HEXAMETHYLENE-N,N' BIS(TERT-BUTYL PEROXYCARBAMATE) AS A CROSSLINKING AGENT FOR ELASTOMERS

by

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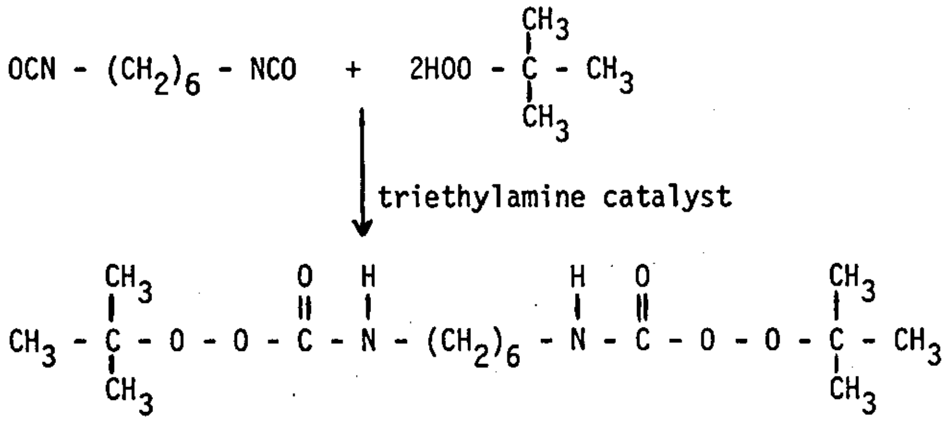
SYNOPSIS

The synthesis of a new bisperoxycarbamate based on a reaction between hexamethylene-1,6 diisocyanate and tertiary butyl hydroperoxide was undertaken. In addition, studies were carried out on an earlier research bisperoxycarbamate based on methylene bis(4-cyclohexylisocyanate) and tertiary butyl hydroperoxide. The equation showing the preparation of the new material is shown below:



$$OCN - (CH_2)_6 - NCO \quad + \quad 2HOO - \overset{CH_3}{\underset{CH_3}{C}} - CH_3$$

$$\Big\downarrow \text{triethylamine catalyst}$$

$$CH_3 - \overset{CH_3}{\underset{CH_3}{C}} - O - O - \overset{O}{\overset{\|}{C}} - \overset{H}{\overset{|}{N}} - (CH_2)_6 - \overset{H}{\overset{|}{N}} - \overset{O}{\overset{\|}{C}} - O - O - \overset{CH_3}{\underset{CH_3}{C}} - CH_3$$

The new material - hexamethylene-N,N' bis (tertiary butyl peroxycarbamate) is shown to be able to crosslink a wide range of elastomers, namely -BIIR, NR, SBR, NR/BR, CR, FKM, NBR, Q, ECO, GPO. However, it has been found to give best results in fluorocarbon rubber which was examined in further detail.

The material is shown to be versatile by using it to cure different grades of fluorocarbon rubber (mainly copolymers of vinylidene fluoride and hexafluoropropylene). The physical properties obtained with the new material as curing agent are comparable with those obtained using standard crosslinking agents for fluoroelastomers. Since carbon dioxide is evolved when bisperoxycarbamates are heated, calcium hydroxide was included in most formulations to act as an absorber system. Calcium oxide and magnesium oxide were found to be suitable metallic oxides to react with any acidic gases (such as hydrogen fluoride) evolved during curing of fluoroelastomer compounds. It was observed that the state of cure was poorer when lead oxides were used (e.g. litharge PbO); also, the use of dibasic lead phosphite as acid acceptor appeared to interfere with HBTBP cure.

Compounding studies, solvent extraction methods and nitrogen tests, and crosslink density measurements were used to postulate possible routes of crosslink formation. These routes of crosslink formation were based on homolytic decomposition of the bisperoxycarbamate, radical abstraction, interaction of a reactive intermediate, and radical-radical interaction. Additional information was obtained from stress relaxation measurements which indicated that new crosslinks were formed during postcuring of fluorocarbon vulcanizates and that this process continued in the initial stages of heat-ageing of postcured FKM vulcanizates.

ACKNOWLEDGEMENTS

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* TBHP is tertiary butyl hydroperoxide

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CHAPTER 1

REVIEW OF VULCANIZATION SYSTEMS

1.1 Introduction

1.1.1 Historical Background

In discussing the historical development of rubber and its vulcanization, we must note that natives of localities where rubber trees grew would have been familiar with rubber long before its existence was recorded in history. However the impetus for developments on rubber and its usage could be attributed to European explorers and scientists who tried to improve rubber which they found stiff when cold and sticky when warm. It was therefore necessary to vulcanize raw rubber in order to improve its properties.

It was speculated in some quarters that hard rubber might have been produced accidentally by P.J. Bergius in Stockholm(1,2) prior to 1791. By 1832, F. Ludersdorff in Germany had noticed that rubber when dissolved in turpentine and heated with sulphur lost its stickiness and exhibited better stability(2). Similar observations were made by van Guens in Holland and Nathaniel Hayward in the US but none of those workers recognised the significance of their discoveries and did not attach any practical value to them.

Meanwhile, Charles Goodyear in about 1831 had been undertaking a series of experiments directed towards the improvement of properties of rubber but without success. He (Goodyear) became acquainted with Nathaniel Hayward and both of them took out a patent on a mixture of rubber and sulphur(2,3). Later on in 1839, Goodyear purchased the process from Hayward and discovered that a mixture of rubber, sulphur and lead compounds heated at elevated temperature gave a product distinctly superior to the raw material both in mechanical properties and in resistance to change of temperature. He did not patent this discovery until 1844.

In another version(3,4) of the historical account of vulcanization, it was narrated that a young Englishman named Stephen Moulton visited the US towards the end of 1841. Whilst there, he came into contact with Goodyear and brought back from the US some samples of rubber for submission to Charles Macintosh and Company, with a view to their purchasing the process by which they had been treated. On returning to England, Moulton at once approached Brockedon for advice from whom the rubber sample finally got to Hancock. The sample which Hancock received must have had some bloom. Hence Hancock observed that the samples had a slight smell of sulphur and did not stiffen on ice. He even thought that a little sulphurous powder had been rubbed on the sample to mislead anyone examining it. Hancock did not analyse the samples from America and without a knowledge of how they had been made, laid out a series of experiments which showed that sulphur alone would vulcanize india rubber. However, the word "vulcanization" was coined by Brockedon(4) who derived it from the vulcan of mythology and the use of sulphur and heat with which this god was supposed to be familiar. Hence, whereas Goodyear filed a patent(5) in which exposure of triple compound of rubber, sulphur and white lead to a high degree of heat would vulcanize rubber, it was Hancock who observed that sulphur alone would vulcanize india rubber at elevated temperature.

Another important discovery is that of Alexander Parkes who in 1846(3,6) found that vulcanization could be brought about by the treatment of rubber with solution of sulphur monochloride in carbon disulphide at room temperature (cold vulcanization). In 1845,Keele also succeeded in effecting vulcanization by treating rubber with sulphur vapour(3). There are reports that suggest that the natives of Brazil had long known a process similar to vulcanization(2). The Indian tribes of the Amazon were reported to have stretched fabrics coated with latex upon frames and let them dry in the sun. The latex used was mixed with sulphur or gunpowder.

In spite of the different versions of the history of vulcanization, the widely held belief that Thomas Hancock and Charles Goodyear are pioneers of rubber vulcanization is still appropriate since they are the earliest people to document the result of their discovery of improving properties of raw rubber by heating it with sulphur at elevated temperature.

Ever since the time of Hancock and Goodyear, a number of significant developments have been made in the field of vulcanization. Among these developments are the use of accelerators, antidegradants, fillers, plasticizers and a host of other rubber additives used to improve vulcanizate properties. Equally noteworthy is the proliferation of different types of vulcanizing agents different from elemental sulphur - partly brought about by the post-World War II development of synthetic and speciality rubbers.

The present chapter attempts a general review of different vulcanization systems.

1.1.2 Definition of Vulcanization

The vulcanization of a rubber compound is an irreversible process during which the rubber compound undergoes a change in its chemical structure (for example crosslinking or formation of a molecular network by a chemical tying together of chain molecules). The vulcanizate (crosslinked rubber compound) loses the tackiness associated with raw rubber, becomes less plastic and more resistant to swelling to organic liquids while elastic properties are conferred, improved or extended over a greater range of temperature(7). Thus vulcanization produces an intermolecular reaction which increases the retractive force and reduces the amount of permanent deformation remaining after the removal of the deforming force.

Crosslinks may be chains of sulphur atoms, single sulphur atoms, carbon-carbon bonds, polyvalent organic radical or polyvalent metal ions.

1.1.3 Effect of Degree of Vulcanization on Rubber Properties

Vulcanizate properties are not only affected by crosslink density only but also by the crosslink type formed, the nature of the polymer, the type and amount of filler etc. However, only the effect of crosslink density on vulcanizate properties will be discussed. Perhaps, an appropriate illustration due to Coran(8), of the effect of crosslink density on vulcanizate properties is shown, Figure 1.1.

He further stated(8) that properties such as tear strength, fatigue life and toughness are related to the energy-to-break and these properties increase with small amounts of crosslinks, but are reduced with increasing crosslink formation. Hysteresis diminishes with increasing crosslink formation and is a measure of the deformation energy that is not stored or borne by the network chains, but instead converted to heat. Properties related to energy-to-break, then increase with increase in the number of network chains and hysteresis. But since hysteresis decreases as more network chains are developed, the energy-to-break related properties peak at some intermediate crosslink density.

Cox and Parks(9) studied the effect of crosslink type and concentration in reinforced natural rubber compounds on their resistance to fatigue failure; the enhancement of this property by antioxidants and its retention during oxidative ageing. Their results showed that accelerated sulphur vulcanization was superior to peroxide and non-elemental sulphur cures.

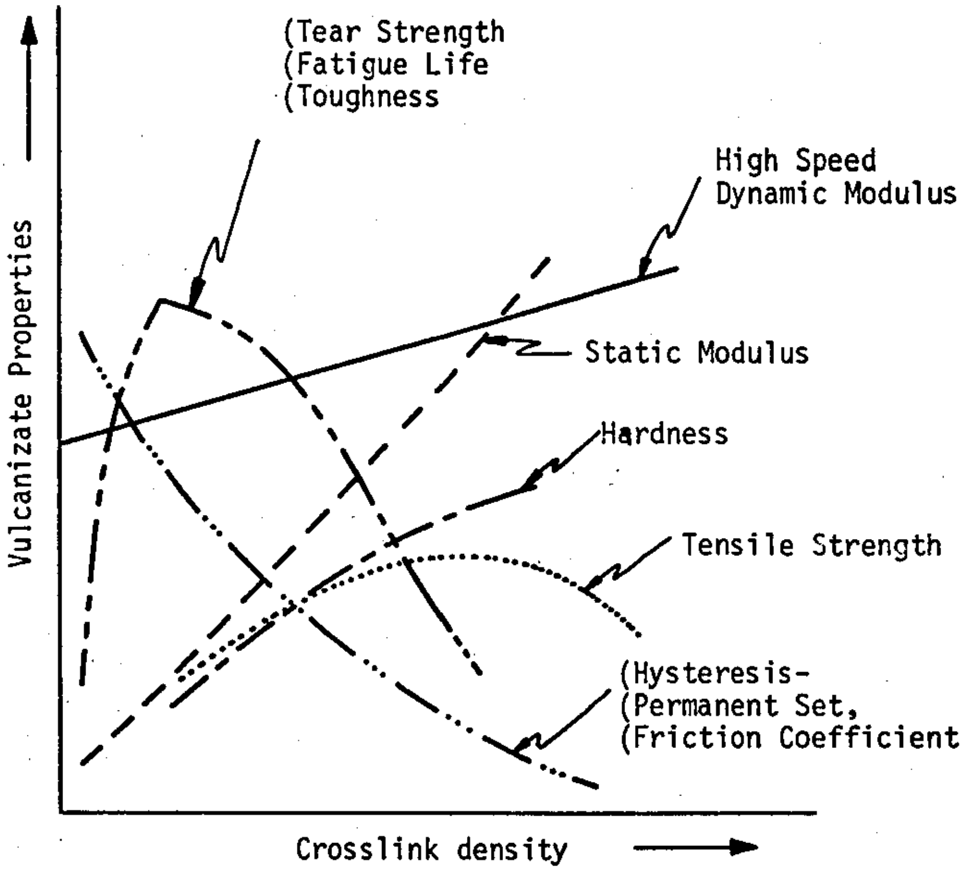


FIGURE 1.1: The Effects of Vulcanization(8)

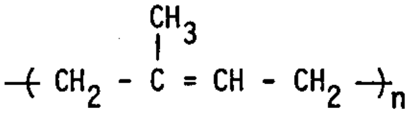
The effect of curing systems on some physical properties was studied by Studebaker(10) while Kuvshinskii and Sidorovich(11) considered the effect of vulcanization on dynamic properties.

1.2 Sulphur Vulcanization

1.2.1 Sulphur Vulcanization of Elastomers

Sulphur vulcanization of elastomers constitutes an area of study to which much contribution has been made by workers at British Rubber Producers' Research Association (later Malaysian Rubber Producers' Research Association). Most of their studies have been limited to natural rubber from which clues are taken in compound formulation for other diene-based elastomers. The extensive nature of the subject limits this discussion to a review of basic principles and a detailed treatment is not intended.

It is necessary to explain at the outset that sulphur vulcanization is not universally applicable to all elastomers. Elastomers which can be vulcanized by sulphur are natural rubber (NR), polyisoprene (IR), polybutadiene (BR), styrene-butadiene (SBR), nitrile rubber (NBR), butyl rubber (IIR), ethylene propylene diene monomer rubber (EPDM) and their respective structures are shown below:

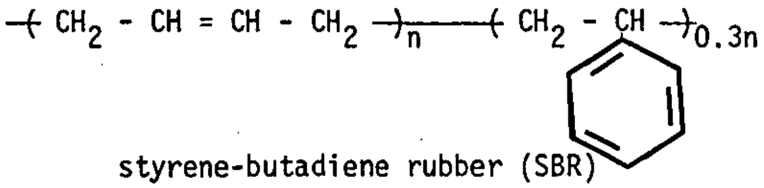


$$-\!\!(\, CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{C} = CH - CH_2 \,)\!\!-_n$$

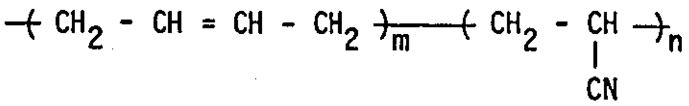
natural rubber (NR) or
synthetic polyisoprene rubber (IR)

$$-\!\!(\, CH_2 - CH = CH - CH_2 \,)\!\!-_n$$

polybutadiene (BR)

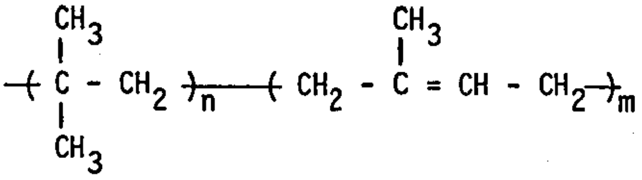


styrene-butadiene rubber (SBR)



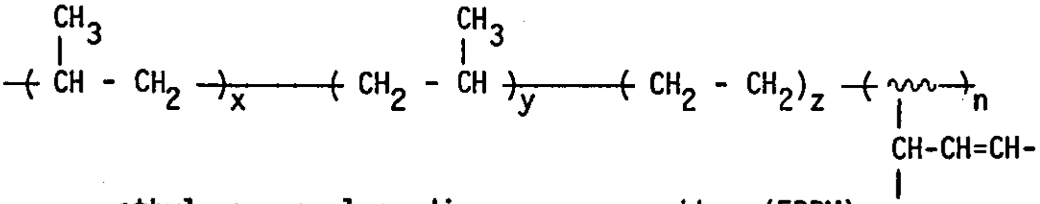
$$\left(CH_2 - CH = CH - CH_2 \right)_m \left(CH_2 - \underset{\displaystyle CN}{\underset{|}{CH}} \right)_n$$

nitrile rubber (NBR)



$$\left(\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}} - CH_2 \right)_n \left(CH_2 - \overset{\displaystyle CH_3}{\overset{|}{C}} = CH - CH_2 \right)_m$$

butyl rubber (IIR)



$$\left(\overset{\displaystyle CH_3}{\overset{|}{CH}} - CH_2 \right)_x \left(CH_2 - \overset{\displaystyle CH_3}{\overset{|}{CH}} \right)_y \left(CH_2 - CH_2 \right)_z \left(\underset{\displaystyle \underset{|}{CH-CH=CH-}}{\underset{|}{\sim\sim}} \right)_n$$

ethylene propylene diene monomer rubber (EPDM)

Examination of the structure of these elastomers reveals a common reactive portion which is simply represented by $>CH - CH = CH -$.

1.2.2 Unaccelerated Sulphur Vulcanization

With the unaccelerated sulphur vulcanization, only the rubber and sulphur are heated to obtain crosslinks; a process similar to that employed by Thomas Hancock. If we take natural rubber as an example, it requires about 8 hours to vulcanize 100 parts of natural rubber and 8 phr* of sulphur. The vulcanizate obtained from this type of vulcanization system suffers from many disadvantages, some of which are:

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* phr - parts per hundred rubber

a) poor mechanical properties
b) poor ageing properties
c) large amounts of sulphur are required and long curing times make the process uneconomic
d) tendency towards reversion
e) formation of sulphur bloom.

The chemistry of unaccelerated sulphur vulcanization of rubber is almost impossible to fully elucidate because of the complicated rubber molecule and its high molecular weight. Furthermore separation and identification of reaction products is difficult. This complexity of the rubber molecule has led many workers to use model olefin-sulphur reactions at elevated temperatures to simulate the unaccelerated sulphur vulcanization. Two major schools of thought have emerged about the mechanism of unaccelerated sulphur vulcanization.

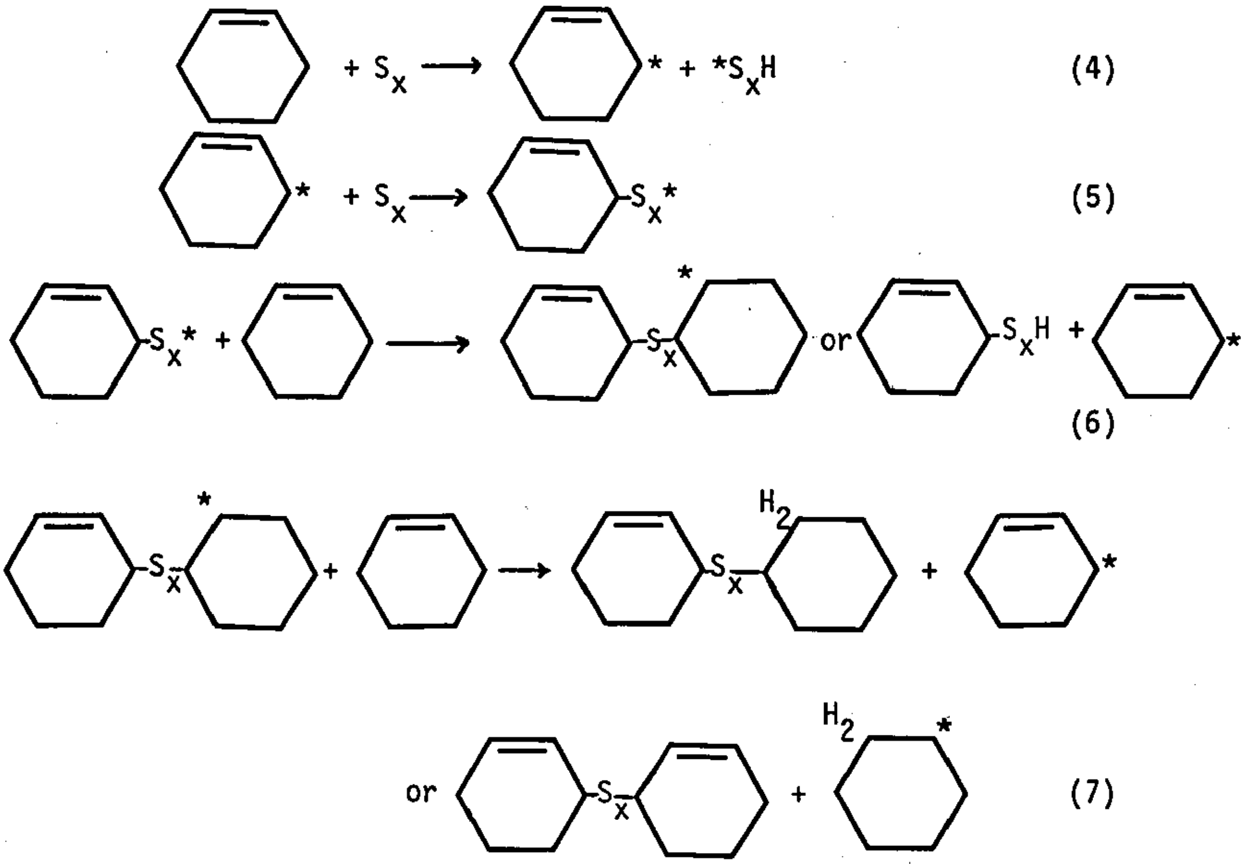
Farmer et al(12,13) compared sulphur to oxygen which contains two unpaired electrons in its outer shell and thought sulphur might well behave in an essentially similar way to oxygen in initiating its attack on olefin. Since oxygen reacts with olefin by a radical mechanism involving chain reactions we have the following equations (1) to (3):

$$\cdot CH_2 \cdot CH{:}CH\cdot + O_2 \rightarrow \cdot \underset{\bullet}{C}H \cdot CH{:}CH\cdot + {}^*OOH \qquad (1)$$

$$\cdot \underset{\bullet}{C}H \cdot CH{:}CH\cdot + O_2 \rightarrow \cdot CH(OO^*)\cdot CH{:}CH\cdot \qquad (2)$$

$$\cdot CH(OO^*)\cdot CH{:}CH\cdot \xrightarrow{\cdot CH_2 \cdot CH{:}CH\cdot} \cdot CH(OOH)\cdot CH{:}CH\cdot + \cdot \underset{\bullet}{C}H \cdot CH{:}CH\cdot \qquad (3)$$

Using cyclohexene and 1-methylcyclohexene which contains the polyisoprenic unit, Farmer et al(12) believed the major product of sulphur-olefin interaction at 140°C to be alkenyl alkyl polysulphide and postulated a non-polar mechanism in which attack by sulphur begins by displacement of α-methylenic hydrogen atoms (i.e. begins substitutively) and ends additively by attachment of a sulpho radical at one end of a double bond. The resulting radical is subsequently stabilized by capture (or less usually by loss) of a hydrogen atom, thus



(4)

(5)

(6)

(7)

It was further emphasized that there was no evidence of direct carbon-to-carbon crosslinking of olefins when cured by sulphur(12,13). Furthermore, some of the sulphur used in unaccelerated sulphur vulcanization is said to be consumed in forming cyclizing links and polysulphidic crosslinks. Cyclizing links are said to be valueless from the point of strengthening the molecular network. This might be a reason for poor crosslinking efficiencies obtained with unaccelerated sulphur vulcanization although vulcanizates may have good low temperature properties(14).

Bateman and his research group(15-18) rejected the free radical mechanism of unaccelerated sulphur vulcanization. They used both structural and kinetic studies to show:

i) that alkenyl alkyl polysulphides are not the sole primary products of the reaction of monoolefins with sulphur;

ii) that the alkenyl alkyl polysulphides formed have not the structures to be expected from reactions (4) to (7);

iii) that 2:6 dimethyl-octa-2:6-diene does not yield cyclic monosulphides having structures consistent with a wholly free radical reaction;

iv) that the kinetic characteristics indicate a polar mechanism and not a free radical mechanism.

Hence Bateman et al(15-18) proposed the polar mechanism below:

Initiation: $\text{Polysulphide} \rightarrow TS_a^{+} + TS_b^{-}$ (8)

Propagation: $TS_a^{+} + RH(C{:}C) \rightarrow TS_aRH^{+}\,(sat)$ (9)

$$\begin{tikzcd}[column sep=small]
 & TS_aRH_2(sat) + R^{+} \quad (10) \\
TS_aRH^{+}(sat) + RH(C{:}C) \arrow[ur] \arrow[dr] & \\
 & TS_aR\,(C{:}C) + RH_2^{+} \quad (11)
\end{tikzcd}$$

$$\begin{tikzcd}[column sep=small]
R^{+} & & & RS_a^{+} \quad (12) \\
 & + & S_8 \arrow[ur] \arrow[dr] & \\
RH_2^{+} & & & RH_2S_a^{+} \quad (13)
\end{tikzcd}$$

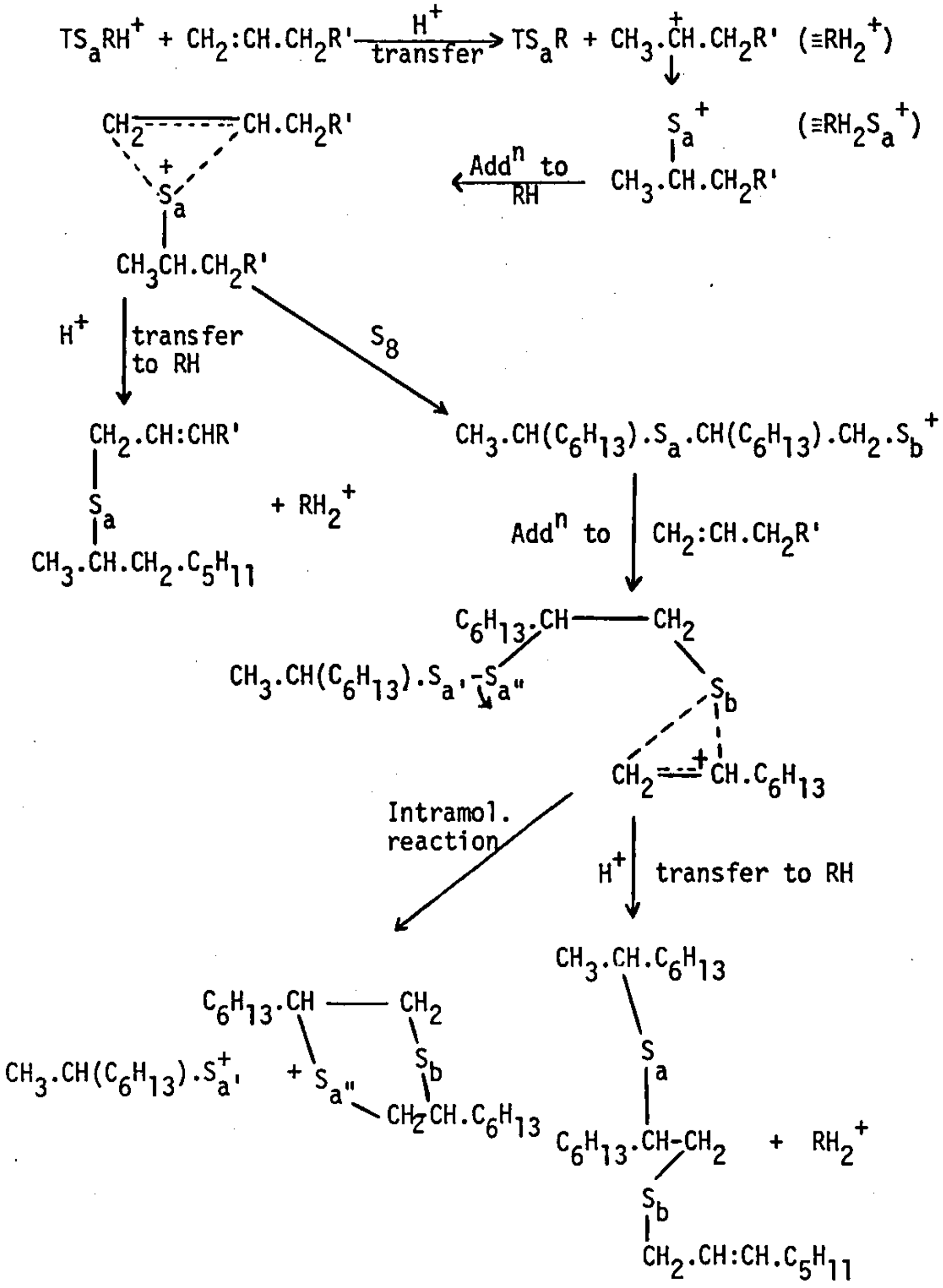
$$\text{Termination:}\quad \left.\begin{array}{l} R^{+} \\ RH_{2}^{+} \\ TS_{a}RH^{+} \end{array}\right\} + TS_{b}^{-} \rightarrow \begin{array}{l} \\ \text{Non-chain} \\ \text{carriers} \end{array} \qquad \begin{array}{r} (14) \\ (15) \\ (16) \end{array}$$

where RH(C:C) is a monoolefin
sat denotes absence of C:C
H is an α-methylenic hydrogen atom
T is R or RH_2 (alkenyl or alkyl)
a and b $\geqslant$ 1
Polysulphide is of average composition RS_xRH_2
$x = a+b$

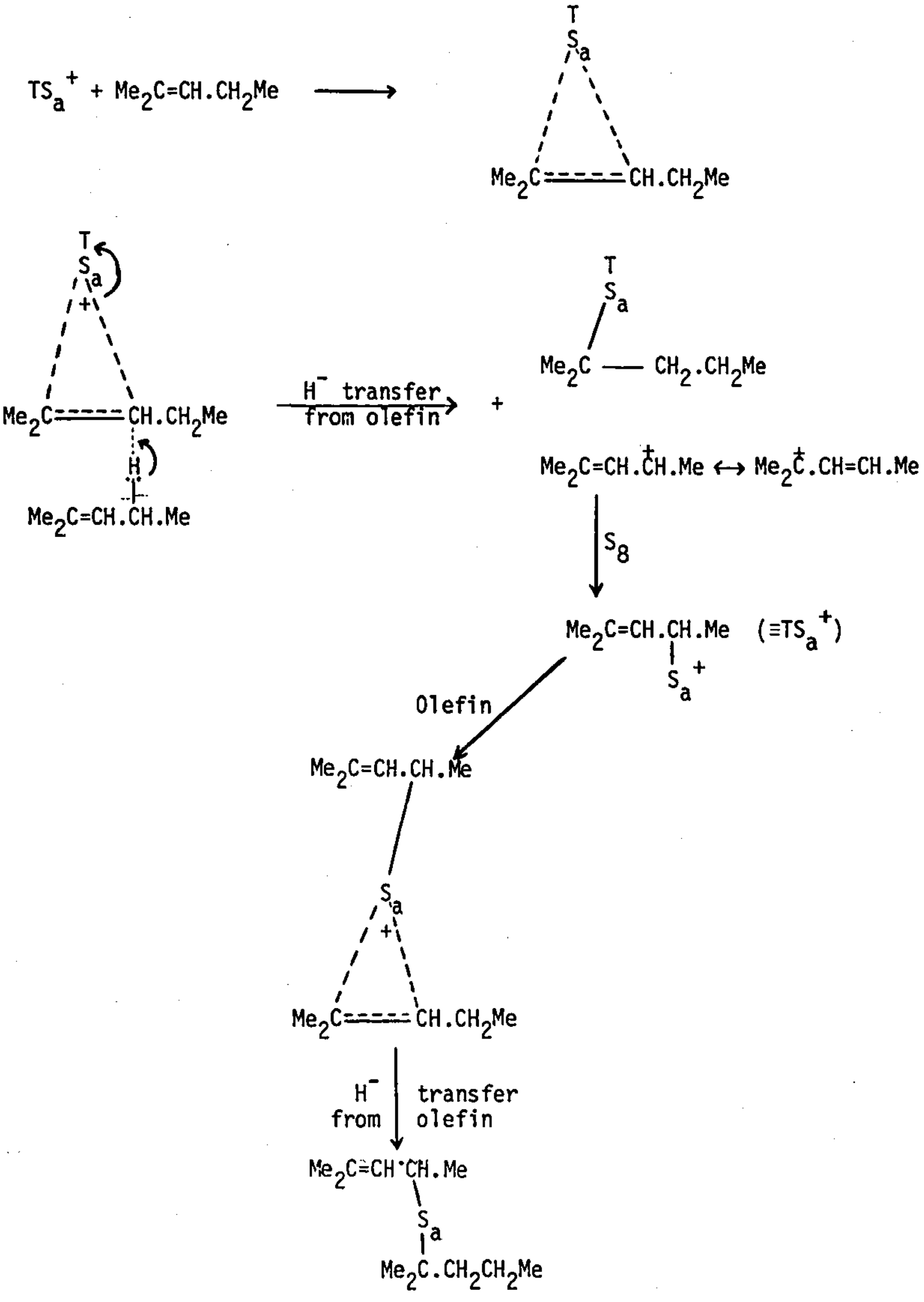
A number of possible reaction schemes based on the above polar mechanism have been discussed by Bateman et al(14,15) and some are listed below.

Reaction Scheme 1: based on oct-1-ene

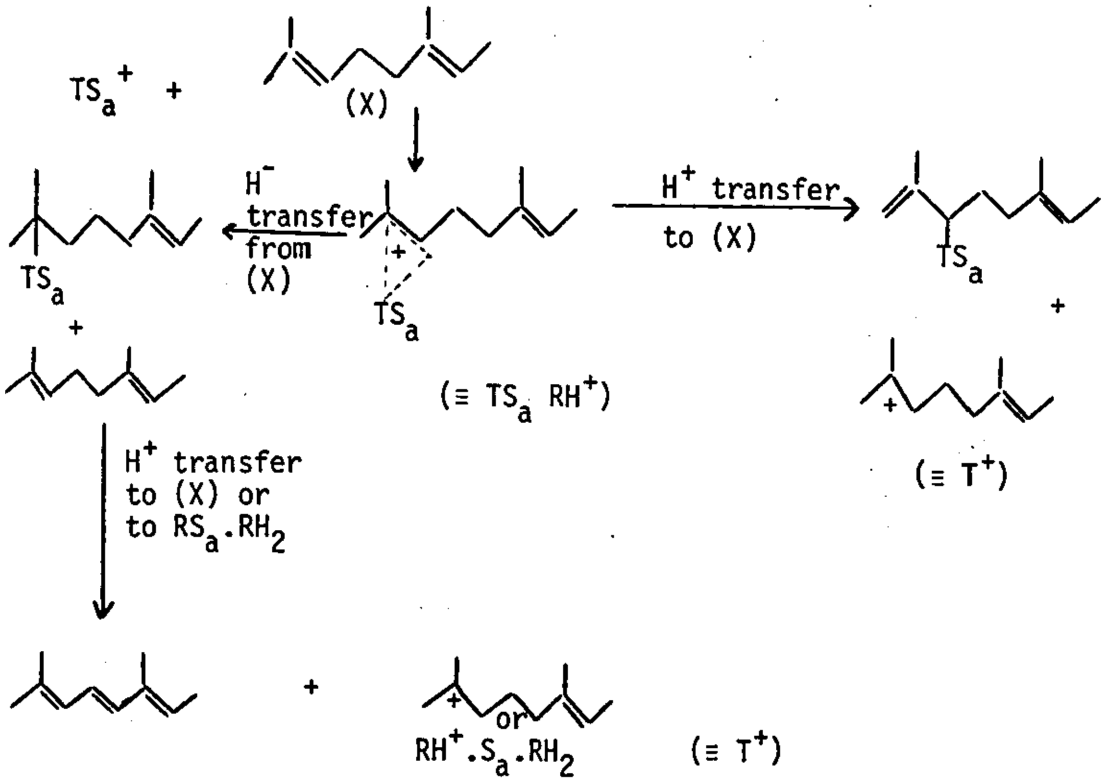
($RH=CH_2:CH.CH_2R'$; $R' = C_5H_{11}$)



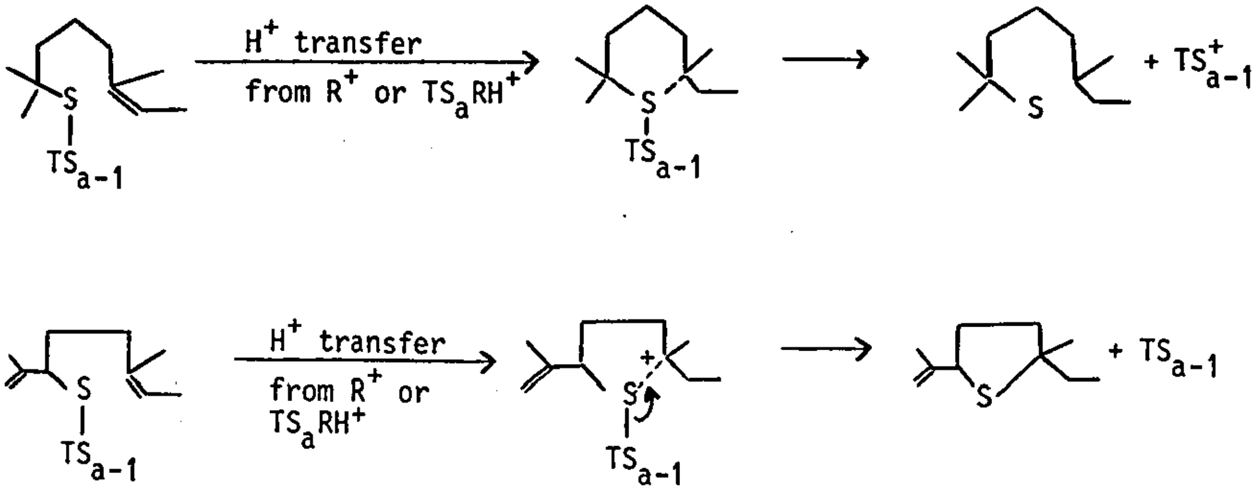
Reaction Scheme 2: based on 2-methylpent-2-ene



Reaction Scheme 3: alternative routes to crosslinked polysulphides



Reaction Scheme 4: formation of cyclic monosulphides



In addition to citing the kinetic analysis of Ross(16) as evidence of the validity of the polar mechanism, Bateman et al(14,15) further stated that purely thermal homolysis of S-S bonds in sulphur and organic di- and polysulphide molecules at temperatures below 140°C had not yet been conclusively demonstrated. Such fission occurs only when induced photolytically or by a radical displacement reaction:

$$R\cdot + R'S\text{-}SR' \rightarrow RSR' + R'S\cdot \tag{17}$$

$$R^{\bullet}_{n} + S_8 \rightarrow R_nS_x + S^{\bullet}_{8-x} \tag{18}$$

whereas S-S bonds in sulphur and organic polysulphides are readily broken by nucleophilic reagents as represented below:

$$X^- + -S-\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}\overset{\curvearrowleft}{-}\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}} \rightarrow -S-\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}-X + {}^{-}\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}- \tag{19}$$

Another investigation examined the role of hydrogen sulphide during sulphur vulcanization of natural rubber(19) while the removal of combined sulphur from vulcanized rubber as trimethyl sulphonium iodide on treatment with methyl iodide was given as evidence of the presence of sulphide sulphur linked to allylic type residues(20,21). The latter investigation cannot be used comparatively since its reactions with sulphides to yield trimethyl sulphonium iodide is nonspecific with respect to the structures of R and R' in R•S•R' and occurs to a negligible extent with di- and poly sulphides(14).

Equally of interest is the fact that when natural rubber is hydrogenated to saturate the double bond present, the hydrogenated product inhibited vulcanization. This demonstrates that sulphur-based vulcanization is associated with the double bond(22).

Although there is no guarantee that reactions of sulphur with model olefins simulate reactions of sulphur in high polymers, they provide strong indications of likely reactions and predictions based on results obtained with the systems may be justified.

Evidence from studies(15) of unaccelerated sulphur-natural rubber vulcanizate led to the proposal of a conceptual structural network shown below (Figure 1.2):

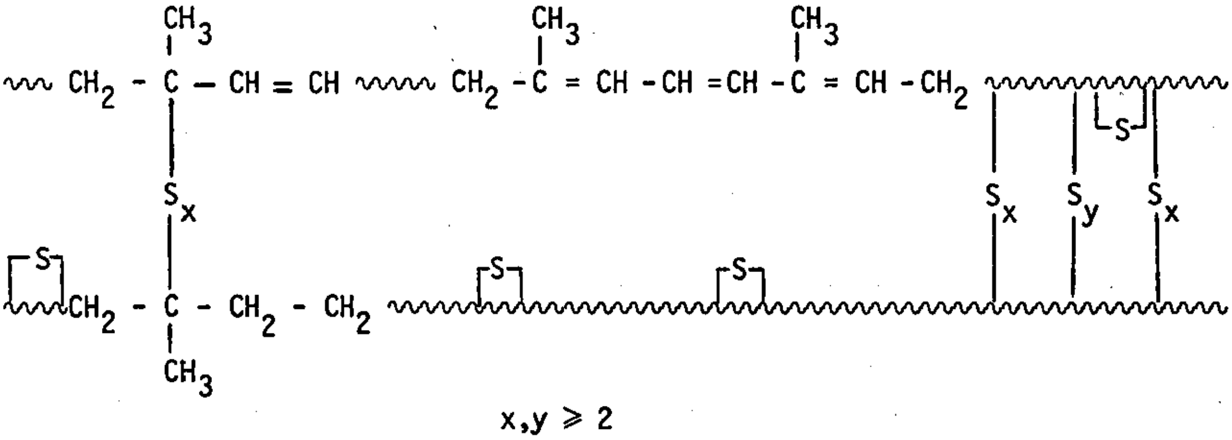


FIGURE 1.2: Conceptual structural features of an unaccelerated sulphur-natural rubber vulcanizate network(15)

1.2.3 Accelerated Sulphur Vulcanization

The earliest basic accelerator (lead carbonate) was used by Charles Goodyear though without him understanding the relationship. Since the discovery of vulcanization, various metal oxides and salts have been used as inorganic accelerators in sulphur vulcanization. Metal oxides e.g. zinc oxide enhance the effect of sulphur during vulcanization and somewhat reduce vulcanization time to about three hours at

140°C. The discovery of aniline in 1906 as an organic accelerator opened the way to the discovery of other organic accelerators which are still used at this present time. The historical development of accelerators is given elsewhere(23).

Accelerators are used in conjunction with auxiliary agents like stearic acid and zinc oxide in accelerated sulphur vulcanization systems to quicken the process. The effect of accelerators on the resulting vulcanizate structure depends on the concentration of auxiliary agents and that of accelerators. Equally important is time and temperature of cure. The functions of accelerators as stated by Bateman et al(15) are:

i) To increase the rate of sulphur combination with the rubber;
ii) Increase in the efficiency of utilization of sulphur as a crosslinking agent and thereby to produce simpler network with the additional advantages given in (iii)-(vii);

iii) Increase in the rate of crosslinking of the rubber and thus to economise time, energy and use of equipment in industrial vulcanization processes;

iv) Greater control over the vulcanization process especially by minimizing modulus and tensile strength reversion, so that vulcanizates with specified physical properties are readily obtained;

v) Improvements in the physical properties and ageing characteristics of the vulcanizates;

vi) Improved appearance of the vulcanizate (e.g. by reducing sulphur bloom);

vii) Reduced variability of cure in different samples of rubber as is especially important with natural rubber.

A general discussion of accelerators and their advantages has been given by Neal(24).

Based on the development of the efficient vulcanization (EV) systems by workers at Natural Rubber Producers' Research Association (NRPRA)(25,26), the accelerated sulphur vulcanization could further be subdivided into three groups, namely: conventional vulcanization (CV); efficient vulcanization (EV) and semi-efficient vulcanization (semi-EV).

A typical recipe for the accelerated vulcanization system is shown in Table 1.1 below:

TABLE 1.1: Recipe for accelerated sulphur vulcanization

	phr[a]
Polymer	100.0
ZnO	2-10
Fatty Acid	1- 4
Accelerator[b]	0.5- 3
Sulphur	0.5- 2

while Table 1.2 shows a typical recipe for the three subdivisions of accelerated sulphur vulcanization.

TABLE 1.2: Subdivisions of accelerated sulphur vulcanization

	EV (phr)	Semi-EV (phr)	CV (phr)
Polymer	100.0	100.0	100.0
ZnO	5.0	5.0	5.0
Fatty Acid	2.0	1.0	1.0
Accelerator	3.0	2.0	1.0
Sulphur	0.3	1.0	2.5

a: phr - parts per hundred rubber. b: accelerators can be used individually or as mixtures.

It should be noted that efficient vulcanization systems have low sulphur to accelerator ratios while the conventional vulcanization systems have high sulphur to accelerator ratios. The semi-efficient vulcanization system is intermediate between the two extreme systems. Vulcanizates from EV systems have been described(25,26) as having better resistance to heat ageing when compared with vulcanizates from CV systems. However, the flex fatigue resistance of vulcanizates from EV systems is somewhat inferior to vulcanizates from CV systems. Vulcanizates from semi-EV systems give a compromise of properties between the other two systems. Other recent reviews(27,28) on accelerated sulphur vulcanization have been published.

Before proceeding to discuss the mechanism of accelerated sulphur vulcanization, a summary due to Brydson(22) of some commercially important accelerators is given in Table 1.3.

1.2.4 Mechanism of Accelerated Sulphur Vulcanization

The chemistry and mechanism of accelerated sulphur vulcanization is an area where different opinions exist and the volume of literature published on this area over the years bears testimony to this.

A summary of the overall reactions taking place during vulcanization was given by Porter(29) and summarised in Figure 1.3 below:

TABLE 1.3(22)

Some Classes of Accelerators Used in Accelerated Sulphur Vulcanization

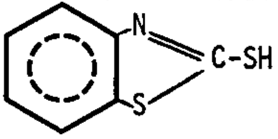
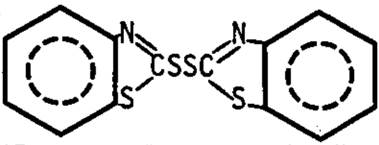
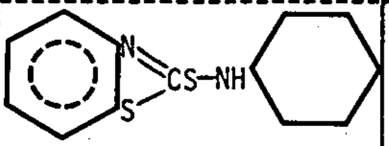
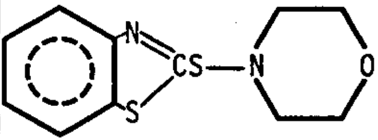
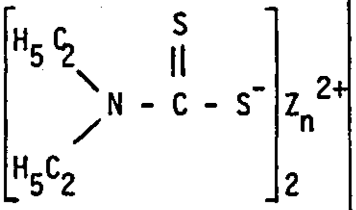
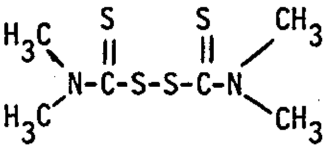
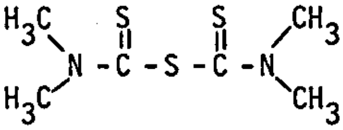
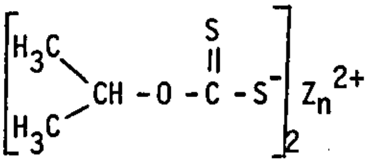
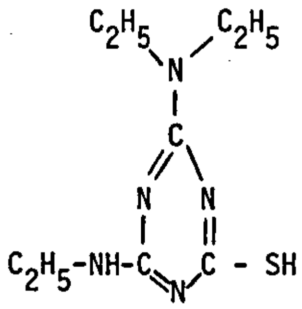
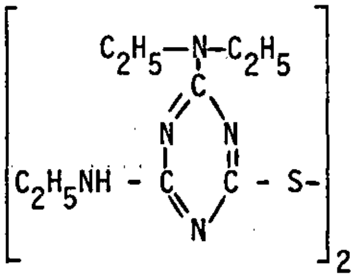
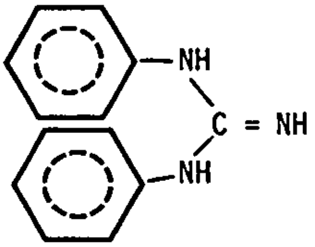
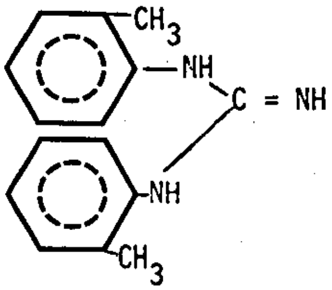
Type and Examples	Chemical Formula	Comments
THIAZOLES Mercaptobenzothiazole (MBT)		MBT and its derivatives form the dominant group of accelerators used with dienes. MBT is powerful but tends to be scorchy
Dibenzothiazyl disulphide (MBTS)		
SULPHENAMIDES N-cyclohexyl benzothiazole sulphenamide (CBS)		Delayed action semi-ultra accelerator. Widely used.
N-oxydiethyl benzothiazyl sulphenamide (NOBS)		Similar to CBS
DITHIOCARBAMATES Zinc diethyl dithiocarbamate (ZDC or ZDEC)		Ultra-accelerator. This and other dithio-carbamates are usually too fast for dry rubber technology. Used in latex work
THIURAM SULPHIDES Tetramethyl thiuram disulphide (TMT or TMTD)		Ultra-accelerator. Also vulcanizing agent.
Tetramethyl thiuram monosulphide (TMTM)		Ultra-accelerator. Like TMTD often used in small quantities in conjunction with other accelerators
XANTHATES Zinc isopropyl xanthate (ZIX)		Ultra-accelerator.

TABLE 1.3 ... continued

Type and Examples	Chemical Formula	Comments
TRIAZINES 2-Ethylamino-4-diethyl amino-6-mercaptotriazine		
Disulphide oxidation product of above		Similar delayed action as CBS - improved reversion resistance
GUANIDINES Diphenyl guanidine (DPG)		Medium-speed accelerator. Now largely used in conjunction with other accelerators. Strong synergism with MBT
Di-o-tolyl guanidine (DOTG)		Medium-speed accelerator. Also used as 'plasticizer' for polychloroprenes.

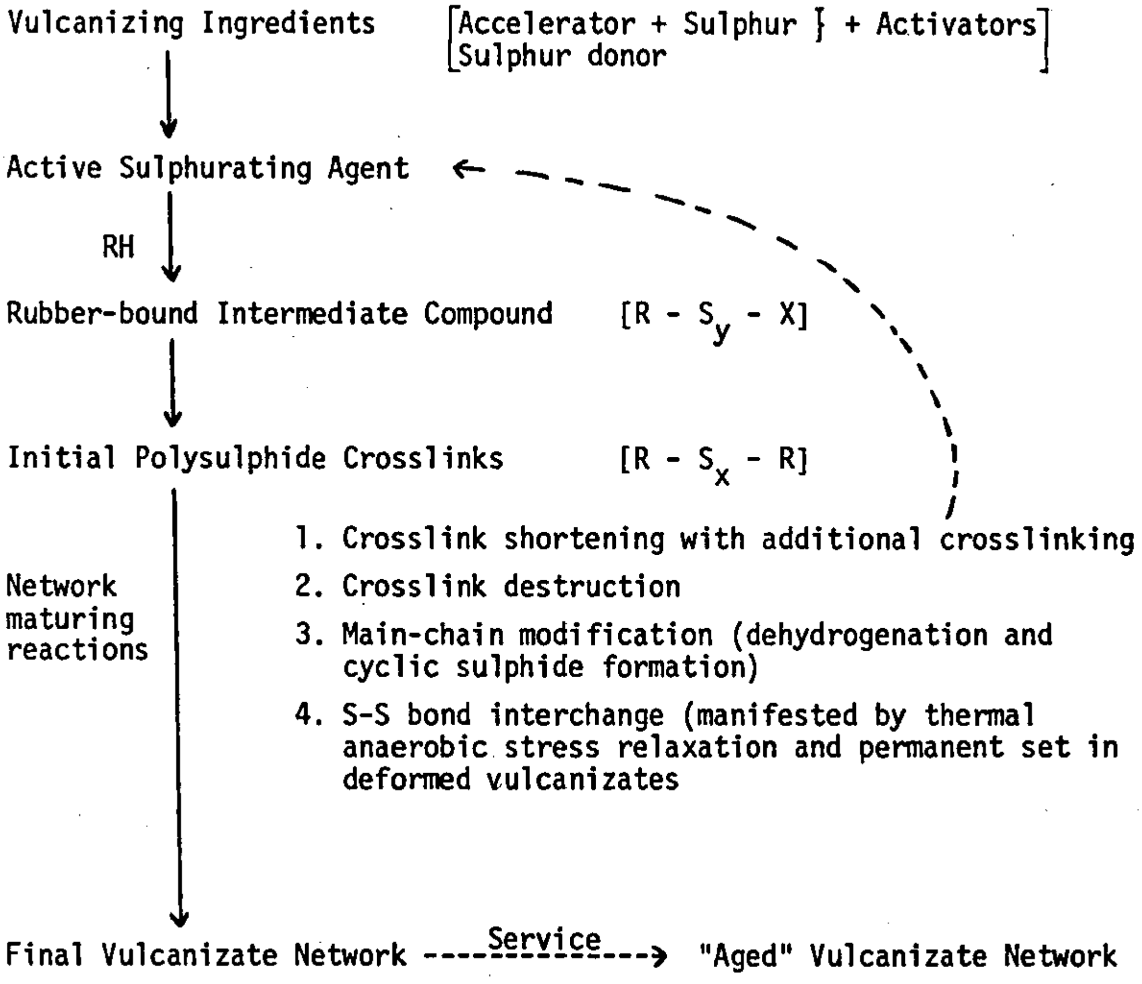
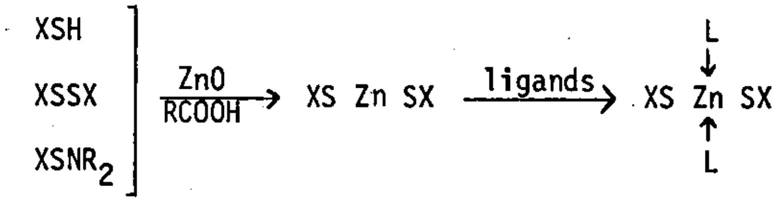


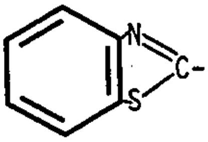
FIGURE 1.3: Overall Course of Accelerated Sulphur Vulcanization

The active sulphurating agent formed by reaction of sulphur with an accelerator complex or from a sulphur donor and zinc oxide reacts directly with the rubber hydrocarbon to give a rubber-bound polysulphidic pendent group terminated by a fragment derived from the accelerator or sulphur donor(29)



$$\left.\begin{array}{l}XSH\\ XSSX\\ XSNR_2\end{array}\right] \xrightarrow[RCOOH]{ZnO} XS\;Zn\;SX \xrightarrow{ligands} XS\;\underset{\underset{L}{\uparrow}}{\overset{\overset{L}{\downarrow}}{Zn}}\;SX \qquad (20)$$

$X = (CH_3)_2\,N - \overset{\overset{S}{\|}}{C} -$ or



L = nitrogen bases (either added as accelerator or present in the raw natural rubber) or zinc carboxylates

Such pendent groups are immediate precursors to polysulphidic crosslinks which they form either by direct reaction with another rubber hydrocarbon molecule or by disproportionation with a second pendent group on a neighbouring rubber chain:

$$\left.\begin{array}{l}2RS_x - C(:S) - N\,Me_2\\ RS_x - C(:S)\,N\,Me_2 + RH\end{array}\right] \xrightarrow{ZnO} R\,S_y\,R + ZD_mC + H_2O \qquad (21)$$

where RH = polyisoprene in which H is α-methylenic or α-methylic and $x \geq 2$; $Z\,D_mC$ is zinc dimethyldithiocarbamate. Polysulphide crosslinks are thermally unstable and chemically reactive and are subject to a number of competing reactions, the relative rates of which depend on the detailed structure of the crosslink termini, the concentration in the vulcanizate of various zinc-containing entities and the temperature of vulcanization. These reactions have been termed "network maturing reactions"(14) and they lead to the final vulcanizate which may have a structure as shown in Figure 1.4 below:

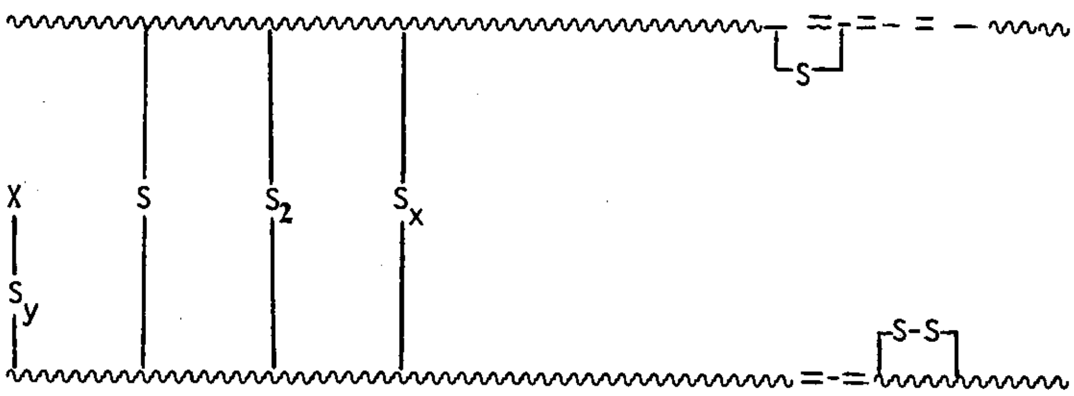


FIGURE 1.4: Structural features of an accelerated sulphur vulcanizate of natural rubber.
(X = accelerator fragment, $x \geqslant 3$, $y \geqslant 1$).

Maturation of the network may continue during the service life of the vulcanizate, especially if this takes place at an elevated temperature where its effects are superimposed on the oxidative ageing reactions of the vulcanized network. Several other factors affect the final vulcanizate structure. Such factors are the presence of nitrogenous bases(30,31), the type of accelerator system and accelerator to sulphur ratio(25,26).

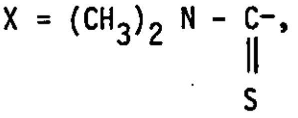
As said earlier on, there are different opinions about the mechanism of accelerated sulphur vulcanization. A school of thought consists of researchers such as E.M. Bevilacqua and B.A. Dogadkin(32-35) and their respective co-workers. These people advanced free radical mechanism for the accelerated vulcanization of unsaturated elastomers (particularly for accelerators involving tetramethylthiuram disulphide (TMTD), 2-mercaptobenzothiazyl disulphide (MBTS), N-cyclohexyl-2-benzothiazole sulphenamide (CBS), and the "sulphurless" TMTD-ZnO system). These free radical schemes are similar. They assume, in principle, the homolysis of the sulphurating complex to yield persulphenyl radicals which could then interact with RH (polyisprene) to give the precursor to the crosslinks. The initial stages of the reaction are shown in the scheme below:

$$XSSX \rightarrow 2XS^{\bullet} \qquad (22)$$

$$XS^{\bullet} + RH \rightarrow XSH + R^{\bullet} \qquad (23)$$

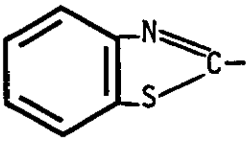
$$R^{\bullet} + S_8 \rightarrow R\text{-}S_8^{\bullet} \qquad (24)$$

$$R^{\bullet} + XSSX \rightarrow RSX + XS^{\bullet} \qquad (25)$$



$$X = (CH_3)_2\,N - \underset{\underset{S}{\|}}{C}-,$$

or



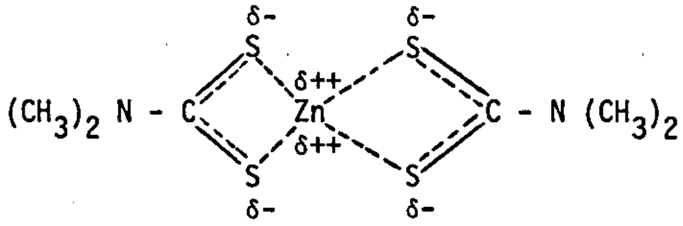
etc

However, Bateman and his co-workers(14) rejected the free radical mechanism on the grounds that it is irrational that the introduction of such obviously polar or polarizable auxiliary vulcanizing ingredients as metal oxides, zinc soaps and accelerators of the amine and complex thiol or disulphide type should change the course of sulphuration from the polar processes obtaining in unaccelerated systems. They also point out that if persulphenyl radicals were formed, they would be expected to undergo additive sulphuration of the olefin in competition with substitutive sulphuration which is contrary to the known disubstitutive sulphuration pattern for "efficient" accelerated sulphuration. Thus Bateman et al(14) put forward a polar mechanism of accelerated sulphur vulcanization which could be regarded as an extension of their studies of unaccelerated vulcanization. The polar mechanism which is condensed below fits the overall course of accelerated sulphur vulcanization of Porter(29) described earlier and more generally accepted.

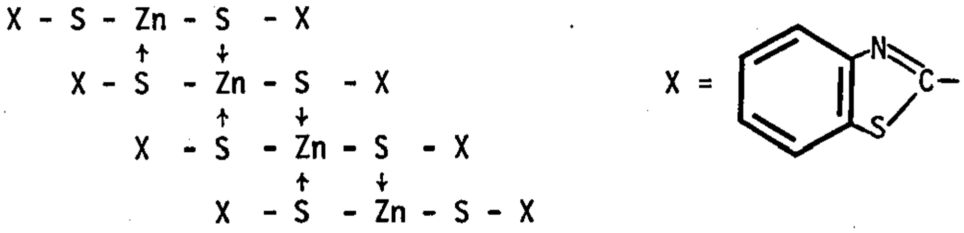
Polar Mechanism

Process (1) - Formation of Sulphurating Agents(14)

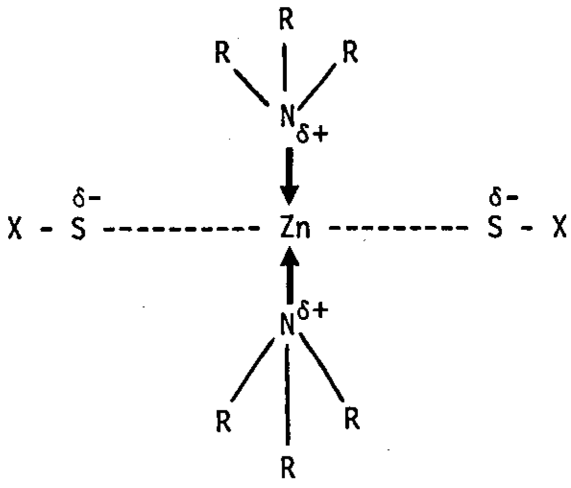
Accelerators are regarded as soluble zinc mercaptide species which are either internally chelated as in zinc dimethyldithiocarbamate (A) or a complex of otherwise insoluble zinc benzothiazyl mercaptide (B) rendered soluble through coordination of amine or carboxylate ligands to the zinc atom as in (C)



[A]

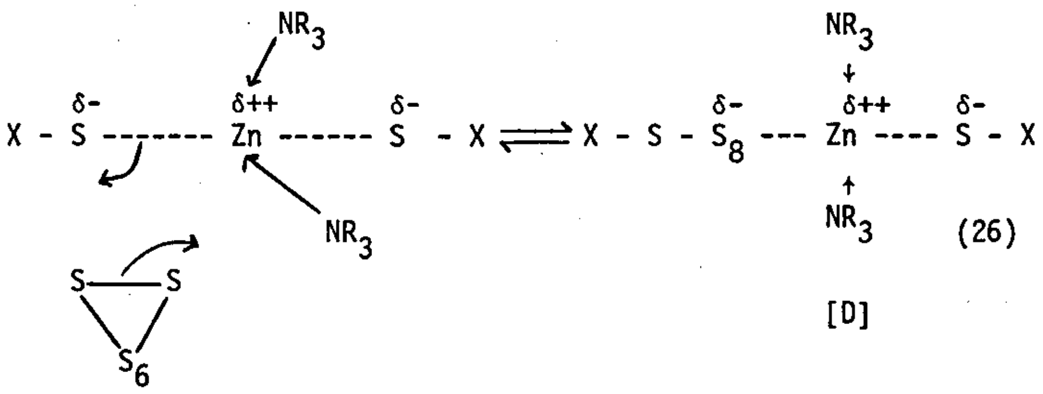


[B]

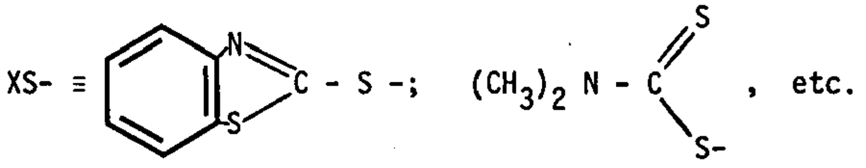


[C]

The fission of the S_8 ring is considered due to attack by the nucleophilic sulphur atom of the accelerator complexes while Krebs(36) was of the view that the addition of a Lewis base e.g. amines aided the ionic scission of the sulphur. However, the fission of the sulphur ring, according to Bateman et al(14), is shown in equation 26 below



(26)



The sulphurating complexes such as [D] will react with other accelerator molecules to yield a spectrum of sulphurating complexes of varying sulphur chain length

$$X-S-S_8-Zn-S-X \xrightleftharpoons{n(XS-Zn-SX)} \underset{[E]}{X-S-Sx-Zn-S-X} \qquad (27)$$

$$\xrightleftharpoons{X-S-Sx-Zn-S-X} \underset{[F]}{X-S-Sx-Zn-Sx-S-X} + X-S-Zn-S-X$$

Complexes D, E and F are thought to act as sulphurating agents for olefin. Formation of these complexes are also possible in a TMTD-Zinc oxide "sulphurless system" and they are probably formed via thiuram polysulphides which result from prior interaction of TMTD with zinc oxide or with a basic zinc salt derived from a naturally occurring acid in the rubber. The interchange between the thiuram polysulphides and zinc dimethyldithiocarbamate would then yield the type of sulphurating complexes discussed above.

Process 2 - Initial Crosslinking of Rubber Molecules(14)

The interaction of olefins and diene rubbers with sulphur in the presence of thiazole and dithiocarbamate classes of accelerators together with soluble entities conform to the equation below under efficient crosslinking conditions:

$$2RH + S_{x+1} + ZnO \xrightarrow[ZD_mC\ etc]{MBT\ CBS} R\ S_x\ R + H_2O + ZnS \qquad (28)$$

Therefore it was deduced that process 2 consists of asequence of reactions: (i) which leads to polysulphidic crosslinks by disubstitutive sulphuration of the olefin at α-methylic and α-methylenic groups, (ii) which is unlikely to involve the intermediate formation of a free hydrocarbon reactive species (either radical or ionic) since allylic rearrangement of alkenyl groups only occurs to a minor extent in the initial crosslinked polysulphides and (iii) which gives one mole of zinc sulphide per crosslink. The reaction sequence of the overall sulphuration reaction is given below:

$$RH + XSS_xZnS_ySX \rightarrow RS_xSX + ZnS + XS_yH \qquad (29)$$

$$2RS_xSX \xrightarrow[(Catalyst)]{XSZnSX} RS_{2z}R + XS_{2(x+1-z)}X \qquad (30)$$

$$ZnS + XS_{2(x+1-z)}X \longrightarrow XS_{(x+2-z)}\ ZnS_{(x+1-z)}X \qquad (31)$$

$$2XS_yH + ZnO \longrightarrow XS_yZnS_yX + H_2O \qquad (32)$$

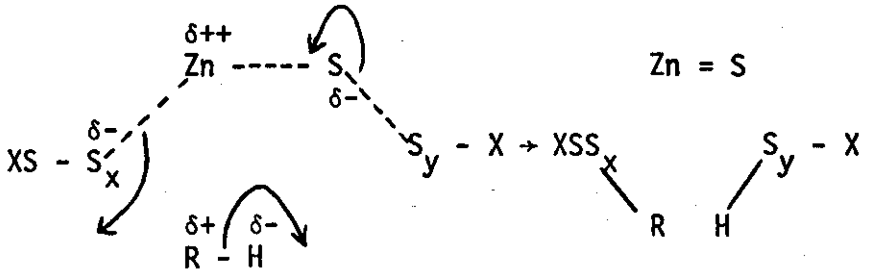
(x, y, z are integers; X = accelerator residue)

and the overall stoichiometry is

$$2RH + 2XSS_xZnS_ySX + ZnO \longrightarrow RS_{2z}R + H_2O + ZnS$$

$$+ XS_{(x+2-z)}\ ZnS_{(x+1-z)}X + XS_yZnS_yX \qquad (33)$$

If zinc oxide or basic soap is absent, accelerated vulcanization is still possible via equations (29)-(31) but the crosslinking potential of the incident sulphur will be diminished since the regenerative path of equation 32 reforming the active sulphurating complex is then lacking. Thus, it was proposed that accelerated sulphuration proceeds by a polar mechanism having many features in common with that of unaccelerated sulphuration(14,15)



(34)

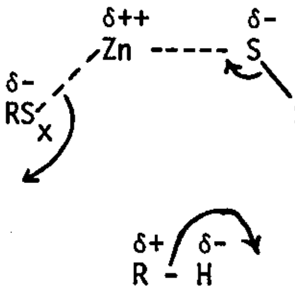
A probable route for the conversion of the sulphurated intermediate RS_xSX into the crosslinked polysulphides is by the disproportionation process (equation 30) involving interchange of S-S bonds catalysed by XS^- ions derived from the zinc mercaptide or by similar persulphenyl anions:

$$RS_xSX + XS^- \rightarrow RS_z^- + XS_{(x+2-z)}X \qquad (35)$$

$$RS_z^- + RS_xSX \rightarrow RS_{2z}R + XS^-_{(x+1-z)} \text{ etc.} \qquad (36)$$

These reactions are judged to be energetically easier than a route involving the further sulphuration of the olefin as depicted below:

$$RS_xSX + XSS_x\ ZnS_ySX \rightarrow RS_xZnS_xSX + XSS_ySX \qquad (37)$$

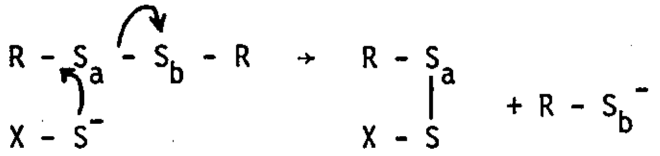


$$\longrightarrow RS_xR + ZnS + HS_xX \qquad (38)$$

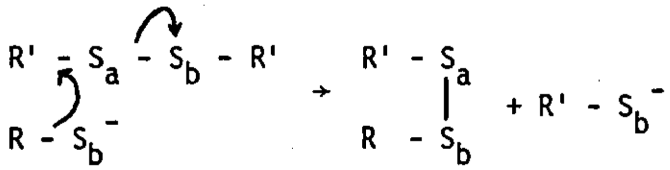
Also, the reaction in equation (38) contributes to the overall crosslinking process.

