbamate III demonstrated comparable ultimate tensile strength and resistance to thermal oxidative stress-relaxation and hot air oven ageing with the DPNR control cured using dicumyl peroxide.

It was found necessary to use a special gas absorption additive system to avoid porosity in vulcanisates cured with high proportions of the bisperoxycarbamates as carbon dioxide is liberated during cure. Three systems were examined and found to eliminate porosity:

i) Trimethylol propane trimethacrylate (Sartomer SR-350).
ii) N,N'-m-phenylene dimaleimide (HVA-2).
iii) $Ca(OH)_2$ + CaO.

Of these the $Ca(OH)_2$ + CaO system was considered the most suitable with respect to the versatility and cost.

For applications involving white and black filled mixes the cyclic bisperoxycarbamate III gave a satisfactory cure in the presence of fillers such as precipitated silica (Ultrasil VN3) and the following carbon blacks: SRF (Regal SRF), MT (Sevacarb MT), and Acetylene (Shawinigan Acetylene). However with SAF black (Vulcan 9) and HAF black (Vulcan 3) cure interference occurred and this was considered due to the presence of relatively high content of organic groups based on H, O and S in the carbon blacks. This cure interference effect is also observed in the traditional dicumyl peroxide cured rubbers.

ACKNOWLEDGEMENTS

I am grateful to Mr C Hepburn for his invaluable advice and guidance throughout the course of this work.

My thanks are also due to Professor A W Birley for providing the research facilities, to the Staff of the Institute of Polymer Technology for considerable assistance and to Mrs J Smith who typed this thesis.

I acknowledge the award of a Malaysian Government Scholarship and study leave from the Rubber Research Institute of Malaysia.

DEDICATION

This thesis is dedicated to my parents, wife and children.

I hereby certify that this work has not been submitted to this or any other institution for consideration of a degree.

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CHAPTER 1

VULCANISATION SYSTEMS FOR NATURAL AND POLYISOPRENE RUBBERS

Introduction

Vulcanisation is a process by which essentially linear polymeric molecules are transformed into a three-dimensional network by the insertion of crosslinks. It is the most essential stage in the processing of rubbers because it is the means of changing the predominantly plastic nature of rubber into highly elastic and stronger rubber state or 'hard rubber' (ebonite). Ebonite is not really 'rubber' since it is still noticeably thermoplastic.

A balance of physical and chemical properties, especially the former is the main criterion by which a curing system is selected for use in rubbers. Major effects of crosslink density on some common physical properties are illustrated by Figure 1.1 (1).

Sulphur vulcanisation in one variant or another has remained the preferred method of curing rubbers since 1839. Considerable research work on sulphur vulcanisation since that year has brought it to a high degree of refinement and versatility. Although sulphur curing systems have remained the preferred methods, considerable research effort has been pursued on sulphurless curing systems.

The present chapter deals with the mechanisms of vulcanisation, structural features of vulcanisates, and a summary of advantages and disadvantages of the common curing systems for natural and polyisoprene rubbers. This is followed by the review of other available curing systems for both these rubbers and finally the objectives of the present research.

1.1 Common Curing Systems for Natural and Polyisoprene Rubbers

1.1.1 Sulphur Vulcanisation

1.1.1.1 Accelerated sulphur vulcanisation

When natural rubber is cured with sulphur alone it does not merely produce simple sulphur linkages, but a variety of types of crosslinks which can be represented pictorially in Figure 1.2. In summary, heating of sulphur with natural rubber at 140°C results

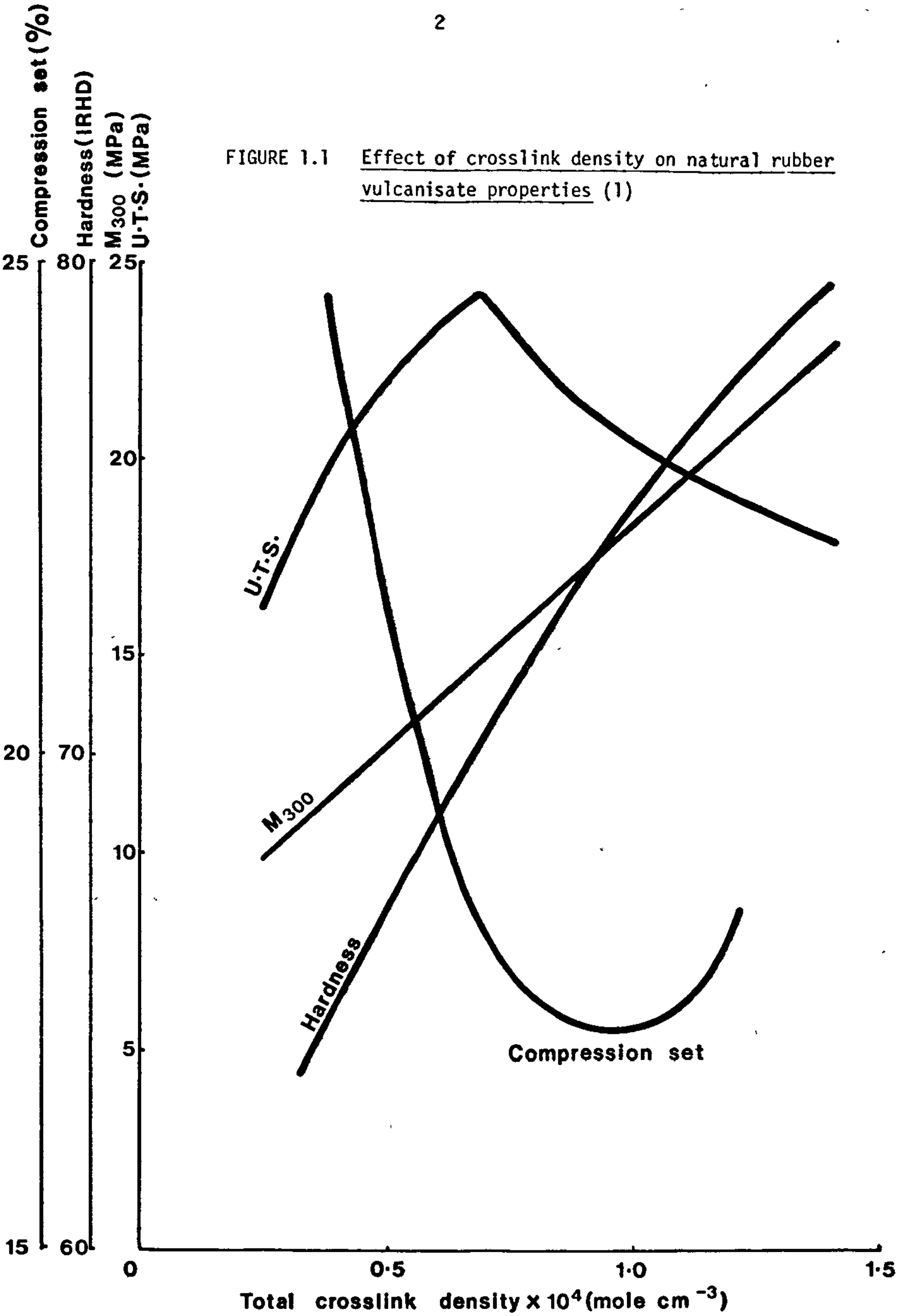


FIGURE 1.1 Effect of crosslink density on natural rubber vulcanisate properties (1)

Start

in the formation of initially long polysulphidic crosslinks. These crosslinks decrease in length with increasing reaction time to give very short sulphurated crosslinks at complete cure and substantial proportional of cyclic monosulphides, together with trienes (2). As a consequence of these structural features, low crosslink yield is obtained with this system. A detailed consideration of sulphur cure (without accelerators or other additives present) is given in Appendix I.

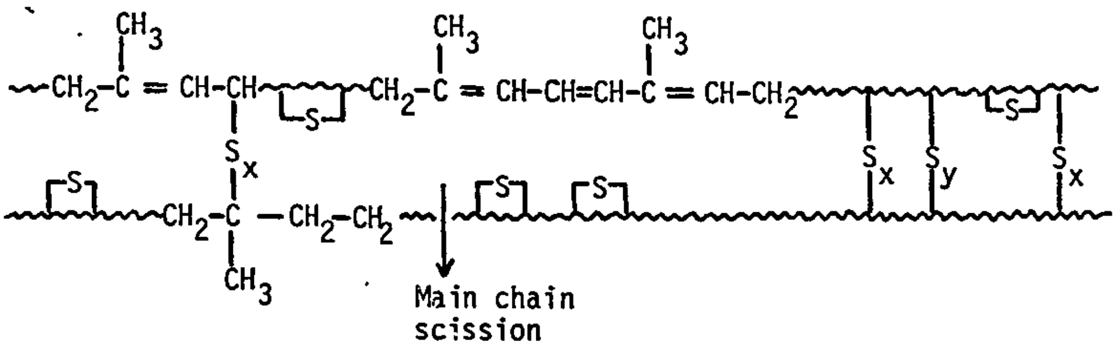


FIGURE 1.2 Structural features of an accelerator-free sulphur vulcanisate of natural rubber (2)

The vulcanisate obtained from this unaccelerated sulphur curing system is of little technical importance for the following reasons:

i) It is an extremely slow process, i.e. long cure time of typically 8 hours at 140°C.

ii) It has a strong tendency to revert.

iii) Its resistance to ageing is poor.

iv) The mechanical properties are inadequate.

v) Large amounts of sulphur are needed.

It is for reason (i) above that accelerators were introduced to reduce the cure time. Inorganic accelerators such as oxides of zinc, calcium, magnesium and lead were the first accelerators used in the rubber industry. Organic accelerators for sulphur vulcanisation were later used in the early years of the present century.

The two major chemical functions of organic accelerators, when used in conjunction with auxiliary agents such as zinc oxide and fatty acids are:

a) To increase the rate of sulphur combination with rubber.
b) To increase the efficiency of utilisation of sulphur as a cross-linking agent and thereby to produce a simple network structure.

Thus the use of organic accelerators in conjunction with zinc oxide and fatty acids overcomes the problems existing with unaccelerated sulphur vulcanisation.

Within the accelerated sulphur vulcanisation there is an accepted terminology. First, conventional systems which contain a much higher concentration of sulphur than accelerator, second, efficient vulcanisation (EV) systems which contain a much lower concentration of sulphur than accelerator and last, semi-efficient vulcanisation (semi-EV) systems which are between the first and second extremes. The approximate concentrations of sulphur and accelerator in the three systems when used in natural rubber are as given in Table 1.1.

TABLE 1.1

The proportions of sulphur and accelerator used for conventional, EV and semi-EV (3)

Curing Systems	Sulphur (phr)	Accelerator (phr)
Conventional	2.0 - 3.5	1.0 - 0.4
EV	0.3 - 0.8	6.0 - 2.5
Semi-EV	1.0 - 1.7	2.5 - 1.0

The use of the conventional sulphur system enables a solution to be obtained to the problems (i), (iv) and (v), whilst the efficient vulcanisation is an ideal system to the solutions of all the five problems that existed with unaccelerated sulphur vulcanisation.

The structural features of an accelerated sulphur vulcanisate of natural rubber are represented pictorially in Figure 1.3. They consist of mono-, di-, and poly-sulphidic crosslinks, cyclic mono-sulphides, pendant sulphide groups containing accelerator fragments and conjugated diene and triene units. The relative proportions of these structures in relation to the properties of the vulcanisate depend on the types of sulphur accelerated vulcanisation systems such as conventional sulphur cure or efficient vulcanisation system and cure conditions.

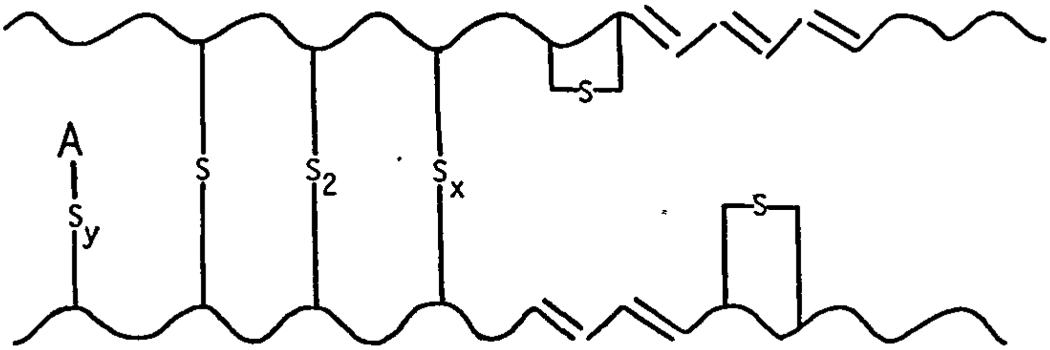


FIGURE 1.3 Structural features of an accelerated sulphur vulcanisate of natural rubber (2)

Sulphenamide accelerators, such as N-cyclohexyl benzothiazole-2-sulphenamide, are commonly used for accelerated sulphur vulcanisation of natural rubber, and have been chosen by the author as a typical model to discuss it. It is appreciated that other mechanisms will apply with other classes of accelerator.

The mechanism of sulphenamide accelerated sulphur vulcanisation is extremely complex. Three reaction mechanisms are postulated namely, the polar mechanisms, the free radical mechanismsand mechanisms with a combined polar/radical nature. The polar mechanism (2) will be discussed in detail here since it is generally accepted as the best way of explaining the numerous features of accelerated sulphur vulcanisation.

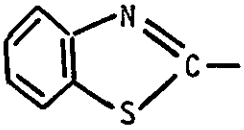
As an extension of the work done by the workers at MRPRA* on unaccelerated sulphur vulcanisation, a polar mechanism was advanced for this accelerated sulphur vulcanisation. As a result of this it has been established that the pathway of the polar mechanism of the accelerated sulphur vulcanisation is as follows:

$$\begin{tikzcd}
\text{Vulcanising ingredients} \arrow[d] \\
\text{Active sulphurating agents} \arrow[d] \\
\text{Rubber-bound intermediates} \arrow[d] \\
\text{Polysulphidic crosslinks} \arrow[d] \\
\text{Matured network}
\end{tikzcd}$$

The interaction between sulphenamide accelerator with activators such as zinc oxide and fatty acid results in the formation of zinc benzothiazole-2-thiolate (ZMBT) (2,4,5,6) given below in equation 1.

$$\underset{\text{(sulphenamide)}}{XSNR_2} \xrightarrow[RCOOH]{ZnO} \underset{\substack{\text{Zinc benzothiazole-2-thiolate}\\ \text{(ZMBT)}}}{XS\ Zn\ SX} \qquad (1)$$

where X =



ZMBT itself is sparingly soluble in rubber but the coordination of it with the amine or carboxylate ligands renders it very soluble. Nitrogenous bases are derived either from dissociation of sulphenamide accelerator or from the nitrogenous proteins of raw natural rubber.

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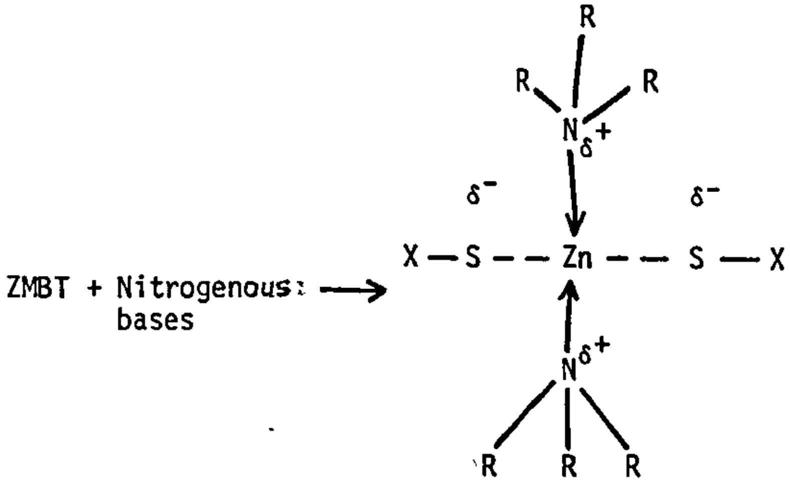
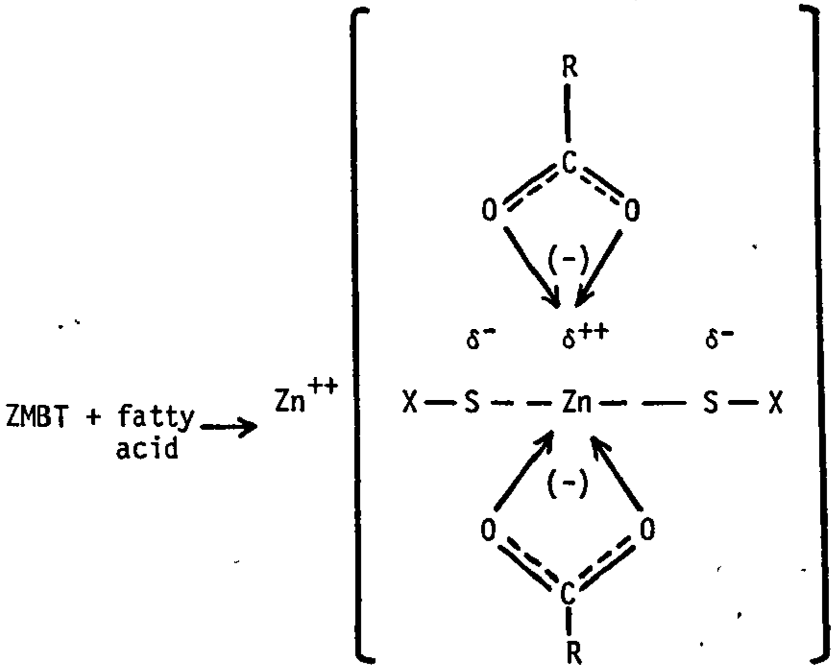
* MRPRA - Malaysian Rubber Producers' Research Association

Carboxylate ligands are derived from the fatty acid added to the compound or that naturally occurring in the raw natural rubber. These steps are detailed in equations 2 and 3.



(2)

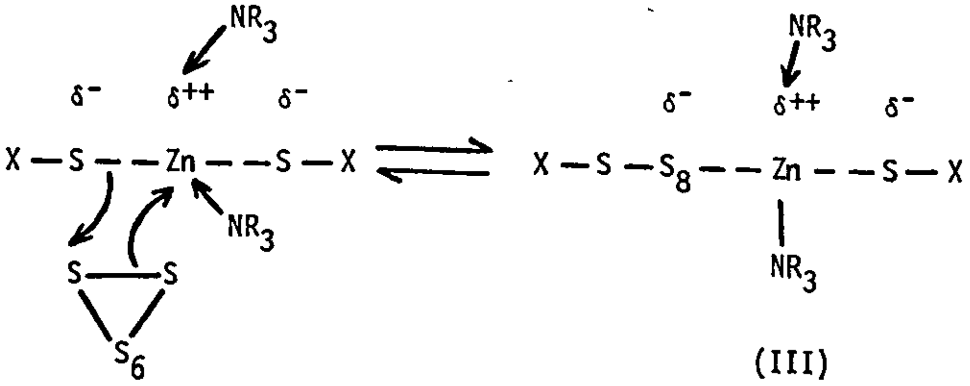
(I)



(3)

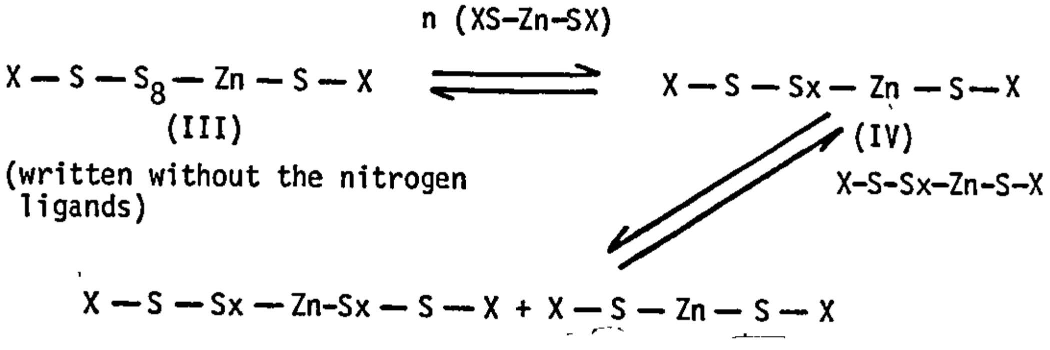
(II)

Next, the complexes formed above in equations 2 and 3 react with sulphur to form zinc perthiomercaptides which are believed to be active sulphurating agents; this event is shown in equation 4.



(4)

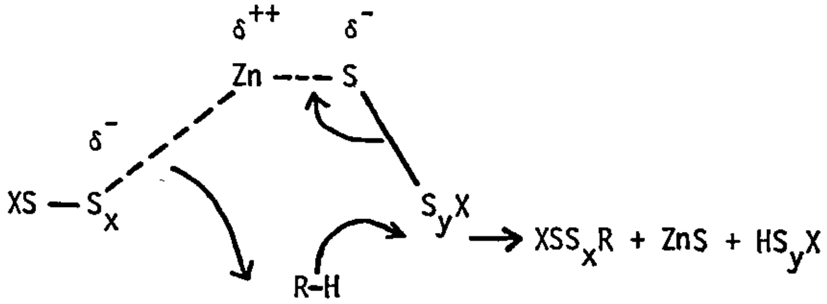
The sulphurating complex (III) is then considered to react with other ZMBT molecules to yield sulphurating complexes of various sulphur ranks shown below. Complexes (IV and V) are also regarded as the sulphurating agents (equation 5)



(V)

(5)

Bateman and co-workers proposed that the formation of the rubber-bound intermediate involves nucleophilic attack of a terminal perthiomercaptide sulphur atom at the side-chain methylic carbon or backbone α-methylenic carbon atom in the rubber hydrocarbon (see equation 6).



(6)

$$2HS_yX \xrightarrow{ZnO} X\,S_y\,Zn\,S_yX + H_2O \qquad (7)$$

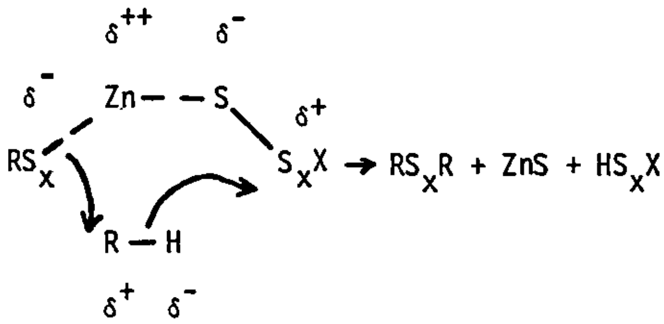
Initial crosslinks may be formed either by nucleophilic displacement (shown below in equations 8 and 9)

$$R\,S_x\,SX + XS^- \rightarrow RS_a^- + X\,S_bX \qquad (8)$$

$$RS_a^- + RS_x\,SX \rightarrow RS_cR + XS_d^-, \text{ etc.} \qquad (9)$$

or interchange between the rubber-bound intermediate and zinc perthiomercaptide (equation 10). This is then followed by sulphuration of another rubber chain (equation 11).

$$RS_xSX + XSS_x\,Zn\,S_y\,SX \rightarrow RS_x\,Zn\,S_xSX + XS\,S_y\,SX \qquad (10)$$



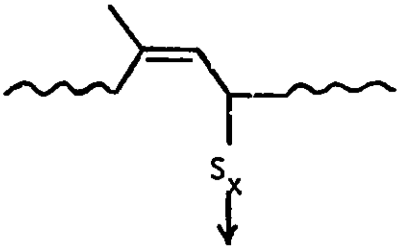
(11)

The initially formed polysulphidic crosslinks undergo maturation which involves several competing reactions namely:

a) The polysulphidic crosslinks can undergo shortening of the sulphur linkages which eventually produces thermally stable monosulphidic crosslinks. The desulphuration may be catalysed by the ZMBT complexes (equation 12)

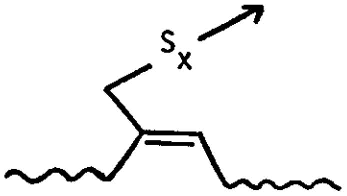
$$RS_xR + XSZnSX \rightarrow RSR + XSS_m\ ZnS_nSX \qquad (12)$$

where R mainly



(VI)

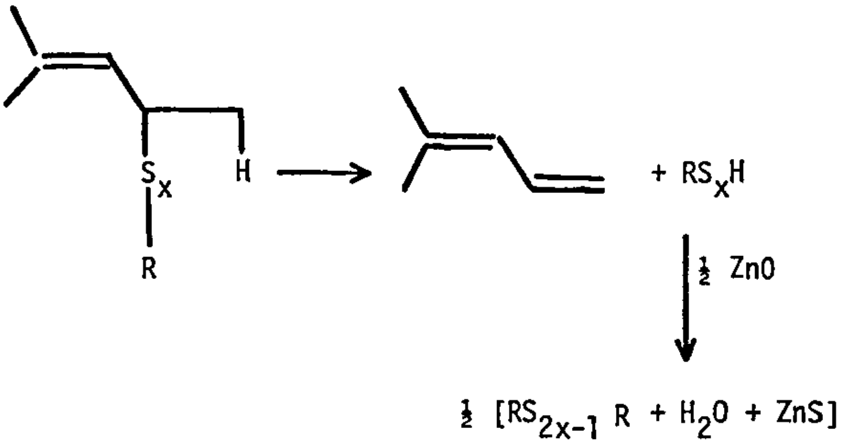
and



(VII)

Crosslinks of (VII) structures desulphurate faster than the crosslinks of (VI) structures.

b) The polysulphidic crosslinks can be thermally decomposed giving rise to cyclic mono- and di-sulphides, conjugated diene and triene and zinc sulphide (equation 13).



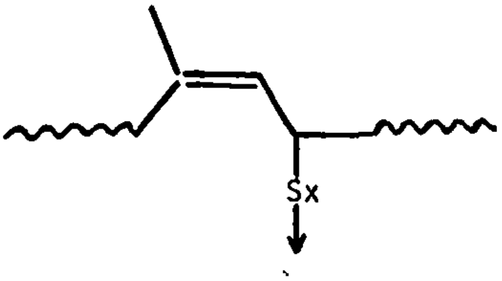
(13)

c) The polysulphidic crosslinks can undergo interchange, which accounts for stress-relaxation, creep, compression set, and permanent set in the deformed vulcanisate. This is due to the interchangeable crosslinks slipping into elastically ineffective positions.

The author wishes not to discuss further the mechanisms involving free radicals and combined polar/radical mechanisms postulated by other workers. However, a brief comment of these two mechanisms can be made. Free radical mechanisms (7-11) may be deficient for a number of reasons such as the non-existence of evidence for polyisoprenyl radicals formed by hydrogen abstraction. Postulation of mixed polar and radical mechanism by Coran (12,13) is fairly well supported by the experimental evidence.

The disadvantages of using a conventional sulphur system are mainly the poor resistance to reversion and ageing. The occurrence of such characteristics can be understood by the maturation process discussed earlier.

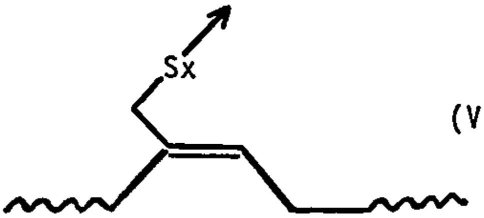
The cure system using low ratio of accelerator : sulphur (ca 1:5) gives a low concentration of zinc perthiomercaptide complexes which could lead to the formation of polysulphidic crosslinks predominantly at position shown below (6):



(VI)

These structures are not efficiently desulphurated to monosulphide due to their slow desulphuration process. As a consequence a substantial degree of total destruction occurs during an extended cure, resulting in reversion processes.

In the case of cure systems with a high ratio of CBS: sulphur (such as 15:1 for efficient vulcanisation system), a high concentration of zinc perthiomercaptide complexes can be formed. These complexes possibly promote the formation of polysulphidic crosslinks at position shown below:



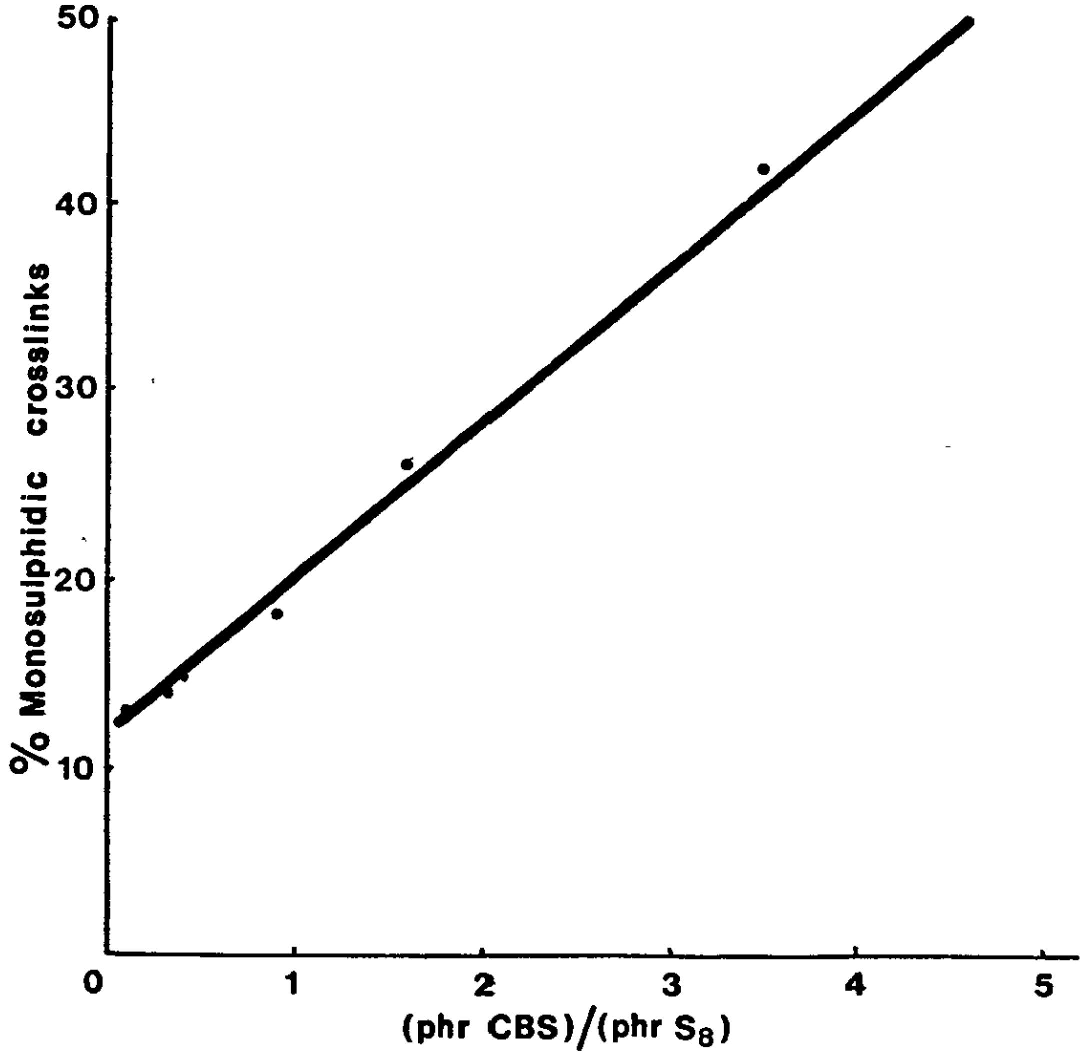
(VII)

Such polysulphidic crosslinks desulphurate very rapidly to form thermally stable monosulphidic crosslinks. Figure 1.4 illustrates the effect of varying the ratio of CBS/S on crosslink type in natural rubber stocks (14).

Natural rubber can be vulcanised to high strength with a conventional sulphur cure or for superior heat resistance with the EV system already described but neither of these provides the ideal spring or elastic material. Among the properties required in the manufacture of rubber products are highly reproducible stiffness or modulus. A further development to meet such requirements was the introduction of soluble EV systems.

It has been shown (15) that normal mixing procedures, using a rubber two roll mill etc. lead to maldispersion of the solid vulcanising ingredients. There appears to be two causes of this maldispersion; first, the loose aggregation of fine powders during mixing and secondly, the sulphur and accelerators in solution in a warm rubber mix, will, if their room temperature solubilities are exceeded, crystallise out as the mix cools or during its subsequent storage, to form a coarsened dispersion. This maldispersion causes some degree of inhomogeneous vulcanisation which

FIGURE 1.4 Crosslink type as a function of accelerator/sulphur ratio (14)



results in variability in physical properties of the vulcanisate. Hence the concept of the all-soluble vulcanisation system was created. An example of this was the soluble-EV system.

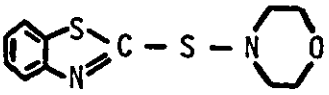
In soluble-EV systems, rubber soluble accelerators and a low sulphur level was used to prevent the formation of crystals. It is known that up to 0.8% of sulphur will normally remain dissolved for a very long time as a supersaturated solution. In the case of accelerators, the solubility of tetramethylthiuram disulphide (TMTD) at 20°C is 0.125% (16), that of CBS is between 0.25% and 0.5%, and many of the other common accelerators are similarly rather insoluble in rubber (16,17). However, tetrabutylthiuram disulphide (TBTD), N-oxydiethylenebenzothiazole-2-sulphenamide (OBS) and diphenylguanidine (DPG) have solubilities of 2% or more at room temperature. Soluble-EV systems have therefore been designed (3) using appropriate amounts of one or more of these three accelerators together with up to 0.8 phr of sulphur and zinc 2-ethyl hexanoate as activator. Zinc 2-ethyl hexanoate was chosen as activator since it is more soluble than zinc stearate which is only sparingly soluble in rubber. A typical formulation for a soluble-EV system is as shown below (Table 1.2):

TABLE 1.2

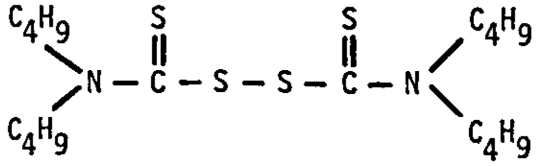
Typical formulation for a soluble-EV system (3)

Natural Rubber	100.00
Zinc 2-ethyl hexanoate	2.00
Sulphur	0.60
OBS[1]	1.44
TBTD[2]	0.60

1. N-oxydiethylenebenzothiazole-2-sulphenamide

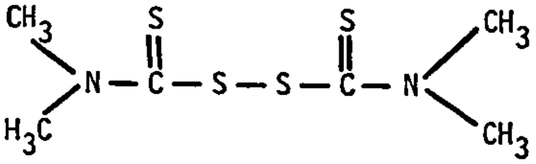


2. Tetrabutylthiuram disulphide

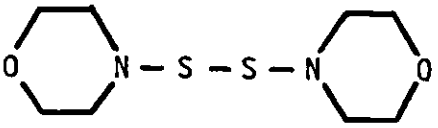


1.1.1.2 Vulcanisation by sulphur donors

Natural or polyisoprene rubbers can be vulcanised by a variety of sulphur-containing organic compounds in the absence of elemental sulphur. These include tetramethylthiuram disulphide, TMTD (VIII), and dithiobismorpholine (IX).



TMTD (VIII)

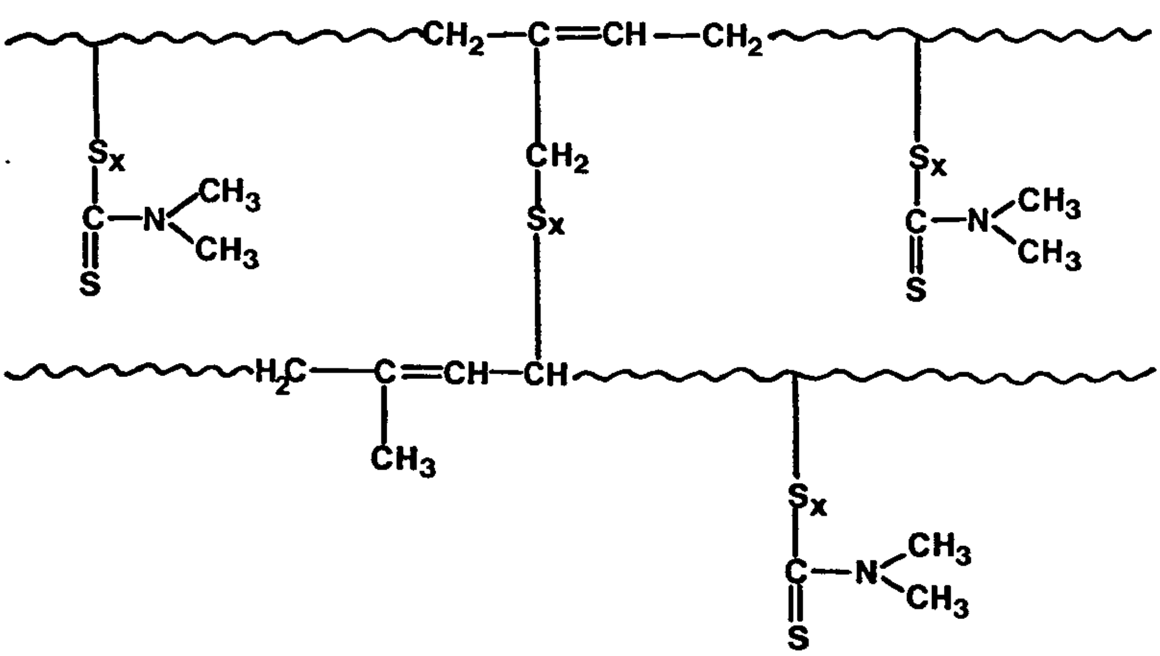


Dithiobismorpholine (IX)

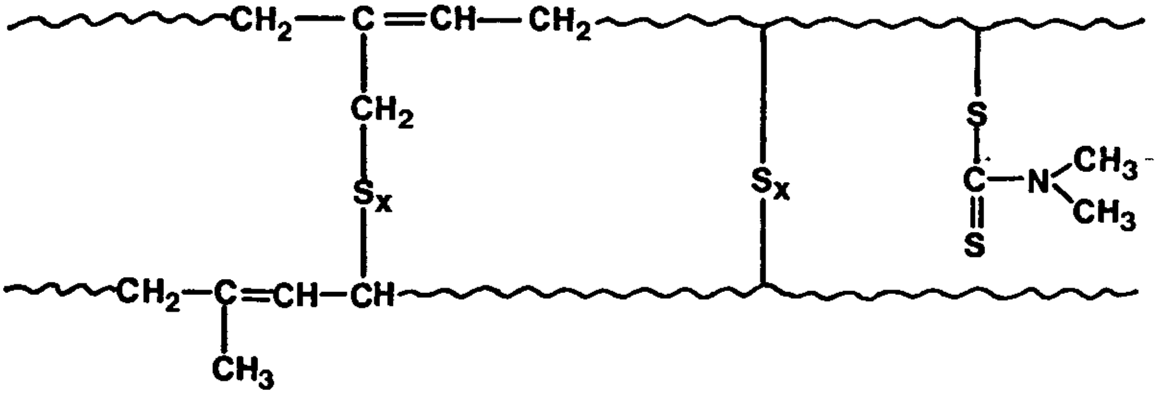
Earlier views (18,19) assumed thiuram vulcanisates to contain of C-C crosslinks. It is now established (20) that they are entirely sulphidic. The number of sulphur atoms in the crosslink depends on the cure time at a given temperature and decreases to mainly $-S_1-$ at long cure times as shown in Figure 1.5.

As contrast to the sulphur accelerated system, sulphurating agents are formed probably via thiuram polysulphides which result from prior interaction of TMTD with zinc oxide or with a basic zinc

FIGURE 1.5 Network structures formed in the natural rubber-TMTD-zinc oxide system at different cure times (2)

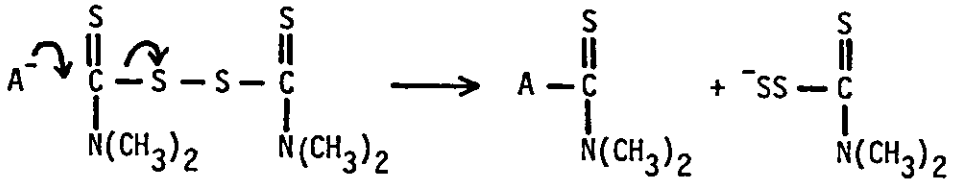


x ⩾ 2 (short cure time)



x mainly 1 (long cure time)

salt derived from a naturally occurring acid in the rubber. The thiuram polysulphides result from nucleophilic attack of a basic oxyanion (e.g. from ---Zn^{++} -- O^{--} -- or RCO_2 Zn^{+}---^{-}OH) on the electrophilic thionocarbon atom of TMTD (20) (see equation 14).

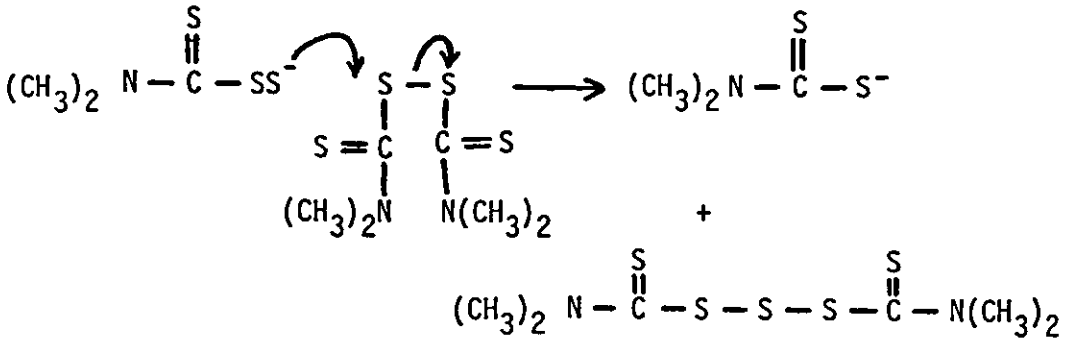


(14)

where A^- from -- Zn^{++} -- O^{--} --

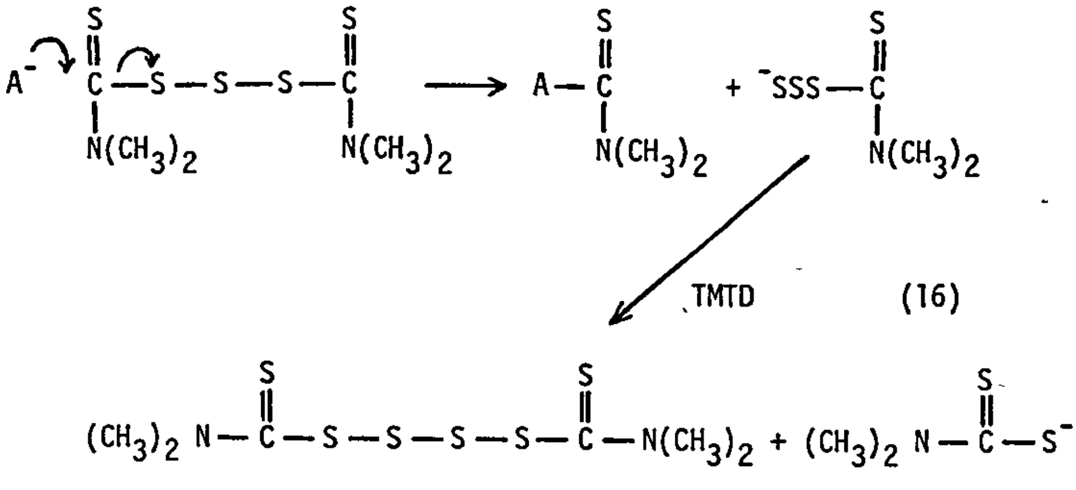
or RCO_2 Zn^{+} --- ^{-}OH

The perthioanion above then preferentially attacks a disulphidic sulphur atom in TMTD to give tetramethylthiuram trisulphide (equation 15):



(15)

Further attack by A^- on the trisulphide yields higher polysulphides (equation 16):



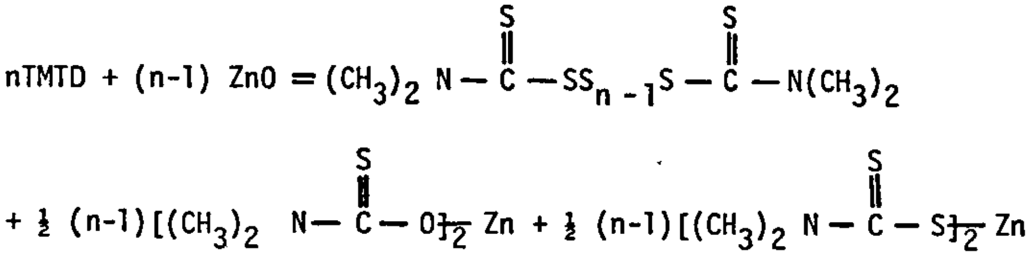
$$A^- + (CH_3)_2N-\overset{S}{\overset{\|}{C}}-S-S-S-\overset{S}{\overset{\|}{C}}-N(CH_3)_2 \longrightarrow A-\overset{S}{\overset{\|}{C}}-N(CH_3)_2 + {}^-SSS-\overset{S}{\overset{\|}{C}}-N(CH_3)_2$$

$$\xrightarrow{TMTD} (CH_3)_2N-\overset{S}{\overset{\|}{C}}-S-S-S-S-\overset{S}{\overset{\|}{C}}-N(CH_3)_2 + (CH_3)_2N-\overset{S}{\overset{\|}{C}}-S^-$$

(16)

Bateman and co-workers (2) believe that, when the reaction is continued further which in the absence of opportunities for other reactions, sulphur may be split off. This has also been observed by Kawaoka (21).

By putting $A^- = ZnO$, the reaction between TMTD (equation 17) and zinc oxide is stoichiometrically formulated in the following way:

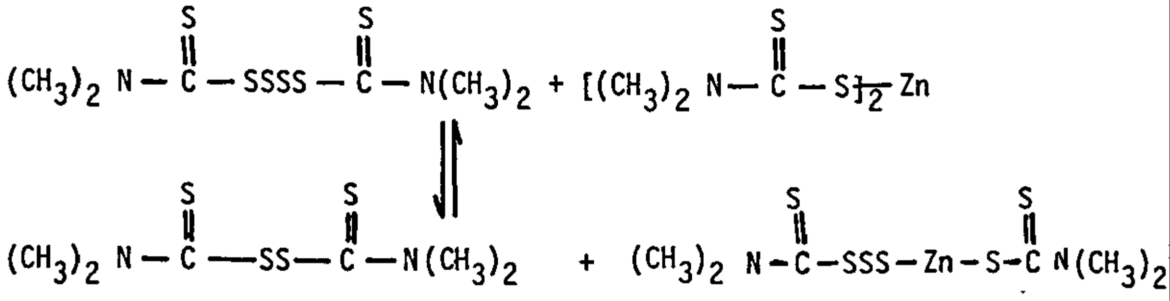


$$nTMTD + (n-1)\ ZnO = (CH_3)_2N-\overset{S}{\overset{\|}{C}}-SS_{n-1}S-\overset{S}{\overset{\|}{C}}-N(CH_3)_2$$

$$+ \tfrac{1}{2}(n-1)[(CH_3)_2N-\overset{S}{\overset{\|}{C}}-O]_2Zn + \tfrac{1}{2}(n-1)[(CH_3)_2N-\overset{S}{\overset{\|}{C}}-S]_2Zn$$

(17)

The actual sulphurating complexes are formed by interchanging between the thiuram polysulphides and zinc dimethyldithiocarbamate as shown below (equations 18 and 19):

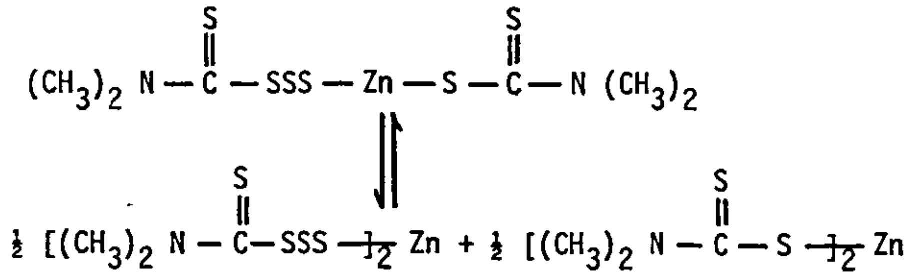


$$(CH_3)_2N-\overset{S}{\overset{\|}{C}}-SSSS-\overset{S}{\overset{\|}{C}}-N(CH_3)_2 + [(CH_3)_2N-\overset{S}{\overset{\|}{C}}-S]_2Zn$$

$$\rightleftharpoons (CH_3)_2N-\overset{S}{\overset{\|}{C}}-SS-\overset{S}{\overset{\|}{C}}-N(CH_3)_2 + (CH_3)_2N-\overset{S}{\overset{\|}{C}}-SSS-Zn-S-\overset{S}{\overset{\|}{C}}N(CH_3)_2$$

(sulphurating complex)

(18)



$$(CH_3)_2N-\overset{\overset{S}{\|}}{C}-SSS-Zn-S-\overset{\overset{S}{\|}}{C}-N(CH_3)_2$$

$$\Big\downarrow\!\Big\uparrow$$

$$\tfrac{1}{2}\,[(CH_3)_2N-\overset{\overset{S}{\|}}{C}-SSS]_2\,Zn+\tfrac{1}{2}\,[(CH_3)_2N-\overset{\overset{S}{\|}}{C}-S]_2\,Zn$$

(sulphurating
complex) (19)

The sulphurating complex is considered to react with the rubber to form a rubber-bound intermediate compound of structure $R-S_x-\underset{\underset{S}{\|}}{C}-N(CH_3)_2$. At short cure time $x \geqslant 2$ and as the cure proceeds the rubber-bound intermediate compound undergoes subsequent reaction to give crosslinks and zinc-dimethyldithiocarbamate. Finally a fully cured vulcanisate consists of $-S_1-$ crosslinks and pendant groups having the structure $-S-\underset{\underset{S}{\|}}{C}-N(CH_3)_2$.

1.1.2 Peroxide Vulcanisation

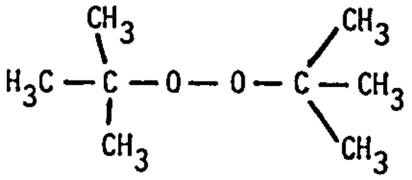
1.1.2.1 Peroxides used for vulcanisation

The use of an organic peroxide as a vulcanising agent for an elastomer was first reported by Ostromyslenski (22) in 1915. In his work dibenzoyl peroxide was used to cure natural rubber. Later additional peroxides (among these was dicumyl peroxide) were used to crosslink natural rubber (23, 24).

With the introduction of saturated rubbers, for which the usual accelerated sulphur systems are unsuitable, interest in the industrial use of peroxides was generated.

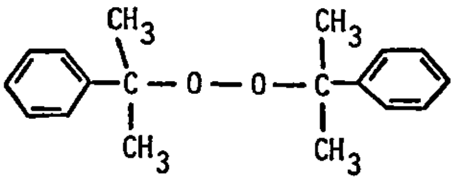
The peroxides commonly available and superficially suitable for rubber applications may be divided into three classes:

A) Dialkyl or aryl-alkyl peroxides such as



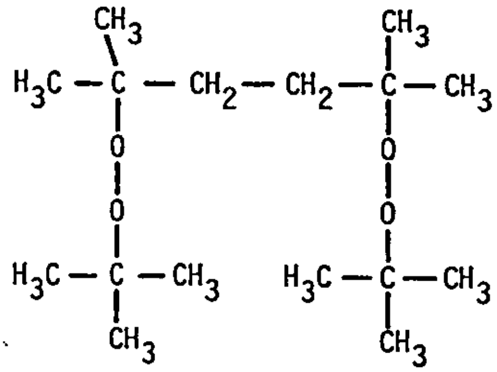
Ditertbutyl peroxide.

(X)



Dicumyl peroxide

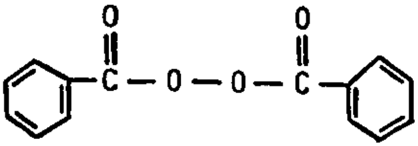
(XI)



(XII)

2,5 Dimethyl 2,5 bis(tert-butylperoxy) hexane

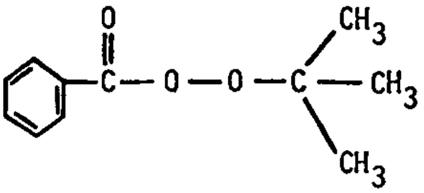
B) Diacyl peroxides such as



Dibenzoyl peroxide

(XIII)

C) Peroxyesters such as



Tert-butyl peroxybenzoate

(XIV)

An investigation of the usefulness of these three classes of peroxides in vulcanising natural rubber has been made by Braden, Fletcher and McSweeny (23, 24). Seven peroxides were studied by them and these include di-tert-butyl peroxide, dicumyl peroxide, 2, 2 di(tert-butyl peroxy) propane, 2,2 di(tert-butyl peroxy) butane, dibenzoyl peroxide and dilauroyl peroxide and tert-butyl perbenzoate. The following general conclusions were made.

a) With diacyl peroxides only low crosslinking efficiencies were obtained; up to 10 phr being required for adequate vulcanisation . There is also an appreciable combination of oxygenated groups with the rubber and this is undesirable since such groups may act as initiating sites for subsequent oxidation.

b) A variety of dialkyl and aryl-alkyl peroxides and tert-butyl perbenzoate lead to high efficiency crosslinking reactions in gum rubber. But only ditertiarybutylperoxide and dicumyl peroxide have been found to give satisfactory vulcanisation of black stocks. Of these two, the former has a rather high volatility and is a liquid, while the latter being relatively nonvolatile and solid appears to be the most generally useful peroxide.

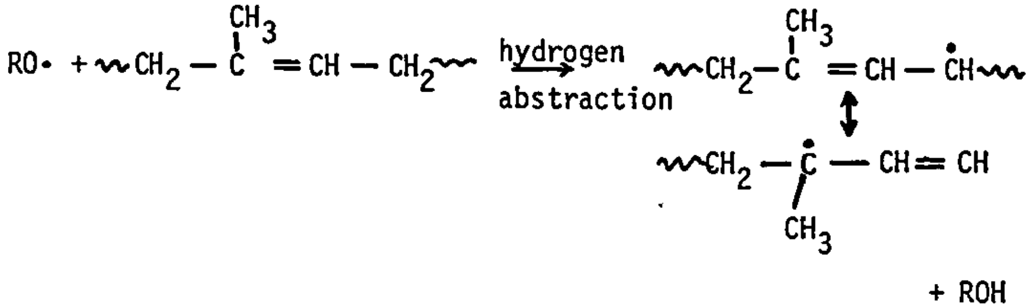
A variety of other peroxides are marketed now for curing both saturated and unsaturated polymers and some of these are reported in the Akzo Chemie Technical Bulletin (25).

1.1.2.2 Basic mechanism of crosslinking by peroxides

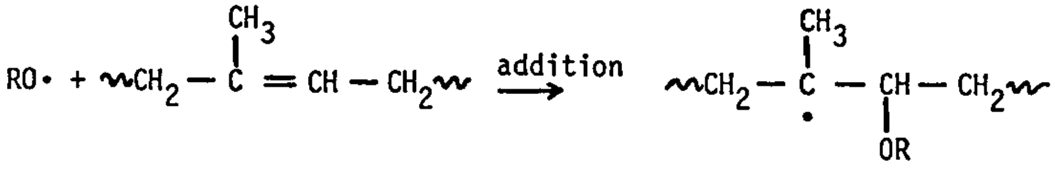
The essential function of any peroxide in curing a rubber is the production of free radicals. The common method in the rubber industry of causing the formation of these free radicals is by heating the peroxide molecule which then decomposes into two *alkoxy* free radicals (equation 20). These free radicals thus produced then react with the rubber chain leading eventually to a chemically crosslinked network.

Early papers on peroxide crosslinking showed that there are two important ways in which olefins, such as natural rubber, and free radicals may react, namely by hydrogen abstraction from an α-methylene group (equation 21) and by addition to the double bond (26-28) (equation 22).

$$ROOR \rightarrow 2RO\bullet \qquad (20)$$

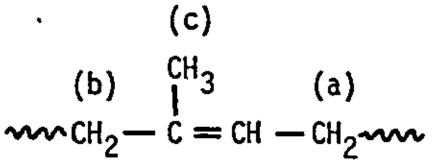


$$RO\bullet + \sim CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2\sim \xrightarrow[\text{abstraction}]{\text{hydrogen}} \sim CH_2-\overset{CH_3}{\overset{|}{C}}=CH-\dot{C}H\sim \;\updownarrow\; \sim CH_2-\underset{CH_3}{\underset{/}{\dot{C}}}-CH=CH \; + ROH \qquad (21)$$



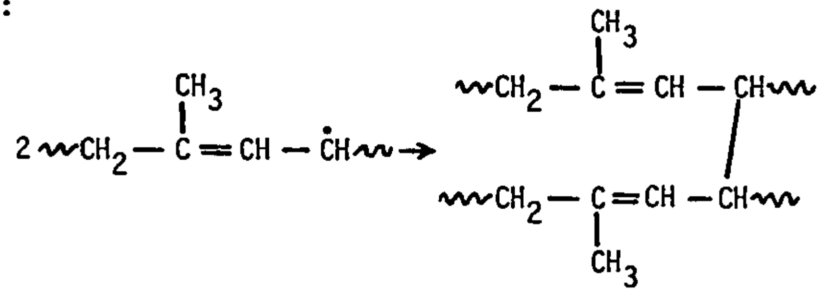
$$RO\bullet + \sim CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2\sim \xrightarrow{\text{addition}} \sim CH_2-\underset{\bullet}{\overset{CH_3}{\overset{|}{C}}}-\underset{OR}{\underset{|}{CH}}-CH_2\sim \qquad (22)$$

In the case of reaction (equation 21), there is a choice of three types of hydrogen atoms in the isoprene unit for the RO· radical to abstract hydrogen. The order of reactivity of these three types of hydrogen atoms (29, 30) had been found to be a>b>c.

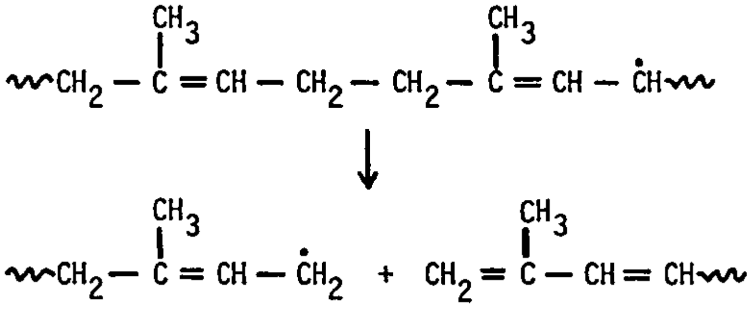


$$\overset{(b)}{\sim CH_2} - \overset{\overset{(c)}{CH_3}}{\overset{|}{C}} = \overset{(a)}{CH - CH_2}\sim$$

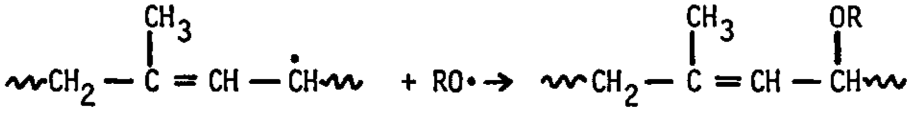
The polymeric radicals formed from reaction of equation 21 may react by several paths leading to crosslinking (equation 23), scission (equation 24), or radical wastage (equation 25) shown below:



$$2\sim CH_2-\overset{CH_3}{\overset{|}{C}}=CH-\dot{C}H\sim\ \rightarrow\ \begin{array}{c}\sim CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH\sim\\ |\\ \sim CH_2-\underset{CH_3}{\underset{|}{C}}=CH-CH\sim\end{array}\qquad (23)$$



$$\begin{array}{c}\sim CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-\dot{C}H\sim\\ \downarrow\\ \sim CH_2-\overset{CH_3}{\overset{|}{C}}=CH-\dot{C}H_2\ +\ CH_2=\overset{CH_3}{\overset{|}{C}}-CH=CH\sim\end{array}\qquad (24)$$

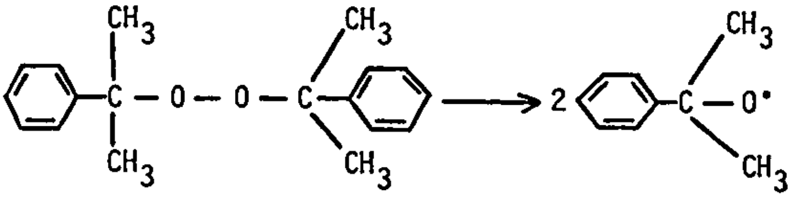


$$\sim CH_2-\overset{CH_3}{\overset{|}{C}}=CH-\dot{C}H\sim\ +\ RO\cdot\rightarrow\ \sim CH_2-\overset{CH_3}{\overset{|}{C}}=CH-\overset{OR}{\overset{|}{C}H}\sim\qquad (25)$$

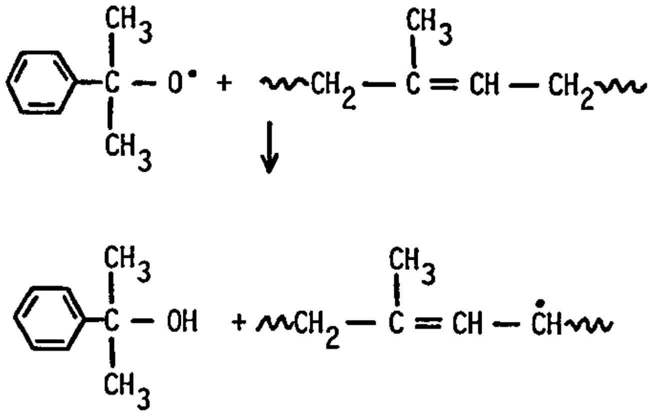
For an efficient use of peroxide (of structure ROOR) in crosslinking, the reactions of equations 24 and 25 must occur to only a small extent.

Moore and Watson (31) found that the number of crosslinks formed per molecule of di-tert-butyl peroxide decomposed is somewhat less than unity and is between 0.70 and 0.85. However, as the gas phase decomposition of the peroxide is reduced higher values are obtained, and for curing in a mould it seems probable that crosslinking efficiencies very close to unity would be obtained.

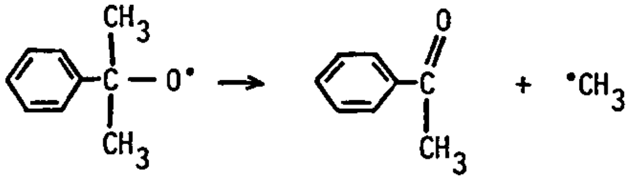
Thomas (32) showed that crosslinking efficiencies very close to unity over a range of curing conditions were obtainable from dicumyl peroxide crosslinker. He managed to obtain complete recovery of the peroxide as cumyl alcohol and acetophenone as would be expected from reactions of equations 26-28 below:



(26)



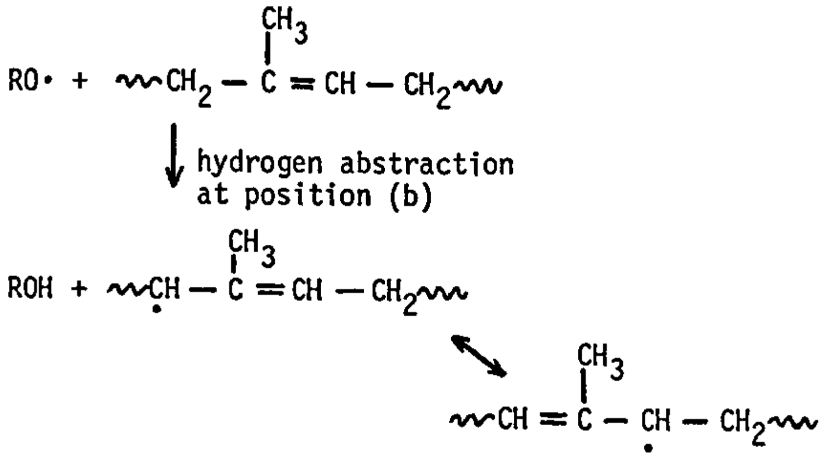
(27)



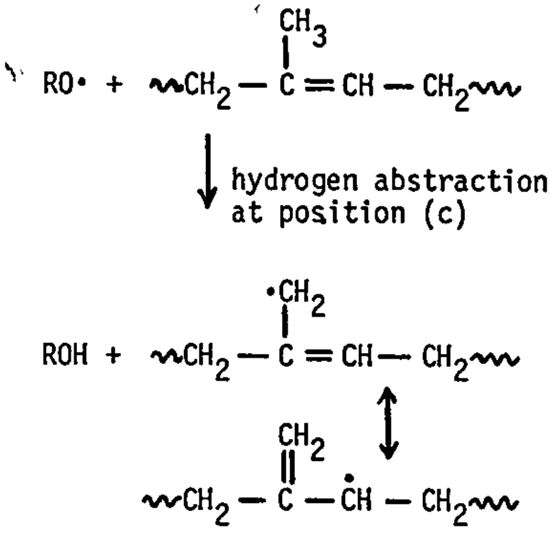
(28)

Based on 2,6 dimethylocta-2,6 diene as a model compound for natural rubber, Parks and Lorenz (33) reported that the polyisoprenyl radicals formed by interaction of the model compound with dicumyl peroxide at 120° - 150°C undergo exclusive combination.

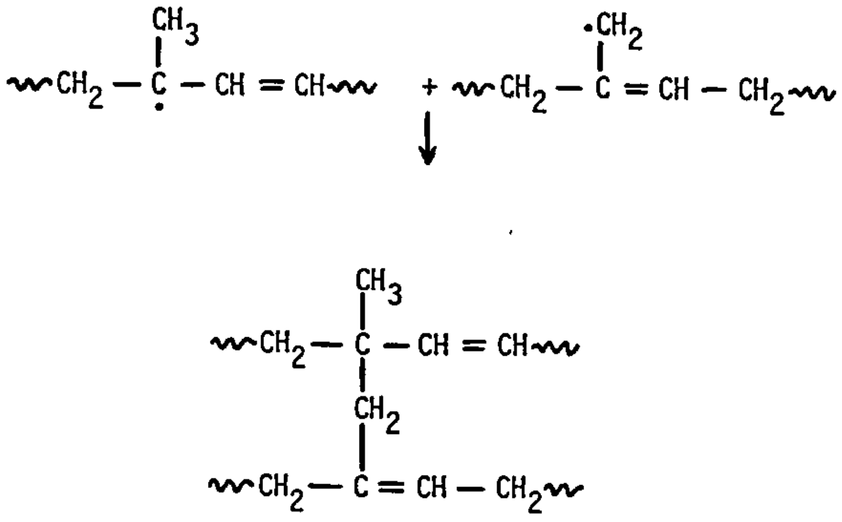
Considering the other two types of hydrogen abstraction (as shown in equations 29 and 30), there are then various possibilities that these macroradicals resulting from the hydrogen abstraction can couple to form crosslink. An example of such possibilities is shown in equation 31.



$$RO\cdot + \sim CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2\sim \;\xrightarrow{\text{hydrogen abstraction at position (b)}}\; ROH + \sim\dot{C}H-\overset{CH_3}{\overset{|}{C}}=CH-CH_2\sim \;\longleftrightarrow\; \sim CH=\overset{CH_3}{\overset{|}{C}}-\dot{C}H-CH_2\sim \qquad (29)$$

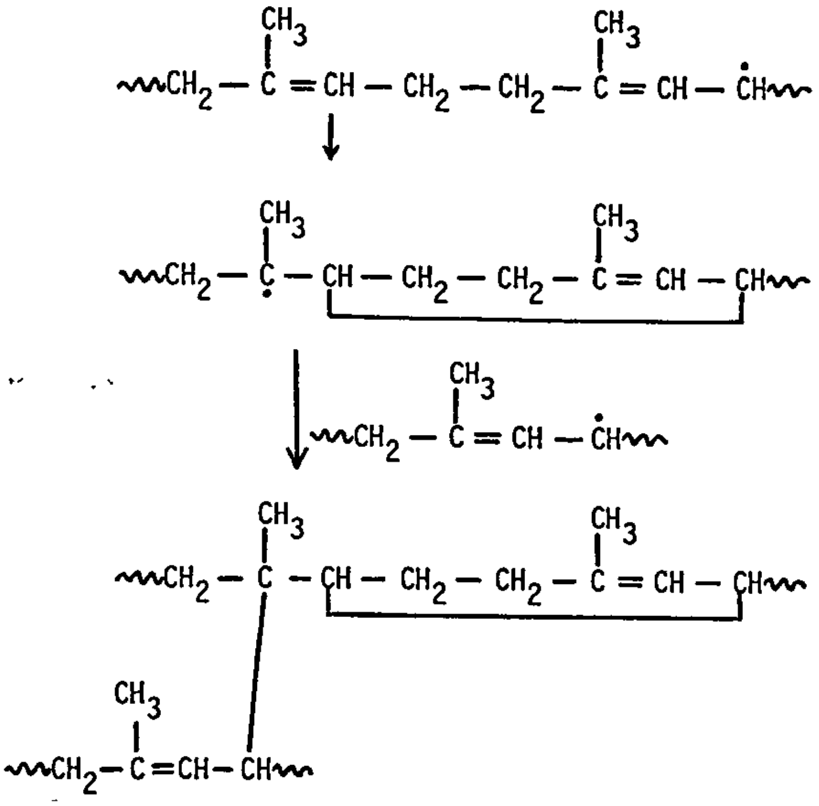


$$RO\cdot + \sim CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2\sim \;\xrightarrow{\text{hydrogen abstraction at position (c)}}\; ROH + \sim CH_2-\overset{\cdot CH_2}{\overset{|}{C}}=CH-CH_2\sim \;\longleftrightarrow\; \sim CH_2-\overset{CH_2}{\overset{\|}{C}}-\dot{C}H-CH_2\sim \qquad (30)$$



(31)

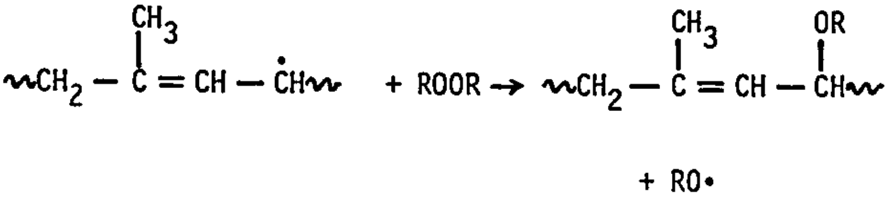
Besides the normal coupling between free radicals for crosslinking purposes (equations 23 and 31), there is the further possibility for the initially formed macroradicals to undergo cyclisation as shown below (equation 32):



(32)

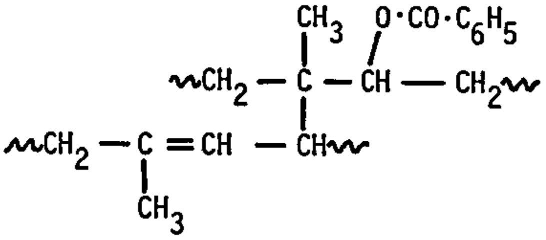
The above cyclisation is based on the estimation of the unsaturation retained in the products obtained from model compounds 2,6-dimethylocta-2,6-diene and digeranyl; the retentions of unsaturation were 82 and 72% respectively (27, 28). In the case of mono-olefins, 100% retention of unsaturation was found.

The inclusion of peroxide fragments does not occur with dialkyl or aryl-alkyl peroxides such as di-tert-butyl peroxide or dicumyl peroxide, indicating that neither reaction of equation 25 nor incidentally reaction of equation 22 occur with these peroxides. However, it has been shown that with other peroxides such as dibenzoyl peroxide, benzoyloxy groups are known to be attached to the polymer chain (34). The causes of this attachment may be due to reactions of equations 22 and 25 or by induced decomposition (35) shown below (equation 33):

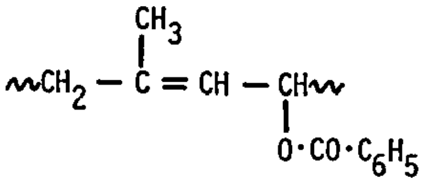


$$\sim CH_2-\overset{CH_3}{\overset{|}{C}}=CH-\dot{C}H\sim \; + ROOR \rightarrow \; \sim CH_2-\overset{CH_3}{\overset{|}{C}}=CH-\overset{OR}{\overset{|}{C}}H\sim \; + RO\bullet \qquad (33)$$

The benzoloxy groups can attach themselves to the main chain either at the site of a crosslink as in (XV) or at isolated points in the chain as in (XVI) (26, 36, 37, 38).



(XV)



(XVI)

Scission may occur since reactions of equations 23 and 24 would be expected to occur to differing extents at different temperatures. Scheele and co-workers (39) showed a gradual decrease in crosslinking efficiency with increasing temperature; overall change being about 20%. Over a slightly more restricted temperature range, 110°-140°C, Thomas (32) obtained an essentially constant value of 1.0. Based on the estimation of scission by the sol-gel technique, Scott (40) and Bristow (41) showed that scission competes only to a small extent with the coupling reaction even by varying normal cure temperatures (130-150°C).

As a consequence of various possible reaction routes discussed above, the structural features of the natural rubber vulcanisate cured with di-tert-butyl and dicumyl peroxides were simplified (2) as in Figure 1.6.

1.1.2.3 Properties of vulcanisates cured with peroxides

Table 1.3 shows the comparative properties of natural rubber gum vulcanisates cured with different peroxides. Dicumyl peroxide gives the highest tensile strength so far obtained with any organic peroxide. However, it is still somewhat inferior in this respect to a conventional sulphur gum vulcanisate.

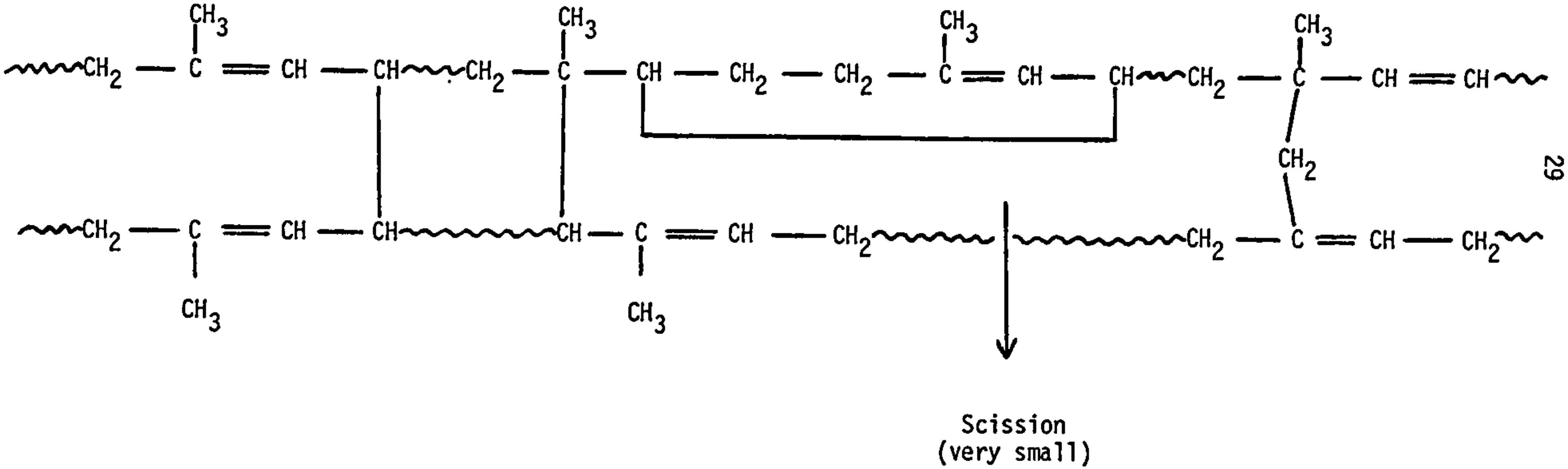
TABLE 1.3

Properties of peroxide-cured natural rubber gum vulcanisates (23,24,28)

	Dicumyl Peroxide	Ditertiary butyl peroxide	Tertiary butyl perbenzoate
Concentration of peroxide (phr)	3	1.45	3
Cure time (min.at 140°C)	50	360	30
Tensile strength (MPa)	17.5	13.8	12.7
Elongation at break (%)	648	645	650
Modulus at 300% strain (MPa)	1.5	1.3	1.2

FIGURE 1.6

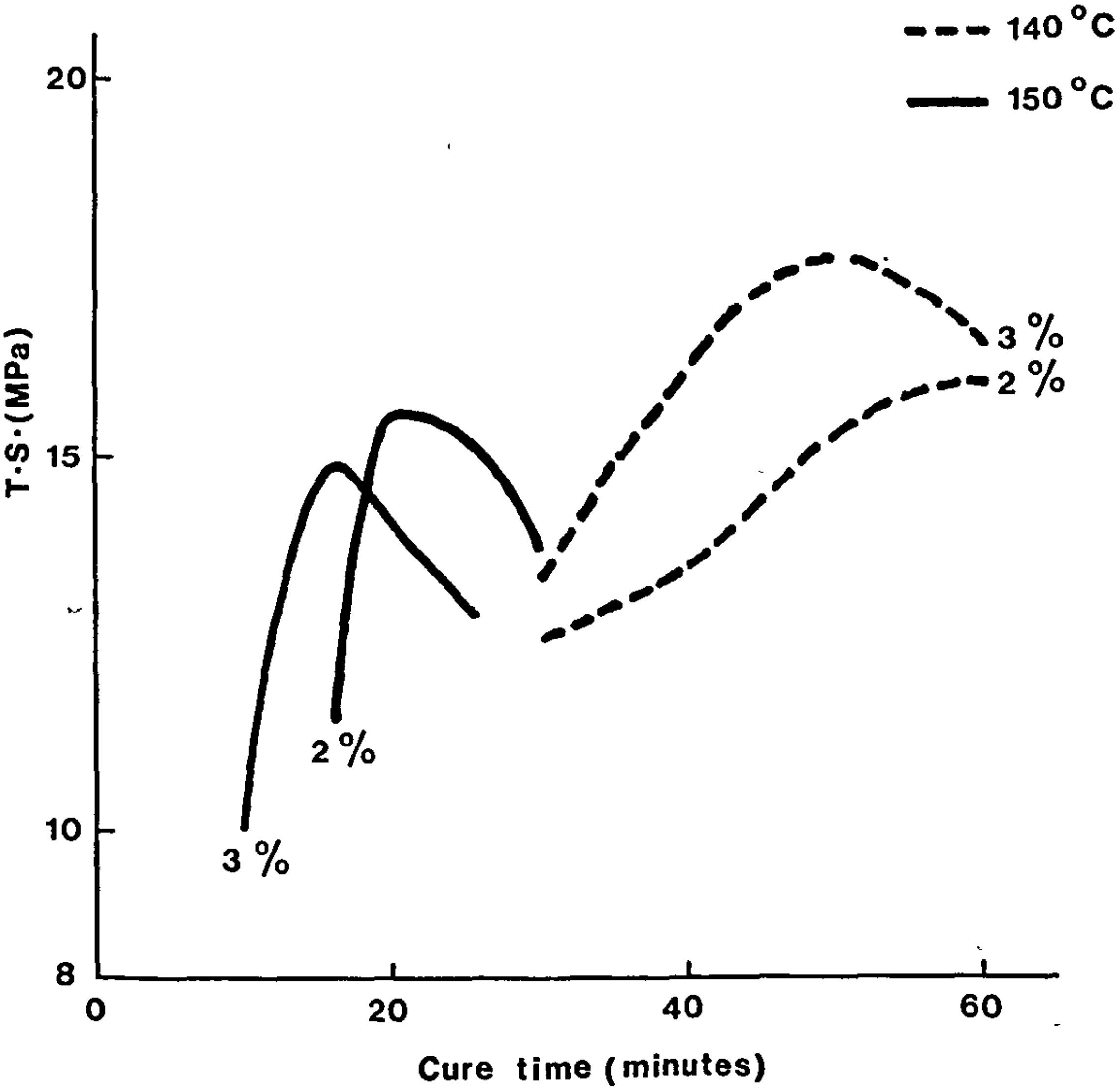
Structural features of natural rubber vulcanisate cured with ditertbutyl or dicumyl peroxides (2)



For maximisation of the tensile strength of natural rubber gum vulcanisate cured with dicumyl peroxide, both the cure conditions and the concentration of the crosslinker are the predominant factors. The effect of these variables on tensile strength is illustrated by Figure 1.7.