Process 3 - "Maturing" of initially formed networks(14)

Chemical probes and anaerobic stress relaxation techniques have been used to identify the reactions which the initially formed polysulphidic crosslinks undergo on further heating. The reactions are (i) crosslink shortening, leading finally to monosulphidic crosslinks, and (ii) catastrophic destruction of the crosslink. The sulphur removed in both reactions may appear as zinc sulphide or **be recycled** through the accelerator sulphur complex into fresh crosslinks while the rate of reaction (ii) is likely to increase with polysulphide chain length. It is also possible during "maturing" that di- and polysulphidic crosslinks undergo dynamic interchange with like crosslinks and with similar sulphidic chains present in pendant groups or intramolecular loops. Such interchange may be facilitated by high temperature or by nucleophilic reagents such as sulphenyl and persulphenyl anions derived from the accelerator complex:



$$\begin{array}{l} R - S_a - S_b - R \\ X - S^- \end{array} \rightarrow \begin{array}{l} R - S_a \\ \quad\;\; | \\ X - S \end{array} + R - S_b^- \qquad (39)$$



$$\begin{array}{l} R' - S_a - S_b - R' \\ R - S_b^- \end{array} \rightarrow \begin{array}{l} R' - S_a \\ \qquad | \\ R \; - S_b \end{array} + R' - S_b^- \qquad (40)$$

$$R' - S_b^- + R - S_a - S - X \rightarrow R' - S_b - S_a - R + X - S^- \text{ etc} \qquad (41)$$

Signs of dynamic interchanges are most noticeable when the vulcanizate is deformed and will be reflected in physical properties as stress relaxation, creep, compression set and permanent set as the interchangeable crosslinks slip into elastically ineffective positions. A schematic diagram of competing processes that take place during "maturing" of initially formed network is shown below in Figure 1.5:

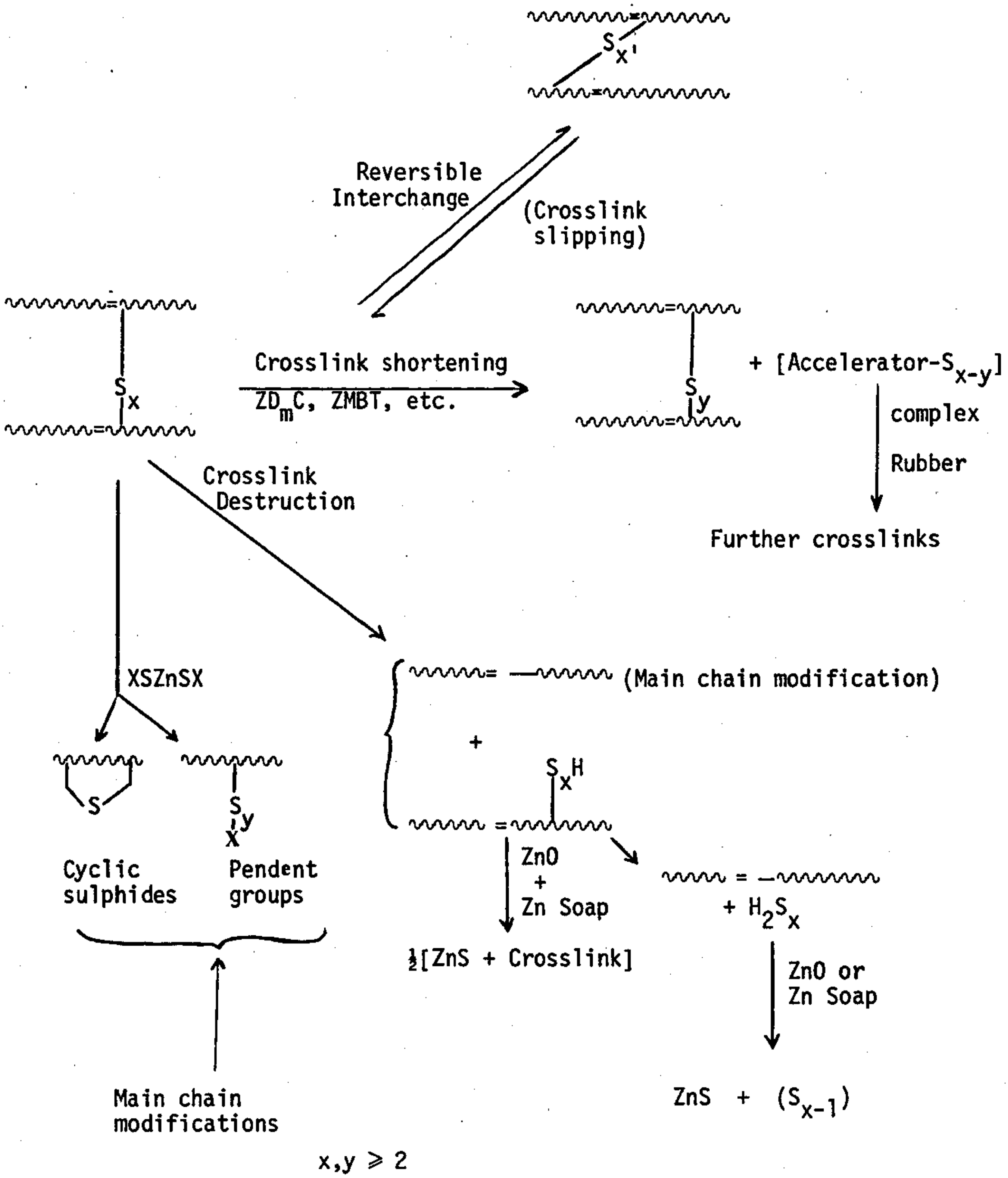


FIGURE 1.5: Competing Processes Involved in the "Maturing" of Initial Polysulphidic Crosslinked Networks(14)

In view of the different opinions about the mechanism of accelerated sulphur vulcanization, Shelton and McDonel(37) attempted to establish the free radical or polar character of curing reactions by determining the effect of free-radical scavengers or traps on the rate of cross-linking in SBR (styrene-butadiene rubber) with a variety of curing systems. The method has a limited use since a retardation effect may result from the scavenger displaying other reactivity and participating in a non-radical process. However, the following classification for a variety of curing systems were given:

Unaccelerated sulphur Guanidine-accelerated sulphur	POLAR
Thiuram disulphide-accelerated sulphur Dithiocarbamate-accelerated sulphur Thiazole-accelerated sulphur	PREDOMINANTLY POLAR
Thiazole/disulphide-accelerated sulphur Sulphenamide-accelerated sulphur	MIXED POLAR AND FREE RADICAL
Thiuram disulphide	INCONCLUSIVE
Peroxide cure Radiation cure	FREE RADICAL

1.3 Vulcanization by "Sulphur Donors"

As the name implies, these are compounds which vulcanize diene-based rubbers by releasing sulphur during curing.

The organic sulphur donor compounds may be accelerators themselves such as the tetraalkylthiuram disulphides while other compounds may require the addition of accelerators as does sulphur. Examples of the latter type are dimorpholinyl disulphide and alkyl phenol polysulphides(38-40). One notable characteristic of sulphur-donor compounds is their resistance to heat ageing without additional antioxidant and exhibiting negligible modulus reversion on extended cure. A typical curing system and crosslink formation will be illustrated with tetramethylthiuram disulphide (TMTD).

Some measure of crosslinking in natural rubber (NR) can be realised by using large proportions of TMTD (10 parts TMTD per 100 parts NR) without any metal activator(35,41). However, a metal oxide or soap or sulphide is necessary to achieve the best crosslinking potential: in this regard, zinc oxide is about the most effective activator(42,43). The network structures obtained from NR-TMTD-ZnO vulcanized to different levels are shown below in Figures 1.6a and 1.6b:

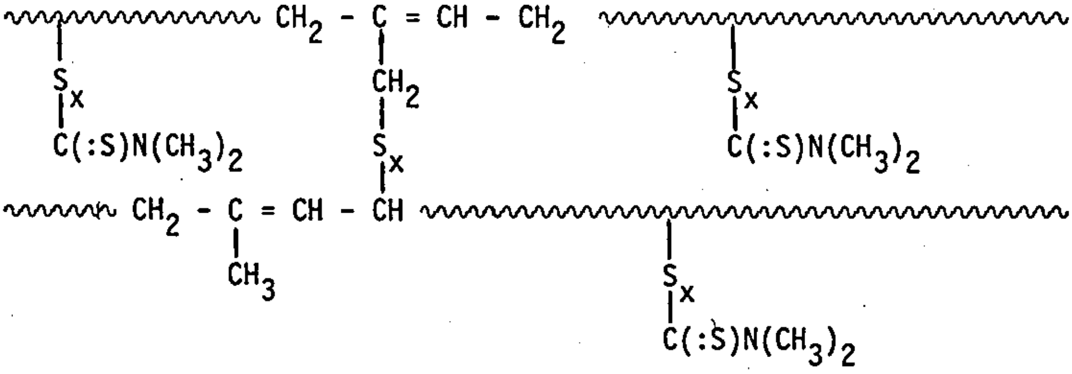


FIGURE 1.6a: ($x \geqslant 2$) (short cure time)

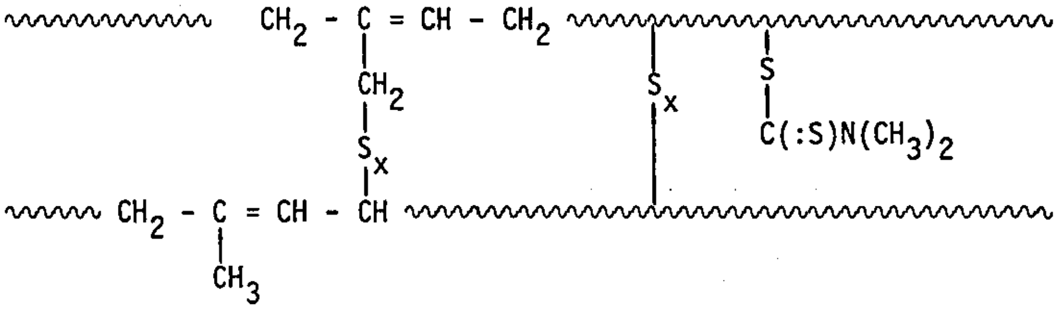
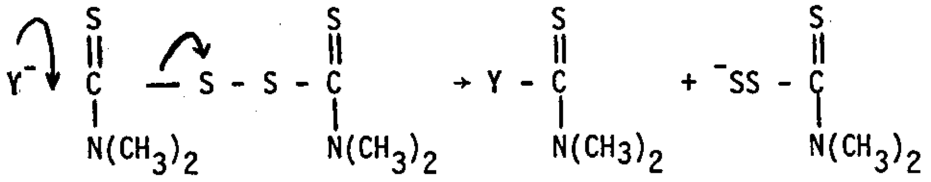


FIGURE 1.6b: (x mainly 1) (long cure time)

FIGURES 1.6a and 1.6b: Network structures formed in the NR-TMTD -zinc oxide system at different cure times(14)

Crosslinks are entirely sulphidic(44) as opposed to earlier views that C-C crosslinks are involved(45). Evidence for this assertion arises from the complete degradation of the network when it is treated with methyl iodide at 80°C whereas an insignificant degradation results when a dicumyl peroxide-cured NR network is treated comparably. Methyl iodide is known to cause the fission of C-S and S-S bonds in variously constituted organic mono- and polysulphides(20,21) and should act thus on a vulcanizate with similar sulphur crosslinks while being without effect on C-C crosslinks. Other studies on the NR-TMTD-ZnO vulcanization have been treated elsewhere(34,46-55).

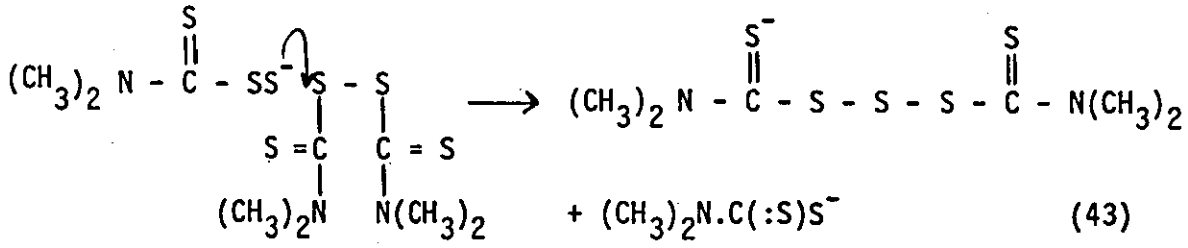
The mechanism of crosslinking in the NR-TMTD-ZnO has been treated as an extension of the accelerated sulphur vulcanization(14) discussed earlier. Sulphurating agents are proposed to be formed via thiuram polysulphides which result from prior interaction of TMTD with zinc oxide or with a basic zinc salt derived from a naturally occurring acid in the rubber. Formation of thiuram polysulphides is probably through a nucleophilic attack of a basic oxyanion (e.g. from Zn^{++} ---O$^=$ or RCO$_2$Zn$^+$ ---- $^-$OH) which is designated Y$^-$ on the electrophilic thionocarbon atom of TMTD(55)



$$Y^- + (CH_3)_2N-\overset{S}{\overset{\|}{C}}-S-S-\overset{S}{\overset{\|}{C}}-N(CH_3)_2 \rightarrow Y-\overset{S}{\overset{\|}{C}}-N(CH_3)_2 + {}^-SS-\overset{S}{\overset{\|}{C}}-N(CH_3)_2 \qquad (42)$$

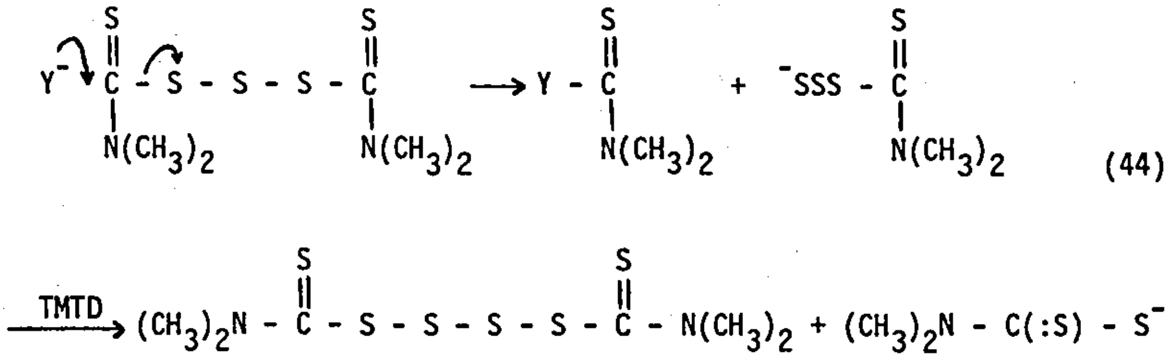
[K]

The perthioanion [K] then preferentially attacks a disulphidic sulphur atom in TMTD to give tetramethylthiuram trisulphide.



$$(CH_3)_2N-\overset{S}{\overset{\|}{C}}-SS^-\;\underset{\underset{(CH_3)_2N}{|}}{\underset{S=C}{|}}{S}-\underset{\underset{N(CH_3)_2}{|}}{\underset{C=S}{|}}{S} \longrightarrow (CH_3)_2N-\overset{S^-}{\overset{\|}{C}}-S-S-S-\overset{S}{\overset{\|}{C}}-N(CH_3)_2 + (CH_3)_2N.C(:S)S^- \qquad (43)$$

Further attack by Y^- on the trisulphide yields higher polysulphides:



$$Y^-\;\underset{\underset{N(CH_3)_2}{|}}{\overset{S}{\overset{\|}{C}}}-S-S-S-\underset{\underset{N(CH_3)_2}{|}}{\overset{S}{\overset{\|}{C}}} \longrightarrow Y-\underset{\underset{N(CH_3)_2}{|}}{\overset{S}{\overset{\|}{C}}} + {}^-SSS-\underset{\underset{N(CH_3)_2}{|}}{\overset{S}{\overset{\|}{C}}} \qquad (44)$$

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

If Y^- is specifically ZnO, then the overall stoichiometry is represented in equation below:

$$nTMTD + (n-1)\,ZnO \longrightarrow (CH_3)_2\,NC(:S)SS_{n-1}\,SC(:S)\,N(CH_3)_2$$

$$+ \quad \tfrac{1}{2}(n-1)[(CH_3)_2NC(:S)O]_2\,Zn + \tfrac{1}{2}(n-1)[(CH_3)_2NC(:S)S]_2\,Zn \qquad (45)$$

Interchange between the thiuram polysulphides and zinc dimethyldithiocarbamate would yield the actual sulphurating complexes (e.g. [L] and [M]) which are examples of the general cases [E] and [F]

$$\text{e.g } (CH_3)_2\,N-C(:S)SSSSC(:S)-N(CH_3)_2 + [(CH_3)_2N-C(:S)S]_2\,Zn \rightleftharpoons$$

$$(CH_3)_2\,N-C(:S)SSS\underset{[L]}{-Zn}-SC(:S)-N(CH_3)_2 + (CH_3)_2N-C(:S)S_2C(:S)-N(CH_3)$$

$$\Big\downarrow\!\Big\uparrow \qquad\qquad (46)$$

$$\tfrac{1}{2}[\underset{[M]}{(CH_3)_2}\,N-C(:S)SSS]_2Zn + \tfrac{1}{2}[(CH_3)_2N-C(:S)S]_2Zn$$

1.4 Peroxide Vulcanization

Ever since Thomas Hancock and Charles Goodyear cured rubber with sulphur in about 1843, sulphur has been the predominant curing agent in the rubber industry. It was not until 1915 that an alternative curing agent was reported when Ostromyslenski(56) published information on the use of benzoyl peroxide for curing caoutchouc. Even then, considerable interest was not generated on the subject of peroxide vulcanization until about 1929. This is evident from the absence of an appreciable amount of work during the time interval between these two periods. A disadvantage of benzoyl peroxide curing however, is due to surface blooming of benzoic acid produced from the decomposition of the peroxide. Also vulcanizates obtained have poor physical properties and poor resistance to heat ageing.

Fisher and Gray(57) investigated the extent to which the degree of saturation of rubber was affected during vulcanization with benzoyl peroxide. They found that the saturation of the rubber was not altered and hence assumed that the vulcanization of rubber does not depend upon a saturation of the double bond of C_5H_8 by oxygen.

Braden and Fletcher(58) have described vulcanization of natural rubber with dicumyl peroxide using different compounding ingredients and compared it with sulphur-cured compounds. Their results showed the oven ageing of dicumyl peroxide-cured vulcanizates to be notably different from that of conventional sulphur-cured rubbers in that modulus of peroxide-cured vulcanizates was little affected. The explanation given was that, whereas rearrangement can take place between polysulphide crosslinks, cyclic sulphides and free sulphur in a conventional vulcanizate on ageing, no such changes are possible in the case of the carbon-carbon crosslink of a peroxide vulcanizate: only chain scission can occur on ageing. However, a limitation on dicumyl peroxide vulcanization reported is the lack of means of accelerating or retarding vulcanization and tendency to scorch.

(It is possible to use free radical acceptors or scavengers to retard vulcanization in peroxide systems(59)).

Through the use of high temperature stress relaxation measurements, it was shown that peroxide vulcanizates of natural rubber have good resistance to degradation(60). Earlier work(58) indicated that ageing resistance of peroxide-cured vulcanizates were improved when lime (CaO) was included in the compounding recipe.

A general survey of peroxide vulcanization was carried out by Braden et al(61). They listed the factors governing the choice of peroxide which are stated below:

i) It must be safe to handle at processing temperatures and must be non-toxic and non-irritant.

ii) Its ultimate decomposition products should be harmless.

iii) It should not combine with rubber in side reactions which are wasteful of peroxide and may introduce groups having an adverse effect on the cured rubber.

iv) Its decomposition temperature in the presence of rubber must not be so low that scorching occurs during compounding but rapid decomposition at curing temperature is desirable for a short cure.

v) It must not be so volatile that losses occur in mixing.

vi) Neither the peroxide nor its decomposition products should catalyse oxidation of the rubber.

vii) It should be effective in the presence of reinforcing fillers in order not to limit its application to gum vulcanizates.

Other areas of peroxide crosslinking of natural rubber include the investigation of crosslinking efficiency in the reaction of dicumyl peroxide with a model olefin 2,6-dimethyloctadiene(62) as well as in natural rubber(63,64). It is worth mentioning that apart from natural rubber, other diene-based elastomers can be crosslinked by peroxides and they can be discussed in terms of the pattern developed for natural rubber. Below is a summary of polymers that can be crosslinked by peroxides(65):

NR - natural rubber
SBR - styrene-butadiene rubber
BR - polybutadiene rubber
IR - polyisoprene rubber
NBR - nitrile rubber
CR - polychloroprene rubber
EPM - ethylene-propylene copolymer
EPDM - ethylene-propylene diene monomer rubber
Si,VSi- silicone rubber
Acrylic rubber
Polysulphide rubber
AU,EU- polyurethane elastomers
ABS - acrylonitrile-butadiene-styrene
PE - polyethylene
CSM - chlorosulphonated polyethylene
CM - chlorinated polyethylene
FKM - fluorocarbon rubber

and polymers that cannot be crosslinked by peroxides are:

IIR - butyl rubber
Polyisobutylene rubber
CO,ECO- polyepichlorohydrin rubber
PP - polypropylene
PVC - poly(vinyl chloride)

TABLE 1.4: Trade Names and Manufacturers of Some Organic Peroxides Used for Crosslinking(65-68)

CHEMICAL NAME	MANUFACTURER AND TRADE NAME					
	Akzo Chemie bv Amersfoort Netherlands	Hercules Europe SA Brussels, Belgium	Luperox GmbH Pennwalt Corp Gunzburg, FRG	Montedison Spa Mailand Italy	Peroxid-Chemie GmbH (Interox) Munchen, FRG	Witco (USP) Richmond, USA
2,5-dimethyl-2,5-di-t.butylperoxy hexyne-3			Luperox 130 Luperox 130XL			
2,5-dimethyl-2,5-di-(t.butylperoxy)-hexane			Luperox 101 Luperox 101XL			
di-t-butyl peroxide	Trigonox B Trigonox B-50E		Luperox DI Luperos Diop 31	Peroximon DB	Interox DIPB	DTBP
bis(t-butylperoxy-isopropyl) benzene	Perkadox 14-90 Perkadox 14-40B Perkadox 14-40K Perkadox 14-40 MB Perkadox 14-40P Perkadox 14-40 MK	Vulcup R Vulcup 40C Vulcup 40KE	Luperco 802G	Peroximon F Peroximon F-40 Peroximon F-40 MG	Interox DIPB-40CA	
t-butyl cumyl peroxide	Trigonox T-95 Trigonox T-50		D-801			

TABLE 1.4: continued

dicumyl peroxide	Perkadox BC-95 Perkadox BC-40B Perkadox BC-40K Perkadox BC-40MB Perkadox BC-40P	Dicup R(T) Dicup 40C Dicup 40KE	Luperco 500R/C Luperco 540G Luperco 500C Luperco 540KE Luperco 540PE	Peroximon DC Peroximon DC-40 Peroximon DC-40K Peroximon DC-40 MG	Interox DCUP Interox DCUP-40CA	
4,4-di-t-butylperoxy-n-butylvalerate	Trigonox 17-40B Trigonox 17-40MB		Luperco 230XL(P)			
1,1-di-t-butylperoxy-cyclohexane	Trigonox 22-B50 Trigonox 22-E50		Luperox 331-50		Interox CH-50FT Interox CH-50AL	USP-400XL USP-400P
1,1-di-t-butylperoxy-3,3,5-trimethyl cyclohexane	Trigonox 29-40B Trigonox 29-40MB		Luperco 231KLP Luperco 231XL,G		Interox TMCH-40BC Interox TMCH-50BC	
t-butylperoxy benzoate	Trigonox C Trigonox C-50D		Luperox P		Interox TBPB Interox TBPB-50IC	Esperox 10 Esperox 10XL
2,2-bis(t-butylperoxy) butane	Trigonox DB-50		Luperox 220		Interox BU-50AL	
dibenzoyl peroxide	Lucidol S-50S		Luperco AST		Interox BP-50PSI	
bis(2,4-dichloro-benzoyl)peroxide	Perkadox PD-50S Perkadox PD-50F		Luperco CST		Interox DCLBP-50-PSI	
bis(p-chlorobenzoyl) peroxide	Perkadox PC-50S				Interox CLBP-50-PSI	

1.4.1 Classification of Peroxides

Peroxides that may be used for curing polymers fall into three groups. These are:

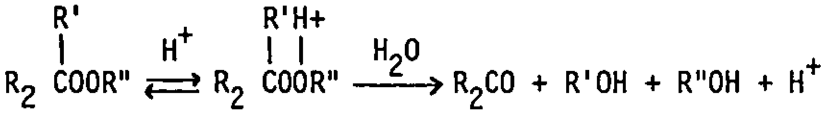
a) diacyl peroxides (ROC-OO-COR) e.g. benzoyl peroxide
b) dialkyl or diaralkyl peroxides (R-OO-R) e.g. di-tertiary butyl peroxide
c) peresters (ROC-OO-R) e.g. tertiary butyl benzoate.

Diacyl peroxides give low crosslinking efficiency and usually require about 10 phr for adequate curing. Some dialkyl peroxides and peresters give high crosslinking efficiencies, however, it is mainly di-tertiary butyl peroxide and dicumyl peroxide (diaralkyl peroxide) that are capable of curing compounds containing reinforcing black fillers. Di-tertiary butyl peroxide has a disadvantage because of its volatile nature thereby leaving dicumyl peroxide as the most generally useful peroxide(40). Several other organic peroxides have been developed recently and are commercially available. Some of the peroxides are listed in Table 1.4.

1.4.2 Effect of Compounding Ingredients on Peroxide Crosslinking

1.4.2.1 Fillers

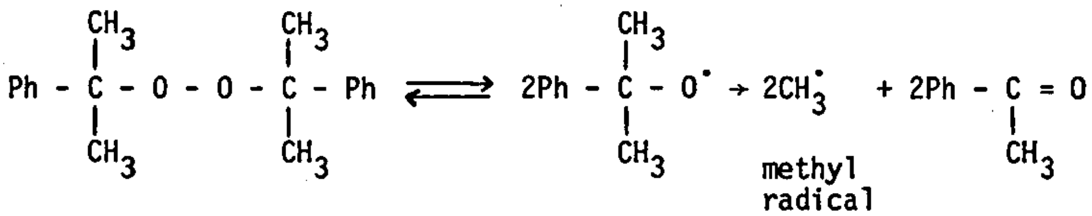
Fillers with acidic surface tend to cause the heterolytic fission of peroxides. The fission reaction leads to peroxide fragments which cannot initiate cure and consequently a reduction in the efficiency of the peroxide as a crosslinking agent. Neutral and basic fillers appear to have no effect on peroxides. A catalysed, non-radical breakdown of the peroxide may be represented in the equation below(69):



$$R_2\overset{\overset{R'}{|}}{C}OOR'' \xrightleftharpoons{H^+} R_2\overset{\overset{R'H+}{||}}{C}OOR'' \xrightarrow{H_2O} R_2CO + R'OH + R''OH + H^+ \qquad (47)$$

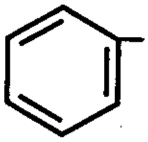
The effect of various media on the decomposition of peroxides could be illustrated with the decomposition of dicumyl peroxide in different media shown in (a) and (b) respectively.

a) *Neutral or alkaline media*



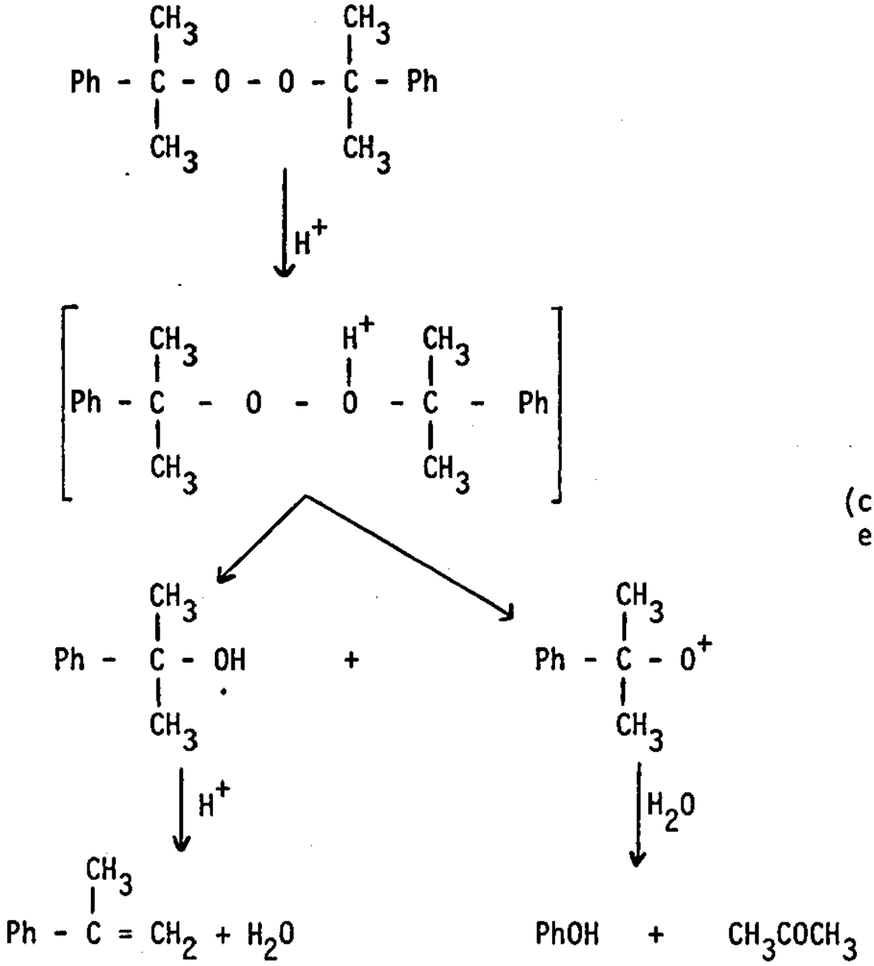
$$Ph-\underset{CH_3}{\overset{CH_3}{C}}-O-O-\underset{CH_3}{\overset{CH_3}{C}}-Ph \rightleftharpoons 2Ph-\underset{CH_3}{\overset{CH_3}{C}}-O^{\bullet} \rightarrow 2CH_3^{\bullet} + 2Ph-\underset{CH_3}{C}=O$$

dicumyl peroxide | cumyloxy radical | methyl radical | acetophenone

Ph - = 

(48)

b) *Acid media*



$$Ph-\underset{CH_3}{\overset{CH_3}{C}}-O-O-\underset{CH_3}{\overset{CH_3}{C}}-Ph \xrightarrow{H^+} \left[Ph-\underset{CH_3}{\overset{CH_3}{C}}-O-\overset{H^+}{O}-\underset{CH_3}{\overset{CH_3}{C}}-Ph\right]$$

$$\rightarrow Ph-\underset{CH_3}{\overset{CH_3}{C}}-OH + Ph-\underset{CH_3}{\overset{CH_3}{C}}-O^+$$

$$Ph-\underset{CH_3}{\overset{CH_3}{C}}-OH \xrightarrow{H^+} Ph-\overset{CH_3}{C}=CH_2 + H_2O$$

$$Ph-\underset{CH_3}{\overset{CH_3}{C}}-O^+ \xrightarrow{H_2O} PhOH + CH_3COCH_3$$

(compare with equation 47)

(methyl styrene) (phenol) (acetone)

It is also possible that adsorption of peroxides onto the surface of the filler may sometimes lead to poor cures; this possibility appears most likely with silica(69). The detrimental influence on the crosslinking process due to acidic fillers can be corrected by the addition of alkaline activators like diphenyl guanidine while the problem due to adsorption of peroxides can be lessened by silanisation.

1.4.2.2 Oils and Plasticizers

All oils and plasticizers reduce the efficiency of peroxides because some of the radicals generated are transferred to the oil and do not lead to crosslinking. The extent to which these materials reduce cure efficiency is dependent on the level of addition and the type of oil or plasticizer used. Aromatic oils have the greatest detrimental effect while paraffinic oils have the least effect; naphthenic oils are intermediate.

1.4.2.3 Antidegradants

All antidegradants reduce the efficiency of peroxides during vulcanization. The amine-type antioxidants are preferred since they have the least effect on cure, while phenolic-type antioxidants inhibit cure to a greater extent. Antiozonants are best avoided in peroxide-cured formulations because they greatly reduce the cure efficiency.

The use of sulphur as an additive in peroxide formulations has been said to cause a reduction in crosslinking efficiency without affecting decomposition rate of peroxides(69). Thus it was suggested that sulphur interferes in free radical crosslinking reaction.

In general, any compounding ingredient that acts as a free radical acceptor or that may cause the heterolytic fission of peroxides leads to wastage, and consequently poor crosslinking.

TABLE 1.5: Properties of Natural Rubber Vulcanizates Cured with Dicumyl Peroxide for 60 Minutes at 150°C (70)
(Dihydroquinoline antioxidant)

SMR L	100	100	100	100	100
HAF Black N330	50	50	50	50	50
Dutrex 729	3	3	3	3	3
Zinc Oxide	5	5	5	5	5
Flectol H	2	2	2	2	2
Dicumyl peroxide	2	2.5	3	3.5	S/CBS*
Initial Vulcanizate Properties					
Hardness (IRHD)	57	60	63	66	64
Relaxed modulus (MR 100) MPa	1.69	2.12	2.64	3.78	2.10
Tensile Strength, MPa	23.0	24.7	23.7	20.4	28
Elongation at break %	370	340	300	235	505
Dunlop resilience, %	68	70	72	74	66
Akron abrasion, mm^3/500 rev	35	38	35	38	35
Ring fatigue 0-100% extn,kcs	58	52	39	10	92
Goodrich heat build-up, °C	40	38	33	33	35
Compression set, 25% (24 hours at 70°C)	10	8	7	6	26
Aged Vulcanizate Properties					
7 days at 100°C					
Tensile Strength, % retention	43	47	50	58	25
Elongation at break % retention	81	79	78	82	24
200% modulus, % retention	64	66	81	76	-
3 days at 125°C					
Tensile Strength, % retention	24	23	43	50	-
Elongation at break % retention	86	72	91	96	-
200% modulus, % retention	33	39	52	55	-

* Stearic Acid, 3; Sulphur, 2.5; CBS, 0.5.
Cured 25 mins at 150°C

TABLE 1.6: Properties of Natural Rubber Vulcanizates Cured with Dicumyl Peroxide for 2 hours at 150°C (70)

(Dihydroquinoline antioxidant)

SMR L	100	100	100	100	100
HAF Black N330	50	50	50	50	50
Dutrex 729	3	3	3	3	3
Zinc Oxide	5	5	5	5	5
Flectol H	2	2	2	2	2
Dicumyl peroxide	2	2.5	3	3.5	S/CBS*
Initial Vulcanizate Properties					
Hardness, IRHD	59	61	63	66	64
Relaxed modulus (MR 100)MPa	1.8	2.28	2.58	3.11	2.1
Tensile Strength, MPa	20.5	21.4	21.8	18.9	28
Elongation at break %	335	310	290	240	505
Dunlop resilience, %	68	72	75	76	66
Akron Abrasion, mm^3/500 rev	35	37	46	47	35
Ring fatigue 0-100% extn.,kcs	94	51	25	18	92
Goodrich heat build-up °C	37	34	32	31	35
Compression Set, 25% (24 hrs at 70%)	13	11	10	8	26
Aged Vulcanizate Properties					
7 days at 100°C					
Tensile Strength, % retention	54	51	50	65	25
Elongation at break, % retention	93	79	78	89	24
200% modulus, % retention	60	78	79	83	-
3 days at 125°C					
Tensile Strength, % retention	35	43	47	55	-
Elongation at break, % retention	100	92	89	93	
200% modulus, % retention	34	53	58	68	

* Stearic Acid, 3; Sulphur, 2.5; CBS, 0.5.
Cured 25 mins at 150°C

TABLE 1.7: Properties of Natural Rubber Vulcanizates Cured with Dicumyl Peroxide for 60 minutes at 150°C (70)

(p-phenylenediamine antioxidant)

SMR L	100	100	100	100	100
HAF Black N330	50	50	50	50	50
Dutrex 729	3	3	3	3	4
Zinc Oxide	5	5	5	5	5
Santoflex 13	2	2	2	2	2
Dicumyl Peroxide	2	2.5	3	3.5	S/CBS*
Initial Vulcanizate Properties					
Hardness IRHD	52	55	57	59	66
Relaxed modulus (MR100) MPa	1.14	1.39	1.61	1.85	2.0
Tensile Strength, MPa	23.1	23.2	24.2	24.1	31.0
Elongation at break, %	455	420	395	360	545
Dunlop resilience, %	64	68	71	72	66
Akron abrasion mm^3/500 rev	41	44	38	38	36
Ring fatigue 0-100% extn,kcs	127	100	115	76	258
Goodrich heat build-up °C	41	39	34	42	32
Compression set (25%, 24 hrs at 70°C) %	16	15	14	11	30
Aged Vulcanizate Properties					
7 days at 100°C					
Tensile Strength, % retention	37	48	57	62	21
Elongation at break, % retention	96	92	102	102	21
200% modulus, % retention	43	51	53	60	-
3 days at 125°C					
Tensile Strength, % retention	15	24	22	37	17
Elongation at break, % retention	103	102	81	100	6
200% modulus, % retention	21	27	33	39	-

* Stearic Acid, 3; Sulphur, 2.5; CBS, 0.5
Cured 40 mins at 140°C.

Typical data on the use of dicumyl peroxide to vulcanize natural rubber was presented by Baker$^{(70)}$ and some of these are shown in Tables 1.5-1.7.

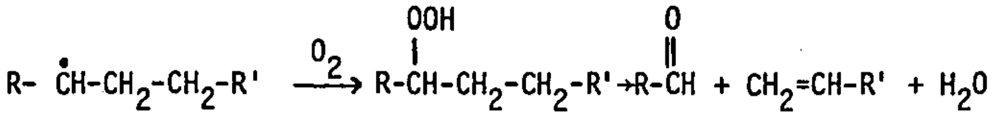
The data demonstrate the excellent compression set resistance of peroxide-cured vulcanizates. However, it was found that the ageing properties of vulcanizates cured for 1 hr at 150°C were relatively poor (Table 1.5). An increase in the cure time led to an improved ageing performance (Table 1.6); hence the conclusion that if the optimum ageing performance is to be achieved with peroxide cures, longer cure times are desirable although this may be at the expense of some initial vulcanizate properties. Table 1.7 also shows that the dihydroquinoline type antioxidant interferes less with peroxide curing than p-phenylenediamine antioxidant.

1.4.3 Advantages and Disadvantages of Peroxide Crosslinking

Obvious advantages of peroxide curing are non-reversion during cure and good ageing resistance (carbon-carbon bonds are thermally stable (e.g. C-C = 343 kJ; cf C-S = 276 kJ, S-S = 205 kJ). Also, peroxide-cured vulcanizates have excellent resistance to compression set at elevated temperatures (70°C ∿ 100°C). Furthermore, peroxide compounding recipes do not usually include stearic acid, and accelerators as in sulphur vulcanization. Also, peroxide-cured recipes do not bloom and coagents could be included in compound recipe to improve modulus and hardness. (Coagents are polyunsaturated compounds e.g. triallylisocyanurate). Perhaps the most important advantage of peroxide vulcanization over other systems is their unique ability to crosslink saturated elastomers e.g. ethylene-propylene copolymer, polyethylene and chlorinated polyethylene.

Particular disadvantages of some peroxide-cured vulcanizates and compounds (e.g. with dicumyl peroxide) are the unpleasant odour during curing, poor fatigue resistance and tendency to scorch.

With regard to the latter problem, Chow and Knight(59) have made an attempt to use free radical scavengers to impart scorch delay to peroxide vulcanization systems. Their use of peroxide-activated maleimide vulcanization compares favourably with delayed-action sulphur systems. Another disadvantage is that any peroxide remaining undecomposed at the end of the vulcanization period may act as a potent pro-oxidant leading to inferior ageing performance and inferior high temperature compression set behaviour(71). Some peroxide-cured vulcanizates (e.g. silicones) require controlled post-curing in air after press-cure to remove decomposition products and to stabilize the vulcanizate. Furthermore some peroxides are not suitable for curing in air as they are inhibited by oxygen. If such a peroxide is used to cure in air, a radical that has been transferred to a polymer chain becomes susceptible to oxidation and a hydroperoxide is formed, which thermally decomposes in a reaction leading to polymer degradation (see equation 49 below):



$$R\text{-}\ \dot{C}H\text{-}CH_2\text{-}CH_2\text{-}R' \xrightarrow{O_2} R\text{-}\overset{\overset{OOH}{|}}{C}H\text{-}CH_2\text{-}CH_2\text{-}R' \rightarrow R\text{-}\overset{\overset{O}{\|}}{C}H + CH_2{=}CH\text{-}R' + H_2O$$

(49)

1.4.4 Cure Conditions

The cure temperature in peroxide formulations depends on the stability of peroxide. Peroxides with acid groups decompose at considerably lower temperatures than dialkyl or diaralkyl peroxide. Thus, dicumyl peroxide offers better processing safety than dibenzoyl peroxide.

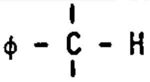
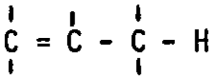
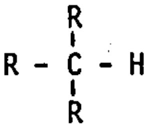
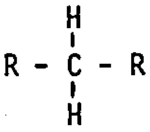
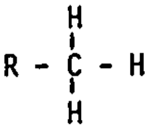
Although the cure conditions of peroxide systems can be determined by Monsanto Oscillating Disc Rheometer, the cure conditions may also be determined by the decomposition rate of the peroxide at the curing temperature. Graphs showing how the decomposition half-lives of peroxides in low molecular weight hydrocarbon solvent vary with temperature are provided by suppliers of organic peroxides(65-67).

Half-life is the time it takes one-half of any quantity of peroxide present to thermally decompose. Thus, to obtain substantially complete reaction of the peroxide, a cure time of at least six half-lives is required (leaving less than 1.6% of peroxide unreacted).

1.4.5 Mechanism of Peroxide Crosslinking

The mechanism of peroxide crosslinking is well known to proceed via a free radical reaction. An initial process is the thermally-induced homolytic cleavage of a peroxide molecule to yield two-oxy radicals. The free radicals abstract some of the more labile (e.g. α-methylenic) hydrogen atoms of the rubber hydrocarbon thus providing randomly distributed active centres which lead to crosslinking by mutual interaction with other rubber radicals(69).

The comparative ease with which hydrogens are abstracted by oxy radicals is a function of the hydrogen atom's reactivity. The following, lists hydrogen atom functionality in descending order of reactivity(65):

Most	$\phi - OH$	phenolic
	 $\phi - \underset{\vert}{\overset{\vert}{C}} - H$	benzylic
	 $\underset{\vert}{\overset{\vert}{C}} = \overset{\vert}{C} - \underset{\vert}{\overset{\vert}{C}} - H$	allylic
	 $R - \underset{R}{\overset{R}{C}} - H$	tertiary
	 $R - \underset{H}{\overset{H}{C}} - R$	secondary
Least	 $R - \underset{H}{\overset{H}{C}} - H$	primary

Another view of peroxide crosslinking was given by van Rossem et al(72) whose experiments showed benzoate groups as combined with rubber. In a later work, Farmer and Michael(73) concurred with van Rossem et al(72).

Loan(69) in a detailed review gave the mechanism of peroxide vulcanization of different elastomers. Unsaturated rubbers were said to be crosslinked by free radicals in either of the following two ways:

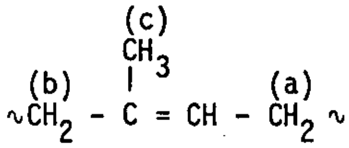
i) by hydrogen abstraction from an α-methylene group, and
ii) by addition to the double bond (illustrated by equations 51 and 52)

$$\mathrm{ROOR} \xrightarrow{\Delta\Delta} 2\mathrm{RO}^{\bullet} \text{ (neutral or basic medium assumed)} \qquad (50)$$

$$\mathrm{RO}^{\bullet} + \sim\mathrm{CH_2CH = CH}\sim \ \rightarrow \sim\mathrm{CH_2{-}CH(OR){-}\dot{C}H}\sim \qquad (51)$$

$$\begin{array}{l} \mathrm{RO}^{\bullet} + \sim\mathrm{CH_2CH = CH}\sim \ \rightarrow \sim\mathrm{ROH} + \sim \mathrm{\dot{C}H - CH = CH}\sim \qquad (52) \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \updownarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad \sim \mathrm{CH = CH - \dot{C}H}\sim \end{array}$$

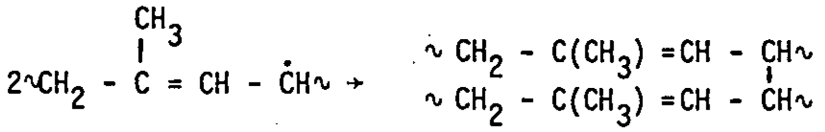
Reaction 51 is considered possible when benzoyl peroxide is used while reaction 52 is considered as the more important of the two reactions. With polyisoprenes, three types of α-methylenic hydrogen are available as shown below:



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

The order of reactivity of the three types of hydrogen atom is a > b > c(69).

The possible reaction paths for the macroradical from reaction 52 are explained in equations 53 through to 55:



(53)

$$2\sim CH_2 - \overset{CH_3}{\overset{|}{C}} = CH - \dot{C}H\sim \rightarrow \begin{array}{l} \sim CH_2 - C(CH_3) = CH - CH\sim \\ \hspace{9em}| \\ \sim CH_2 - C(CH_3) = CH - CH\sim \end{array} \qquad (53)$$

$$\begin{array}{c} \sim CH_2 - C(CH_3) = CH - CH_2 - CH_2C(CH_3) = CH - \dot{C}H\sim \\ \downarrow \\ \sim CH_2 - C(CH_3) = CH - \dot{C}H_2 + CH_2 = C(CH_3) - CH = CH \sim \end{array} \qquad (54)$$

$$\sim CH_2 - C(CH_3) = CH - \dot{C}H\sim + RO\cdot \rightarrow \sim CH_2 - C(CH_3) = CH - CH(OR)\sim \qquad (55)$$

Reaction 54 leads to scission while reaction 55 leads to radical wastage. Both reactions 54 and 55 must be at the possible minimum in order to have an efficient use of peroxide in crosslinking. Moore and co-workers$^{(74,75)}$ however, have discounted the possibility of scission during peroxide crosslinking of natural rubber.

There had been some investigation on the peroxide crosslinking of polybutadiene$^{(76-79)}$. Relatively high crosslinking efficiencies were obtained which were attributed to the polymer structure. As with polyisoprenes, the reaction between alkoxy radicals and polybutadiene could proceed via (i) the route illustrated in equation 51 and thus producing radical $\sim CH_2CH(OR) - \dot{C}HCH_2\sim$ or (ii) the route illustrated in equation 52 and thereby producing a radical $\sim\dot{C}HCH = CHCH_2\sim$; the latter radical is thought to be more reactive than the usual radical formed from polyisoprene ($\sim CH_2\dot{C}(CH_3)CH = CH\sim$). It may therefore add to a nearby double bond and initiate a sequence of further additions.

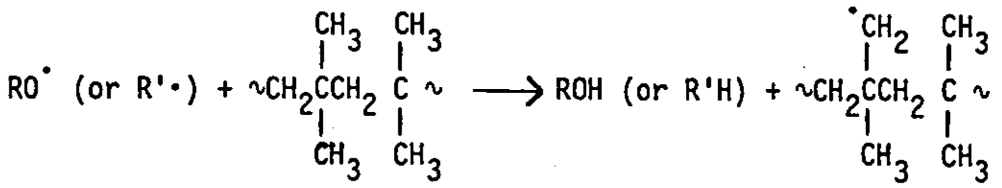
The crosslinking behaviour of styrene-butadiene rubber with peroxides has been shown to be similar to that of cis-polybutadiene(79). However, the relatively low crosslinking efficiency (<1) of nitrile rubber with peroxides led to a suggestion that the chain reaction observed with the homopolymer (butadiene) is probably suppressed in nitrile rubber by acrylonitrile residues.

A unique feature of peroxides as crosslinking agents is their ability to crosslink saturated elastomers for which there is hardly an alternative curing system (except radiation curing). Saturated elastomers that are peroxide-curable are ethylene-propylene copolymer and polydimethyl siloxane (silicone rubber). The curing system for ethylene-propylene copolymer has been studied(80-82) and another work demonstrated the extent of scission during crosslinking(83).

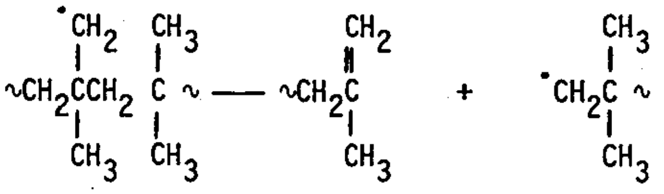
Silicone rubbers are normally cured with a diacyl peroxide e.g. benzoyl peroxide since dialkyl peroxides are less effective. The crosslinking reaction is by abstraction of methyl hydrogen followed by combination of polymeric radicals(69,84).

Polychloroprene may be crosslinked by cumyl peroxide with a rather low efficiency of about 0.5(69) while polyurethane elastomers are also peroxide-curable(85,86).

Some elastomers which may not be cured by peroxides are butyl rubber and polyisobutylene. In these elastomers, scission predominates over crosslinking. In butyl rubber however, some crosslinking is possible at higher concentration of isoprene residue(87). Loan(87) has proposed a mechanism of scission based on an initial hydrogen abstraction and this is stated below in equations 56 and 57:



$$\mathrm{RO^{\bullet}\ (or\ R'\cdot) + \sim CH_2\underset{CH_3}{\overset{CH_3}{C}}CH_2\underset{CH_3}{\overset{CH_3}{C}}\sim \longrightarrow ROH\ (or\ R'H) + \sim CH_2\underset{CH_3}{\overset{{}^{\bullet}CH_2}{C}}CH_2\underset{CH_3}{\overset{CH_3}{C}}\sim} \qquad (56)$$



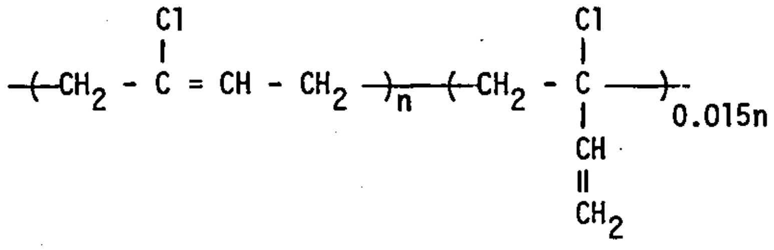
$$\mathrm{\sim CH_2\underset{CH_3}{\overset{{}^{\bullet}CH_2}{C}}CH_2\underset{CH_3}{\overset{CH_3}{C}}\sim \longrightarrow \sim CH_2\underset{CH_3}{\overset{CH_2}{\overset{\|}{C}}} + {}^{\bullet}CH_2\underset{CH_3}{\overset{CH_3}{C}}\sim} \qquad (57)$$

In general, the mechanism of crosslinking in peroxide-cured elastomers may be stated in the following three steps:

i) Thermally-induced homolytic decomposition of peroxide
ii) Abstraction of hydrogen atoms from polymer to give polymeric radicals
iii) Interaction of polymeric radicals to form crosslinks.

1.5 Vulcanization by Metal Oxides

Vulcanization by metal oxides is not a versatile method for crosslinking elastomers and it is used mainly for polychloroprene rubbers whose general structure is represented below:

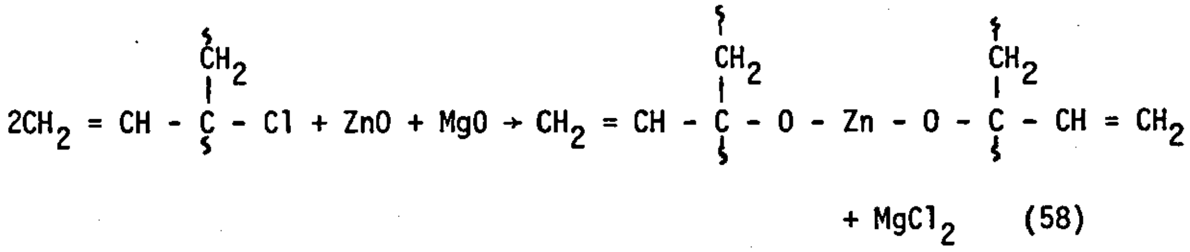


$$\mathrm{-\!\!\left(CH_2 - \overset{Cl}{C} = CH - CH_2\right)_{n}\!\!-\!\!\left(CH_2 - \underset{\underset{CH_2}{\overset{\|}{CH}}}{\overset{Cl}{C}}\right)_{0.015n}\!\!-}$$

Chlorosulphonated rubbers are also able to be vulcanized by metal oxides but polychloroprene will be the reference point in this instance.

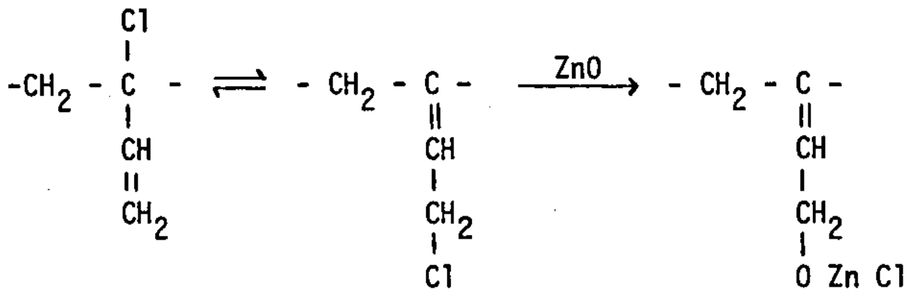
The primary crosslinking agent is zinc oxide and it is often used in conjunction with magnesium oxide or, lead oxide when low water absorption is required. Any of the metal oxides would vulcanize rubber; however the combination is better than either one alone. Zinc oxide by itself tends to be scorchy whereas magnesium oxide alone is inefficient. The accelerators used in accelerated sulphur vulcanization are generally not applicable to metal oxide vulcanization. The accelerator most widely used with metal oxide cures is ethylene thiourea or 2-mercaptoimidazoline.

Some different mechanisms of crosslink formation have been proposed. The first mechanism which requires the incorporation of zinc atoms in the crosslink(8) is summarized in the overall reaction equation 58:

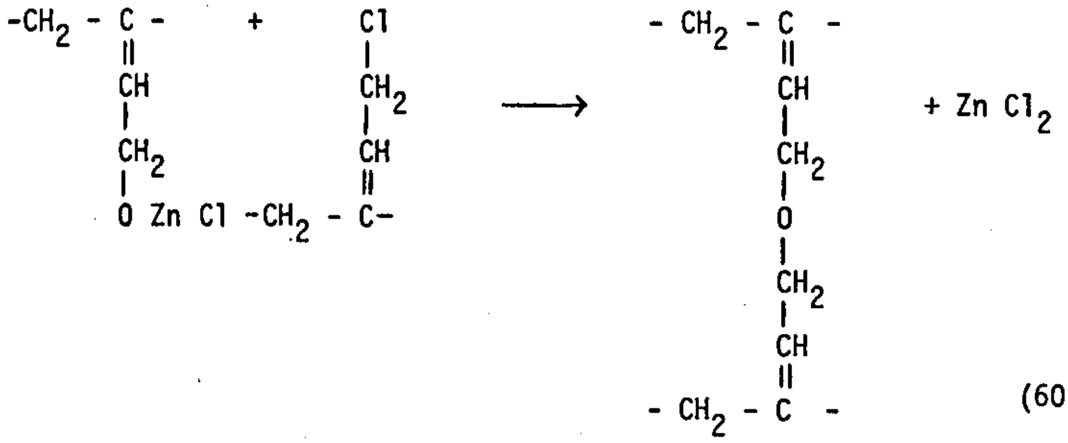


$$2CH_2 = CH - \overset{\overset{\wr}{CH_2}}{\underset{\wr}{\overset{|}{C}}} - Cl + ZnO + MgO \rightarrow CH_2 = CH - \overset{\overset{\wr}{CH_2}}{\underset{\wr}{\overset{|}{C}}} - O - Zn - O - \overset{\overset{\wr}{CH_2}}{\underset{\wr}{\overset{|}{C}}} - CH = CH_2 + MgCl_2 \qquad (58)$$

The second crosslink mechanism(8,40,88) which leads to the formation of ether crosslinks is represented in equations 59 through to 61 below:



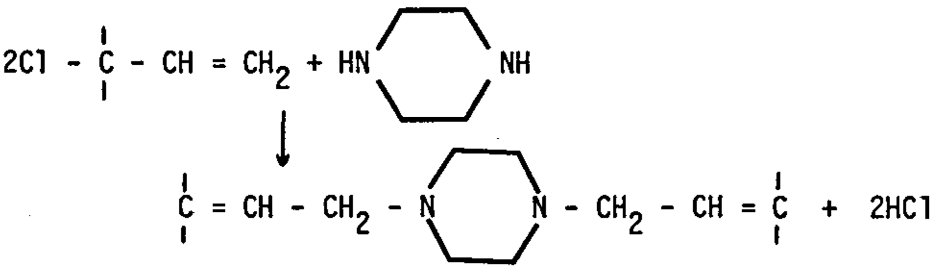
$$-CH_2 - \underset{\underset{\underset{CH_2}{\|}}{\underset{CH}{|}}}{\overset{\overset{Cl}{|}}{C}} - \rightleftharpoons - CH_2 - \underset{\underset{\underset{\underset{Cl}{|}}{CH_2}}{\underset{CH}{|}}}{\underset{\|}{C}} - \xrightarrow{ZnO} - CH_2 - \underset{\underset{\underset{\underset{O\,Zn\,Cl}{|}}{CH_2}}{\underset{CH}{|}}}{\underset{\|}{C}} - \qquad (59)$$



(60)

$$ZnCl_2 + MgO \rightarrow ZnO + MgCl_2 \qquad (61)$$

In his own work, Kovacic(89) emphasised the role of the 'active chlorine' in the vulcanization of polychloroprene by difunctional amines. He suggested that the vulcanization of polychloroprene by piperazine proceeds through bisalkylation of the vulcanizing agent by the polymer chains at the active chlorine position. The cross-linking reaction in the case of piperazine was illustrated according to equation 62 below:

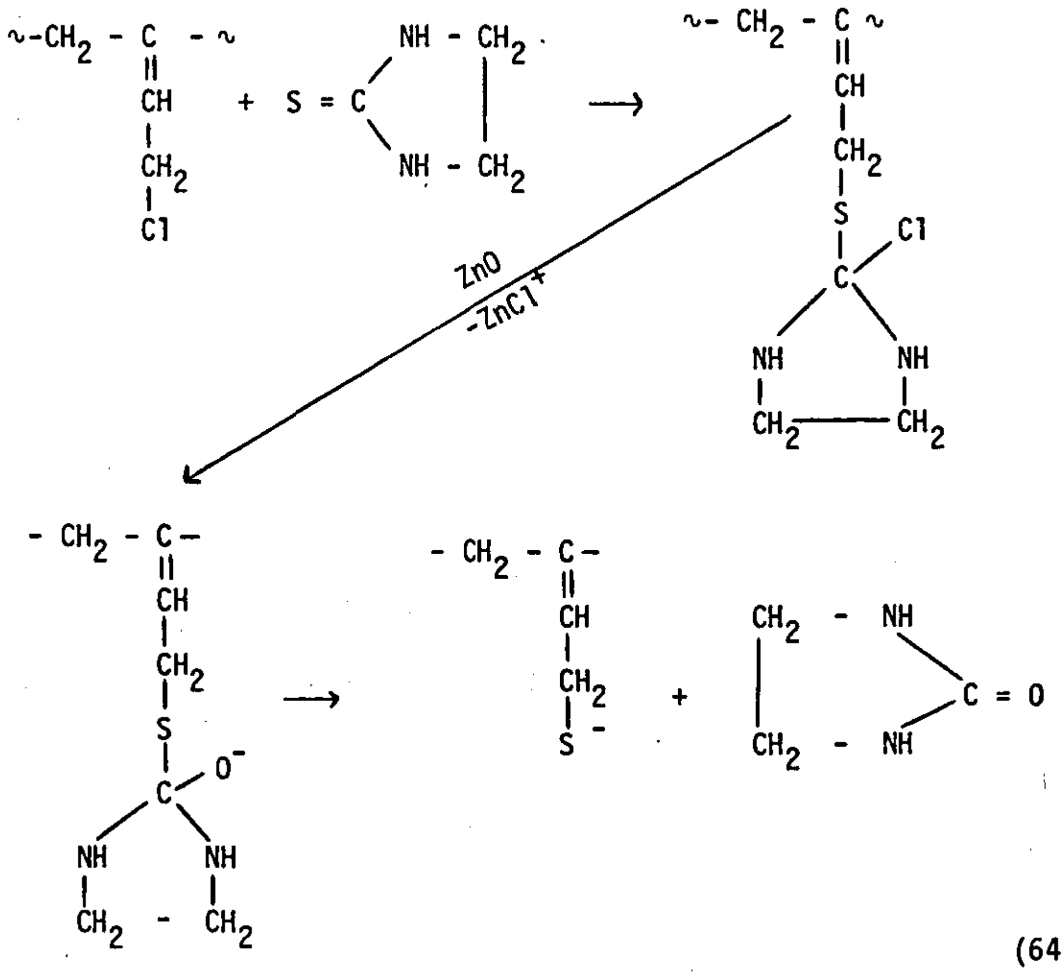


(62)

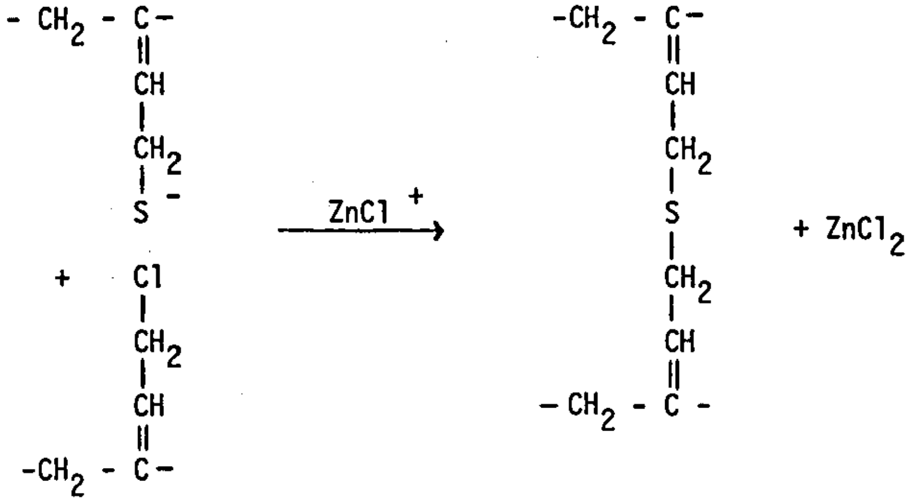
$$2HCl + MgO \rightarrow MgCl_2 + H_2O \qquad (63)$$

Also, the use of some novel crosslinking systems for polychloroprene has been reported(90) but no crosslink mechanism was advanced.

Equally noteworthy is a mechanism of ethylene thiourea acceleration of polychloroprene cure due to Pariser(8) and summarised in equations 64 and 65 below:



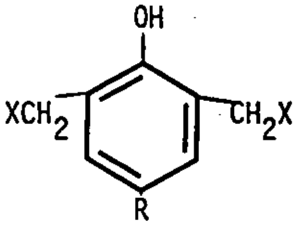
(64)



(65)

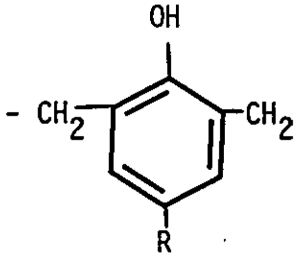
1.6 Resin Vulcanization

Elastomers appropriate for accelerated sulphur vulcanization (especially diene-based elastomers) can be crosslinked by resins of the structure:



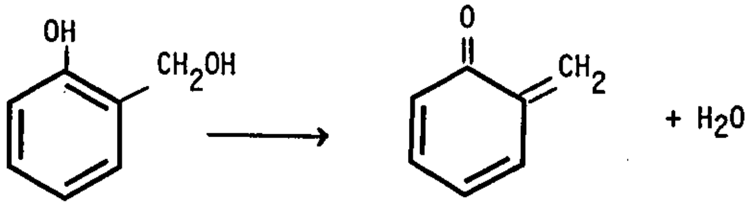
R = alkyl radical

where X is -OH, halogen atom, or



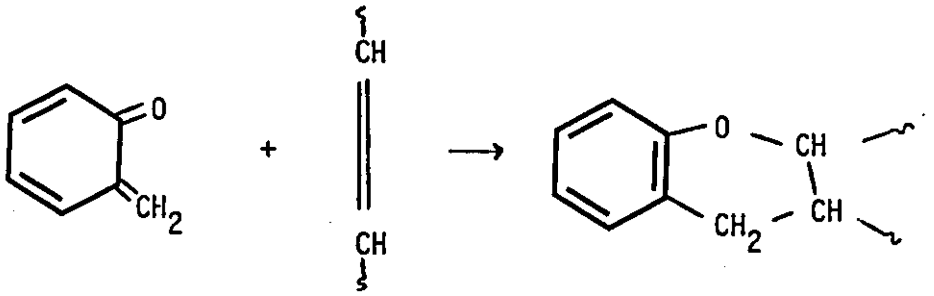
Resin cures are slower than accelerated sulphur cures and higher temperatures are required, but they can be activated by zinc oxide or by heavy metal halides (eg $ZnCl_2$ or $SnCl_2.H_2O$). Resin cures are also used extensively for curing butyl rubber(91) and two mechanisms of crosslinking have been postulated(92,93).

Both routes of crosslink formation assume that reaction takes place via an intermediate methylene-quinone structure which results from the elimination of water from ortho-methylol phenols at high temperature:



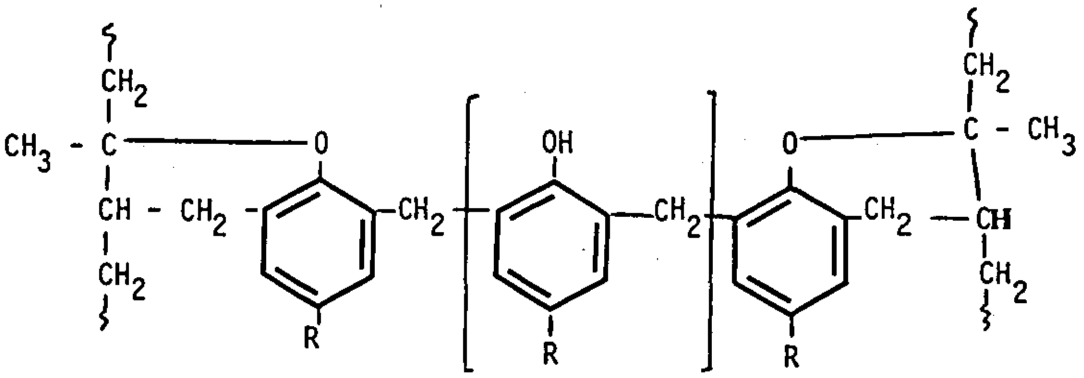
(66)

One route of crosslink formation is through the condensation of ortho-methylolphenol with a double bond to produce a chroman ring(94)

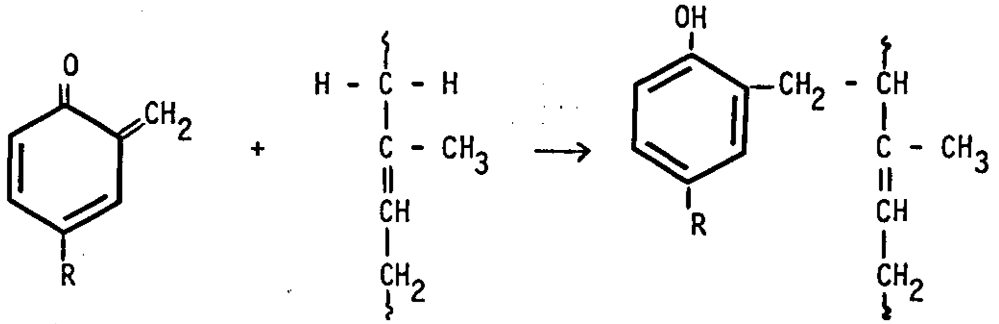


(67)

If the crosslinking agent is para-alkylphenol/formaldehyde resin, crosslinking is thought to occur concurrently with self-condensation of the resin involving elimination of water from two methylol groups(95). A possible crosslink structure formulated is shown below:

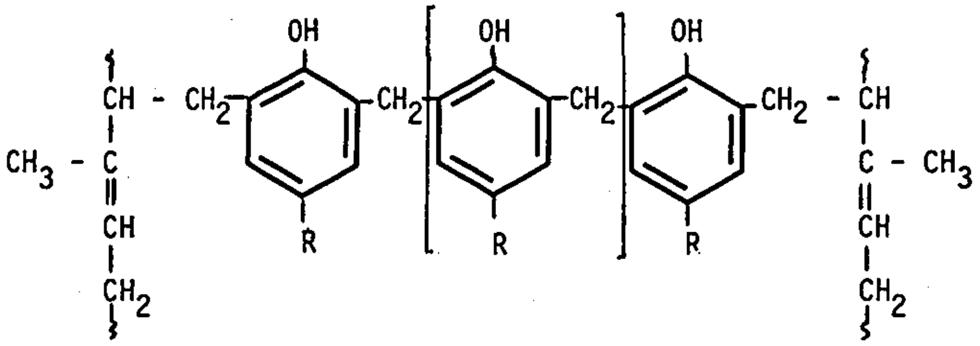


Another route of crosslink formation(96) assumes that reaction takes place at the α-carbon atom of the rubber as follows:



(68)

and the crosslink structure in this instance is:

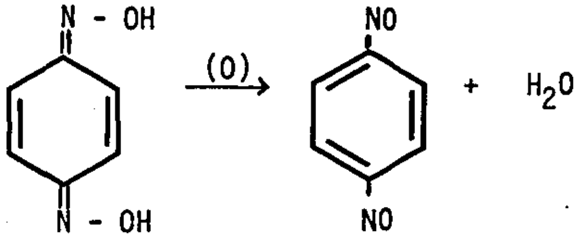


1.7 Vulcanization by Quinone. Derivatives

As with resins, benzoquinone and many of its derivatives can vulcanize natural rubber(97-101) and other diene rubbers that are cured by accelerated sulphur systems. Benzoquinone may also be used to cure butyl rubber. Only benzoquinone dioxime is of technical significance among the series and it is expected to be initially oxidized to nitrosobenzene; hence the inclusion of oxidizing agents like lead peroxide (PbO_2) in compound formulations. Indeed, dinitrosobenzene would vulcanize diene rubbers readily.(8,40)

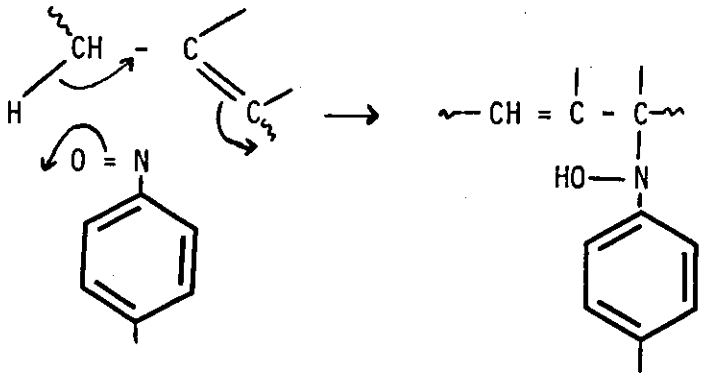
Flory and Rehner(99) established that the nitroso groups could be placed in meta- or para- but not ortho- to each other. Their mechanism of crosslink formation was through the diolefin unit of the polymer chain, in which the crosslink is through the polymer double bond and the nitrogen is in a nitrone configuration. It was further shown that (a) polymer unsaturation is required for dinitrosobenzene crosslinking , (b) the rate and state of reaction is not very sensitive to the polymer unsaturation level in contrast to the extreme dependence of the sulphur cures, (c) due to the greater stability of the carbon-nitrogen crosslink, the cure expands the practical limit of heat-ageing resistance to 150°C.

The oxidation of benzoquinone dioxime to dinitrosobenzene is represented by equation (69) below:



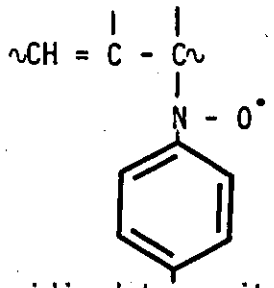
(69)

while the reaction of the nitroso group with rubber was postulated by Sullivan(101) as follows:



(70)

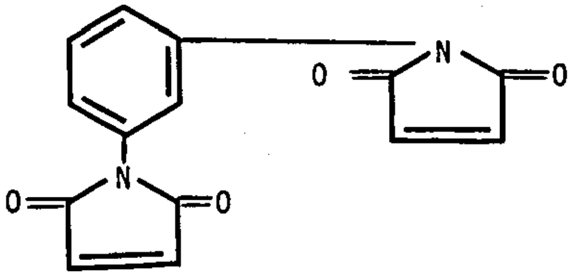
Stable free radicals were indicated by electron spin resonance with the structural assignment represented as:



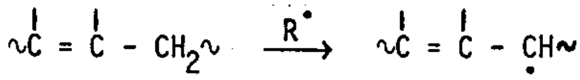
and could be oxidized to a nitrone.

1.8 Vulcanization by Maleimide Derivatives

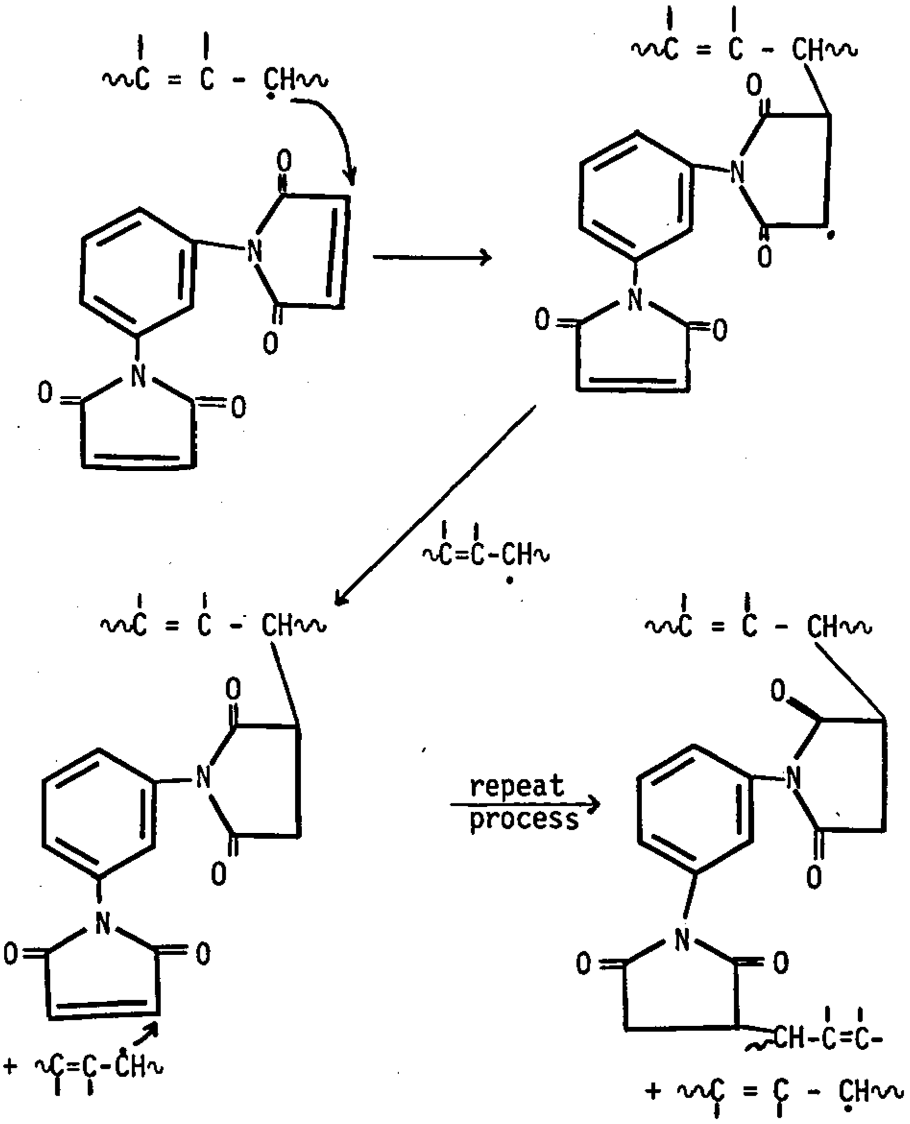
Derivatives of maleimides may also be used as crosslinking agents for diene rubbers. The most efficient ones contain more than one maleimide moiety per molecule and the most common of these is m-phenylene bismaleimide with the structure below:



A catalytic free radical source such as dicumyl peroxide is usually required to initiate the reaction(102,103). Alternatively, the reaction may be induced by high energy radiation(104) or even materials like bis-2,2-dithiobenzothiazole (MBTS). A mechanism of crosslink formation(102,105) is given below in equations 71 and 72:



$$\sim\overset{|}{C} = \overset{|}{C} - CH_2\sim \xrightarrow{R^{\bullet}} \sim\overset{|}{C} = \overset{|}{C} - \underset{\bullet}{CH}\sim \tag{71}$$



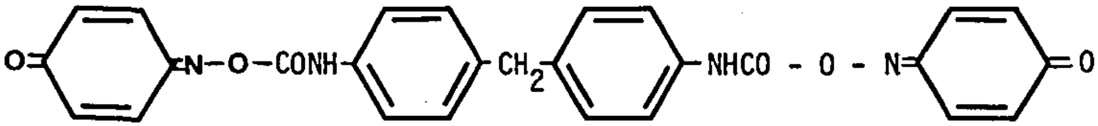
(72)

It has also been reported(106) that maleimides will react with rubber without catalyst at temperatures well above the usual vulcanization temperatures.

In general, vulcanizates based on crosslinking by phenolic resins, quinone derivatives or derivatives of maleimides are particularly useful in cases where thermal stability is required and some of them are important in rubber adhesion technology.

1.9 Urethane Crosslinking

The use of urethane crosslinking agents for natural rubber was developed by workers at the Malaysian Rubber Producers' Research Association. Urethane crosslinking agents comprise condensation products of p-benzoquinonemonooximes (nitroso phenols) and diisocyanates with a structure shown below:



The physical properties of urethane vulcanizates were said to be good because of the stability of urea type crosslinks(95,107).

The mechanism of crosslink formation was explained by the thermal dissociation of urethane agent during curing, addition of nitrosophenols to the rubber chains to give pendent aminophenol groups and consequent crosslinking by diisocyanates. An illustration of crosslink mechanism is shown (95,107) in Figure 1.7.

1.10 Radiation Crosslinking

Crosslinking in polymers can be effected by means of high energy radiation. Polymers that may be crosslinked by high energy radiation are: polyacrylic esters, polystyrene, polyesters, nylon, chlorinated polyethylene, chlorosulphonated polyethylene, natural rubber, styrene-butadiene rubber, butadiene-acrylonitrile copolymers, polychloroprene and styrene-acrylonitrile copolymers(108). Also, the following polymers viz. polyisobutylene and butyl rubber cannot be crosslinked by high energy radiation but are degraded. However, it has been possible to effect radiation-induced crosslinking of polyvinyl chloride and polypropylene when each of these polymers is mixed with polyfunctional monomers(109,110).

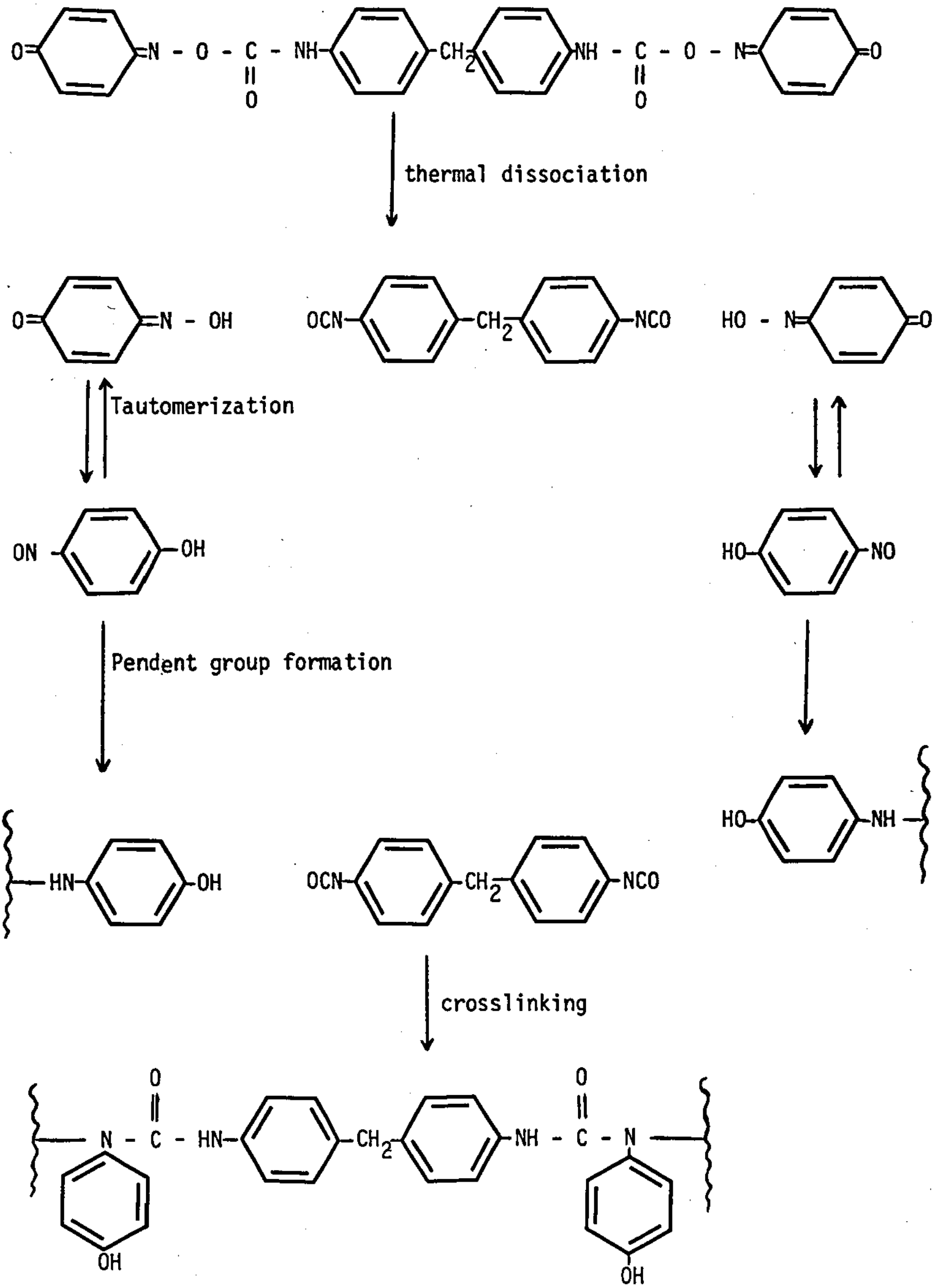
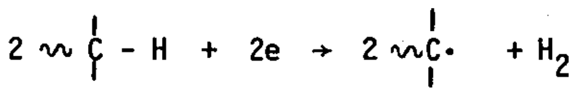
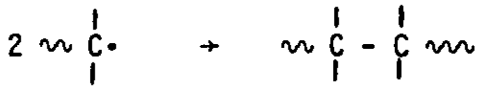


FIGURE 1.7: Mechanism of Urethane Crosslinking(95,107)

A general theory of radiation crosslinking explains that when a polymer is exposed to high energy radiation, dehydrogenation takes place and the resultant formation of free radicals. The interaction between polymer radicals leads to the formation of carbon-carbon crosslinks (equations 73 and 74) which may be expected to have good resistance to heat ageing.



$$2 \sim \overset{|}{\underset{|}{C}} - H \; + \; 2e \; \rightarrow \; 2 \sim \overset{|}{\underset{|}{C}}\cdot \; + H_2 \qquad (73)$$



$$2 \sim \overset{|}{\underset{|}{C}}\cdot \; \rightarrow \; \sim \overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}} \sim\sim \qquad (74)$$

Even though the participation of radicals in radiation crosslinking has been established, it has been suggested that reactions involving ions and radicals will also contribute to crosslinking(111,112).

The majority of industrial applications have involved the crosslinking of polyethylene in wire insulation and heat shrinkable films while radiation crosslinking in tyre production is still being explored(113). In spite of the limited application of radiation crosslinking, a considerable amount of work has been done and useful references are available(114-119).

1.11 Miscellaneous Vulcanization Systems

Several crosslinking systems exist for different elastomers. Some crosslinking agents have been developed either to meet special service requirements of vulcanizates or because of the peculiarity of the rubber involved while other crosslinking systems have been developed out of pure academic interest. It is therefore worth mentioning some of these different crosslinking agents.

The use of polyhalogenated compound for the vulcanization of styrene-butadiene rubber has been reported(120) while it is also possible to crosslink vinyl polybutadiene with dithiols(121). Butadiene and some of its copolymers have been reported to undergo thermal vulcanization although vulcanizates obtained from this method were poor(122). Other vulcanizing agents/systems are amine-boranes(123), aldehydes(124), bisperoxycarbamates(125,126), bisazoesters(127-129), bisazidoformates(130), aromatic diazoaminocompounds(131), diamines for fluoropolymers(122), selenium and tellerium(40) and nascent sulphur(132).

The list is by no means exhaustive as information on different crosslinking systems for different elastomers is scattered in the literature and further treatment of vulcanization and vulcanizing agents could be found elsewhere(40,88).

1.12 Objectives of the Present Research Project

An objective of the present research project is to undertake the preparation of a new vulcanizing agent for rubber, namely, a bisperoxycarbamate based on hexamethylene-1, 6-diisocyanate and to evaluate its crosslinking ability in various elastomer compounds. It is intended to select a particular elastomer in which the bisperoxy carbamate gives a good cure response as reference material for studying the crosslinking system using conventional rubber technology methods.

CHAPTER 2

PREPARATION OF BISPEROXYCARBAMATES

2.1 Introduction

Preparation of organic peroxycarbamates, which are esters of the unknown percarbamic acids have been based on the tendency of organic isocyanates to react with compounds having active hydrogens to produce addition products.

Davies and Hunter(133) has prepared tertiary butyl percarbamate and four of its N-monosubstituted derivatives (phenyl, α-naphthyl, p-xenyl and -methyl). Their method of preparation was selected from one of the following three procedures:

i) $R - N = C = O + t\text{-}C_4H_9 - O - OH$ with pyridine as catalyst

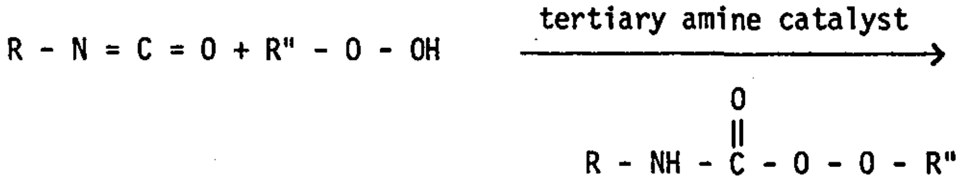
ii) $R - NHCOCl + t\text{-}C_4H_9 - O - OH$ with pyridine as acid acceptor

iii) $RNH_2 + t\text{-}C_4H_9 - O - O - COCl$

One of the products obtained (tert-butyl N-phenylpercarbamate) was shown to catalyse the polymerization of styrene at 85°C; this confirmed the presence of a peroxide linkage which can undergo homolysis under the condition of the experiment.

Also, Pederson(134a,134b) synthesized some other peroxycarbamates which are tertiary butyl and α-cumyl esters of N-substituted peroxycarbamic acids. He used two methods of preparation which are stated below:

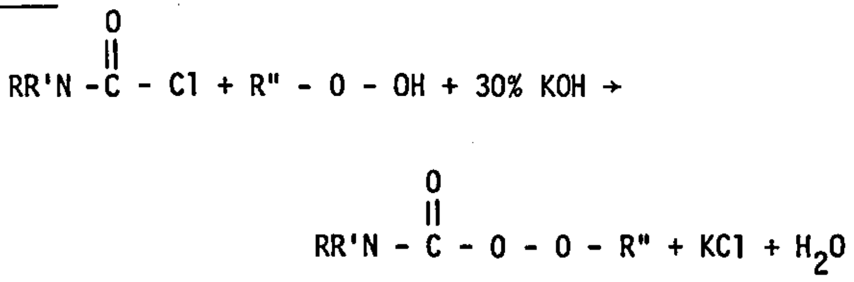
Method 1:



$$R - N = C = O + R'' - O - OH \xrightarrow{\text{tertiary amine catalyst}} R - NH - \overset{\overset{\displaystyle O}{\|}}{C} - O - O - R''$$

i.e. reacting isocyanates with hydroperoxides in the presence of a solvent and a tertiary amine as catalyst; a method which he claimed can only be used for peroxycarbamate containing the -NH group.

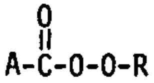
Method 2:

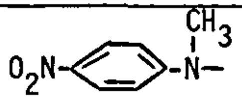
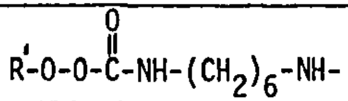
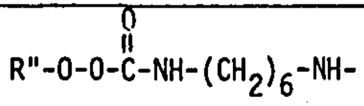


$$RR'N - \overset{\overset{\displaystyle O}{\|}}{C} - Cl + R'' - O - OH + 30\%\ KOH \rightarrow RR'N - \overset{\overset{\displaystyle O}{\|}}{C} - O - O - R'' + KCl + H_2O$$

His second method involved the reaction of N-substituted carbamoyl chlorides with hydroperoxides in the presence of 30% aqueous potassium hydroxide, which is applicable to the synthesis of all types but less suitable for the N-monosubstituted compounds.

In addition to his preparations, Pederson(134a) investigated the thermal stability of peroxycarbamates, thus establishing tert-butyl N-ethylperoxycarbamate, hexamethylene-N, N"-bis (tertiary butyl peroxycarbamate) and tert-butyl N-(p-nitrophenyl) peroxycarbamate as the most stable compounds among his preparations. He also reported the use of peroxycarbamates to initiate the polymerization of vinyl monomers and the bulk polymerization of styrene. A summary of Pederson's preparations is given in Table 2.1 below:

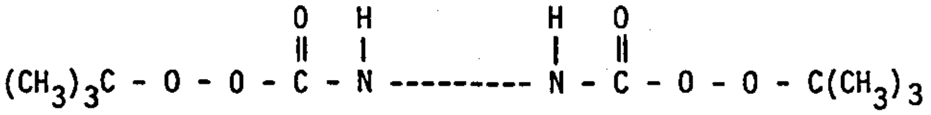
TABLE 2.1: PREPARATION AND PROPERTIES OF  $A-\overset{O}{\overset{\|}{C}}-O-O-R$ (134a)

A	R^a	Method	Solvent	Catalyst	Yieldb %	M.Pt °C	Purity by KI%	% Nitrogen Content	
								Calc.	Found
1. C_2H_5NH-	R'	1	Benzene	Pyridine	18	$39-40^d$	99	8.7	8.7
2. $(CH_3)_2N-$	R'	2	None	-	54	Liquid^e	100	8.7	8.7
3. $(CH_3)_2N-$	R"	2	None	-	40	60^d	100	6.3	6.3
4. $(C_2H_5)_2N-$	R'	2	None	-	43	Liquid^f	100	7.4	7.4
5. 	R'	2	None	-	81	Liquid^g	99	7.0	7.1
6. 	R'	1	Benzene	Triethyl-Amine	59	93^h	100	11.0	10.9
7. 	R'	2	Petrol ether	-	68	66^h	100	10.5	10.4
8.  $R'-O-O-\overset{O}{\overset{\|}{C}}-NH-(CH_2)_6-NH-$	R'	1	Benzene	Pyridine	6	$64-5^d$	100	8.0	8.1
9.  $R''-O-O-\overset{O}{\overset{\|}{C}}-NH-(CH_2)_6-NH-$	R"	1	Benzene	Triethyl-Amine	57	105^d	98	5.9	6.3

a: R' is tertiary-butyl and R" is α-cumyl. b: Yields are based on isocyanate or carbamoylchloride. They are approximate and no effort was made to secure maximum yields. c: These points were determined on a bronze block and are uncorrected. In general, the compounds decomposed on melting. d: White crystals. e: Colourless; boiling at 43-45°/0.1-0.2 mm without decomposition. f: Undistilled; g: Undistillable at 0.005 mm. Pale yellow.

While studying the thermal decomposition of peroxycarbamates in solvents, O'Brien and co-workers(135,136) prepared tertiary butyl and cumyl N-phenylperoxycarbamates by the reaction of t-butyl and cumyl hydroperoxides with phenyl isocyanate. Also, they prepared tertiary butyl N-α-naphthylperoxycarbamate by reacting t-butyl hydroperoxide with α-naphthyl isocyanate.

In another work, Tobolsky and Rembaum(137) reacted polypropylene oxide diisocyanate with tertiary butyl hydroperoxide to form a diperoxycarbamate represented by the following formula:

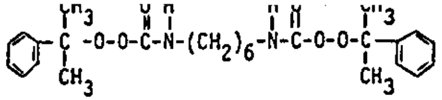
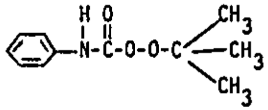
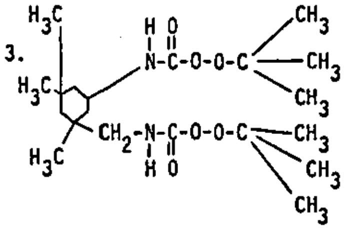
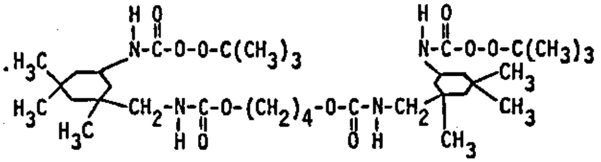
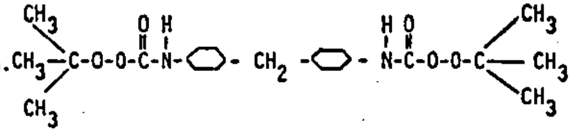
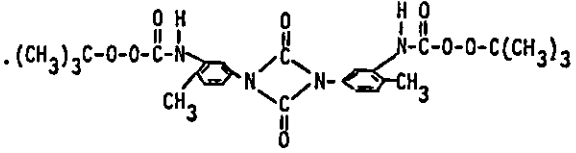
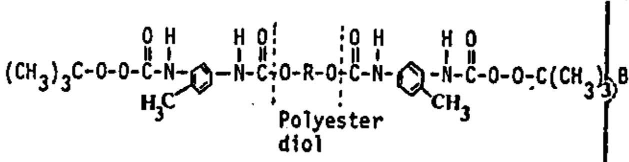
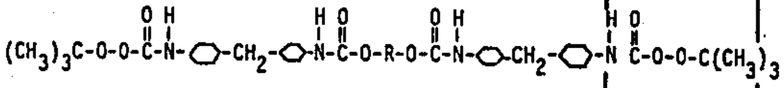


$$(CH_3)_3C - O - O - \overset{O}{\overset{\|}{C}} - \overset{H}{\overset{|}{N}} \text{ --------- } \overset{H}{\overset{|}{N}} - \overset{O}{\overset{\|}{C}} - O - O - C(CH_3)_3$$

where the dashed line represents a polypropylene oxide chain.

The preparation of two peroxycarbamates 2,6-tolyl N,N'-bis-(t-butyl) peroxycarbamate and hexamethylene N,N'-bis-(t-amyl) peroxycarbamate was described in a German patent(138) while an American patent in 1960(139) mentioned the use of a percarbamate to crosslink a copolymer of vinylidene fluoride and hexafluoropropene.

In a recent work, Abu Amu(126) prepared a number of bisperoxycarbamates and evaluated their ability to cure natural and polyisoprene rubbers. A summary of his preparations is given in Table 2.2. His first preparation (No 1, Table 2.2) was based on the work of Pederson(134a) while No. 2 preparation was based on the work of O'Brien et al(135,136). Three of the preparations (Nos. 3, 5, 6) were principally based on reacting isocyanates with cumyl or tertiary butyl hydroperoxide. Other preparations are Nos. 4, 7 and 8 which are based on polyurethane prepolymer routes. One of his findings(126) is that the time to completion of reaction of hydroperoxides with various isocyanates is dependent on the structures of the backbones of the isocyanates in the following order: aromatic < aliphatic < aliphatic/cyclic < cyclic. Also three of the bisperoxycarbamates

1. 	Benzene	TEA[b]	55	105	C-O → 1160 cm^{-1} 3080 cm^{-1} -C(CH$_3$)$_3$1375 cm^{-1} C=O → 1715 cm^{-1} CH stretching→2890 cm^{-1} and 2950 cm^{-1}
2. 	Benzene	Pyridine	68	83	O-O → 850 cm^{-1} C-H aromatic 3030 cm^{-1},3060 cm^{-1} 314) cm^{-1} C-O →1190 cm^{-1} -C(CH$_3$)$_3$→1375 cm^{-1},1400 cm^{-1} N-H→ 3210 cm^{-1} C=O →1735 cm^{-1} C-H stretching→2950 cm^{-1}
3. 	Benzene	TEA	69	167	O-O → 854 cm^{-1} C-H stretching → 2920 cm^{-1} 2940 cm^{-1} 2964 cm^{-1} C-O →1187 cm^{-1} -C(CH$_3$)$_3$→1365 cm^{-1}, 1385 cm^{-1} C=O →1715 cm^{-1} N-H →3340 cm^{-1}
4. 	Benzene	TEA	88	163	O-O →850 cm^{-1} C-H stretching → 2948 cm^{-1} C-O→1193 cm^{-1} -C(CH$_3$)$_3$ →1363 cm^{-1}, 1383 cm^{-1} C=O → 1714 cm^{-1} N-H → 3327 cm^{-1}
5. 	benzene	TEA	65	163	O-O → 860 cm^{-1} C-H stretching →2860 cm^{-1}, 2935 cm^{-1} 2985 cm^{-1} C-O →1192 cm^{-1} -C(CH$_3$)$_3$ →1370 cm^{-1}, 1393 cm^{-1} C=O → 1720 cm^{-1} N-H → 3360 cm^{-1}
6. 	Trichloro-Benzene	Pyridine	26	66	O-O → 833 cm^{-1} C-H stretching → 2870 cm^{-1} 2932 cm^{-1}, 2980 cm^{-1} C-O → 1200 cm^{-1} -C(CH$_3$)$_3$ →1410 cm^{-1} C-H aromatic → 3040 cm^{-1} 3083 cm^{-1} C=O → 1720 cm^{-1} N-H → 3328 cm^{-1}
7. 	Benzene	Pyridine	21	64	O-O → 830 cm^{-1} C-H aromatic →3070 cm^{-1} C-O →1172 cm^{-1} C-H stretching →2890 cm^{-1}, 2977 cm^{-1} -C(CH$_3$)$_3$ →1392 cm^{-1} C=O → 1735 cm^{-1} N-H → 3230 cm^{-1}
8. 	Benzene	TEA	Very low	166.5	O-O → 857 cm^{-1} C-H stretching→ 2880 cm^{-1} 2953 cm^{-1} C-O → 1185 cm^{-1} -C(CH$_3$)$_3$→ 1377 cm^{-1} and 1400 cm^{-1} C=O → 1737 cm^{-1} N-H → 3390 cm^{-1}

a) Generally, compounds decomposed on melting; b) TEA = trimethylamine; c) ≡→ absorbs at

(Nos. 1, 4, 5) were found to be effective crosslinking agents in natural and polyisoprene rubbers.

There are two objectives for the synthesis work described in this chapter. The first objective is to carry out further work on the bisperoxycarbamate [methylene-bis-4-cyclohexyl N,N'(tertiary butyl peroxycarbamate)] which was reported to have been used in crosslinking natural and polyisoprene rubbers(126). The other objective is to prepare a new type of bisperoxycarbamate, not previously investigated, namely, hexamethylene-N,N' bis (tertiary butyl peroxycarbamate) for consequent examination as crosslinking agent in elastomer compounds. Although this material was originally prepared by Pederson(134a) in one of his numerous preparations, he obtained a very low yield and the method used in this work is different.

2.2 Experimental Section

2.2.1 Materials

Materials used in various preparations and tests were obtained from commercial sources and used as received except as otherwise stated.

1. Methylene bis(4-cyclohexyl isocyanate) and hexamethylene-1, 6-diisocyanate were supplied as solvent-free clear liquid by Bayer (UK) Ltd as Desmodur W and Desmodur H respectively.

2. The following chemicals and solvents, viz. toluene, hexane, petroleum ether 30/40°C, magnesium sulphate, triethylamine, were obtained from Fisons Scientific Supplies Ltd, Loughborough.

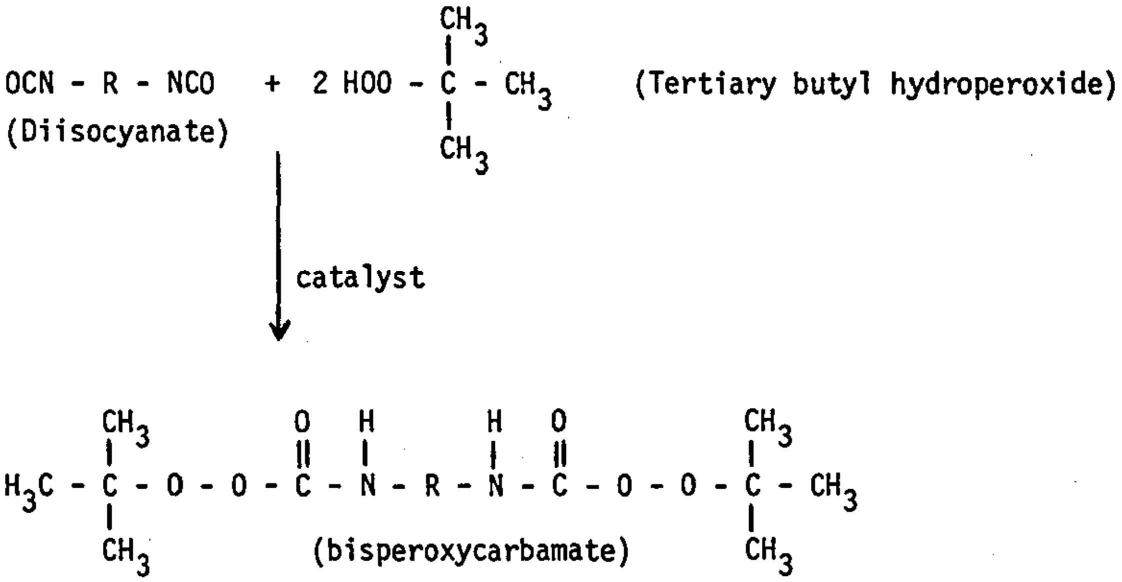
3. Stannous octanoate was obtained as Nuocure 28 from Durham Chemicals Group, UK.

4. Dried nitrogen was obtained from British Gas Ltd.
5. 50% solution of tertiary butyl hydroperoxide 'dissolved in toluene' was obtained from Interox Ltd, UK.
6. Another grade of tertiary butyl hydroperoxide was obtained from Koch Light Industries Ltd in 70% aqueous form. This cannot be used as received because the water in the aqueous solution reacts with diisocyanates to form urea and urea derivatives. Water was extracted from this solution by mixing it with petroleum ether. Two phases were formed - one with the bottom layer consisting of water and some petroleum ether. This layer was decanted using a separating flask. To the upper layer was added dried magnesium sulphate to further extract the remaining water in the solution. The remaining solution was later filtered and transferred into a dry, open beaker which was placed in a vacuum chamber to evaporate the remaining petroleum ether. The tertiary butyl hydroperoxide extracted in the manner described above was used in a number of preparations described later.

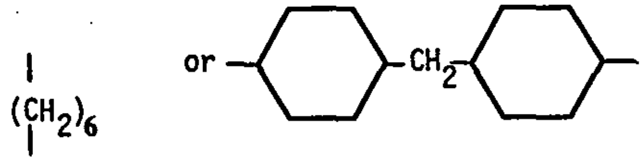
2.2.2 Procedure

The primary chemical reaction of the various preparations was to react tertiary butyl hydroperoxide with diisocyanate in solvent medium (toluene was used in most of the reactions) and in the presence of catalyst(s). Some variations in the preparations were made and are due to different diisocyanates, catalysts and their levels in the reaction medium. Another difference worth stating is the use of extracted tertiary butyl hydroperoxide and 50% tertiary butyl hydroperoxide 'dissolved in toluene'; the latter being used as received.

The chemical equation representing the various preparations can be given in the general form below [Note: stoichiometry is based on the chemical formula of the reactants e.g. if only one -NCO group is present, then 1 mole of t-butyl hydroperoxide would be required]:



where R is either



A general method of reaction was followed in most of the studies carried out, using a clean, dry glassware, stirrer and other ancillary items. Material quantities used for the various reactions are shown in Table 2.3 and the individual preparation steps are itemised below.

A. Dissolve 0.2 mole of isocyanate in about 300 cm^3 of toluene in the reaction flask (some toluene was also used to wash the beakerwhich contained the diisocyanate into the reaction flask).

B. Add triethylamine (as indicated in Table 2.3) and wash out the beaker with toluene into the reaction flask [overall about 500 cm^3 of toluene was used].

C. Pass dry nitrogen into the reaction flask to exclude air and moisture, and commence stirring.

D. Add tertiary butyl hydroperoxide from the dropping funnel to the contents of the reaction flask. (Tertiary butyl hydroperoxide was calculated to give a 20% excess of the stoichiometric requirements (see Appendix 1)).

Extent of reaction was monitored by observing the disappearance of the characteristic isocyanate absorption band (-NCO at 2270 cm^{-1}) on the infra-red spectra with time. At the end of the reaction, a sludge was formed, to which was added about 200 cm^3 of hexane; this was stirred for a few minutes and the contents of the reaction flask was left to stand for a day. Afterwards, the sludge of reaction product, toluene, hexane and excess tertiary butyl hydroperoxide was filtered.

The filter cake was returned to the reaction vessel and again washed with about 1 litre of hexane and then filtered to obtain the final product. A Buchner filter/water pump assembly was used to speed up filtration. The white filter cake was spread on a flat plate, placed in a vacuum chamber at room temperature and left to dry to constant weight. (The use of room temperature-drying which took about 2 days, was strictly adhered to. An attempt to dry the material at a higher temperature (50°C) in hot air resulted in an explosion in another laboratory).

A summary of the studies concerning the reaction variables carried out in the preparation of methylene-bis-4-cyclohexyl N,N'(tertiary butyl peroxycarbamate) is listed in items (1) through to (7) in Table 2.3. These variables are now given below:

1. Synthesis using toluene as solvent and hexane for precipitating the product.

TABLE 2.3: Material Contents and Results of Various Reactions

Reaction No.	TBHP[a] (g)	Isocyanate (g)		Catalyst (g)		Toluene cm^3	Yield[f] %	Reaction Time (hrs)
		DESW[b]	DESH[c]	TEA[d]	SO[e]			
1	61.7(1)	52.4	-	5.3	-	500	60	>144
2	61.7(1)	52.4	-	5.3	-	500[g]	65	144
3	61.7(1)	52.4	-	5.3	-	500	60	>144
4	61.7(1)	52.4	-	8.0	-	500	61	>72
5	61.7(1)	52.4	-	-	5.3	500	40	>72
6	61.7(1)	52.4	-	2.65	2.65	500	46	>72
7	86.4(2)	52.4	-	5.3	-	400	69	48
8	61.7(1)	-	33.6	-	-	500	-	>144
9	61.7(1)	-	33.6	2.65	2.65	500	59	10
10	61.7(1)	-	33.6	-	5.4	500	-	>48
11	86.4(2)	-	33.6	3.0	-	400	90	8

a TBHP = tertiary butyl hydroperoxide (1) extracted
(2) dissolved in toluene (Interox)

b DESW = methylene bis-(4-cyclohexylisocyanate)

c DESH = hexamethylene-1, 6-diisocyanate

d TEA = triethylamine

e SO = stannous octanoate

f Yield is based on assumed molecular weights of product;
442 for product from DESW
348 for product from DESH

g Benzene was used instead of toluene

2. Synthesis using benzene as solvent and hexane for precipitating the product.

3. Rate of disappearance of isocyanate with time was studied using quantitative methods of infrared analysis (see Appendix 2). Direct methods of standard chemical analysis may be used though they are not always convenient(140). Rate studies were obtained individually for extracted tertiary butyl hydroperoxide and tertiary butyl hydroperoxide 'dissolved in toluene'.

4. Since the use of low concentration of triethylamine catalyst was reported(126) as giving a slow reaction, a higher concentration of catalyst was investigated to find out the effect on yield and time to completion of reaction.

5. Use of stannous octanoate as catalyst was investigated.

6. A combination of stannous octanoate and triethylamine were used as catalyst to find out if there was any synergistic effect on the reaction.

7. Use of tertiary butyl hydroperoxide dissolved in toluene (supplied by Interox Ltd) was investigated and compared with its water analogue.

Also, stated below initems (8) through to (11) are the studies carried out on the preparation of hexamethylene-N,N' bis(tertiary butyl peroxycarbamate) with the corresponding material contents shown in Table 2.3.

8. The effect of reacting diisocyanate with tertiary butyl hydroperoxide in the absence of catalyst was investigated.

9. The effect of combination of catalysts (triethylamine and stannous octanoate) was investigated to test any synergistic effect on the reaction.

10. Also, the use of stannous octanoate as the only catalyst was investigated.

11. Hitherto, extracted tertiary butyl hydroperoxide had been used, hence tertiary butyl hydroperoxide dissolved in toluene (obtained from Interox) was also used in the preparation of hexamethylene-N,N' bis(tertiary butyl peroxycarbamate).

2.3 Results and Discussion

2.3.1 Preparation of Methylene bis-4-cyclohexyl N,N'(tertiary butyl peroxycarbamate)

In the initial preparation of methylene bis-4-cyclohexyl N,N'(tertiary butyl peroxycarbamate) using extracted tertiary butyl hydroperoxide, a product yield of 60% was obtained (Reaction 1, Table 2.3). Although the reaction time was extended to 144 hours, a noticeable peak was still obtained in the infrared spectrum which showed that the reaction did not go to completion when toluene was used as a solvent medium. When benzene was substituted for toluene as solvent (reaction 2, Table 2.3), a product yield of 65% was obtained and the reaction was completed in 144 hours after which time no isocyanate peak was observed in the infrared spectrum. In spite of the fact that the synthesis reaction went to completion when benzene was used and with higher product yield, the use of toluene is thought to be less dangerous than the use of benzene which is thought to be carcinogenic.

Extracted TBHP* was also used for reaction rate studies again using the disappearance of isocyanate peak with time-technique. The isocyanate concentration showed a steady decrease with time for the initial 30 hours of reaction i.e. reducing from 0.28g-mole/litre to 0.14g-mole/litre, after which no further decrease in concentration was obtained (see Figure 2.1).

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* TBHP = tertiary butyl hydroperoxide

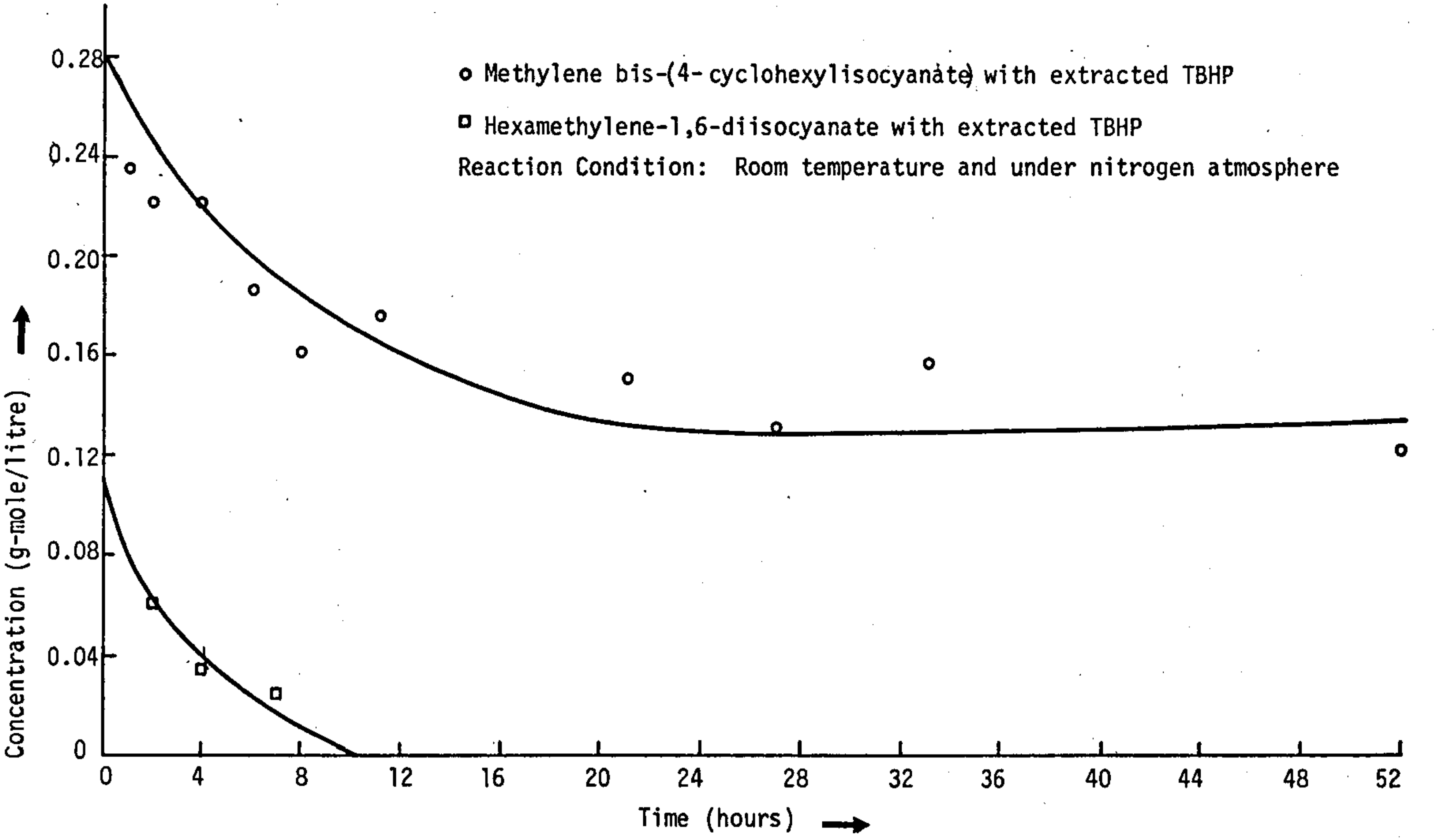


FIGURE 2.1: Rate of Disappearance of Diisocyanates in preparation of bisperoxycarbamates (diisocyanates with extracted TBHP)

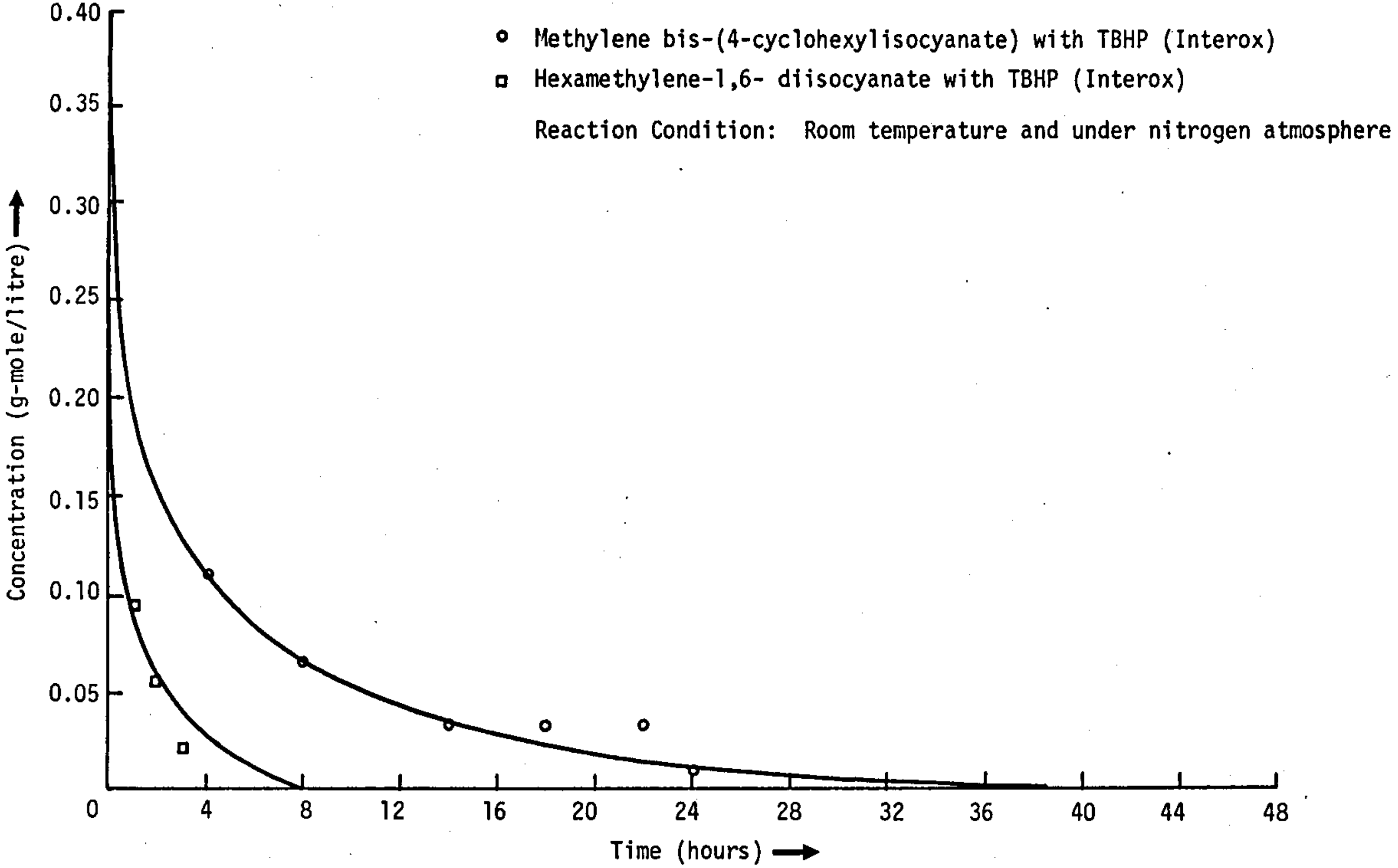


FIGURE 2.2: Rate of disappearance of diisocyanates in preparation of bisperoxycarbamates (diisocyanates reacted with TBHP 'dissolved in toluene)

However, when 'TBHP dissolved in toluene' was used as a reagent for the reaction and the extent of reaction monitored, a gradual and continual decrease in isocyanate concentration was observed and the reaction was completed in about 48 hours (see Figure 2.2).

Though not conclusive, the rate study gave an approximate guide to the time to completion of reaction which was about three days when extracted TBHP was used (using extracted TBHP, product yield when the reaction was carried out in three days was not different from that obtained when the reaction was carried out in six days).

An increase in catalyst (triethylamine) concentration from 26.5g to 40g per stoicheiometric quantities of reactants gave a 61% product yield which is not considered a significant difference from the 60% yield obtained using 26.5g of catalyst (Table 2.3; reactions 3 and 4). The use of stannous octanoate (26.5g per stoicheiometric quantities of reactants) as catalyst gave a 40% product yield while a combination of stannous octanoate and triethylamine (13.25g of each catalyst per stoicheiometric value of reactants) gave a 46% yield of product. From the foregoing, it is evident that the use of stannous octanoate or its combination with triethylamine is inferior to the use of triethylamine alone as catalyst. The use of TBHP 'dissolved in toluene' (obtained from Interox Ltd) for the preparation of methylene bis-4-cyclohexyl N,N'(tertiary butyl peroxycarbamate) was also investigated.

The quantities of the materials reacted are shown in Table 2.3 (reaction 7) and 69% product yield was obtained. In this case, time to completion of reaction was about 48 hours. Compared to the reaction involving the use of extracted TBHP, this reaction offers the following advantages: better yield, shorter reaction time and a more straightforward preparation method since all the reactants were used as received. Furthermore, a disadvantage with the ether extraction of aqueous TBHP is the fact that if there is any trace of water in the extracted TBHP, the isocyanate reacts with water quickly to form urea and urea derivatives which are unwanted by-products.

2.3.2 Preparation of Hexamethylene-N,N'bis (tertiary butyl peroxycarbamate)

The preparation of hexamethylene-N,N' bis(tertiary butyl peroxycarbamate) (HBTBP) was based on the procedure used to prepare methylene bis-4-cyclohexyl-N,N'(tertiary butyl peroxycarbamate).

In the first instance (Table 2.3, Reaction 8) the reaction was carried out without catalyst for about 144 hours. There was no product formation and the level of isocyanate remained constant throughout the course of the reaction. This is evidence that the reaction could not occur without catalyst and that the catalyst is a vital ingredient of the reaction mixture.

2.3.2.1 Effect of catalyst(s)

An investigation of the effect of catalyst concentration on product yield and time to completion of reaction was also considered, using extracted TBHP. Variation of catalyst concentration (expressed in grams per stoicheiometric quantities of reactants) with the consequent product yield and time to completion of reaction is shown in Table 2.4 below.

TABLE 2.4: Effect of catalyst (triethylamine and stannous octanoate) concentration on product yield and time to completion of reaction in the preparation of HBTBP

Quantity of Catalyst[a] g	Product Yield %	Time to Completion of Reaction (hrs)
0	0	>144
7.5 (TEA)[b]	85	36
15.0 (TEA)	90	10
27.0 (TEA)	90	8
40.0 (TEA)	80	4
13.5 TEA/13.5 SO[c]	59	10
27.0 (SO)	-	>48

a: Quantities of catalyst expressed per stoicheiometric values of reactants
b: TEA = triethylamine c: SO = stannous octanoate

The above result shows little difference in product yield when catalyst (TEA) concentration was varied between 7.5g and 40g. However the time to completion of reaction was shorter at increased catalyst concentration. The result also shows that about 15.0g of catalyst would be optimum for large scale preparation of hexamethylene-N,N' bis(tertiary butyl peroxycarbamate). Once again, the use of stannous octanoate as catalyst or its combination thereof has been shown to be inferior to the use of triethylamine alone. Using the tertiary butyl hydroperoxide 'dissolved in toluene' (obtained from Interox Ltd) the reaction was completed in eight hours with a product yield of about 90%. Although TBHP 'dissolved in toluene' is preferred in this reaction, the time to completion of reaction was approximately the same in the case of TBHP 'dissolved in toluene' as well as extracted TBHP.

2.3.3 Product Characterization

The methods of characterizing the bisperoxycarbamates prepared are (1) melting point/decomposition temperature using the differential thermal analysis method, (2) infra-red spectra analysis, (3) elemental analysis, and (4) curing capability of the bisperoxycarbamate in elastomer systems.

2.3.3.1 Differential Thermal Analysis (DTA)

This is a method by which thermal behaviour of polymer materials are studied. The difference in temperature of a substance and that of an inert reference material is measured as a function of time or temperature when subjected to a controlled heating or cooling programme. It is important that the inert reference material does not undergo any transition within the range of temperature under investigation and an empty sample pan was used as a reference material.

Before testing, the equipment (a Dupont 990 Thermal Analyser) was calibrated by obtaining the melting point of a known pure substance (indium: m.pt = 156.4). The value obtained from the equipment agreed with values quoted in the literature.

In measuring the melting point/decomposition temperature, the temperature difference of the product and an inert sample pan were measured as a function of temperature to obtain a plot known as a thermogram. Plots on the differential scanning calorimetry (DSC) are similar to that obtained from the DTA. The difference lies in the fact that DSC measures the heat flow into or from a sample as a function of time or temperature which makes it suitable for quantitative work. The DTA plots or thermograms were obtained for the two products and these are shown in Figures 2.3 and 2.4. From the thermograms, the following estimates could be made:

a) Melting point/decomposition peak temperature of methylene bis-4-cyclohexyl N,N'(tertiary butyl peroxycarbamate) = 163^{o}C.

b) Decomposition peak temperature of hexamethylene-N,N' bis(tertiary butyl peroxycarbamate) = 142^{o}C

c) Melting point of hexamethylene-N,N' bis(tertiary butyl peroxycarbamate) = 93^{o}C.

2.3.3.2 Infra-red spectra analysis

The infra-red method of analysis is based on the absorption of electromagnetic radiation by the molecules of the sample under examination. Different chemical groups absorb at different frequencies and the instrumental output consists of a measure of the degree of this energy absorption as a function of frequency typically over the range 600-4000 cm^{-1}. In this way, a chemical fingerprint is built up of the composition of the sample.

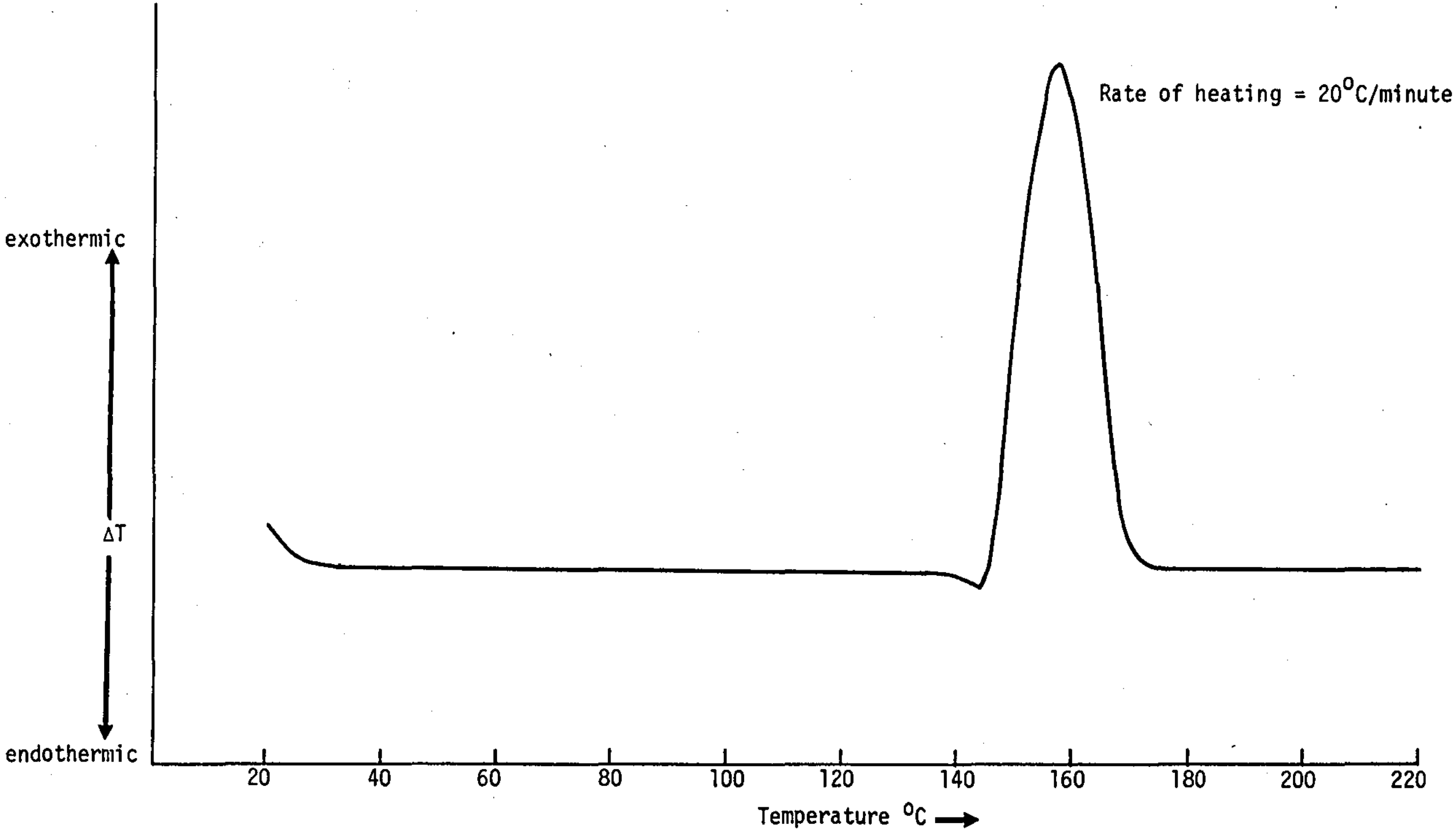


FIGURE 2.3: Differential thermal analysis of methylene bis-4-cyclohexyl N,N'(tertiary butyl peroxycarbamate)

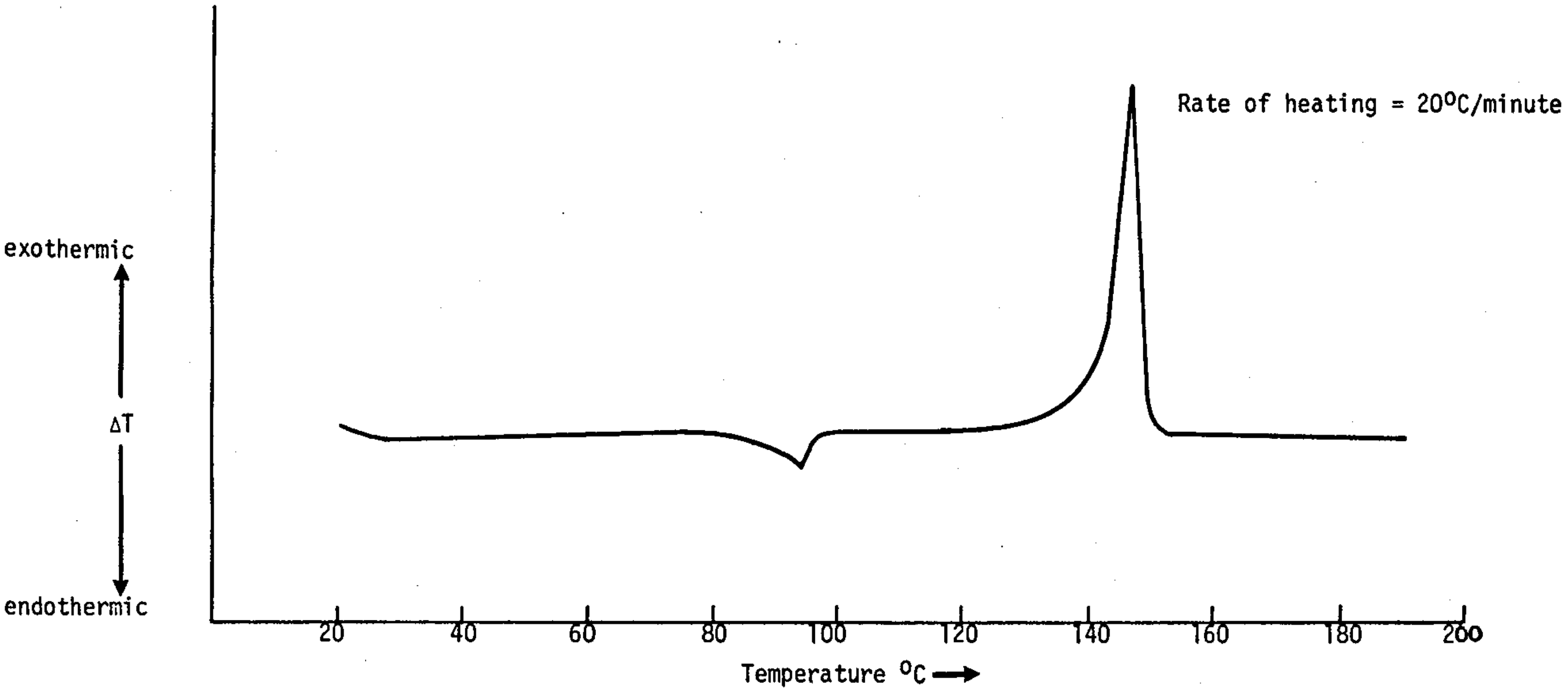


FIGURE 2.4: Differential thermal analysis of hexamethylene-N,N' bis(tertiary butyl peroxycarbamate)

Generally, an infra-red spectrophotometer consists of a radiation source emitting over the entire wavelength region. The radiation from the source is split into two beams - one of which passes through the sample, the other passes directly through to the detector. The difference between the intensities of these two beams provides the output signal for the instrument(141-143).

The instrument used to obtain the infra-red spectra was the Pye-Unicam SP3-200 Grating Infra-red Spectrophotometer. Samples used in the analysis were prepared by dispersing the dried powdered product in a matrix of pure, dry alkali halide (potassium bromide was used) and compressing to form an almost transparent disc - the occluded air having been removed by means of a vacuum pump.