FIGURE 1.7

The effect of dicumyl peroxide concentration and cure conditions on tensile strength (24)



When curing the dicumyl peroxide mixes at 140° or 150°C, it is a common practice to choose the cure time in the region of within 1 hour. However, it has been shown (42) that complete decomposition of the dicumyl peroxide (ca 99.9%) at 150°C takes place in about 3 hours. Thus there is usually some dicumyl peroxide that remains undecomposed, in the vulcanisate if the normal cure time of 1 hour is chosen.

Dicumyl peroxide has been shown to work satisfactorily in vulcanisates containing reinforcing carbon blacks. The resulting vulcanisates compare favourably with conventionally cured black compounds as shown in Table 1.4.

TABLE 1.4

Properties of HAF black loaded compounds (24)

Natural Rubber	100	100
HAF black	45	45
Phenyl β naphthylamine	1	1
Pine tar	1	2.5
Stearic acid	-	2.5
Zinc oxide	-	5
CBS	-	0.6
Sulphur	-	2.5
Dicumyl peroxide	3.5	-
Cure time (min. at 140°C)	50	40
Tensile strength (MPa)	23.5	24.5
Elongation at break (%)	373	500
Modulus at 100% strain (MPa)	2.1	2.7
Modulus at 300% strain (MPa)	18.4	13.1
Hardness B.S. degrees	57	66
De Mattia cut growth (Kc to 4 mm)	250	165
(Kc to 8 mm)	1544	709
De Mattia Flex life	Better than Grade A after 1000 Kc	1530 Kc to Grade C

The three major differences between these two curing systems are:

i) Elongation is lower in the case of the peroxide cured compound.

ii) Resistance to cyclic deformation fatigue (De Mattia) is better in the case of the conventional sulphur cured compound.

iii) Resistance to cut growth (De Mattia) is better with the peroxide cured compound.

1.2.3 Radiation Vulcanisation

Radiation vulcanisation of rubber was discovered in 1929 by Newton (43) who crosslinked rubber by exposure to electrons from a cathode ray tube. Both natural rubber and polyisoprene can be cured when they are exposed to various types of high energy radiation. A dose of 30-50 Mrad (1 Mrad = 10^4 J kg^{-1} absorbed energy) is required to produce an acceptable vulcanisate in a natural rubber gum stock, and similar doses are necessary for filled rubbers. The number of crosslinks formed is proportional to the dose and independent of the dose rate (44).

The common types of radiation used include gamma rays, fast electrons and slow neutrons. There are no substantial differences between the effects of these types of radiation on polymers (45).

The mechanism of radiation crosslinking of natural rubber is almost similar to that of ditertbutyl peroxide/dicumyl peroxide vulcanisation. During irradiation homolytic fission of carbon-hydrogen bonds occurs with the formation of polyisoprenyl and hydrogen radicals (equation 34). A large proportion of the hydrogen radicals will abstract α-methylenic hydrogen atoms to form molecular hydrogen and polyisoprenyl radicals (44) as shown in equation 35. The polyisoprenyl radicals couple to form crosslinks (equation 36).

$$RH \rightarrow R\cdot + H\cdot \qquad (34)$$

$$H\cdot + RH \rightarrow R\cdot + H_2 \qquad (35)$$

$$2R\cdot \rightarrow R\text{-}R \qquad (36)$$

Some scission of the backbone of the rubber molecules (and hence degradation) also occurs, but the ratio of fractures to crosslinks is only about 1:10 (46).

Various types of additives have been employed to increase the extent of crosslinking. Examples of such additives are dimaleimides (44) and polyester acrylate resins (47).

1.2.4 Urethane Vulcanisation (Novor System)

1.2.4.1 Basic mechanism

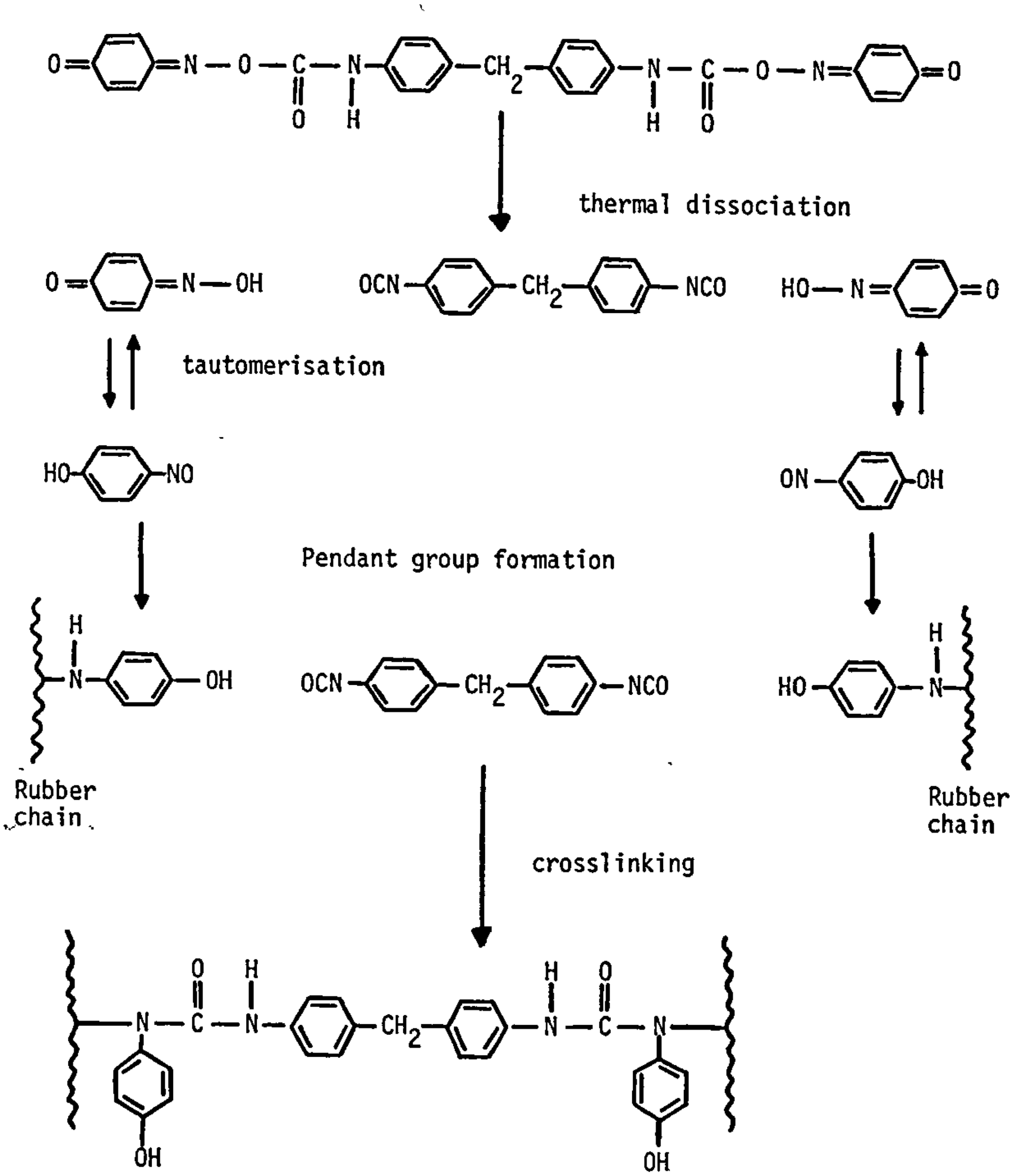
The chemical basis of urethane crosslinking relies on the attachment of pendant aminophenol groups into natural rubber chains, which are then crosslinked with diisocyanates (48). These two processes are achieved in a single operation by the use of diurethane crosslinking agents which are adducts of p-benzoquinonemonooximes and diisocyanates as shown in Figure 1.8.

On the formation of pendent aminophenol groups, as illustrated in Figure 1.8, a substantial proportion of the diisocyanates will react with the more reactive NH than with the OH group, forming a majority of urea crosslinking rather than urethane crosslinking. This preferential reaction mechanism is based on the knowledge of the vulcanisate's thermal and hydrolytic stability properties, coupled with chemical probe work (50) and experiments with model olefins. The chemical probe work on urethane-cured vulcanisates indicated that only 15-20% of the crosslinks were urethanes. However in the absence of ZDMC(1), isocyanates react with model alkylaminophenols at the NH groups almost exclusively, but in the presence of ZDMC, some reaction at the phenolic OH group is also found. The presence of ZDMC also facilitates the decomposition of the diurethane (51).

(1) - Zinc dimethyl dithiocarbamate

FIGURE 1.8

Schematic representation of the mechanism of crosslinking by a diurethane crosslinker (48)



The absence of water in mixes containing diurethane is important to prevent the undesirable reaction of diisocyanate with water. It is for this particular reason that a dessicant, such as calcium oxide, is added to diurethane mix.

1.2.4.2 Performance

The performance of diurethane systems in natural rubber has been widely reported. A few of the outstanding characteristics are: excellent age-resistance (Figure 1.9), outstanding reversion resistance (Figure 1.10) and excellent aged fatigue resistance (Figure 1.11). However the high cost of the curatives in comparison with the presently available sulphur curing systems restricts its commercial exploitation. With the recently introduced mixed diurethane/sulphur system, the cost of vulcanisation ingredients is reduced to some extent.

FIGURE 1.9

Comparative ageing behaviour of sulphur and diurethane curing systems in natural rubber (51) (air-oven ageing at 100°C)

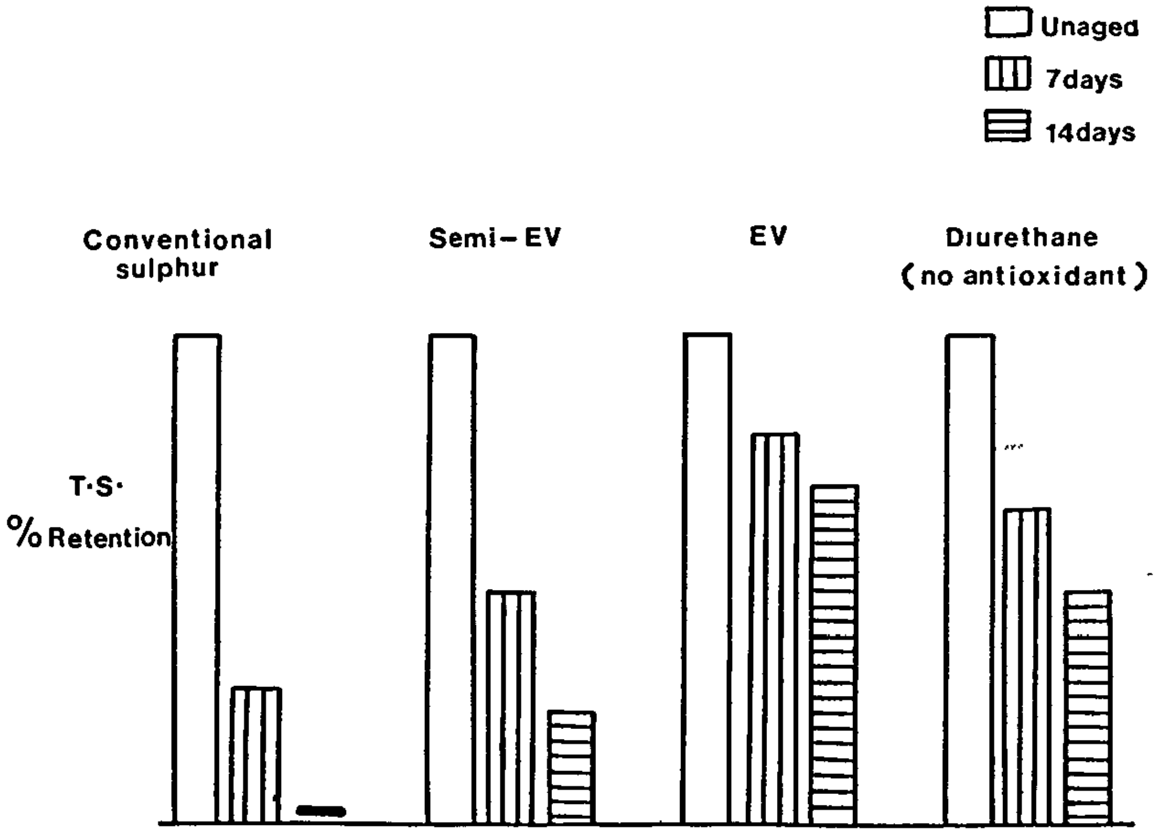


FIGURE 1.10

Reversion resistance at 180°C for diurethane vs sulphur crosslinkers (52)

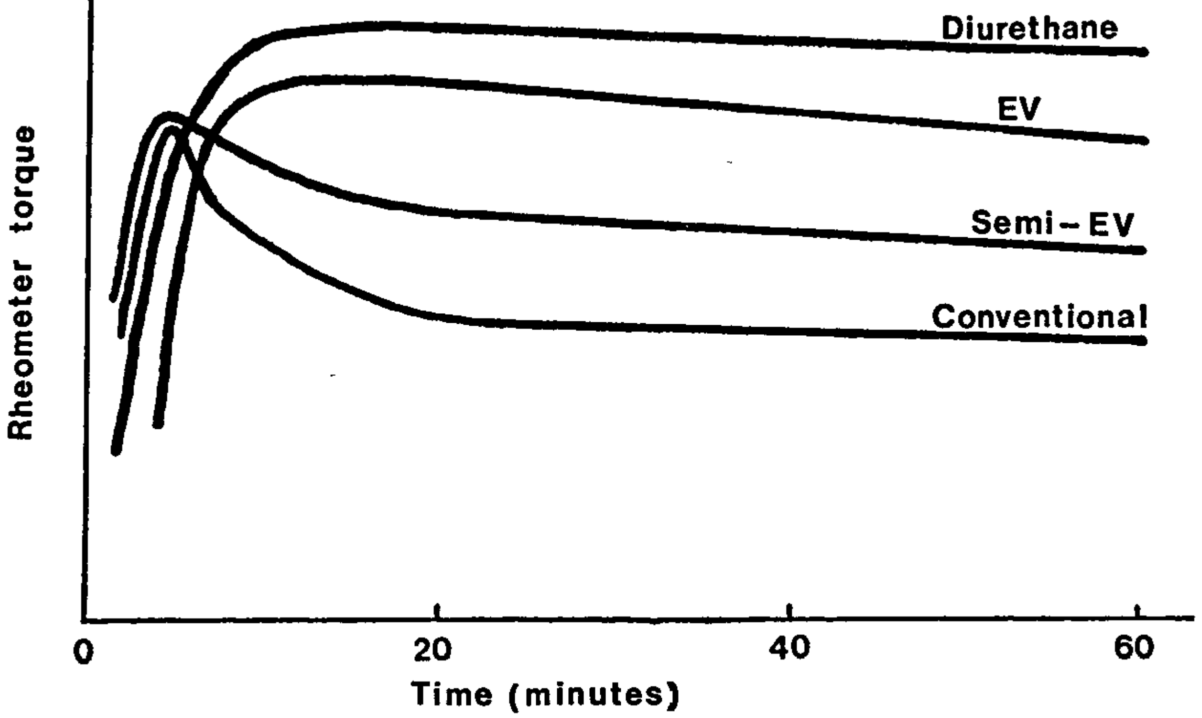
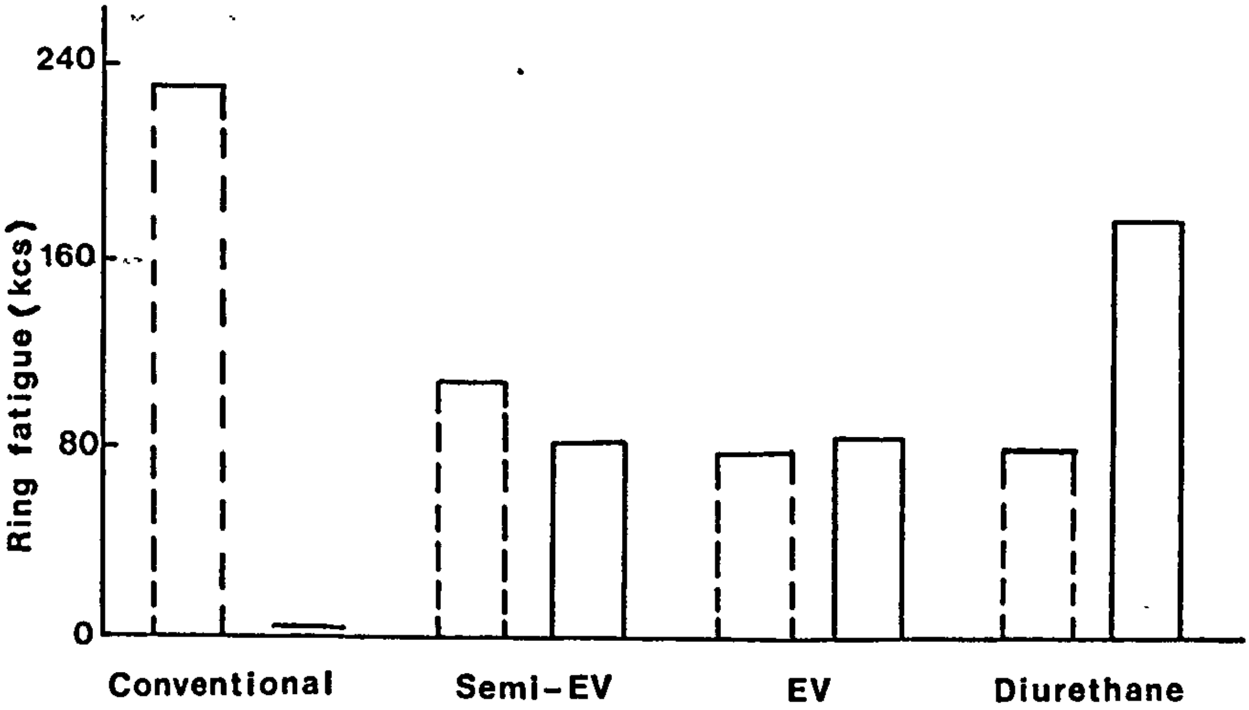


FIGURE 1.11

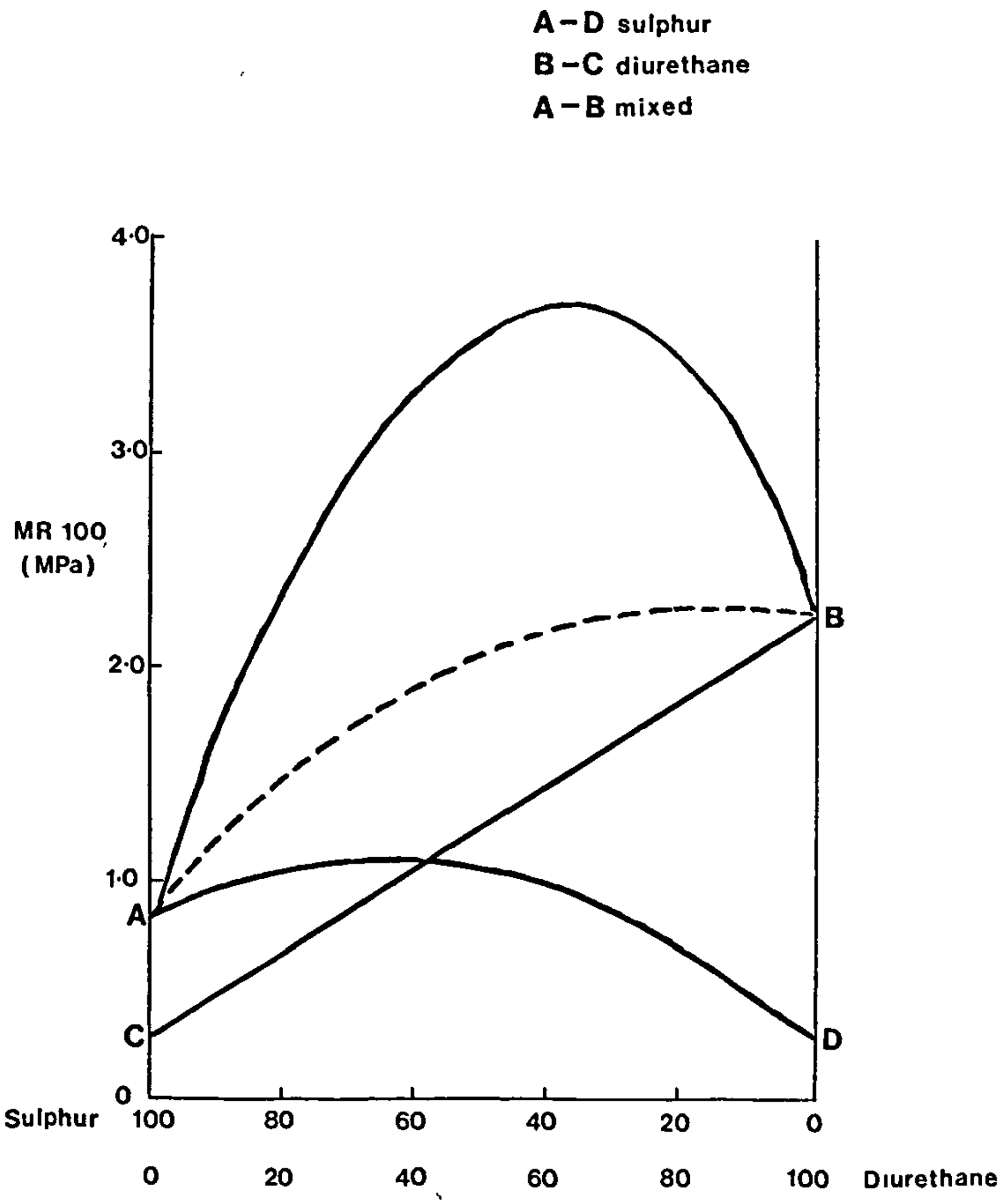
Initial and aged fatigue performance for diurethane vs sulphur crosslinkers (52)



1.2.4.3 Mixed urethane/sulphur system

Urethane crosslinking systems are compatible with sulphur curing systems, giving a very fast curing combination which exhibits very marked modulus synergism (51). This modulus synergism, as shown in Figure 1.12, allows a substantial reduction in the total amount of curatives required to produce a given modulus and thus lowers the cost of vulcanisation ingredients considerably.

FIGURE 1.12
Modulus synergism (51)



The initially low scorch times of these systems has been overcome and several methods are available for increasing the scorch time:

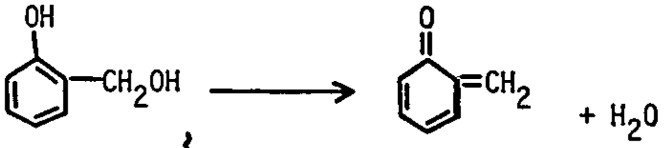
a) Replacement of part of the urethane by TDI dimer*, which also reduces the cost (53).

[illegible]

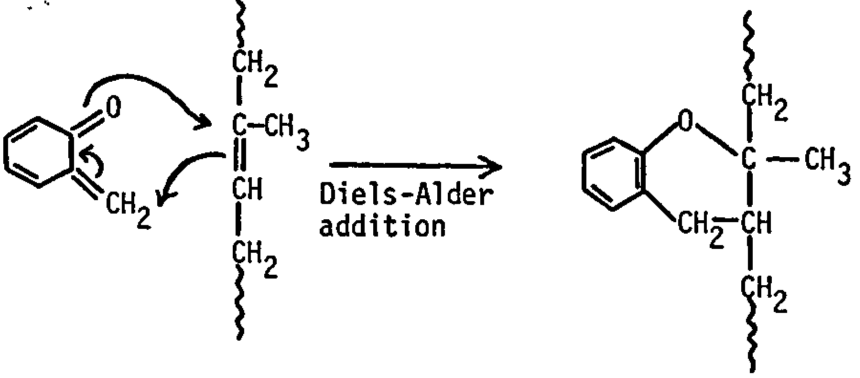
b) Replacement of ZDMC by TMTM and zinc oxide (53).

1.2.5 Resin Vulcanisation

Alkylphenol formaldehyde resins can be used to vulcanise both high and low unsaturated rubbers, usually in the presence of a catalyst. The mechanism of the crosslinking is *not fully clarified*. One theory is based on the observation that ortho-methylolphenol, presumably after elimination of water (equation 37) condenses with a double bond of natural rubber to produce a chroman ring (54, 55) (equation 38).



(37)



(38)

Based on 2,6 dihydroxymethyl-4-methylphenol/formaldehyde resin, crosslinking reactions similar to the above occurs concurrently with self-condensation of the resin involving elimination of water from the two methylol groups to form a crosslink of structure shown below (XVII):

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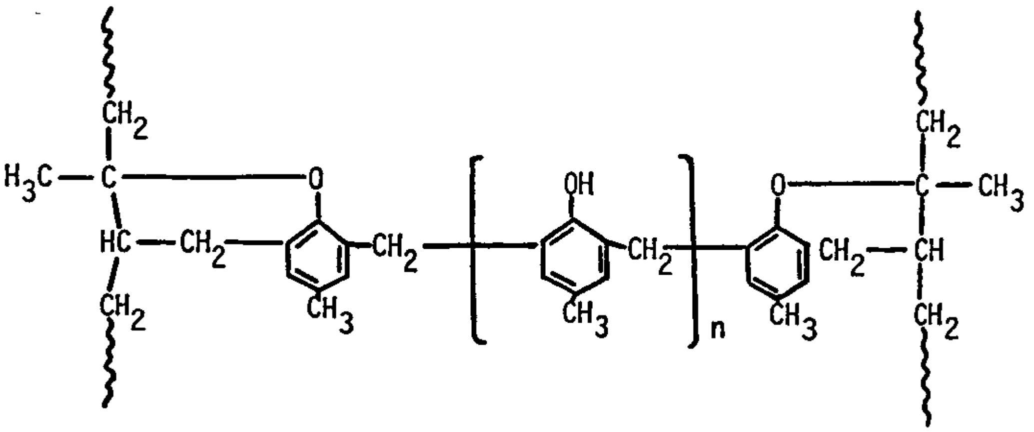
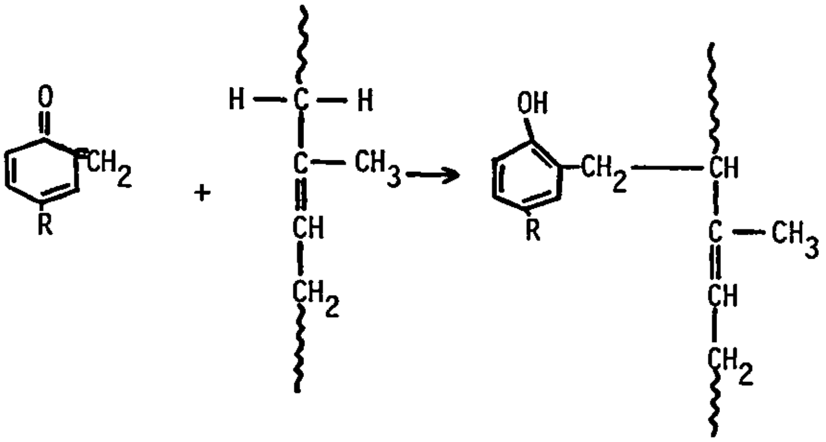
* Desmodur TT of Bayer



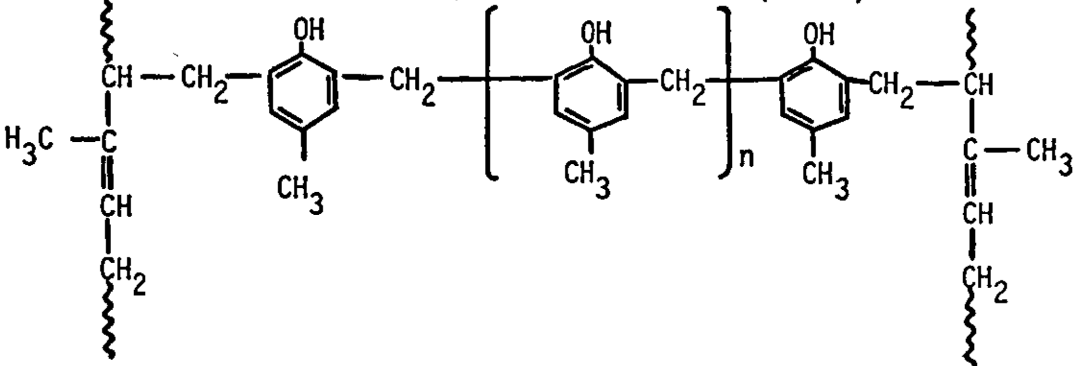
Crosslink (XVII)

Resins in which the phenolic and methylol hydroxyl groups are in the para-position could not possibly form chroman rings as predicted from the above theory. However it was shown that the product vulcanised rubber. In view of this observation and other experimental evidence, a methylene quinone intermediate was postulated to substitute the hydrogen at the alpha methylenic site (56) as shown below (equation 39):



(39)

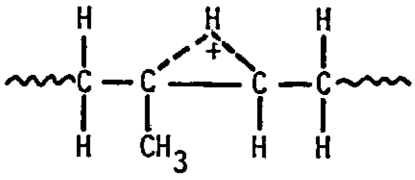
In the above case the structure of crosslink based on 2,6 dihydroxymethyl-4-methylphenol/formaldehyde resin would be (XVIII):



Crosslink (XVIII)

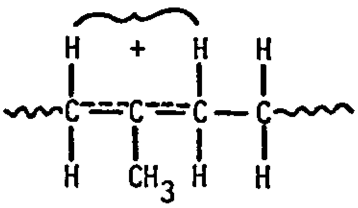
Ginzburg et al (57) found that the concentration of phenolic hydroxyl groups did not diminish, but that the methylol groups disappeared as ether groups were formed. The ether groups subsequently also gradually disappeared. These authors proposed that crosslinking was due to radicals formed by thermal degradation of the ether bonds, and this was confirmed by experiments in which MBT was used as a radical trap.

When stannous chloride was used as catalyst in the study by Ginzburg et al, it was found that ether bonds were not formed, and the phenolic hydroxyl group concentration fell by 50%. It was considered that stannous chloride (Sn $Cl_2.2H_2O$) accelerated the reaction at the double bonds of the rubber by transforming them into either of two possible intermediate π-complexes by proton donation as shown below [(XIX) and (XX)]:



(XIX)

or



(XX)

From the above complexes, two types of crosslinks were formed: one having a chroman structure with the other having a methylene bridge as discussed earlier.

Table 1.5 illustrates the mechanical properties of natural rubber cured with 2,6 dihydroxymethyl-4-methylphenol/formaldehyde resin. The tensile properties were based on ring samples.

TABLE 1.5

Mechanical properties of natural rubber cured with phenol/formaldehyde resin (56)

Concentration of resin (phr)	30	40
Cure time at 155°C (hr)	2	2
Tensile strength (MPa)	13.6	15.6
Elongation at break (%)	550	510
Modulus at 100% strain (MPa)	0.9	1.0
Hardness (Shore A)	40	45

1.2 A Summary of the Comparative Structural Features, Advantages and Disadvantages of Vulcanisates Cured with Common Curing Systems

The comparative structural features, advantages and disadvantages of natural rubber vulcanisates cured with the common curing systems can be summarised by means of a chart shown in Table 1.6.

1.3 Other Available Curing Systems for Natural and Polyisoprene Rubbers

1.3.1 Vulcanisation with Maleimides

Natural rubber can be vulcanised with certain monomaleimides or dimaleimides if a small quantity of peroxide is present to initiate the reaction (58,59). Thermal initiation was shown to produce a lesser extent of crosslinking than the peroxide initiation. The crosslinking reaction may also be induced by high energy radiation (44). Typical properties of vulcanisates cured with dimaleimides are shown in Table 1.7.

TABLE 1.6

A summary of the comparative structural features, advantages and disadvantages of natural rubber vulcanisates cured with common curing systems

Curing Systems	Structural Features	Advantages	Disadvantages
Conventional sulphur cure	Mainly polysulphidic linkages	Excellent initial vulcanisate properties; such as resistance to cyclic deformation, fatigue, tensile strength, tear strength and abrasion resistance	Poor thermal reversion characteristic and oxidative ageing.
Semi-EV	Intermediate between conventional sulphur cure and EV		
EV	Mainly mono sulphidic linkages	Thermally stable networks and the monosulphidic networks being more easily protected against oxidation than the polysulphidic networks. Good aged flex fatigue.	Poor resistance to flexing if the specimen passes through zero strain. Tensile strength, tear strength and abrasion resistance are usually not as high as the conventional cured vulcanisates. Resilience is often inferior.
Sulphur donor curing system	Similar to the EV		
Soluble-EV	Mainly mono sulphidic linkages	Similar to EV plus highly reproducible with respect to stiffness or modulus; less variation in strength and dynamic fatigue properties, improved resilience at high temperature and very low levels of creep and set.	Similar to EV.

TABLE 1.6 (continued)

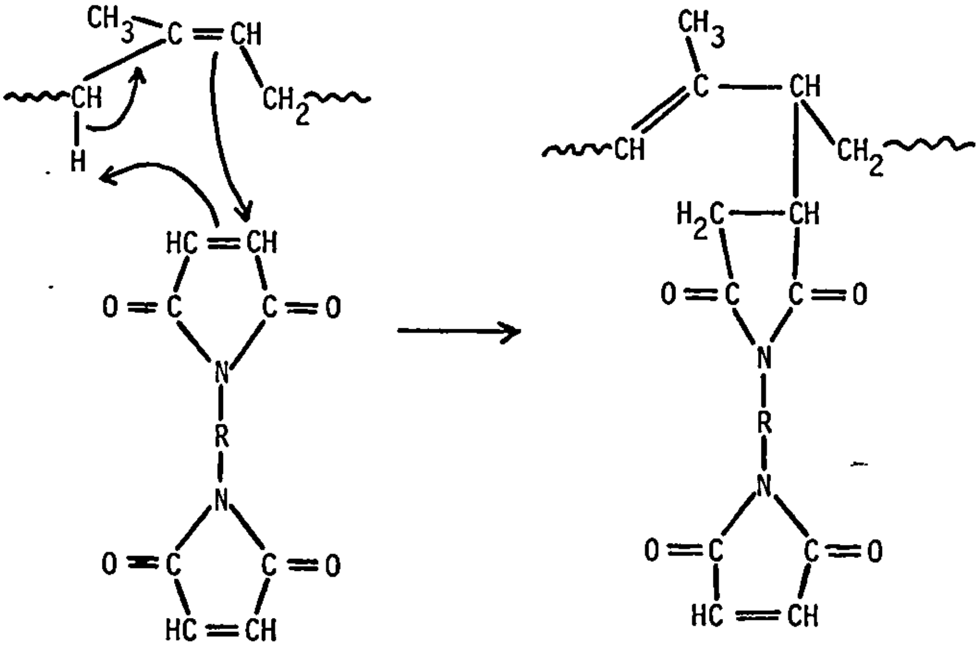
Curing Systems	Structural Features	Advantages	Disadvantages
Peroxides such as dicumyl peroxide	Consists of carbon-carbon linkages	Thermally stable networks and good resistance to oxidative ageing	Inferior strength to the conventional sulphur cure, poor resistance to cyclic deformation fatigue and unpleasant odours in the vulcanisate
Radiation cure	Consists of carbon-carbon linkages	Similar to the above peroxide cure	The vulcanisate has slightly lower tensile strength than the peroxide cured vulcanisate
Diurethane (Novor system)	Mainly urea linkages with some urethane linkages	Outstanding reversion resistance, physical properties unaffected by cure temperature, and excellent thermal stability	Inferior unaged flex fatigue as compared to the conventional sulphur cure.
Resin cure	Ambiguous	Good set resistance, low hysteresis, and non-reverting up to around 220°C	Age-resistance is poor

TABLE 1.7

Properties of natural rubber vulcanisates cured with dimaleimides (58)

Natural rubber (Pale Crepe)	100	100	100	100
N,N' m-Phenylenedimaleimide	3	3	3	3
Dicumyl peroxide	0.3	-	-	-
Cure conditions	45'/155°C	45'/155°C	45'/170°C	30'/184°C
Tensile strength (MPa)	13.4	7.9	6.9	10.3
Elongation at break (%)	525	800	700	750
Resilience (%)	85	72	77	79

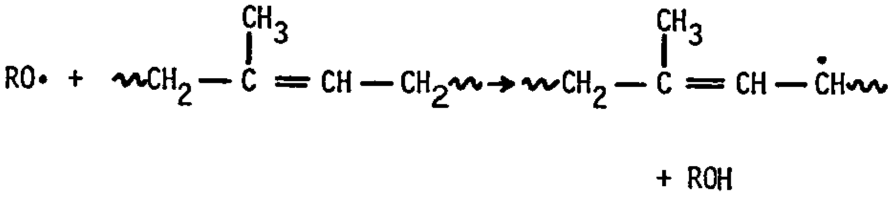
Evidence of the thermal induced vulcanisation occurring as shown above suggests either free radicals formed by thermal initiation or by the following reaction (equation 40):



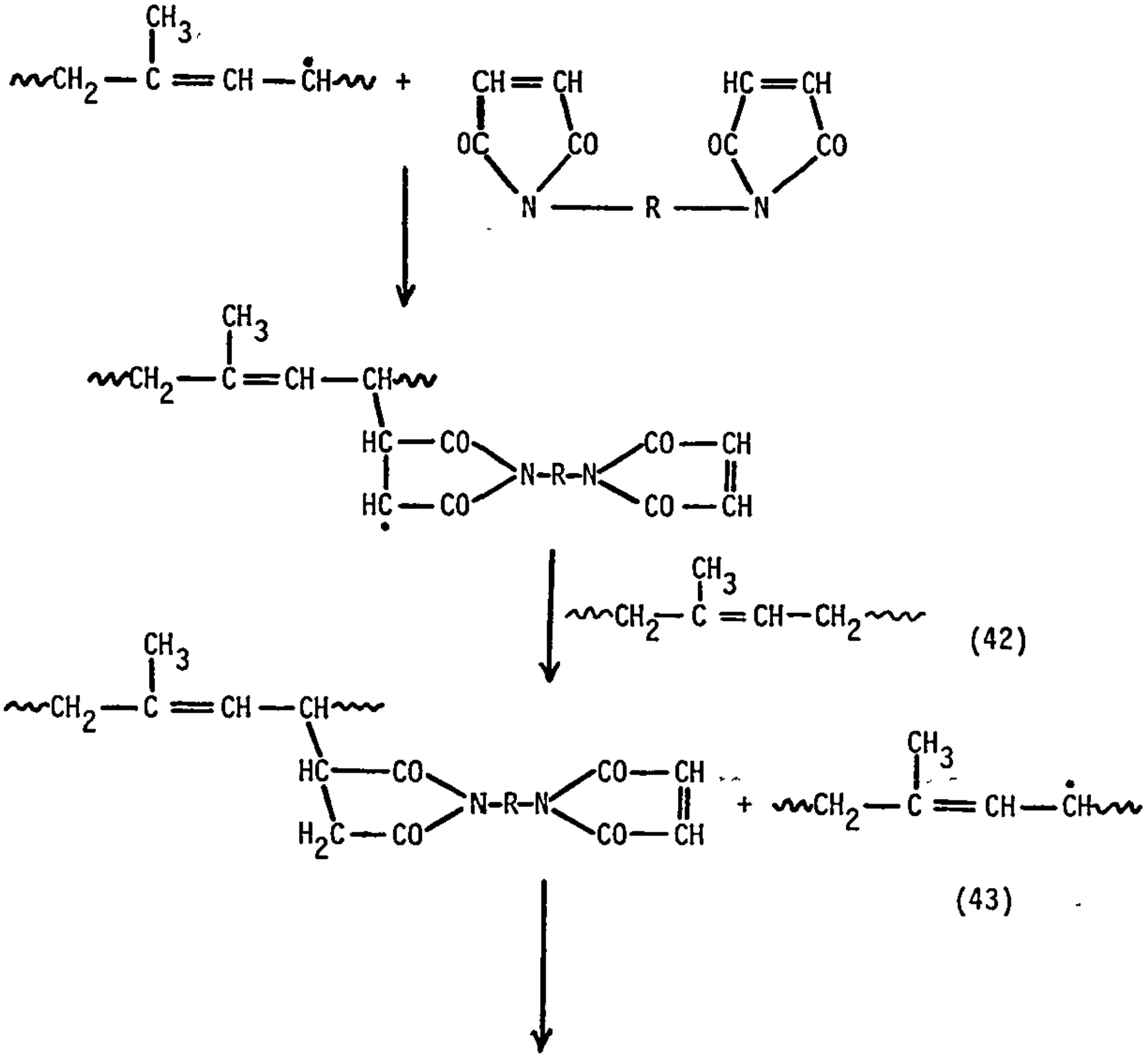
(40)

The principal mode of vulcanisation by dimaleimides in the presence of peroxide as initiator was proposed (58) as follows (equations 20 and 41-45):

$$ROOR \rightarrow 2RO\cdot \qquad (20)$$

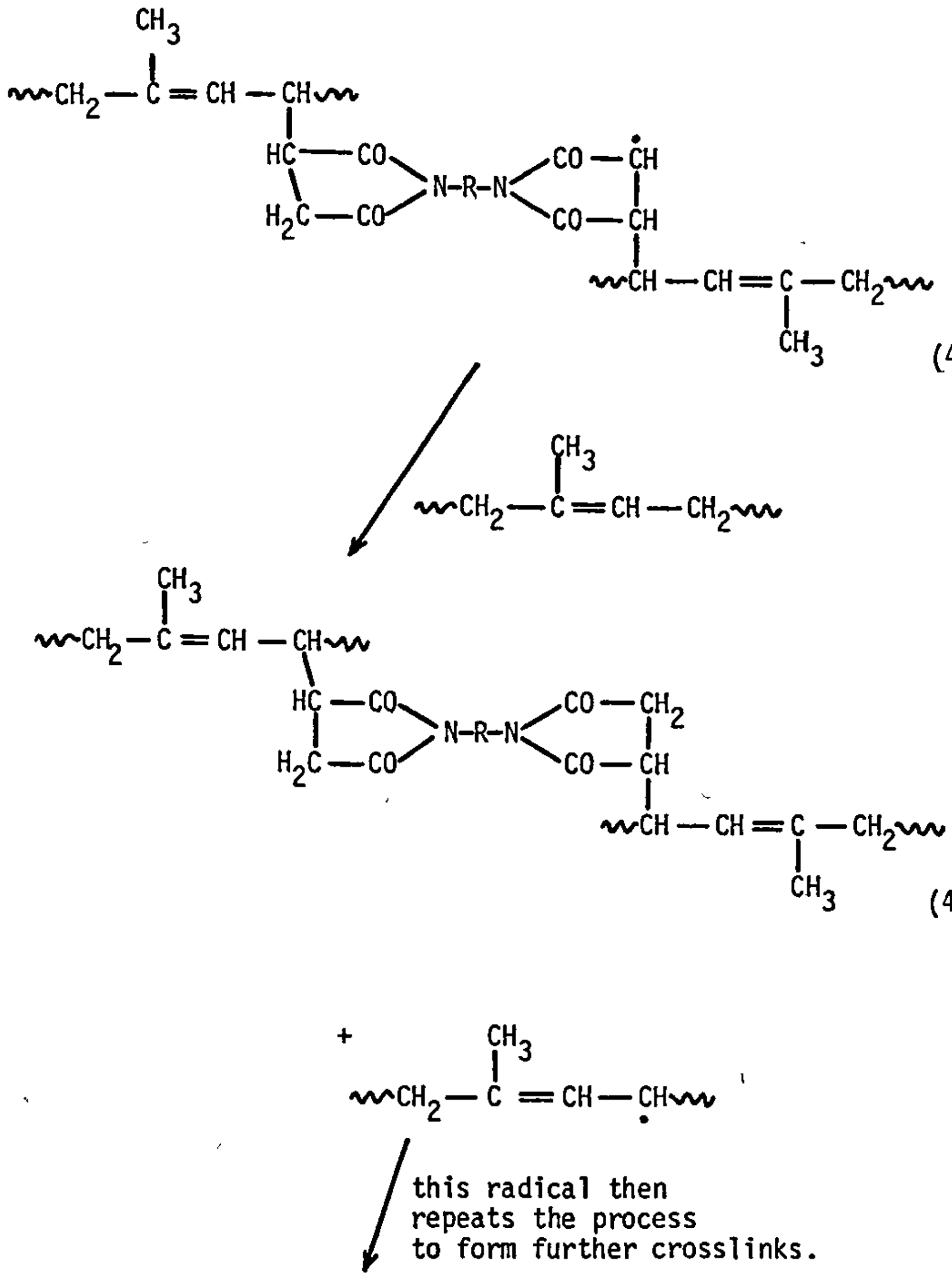


$$RO\cdot + \sim CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2\sim \rightarrow \sim CH_2-\overset{\overset{CH_3}{|}}{C}=CH-\dot{C}H\sim + ROH \qquad (41)$$



(42)

(43)

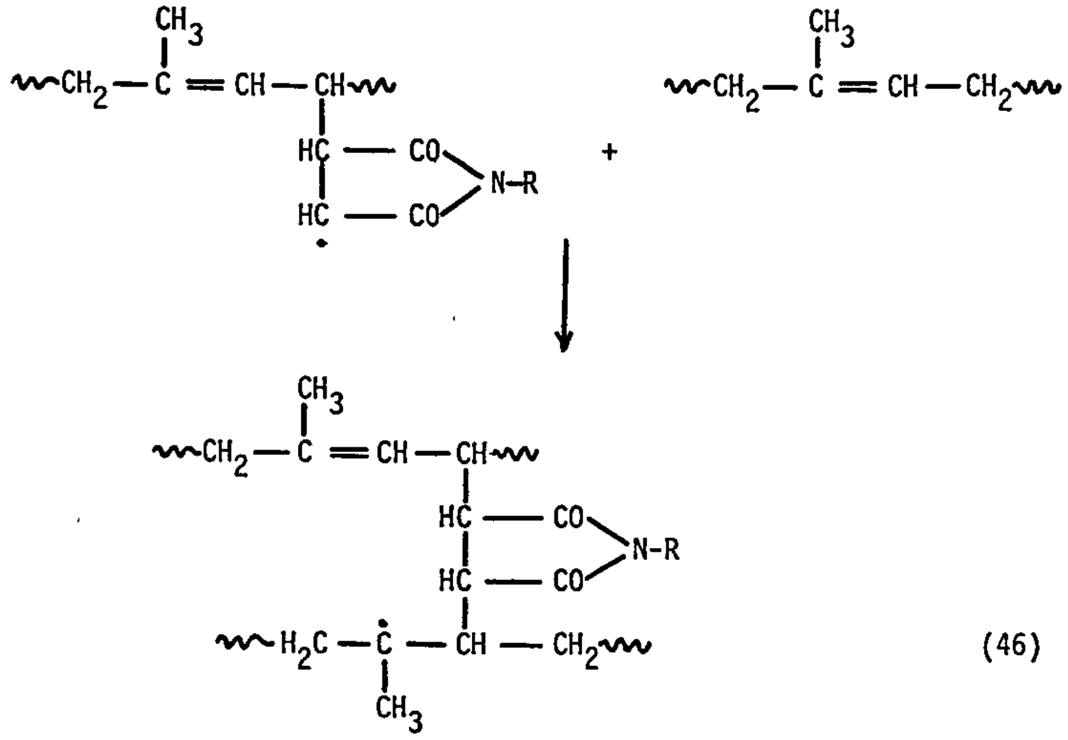


(44)

(45)

this radical then repeats the process to form further crosslinks.

Since the monomaleimide, N-phenylmaleimide, was shown to crosslink natural rubber in the presence of peroxide, but to a much lesser extent than does the corresponding dimaleimide it was suggested that the following mechanism (equation 46) could represent the primary crosslinking reaction for monomaleimides, but it is only a secondary reaction for dimaleimides.

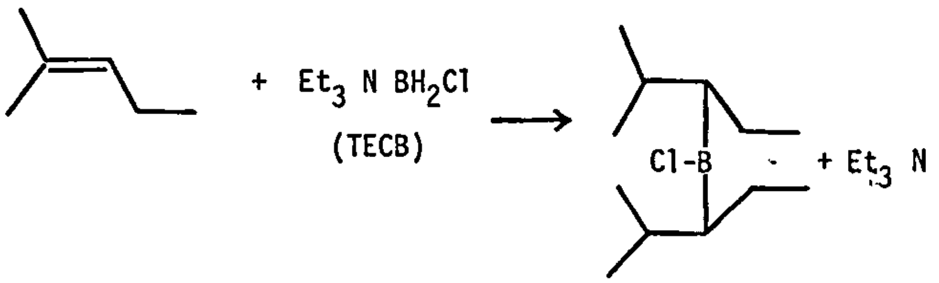

(46)

The above new radical may continue the propagation reaction or effect a chain transfer to form crosslinks.

1.3.2 Vulcanisation with Amine-Boranes

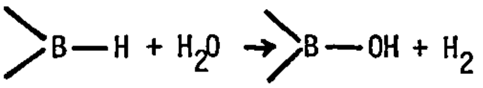
Natural rubber can be vulcanised by amine-boranes or amine-chloroboranes at normal vulcanisation temperatures (48). For example natural rubber vulcanisate prepared from RSS 1 100, HAF 50 and triethylamine-borane 3.2 possessed a relaxed modulus at 100% extension (MR 100) of 2.5 MPa and a tensile strength of 20.6 MPa.

The vulcanisation mechanism, believed to be analogous to that of the reaction of 2-methylpent-2-ene with triethylamine-chloroborane, can be represented as follows (equation 47):



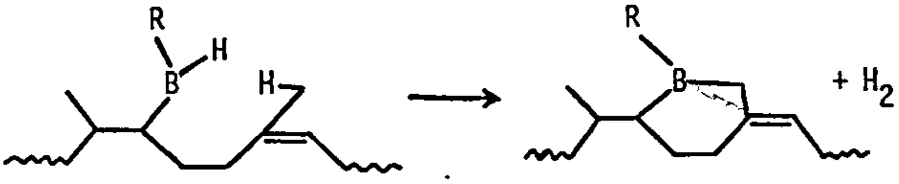
(47)

Porosity was observed in vulcanisates cured with amine-boranes and it was shown to be due to evolution of hydrogen. Porosity was found to arise in two ways. The first, and more substantial source was the reaction of borane with moisture in the rubber (equation 48).



(48)

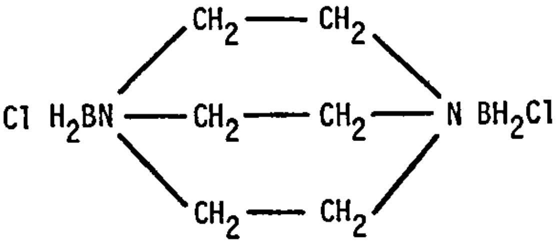
The second source of evolution of the gas is the reaction (equation 49) of the boron hydrogen with the hydrogen of the methyl group in the same natural rubber molecule to give hydrogen gas and a boron heterocycle.



(49)

(R = a second rubber chain)

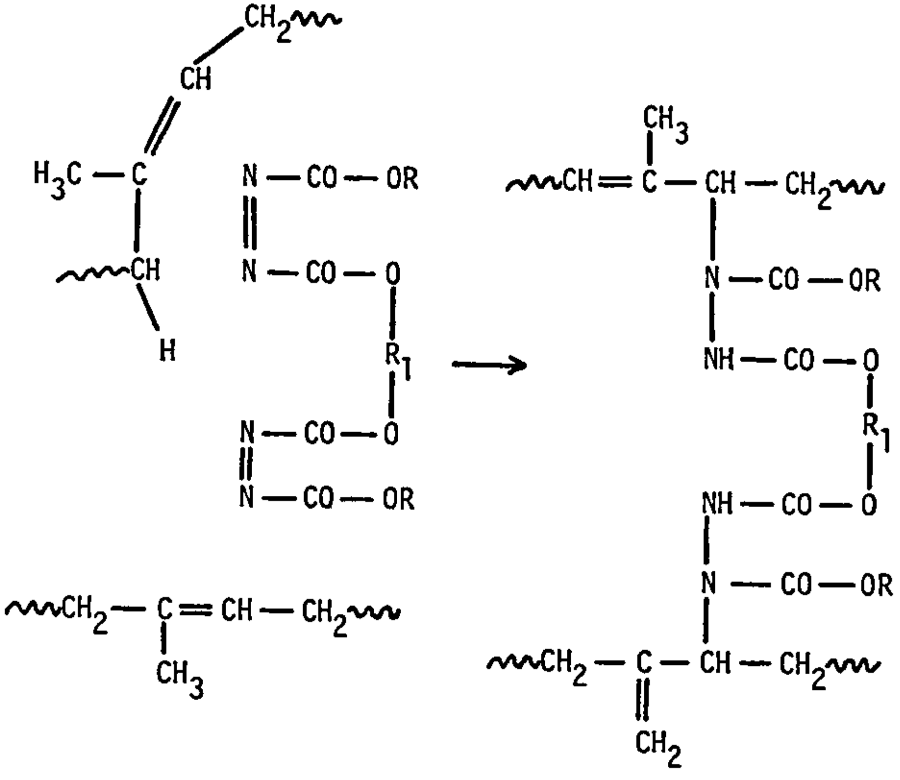
The problem of porosity was overcome by using a monosubstituted borane, BH_2X (in the form of a complex). For example, triethylamine chloroborane (TECB) and triethylenediamine chloroborane (TEDCB, XXI) both vulcanised gum or black-filled natural rubber in the presence of a drying agent (Caloxol C31) without porosity.



TEDCB (XXI)

1.3.3 Bisazoester Vulcanisation

The bisazoester curing system has been known for many years and so far they have not yet been used for technical purposes. The mechanism of the vulcanisation reaction, known chemically as an 'ene' reaction, can be represented as shown below (60,61) (equation 50):



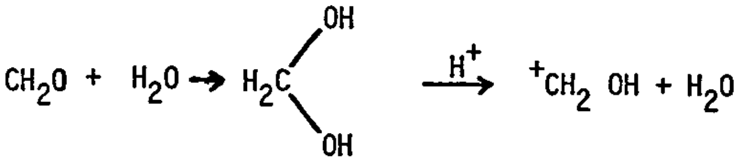
(50)

Natural rubber was vulcanised with bisazoesters by Rabjohn and co-workers (62,63) to various degrees of crosslinking and they found that the mechanical properties of the vulcanisates did not differ substantially from those of sulphur vulcanisates. In contrast to Rabjohn and co-workers (63), some workers (64) found that the properties of natural rubber vulcanisates produced with bisazoester differ from those of natural rubber vulcanisates produced with sulphur.

1.3.4 Vulcanisation by Aldehydes

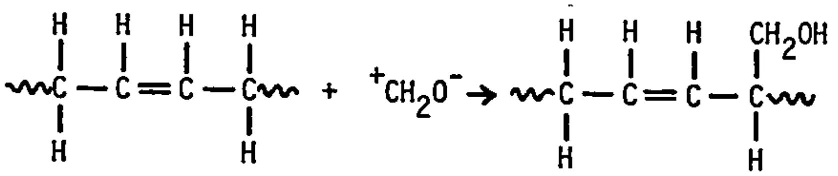
Aldehydes in the presence of acid catalysts will crosslink natural rubber (65). The crosslinking reaction in this vulcanisation system was not fully clarified. It was thought to be an ionic reaction, involving formation of the carbonium cation by aldehydes in the presence of an acid. The carbonium cation can be formed by either one of the following equations (equations 51 or 52).

$$CH_2O \rightarrow {}^{+}CH_2O^{-} \qquad (51)$$



(52)

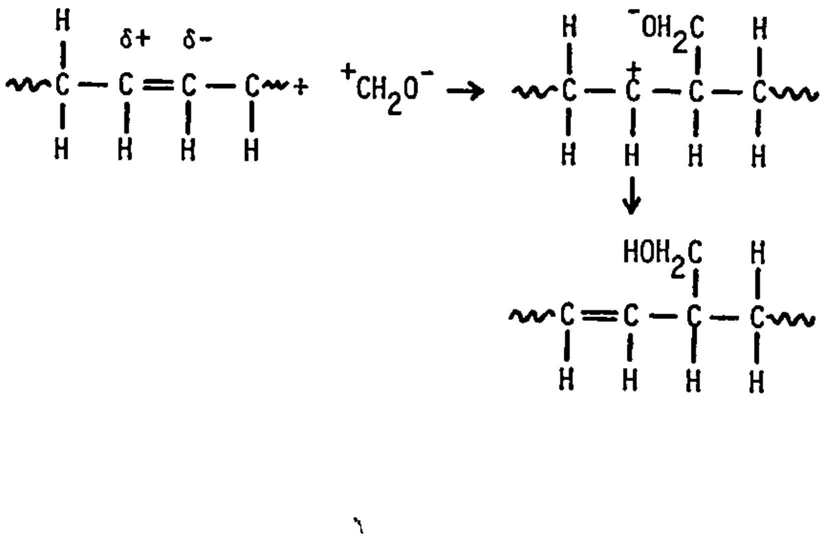
The carbonium cation can add either to the active α-carbon (equation 53) or to the polarised double bond (equation 54).



$$\sim CH_2-CH=CH-CH_2\sim + {}^{+}CH_2O^{-} \rightarrow \sim CH_2-CH=CH-CH(CH_2OH)\sim$$

(53)

or



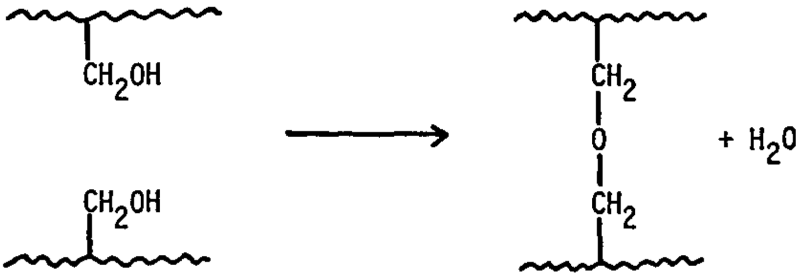
$$\sim CH_2-\overset{\delta+}{C}H=\overset{\delta-}{C}H-CH_2\sim + {}^{+}CH_2O^{-} \rightarrow \sim CH_2-\overset{+}{C}H-CH(CH_2O^{-})-CH_2\sim$$

$$\downarrow$$

$$\sim CH=CH-CH(CH_2OH)-CH_2\sim$$

(54)

An ether crosslink is formed by dehydration of the pendant methylol groups in the presence of acid during heating as shown below (equation 55):



(55)

Various aldehydes and acids have been studied (65) and the most efficient combination found for crosslinking natural rubber was α-polyoxymethylene and $SnCl_2.2H_2O$. The performance of this curing system in silica-filled natural rubber vulcanisate is shown below (Table 1.8):

TABLE 1.8

Physical properties of aldehyde cured vulcanisate* (65)

Cure time at 150°C (min)	10
Tensile strength (MPa)	12.3
Modulus at 300% strain (MPa)	9.2
Elongation at break (%)	380
Resilience (%)	22

1.3.5 Sulphur Chloride

Sulphur chloride was discovered as a vulcanising agent as early as 1846 by Alexander Parkes (66). The vulcanisation process can be done by dipping thin sections of natural rubber in a solvent of sulphur monochloride or by exposure to the vapour.

The mechanism of sulphur monochloride vulcanisation is not fully clarified. A free radical mechanism is favoured, particularly

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* Pale Crepe 2-100, α-polyoxymethylene-10, $SnCl_2.2H_2O$ - 10, Antioxidant-1, Stearic acid-1 and Nipsil VN3-58.

in the presence of an active hydrogen compound such as MBT initiators, although a polar reaction cannot be discounted (67,68); the crosslinks are probably disulphidic (68).

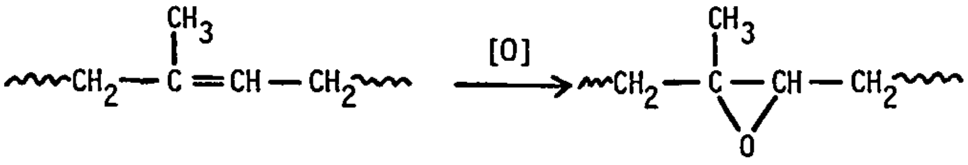
An acid scavenger, usually magnesium oxide, is included in the formulation to neutralise traces of hydrochloric acid formed during the reaction. The vulcanisates have a characteristic sulphurous odour, good strength but poor age-resistance.

1.3.6 Vulcanisation Through Chemical Modified Forms of Natural and Polyisoprene Rubbers

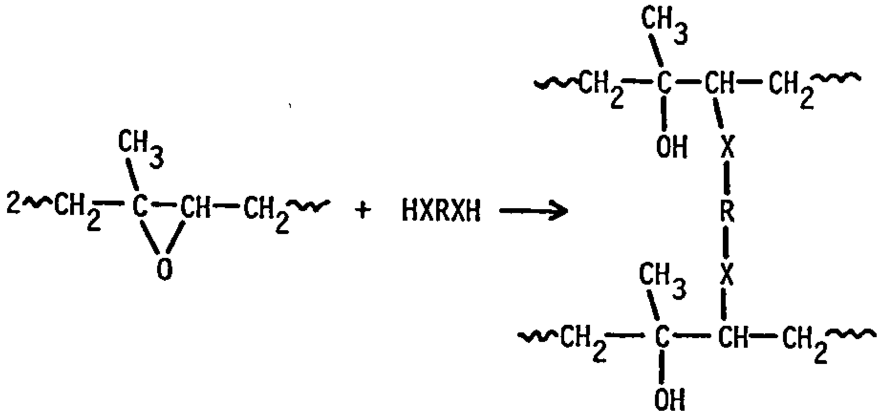
A number of curing systems have depended on a separate initial stage whereby reactive chemical groups are attached to the rubber molecule before vulcanisation.

Among these vulcanisation studies include the investigations done by the workers at MRPRA. Stabilised natural rubber latex was treated with perbenzoic acid (69), monochlorothiolacetic acid (70) or ethyl thioglycollate (71) to give epoxide groups (equation 56), chlorine-containing groups, and ester groups, respectively, on the rubber.

The epoxide groups can be crosslinked with diamines, dithiols, dibasic acids and acid anhydrides (equation 57), but the crosslinking was much slower than by conventional methods of vulcanisation.



(56)


(57)

The mono-chlorothiolacetic acid modified natural rubber can be crosslinked by dibasic pyridine compounds but the vulcanisate obtained was weak (72).

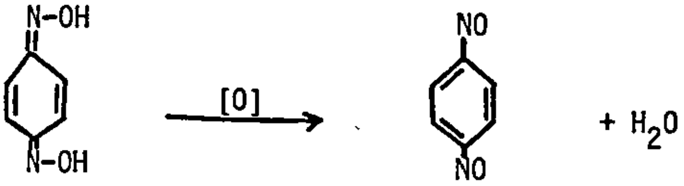
The ester groups attached to the natural rubber chain needs to be hydrolysed before crosslinking. The most effective method of crosslinking was a combination of calcium hydroxide and propylene glycol (71). The vulcanisates obtained showed marked creep under load, rapid stress relaxation at fixed strain and marked sensitivity of their properties to the rate of extension and to water.

Natural rubber was recently chemically modified to give pendant hydroxyl groups (73). These hydroxyl groups were then crosslinked by diphenyl acetonedicarboxylate and diphenyl malonate to form β-keto-ester or malonate crosslinks. The resulting vulcanisates showed high stress relaxation rates in the temperature range 120 to 160°C and some degree of remouldability at 180°C.

1.3.7 Quinoid Systems

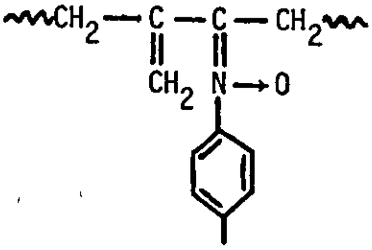
The term quinoid cure usually refers to the crosslinking of rubbers, which have allylic hydrogens, by quinone dioxime or its esters; although other quinone derivatives are also effective. Examples of quinone derivatives used to crosslink natural rubber include: chloranil and GMF (commercial p-quinone dioxime) (74).

In most cases, oxidising agents are required; the oxides of lead, Pb_3O_4 and PbO_2, are most commonly used. The mechanism is thought to involve the formation of nitroso groups by oxidation (75) (equation 58):



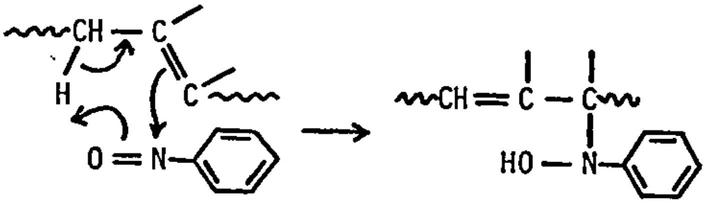
(58)

Early workers felt that the nitroso groups reacted with rubber to give nitrones (76-79). In the case of natural rubber a structure of the type shown below would be formed (XXII).



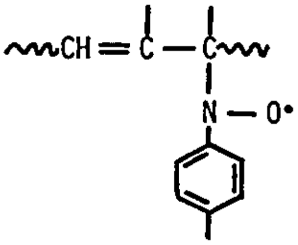
(XXII)

More recently, Sullivan (80) has postulated that the nitroso group reacts with rubber as follows (equation 59):



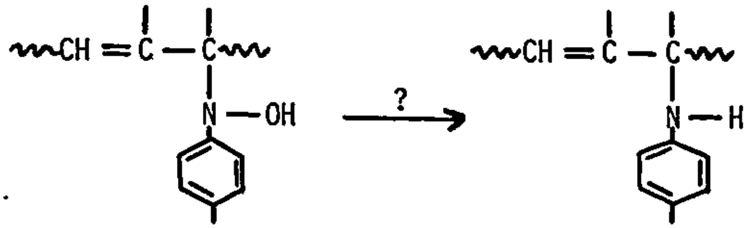
(59)

Stable free radicals were indicated by electron spin resonance spectra. A structural assignment for the radicals can be represented as (XXIII).



(XXIII)

This could conceivably be oxidised to a nitrone. However, there is recent evidence that ultimately the attachment to rubber occurs through an amine linkage which is formed by an unknown mechanism (48) (equation 60).



(60)

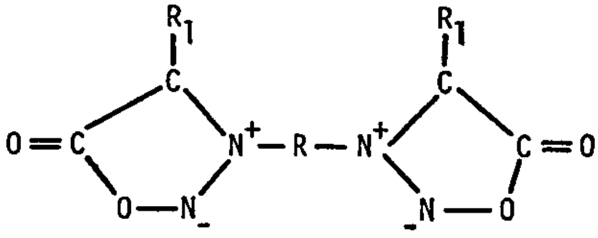
Quinoid cures of natural rubber show little tendency to revert at elevated temperature. However the retention of tensile strength on heat ageing is poor which suggests the occurrence of some reaction which inhibits stress-crystallisation (81). Short scorch times are also encountered in natural rubber mixes.

1.3.8 Vulcanisation Using Organic Halogen Compounds

Most of the investigations on organic halogen compounds, such as octachloro-3-cyclohexen-1-one (OCTA) and di(trichloromethyl) sulfone, were used in combination with sulphur and certain metal compounds, such as magnesium oxide for curing EPR (82-87). Some of these halogenated compounds will vulcanise natural or polyisoprene rubbers, but the onset of reaction tends to be very rapid. Mixes particularly in the presence of carbon black, are extremely scorchy. The vulcanisation process involves hydrogen abstraction to form polymer radicals, which combine to form carbon-carbon crosslinks (82,88).

1.3.9 Vulcanisation using Bis Sydnones

Bis sydnones of general structure (XXIV) shown will crosslink either natural or polyisoprene rubbers which contain carbon-carbon double bonds bearing at least one hydrogen atom (89).

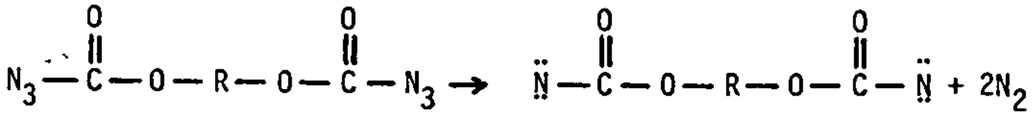


(XXIV)

The crosslinking agents are not affected by air or moisture, and the products are said to be tough and solvent-resistant.

1.3.10 Vulcanisation using Bisazidoformates and Bisazides

Bisazidoformates and bisazides are effective crosslinkers for unsaturated rubbers (90,91). Bisazidoformate decomposes under the influence of heat (equation 61) whilst bisazide decomposes under the influence of ultraviolet light (equation 62) to give a highly reactive bis-nitrene which adds to the double bonds of the unsaturated rubbers to give a crosslinked product (equation 63).

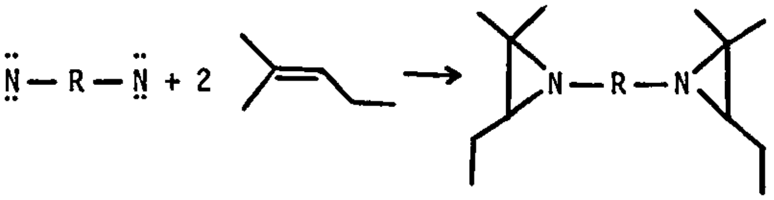


$$N_3-\overset{\overset{O}{\|}}{C}-O-R-O-\overset{\overset{O}{\|}}{C}-N_3 \rightarrow \underset{\cdot\cdot}{\overset{\cdot\cdot}{N}}-\overset{\overset{O}{\|}}{C}-O-R-O-\overset{\overset{O}{\|}}{C}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{N}} + 2N_2$$

(Bisazidoformate) (61)

$$N_3-R-N_3 \rightarrow \underset{\cdot\cdot}{\overset{\cdot\cdot}{N}}-R-\underset{\cdot\cdot}{\overset{\cdot\cdot}{N}} + 2N_2 \qquad (62)$$

(Bisazide)

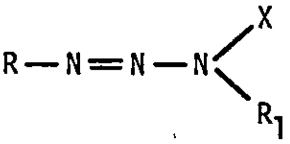


(63)

Bisazide (91) is particularly recommended for crosslinking cyclised natural rubber, whilst bisazidoformate such as tetramethylene bis-azidoformate (90) is used to cure uncyclised natural rubber containing HAF black to a high strength (25 MPa). Blowing, as the result of evolution of nitrogen, appears in general to be a function of compound viscosity, state of cure and mould pressure. No porosity was detected in the vulcanisates investigated.

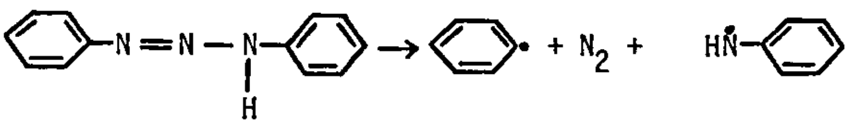
1.3.11 Aromatic Diazoamino Compounds

Aromatic diazoamino compounds of the general formula

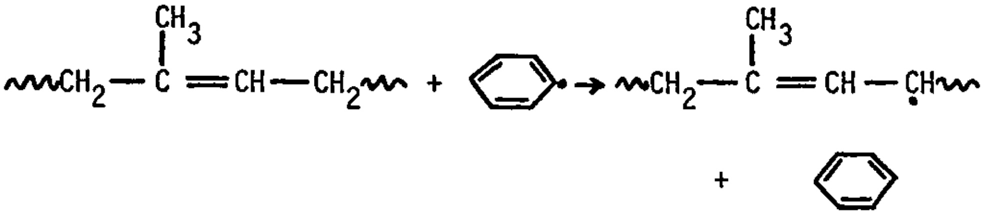


, such as phenyldiazoaminobenzene and p-tolyl disazoamino-p-toluene will crosslink both natural and polyisoprene rubbers (74,92,93).

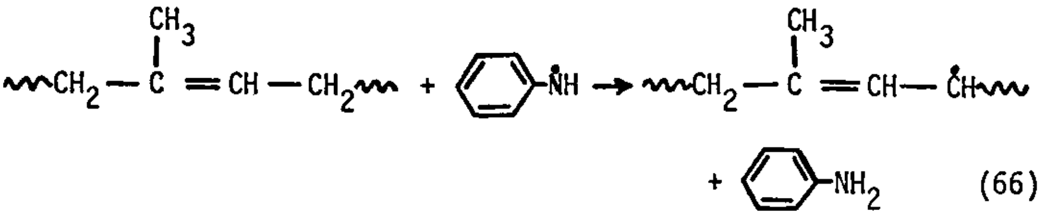
Cure is rapid in natural rubber (93) at moderate temperature (e.g.. 5 minutes at 143°C). Phenyldiazoaminobenzene crosslinks natural rubber according to the proposed reaction scheme of equations 64-67 (93).



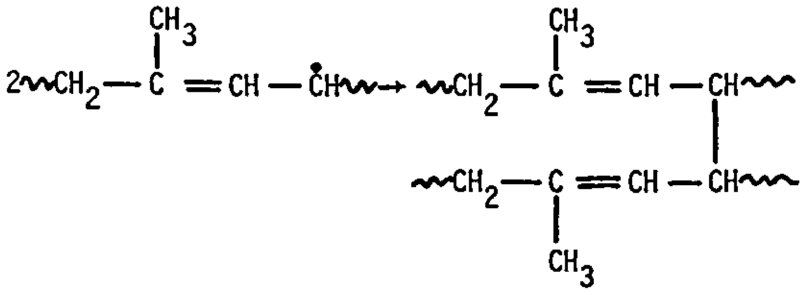
(64)



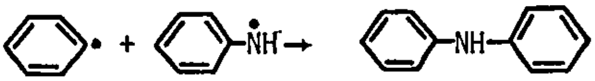
(65)



(66)



(23)



(67)

The products obtained by vulcanisation with diazoamino compounds have a tendency to be porous, and when prepared from natural rubber, age poorly and become sticky (93).

1.3.12 Polynitroarenes

Aromatic polynitro-compounds, such as m-dinitrobenzene and 1,3,5 trinitrobenzene, are active crosslinking agents for unsaturated polymers (74,94,95,96). Basic oxides, such as lead oxide and barium oxide, are essential activators (95,96).

1.3.13 Selenium and Tellurium

Selenium and tellurium, in the same atomic group as sulphur, vulcanise natural rubber in the presence of organic accelerators (97). Vulcanisate properties are good with selenium, but the rate of crosslinking is slower than achieved with sulphur. Both Se and Te reduce the tendency to reversion when used as partial replacements for sulphur (98,99).

1.3.14 Nascent Sulphur

Thin sections of natural rubber were vulcanised by dipping successively in solvent solutions of H_2S and SO_2 at room temperature (100).

1.3.15 Miscellaneous Curing Systems

The above includes nitrogen sulphide (101), phosphorous sulphide (102) and sulphur thiocyanates (103), which were used to vulcanise natural rubber.