The characteristic peaks of the infra-red spectra are listed below and the spectra shown in Figures 2.5 and 2.6. Methylene bis-4-cyclohexyl N,N' (tertiary butyl peroxycarbamate)

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

Hexamethylene-N,N' bis(tertiary butyl peroxycarbamate)

$O-O$ → 860 cm^{-1}
$C-O$ → 1198 cm^{-1}
$-C(CH_3)$ → 1380 cm^{-1} and 1395 cm^{-1}
$C=O$ → 1720 cm^{-1}
C-H stretching → 2280 cm^{-1}, 2980 cm^{-1} and 2995 cm^{-1}
$N-H$ → 3360 cm^{-1}
$-(CH_2)_6$ → 720 cm^{-1}

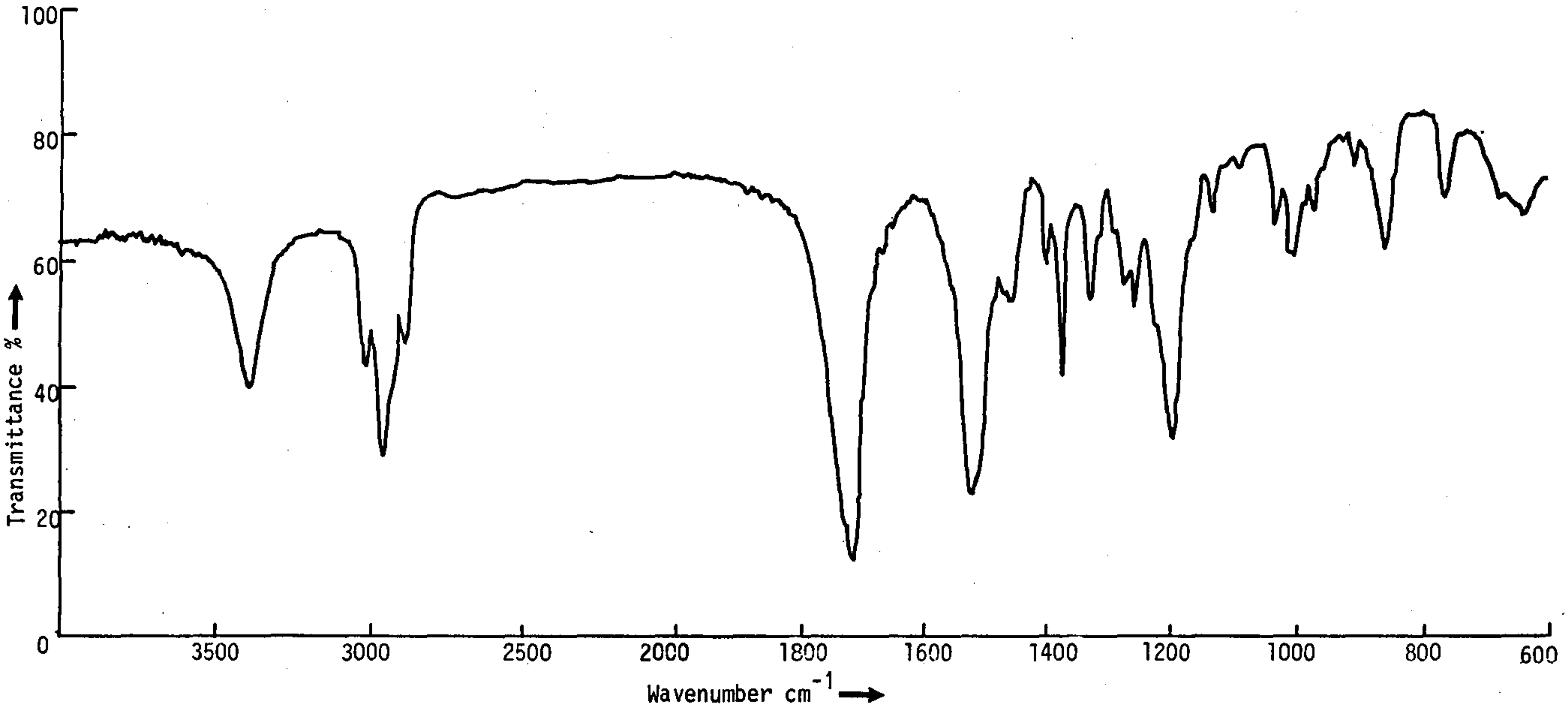


FIGURE 2.5: Infra-red Spectrum of Methylene bis 4-cyclohexyl N,N'(tertiary butyl peroxycarbamate)

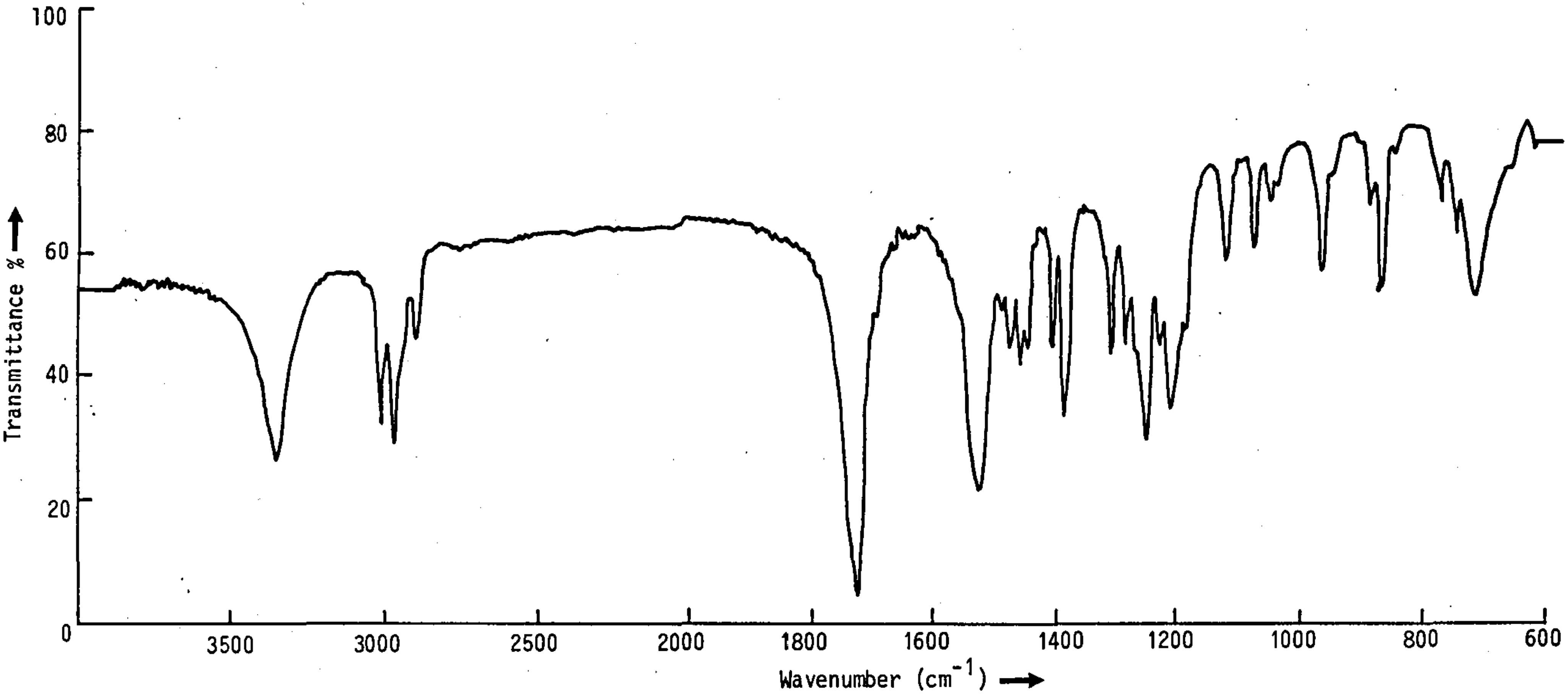


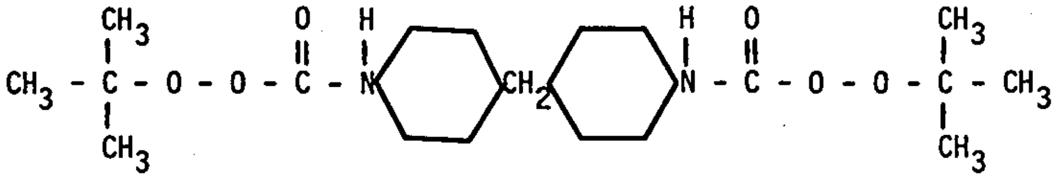
FIGURE 2.6: Infra-red Spectrum of Hexamethylene-N,N'bis (tertiary butyl peroxycarbamate)

If we take a close look at the characteristic peaks of the two products above, a close similarity is noted. The main difference however is the absorption band at 720 cm^{-1} in the spectrum of hexamethylene-N,N' bis(tertiary butyl peroxycarbamate) which is absent in the spectrum of methylene bis-4-cyclohexyl N,N'(tertiary butyl peroxycarbamate). A band at 720 cm^{-1} indicates an open chain of four or more adjacent methylene groupings ; here alycylic derivatives do not yield any absorption.

2.3.3.3 Elemental analysis

The percentage composition of elements in the products were determined at the Micro Analytical Laboratory of the University of Manchester. The elemental composition determined is compared with the theoretical composition based on the assumed structures written for the products.

For methylene bis-4-cyclohexyl N,N'(tertiary butyl peroxycarbamate), the proposed structure is:

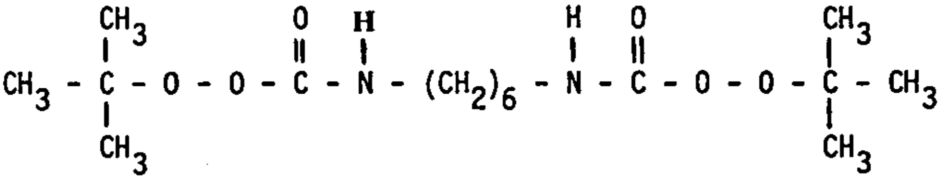


The experimentally determined composition for the above compound and the theoretical composition is given in Table 2.5 below.

TABLE 2.5: Comparison Between Theoretical and Actual Percentage Elemental Composition of Methylene bis-4-cyclohexyl N,N'(tertiary butyl peroxycarbamate)

Element	Percentage Composition Expected (Theoretical)	Percentage Composition Determined (Actual)
Carbon	62.44	63.3
Hydrogen	9.51	10.2
Nitrogen	6.33	7.0
Oxygen (by subtraction)	21.72	19.5

Similarly, in Table 2.6, the elemental composition determined for hexamethylene-N,N'bis(tertiary butyl peroxycarbamate) is compared with the expected composition based on the structure below:



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-O-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-(CH_2)_6-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-O-O-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

TABLE 2.6: Comparison Between Theoretical and Actual Percentage Elemental Composition of Hexamethylene-N,N'bis(tertiary butyl peroxycarbamate)

Element	Percentage Composition Expected (Theoretical)	Percentage Composition Determined (Actual
Carbon	55.1	55.8
Hydrogen	9.2	9.7
Nitrogen	8.0	8.4
Oxygen (by subtraction)	27.7	26.1

The differences between the expected composition and the experimentally determined values could be attributed to some unknown side reactions. However, within limits of experimental error, the infrared spectra analysis with elemental analysis justifies the assumed structures of the products.

2.3.3.4 Curing capability of bisperoxycarbamates in elastomer Compounds

This aspect of product characterization will only be mentioned in passing in this chapter. The use of methylene bis-4-cyclohexyl N,N' (tertiary butyl peroxycarbamate) as crosslinking agent in elastomers has been treated by Abu Amu(126) while the evaluation of hexamethylene-N,N' bis(tertiary butyl peroxycarbamate) as crosslinking agent in elastomer compounds forms the basis of the next chapter.

2.4 Conclusion

A general study of preparation of bisperoxycarbamates has been undertaken and the main variable studied has been the effects of catalysts and their levels in the reaction mixture. Based on the product yield and time to completion of reaction obtained, the ratio of materials stated in Table 2.7 are suggested as optimum.

Indeed, the large scale preparation of bisperoxycarbamates used in this work was based on the formulation shown in Table 2.7.

TABLE 2.7: Optimum Material Ratio for Preparation of Bisperoxycarbamates

	TBHP[a] g	Isocyanate (g)		Catalyst TEA[d] (g)	Toluene cm^3	Yield %	Reaction Time (hrs)
		DESW[b]	DESH[c]				
Methylene bis-4-cyclohexyl N,N'(tertiary butyl peroxycarbamate)	86.4	52.4	-	5.3	~400	69	48
Hexamethylene-N,N' bis (tertiary butyl peroxycarbamate)	86.4	-	33.6	3.0	~400	90	8

a: TBHP = tertiary butyl hydroperoxide dissolved in toluene (Interox)

b: DESW = methylene bis(4-cyclohexylisocyanate)

c: DESH = hexamethylene-1, 6-diisocyanate

d: TEA = triethylamine

CHAPTER 3

EVALUATION OF HEXAMETHYLENE-N,N' BIS (TERTIARY BUTYL PEROXYCARBAMATE) AS THE CROSSLINKING AGENT FOR VARIOUS ELASTOMERS

3.1 Introduction

Having prepared hexamethylene-N,N' bis(tertiary butyl peroxycarbamate) (HBTBP), the next objective of this work is to evaluate the curing capability of the material in various elastomer types. An interest in this particular material is due to the fact that it has not been used for such a purpose before and a substantial amount of work in the past had proven the curing capability of a similar material [methylene bis-4-cyclohexyl-N,N'(tertiary butyl peroxycarbamate)] in natural and polyisoprene rubbers(126).

Most evaluations were carried out using filled vulcanizates to test whether the product is suitable as a crosslinking agent for a particular elastomer. Where tests proved positive, limited compounding studies were carried out to enable the comparison of physical properties of vulcanizates cured with the product (HBTBP) and those cured by conventional vulcanization systems. The range of elastomers used are natural rubber (NR), blend of natural rubber and polybutadiene rubber (NR/BR), styrene-butadiene rubber (SBR), ethylene-propylene diene monomer (EPDM), silicone rubber (Q), chlorosulphonated polyethylene rubber (CSM), polychloroprene rubber (CR), bromobutyl rubber (BIIR), copolymer of polypropylene oxide and allyl glycidyl ether (GPO), nitrile rubber (NBR), epichlorohydrin rubber (ECO), fluorocarbon rubber (FKM). A previous study(126) served as a guide in designing the HBTBP formulations, thus, semi-reinforcing furnace black was used as filler while a combination of calcium oxide and calcium hydroxide was used as an absorber system for any carbon dioxide or moisture that might be evolved during curing.

Some of the vulcanizates were subjected to a short-term air cell-oven ageing procedure (24 hours at 100°C) which enabled comparison to be made of physical properties of aged and unaged vulcanizates.

A number of standard formulations were used as 'controls' and the properties of these control formulations were compared with the properties obtained using HBTBP.

3.2 Experimental Section

Here, mention is made of materials, experimental methods and tests used in this work.

3.2.1 Materials

Hexamethylene-N,N' bis(tertiary butyl peroxycarbamate) (HBTBP) was prepared as described in Chapter 2. Dicup 40C was supplied by Hercules Powder Company as a 40% active dicumyl peroxide supported on precipitated calcium carbonate. Semi-reinforcing furnace carbon black was supplied by Cabot Corporation Ltd while rubber grade calcium oxide and calcium hydroxide were made available by John and E Sturge Ltd. Poly-2,2,4-trimethyl-1, 2-dihydroquinoline was supplied as Flectol H by Monsanto Rubber Chemicals. The various elastomers were of commercial grade and, other compounding ingredients were standard materials used in rubber formulations and used as received.

3.2.2 Mill Mixing

Milling of uncured elastomer compounds is an important operation in the processing of rubber goods and the main aim is to ensure the uniform dispersion of compounding ingredients in the rubber.

The various rubber batches for the experiment were compounded on a two-roll mill of 850 cm^3 capacity. Generally, the mixing and milling procedures adopted were along the guidelines set by BS 1674:1976.

Although the rubber compound was cut and folded several times to ensure homogeneity, a possible defect of two-roll mixing exists in the maldispersion of compounding ingredients caused by the loose aggregation of fine powders with possible variability in the physical properties of vulcanizates (further description of the two-roll mill is given in Appendix 3).

A typical formulation for elastomers cured by HBTBP is shown below:

	phr*
Polymer	100
SRF black (N762)	30
CaO	4.0
$Ca(OH)_2$	6.0
HBTBP	2-6

The semi-reinforcing black is moderately reinforcing and does not interfere with HBTBP cures. Calcium oxide and calcium hydroxide serve as an absorber system for both moisture and carbon dioxide. The control formulations for the various elastomers are shown in the Results and Discussion section and are regarded as standard formulations for the general evaluation undertaken in this chapter.

3.2.3 Mooney Test

Although the Mooney viscometer can be used to measure the viscosity and scorch characteristics of elastomeric compounds (both in the raw and the compounded state), only the Mooney scorch was determined as this appears to be more meaningful. The scorch characteristics of a rubber compound could also be found using the Monsanto Oscillating Disk Rheometer. The principles laid down in BS 1673, Part 3, 1969 were followed in the determination of Mooney scorch i.e. use of a large rotor, 1 minute preheat time, test temperature of 120°C and scorch time was taken as 5 Mooney units above the minimum reading

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* phr = parts per hundred rubber

(description of Mooney viscometer is given in Appendix 3).

3.2.4 Cure Characteristics

The cure characteristics of the compounds were studied with the aid of a Monsanto Oscillating Disc Rheometer TM 100 using test procedure specified in BS 1673 Part 10, Method B, 1977. (A description of the Monsanto Oscillating Disc Rheometer is given in Appendix 3).

3.2.5 Moulding

The compression moulding techniques specified in BS 1674: 1976 were used to obtain vulcanized rubber sheets of 2 mm thickness (see Appendix 3 for further details).

3.2.6 Tensile Stress-Strain Tests

The tensile stress-strain properties were determined according to BS 903 Part A2, 1971 using Type 2 dumb-bell specimens (further information is given in Appendix 3).

3.2.7 Other Tests

Other tests are tear strength, which was determined according to BS 903 Part A3, 1982; rebound resilience, which was determined according to DIN 53512; hardness test, which was determined according to BS 903 Part A26, 1969 and compression set measurements which was determined according to BS 903 Part A6, 1969. Each of these other tests are discussed further in Appendix 3.

3.2.8 Heat Ageing

Heat ageing tests in general depend upon accelerating the ageing process by exposing the rubber compound to high temperatures and then measuring the changes in physical properties which have resulted. In some cases (e.g. engine components), the temperature of the test will not be widely different from the highest service temperature, and the test may not be so much accelerated relative to service, as more fully and accurately controlled. However, in the majority of cases, the test is truly accelerated and interpretation of results depends upon the assumption that the higher temperature has not significantly distorted the pattern of relative ageing behaviour of the compounds being compared. This assumption may not be invariably valid.

The basic method of test in many cases consists first in preparing the rubber compound as sheets of carefully controlled and uniform thickness (usually 2 mm).From such sheets a number of standardised test pieces (dumb-bells or other types as the case may be) are stamped out; the numbers used will vary with particular test specifications, but in general should not be fewer than three test pieces for each period of ageing, plus three required as unaged controls. Groups of three (or more) test pieces are then aged for selected periods at the elevated temperature chosen. The usual mechanical properties (tensile strength, elongation-at-break, hardness and tensile modulus) are subsequently measured and compared with the values obtained from the unaged compounds.

In most heat-ageing tests, care is required in selecting properties for study as measures of ageing resistance. In the case of polymers which predominantly soften on ageing (NR, IIR), tensile strength or tensile modulus is a sensitive indicator of the progress of ageing. By contrast, polymers which harden on ageing (SBR, CR) show little change in tensile strength until the final stages of ageing, when degradation has progressed to a disastrous level. For these polymers, elongation-at-break is a much more sensitive indicator, particularly in the intermediate stages of ageing.

The actual ageing (heating) can be carried out in one or more of three types of equipment viz. (a) oxygen bomb (b) fan circulated air oven (c) multi-cell air oven.

In the oxygen bomb, test pieces are aged in an atmosphere of high-pressure oxygen at moderately elevated temperatures. Because of the enriched oxygen atmosphere, a full ageing test can be accomplished in a relatively short time without resorting to temperatures higher than 70°C compared with 100°C to 150°C used in the air oven. However, the test has been criticised as being too severe and does not necessarily simulate practical conditions.

Heat-ageing tests may also be carried out in the ordinary fan-circulation air-oven. This is however, a fairly crude test because of the difficulties of obtaining even temperatures or consistent air flow throughout the oven and also due to contamination of adjacent specimens by volatiles. Hence this method and that of the oxygen bomb technique were not used in this research.

The ageing equipment selected for use in this work was the Wallace multi-cell air oven. It is the most common and probably (considered in broadest terms) the most widely applicable of the three methods. Essentially, it is an air-oven having separate single cells to contain each set of replicate samples, with provision for close control of air temperature and individual, metered air-flow through the sample in the cells. With careful maintenance, it provides accurate control and reproducibility of conditions and prevents cross-contamination between compounds.

3.3 Results and Discussion

The cure trace obtained using hexamethylene-N,N' bis(tertiary butyl peroxycarbamate (HBTBP) in various elastomers is compared with those of conventional curing systems (used as controls) in Figures 3.1 to 3.11. The various cure traces bear testimony to the wide applicability of HBTBP as crosslinking agents in elastomer systems. It is able to cure the following elastomers viz NBR (Figure 3.1), SBR (Figure 3.2), NR (Figure 3.3), NR/BR (Figure 3.4), Q (Figure 3.5), CR (Figure 3.6), FKM (Figure 3.7), ECO (Figure 3.8), BIIR (Figure 3.9), GPO (Figure 3.10). It is however not suitable for EPDM and CSM elastomers (Figure 3.11) as little or no cure response was obtained when HBTBP was used as crosslinking agent in these elastomers.

In diene-containing elastomers (NBR, SBR, NR and NR/BR), sulphur vulcanization systems gave the best cure response while HBTBP curing systems gave the least cure response; peroxide vulcanization systems were intermediate. In polychloroprene rubber, metal oxide curing system gave the best cure response, followed by peroxide curing system and HBTBP curing system. Also, the peroxide curing system in silicone rubber was found to give better cure response than the HBTBP curing system. The cure responses of HBTBP in FKM, BIIR and GPO were comparable to those of their respective controls. In epichlorohydrin homopolymer, HBTBP curing system gave a slightly better cure response than the ethylene thiourea curing system.

In general, conventional curing agents (sulphur, peroxide, metal oxide, etc) appear to give better cure response than HBTBP in most of the elastomers investigated. Nevertheless the major objective of the present exercise has been to demonstrate the use of HBTBP as a curing agent. Its use in the various elastomer systems has been peripheral and detailed studies were not carried out on each elastomer system. Also, it was observed that most HBTBP curing systems have the tendency to scorch and some of the compounds produced a disagreeable odour during curing. One further observation is the need to cure the compounds longer than the estimated t_{95} times to ensure that the carbon dioxide evolved during cure is sufficiently absorbed by the $Ca(OH)_2$ system.

Tensile sheets were prepared from the various compounds and the physical properties in both the unaged and aged conditions were obtained. The detailed results are shown in Tables 3.1-3.8. In most of the elastomers, the physical properties of vulcanizates cured with conventional crosslinking agents were better than those obtained from vulcanizates cured with HBTBP. However, it is unknown whether further studies on the use of HBTBP as a crosslinking agent in a specific elastomer would produce comparable properties to that obtained using a conventional crosslinking system. A comparison of physical properties obtained using different curing systems in nitrile rubber is shown in Table 3.1 as an example.

Although the ageing conditions were relatively mild (24 hours at 100°C in air-cell oven) some vulcanizates used as controls were protected with antioxidants while HBTBP-cured systems were deliberately unprotected. Still, retention of tensile properties in most HBTBP systems were good or even better than those of the controls after ageing. Though the ageing conditions used were mild for all systems, the fact that improved properties were obtained after ageing makes it possible that post-curing in an air-oven might be desirable to optimise HBTBP-cured systems (to be further investigated). A net loss in weight of about 0.5% was recorded for the test samples from all the vulcanizates after ageing, thus suggesting that some volatiles had been driven out.

Another interesting aspect of this work is the good cure response obtained when HBTBP was used to cure a fluorocarbon rubber (Viton GF*) and it compared favourably with the cure response obtained from the control compound (see Figure 3.7). Further studies on the use of HBTBP as crosslinking agent in fluorocarbon rubbers are described in the latter part of this work.

Rather surprisingly, HBTBP was found to be capable of curing epichlorohydrin homopolymer, bromobutyl and, copolymer of polypropylene oxide and allyl glycidyl ether (Figures 3.8-3.10). It must be stressed, however, that cure responses were poor in the three elastomer compounds. This notwithstanding, these types of rubbers (ECOH, CIIR, GPO) are known to have special structural features which undergo beta cleavage in the presence of decomposing peroxides or free radicals and hence are degraded.

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* Viton GF is a trade name of Du Pont.

In the case of epichlorohydrin, the use of 5 phr HBTBP did not produce a cure response; however at 3 phr HBTBP, a modest cure response was obtained. Thus, it would seem that high levels of crosslinking agent degrades the polymer or neutralises any crosslinking, whereas crosslinking predominates at lower concentrations of crosslinking agent. Also, it is worth noting that halogenated elastomers generally respond better to HBTBP curing than diene-based elastomers.

The cure capability of HBTBP has been examined in many elastomers. However, it is only in natural rubber that the mechanism of crosslink formation has been suggested. Hepburn(125) proposed a free radical mechanism for the crosslinking of natural rubber by bisperoxycarbamates which is stated from steps 1 through to step 7 in the next section.

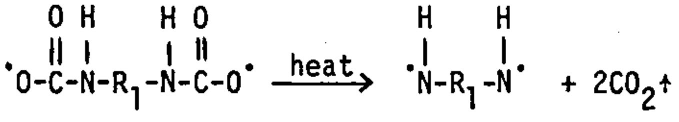
3.3.1 Cure Mechanism of Bisperoxycarbamates(125)

Thermal decomposition of the bisperoxycarbamate to produce free radicals (steps 1 and 2):

Step 1

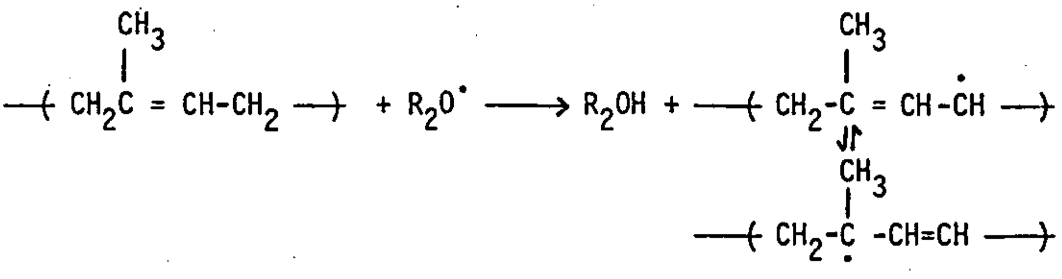
$$R_2\text{-O-O-}\overset{\overset{O}{\|}}{C}\text{-}\overset{\overset{H}{|}}{N}\text{-}R_1\text{-}\overset{\overset{H}{|}}{N}\text{-}\overset{\overset{O}{\|}}{C}\text{-O-O-}R_2 \xrightarrow{heat} {}^{\bullet}\text{O-}\overset{\overset{O}{\|}}{C}\text{-}\overset{\overset{H}{|}}{N}\text{-}R_1\text{-}\overset{\overset{H}{|}}{N}\text{-}\overset{\overset{O}{\|}}{C}\text{-O}^{\bullet} + 2R_2O^{\bullet} \qquad (1)$$

Step 2



$${}^{\bullet}\text{O-}\overset{\overset{O}{\|}}{C}\text{-}\overset{\overset{H}{|}}{N}\text{-}R_1\text{-}\overset{\overset{H}{|}}{N}\text{-}\overset{\overset{O}{\|}}{C}\text{-O}^{\bullet} \xrightarrow{heat} {}^{\bullet}\overset{\overset{H}{|}}{N}\text{-}R_1\text{-}\overset{\overset{H}{|}}{N}{}^{\bullet} + 2CO_2\uparrow \qquad (2)$$

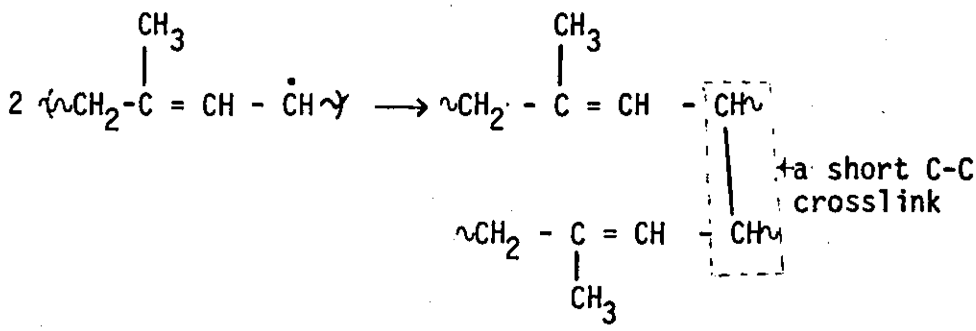
Step 3: Activation of the rubber molecule



$$\text{—(}CH_2\overset{\overset{CH_3}{|}}{C} = CH\text{-}CH_2\text{—)} + R_2O^{\bullet} \longrightarrow R_2OH + \text{—(}CH_2\text{-}\overset{\overset{CH_3}{|}}{C} = CH\text{-}\dot{C}H\text{—)} \rightleftharpoons \text{—(}CH_2\text{-}\underset{\bullet}{\overset{\overset{CH_3}{|}}{C}}\text{-}CH{=}CH\text{—)} \qquad (3)$$

Crosslink formation (Steps 4, 5 and 6)

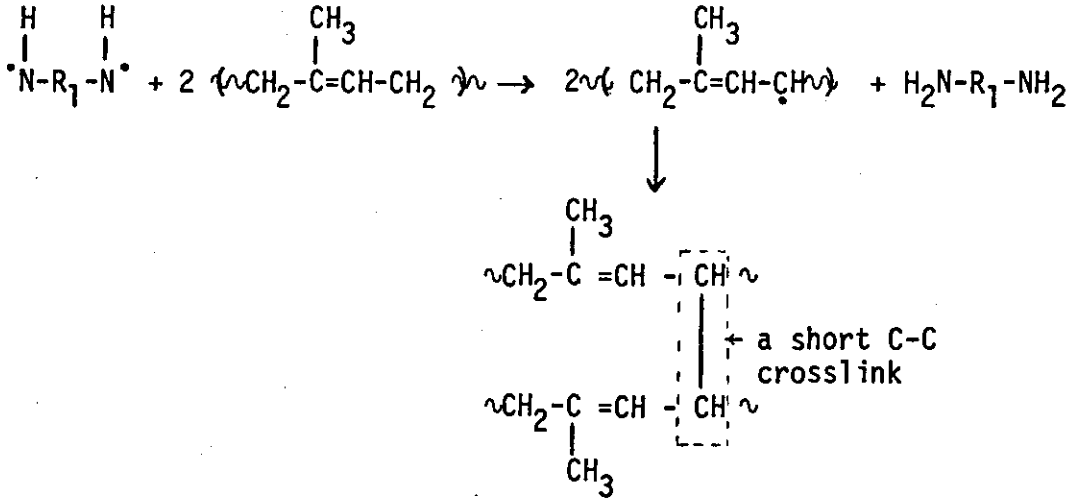
Step 4



$$2\ \{\sim CH_2-\overset{CH_3}{\overset{|}{C}}=CH-\dot{C}H\sim\} \longrightarrow \begin{array}{l} \sim CH_2-\overset{CH_3}{\overset{|}{C}}=CH-\boxed{CH}\sim \\ \qquad\qquad\qquad\qquad\quad | \\ \sim CH_2-\underset{CH_3}{\underset{|}{C}}=CH-\boxed{CH}\sim \end{array}$$

← a short C-C crosslink

(4)



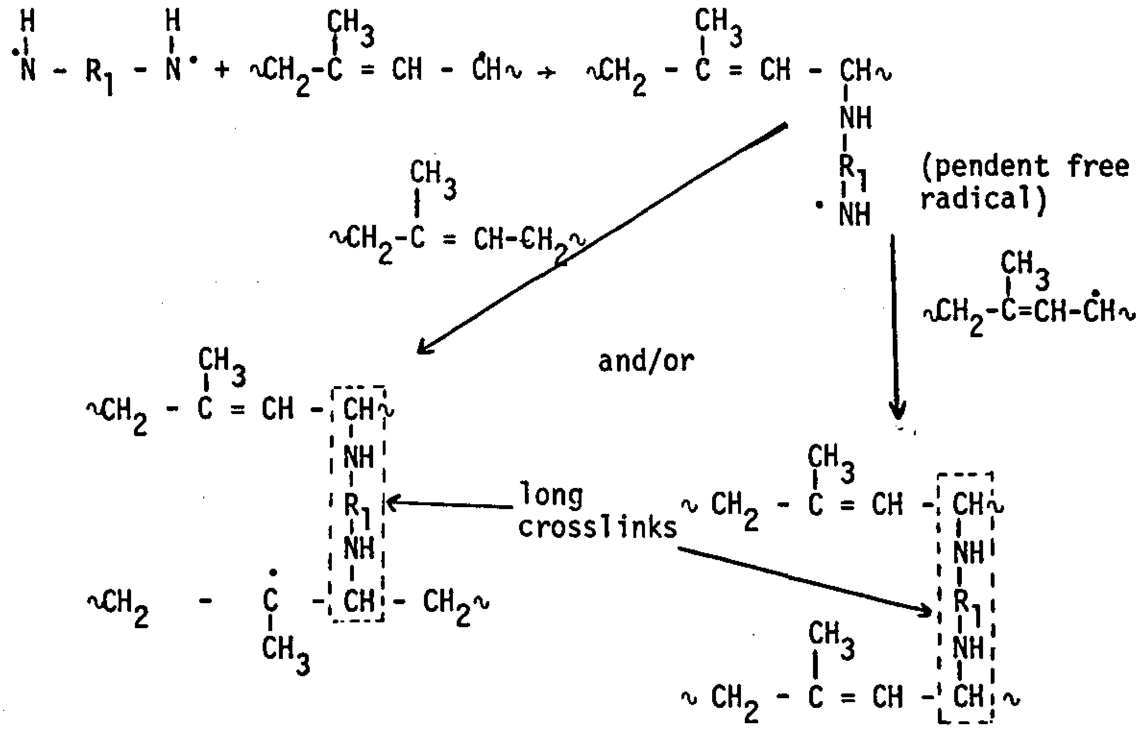
$$\overset{H}{\overset{|}{\dot{N}}}-R_1-\overset{H}{\overset{|}{\dot{N}}} + 2\ \{\sim CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2\sim\} \longrightarrow 2\sim\{CH_2-\overset{CH_3}{\overset{|}{C}}=CH-\underset{\bullet}{C}H\sim\} + H_2N-R_1-NH_2$$

$$\downarrow$$

$$\begin{array}{l} \sim CH_2-\overset{CH_3}{\overset{|}{C}}=CH-\boxed{CH}\sim \\ \qquad\qquad\qquad\qquad\quad | \\ \sim CH_2-\underset{CH_3}{\underset{|}{C}}=CH-\boxed{CH}\sim \end{array}$$

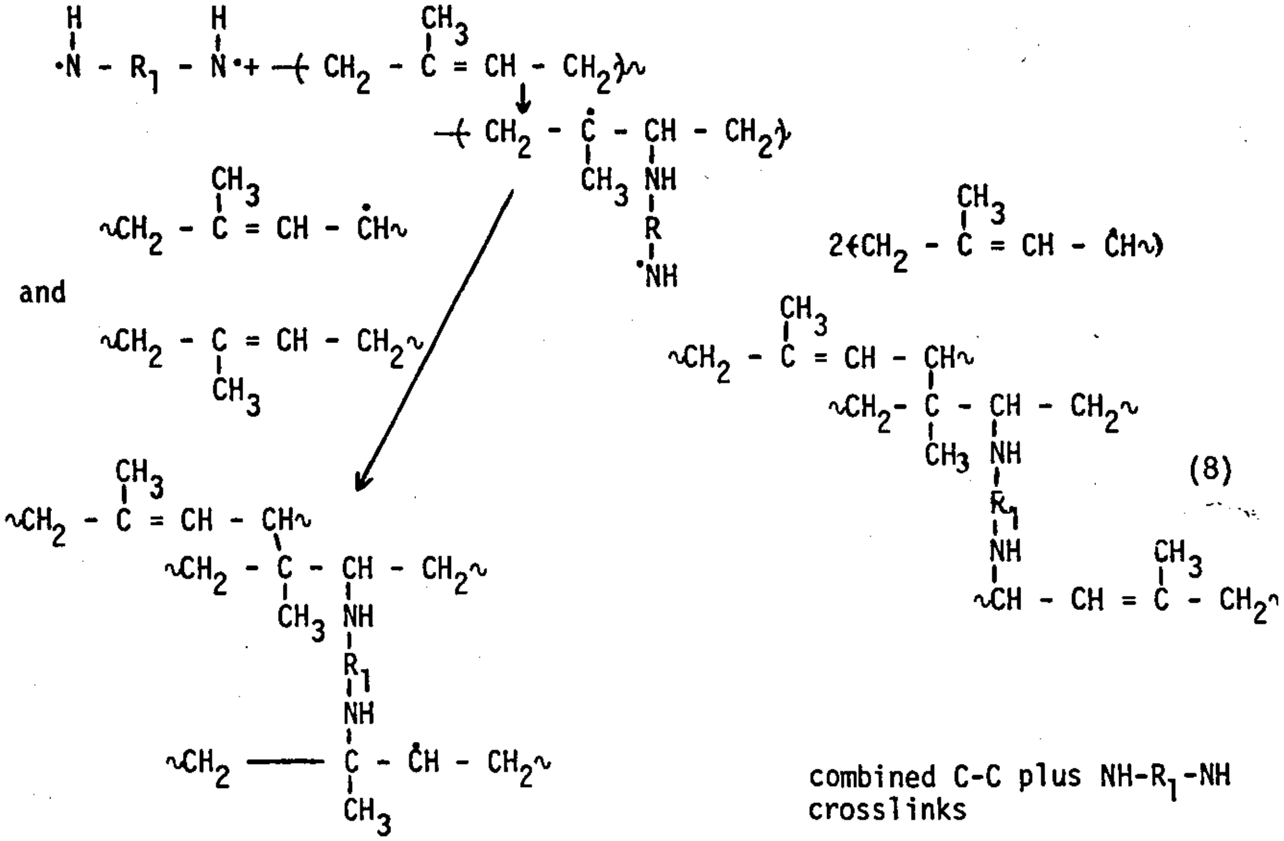
← a short C-C crosslink

Step 5



(6)

Step 6



(8)

combined C-C plus NH-R_1-NH crosslinks

combined C-C plus NH-R_1-NH crosslinks with a spare free radical site

Step 7

Simultaneous short C-C and long NH-R_1-NH crosslink formation.

3.4 Conclusion

The cure capability of HBTBP in elastomer compounds has been discussed in general terms since the primary objective behind this work was to scan a range of elastomers that can be crosslinked by HBTBP. Because of the general nature of this work, no attempt has been made at studying the mechanism of crosslinking or optimum crosslinking of any particular elastomer. Heat stability of vulcanizates which is of primary concern, has not been exhaustively studied. However, it can be said that HBTBP has been used successfully to crosslink the following elastomers viz. NR, SBR, NBR, FPM, Q, CR, ECOH, GPO, NR/BR and SBR/BR. It has not been found suitable as a crosslinker for EPDM, CSM and IIR.

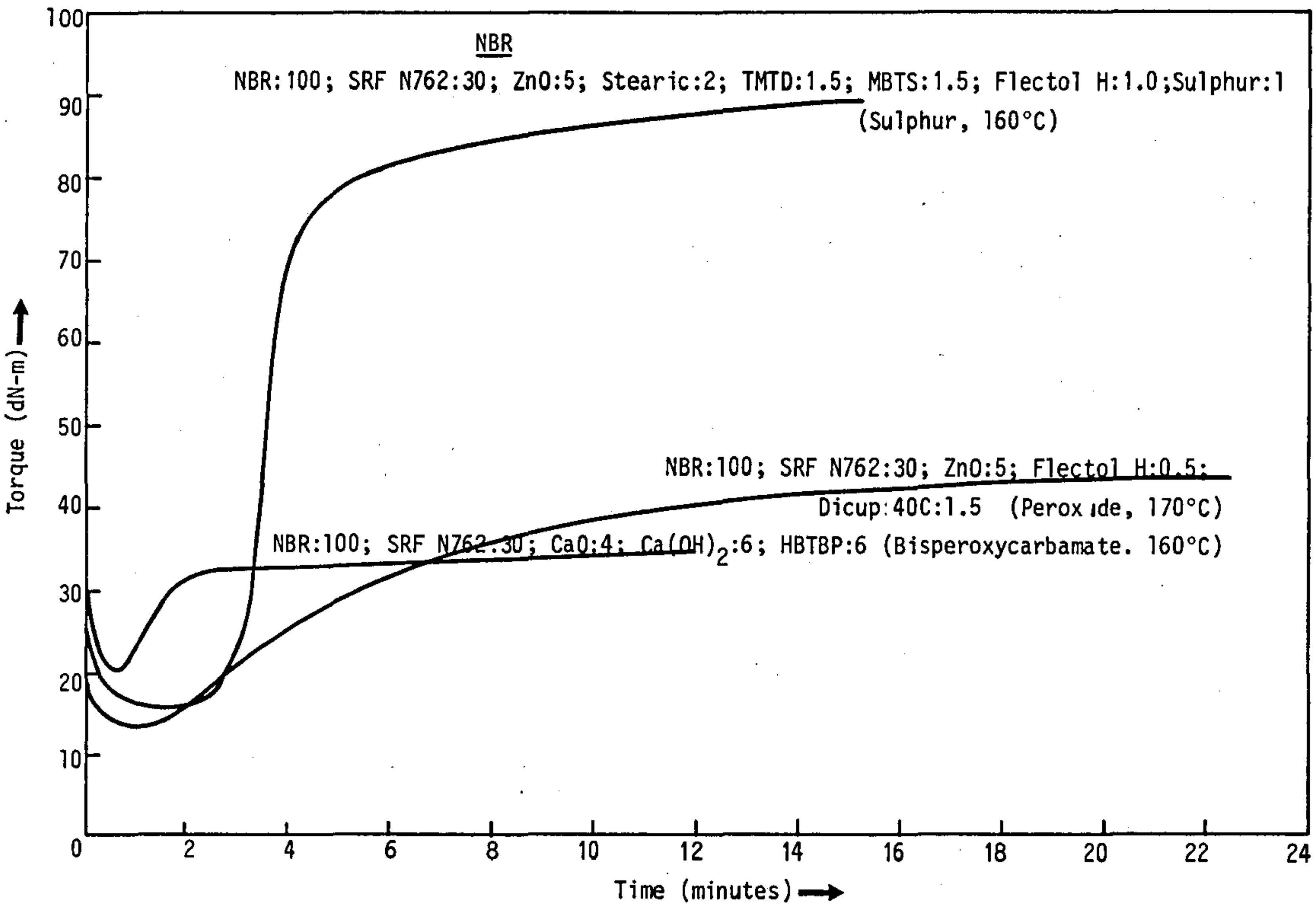


FIGURE 3.1: Monsanto ODR Cure Traces of Nitrile Rubber Using Different Crosslinking Systems

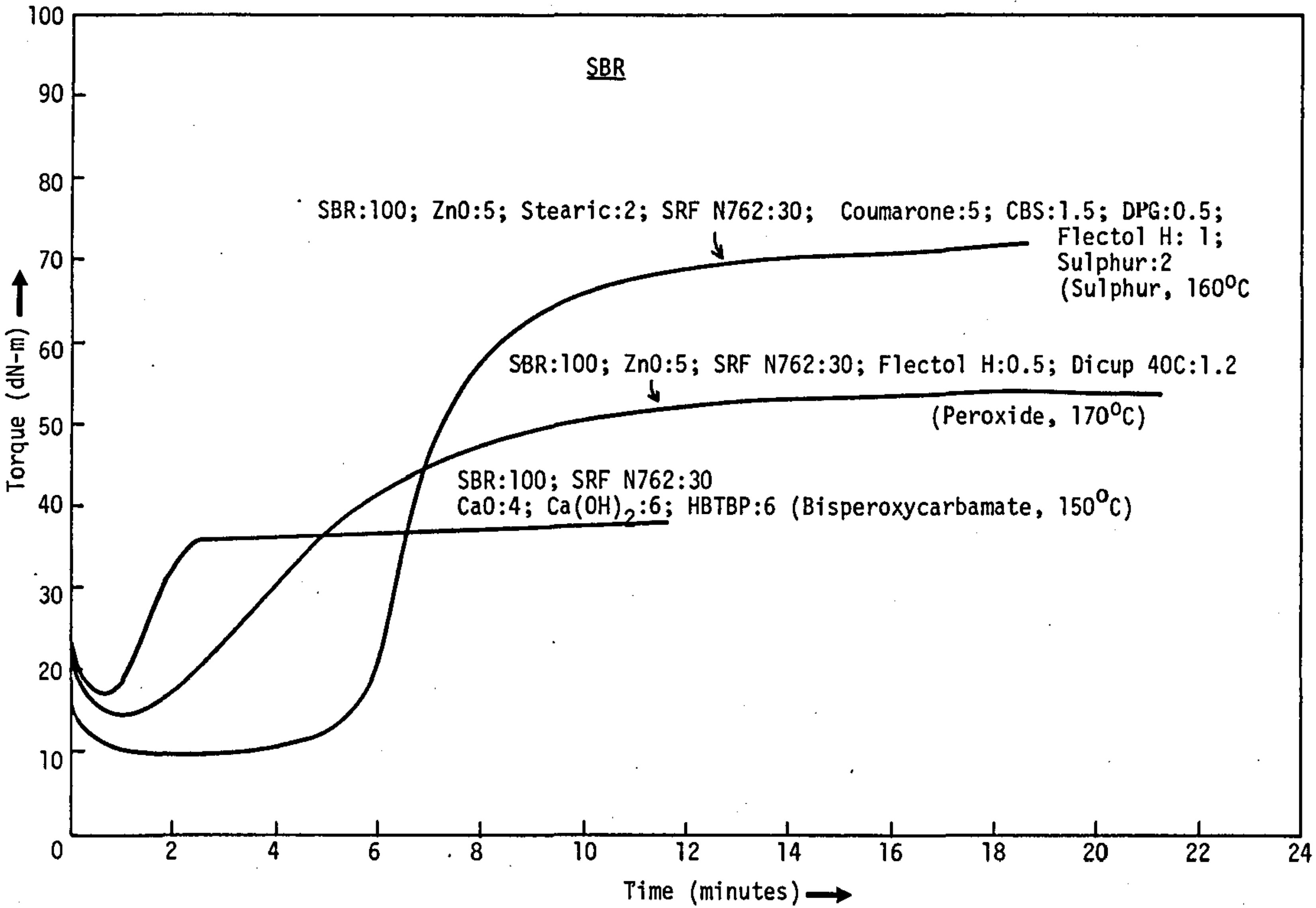


FIGURE 3.2: ODR Cure Traces of Styrene-Butadiene Rubber Using Different Crosslinking Systems

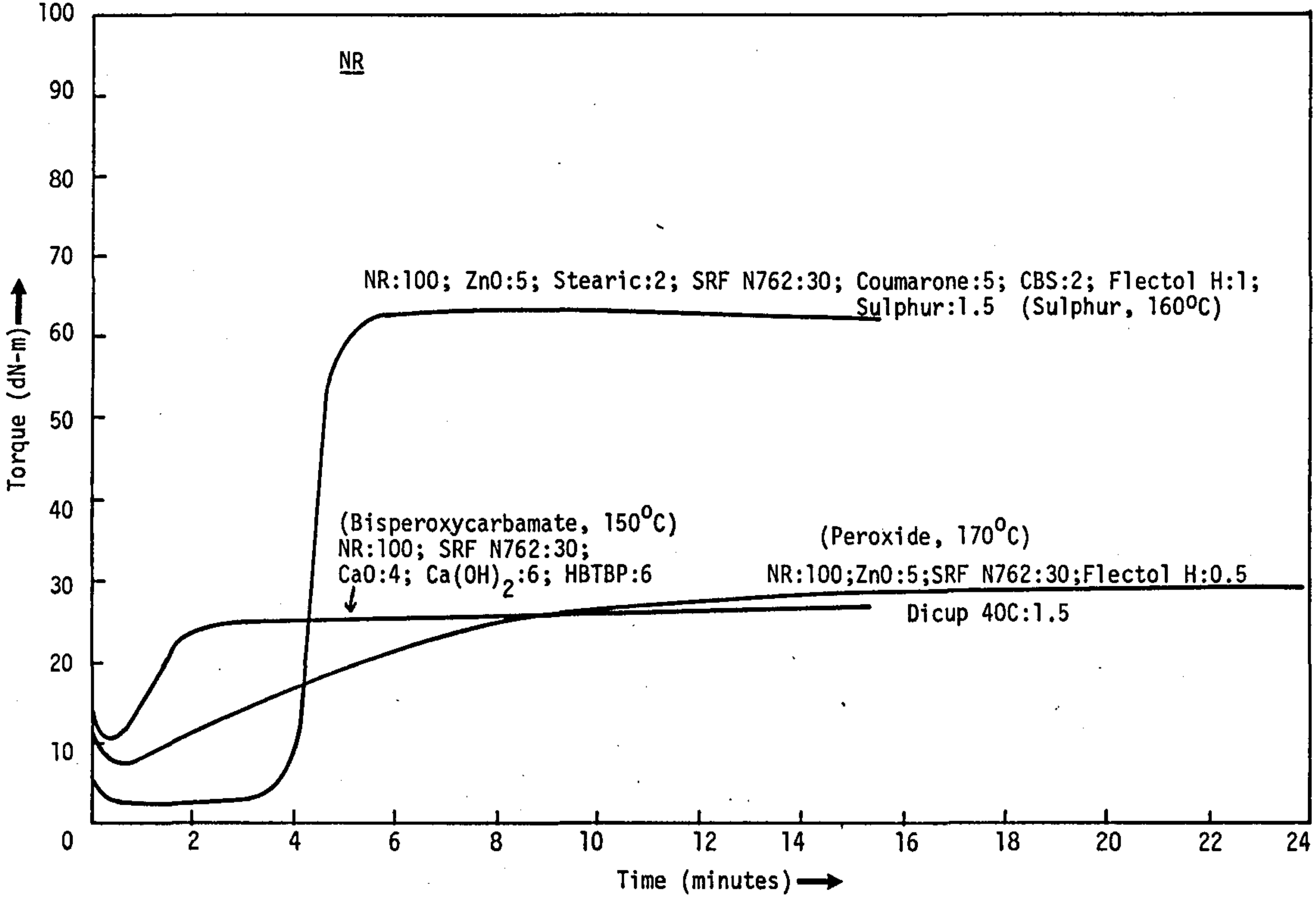


FIGURE 3.3: ODR Cure Traces of Natural Rubber Using Different Crosslinking Systems

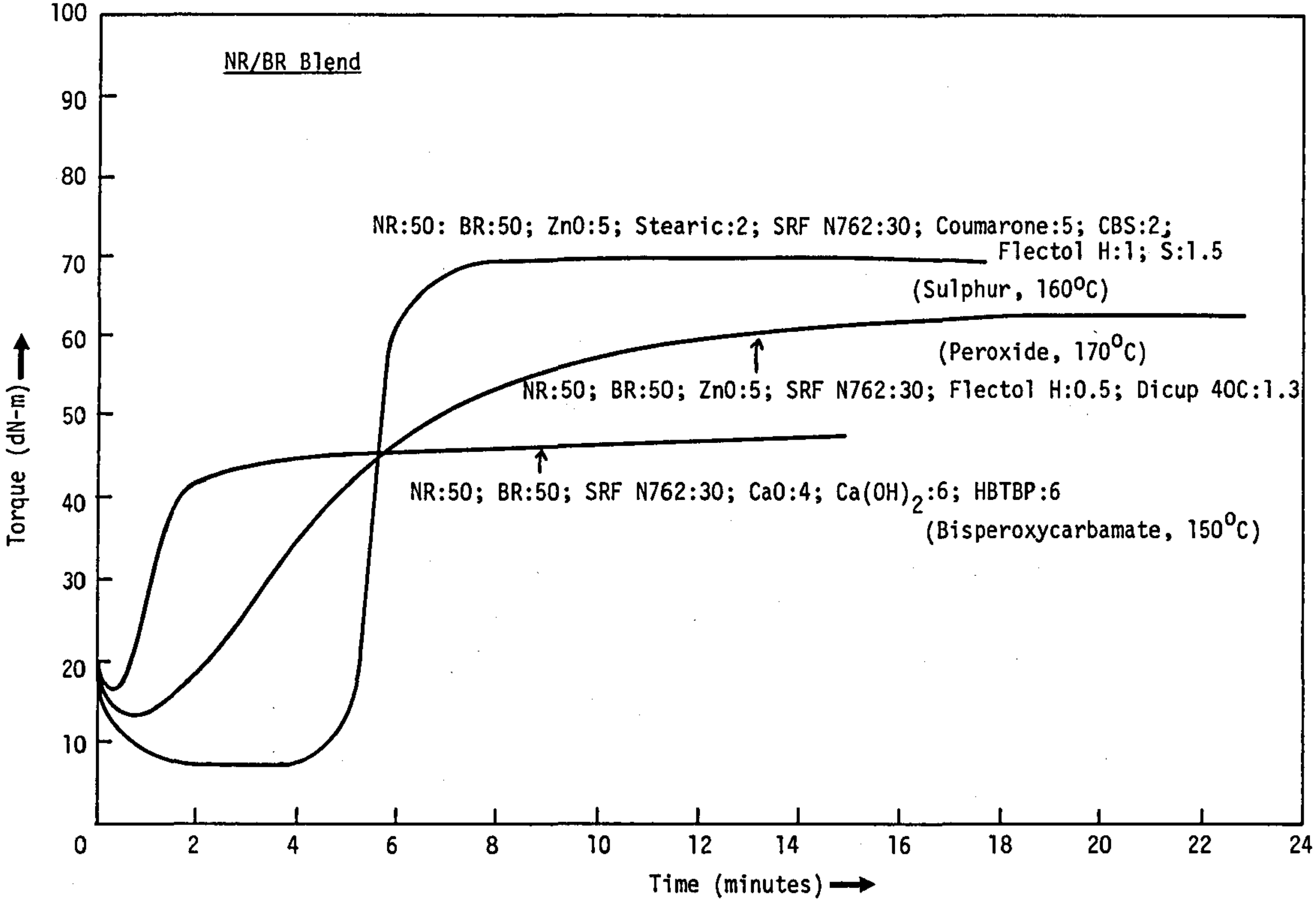


FIGURE 3.4: ODR Cure Traces of Natural Rubber/Polybutadiene Blend Using Different Crosslinking Systems

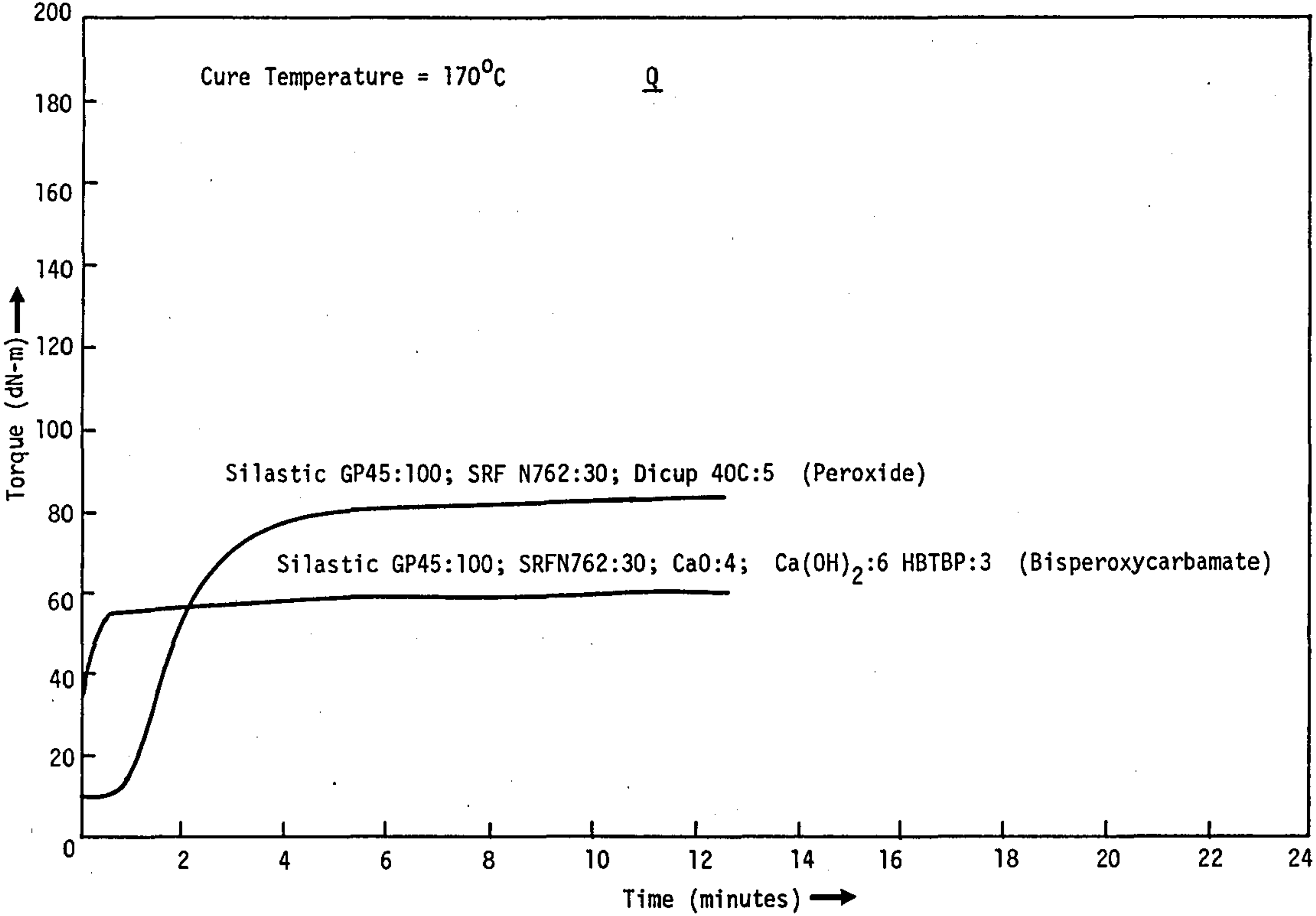


FIGURE 3.5: ODR Cure Traces of Silicone Rubber Using Different Crosslinking Systems

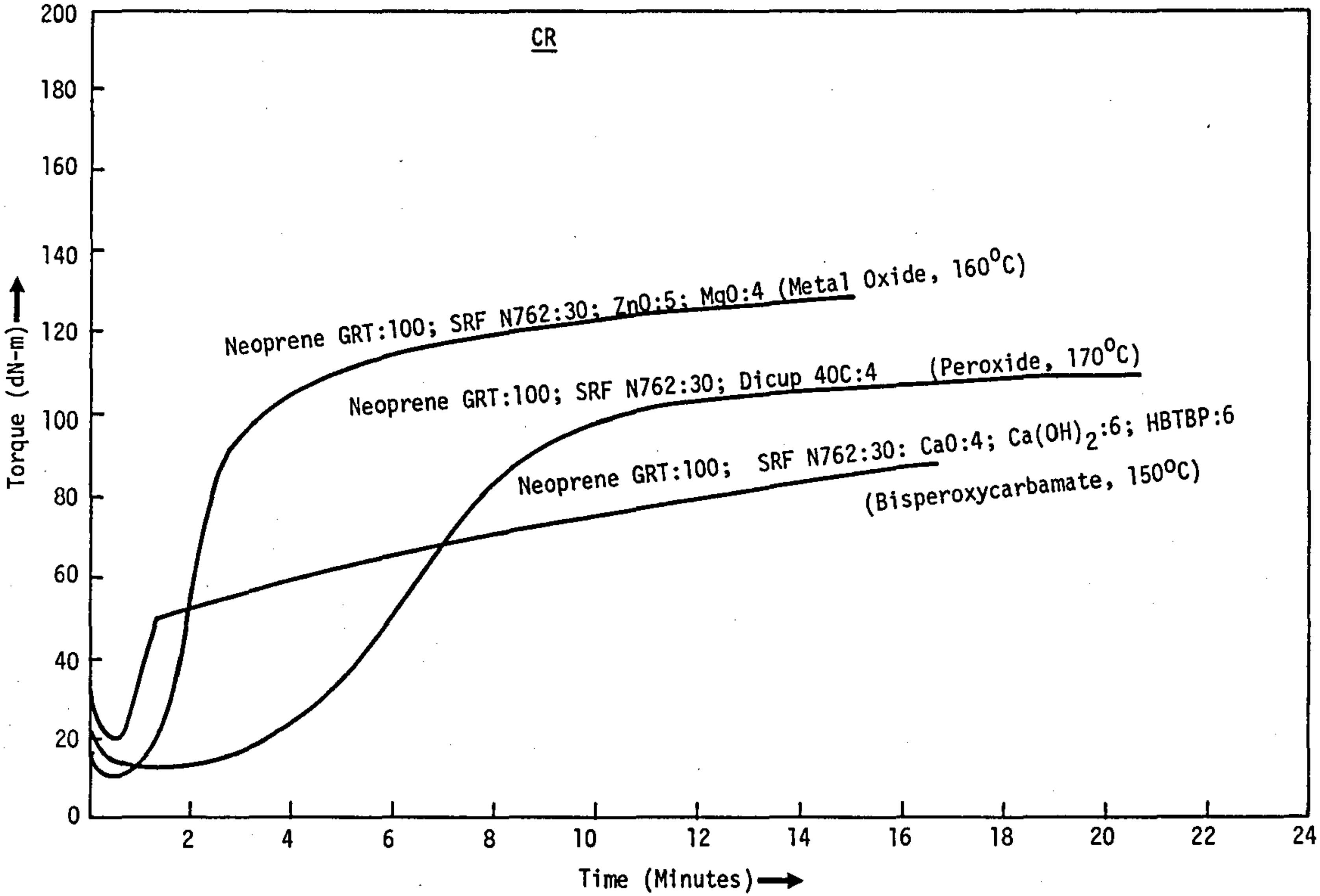


FIGURE 3.6: ODR Cure Traces of Polychloroprene Rubber Using Different Crosslinking Systems

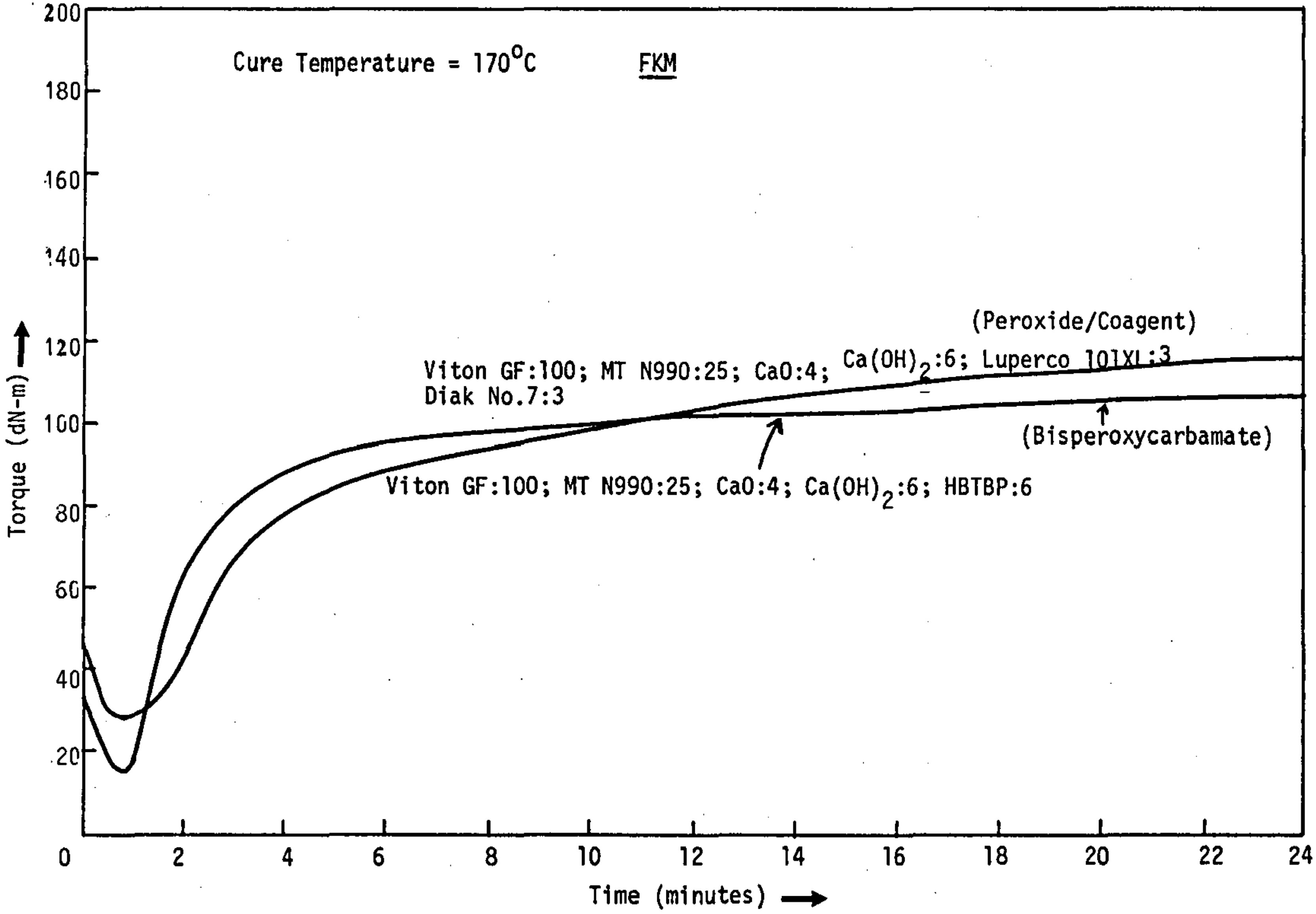


FIGURE 3.7: ODR Cure Traces of Fluororubber Using Different Crosslinking Systems

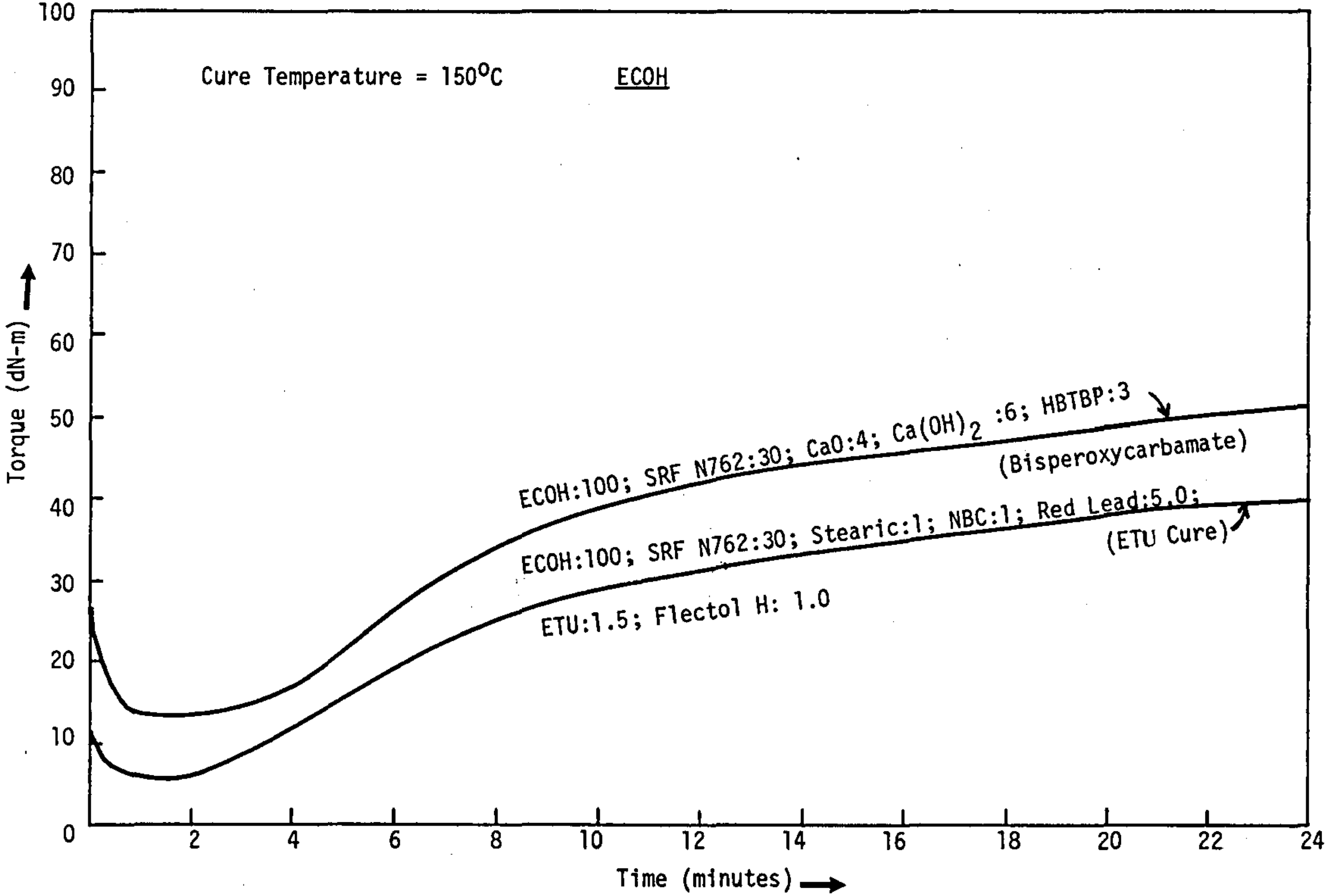


FIGURE 3.8: ODR Cure Traces of Epichlorohydrin Homopolymer using Different Crosslinking Systems

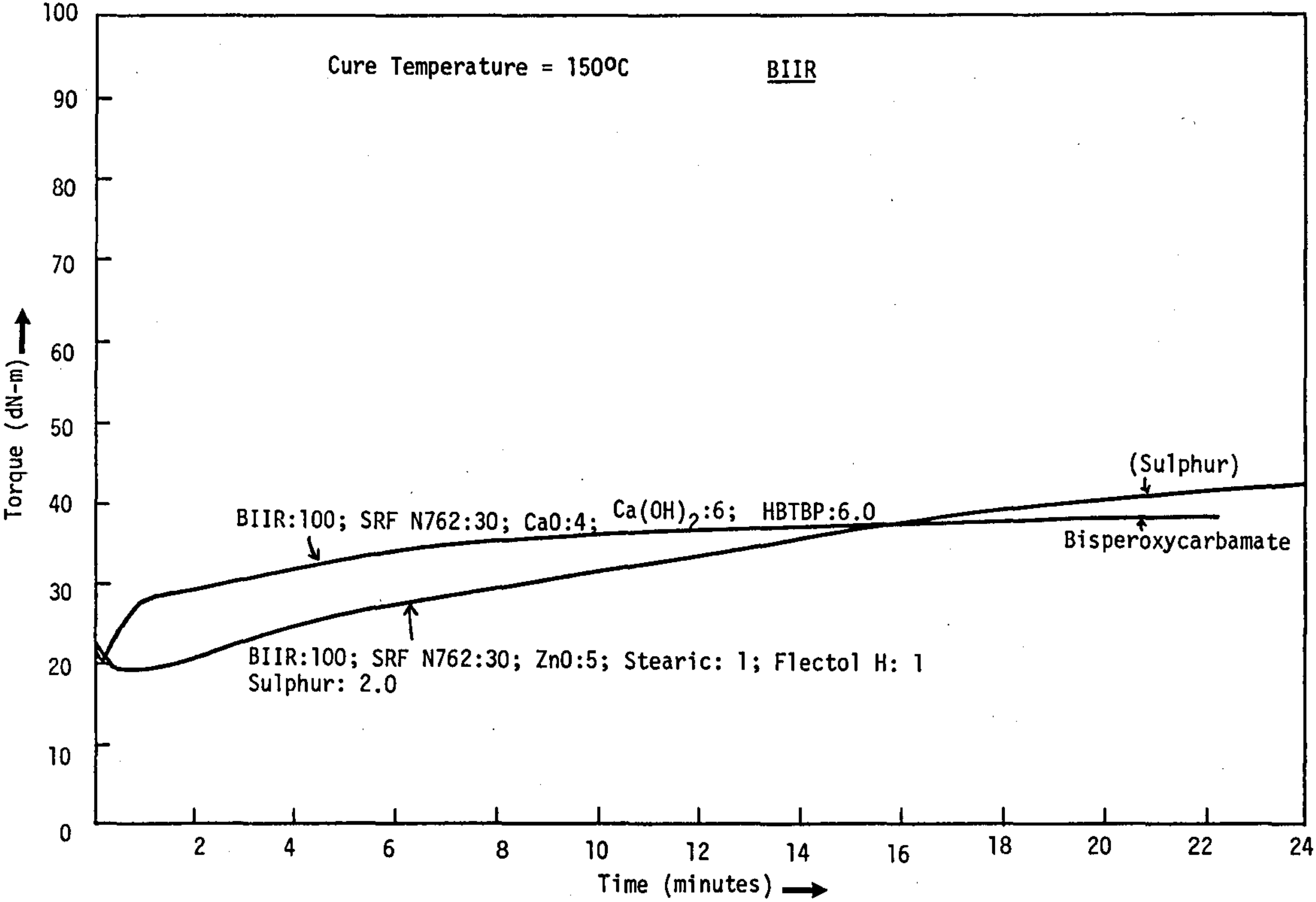


FIGURE 3.9: ODR Cure Traces of Bromobutyl Rubber Using Different Crosslinking Systems

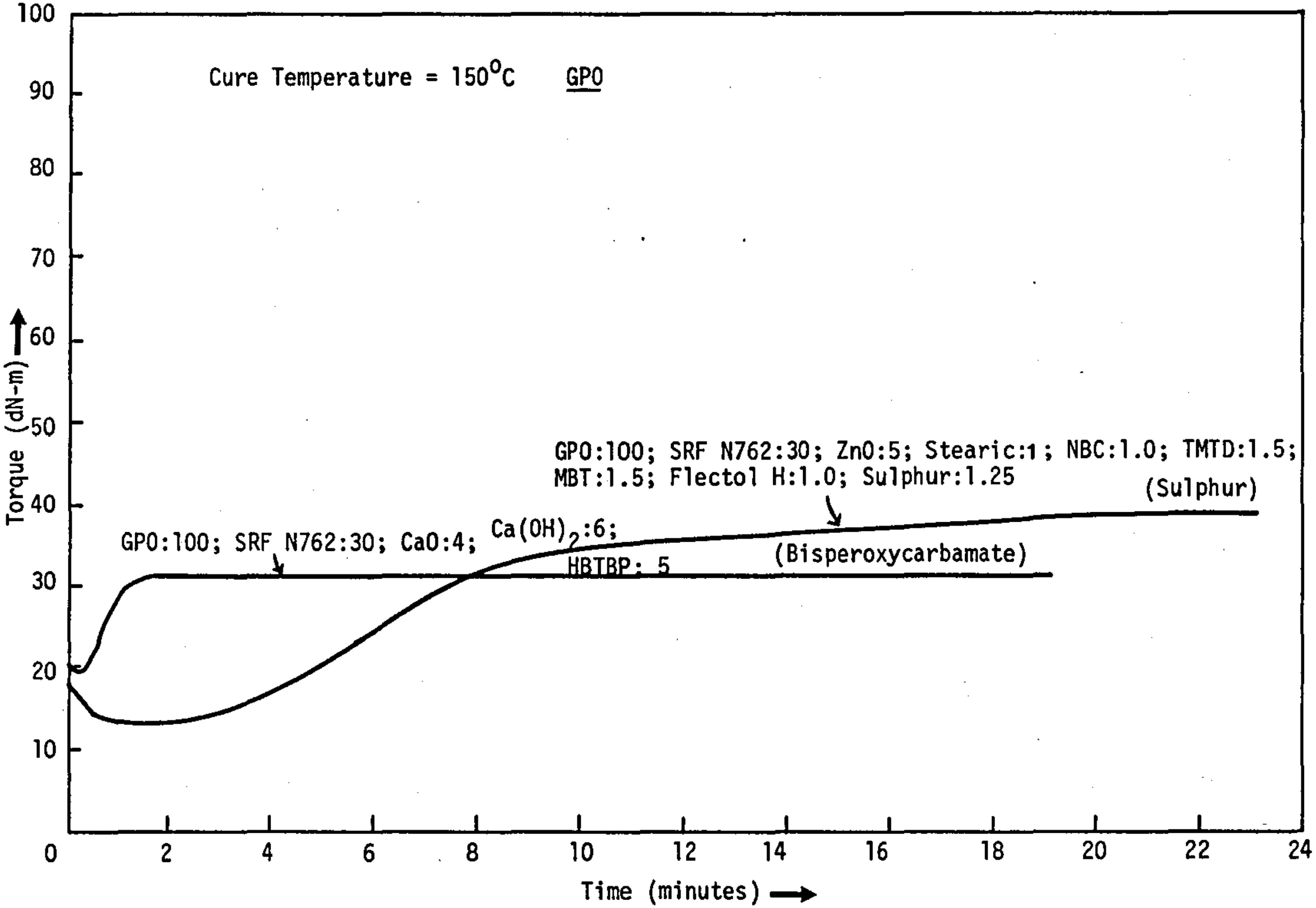


FIGURE 3.10: ODR Cure Traces for Copolymer of Polypropylene Oxide and Allyl Glycidyl Ether Using Different Curing Systems

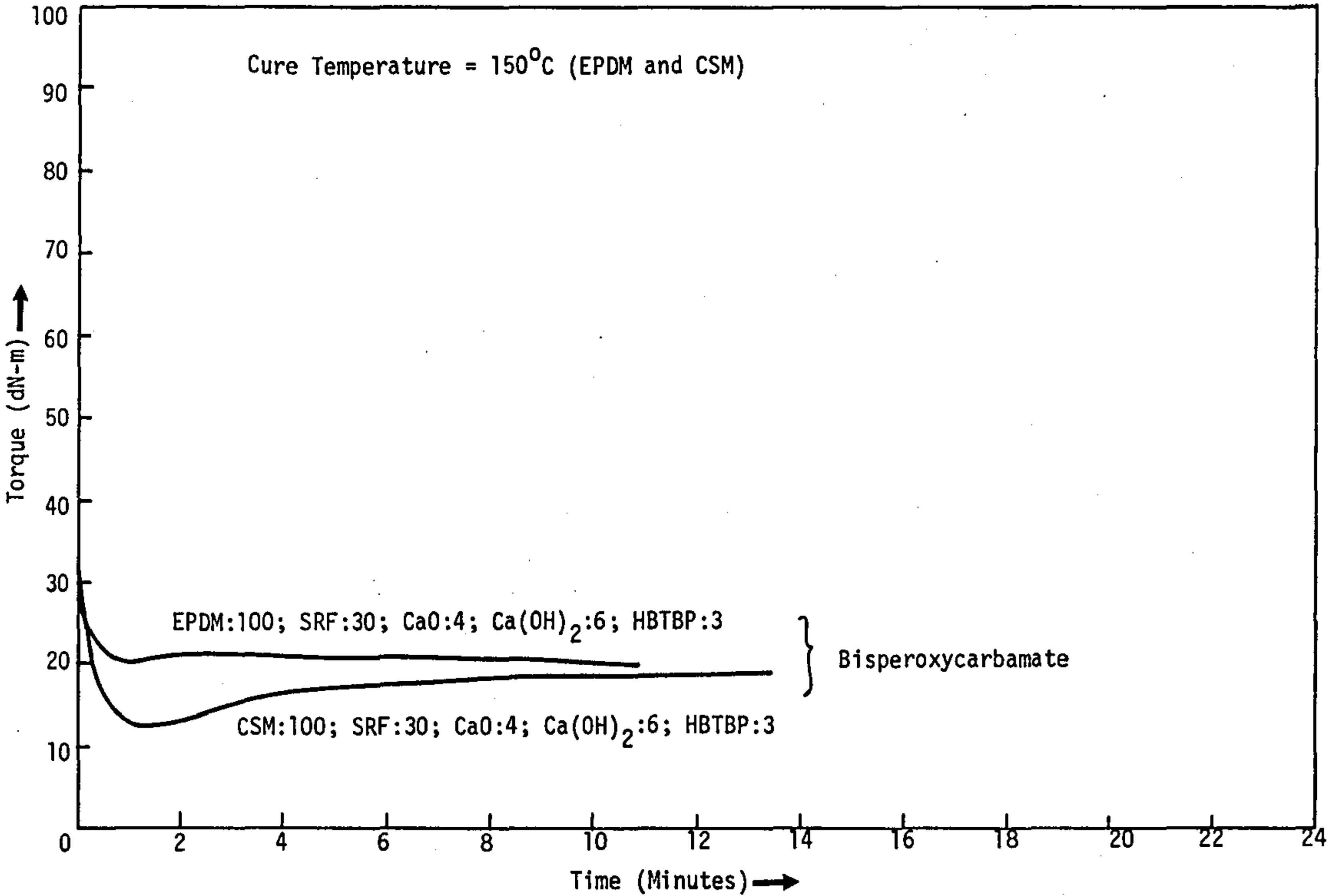


FIGURE 3.11: ODR Cure Traces of EPDM and CSM

Comparison of physical properties of vulcanizates obtained using HBTBP curing agent and 'controls' for various elastomers (Tables 3.1-3.8).