1.4 Objectives of the Research

Vulcanisation of unsaturated rubber by peroxides is traditionally practiced when maximum heat stability is required in the vulcanisate. Such vulcanisates usually have the disadvantages of relatively poor strength and resistance to cyclic deformation fatigue to that of the conventional polysulphidic sulphur cure (23,24) and sometimes are accompanied by unpleasant odours. The objective of this research work is to find an alternative method of vulcanisation of unsaturated rubber, with particular reference to natural and polyisoprene rubbers, to give heat stable vulcanisate of reasonable strength.

Earlier pioneering efforts to use peroxycarbamate as crosslinker for copolymer of vinylidene fluoride and hexafluoropropene were unsuccessful for many reasons (104). Porosity was observed in the vulcanisate and required coagent to eliminate porosity and also to increase the crosslink density. Against this background a research programme was planned to investigate whether bisperoxycarbamates could be used as vulcanising agents for diene rubbers; it had the following sequence:

1. Synthesise various bisperoxycarbamates and investigate the crosslinking ability of this class of peroxides in natural and polyisoprene rubbers. Polyisoprene rubber (Cariflex IR 305) was chosen so as to investigate the effect of vinyl content on crosslinking efficiency.

2. To investigate the effect of variable structures of the bisperoxycarbamates on cure characteristics, crosslinking efficiency, tensile properties and ageing behaviour.

3. To apply the bisperoxycarbamate cure system to black and silica-filled vulcanisates.
4. To extend the use of the bisperoxycarbamates in other types of unsaturated rubbers such as polychloroprene, styrene-butadiene, acrylonitrile-butadiene and EPDM rubbers.

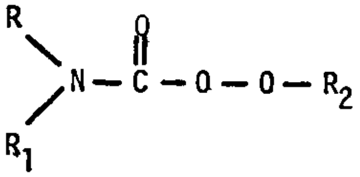
CHAPTER 2

PEROXYCARBAMATES - SYNTHESIS AND REACTIONS WITH POLYISOPRENE RUBBER

2.1 Introduction

2.1.1 Historical development in the synthesis of peroxycarbamates

Organic peroxycarbamates are esters derived from the unknown peroxycarbamic acids and may be represented by the general formula:



(XXV)

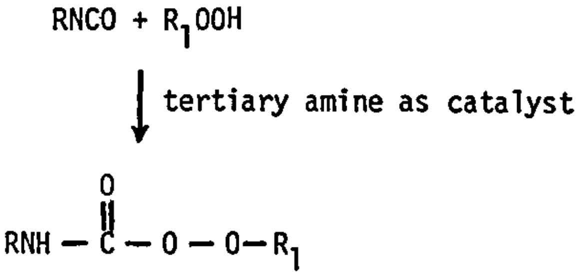
Davies and Hunter (105) were the pioneers in the synthesis of such compounds and they successfully prepared tertiary butyl peroxycarbamate and four of its N-monosubstituted derivatives (phenyl, α-naphthyl, p-xenyl, (-)-menthyl) by three methods:

i) RNCO + t C_4H_9OOH with pyridine as catalyst.

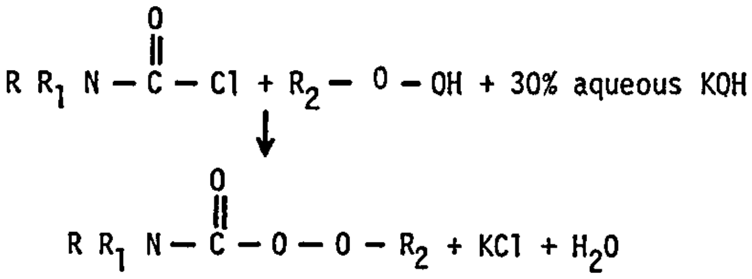
ii) RNHCO Cl + t C_4H_9OOH with pyridine as acid acceptor.

iii) RNH_2 + t $C_4H_9OOCO\ Cl$.

Later in 1957, additional esters of N-substituted peroxycarbamic-acids were prepared by Pederson (106) by the two general methods (equations 68 and 69):



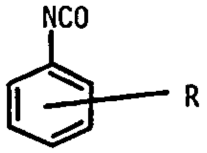
$$\mathrm{RNCO} + \mathrm{R_1OOH} \xrightarrow{\text{tertiary amine as catalyst}} \mathrm{RNH-\overset{O}{\overset{\|}{C}}-O-O-R_1} \qquad (68)$$



$$R\,R_1\,N-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + R_2-O-OH + 30\%\ \text{aqueous KOH} \longrightarrow R\,R_1\,N-\overset{\overset{\displaystyle O}{\|}}{C}-O-O-R_2 + KCl + H_2O \qquad (69)$$

The first method is applicable to the synthesis of only peroxycarbamates containing the -NH- group, while the second method can be used for the preparation of all types although it is less suitable for the N-monosubstituted compounds. Lists of the peroxycarbamates prepared by Pederson are shown in Table 2.1.

In an attempt to study the decomposition of peroxycarbamates and their efficiency as initiators in vinyl polymerisation, O'Brien et al (107) added another peroxycarbamate (cumyl N-phenylperoxycarbamate) to the above list. Later in 1959 the same workers (108) synthesised a series of substituted t-butyl N-phenyl peroxycarbamates by addition of t-butyl hydroperoxide to substituted phenyl isocyanate as shown below:



(XXVI)

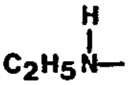
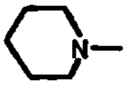
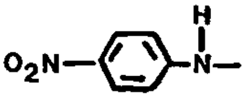
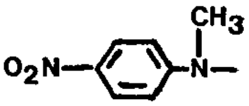
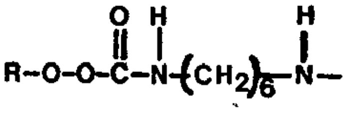
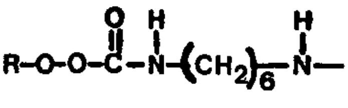
where R = mCH_3, o-Cl, m-Cl, p-Cl, 2,5-Cl_2, p-Br, m-NO_2, p-NO_2.

M Lederer and O Fuchs patented another two new peroxycarbamates (109) 2,6-tolyl N,N'-bis (tert-butyl) peroxycarbamate and hexamethylene N,N'-bis-(t-amyl) peroxycarbamate.

All the above peroxycarbamates were prepared using diisocyanates which were small molecules. However, the first peroxycarbamate based on urethane type pre-polymer diisocyanate was successfully prepared by Tobolsky et al (110). These peroxycarbamates were synthesised by the reaction of polyester or polyether based urethane

TABLE 2·1 Preparation and properties

of $A{-}\overset{O}{\overset{\|}{C}}{-}O{-}O{-}R$ (106)

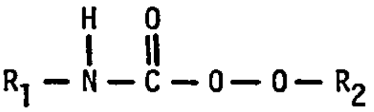
A	R^a	Method by equations	Solvent	Catalyst	Yield %	m.p.t.^{d} ^oC
 $C_2H_5\overset{H}{\overset{\vert}{N}}{-}$	R'	68	Benzene	Pyridine	18	40
$(CH_3)_2N{-}$	R'	69	None	-	54	Liquid
$(CH_3)_2N{-}$	R"	69	None	-	40	60
$(C_2H_5)_2N{-}$	R'	69	None	-	43	Liquid
	R'	69	None	-	81	Liquid
	R'	68	Benzene	Triethyl-amine	59	93
	R'	69	Petrol ether	-	68	66
 $R{-}O{-}O{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{\overset{\vert}{N}}{-}(CH_2)_6{-}\overset{H}{\overset{\vert}{N}}{-}$	R'	68	Benzene	Pyridine	6	65
 $R{-}O{-}O{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{\overset{\vert}{N}}{-}(CH_2)_6{-}\overset{H}{\overset{\vert}{N}}{-}$	R"	68	Benzene	Triethyl-amine	57	105

a— R' is tertiary butyl
R" is alpha-cumyl

d— In general the compounds decomposed on melting prepolymers containing one or several isocyanate groups per chain with tertiary-butyl hydroperoxide yielding long-chain peroxycarbamates.

2.1.2 Structures of peroxycarbamates

There are two possible structures for a peroxycarbamate namely:

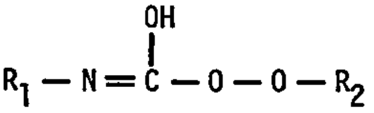


$R_1-N(H)-C(=O)-O-O-R_2$

(lactam form)

(XXVII)

or



$R_1-N=C(OH)-O-O-R_2$

(lactim form)

(XXVIII)

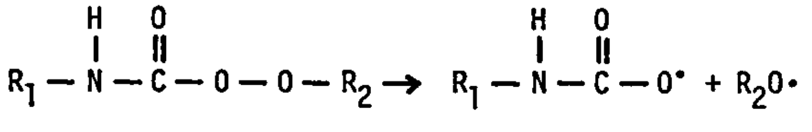
The proportion of lactim form would be expected to be largest in the case of N-arylamides where stabilisation of this form will result from conjugation between the C=N double bond and the aromatic ring. Davies and Hunter (105) have demonstrated the presence of lactam forms in the infra-red absorption spectra of tertiary-butyl N-phenyl and N-1-naphthyl peroxycarbamate but the evidence for the existence of a proportion of the lactim forms was inconclusive. No evidence for a lactim form was found in the i.r. spectra of the bisperoxycarbamates.

2.1.3 Properties of peroxycarbamates

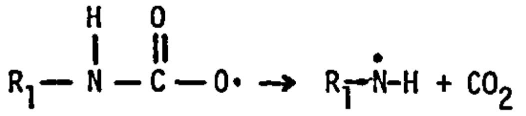
Davies and Hunter (105) have shown that peroxycarbamates such as tert-butyl N-phenylperoxycarbamate catalysed the polymerisation of styrene at 85°C, confirming that it contains a peroxide linkage.

Further confirmation of the ability of peroxycarbamates in initiating vinyl polymerisation was given by O'Brien et al (107). They have shown that tertiary-butyl and cumyl N-phenyl peroxycarbamates exhibit normal free-radical polymerisation kinetics in styrene with rate of polymerisation proportional to the first power of monomer concentration and to the half power of initiator concentration. It was shown that the radicals formed from tertiary-butyl N-phenyl peroxycarbamate efficiently initiate chains while the radicals from cumyl derivative are less efficient. The tertiary-butyl N-naphthyl peroxycarbamate, however, exhibits induced decomposition and consequently a strong dependence of initiating efficiency with initiator concentration.

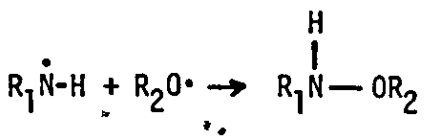
The decomposition products of the three peroxycarbamates studied appear to be carbon dioxide, imino radical, and an alkoxy or aralkoxy radical. This is supported by the evidence of hydrazo and azo compound formation in decomposition studies. Carbon dioxide is lost simultaneously with cleavage of the peroxide. Alternatively decarboxylation of the carbamate free radical is a more rapid reaction than that involving its addition to styrene; the reason for this conclusion is the absence of a carbonyl absorption in the infra-red spectrum of polystyrene when polymerisation of styrene is initiated by tert-butyl N-phenyl peroxycarbamate. The observations of O'Brien and co-workers (108) suggest that the decomposition of peroxycarbamates in the solid state, in solution or in the presence of vinyl monomers can be represented as shown in equations 70-76:



$$R_1-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-O-O-R_2 \rightarrow R_1-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-O^{\cdot} + R_2O\cdot \qquad (70)$$



$$R_1-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-O\cdot \rightarrow R_1-\dot{N}-H + CO_2 \qquad (71)$$



$$R_1\dot{N}-H + R_2O\cdot \rightarrow R_1\overset{H}{\overset{|}{N}}-OR_2 \qquad (72)$$

$$2R_1\dot{N}\text{-H} \rightarrow R_1NHNHR_1 \xrightarrow{-2H} R_1N{=}NR_1 \qquad (73)$$

$$R_1\dot{N}\text{-H} + \underset{\text{(solvent)}}{HS} \rightarrow R_1NH_2 + S\cdot \qquad (74)$$

$$R_1\dot{N}\text{-H} + CH_2{=}CHX \rightarrow R_1NHCH_2-\dot{C}HX \qquad (75)$$

$$R_2O\cdot + CH_2{=}CHX \rightarrow R_2OCH_2-\dot{C}HX \qquad (76)$$

The reactivities of peroxycarbamates in vinyl polymerisation with related compounds have been studied by Russian workers (111). They found that compounds containing the group $>N-\overset{O}{\overset{\|}{C}}-O-O$ are generally more active than the corresponding peroxide with the grouping $>N-CH_2-O-O-$.

Long chain peroxycarbamates, synthesised by Tobolsky and Rembaum (110), were similarly found to initiate the polymerisation of a wide variety of vinyl monomers and dienes leading to a new class of block polymers of very interesting physical properties. In contrast to the findings of O'Brien and co-workers (107) evolution of carbon dioxide was not observed during the formation of the block polymer. Furthermore the weight losses after polymerisation were too small to account for complete loss of carbon dioxide.

All the above studies on peroxycarbamates concerned their synthesis, decomposition and use - as initiators in vinyl or diene polymerisation. The only attempt to use one as a crosslinking agent was reported in 1960 (104). In this particular work N,N-dimethyl tertiary-butyl peroxycarbamate was used as a free radical generator, in combination with free radical acceptors, in curing a copolymer of vinylidine fluoride and hexafluoropropene.

2.2 Reactions of Polyisoprene Rubber with Mono or Bisperoxycarbamates

2.2.1 Materials

Hydroperoxide

Tertiary butyl hydroperoxide (70% solution in water) was obtained from Koch Light Laboratories Ltd. The hydroperoxide was extracted by petroleum-ether 30/40°C in a separating funnel. The petroleum-ether was then removed under reduced pressure and the hydroperoxide obtained was dried with anhydrous Mg SO_4.

Cumene hydroperoxide of Koch Light (a product stabilised with 6% of a 15% w/w slurry of sodium bicarbonate and water) was added to a 25% solution of sodium hydroxide below 30°C. Crystals of the sodium salt of the hydroperoxide were collected and washed twice with benzene. The crystals were then dissolved in distilled water, and the pH was adjusted to 7.5. The hydroperoxide was extracted from the solution by petroleum-ether and then dried with anhydrous Mg SO_4.

Peroxide

Dicumyl peroxide (Perkadox SB) of 95% purity was obtained from Akzo Chémie.

Diisocyanate

Phenyl isocyanate (98%, Aldrich Chemical Co Ltd) and 1,6 hexamethylene diisocyanate (Bayer) were used as received.

Solvent

Benzene (Analar grade) was distilled over sodium and dried with anhydrous Mg SO_4. Petroleum ether 30/40°C, n-heptane, toluene, methanol and acetone were of highest available commercial purity and used as received.

Catalyst

Pyridine and triethylamine were of highest available commercial purity and were used as received.

Nitrogen

White spot nitrogen (B.O.C) was dried by passing through silica gel guard tubes before use.

Polymer

Polyisoprene rubber (Cariflex IR-305) was obtained from Shell Chemicals (UK) Ltd and had the following specified properties:

Structural purity,	% cis-1,4	-	92.0
	% trans-1,4	-	3.0
	% 3,4	-	5.0
Volatile matter, % wt			0.2
Ash content, % wt			0.05
Stabiliser (non-staining) content, % wt			0.13
Specific gravity at 25°C			0.90

The rubber was purified by dissolving in toluene and then precipitated by methanol addition. The precipitated rubber was dried under reduced pressure and kept in a flask which was then filled with nitrogen and stored in a refrigerator.

In the case of preparation of vulcanisates based on dicumyl peroxide as a control, the polyisoprene rubber was not purified.

2.2.2 Reaction of polyisoprene rubber with monoperoxycarbamate (t-butyl N-phenyl peroxycarbamate)

2.2.2.1 Synthesis of t-butyl N-phenylperoxycarbamate

t-butyl N-phenylperoxycarbamate was prepared as follows. One-tenth of a mole each of t-butyl hydroperoxide (9.0 gm) and phenyl isocyanate (21.9 ?? gm) and a few drops of pyridine were dissolved in

11.9

1mole of phenyl isocyanate = 119

Based on reference (108)

100 ml dry benzene in a N_2 atmosphere obtained with the passage of dry nitrogen gas. The temperature was maintained below $30^{o}C$. After 30 minutes benzene was removed under reduced pressure, and the residue was recrystallised from petroleum-ether $30/40^{o}C$. The t-butyl N-phenylperoxycarbamate was stored in a refrigerator at $4^{o}C$. Infra-red spectrum and melting point of the peroxycarbamate was taken using Pye-Unicam SP 200G Grating Infra-red Spectrophotometer and by DSC observation using a Du Pont 990 Thermal Analyser respectively. A detailed description of the Thermal Analyser is given in Chapter 3.

Theoretical yield	=	20.9 gm
Practical yield	=	14.2 gm
	=	68%
Decomposition Temperature	=	$83^{o}C$ (Figure 2.1)
Infra-red peaks,		O-O - 850 cm^{-1}
observed as		C-O - 1190 cm^{-1}
characteristic		$C-(CH_3)_3$ - 1375 cm^{-1} and 1400 cm^{-1}
spectra, were:		C=O - 1735 cm^{-1}
(Figure 2.2)		CH stretching - 2950 cm^{-1} and 2997 cm^{-1}
		CH aromatic - 3030 cm^{-1}, 3060 cm^{-1} and 3140 cm^{-1}
		NH - 3240 cm^{-1}

2.2.2.2 Heat treatment of a mixture of polyisoprene rubber and t-butyl N-phenyl peroxycarbamate

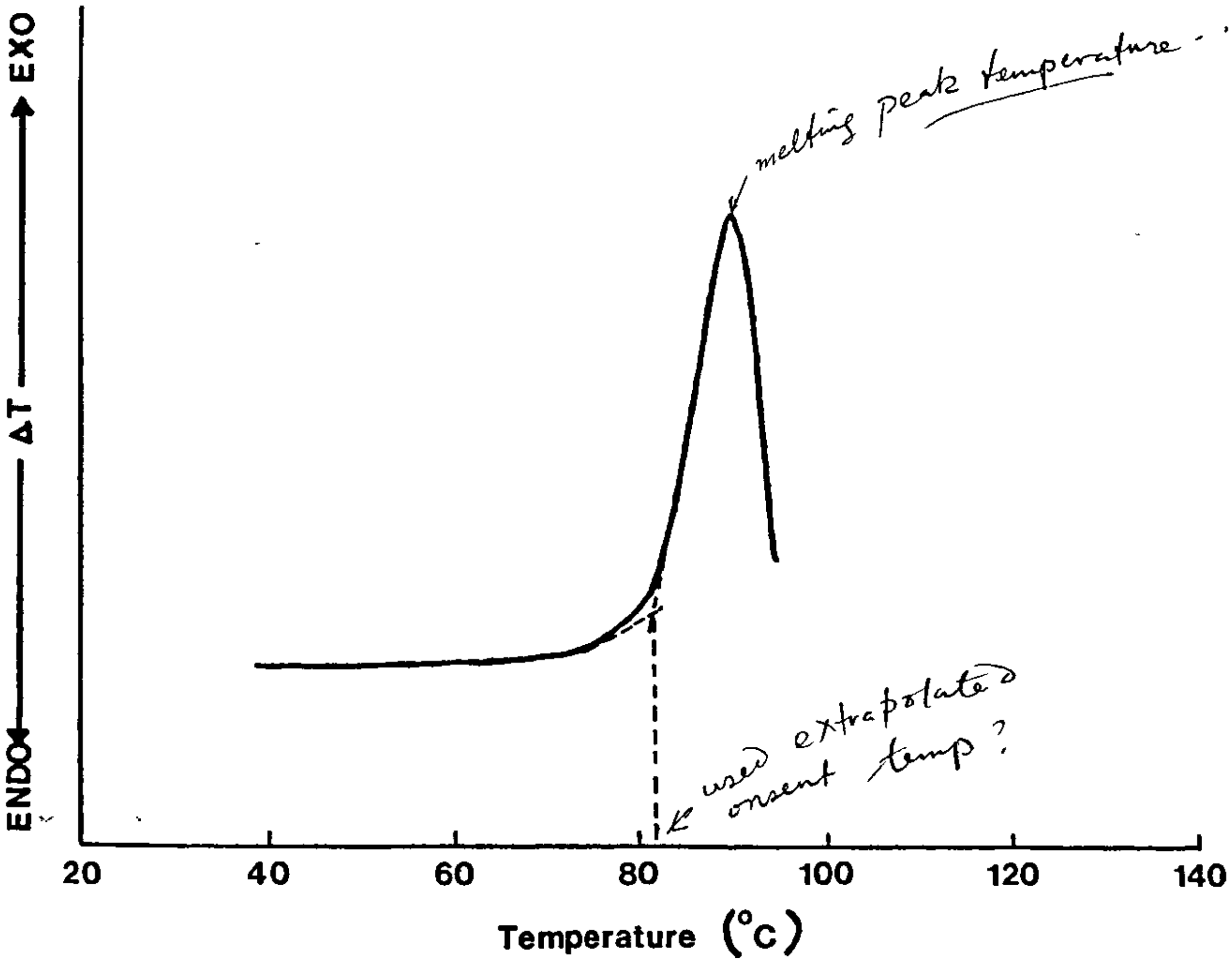
The recrystallised t-butyl N-phenylperoxycarbamate (0.5g) was stirred into purified polyisoprene rubber (2.0g) dissolved in benzene to give a 2% solution. After vigorous stirring, the benzene was removed under reduced pressure. The solid mix was heated under pressure in a mould for 3 hours at $80^{o}C$. The pressed sheet was extracted by methanol (B.S 903, Parts B1 and B2, 1958; methanol was used instead of acetone) for 24 hours and then dried under reduced pressure. The extracted polymer(1) was characterised by the Infra-red Spectrophotometer (Figure 2.4) while the methanol extract was dried

(1) The loss in the extraction was 14·1% by weight

under reduced pressure and similarly analysed by the Infra-red Spectrophotometer (*Figure 2.5*).

FIGURE 2.1

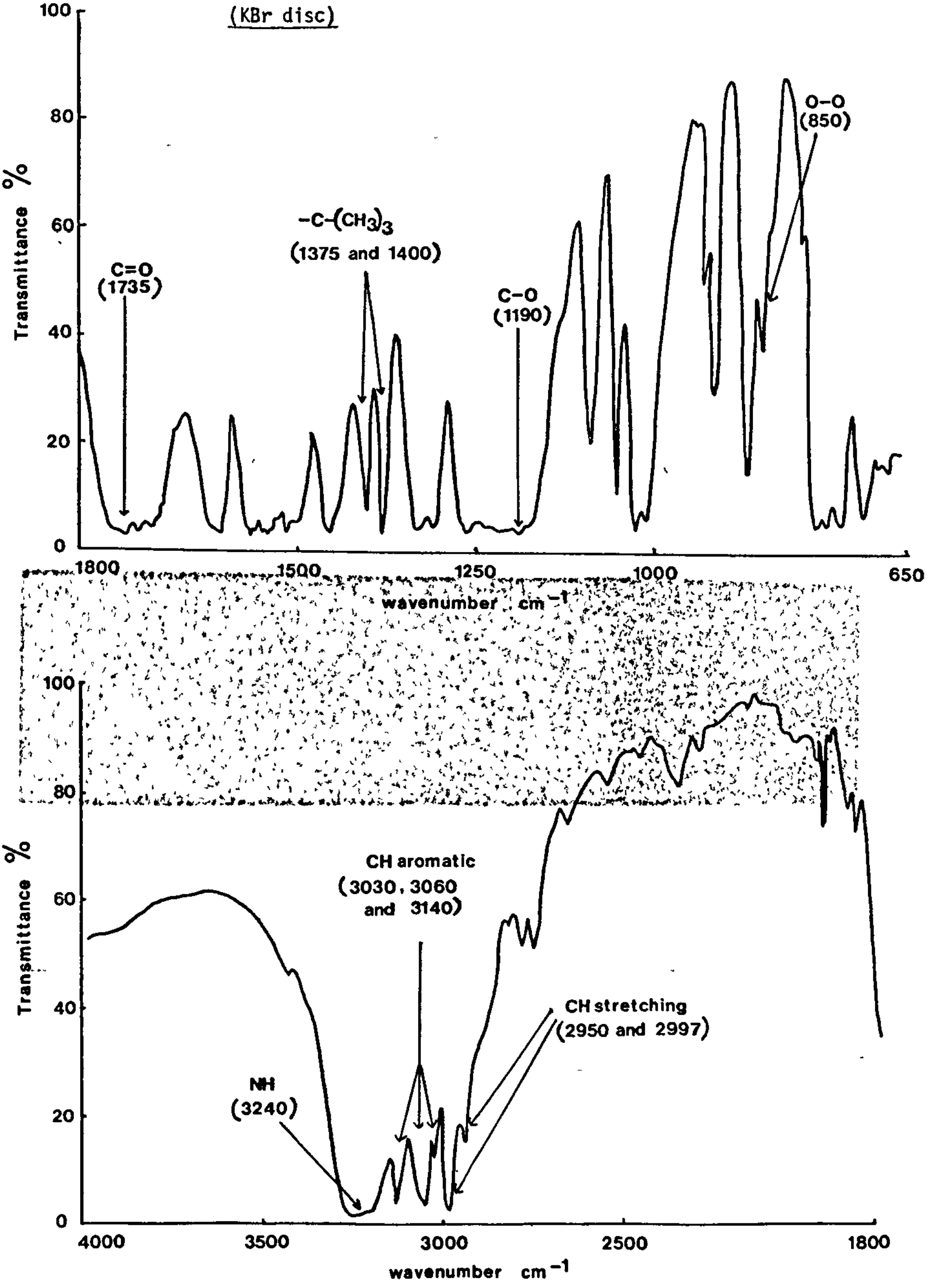
DSC trace of recrystallised t-butyl N-phenyl peroxycarbamate



2.2.2.3 Results and discussion

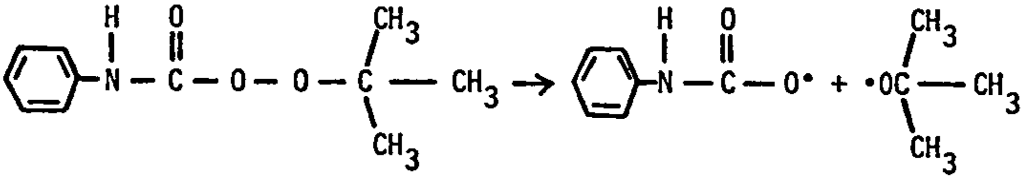
It was concluded that amino groups had been grafted onto the polyisoprene by this process; this is shown by the presence of NH (3390 cm^{-1}) and phenyl peaks (in the region 3020-3070 cm^{-1}) in the spectrum of the extracted polymer in contrast to the absence of these peaks of the spectrum of cast film of polyisoprene rubber (Figures 2.3 and 2.4). The absence of the C=O peak and observation

FIGURE 2.2 Infra-red spectrum of recrystallised t-butyl N-phenyl peroxycarbamate
(KBr disc)

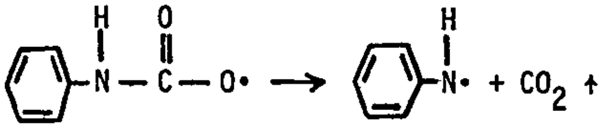


The monoperoxycarbamate caused a degree of crosslinking in polyisoprene rubber as indicated by the insolubility of the pressed sheet in toluene.

of porosity in the heated polyisoprene/t-butyl N-phenyl peroxycarbamate mix was considered to indicate that carbon dioxide was liberated during thermal decomposition of the peroxycarbamate in the rubber. The following reaction scheme, equations 77 and 78, suggested by O'Brien and co-workers (108) and Pederson (106) is considered to apply:



(77)



(78)

Infrared analysis of the extracted materials showed the presence of the following peaks (Figure 2.5);

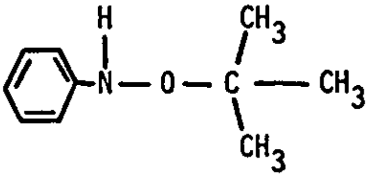
C-$(CH_3)_3$ - 1375 cm^{-1} and 1398 cm^{-1}

CH stretching - 2860 cm^{-1} and 2940 cm^{-1}

CH aromatic - 3050 cm^{-1} and 3080 cm^{-1}

NH - 3330 cm^{-1}

From the above peaks and the proposed decomposition mechanisms of equations 77 and 78, it would seem that one of the extracted materials could have the following structure:



(XXIX)

FIGURE 2.3 Infra-red spectrum of pure polyisoprene rubber (film)

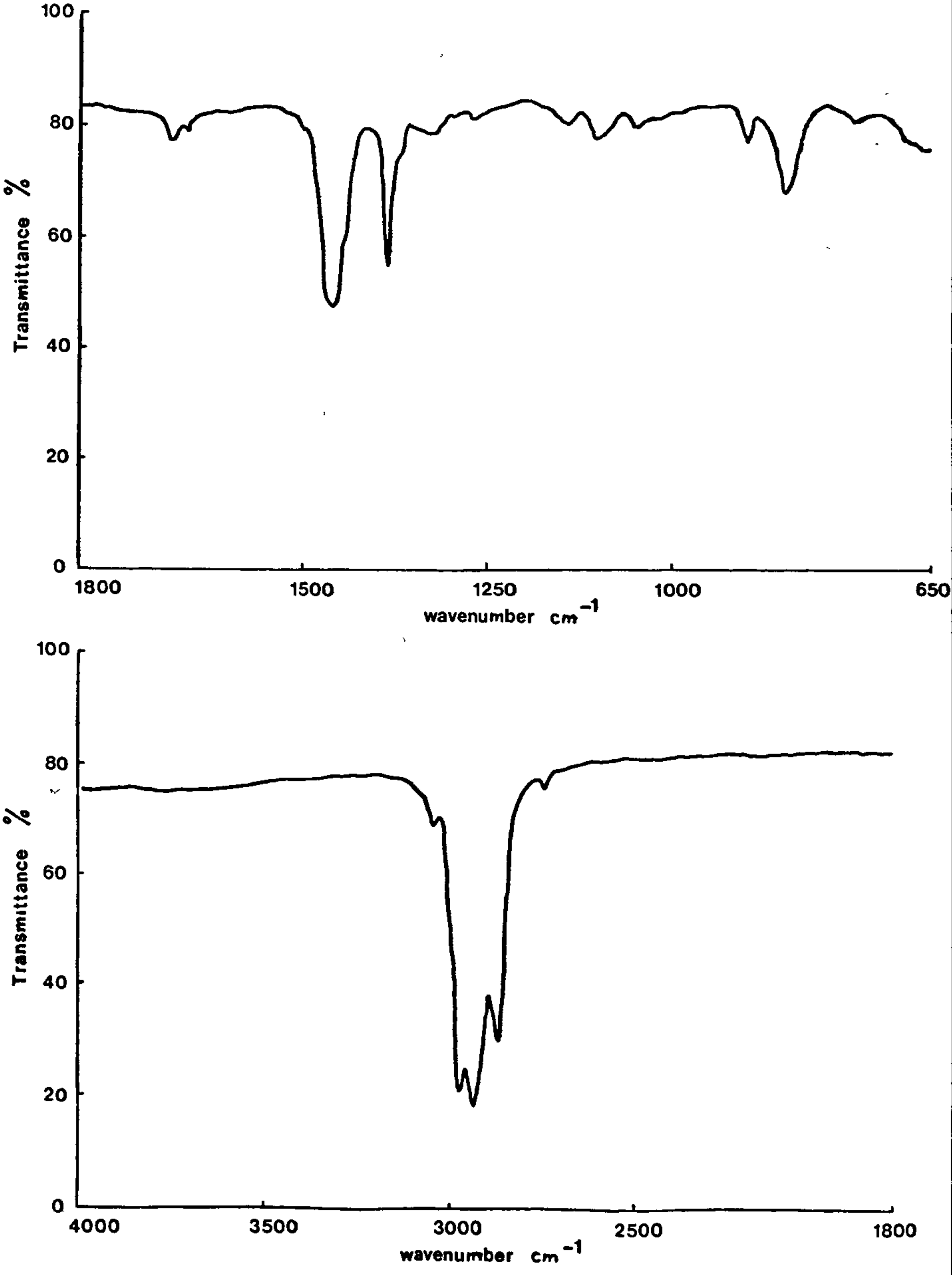


FIGURE 2.4 Infra-red spectrum of extracted polyisoprene rubber/ t-butyl N-phenyl peroxycarbamate (heated sample)

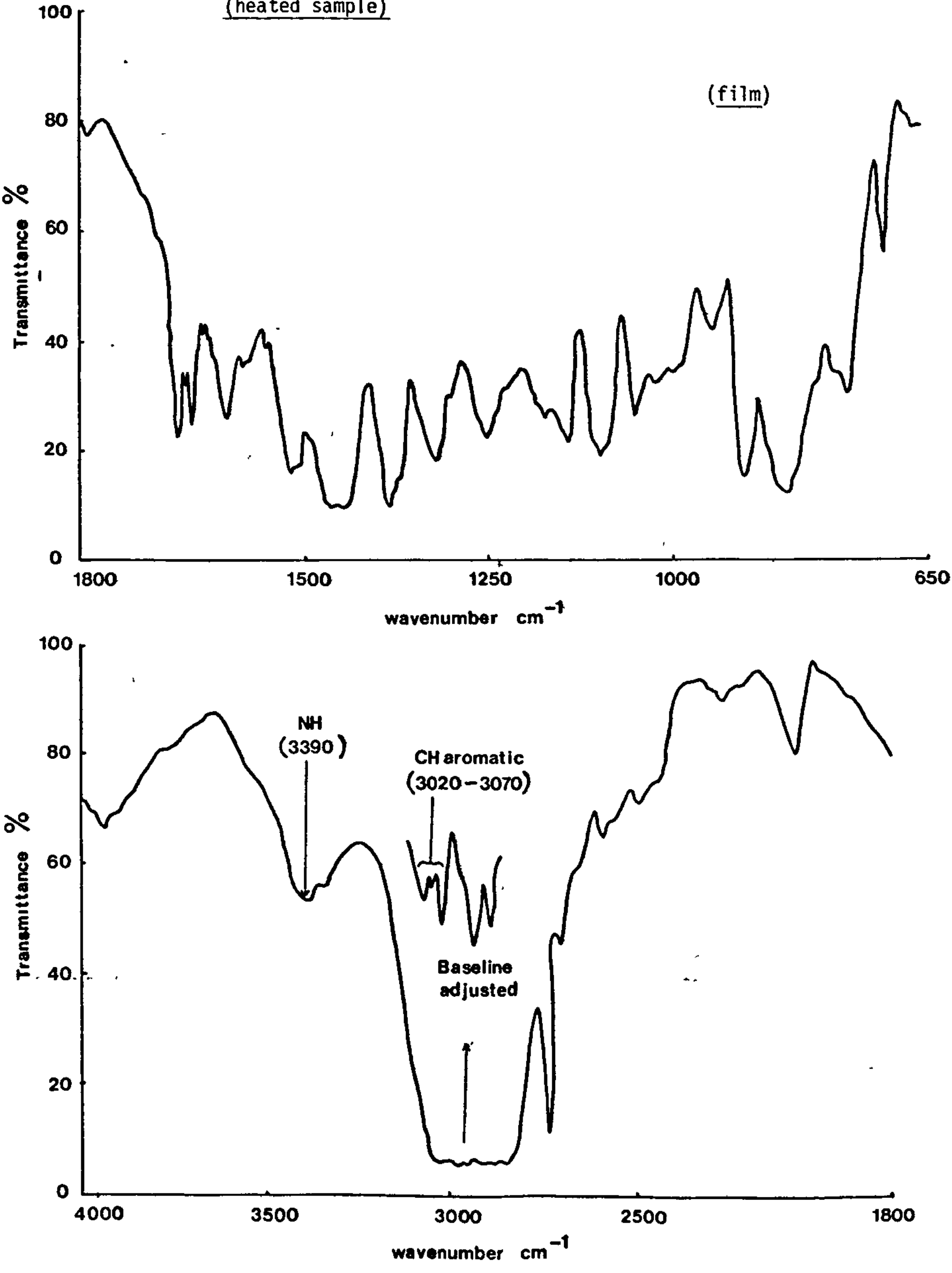
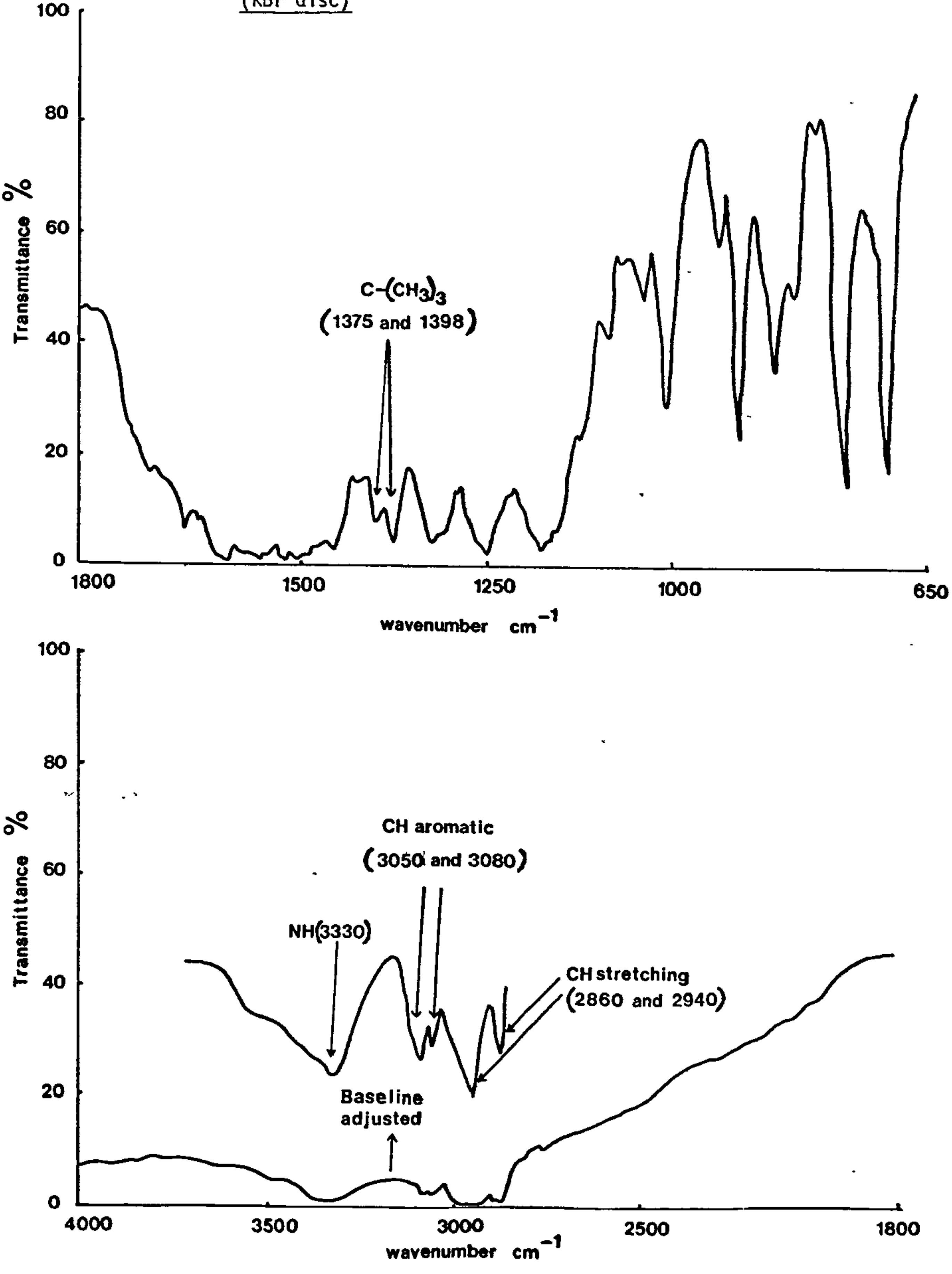


FIGURE 2.5 Infra-red spectrum of the extractable materials (KBr disc)



2.2.2.4 Conclusions

Based on the above monoperoxycarbamate reaction sequences a bisperoxycarbamate could be deduced by theory as potentially able to vulcanise polyisoprene rubber to give a certain proportion of amino linkages, $\mathrm{C}-\overset{\overset{\mathrm{H}}{|}}{\mathrm{N}}-\mathrm{R}-\overset{\overset{\mathrm{H}}{|}}{\mathrm{N}}-\mathrm{C}$. The present research work was therefore directed towards synthesis of a known bisperoxycarbamate, preferably a solid, such as hexamethylene bis N,N' (cumyl peroxycarbamate) and to exploring experimentally its ability to behave as a crosslinking agent for the polyisoprene rubber.

2.2.3 Reaction of Polyisoprene Rubber with a Bisperoxycarbamate

2.2.3.1 Synthesis of hexamethylene bis N,N' (cumyl peroxycarbamate

Hexamethylene diisocyanate (10.0g = 0.060 Mole) was dissolved in 200 ml of dry benzene, and the temperature maintained at 5°C. Triethylamine (0.54g) was added and the mixture kept under a dry nitrogen atmosphere. Dried cumyl hydroperoxide (21.9g = 0.120 Mole + 20% excess by weight) was added. Excess hydroperoxide was used to ensure complete reaction of the diisocyanate with the hydroperoxide. The reaction mixture was kept cool for 2 hours and at room temperature for 22 hours. The reaction product was obtained by removal of the benzene under reduced pressure at room temperature. The product obtained was dissolved in benzene and filtered and then benzene removed as before. It was then washed several times with n-heptane and dried.

Theoretical yield = 28.2 gm
Practical yield = 15.5 gm
= 55%
Melting point = 105°C (DSC spectrum of Figure 2.6)

Infrared peaks, observed as characteristic spectra (Figure 2.7) were:

O-O - 860 cm^{-1}
C-O - 1160 cm^{-1}
$\mathrm{C\text{-}(CH_3)_2}$ - 1375 cm^{-1} and 1390 cm^{-1}

C=O - 1715 cm^{-1}
CH stretching - 2890 cm^{-1}, 2950 cm^{-1} and 3000 cm^{-1}
CH aromatic - 3050 cm^{-1}, 3080 cm^{-1} and 3100 cm^{-1}
NH - 3370 cm^{-1}

FIGURE 2.6

DSC Spectrum of Hexamethylene bis N,N' (cumyl peroxycarbamate)
(used for characterisation and m.pt. determination)

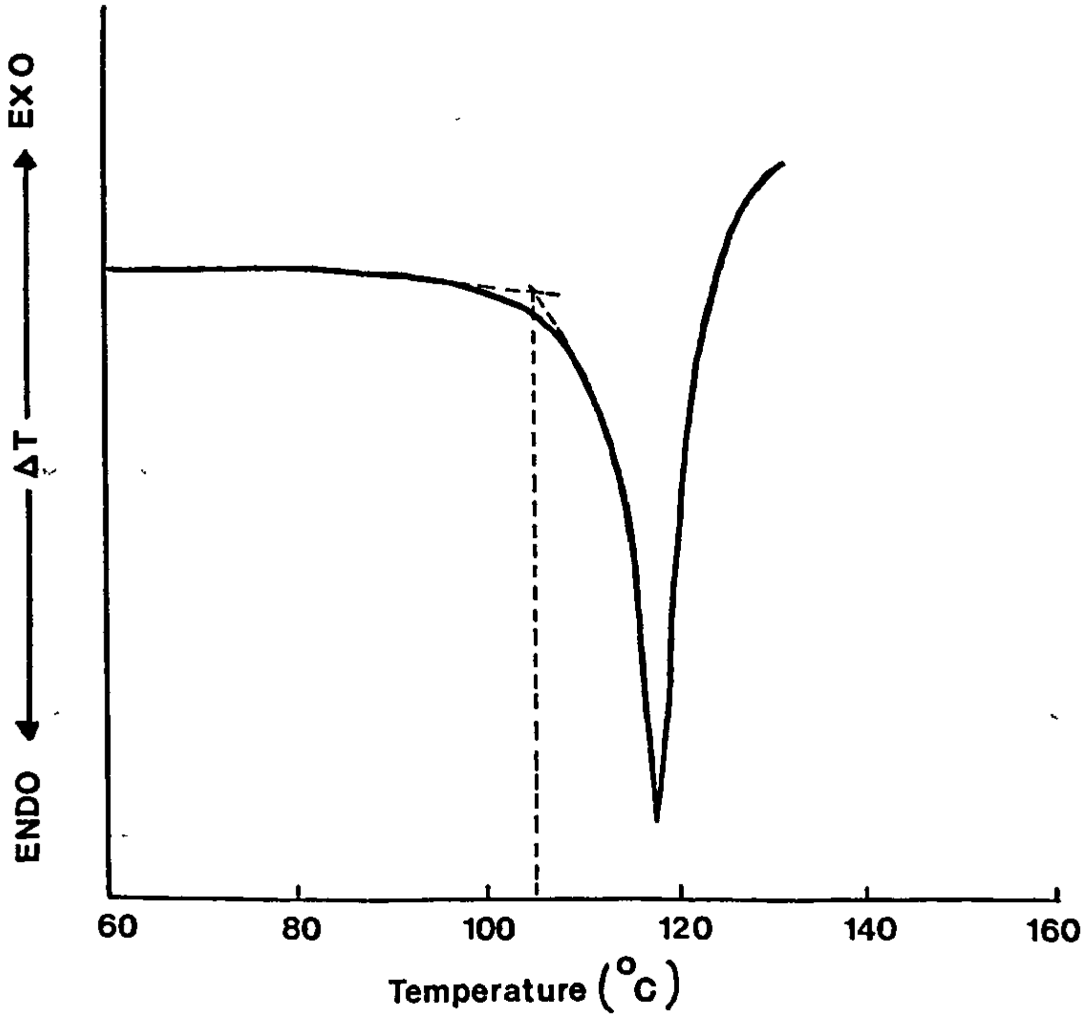
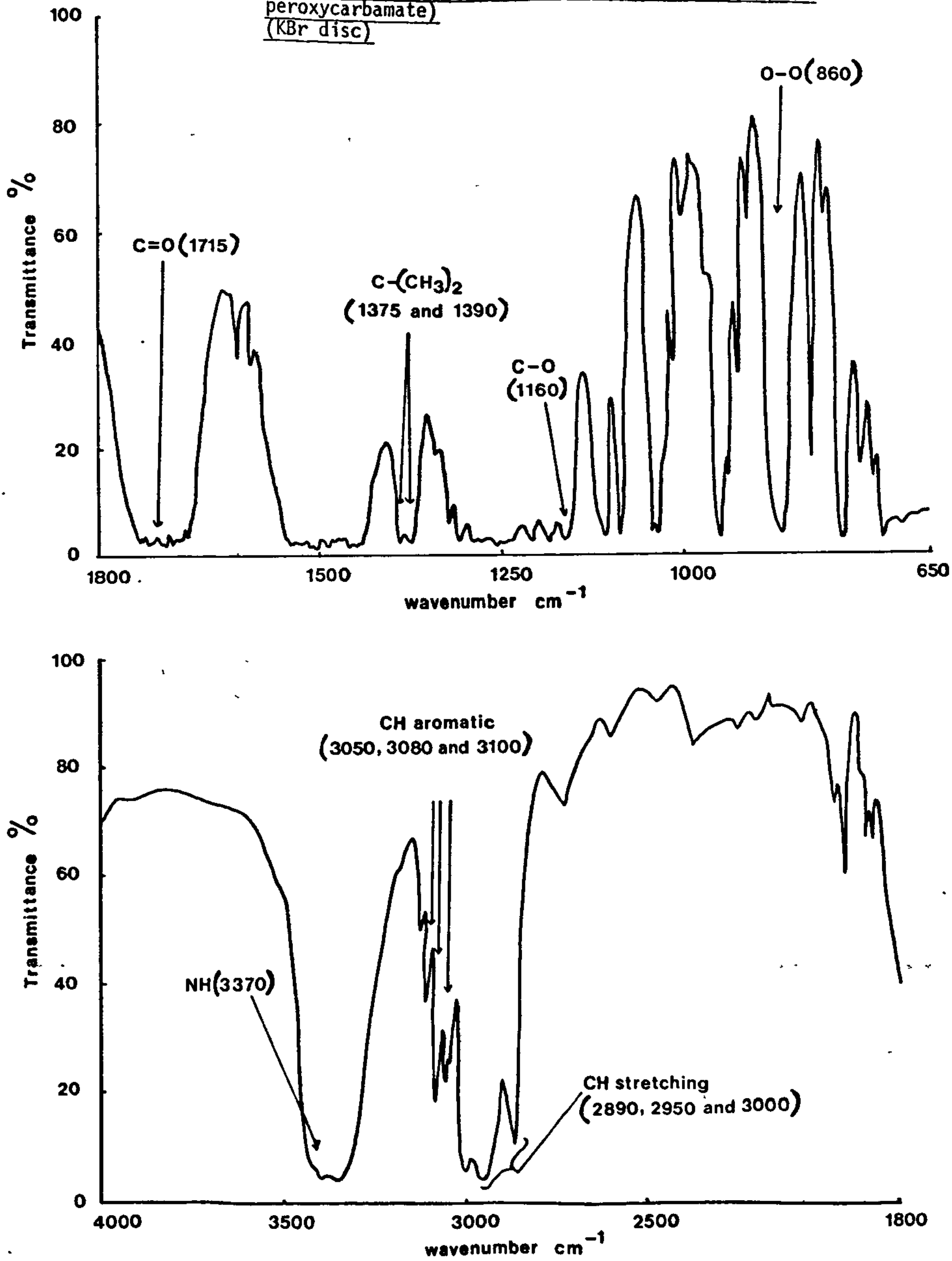


FIGURE 2.7 Infra-red spectrum of hexamethylene bis N,N' (cumyl peroxycarbamate) (KBr disc)



2.2.3.2 Heat Treatment of Rubber Mixes Consisting of Polyisoprene Rubber and Hexamethylene bis N,N' (cumyl peroxycarbamate)

Hexamethylene bis N,N' (cumyl peroxycarbamate) was mixed at various concentration levels into the purified polyisoprene rubber using a two roll mill at room temperature. The mixes were then analysed by DSC using the Du Pont 990 Thermal Analyser to obtain an indication of cure activation temperature of the mixes as described in Chapter 3. Figure 2.8 shows the typical DSC [illegible] of the mix. The amount of exothermic energy evolved in each mix was determined from the DSC [illegible] according to the method shown in Appendix II. This DSC data indicated that 140^{0}C could be a practical cure temperature, then the conventional cure times of the mixes were determined using an oscillating Disc Rheometer at 140^{0}C (Monsanto) to confirm the DSC observations. The essential features of this rheometer are described in Chapter 3. From the rheometer traces of the mixes, typified by Figure 2.9, all the mixes were cured for 15 minutes at 140^{0}C. The vulcanisates were kept at room temperature for 24 hours before the following procedures were carried out:

1. Observation of the NH peak of the acetone extracted vulcanisate by an Attenuated Total Reflectance (ATR) spectroscopy as described in Appendix III.

2. Determination of presence of any bound nitrogen in the extracted vulcanisate by Lassaigne's test.

3. Determination of the physical crosslink densities of the vulcanisates by the swelling method according to the technique described in Chapter 3.

4. Determination of tensile properties of the vulcanisates according to the method described in Chapter 4.

FIGURE 2.8 DSC trace of polyisoprene rubber mix containing hexamethylene bis N, N' (cumyl peroxycarbamate)

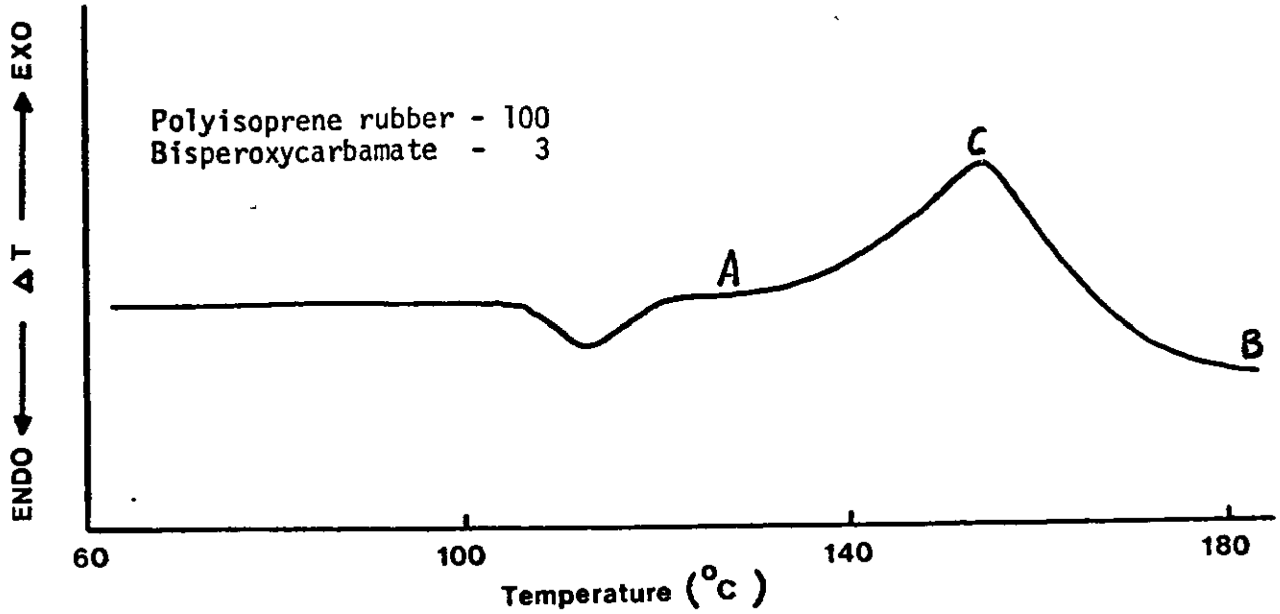


FIGURE 2.9 ODR trace of polyisoprene rubber mix containing hexamethylene bis N,N' (cumyl peroxycarbamate)
(Cure temperature = 140°C)

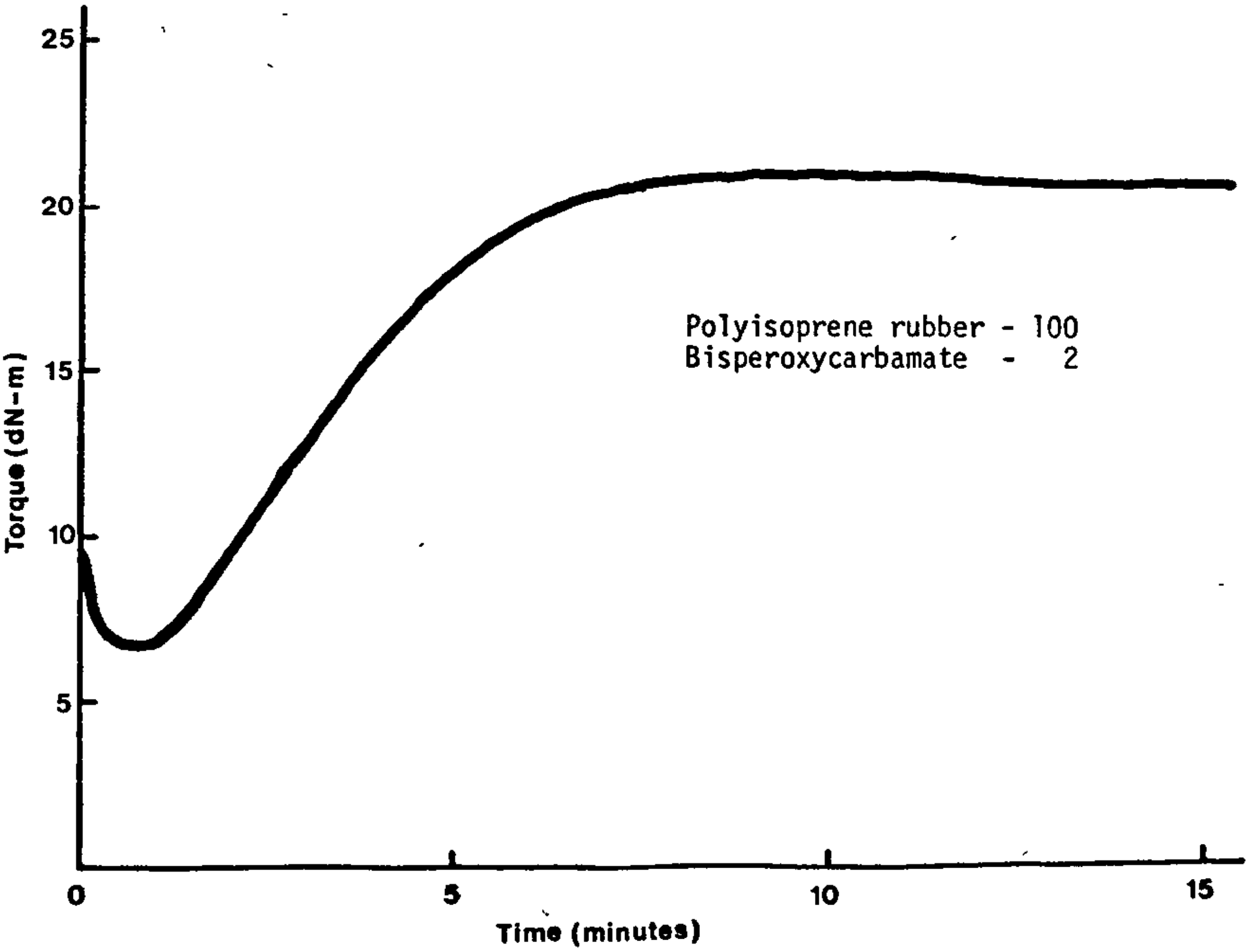
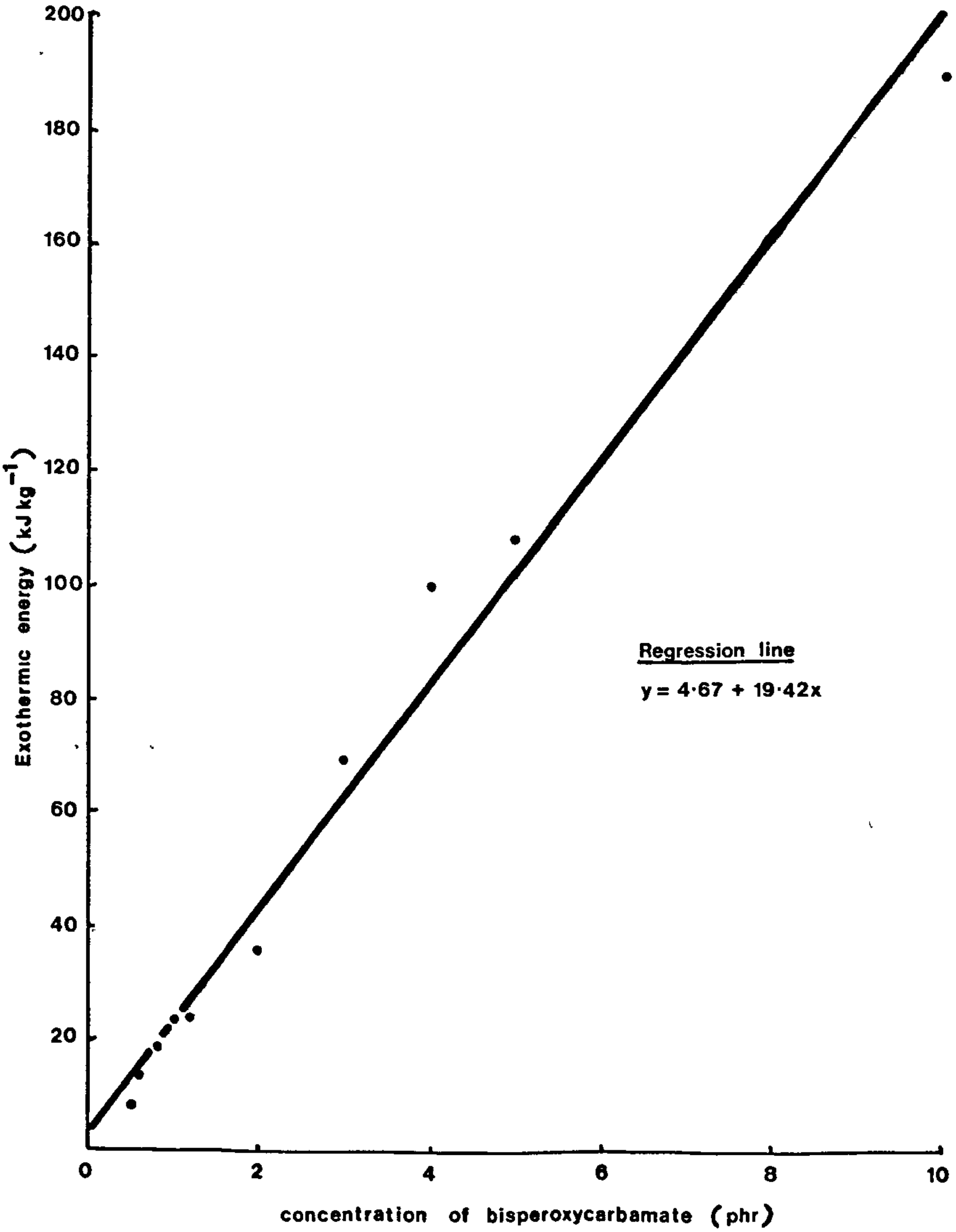


FIGURE 2.10 Exothermic energy as a function of concentration of bisperoxycarbamate



5. Examination of the ageing performance of the vulcanisates according to the method described in Chapter 5.

2.2.3.3 Results and Discussion

From the DSC data the exothermic energy which is related to the curing energy was found to be dependent on the amount of bisperoxycarbamate present in the mix. A linear relationship as shown in Figure 2.10 was found to apply and is given in the following equation:

Equation showing relationship between exothermic energy and concentration of bisperoxycarbamate

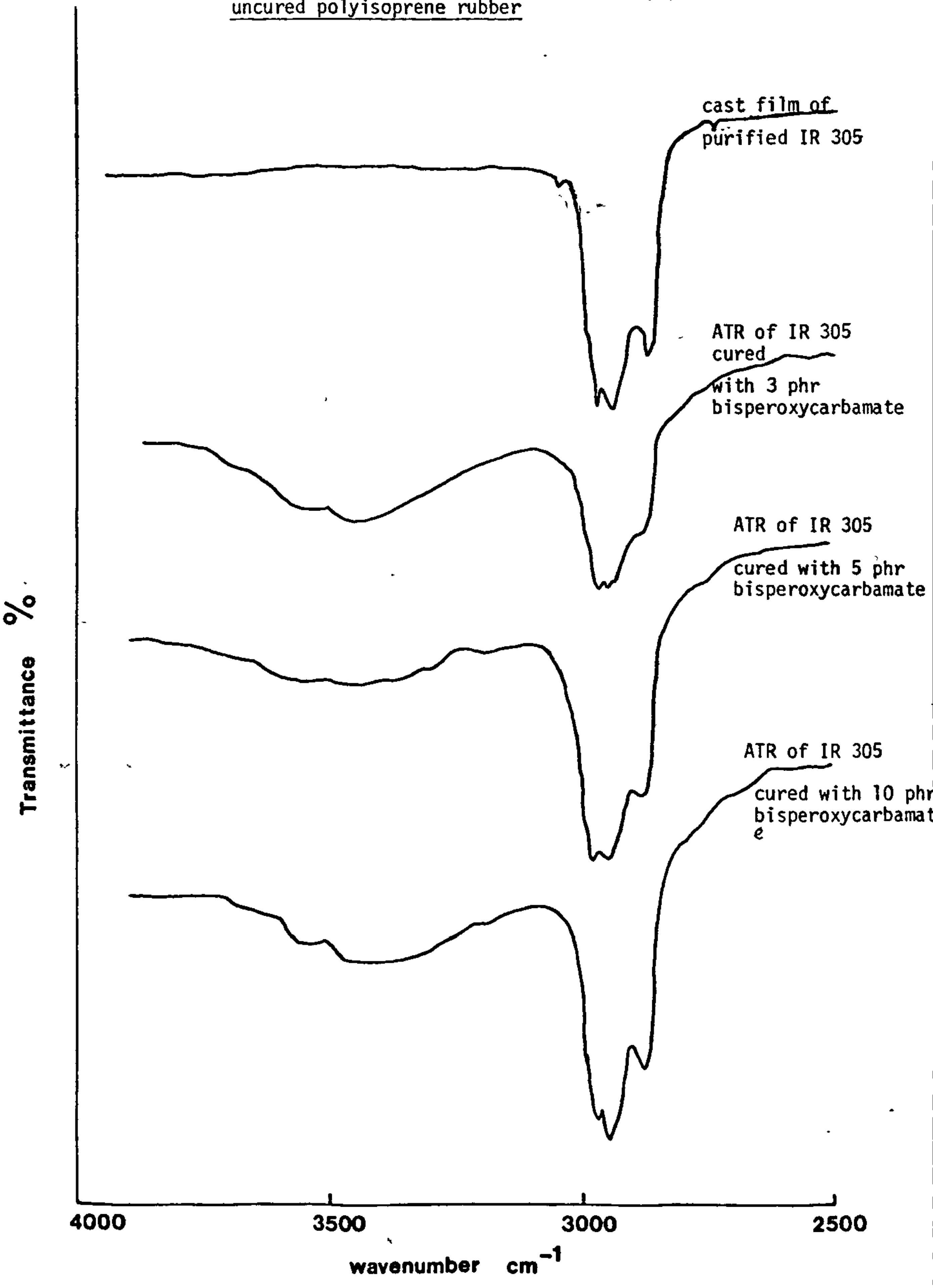
$$y = 4.67 + 19.42x$$

where y is the exothermic energy and x is the concentration of bisperoxycarbamate.

The ATR traces of the extracted vulcanisates in comparison with the spectrum of cast film of uncured polyisoprene rubber are shown in Figure 2.11. In the case of the uncured polyisoprene rubber the spectrum of its cast film was obtained since the normally rough surfaces of the uncured solid milled rubber restricted the application of the ATR technique. The presence of NH group in the extracted vulcanisate was shown by the peak in the region of 3100 cm^{-1} to 3700 cm^{-1}. However, it could be argued that this peak could also be due to the presence of water in the investigated samples. To substantiate the evidence of bound nitrogen, a Lassaigne's test was performed on each of the extracted vulcanisates. The results in Table 2.2 indicate that nitrogen was chemically bound to the polyisoprene rubber.

Figure 2.12 illustrates the effect of the concentration of the bisperoxycarbamate on the physical crosslink density of the vulcanisate. Dicumyl peroxide (Perkadox SB) was used as a control and

FIGURE 2.11 Spectra of extracted vulcanisates in comparison with uncured polyisoprene rubber



cure conditions of the mixes were 60 minutes at 150°C. Initially the crosslink density increased almost proportionally with the concentration of the bisperoxycarbamate. A maximum crosslink density was reached at about 4 phr concentration of the bisperoxycarbamate which then decreased at a higher concentration of the bisperoxycarbamate. This phenomenon was also observed in the case of the plot of M_{300} vs. concentration (see Figure 2.14). It was possible that at higher concentrations the scission reaction took place preferentially with this particular curing agent and thus affecting the crosslink density.

At equivalent molar concentrations of the curing agent in the polyisoprene rubber, the dicumyl peroxide vulcanisates have higher crosslink densities and M_{300} values than the bisperoxycarbamate vulcanisates. Studies by early workers had shown that the dicumyl peroxide decomposed to radicals in which the efficiency in the formation of crosslinks is nearly unity in natural rubber (32,40,41) and greater than unity in polyisoprene rubber (112). Such differences in crosslink efficiency could be due to the wastage of some of the radicals formed during decomposition of the bisperoxycarbamate through the termination process (106,108) as shown in the reaction

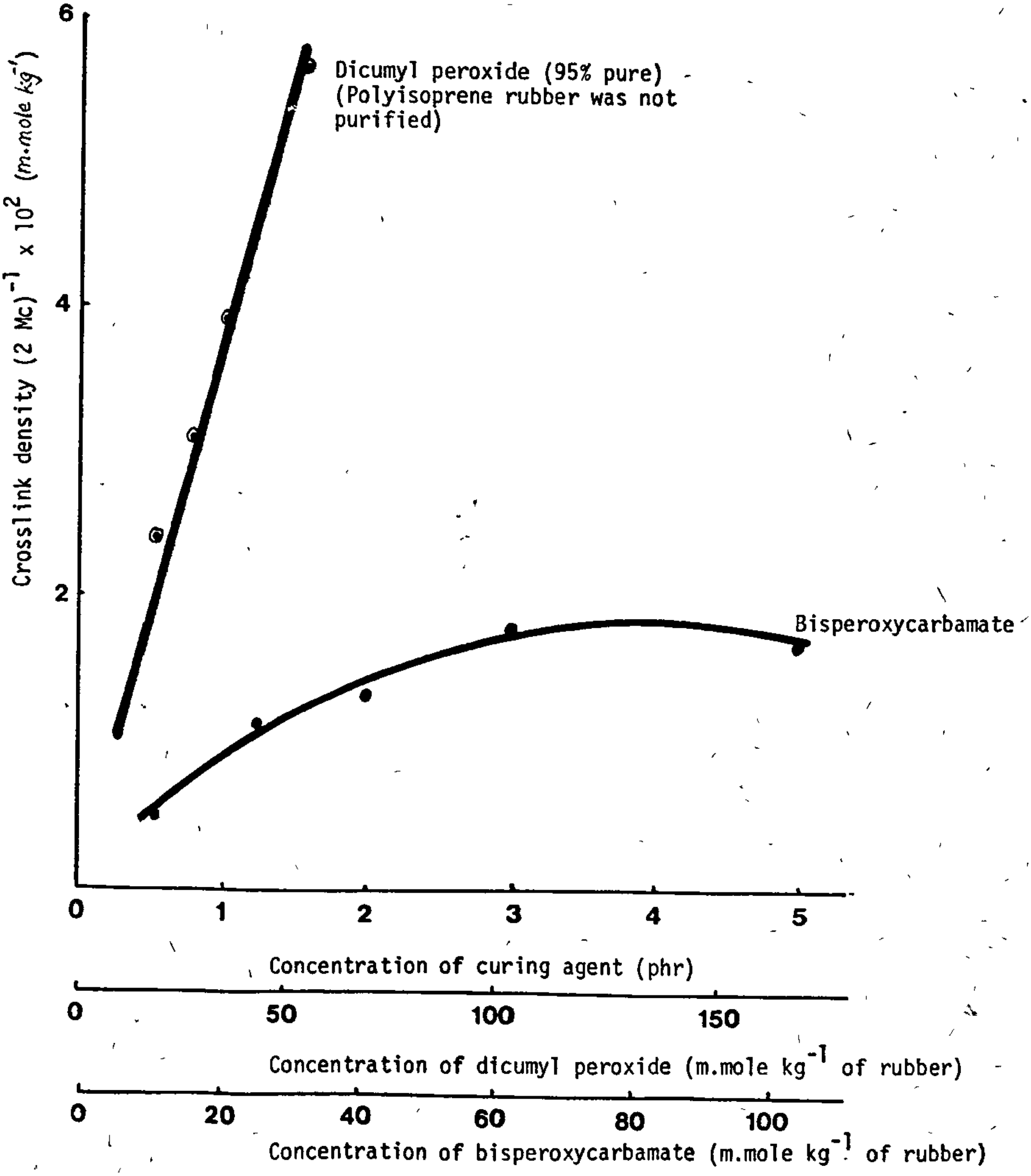
TABLE 2.2

Results of Lassaigne's Test

Samples	Results*
Pure IR 305	Negative
Pure IR 305 cured with 3 phr bisp.	Positive
5 phr bisp.	Positive
10 phr bisp.	Positive

* For each sample, three tests were carried out to confirm the presence of bound nitrogen.

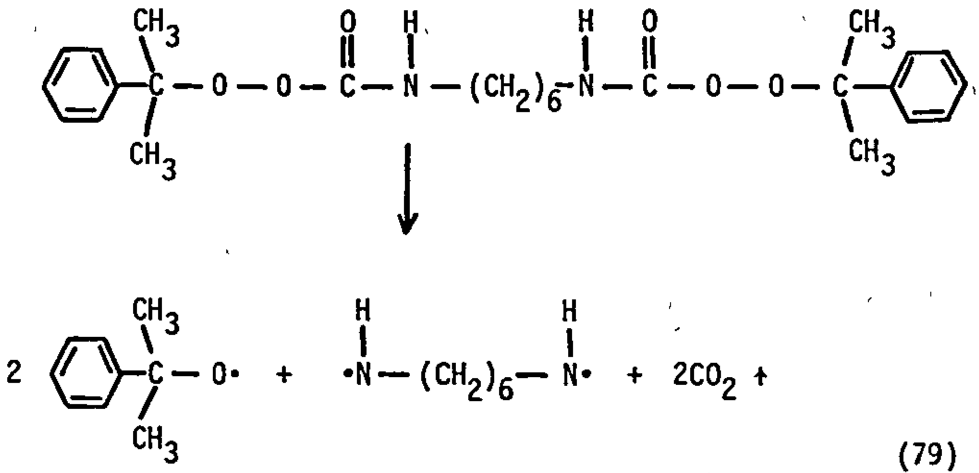
FIGURE 2.12 Crosslink density $(2\ Mc)^{-1}$ vs. concentration of curing agent



scheme of equations 79 and 80 below:

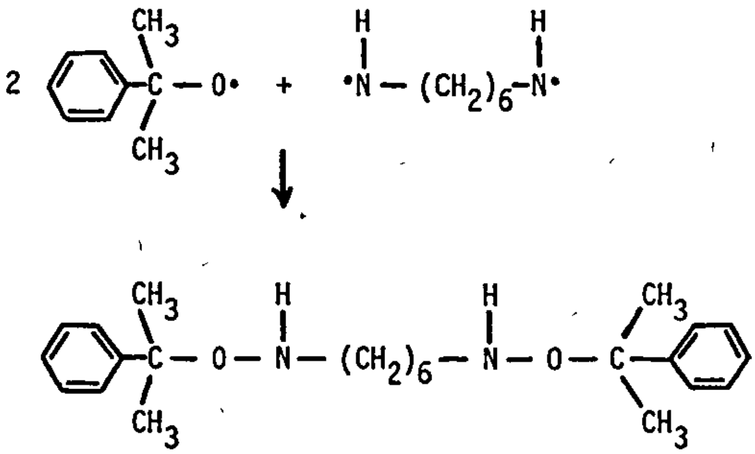
Reaction scheme involving decomposition and termination of the bisperoxycarbamate

Decomposition



(79)

Termination



(80)

The performance of the bisperoxycarbamate vulcanisates on mechanical properties was based on the tensile properties and these data are shown in Figures 2.13 - 2.15. The bisperoxycarbamate vulcanisate is seen to have better strength than the equivalent dicumyl peroxide vulcanisates; the tensile strength of the vulcanisate cured with 0.04 mole kg^{-1} of rubber of dicumyl peroxide is 5.8 MPa whilst that cured with 0.1 mole kg^{-1} of rubber of bisperoxycarbamate has a tensile strength of 7.3 MPa.

For a given weight concentration of curing agent, the bisperoxycarbamate vulcanisates are considered more flexible than the equivalent dicumyl peroxide vulcanisates and this is thought primarily due to the difference in the degree of cross-linking.

Porosity in the bisperoxycarbamate vulcanisates, especially in those with a high concentration of the bisperoxycarbamate, was observed. Based on earlier experiments using tertiary butyl-N-phenylperoxycarbamate and suggested equation (106,108), this porosity was thought to be due to the evolution of carbon dioxide.

Figures 2.16 and 2.17 show the performance of the bisperoxycarbamate vulcanisate under ageing conditions. Under a continuous stress-relaxation process, the dicumyl peroxide vulcanisate failed by rupture tearing of the specimen after 280 minutes at 100°C, whereas the bisperoxycarbamate vulcanisate did not undergo failure but relaxed. Such stability of the bisperoxycarbamate vulcanisate was further confirmed by the hot air oven ageing data.

2.2.3.3 Conclusions

Hexamethylene bis N,N' (cumyl peroxycarbamate) was shown to be able to cure polyisoprene rubber to vulcanisates of superior strength and thermal stability than the equivalent dicumyl peroxide vulcanisates. Based on this promising finding, the present research work was directed to synthesis of a few new bisperoxycarbamates of various structures and to investigate their performance as vulcanising agents in both natural and polyisoprene rubbers.