TABLE 3.1 Nitrile Rubber

	Sulphur (phr)*	Peroxide (phr)	HBTBP (phr)
NBR Breon 1042	100	100	100
SRF Black (N762)	30	30	30
ZnO	5.0	5.0	-
CaO	-	-	4.0
$Ca(OH)_2$	-	-	6.0
Stearic Acid	2.0	-	-
TMTD	1.5	-	-
MBTS	1.5	-	-
Flectol H	1.0	0.5	-
Sulphur	1.0	-	-
Dicup 40C	-	1.5	-
HBTBP	-	-	6.0
Mooney Scorch at 120°C	24 mins	>40 mins	5 mins
Cure Conditions (mins/Temp°C)	12/160	16/170	10/160
Unaged Properties			
Tensile Strength (MPa)	14.26	21.07	4.61
300% Modulus (MPa)	10.27	3.61	2.96
Elongation-at-break (%)	350	850	575
Tear Strength (kN/m)	24.75	30.02	34.60
Hardness IRHD	47	42	36
Resilience %	21	31	39
Aged Properties (24 hours at 100°C)			
Tensile Strength (MPa)	12.79	20.41	7.56
300% Modulus (MPa)	9.18	4.25	4.02
Elongation-at-break (%)	325	750	600
Tear Strength (kN/m)	22.39	24.46	44.39
Compression Set (%) (24 hrs @ 100°C, 25% strain)	8	25	72
% Retention of Tensile Strength	90	97	164

* phr - parts per hundred rubber

TABLE 3.2: Styrene-Butadiene Rubber

	Sulphur (phr)	Peroxide (phr)	HBTBP (phr)
SBR Intol 1502	100	100	100
ZnO	5.0	5.0	-
CaO	-	-	4.0
$Ca(OH)_2$	-	-	6.0
Stearic Acid	2.0	-	-
SRF Black (N762)	30	30	30
Coumarone Resin	5.0	-	-
CBS	1.5	-	-
DPG	0.5	-	-
Flectol H	1.0	0.5	-
Sulphur	2.0	-	-
Dicup 40C	-	1.2	-
HBTBP	-	-	6.0
Mooney Scorch at 120°C	43 mins	>40 mins	2.5 mins
Cure Conditions mins/°C	14/160	13/170	10/150
Unaged Properties			
Tensile Strength (MPa)	14.67	13.30	8.00
300% Modulus (MPa)	5.79	3.09	4.50
Elongation-at-break %	525	800	500
Tear Strength (kN/m)	28.57	27.89	28.37
Hardness IRHD	41	40	36
Resilience (%)	56	60	62
Aged Properties (24 hours at 100°C)			
Tensile Strength (MPa)	10.85	7.06	8.48
300% Modulus (MPa)	9.77	2.42	4.28
Elongation-at-break %	325	600	500
Tear Strength (kN/m)	18.18	36.2	22.15
Compression Set (%) (24 hrs @ 100°C, 25% strain)	31	15	50
% Retention of Tensile Strength	74	53	106

TABLE 3.3: Natural Rubber

	Sulphur (phr)	Peroxide (phr)	HBTBP (phr)
NR SMR 5 CV	100	100	100
ZnO	5.0	5.0	-
CaO	-	-	4.0
$Ca(OH)_2$	-	-	6.0
Stearic Acid	2.0	-	-
SRF Black (N762)	30	30	30
Coumarone Resin	5.0	-	-
CBS	2.0	-	-
Flectol H	1.0	0.5	-
Sulphur	1.5	-	-
Dicup 40C	-	1.5	-
HBTBP	-	-	6.0
Mooney Scorch at 120°C	40 mins	>40 mins	2 mins
Cure Conditions (mins/°C)	9/160	14/170	10/150
Unaged Properties			
Tensile Strength (MPa)	23.54	17.37	4.97
300% Modulus (MPa)	5.12	10.68	4.07
Elongation-at-break (%)	600	525	375
Tear Strength (kN m^{-1})	89.43	27.93	8.75
Hardness IRHD	36	36	<36
Rebound Resilience (%)	63	57	-
Aged Properties (24 hours at 100°C)			
Tensile Strength (MPa)	21.55	14.81	5.17
300% Modulus (MPa)	5.99	9.88	3.11
Elongation-at-break %	525	550	400
Tear Strength (kNm^{-1})	63.37	23.42	16.89
Compression Set % (24 hours at 100°C, 25% strain)	46	32	-
% Retention of Tensile Strength	92	85	104

phr - parts per hundred rubber

TABLE 3.4: Natural Rubber/Polybutadiene Blend

	Sulphur (phr)	Peroxide (phr)	HBTBP (phr)
NR SMR 5 CV	50	50	50
BR Intene*50	50	50	50
ZnO	5.0	5.0	-
CaO	-	-	4.0
$Ca(OH)_2$	-	-	6.0
Stearic Acid	2.0	-	-
SRF Black (N762)	30	30	30
Coumarone Resin	5.0	-	-
CBS	2.0	-	-
Flectol H	1.0	0.5	-
Sulphur	1.5	-	-
Dicup 40C	-	1.3	-
HBTBP	-	-	6.0
Mooney Scorch at 120°C	45 mins	>45 mins	2 mins
Cure Conditions (mins/°C)	12/160	12/170	10/150
Unaged Properties			
Tensile Strength (MPa)	14.31	6.35	4.39
300% Modulus (MPa)	6.08	3.97	3.18
Elongation-at-break (%)	525	400	400
Tear Strength (kNm^{-1})	25.74	8.67	10.95
Hardness IRHD	39	40	35
Rebound Resilience (%)	67	68	58
Aged Properties (24 hours at 100°C)			
Tensile Strength (MPa)	9.90	5.48	4.26
300% Modulus (MPa)	7.31	3.70	2.71
Elongation-at-break (%)	375	375	425
Tear Strength (kNm^{-1})	18.05	9.77	10.49
Compression Set (%) (24 hours at 100°C, 25% strain)	36	16	53
% Retention of Tensile Strength	69	86	97

*Intene is a trade name of Enichem

TABLE 3.5: Silicone Rubber

	Peroxide (phr)	HBTBP (phr)
Silastic* GP 45	100	100
SRF Black (N762)	30	30
CaO	-	4.0
$Ca(OH)_2$	-	6.0
HBTBP	-	3.0
Dicup 40C	5.0	-
Cure Conditions (mins/°C)	8/170	8/170
Unaged Properties		
Tensile Strength (MPa)	6.18	5.00
300% Modulus (MPa)	5.81	3.70
Elongation-at-break (%)	325	425
Tear Strength (kNm^{-1})	12.55	17.55
Hardness IRHD	46	44
Rebound Resilience (%)	52	41
Aged Properties (24 hours at 100°C)		
Tensile Strength (MPa)	5.93	5.21
300% Modulus (MPa)	-	5.21
Elongation-at-break (%)	225	300
Tear Strength (kNm^{-1})	10.73	17.2
Compression Set (%) (24 hours at 100°C, 25% strain)	7	46
% Retention of Tensile Strength	96	104

* Silastic is a trade name of Dow Corning Corporation

TABLE 3.6: Polychloroprene Rubber

	Metal Oxide (phr)	Peroxide (phr)	HBTBP (phr)
Neoprene* GRT	100	100	100
SRF Black (N762)	30	30	30
ZnO	5.0	-	-
MgO	4.0	-	-
CaO	-	-	4.0
Ca(OH)$_2$	-	-	6.0
HBTBP	-	-	6.0
Dicup 40C	-	4.0	-
Mooney Scorch at 120°C	15 mins	>40 mins	3 mins
Cure Conditions (mins/°C)	25/160	10/170	8/150
Unaged Properties			
Tensile Strength (MPa)	19.22	16.38	12.75
300% Modulus (MPa)	8.63	9.39	11.45
Elongation-at-break (%)	525	425	325
Tear Strength kNm^{-1}	71.17	54.22	28.32
Hardness IRHD	46	44	46
Resilience (%)	54	56	56
Aged Properties (24 hours at 100°C)			
Tensile Strength (MPa)	15.77	12.61	9.70
300% Modulus (MPa)	11.98	12.61	-
Elongation-at-break (%)	375	300	250
Tear Strength (kNm^{-1})	42.63	37.32	21.07
Compression Set (%) (24 hours at 100°C, 25% strain)	56	58	72
% Retention of Tensile Strength	82	77	76

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* Neoprene is a trade mark of Dupont

TABLE 3.7: Fluorocarbon Rubber

	Peroxide (phr)	HBTBP (phr)
Viton GF*	100	100
MT Black (N990)	25	25
CaO	4.0	4.0
$Ca(OH)_2$	6.0	6.0
HBTBP	-	4.0
Luperco 101XL**	3.0	-
TAIC*** (Diak No. 7)	3.0	-
Mooney Scorch at 120°C	>45 mins	5.5 mins
Cure Conditions (mins/°C)	15/170	15/170
Unaged Properties		
Tensile Strength (MPa)	16.52	11.06
300% Modulus (MPa)	-	-
Elongation-at-break (%)	175	250
Hardness IRHD	53	50
Aged Properties (24 hours at 100°C)		
Tensile Strength (MPa)	16.70	14.27
300% Modulus (MPa)	-	-
Elongation-at-break (%)	200	200
Hardness IRHD	53	53
Compression Set (%) (24 hours at 100°C, 25% strain)	-	45
% Retention of Tensile Strength	101	129

* Trade name of Du Pont

** 2,5-dimethyl-2,5-bis[t-butylperoxy]hexane (45% active)

*** Triallylisocyanurate

TABLE 3.8: GPO, ECOH and BIIR

	GPO		ECOH		BIIR	
	Sulphur (phr)	HBTBP (phr)	ETU (phr)	HBTBP (phr)	Sulphur (phr)	HBTBP (phr)
GPO Parel* 58	100	100	-	-	-	-
ECO H	-	-	100	100	-	-
Bromobutyl	-	-	-	-	100	100
ZnO	5.0	-	-	-	5.0	-
CaO	-	4.0	-	4.0	-	4.0
$Ca(OH)_2$	-	6.0	-	6.0	-	6.0
SRF Black	30	30	30	30	30	30
HBTBP	-	5.0	-	3.0	-	6.0
Stearic Acid	1.0	-	1.0	-	1.0	-
NBC	1.0	-	1.0	-	-	-
TMTD	1.5	-	-	-	-	-
MBT	1.5	-	-	-	-	-
Sulphur	1.25	-	-	-	2.0	-
Red Lead	-	-	5.0	-	-	-
ETU	-	-	1.5	-	-	-
Flectol H	1.0	-	1.0	-	1.0	-
Mooney Scorch at 120°C	9.5mins	1.5mins	8mins	15mins	6.5mins	1.0mins
Cure Conditions (mins/°C)	20/150	12/150	22/150	30/150	28/170	20/150
Unaged Properties						
Tensile Strength (MPa)	6.95	2.70	10.81	8.24	11.53	6.40
300% Modulus MPa	4.81	-	6.15	3.45	7.36	-
Elongation-at-break (%)	450	225	500	600	500	275
Tear Strength (kNm^{-1})	18.28	-	33.6	41.56	23.02	15.07
Hardness IRHD	41	36	38	<35	35	35
Rebound Resilience (%)	70	45	13	14	12	19
Aged Properties (24 hours at 100°C)						
Tensile Strength (MPa)	7.73	3.52	15.33	8.69	8.80	6.18
300% Modulus MPa	-	3.52	14.06	4.25	6.61	-
Tear Strength (kNm^{-1})	15.92	-	31.42	51.89	22.54	15.83
Elongation-at-break (%)	250	300	325	625	400	225
Compression Set % (24 hours at 100°C 25% strain)	65	40	68	42	43	28
% Retention of Tensile Strength	111	130	142	105	76	97

* Parel is a trade name of Hercules Chemicals

CHAPTER 4

CURING OF FLUOROCARBON RUBBERS BY HBTBP

4.1 Introduction

The results of previous work in Chapter 3 has shown that a relatively good cure response was obtained when HBTBP was used as crosslinking agent in a fluoroelastomer compound. Hence, further studies on the use of HBTBP as crosslinking agent would be specifically limited to fluoroelastomer compounds. However, before describing the experimental work on the use of HBTBP as crosslinking agent in fluoroelastomers, some background information on fluoroelastomers and their established crosslinking systems are discussed.

4.1.1 Fluoroelastomers

Commercial fluoroelastomers are co- or terpolymers of vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene or chlorotrifluoroethylene. These fluoroelastomers are identified as "Viton" brand (E I du Pont de Nemours and Company, USA); "Fluorel" brand elastomers and "Kel-F" elastomer (Minnesota Mining and Manufacturing Company, USA); "Technoflon" (Montecatini Edison, Italy); SKF-26 and SKF-32 (USSR); and "Daiel"-501 (Daikin Kogyo Company Ltd, Japan). The monomers from which these fluoroelastomers are believed to be polymerized are shown in Table 4.1(144).

There are reports of fluoroalkylsiloxanes(145-147) and various developments have led to the production of uncompounded fluorosilicone gum which is designated "Silastic" LS-420 (Dow Corning Corporation, USA). Other fluorocarbon/fluorinated elastomers are available(144) and new types are still being developed(148,149); however this work will be limited to the Viton brand of fluoroelastomers which are widely used.

TABLE 4.1: Commercial Fluoroelastomers

Trade Name	Monomers
Viton A, AHV, A-35 E-60, E-60C "Fluorel" 2140, 2141, 2143, 2146, 2160, 2170 SKF-26	Vinylidene fluoride and hexafluoropropylene
Viton B, B-50 Daiel G-501	Vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene
Kel-F 3700, 5500 SKF-32	Vinylidene fluoride and chlorotrifluoroethylene
Tecnoflon SL	Vinylidene fluoride and 1-hydropentafluoropropylene
Tecnoflon T	Vinylidene fluoride, tetrafluoroethylene, and 1-hydropentafluoropropylene

Structural formulae of monomers

Vinylidene fluoride (VF_2)

$CH_2 = CF_2$

Hexafluoropropylene (HFP)

$CF_3 - CF = CF_2$

Tetrafluoroethylene (TFE)

$CF_2 = CF_2$

Chlorotrifluoroethylene (CITFE)

$CFCl = CF_2$

1-Hydropentafluoropropylene (HFPE)

$CF_3 - CF = CHF$

4.1.2 Curing System

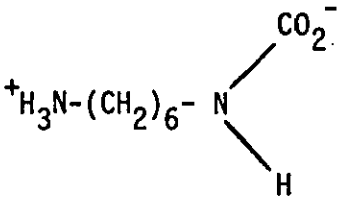
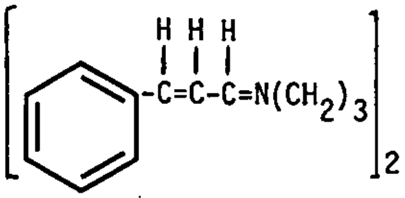
Several curing systems have been investigated or developed for vinylidene fluoride copolymers. Some of them are (i) diamines and their derivatives(150), (ii) peroxides with or without coagents(151-154), (iii) aromatic polyhydroxy compounds(144,155), (iv) dithiols in combination with amines(156), (v) high-energy radiation(117,157). Most of these curing systems require the inclusion of a basic metal oxide/ hydroxide in the compound formulation.

Aliphatic polyamines produce a good balance of properties but are much too reactive i.e. tend to scorch during cure. This led to the development of carbamate salts of diamines which are less reactive and therefore more practical. The use of aromatic diamines has also been employed(144) but has so far yielded little success. A recent work(151) described the use of peroxides with suitable coagents to cure fluoroelastomers which resulted in vulcanizates with outstanding heat and compression resistance. Fluorinated elastomers may also be cured with nitrogenfluoride(144,158) by exposing a premoulded film of the polymer to various concentrations of the gas at temperatures from 0°C to 125°C. Vulcanizates were reported to have excellent resistance to creep and heat ageing. However, nitrogen fluoride (N_2F_2) has limited application because of its explosive nature. The use of dithiols for curing fluoroelastomers in the presence of tertiary amines was reported by Smith(156) and compounds obtained were reported to have good scorch resistance.

In general, the practical curing systems of importance for vinylidene fluoride copolymers are:

1. aliphatic diamine derivatives in combination with metal oxides;
2. aromatic polyhydroxy compounds in combination with strong alkyl or aryl bases or their derivatives and basic metal oxides and hydroxides;
3. peroxides in combination with suitable coagents.

Examples of diamine derivatives are shown below:

Diak No. 1	Hexamethylene diamine carbamate	
Diak No. 3	N,N'-Dicinnamylidene-1,6-hexanediamine	
Diak No. 4.	An alicyclic amine salt, not specified.	

4.1.3 Compounding Practice

Most fluoroelastomer compounds have a typical formulation shown below:

	phr
Fluoroelastomer*	100.0
Metal Oxide	3-15
Filler	10-30
Processing Aid	0.5-2.0
Curing Agent	0.5-4.0

The metal oxide in the formulation is used as acid acceptor in curing reactions. Zinc oxide and dibasic lead were the earliest forms of acid acceptors. However, they give a rather low state of cure and their use is limited. Litharge is used in acid and water resistance compositions, while magnesium oxide has a more or less general use.

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* Fluoroelastomers will be referred to by their trade names as they are not easily discernible by their chemical structure - some of which are not completely disclosed.

Calcium oxide is useful for articles with thick cross-sections and helps to reduce void formation. Also shrinkage is less with calcium oxide but there is a possible disadvantage of moisture pick-up by the vulcanizate when exposed to atmospheric conditions.

As in other elastomers, fillers are used in fluoroelastomers for the following reasons viz:

a) to reduce cost;
b) to facilitate processing by reducing nerve of the uncured stock, and
c) to adjust hardness and modulus.

Medium thermal black (N990 or N908) is most commonly used in fluoroelastomers because of its combination of good processing and good vulcanizate properties. However filler loadings are generally low to allow easy processability. If high loadings are used or highly reinforcing fillers are chosen, the viscosity becomes too high and consequently processing would be difficult.

Whereas petroleum hydrocarbons and organic esters are used as plasticizers in general purpose elastomers, they are not often used with fluoroelastomers because of their solvent resistance which makes few of the plasticizers compatible and some plasticizers may interfere with cure. Furthermore, the plasticizers may vaporize during postcure or heat ageing so that vulcanizates containing them shrink in direct proportion to the amount used. In thick sections, plasticizers may cause sponging or fissuring due to evaporation during postcure.

4.2 Experimental Section

4.2.1 Materials

The "Viton" brand of fluoroelastomers were obtained from du Pont (UK) Ltd. Diak No. 7 (triallylisocyanurate), Viton Curative No 20 (Organophosphonium salt), and Viton Curative No 30 (Dihydroxy aromatic compound) are proprietary materials obtained from du Pont (UK) Ltd. Calcium hydroxide ($Ca(OH)_2$-VE) and calcium oxide (CaO-VG) are rubber-grade materials obtained from John and ESturge Ltd, UK. Luperco 101-XL (2,5-dimethyl-2,5-bis[t-butyl peroxy] hexane, 45% active ingredient on inert carrier) was obtained from K and K Greef Chemicals Ltd, UK. Other materials are standard compounding ingredients and were obtained from commercial sources.

4.2.2 Mix Formulation

The effect of increasing concentration of HBTBP curing agent in Viton GF was investigated using the formulation below

	phr
Viton GF	100
CaO VG	4
$Ca(OH)_2$ VE	6
MT black N990	25
HBTBP	1-5

The formulation used as control was developed from du Pont's technical literature(159) and stated appropriately in the results and discussion section. Polymer and compounding ingredients were mixed on a two-roll mill as described in Chapter 3. A modification however, is the preblending of all compounding ingredients before addition on the mill and batch was refined on a tight mill 24 hours after mixing to enhance dispersion. Also, a two-step cure was used as it is the practice with fluorocarbon rubbers. However the physical properties of vulcanizates were determined after press-cure to examine the changes brought about by postcuring. A cure temperature of 170°C was used in moulding vulcanizate specimens and air-oven postcuring at 250°C for 24 hours.

4.3 Results and Discussion

4.3.1 HBTBP in Viton GF

Using increasing levels of HBTBP curing agent in Viton GF, the cure traces shown in Figure 4.1 were obtained. The Oscillating Disc Rheometer (ODR) trace for the control compound is shown in Figure 4.2 with the cure trace of another compound containing 6 phr of HBTBP; this demonstrates that Viton GF could be formulated with HBTBP to obtain about the same level of cure with the control compound.

A particular problem with the use of HBTBP is the evolution of carbon dioxide during cure. Although this problem was overcome by the inclusion of calcium hydroxide in the formulation, it was more pronounced at increased levels of HBTBP. Based on compounding experience, it would be necessary that, for every phr of HBTBP used, a minimum of 2 phr of calcium hydroxide would be required to overcome porosity. It is also worth mentioning that the Mooney scorch values (Table 4.2) and the ODR traces show that the compounds formulated with HBTBP were rather scorchy. No attempt was made to improve the safe processing times of the compound. The maximum torque values obtained from the Oscillating Disc Rheometer (ODR) after 24 minutes, for the various compounds, increases with increase in the concentration of HBTBP. This suggests that more crosslinks are introduced as the concentration of crosslinking agent is increased. Conversely, the minimum ODR torque values of the compounds decreases as the concentration of crosslinking agent is increased. Hence it may be possible that HBTBP, in addition to its use as a curative in Viton GF, has a slight plasticising effect as well. The reason for this observation is probably due to initial main chain scission due to increasing free-radical concentration.

Vulcanizates of the compounds containing HBTBP and that of the control compound were prepared using moulding techniques as described in Chapter 3. The physical properties shown in Table 4.2 were obtained for samples that were postcured and for samples without postcuring. The results clearly demonstrate that fluoroelastomer compounds cured with HBTBP respond to postcuring operation as with other established

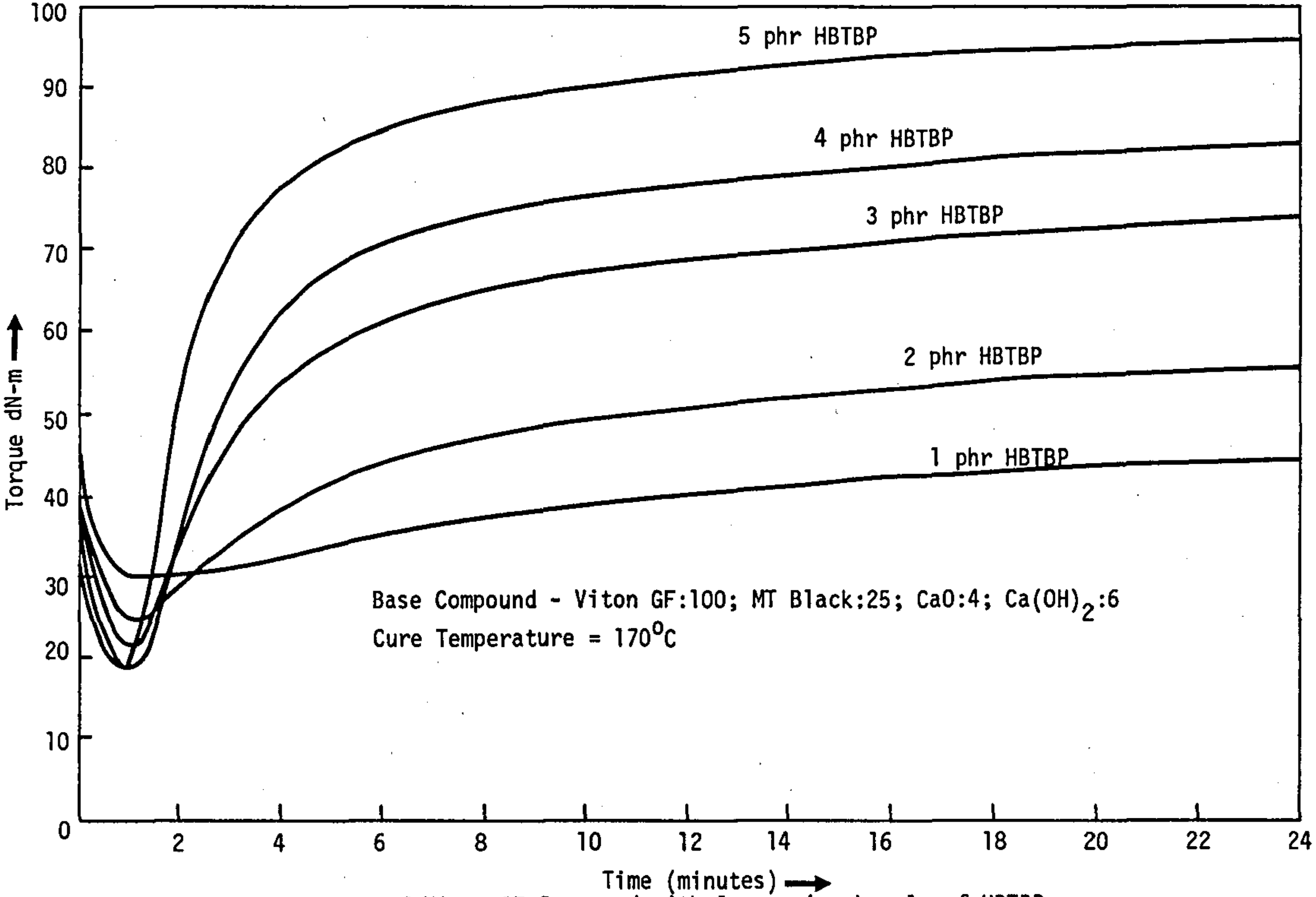

FIGURE 4.1: ODR Cure Traces of Viton GF Compound with Increasing Levels of HBTBP

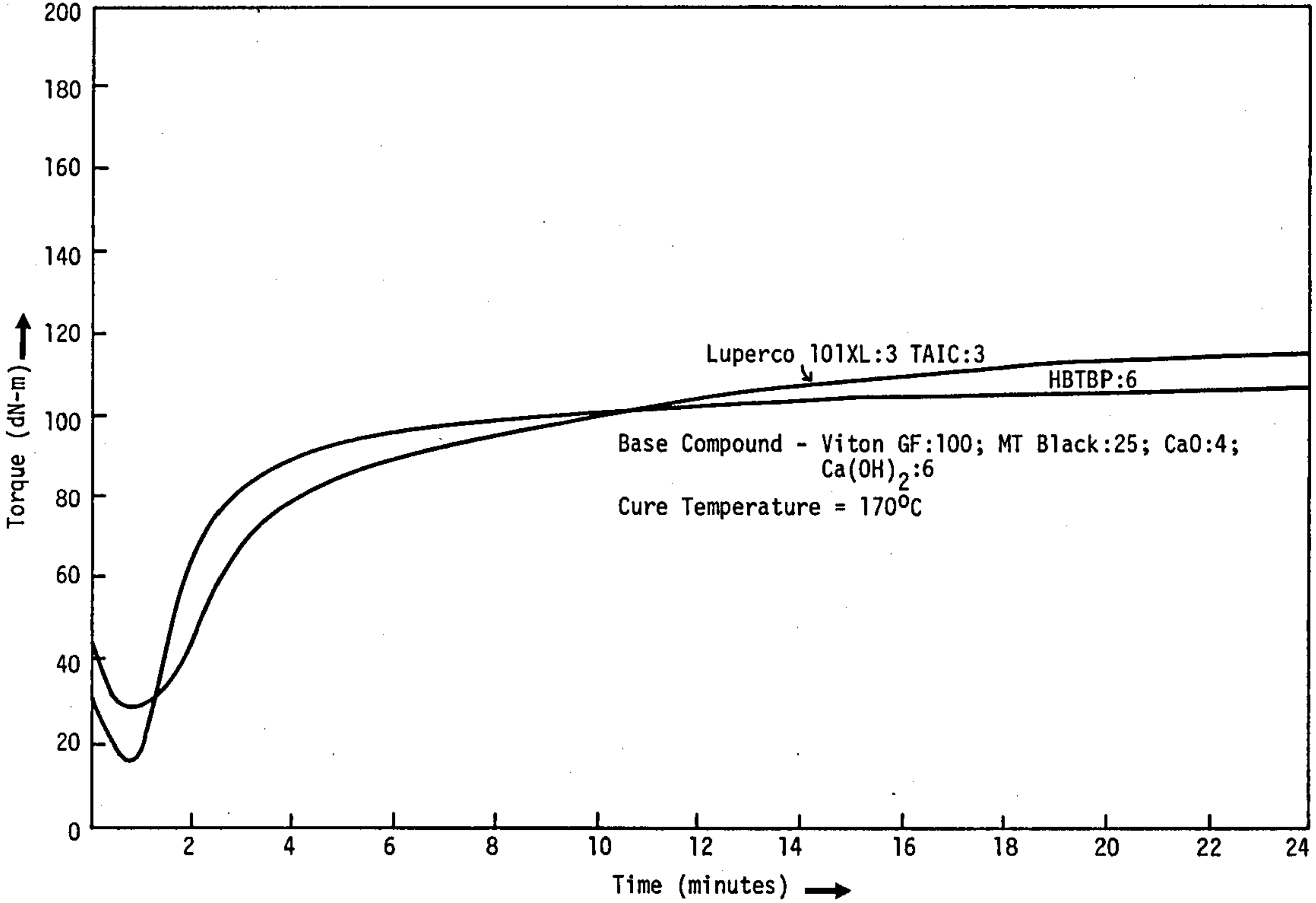

FIGURE 4.2: Comparison of Cure Traces Obtained using HBTBP and Peroxide Cures in Viton GF Respectively

TABLE 4.2: The effect of increase of HBTBP curing agent on physical properties of Viton GF vulcanizates

	C1	C2	C3	C4	C5	Control
Viton GF	100.0	100.0	100.0	100.0	100.0	100.0
MT Black (N990)	25.0	25.0	25.0	25.0	25.0	25.0
CaO (VG)	4.0	4.0	4.0	4.0	4.0	4.0
$Ca(OH)_2$(VE)	6.0	6.0	6.0	6.0	6.0	6.0
HBTBP*	1.0	2.0	3.0	4.0	5.0	-
Luperco 101-XL**	-	-	-	-	-	3.0
TAIC (Diak No 7)	-	-	-	-	-	3.0
Mooney Scorch at 120°C (large rotor, minutes to 5-pt rise)	7.5	6.5	6.0	5.5	5.5	>40
Cure Conditions	← 15 minutes at 170°C →					
Original Vulcanizate Properties (No Postcuring)						
Tensile Strength, MPa	7.39	11.14	11.24	11.11	11.32	-
Elongation-at-break %	575	400	300	275	250	-
100% Modulus, MPa	4.13	3.80	3.20	4.07	3.54	-
Compression set, 70 hrs at 250°C (25% strain)%	Samples were permanently deformed					
Hardness IRHD	52	51	51	Samples cracked		-
Vulcanizate Properties (Air-oven Postcured at 250°C for 24 hours)						
Tensile Strength, MPa	12.05	14.28	14.48	13.26	13.73	18.47
Elongation-at-break %	375	250	200	150	150	200
100% Modulus, MPa	5.02	5.71	6.72	8.52	9.59	11.08
Compression set, 70 hrs at 250°C (25 strain)%	Deformed	98	98	samples cracked or contained voids		68
Hardness, IRHD	53	54	54			58

* HBTBP is Hexamethylene-N,N' bis(tert-butyl peroxycarbamate)

** Luperco 101-XL is 2,5-dimethyl-2,5-bis [t-butyl peroxy] hexane and a trade name of Luperox GmbH

Note The cracking and voiding of mixes C4-C6 is considered due to insufficient $Ca(OH)_2$ being present in the mix.

crosslinking systems. Also the physical properties obtained in HBTBP-cured fluoroelastomers are comparable to the properties obtained for other crosslinking systems (Table 4.3). The results in Table 4.2 further show that about 2 or 3 phr of HBTBP would give optimum properties in Viton GF. However, compression set resistance of HBTBP-cured vulcanizates were rather poor (further studies on compression set are to be reported later).

It was further observed that the modulus values of postcured vulcanizates (Table 4.2) increase with the increase in concentration of HBTBP curing agent which indicates that more crosslinks are introduced as the concentration of crosslinking agent is increased.

TABLE 4.3: Physical Properties of Other Curing Systems for Viton GF(159)

	Peroxide	Dihydroxy	Diamine
Viton GF	100.0	100.0	100.0
MT Black (N908)	30.0	30.0	30.0
Maglite D	-	3.0	-
Calcium Hydroxide	-	6.0	-
Sublimed Litharge	3.0	-	15.0
Viton Curative No. 20	-	4.0	-
Viton Curative No. 30	-	6.0	-
Diak No. 7	3.0	-	-
Luperco 101-XL	3.0	-	-
Diak No. 3	-	-	3.0
Cure Conditions	- 10 minutes press cure at 177°C; 24 hours air-oven postcure at 232°C		
Vulcanizate Properties			
Tensile Strength, MPa	18.8	13.0	13.0
100% Modulus MPa	5.8	7.4	4.4
Elongation-at-break %	240	200	290
Compression set, Method B, % (70 hours at 232°C)	61	65	91

Furthermore, a plot of modulus values of postcured vulcanizates versus concentration of crosslinking agent (Figure 4.3) can be compared with a plot of the maximum ODR torque values versus concentration of crosslinking agent (Figure 4.3). The apparent similarity between the two plots suggest a relationship between the maximum ODR torque for each compound and the modulus values of the corresponding postcured vulcanizate. A relatively high correlation coefficient of 0.98 was obtained between the two values (maximum ODR torque and 100% modulus of postcured vulcanizate) and it showed good agreement between two different methods of assessing the state of cure in vulcanizates. The irregular pattern of the modulus of unpostcured vulcanizates shown in Table 4.2 is probably due to the incompleteness of the network-forming process.

4.3.2 Effect of Coagent

According to technical literature(159) Viton GF is cured by peroxides only in combination with coagents; the coagent recommended being triallylisocyanurate (Diak No. 7). Hence it was investigated whether triallylisocyanurate is compatible with HBTBP and the effect of increasing coagent concentration on vulcanizate properties. The formulation used is shown below:

	phr
Viton GF	100
CaO VG	4
$Ca(OH)_2$ VE	6
MT black N990	25
HBTBP	2
Diak No. 7	0-4

The cure traces obtained for the various concentrations of coagent are shown on Figure 4.4 while the physical properties of the corresponding vulcanizates are shown on Table 4.4. The use of coagents has decreased

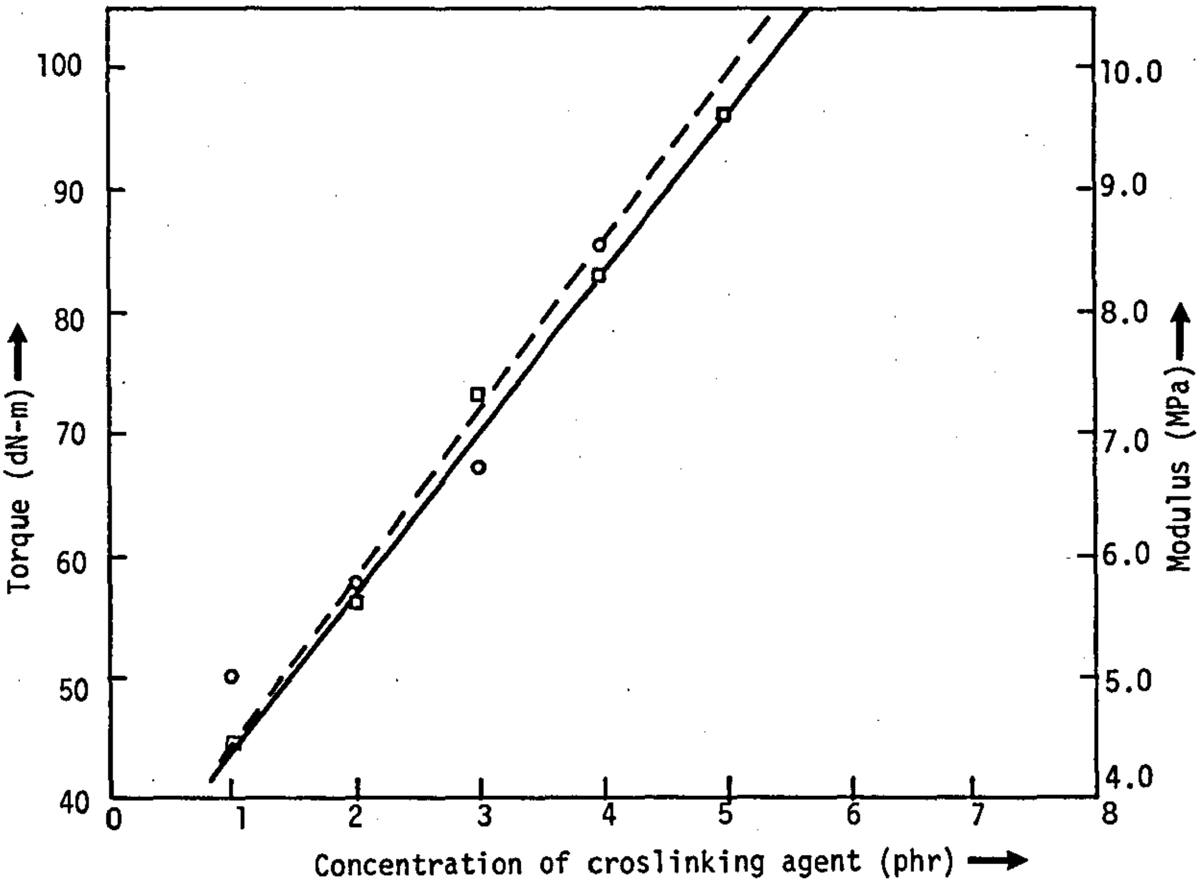

FIGURE 4.3: Plot of 100% Modulus vs Concentration of Crosslinking Agent--□--□--, and Plot of Maximum Torque (ODR) vs Concentration of Crosslinking Agent-O-O- .

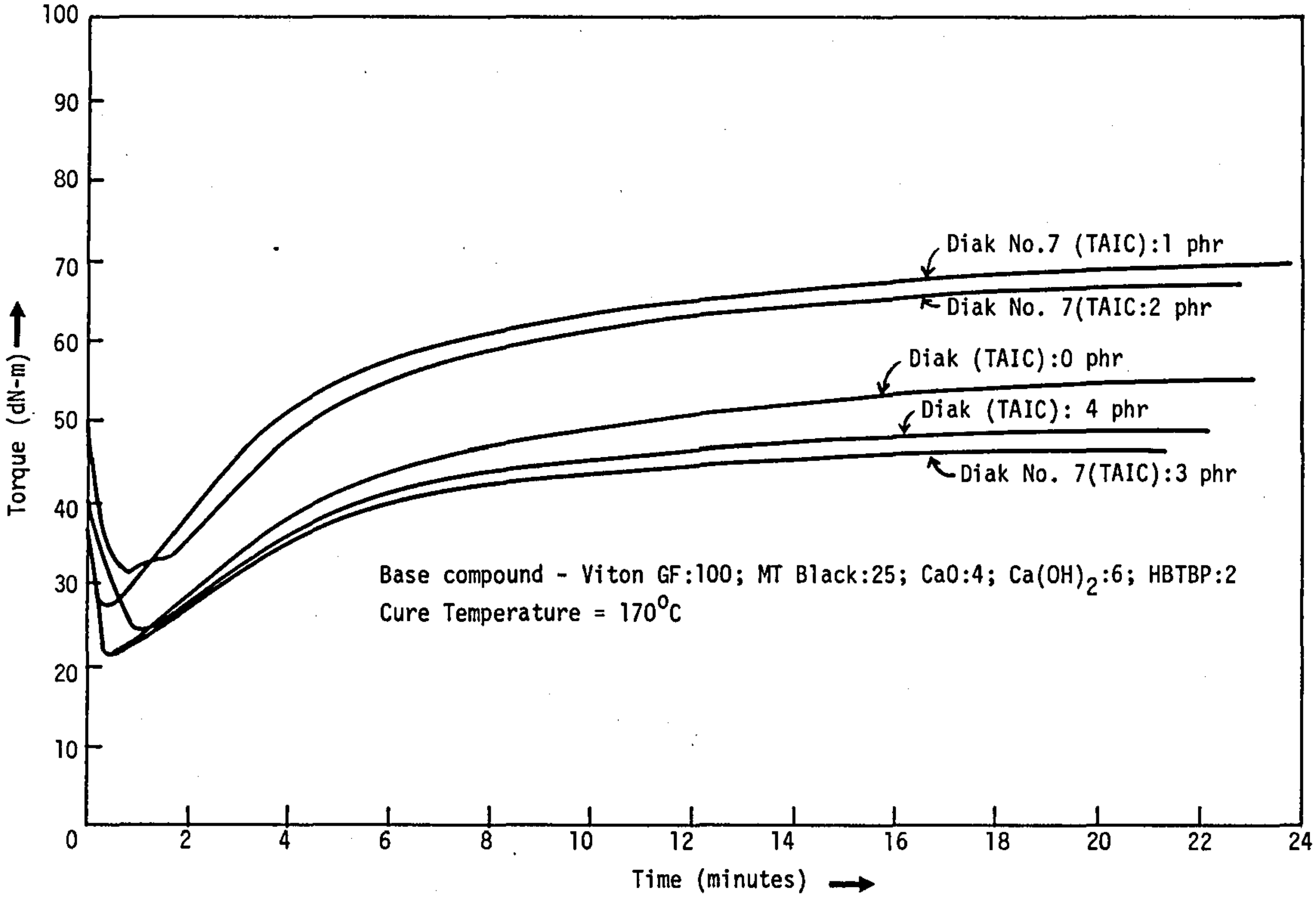

FIGURE 4.4: Effect of Coagent on HBTBP-cure of Viton GF

TABLE 4.4: Variation of Triallylisocyanurate (TAIC) Concentration in a Constant - HBTBP, Viton GF Compound

	Control	C7	C8	C9	C10
Viton GF	100.0	100.0	100.0	100.0	100.0
MT Black (N990)	25.0	25.0	25.0	25.0	25.0
CaO VG	4.0	4.0	4.0	4.0	4.0
$Ca(OH)_2$ VE	6.0	6.0	6.0	6.0	6.0
HBTBP	2.0	2.0	2.0	2.0	2.0
TAIC*	-	1.0	2.0	3.0	4.0
Mooney Scorch at 120°C (large rotor - minutes to 5-pt rise)	6.5	2.0	2.0	2.0	2.0
Cure Conditions	← 15 minutes at 170°C →				
Original Vulcanizate Properties (No Postcuring)					
Tensile Strength MPa	11.14	10.68	10.71	10.39	10.25
Elongation-at-break %	400	325	350	375	350
100% Modulus MPa	3.8	4.13	3.81	3.87	3.95
Compression set, 70 hrs at 250°C (25% strain)	Samples were permanently deformed				
Hardness IRHD	51	52	54	54	54
Vulcanizate Properties (Air-Oven Postcured at 250°C for 24 Hours)					
Tensile Strength, MPa	14.28	16.03	14.66	15.75	15.32
Elongation-at-break %	250	200	200	200	200
100% Modulus MPa	5.71	10.33	7.69	8.63	9.07
Compression set, 70 hours at 250°C (25% strain)	98	86	88	89	87
Hardness IRHD	54	57	58	56	59

* Triallylisocyanurate (Diak No. 7)

the safe processing times as shown by the Mooney scorch values. The ODR cure traces do not seem to follow any definite pattern. It is however noteworthy that the use of 1 phr and 2 phr of Diak No. 7 with HBTBP respectively gave higher ODR torques than the compound without coagent.

Explanation for the nature of the ODR traces is unknown but it was satisfying that the use of coagent gave an improvement to compression set resistance while the effectson other properties were rather insignificant. In the light of the available results, it could be said that HBTBP, whilst being compatible with coagent (Diak No.7) in fluoroelastomer, it does not necessarily require a coagent to cure effectively.

4.3.3 Effect of Metal Oxides

Some formulations (Table 4.5) were prepared to find out whether other metal oxides apart from calcium oxide could be used in HBTBP curing of fluoroelastomers. The metal oxides investigated are mainly magnesium oxide and lead oxide (litharge). It must be stressed however that whatever oxide is used, a material that would absorb the carbon dioxide evolved during vulcanization is always an essential part of the formulation - hence the inclusion of calcium hydroxide in the formulations. The tensile properties of the vulcanizate containing magnesium oxide is compared with that containing calcium oxide in Table 4.5.

Lead oxide and dibasic lead phosphite (Dyphos) were also used in HBTBP curing of fluoroelastomer. The use of both materials gave formulations with low state of cure and the vulcanizates produced were porous despite the inclusion of calcium hydroxide. This would seem to indicate that the use of litharge or dibasic lead phosphite interferes with cure in HBTBP systems. So far, calcium oxide and magnesium oxide are the metal oxides found to be compatible with HBTBP curing system .

TABLE 4.5: Effect of Metal Oxides on Vulcanizate Properties (Viton GF)

	Calcium Oxide	Magnesium Oxide
Viton GF	100.0	100.0
MT Black (N-990)	25.0	25.0
CaO	4.0	-
MgO (Maglite D)	-	3.0
$Ca(OH)_2$	6.0	6.0
HBTBP	3.0	3.0
Cure Conditions	15 minutes at 170°C	
Original Vulcanizate Properties (No Postcuring)		
Tensile Strength (MPa)	11.24	12.84
Elongation-at-break (%)	300	325
100% Modulus (MPa)	3.20	3.55
Hardness IRHD	51	51
Vulcanizate Properties (Postcured at 250°C in Air-oven for 24 Hours		
Tensile Strength (MPa)	14.48	13.14
Elongation-at-break (%)	200	275
100% Modulus (MPa)	6.72	5.43
Hardness (IRHD)	54	52

4.3.4 Cure-Capability of HBTBP in Viton B and Viton E60

The cure response of HBTBP was further examined in other grades of Viton (Viton B and Viton E60) using HBTBP formulations and the respective controls shown in Table 4.6. ODR cure traces of Viton B compound containing HBTBP and the control formulation are shown in Figure 4.5. Similar cure traces for Viton E60 are also shown in Figure 4.6. In both

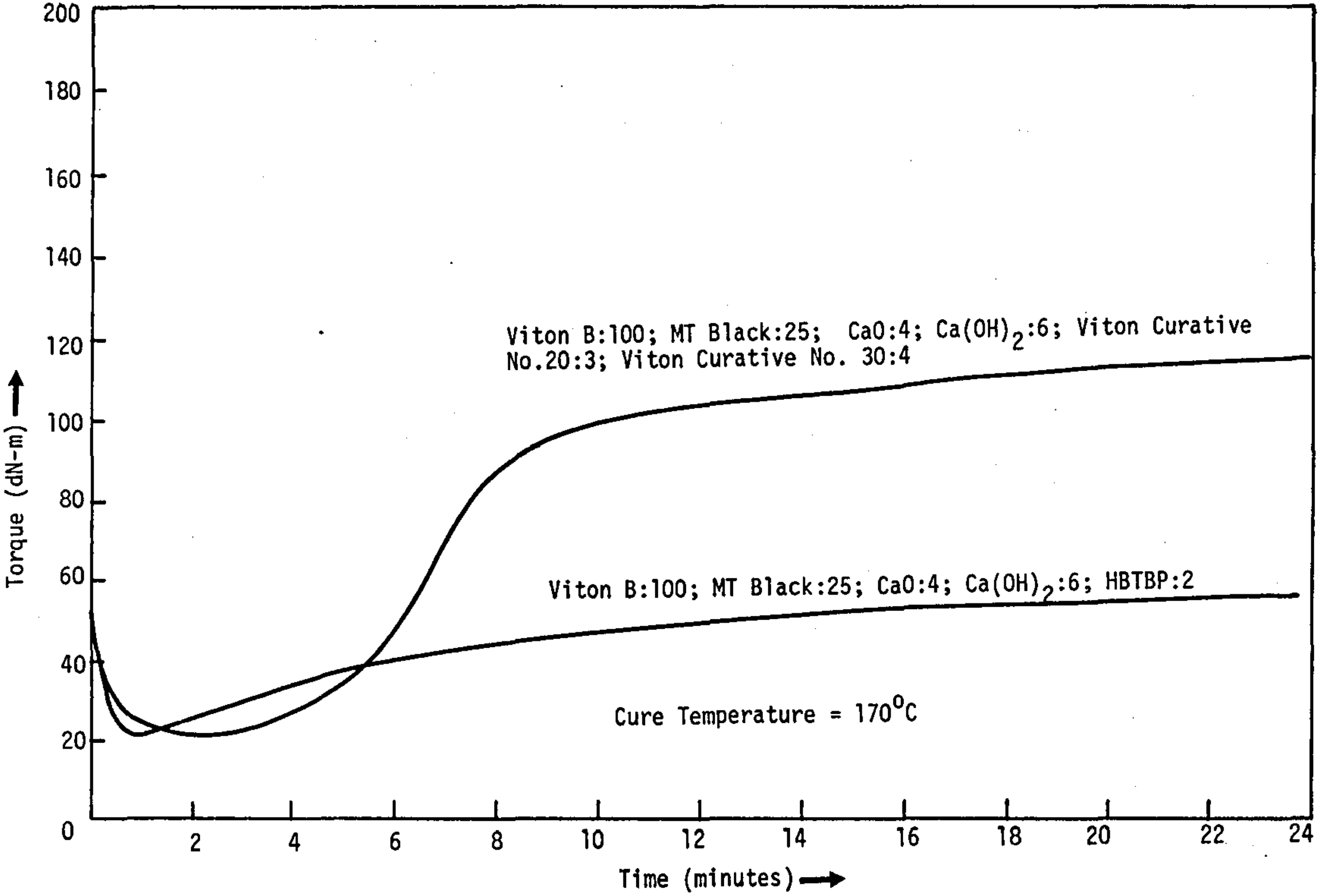

FIGURE 4.5: ODR Cure Traces of Viton B Compound Using Different Crosslinking Systems

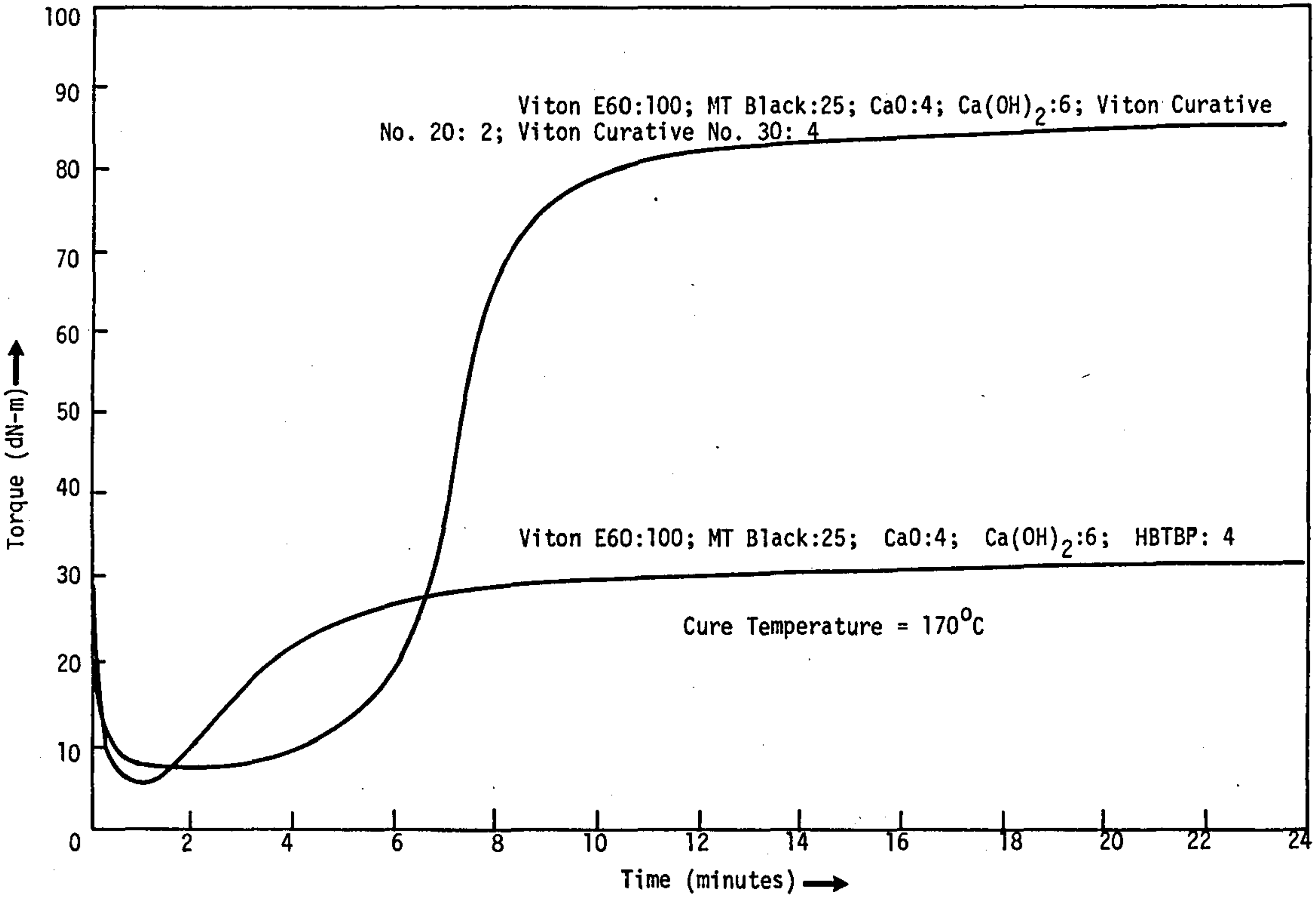

FIGURE 4.6: ODR Cure Traces of Viton E60 Using Different Crosslinking Systems

Viton B and Viton E60, the respective controls gave better cure response than the HBTBP curing system. However no attempts were made at optimising the state of cure of compounds containing HBTBP. Moderate tensile properties were obtained for vulcanizates cured with HBTBP although they were somewhat inferior to the tensile properties of the control formulation (Table 4.6). Nevertheless, the cure-capability of HBTBP in Viton brand of fluoroelastomers has been demonstrated by the cure traces obtained (Figures 4.5 and 4.6).

TABLE 4.6: Physical Properties of HBTBP-cured Vulcanizates (Vitons B and E60), and their Respective Controls

	Viton-B (Control)	Viton-B (HBTBP)	Viton-E60 (Control)	Viton-E60 (HBTBP)
Viton E60	-	-	100.0	100.0
Viton B	100.0	100.0	-	-
MT Black (N990)	25.0	25.0	25.0	25.0
CaO (VG)	4.0	4.0	4.0	4.0
$Ca(OH)_2$ (VE)	6.0	6.0	6.0	6.0
HBTBP	-	2.0	-	4.0
Viton Curative No.20	3.0	-	2.0	-
Viton Curative No.30	4.0	-	4.0	-
Cure Conditions	← 15 minutes at 170°C →			
Original Vulcanizate Properties (No Postcuring)				
Tensile Strength, MPa	11.01	9.70	9.09	8.47
Elongation-at-break %	275	600	250	425
100% Modulus, MPa	3.57	2.33	3.64	1.98
Hardness, IRHD	51	47	52	37
Vulcanizate Properties (Postcured in Air-oven at 250°C for 24 Hours)				
Tensile Strength, MPa	15.69	10.05	15.29	13.18
Elongation-at-break %	250	300	225	225
100% Modulus, MPa	5.72	3.96	6.05	6.21
Hardness, IRHD	52	48	53	44

4.4 Conclusion

A general compounding study of fluoroelastomer compounds has been undertaken. It was found that about 2-3 phr of HBTBP curing agent is required in Viton GF compound to obtain optimum properties and that a HBTBP-cure does not necessarily require a coagent to cure effectively. The versatility of HBTBP was demonstrated by using it to cure Viton B and Viton E60. Also, magnesium and calcium oxides were found to be compatible with the HBTBP curing system while lead oxide appeared to interfere with HBTBP-cure.

CHAPTER 5

HEAT AND FLUID RESISTANCE OF FLUOROELASTOMER COMPOUNDS

5.1 Introduction

Fluoroelastomers are well known for their outstanding heat and fluid resistance. Heat resistance is especially important since fluoroelastomer vulcanizates are able to withstand service temperatures of about 200°C for a long period of time: a service condition well beyond the limit for other common elastomers. The heat and fluid resistance of fluoroelastomers have thus dictated their use in aircraft and automotive sealing applications, shaft seals, packings and gaskets. The wide use of fluoroelastomers in sealing applications makes compression set resistance a criterion for service performance. Fluoroelastomers are also used in pump and valve parts, hydraulic hose and tank linings because of their chemical resistance. Generally, most fluoroelastomer vulcanizates are resistant to aliphatic and aromatic hydrocarbons, chlorinated solvents, petroleum fluids and most mineral acids. They swell excessively however, in polar solvents such as ketones, esters and ethers.

It is with respect to the established fluoroelastomer properties that comparative study of HBTBP vulcanization and standard vulcanization systems were undertaken. In the case of Viton B and Viton E60, HBTBP-cured vulcanizates were compared with vulcanizates cured by recommended systems(159) for resistance to heat ageing and compression set resistance. Similar tests were performed for Viton GF grade of fluoroelastomers but in addition, the solvent resistance in various media were also examined (the manufacturer claims that Viton GF grade has been developed to meet special fluid resistance requirements).

5.2 Experimental Section

5.2.1 Compounding and Vulcanization

Compounding and preparation of vulcanizates were as previously described. Various compound formulations are specified in the results and discussion section (a two-step cure i.e. press curing followed by air-oven postcuring, was used for all vulcanizates used in this section).

5.2.2 Heat Ageing

The detailed description of heat ageing equipment and procedures were given in Chapter 3. However, a test temperature of 230°C was chosen while the period of ageing at the test temperature was for 1 day, 3 days, 5 days, 7 days and 10 days respectively.

5.2.3 Compression Set Measurements

Compression set measurements were along guidelines of ASTM-D395 Method B or BS 903 Part A6, 1969. Test pieces were compressed at 25% strain for 70 hours and at each of the following temperatures: 70°C, 100°C, 150°C, 200°C and 250°C.

5.2.4 Fluid Resistance

The test samples were completely immersed in the test fluid for 7 days. Immersion was at room temperature in all cases except where distilled water, and water/ethylene glycol mixtures were used at 90°C. Volume change was measured immediately after tests while tensile properties were measured after allowing the samples to dry.

5.3 Results and Discussion

5.3.1 Viton B

The aged and unaged physical properties of HBTBP-cured vulcanizate and the control compound are shown in Table 5.1. The unaged physical properties of HBTBP-cured vulcanizate are low compared to that of the control compound though both compounds show relatively good stability to heat ageing. A histogram comparing the percentage retention of tensile strength in both compounds is shown in Figure 5.1. Also, a comparison of the compression set resistance of both compounds in Figure 5.2 shows that HBTBP-cured vulcanizates have inferior compression set resistance to the control compound. It may be possible however to formulate HBTBP compounds to give improved resistance to compression set.

5.3.2 Viton E60

Viton E60 compounds were also compared for aged and unaged physical properties in Table 5.2. HBTBP-cured vulcanizates of Viton E60 are comparable in many respects to the control formulation and the histogram showing the percentage retention of tensile strength further attests to this (Figure 5.3). Compression set resistance was however better in the control formulation (Figure 5.4)

5.3.3 Viton GF (Heat Ageing)

The results of the heat ageing tests for Viton GF crosslinked with HBTBP and that for a control formulation are shown in Table 5.3 while a histogram in Figure 5.5 shows the percentage retention of tensile strength with the two formulations. Although the control formulation has a high initial tensile strength, the retention of tensile strength on ageing is better in the HBTBP-cured vulcanizates as shown by the histogram in Figure 5.5. As in other fluoroelastomer compounds, resistance to compression set of HBTBP-crosslinked vulcanizate is inferior to that of the control formulation (Figure 5.6 and Table 5.5)

TABLE 5.1: Heat Ageing Tests of Viton B Vulcanizates

	Control	HBTBP
Viton B	100.0	100.0
CaO VG	4.0	4.0
Ca(OH)$_2$ VE	6.0	6.0
MT Black N990	25.0	25.0
HBTBP	-	2.0
Viton Curative No. 20	3.0	-
Viton Curative No. 30	4.0	-
Cure Conditions	15 minutes at 170°C; 24 hours air-oven postcuring at 250°C	
Unaged Physical Properties		
Tensile Strength, MPa	15.69	10.05
100% Modulus, MPa	5.72	3.96
Elongation-at-break %	250	300
Hardness, IRHD	52	48
Physical Properties (Aged 1 day at 230°C)		
Tensile Strength, MPa	15.73	10.29
100% Modulus, MPa	5.62	4.26
Elongation-at-break %	225	350
Hardness, IRHD	51	48
Physical Properties (Aged 3 days at 230°C)		
Tensile Strength, MPa	16.94	10.49
100% Modulus, MPa	5.42	3.74
Elongation-at-break %	250	300
Hardness, IRHD	52	49
Physical Properties (Aged 5 days at 230°C)		
Tensile Strength, MPa	16.00	10.52
100% Modulus, MPa	5.67	4.27
Elongation-at-break %	250	300
Hardness, IRHD	51	48
Physical Properties (Aged 7 days at 230°C)		
Tensile Strength, MPa	16.43	10.12
100% Modulus, MPa	6.18	4.32
Elongation-at-break %	225	275
Hardness, IRHD	51	48
Physical Properties (Aged 10 days at 230°C)		
Tensile Strength, MPa	15.79	8.88
100% Modulus, MPa	5.85	4.14
Elongation-at-break %	200	250
Hardness, IRHD	51	48

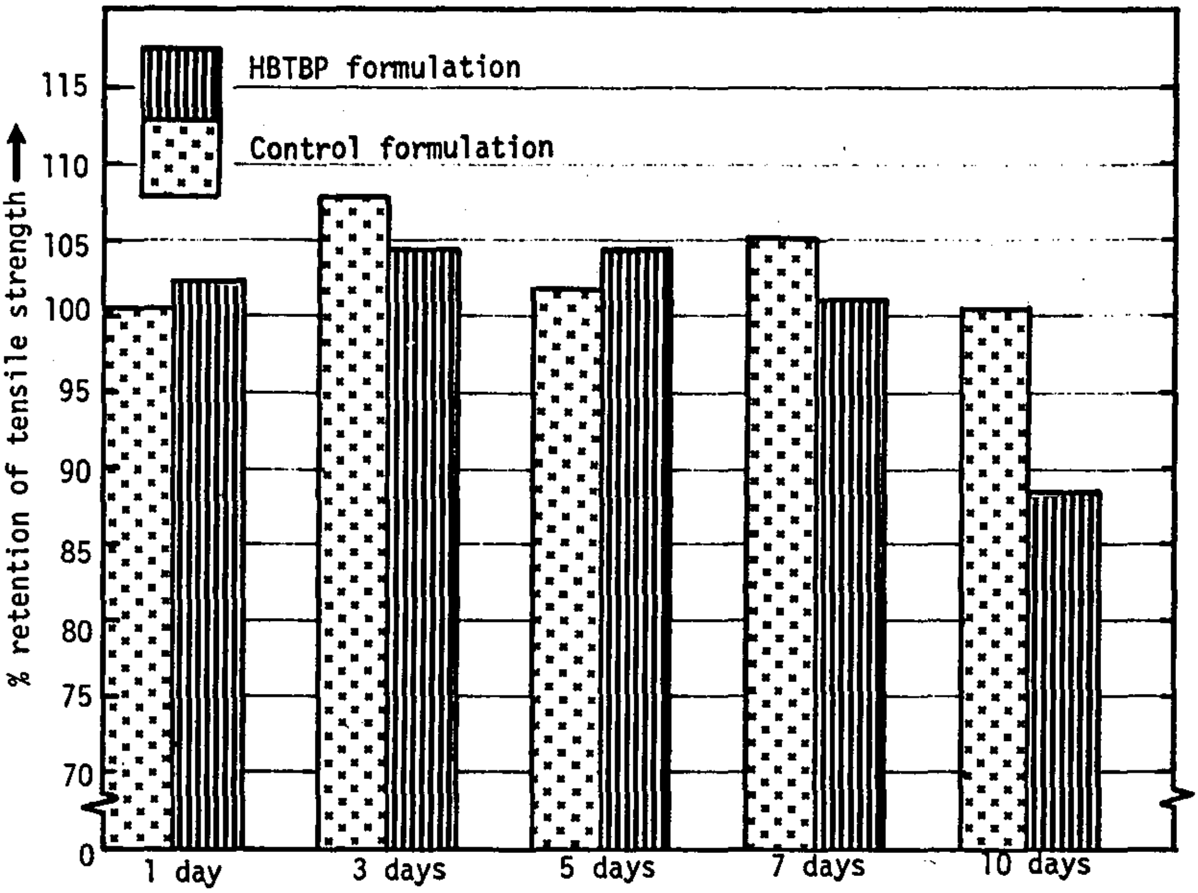

FIGURE 5.1: Percentage retention of tensile strength for Viton B vulcanizates after heat ageing at 230°C

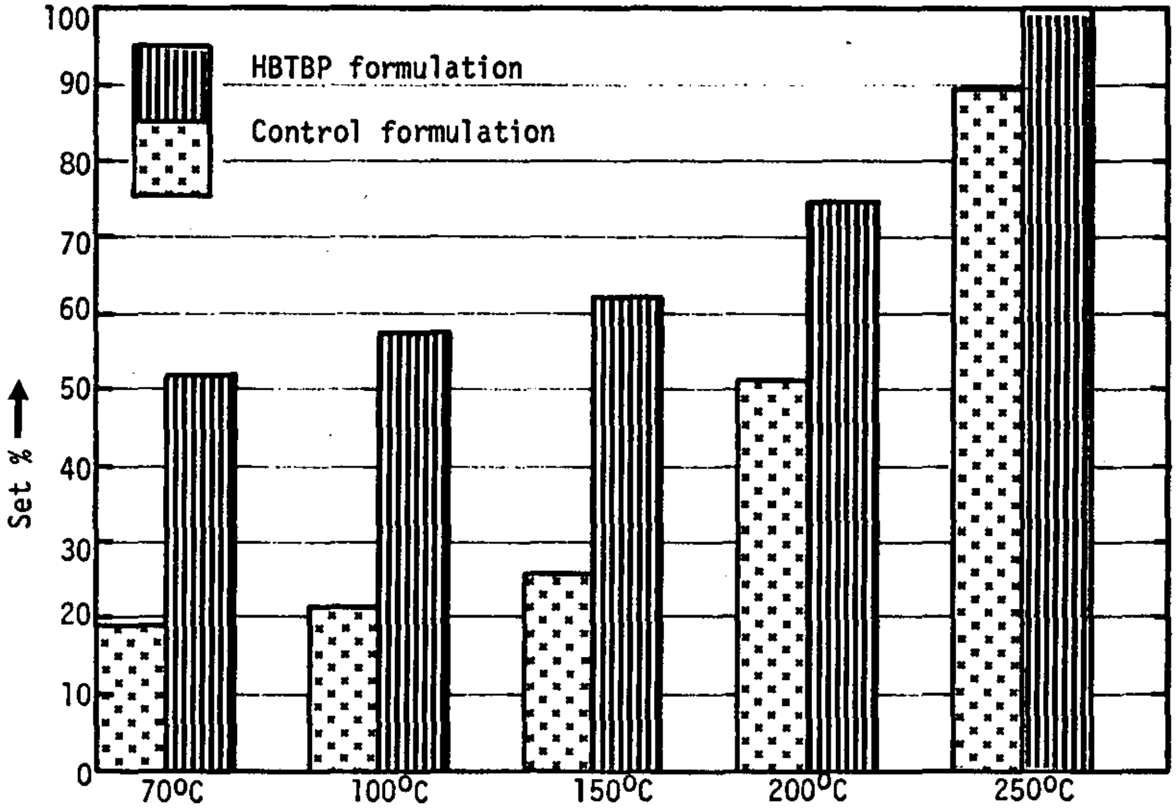

FIGURE 5.2: Compression set of Viton B vulcanizates (70 hours, 25% strain)

TABLE 5.2: Heat Ageing Tests of Viton E60 Vulcanizates

	Control	HBTBP
Viton E60	100.0	100.0
CaO VG	4.0	4.0
Ca(OH)$_2$ VE	6.0	6.0
MT Black N990	25.0	25.0
HBTBP	-	4.0
Viton Curative No. 20	2.0	-
Viton Curative No. 30	4.0	-
Cure Conditions	15 minutes at 170°C; 24 hours air-oven postcuring at 250°C	
Unaged Physical Properties		
Tensile Strength, MPa	15.29	13.18
100% Modulus, MPa	6.05	6.21
Elongation-at-break %	225	225
Hardness, IRHD	53	44
Physical Properties (Aged 1 day at 230°C)		
Tensile Strength, MPa	15.29	13.40
100% Modulus, MPa	5.57	7.40
Elongation-at-break %	225	200
Hardness, IRHD	56	46
Physical Properties (Aged 3 days at 230°C)		
Tensile Strength, MPa	13.46	13.06
100% Modulus, MPa	6.41	7.22
Elongation-at-break %	200	200
Hardness, IRHD	54	46
Physical Properties (Aged 5 days at 230°C)		
Tensile Strength, MPa	13.72	14.54
100% Modulus, MPa	5.79	7.45
Elongation-at-break %	200	200
Hardness, IRHD	54	45
Physical Properties (Aged 7 days at 230°C)		
Tensile Strength, MPa	14.46	12.58
100% Modulus, MPa	6.33	7.19
Elongation-at-break %	200	200
Hardness, IRHD	53	45
Physical Properties (Aged 10 days at 230°C)		
Tensile Strength, MPa	15.00	12.57
100% Modulus, MPa	7.58	7.14
Elongation-at-break %	200	175
Hardness, IRHD	54	45

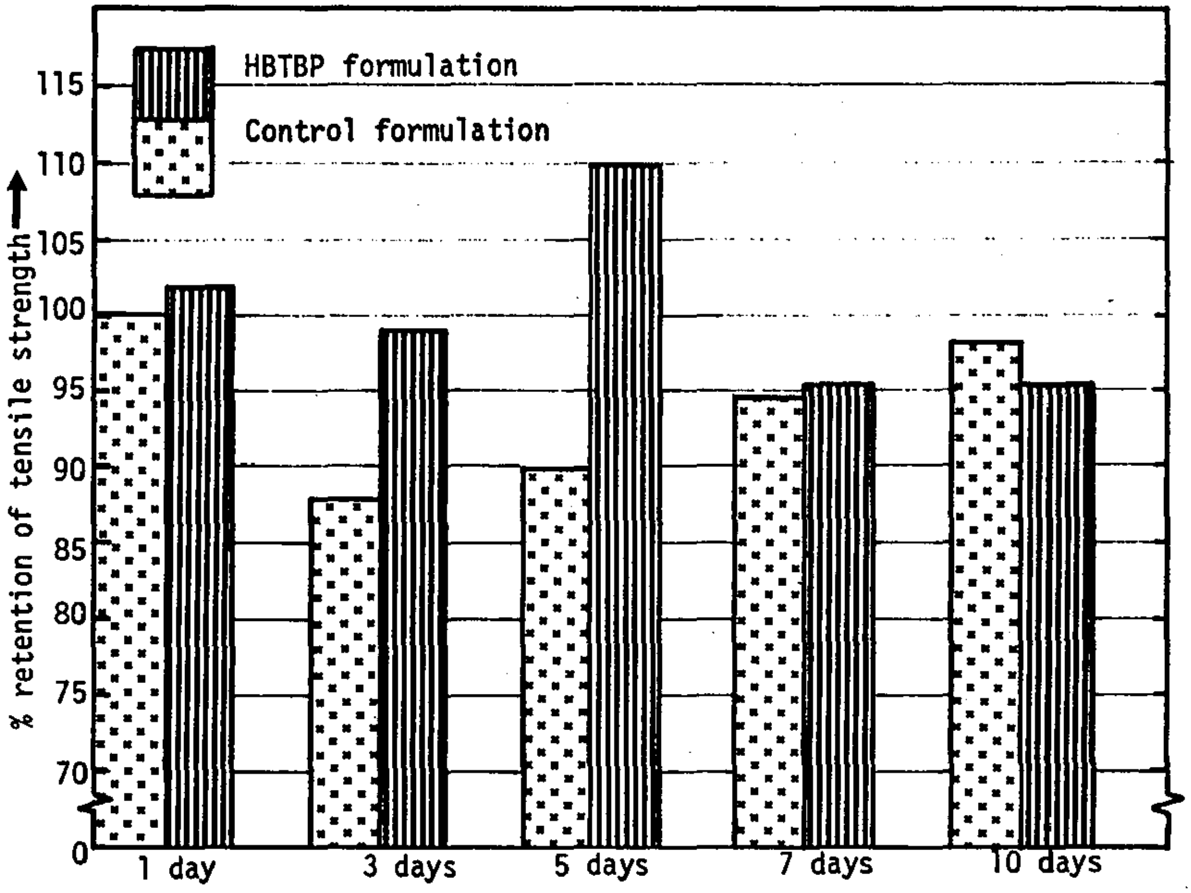

FIGURE 5.3: Percentage retention of tensile strength for Viton E60 vulcanizates after heat ageing at 230°C

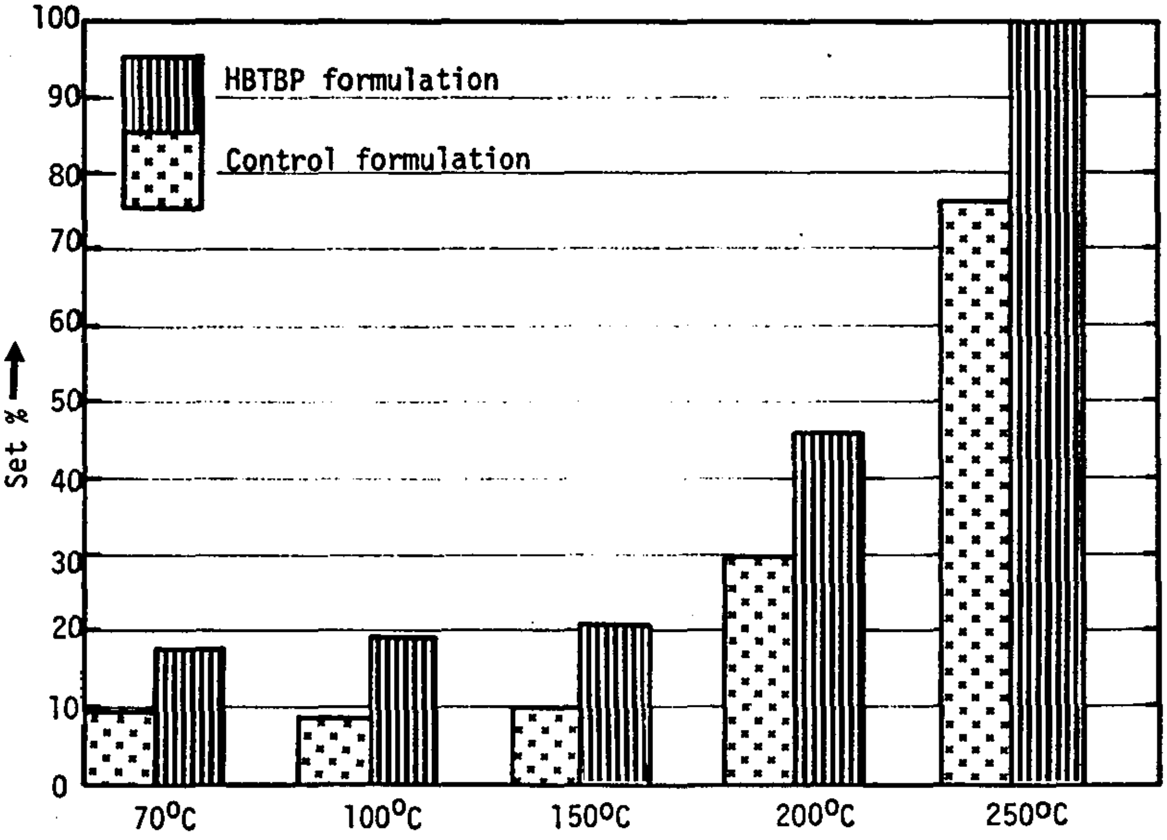

FIGURE 5.4: Compression set of Viton E60 vulcanizates (70 hours, 25% strain)

TABLE 5.3: Heat Ageing Tests of Viton GF Vulcanizates

	Control	HBTBP
Viton GF	100.0	100.0
CaO VG	4.0	4.0
Ca(OH)$_2$ VE	6.0	6.0
MTBlack N990	25.0	25.0
HBTBP	-	2.0
Luperco 101-XL	3.0	-
TAIC(Diak No. 7)	3.0	-
Cure Conditions	15 minutes at 170°C; air-oven postcured at 250°C for 24 hours	
Unaged Physical Properties		
Tensile Strength, MPa	18.47	15.43
100% Modulus, MPa	11.08	6.65
Elongation-at-break %	200	275
Hardness, IRHD	58	54
Physical Properties (Aged 1 day at 230°C)		
Tensile Strength, MPa	16.49	15.83
100% Modulus, MPa	10.43	6.94
Elongation-at-break %	200	275
Hardness, IRHD	58	55
Physical Properties (Aged 3 days at 230°C)		
Tensile Strength, MPa	16.98	15.75
100% Modulus, MPa	9.12	7.31
Elongation-at-break %	225	275
Hardness, IRHD	57	55
Physical Properties (Aged 5 days at 230°C)		
Tensile Strength, MPa	14.74	14.83
100% Modulus, MPa	9.54	6.07
Elongation-at-break %	200	275
Hardness, IRHD	56	54
Physical Properties (Aged 7 days at 230°C)		
Tensile Strength, MPa	11.05	12.81
100% Modulus, MPa	7.27	6.88
Elongation-at-break %	250	225
Hardness, IRHD	56	54
Physical Properties (Aged 10 days at 230°C)		
Tensile Strength, MPa	11.48	9.94
100% Modulus, MPa	6.76	4.39
Elongation-at-break %	225	325
Hardness, IRHD	56	52

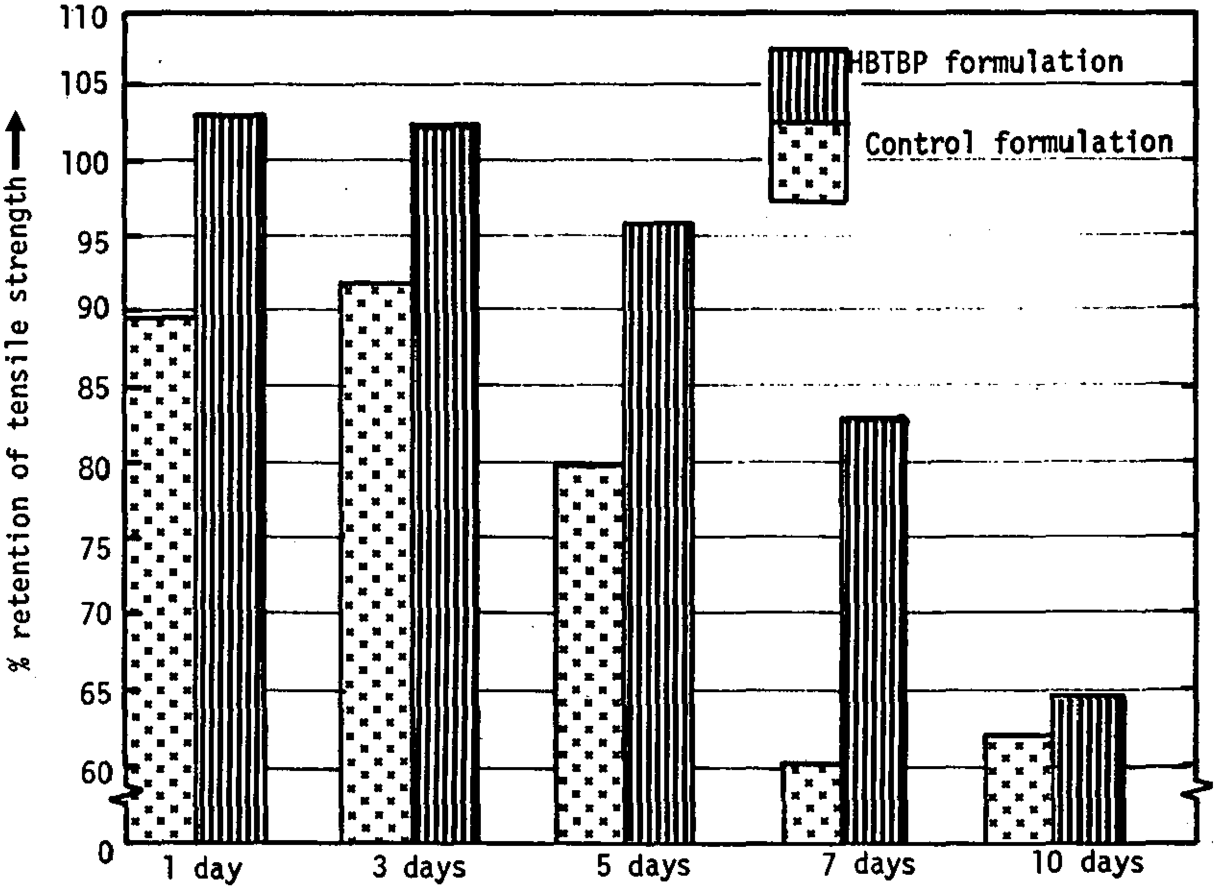

FIGURE 5.5: Percentage retention of tensile strength for Viton GF vulcanizates after heat ageing at 230°C

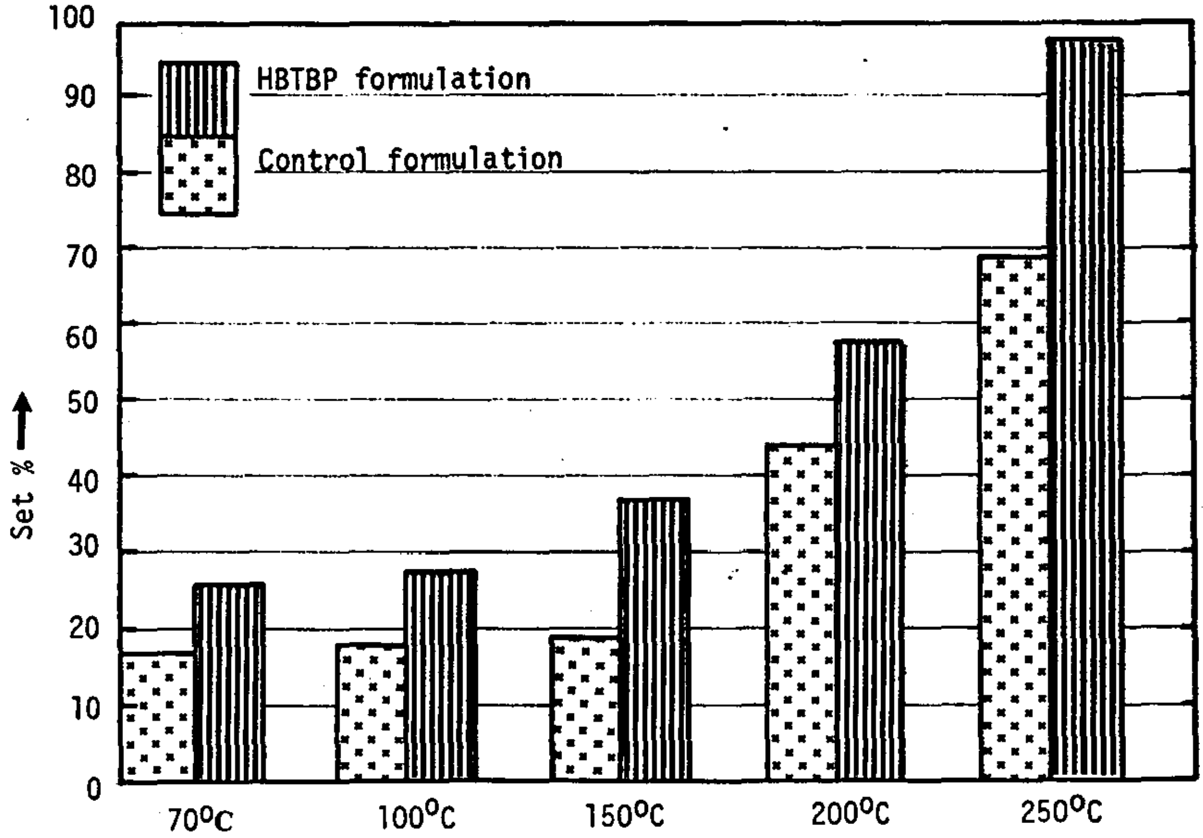

FIGURE 5.6: Compression set of Viton GF vulcanizates (70 hours, 25% strain)

5.3.4 Viton GF (Solvent Resistance)

The two crosslinking systems used for Viton GF were compared for their solvent resistance using some fluids which vulcanizates are likely to encounter during their service life(159). The results in Table 5.4 show the volume change after immersion; and physical properties of vulcanizates after immersion and evaporation of the respective fluids from swollen vulcanizates. In terms of volume change, vulcanizates used as controls appear to swell less than the HBTBP-cured vulcanizates. In general, the use of calcium oxide and calcium hydroxide in both formulations might have caused the high swelling of the vulcanizates as their salts are more readily soluble. This is evident from the 15% increase in volume obtained for the different vulcanizates when immersed in distilled water. It is thought that the use of lead oxide whose salts are less soluble than calcium salts would offer better swelling resistance in the vulcanizates. Whereas the use of lead oxide is possible with peroxide-coagent cure, compounding studies so far indicate limited compatibility of lead oxide with HBTBP cure and this is another area where the peroxide-coagent cure offers an advantage over the HBTBP-cure.

5.4 Conclusion

The investigations carried out so far indicate that vulcanizates obtained from peroxide-coagent vulcanization of Viton GF and from other control formulations appear to have superior physical properties, as well as better resistance to swelling and compression set when compared to vulcanizates cured with HBTBP. Although the results obtained show that HBTBP-cured vulcanizates have good retention of properties on exposure to dry heat, it is thought that the general thermal stability of fluoroelastomer vulcanizates owe more to the structure of the raw polymers than to the curing system used.

TABLE 5.4: Solvent Resistance of Viton GF Vulcanizates

	Control	HBTBP
Viton GF	100.0	100.0
CaO VG	4.0	4.0
$Ca(OH)_2$	6.0	6.0
MT Black N990	25.0	25.0
HBTBP	-	2.0
Luperco 101-XL	3.0	-
TAIC (Diak No. 7)	3.0	-
Cure Conditions	15 minutes at 170°C; air-oven postcured at 250°C for 24 hours	
Physical Properties of Vulcanizate		
Tensile Strength, MPa	18.47	15.43
100% Modulus, MPa	11.08	6.65
Elongation-at-break %	200	275
Hardness, IRHD	58	54
Physical Properties After 1 Week in 37% HCl at 24°C		
Tensile Strength, MPa	13.84	13.77
100% Modulus, MPa	7.55	4.43
Elongation-at-break %	200	325
Hardness, IRHD	55	50
Volume Change, %	+6	+7
Physical Properties After 1 Week in 70% HNO_3 at 24°C		
Tensile Strength, MPa	14.62	11.84
100% Modulus, MPa	7.02	4.09
Elongation-at-break %	225	300
Hardness, IRHD	47	41
Volume Change, %	+8	+13
Physical Properties After 1 Week in ASTM Fuel C at 24°C		
Tensile Strength, MPa	13.40	11.03
100% Modulus, MPa	7.83	3.97
Elongation-at-break %	200	325
Hardness, IRHD	54	48
Volume Change, %	+5	+11
Physical Properties After 1 Week in Methanol at 24°C		
Tensile Strength, MPa	10.86	9.54
100% Modulus, MPa	6.00	3.18
Elongation-at-break %	200	325
Hardness, IRHD	54	49
Volume Change, %	+3	+5

/Continued....

TABLE 5.4 ... continued

	Control	HBTBP
Physical Properties After 1 Week in Toluene at 24^oC		
Tensile Strength, MPa	11.32	11.08
100% Modulus, MPa	6.32	3.89
Elongation-at-break %	200	300
Hardness, IRHD	54	50
Volume Change, %	+2	+8
Physical Properties After 1 Week in Fuel C/Methanol (85/15) at 24^oC		
Tensile Strength, MPa	8.48	8.19
100% Modulus, MPa	4.60	2.54
Elongation-at-break %	175	300
Hardness, IRHD	53	48
Volume Change, %	+13	+12
Physical Properties After 1 Week in Dichloromethane at 24^oC		
Tensile Strength, MPa	8.89	8.90
100% Modulus, MPa	6.02	2.91
Elongation-at-break %	175	250
Hardness, IRHD	46	41
Volume Change, %	+1	+14
Physical Properties After 1 Week in Trichloroethylene at 24^oC		
Tensile Strength, MPa	10.51	9.94
100% Modulus, MPa	6.25	3.31
Elongation-at-break %	175	275
Hardness, IRHD	52	47
Volume Change %	+6	+6
Physical Properties After 1 Week in Distilled Water at 90^oC		
Tensile Strength, MPa	13.04	10.11
100% Modulus, MPa	5.38	4.51
Elongation-at-break %	200	325
Hardness, IRHD	50	42
Volume Change %	+15	+15
Physical Properties After 1 Week in Ethylene Glycol/Water (50/50) at 90^oC		
Tensile Strength, MPa	14.11	10.82
100% Modulus, MPa	8.13	4.88
Elongation-at-break %	225	350
Hardness, IRHD	52	43
Volume Change, %	+8	+9

TABLE 5.5: Comparison of Set Measurements for Viton GF Pellets at Various Temperatures (70 hours and 25% strain)

Temperature	70°C	100°C	150°C	200°C	250°C
* Control (% set)	17	18	19	44	68
** HBTBP (% set)	26	28	37	58	98

* Control formulation is the same as in Table 5.3

** HBTBP formulation is the same as in Table 5.3.

CHAPTER 6

STUDIES ON THE CURE MECHANISM OF HBTBP IN VITON GF

6.1 Introduction

The elucidation of crosslink formation in any vulcanization system is of considerable importance in designing a compound to meet specific applications. An understanding of the mechanism can often be used to predict vulcanizate behaviour, offer an explanation for the physical and chemical properties obtained in vulcanizates and to predict their long term behaviour. Obtaining information on the structure of the vulcanizate is complicated. Insolubility of vulcanizates in organic solvents and their heterogeneity prevent application of conventional analytical techniques. However, a number of experimental approaches have been developed which enable some information to be obtained on possible routes of crosslink formation. These involve a combination of (i) compounding studies, (ii) thermal analysis, (iii) solvent extraction, and (iv) swelling measurements.

6.2 Compounding Studies

The formulations given in Table 6.1 represent compounding studies undertaken with the following objectives:

i) to investigate whether HBTBP alone would cure a Viton GF type fluoroelastomer (mix A)

ii) examination of the effect of certain compounding ingredients on the state of cure of Viton GF; these will be CaO + $Ca(OH)_2$, medium thermal carbon black (mixes B and C)

iii) comparison of curing characteristics of another analogous bis-peroxycarbamate having an aliphatic/cyclic backbone i.e. MBTBP* with HBTBP in Viton GF (mixes C and E)

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* MBTBP is Methylene bis-4-cyclohexyl N,N'(tertiary butyl peroxycarbamate)

iv) comparison of the cure responses of different Viton grades which possess some dissimilarity in chemical structure using HBTBP as the curing agent (mixes C, F and G).

TABLE 6.1: Formulations for Compounding Studies

	A	B	C	D	E	F	G
Viton GF	100	100	100	100	100	-	-
Viton B	-	-	-	-	-	100	-
Viton E60	-	-	-	-	-	-	100
MT Black N990	-	-	25	-	25	25	25
CaO VG	-	4.0	4.0	4.0	4.0	4.0	4.0
$Ca(OH)_2$ VE	-	6.0	6.0	6.0	6.0	6.0	6.0
HBTBP	4.0	4.0	4.0	-	-	4.0	4.0
MBTBP	-	-	-	-	4.0	-	-

6.2.1 Cure Studies of Viton GF Compounds

The ODR cure traces for the compounds A, B, C and D are shown in Figure 6.1. It was observed that whilst the HBTBP alone would cure the Viton GF (compound A), the vulcanizates were porous. Inclusion of calcium oxide and calcium hydroxide (compound B) improved the level of cure and was found to eliminate porosity. As expected, compound C which contained the medium thermal carbon black possessed the highest ODR maximum torque of all the mixes in Figure 6.1 and this is attributed to modulus enhancement by the filler.

Additionally, it was established that Viton GF cannot be cured by a combination of calcium oxide and calcium hydroxide alone as shown by the flat ODR cure trace of compound D in Figure 6.1. When the ODR cure time of compound D was extended to 2 hours, there was still no appreciable increase in the ODR torque and the resulting compound was

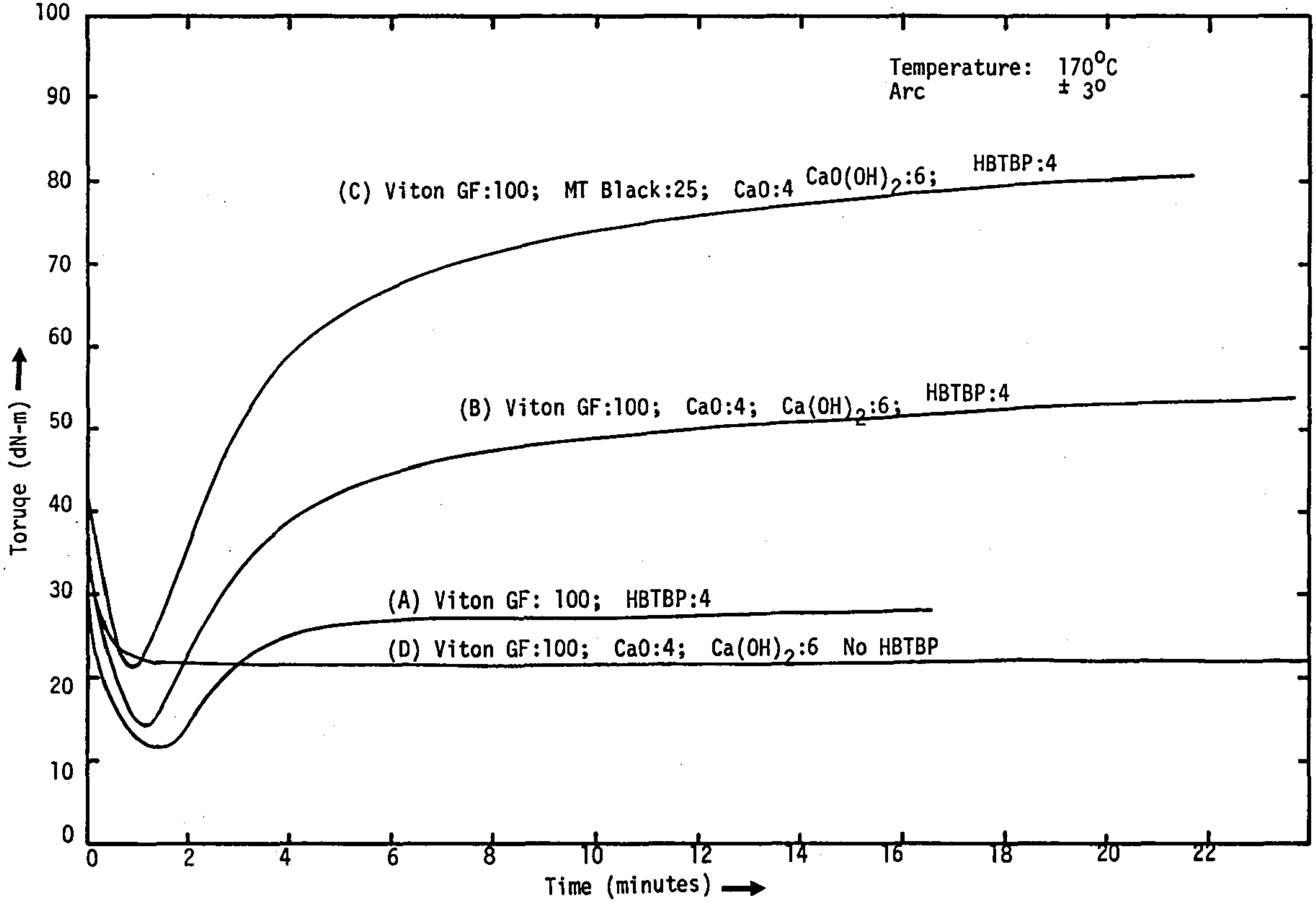


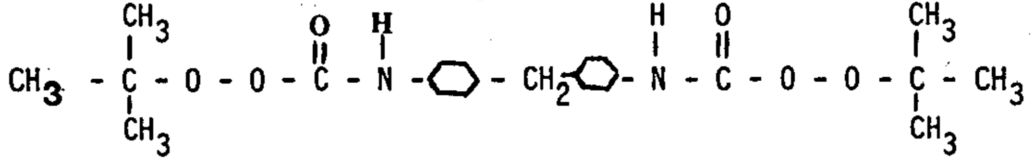
FIGURE 6.1: ODR cure traces of Viton GF compounds crosslinked with HBTBP

found to be soluble in methyl ethyl ketone which conclusively proved that no crosslinking had occurred. It is recorded in the literature that thermal crosslinking of Viton A-HV with magnesium oxide has been obtained(154,160) although the physical properties obtained were rather poor.

It is deduced from these ODR studies of compounds A, B, C and D in Figure 6.1 that while in principle HBTBP alone would cure Viton GF, the inclusion of calcium oxide and calcium hydroxide is beneficial as their presence improves the state of cure. Also calcium hydroxide eliminates any tendency towards porosity by absorbing the carbon dioxide evolved during cure as a by-product in the thermal dissociation of the bisperoxycarbamate. The contribution made to crosslinking by the inclusion of calcium oxide and calcium hydroxide to a HBTBP mix (mix B) could not be assessed by swelling measurements because the vulcanizate containing only the HBTBP crosslinking agent (mix A) was porous.

6.2.2 HBTBP Compared with MBTBP as Crosslinking Agent in Viton GF

In Figure 6.2, a comparison is made between the ODR cure traces of compounds C(HBTBP) and E(MBTBP). Compound C is seen to possess a higher state of cure than compound E. The two crosslinking agents (HBTBP and MBTBP) have similar though not identical chemical structures which are shown below and must account for the observed variation in cure response with Viton GF; this difference will be discussed later when mechanisms are being considered



Methylene bis-4-cyclohexyl N,N'(tertiary butyl peroxycarbamate)
(MBTBP)

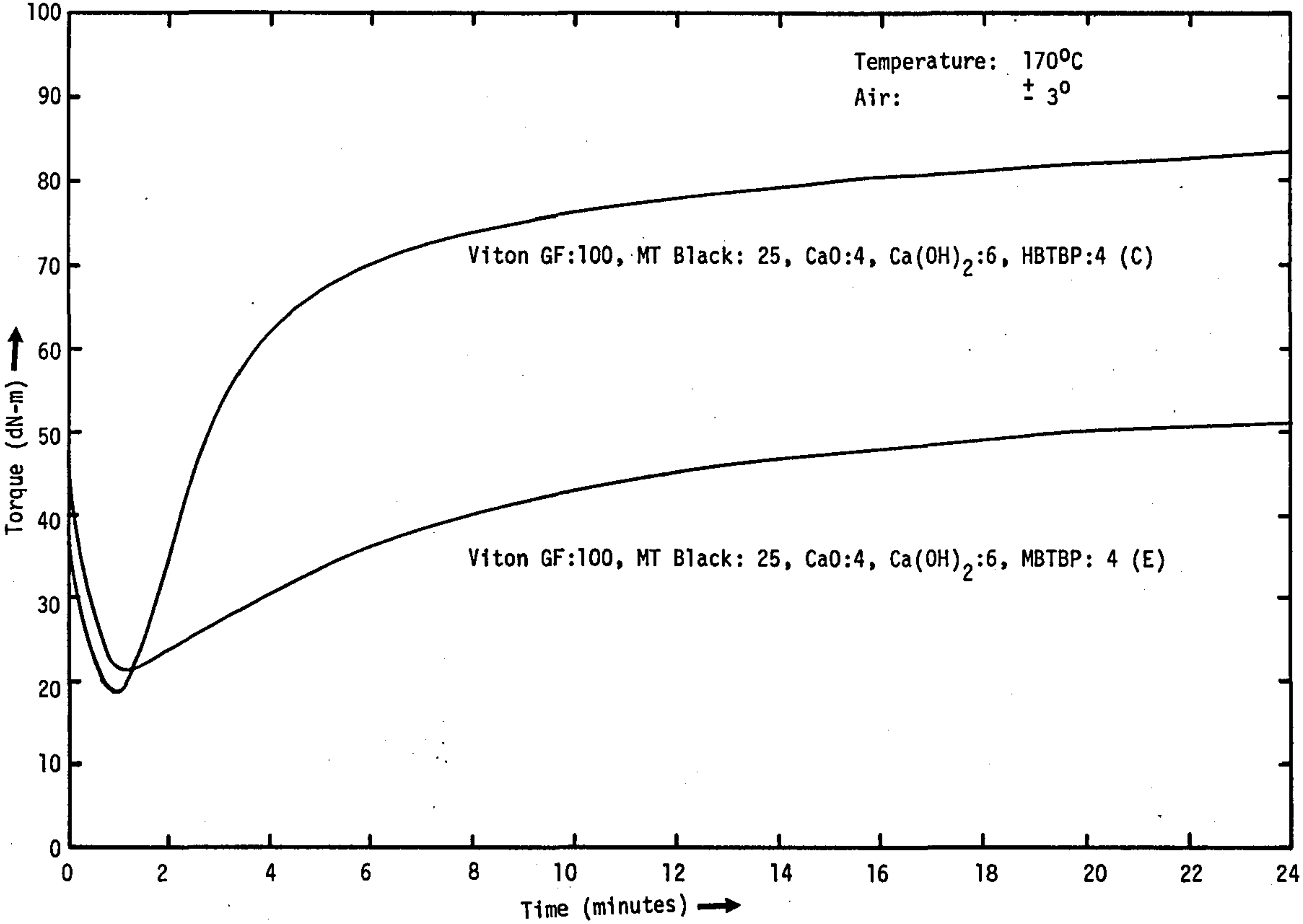
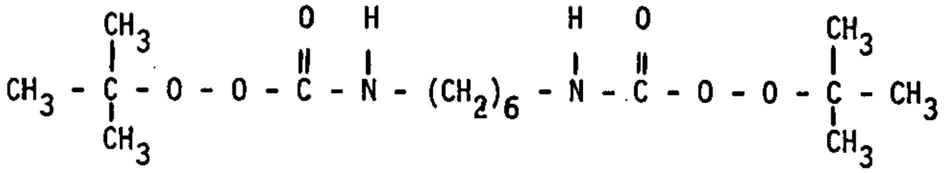


FIGURE 6.2: Comparison of ODR cure traces of Viton GF crosslinked with HBTBP and MBTBP



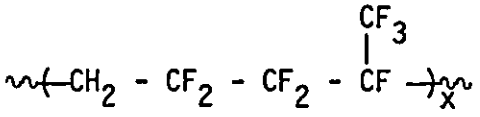
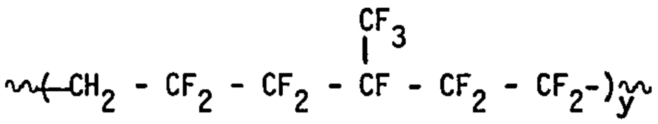
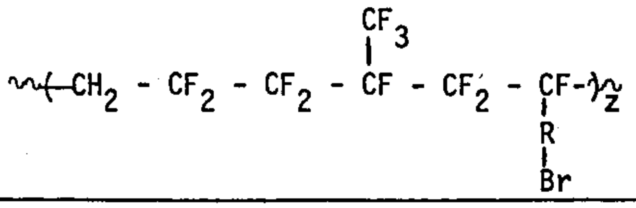
$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O-O-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-O-O-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$

Hexamethylene-N,N'bis(tertiary butyl peroxycarbamate) (HBTBP)

6.2.3 Cure Response of Viton Grades GF, B and E60 to HBTBP

The ODR cure traces of compounds C, F and G are shown in Figure 6.3. Here, comparison is made of the cure responses of different grades of Viton which possess different chemical structure (see Table 6.1a) with the HBTBP crosslinking agent. These various Viton grades all show different responses to the curing agent HBTBP: Viton GF exhibits the fastest rate and highest state of cure, followed by Viton B. Viton E60 shows the poorest cure response to HBTBP. However, equally all the Viton grades examined gave good resilient vulcanizates. Reference will be made in the mechanism section to the reason for the different cure responses of these various Viton grades to HBTBP.

TABLE 6.1a: Structures of the various Viton grades of fluoroelastomers used in the compounds of Table 6.1

Grade	Structure
Viton E60	 $\sim(-CH_2-CF_2-CF_2-\overset{CF_3}{\overset{\vert}{CF}}-)_x\sim$
Viton B	 $\sim(-CH_2-CF_2-CF_2-\overset{CF_3}{\overset{\vert}{CF}}-CF_2-CF_2-)_y\sim$
Viton GF(161)	 $\sim(-CH_2-CF_2-CF_2-\overset{CF_3}{\overset{\vert}{CF}}-CF_2-\underset{\underset{Br}{\vert}}{\underset{R}{\underset{\vert}{CF}}}-)_z\sim$

x, y and z are integers

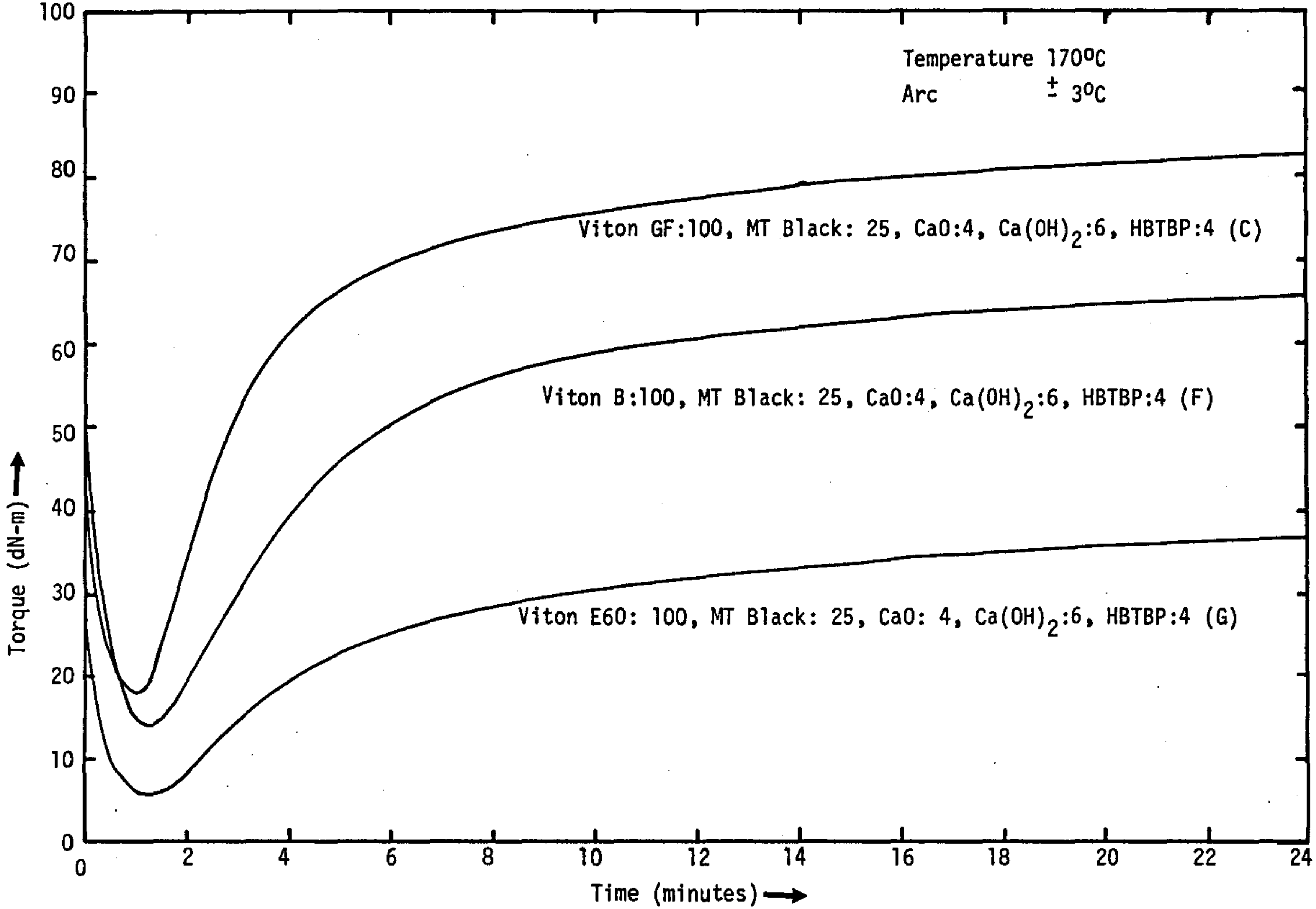


FIGURE 6.3: ODR cure traces of different grades of Viton with HBTBP

From the studies so far, it is concluded that

i) whilst HBTBP alone would cure Viton GF, the inclusion of calcium oxide and calcium hydroxide improves the state of cure and eliminates porosity

ii) in the curing of Viton GF, the backbone structure of the HBTBP is more reactive than that of MBTBP since HBTBP gives a better cure response than MBTBP

iii) using HBTBP as crosslinking agent, comparison of the different Viton grades GF, B and E60 shows that the Viton GF is the most responsive and has an improved cure response over other grades. Hence the different structures of the fluoroelastomers must be accountable for the different cure responses.

6.2.4 Thermal Analysis

The thermal analysis study was undertaken using a Du Pont 990 Thermal Analyser (principle of operation was described in Section 2.3.3.1). Its aims were (i) to examine the thermal changes taking place in the uncured compound during cure, (ii) to examine the changes taking place when the non-postcured vulcanizate was postcured to various degrees.

Towards this end, the formulations shown in Table 6.2 were prepared.

A portion of compound Y was press-cured at 170°C for 15 minutes to provide the non-postcured sample; another was both press-cured at 170°C for 15 minutes and postcured by heating in a hot air-oven at 250°C for 24 hours.

TABLE 6.2: Formulations for the thermal analysis study

	X	Y
Viton GF	100	100
CaO (VG)	4.0	4.0
$Ca(OH)_2$ (VE)	6.0	6.0
HBTBP	-	5.0

6.2.4.1 Thermal analysis of uncured compounds

The differential thermal analysis (DTA) traces for the uncured compounds X and Y are shown in Figure 6.4a. Examination of the DTA trace for compound X shows that there is no thermal change of state or any indication of chemical reaction up to a temperature of 260°C: this further proves that calcium oxide or its hydroxide cannot bring about the curing of Viton GF. However, the DTA trace of compund Y shows a melting endotherm at 93°C and this is attributed to the melting of the HBTBP curing agent. Further inspection of the thermogram of compound Y shows an exotherm with a maximum at 166°C: this exotherm is attributed to the crosslinking reaction that occurs between Viton GF and HBTBP. It also indicates that the choice of 170°C as the press-curing temperature for Viton GF/HBTBP compounds is justified.

6.2.4.2 Thermal analysis of postcured and non-postcured vulcanizates

DTA traces of both postcured and non-postcured vulcanizates of compound Y are shown in Figure 6.4b. The DTA trace for the postcured vulcanizate shows no thermal change up to 280°C and this indicates that the postcured vulcanizate does not undergo any other DTA-sensitive thermal changes within the range of temperature investigated. In the case of the non-postcured vulcanizate, a trough is obtained at about 140°C which is

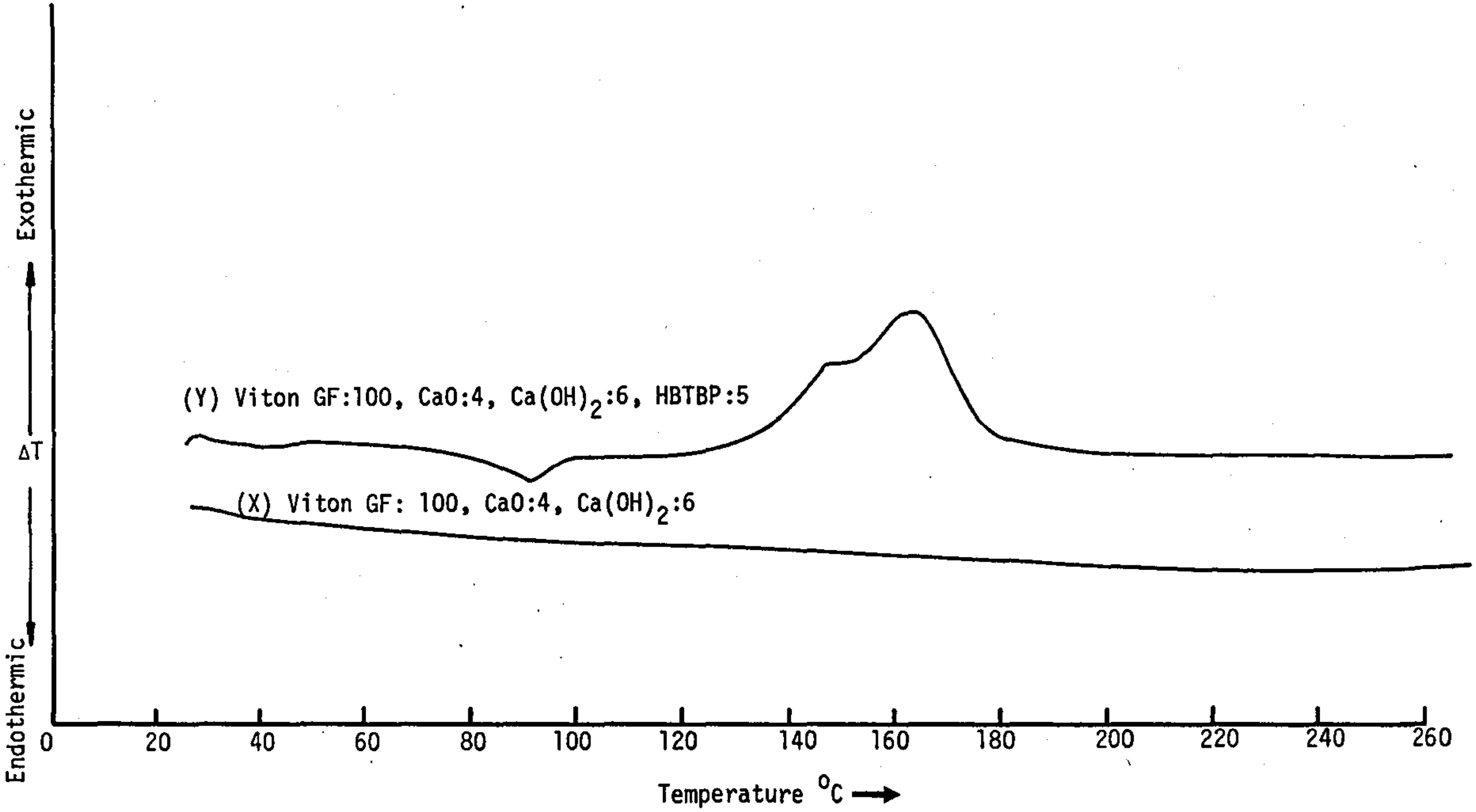


FIGURE 6.4a: Differential thermal analysis of Viton GF compounds X and Y of Table 6.2

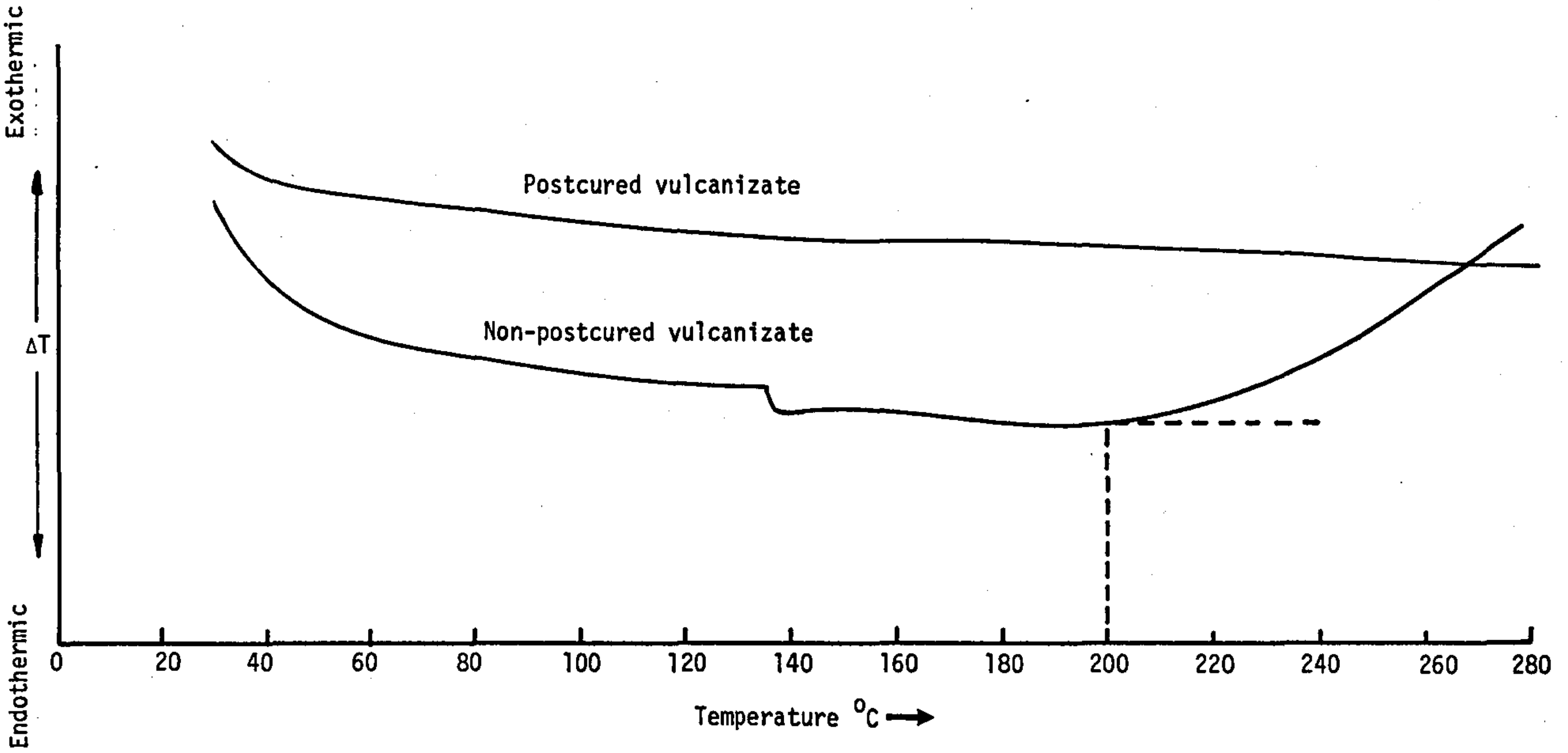


FIGURE 6.4b: Differential thermal analysis of postcured and non-postcured vulcanizates of compound Y of Table 6.2

probably due to the volatilization of low molecular weight products (e.g. moisture). The thermogram for the non-postcured vulcanizate also shows the beginning of an exotherm at 200°C which indicates further crosslinking reaction(s) to be occurring (possibly due to aromatization which is to be discussed in Section 6.6.3).

On the basis of the results of the thermal analysis study, it was concluded that a press or 'set' curing temperature of 170°C is found to be appropriate for Viton GF/HBTBP compounds while a suitable post-curing temperature is indicated to be from 200°C or above. It is also considered that the DTA data implies that volatilization of low molecular weight products can occur between 138°C and 145°C in non-post-cured vulcanizates. The DTA study of non-postcured vulcanizate also suggests the absence of by-products of vulcanization with melting or boiling points outside the 138°C - 145°C range. There is also an indication that a temperature of 200°C or above may be used to postcure HBTBP-cured Viton GF vulcanizates.

6.3 Solvent Extraction

6.3.1 Solvent Extraction with Methyl Ethyl Ketone

For the purposes of the solvent extraction investigation, the compound specified below was prepared:

Viton GF : 100
CaO (VG) : 4.0
$Ca(OH)_2$ (VE): 6.0
HBTBP : 5.0

(Cure conditions - 15 minutes at 170°C).

A portion of the above compound was press-cured while another portion was both press-cured and postcured (24 hours at 250°C in hot air).

Postcured, as well as non-postcured vulcanizates of the HBTBP-cured fluoroelastomer were extracted with hot methyl ethyl ketone using the Soxhlet apparatus and using procedures described in British Standard 903 Parts B1 and B2, 1958. The period of extraction was 72 hours. After extraction, the swollen vulcanizates were placed in an air-oven at 100°C until constant weight was obtained; this took about 24 hours and the samples shrank back to their approximate original dimensions. Then, these dried and extracted vulcanizates were tested qualitatively for nitrogen using Lassaigne's test. Similar tests were carried out on the unextracted samples of postcured and non-postcured vulcanizates. In all cases, tests were positive with nitrogen being detected. A possible deduction from these tests is that some nitrogen-containing fragments of the crosslinking agent (HBTBP) are chemically bound to the vulcanizate network. In this instance, the HBTBP is the only compounding ingredient present in the Viton GF vulcanizate to contain nitrogen; it is known that no nitrogen is contained in the raw Viton GF polymer. (Viton GF analysis: fluorine - 66.2%; Bromine 0.6%; Nitrogen - nil).

Quantitative estimates of nitrogen contents were now made* and the results are presented in Table 6.3a.

In Table 6.3a, the quantitative values of nitrogen vary widely as it was found that samples from the same specimen gave different results. Also the theoretical maximum content of nitrogen derived from the HBTBP would be 0.35% calculated on the unextracted vulcanizate (based on 5 phr HBTBP),

$$\text{i.e. 5 phr HBTPB in 115 of mix} = \frac{5 \times 28.014 \times 100}{115 \times 348.43} \ \%\text{N}$$

$$= 0.35\% \text{ N.}$$

---

* Acknowledgement is made to the staff of the Microanalytical Laboratory of the University of Manchester for these determinations.

TABLE 6.3a: Nitrogen contents of fluoroelastomer vulcanizates

Viton GF Vulcanizate Samples	Percentage Nitrogen Content	
	Test No 1	Test No 2
Non-postcured (unextracted)	0.9	0.8
Non-postcured (extracted)	0.7	0.8
Postcured (unextracted)	1.7	1.0
Postcured (extracted)	1.4	0.4

However, the experimentally determined values of nitrogen in the various vulcanizates were higher than the theoretical quantity of 0.35%. The wide disparity in these levels may be due to the extreme difficulty of determining low nitrogen contents in samples with high fluorine content. Thus, the significance of the quantitative nitrogen tests carried out with the extracted and unextracted vulcanizates is to confirm the Lassaigne qualitative tests on HBTBP-cured Viton GF vulcanizates and to show further that some nitrogen-containing fragments of the HBTBP crosslinking agent are chemically bound within the vulcanizate network.

6.3.2 Solvent Extraction with Hot Distilled Water

An identical sample of non-postcured, HBTBP-cured Viton GF vulcanizate used in Section 6.3.1 was extracted with hot distilled water in a Soxhlet apparatus for 72 hours. A qualitative test was conducted by reacting some of the water extract with silver nitrate acidified with dilute nitric acid. During the test, the solution formed a whitish cloud which subsequently tended to darken upon exposure to light; this was taken to indicate the presence of a halogen. Similar hot water extraction procedures were performed for the raw polymers of the various grades of fluoroelastomers (Viton GF, Viton B and Viton E60). The water extract obtained for each of these raw fluoroelastomers, when similarly tested was found to contain halogens. Quantitative analysis of the amount of halogens present in the water extracts is given in Table 6.3b.

TABLE 6.3b: Analysis of halogens present in hot water extracts of raw and vulcanized fluoroelastomers

Water extract sample of:	Halogens present and their content	Extractable quantity of halogen per gram of rubber
HBTBP-cured Viton GF (non-postcured)	Chlorine (4.68 μg/cm³)[a] Fluorine (2.07 μg/cm³)	Chlorine (117.7 μg) Fluorine (52.0 μg)
Raw Viton GF polymer	Chlorine (4.35 μg/cm³) Fluorine (5.8 μg/cm³)	Chlorine (87.0 μg) Fluorine (116.0 μg)
Raw Viton B polymer	Chlorine (4.85 μg/cm³) Fluorine (5.82 μg/cm³)	Chlorine (194.0 μg) Fluorine (232.8 μg)
Raw Viton E60 polymer	Chlorine (5.79 μg/cm³) Fluorine (1.21 μg/cm³)	Chlorine (115.8 μg) Fluorine (24.2 μg)

a) μg of halogen per cubic centimetre of water extract

These water extraction experiments of the various raw Viton polymers were undertaken to examine the ease of halogen removal from the raw rubber. The extraction of the HBTBP-cured Viton GF vulcanizate with hot water was undertaken to find out if any calcium halides were formed during vulcanization as a result of calcium oxide and calcium hydroxide being present. The results in Table 6.3b show that only trace quantities of halogens are present in all cases.

Calcium halides may be formed as a result of calcium oxide and calcium hydroxide being present during the vulcanization of Viton GF with HBTBP, but the evidence is not considered conclusive. It is possible that the halogens present in the various water extracts are due to catalyst residues in the Viton polymers(144). For example,an additional experiment was performed as follows: raw Viton GF which was extracted with hot water, dried and later cured with HBTBP showed no difference in cure and physical properties when it was compared with unextracted Viton GF polymer cured with HBTBP.

Paciorek and co-workers(162) have used solution studies to propose dehydrohalogenation as a primary step in the amine crosslinking of fluoroelastomers while Smith(163) has also suggested hydrogen fluoride elimination to occur in the diamine vulcanization of Viton A fluoroelastomer.

In general, the extraction of the HBTBP-cured vulcanizate with methyl ethyl ketone and the tests to detect nitrogen in dry and extracted vulcanizates demonstrate that some nitrogen-containing fragments of the HBTBP crosslinking agent are chemically bound within the Viton GF vulcanizate network. However, the results of hot water extraction of Viton GF vulcanizate and raw Viton polymers are considered inconclusive as traces of halogens in their respective water extracts could, it is thought, be due to catalyst residues in Viton polymers.

6.4 Swelling Measurements

Unfilled or gum Viton GF fluoroelastomer compounds were prepared to contain between 1 and 3 phr of HBTBP curing agent. Vulcanizates were obtained using a two-stage curing process (i.e. press-cure at 170°C for 15 minutes and followed by a postcure in hot air-oven at 250°C for 24 hours). However, some samples of each compound were only press-cured, to enable an assessment to be made of crosslink changes brought about by postcuring. In addition, postcured, gum vulcanizates containing 2 phr HBTBP were aged at 230°C for 1 day, 3 days, 5 days, 7 days and 10 days respectively; this enabled measurements of changes in crosslink density due to ageing to be made.

Weighed samples of the vulcanized fluoroelastomer were immersed in an excess of methyl ethyl ketone at 24°C. After a period of 72 hours, the swollen samples having attained equilibrium, were surface-dried using blotting paper and weighed. The swollen samples were dried to constant weight in a vacuum oven at 60°C.

6.4.1 Methods of Calculating Volume Fraction of Rubber in the Swollen Gel

The first method of calculating volume fraction of rubber in the swollen gel is as follows. Volume of solvent in the swollen samples was determined from the difference between swollen and desorbed samples while the volume fraction of rubber at equilibrium was calculated by assuming simple additivity of volume(164).

Another valid method(165) measures the weight increase (S) of each sample as:

$$S = \frac{m - m_o}{m_o} . 100$$

where m = weight of swollen sample

m_o = weight of dry, desorbed sample

and volume fraction (V_r) of elastomer in the swollen gel is given by:

$$V_r = \frac{1}{1 + 10^{-2} \frac{P_2}{P_1} .S}$$

where P_1 and P_2 denote the densities of the swelling liquid and the elastomer respectively. It is to be noted that V_r values from both methods agree.