FIGURE 2.13 Tensile strength vs concentration of curing agent

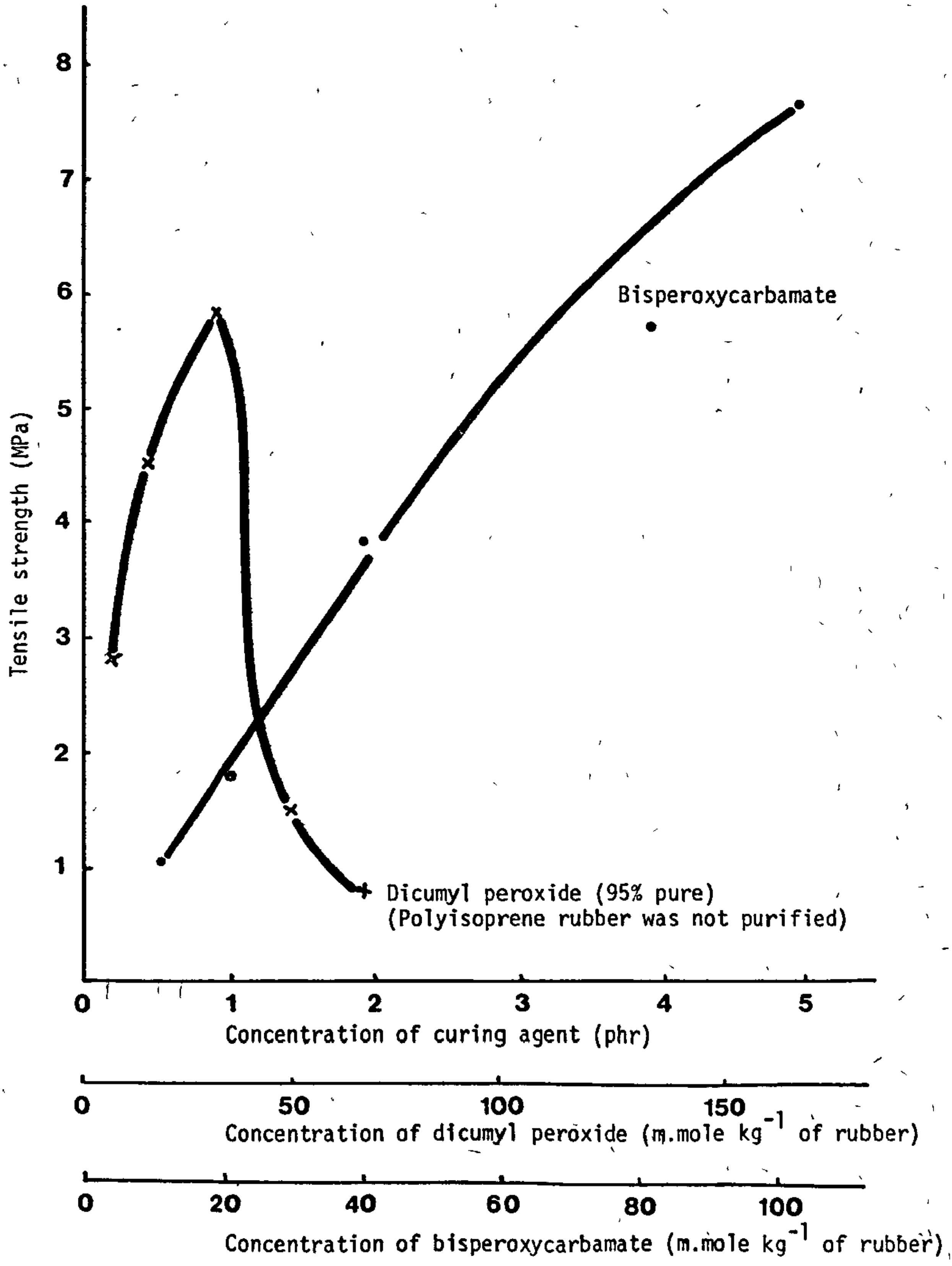


FIGURE 2.14 M_{300} vs concentration of curing agent

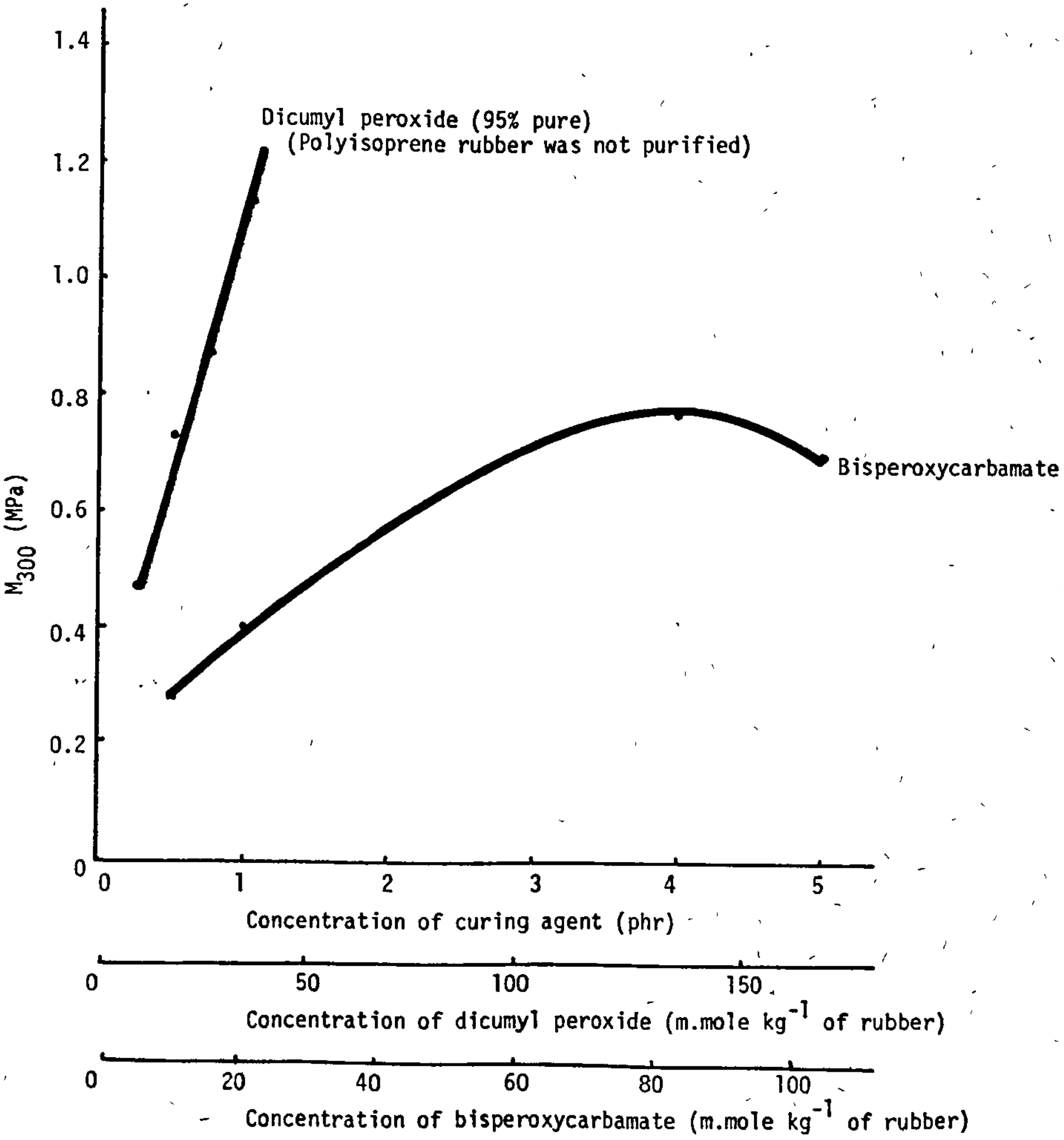


FIGURE 2.15 Elongation at break vs concentration of curing agent

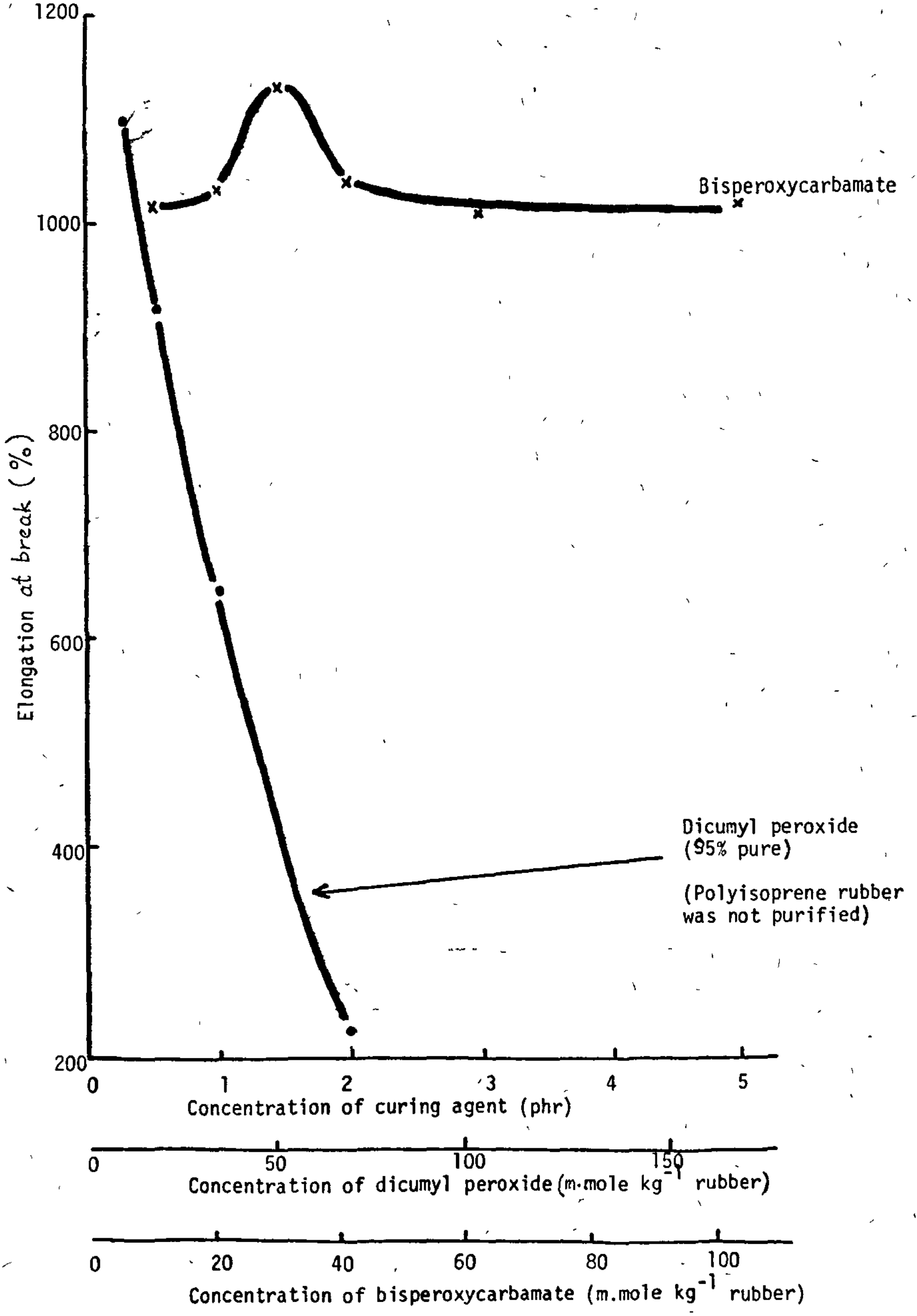


FIGURE 2.16 Continuous stress-relaxation in hot air at 100°C

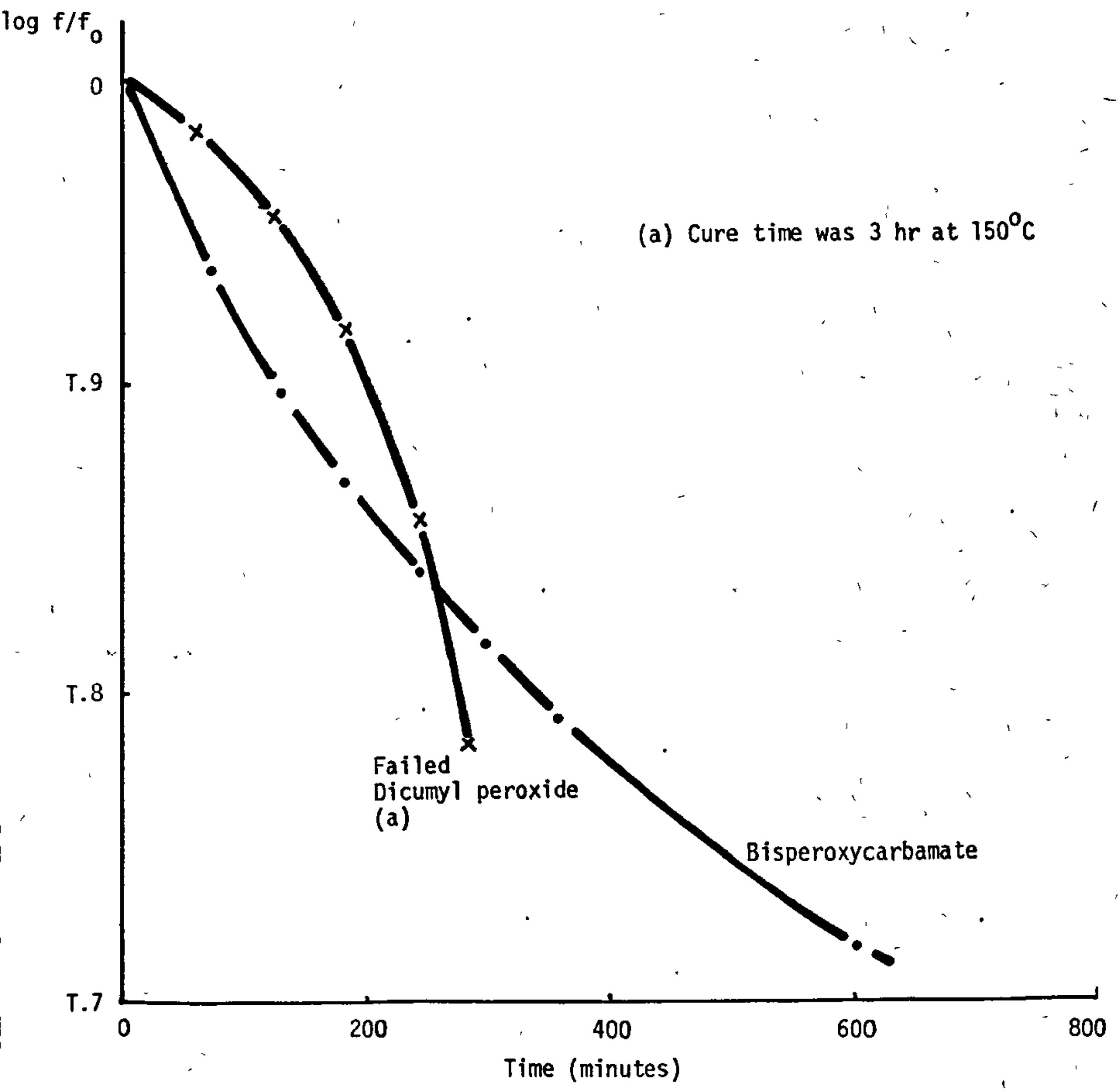
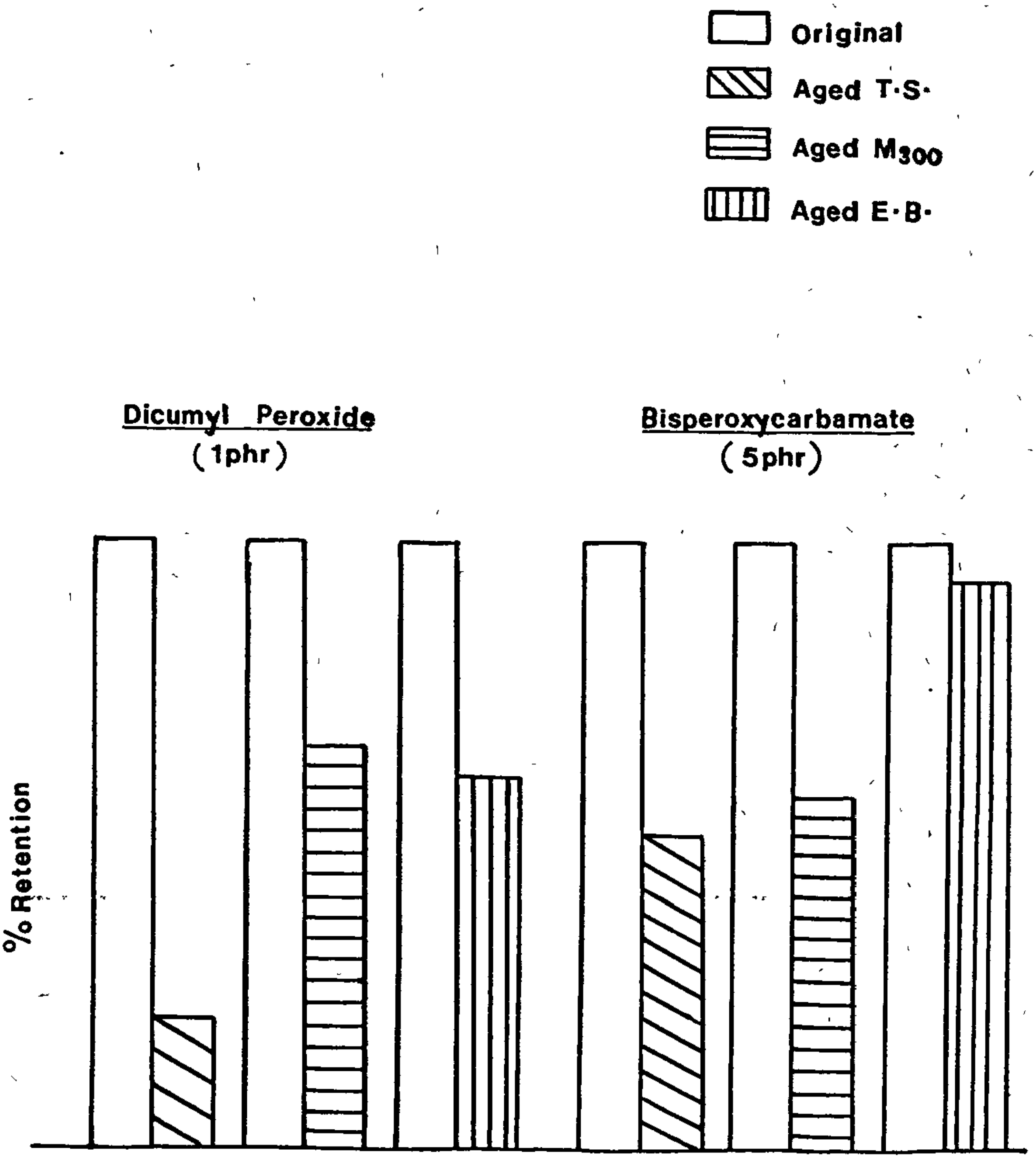


FIGURE 2.17 Tensile property retention (7 days/70^{0}C) of polyisoprene rubber vulcanisates



2.3 Synthesis of Various Bisperoxycarbamates

2.3.1 Materials

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In addition to the materials mentioned in Section 2.2.1 the following were used:

Diisocyanates

Methylene diphenylene diisocyanate, MDI (Desmodur 44 obtained from Elastogran, U.K).

3-Isocyanatomethyl-3,5,5-trimethyl-cyclohexyl-isocyanate, IPDI (obtained from Veba-Chemie).

Methylene-bis-(4-cyclohexyl isocyanate). This diisocyanate was first obtained from E I Du Pont De Nemours Co. Inc. under the trade name of Hylene W, but due to the stoppage of production by this company, the diisocyanate was kindly presented to the author by Bayer AG under the trade name of Desmodur W.

2,4 Tolylene diisocyanate dimer, Desmodur TT (obtained from Bayer AG).

Prepolymer based on polyester diol and 2,4 tolylene diisocyanate (TDI) of 4.51% excess NCO (obtained from Thiokol Corporation under the trade name, Solithane 790).

These diisocyanates were used as received.

Polyester and diol

1,4-butane diol (obtained from GAF (Great Britain) Ltd.).

Polycaprolactone under trade name, Capa 222 of molecular weight 2000 (obtained from Laporte Industry).

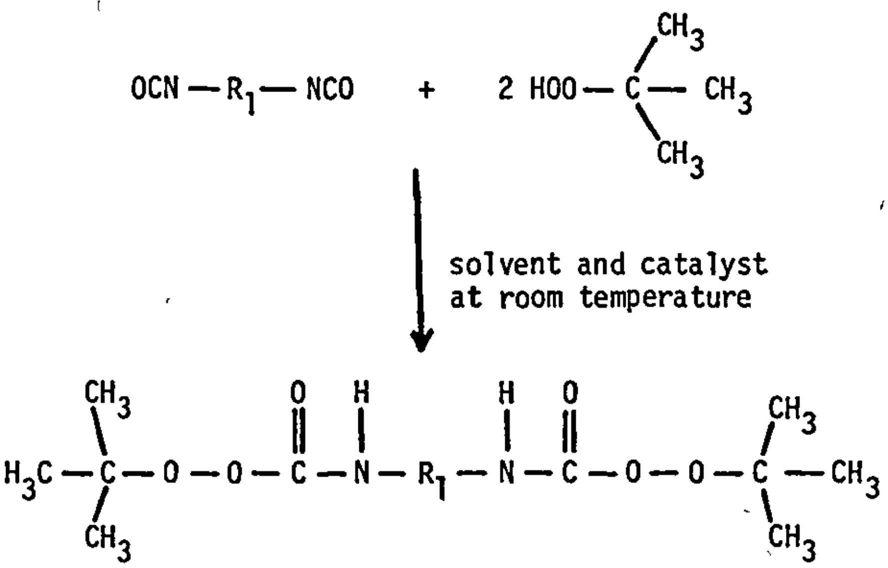
Solvent

Trichlorobenzene (BDH Laboratory reagent).

2.3.2 Experimental

The following general procedure was adopted for synthesis of the bisperoxycarbamates:

Method of preparing bisperoxycarbamates



The diisocyanate of known molecular weight (0.02 Mole) was first dissolved in benzene; all the diisocyanates were soluble in benzene with the exception of TDI dimer which was soluble in trichlorobenzene. In the case of TDI prepolymer and Hylene W prepolymer, 10g. weight of the prepolymer was used. Tertiary butyl hydroperoxide (4.3g. i.e. 20% excess by weight) and catalyst (0.18g) were added to the solution and allowed to react in a nitrogen atmosphere obtained with the passage of dry nitrogen gas at room temperature.

In all cases triethylamine was used as catalyst with the exception of methylene diphenylene diisocyanate, TDI dimer and TDI prepolymer where pyridine was used instead.

The extent of reaction of the diisocyanate with the hydroperoxide was followed by observing the disappearance of the characteristic (-N=C=O) absorption band (i.e. 2270 cm^{-1}) with time of reaction. A typical example of the infrared spectra, showing the disappearance of the -N=C=O peak with reaction time is shown in Figure 2.18. After reaction was complete, benzene or trichlorobenzene was removed under reduced pressure. The residue was washed several times with n-heptane and dried at room temperature in a desiccator under vacuum.

The prepared bisperoxycarbamates were analysed to determine their characteristic IR peaks and also the decomposition or melting temperatures which were obtained by DSC observation using the Du Pont 990 Thermal Analyser. In the case of solid bisperoxycarbamates, the infrared spectra of the bisperoxycarbamates were taken of 1.5% of the bisperoxycarbamates in potassium bromide disc (200 mg). For bisperoxycarbamates (f) and (g) shown below, their spectra was obtained from thin films between sodium chloride windows.

2.3.3 Results and Discussion

Synthesis of the following bisperoxycarbamates were attempted. In all cases the syntheses were first based using a micro scale procedure and later this was scaled up to obtain enough bisperoxycarbamates for technological evaluation.

a) Bisperoxycarbamate from methylene diphenylene diisocyanate and tertiary butyl hydroperoxide.

The reaction between the two materials is too violent and was omitted for safety reasons.

b) Bisperoxycarbamate from 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl-isocyanate (IPDI) and tertiary butyl hydroperoxide.

The total reaction time required for complete disappearance of the -N=C=O peak was 70 hours. The yield obtained was 69% by weight. The infrared peaks (see Figure 2.21), observed as characteristic spectra, were:

O-O - 854 cm^{-1}
C-O - 1187 cm^{-1}
$C-(CH_3)_3$ - 1365 cm^{-1} and 1385 cm^{-1}
C=O - 1715 cm^{-1}
CH stretching - 2920 cm^{-1}, 2940 cm^{-1} and 2964 cm^{-1}
N-H - 3340 cm^{-1}

This compound exhibits two separate decomposition points (Figure 2.19). It begins to melt at 113°C and shows two distinct decompositions DSC peaks at 167°C and 177°C. These peaks were thought to correspond to the cleavage of the O-O bonds of the aliphatic peroxycarbamate and the cyclic peroxycarbamate.(1)

c) <u>Bisperoxycarbamate prepared from a polyurethane prepolymer based on 1,4 butane diol reacted with excess IPDI (block ratio 1:2); this polyurethane type was then reacted with tertiary butyl hydroperoxide to form the bisperoxycarbamate.</u>

In the case of this bisperoxycarbamate a prepolymer was initially prepared. 1,4 butane diol was reacted under nitrogen with excess IPDI for 2.5 hours at 120°C to form the prepolymer. The total reaction time required to form the prepolymer was determined according to the method described in Appendix IV and V. The excess diisocyanate monomer was removed by washing several times the reaction product with dry petroleum ether and the product dried. The dry product was reacted with tertiary butyl hydroperoxide using a similar procedure to that described before.
The total reaction time required for complete disappearance of the -N=C=O peak was 89 hours. The yield obtained was 88% by weight. This compound begins to melt at 117°C and shows one DSC decomposition peak at 163°C (Figure 2.19). The infrared peaks (Figure 2.22), observed as characteristic spectra, were:

O-O - 850 cm^{-1}
C-O - 1193 cm^{-1}
$C-(CH_3)_3$ - 1363 cm^{-1} and 1383 cm^{-1}

(1) $R_1-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-O-O-R$ - aliphatic peroxycarbamate when R is an aliphatic
- cyclic peroxycarbamate when R is a cyclic

C=O - 1714 cm^{-1}
CH stretching - 2948 cm^{-1}
N-H - 3327 cm^{-1}

d) Bisperoxycarbamate from methylene-bis-(4-cyclohexyl isocyanate) and tertiary butyl hydroperoxide

The total reaction time for complete disappearance of the -N=C=O peak was very slow, i.e. after one week the -N=C=O peak was still present. The experiment was repeated but using higher concentration of catalyst, 0.53g. of triethylamine, and the total reaction time observed was 142 hours. An experiment was also attempted by using cumene hydroperoxide instead of tertiary butyl hydroperoxide and the reaction time observed was slower in the case of cumene hydroperoxide. The yield obtained was 71% by weight. The compound begins to decompose at 147°C with DSC decomposition peak at 162.5°C (Figure 2.19). The infrared spectrum of the bisperoxycarbamate is shown in Figure 2.23 and with the following characteristic peaks:

O-O - 860 cm^{-1}
C-O - 1192 cm^{-1}
$C-(CH_3)_3$ - 1370 cm^{-1} and 1393 cm^{-1}
C=O - 1720 cm^{-1}
CH stretching - 2860 cm^{-1}, 2935 cm^{-1} and 2985 cm^{-1}
N-H - 3360 cm^{-1}

e) Bisperoxycarbamate from 2,4,tolylene diisocyanate dimer and tertiary butyl hydroperoxide

The total reaction time for complete disappearance of the -N=C=O peak was about 48 hours. The yield obtained was 26% by weight. The compound begins to decompose at 66°C (Figure 2.20). The infrared spectrum of the bisperoxycarbamate is shown in Figure

2.24 and shows the following characteristic peaks:

O-O	-	833 cm^{-1}
C-O	-	1200 cm^{-1}
$C-(CH_3)_3$	-	1410 cm^{-1}
C=O	-	1720 cm^{-1}
CH stretching	-	2870 cm^{-1} and 2932 cm^{-1}, 2980 cm^{-1}
CH aromatic	-	3040 cm^{-1} and 3083 cm^{-1}
NH	-	3328 cm^{-1}

f) <u>Bisperoxycarbamate from Polyester/TDI prepolymer (Solitane 790) and tertiary butyl hydroperoxide</u>

The total reaction time for complete disappearance of the -N=C=O peak was 54 hours. The yield obtained was 2.8g. The compound begins to decompose at 64°C (Figure 2.20). Infrared spectrum of the bisperoxycarbamate is shown in Figure 2.25 and shows the following characteristic peaks:

O-O	-	830 cm^{-1}
C-O	-	1172 cm^{-1}
$C-(CH_3)_3$	-	1392 cm^{-1}
C=O	-	1735 cm^{-1}
CH stretching	-	2890 cm^{-1} and 2977 cm^{-1}
CH aromatic	-	3070 cm^{-1}
NH	-	3230 cm^{-1}

g) Bisperoxycarbamate from Polycaprolactone/Methylene-bis-(4-cyclohexyl isocyanate) prepolymer and tertiary butyl hydroperoxide

The total reaction time to form a polyurethane prepolymer having an excess NCO from the polycaprolactone and the diisocyanate was first determined according to the method described in Appendix IV. The amount by weight of the diisocyanate and caprolactone required to give 4% excess free NCO was estimated according to the calculations shown in Appendix V. These two reagents of known weights were allowed to react under nitrogen for 2 hours at 120°C.

The prepolymer with excess free NCO was reacted with tertiary butyl hydroperoxide using the similar method described for the other bisperoxycarbamates but using 0.53g of triethylamine. The total reaction time required for complete disappearance of the -N=C=O peak was very slow. The yield obtained was 7.1g. Almost similar to the bisperoxycarbamate (d), the prepolymer bisperoxycarbamate begins to decompose at 138°C with DSC decomposition peak at 166.5°C (Figure 2.20). The characteristic peaks (Figure 2.26) observed in the infrared spectra were:

O-O - 857 cm^{-1}

C-O - 1185 cm^{-1}

$C-(CH_3)_3$ - 1377 cm^{-1} and 1400 cm^{-1}

C=O - 1737 cm^{-1}

CH stretching - 2880 cm^{-1} and 2953 cm^{-1}

N-H - 3390 cm^{-1}

2.3.4 Conclusions

The rates of reaction of a given hydroperoxide with various diisocyanates were observed to be dependent on the structures of the backbones of the diisocyanates; aromatic > aliphatic > aliphatic/cyclic > cyclic.

It is to be noted that by no means should any reactive aromatic diisocyanate be reacted with hydroperoxide, since the reaction is too violent which may result in explosion. For this reason the less reactive diisocyanates, such as aliphatic, aliphatic/cyclic or cyclic were preferred in programme of synthesis.

New bisperoxycarbamates have been synthesised and these will now be investigated as crosslinking agents for rubbers.

FIGURE 2.18 The disappearance of the -N=C=O peak with time of reaction (IPDI and tert-butyl hydroperoxide)

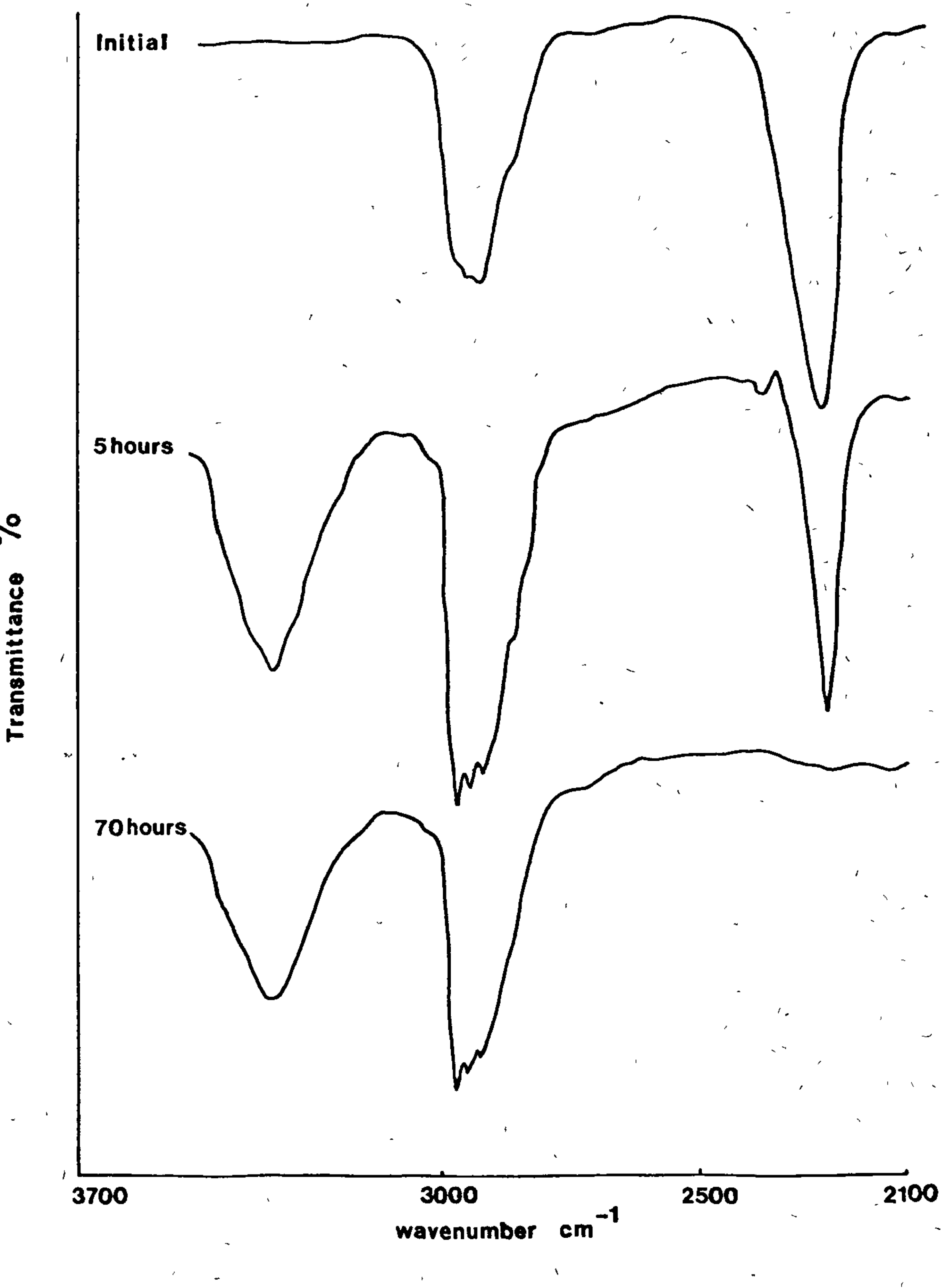


FIGURE 2.19 DSC traces of bisperoxycarbamates (b)-(d)

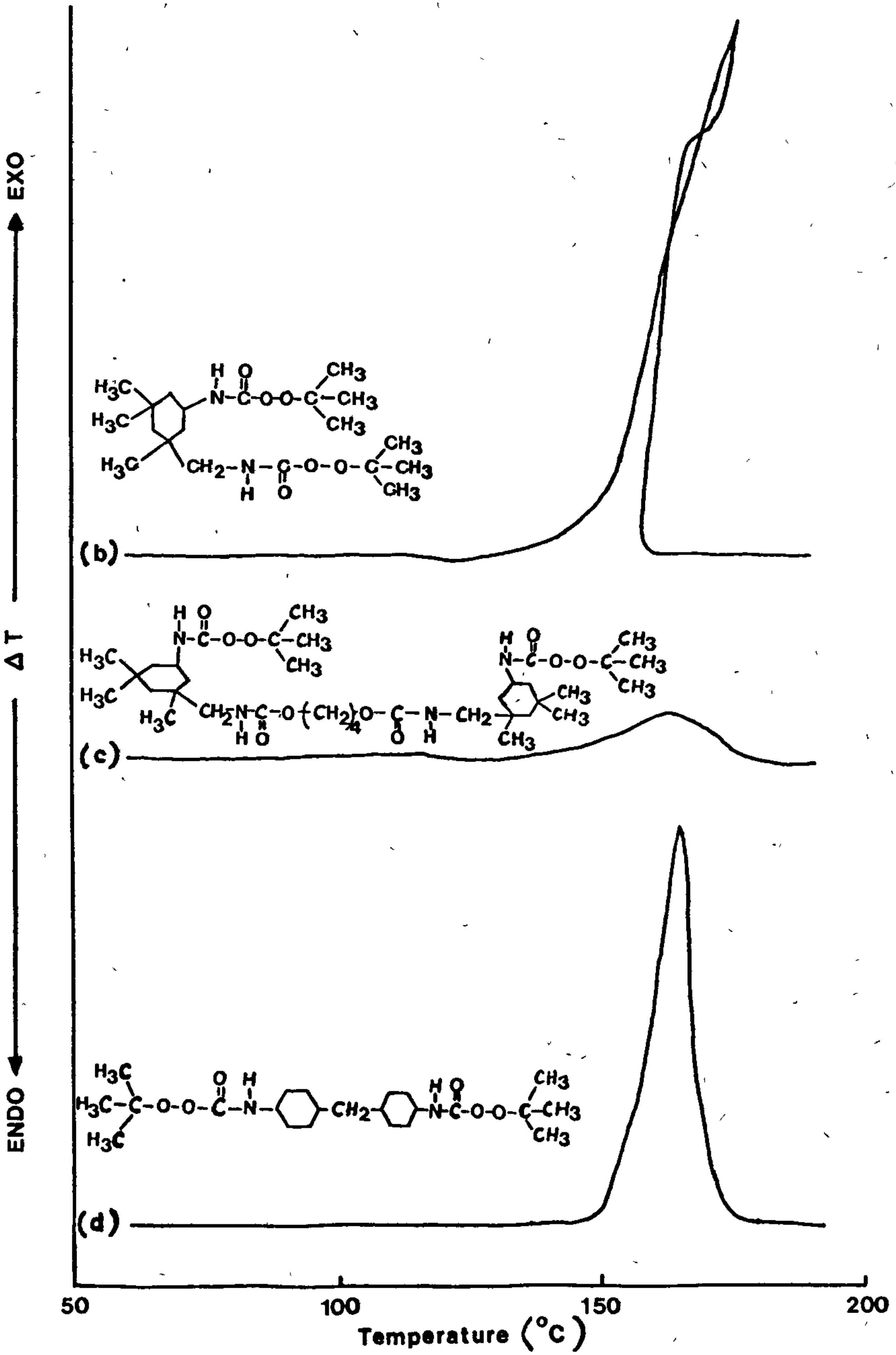


FIGURE 2.20 DSC traces of bisperoxycarbamates (e)-(g)

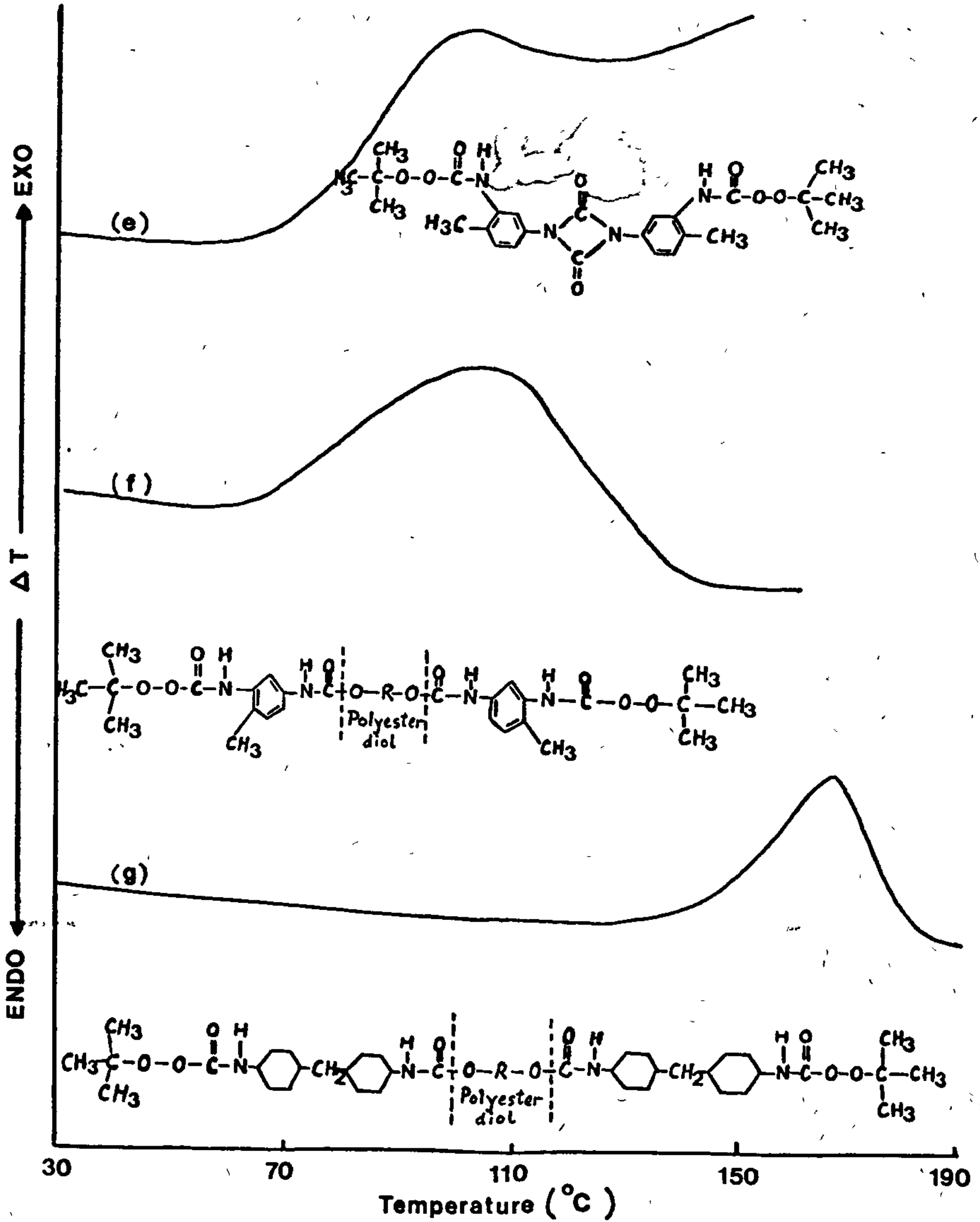


FIGURE 2.21 Infra-red spectrum of bisperoxycarbamate (b) (KBr disc)

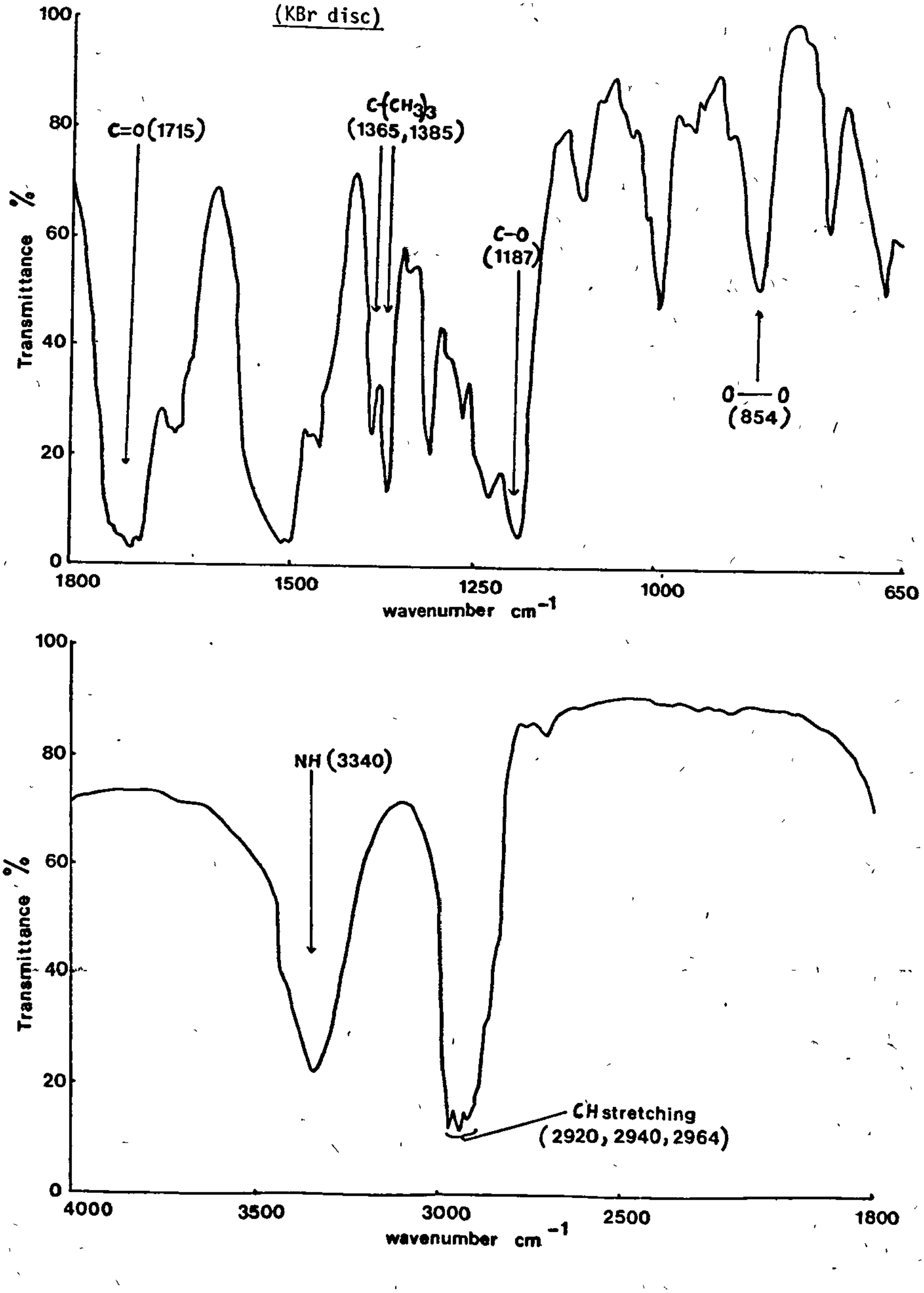
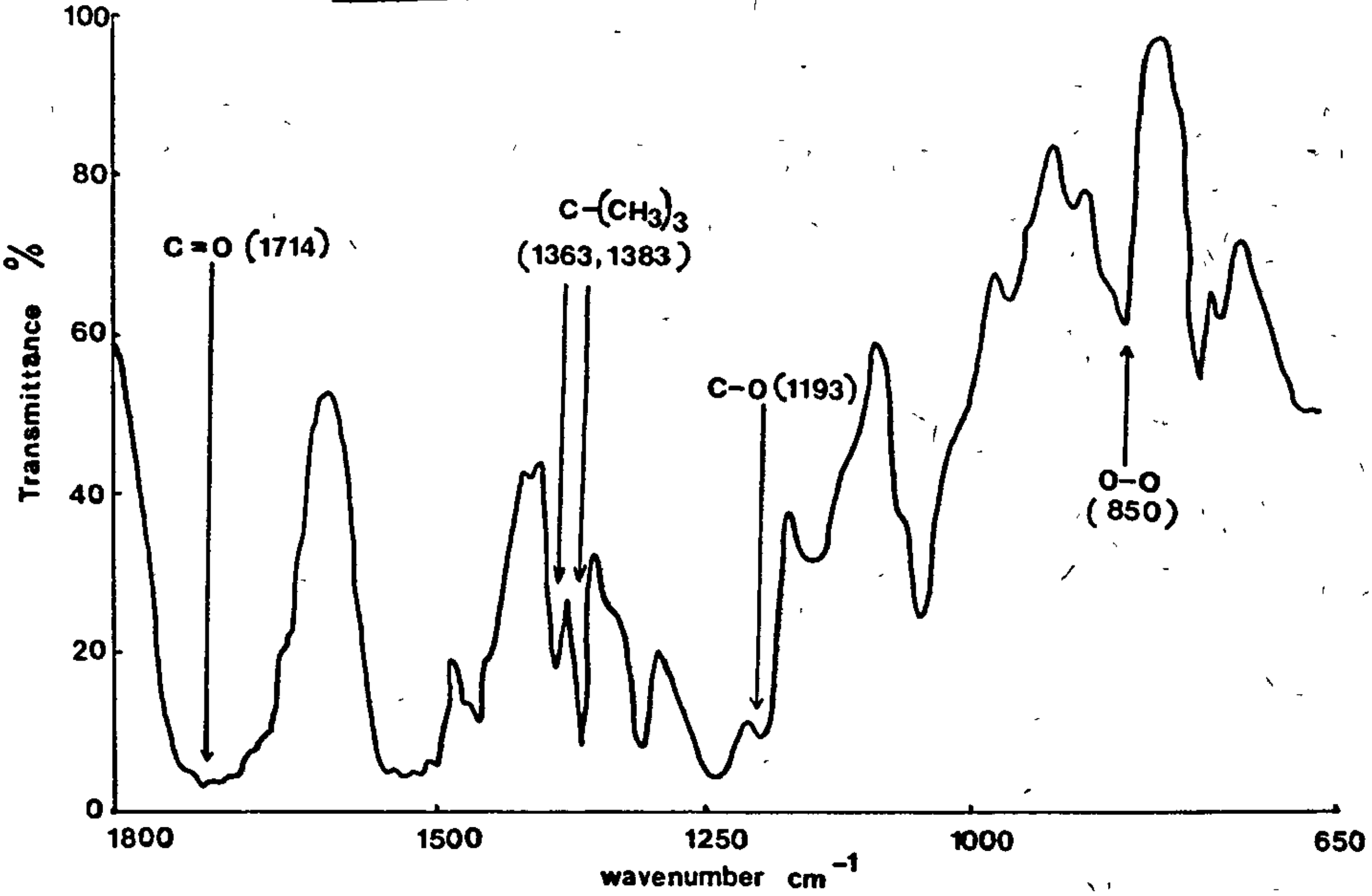


FIGURE 2.22 Infra-red spectrum of bisperoxycarbamate (c) (KBr disc)



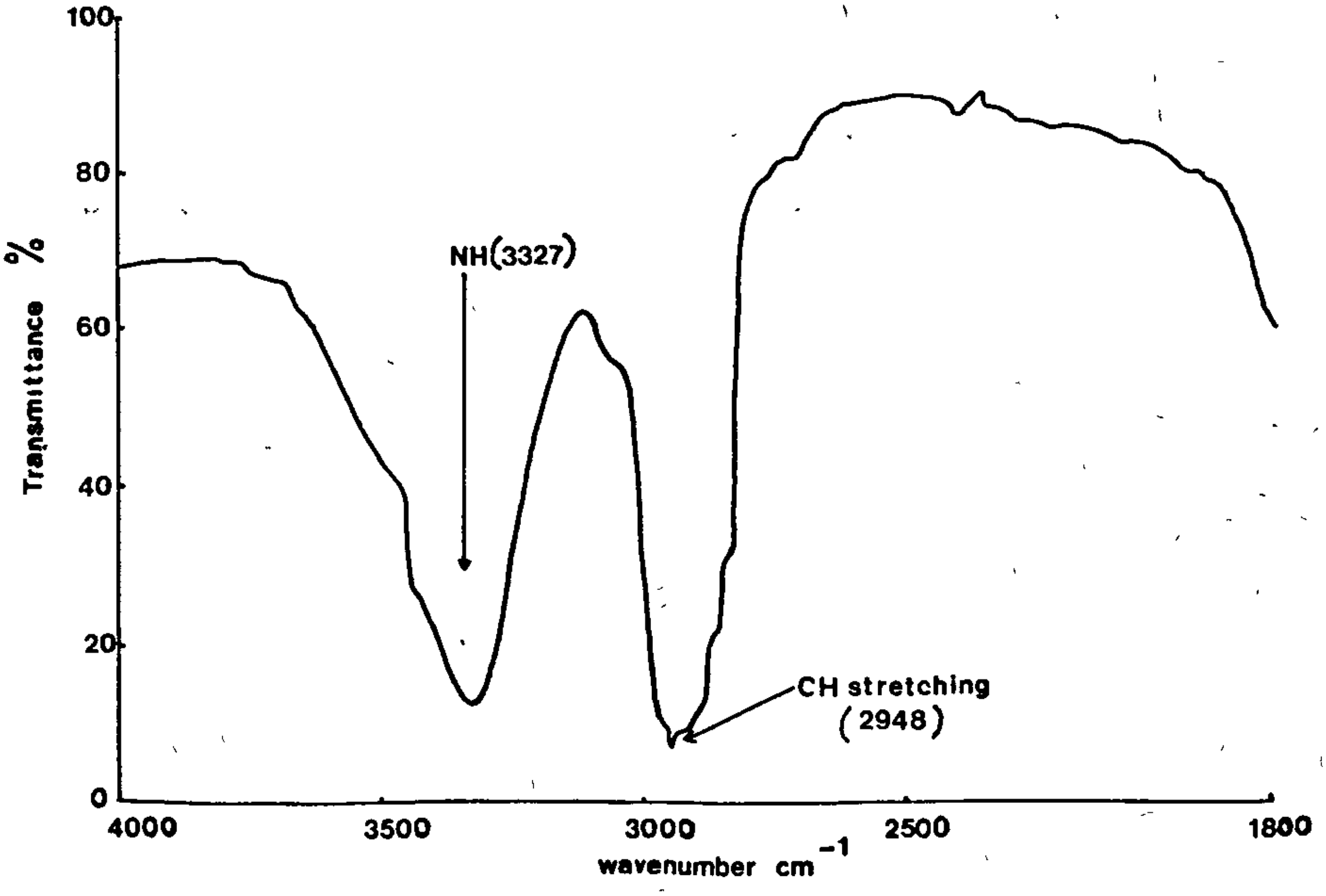
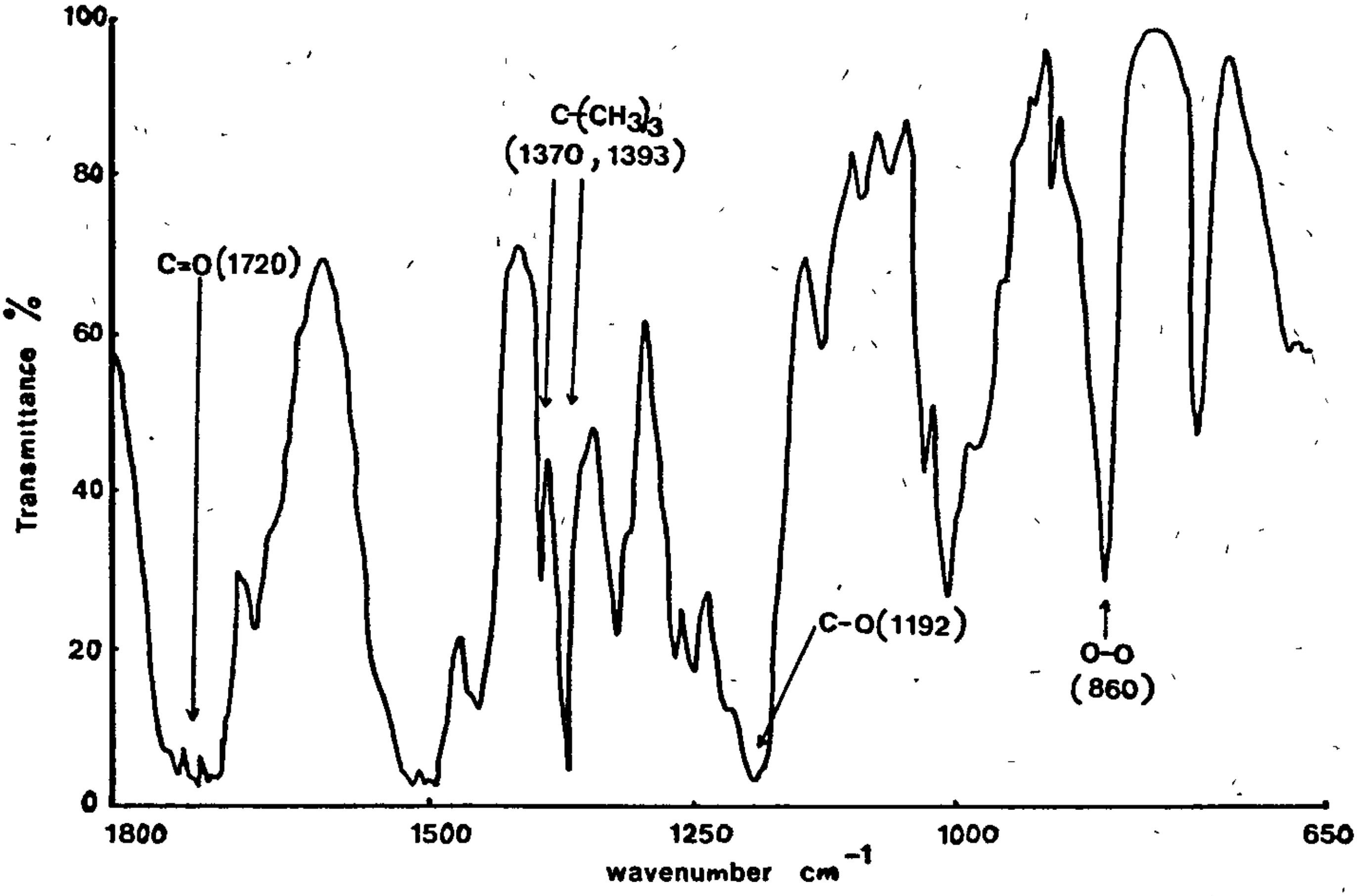


FIGURE 2.23 Infra-red spectrum of bisperoxycarbamate (d) (KBr disc)



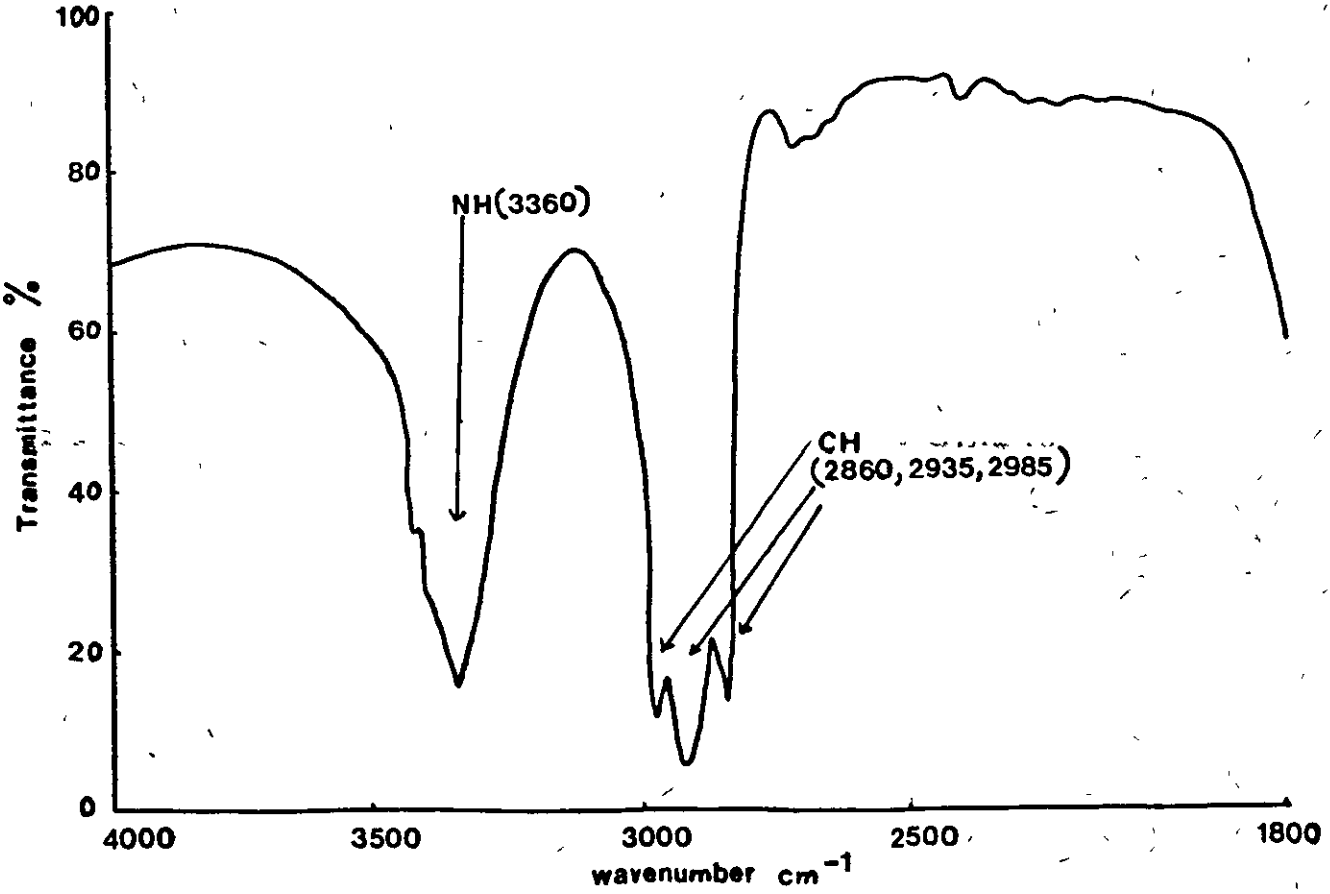


FIGURE 2.24 Infra-red spectrum of bisperoxycarbamate (e) (KBr disc)

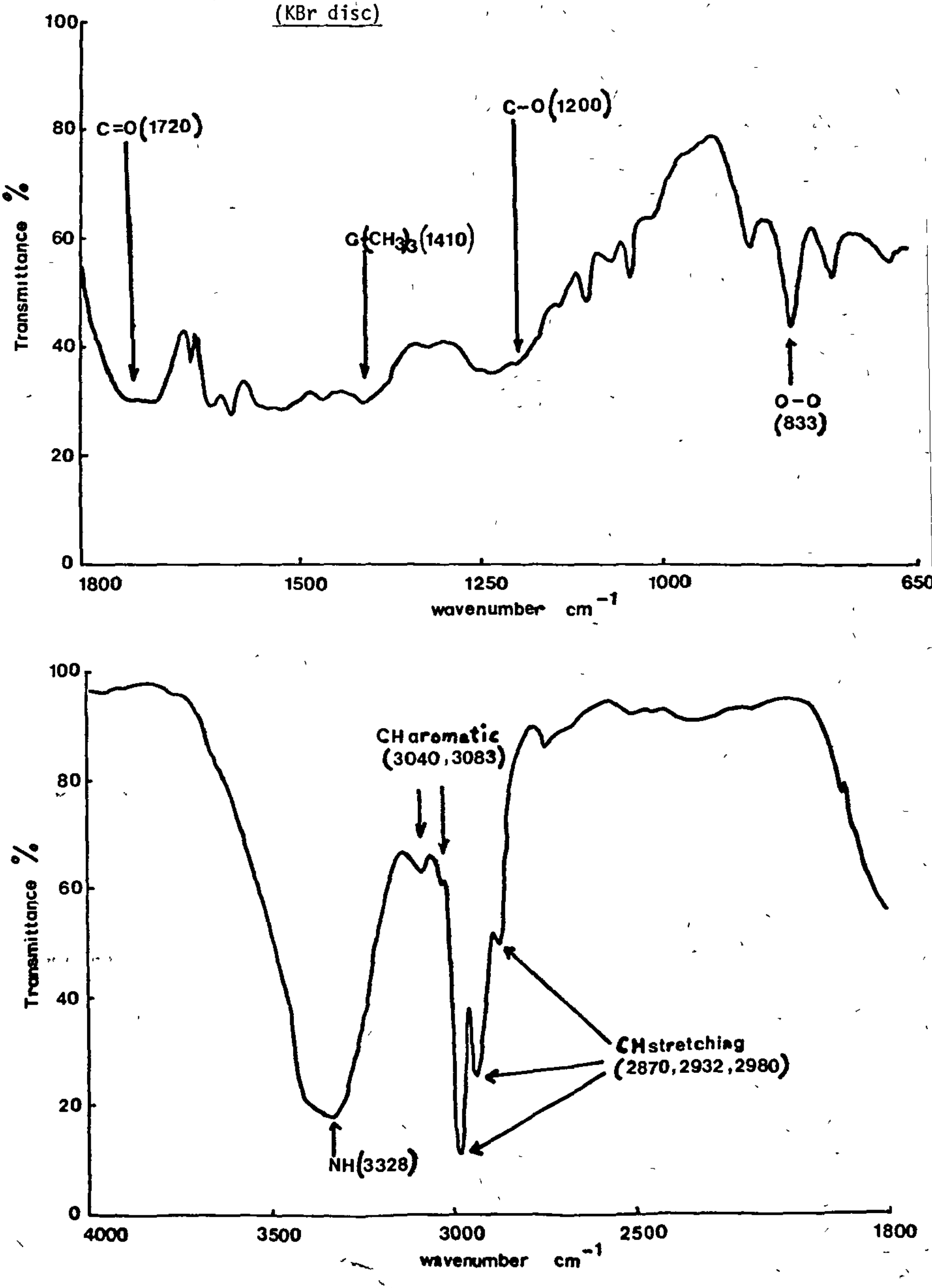


FIGURE 2.25 Infra-red spectrum of bisperoxycarbamate (f) (KBr disc)

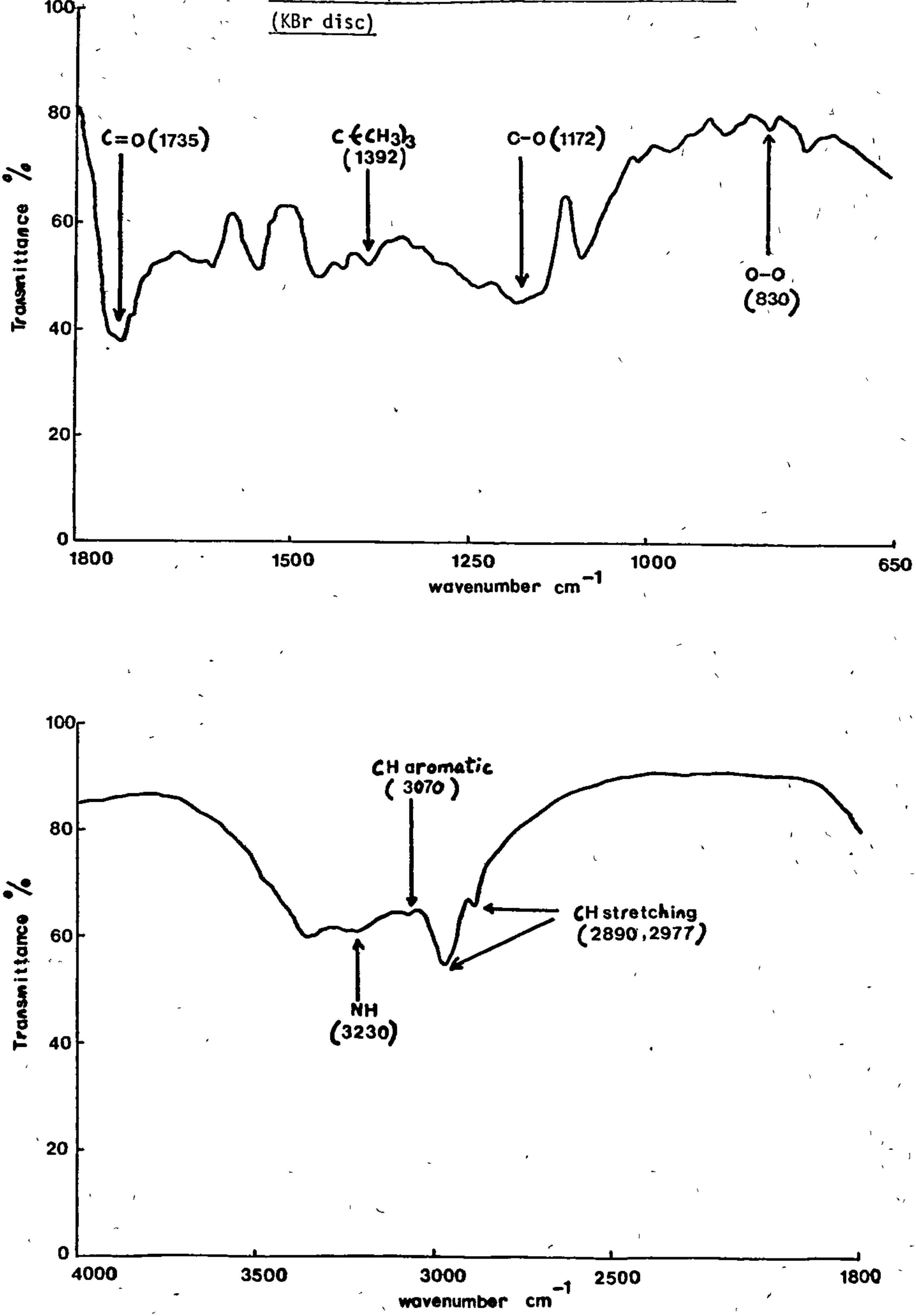
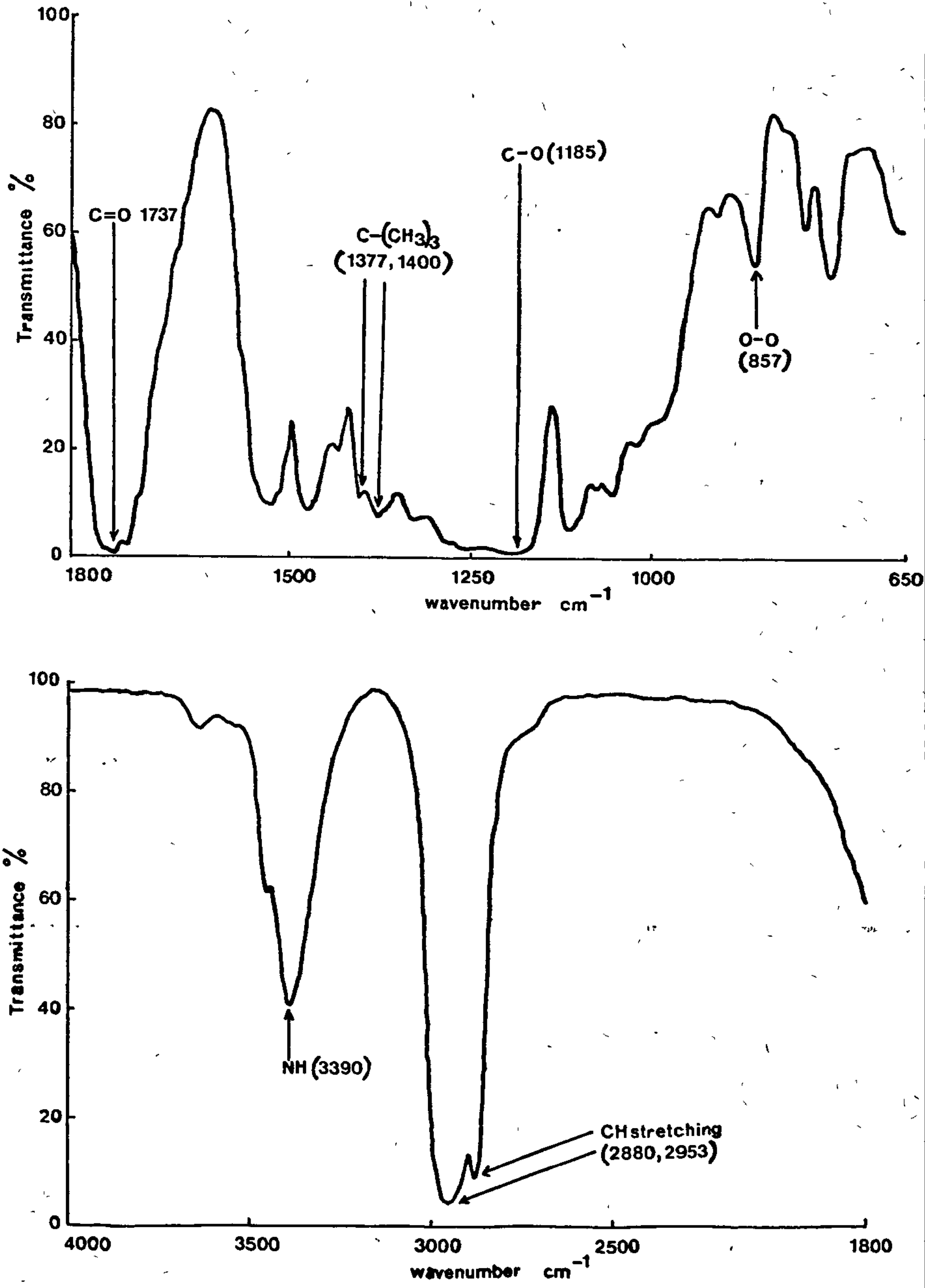


FIGURE 2.26 Infra-red spectrum of bisperoxycarbamate (g) (Film)



CHAPTER 3

CURING ABILITY OF BISPEROXYCARBAMATES IN NATURAL AND POLYISOPRENE RUBBERS

Introduction

The determination of the minimum cure activation temperature of mixes containing new curing agents, such as bisperoxycarbamates, using any given technique needs to be resolved before proceeding to further work. Determination by a fundamental technique was sought in place of the more usual trial and error method using the Monsanto Oscillating Disc Rheometer at varying temperatures. Differential Thermal Analysis (DTA) had previously been shown to provide us with such information (113) and in that instance the researcher defined the curing region as the interval between point A (see Figure 3.1), the temperature at which the thermogram begins to rise from a baseline, and point B, the temperature at which the thermogram returns to a stable baseline. Based on this reference (113), the author used the DTA as a means of detecting the minimum cure activation temperatures of the bisperoxycarbamate mixes.

To confirm and extend the DTA cure activation temperature data, the vulcanisation characteristics of the bisperoxycarbamate mixes would have to be further investigated and confirmed by means of an established technique. Methods for determining the vulcanisation characteristics of rubber mixes have been the subject of extensive investigations. One of these methods, the Monsanto Oscillating Disc Rheometer (ODR), is an instrument well established as appropriate for such investigations.

The ODR technique provides us with information such as state of cures of rubber mixes in terms of torque values. Hence to extend this investigation further the fundamental values of physical cross-link density were used to confirm the data obtained from the ODR technique.

3.2 Differential Thermal Analysis

3.2.1 Basic Principles

The basis of the DSC technique is as follows.

An inert reference material which undergoes no thermal transition in the temperature range investigated is normally used in conjunction with the experimental material. They are both heated at a same constant rate and the temperature difference between the sample and the reference is measured using thermocouples connected in opposition. When the temperature of the sample is equal to the reference, the two thermocouples produce identical voltages and therefore the net voltage equals zero. When the temperatures differ there is a net voltage which is proportional to the difference in temperature. This net voltage is amplified and recorded on the y-axis of an x-y recorder. The temperature of the experimental material and reference,which is varied at a programmed constant rate, is monitored on the x-axis.

It is to be noted that Differential Scanning Calorimeter (DSC) measures the amount of energy required or removed to keep the sample and reference at the same temperature. Since the net voltage is proportional to the difference in temperature, it is normally quoted as ΔT.

3.1.2 Materials

Polyisoprene rubber of similar grade as before was used but without purification since a large amount of rubber was required for technological evaluation.

Natural rubber of grade deproteinised natural rubber was obtained from MRPRA and was similarly used without purification. The DPNR had the following specified properties:

Volatile matter, % wt	0.19
Ash content, % wt	0.14

Dirt,	% wt	0.002
Nitrogen,	% wt	0.11

3.2.3 Experimental

DSC traces of the gum mixes which were prepared on a two roll mix at room temperature were recorded using a Du Pont 990 Thermal Analyser equipped with a standard Du Pont heating cell. A single piece of each rubber mix weighing approximately 13 mg was encapsulated in small closed aluminium pans. An empty pan was used as the reference. For every experiment a new empty pan was used to avoid any changes occurring due to the thermal activity of the used pan.

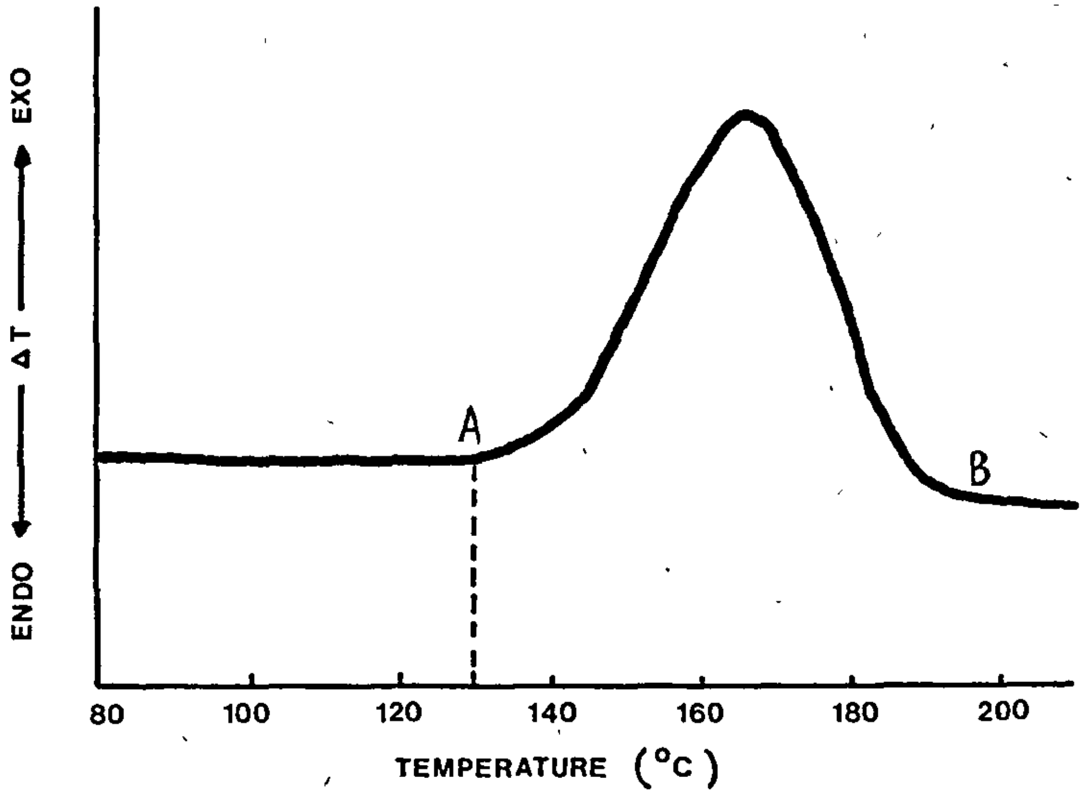
The mix was placed on the left hand thermocouple of the heating cell while the reference was placed on the right hand thermocouple. The cell was cooled to approximately 0°C by pouring liquid nitrogen into a surrounding steel jacket. In every experiment the liquid nitrogen was prevented from going into the cell and thus prevented undesirable transitions due to water condensation. When the temperature had reached about 0°C, the cooling jacket was quickly removed and replaced by a steel cover and a pyrex glass surround. The digit of the starting temperature was then adjusted until the control light extinguished indicating that the starting temperature corresponded to the recorded temperature. When this condition was achieved, the cell was immediately heated at a programmed constant rate of 20°C/min with a steady purge of pure dry nitrogen.