6.4.2 Experimental Crosslink Density

The experimental crosslink density $(2\ M_c)^{-1}$ was estimated from the Flory-Rehner equation(166) below:

$$-[\ln (1 - V_r) + V_r + \chi V_r^2] = \rho V_o\ M_c^{-1}\ (V_r^{1/3} - V_r/2) \qquad (6.1)$$

where V_r is the volume fraction of polymer in the swollen gel;

χ, the polymer-solvent interaction parameter which was estimated from a relationship given by Fogiel$^{(167)}$; ρ is the density of the elastomer; V_0, the molar volume of the swelling liquid and M_c is the molecular weight between crosslinks. Network imperfections due to chain entanglements are neglected while the correction for loose chain ends$^{(166)}$ was made by replacing M_c^{-1} by M_c^{-1} $(1-2\ M_cM^{-1})$ where M designates the number average molecular weight of the non-crosslinked elastomer (100,000 in the case of Viton GF).

6.4.3 Results and Discussion of Swelling Measurements

The elastically effective crosslink density, corrected for loose chain ends, is plotted as a function of concentration of the HBTBP crosslinking agent in Figure 6.5a. If the stoichiometry of crosslinking is assumed to be one mole of crosslinks per mole of crosslinking agent, then the broken line in Figure 6.5a would be obtained. However, the actual experimental plot (continuous line, Figure 6.5a) shows that HBTBP yields crosslink density values which are in excess of the assumed stoichiometry. The slope of the actual plot gives a crosslinking efficiency of 1.48 and shows that the crosslinking of Viton GF by HBTBP cannot be represented by simple stoichiometry. It must be recognised that no correction has been made for physical factors like chain entanglement which contribute to the elastically effective crosslink density and this may be responsible for the apparent high crosslink efficiency of HBTBP. A further source of error in the determination of elastically effective crosslink density may be due to unknown complex chemical reactions taking place during vulcanization or overcuring at higher levels of crosslinking agent.

Another plot of the variation of actual experimental crosslink density with concentration of crosslinking agent is presented in Figure 6.5b. Although a higher crosslinking efficiency (1.84) is estimated from this plot, extrapolation of the plot to the HBTBP axis shows that a minimum quantity of HBTBP crosslinking agent is

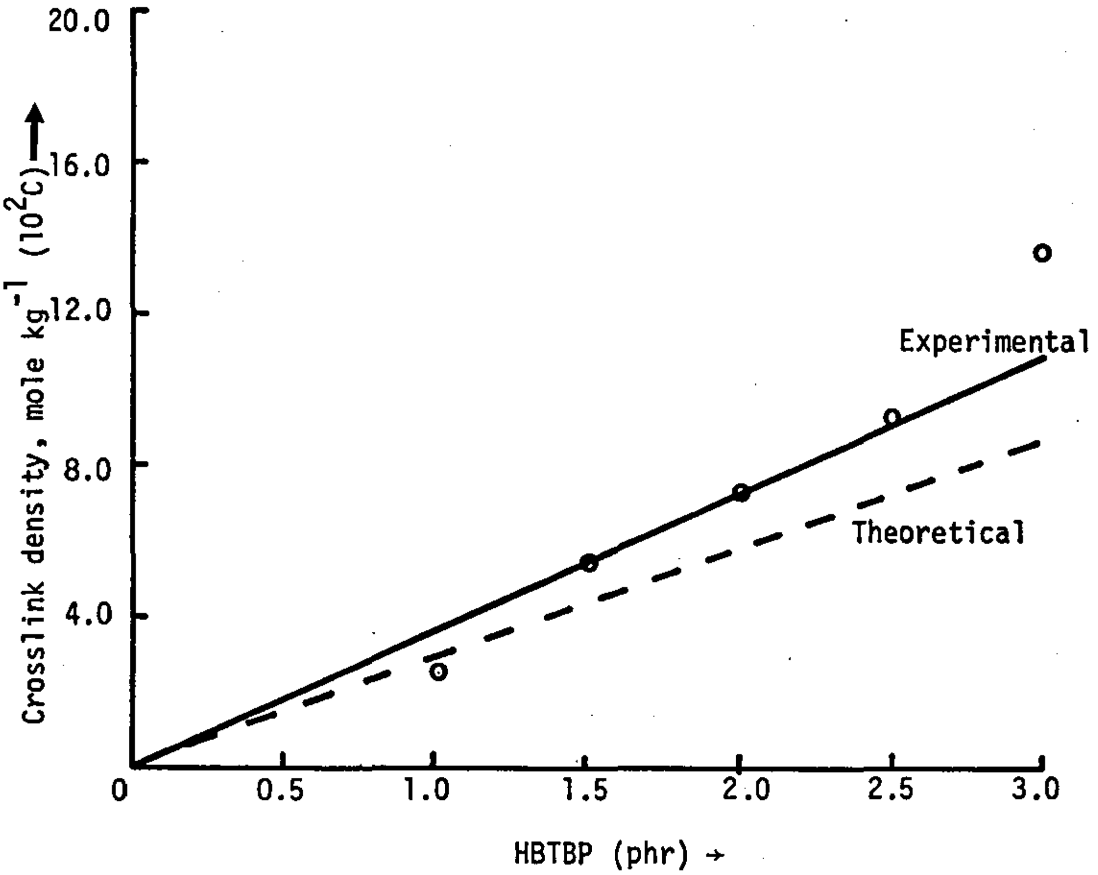


FIGURE 6.5a: Effect of HBTBP concentration on the crosslink density of Viton GF; (—) crosslink density corrected for loose chain ends; (----) theoretical plot of one mole of crosslinks per mole of HBTBP crosslinking agent

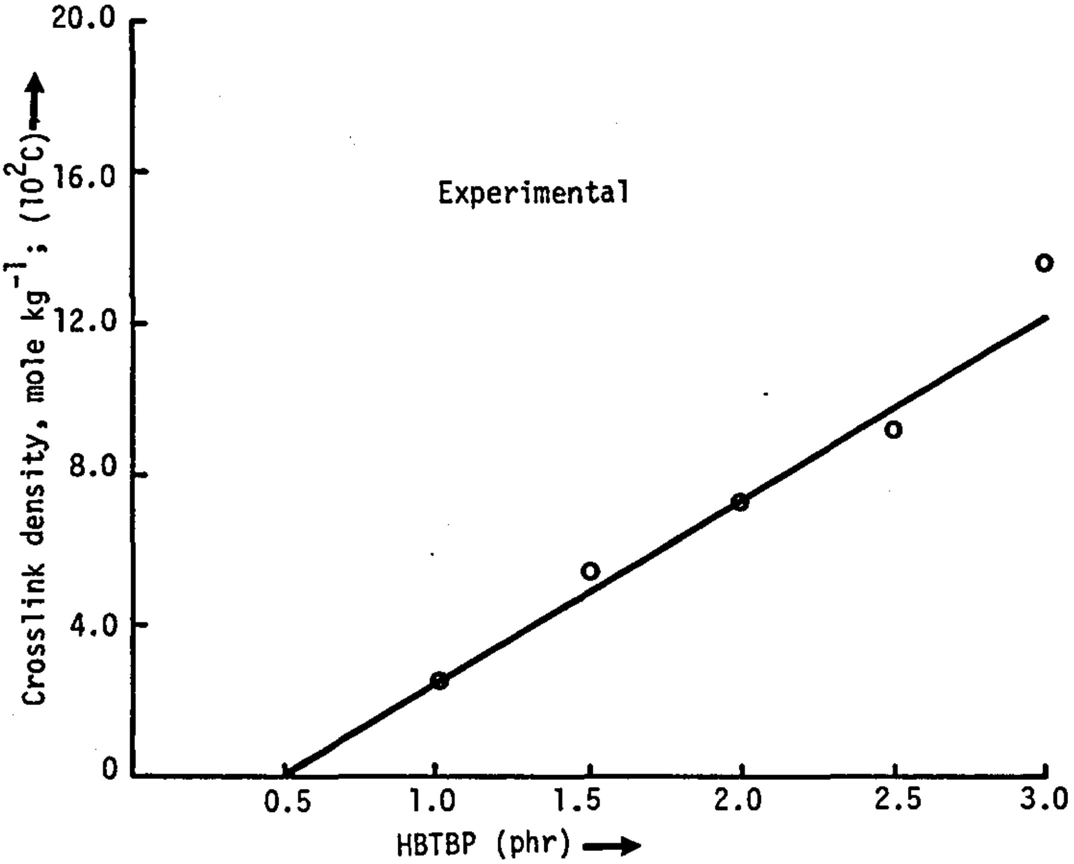


FIGURE 6.5b: Effect of HBTBP concentration on the crosslink density of Viton GF (corrected for loose chain ends)

required before any formation of crosslinks can occur. This suggests that some small quantity of the crosslinking agent is either adsorbed by the calcium oxide and/or calcium hydroxide present in the mix or possibly used in some unknown reactions.

6.4.4 State of Cure and Crosslink Density

The results in Table 6.4 which show crosslink density values of Viton GF vulcanizates in both set and postcured states, demonstrate that a substantial increase in crosslink density occurs as a result of postcuring. Thus, it may be deduced that additional crosslinks are formed when non-postcured, HBTBP-cured Viton GF vulcanizates are postcured.

TABLE 6.4: Influence of Curative Proportions and Cure State on Crosslink Density

Formulation	P1	P2	P3	P4	P5
Viton GF	100	100	100	100	100
CaO VG	4.0	4.0	4.0	4.0	4.0
$Ca(OH)_2$VE	6.0	6.0	6.0	6.0	6.0
HBTBP	1.0	1.5	2.0	2.5	3.0
Cure conditions	15 minutes at 170°C				
NO POSTCURE					
Volume fraction V_r	0.033	0.067	0.100	0.147	0.150
Int*Parameter, χ	0.420	0.370	0.317	0.240	0.240
Cross.** density (mole kg^{-1})	1.05(10^{-3})	5.9(10^{-3})	6.8(10^{-3})	37.2(10^{-3})	39.2(10^{-3})
AFTER POSTCURE AT 250°C FOR 24 HOURS					
Volume fraction V_r	0.132	0.166	0.182	0.195	0.224
Int.Parameter, χ	0.267	0.220	0.200	0.167	0.133
Cross.density (mole kg^{-1})	2.43(10^{-2})	5.4(10^{-2})	7.14(10^{-2})	9.2(10^{-2})	13.58(10^{-2})

* Int = Interaction
** Cross = Crosslink

6.4.5 Heat Ageing and Crosslink Density Changes in Postcured Vulcanizates

The results in Table 6.5 show that the crosslink density values of heat-aged samples of the HBTBP-cured, gum Viton GF vulcanizates undergo little change during heat ageing and this presents evidence that these fluoroelastomer vulcanizates are thermally stable.

TABLE 6.5: Crosslink Density of Postcured, HBTBP-crosslinked Gum Fluoroelastomer Vulcanizates after Heat-ageing at 230°C

Period of heat ageing (days)	0	1	3	5	7	10
Volume fraction V_r	0.176	0.184	0.179	0.168	0.168	0.168
Interaction parameter χ	0.200	0.200	0.200	0.200	0.200	0.200
Crosslink density (mole kg^{-1})	6.60 (10^{-2})	7.32 (10^{-2})	6.80 (10^{-2})	5.94 (10^{-2})	5.94 (10^{-2})	5.94 (10^{-2})

6.5 Simulation of Postcuring

A further study of the postcuring operation was undertaken with a view towards determining whether any unreacted intermediate product was present in HBTBP-cured vulcanizates that were only press-cured. Vulcanizates were prepared from the following compound formulation: Viton GF:100, CaO:4, $Ca(OH)_2$: 6, HBTBP:5. Press-curing was at 170°C for 15 minutes while the temperature used to simulate the postcure was 250°C.

Vulcanizate strips were suspended in a glass flask which was in turn immersed in an oil bath at 250°C. The gases given off from the vulcanizate strips during the simulated study were passed through a U-tube immersed in dry ice at -80°C and the uncondensed gases were absorbed in distilled water. The test was carried out over a period of 24 hours.

Some liquid was found to condense in the U-tube and its refractive index was found to be 1.334 (it is to be noted that water has a refractive index of 1.333). An attempt to test the condensed liquid qualitatively for nitrogen (Lassaigne's test) was unsuccessful as the metallic sodium used in the Lassaigne's test reacted violently with the liquid. The normal reaction of sodium with water is similarly explosive. Completion of the Lassaigne's test did not reveal the presence of any nitrogen. It is considered on the basis of the refractive index and the reaction with sodium, that the condensed liquid found in the U-tube is probably water. Infra-red analysis of this liquid was not undertaken because water and the -NH group absorb within the same frequency range and it would thus be difficult to distinguish between them.

Also, the quantity of the liquid condensate was small and this prevented further analysis. However, the water solution in which the uncondensed gases were passed and subsequently dissolved, was analysed and found to contain trace quantities of fluorine (2.0 μg/cm^3) and chlorine (8.5 μg/cm^3) respectively.

It is considered that the water evolved (the condensate) when these vulcanizate strips were heated to simulate a postcure may simply be formed from the reactions occurring during the press cure (see page 188, Step 2), since calcium hydroxide does not lose water until about 580°C. (The temperature used to simulate postcure was 230°C). The halogens detected in water used to dissolve the uncondensed gases were probably given off as hydrogen halides.

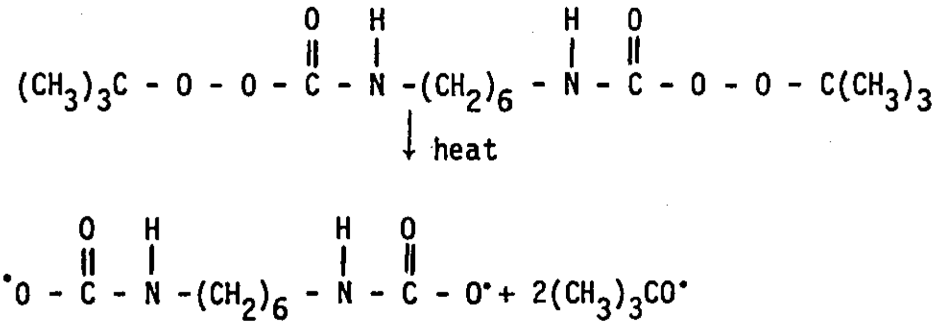
6.6 Mechanism of Crosslink Formation

6.6.1 Thermal Decomposition of HBTBP

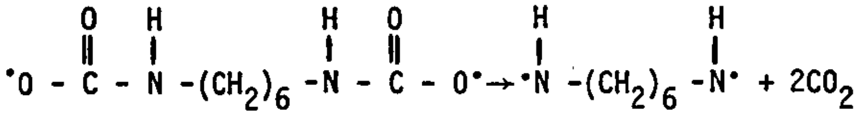
It is necessary to understand the thermal decomposition of HBTBP as a first step towards formulating a mechanism for its use as a crosslinking agent in Viton GF fluoroelastomer compounds.

Pederson[134a,134b] and others[135,136] have postulated mechanisms of thermal decomposition of peroxycarbamates to give free radicals in suitable medium. Products of thermal decomposition of peroxycarbamates were suggested to be carbon dioxide, an imino radical and an alkoxy or aralkoxy radical. This was supported by the evidence of a hydrazo and azo compound being formed when peroxycarbamates are decomposed. It was therefore postulated that the primary step in the decomposition of peroxycarbamates is the homolytic scission of the oxygen-oxygen bond, accompanied or followed by loss of carbon dioxide.

Based on the work of Pedersen(134a,134b) and others(135,136), HBTBP can be similarly considered to undergo a homolytic, thermal decomposition which is represented in equations 6.2 through to 6.4.



$$(CH_3)_3C - O - O - \overset{\overset{O}{\|}}{C} - \overset{\overset{H}{|}}{N} - (CH_2)_6 - \overset{\overset{H}{|}}{N} - \overset{\overset{O}{\|}}{C} - O - O - C(CH_3)_3 \xrightarrow{heat} {}^{\bullet}O - \overset{\overset{O}{\|}}{C} - \overset{\overset{H}{|}}{N} - (CH_2)_6 - \overset{\overset{H}{|}}{N} - \overset{\overset{O}{\|}}{C} - O^{\bullet} + 2(CH_3)_3CO^{\bullet} \tag{6.2}$$



$${}^{\bullet}O - \overset{\overset{O}{\|}}{C} - \overset{\overset{H}{|}}{N} - (CH_2)_6 - \overset{\overset{H}{|}}{N} - \overset{\overset{O}{\|}}{C} - O^{\bullet} \rightarrow {}^{\bullet}\overset{\overset{H}{|}}{N} - (CH_2)_6 - \overset{\overset{H}{|}}{N}{}^{\bullet} + 2CO_2 \tag{6.3}$$

$$(CH_3)_3\ CO^{\bullet} \rightarrow (CH_3)_2CO + CH_3^{\bullet} \tag{6.4}$$

(If any acetone is formed, it would be evaporated at the temperature of vulcanization, 170°C).

6.6.2 Reaction Mechanism of Crosslink Formation

From the homolytic decomposition of HBTBP, the results of compounding studies, thermal analysis and nitrogen tests, two possible routes of crosslink formation are proposed.

Scheme 1

The first scheme which is represented on page 187, is proposed to occur through the abstraction of methylenic hydrogen from the Viton GF fluoroelastomer to form free radicals on the polymer main chain and interaction of the resulting radicals to form crosslinks; also considered formed is hexamethylene diamine as an intermediate product and this in turn reacts further with the Viton GF polymer to form additional crosslinks.

A separate experiment was performed in which hexamethylenediamine, in its pure form, was mill-mixed into Viton GF and the resulting compound was found to scorch during mixing. This is some evidence that any hexamethylenediamine formed during the vulcanization of Viton GF/HBTBP compound would react further with the polymer to form additional crosslinks.*

This first scheme is supported by the difference in the relative crosslinking efficiencies of MBTBP and HBTBP in Viton GF respectively (measured by ODR in Figure 6.2). MBTBP and HBTBP have similar types of chemical structures (Section 6.2.2) but have some differences in the particular groups present. The comparable formulations used to examine both MBTBP and HBTBP in Viton GF (see the ODR of Figure 6.2) showed the HBTBP formulation to be the more reactive of the two. This superior cure response of HBTBP in Viton GF may be attributed to the formation of a more reactive hexamethylenediamine intermediate than its MBTBP analogue. It is probable that the hexamethylenediimino radical obtained from the decomposition of HBTBP abstracts methylenic hydrogen from Viton GF to form hexamethylenediamine. The hexamethylenediamine thus formed will be present as an intermediate that then further reacts with the elastomer to form more crosslinks. This proposal is further supported

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* Viton B shows similar scorch tendencies with hexamethylene diamine as curing agent (144)

by the thermal analysis of the non-postcured vulcanizate (Section 6.2.4.2) as well as the simulated postcuring studies (Section 6.5) which found free hexamethylenediamine to be absent.

Additional evidence for this view of the mechanism can be deduced from the experiment which was carried out and involved solvent extraction of non-postcured and postcured vulcanizates of Viton GF. These vulcanizates were extracted with methyl ethyl ketone and dried; they were found to contain nitrogen which could only have been obtained from fragments of the HBTBP crosslinking agent being chemically bound to the vulcanizates.

More supporting evidence for the presence of bound nitrogen within the HBTBP-cured Viton GF vulcanizate was obtained by infrared analysis. In this experiment, HBTBP only was mixed at the 1 phr level into Viton GF fluoroelastomer and the mix was press-cured for 15 minutes at 170°C to produce a lightly crosslinked thin vulcanizate film (0.6 mm). A non-porous section of the crosslinked film was extracted with methyl ethyl ketone in a Soxhlet apparatus for 48 hours after which it was left to dry to constant weight in an air-oven at 100°C, and thus to exclude any moisture or solvent present (a temperature higher than 100°C was not used for drying to prevent the film from darkening). Using a 5% solution of raw Viton GF polymer dissolved in methyl ethyl ketone, a control film of pure Viton GF (uncrosslinked) was prepared by spreading some of the solution onto a sodium chloride disc, and evaporating the solvent from the film with an infrared heat lamp.

The infrared traces for the crosslinked and the uncrosslinked film are shown in Figure 6.6. It should be noticed that the infrared trace for the crosslinked film absorbed at 3540 cm^{-1}, whereas the infrared trace for the uncrosslinked film showed no such absorption. The peak at 3540 cm^{-1} is attributed to the presence of an -NH group since moisture has been excluded from the crosslinked sample by drying. Thus, it can be said that nitrogen-containing fragments of the HBTBP crosslinking agent are chemically bound to the Viton GF polymer network (possibly in the form of an $-NH-(CH_2)_6-NH-$ crosslink).

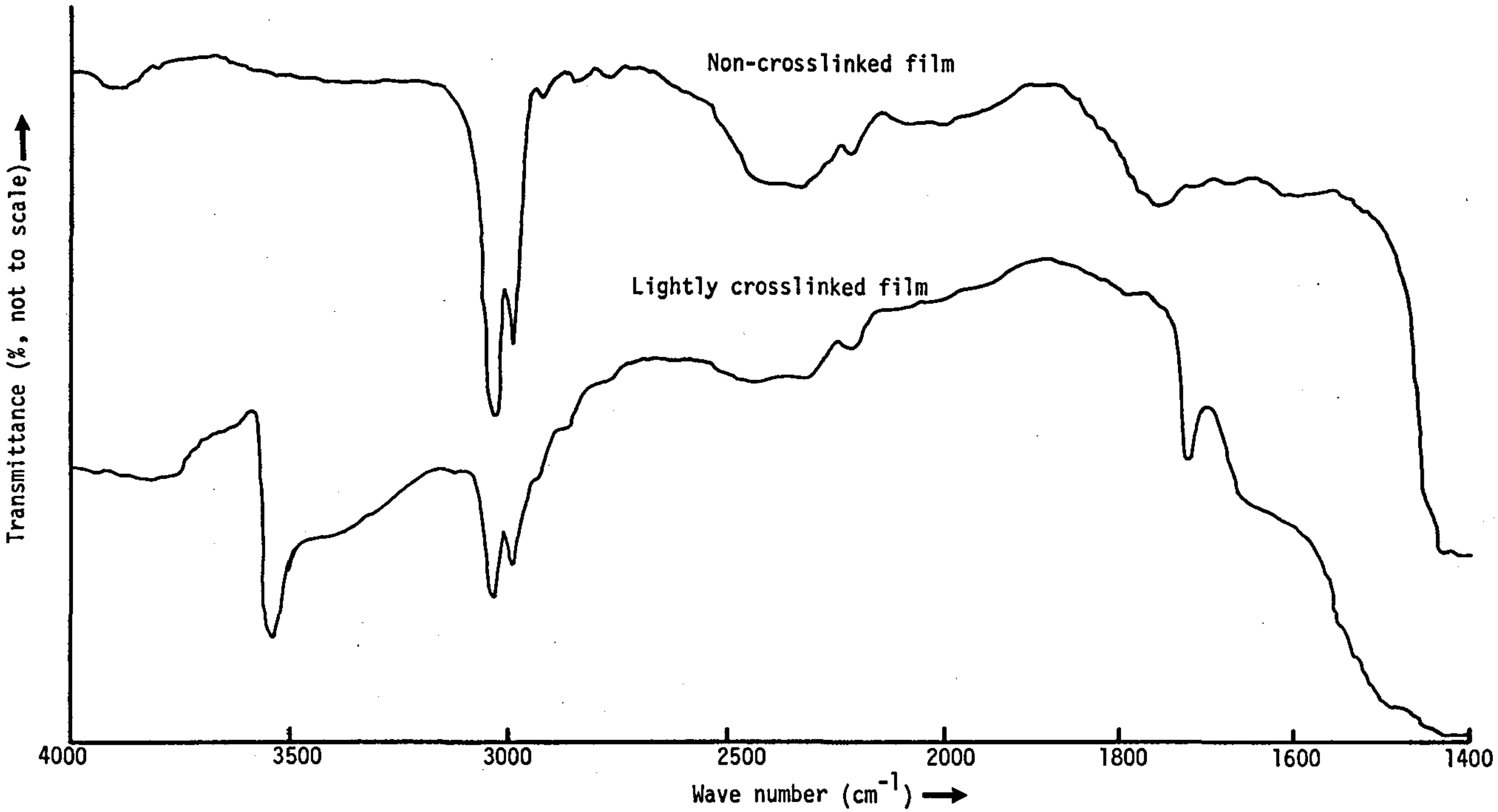
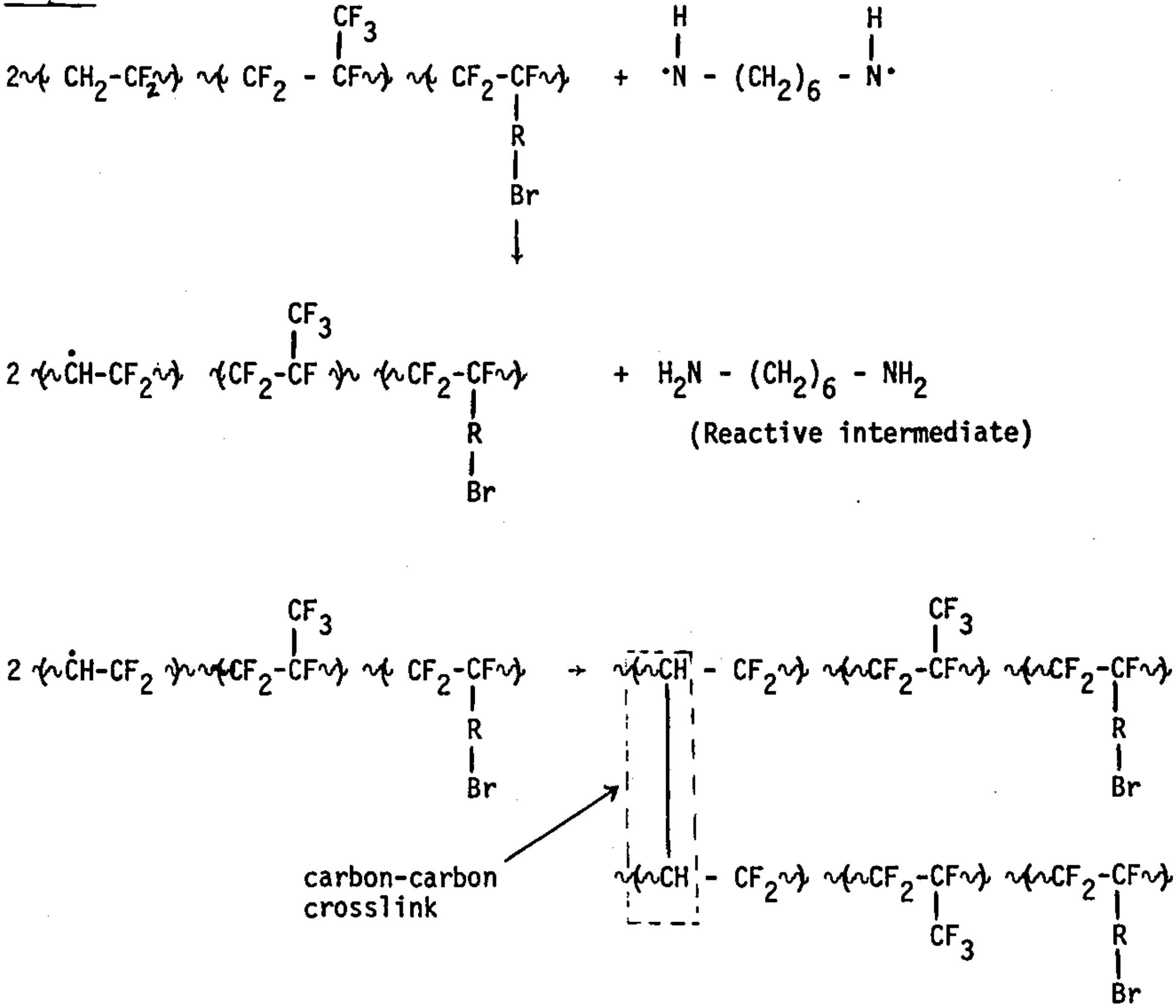


FIGURE 6.6: Infrared spectra of crosslinked and non-crosslinked Viton GF fluoroelastomer films

Combining the homolytic decomposition of HBTBP with the results of compounding studies, thermal analysis, quantitative and qualitative nitrogen tests, and infrared studies, Scheme 1 (below) is proposed to depict possible routes of crosslink formation:

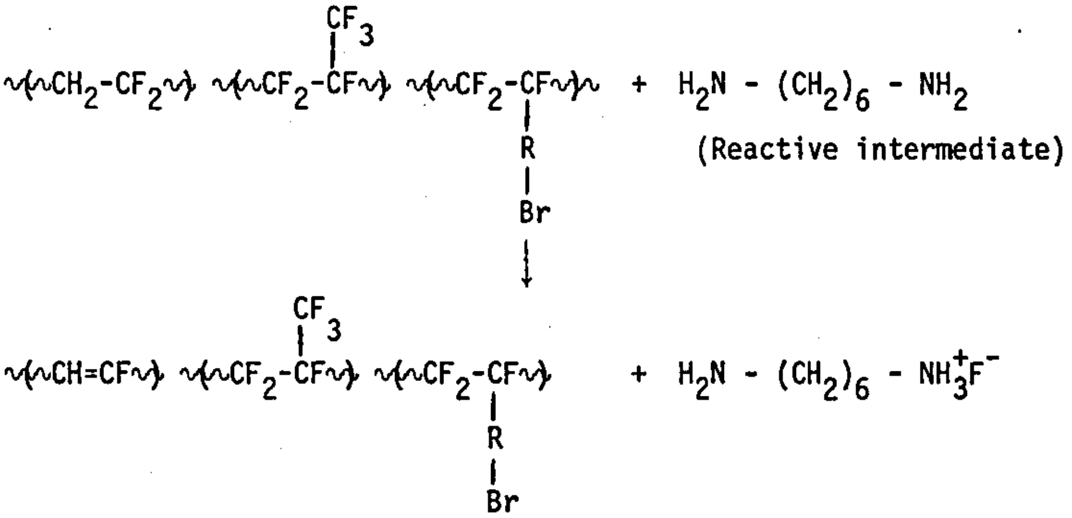
Scheme 1: Crosslink formation in Viton GF obtained through hydrogen abstraction, radical-radical addition and further interaction with hexamethylenediamine formed as an intermediate

Step 1



Step 2

Further interaction of the reactive intermediate (hexamethylene-diamine) is represented in the equations below and similar to that of Smith and Perkins(168):



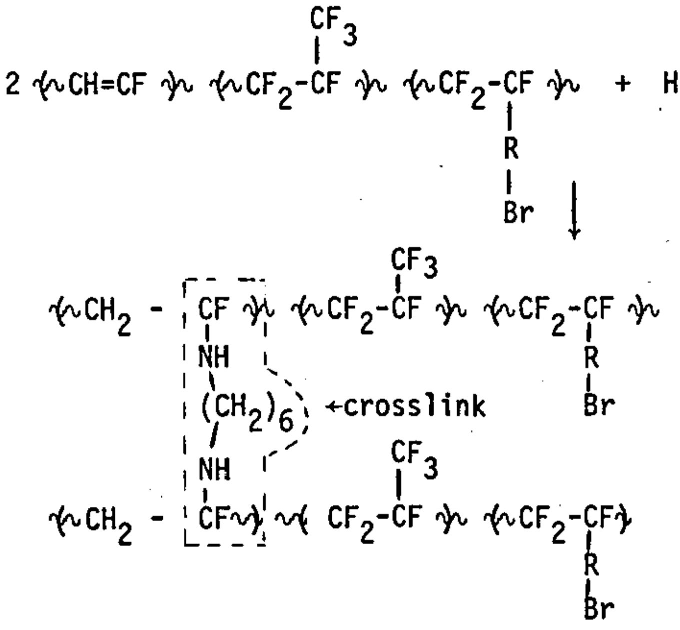
$$\sim\!CH_2\text{-}CF_2\!\sim\ \sim\!CF_2\text{-}\underset{}{\overset{CF_3}{\overset{|}{C}}}F\!\sim\ \sim\!CF_2\text{-}\underset{\underset{Br}{\overset{|}{R}}}{\underset{|}{C}}F\!\sim\ +\ H_2N - (CH_2)_6 - NH_2 \text{ (Reactive intermediate)}$$

$$\downarrow$$

$$\sim\!CH{=}CF\!\sim\ \sim\!CF_2\text{-}\overset{CF_3}{\overset{|}{C}}F\!\sim\ \sim\!CF_2\text{-}\underset{\underset{Br}{\overset{|}{R}}}{\underset{|}{C}}F\!\sim\ +\ H_2N - (CH_2)_6 - NH_3^+F^-$$

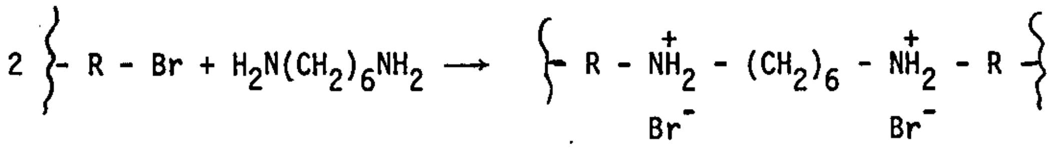
$2H_2N\text{-}(CH_2)_6 - NH_3^+F^- + CaO \rightarrow CaF_2 + H_2O + 2H_2N - (CH_2)_6 - NH_2$

(Note: CaF_2 is sparingly soluble in water and hence will not be extracted easily from the vulcanizate by aqueous media).



$$2\ \sim\!CH{=}CF\!\sim\ \sim\!CF_2\text{-}\overset{CF_3}{\overset{|}{C}}F\!\sim\ \sim\!CF_2\text{-}\underset{\underset{Br}{\overset{|}{R}}}{\underset{|}{C}}F\!\sim\ +\ H_2N - (CH_2)_6 - NH_2$$

It is also considered that the hexamethylenediamine formed as an intermediate vulcanization product should be capable of quaternizing the pendent bromine groups to form crosslinks as depicted below(a)



$$2\,\}\!-R-Br+H_2N(CH_2)_6NH_2\longrightarrow\ \}\!-R-\underset{Br^-}{\overset{+}{N}H_2}-(CH_2)_6-\underset{Br^-}{\overset{+}{N}H_2}-R-\{$$

Scheme 2

Another possible route of crosslink formation is postulated on the basis of free radical abstraction of the bromine group from Viton GF (C-Br has the lowest bond strength in the Viton GF polymer structure). The evidence for this route of crosslink formation derives from the result obtained when the cure responses of different grades of "Viton" with HBTBP crosslinking agent are investigated (Figure 6.3). The difference in the relative crosslink efficiencies of each Viton grade can be attributed mainly to their different structures (see Table 6.1a). Since Viton GF, which gives the best cure response with HBTBP is the only polymer that is brominated, it is considered that the pendent bromine group in the polymer structure is partly involved in the crosslinking reactions. Methyl radical abstraction of the bromine group as methyl bromide would thus seem to be the simplest route of generating radicals on the Viton GF polymer.

An experiment to try and detect the presence of methyl bromide vapour, and if possible collect some was not successful (possibly due to equipment limitations). Also a quantitative determination was made of bromine in the raw Viton GF polymer and found to be 0.6%; also in the vulcanizate, bromine content was measured and a value of 0.58% was obtained. It is considered that these two values are not significantly different. This use of quantitative analysis to determine bromine assumes that the polymerized monomers in raw Viton GF are uniformly

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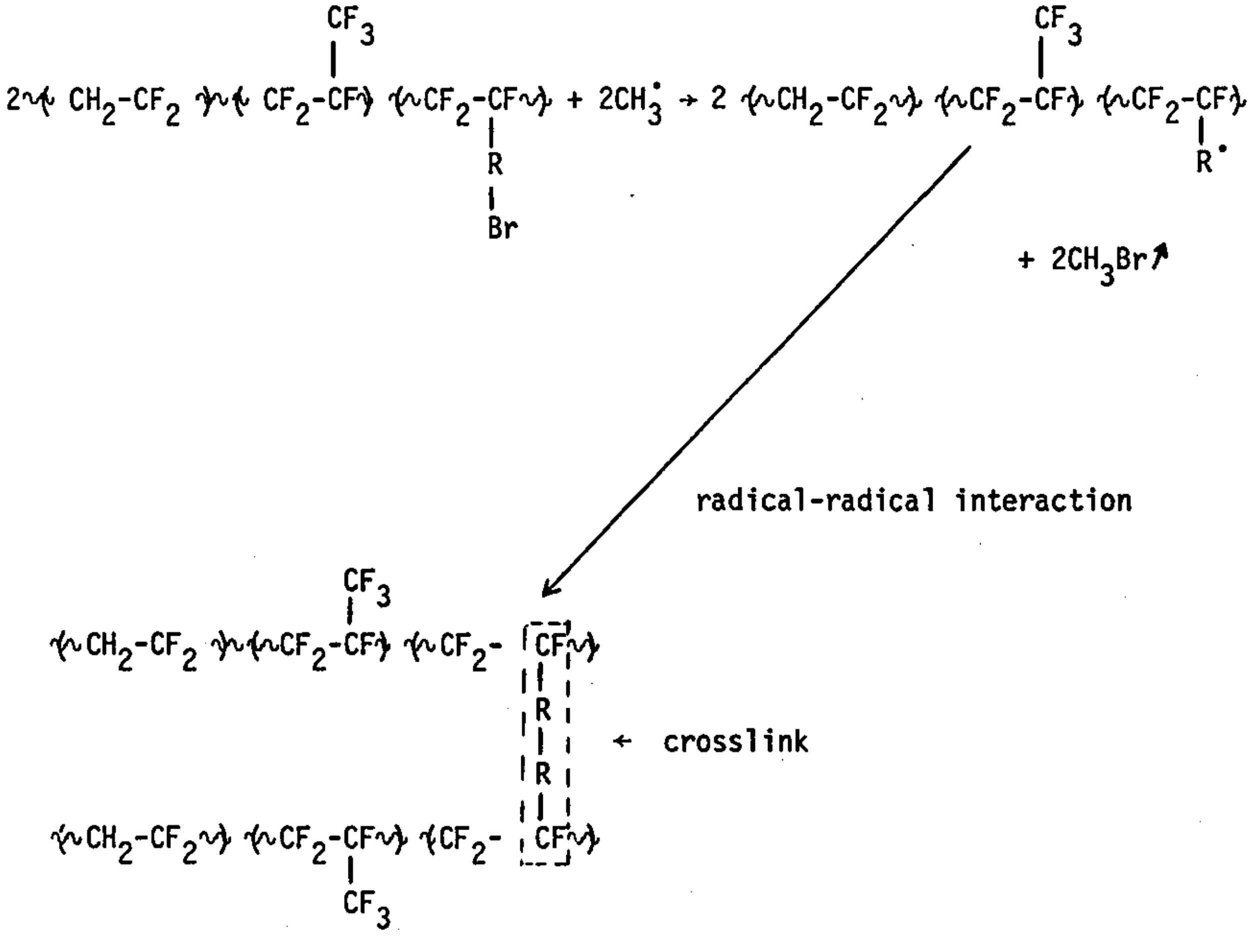
(a) This concept was suggested to the author by Dr M Porter of the Malaysian Rubber Producers' Research Association distributed. As a result of these experiments, it was not possible to conclude whether any bromine in the polymer was lost as methyl bromide when Viton is crosslinked with HBTBP.

However, a theoretically possible route of obtaining crosslinks in Viton GF with HBTBP is depicted in Scheme 2 below:



Scheme 2: Bromine abstraction from Viton GF and crosslink formation through radical-radical interaction

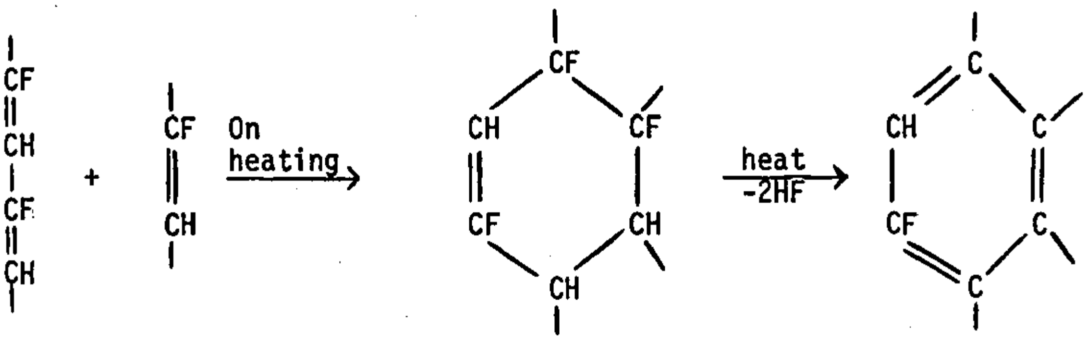
From what has been discussed so far on crosslinking mechanism, it is possible now to re-examine Figures 6.5a and 6.5b. To explain the results shown by these figures, 'physical' crosslinks, such as chain entanglements were suggested as one reason for the apparent crosslinking efficiencies demonstrated by the 1.48 of Figure 6.5a and the 1.84 of Figure 6.5b.

However, as an alternative, there could be another chemical reason for the stoichiometric values obtained in Figures 6.5a and 6.5b. Decomposition of one molecule of HBTBP could give two t-butoxy radicals and one hexamethylenediimino radical. If these were 100% efficient in hydrogen or bromine abstraction, and the reactive intermediate was also 100% efficient in forming crosslinks, it would be possible to obtain three crosslinks per mole of HBTBP. Both physical and chemical factors could then be responsible for the apparent crosslinking efficiencies obtained although the extent of physical crosslinks within the vulcanizate network remains uncertain.

A recent work(151) has described the crosslinking of bromine-containing fluoroelastomers by peroxides in combination with coagents. The cure mechanism which was proposed to occur involved (a) generation of alkyl radicals via the aliphatic peroxide decomposition, (b) generation of radicals on the polymer backbone via a chain reaction in which the residual bromine atom of the Viton GF is abstracted, and (c) addition of the polymeric radicals to the trifunctional coagent to form crosslinks (the coagent was regarded as the crosslinking molecule).

6.6.3 Mechanism of Postcuring

The detailed chemical changes which obviously take place during the postcure step (Table 6.4) are not fully understood. Also, infrared studies of the changes taking place in the Viton GF vulcanizate during postcure did not produce meaningful results as the samples darkened on prolonged exposure to heat (24 hours in hot air at 250°C). It was also found that a white sheet of raw Viton GF polymer which was exposed to an air-oven temperature of 250°C for 24 hours darkened (probably due to in-situ double bond formation), and would not dissolve completely in methyl ethyl ketone whereas an untreated, raw Viton GF polymer formed a homogeneous solution with methyl ethyl ketone. This qualitative test and the results of the simulated study of postcuring (Section 6.5) suggest some network-forming reactions taking place during postcuring. Indeed, the following explanation offered by Smith(163) for postcuring of fluoroelastomer may apply in this instance; a conjugated centre which is formed by dehydrofluorination of the Viton GF may react with a double bond in an adjacent chain by means of a Diels-Alder addition (see scheme 3 below). Subsequently, by further dehydrofluorination, a benzenoid ring can form which explains the stability of the network through the formation of the new thermally stable crosslinks.



Scheme 3: The Diels-Alder reaction, which it is proposed can occur during postcuring of Viton GF to form an aromatic ring, with loss of HF (163)

6.7 Stress Relaxation Measurements

6.7.1 Introduction and Theory

Stress relaxation measurements can be used as a sensitive method for following stress changes in vulcanizate strips when heat-aged at elevated temperatures and these changes can be correlated with the 'making and breaking' of bonds in the elastic network. It must be recognised however that there are two mechanisms which can lead to stress relaxation occurring in a crosslinked elastomer. These are (i) physical stress relaxation processes which involve molecular rearrangement that require little primary bond formation or breakage e.g. relaxation of entanglements, (ii) chemical stress relaxation (chain scission, crosslink scission and crosslink formation). Physical stress relaxation is considered to be of little consequence here and the remaining discussion pertains mainly to chemical stress relaxation.

The general principles(169-171) underlying the stress relaxation technique are based upon the kinetic theory of rubber elasticity where stress f(o) exerted on a stretched rubber sample is directly proportional to the number N(o) of stress supporting network chains

i.e. $$f(o) = N(o)k\,T(\alpha - \alpha^{-2}) = n(o)\,RT(\alpha - \alpha^{-2}) \qquad (6.5)$$

k is Boltzmann's constant, T is the absolute temperature, R is the gas constant, n(o) is the moles of network chains and α is the ratio of the stretched length to the initial length of the sample (extension ratio).

If at a time t there has been a cleavage of N_0-N_t of network chains at extension ratio α and constant temperature, then

$$\frac{f_t}{f_o} = \frac{N_t}{N_o} \tag{6.6}$$

Hence the decrease in stress of a continuously extended strip (continuous stress relaxation measurements) can be used as a measure of the number of network chains removed by scission since it is assumed that any new network formed by crosslinking is in equilibrium in the extended state and does not contribute to the stress as long as the extension is unchanged. The limitations of this theory in the interpretation of stress relaxation data has been discussed elsewhere(172). However, the balance between the retractive force of the original network and the newly formed ones will result in permanent set i.e. increase in the unstrained length when the strain is removed.

Also intermittent stress relaxation experiments can be performed on a vulcanizate strip by extending it only for short periods at such times as the stress is to be measured so that any new network will be formed with the sample in the unstretched state and will only contribute to the stress when extended. It can be said therefore that whilst continuous stress relaxation measurements provide an estimate of network chain scission, intermittent stress relaxation measures the net rate of scission and crosslinking. Hence the difference between the two measurements is a measure of crosslinking which is expressed in the form below(173).

If the original network structure is characterized by $C(o)$ moles of effective tetrafunctional crosslinkages per cubic centimetre, the relation between $n(o)$ moles of network chains per cubic centimetre and $C(o)$ is given by

$$n(o) = = C(o) \tag{6.7}$$

The number of moles of additional crosslinks per cubic centimetre that have subsequently formed up to time t will be denoted by $\Delta C(t)$, and the number of moles of chain cleavages per cubic centimetre by $q(t)$. Then the crosslinking density of the network chains up to time t, $n(t)$ is given by:

$$n(t) = 2C(t) = 2C(o) - q(t) + 2\,\Delta C(t) \tag{6.8}$$

Therefore the intermittent stress measurement at time t, $f_i(t)$ is denoted by

$$f_i(t) = \{2C(o) - q(t) + 2\Delta C(t)\}\ RT(\alpha - \alpha^{-2}) \tag{6.9}$$

On the other hand, the stress $f_c(t)$ measured in a continuous relaxation of stress experiment, where the sample is maintained at a fixed elongation is

$$f_c(t) = \{2C(o) - q(t)\}\ \ RT(\alpha - \alpha^{-2}) \tag{6.10}$$

If the difference between curves of intermittent stress relaxation and the continuous stress relaxation is represented by X, the following equation is derived from equations 6.5 through to 6.10

$$X = \frac{f_i(t)}{f(o)} - \frac{f_c(t)}{f(o)} = \frac{2\Delta C(t)}{n(o)} = \frac{\Delta C(t)}{C(o)} \tag{6.11}$$

Thus, the difference value X, the additional crosslinkages formed up to time t could be estimated. If only scission were occurring, the continuous stress-relaxation curves and the intermittent stress curves would be identical.

From the foregoing discussion, it was considered that the stress relaxation data which is normally used to assess heat ageing could also be used to assess crosslink changes which occur during postcuring of Viton GF vulcanizates.

The following experiments were carried out to examine crosslink changes when the Viton GF cured with HBTBP is exposed to high degree of heat in different environments. Both non-postcured and postcured Viton GF vulcanizates were examined.

6.7.2 Specimen Preparation

For the purpose of stress relaxation measurements the formulations (Table 6.6) below were used and method of preparation was as described in Chapter 3.

TABLE 6.6: Compound Formulation for Stress Relaxation Measurements

	S1	S2	S3
Viton GF	100	100	100
MT Black N990	25	-	-
CaO VG	4.0	4.0	4.0
$Ca(OH)_2$ VE	6.0	6.0	6.0
HBTBP	2.0	2.0	-
Luperco 101 XL	-	-	3.0
Diak No 7	-	-	3.0
Cure conditions	15 minutes at 170°C		

One half of each compound was press-cured only while the other half was both press-cured and postcured. Vulcanized sheets obtained were 0.6 mm thick.

The description of the stress relaxation unit used is given in Appendix 4. A test temperature of 200^{o}C was used while vulcanizates were extended to 30% of their original length and measurements were obtained over a 24-hour period.

6.7.3 Results and Discussion

6.7.3.1 Stress relaxation and postcuring operation

All the vulcanizate samples used here had not undergone postcuring so as to enable the monitoring of network changes that occurred in the non-postcured samples during 'heat ageing' to be possible; thus the heat ageing simulated the postcuring operation. A test temperature of 200^{o}C was used for this heat ageing; a higher temperature was not possible due to equipment limitations. This test temperature (200^{o}C) was lower than the postcuring temperature which was 250^{o}C. However the results obtained at 200^{o}C are considered to some extent to simulate the 250^{o}C postcure situation. [*Note*: Postcure temperatures for Viton GF are usually between 200^{o}C and 260^{o}C].

For the gum HBTBP-cured Viton GF, the results of the stress relaxation measurements are plotted in Figure 6.7 as $\log(f_t/f_o)$ against time (f_t and f_o are tensile stresses at times t and t=0 respectively). The results were obtained for continuous and intermittent measurements made in air and in nitrogen.

Examination of this data for the non-postcured samples indicated that a stable network was attained in both air and nitrogen environments after the initial 12 hours of exposure to heat.

Equation 6.11 was used to obtain the additional crosslinks formed during the simulated postcure. The plots in Figure 6.8 demonstrated clearly that additional crosslinks must be formed when a gum, non-postcured Viton GF vulcanizate is exposed to an elevated temperature in both air and nitrogen environments. Larger amounts of crosslinks

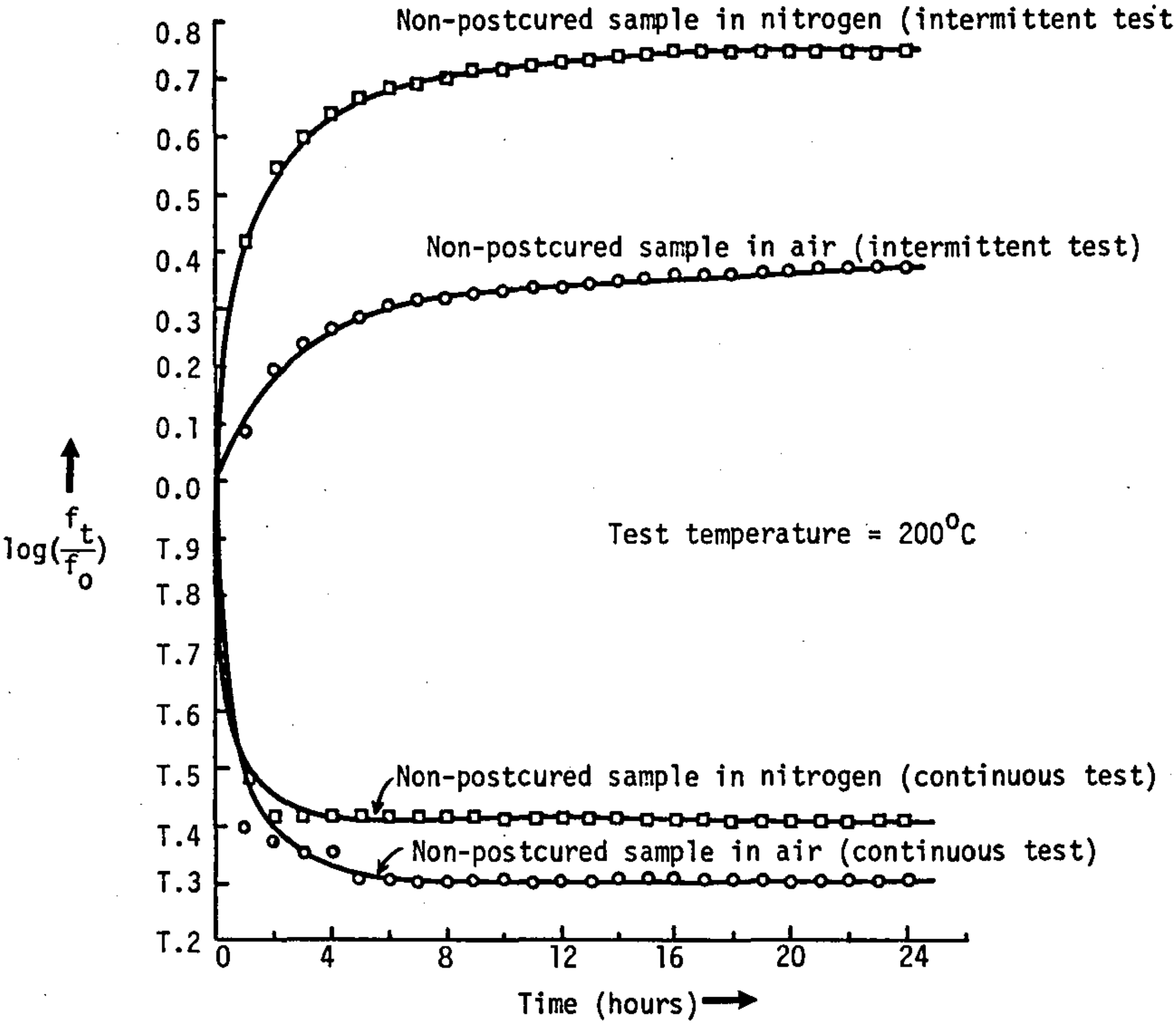


FIGURE 6.7: Stress relaxation measurements of non-postcured, HBTBP-cured gum fluoroelastomer

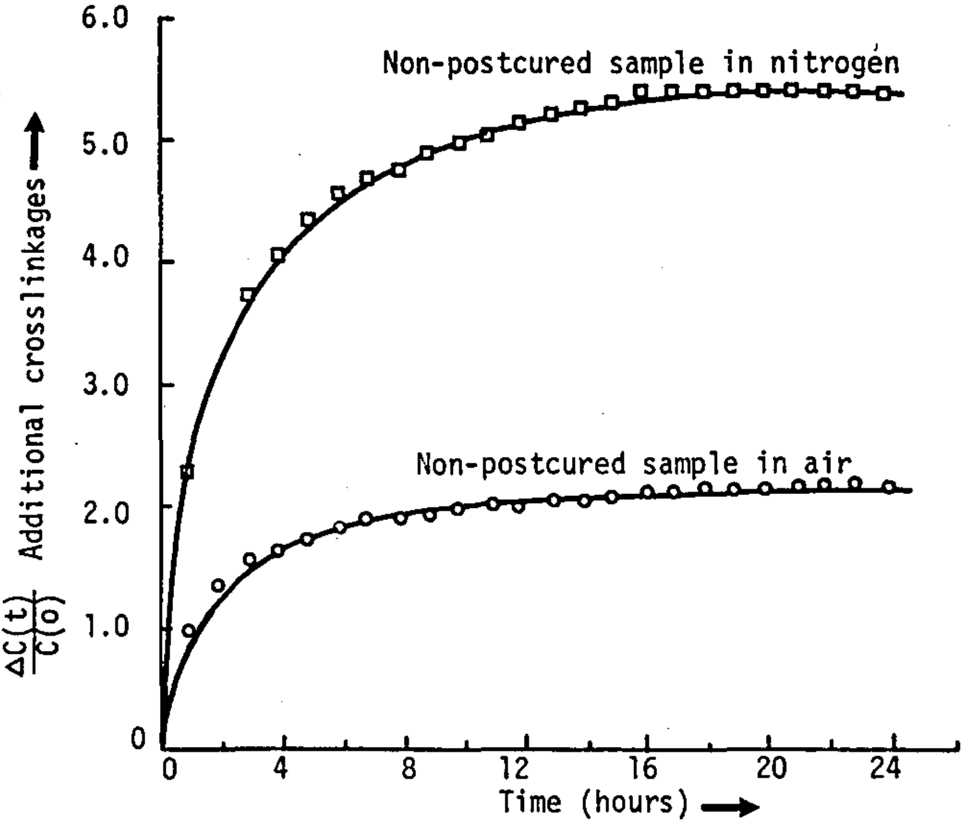


FIGURE 6.8: Additional crosslinkages formed in non-postcured, HBTBP-cured gum fluoroelastomers at 200°C

are formed in the nitrogen environment whereas in the air atmosphere, it is considered that oxidative scission effects occur and a lower overall crosslink density results.

Stress relaxation measurements were also performed on the unfilled Viton GF fluoroelastomer crosslinked with peroxide and coagent (S3 of Table 6.6). Results of continuous and intermittent stress relaxation measurements in this case, obtained in both nitrogen and air, are presented in Figure 6.9 and the additional crosslinks formed are shown in Figure 6.10. The stress relaxation behaviour of the peroxide/coagent-cured Viton GF vulcanizate followed a similar trend to that of the HBTBP-cured Viton GF vulcanizate.

Though quantitative considerations of stress relaxation usually relate only to gum vulcanizates, the use of a non-postcured but carbon black filled Viton GF vulcanizate in these stress relaxation experiments followed the same course as its gum analogues (Figures 6.11 and 6.12). Hence stress relaxation curves were found to be nearly independent of the presence or absence of carbon black.

The relevance of the stress relaxation measurements obtained so far, has been to show that the formation of additional, stable crosslinks is the predominating feature to occur during such 'ageing' of non-postcured Viton GF vulcanizates; this ageing is considered to simulate the postcuring operation. This observation is consistent with results of swelling measurements (see Table 6.4). When swelling measurements were used to estimate the crosslink densities of non-postcured and postcured vulcanizates, it was found that the postcuring of HBTBP-cured Viton GF vulcanizate led to an increase in crosslink density.

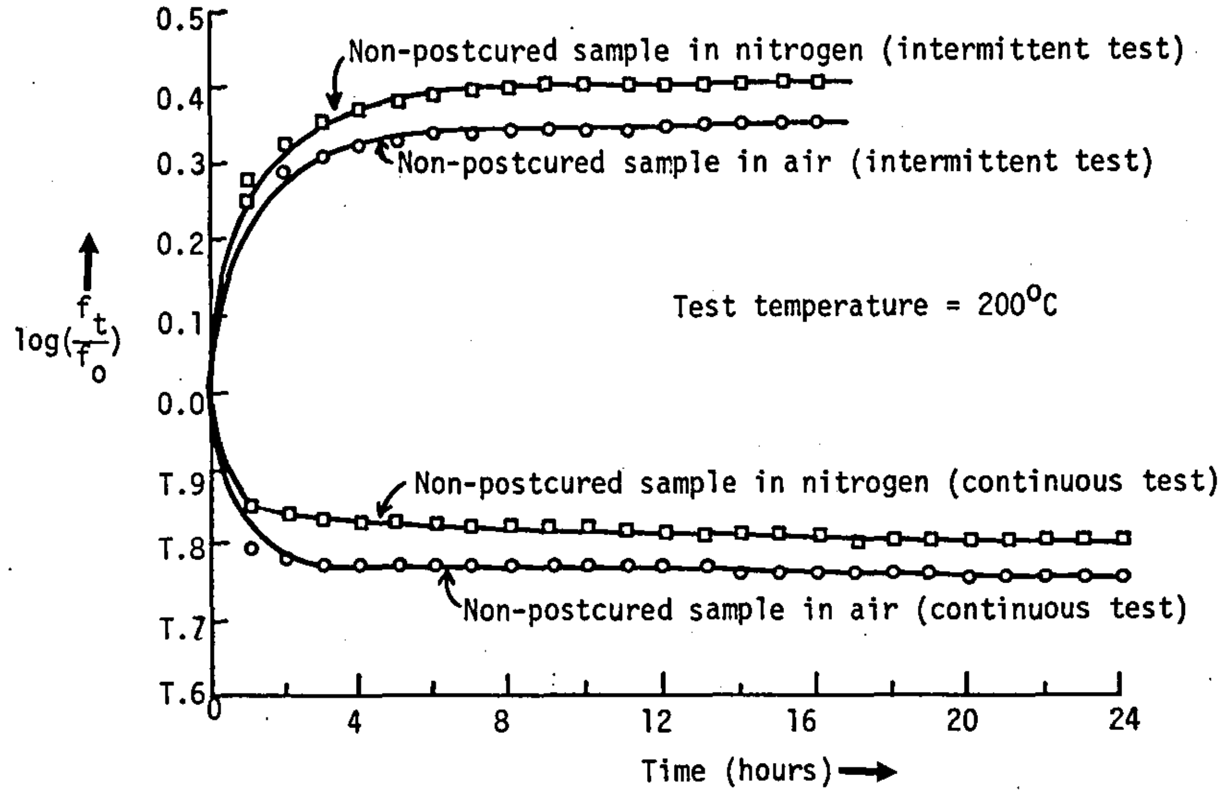


FIGURE 6.9: Stress relaxation measurements of non-postcured, peroxide-cured gum fluoroelastomer

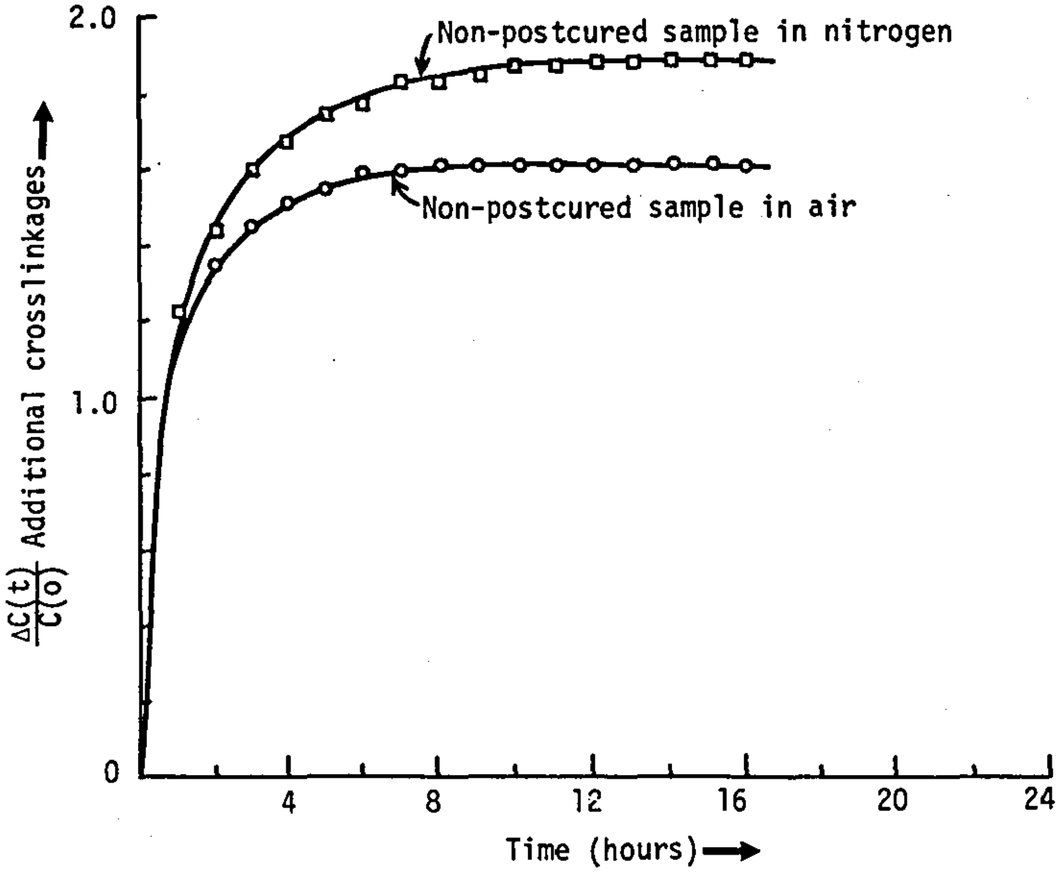


FIGURE 6 10: Additional crosslinkages formed in non-postcured, peroxide-cured gum fluoroelastomer at 200°C

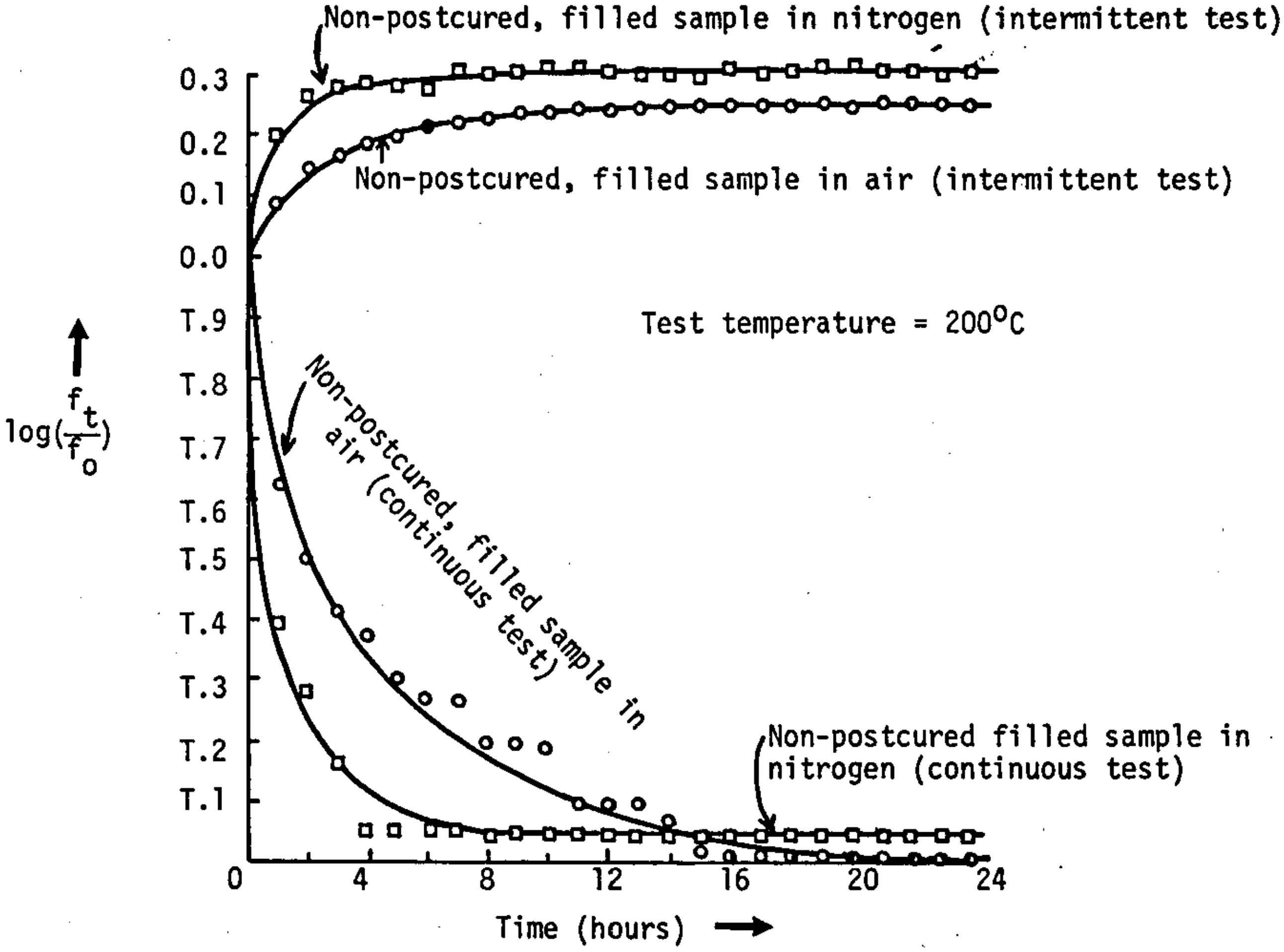


FIGURE 6.11: Stress-relaxation measurements of non-postcured, HBTBP-cured, filled fluoroelastomer

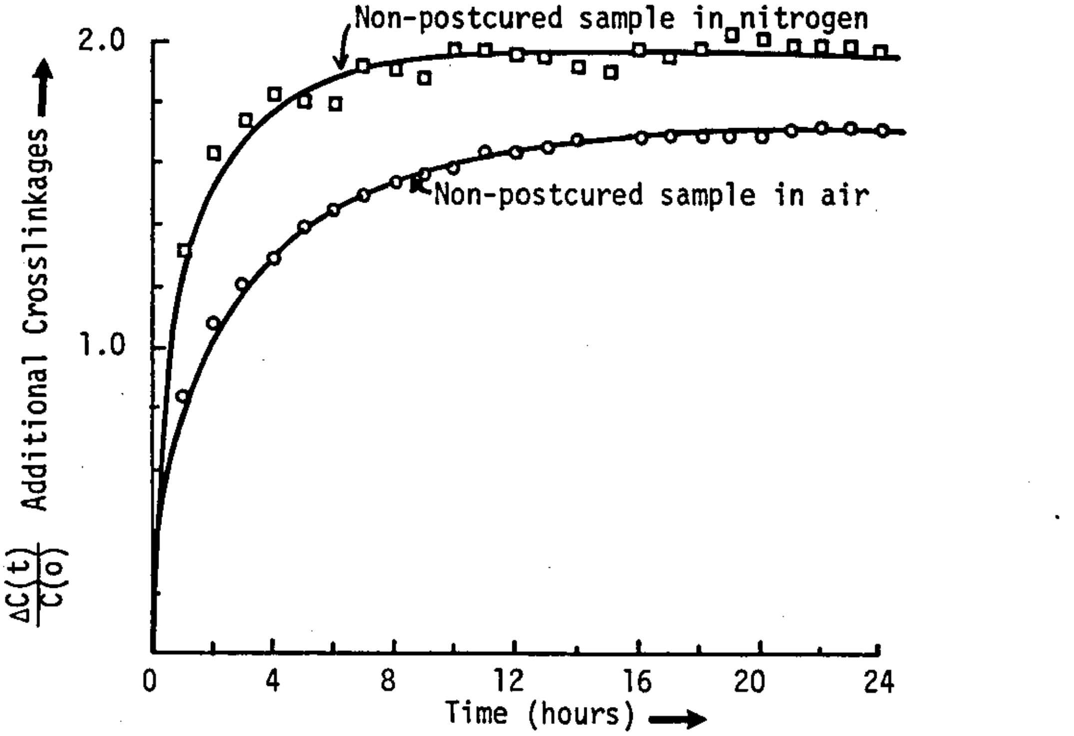


FIGURE 6.12: Additional crosslinkages formed in non-postcured, HBTBP-cured filled fluoroelastomer at 200°C

6.7.3.2 Stress relaxation and heat ageing of postcured Viton GF

The samples used in this series of stress relaxation tests were all both press-cured and then postcured since this represents the most likely state in which they will find service. Hence the stress relaxation measurements can be used to assess heat ageing in this instance.