A known sensitivity of the net voltage (i.e. y-axis) was chosen to give optimum resolution on the y-axis of the chart. DSC [illegible] were recorded between approximately room temperature and 200°C.

3.2.4 Results and Discussion

A typical DSC [illegible] of a rubber mix containing a bisperoxycarbamate is shown in Figure 2.8. In some cases where the bisperoxycarbamates do not melt but decompose, a typical DSC [illegible] of such mix is shown in Figure 3.1. The minimum cure temperature considered realistic for practical cure rate with the bisperoxycarbamate was chosen from the DSC spectrum as the temperature at which the mix begins to show an exothermic response i.e. at 130°C in Figure 3.1.

FIGURE 3.1 DSC spectrum of DPNR mix containing 4 phr bisperoxycarbamate*



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* Bisperoxycarbamate from methylene-bis-(4-cyclohexyl isocyanate) and tertiary butyl hydroperoxide

For simplicity the following abbreviations are used to denote the various bisperoxycarbamates:

Bisperoxycarbamate I - Hexamethylene bis N,N' (cumyl peroxycarbamate) (aliphatic)

Bisperoxycarbamate II - Bisperoxycarbamate prepared from 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl-isocyanate (IPDI) and tertiary butyl hydroperoxide (aliphatic/cyclic)

Bisperoxycarbamate III - Bisperoxycarbamate prepared from methylene-bis-(4-cyclohexyl isocyanate) and tertiary butyl hydroperoxide (cyclic)

Bisperoxycarbamate IV - Bisperoxycarbamate prepared from a polyurethane prepolymer based on 1,4 butane diol reacted with excess IPDI (block ratio 1:2); this polyurethane type was then reacted with tertiary butyl hydroperoxide to form the bisperoxycarbamate (prepolymer).

Bisperoxycarbamate V - Bisperoxycarbarmate prepared from 2,4 tolylene diisocyanate dimer and tertiary butyl hydroperoxide (aromatic)

Bisperoxycarbamate VI - Bisperoxycarbamate prepared from Polyester/TDI prepolymer (Solithane 790) and tertiary butyl hydroperoxide (prepolymer).

Bisperoxycarbamate VII - Bisperoxycarbamate prepared from Caprolactone/methylene bis-4-(cyclohexyl isocyanate) prepolymer and tertiary butyl hydroperoxide (prepolymer).

Table 3.1 shows the minimum cure activation temperatures derived from the technique by which a satisfactory cure rate was found possible for the bisperoxycarbamates in natural and polyisoprene gum stocks. It is appreciated that a higher temperature can be used if shorter cure time is preferred.

As shown in Table 3.1, the bisperoxycarbamates based on aromatic diisocyanate backbones are the least stable bisperoxycarbamates; this comment is based on the decomposition temperature of Figures 219 & 220 and the data in Table 3.1. If bisperoxycarbamates are to be used industrially, then the most stable bisperoxycarbamate, i.e. the bisperoxycarbamate based on cyclic diisocyanate backbone, is preferred as this is close to the present conventional industrial processing temperatures. The minimum cure activation temperaturesof some of these bisperoxycarbamates are similar to that of the traditional rubber cure temperatures.

3.3 Cure Characteristics by Monsanto ODR

To confirm and extend the DSC cure activation temperature data the vulcanisation characteristics of the bisperoxycarbamates were further investigated by means of the ODR.

3.3.1 Basic Principles

Monsanto ODR TM 100 consists of a die cavity located in large electrically heated platens as shown in Figure 3.2. The temperatures of the platens and dies are maintained to within ±0.5°C by proportional temperature controllers. A mix is placed within the vulcanisation chamber so that a reciprocating biconical disc is embedded in the mix and the mix is maintained under high pressure throughout the test. The sinusoidal oscillation of the biconical disc at constant amplitude exerts a shear strain on the mix. As vulcanisation proceeds the torque required to shear the mix increases and a curve of torque versus cure time is generated. The torque value

TABLE 3.1

Minimum temperature considered to give practical cure rates with bisperoxycarbamates using the DSC technique

Bisperoxycarbamate	Minimum cure activation temperature (as determined by Du Pont DSC)
I	116°C
II	125°C
III	130°C
IV	130°C
V	59°C
VI	60°C
VII	129°C
dicumyl peroxide	140°C

FIGURE 3.2 Basic principles of Monsanto ODR

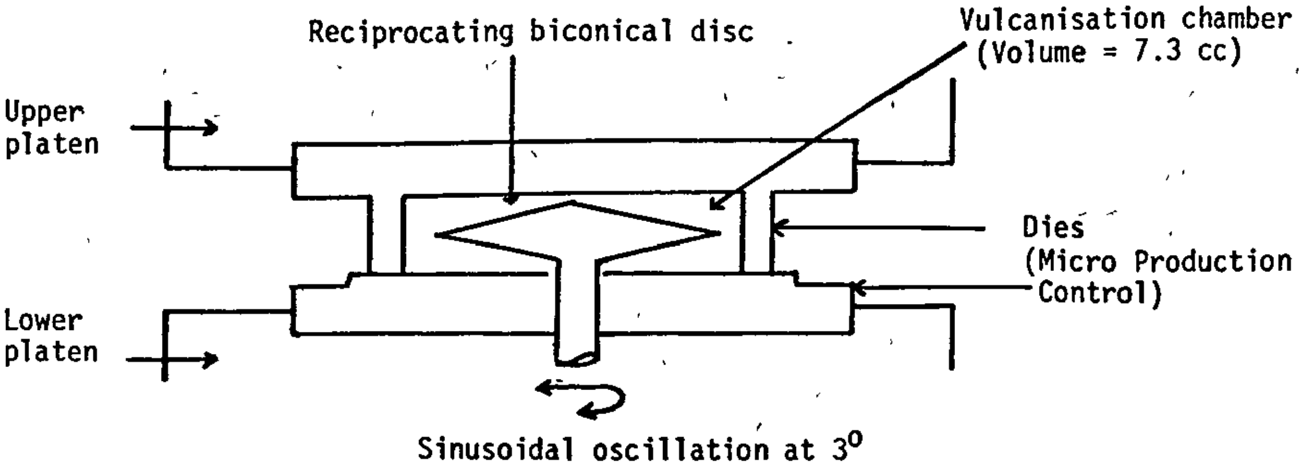
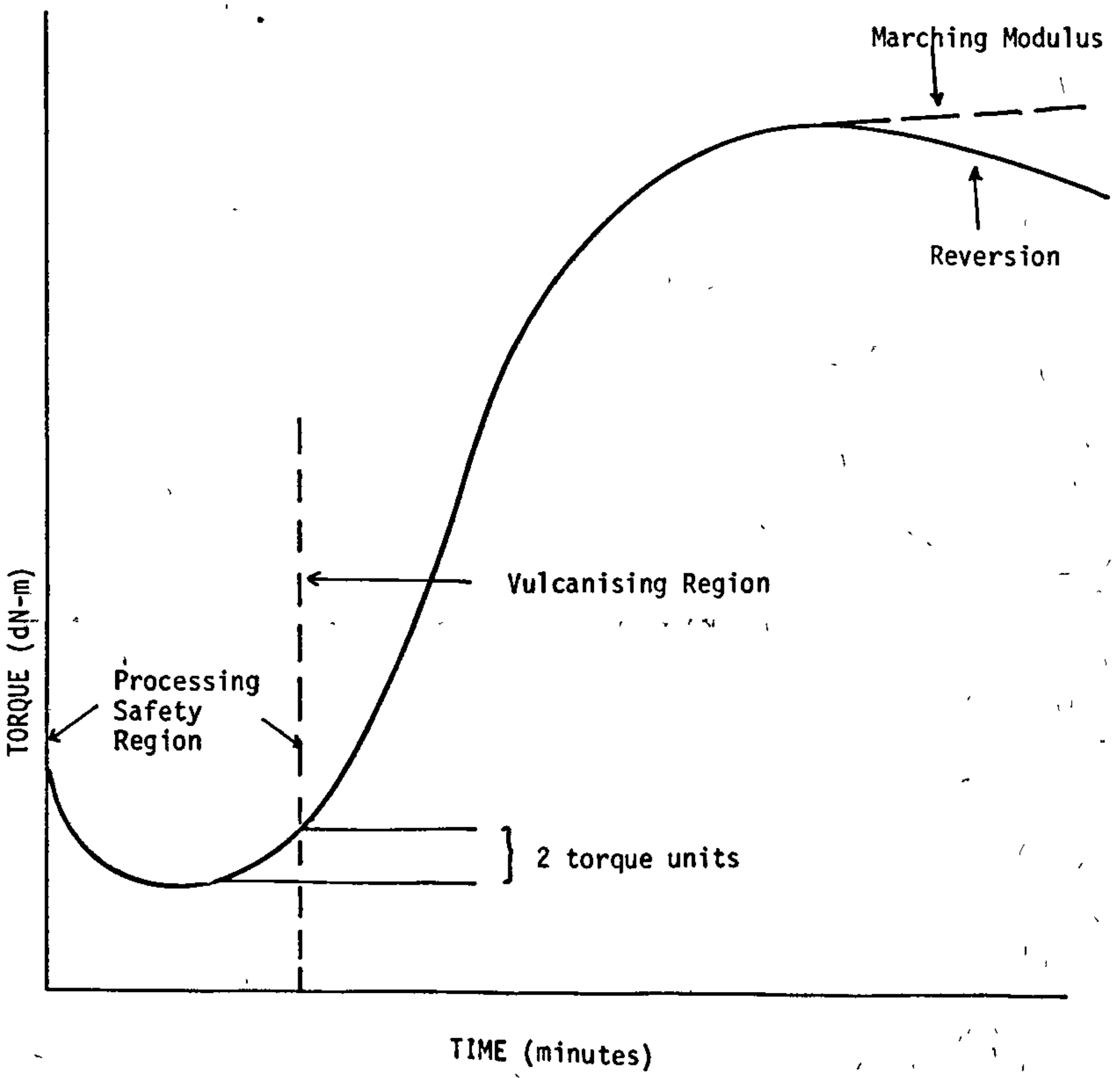


FIGURE 3.3 Rubber vulcanisation features as measured by ODR



is directly related to the shear modulus of the mix; see Figure 3.3 for properties available from an ODR.

3.3.2 Experimental

The temperature of the platens and dies was maintained at the required cure temperature and the biconical disc was kept in engaged or driven position. A mix of 9g. was placed within the vulcanisation chamber and high pressure was applied so that the biconical disc was embedded in the mix. The motor which oscillates the disc was immediately switched on and the trace was recorded on a chart.

3.3.3 Results and Discussion

The cure characteristics of the bisperoxycarbamate mixes are shown in Figures 3.4 and 3.5. Only the bisperoxycarbamates I-III show reasonable states of cure while the bisperoxycarbamates IV-VII have very low cure state efficiency even when high weight concentrations of the bisperoxycarbamates are added to the rubbers; it was therefore decided to omit these latter bisperoxycarbamates in the subsequent evaluation.

At equivalent molar concentration, the order of the cure state efficiency of the bisperoxycarbamates in both rubbers was found to be dependent on the structures of the diisocyanate backbones; cyclic > aliphatic/cyclic > aliphatic > prepolymer. All these bisperoxycarbamates have a lower cure state efficiency than the dicumyl peroxide system.

The cure rates of the four bisperoxycarbamates I-IV in both natural and polyisoprene rubbers were found to be faster than that of the dicumyl peroxide system. For example, maximum ODR torque occurs within 10 minutes at 160°C for the bisperoxycarbamate III whereas with the dicumyl peroxide about 3 hours at 150°C (42) must elapse before maximum or cure state equilibrium occurs.

FIGURE 3.4 Curing characteristis of bisperoxycarbamates and dicumyl peroxide in DPNR (ODR)

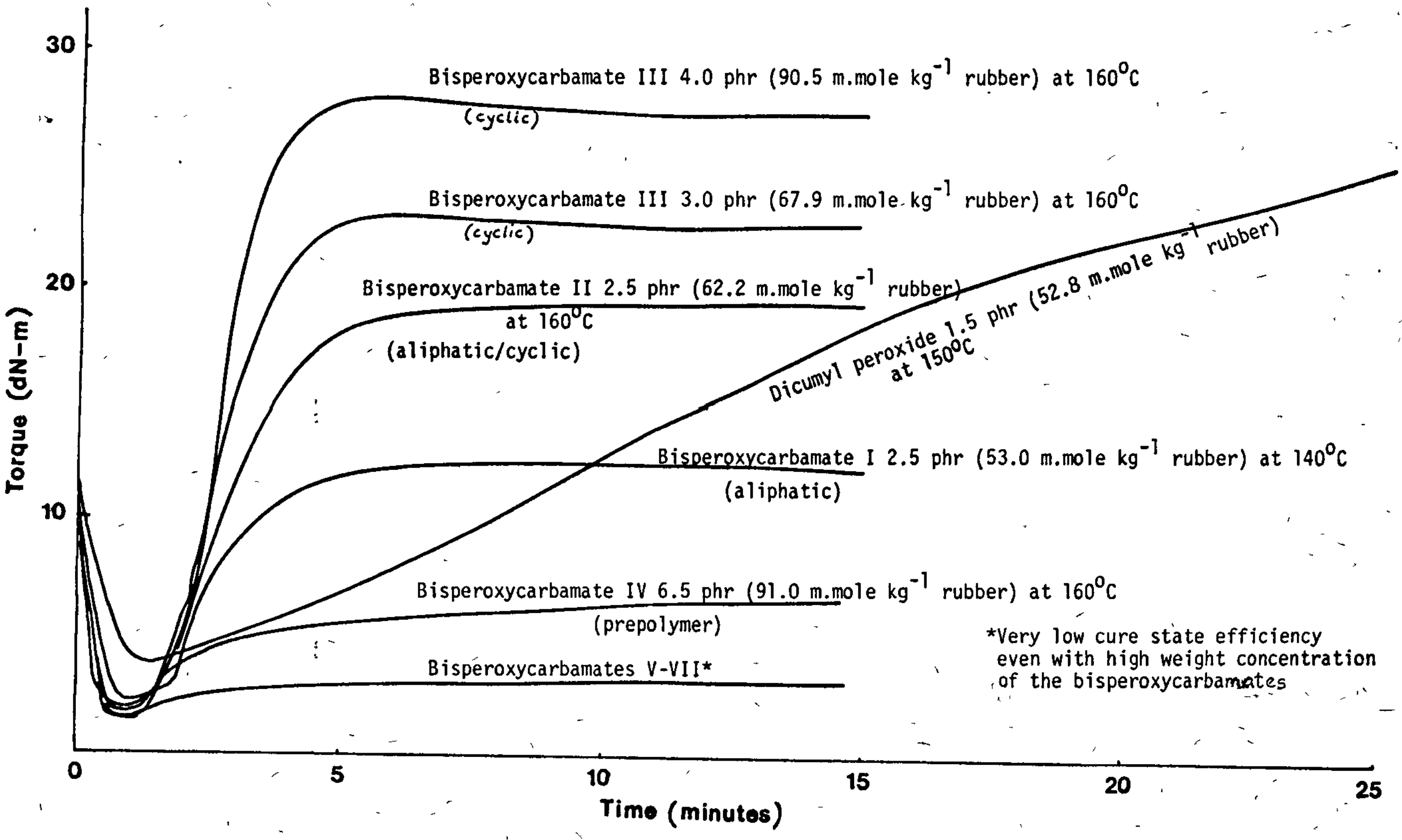
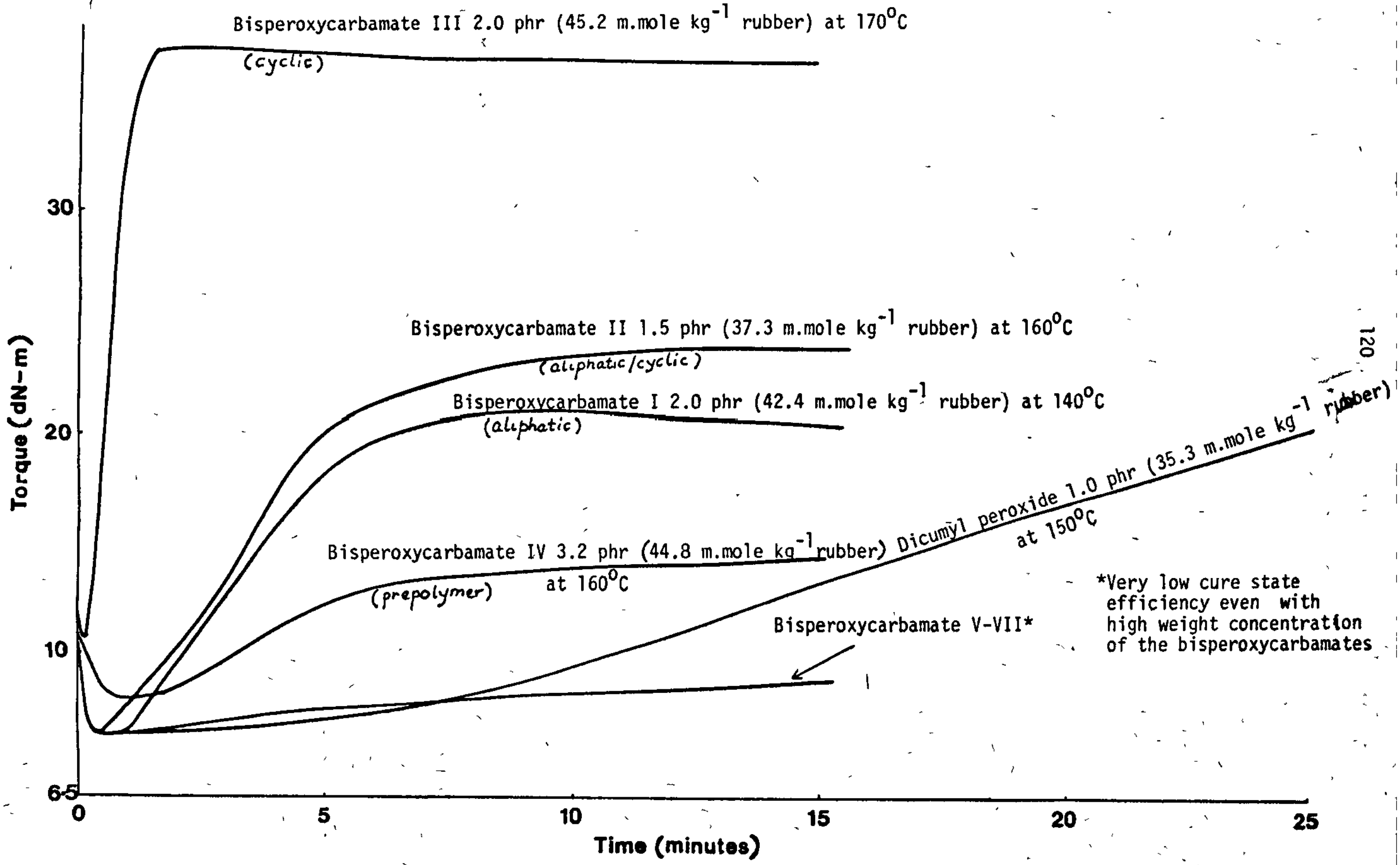


FIGURE 3.5 Curing characteristics of bisperoxycarbamates and dicumyl peroxide in IR 305 (ODR)



*Very low cure state efficiency even with high weight concentration of the bisperoxycarbamates

3.4 Physical Crosslink Density

3.4.1 Theory

Basically there are two equations conventionally used in calculating crosslink density of a gum vulcanisate from swelling measurements, namely the simpler original form of the Flory-Rehner equation (114), (equation 81), or this in a modified form equation (115) (equation 82). Both the equations are derived from assumptions based on the validity of the statistical theory of rubber-like elasticity.

$$-\ln (1 - V_r) - V_r - \chi V_r^2 = \rho V_o M_c^{-1} V_r^{1/3} \qquad (81)$$

$$-\ln (1 - V_r) - V_r - \chi V_r^2 = \rho V_o M_c^{-1} (V_r^{1/3} - V_r/2) \qquad (82)$$

where M_c is the number average molecular weight between crosslinks
ρ is the density of rubber
V_o is the molar volume of solvent
V_r is the volume fraction of rubber in swollen vulcanisate
χ is the polymer solvent interaction constant
$(2M_c)^{-1}$ is the crosslink density

The value of χ used for the rubber-toluene was 0·42

For the present research, the author prefers to use the equation 81 for two reasons: first there is no experimental verification to support the theoretical preference for the modified equation 82 and second the advantage that values of χ derived are less dependent upon V_r (116).

3.4.2 Experimental

Optimum cure times of the natural and polyisoprene gum stocks were obtained from their ODR traces and the following cure conditions were used to cure these gum stocks for technological evaluations.

TABLE 3.2 Cure conditions for the natural and polyisoprene gum stocks

Curing Systems	Cure conditions	
	DPNR	IR 305
Bisperoxycarbamate I	15 min/140°C	15 min/140°C
Bisperoxycarbamate II	10 min/160°C	15 min/150°C
Bisperoxycarbamate III	10 min/160°C	15 min/170°C
Dicumyl peroxide	60 min/150°C	60 min/150°C

Approximately 2 cm^3 of a vulcanisate was weighed accurately and then immersed in toluene at room temperature for 24 hours. After 24 hours the sample was removed, rapidly blotted with tissue and transferred to a previously weighed stoppered sample tube. The stoppered sample tube was weighed to obtain swollen weight of sample. The crosslink density was calculated from the results obtained using equation 81. The experiment was repeated and an average crosslink density was quoted.

3.4.3 Results and Discussion

Figures 3.6 - 3.9 illustrate the effect of curing agent type and molar or weight concentration on crosslink density. At equivalent molar and weight proportions the crosslink efficiencies of the bisperoxycarbamates in the two rubbers were observed to be dependent on the structures of their diisocyanate backbones: cyclic > aliphatic/cyclic > aliphatic > prepolymer.

In natural rubber for a given concentration in terms of parts by weight or moles of curing agent the dicumyl peroxide vulcanisates gave higher crosslink density than their corresponding bisperoxycarbamate vulcanisates. Also, the polyisoprene rubber (Cariflex IR 305) vulcanisates have higher crosslink densities for a given concentration of curing agent in terms of parts by weight or mole than the equivalent natural rubber. This is considered due

FIGURE 3.6 Crosslink density vs concentration of bisperoxycarbamate curing agent (phr) in DPNR

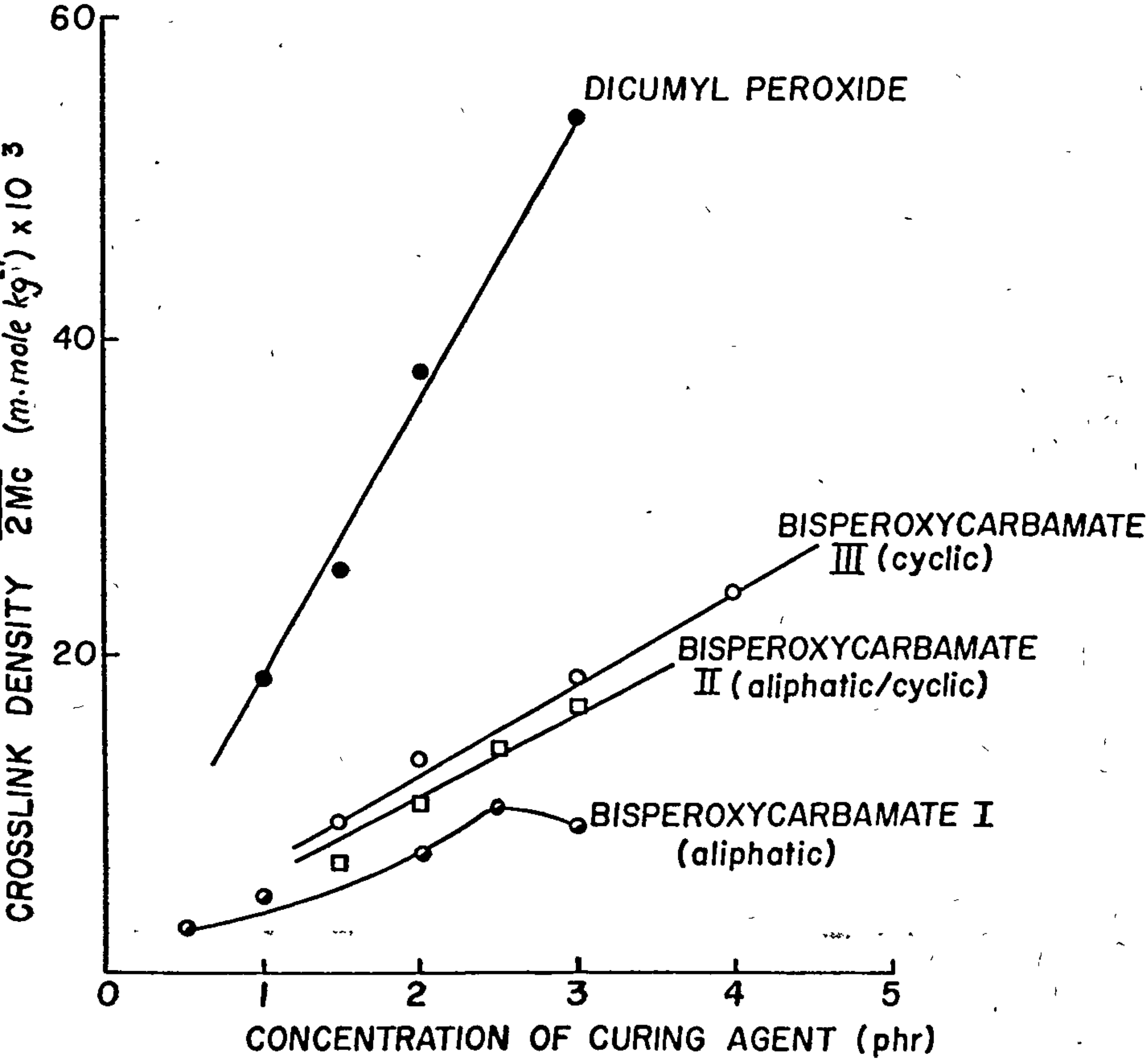


FIGURE 3.7 Crosslink density vs concentration of bisperoxycarbamate curing agent (phr) in IR 305

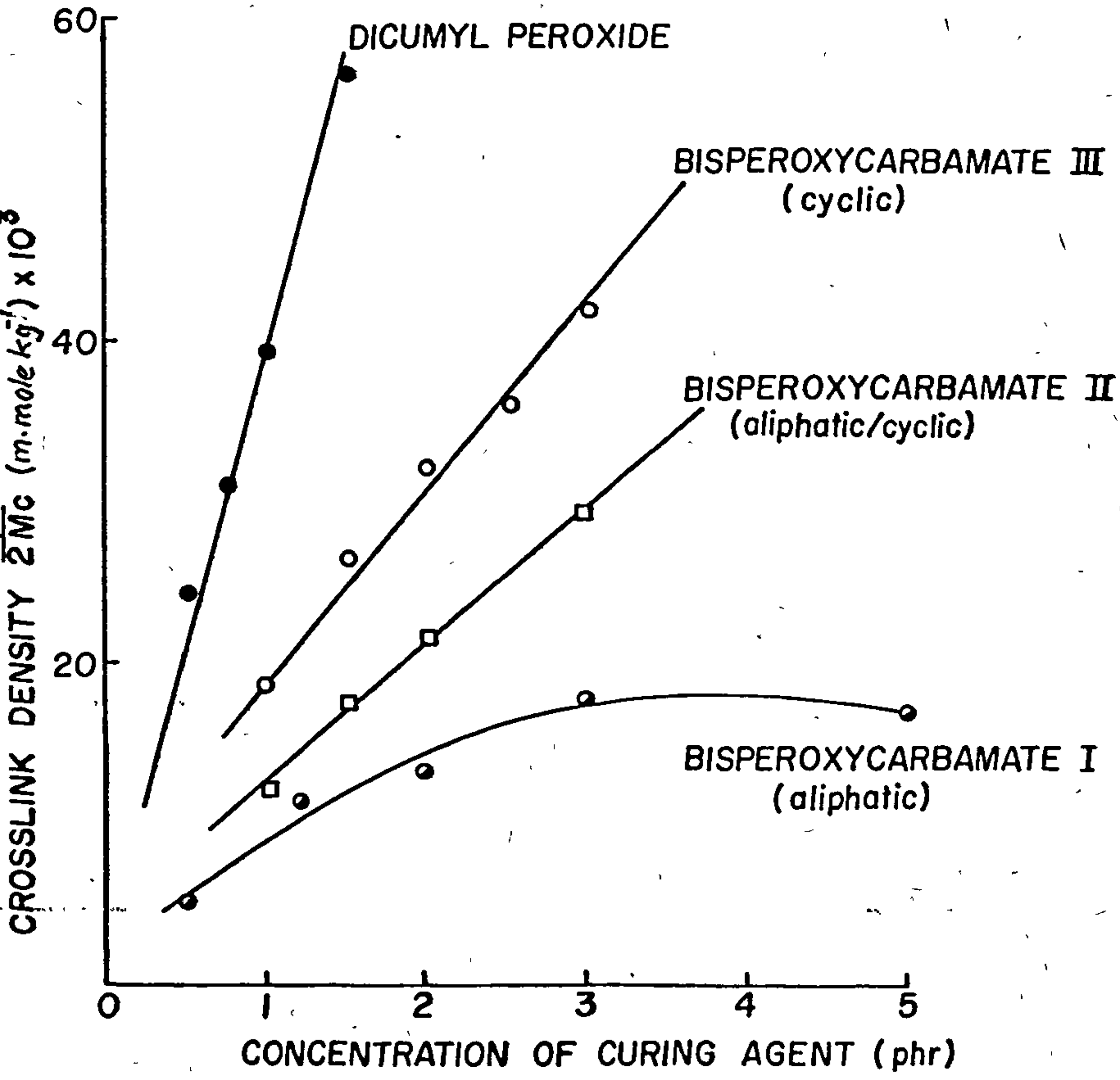


FIGURE 3.8 Crosslink density vs concentration (m.mole kg^{-1} rubber) of bisperoxycarbamate in DPNR

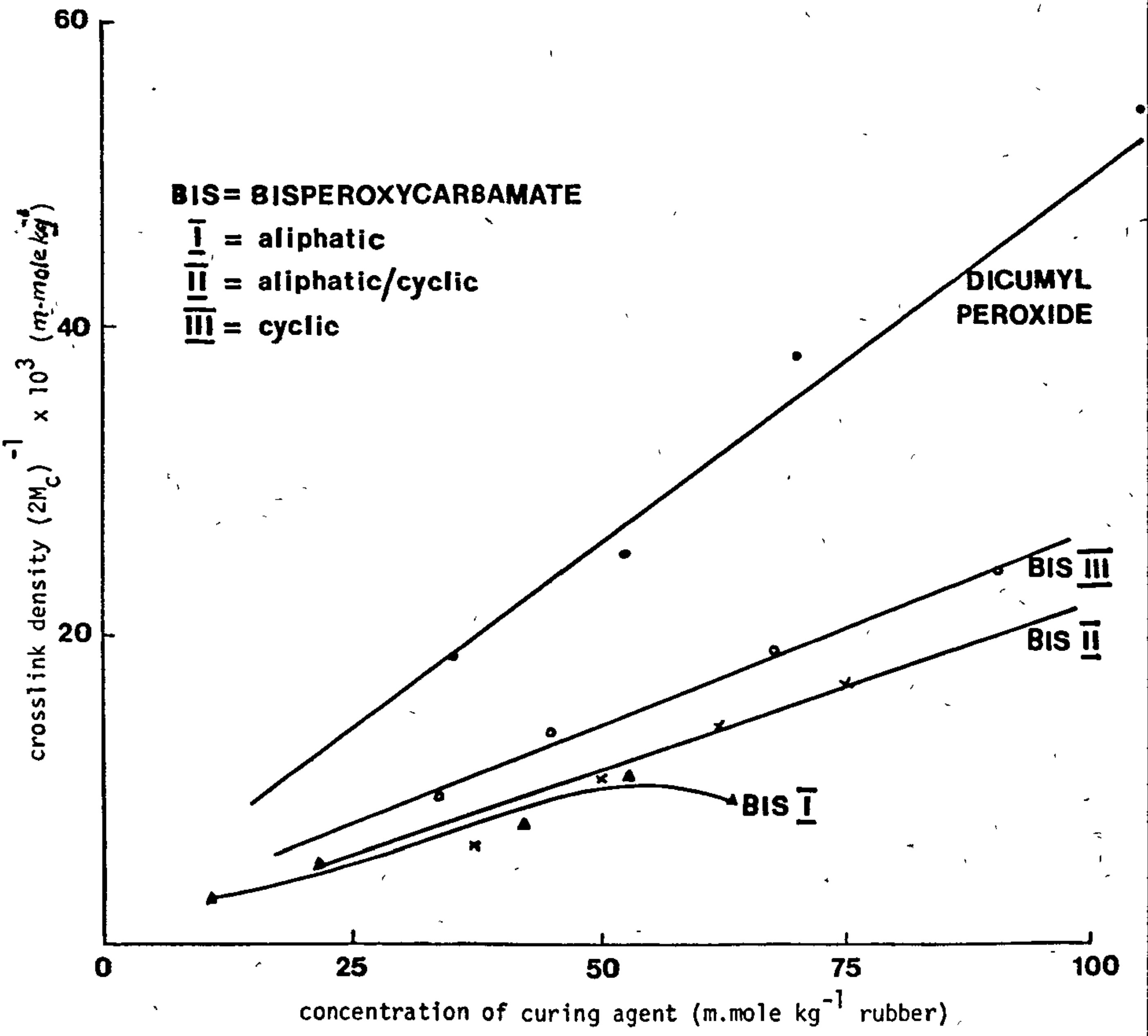
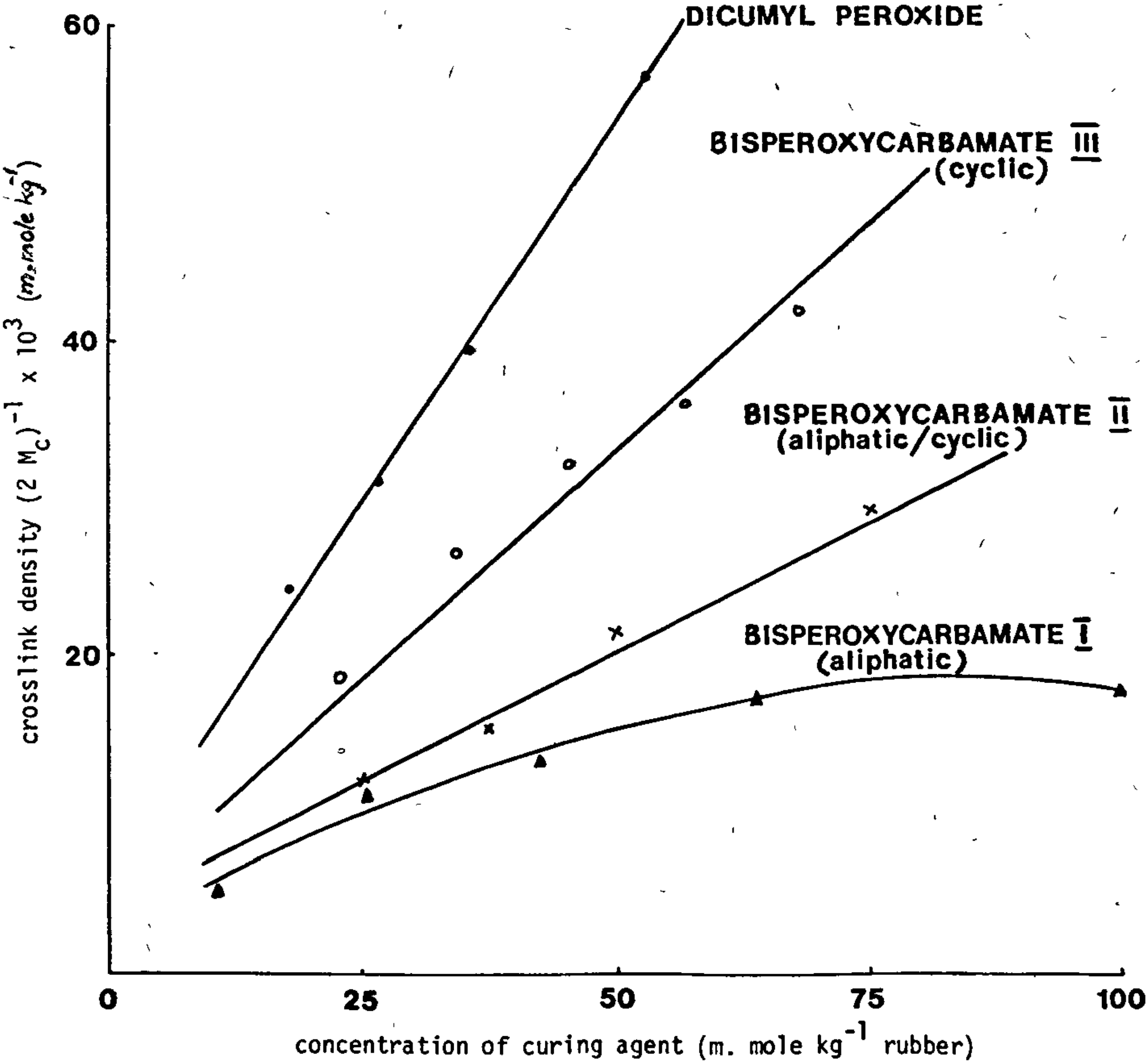
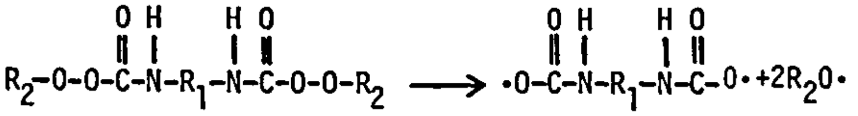


FIGURE 3.9 Crosslink density vs concentration (m.mole kg^{-1} rubber) of bisperoxycarbamate IR 305

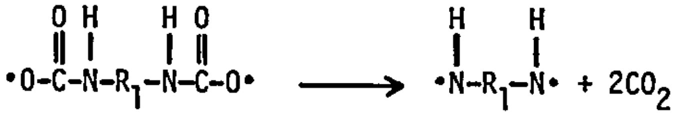


to the presence of vinyl structures (5% vinyl content) in the polyisoprene macromolecules.

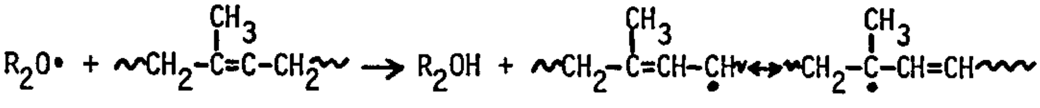
Considering the decomposition mechanisms of bisperoxycarbamates, crosslinking of natural or polyisoprene rubbers with ditertiary butyl or dicumyl peroxides and the evidence of the grafted amino group onto polyisoprene rubber, the crosslinking mechanism of bisperoxycarbamates is proposed represented by the following equations 83-89. It is to be noted the reactions involving the vinyl structures are not considered here.



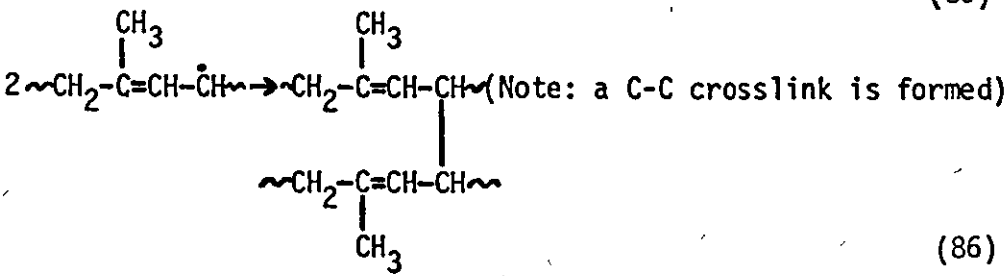
$$R_2-O-O-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-R_1-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-O-O-R_2 \longrightarrow \cdot O-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-R_1-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-O\cdot + 2R_2O\cdot \qquad (83)$$



$$\cdot O-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-R_1-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-O\cdot \longrightarrow \cdot\overset{H}{\overset{|}{N}}-R_1-\overset{H}{\overset{|}{N}}\cdot + 2CO_2 \qquad (84)$$

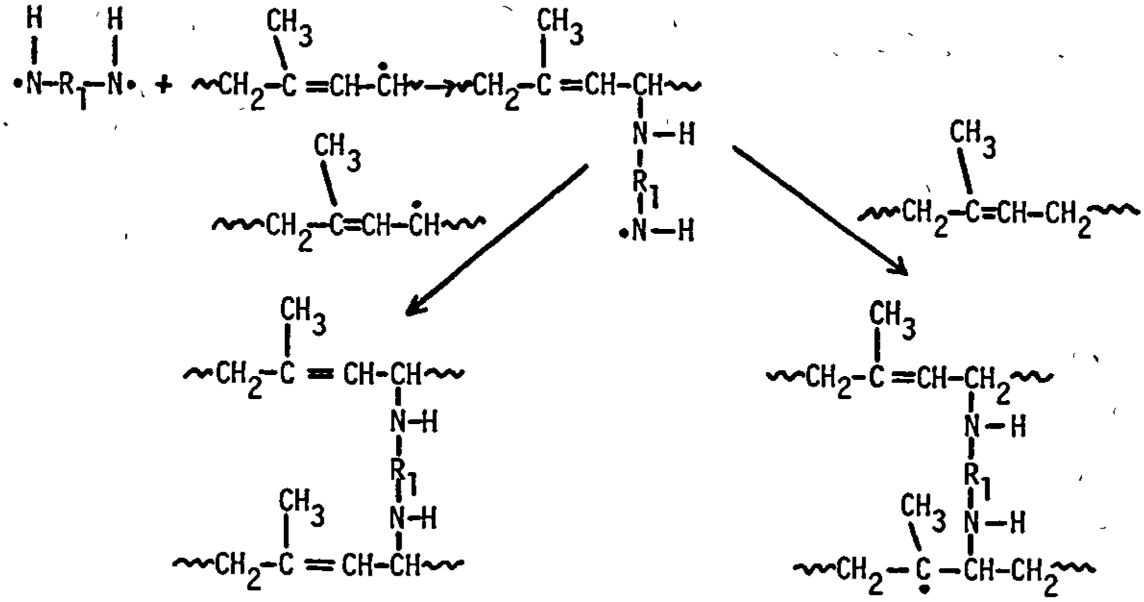


$$R_2O\cdot + \sim CH_2-\overset{CH_3}{\overset{|}{C}}=C-CH_2\sim \longrightarrow R_2OH + \sim CH_2-\overset{CH_3}{\overset{|}{C}}=CH-\underset{\bullet}{C}H\sim \longleftrightarrow \sim CH_2-\underset{\bullet}{\overset{CH_3}{\overset{|}{C}}}-CH=CH\sim \qquad (85)$$



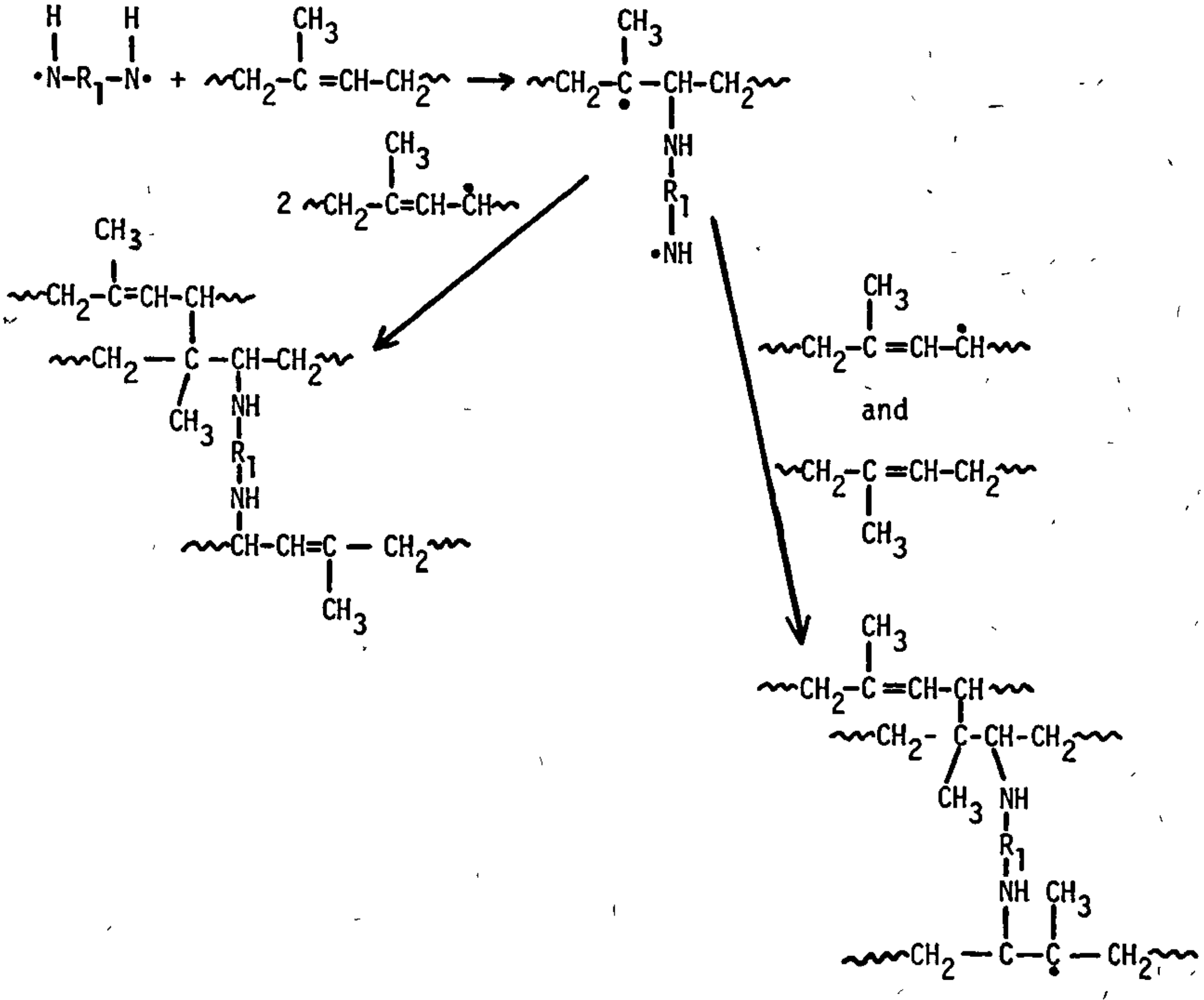
$$2\sim CH_2-\overset{CH_3}{\overset{|}{C}}=CH-\dot{C}H\sim \longrightarrow \sim CH_2-\overset{CH_3}{\overset{|}{C}}=CH-\underset{\displaystyle \sim CH_2-\underset{CH_3}{\underset{|}{C}}=CH-CH\sim}{\underset{|}{C}H}\sim \text{(Note: a C-C crosslink is formed)} \qquad (86)$$

It is to be noted that a monoperoxycarbamate causes a degree of crosslinking in polyisoprene rubber as indicated by the insolubility of the investigated sample in toluene (see Section 2.2.2.3).

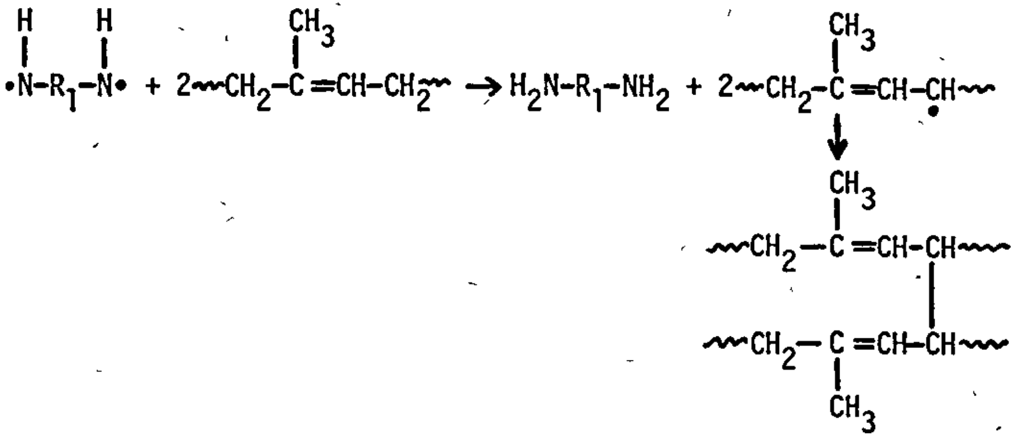


(Note: a $-NH-R_1-NH$ crosslink is formed)

(87)



(88)

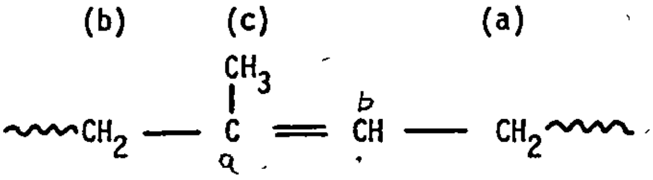


$$\cdot\overset{H}{\overset{|}{N}}-R_1-\overset{H}{\overset{|}{N}}\cdot + 2\sim CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2\sim \rightarrow H_2N-R_1-NH_2 + 2\sim CH_2-\overset{CH_3}{\overset{|}{C}}=CH-\dot{C}H\sim$$

(89)

It is considered that a bisperoxycarbamate decomposes thermally with formation of free radicals, as shown in equations 83 and 84, and these vulcanise the rubber. Porosity was observed in these vulcanisates, especially in those with a high concentration of bisperoxycarbamate. This can be explained if equation 84 takes place as CO_2 is generated. A more detailed treatment of this subject will be discussed later in Chapter 6.

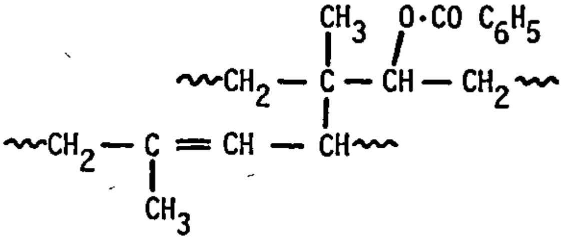
It is considered that an $R_2O\bullet$ radical abstracts hydrogen from the α-methylene group of the polyisoprene unit (equation 85) in an analogous manner to that of the free radicals produced during the well known decomposition of dicumyl and ditertiary butyl peroxides in their crosslinking reactions. Two polymer macroradicals resulting from this reaction can couple giving rise to a carbon-carbon crosslink (equation 86). Experiments by other workers with 2,6-dimethylocta-2,6-diene (a model compound that simulates polyisoprene) suggested that equation 86 is the preferred mode in the C-C crosslinking reaction (31,33). However, there is known to be a choice of three types of hydrogen atoms in the isoprene unit for the $R_2O\cdot$ radical to abstract hydrogen. The order of reactivity of these three types of hydrogen atoms, identified below, has been found to be a > b > c (29,30).



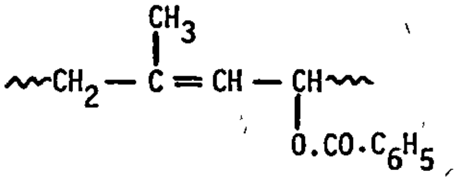
$$\sim\!CH_2 - \overset{\displaystyle CH_3}{\overset{|}{C}} = CH - CH_2\!\sim$$

Since the equation 86 is considered the predominant C-C forming reaction, the other two types of macroradicals are not considered in this chapter, but were discussed in Chapter 1 for dicumyl or ditertiary butyl peroxides.

Previous workers have shown that, based on dibenzoyl peroxide or an alkyl perbenzoate as curing agents for natural rubber, the benzoyloxy groups are proved to attach themselves to the rubber main chain either at the site of a crosslink as in (XV) below, or at isolated points in the chain as in (XVI) below (34,26,36,37,38).



(XV)

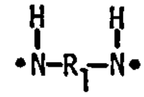


$$\sim\!CH_2 - \overset{\displaystyle CH_3}{\overset{|}{C}} = CH - \underset{\displaystyle O.CO.C_6H_5}{\underset{|}{CH}}\!\sim$$

(XVI)

Using the above attachments (XV) and (XVI) as proven models it is postulated that the amino group in the bisperoxycarbamate could become grafted to the rubber main chain as shown in equations 87 and 88. In the case of the polyisoprene rubber it was experimentally established that an amino group has attached itself to the polymer since investigations showed the presence of chemically bound nitrogen in the vulcanisate which had been previously extracted with solvent (acetone) to remove any excess and unreacted bisperoxycarbamate crosslinker.

It is considered that the amino radical can also, in principle, abstract hydrogen from the α-methylene group of the isoprene unit (93,117) as in equation 89. Besides the reactions quoted above, other side reactions may occur but they are not considered in this discussion.

Based on theoretical considerations and observed cure efficiency the stability of  $\cdot\overset{H}{N}-R_1-\overset{H}{N}\cdot$ is observed to depend on the structure of R_1; aromatic > aliphatic > cyclic. The more reactive radicals would be those derived from cyclic structures and thus these would have higher crosslink efficiency. This is the experimentally observed situation as shown in Figures 3.8 and 3.9.

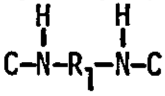
3.5 Conclusions

Some new bisperoxycarbamates were evaluated in natural and polyisoprene gum stocks for minimum cure activation temperatures, cure characteristics and crosslink densities and relative efficiencies, and these data was compared with the dicumyl peroxide curing system used as a control.

The bisperoxycarbamate based on a cyclic diisocyanate backbone is the most stable of all the bisperoxycarbamates studied and is particularly suitable for the conventional cure temperatures.

The cure rates of all the bisperoxycarbamates studied in both natural and polyisoprene rubbers were found to be faster than that of the dicumyl peroxide system. However the crosslink efficiency, in terms of crosslink density, of these bisperoxycarbamates in both rubbers was found to be lower than the equivalent dicumyl peroxide system. In all the curing systems evaluated, the polyisoprene rubber vulcanisates have higher crosslink densities for a given concentration of curing agent than the equivalent natural rubber.

In both natural and polyisoprene gum rubbers the relative effectiveness of the bisperoxycarbamates as curing agents was found to be dependent on the structures of their diisocyanate backbones; cyclic > aliphatic/cyclic > aliphatic > prepolymer. The bisperoxycarbamates studied, based on the aromatic and prepolymer backbones, were found to be relatively ineffective crosslinking agents for natural and polyisoprene rubbers.

The crosslinking reactions of these bisperoxycarbamates were thought to be based on free radical mechanisms. They are considered to differ in action from conventional peroxide free radical crosslinkers, typified by dicumyl or ditertiary butyl peroxides, by the formation of a combination of C–C and  $C-\overset{H}{\overset{|}{N}}-R_1-\overset{H}{\overset{|}{N}}-C$ crosslinks.

CHAPTER 4

TENSILE PROPERTIES OF BISPEROXYCARBAMATE GUM VULCANISATES

4.1 Introduction

Rupture can occur in rubbers under various imposed mechanical conditions and in this present research only tensile rupture was considered for it is the simplest so far as measurement is concerned.

Various theories have attempted to explain the origin of the failure process. Bueche (118) attempted to estimate the strength of a rubber by summing the strengths of single chains. The strength obtained was much greater than the usual strength observed. He suggested that rupture takes place through high local stresses which are concentrated upon a few chains in the rupture cross-section. These regions of high local stresses are caused by a distribution of molecular weights between crosslinks, so short-network chains experienced abnormally high stresses because of finite extensibility. Besides these inhomogeneities on a molecular scale tensile failure would also be expected from solid impurities or surface flaws (119, 120) which can be caused by chemical attack or even defects in the mould used to shape the vulcanisates during curing.

Tensile rupture has provided considerable information on the effects of such factors as crystallisation, filler reinforcement, and degree of crosslinking. Figure 4.1 illustrates the general effect reported in the literature of one of the factors, degree of crosslinking, on tensile strength.

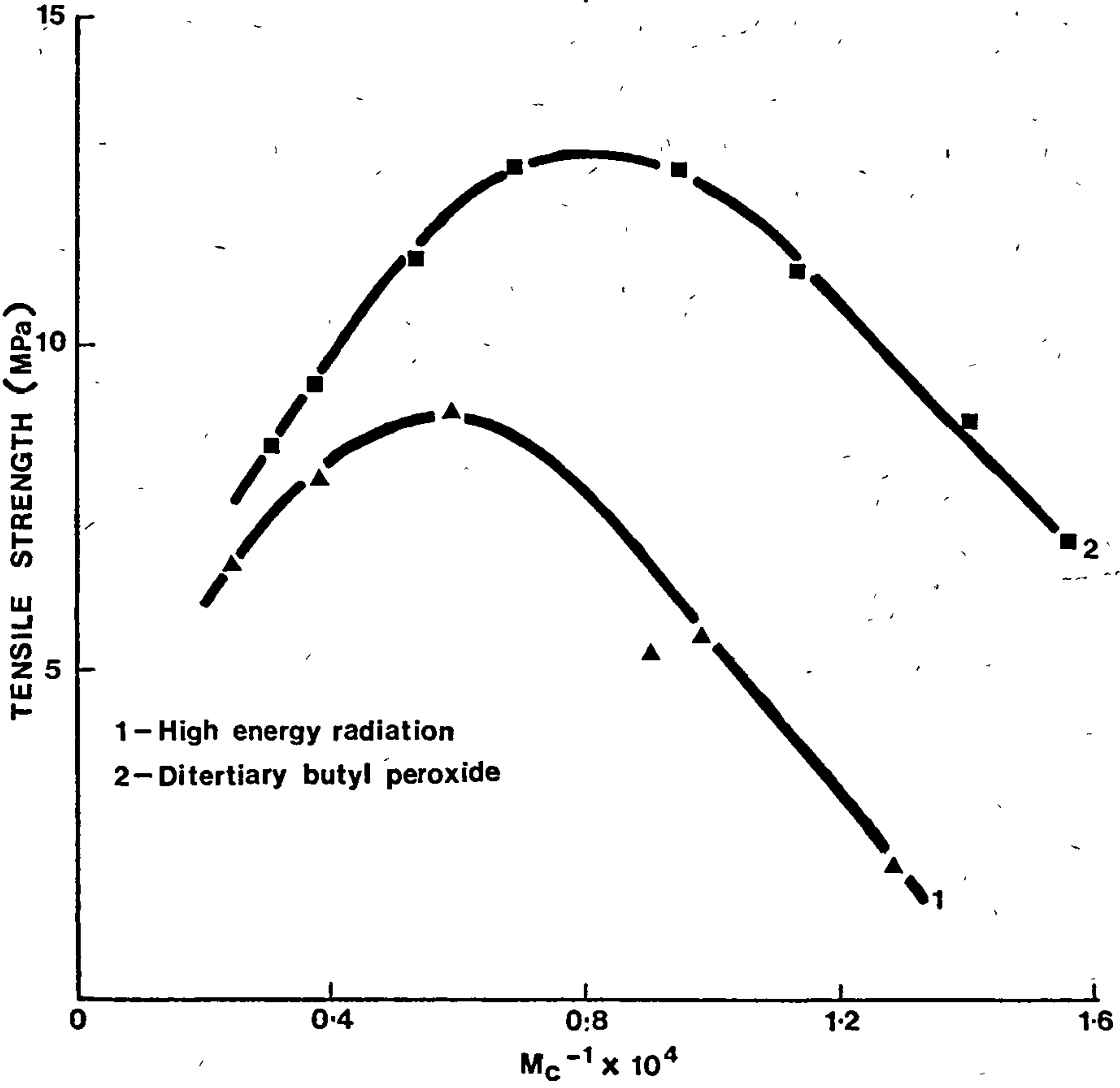


FIGURE 4.1 Tensile strength of natural rubber vulcanisates plotted against Mc^{-1}*for peroxide and high energy radiation vulcanising systems (121)

In Figure 4.1 it is observed that the tensile strength passes through a maximum as the degree of crosslinking is increased. At low degrees of crosslinking it has been suggested that plastic flow could occur and thus prevent orientation of the rubber chains to form crystallites on extension, resulting in low tensile strength (122). At the other extreme, i.e. at high degrees of crosslinking, the tensile strength is low and it had been supposed that the breaking point is attained before the extension is sufficiently high for crystallisation to develop (122, 123).

* Mc^{-1} derived from stress-strain data.

4.2 Experimental

The tensile properties of rubbers using three different sample geometries, i.e. dumbbell, ring and oval, have been compared by Myers and Wenrick (124). Scott (125) discussed the relative merits of dumbbells and rings. Here the author's discussion was only directed to compare the two most widely accepted geometries, i.e. the dumbbell and the ring (used in the present work).

The stress and strain values at failure in dumbbell specimens are usually higher than those from ring specimens. It was quoted that ring specimens based on natural rubber give tensile strengths 33% below their true strength. When a ring specimen undergoes stretching the tensile stress and strain are not uniform over its cross-section, but vary from a maximum on the inside circumference to a minimum at the outside. Hence when the specimen breaks, the force registered at break does not correspond to the true tensile strength. Furthermore during the duration of testing the material in contact with the specimen grip spindles experiences non-uniaxial deformation leading to failure in these regions. Appendix VI shows typical differences of the ultimate tensile strength values obtained using these two sample geometries.

Ring geometry was preferred in the present work primarily because of the following reasons:

1. The existing JJ machine optical extensometer is incapable of measuring the strain for *an unfilled* vulcanisate.

2. Preliminary work based on micro-dumbbells so that the strain could be directly measured from the distance of the two grips was unsuccessful. These micro-dumbbells were shown to undergo slippage in the standard grips and hence no reliable data could be obtained by this technique.

3. The present work was based on very small quantities of rare chemicals and the use of ring samples avoided the unnecessary wastage of the small amount of experimental vulcanisate available.

4. The present research work is concerned with comparative tensile properties of various vulcanisates.

Tensile properties were determined on vulcanisates in the form of microrings of internal diameter 23 mm and external diameter 27 mm. Rings were cut by means of a fly press from vulcanisates approximately 1.0 mm thick, using a specially designed cutting tool (Figure 4.2).

The J.J. Tensile Testing Machine of Model T5002 (J.J. Lloyd Instruments Ltd) was used in order to obtain tensile properties of vulcanisates, in conjunction with an X-Y plotter (PL 100 of JJ).

A prepared vulcanisate was placed in the form of a ring between the two grips shown in Figure 4.3. These grips were designed to give good distribution of stress in the ring sample on stretching by positioning the ring around four freely rotating spindles (Figure 4.4). Tensile measurements were made using a load cell of 500N and sensitivity was chosen to give the optimum load on the chart. Similarly the chart to crosshead ratio was set to give the optimum extension on the chart. A separation of 15 mm distance between the grips was kept at the start of extension since this distance was found to be suitable to avoid any force exerted on the vulcanisate due to small extension at the beginning of the test. A crosshead speed of 500 mm min^{-1} was used throughout. A trace indicating the load (newtons) and extension (mm) was plotted by means of an X-Y recorder. From the load/extension trace obtained, the following tensile parameters were calculated:

a) Ultimate Tensile Strength

Ultimate tensile strength is calculated from the recorded load at break using the following formula:

$$\left[\frac{\text{Load (N)}}{\text{2 x sample thickness (m) x sample radial width (m)}}\right] \ \text{Nm}^{-2}$$

FIGURE 4.2 Ring sample cutting tool

FIGURE 4.3 Ring sample in place over tensile grips

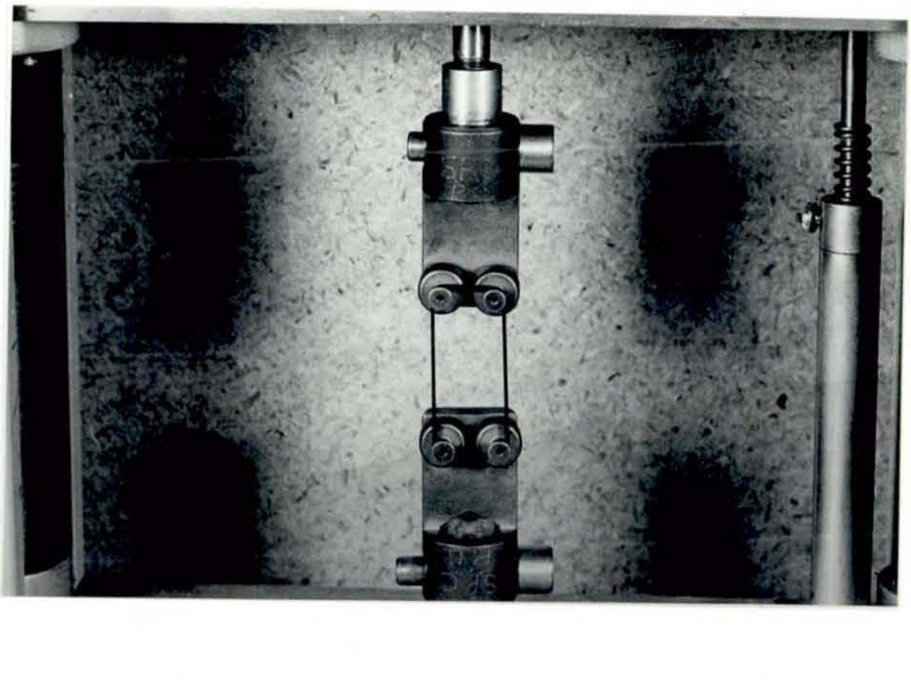


FIGURE 4.4 Ring sample tensile grips

Sample radial width = 2×10^{-3}m (from dimensions of cutting die)

$$\therefore \text{ Ultimate Tensile Strength} = \left[\frac{\text{Load (N)}}{4 \times 10^{-6} \times \text{sample thickness (mm)}}\right] \text{Nm}^{-2}$$

$$= \left[\frac{\text{Load (N)}}{4 \times \text{sample thickness (mm)}}\right] \text{MPa}$$

6) Elongation at Break

Sample elongation (%) is calculated from the following:

$$\text{Sample elongation, E\%} = \frac{100}{M}(2D + G - M) \qquad (90)$$

where M = mean circumference of sample
G = constant of grip geometry (see Figure 4.5).
D = vertical separation of grip spindle centres.

For grips used, G ≐ 38.74 mm.
For ring samples used, M = 78.55 mm.

$$\therefore (90) \text{ becomes E\%} = 2.5462D - 50.682 \qquad (91)$$

where D = extension recorded on the chart (mm) (i.e. vertical displacement of grips) + 15 mm (initial setting of grip separation).

Elongation at break is obtained from equation 91 by inserting value of D at break.

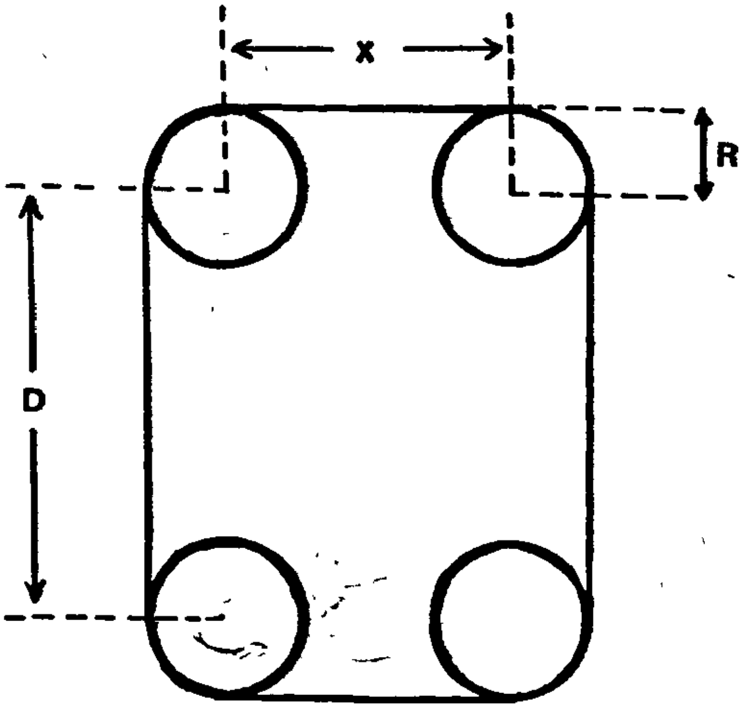
c) Modulus at 300% strain

For 300% strain, the equation 91 becomes

$$300 = 2.5462D - 50.682$$

$$\therefore D = 137.73 \text{ mm}$$

FIGURE 4·5 Sample geometry around grips



$$\text{Sample length} = 2D + 2x + 2\pi R$$

$$2x + 2\pi R = \text{Constant, } G$$

$$\therefore \text{Sample length} = 2D + G$$

∴ Strain recorded on the chart = 122.73 mm.

Modulus at the above strain is given by:

$$\left[\frac{\text{Load (N)}}{4 \times \text{sample thickness (mm)}}\right] \text{MPa}$$

where load (N) is taken from the load/extension trace at the recorded strain given above.

It is to be noted that tensile properties were determined on three samples from each vulcanisate and the median value was quoted throughout.

4.3 Results and Discussion

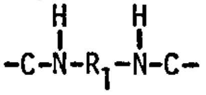
The effect of concentration (m mole kg^{-1} rubber) of the bisperoxycarbamates and of dicumyl peroxide on tensile strength of gum vulcanisates of natural and polyisoprene rubbers are shown in Figures 4.6 - 4.9. In the case of natural rubber (see Figure 4.6), the tensile strength of the vulcanisate cured with bisperoxycarbamate III does not reach its optimum with 90.5m mole kg^{-1} rubber (4 phr) of the curing agent. However, increasing the level of this bisperoxycarbamate, in DPNR, beyond 4 phr was observed to give rise to porosity in the vulcanisate. As a result of this observation which was thought to be due to evolution of carbon dioxide, absorbing systems were then investigated to remove the liberated carbon dioxide. A more detailed study of this problem was considered and will be discussed in Chapter 6.

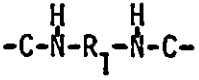
In natural rubber the two bisperoxycarbamates (I and II) demonstrated poorer tensile strength than the vulcanisates cured using dicumyl peroxide. However, in the case of the polyisoprene rubber (see Figure 4.7), the bisperoxycarbamate I vulcanisates had much better tensile strength than any of the vulcanisates cured with the crosslinking agents studied. Furthermore the vulcanisate did not reach its optimum tensile strength with 105.9m mole kg^{-1} (5 phr) rubber of the curing agent.

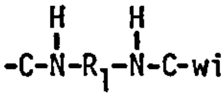
On observation of all the cured samples, it was found that vulcanisates cured with dicumyl peroxide had a strong and unpleasant smell, whilst the odour in some of the bisperoxycarbamate vulcanisates is hardly perceptible.

The product of tensile strength and elongation at break is approximately proportional to the strain energy (the energy required to break a vulcanisate) and is considered a useful alternative method of comparing the strengths of vulcanisates (125).

As shown in Figure 4.8 all the natural rubber vulcanisates show comparable optimum strength with the exception of the bisperoxycarbamate III vulcanisate which does not reach its optimum strength with 90.5m mole kg^{-1} rubber (4 phr) of the curing agent. In the case of polyisoprene rubber (see Figure 4.9), the bisperoxycarbamate I vulcanisate had much better strength than the other three vulcanisates which had comparable optimum strength between them.

It is appreciated that there are various theories which attempt to explain the causes of tensile rupture (118-120). However, with limited knowledge of the complete structural features of the vulcanisate cured with bisperoxycarbamate and the origins of tensile rupture the author now attempts to consider that the long flexible  $-C-\overset{H}{\overset{|}{N}}-R_1-\overset{H}{\overset{|}{N}}-C-$ crosslinks which are thought to be part of the structural features of the bisperoxycarbamate vulcanisate may be able to reduce the regions of high local stresses presumed to exist when short-network chains predominate as formed through the C-C crosslinks. Hence this consideration could explain one of the causes of high strength in some of the bisperoxycarbamate vulcanisates as compared to the dicumyl peroxide vulcanisates.

Figures 4.10 and 4.11 illustrate the effect of concentrations and types of structures of bisperoxycarbamates on the extensibility of the natural and polyisoprene gum vulcanisates. In both these rubbers, the order of flexibility of the vulcanisates at equivalent concentration was found to be aliphatic > aliphatic/cyclic > cyclic. All these bisperoxycarbamate vulcanisates had higher elongation at break than the equivalent dicumyl peroxide system. Such differences in flexibility between the bisperoxycarbamate and dicumyl peroxide vulcanisates may be due to the differences in the degree of crosslinking between these two systems. To consider such behaviour more closely the data on the effect of crosslink density on elongation at break of these vulcanisates was reconsidered and this is shown in Figures 4.12 and 4.13. For a given crosslink density, especially at high levels, the bisperoxycarbamate vulcanisates are considered more flexible than the equivalent dicumyl peroxide vulcanisates. For example, at the crosslink density of 40 x 10^{-3} kg mole^{-1} the natural rubber cured with the cyclic bisperoxycarbamate has about 37% higher breaking strain than the equivalent dicumyl peroxide vulcanisate. This is considered a direct consequence of the crosslink structures involved. Dicumyl peroxide is well established as forming short C-C crosslinks between rubber chains whilst the bisperoxycarbamates are considered to form a predominance of the much larger and hence more flexible  $-C-\overset{H}{N}-R_1-\overset{H}{N}-C-$ crosslinks.

At low crosslink density, the M_c is high and hence the length of the crosslink on strength is relatively insignificant compared to the number average molecular weight between crosslinks (M_c). The length of the crosslink in this instance is therefore not thought to contribute significantly towards the flexibility of the vulcanisate. On the other extreme, i.e. at high crosslink density, the M_c is low and hence the length of crosslinks which are relatively long such as  $-C-\overset{H}{N}-R_1-\overset{H}{N}-C-$ will somehow contribute towards the flexibility of the vulcanisate.

In both natural and polyisoprene rubber, the dicumyl peroxide vulcanisates show a continuous drop in elongation at break with increasing crosslink density. Since it is well established that the dicumyl peroxide vulcanisates give solely short C-C crosslinks it is considered that the contributing factor of this drop in elongation at break with increasing crosslink density is mainly the length of M_c.

The above consideration is applicable to the system where the elongation at break of vulcanisates is a function of crosslink density only. However, it is appreciated ultimate tensile failure of the natural and polyisoprene vulcanisates also depends on various factors, such as crystallisation (122, 123), presence and dispersion of solid ingredients or microflaws (119, 120), and others (126).

The moduli at 300% values for each of the curing systems in both natural and polyisoprene gum vulcanisates are shown as a function of crosslink density in Figures 4.14 and 4.15. In natural rubber the relative positions of the curves relating modulus and crosslink density of the bisperoxycarbamate and dicumyl peroxide vulcanisates are reflected by the order of crosslink length; dicumyl peroxide (solely C-C crosslinks) > bisperoxycarbamates (C-C and $-C-\overset{H}{N}-R_1-\overset{H}{N}-C-$ crosslinks). However, in the case of polyisoprene, the curves relating modulus and crosslink density of all the vulcanisates are comparable. A more detailed investigation needs to be carried out to provide an explanation of such phenomena.

4.4 Conclusions

In natural rubber, all the vulcanisates have comparable optimum tensile products (i.e. strength) with the exception of the bisperoxycarbamate III vulcanisate which does not attain its optimum strength with 4 phr of the curing agent. In the case of polyisoprene rubber the bisperoxycarbamate I vulcanisate exhibits superior strength to the dicumyl peroxide vulcanisate.

For a given crosslink density, especially at high levels, the bisperoxycarbamate vulcanisates are considered more flexible than the equivalent dicumyl peroxide vulcanisates.

In natural rubber, the dicumyl peroxide vulcanisate has higher M_{300} than its bisperoxycarbamate vulcanisate equivalent at the same crosslink density. In the case of polyisoprene rubber, the bisperoxycarbamate II and III vulcanisates have comparable M_{300} values with the dicumyl peroxide vulcanisate at equivalent crosslink density.

Figure 4·6 Tensile strength vs concentration of bisperoxycarbamate (DPNR)

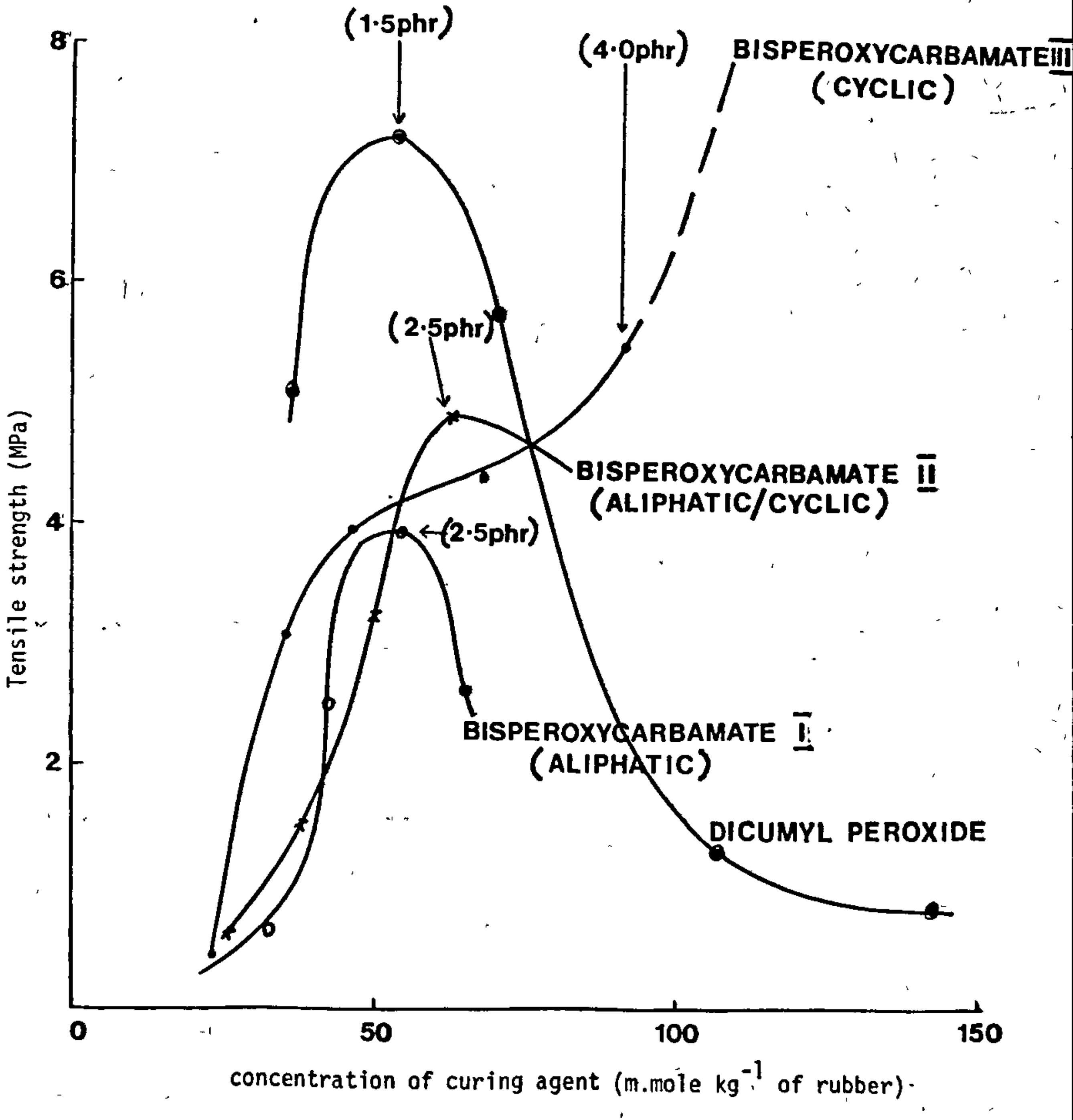


FIGURE 4.7 Tensile strength vs concentration of bisperoxycarbamate (IR 305)

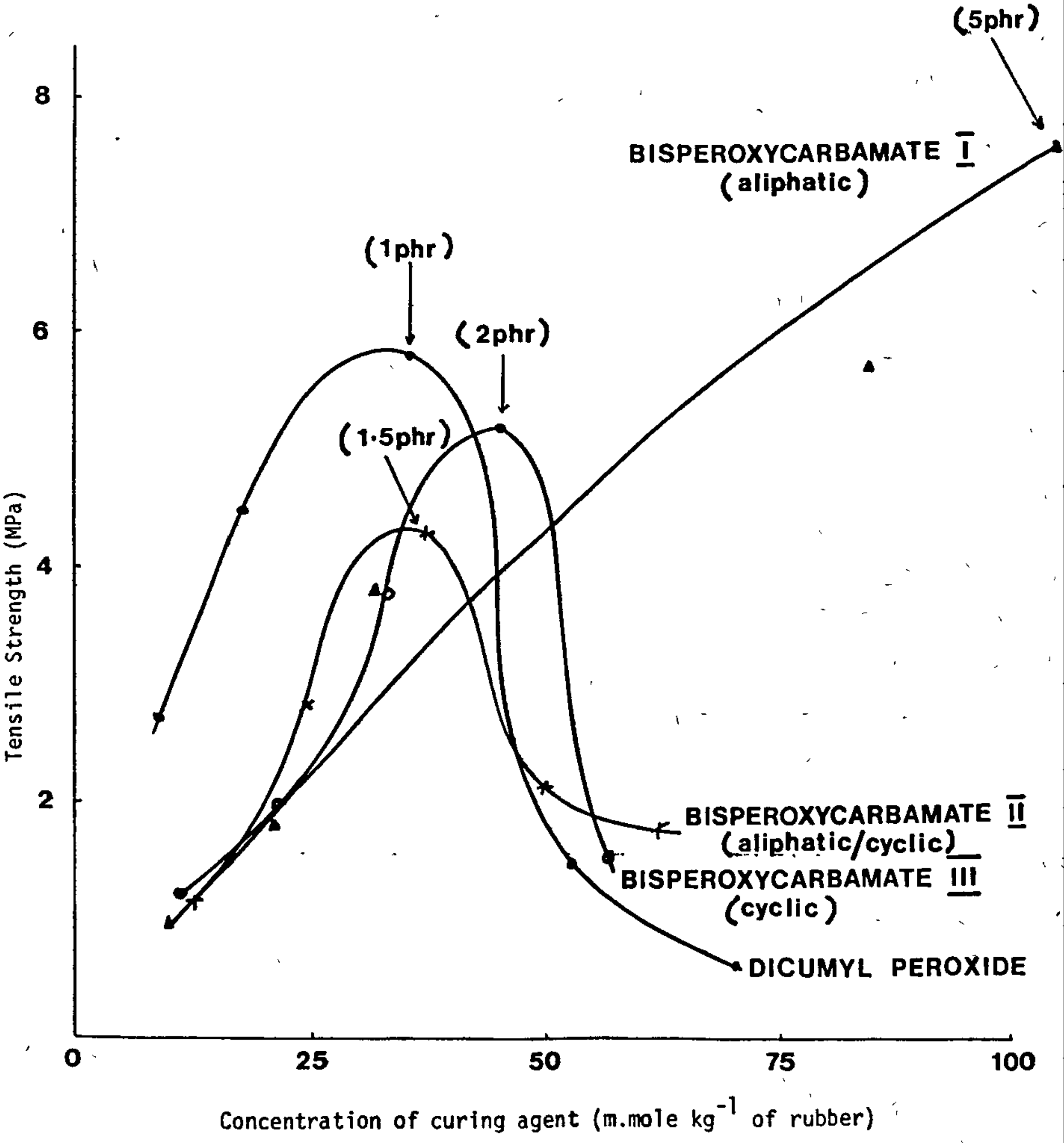


FIGURE 4.8 Tensile product vs. concentration of bisperoxycarbamate (DPNR)

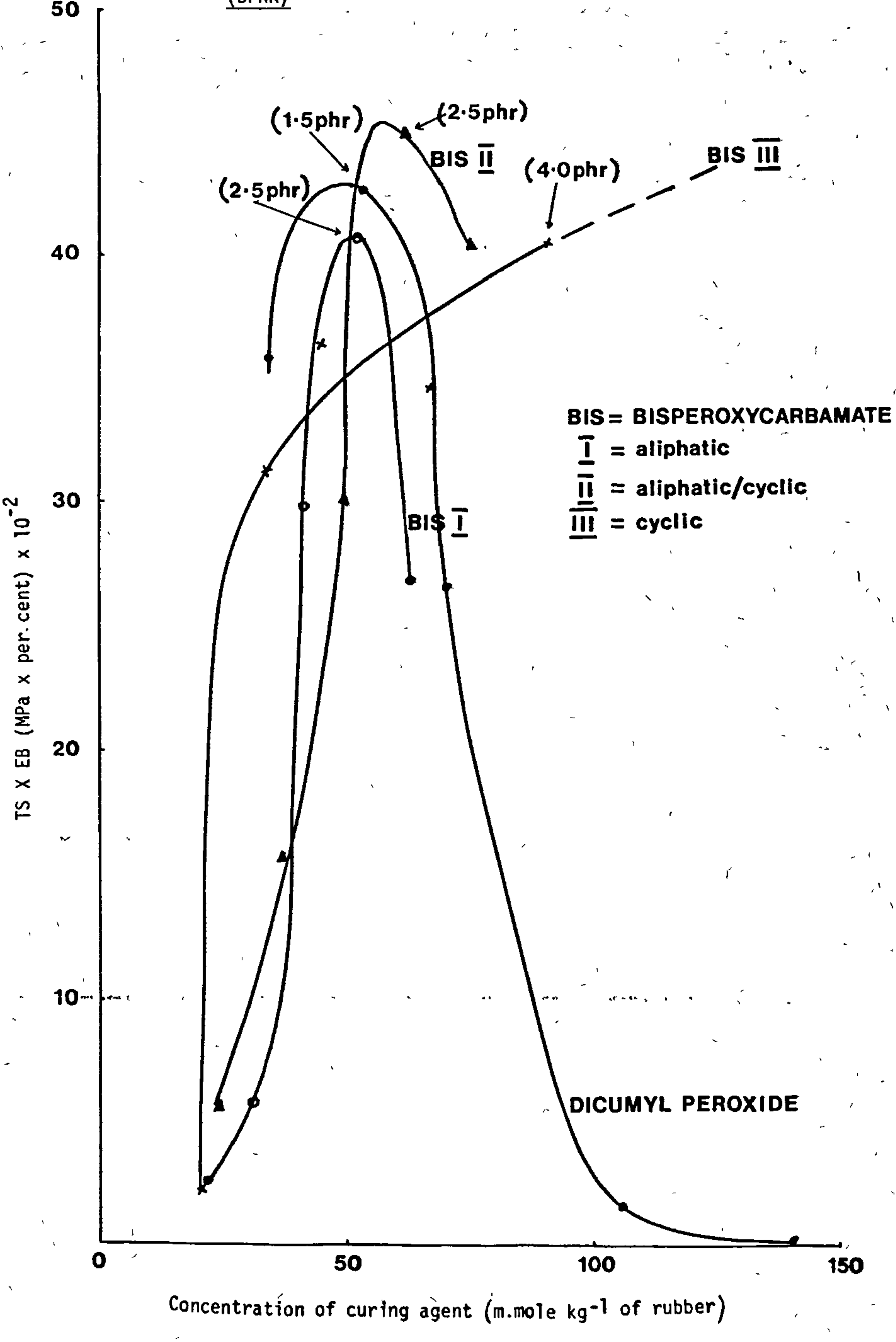


FIGURE 4.9 Tensile product vs concentration of bisperoxycarbamate (IR 305)

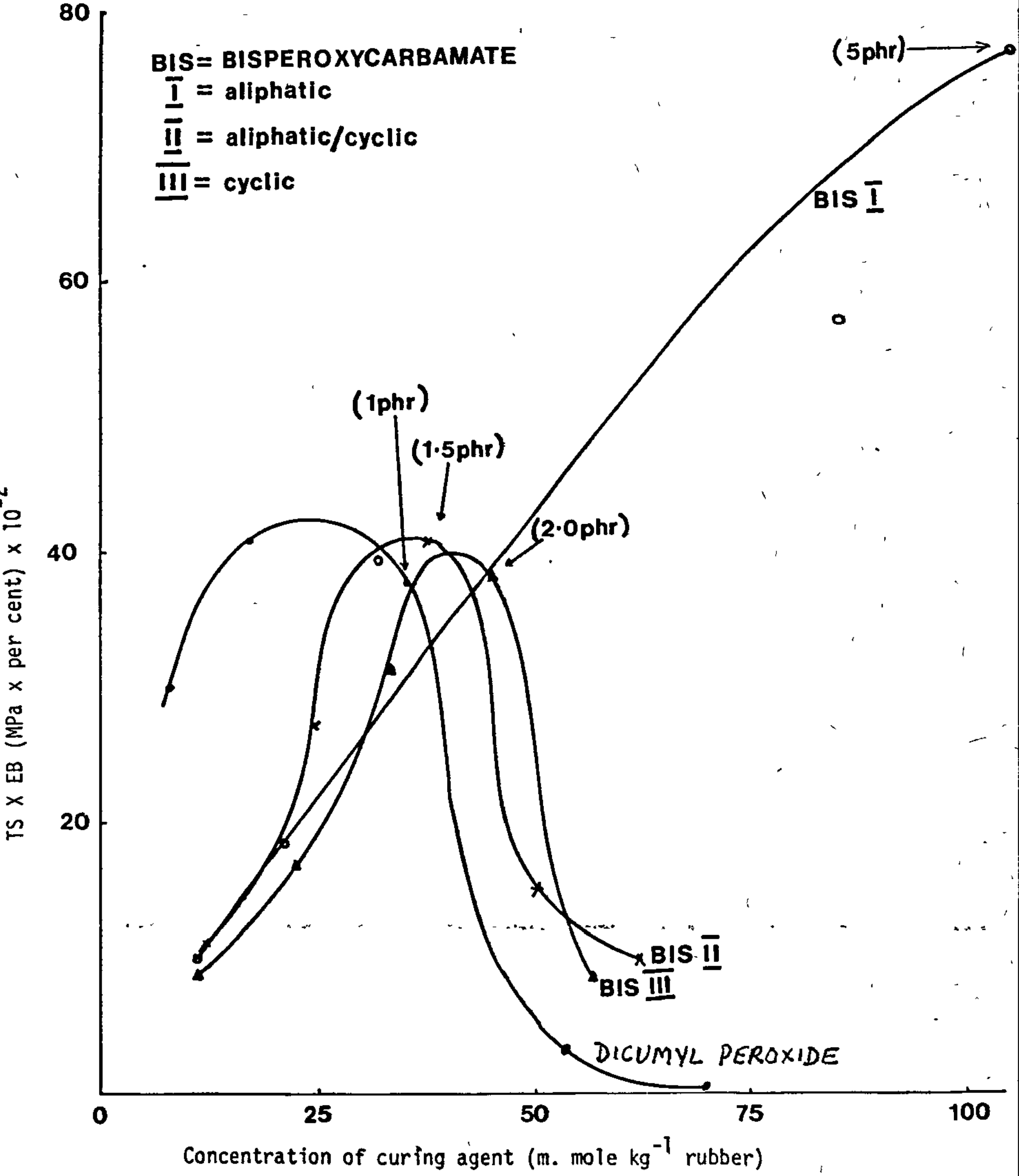


FIGURE 4.10 Elongation of break vs. concentration of bisperoxycarbamate (DPNR)

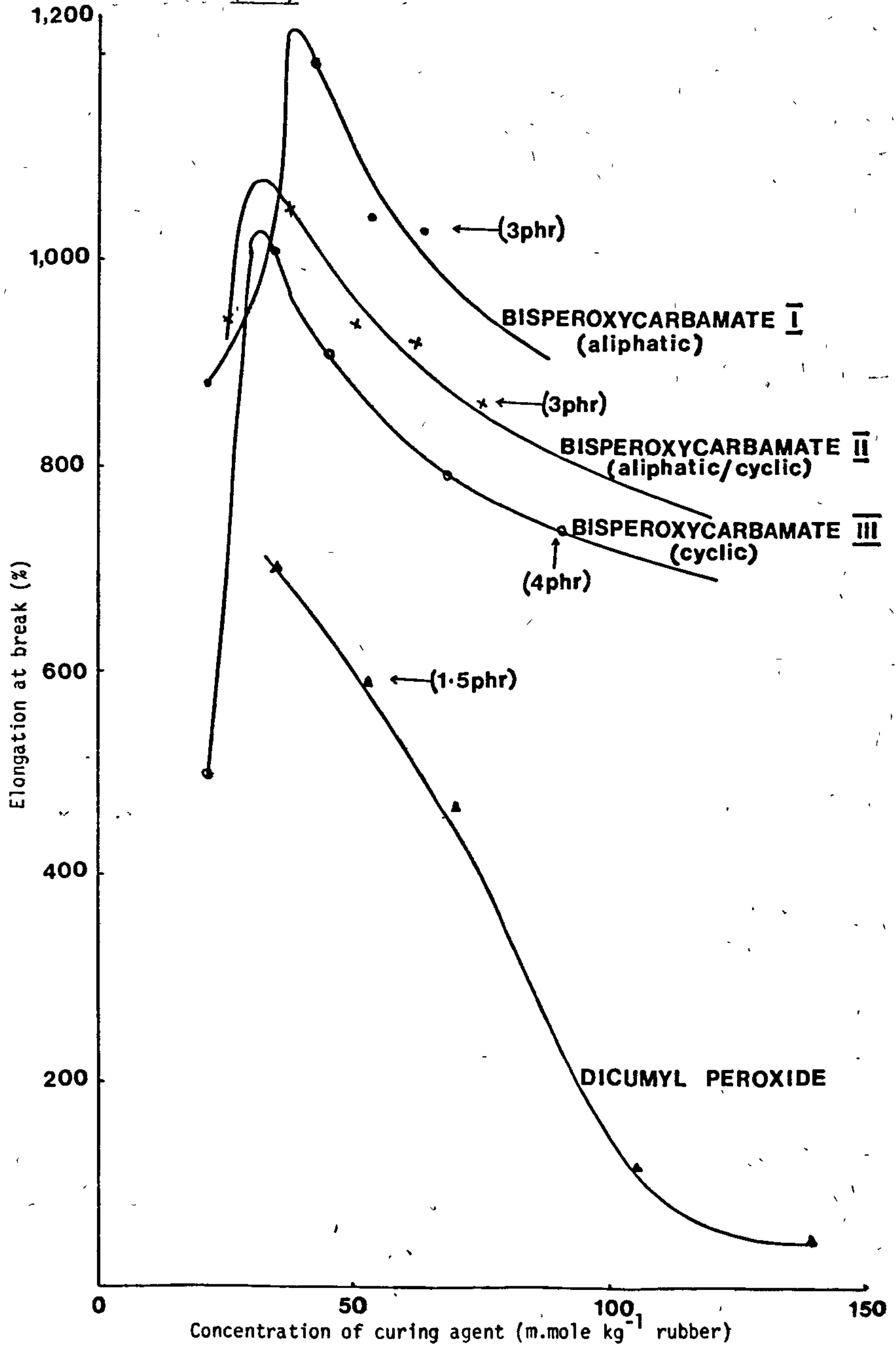


FIGURE 4.11 Elongation at break vs concentration of bisperoxycarbamate (IR 305)

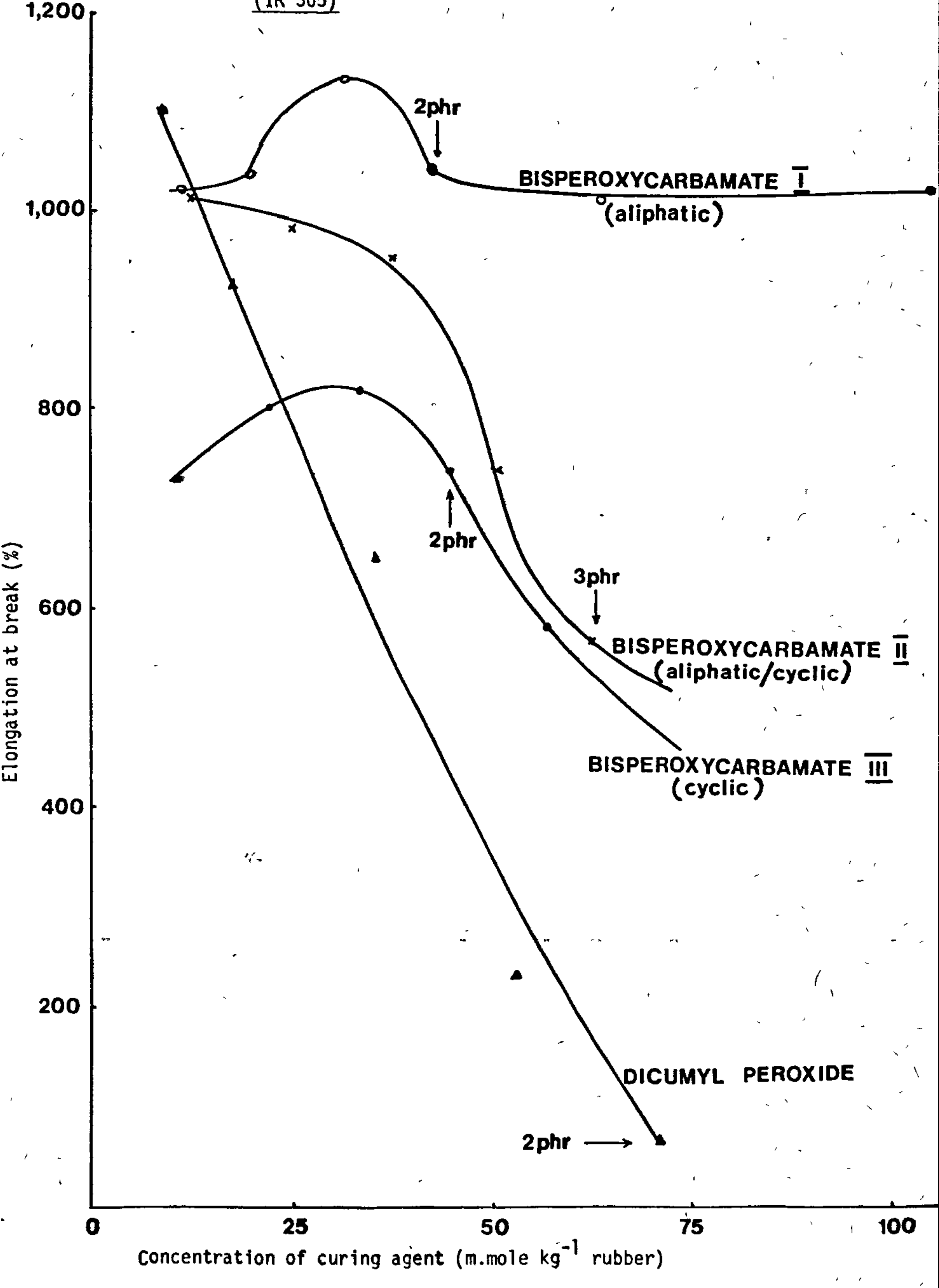


FIGURE 4.12 Effect of crosslink density on Elongation at break of DPNR vulcanisates

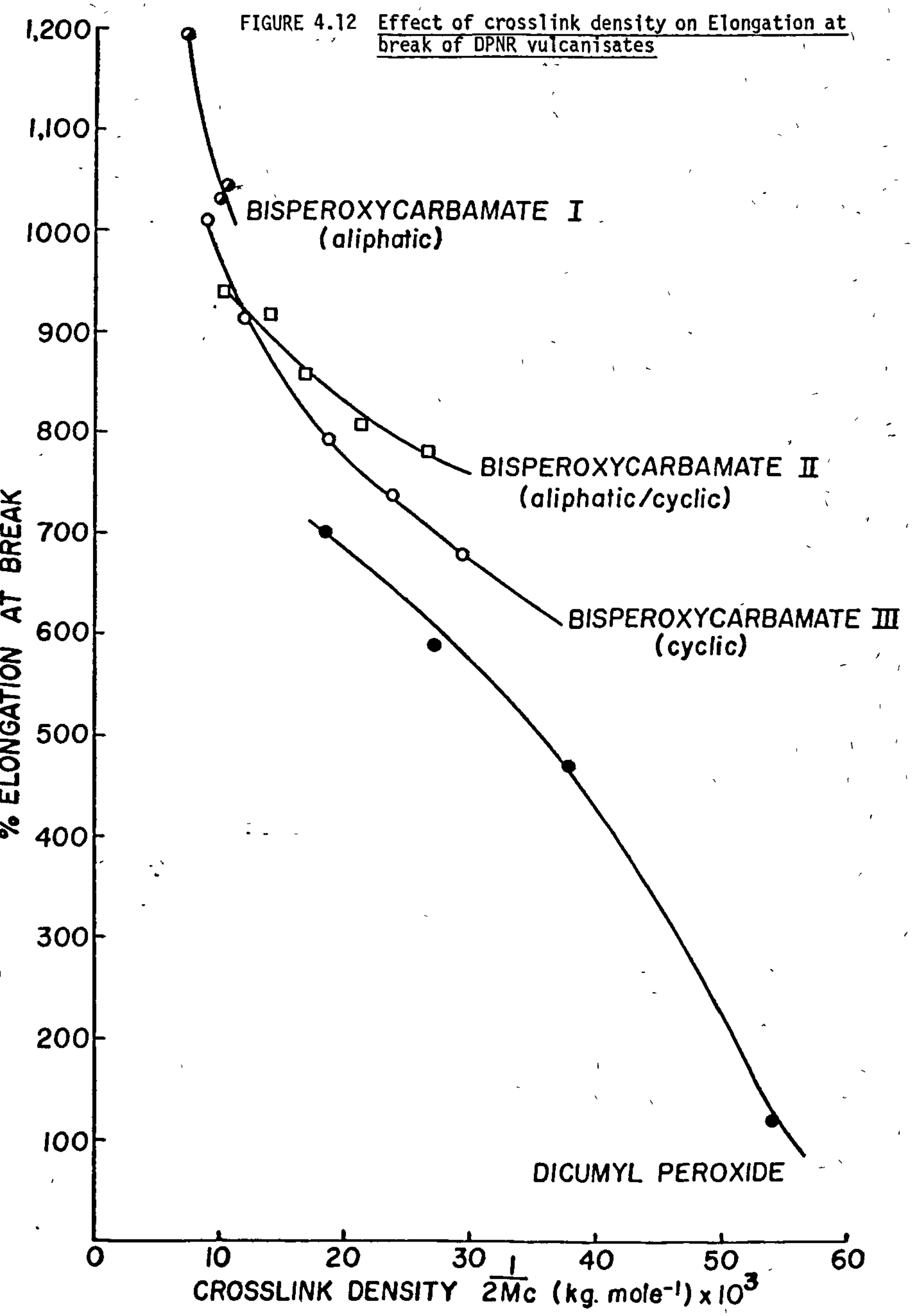


FIGURE 4.13 Effect of crosslink density on Elongation at break of IR 305 vulcanisates

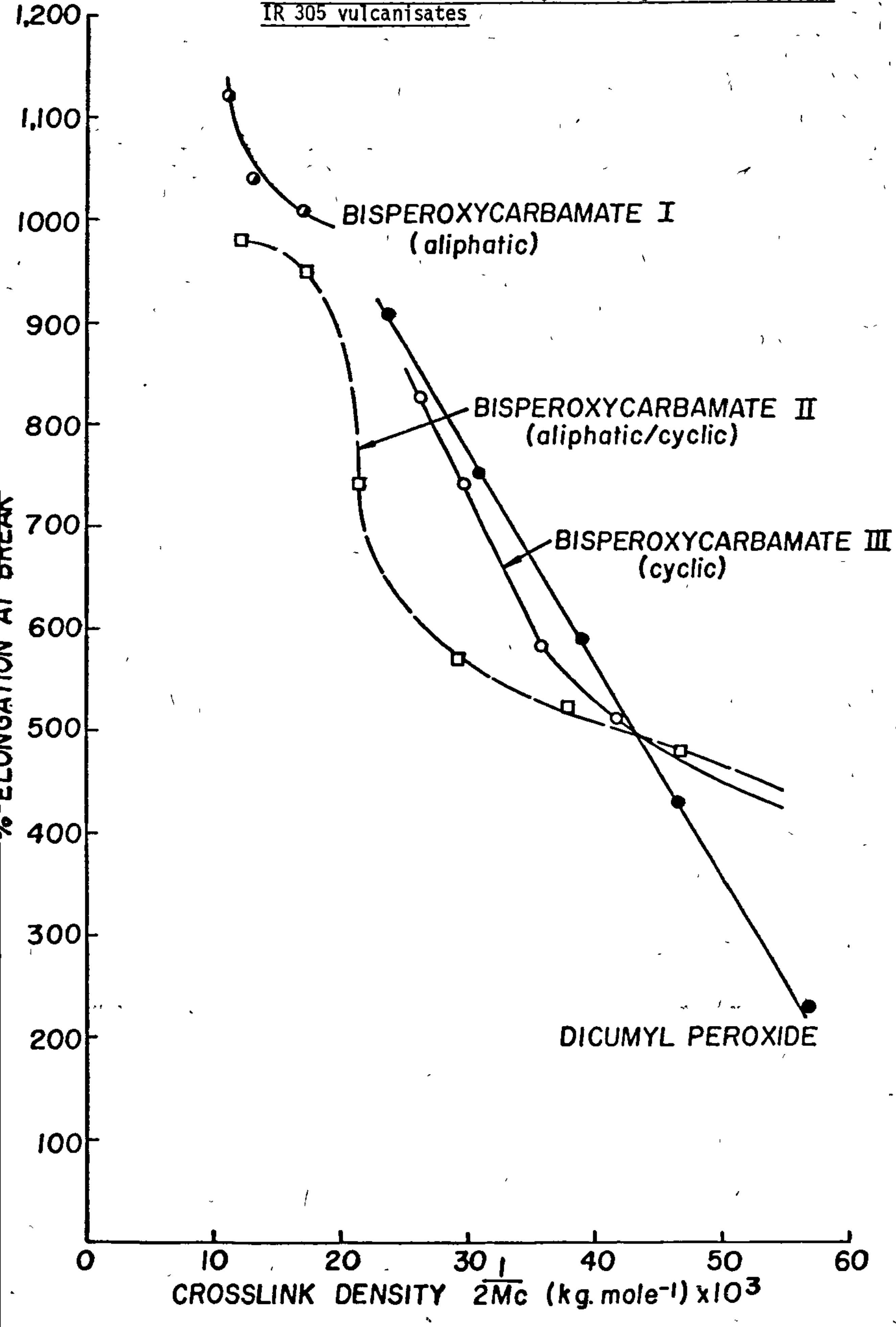


FIGURE 4.14 Effect of crosslink density on M_{300} of DPNR vulcanisates.

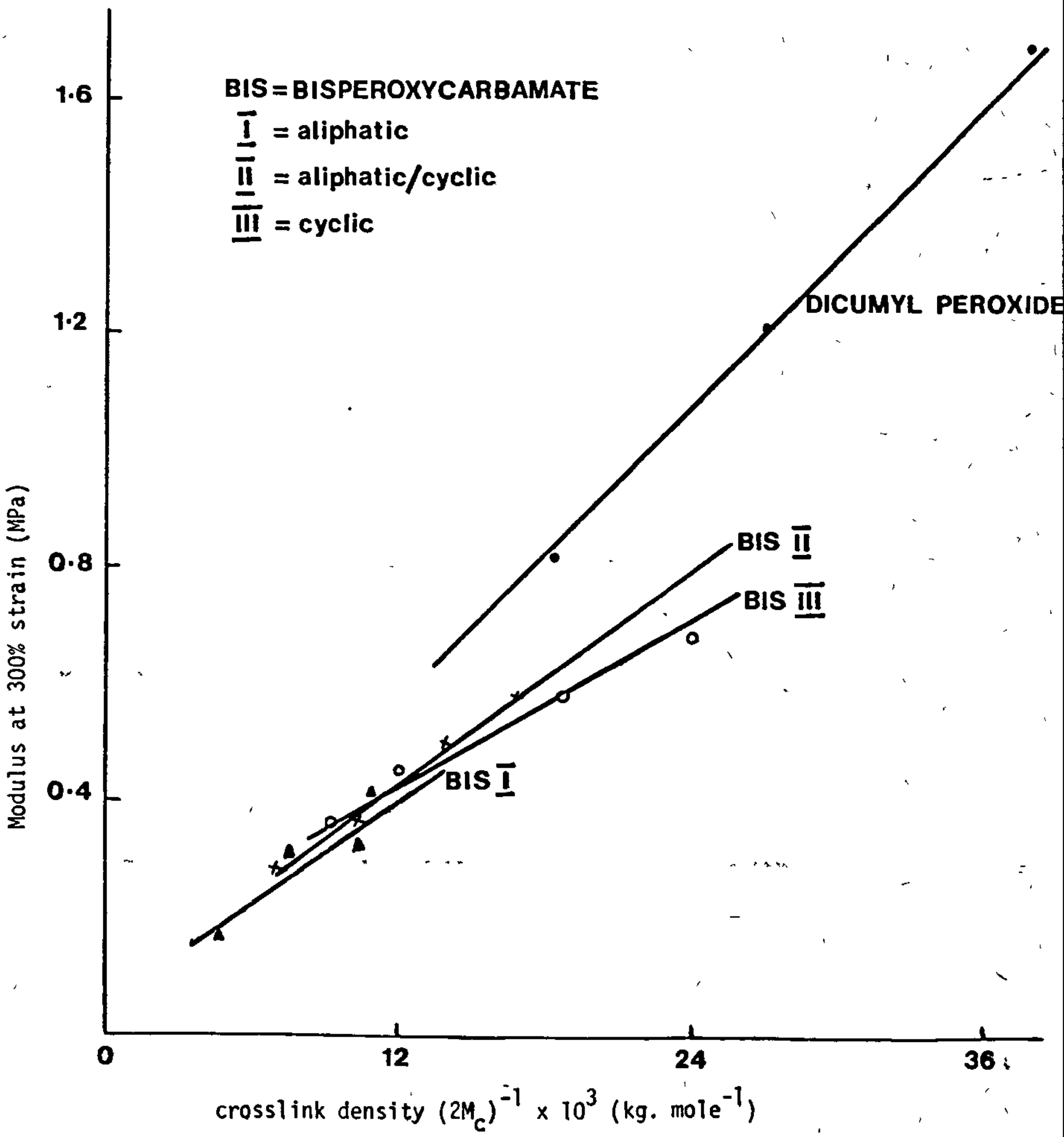
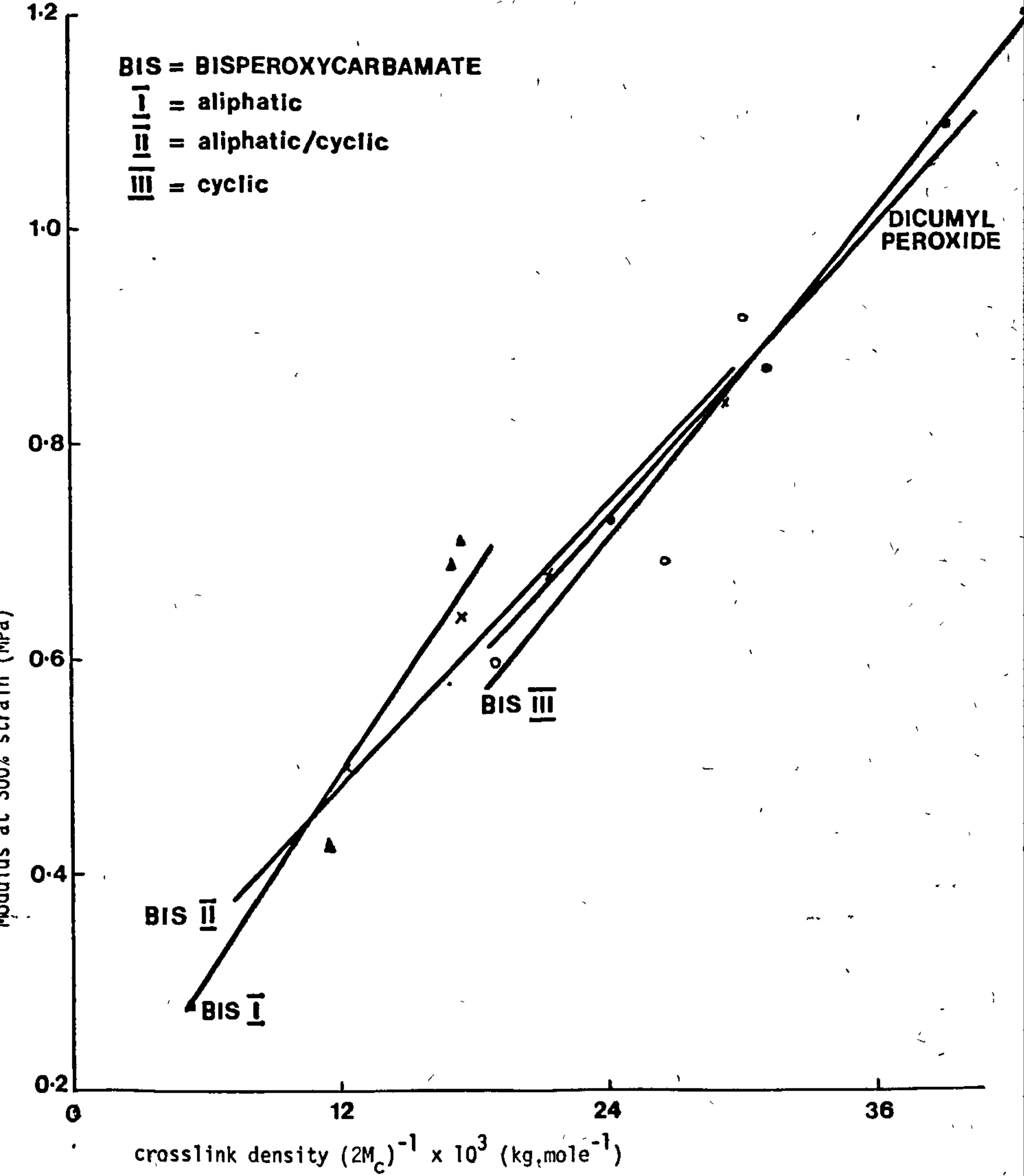


FIGURE 4.15 Effect of crosslink density on M_{300} of IR 305 vulcanisates



CHAPTER 5

AGEING PERFORMANCE OF UNFILLED BISPEROXYCARBAMATE VULCANISATES

5.1 Introduction

Observing the initial physical properties of vulcanisates is one aspect of their technology but maintaining these properties during service is another of no less importance. It has long been known that one of the serious causes of the deterioration of rubber products is *the* reaction *of the rubber* with atmospheric oxygen; for example an absorption of a few tenths of 1% of oxygen is sufficient to reduce the tensile strength of a rubber vulcanisate by 50% (127). Because of this sensitivity various methods have been developed to provide information on the stability of rubber vulcanisates against oxidative degradation. One of these methods, which has a good fundamental basis, is the Stress-Relaxation method; this is supported by several technological methods, e.g. oxidative hot air oven ageing is well documented for specification and evaluation purposes. In the present research both these methods were utilised in evaluating the *resistance* of unfilled bisperoxycarbamate vulcanisates to oxidative degradation.

5.2 Stress-Relaxation

5.2.1 Basic Principles

The stress-relaxation method is based upon the kinetic theory relationship shown below:

$$f = NkTA\,[\Lambda - \Lambda^{-2}] \qquad (92)$$

where f is the tension exerted by an extended rubber sample

N chain segments between junction points in the network per unit volume

k is Boltzmann's constant

T is the absolute temperature
A is the unstrained cross-section area
Λ is the ratio of the stretched to the initial length of the sample

At sufficiently high temperatures a state of 'ideal' rubbery behaviour is approached and equation 92 can be applied. In the continuous stress-relaxation method, the temperature and the extension ratio Λ are kept constant, and hence from equation 92 it is implied that the stress is proportional to the number of stress-supporting network chains N. Suppose N_0 is the number of stress-supporting network chains originally present and N_t is the residual number of stress-supporting network chains remaining after a given time, t, during degradation, the ratio of the tension f_t at time t, to the initial tension f_0 is given by the equation 93:

$$\frac{f_t}{f_0} = \frac{N_t}{N_0} \qquad (93)$$

Therefore at constant extension and temperature during ageing the decay in stress is a direct measure of the degradation of the elastic network.

The Wallace Extension Stress-Relaxometer is an instrument which enables one to follow the changes in stress of a vulcanisate strip. These changes of stress in a 'continuous' mode can then be correlated with the breaking of chemical bonds in the elastic network.

The stress-relaxometer may be operated in 'continuous' mode or 'intermittent' mode. In the continuous stress-relaxation mode a sample is held extended throughout the experiment and the decrease of stress with time is recorded. In the case of intermittent stress-relaxation, the sample is strained only at such times as that at which the stress is to be measured (128).

During the continuous stress-relaxation process, the stress recorded at a given time is the measure of the residual stress remaining after the degradation of the elastic network. It is to be noted that any chains which are formed by crosslinking during the relaxation process are part of a new network in equilibrium in the extended state and do not contribute to the stress so long as the extension is unchanged. This new network will, however, give rise to 'permanent set'. In the case of intermittent stress-relaxation, the stress recorded at a given interval of time is the measure of the residual stress remaining after the degradation of the elastic network plus the stress due to the new network.

5.2.2 Experimental

In the present research only continuous stress-relaxation of the vulcanisates in air at elevated temperature was measured in order to determine the stability of the networks investigated.

Stress-relaxation in vulcanisates was investigated using a Wallace Extension Stress-Relaxometer (see Figure 5.1). The equipment consists of a thermostatically controlled cast aluminium block heating unit having a series of circular chambers. Each chamber is used in conjunction with a single stress-relaxation unit.

Figure 5.2 illustrates the essential features of the Stress-Relaxation apparatus. A sample in the form of strip 4.0 mm wide, and 0.4 mm thick (A) was held at constant extension. The sample was connected to one end of the cantilever beam (C). The beam is pivoted at the other extreme. The stress caused by the downward extension of the sample is balanced by a helical spring (D) arranged centrally above the beam. The helical spring operates within its Hooke's law range. Any change in stress of the sample due to relaxation is automatically compensated by a change in the extension of the spring. A marker pencil attached directly to the spring is placed in contact with a drum chart (E) rotating at a constant rate of one revolution every 12 hours. The relaxation of the spring during the ageing process is recorded on the chart.

FIGURE 5.1 Wallace Extension Stress-Relaxometer

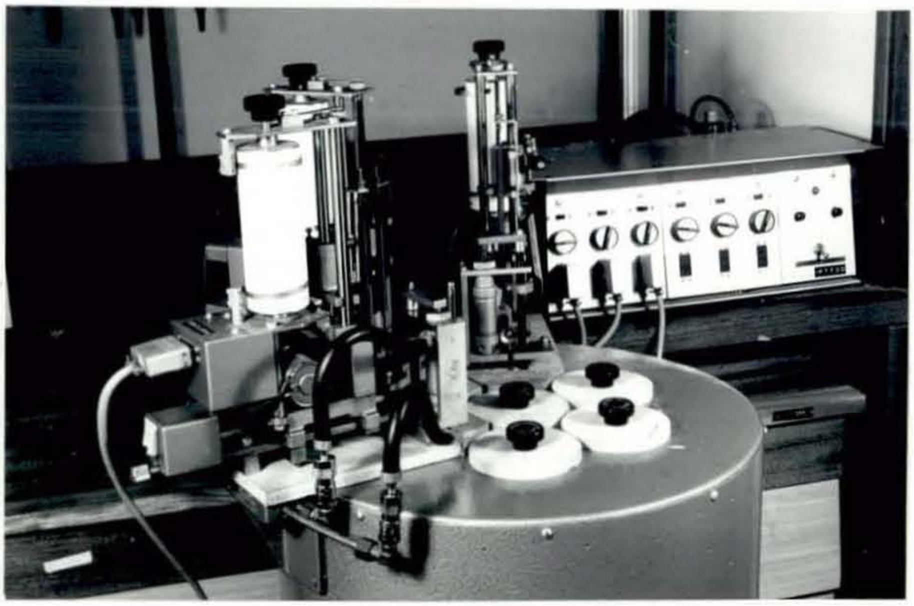
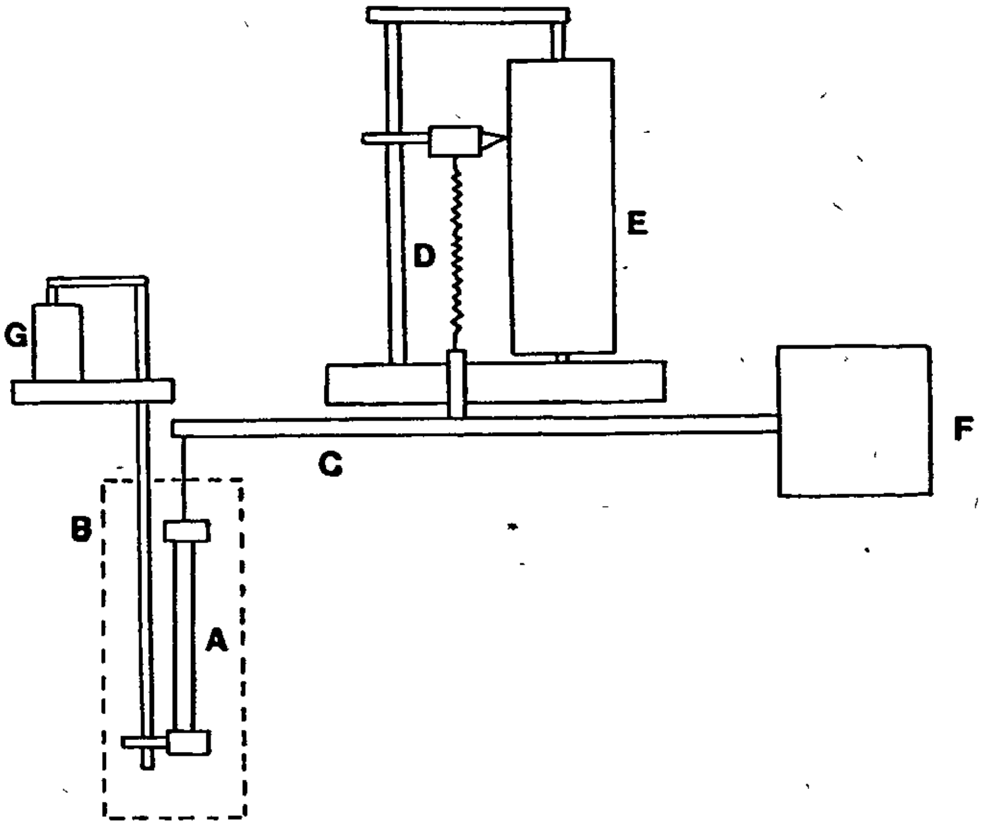


FIGURE 5.2 Block diagram of stress-relaxation apparatus



KEY:

A = Sample under elongation

B = Thermostatted cast aluminium block heating unit

C = Cantilever beam

D = Compensating spring

E = Rotating drum chart

F = Cantilever beam electronic balancing unit

G = Pneumatic piston

The air-flow indicator was adjusted to read 0.057 m^3 per hour (2.0 cubic feet per hour). The chambers were preheated to 100 ± $1^{o}C$ before commencing the experiment.

In every experiment, the strip was extended to approximately 100% extension. Since the scission rate is independent of elongation up to about 150% (129), the extension of every vulcanisate was kept near to 100%.

5.2.3. Results and Discussion

The formulations and cure conditions used to obtain various vulcanisates for the thermal oxidative stress-relaxation data of Figures 5.3 and 5.4 are shown in Table 5.1. As shown in those two figures the order of thermal oxidative stability of the bisperoxycarbamate vulcanisates was found to be cyclic > aliphatic/cyclic > aliphatic. Of the three bisperoxycarbamates in natural rubber the bisperoxycarbamate III vulcanisate demonstrated comparable stability to natural rubber cured with dicumyl peroxide, diurethane and sulphur-EV systems. In the case of IR 305, all three bisperoxycarbamate vulcanisates are more stable than the vulcanisates cured with dicumyl peroxide and the conventional sulphur system, but its bisperoxycarbamate III vulcanisate is of comparable stability with the vulcanisate cured with the sulphur-EV system.

The lower scission rate in the natural rubber vulcanisate, cured with dicumyl peroxide, when compared with the polyisoprene vulcanisate is considered due to the presence of naturally occurring antioxidants in the natural rubber (130). Further this consideration is substantiated by the earlier work of Dunn et al (131). They showed that the thermal oxidative stress-relaxation of 'highly purified' rubber (weight percentage of nitrogen was 0.05%) cured with dicumyl peroxide was autocatalytic in type after an initial slow period. This behaviour is almost identical to that of the polyisoprene vulcanisate shown in Figure 5.4. However, the scission rate has been shown by other workers (131) to be markedly retarded in

TABLE 5.1

The formulations and cure conditions used to obtain the vulcanisates for the thermal oxidative stress-relaxation data of Figures 5.3 and 5.4

Curing systems	Conventional sulphur		Sulphur-EV		Diurethane	Dicumyl peroxide		Bisperoxycar-bamate I		Bisperoxycar-bamate II		Bisperoxycar bamate II	
Types of Rubbers	DPNR	IR305	DPNR	IR305	DPNR	DPNR	IR305	DPNR	IR305	DPNR	IR305	DPNR	IR305
Rubber (pbw)	100	100	100	100	100	100	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	-	-	-	-	-	-	-	-	-
Stearic acid	1	1	1	1	-	-	-	-	-	-	-	-	-
Sulphur	2.5	2.5	0.33	0.33	-	-	-	-	-	-	-	-	-
CBS	0.5	0.5	5.0	5.0	-	-	-	-	-	-	-	-	-
Diurethane (Novor 924)	-	-	-	-	6.7	-	-	-	-	-	-	-	-
ZDEC	-	-	-	-	2.0	-	-	-	-	-	-	-	-
Caloxol W5G	-	-	-	-	3.0	-	-	-	-	-	-	-	-
Dicumyl peroxide (Perkadox SB)	-	-	-	-	-	1.5	1.0	-	-	-	-	-	-
Bisperoxycar-bamate I	-	-	-	-	-	-	-	2.5	5.0	-	-	-	-
Bisperoxycar-bamate II	-	-	-	-	-	-	-	-	-	2.5	1.5	-	-
Bisperoxycar-bamate III	-	-	-	-	-	-	-	-	-	-	-	4.0	2.0
Cure conditions	19min/150°C		60min/140°C		50min/160°C	3hr/150°C		15min/140°C		10min/ 160°C	15min/ 150°C	10min/ 160°C	15min/ 170°C

Figure 5·3 Continuous stress-relaxation of DPNR vulcanisates in air at 100°C

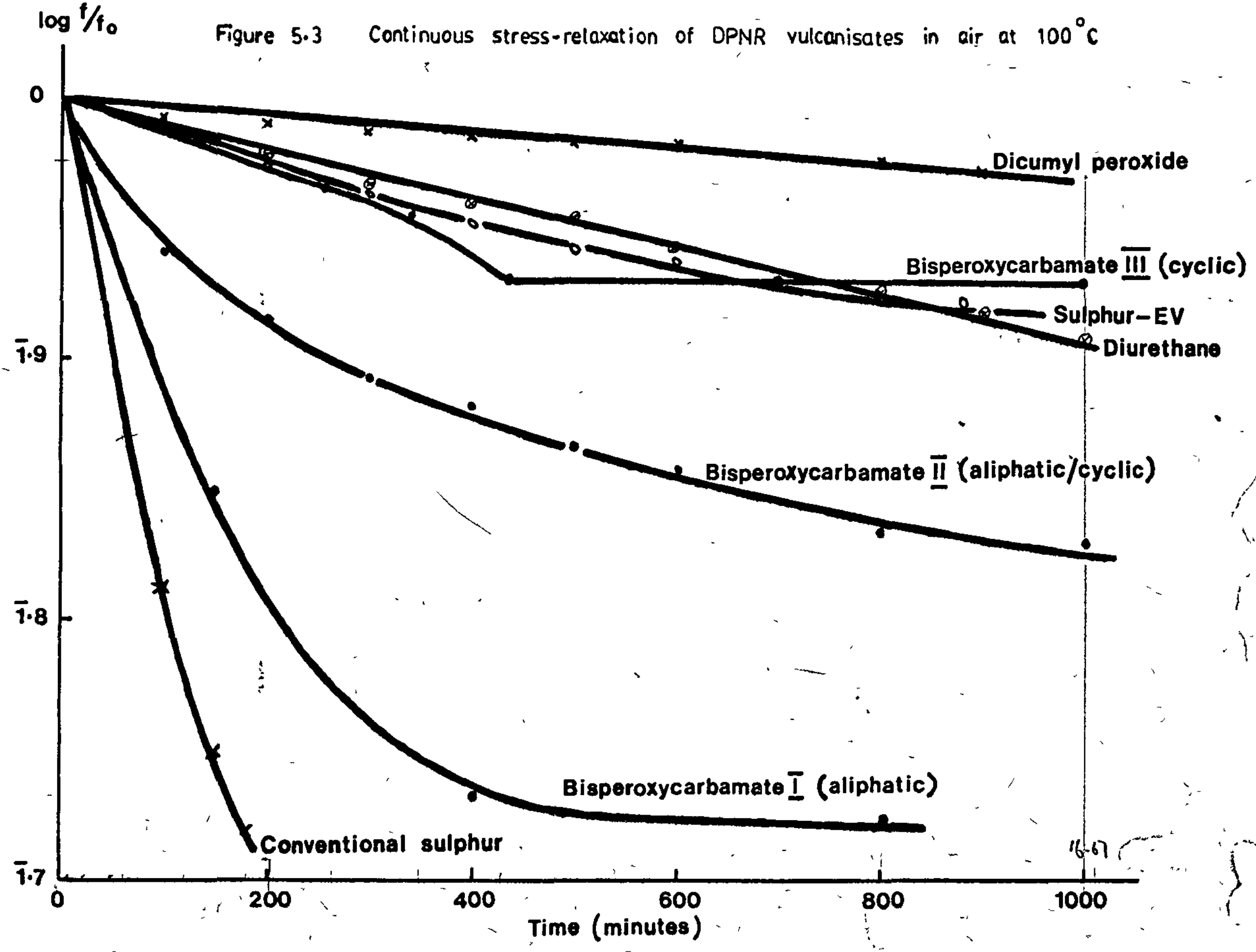
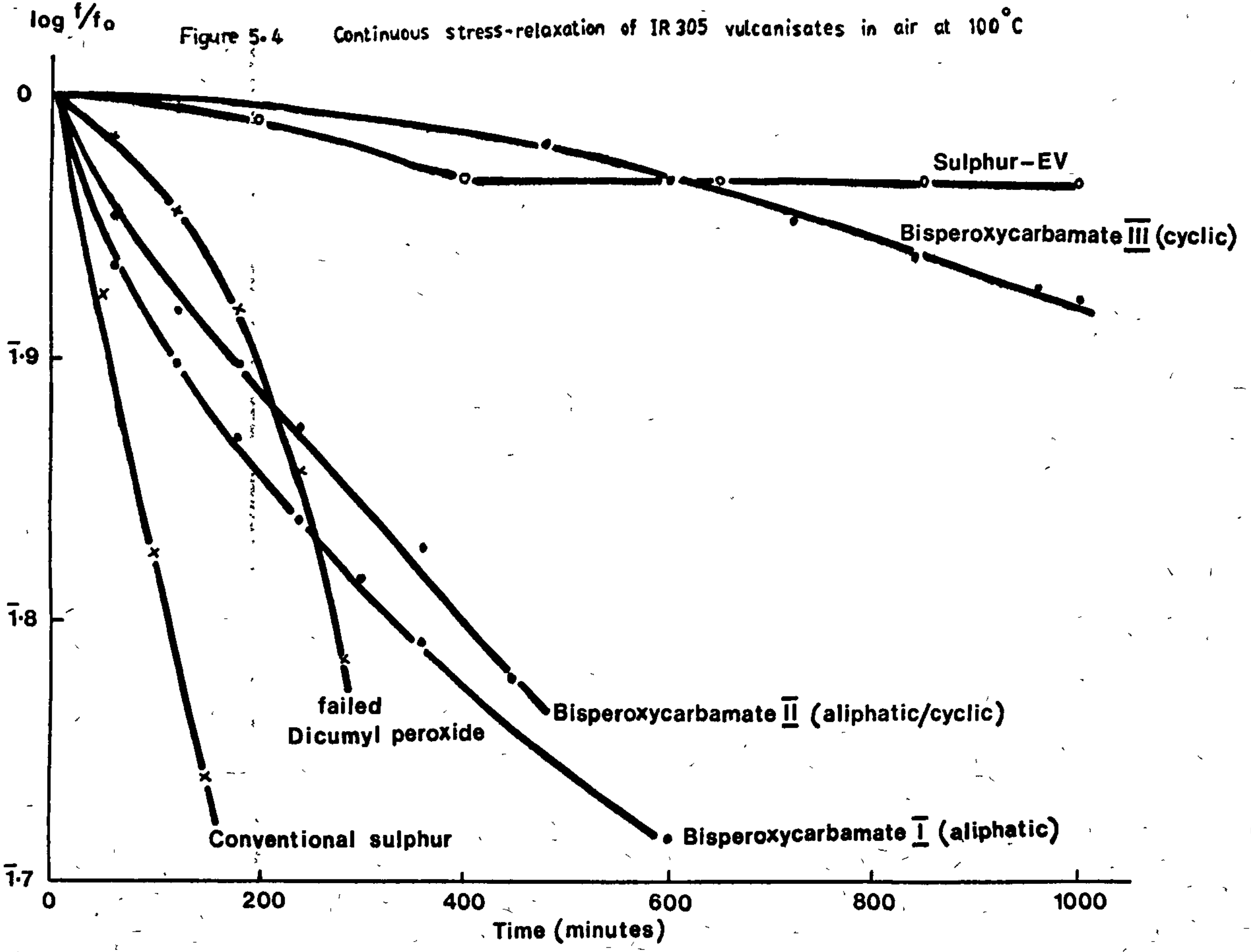


Figure 5.4 Continuous stress-relaxation of IR 305 vulcanisates in air at 100°C



the presence of as little as 0.2% by weight of phenolic antioxidant and with stress-relaxation characteristics comparable to that of the author's natural rubber vulcanisate shown in Figure 5.3.

In both natural and polyisoprene rubbers, the vulcanisates cured with an EV system are known to be more stable than the vulcanisates cured with conventional sulphur systems. The author considers that the differences between these two systems are due to the predominant presence of polysulphidic linkages in conventional systems; polysulphide linkages have been shown to be more susceptible to oxygen degradation than the monosulphide linkages (132).

In the case of vulcanisates investigated in this research those cured with the conventional sulphur system, both the natural and polyisoprene vulcanisates had comparable stability. In this instance the effect of naturally occurring antioxidants on the retardation of the scission rate in the natural rubber vulcanisates was not observed in contrast to the previous observation with the dicumyl peroxide vulcanisate. This adverse behaviour can be explained by an informative result provided by Cunneen (132). In his work a model trisulphide $A_1S_3A_1$ was added to: (i) purified rubber and (ii) smoked sheet (RSS1), and the compounds were then crosslinked using a peroxide system. In this case oxidation was studied by following oxygen absorption and the data obtained is shown in Figure 5.5.

The large differences in the rates of oxidation of the two vulcanisates A and D (in the absence of $A_1S_3A_1$) was considered due to natural inhibitors present in the RSS1 vulcanisate even though it has been extracted after cure. In the case of the purified rubber (B) the trisulphide retarded oxidation but with the RSS1 (C) the trisulphide was a pro-oxidant.

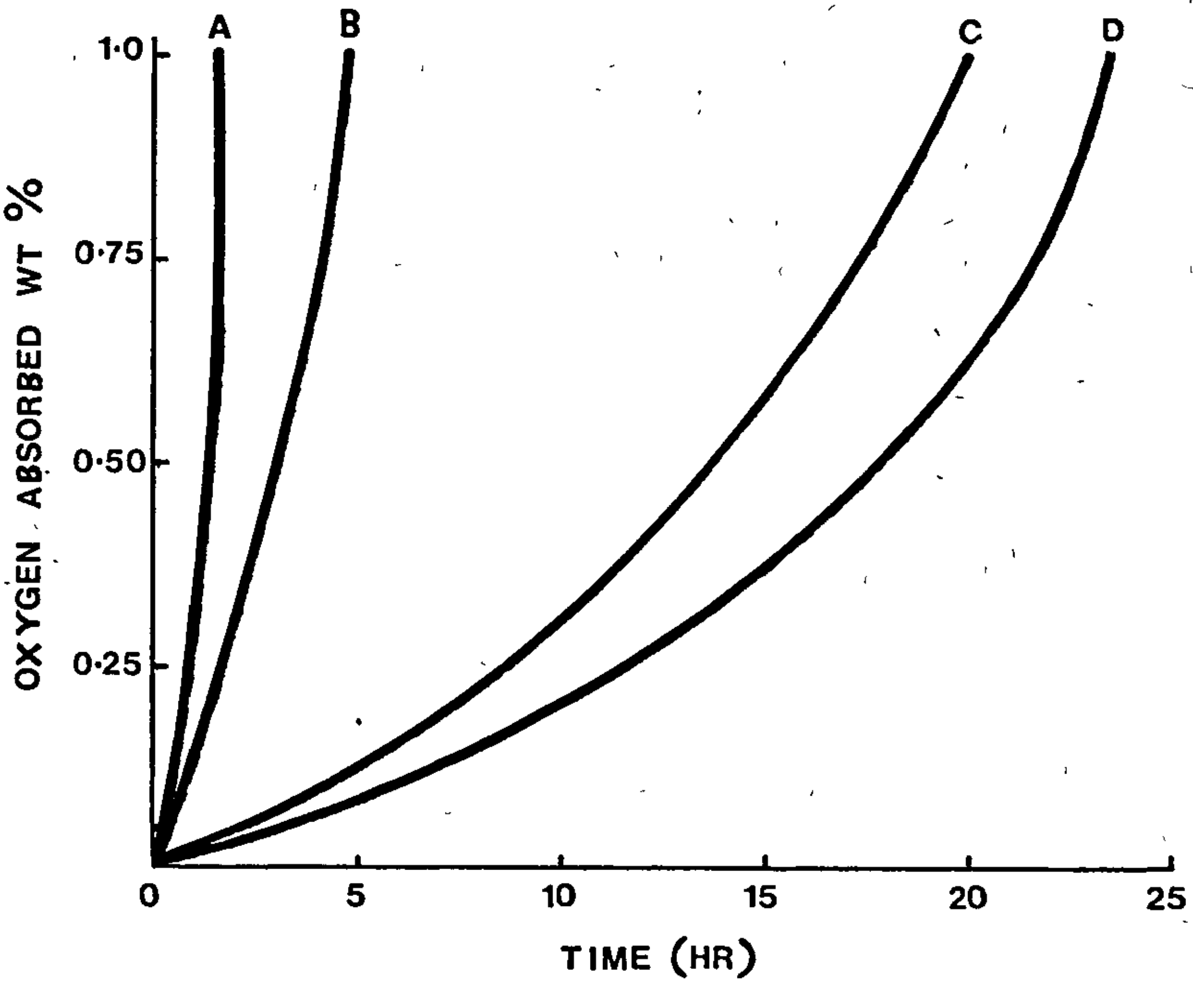


FIGURE 5.5 Effect of $A_1S_3A_1$ (0.25M) on the autoxidation of peroxide vulcanisates from purified natural rubber and RSS1 at 100°C and 760 mm oxygen pressure. (A) Purified natural rubber, no addition; (B) purified natural rubber, $A_1S_3A_1$ added; (C) RSS1, $A_1S_3A_1$ added; (D) RSS1, no addition (132).

The stress-relaxation data (see Figures 5.3 and 5.4) of the natural and polyisoprene vulcanisates cured with dicumyl peroxide was based on samples which were previously cured for 3 hours at 150°C in order to ensure complete decomposition of dicumyl peroxide. However, in practice, vulcanisation of rubbers with dicumyl peroxide was performed within a short period of time at a given cure temperature. In order to investigate further the effect of unreacted dicumyl peroxide and also side products remaining in the vulcanisate cured, after the usual practical cure conditions, on its stress-relaxation behaviour, an experiment was designed using a DPNR vulcanisate cured with dicumyl peroxide (1.5 phr) for 35 minutes at 140^{0}C so that some of the peroxide remained undecomposed in the vulcanisate. Stress-relaxation measurements were then taken of this vulcanisate after it had been conditioned as follows; one sample without devolatilisation and the other had been previously devolatilised for 24 hours at 120°C under vacuum to remove any unreacted peroxide and side products remaining in the vulcanisate. The data obtained is shown in Figure 5.6. The scale of log f/f_0 has been magnified to observe the differences between the two samples. It seems that the devolatilisation process reduces the rate of oxidative stress-relaxation though by an insignificant amount.

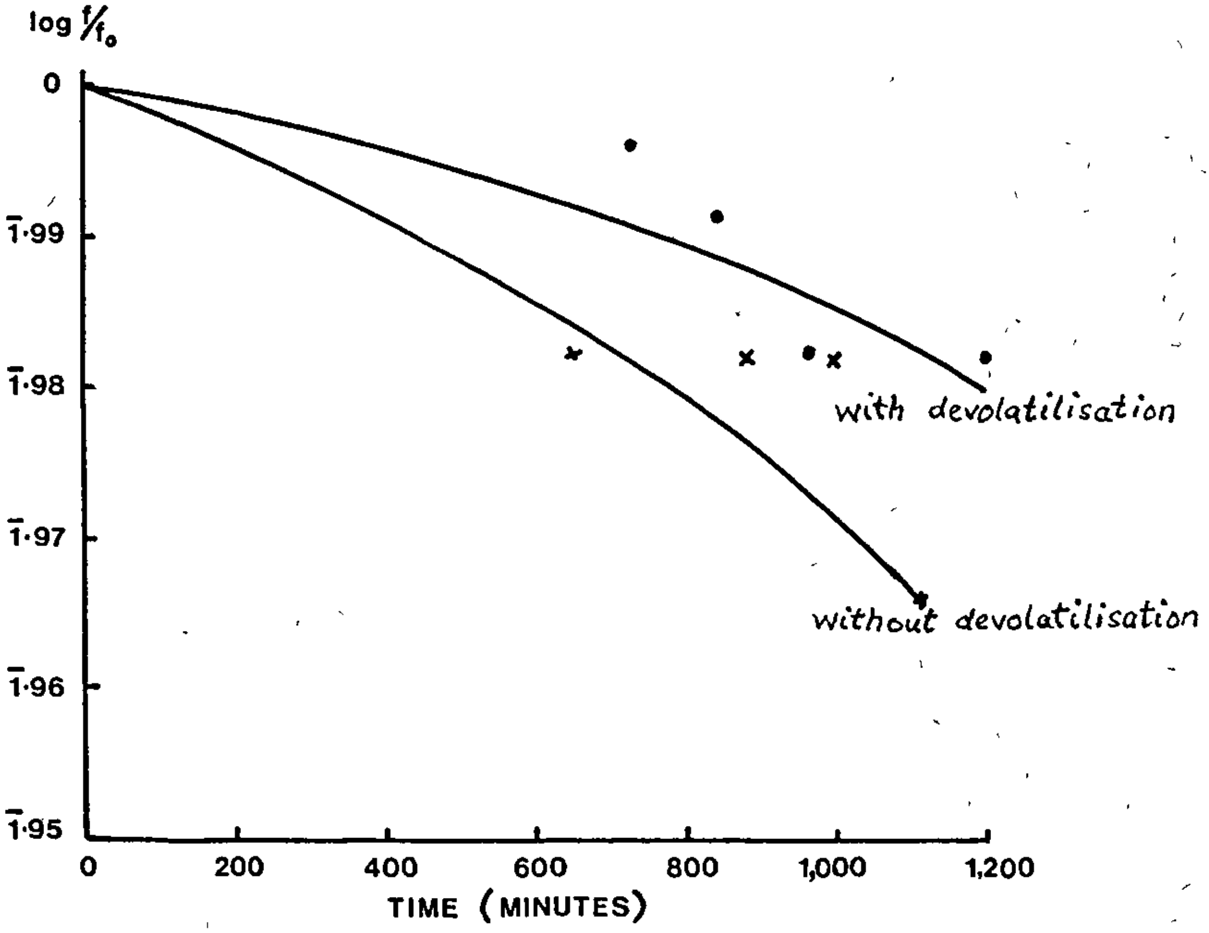


FIGURE 5.6 Continuous stress-relaxation of dicumyl peroxide vulcanisate with and without devolatilisation (in air at 100°C)

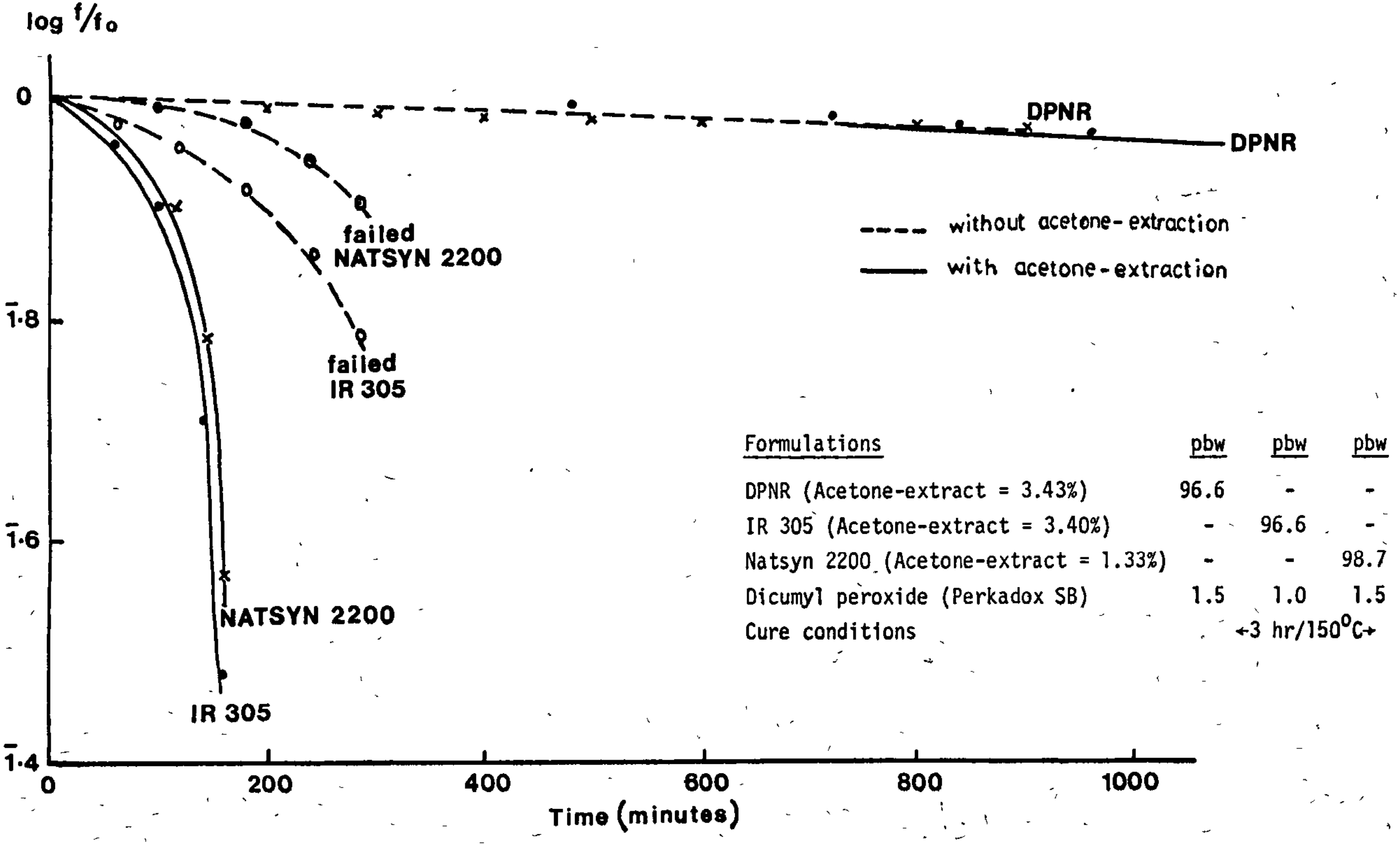
The previous thermal oxidative stress-relaxation data of natural and polyisoprene vulcanisates cured with dicumyl peroxide and bisperoxycarbamates (see Figures 5.3 and 5.4) was based on DPNR and IR 305 which were not previously acetone-extracted. To observe the effect of acetone-extraction on the thermal oxidative stress-relaxation behaviour of these vulcanisates, both DPNR and IR 305 were initially acetone-extracted and then vulcanised with the appropriate curing agents. The thermal oxidative stress-relaxation behaviour of the vulcanisates obtained is shown in Figures 5.7 and 5.8. Additional data based on Natsyn 2200 was utilised to observe the effect of types of polyisoprene rubbers on thermal oxidative stress-relaxation behaviour.

As shown in Figure 5.7 the effect of acetone-extraction did not show any significant consequence on the relaxation rate of the DPNR vulcanisate cured with dicumyl peroxide. The naturally occurring antioxidants present in DPNR are considered to be bound to the rubber and are not easily removed by the acetone-extraction technique. It is the presence of these bound antioxidants which are considered to retard the relaxation rate of the DPNR vulcanisate.

In the case of Natsyn 2200 and IR 305, the relaxation rates of their dicumyl peroxide vulcanisates which were based on the unextracted raw rubbers were significantly slower than their equivalent vulcanisates based on the raw rubbers which had been previously acetone-extracted. By means of the acetone-extraction technique, which removed the stabilisers present in IR 305 and Natsyn 2200, it was shown that the presence of small amounts of antioxidants incorporated during synthesis of these rubbers had a significant effect on the retardation of the relaxation rates.

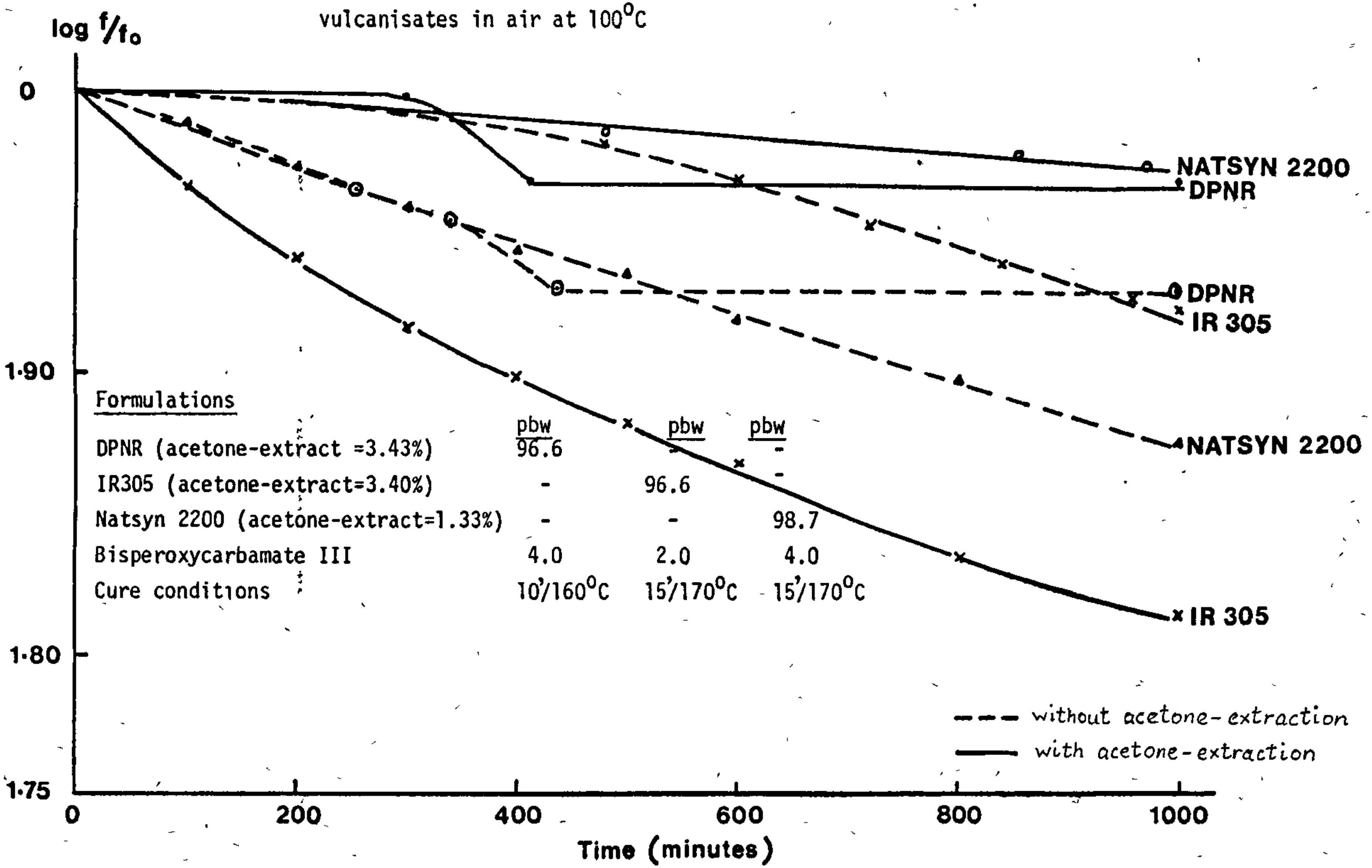
Figure 5.8 shows the performance of bisperoxycarbamate III vulcanisates based on DPNR, IR 305 and Natsyn 2200 which had been previously acetone-extracted before compounding in contrast to their equivalent vulcanisates which had not been previously acetone-extracted before compounding.In DPNR and Natsyn 2200, the vulcanisates based on acetone-extracted rubbers showed relatively slower relaxation rates than the vulcanisates based on unextracted rubbers

FIGURE 5.7 Effect of acetone-extraction on continuous stress-relation of dicumyl peroxide vulcanisates in air at 100^{0}C



Formulations	pbw	pbw	pbw
DPNR (Acetone-extract = 3.43%)	96.6	-	-
IR 305 (Acetone-extract = 3.40%)	-	96.6	-
Natsyn 2200 (Acetone-extract = 1.33%)	-	-	98.7
Dicumyl peroxide (Perkadox SB)	1.5	1.0	1.5
Cure conditions	←3 hr/150^{0}C→		

FIGURE 5.8 Effect of acetone-extraction on continuous stress-relaxation of bisperoxycarbamate III vulcanisates in air at 100°C



Formulations

	pbw	pbw	pbw
DPNR (acetone-extract =3.43%)	96.6	-	-
IR305 (acetone-extract=3.40%)	-	96.6	-
Natsyn 2200 (acetone-extract=1.33%)	-	-	98.7
Bisperoxycarbamate III	4.0	2.0	4.0
Cure conditions	10'/160°C	15'/170°C	15'/170°C

but in the case of IR 305 the situation was reversed.

Special attention concerning. causes of the relaxation process was not considered in detail in the preceding discussion. An attempt based on the literature is now considered by the author. During the process of thermal oxidative stress-relaxation of vulcanisates, the relaxation of stress can be caused by (i) main chain scission, (ii) crosslink scission or (iii) both scissions (i) and (ii) occurring simultaneously. From previous studies (129,131,133) of stress-relaxation it has been suggested that only main chain scission occurs during the thermal oxidative stress-relaxation process of vulcanisates. On the other hand Berry and Watson (134) consider that the relaxation of stress is the result of crosslink scission. The case in which both types of scissions occur simultaneously was suggested by Horikx (135) and Lyubchanskaya et al (136). However, difficulties arise in attempting to analyse the individual processes that occur during the simultaneous occurrence of both these types of scissions; no report of a method has been found in the literature to solve this problem.

5.3 Hot Air Oven Ageing

5.3.1 Significance

Hot air oven ageing has been used extensively in the rubber industry as an accelerated process for evaluation of rubber products which are exposed to ~~the~~ conditions existing in service. A review (137) of the work of Schoch and Juve, Youmans and Massens and of Du Bois and Hennickers indicates that the air-oven ageing method is valid for predicting long-term performance under moderate climatic conditions.

As an extension of the work on thermal oxidative stress-relaxation, the hot air oven ageing method was utilised in the technological evaluation of the bisperoxycarbamate vulcanisates.

5.3.2 Experimental

Test pieces in the form of microrings were used and they were aged by means of the Wallace-Cell Ageing Block kept at 70 ± 1°C with a constant rate of air circulation. Further details concerning this method are given in BS 903: Part A 19: 1975. Test results were expressed as percentage retention in property.

5.3.3 Results and Discussion

Of the three bisperoxycarbamates studied, the bisperoxycarbamate III vulcanisates based on natural and polyisoprene rubbers showed the most resistance to hot air ageing (see Figures 5.9 and 5.11).

In natural rubber, both the bisperoxycarbamate II and III vulcanisates had comparable stability to the dicumyl peroxide or sulphur-EV vulcanisates at the specified hot air oven ageing conditions (see Figures 5.9 and 5.10). The conventional sulphur vulcanisate was the least stable of all the vulcanisates studied.

In polyisoprene rubber, only the sulphur-EV vulcanisate had comparable stability to the bisperoxycarbamate II and III vulcanisates (see Figures 5.11 and 5.12). Both the dicumyl peroxide and conventional sulphur vulcanisates had poor aged properties.

5.4 Conclusions

The order of stability of the unfilled bisperoxycarbamate vulcanisates based on natural and polyisoprene rubbers to the thermal oxidative stress-relaxation and hot air oven ageing was found to be dependent on the structures of the bisperoxycarbamates; cyclic > aliphatic/cyclic > aliphatic. Of these curing systems, bisperoxycarbamate III vulcanisate based on natural rubber demonstrated comparable stability to its equivalent vulcanisates cured with dicumyl peroxide, Diurethane (Novor 924) and sulphur-EV systems. In the case of polyisoprene rubber, the bisperoxycarbamate III vulcanisate had comparable stability to its equivalent vulcanisate cured with sulphur-EV system.

FIGURE 5.9 Tensile property retention (7 days at 70°C) of DPNR vulcanisates

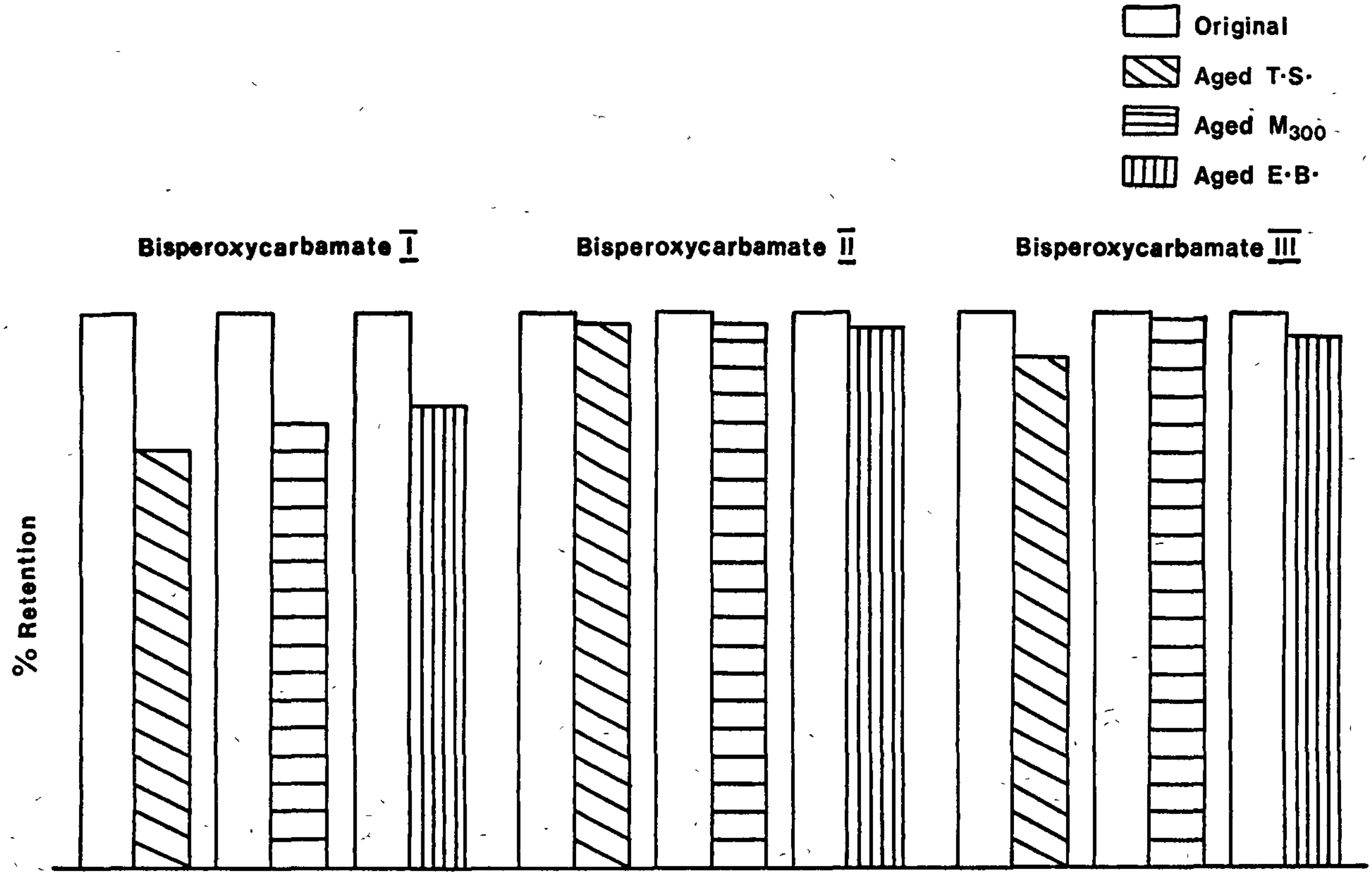


FIGURE 5.10 Tensile property retention (7 days at 70°C) of DPNR vulcanisates

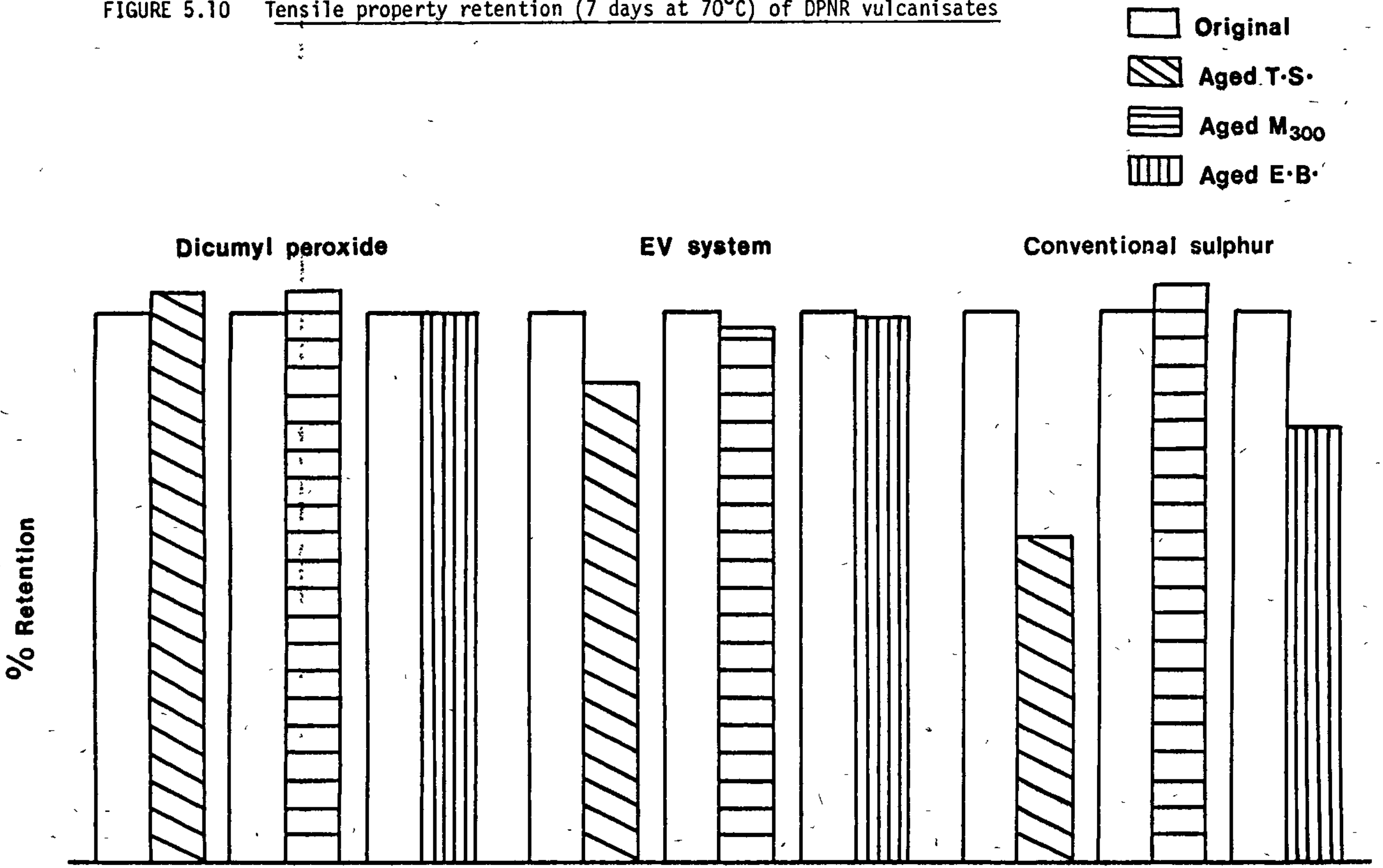


FIGURE 5.11 Tensile property retention (7 days at 70°C) of IR 305 vulcanisates

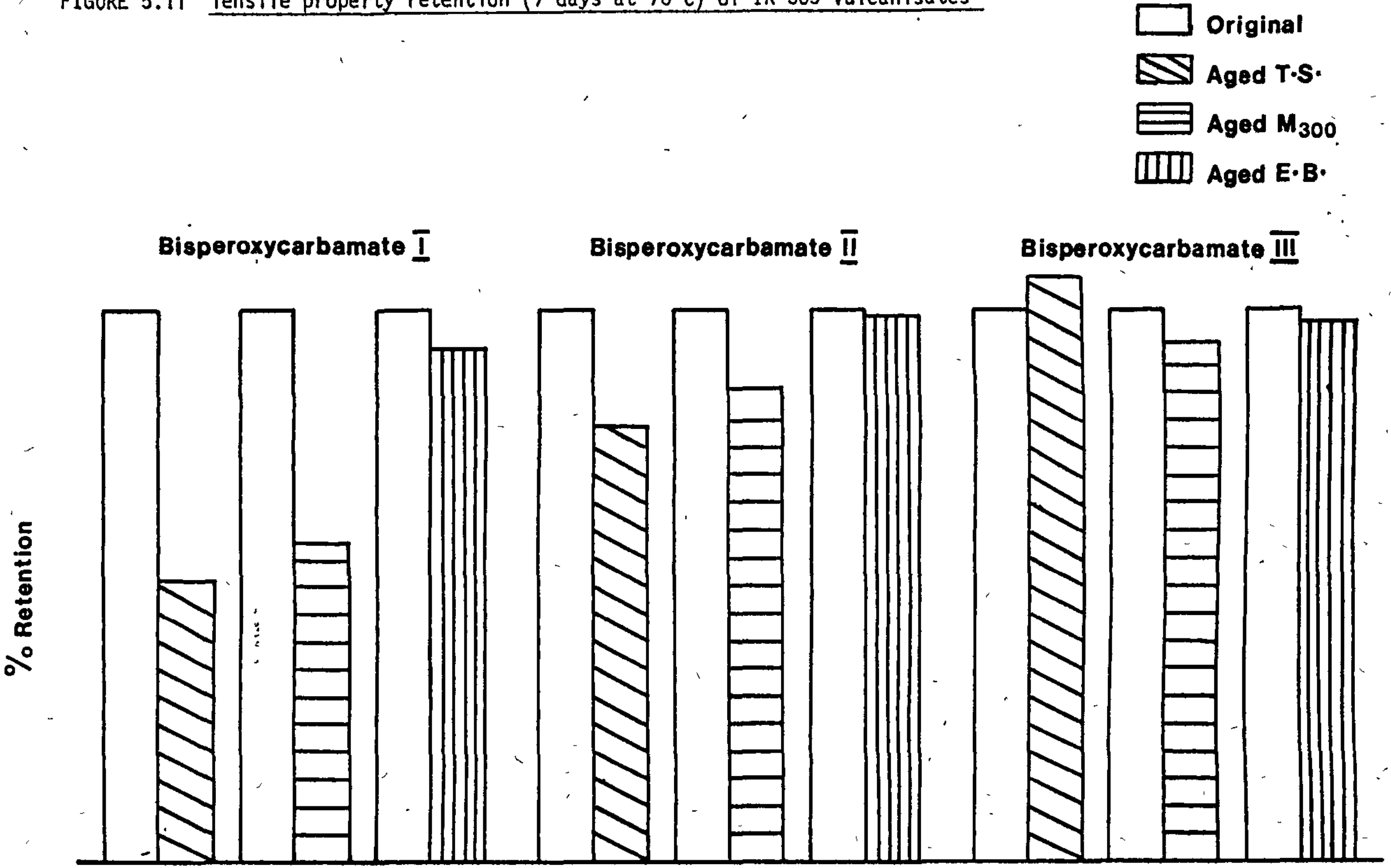
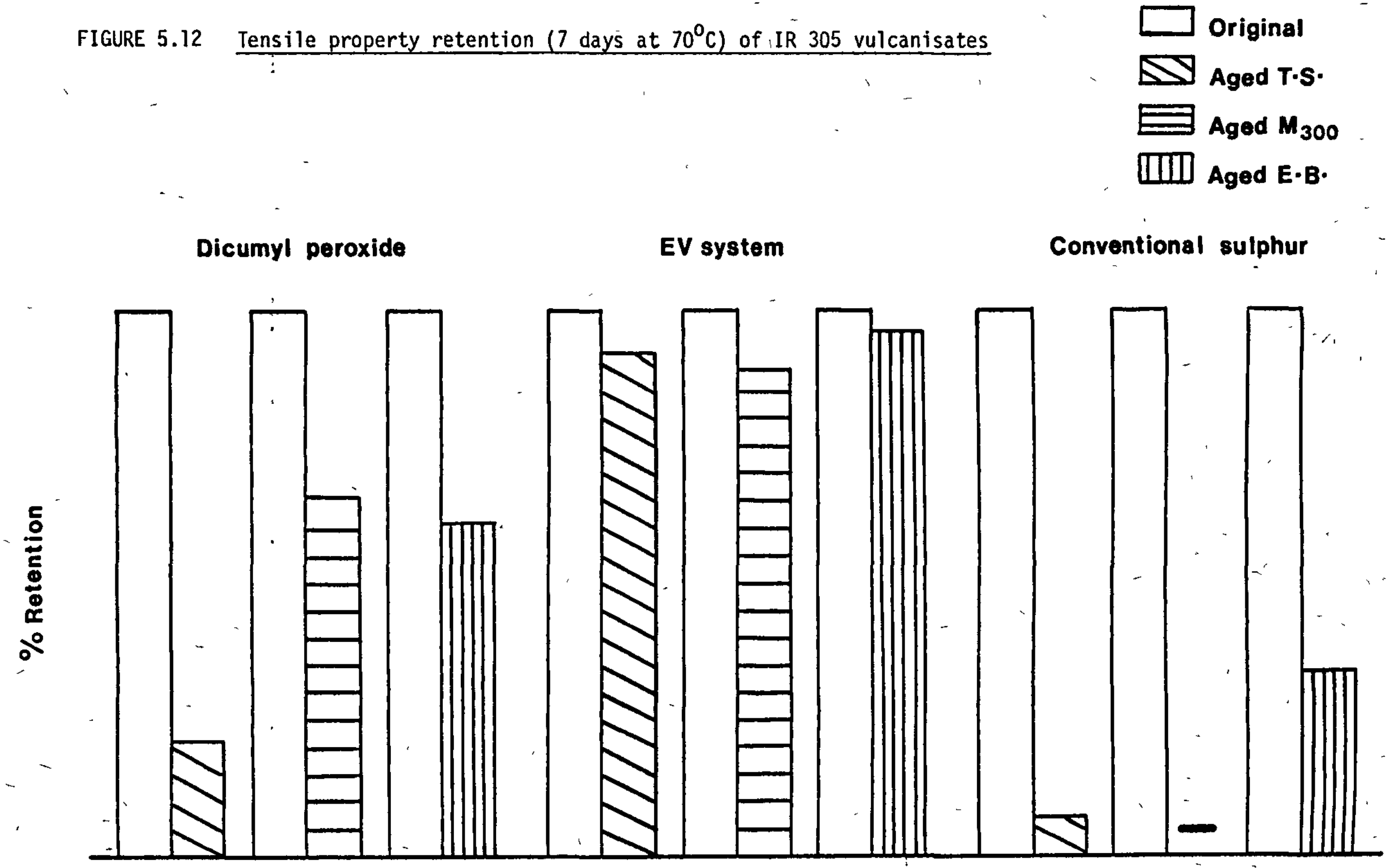


FIGURE 5.12 Tensile property retention (7 days at 70°C) of IR 305 vulcanisates

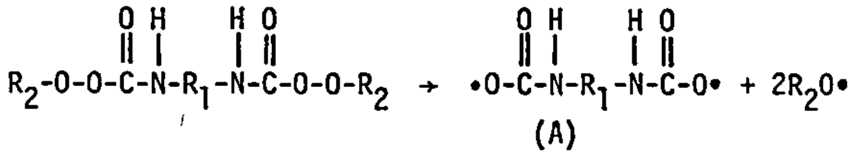


CHAPTER 6

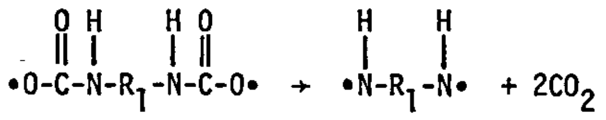
POROSITY IN BISPEROXYCARBAMATE VULCANISATES

6.1 Introduction

In earlier chapters the author observed that sometimes porosity occurred and was due to the evolution of carbon dioxide, via equations 83 and 84, during the vulcanisation of the rubber when a high concentration of bisperoxycarbamate was present. To substantiate such a consideration an investigation was designed at finding absorbing systems to remove the liberated carbon dioxide.



$$R_2\text{-O-O-}\overset{\overset{O}{\|}}{C}\text{-}\overset{\overset{H}{|}}{N}\text{-}R_1\text{-}\overset{\overset{H}{|}}{N}\text{-}\overset{\overset{O}{\|}}{C}\text{-O-O-}R_2 \rightarrow \underset{(A)}{\bullet O\text{-}\overset{\overset{O}{\|}}{C}\text{-}\overset{\overset{H}{|}}{N}\text{-}R_1\text{-}\overset{\overset{H}{|}}{N}\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\bullet} + 2R_2O\bullet \qquad (83)$$



$$\bullet O\text{-}\overset{\overset{O}{\|}}{C}\text{-}\overset{\overset{H}{|}}{N}\text{-}R_1\text{-}\overset{\overset{H}{|}}{N}\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\bullet \rightarrow \bullet\overset{\overset{H}{|}}{N}\text{-}R_1\text{-}\overset{\overset{H}{|}}{N}\bullet + 2CO_2 \qquad (84)$$

An earlier worker (104) used coagents to eliminate porosity and also to increase the crosslink density of the copolymer of vinylidene fluoride and hexafluoropropene cured with di-N-methyl tertiary-butyl peroxycarbamate. Based on this reference two common commercially available coagents for peroxide vulcanisation were chosen for examination to eliminate porosity, coupled with the purpose of increasing the crosslink density of the bisperoxycarbamate vulcanisates.

In addition to the above technique, it is known that when calcium hydroxide is exposed to air it absorbs carbon dioxide and the crystals of the calcium hydroxide become opaque due to the following reaction scheme (equation 94):

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \qquad (94)$$

On the basis of the above reaction scheme, the author considered that calcium hydroxide could also be an appropriate absorbing system. However, using this technique water is formed and is considered as an undesirable product in rubber. It was considered that the elimination of the water could possibly be overcome by means of a commonly used dessicant in the rubber industry, i.e. calcium oxide (see equation 95). (Calcium oxide is usually dispersed in paraffin wax or plasticizer).

$$CaO + H_2O \rightarrow Ca(OH)_2 \qquad (95)$$

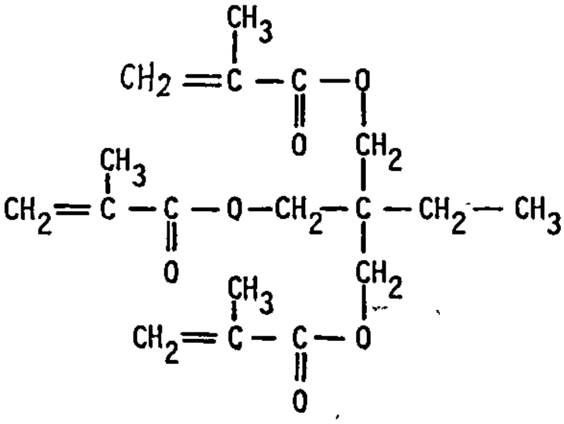
6.2 The Use of Coagents, Sartomer SR-350 and HVA-2

6.2.1 Materials

Two coagents were chosen for examination and will now be described.

Sartomer SR-350

Its structure (XXX) is shown below and it was obtained from the Anchor Chemical (UK) Ltd.

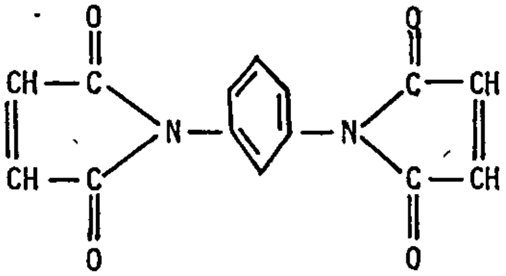


Trimethylol propane trimethacrylate

(XXX)

HVA-2

Its structure is shown below (XXXI) and was obtained from E I Du Pont De Nemours and Company.



N,N'-m-phenylene dimaleimide (XXXI)

Bisperoxycarbamate III was chosen for this investigation as it produces natural and polyisoprene rubber vulcanisates that appear to have the best compromise of strength and resistance to oxidative ageing when compared to equivalent vulcanisates cured with the other bisperoxycarbamates.

6.2.2 Experimental

The bisperoxycarbamate III and the selected coagents were added at varying concentrations into DPNR on the two roll mill at room temperature. The mixes were then analysed for curing characteristics by the Monsanto ODR and vulcanised for observation of porosity and tensile properties.

6.2.3 Results and discussion

The observation of porosity in the vulcanisates cured with bisperoxycarbamate III/Sartomer SR-350 and bisperoxycarbamate III/HVA-2 is represented in Tables 6.1 and 6.2 respectively.

TABLE 6.1

The observation of porosity in the bisperoxycarbamate III/Sartomer SR-350 vulcanisates:(1)

Bisperoxycarbamate III (phr)	Sartomer SR-350 (phr)	Visible porosity
4.0	4.0	Nil
4.0	6.0	Nil
6.0	4.0	Very slight
6.0	6.0	Nil

TABLE 6.2

The observation of porosity in the bisperoxycarbamate III/HVA-2 vulcanisates: (1)

Bisperoxycarbamate III (phr)	HVA-2 (phr)	Visible porosity
4.0	0.5	Nil
4.0	1.0	Nil
5.0	0.5	Very slight
6.0	1.5	Very slight
6.0	2.0	Nil

(1) Samples were cured for 10 minutes at 160°C

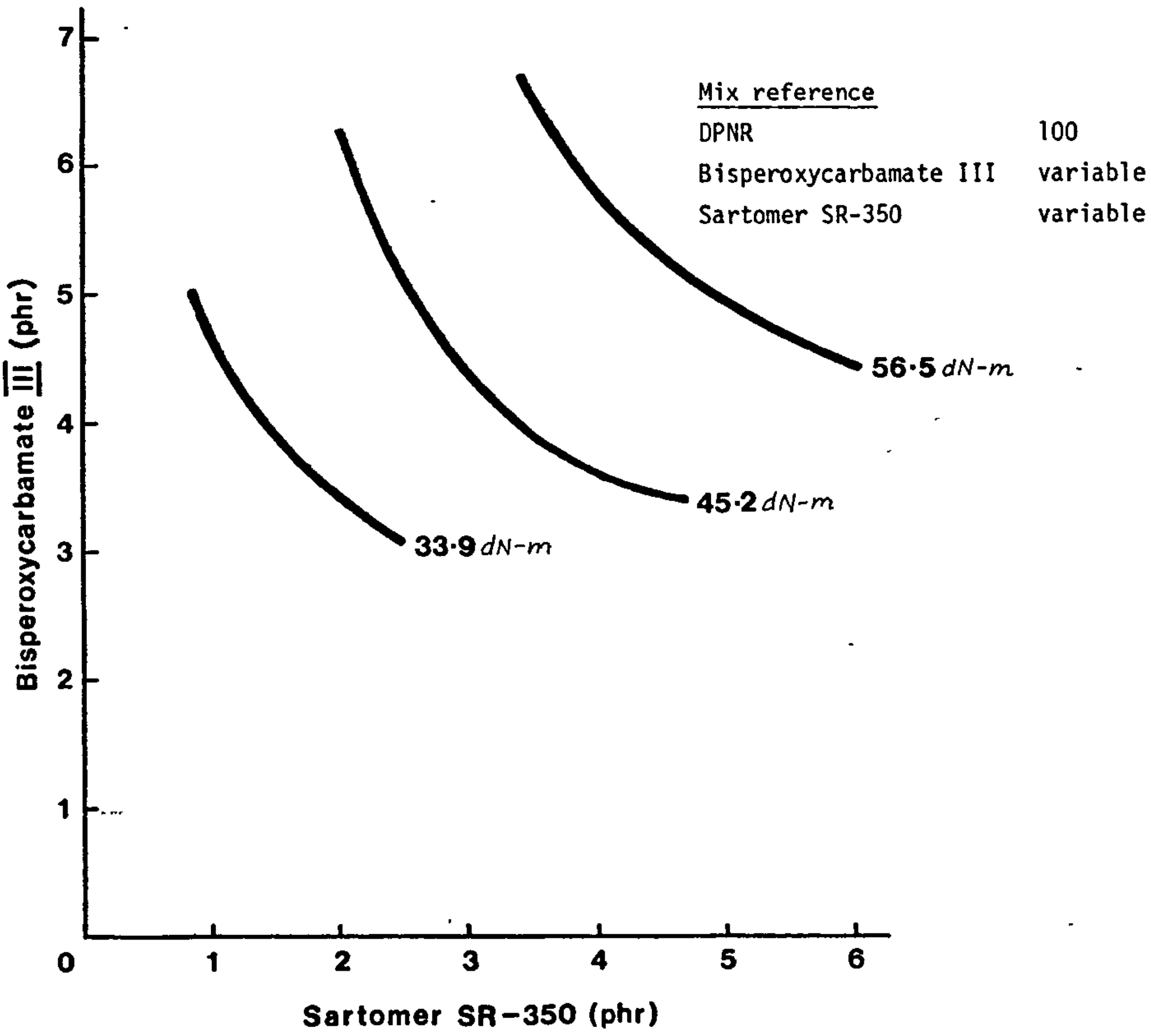
The inclusion of Sartomer SR-350 or HVA-2 into the bisperoxycarbamate III mixes was shown to reduce and eventually eliminate the occurrence of porosity in the cured samples. The concentrations of these coagents determined the extent of porosity elimination.

In the earlier chapters it was considered that a bisperoxycarbamate decomposes thermally with formation of free radicals, as shown in equations 83 and 84, and these vulcanise the rubber. The hypothetical interpretation that equation 84 takes place is considered to be further substantiated by the addition of these coagents which presumably prevents the liberation of carbon dioxide by reacting with radical (A) of equation 83, before it liberated the carbon dioxide of equation 84.

Besides the use of these coagents to eliminate porosity in the vulcanisates, it was considered interesting to observe the effect of these coagents on the optimum ODR torque of the mixes and the vulcanisate properties. These data are shown in Figures 6.1 - 6.6.

The inclusion of these coagents in the formulations of the bisperoxycarbamate III mixes resulted in an increase of crosslink density of the vulcanisates as interpreted from the data of Figures 6.1 and 6.2 and 6.4 and 6.5. Hence it was considered that the presence of a coagent in a rubber mix gives more reactive sites during vulcanisation for the crosslinking reaction to occur (138). Although the use of coagents serves the purpose of increasing crosslink density, they do not give any significant advantageous effect on the tensile strength of the vulcanisates cured with bisperoxycarbamate III as shown by Figures 6.3 and 6.6. As a consequence of this observation another absorbing system was investigated and is discussed in Section 6.3.

FIGURE 6.1 Contour graph of optimum ODR torque of bisperoxycarbamate III/Sartomer SR 305 vulcanisates



Mix reference	
DPNR	100
Bisperoxycarbamate III	variable
Sartomer SR-350	variable

FIGURE 6.2 Contour graph of M_{300} of bisperoxycarbamate III/Sartomer SR-350 vulcanisates

Mix reference

DPNR	100
Bisperoxycarbamate III	variable
Sartomer SR-350	variable

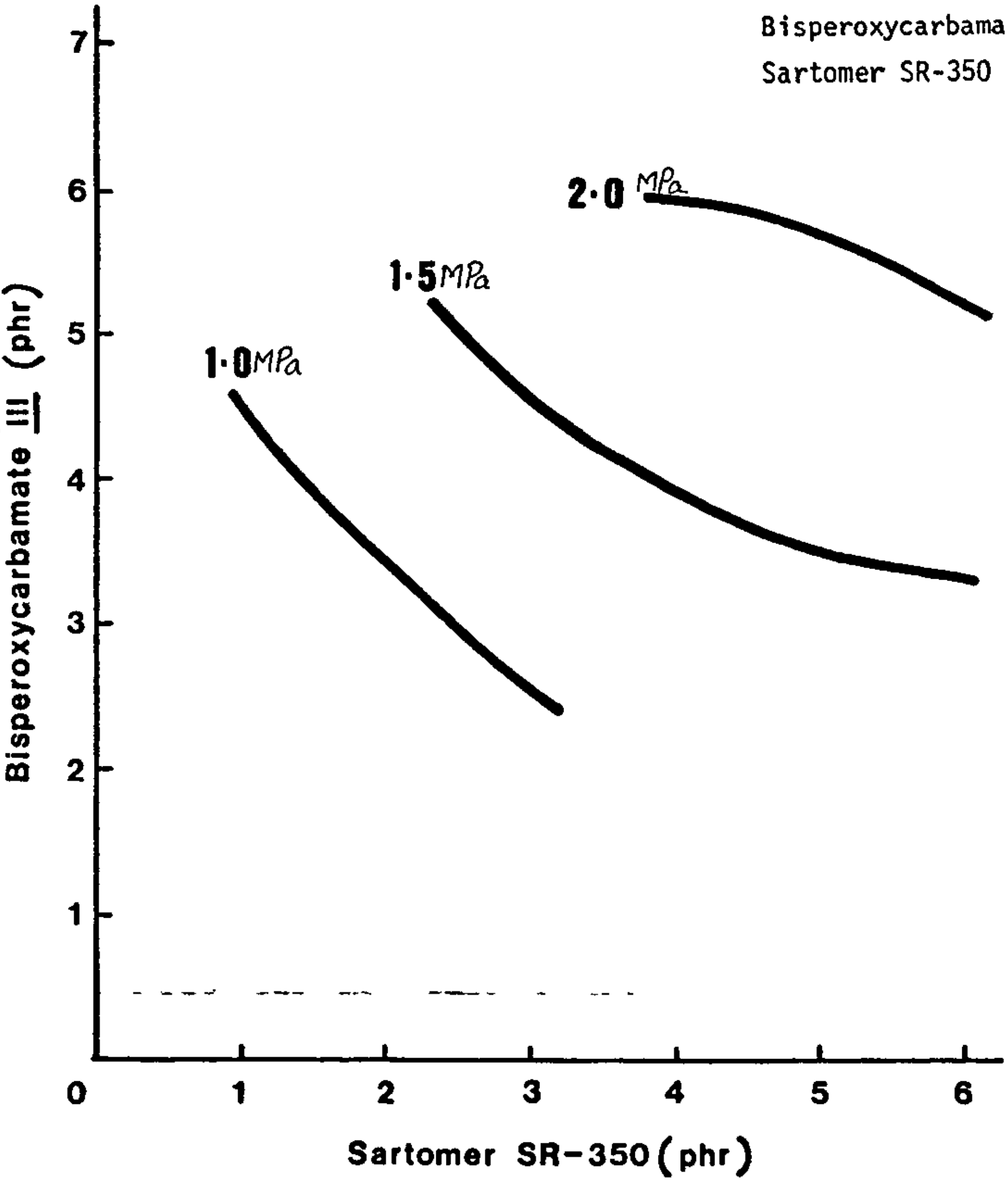


FIGURE 6.3 Effect of varying bisperoxycarbamate III and Sartomer SR-350 on ultimate tensile strength

Mix reference	
DPNR	100
Bisperoxycarbamate III	variable
Sartomer SR-350	variable

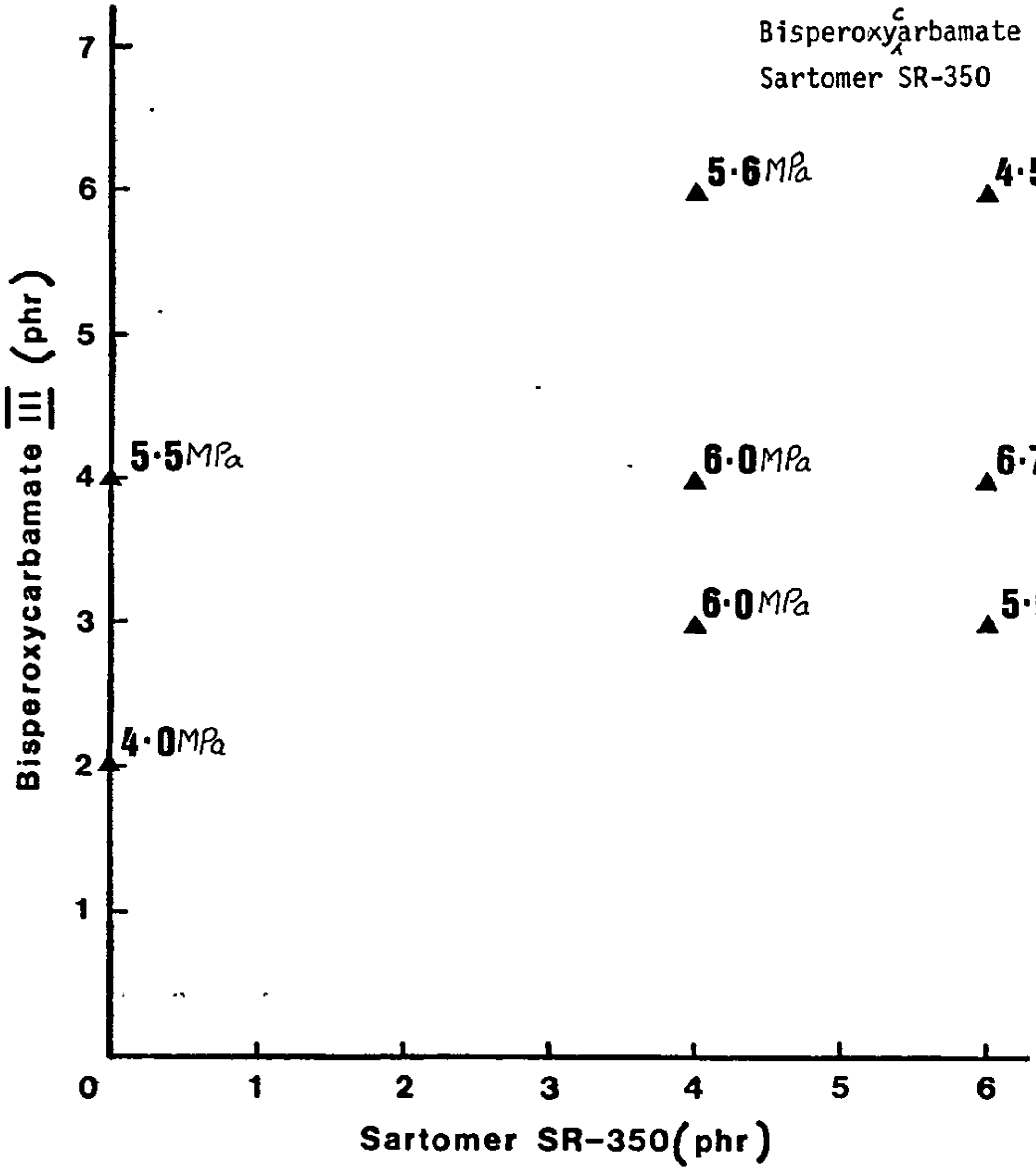


FIGURE 6.4 Contour graph of optimum torques of bisperoxycarbamate III/HVA-2 vulcanisates

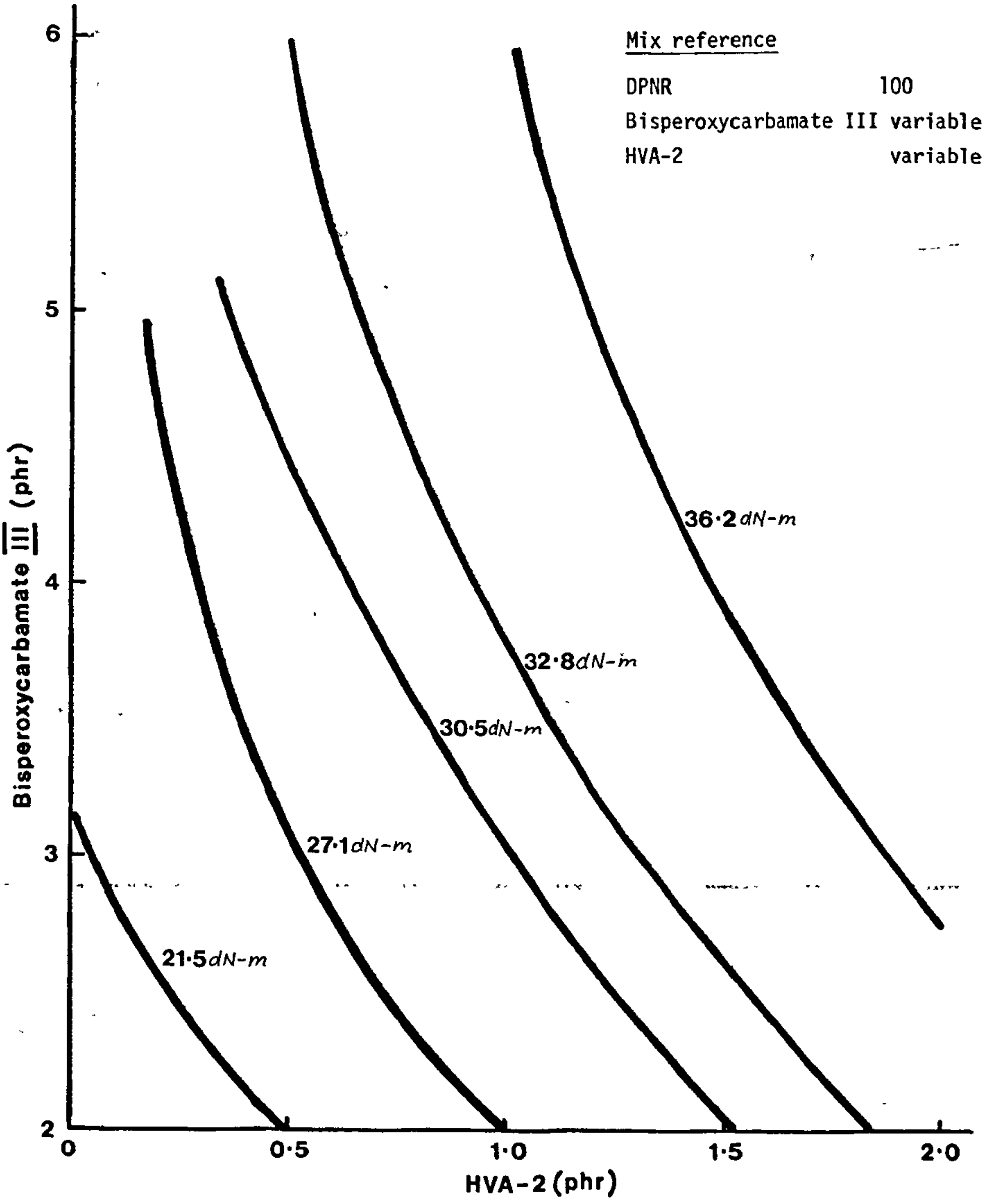


FIGURE 6.5 Contour graph of M_{300} of bisperoxycarbamate III/HVA-2 vulcanisates

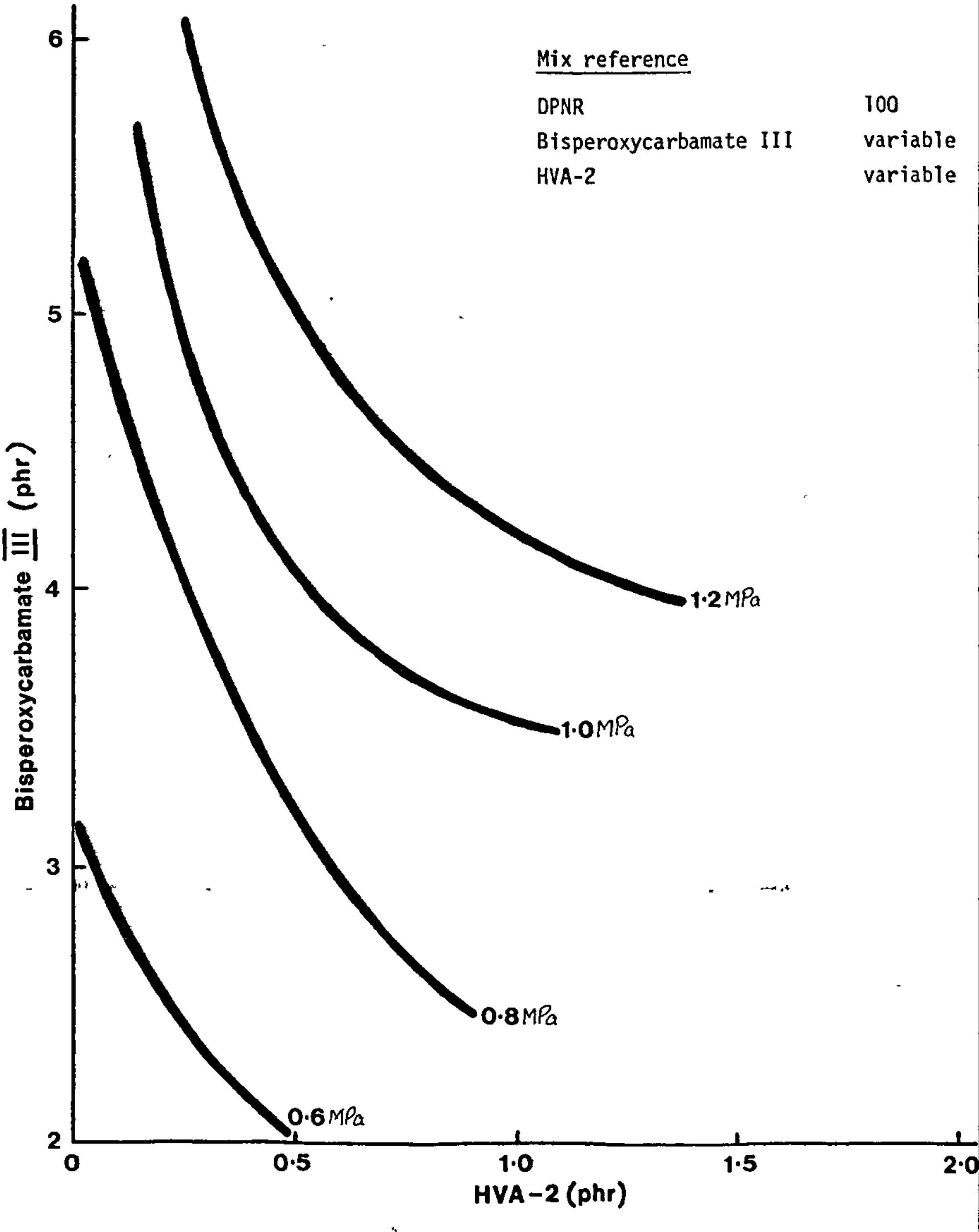
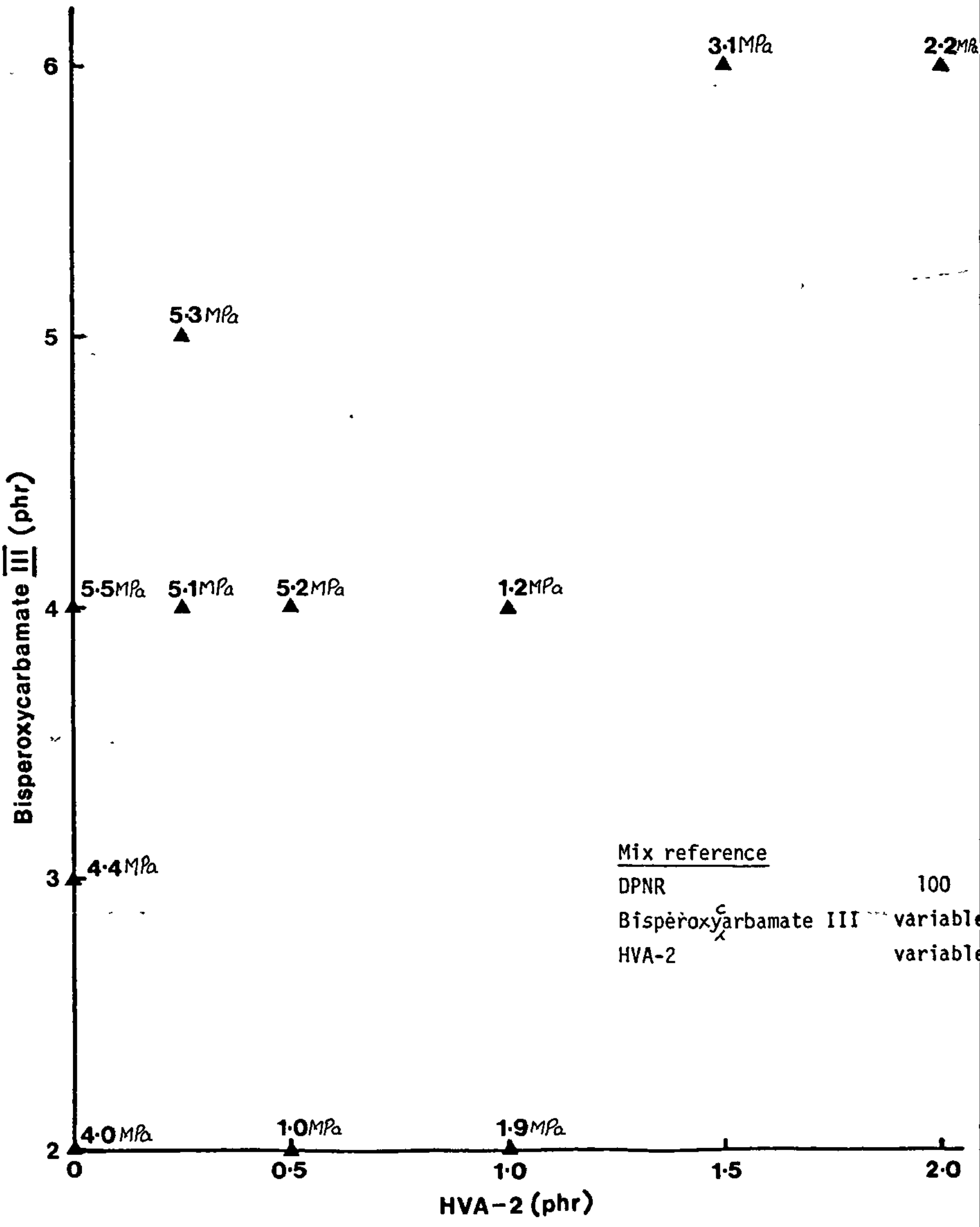


FIGURE 6.6 Effect of varying bisperoxycarbamate III and HVA-2 on ultimate tensile strength



Mix reference	
DPNR	100
Bisperoxycarbamate III	variabl
HVA-2	variabl

6.3 The Use of $Ca(OH)_2/CaO$ System

$Ca(OH)_2/CaO$ powder examination

Initially it was decided to examine the effect of the undiluted $Ca(OH)_2/CaO$ powders in rubber. $Ca(OH)_2$ of 98% purity and Analar grade was obtained from BDH. CaO of pure grade with low chlorine and sulphur was obtained from BDH. The following mixing procedure was used:

DPNR was masticated on a two-roll mill and allowed to form a smooth bank. $Ca(OH)_2$ and CaO were then added and dispersed and finally followed by the bisperoxycarbamate III.

An experiment was designed using a fixed concentration of absorbers guaranteed to eliminate porosity by means of the reaction scheme of equations 94 and 95 whilst the concentration of the bisperoxycarbamate III was varied from 5 phr to 8 phr. The tensile properties of the vulcanisates thus obtained are shown in Table 6.3.

As shown in Table 6.3, the optimum concentration of bisperoxycarbamate III for overall strength and economy reasons would be 5 phr. However, this was achieved using an unnecessarily high level of absorbers and a second step to complete optimisation would be to try and reduce the concentration of absorber. An additional problem is that CaO absorbs moisture from the atmosphere and also $Ca(OH)_2$ absorbs carbon dioxide from the atmosphere, both of which would render the $Ca(OH)_2/CaO$ absorber system inert after a period of storage. Furthermore both are difficult to disperse in rubber. To solve this problem and to aid the dispersion of CaO and $Ca(OH)_2$ in rubber the common aromatic processing oil, Shellflex 729 UK, was utilised to make a $Ca(OH)_2/CaO$ paste.

Oil Dispersed $Ca(OH)_2/CaO$

The weight ratio of $Ca(OH)_2$/CaO/Shellflex 729 UK used to make the oil dispersed $Ca(OH)_2/CaO$ was 3/3/4. The paste was kept in a closed container for 48 hours to obtain a homogeneous paste. Shellflex 729 UK was obtained from Shell Chemicals (UK) Limited.

TABLE 6.3

Formulations and tensile properties for optimisation of the level of the bisperoxycarbamate III in DPNR

DPNR	100	100	100	100
$Ca(OH)_2$	15	15	15	15
CaO	15	15	15	15
Concentration of Bisperoxycarbamate III (phr)	5	6	7	8
Cure conditions	← 30 minutes/140°C →			
Tensile strength (MPa)	8.6	8.2	8.1	9.1
Modulus at 300% strain (MPa)	1.70	1.81	2.02	2.35
Elongation at break (%)	550	520	500	410
Tensile product (MPa x per cent)	4730	4264	4050	3731
Porosity	← no visible porosity →			

The tensile properties of vulcanisates prepared using this oil dispersed absorber system are shown in Table 6.4. The minimum level suitable for elimination of porosity was found to be between 5 - 7.5 phr absorber dispersed in oil.

TABLE 6.4

To reduce and optimise the level of absorber system (5 phr of bisperoxycarbamate III present)

Concentration of absorber system in oil (60% active) (phr)	5	7.5	10	12.5	15
Cure conditions	← 30 minutes/140°C →				
Tensile strength (MPa)	8.8	8.5	7.8	7.2	7.2
Modulus at 300% strain (MPa)	1.20	1.25	1.21	1.13	1.14
Elongation at break (%)	640	630	630	650	640
Tensile product (MPa x per cent)	5632	5355	4914	4680	4608
Porosity	Visible porosity	no visible porosity			

A theoretical calculation of the quantity of the absorber system required can be made as follows:

Theory

5 grams of bisperoxycarbamate III $= \frac{5}{442}$ moles

No. of moles of CO_2 liberated during cure (see equation 84) $= \frac{5 \times 2}{442}$

Weight of $Ca(OH)_2$ required to absorb the CO_2 $= \frac{5}{442} \times \cancel{2} \times 74.08$

$= 1.68 g$

No. of moles of H_2O liberated (see equation 94) $= \frac{5}{442} \times 2$

Weight of CaO required to absorb the liberated H_2O $= \frac{5}{442} \times 2 \times 56.08$

$= 1.27 g$

The above consideration shows that the amount of $Ca(OH)_2$ added in the mix (i.e. 2.25g of $Ca(OH)_2$ in the case of 7.5 phr of 60% paste) is close to the minimum theoretical value required to absorb all the carbon dioxide produced. The weight of CaO added in the mix was based on the same weight of $Ca(OH)_2$ for convenience. However, it is to be noted that the calculation above does not take into consideration the possibility that side reactions may occur where an amount of free radicals are consumed in the presence of aromatic processing oil.

During the vulcanisation step, an additional reaction product was considered to be generated i.e. $Ca(OH)_2$ from the CaO and water produced during crosslinking and this was thought to be available for use in absorbing the liberated carbon dioxide. Since the amount of water liberated during the reaction is low when compared to the naturally occurring water present in rubber and fillers the author considered it is possible in theory to eliminate the use of CaO in the bisperoxycarbamate formulations. In technological practice it would probably always be desirable to add some additional CaO to cope with side reactions such as water present in fillers and the raw rubber. However, the relationship between practical formulation need and chemical stoichiometry is good and remarkable in the history of rubber compounding technology.

6.4 Conclusions

Three systems were examined and found to eliminate porosity namely:

i) Sartomer SR-350
ii) HVA-2
iii) $Ca(OH)_2$/CaO

Of these the $Ca(OH)_2$/CaO system was considered the most suitable with respect to versatility and cost as the $Ca(OH)_2$ absorbed the reaction produced carbon dioxide and the CaO absorbed the water by means of reactions of equations 94 and 95.

Increasing the level of bisperoxycarbamate III in combination with the above additives in DPNR resulted in vulcanisates of better strength than the control dicumyl peroxide vulcanisates e.g. a tensile product value of 5632 MPa x per cent in Table 6.4, compared with vulcanisates cured with dicumyl peroxide, e.g. a tensile product value of 4248 Mpa x per cent in Figure 4.5.

CHAPTER 7

INVESTIGATION OF BISPEROXYCARBAMATE III IN FILLED NATURAL RUBBER AND SOME UNFILLED SYNTHETIC RUBBERS

7.1 Examination of the Bisperoxycarbamate III in Silica-Filled DPNR

7.1.1 Introduction

In all the previous work the investigations of bisperoxycarbamates as crosslinking agents for natural and polyisoprene rubbers were performed on unfilled gum rubbers used as models to eliminate any possible cure reaction interference. However, practical systems contain fillers which are now considered. It is appropriate to consider white fillers first since one would envisage less or no interference by the white fillers than the carbon blacks on cure reactions of the bisperoxycarbamate III.

Many white fillers have been used in the rubber industry and among these the fine particle silicas and silicates are the most highly reinforcing. Intensive literature reviews on these fillers had been previously reported by Bachman et al (139) and Wagner (140). As precipitated silica is one of the most commonly used white reinforcing fillers in rubber product fabrication, it was chosen for the present work to assess the curing ability of the bisperoxycarbamate III in such white-filled DPNR.

In addition to the incorporation of silica into rubber to attain certain desired mechanical properties, the inclusion of coupling agents in a silica-filled compound has been previously shown (141-147) to produce some remarkable property enhancement, such as an increase in modulus at 300% strain and tensile strength and significant reductions in heat build-up and compression set. The enhancement of the properties is generally considered due to the formation of covalent bonds between silica and rubber and the role of coupling agents is to promote the formation of these covalent bonds.

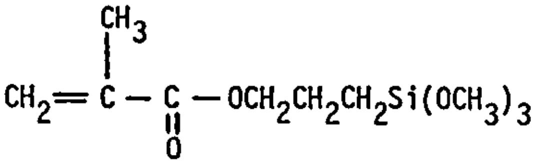
For the purpose of property enhancement of silica-filled vulcanisates cured with the bisperoxycarbamate III, two coupling agents were chosen for the present investigation.

7.1.2 Materials

Precipitated silica of grade Ultrasil VN3 was obtained from Degussa.

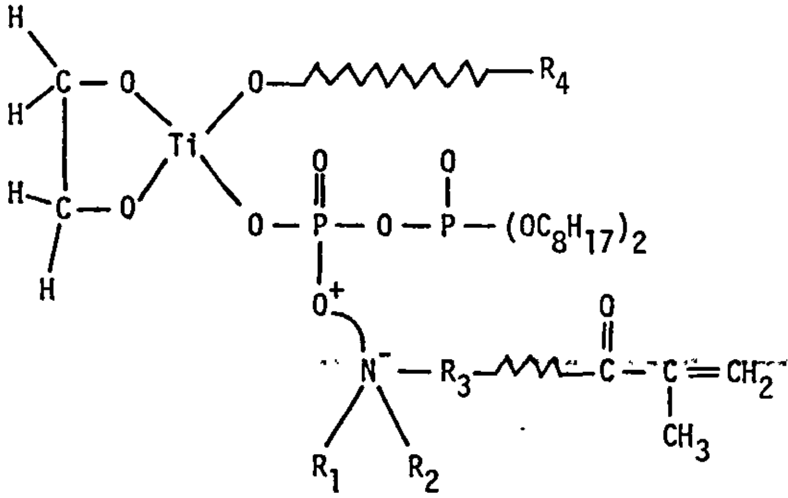
Silica A-174 of structure (XXXII) was obtained from Union Carbide UK Ltd.

Titanate KR-238 of structure (XXXIII) was obtained from Kenrich Petrochemicals Inc.



$$CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}-\underset{\displaystyle O}{\underset{\|}{C}}-OCH_2CH_2CH_2Si(OCH_3)_3$$

gamma-methacryloxypropyltrimethoxysilane (XXXII)
(Silane A-174)



Di(dioctyl pyrophosphato) ethylene titanate chelate, methacrylic amine quat coupling agent (XXXIII)
(Titanate KR-238M)
ernary .

7.1.3 Experimental

A masterbatch of DPNR/Silica (100/20) was prepared on a two-roll mill. Other necessary ingredients were then added on the batches obtained from the masterbatch.

7.1.4 Results and discussion

The formulations and tensile properties of silica-filled DPNR cured with the bisperoxycarbamate III and dicumyl peroxide as control are shown in Table 7.1.

TABLE 7.1

Formulations and tensile properties of silica-filled DPNR (Bisperoxycarbamate III compared with dicumyl peroxide)

DPNR	100	100
Ultrasil VN3	20	20
Bisperoxycarbamate III	5	-
Dicumyl peroxide	-	1.5
$Ca(OH)_2$) 60% dispersion CaO) in Shellflex 729UK	6	-
Cure conditions	30 min/140^{o}C	60 min/150^{o}C
Tensile strength (MPa)	12.4	10.0
Modulus at 300% strain (MPa)	2.41	2.26
Elongation at break (%)	540	500
Tensile product (MPa x per cent)	6696	5000

The concentration of 20 phr of the precipitated silica was chosen as according to the literature; this proportion approximates to the highest tensile strength available from a dicumyl peroxide/natural rubber vulcanisate of this type. As shown in the Table 7.1, the bisperoxycarbamate III curing system exhibits superiority in strength of about 34% over the dicumyl peroxide one and it also requires a much shorter time to reach optimum cure state.

The effect of silane and titanate coupling agents on the tensile properties of silica-filled DPNR cured with the bisperoxycarbamate III is shown in Tables 7.2 and 7.3 respectively.

TABLE 7.2

The effect of silane coupling agent on the tensile properties of silica filled vulcanisates cured with 5 phr of the bisperoxycarbamate III

DPNR	100				
$Ca(OH)_2$)60% dispersion	6				
CaO)in Shellflex 729UK					
Ultrasil VN3	20				
Silane A-174	0	0.5	1.0	1.5	2.0
Cure conditions	← 30 min/140°C →				
Tensile strenth (MPa)	12.4	6.6	9.4	7.3	5.5
Modulus at 300% strain (MPa)	2.41	3.94	5.24	5.26	5.48
Elongation at break (%)	540	340	350	330	300
Tensile product (MPa x per cent)	6696	2244	3290	2409	1650

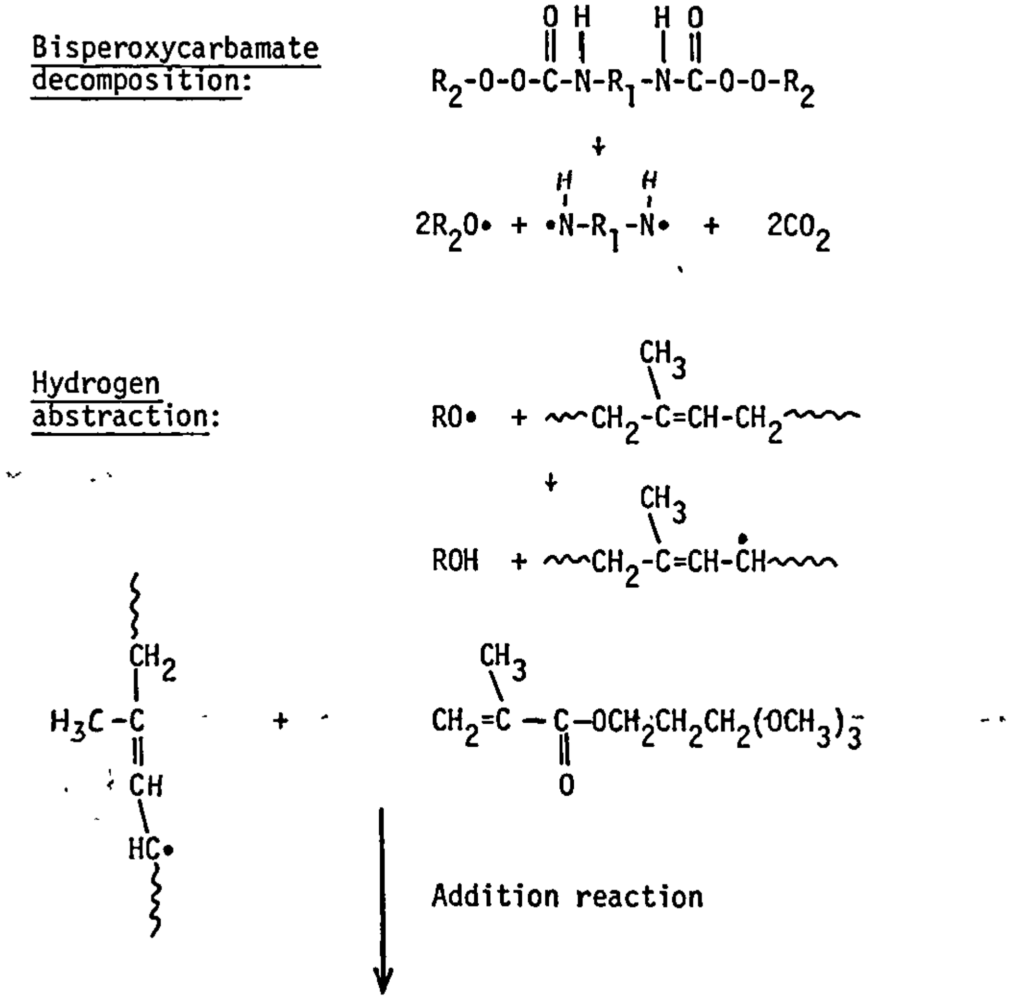
TABLE 7.3

The effect of titanate coupling agent on the tensile properties of silica-filled vulcanisates cured with 5 phr of the bisperoxycarbamate III

DPNR	100				
$Ca(OH)_2$)60% dispersion	6				
CaO)in Shellflex 729UK					
Ultrasil VN3	20				
Titanate KR-238M	0	0.5	1.0	1.5	2.0
Cure conditions	← 30 min/140°C →				
Tensile strength (MPa)	12.4	8.5	9.6	8.6	7.4
Modulus at 300% strain (MPa)	2.41	2.33	2.37	2.18	1.43
Elongation at break (%)	540	480	500	500	590
Tensile product	6696	4080	4800	4300	4366

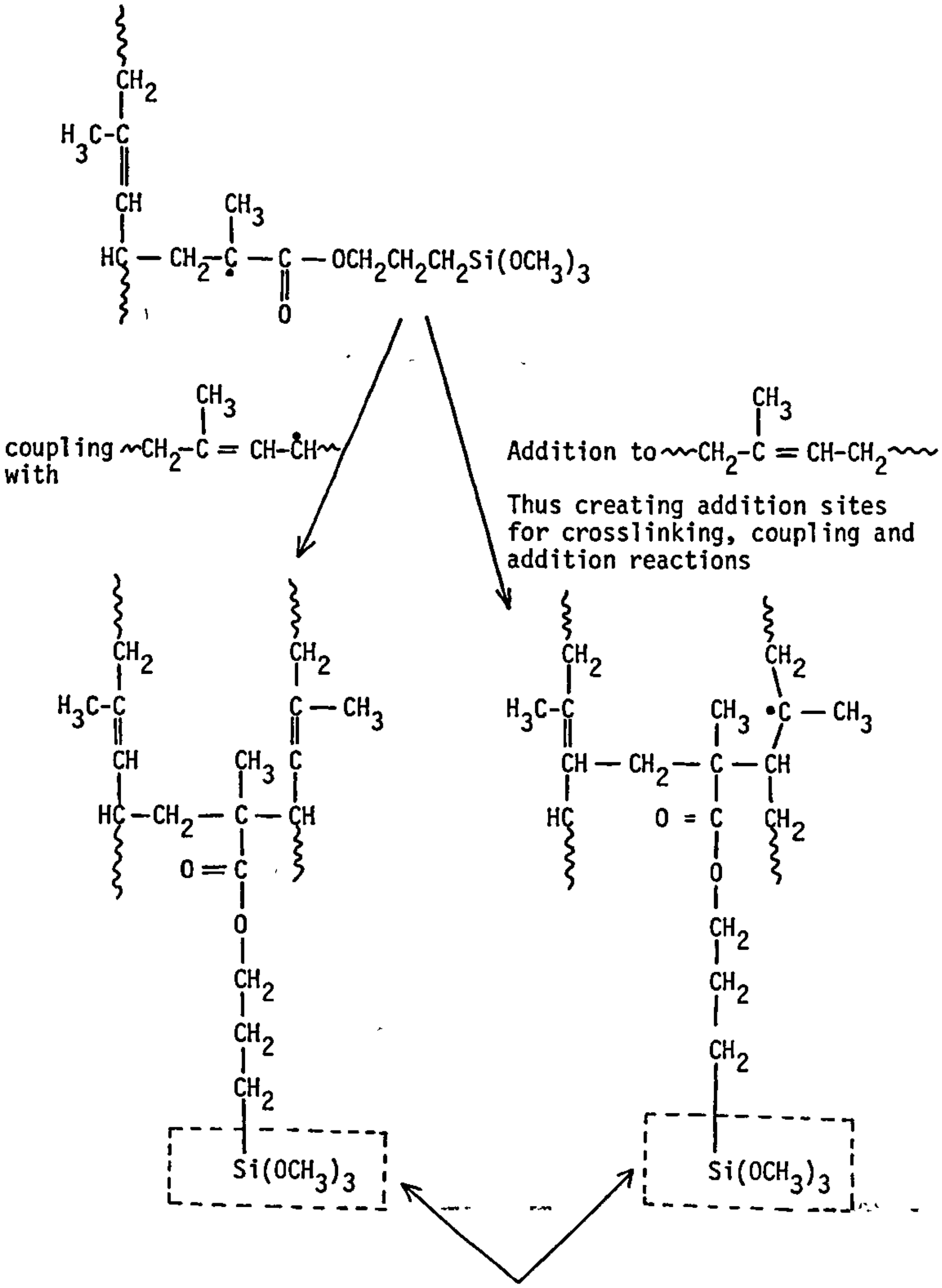
As shown in Table 7.2, both the tensile strength and tensile product of the silica-filled vulcanisates decrease on inclusion of the silane coupling agent. On the other hand, the modulus at 300% increases with increasing silane. The increase of the modulus at 300% strain was thought to be due to the presence of acrylic group in the molecular structure of Silane A-174. This acrylic group was considered to be capable of creating more reactive sites during vulcanisation for crosslinking reaction to occur (138).

The reduction of the strength of the silica-filled vulcanisates on incorporation of Silane A-174 seems to be due to lack of rubber-filler interaction which is generally accepted to be promoted by the coupling agent as shown by an example of mechanisms involving crosslinking, coupling and addition reactions (Figure 7.1).



(continued)

FIGURE 7.1 Schematic representation of free radical mechanism for crosslinking, coupling and addition reactions



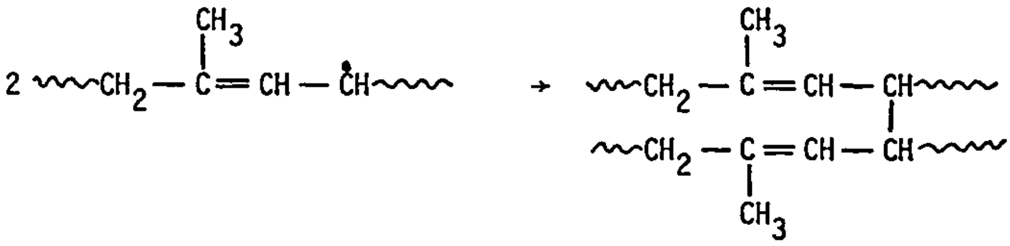
coupling with $\sim CH_2-\overset{CH_3}{C}=CH-\dot{C}H\sim$

Addition to $\sim CH_2-\overset{CH_3}{C}=CH-CH_2\sim$

Thus creating addition sites for crosslinking, coupling and addition reactions

Lack of interaction of the OCH_3 groups of Silane A-174 with the OH groups of the silica presumably due to insufficient water available for promoting the interaction

Crosslinking:



$$2\ \sim\!CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-\dot{C}H\!\sim \;\rightarrow\; \begin{array}{l} \sim\!CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-\underset{|}{CH}\!\sim \\ \sim\!CH_2-\underset{\underset{\displaystyle CH_3}{|}}{C}=CH-CH\!\sim \end{array}$$

In the case of Titanate KR-238M, no enhancement in both the strength and the modulus at 300% strain of the vulcanisates was observed (see Table 7.3).

7.2 Examination of the Bisperoxycarbamate III in Black-Filled DPNR

7.2.1 Introduction

Most practical rubber compounds contain fillers used to decrease cost and to improve processing characteristics and vulcanisate properties. As a reinforcing filler, carbon black is almost a universal ingredient in rubber compounds. Hence the ability of the bisperoxycarbamate III in satisfactorily curing a rubber compound containing a carbon black needs to be resolved first before proceeding to any commercial exploitation (148) of this new curing agent. This factor is considered now.

Various types of carbon blacks are available in the market and they vary between one and another by their specific surface activity, pH value, particle size, surface area and structure. The pH value, surface activity and surface area of carbon black are believed to largely determine its effect on the vulcanisation characteristics of peroxide curing agents.

7.2.2 Materials

The following carbon blacks were used in the present investigation:

Super abrasion furnace, SAF (Vulcan 9 obtained from Cabot Carbon Ltd).

High abrasion furnace, HAF (Vulcan 3 obtained from Cabot Carbon Ltd).

Semi-reinforcing furnace, SRF (Regal SRF obtained from Cabot Carbon Ltd).

Medium thermal, MT (Sevacarb MT obtained from Phillips Co).

Acetylene black (Shawinigan Acetylene obtained from Cairn Chemicals Ltd).

7.2.3 Experimental

All the black mixes were prepared on a two-roll mill at room temperature or otherwise at specific temperatures. The order of mixing schedule was as follows:

DPNR		2 minutes mastication
Carbon blacks	-	13-20 minutes depending on the amount of carbon blacks used
$Ca(OH)_2$, CaO and bisperoxycarbamate III	-	12 minutes addition and dispersion 6 passes through a tight nip

The pH values of the carbon blacks were determined according to ASTM D 15/2, Part 38, July 1975.

7.2.4 Results and discussion

It has been shown previously (23) that many types of carbon blacks strongly inhibit the vulcanising action of peroxides and this behaviour was considered to be due to inducement of the decomposition of the peroxide by the carbon black rather than adsorption of the peroxide on the carbon black. This factor was examined by preparing a SAF black mix (DPNR 100,SAF black 25, $Ca(OH)_2$ 1.8, CaO 1.8 and bisperoxycarbamate III 5.0) on a two-roll mill at room temperature. This mix was then divided into four portions and each was refined on the two-roll mill at a specified temperature. The gap of the nip of the two-roll mill and refining time were kept uniform throughout the experiment. The ODR traces of the refined mixes were then taken.

As shown in Figure 7.2 when the temperature of the mix reached 87°C, it began to give higher minimum torque value and lower state of cure. The increase of the minimum torque value was considered to be due to premature vulcanisation whilst the loss of radicals available for the crosslinking reaction during the milling process had resulted in a decrease of the state of cure.

The presence of SAF black is thus seen to induce the decomposition of the bisperoxycarbamate III and this is further substantiated by the DSC traces shown in Figure 7.3. The onset temperature of decomposition measured by DSC of the bisperoxycarbamate III was reduced from 141°C to 85°C by incorporation of the SAF black in the bisperoxycarbamate III mix. The effect of other types of carbon blacks and precipitated silica (Ultrasil VN3) on the onset temperature of decomposition of the bisperoxycarbamate III is shown in Table 7.4. The precipitated silica did not confer a significant effect as compared to the carbon blacks on the onset temperature of decomposition of the bisperoxycarbamate III. In the case of MT black, the onset temperature of decomposition of the bisperoxycarbamate III could be theoretically determined by extrapolation; it will be lower than shown in Table 7.4, if the theoretical amount of the MT black equivalent in surface area to 25 parts of SAF black was present.

FIGURE 7.2 Effect of mill temperature on cure characteristics of SAF/bisperoxycarbamate III mix

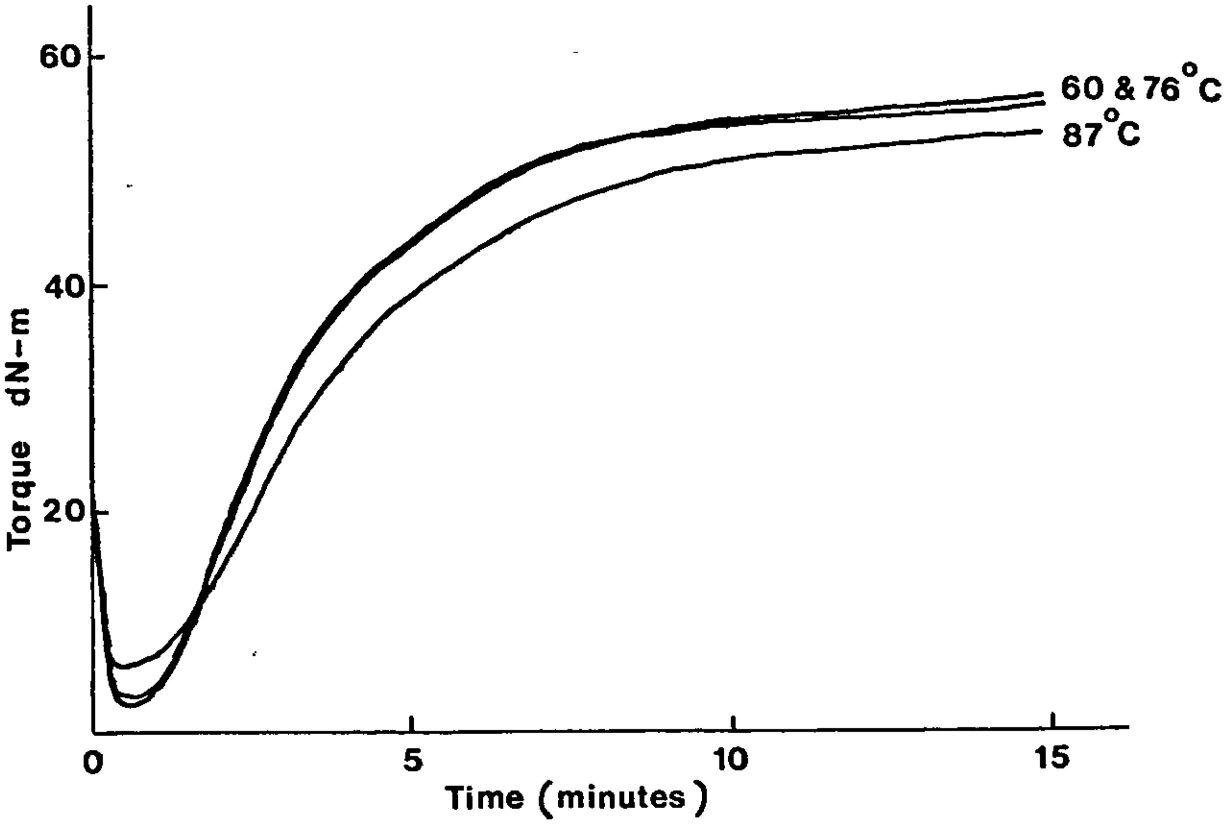


FIGURE 7.3 Effect of SAF black on onset temperature of decomposition of the bisperoxycarbamate III determined by DSC (Du Pont 990: 20°C/min)

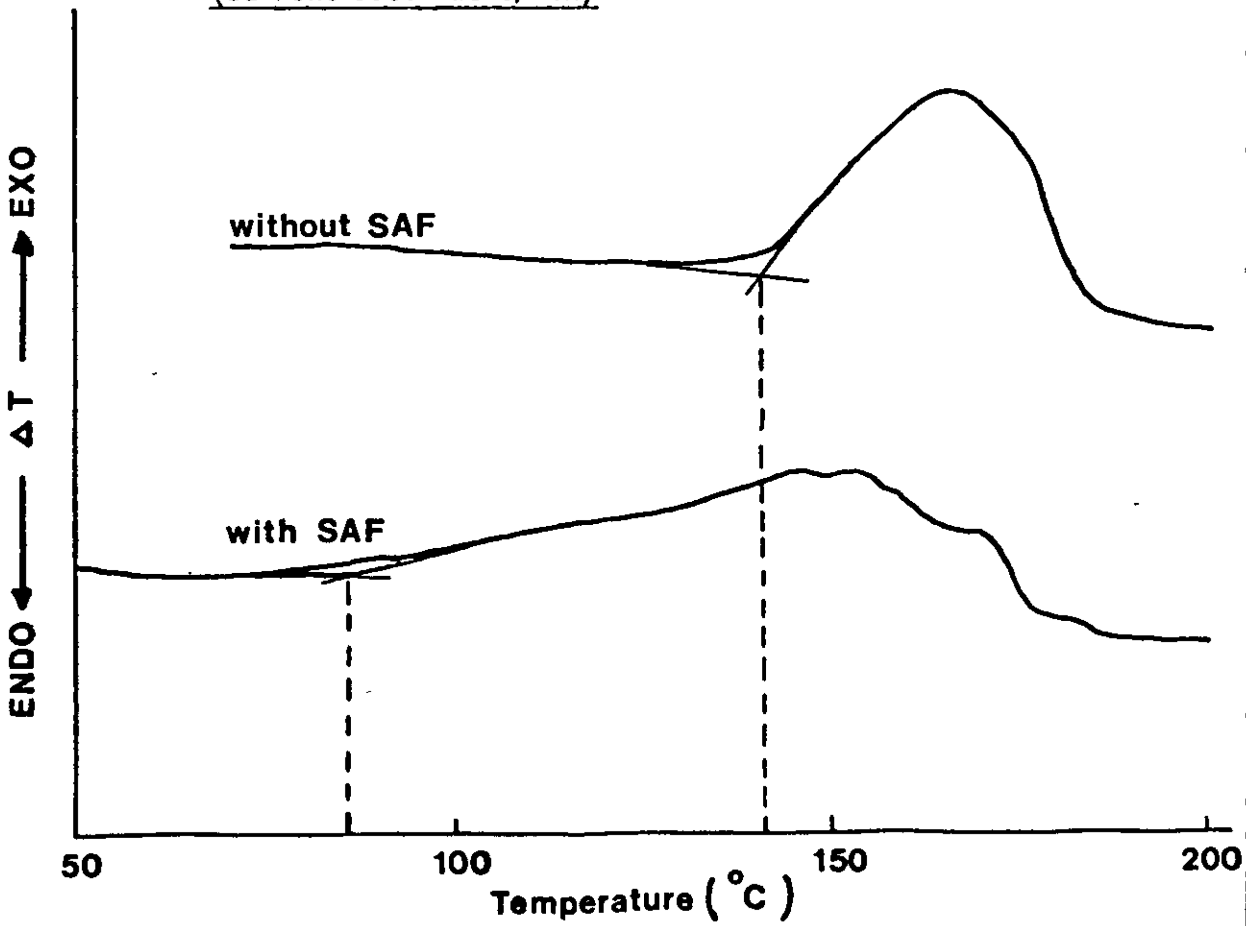


TABLE 7.4

The effect of various types of carbon blacks and Ultrasil VN3 on the onset temperatures of decomposition of the bisperoxycarbamate III

Types of fillers	Normalised concentration (phr) based on the surface area of 25 parts of SAF	Onset temperature of decomposition of the bisperoxycarbamate III (°C).
Control	without carbon black	141
Vulcan 9 (SAF)	25.0	85
Vulcan 3 (HAF)	35.5	86
Regal SRF	92.1	88
Sevacarb MT	120.0(1)	97
Acetylene black	50.5	86.
Ultrasil VN3 (precipitated silica)	20.0(2)	135

(1) Maximum possibility level on the two-roll mill.

(2) Concentration that approximates to the highest tensile strength.

In order to investigate the effect of the series of the carbon blacks on the properties of vulcanisates cured with the bisperoxycarbamate III, mixes containing the blacks were prepared on the two-roll mill at room temperature to prevent premature vulcanisation, as shown earlier. The concentration of the various carbon blacks used in the rubber mix was based on the concept of equivalent surface areas and normalised on 25 phr of SAF black; this level is known to approximate to the highest tensile strength available in a SAF reinforced natural rubber vulcanisate. Calculations of the surface area of individual carbon blacks was based on the following equation (149):

$$\text{Surface area} = \frac{6000}{\rho d}$$

where ρ is the density of the carbon black in $g.cm^{-3}$ and d is the diameter of the carbon black particle in nm.

The properties of the carbon blacks and their natural rubber vulcanisate properties, based on bisperoxycarbamate III as curing agent, are shown in Tables 7.5 and 7.6 respectively. Bisperoxycarbamate III gives satisfactory vulcanisates of good tensile strength with carbon blacks of medium to large particle size as represented by SRF, MT, and Acetylene types. However, at present, only relatively low strength vulcanisates have been obtained with the more highly reinforcing blacks typified by SAF (N 110) and HAF (N 330). From Table 7.5, for bisperoxycarbamate vulcanisates, it would seem that the purity (i.e. non-carbon content) of the black plays a predominant role in their strength as both SAF and HAF blacks respectively contain 2.2% and 1.7% of organic groups based on H, O and S and these blacks give low strength rubbers, whereas the higher carbon content blacks, SRF, MT and Acetylene give high strength vulcanisates. It is considered that it is this organic content factor that seems to predominate in this instance and not the more usual pH and surface absorption factors.

TABLE 7.5

Properties of the carbon blacks (149-151)

Carbon black type	Mean particle size diameter (nm)	Actual density (g.cm^{-3})	pH Values	% composition					Ash
				C	H	O	S	Total organic content by addition	
SAF	22.5	1.80	7.9	97.4	0.4	1.1	0.70	2.20	0.50 ?
HAF	32.0	1.80	7.7	97.9	0.4	0.7	0.60	1.70	0.40
Regal SRF	83.0	1.80	7.3	99.2	0.4	0.2	0.01	0.61	0.20
Sevacarb MT	300.0	1.80	4.7	99.3	0.3	0.1	0.01	0.41	0.30
Shawinigan Acetylene	42.0	1.95	5.5	99.7	0.1	0.2	0.01	0.31	0.04

TABLE 7.6

Tensile properties of carbon black vulcanisates$^{(1)}$ crosslinked with the cyclic bisperoxycarbamate III

Carbon black type	Normalised concentration (phr) based on the surface area of 25 parts SAF	U.T.S. (MPa)	E.B. (%)
SAF	25.0	4.1$^{(3)}$	260
HAF	35.5	6.8$^{(3)}$	270
Regal SRF	92.1	9.0	160
Sevacarb MT	120.0$^{(2)}$	9.3	150
Shawinigan Acetylene	50.5	9.0	190

(1) Formulation used - DPNR 100, $Ca(OH)_2$ 1.8, CaO 1.8, Bisperoxycarbamate III 5, and black as shown in Table 7.6. Samples were cured for 60 min/130°C.

(2) Maximum processibility level on the two-roll mill.

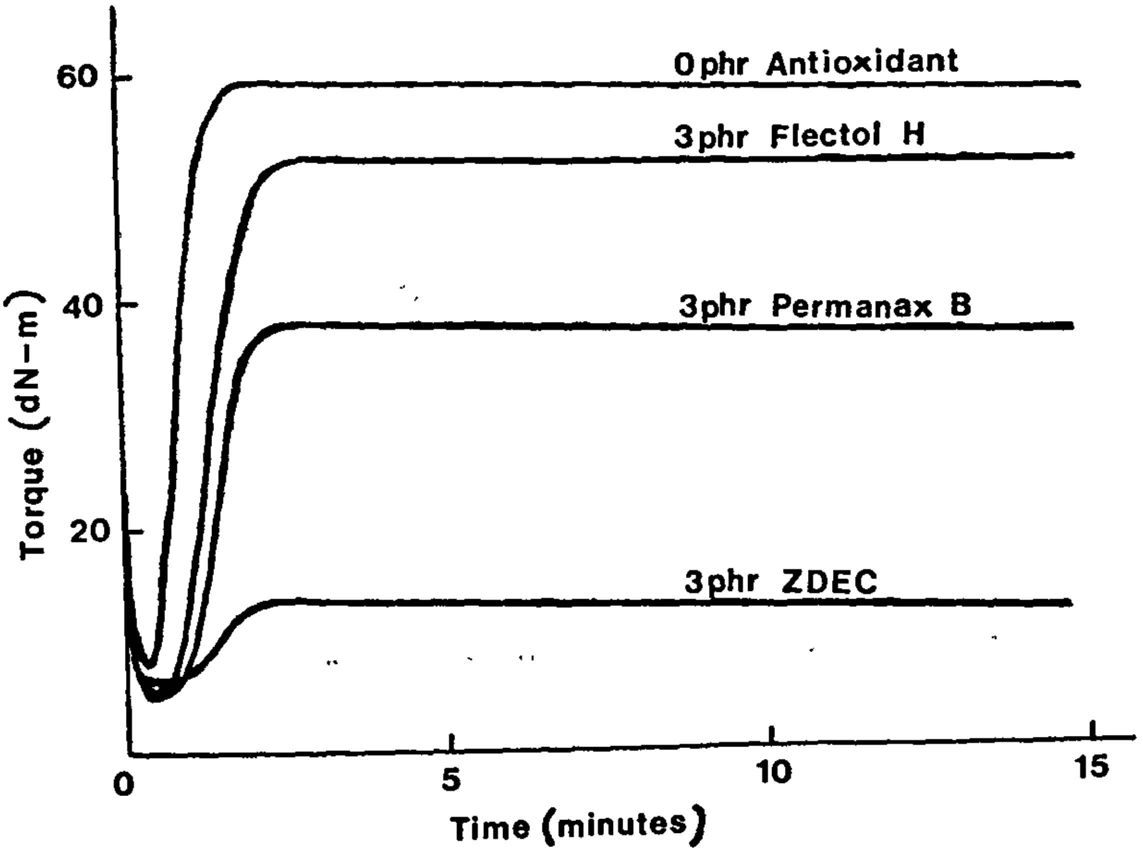
(3) Slight porosity.

7.3. The Effect of Antioxidants on the Bisperoxycarbamate III vulcanisation of DPNR

Three antioxidants, ZDEC (Zinc diethyl dithiocarbamate), Permanax B (Diphe nylamine-acetone condensation product) and Flectol H (Polymerised 1,2-dihydro-2,2,4-trimethyl quinoline) were chosen in the present investigation. In the initial investigation 3 phr of each antioxidant was added to the DPNR gum mixes and ODR traces taken. As shown in Figure 7.4 all the antioxidants reduce the state of cure of the DPNR gum mixes containing the bisperoxycarbamate III; the most severe is the effect of ZDEC whilst Flectol H has relatively least effect on the state of cure.

FIGURE 7.4 ODR traces of gum mixes(1) containing antioxidants (180°C)

(1) Mix reference was based on Table 7.7



The problem of Flectol H interference with the bisperoxycarbamate III was further investigated since it is known that Flectol H is a peroxide-compatible antioxidant. The effect of concentration of this antioxidant on the state of cure of the bisperoxycarbamate III mixes and the vulcanisate properties is shown in Table 7.7. An enhancement in state of cure and modulus at 300% was observed by incorporation of Flectol H between 0.25 - 1.00 phr but its presence had an adverse effect on the strength of the vulcanisates. With higher concentration of Flectol H a reduction in state of cure and modulus at 300% was demonstrated.

TABLE 7.7

The effect of Flectol H on the state of cure of the bisperoxycarbamate III mixes and the vulcanisate properties

DPNR	100					
$Ca(OH)_2$	1.8					
CaO	1.8					
Bisperoxycarbamate III	5.0					
Flectol H	0	0.25	0.50	0.75	1.00	2.00
Torque at 30 min/140°C (dN.m)	43	46	50	47	49	42
Cure conditions	30 min/140°C					
Tensile strength (MPa)	10.2	8.6	7.8	6.6	5.9	6.2
Modulus at 300% strain (MPa)	1.31	1.68	1.84	1.93	1.94	1.59
Elongation at break (%)	670	540	510	480	460	500
Tensile product (MPa x per cent)	6834	4644	3978	3168	2714	3100

7.4 Curing Ability of Bisperoxycarbamate III in Other Synthetic Rubbers

The effectiveness of bisperoxycarbamate III as a curing agent in other synthetic rubbers was investigated (148). Only four synthetic rubbers were investigated in the present work and these were polychloroprene rubber (Neoprene WRT), styrene-butadiene rubber (Cariflex 1500), butadiene-acrylonitrile rubber (Breon 1042), and ethylene-propylene terpolymer (Intolan 170A).

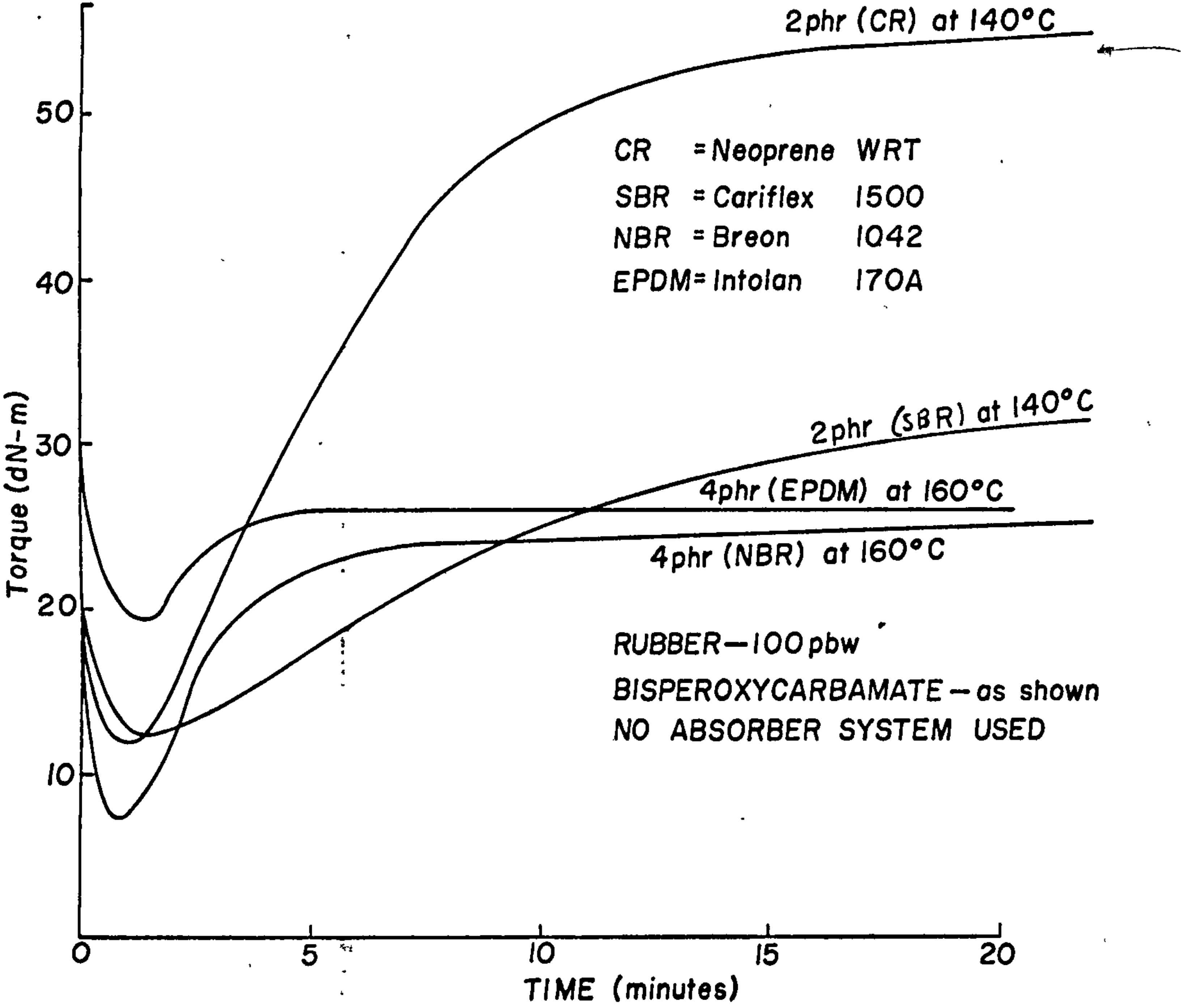
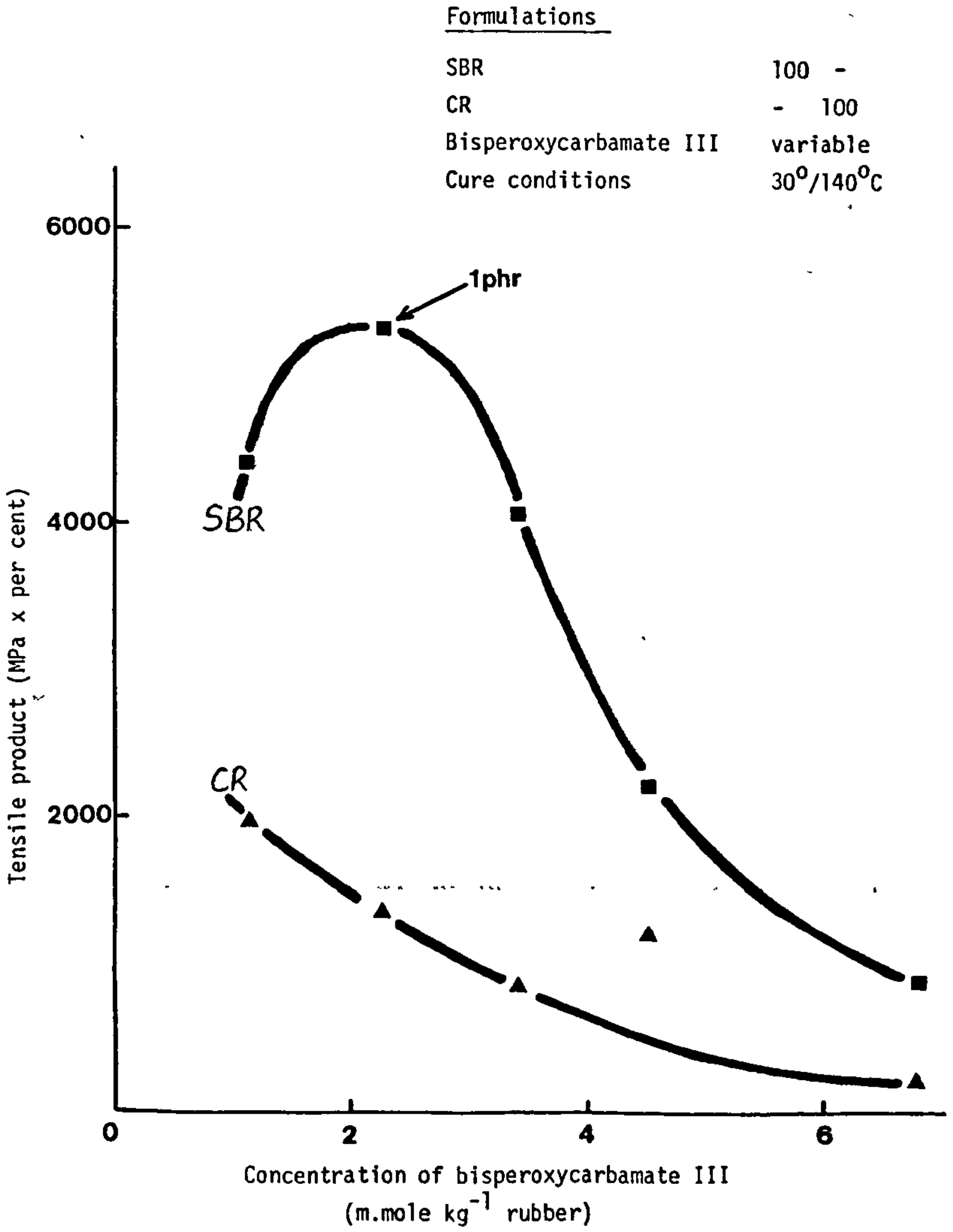

2phr (CR) at 140°C
CR = Neoprene WRT
SBR = Cariflex 1500
NBR = Breon 1042
EPDM = Intolan 170A
2phr (SBR) at 140°C
4phr (EPDM) at 160°C
4phr (NBR) at 160°C
RUBBER—100 pbw
BISPEROXYCARBAMATE—as shown
NO ABSORBER SYSTEM USED
Torque (dN-m)
50
40
30
20
10
0
5
10
15
20
TIME (minutes)

FIGURE 7.6 Effect of concentration of bisperoxycarbamate III on tensile product of SBR and CR gum vulcanisates



Formulations

SBR	100	-
CR	-	100
Bisperoxycarbamate III	variable	
Cure conditions	30°/140°C	

Figure 7.5 shows the ODR traces of gum stocks of the rubbers investigated. No absorber system was used in this investigation as only low levels of bisperoxycarbamate III were involved. As shown in Figure 7.4, both polychloroprene and styrene-butadiene rubbers require a lower concentration of bisperoxycarbamate III to achieve a technical state of cure than ethylene-propylene terpolymer and butadiene-acrylonitrile rubber. The bisperoxycarbamate III has a particularly fast rate of cure in the polychloroprene rubber.

The performance of gum vulcanisates of polychloroprene rubber and styrene-butadiene rubber in terms of tensile product was sought as these rubbers require relatively less curing agent to achieve technical state of cure and hence could be economically more feasible for industrial exploitation. Figure 7.6 shows the effect of concentration of the bisperoxycarbamate III on the tensile products of their gum vulcanisates. Styrene-butadiene rubber vulcanisates cured with the bisperoxycarbamate III confers better strength than the equivalent polychloroprene rubber vulcanisates. Since styrene-butadiene rubber is a non-crystalline rubber, the strength of its gum vulcanisates can be, theoretically, enhanced by incorporation of reinforcing filler.

7.5 Conclusions

In white and black filled DPNR mixes, bisperoxycarbamate III gave satisfactory vulcanisate properties in the presence of fillers such as precipitated silica and the following carbon blacks: Regal SRF, Sevacarb MT, and Shawinigan Acetylene.

Incorporation of Silane A-174 and Titanate KR-238M into silica-filled DPNR containing the bisperoxycarbamate III conferred no enhancement in the strength of the vulcanisates.

Three antioxidants namely, ZDEC, Permanax B and Flectol H were investigated to observe their effect on the bisperoxycarbamate III vulcanisation of DPNR. It was found that their presence in high concentration (3 phr) in the bisperoxycarbamate III mixes reduced the state of cure; the most severe was the effect of ZDEC whilst Flectol H conferred [illegible] least effect on the state of cure.

The cyclic bisperoxycarbamate III as curing agent can also be used satisfactorily with other synthetic rubbers such as CR, SBR, EPDM and NBR. The effectiveness of this bisperoxycarbamate as a curing agent depends on the types of synthetic rubbers, for example, a polychloroprene rubber required relatively less bisperoxycarbamate to achieve a technical state of cure than did the other rubbers. It was found that SBR (Cariflex 1500) can be cured satisfactorily with the bisperoxycarbamate III to give [illegible] stronger gum vulcanisates than the equivalent polychloroprene rubber (Neoprene WRT).

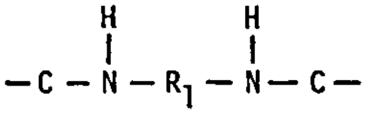
CHAPTER 8

DISCUSSION, CONCLUSIONS AND RECOMMENDATIONS

8.1 Discussion and Conclusions

In the author's literature review, it was seen that most of the early studies using peroxycarbamates concerned their synthesis, decomposition and use as initiators in vinyl or diene polymerisation. The only attempt to use one as a crosslinking agent was reported in 1960 for a plastic. The author's research work is an attempt to synthesise new bisperoxycarbamates and investigate their ability in crosslinking natural rubber (DPNR) and polyisoprene rubber (Cariflex IR 305).

As this is the first attempt at such an investigation a known bisperoxycarbamate, preferably a solid, such as hexamethylene bis N,N' (cumyl peroxycarbamate) was chosen initially in exploring experimentally its ability to behave as a crosslinking agent for polyisoprene rubber. Polyisoprene rubber was preferred since it is easier to purify as compared with natural rubber in order to eliminate the presence of any nitrogen in the rubber. In this particular investigation it was shown that hexamethylene bis N,N' (cumyl peroxycarbamate) can cure polyisoprene rubber and produce vulcanisates which were considered to contain a proportion of amino linkages



$$-\mathrm{C}-\overset{\mathrm{H}}{\overset{|}{\mathrm{N}}}-\mathrm{R}_1-\overset{\mathrm{H}}{\overset{|}{\mathrm{N}}}-\mathrm{C}-$$

①

(see Section 2.2.). In addition to this characteristic, the investigated bisperoxycarbamate vulcanisate was found to have superior ② strength and thermal oxidative stability compared to the equivalent dicumyl peroxide (Perkadox SB) vulcanisate used as a control. However, the crosslinking efficiency of the bisperoxycarbamate was found to be lower than the control dicumyl peroxide.③

Based on this *finding*, i.e. the ability of this model bisperoxycarbamate to cure polyisoprene rubber, the present research work was then directed to synthesis of some new bisperoxycarbamates.

Attempts were made to synthesise seven bisperoxycarbamates by reacting diisocyanates with hydroperoxides in the presence of solvents and catalysts. Various diisocyanates ranging from reactive diisocyanates such as methylene diphenylene diisocyanate to least reactive diisocyanates such as methylene bis-(4-cyclohexyl isocyanate) were chosen to investigate the effect of structures of the diisocyanates on rate of formation of bisperoxycarbamates (see Section 2.3). The rate of formation of the bisperoxycarbamates from a given hydroperoxide was found to be dependent on the specific structures and steric effect of the diisocyanates. The order in the rate of formation of the bisperoxycarbamates from the investigated diisocyanates was found to be aromatic diisocyanate > aliphatic diisocyanate > aliphatic/cyclic diisocyanate > cyclic diisocyanate.

From this program two hydroperoxides namely, tertiary butyl hydroperoxide and cumene hydroperoxide were chosen in order to examine their effect on the rate of formation of bisperoxycarbamates. As an example of this particular examination, methylene bis-(4-cyclohexyl isocyanate) was reacted with tertiary butyl hydroperoxide and cumene hydroperoxide and the rates of formation of the corresponding bisperoxycarbamates were compared. It was found that the rates of formation of the bisperoxycarbamates were slower in the case of cumene hydroperoxide and this is presumably due to the steric effect of the cumene hydroperoxide.

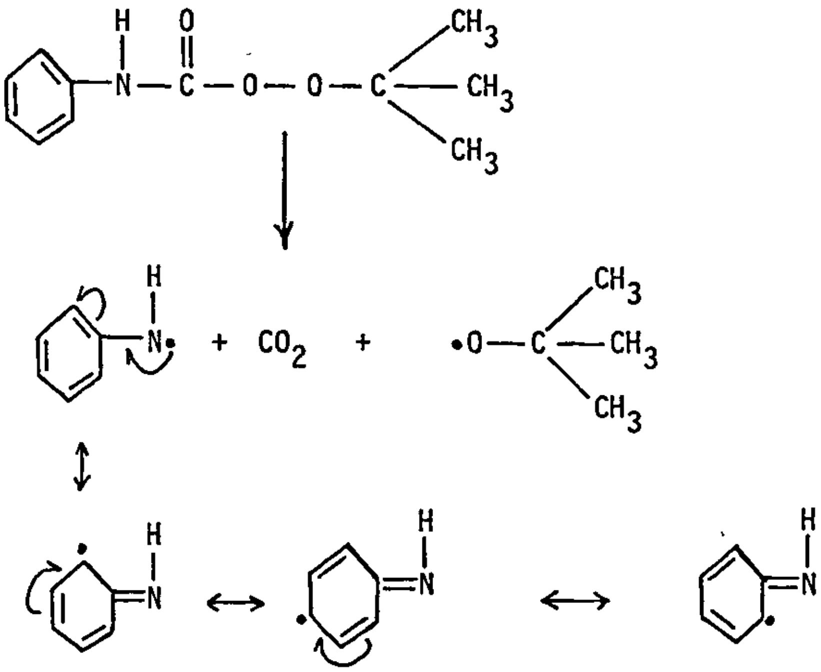
The use of solvents was preferred in the synthesis of the bisperoxycarbamates in order to prevent any undesirable reaction exotherms between the diisocyanates and the hydroperoxides.

Two common catalysts for the synthesis of the bisperoxycarbamates were chosen and these were triethylamine and pyridine. Both these catalysts were chosen on the basis of references of earlier workers.

The prepared bisperoxycarbamates were initially evaluated as crosslinking agents in natural and polyisoprene rubber gum stocks which were used as models to eliminate any possible cure reaction interference.

The minimum cure activation temperatures of the bisperoxycarbamates were determined by DSC technique (see Section 3.2). From this DSC technique it was shown that the bisperoxycarbamate based on the cyclic diisocyanate backbone had a relatively higher cure activation temperature and was considered to give practical cure rates as this temperature is close to the present conventional industrial processing temperatures.

The general trend of the minimum cure activation temperatures of the bisperoxycarbamates was observed to be aromatic < aliphatic < aliphatic/cyclic < cyclic. This observed trend can be explained by considering the stability of the bisperoxycarbamates against decomposition via cleavage of the peroxy bonds, O-O, of the bisperoxycarbamates. For example, the aromatic bisperoxycarbamate was the least stable of the investigated bisperoxycarbamates and this was considered to be due to its ability to form a stable aromatic amino radical via resonance as shown below:

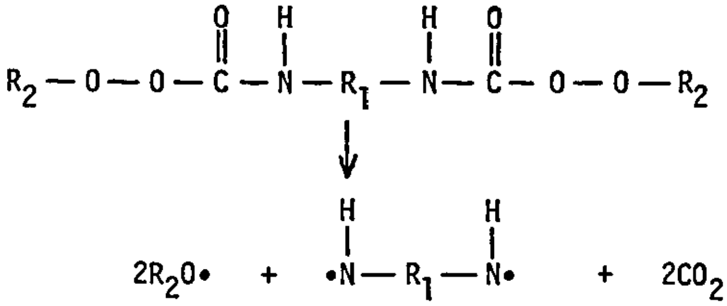


The Monsanto ODR traces of the unfilled bisperoxycarbamate mixes were determined to find their cure times and also to confirm the previous DSC observations (see Section 3.3). The ODR traces of the bisperoxycarbamate mixes indicated that the relative effectiveness of the bisperoxycarbamates as curing agents in natural and polyisoprene rubbers depends on the structures of their diisocyanate backbones. The relative order was found to be cyclic > aliphatic/cyclic > aliphatic. These three bisperoxycarbamates were found to be effective crosslinking agents for both the rubbers, whilst the bisperoxycarbamates studied, based on the aromatic and prepolymer diisocyanate backbones, were found to be relatively ineffective crosslinking agents for natural and polyisoprene rubbers. For this reason only three of the investigated bisperoxycarbamates were evaluated in detail as crosslinking agents for both the rubbers and compared with control dicumyl peroxide vulcanisates. The three bisperoxycarbamates were those based on the aliphatic, aliphatic/cyclic and cyclic diisocyanate backbones. The detailed evaluation of these three bisperoxycarbamates had the following sequence:

1. Determination of crosslink density of the vulcanisates (see Section 3.4).
2. Determination of tensile properties of the vulcanisates (see Section 4).
3. Determination of ageing performance of the vulcanisates (see Section 5).

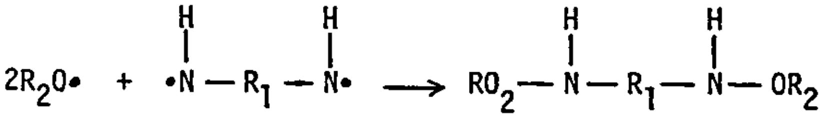
In both rubbers for a given molar concentration of curing agent the dicumyl peroxide vulcanisates gave a higher crosslink density than their corresponding bisperoxycarbamate vulcanisates. Studies by early workers had shown that the dicumyl peroxide decomposed to radicals in which the efficiency in the formation of crosslinks is nearly unity in natural rubber (32, 40, 41) and greater than unity in polyisoprene rubber (112). The differences in crosslink efficiency between the dicumyl peroxide and bisperoxycarbamates were considered to be due to the wastage of the radicals formed ③ during decomposition of the bisperoxycarbamates through the termination process (106, 108), as shown in the reaction scheme below:

Decomposition



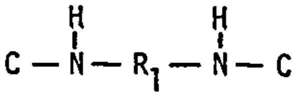
$$\begin{gathered}R_2-O-O-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-R_1-\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-O-O-R_2\\ \downarrow\\ 2R_2O\bullet \quad + \quad \bullet\overset{\overset{H}{|}}{N}-R_1-\overset{\overset{H}{|}}{N}\bullet \quad + \quad 2CO_2\end{gathered}$$

Termination



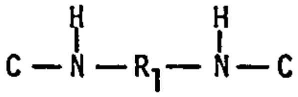
$$2R_2O\bullet + \bullet\overset{\overset{H}{|}}{N}-R_1-\overset{\overset{H}{|}}{N}\bullet \longrightarrow RO_2-\overset{\overset{H}{|}}{N}-R_1-\overset{\overset{H}{|}}{N}-OR_2$$

The polyisoprene rubber vulcanisates were found to have higher crosslink densities for a given molar concentration of bisperoxycarbamate or dicumyl peroxide than the equivalent natural rubber. This was considered to be due to the presence of vinyl structures in the polyisoprene macromolecules (5% 3,4 structures). These vinyl structures are considered to be able to create sites for promoting addition reaction by free radicals which eventually lead to additional crosslinks to be formed. This situation was similarly observed in the case of coagents which were used to increase the crosslink density of the cyclic bisperoxycarbamate vulcanisates based on natural rubber (see Section 6.2).

A mechanism of bisperoxycarbamate vulcanisation was proposed (see Section 3.4.3) and it is thought to be based on free radical mechanisms. They are considered to differ in action from conventional peroxide free radical crosslinkers, typified by dicumyl or ditertiary butyl peroxides, by the formation of a combination of C-C and  $C-\overset{\overset{H}{|}}{N}-R_1-\overset{\overset{H}{|}}{N}-C$ crosslinks.

In the determination of the tensile properties of the unfilled natural rubber vulcanisates cured with the bisperoxycarbamates (see Section 4), it was found that the vulcanisates cured with the aliphatic and aliphatic/cyclic bisperoxycarbamates have comparable optimum tensile products (i.e. strength) with the control dicumyl peroxide vulcanisates. In the case of the cyclic bisperoxycarbamate the strength of its gum vulcanisate does not reach its optimum ④ with 90.5 m.mole kg^{-1} rubber (4 phr) of the curing agent (see Section 4.3). However, increasing the level of this bisperoxycarbamate in natural rubber, beyond 4 phr was observed to give rise to porosity in the vulcanisate.

In the case of the investigated unfilled polyisoprene rubber vulcanisates cured with the bisperoxycarbamates and the control dicumyl peroxide, it was demonstrated that the aliphatic bisperoxycarbamate vulcanisates had much better optimum strength than their equivalent dicumyl peroxide vulcanisate.

The elongation at break data (see Section 4.3) indicated that for a given crosslink density, especially at high levels, the bisperoxycarbamate vulcanisates are considered more flexible than ⑤ the control dicumyl peroxide vulcanisates. This was considered due to the crosslink structures involved. Dicumyl peroxide is well established as forming short C-C crosslinks between rubber chains whilst the bisperoxycarbamates are considered to form a combination of C-C and  $C-\overset{H}{\overset{|}{N}}-R_1-\overset{H}{\overset{|}{N}}-C$ crosslinks.

The performance of the unfilled bisperoxycarbamate vulcanisates based on natural and polyisoprene rubbers to thermal oxidative stress-relaxation and hot air oven ageing was evaluated and compared with vulcanisates cured with the commercially available curing systems (see Sections 5.2 and 5.3). In both rubbers, the cyclic bisperoxycarbamate vulcanisate was shown to be the most stable of the three bisperoxycarbamate vulcanisates studied. For example the cyclic bisperoxycarbamate vulcanisate based on natural rubber demonstrated comparable stability to its equivalent vulcanisates cured with dicumyl peroxide, Diurethane (Novor 924) and Sulphur-EV systems whilst the cyclic bisperoxycarbamate vulcanisate based on polyisoprene rubber had comparable stability with its equivalent vulcanisate cured with Sulphur-EV system.

The porosity problem in the bisperoxycarbamate vulcanisates, especially in those containing high concentrations of the bisperoxycarbamates, had resulted in a detailed examination of systems to eliminate the porosity (see Section 6). In this examination the cyclic bisperoxycarbamate was chosen as a model bisperoxycarbamate for it produces the best compromise of strength and thermal oxidative stability with the natural and polyisoprene vulcanisates as compared with the vulcanisates cured by the other two bisperoxycarbamates. Three systems, trimethylol propane trimethacrylate (Sartomer SR-350), N,N'-m-phenylene dimaleimide (HVA-2), and $Ca(OH)_2$ + CaO, were examined and the last system was considered the most suitable with respect to versatility and cost as the $Ca(OH)_2$ absorbed the reaction produced CO_2 and the CaO absorbed the water by means of reactions 94 and 95 (see Section 6.3). Increasing the level of the cyclic bisperoxycarbamate in combination with $Ca(OH)_2$ and CaO resulted in vulcanisates of better strength than the control dicumyl peroxide vulcanisates.

The original investigations were performed on unfilled gum rubbers used as models to eliminate any possible cure reaction interference. Since practical systems contain fillers, the application of bisperoxycarbamate vulcanisation to filled systems was considered in the later part of the present investigation.

In silica-filled natural rubber vulcanisates it was demonstrated that the cyclic bisperoxycarbamate curing system exhibits superiority in strength of 34% over the dicumyl peroxide one and it also requires a much shorter time to reach optimum cure time (see Section 7.1). Incorporation of gamma-methacryloxypropyltrimethoxysilane (Silane A-174) and Di(dioctyl pyrophosphato) ethylene titanate chelate, methacrylic amine quat coupling agent (Titanate KR-238M) into silica-filled natural rubber containing the cyclic bisperoxycarbamate conferred no enhancement to the strength of the vulcanisates. This was considered to be due to lack of rubber-filler interaction which is generally accepted to be promoted by the coupling agents.

The cyclic bisperoxycarbamate as curing agent was applied to a series of carbon black filled mixes to investigate whether it could vulcanise such mixes to a reasonable strength (see Section 7.2). At present only relatively low ultimate tensile strength vulcanisates have been obtained with the more highly reinforcing blacks typified by SAF (N 110) and HAF (N 330), whereas the relatively higher carbon content blacks, SRF, MT and Acetylene, give relatively high ultimate tensile strength vulcanisates.

With SAF and HAF blacks cure interference occurred with the cyclic bisperoxycarbamate vulcanisation and this was considered to be due to the presence of a relatively high content of organic groups based on H, O and S in the SAF and HAF blacks. This cure interference effect is also observed in the traditional dicumyl peroxide cured rubbers. ⑥

In the application of the cyclic bisperoxycarbamate as curing agent for other synthetic rubbers such as CR, SBR, EPDM and NBR, it was found that the effectiveness of this bisperoxycarbamate as a curing agent depends on the types of synthetic rubbers, for example, a polychloroprene rubber required relatively less bisperoxycarbamate to achieve a satisfactory technical state of cure than did the other rubbers (see Section 7.4). In the evaluation of the tensile properties of the gum vulcanisates of CR and SBR cured with the cyclic bisperoxycarbamate it was found that SBR (Cariflex 1500) vulcanisates had relatively better strength than the equivalent polychloroprene rubber (Neoprene WRT) vulcanisates.

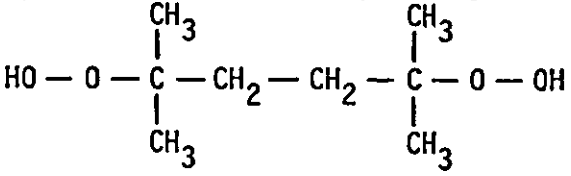
8.2 Recommendations

1. In the present research work only two catalysts were used in the synthesis of the bisperoxycarbamates. It would be useful to investigate other types of catalysts such as stannous octoate and N-ethylmorpholine on the rate of formation of the cyclic bisperoxycarbamate which was found to be slow in the case of triethylamine.

2. To investigate methods in order to optimise the product yield in the synthesis of the cyclic bisperoxycarbamate which was found to be 71% by weight in the present investigation.

3. Since the cyclic bisperoxycarbamate based on methylene bis-(4-cyclohexyl isocyanate) diisocyanate was found to be the most suitable and effective crosslinking agent for rubbers it would be interesting to investigate other types of cyclic bisperoxycarbamates, such as those based on cyclohexyl diisocyanate, on their behaviour as crosslinking agents for rubbers.

4. To investigate other types of hydroperoxides as starting materials for synthesis of peroxycarbamates, especially a difunctional hydroperoxide



$$HO-O-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-O-OH$$

to yield a polyperoxycarbamate. It would be interesting to examine this polyperoxycarbamate as a crosslinking agent for rubbers.

5. To attempt the cyclic bisperoxycarbamate as a free radical initiator for polymerisation or copolymerisation of vinyl or diene monomers. This process would produce polymers or copolymers which contain a certain proportion of bound nitrogen. If the proportion of NH groups in the polymer or copolymer is high enough, they could be used as sites for diisocyanate crosslinking.

6. To attempt to use the absorbant system, $Ca(OH)_2$ + CaO, to other processes where carbon dioxide liberation is a problem.

7. To explore the ability of the cyclic bisperoxycarbamate as a crosslinking agent in rubbers which contain vinyl structures

in their macromolecules, such as silicone rubber.

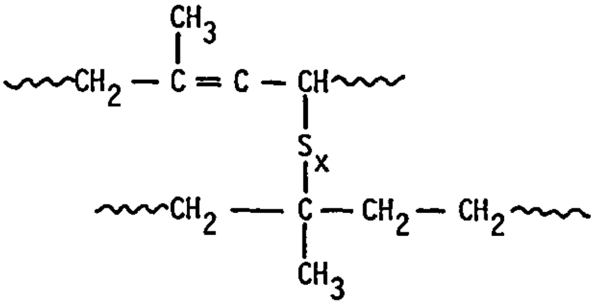
8. To explore the ability of the cyclic bisperoxycarbamate as a crosslinking agent for saturated polymers.

APPENDIX I

Mechanisms postulated for accelerator-free sulphur vulcanisation of natural rubber

Two mechanisms were postulated for accelerator-free sulphur vulcanisation of natural rubber. Bateman and coworkers (2) have postulated mechanisms proceed through polar in nature whilst some investigatorsfelt that the sulphuration process involve free radicals (152-154).

The polar mechanism postulated by Bateman and co-workers is generally accepted as the best way of explaining the numerous structural features of the accelerated-free sulphur vulcanisation of natural rubber. The deduction of these structural features were based on the reaction products obtained from heating sulphur with olefins. The main structural feature (XXXIV) was based on the reaction scheme (A) of 2-methylpent-2-ene with sulphur.

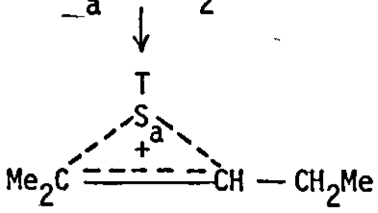


(XXXIV)

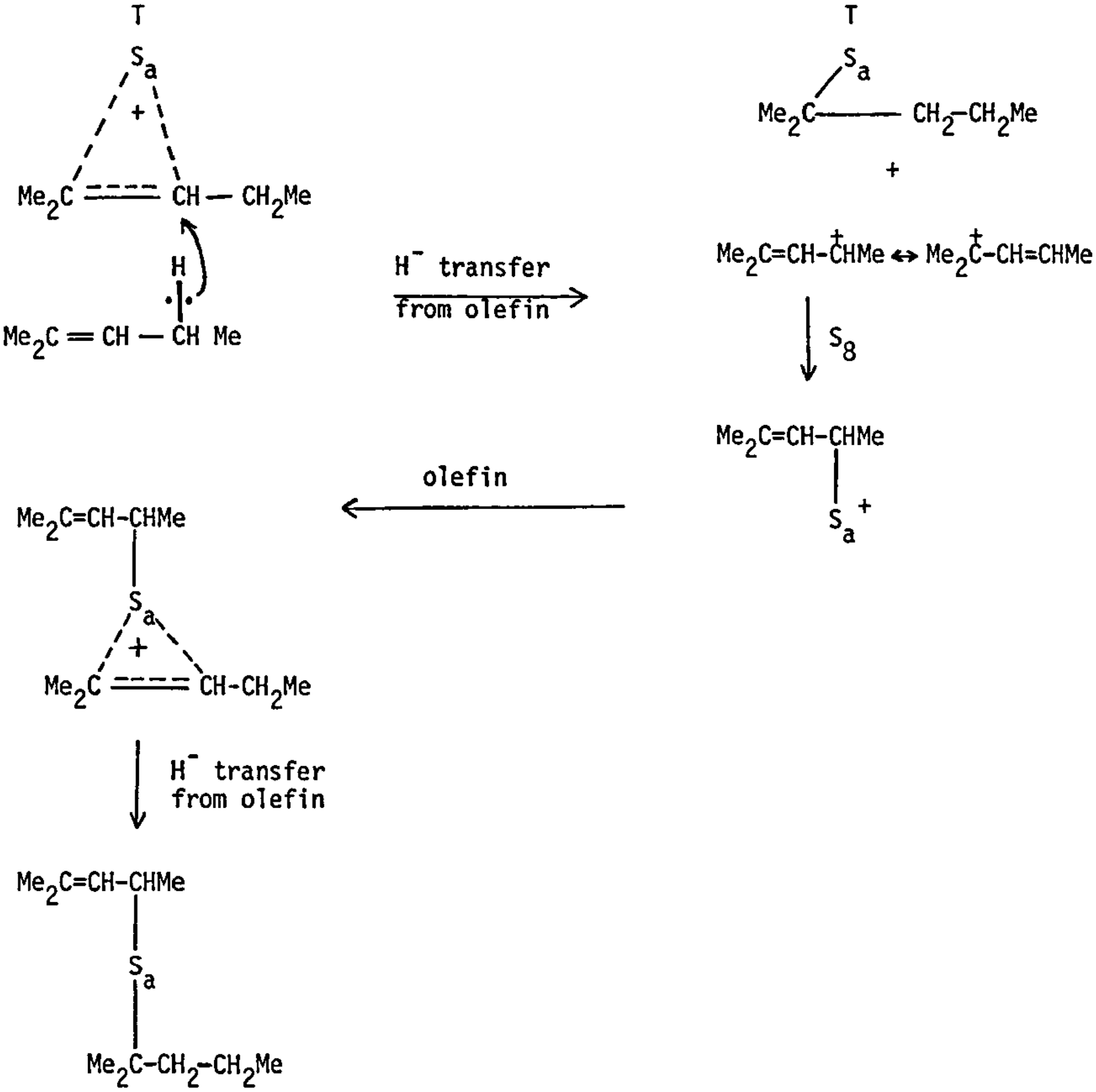
Reaction Scheme (A)

Initiation: Polysulphide, P → $TS_a^+ + TS_b^-$

Propagation: $TS_a^+ + Me_2C = CH - CH_2\,Me$



(XXXV)

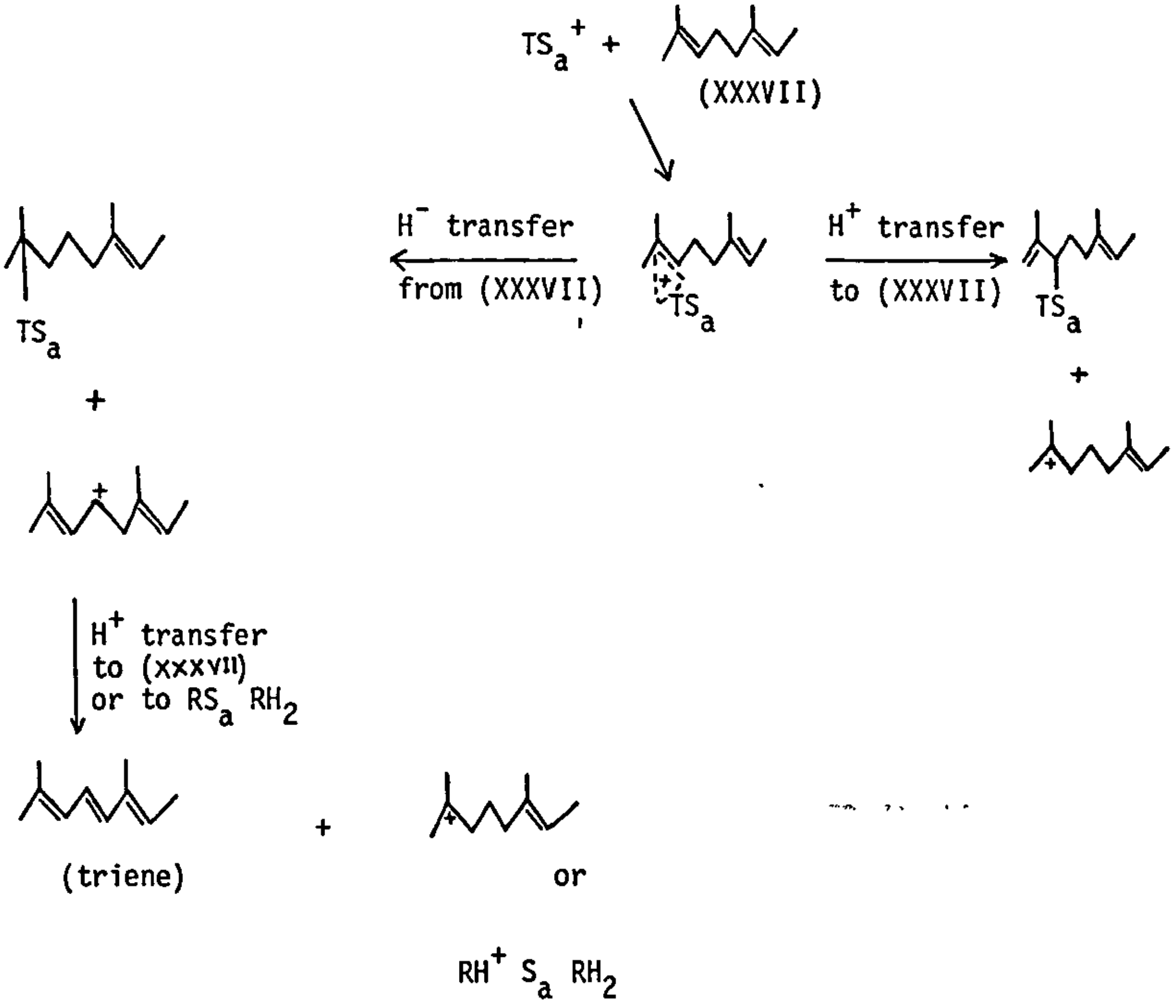


(XXXVI)

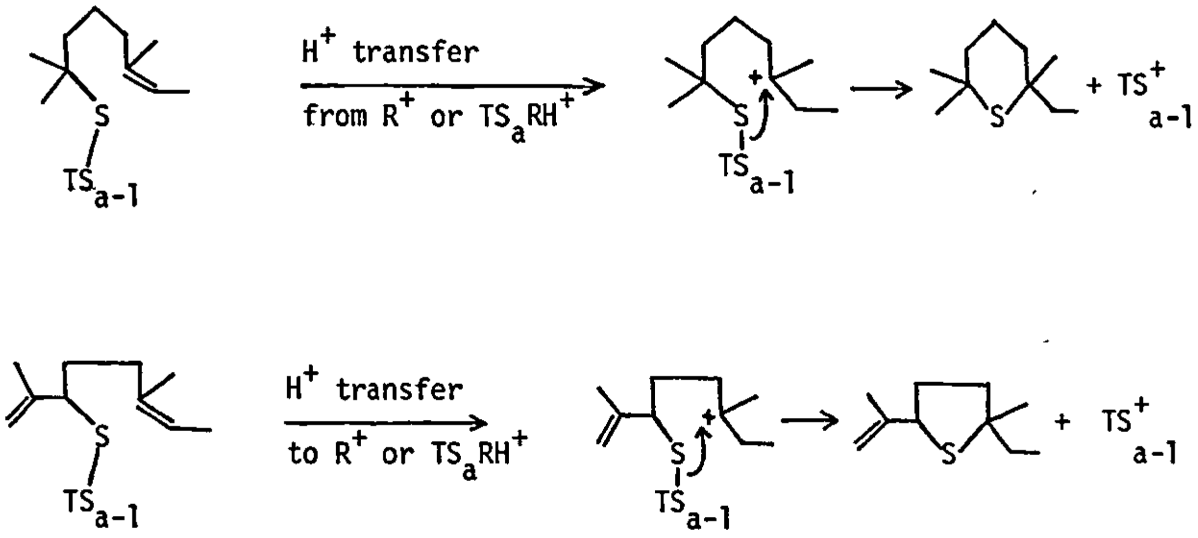
As shown in the reaction scheme (A), the polar mechanism involves the essential heterolysis of S-S bonds in the initially formed polysulphide (or in molecular sulphur in the first instance) to give persulphenium ions, TS_a^+, and persulphenyl anions, TS_b^-. The TS_a^+ propagates the reaction by addition to the olefinic double bond to give structure (XXXV). The persulphenyl anions act merely as chain terminators. The main product, polysulphidic (XXXVI) from the reaction of 2-methylpent-2-ene with sulphur is consistent with the structural feature (XXXIV).

The other structural features, *cyclic monosulphides* and trienes, were based on the reaction schemes of 2,6 dimethyloct-2,6 diene with sulphur. The formation of triene is shown in reaction scheme (B) whilst the formation of *cyclic monosulphides* is shown in the reaction scheme (C).

Reaction Scheme (B)



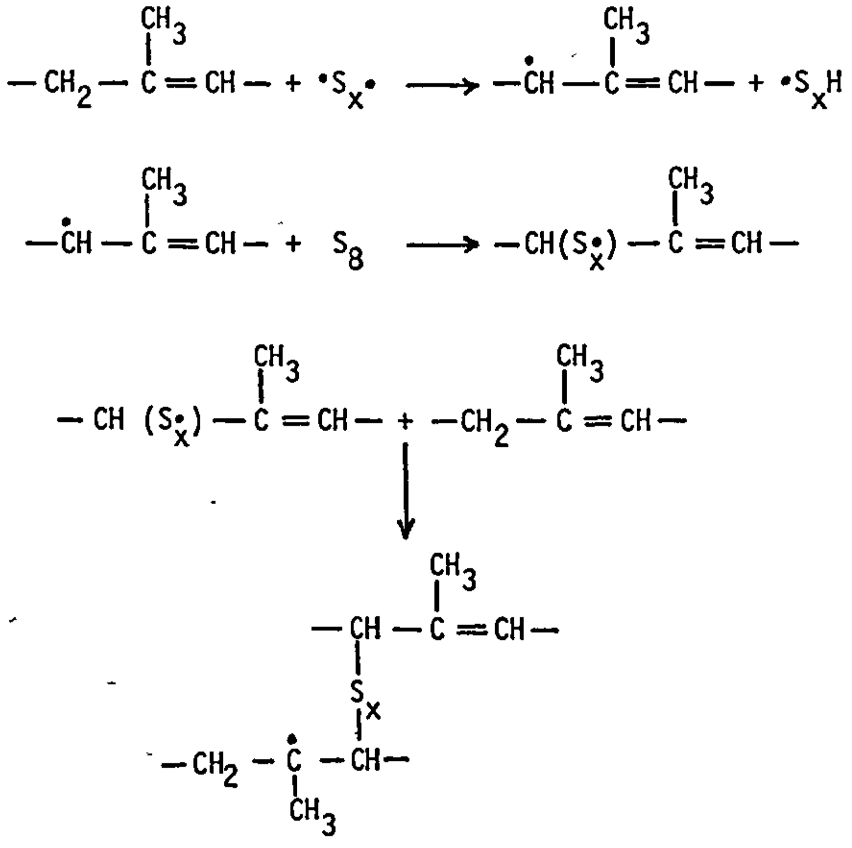
Reaction Scheme (C)



The free-radical mechanism advanced earlier (152-154) is shown by the reaction scheme (D)

Reaction Scheme (D)

$$S_8 \xrightarrow{\text{heat}} \cdot S_x \cdot$$



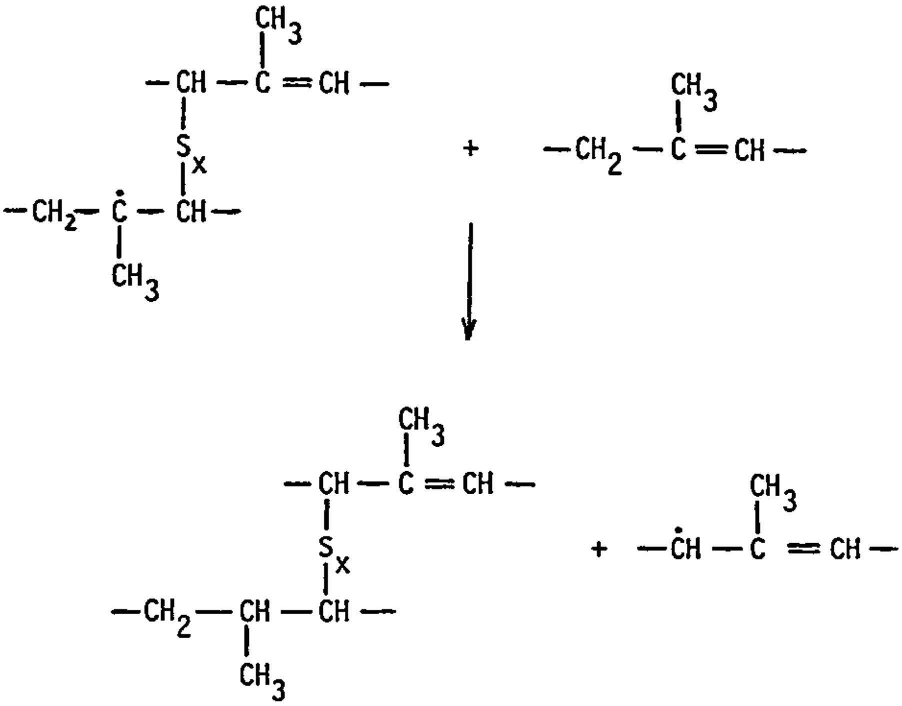
$$-CH_2-\overset{CH_3}{\overset{|}{C}}=CH- + \cdot S_x\cdot \longrightarrow -\dot{C}H-\overset{CH_3}{\overset{|}{C}}=CH- + \cdot S_xH$$

$$-\dot{C}H-\overset{CH_3}{\overset{|}{C}}=CH- + S_8 \longrightarrow -CH(S_x^{\bullet})-\overset{CH_3}{\overset{|}{C}}=CH-$$

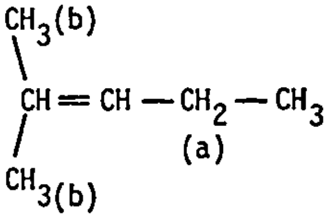
$$-CH\,(S_x^{\bullet})-\overset{CH_3}{\overset{|}{C}}=CH- + -CH_2-\overset{CH_3}{\overset{|}{C}}=CH-$$

$$\downarrow$$

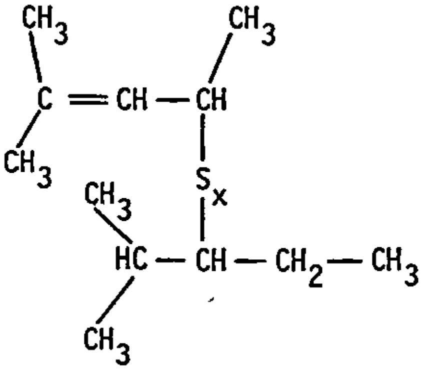
$$\begin{array}{c} -\underset{\substack{|\\ S_x\\ |}}{CH}-\overset{CH_3}{\overset{|}{C}}=CH- \\ -CH_2-\underset{\substack{|\\ CH_3}}{\dot{C}}-CH- \end{array}$$



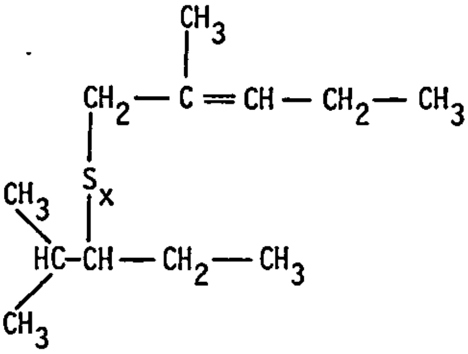
Considering 2-methylpent-2-ene for the reaction scheme (D), there is a choice of two types of α-methylenic hydrogen that can effect in hydrogen abstraction, namely (a) and (b) shown below:



The order of reactivity of these two types of hydrogen atoms is a > b, but there are two possibilities at position (b). Considering both hydrogen abstraction at positions (a) and (b) takes place it would necessitate the polysulphides (XXXVIII) and (XXXIX) to be dominant products which is contrary to fact.



(XXXVIII)



(XXXIX)

APPENDIX II

Determination of exothermic energy of polyisoprene rubber mix containing hexamethylene bis N,N' (cumyl peroxycarbamate)

The typical DSC trace of polyisoprene rubber mix containing hexamethylene bis N,N' (cumyl peroxycarbamate) was shown in Figure 2.8. The exothermic energy of the mix was based on the area under the curve ABC which was converted in terms of energy by obtaining the value of K from a DSC trace of a given weight of tin with known heat of fusion as shown below:

$$A = KW\Delta H_f \tag{96}$$

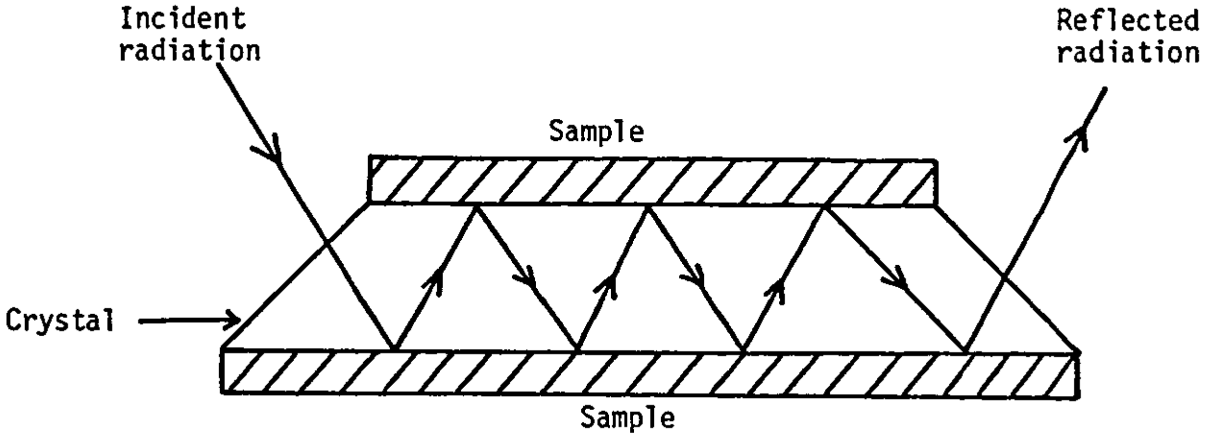
where A is the area involved in the melting of tin
K is a constant
W is the weight of tin
ΔH_f is the heat of fusion of tin (5.94×10^4 J.kg^{-1})

APPENDIX III

Basic principles of ATR spectroscopy

The basic principles of Attenuated Total Reflectance (ATR) spectroscopy are shown in Figure A.1 below:

FIGURE A.1 Basic principles of ATR spectroscopy



The infra-red ATR unit consists essentially of a flat crystal (usually Thallium iodide), arranged in the sample beam of the spectrophotometer so that infra-red radiation can pass through it by total internal reflection. Samples are clamped firmly on either surface of the crystal. When radiation is totally internally reflected at the surface of the crystal, a small proportion actually passes through the surface of the sample, and may be absorbed. On repeated internal reflection along the crystal, the sum intensity of absorption increases. Therefore the emerging radiation has a lower intensity than the reference beam, and a spectrum is obtained in the usual way.

APPENDIX IV

Determination of the total reaction time required to react Hylene W with Capa 222 to form a prepolymer

Hylene W (6.6g) was allowed to react with excess Capa 222 (120g) in a nitrogen atmosphere. The initial infra-red spectrum (immediately after the addition of all the reactants) was recorded using sodium chloride discs. Then at timed intervals during the reaction drops of the reaction mixture were removed and their infra-red spectra were taken.

Using the (-CH) absorption band (2935 cm^{-1}) as an internal reference to overcome the problem of variation in sample thickness between the sodium chloride discs the concentration of isocyanate in the reaction mixture was calculated as follows:

The Beer-Lambert law of absorption states:

$$A = \log_{10} \frac{I_o}{I} = ec\ell \qquad (97)$$

where
A = Absorbance
I_o = Intensity of incident radiation
I = Intensity of transmitted radiation
e = Extinction coefficient
c = Concentration (moles ℓ^{-1})
ℓ = Path length (cm)

From equation 97:

$$\frac{A_{NCO}}{A_{CH}} = \frac{\overset{\checkmark}{e}_{NCO}\ c_{NCO}\ \ell}{\underset{\checkmark}{e_{CH}}\ \underset{\checkmark}{c_{CH}}\ \ell} = \frac{e_{NCO}\ c_{NCO}}{e_{CH}\ c_{CH}}$$

Values of e_{NCO}, e_{CH} and c_{CH} are constant during the extent of the reaction and hence $\frac{A_{NCO}}{A_{CH}}$ is proportional to c_{NCO}.

Values of A_{NCO} and A_{CH} were calculated from the infra-red spectra using the 'base line density' method (155, 156) as shown in the following example:

From Figure A.2

$$A_{NCO} = \log_{10} \left(\frac{I_o}{I}\right)_{NCO} = \log_{10} \frac{AB}{BC}$$

and

$$A_{CH} = \log_{10} \left(\frac{I_o}{I}\right)_{CH} = \log_{10} \frac{XY}{YZ}$$

$$\therefore \quad \frac{A_{NCO}}{A_{CH}} = \log_{10} \frac{AB}{BC} \Big/ \log_{10} \frac{XY}{YZ}$$

The plot of $\frac{A_{NCO}}{A_{CH}}$ with extent of reaction between Hylene W and Capa 222 obtained is shown in Figure A.3. The total reaction time was taken when the $\frac{A_{NCO}}{A_{CH}}$ value remained uniform, i.e. 2 hours at 120°C in this instance.

FIGURE A.2 Infra-red spectrum of Capa 222/Hylene W mixture

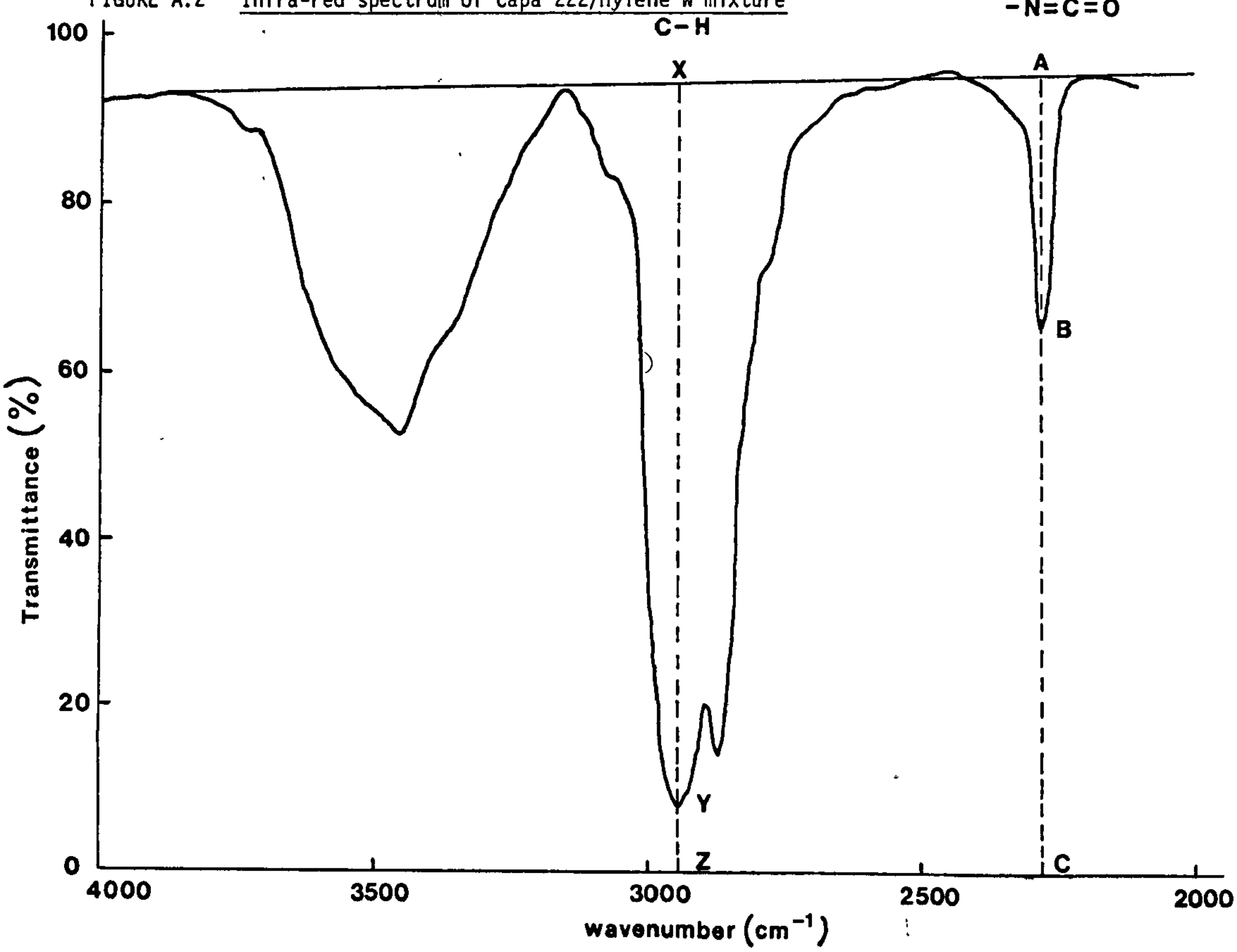
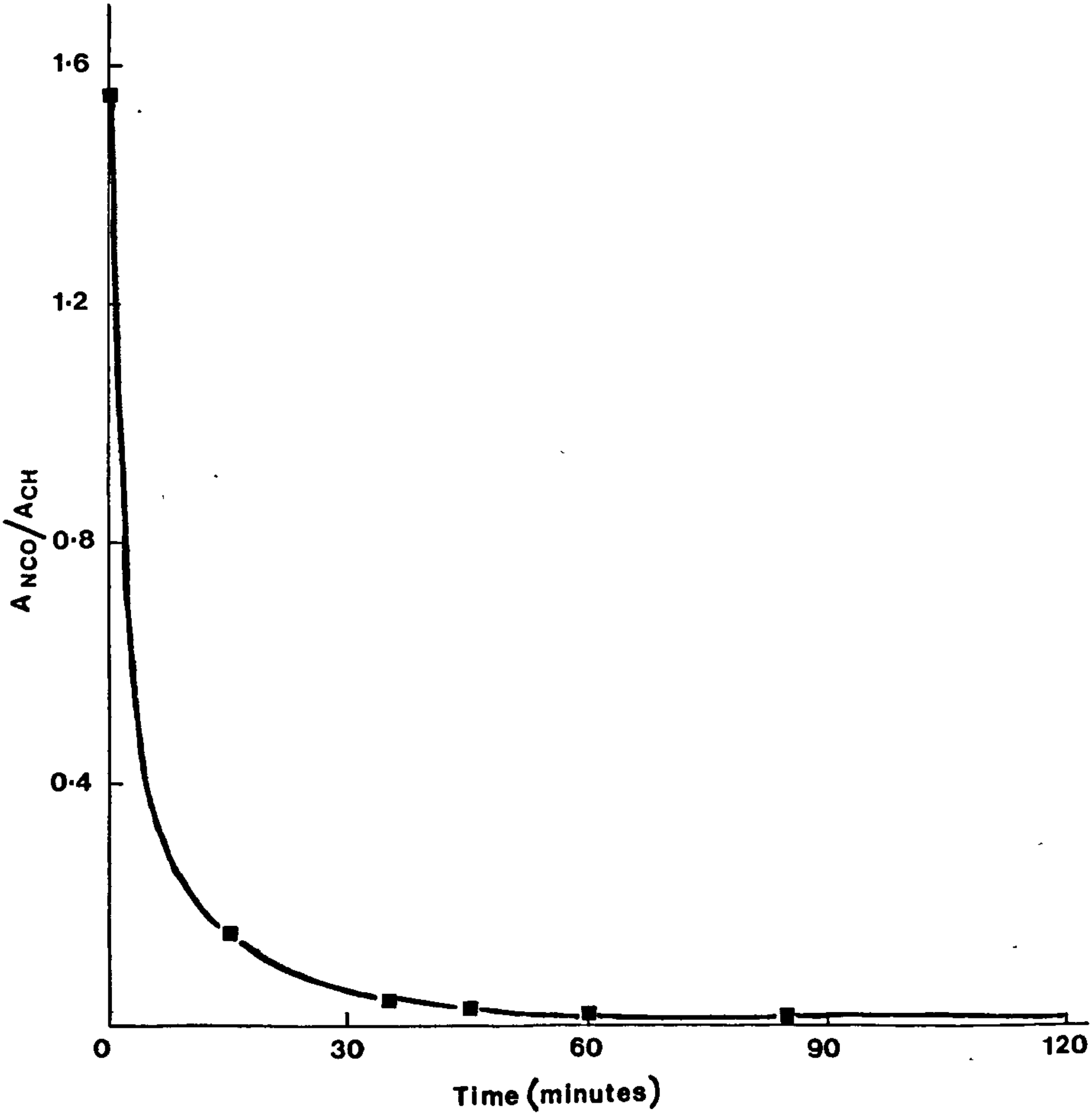


FIGURE A.3 Reactivity of Hylene W with Capa 222 at 120°C



APPENDIX V

Estimation of the amount by weight of diisocyanate required to form a prepolymer of given % of free -NCO

Equivalent weight of CAPA 222 $= \frac{56.1 \times 1000}{\text{OH No.}}$

$$= \frac{56.1 \times 1000}{56}$$

$$= 1001.8$$

Equivalent weight of Hylene W $= \frac{4.2}{\text{\% Free NCO}} \times 1000$

$$= \frac{4200}{31.8}$$

$$= 132.08$$

Let x be the additional weight of Hylene W required to give 4% free -NCO prepolymer.

Then $\frac{x}{132.08}$ is additional number of equivalents of Hylene W required and $\frac{x}{132.08} \times 42$ is the additional weight of isocyanate that will give a prepolymer of 4% free NCO

$$\therefore \frac{\frac{x}{132.08} \times 42}{1133.88 + x} = \frac{4}{100}$$

$$\therefore 0.04\,(1133.8 + x) = 0.318x$$

$$\therefore x = 163.15\text{g}$$

The total weight of Hylene required to react with 1001.8g of CAPA 222 to give a prepolymer of 4% free NCO = 132.08g + 163.15g

= 295.23g

APPENDIX VI

Comparison of ultimate tensile strength values for ring and dumb-bell samples (1)

Ring (MPa)	Dumb-bell (MPa)
16.4	26.3
18.5	26.9
18.6	28.1
19.1	30.1
21.4	30.5
23.2	31.2
Average = 19.5	Average = 28.9
Standard deviation = ±2.2	Standard deviation = ±1.9

(1) The samples used were based on the following formulation and cure conditions:

DPNR	100
ZnO	5
Stearic acid	1
Sulphur	2.5
CBS	0.5
Cure conditions	19 min/150°C

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Patent and Publication Arising from this Thesis

1. A patent has been applied for concerning bisperoxycarbamates as crosslinking agents for rubbers and was filed in May 1981 at the British Patent Office.

2. A paper entitled: *"Bisperoxycarbamates: Crosslinking Agents for Natural, Polyisoprene and other Rubbers"*, has been accepted for presentation in the International Rubber Conference to be held in Harrogate on June 8-12, 1981.