Continuous and intermittent stress relaxation measurements were obtained for gum HBTBP-cured Viton GF vulcanizates in both air and nitrogen environments. The results obtained are shown in Figure 6.13. It is interesting to note that the continuous stress relaxation plots do not exhibit any sudden relaxation during the initial test period. This is in contrast to the non-postcured samples where possible molecular rearrangements might have led to the greater initial relaxation of stress seen to occur in that instance.

Also, if the plots of continuous stress relaxation are compared with the respective intermittent stress relaxation plots in both air and nitrogen (Figure 6.13), a significant difference between the two is noticed which is a further indication that crosslinks are still being formed during the initial stages of heat ageing. Equation 6.11 was used to estimate the quantities of these additional crosslinks thus formed and the results are shown in Figure 6.14. Thus, it is evident that the process of crosslink formation continues after postcure. The additional crosslinks formed in nitrogen environment is less than that of air. No reasons are advanced for this unusual observation.

Stress relaxation tests were also performed for postcured samples of the filled HBTBP-cured Viton GF vulcanizates. The results of continuous and intermittent stress relaxation measurements obtained in air and in nitrogen are shown in Figure 6.15. Plots in Figure 6.16 show that additional crosslinks are also formed in filled Viton GF vulcanizates when heat-aged. The effect of carbon black on heat-

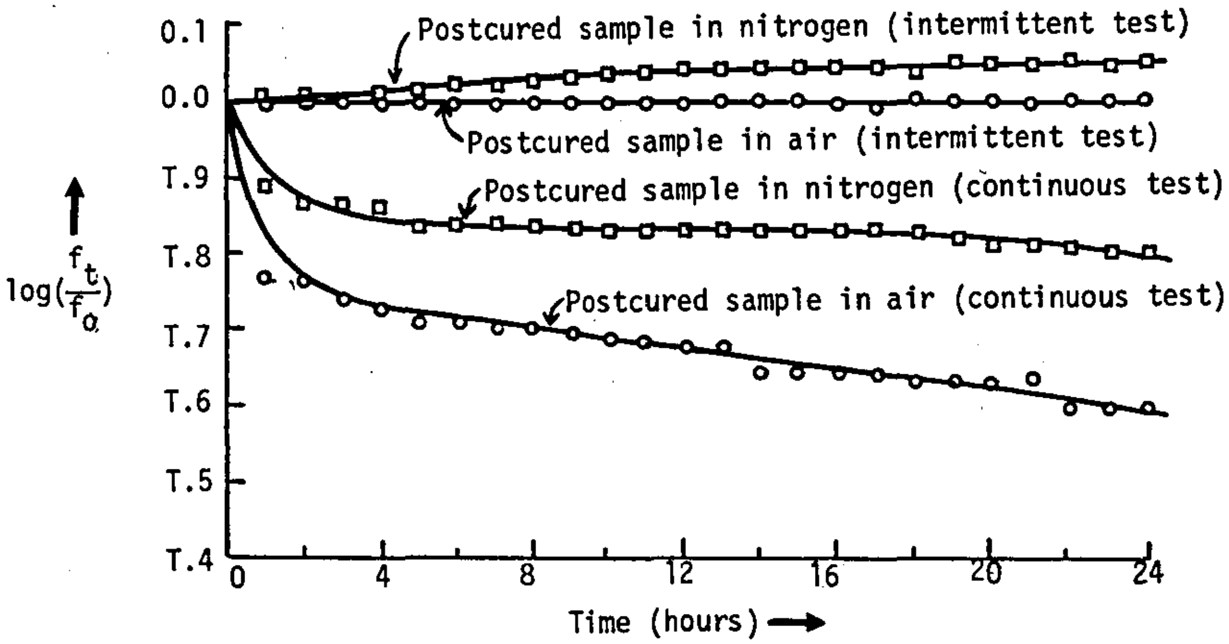


FIGURE 6.13: Stress relaxation measurements of postcured, HBTBP-cured gum fluoroelastomer at 200°C

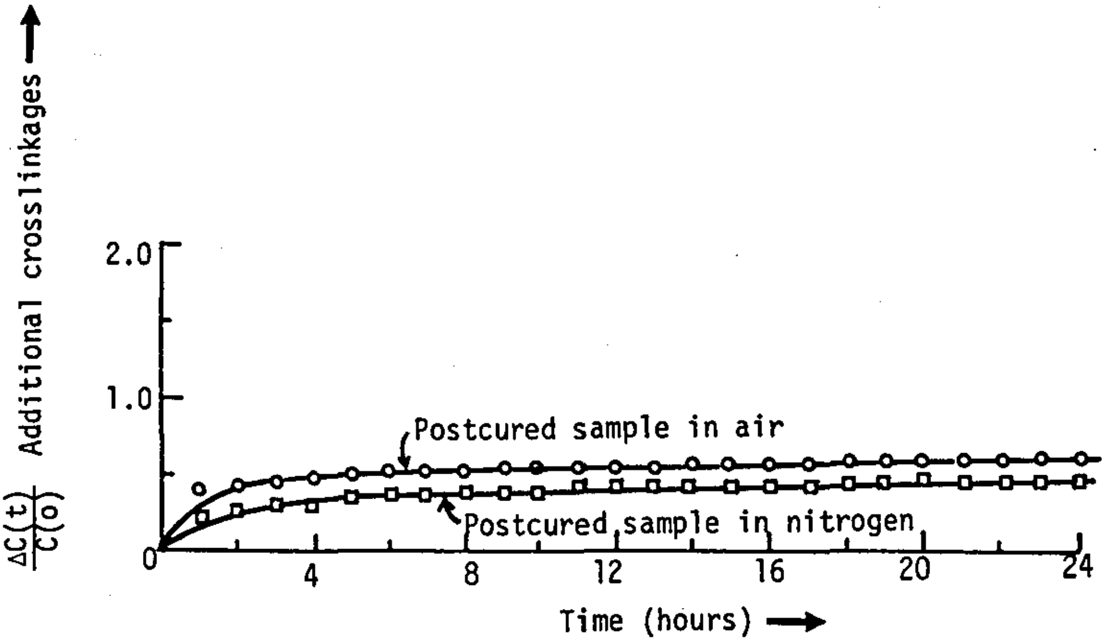


FIGURE 6.14: Additional crosslinkages formed in postcured, HBTBP-cured gum fluoroelastomer at 200°C

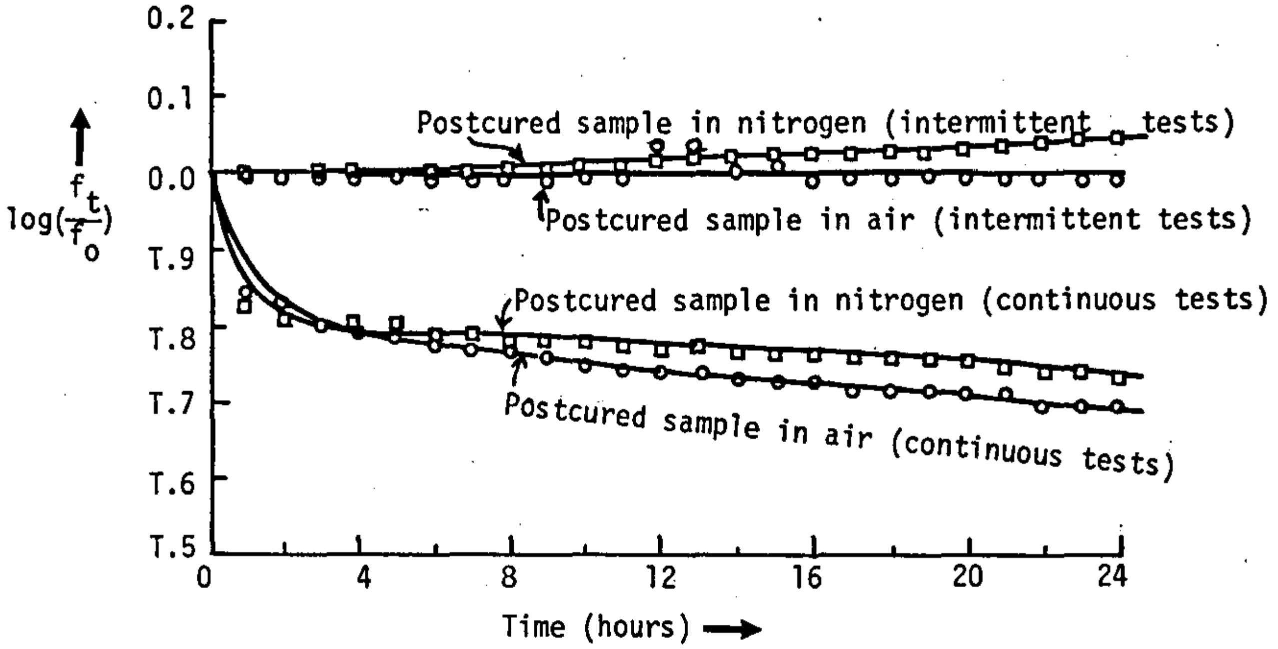


FIGURE 6.15: Stress relaxation measurements of postcured, HBTBP-cured. filled fluoroelastomer at 200°C

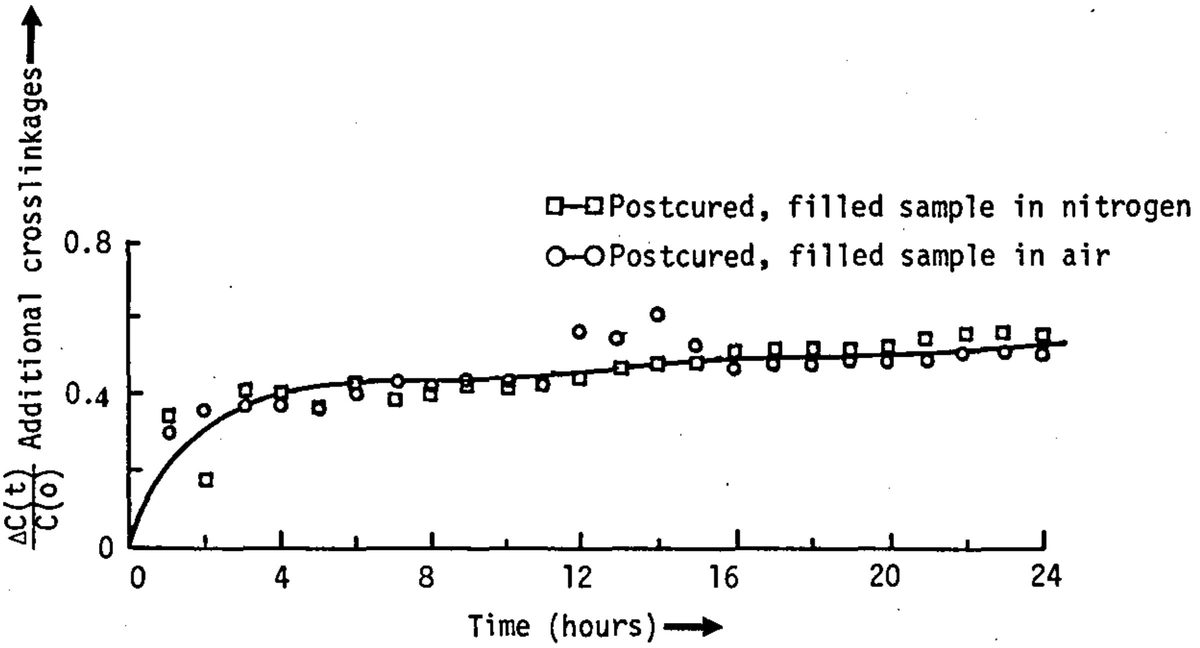


FIGURE 6.16: Additional crosslinkages formed in postcured, HBTBP-cured, filled fluoroelastomer at 200°C

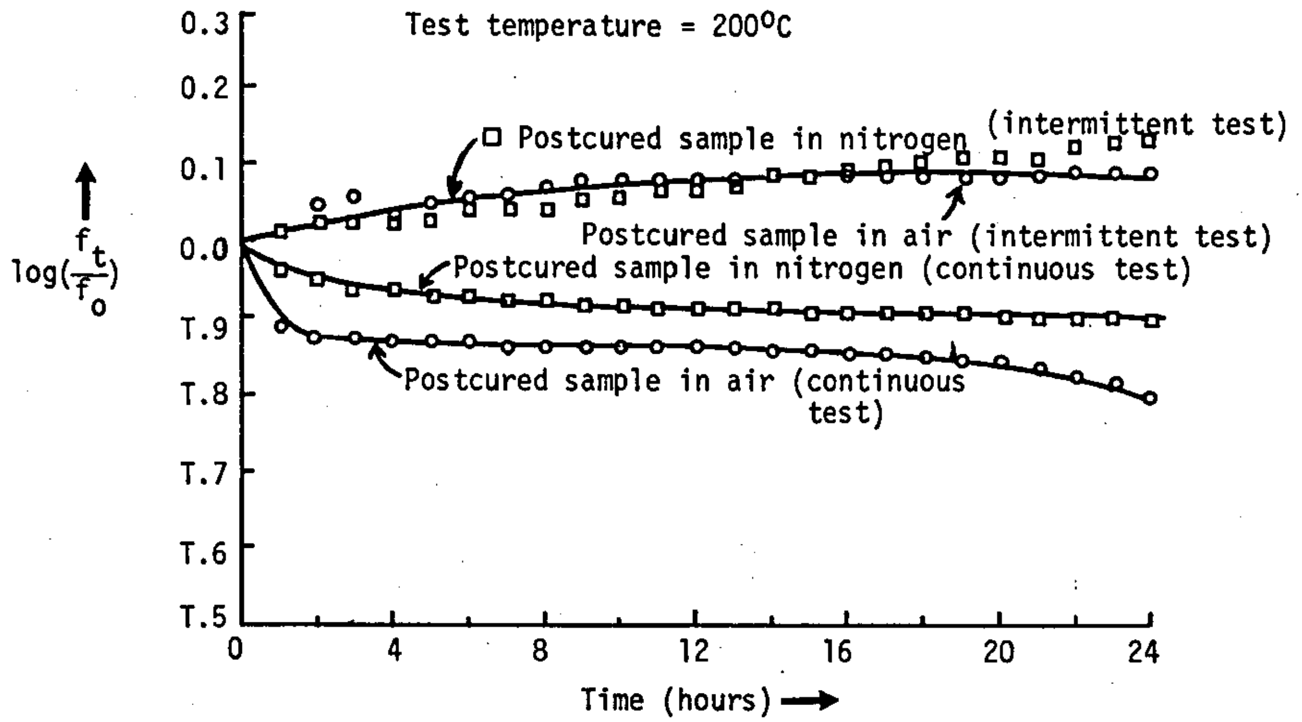


FIGURE 6.17: Stress relaxation measurements of postcured, peroxide-cured gum fluoroelastomer

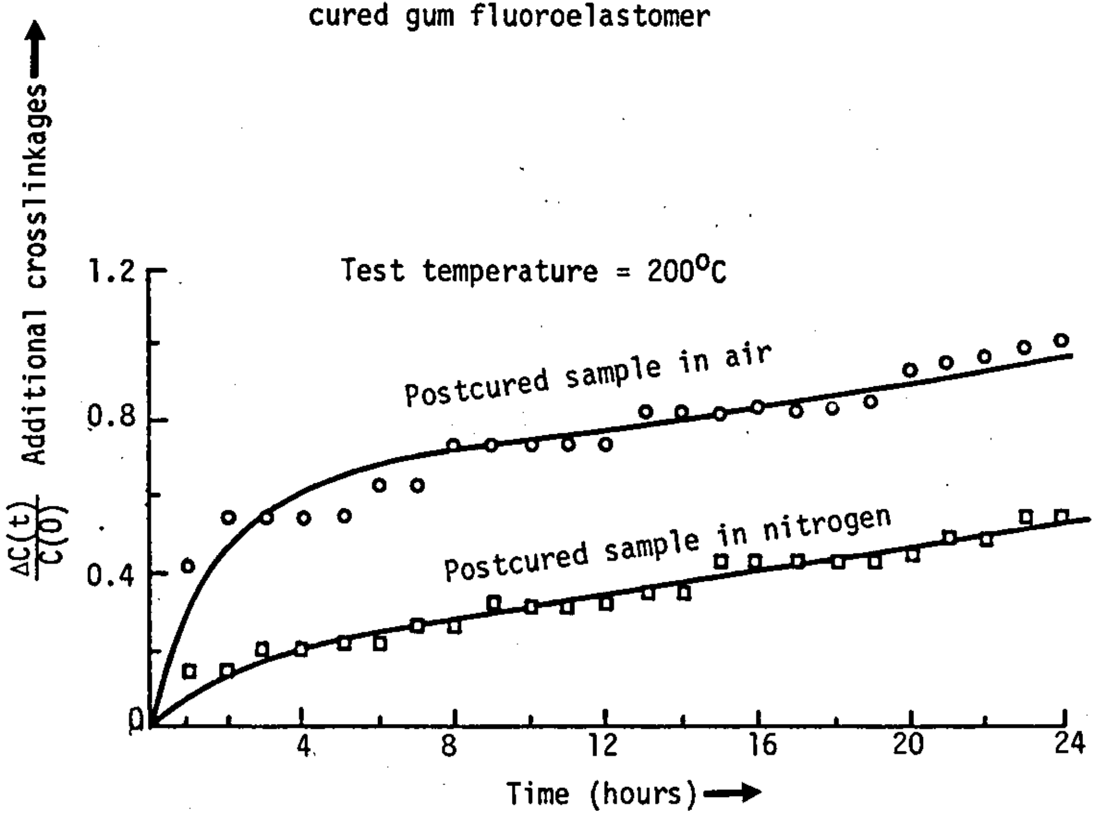


FIGURE 6.18: Additional crosslinkages formed in postcured, peroxide-cured gum fluoroelastomers

ageing is seen to be minimal as the stress-relaxation plots of filled and unfilled vulcanizates are similar.

For purposes of comparison, stress relaxation measurements of postcured, peroxide-cured Viton GF vulcanizates were obtained. The results are expressed in Figures 6.17 and 6.18. It can be observed that postcured, peroxide-cured vulcanizates also form additional crosslinks at the initial stages of heat-ageing (Figure 6.18). However, the relative amount of additional crosslinks formed in the case of gum, peroxide-cured Viton GF vulcanizates is more than that of the analogous gum, HBTBP-cured Viton GF vulcanizates (cf Figures 6.14 and 6.18). The implication of this observation as it relates to permanent set measurements is unclear and no explanation is offered. Also, it would be noticed that more additional crosslinks are formed in air than in nitrogen for postcured, gum, peroxide-cured Viton GF vulcanizate. The reason for this observation is unknown.

Stress relaxation measurements have been used to show that postcured, Viton GF fluoroelastomer vulcanizates, crosslinked with the use of either HBTBP or peroxide, can still form additional crosslinks at the initial stages of heat ageing. It was however found that when Viton GF vulcanizates are exposed to heat in different environments, the additional crosslinks formed, did not follow a particular pattern. Within limits of the experimental conditions used, these Viton GF fluoroelastomer vulcanizates are judged to be thermally stable.

6.8 Conclusion

A variety of methods have been used in an attempt to elucidate the crosslinking mechanism that applies when HBTBP is used to cure Viton GF fluoroelastomer. Based on these findings, crosslink formation is proposed to occur through one or a combination of the following (i) radical abstraction of the methylenic hydrogen in Viton GF, crosslink formation through the interaction of the resulting radicals; also further crosslink formation was proposed to occur through the interaction of a reactive intermediate with the raw Viton GF polymer, (ii) radical abstraction of the pendant bromine group and crosslink formation through interaction of the resulting radicals.

The results of swelling measurements and stress relaxation measurements demonstrate clearly that the formation of additional, stable crosslinks predominate during the postcuring of the Viton GF vulcanizate. Postcured, HBTBP-cured Viton GF vulcanizates are thermally stable though stress relaxation measurements show that additional crosslinks are formed during the early stages of heat ageing.

CHAPTER 7

GENERAL DISCUSSIONS, CONCLUSIONS AND RECOMMENDATIONS

7.1 Discussions

The initial work undertaken concerned the preparation of bisperoxycarbamates based on methylene bis(4-cyclohexylisocyanate) and hexamethylene diisocyanate (Chapter 2). Methods of preparation in both cases involved the reaction of the respective diisocyanates with tertiary butyl hydroperoxide in toluene and in the presence of triethylamine as catalyst. The time to completion of reaction in the preparation of methylene bis-4-cyclohexyl N,N'(tertiary butyl peroxycarbamate) was 48 hours while the reaction time in the preparation of hexamethylene-N,N' bis(tertiary butyl peroxycarbamate) was 8 hours (Table 2.7). Extent of reaction was monitored by observing the disappearance of the isocyanate peak on the infrared spectrum (Figures 2.1 and 2.2). Also, the reaction times quoted above were obtained using tertiary butyl hydroperoxide 'dissolved in toluene' in preference to the extracted aqueous solution formerly used. Although the tertiary butyl hydroperoxide may be extracted from the aqueous solution, its use in this form increases the possibility of side reactions due to unextracted moisture being present. Stannous octanoate was found to be a suitable catalyst for the preparation involving methylene bis(4-cyclohexylisocyanate) but its use was less efficient than triethylamine (Table 2.3) which was a more vigorous catalyst.

The bisperoxycarbamates were characterised by the methods of differential thermal analysis, infrared analysis and elemental analysis (Sections 2.3.3.1, 2.3.3.2 and 2.3.3.3). However, no attempt was made to estimate the shelf life of the bisperoxycarbamates.

The next stage of the work (Chapter 3) involved the general examination of hexamethylene-N,N'bis(tertiary butyl peroxycarbamate) as crosslinking agent in various elastomers; similar studies having been carried out with methylene bis-4-cyclohexyl-N,N'(tertiary butyl peroxycarbamate)(126). Compound formulations containing HBTBP were of the general type shown below:

Elastomer : 100
SRF Black* : 30
CaO : 4
$Ca(OH)_2$: 6
HBTBP : 1∿6

Calcium oxide/calcium hydroxide system was used as an absorber to remove any carbon dioxide that might be evolved during curing. Generally, all HBTBP formulations contained calcium hydroxide in order to avoid porosity due to carbon dioxide evolution. Other formulations were also prepared as 'controls' (Tables 3.1-3.8). Such formulations were based on either the conventional sulphur vulcanization system or peroxide vulcanization. In elastomers that are not cured by either sulphur or peroxide systems, their standard vulcanization systems were obtained from literature(40,88) and used as controls. The cure response of the bisperoxycarbamate formulation wasthen compared with their respective controls (Figures 3.1-3.11) using the Monsanto Oscillating Disk Rheometer. The elastomers investigated were natural rubber, styrene-butadiene rubber, butyl rubber, a natural rubber/polybutadiene rubber blend, polychloroprene rubber, fluorocarbon rubber, nitrile rubber, silicone rubber, epichlorohydrin rubber, chlorosulphonated polyethylene, ethylene-propylene diene monomer, bromobutyl rubber and, the copolymer of polypropylene oxide and allyl glycidyl ether. In all of these elastomers, HBTBP gave some cure response except in butyl rubber, chlorosulphonated polyethylene and ethylene-propylene-diene monomer where little or no cure response was obtained. Also, in the elastomers where HBTBP produced a cure

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* MT Black at 25 phr was used in the fluoroelastomer compounds

response (Figures 3.1-3.11), it was often inferior to the cure response of the respective control formulations. However, it was in epichlorohydrin and a fluorocarbon rubber that the bisperoxycarbamate gave cure traces that were comparable with that of the respective controls (Figures 3.7 and 3.8) and further compounding studies were then restricted to fluorocarbon rubbers (Viton series).

The effect of increasing the bisperoxycarbamate (HBTBP) levels in Viton GF was to produce a corresponding increase in modulus values of the postcured vulcanizates (Table 4.2). However, optimum overall physical properties were obtained at about 2-3 phr of bisperoxycarbamate. Using a peroxide/coagent crosslinking system in Viton GF as control, superior physical properties were obtained with the vulcanizates from the control system (Table 4.2). It was however noted that the HBTBP-cured vulcanizates gave better properties than the Viton GF vulcanizates cured by amine derivatives and dihydroxy aromatic compounds (Table 4.3). Also the HBTBP curing system can be used with the following metal oxides viz: magnesium oxide and calcium oxide (Table 4.5). The use of lead oxide and dibasic lead phosphite in a HBTBP system appears to interfere with cure. However, all the three metal oxides referred to earlier do not interfere with the peroxide/coagent system used as the control for Viton GF curing(159). It is also worth stating that HBTBP can be used together with triallylisocyanurate (a common coagent for Viton GF) although coagents are not necessary for it to cure effectively (Figure 4.4 and Table 4.4).

A general use of HBTBP as a curative was further demonstrated by using it to cure other grades of fluoroelastomers (Viton E60 and Viton B; Figures 4.5 and 4.6). Moderate physical properties were obtained from their respective vulcanizates (Table 4.6) and no attempt was made to optimise the use of HBTBP in Vitons B and E60.

Using the HBTBP curing system and peroxide/coagent curing, a comparative study of the two curing systems in Viton GF were undertaken (Tables 5.3-5.5). The area of study includes heat ageing resistance, compression set resistance and solvent resistance. Vulcanizates from both systems are judged to be thermally stable at 230°C with the HBTBP-cured vulcanizate showing a better retention of properties on exposure to dry heat (Figure 5.5). However, the compression set resistance of the peroxide-cured vulcanizates were superior to the values obtained for HBTBP-cured vulcanizates (Figure 5.6).

Solvent resistance was assessed by means of the percentage volume change and there was no large difference in the solvent resistance of the vulcanizates obtained from the different crosslinking systems (Table 5.4).

It should be noticed however that the use of calcium oxide and calcium hydroxide might have contributed to the excessive swelling of the vulcanizates in water (15% volume increase in vulcanizates from the two systems). It is thought that the use of lead oxide in the compound formulation would give vulcanizates with better resistance to water swelling since lead oxide is less readily soluble in water. The peroxide/coagent system which can be used together with lead oxide offers an advantage over the HBTBP system - where lead oxide interferes with cure.

After a general study of the use of HBTBP as a curative in Viton GF, attempts were made at obtaining information on the possible routes of crosslink formation in HBTBP-cured vulcanizates. The first approach used involved a compounding study which showed that HBTBP alone would cure Viton GF (Figure 6.1). Addition of calcium oxide and calcium hydroxide gave an improvement in the torque values obtained from the Oscillating Disk Rheometer (ODR). It is known that calcium oxide and hydroxide act as absorbers for the water and carbon dioxide evolved during cure. Also, calcium oxide and calcium hydroxide may themselves contribute to crosslink development; this effect could not be assessed by swelling measurements since the vulcanizate containing only Viton GF and HBTBP was porous. Hence the relative crosslink development of Viton GF compounds was assessed by the Monsanto ODR (Figure 6.1).

Compounding studies showed that the structural differences of Viton grades were responsible for the different cure responses of the various Viton fluoroelastomer grades (Figure 6.3).

Similarly the structural differences of two crosslinking agents (HBTBP and MBTBP; Figure 6.2) were suggested to be responsible for their different cure responses in Viton GF.

Using the differential thermal analysis technique, it was indicated that a temperature of about 170^{o}C would be found suitable for the vulcanization of Viton GF/HBTBP compounds. This proved to be correct in practice. Also, the DTA trace of a non-postcured vulcanizate of Viton GF suggested that during cure, low molecular weight products are formed in the vulcanizate and these are volatilized at about 140^{o}C (Figures 6.4a and 6.4b).

Another approach towards understanding the mechanism of HBTBP-cure in Viton GF was to use hot methyl ethyl ketone to extract the Viton GF vulcanizate in order to establish whether the HBTBP was chemically bound to the fluoroelastomer (Viton GF). After the vulcanizates were extracted and dried, they were tested for nitrogen (HBTBP was the only compounding ingredient containing nitrogen) and the tests were positive (Table 6.3a). It was thus concluded that some fragments of the HBTBP curing agent were chemically bound to the vulcanizate network; this was a useful piece of information to have in deducing a mechanism of crosslink formation.

Other extraction tests were carried out on the Viton GF vulcanizate as well as with the raw polymer, with hot water being used as the extracting solvent. The water extracts were found to contain only small traces of halogens, possibly extracted from catalyst residues. (Section 6.3).

Also, the variation of crosslink density (estimated from swelling measurements) with concentration of HBTBP crosslinking agent was obtained. The result of Figure 6.5a gave an estimate of 1.48 crosslinks per molecule of crosslinking agent while a different plot of the same results on Figure 6.5b gave an estimate of 1.84 crosslinks per molecule of crosslinking agent. It is possible however, that the crosslinking efficiency had been overestimated since no correction was made for chain entanglements which may act as physical crosslinks. Crosslink density measurements tend to indicate that simple stoichiometry cannot be written to account for the crosslinking reaction. Also, the relative efficiency of the HBTBP crosslinking agent cannot be assessed since the peroxide/coagent curing system involved a combination of two different ingredients (peroxide and coagent).

Another study was carried out to simulate the postcuring operation and to find out the nature of the volatiles given off. It was found that moisture and possibly traces of hydrogen fluoride and hydrogen chloride were evolved, thus discounting the likelihood of any nitrogen-containing compound being given off during postcuring (Section 6.5).

In addition, the information obtained from literature was used to propose the mechanism of thermally-induced homolytic decomposition of HBTBP (Section 6.6.1).

On collating the available information given earlier, two possible routes of crosslink formation were advanced (Section 6.6.2 Schemes 1 and 2). The first scheme was based on free radical abstraction of the methylenic hydrogen from the elastomer; interaction of the resulting radicals to form carbon-carbon crosslinks; formation of a reactive intermediate (hexamethylene diamine) which reacts further with the polymer to form more crosslinks.

Viton GF gave a better cure response than other Viton grades with HBTBP (Figure 6.3) and a second scheme was proposed on the basis of free radical abstraction of the bromine group in Viton GF and the resulting interaction of the radicals on the side chain to form crosslinks.

The chemical reaction leading to the formation of additional crosslinks is uncertain but it is thought that the Diels-Alder reaction which subsequently leads to aromatization may be responsible.

Stress relaxation measurements at elevated temperature were also used to obtain information about the network changes during postcuring (Section 6.7). For this purpose, non-postcured gum vulcanizate strips were used to obtain stress relaxation measurements in the continuous and in the intermittent modes(Section 6.7.3.1). The results demonstrated that new and stable networks were formed during postcuring. The HBTBP-cured vulcanizate, as well as the peroxide-cured vulcanizates, gave a similar trend of results and the trend of results were little affected by the use of the filled vulcanizate (Figures 6.7-6.12).

Network changes during heat ageing were also examined by obtaining stress relaxation measurements for postcured vulcanizate strips (Section 6.7.3.2; Figures 6.13-6.18). The results indicated that crosslink formation continued after postcuring, although the extent of additional crosslink formation for postcured samples was less than for the non-postcured samples. It is possible that there might have been a degree of network scission in the postcuring and heat ageing tests, however, the net rate of crosslinking obtained in both cases would lead to the conclusion that network formation predominates during postcuring and the initial period of heat ageing.

7.2 Conclusions

While HBTBP may be said to have widespread potential as a crosslinking agent it was in Viton GF that it gave vulcanizates with the best properties which were comparable to the standard commercial vulcanization system used as a control. The mechanism of crosslink formation proposed was on the basis of a free radical process. Also stress relaxation measurements were used to show that the formation of additional crosslinks predominate during postcuring.

7.3 Recommendations

1. A bench-scale study is required to find out the possibility of re-using the mother-liquor (obtained from preparation of cross-linking agent) and thereby improving the economics of preparation.

2. It would be necessary to determine the shelf-life ofthe HBTBP.

3. HBTBP was found to be a suitable crosslinking agent in a number of elastomers. Some of these, notably polychloroprene and epichlorohydrin could be further investigated with a view towards improving the physical properties of their vulcanizates. Also, the use of coagents could be examined in elastomers where HBTBP gave a low cure response.

4. Further compounding studies are also required to optimise the use of HBTBP as crosslinking agent in Viton GF, Viton E60 and Viton B.

5. Only the Viton series of fluoroelastomers were examined in the present study. The examination of HBTBP as crosslinking agent in other fluoroelastomers e.g. Kel-F, Fluorel and Technoflon series would be worthwile.

6. Compression set resistance is quite important in the application of Viton GF, hence further compounding studies are needed to improve the compression set resistance of HBTBP-cured Viton GF.

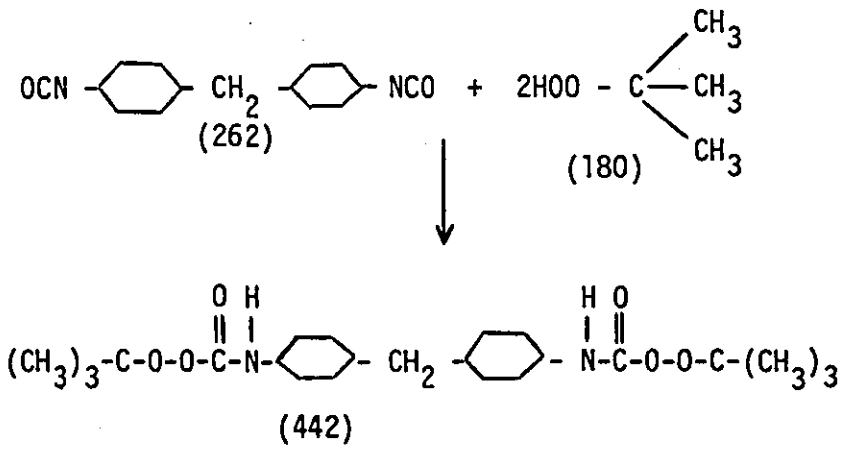
7. Further investigations are required as well to improve the solvent resistance of HBTBP-cured Viton GF. Since lead oxide appeared to interfere with HBTBP cure, polytharge V (dispersion of lead oxide in fluoroelastomer) could be investigated for compatibility with HBTBP curing system.

8. Further stress relaxation measurements are required to determine network changes when vulcanizates are exposed to elevated temperature for a lengthy period. Also, a better understanding of the degradative processes in fluorocarbon rubber is needed.

APPENDIX 1

METHOD FOR CALCULATING THE VALUE OF REACTANTS

For the preparation of methylene bis-4-cyclohexyl N,N'(tertiary butyl peroxycarbamate), the assumed reaction equation is stated below:



Using 20% excess of TBHP to ensure the reaction goes to completion, 1.2 x 180g = 216g of TBHP is required. But TBHP is available at 70% purity (Koch Light Industries Ltd)

∴ Quantity of TBHP required at 70% purity

$$= 216 \times 1/0.7 = 308.6\text{g}$$

i.e. 1 mole of isocyanate ≡ 308.6g of TBHP at 70% purity. Hence 0.2 mole of Desmodur W (52.4g) will require 61.7g of 70% TBHP.

Similarly, 0.2 mole of Desmodur H (33.6g) will require 61.7g of 70% TBHP.

In the case of TBHP dissolved in toluene (Interox Ltd) this is present at 50% purity. Since 1 mole of Desmodur W (262g) required 216g of pure TBHP,

1 mole of Desmodur W will require 432g of TBHP at 50% purity

i.e. 0.2 mole of Desmodur W will require 86.4g TBHP at 50% purity

and 0.2 mole of Desmodur H will require 86.4g TBHP at 50% purity.

APPENDIX 2

METHOD OF QUANTITATIVE INFRARED ANALYSIS

Most quantitative infrared analyses are carried out by comparing directly or indirectly the absorbance of the unknown material at a given wavelength (often the peak of a strong absorption band) with the absorbance of the same material in a standard of known concentration using solution sampling techniques.

Quantitative infrared measurements are based on Beer-Lambert law which relates the intensity of absorption to changes in concentration and sample thickness

i.e.
$$A = kcd = \log_{10} I_o/I \qquad (1)$$

where A = absorbance
k = absorptivity
c = concentration of sample
d = thickness of sample
I_o = intensity of incident radiation
I = intensity of transmitted radiation.

Since the objective is to obtain the concentration of isocyanates, a calibration curve of absorbance versus concentration of isocyanate in toluene is plotted which nearly simulates the contents of the reaction mixture.

In order to eliminate the effect of thickness, an internal reference standard was chosen among the various peaks and a peak at 1500 cm^{-1} corresponding to a C=C bond was found suitable.

Isocyanates have a characteristic absorption peak at 2270 cm^{-1}

$$\therefore \qquad A_{2270} = k_{2270}\, c_{2270}\, d_{2270} \qquad (2)$$

Also

$$A_{1500} = k_{1500}\, c_{1500}\, d_{1500} \qquad (3)$$

However $d_{2270} = d_{1500}$ since the same sodium chloride was used for both peaks.
Dividing (2) by (3)

$$\frac{A_{2270}}{A_{1500}} = \frac{k_{2270}\, c_{2270}}{k_{1500}\, c_{1500}} \qquad (4)$$

since k_{2270}, k_{1500} and c_{1500} are constant during the reaction

$$\frac{A_{2270}}{A_{1500}} \propto c_{2270} \qquad (5)$$

Values of A_{2270} and A_{1500} could be calculated using a transparent ruler calibrated in absorbance units.

Hence, during most of the reactions, the values of A_{2270}/A_{1500} were calculated from the infrared spectra and the concentration plots were interpolated from the calibrated concentration plot (see Figure A2).

In this type of measurement, sources of error could be due to a number of factors viz (a) intermolecular effects such as hydrogen bonding and micelle formation, and (b) instrumentation(141-143).

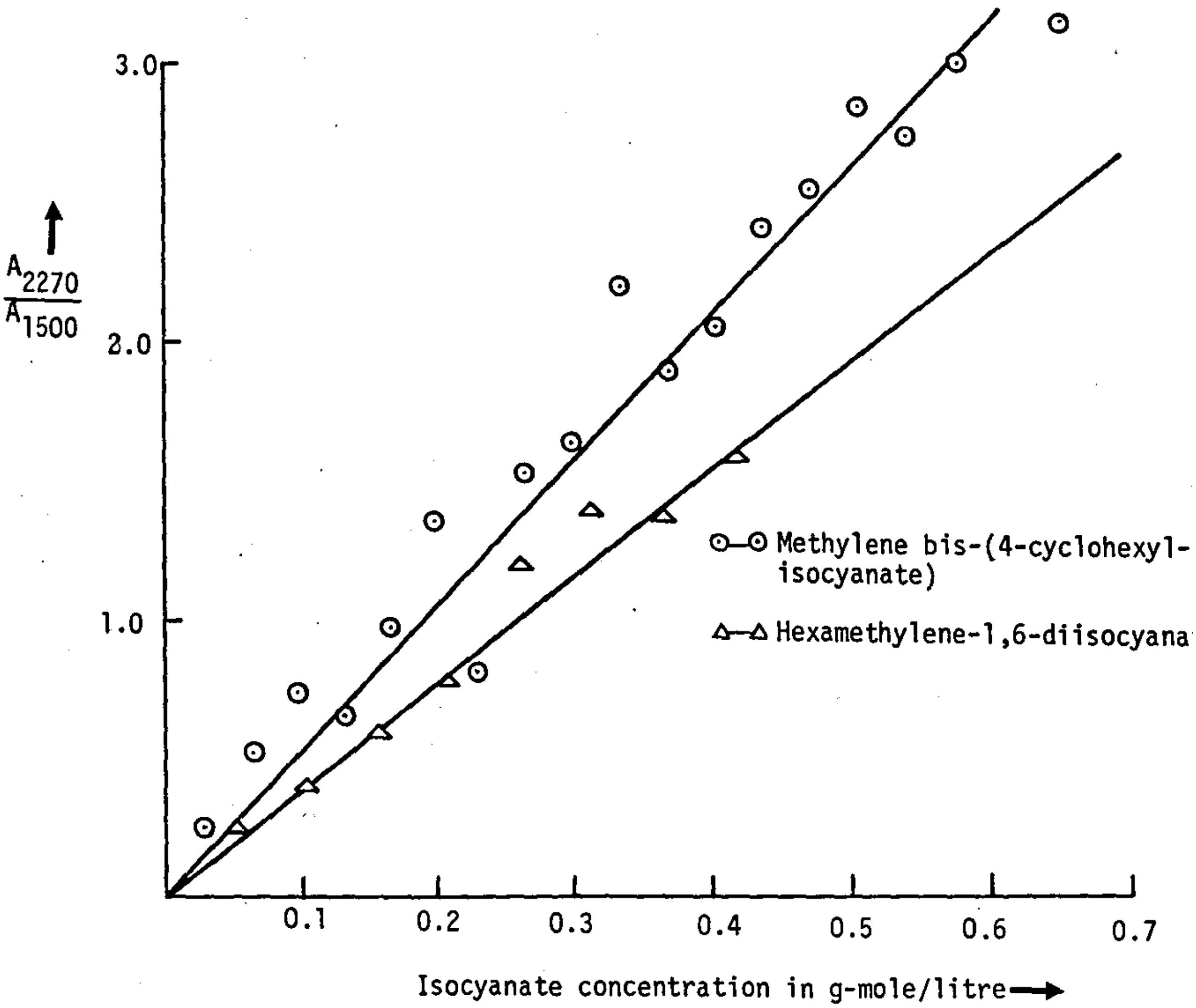


FIGURE A2: Calibration Plots of Diisocyanates

APPENDIX 3

MISCELLANEOUS TEST METHODS AND DESCRIPTIONS

A: Two-roll mill

The two-roll mill consisted of two opposite rotating parallel rollers placed closed to one another with the roll axes lying in a horizontal plane, so that a relatively small space or nip between the cylindrical surface exists. Material reaching the nip is deformed by friction forces between itself and the rollers, and made to flow through the nip in the direction of the roll motion. Cooling of the roll-mills was possible by passing cold water in holes bored inside the mills. This was to prevent excessive heat build-up (due to friction between the rolls) which may cause the rubber compound to scorch.

Usually, the milling operation was started by forming a band of rubber on the mill around the front roll with a full flow of cold water. Powders, fillers etc. were added onto the nip and any which fell into the tray underneath the rollers was returned to the nip until they were absorbed by the rubber. (Scorch producing agents may be held until later).

B: Mooney Viscometer

The Mooney Viscometer consisted of a motor-driven disc device for measuring the effect of temperature and time on the viscosity of rubber mixes. The rubber under test was placed in a shallow cavity containing the rotating disc and embedded under positive pressure. The surfaces of the dies and the disc are grooved to prevent slippage. The torque required to rotate the disc at a speed of about 2 rpm was recorded on a linear scale graduated in Mooney units. A sketch of Mooney chamber and rotor is shown in Figure A3.1.

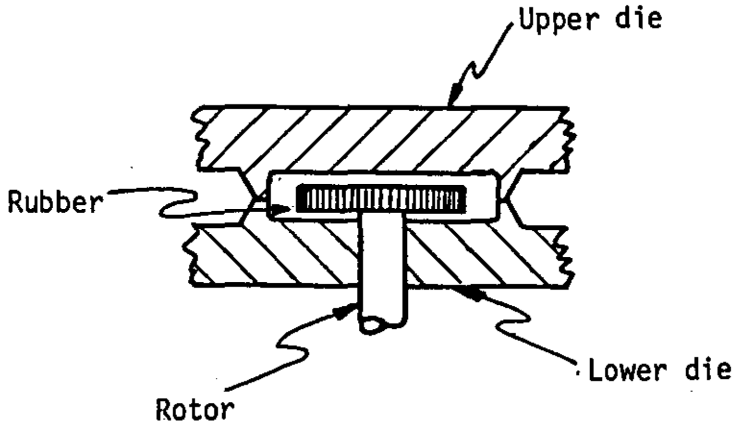


FIGURE A3.1: Mooney Chamber and Rotor

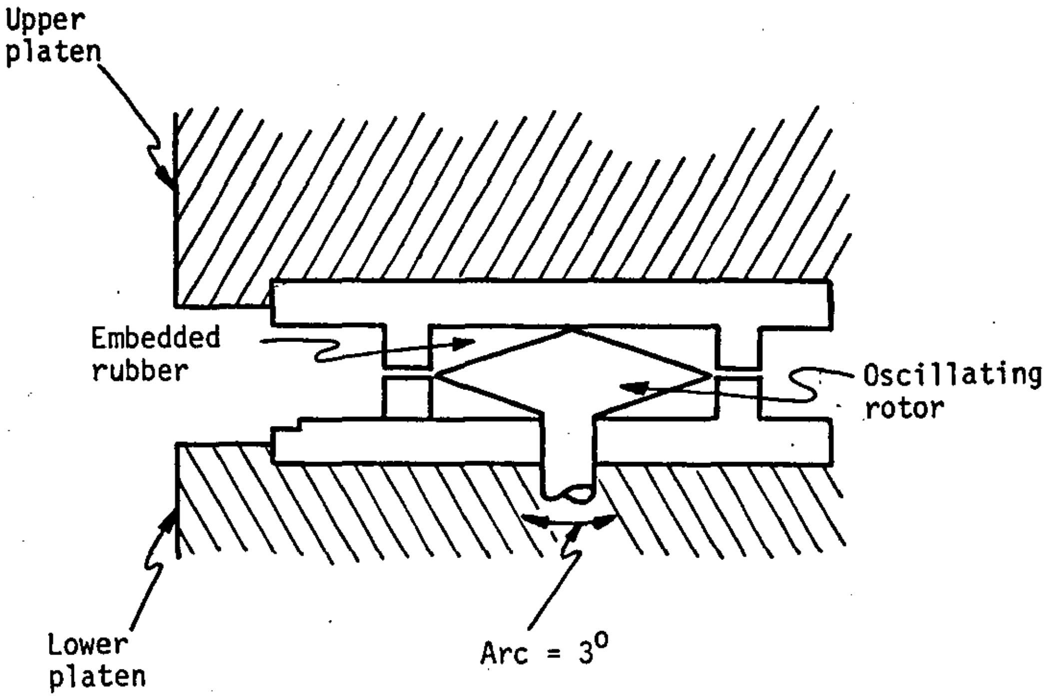


FIGURE A3.2: Basic Principle of the Monsanto Oscillating Disk Rheometer

M_L - Minimum torque

M_{HM} - Maximum torque at specified time of marching modulus curve

M_{HP} - Maximum torque of plateau curve

M_{HR} - Maximum torque of reversion curve

T_2 - Scorch time taken as time to 2 dN-m rise above M_L (3^o arc)

T_{95} - Time to 95% of maximum torque (usually taken as optimum cure time

MMC - Marching Modulus Curve

PC - Plateau Curve

RC - Reversion Curve

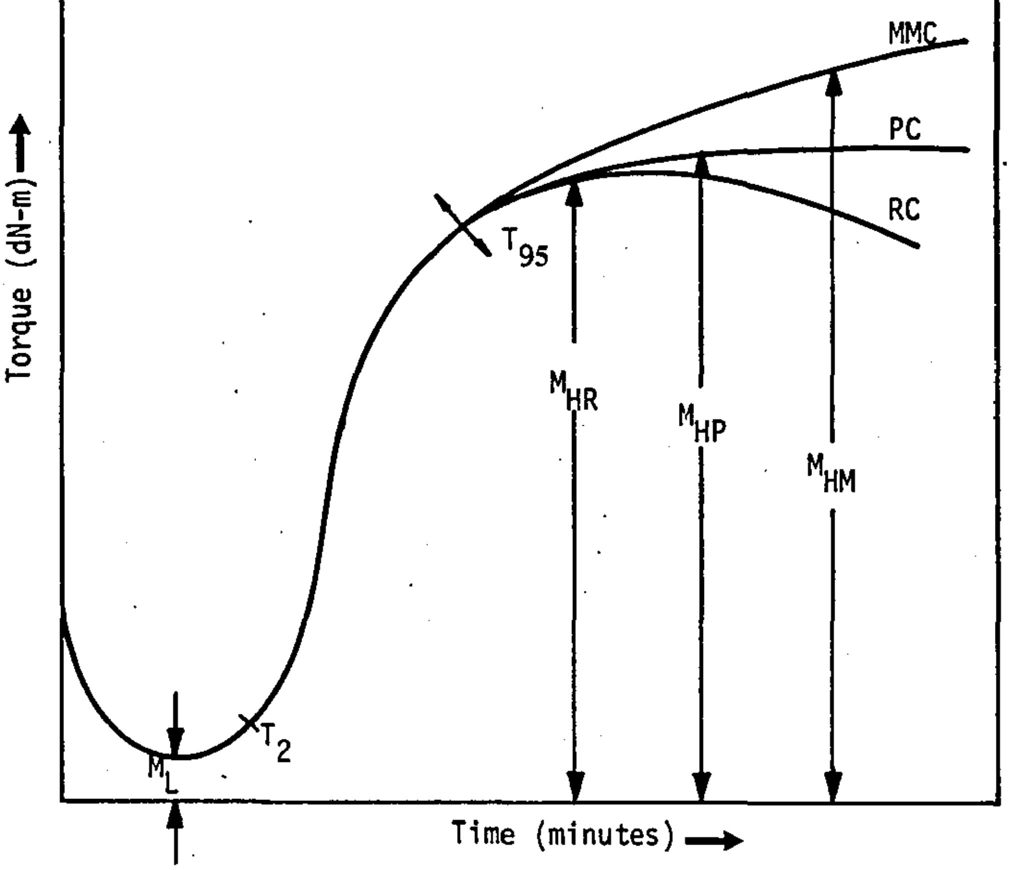


FIGURE A3.3: Types of Monsanto ODR Traces of Rubber Compounds

C: Monsanto Oscillating Disk Rheometer (ODR)

The ODR consisted of a biconical disk which is secured to a drive shaft and rotationally oscillated about the shaft axis through a small arc. The compounded rubber, having been stored for about twenty-four hours was re-milled and a test sample placed in a sealed test cavity under positive pressure, and maintained at an elevated test temperature (stated for different compounds with the formulation).

The sinusoidal oscillation of the biconical disk at constant amplitude exerts a shear strain on the mix and the variation of torque with time was recorded autographically on a chart paper. The diagrams in Figures A3.2 and A3.3 explain the principle and a typical chart obtainable from an Oscillating Disk Rheometer.

D: Moulding

Vulcanized rubber sheets of 2 ± 0.2 mm thickness were prepared using a mould of 93 cm^3 cavity volume and the procedure of BS 1674:1976. Some of the compounds containing HBTBP were vulcanized longer than their respective optimum cure times to ensure enough time for absorption of carbon dioxide evolved during cure by the calcium oxide/ calcium hydroxide system. Other compounds were cured at their respective optimum cure times. A steam-heated platen press was used and compression moulding techniques were employed. Afterwards, vulcanized sheets were stored in polythene bags for at least 24 hours prior to physical testing.

E: Stress-Strain Tests

These are widely used in the rubber industry as a general guide to the quality of a rubber, being sensitive to filler or plasticizer content as well as to mixing and curing efficiency.

The tensile properties of the vulcanizates were determined using a J J Tensile Testing Machine (J J Lloyd Instruments Ltd Model T5002) in conjunction with an X-Y plotter PL100. Three specimens were tested for each vulcanizate sample and speed of testing was at 500 mm/min.

Specimen preparation was made by stamping dumb-bell shapes from the prepared sheets. (Type 2 specified in BS 903 Part A2). Ring test pieces were not used because they give lower values of tensile strength than dumb-bells, the latter being nearer to the true tensile strength of the rubber. Dumb-bell shapes are also preferred because of easy preparation, breakage in a predetermined area and means for following the elongation; the chief disadvantage being slippage at clamp separation. With rings there are no gripping problems but the strain distribution in the ring is not uniform. Tensile strength could be obtained by dividing the force at break by the area of the unstrained cross-section of the test piece. Perhaps it is worth mentioning that reproducibility of tensile strength measurements may be less than satisfactory. This is probably due to the impossibility of making a perfect test sample. Flaws which introduce error into the tensile strength measurements are always present in specimens used in a tensile test. These flaws may be due to foreign inclusions, density fluctuations, variation in filler concentration or even statistical errors during sample preparation. A blunt or a rough-edged cutter may also introduce flaws in test specimens.

Elongation-at-break was expressed as percentage elongation, i.e. the increase in length as a percentage of original gauge length. Modulus was determined at either 100% or 300% tensile strain during the uninterrupted stretching of the test piece. Values used in calculating the modulus values above were evaluated from a recorded stress-strain curve.

F: Tear Strength

This test measures the force required to propagate a nick already produced in the test piece by applying force in a direction normal to the plane of the nick. A crescent test piece was used and the procedures adopted were as specified in BS 903 Part A3. A stretching rate of 500 mm/min was used and tear strength calculated as:

$$\text{Tear Strength} = \frac{\text{Maximum force recorded}}{\text{Thickness of test piece}}$$

G: Rebound Resilience

Resilience may be defined as the ability of a rubber vulcanizate to return the energy used to deform it. It is also the proportion of the applied energy usefully returned after an impact and tests could be used to assess the elastic behaviour of elastomers in the range of 30-85 IRHD in the case of shock stressing. The test was performed according to DIN 53512. A pendulum was dropped on the vulcanized rubber test piece (about 12 mm thick) to condition the test specimen. Afterwards, the pendulum was dropped again on the test piece and the percentage resilience read off the scale. The tests were performed three times and the median reading taken.

H: Hardness Tests

Hardness measurement is a way of obtaining a measure of the elastic modulus of a rubber by determining its resistance to a rigid indentor to which is applied a force. Generally, hardness measurements are better adapted to rapid quality control checks on finished products than to accurate laboratory investigation of vulcanization efficiency or ageing performance. Also hardness changes are less discriminating than a correctly chosen tensile property as a means of following vulcanization efficiency. However, the method is simple, cheap, rapid and non-destructive; hence its value in industrial quality control specifications. In this work, measurement was obtained using a Wallace Hardness Tester calibrated in International Rubber Hardness degrees.

I: Compression Set Tests

Set measurements are simple quality control tests and are sensitive to state of cure. Also, it could be used as a measure of crosslink stability in a vulcanizate.

For each rubber compound, three specimens of about 12.50 mm thick* were moulded, and curing for these specimens was extended by about four minutes more than ordinary tensile sheets in order to ensure the complete curing of the specimens.

Having stored the moulded specimens for at least 24 hours, they were compressed to 25% strain on very smooth platens at room temperature and then held at the test temperature (70°C or any other specified temperature) for a specified period of time (usually 22 hours, 24 hours, 48 hours or 70 hours). After the specified time, the compressive strain was released and the specimens were allowed to recover at room temperature (24°C) for 30 minutes and the recovered thickness obtained.

Set was expressed as a percentage of the applied deformation

i.e.
$$\frac{t_o - t_r}{t_o - t_s} \times 100\%$$

where t_o = initial thickness
t_s = compressed thickness
t_r = recovered thickness.

For each rubber compound, set was calculated for each of the three test specimens and the average taken. Further relevant details about set measurements can be found in ASTM D395 or BS 903 Part A6, 1969.

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* Specimens of fluoroelastomers were 6.3 mm thick.

APPENDIX 4

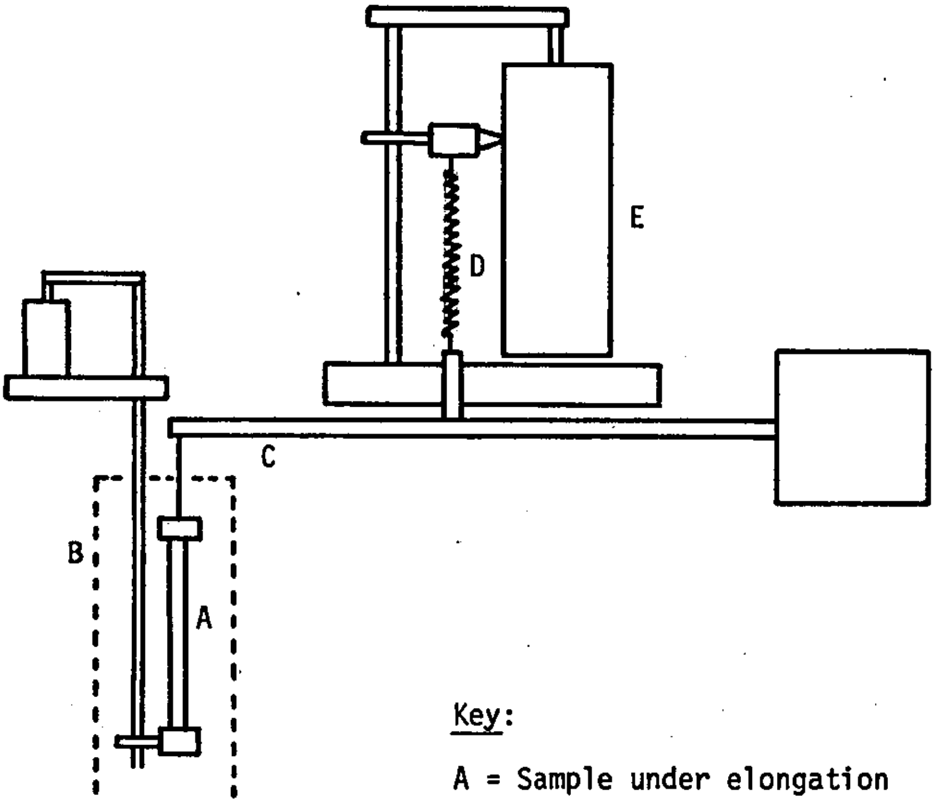
DESCRIPTION OF STRESS RELAXATION UNIT

Stress relaxation measurements were obtained by using the Wallace Extension Stress Relaxometer. It consisted of thermostatically-controlled cast aluminium block heating unit with cells that can be equipped with stress relaxation units. The equipment is capable of operating in the continuous as well as in the intermittent mode and has a maximum operating temperature of about $200^{\circ}\sim 230^{\circ}$C. A sketch of the basic features of the equipment is shown in Figure A4.1 and the illustration of the equipment in Figure A4.2. Vulcanizate strips (4.00 mm wide and 0.6 mm thick) A was held to one end of the cantilever beam C. The beam is pivoted at the other extreme and 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. As the specimen relaxes, the change in stress is automatically compensated for by a change in the extension of the spring. Attached to the spring is a pencil lead which is in contact with chart paper mounted on a drum E. This drum is rotated by a small synchronous electric motor to provide a time base of one revolution in 12 hours. Hence stress relaxation measurements can be obtained. A small pump (not shown) supplies a constant air-flow rate through a duct and this can be connected to a nitrogen cylinder if the need to use the gas arises.

In the continuous extension, the specimen was held continuously at a fixed extension and the pencil gave a continuous trace of relaxation on the chart vertical axis. However, the intermittent extension was controlled pneumatically with a timer so that the specimen was extended for a period of 15 seconds during each 30 minute period (specimen extends for 15 seconds and relaxes 29 minutes, 45 seconds). The chart pencil in the intermittent extension moves on the vertical axis during the 15 second period only.

Vulcanizates were used at 30% extension and a test temperature of 200°C was used while stress relaxation measurements were obtained through a 24 hour period.

Block diagram of stress-relaxation apparatus



Key:

A = Sample under elongation

B = Thermostated cast aluminium block heating unit

C = Cantilever beam

D = Compensating spring

E = Rotating drum chart

FIGURE A4.1

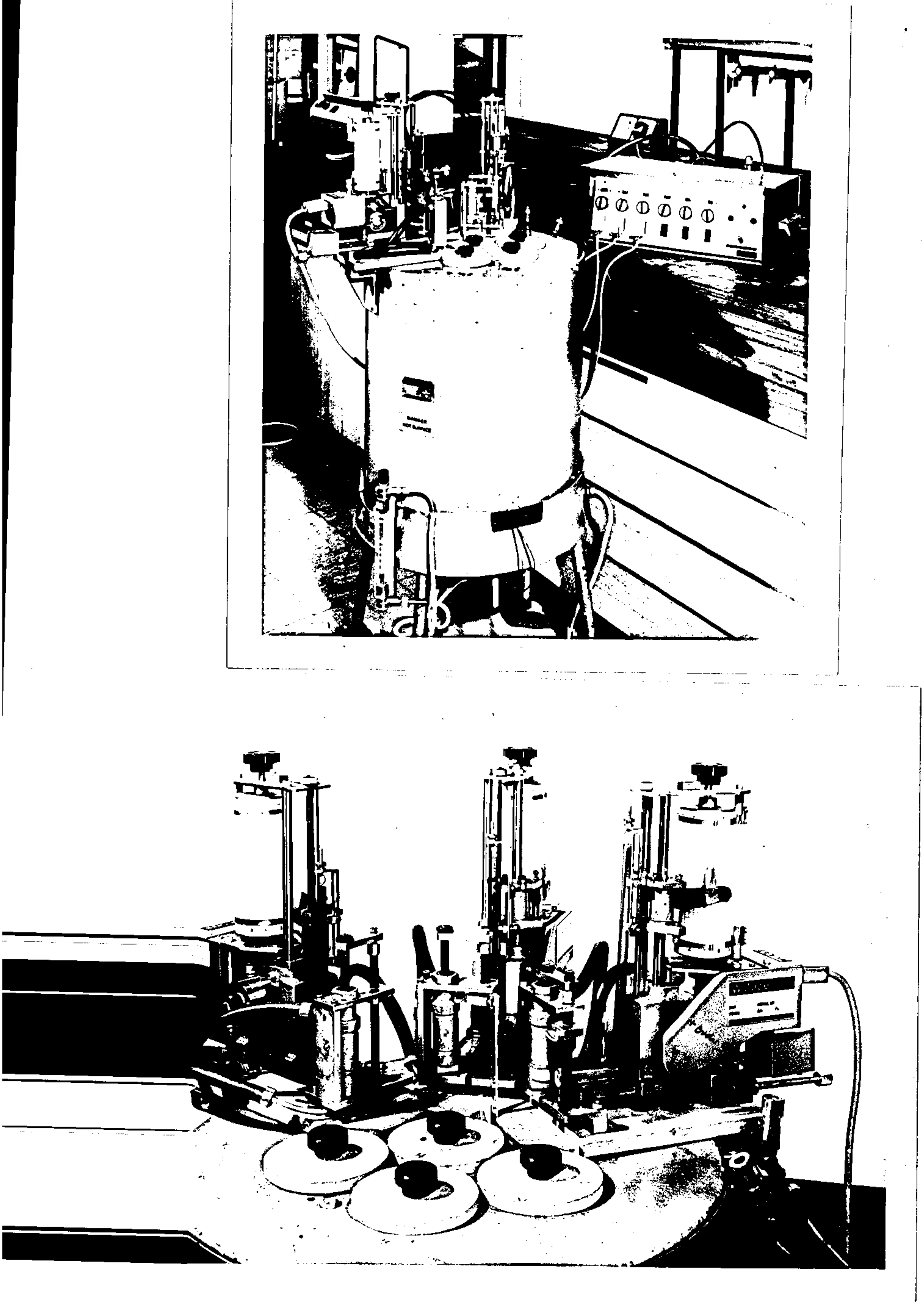


FIGURE A4.2: Views of the Stress-Relaxation Equipment

REFERENCES

1. Porrit, B.D. and Rogers, H.
"A note on the discovery of ebonite". India Rubber J. 1924, 68, 274.

2. Memmler, K. (ed).
"The science of rubber". English translation by Dunbrook, R.F. and Morris, V.N. (eds). Reinhold Publishing Corporation, New York, 1934.

3. Stern, H.J.
"Rubber: natural and synthetic" (2nd ed). Maclaren and Sons Ltd., London, 1967.

4. Stern, H.J.
"William Brockedon and the discovery of vulcanization". India Rubber J., 1945, 108, 645.

5. US Patent 3633.

6. British Patent 11 146.

7. ASTMD 1566-83a.

8. Coran, A.Y.
'Vulcanization" in: Science and Technology of Rubber (ed) Eirich F.R. Academic Press, New York, 1978.

9. Cox, W.L. and Parks, C.R.
"Effect of curing systems on fatigue of natural rubber vulcanizates". Rubber Chem. Technol., 1966, 39, 785.

10. Studebaker, M.L.
"Effect of curing systems on selected physical properties of natural rubber vulcanizates". Rubber Chem. Technol. 1966, 39 1359.

11. Kuvshinskii, E.V. and Sidorovich, E.A.
"Effect of vulcanization on the dynamic properties of rubber". Rubber Chem. Technol., 1959, 32, 662.

12. Farmer, E.H. and Shipley, F.W.
"Modern views on the chemistry of vulcanization changes. I. Nature of the reaction between sulphur and olefins". J. Polym. Sci., 1946, 1, 293.

13. Farmer, E.H. and Shipley, F.W.
"The reaction of sulphur and sulphur compounds with olefinic substances. Part I. The reaction of sulphur with mono-olefins and with $\Delta^{1:5}$ *diolefins".* J. Chem. Soc. 1947, p. 1519.

14. Bateman, L. (ed).
"Chemistry and physics of rubber-like substances". Maclaren and Sons Ltd., London, 1963.

15. Bateman, L., Moore, C.G. and Porter, M.
"The reaction of sulphur and sulphur compounds with olefinic substances. Part XI. The mechanism of interaction of sulphur with mono-olefins and 1:5 dienes". J. Chem. Soc., 1958, p.2866.

16. Ross, G.W.
"The reaction of sulphur and sulphur compounds with olefinic substances. Part X. The kinetics of the reaction of sulphur with cyclohexene and other olefins". J. Chem. Soc., 1958, p. 2856.

17. Bateman, L., Glazebrook, R.W. and Moore, C.G.
"The reaction of sulphur and sulphur compounds with olefinic substances. Part IX. The reaction of sulphur with 2:6-dimethylocta-2:6-diene". J. Chem. Soc., 1958, p.2846.

18. Bateman, L., Glazebrook, R.W., Moore, C.G., Porter, M., Ross, G.W. and Saville, R.W.
"The reaction of sulphur and sulphur compounds with olefinic substances. Part VIII. The reaction of sulphur with mono-olefins". J. Chem. Soc., 1958, 2838.

19. Naylor, R.F.
"Modern views on the chemistry of vulcanization changes. II. Role of hydrogen sulphide". J. Polym. Sci., 1946, 1, 305.

20. Selker, M.L.
"Sulphur linkage in vulcanized rubber—reaction of methyl iodide with sulphur compounds". Ind. Eng. Chem., 1948, 40, 1467.

21. Selker, M.L. and Kemp, A.R.
"Sulphur linkage in vulcanized rubber - acetone extraction of vulcanizates". Ind, Eng. Chem., 1948, 40, 1470.

22. Brydson, J.A.
"Rubber chemistry". Applied Science Publishers Ltd., London, 1978.

23. Van Valkenburgh, E.A.
"Organic accelerators". Rubber World 1937, 96, 51.

24. Neal, A.M.
"Aims of present day accelerator research". Rubber Age 1940, 46, 289.

25. Skinner, T.D. and Watson, A.A.
"EV systems for NR - Part I". Rubber Age 1967, 99, 76.

26. Russell, R.M., Skinner, T.D. and Watson, A.A.
"EV systems for NR - Part 2". Rubber Age 1967, 99, 69.

27. Coran, A.Y.
"The art of sulphur vulcanization". Chemtech 1983, p.106.

28. Hertz, D.L.
"Theory and practice of vulcanization". Elastomerics 1984, 116, 17.

29. Porter, M.
"The chemistry of the sulphur vulcanization of natural rubber" in: The Chemistry of Sulphides (ed) Tobolsky, A.V. Interscience New York 1968.

30. McColm, E.M. and Haefele, J.W.
"Variability of crude rubber - effect of latex nonrubber substances on vulcanization and ageing characteristics of crude rubber". Ind. Eng. Chem., 1948, 40, 311.

31. Horne, S.E., Kiehl, J.P., Shipman, J.J., Folt, V.L., Gibbs, C.F., Wilson, E.A., Newton, E.B. and Reinhart, M.A.
"Ameripol SN - a cis-1,4-polyisoprene". Ind. Eng. Chem . 1956, 48, 784.

32. Dogadkin, B.A., Feldshtein, M.S., Belyaeva, E.N.
"The action of binary accelerator systems of vulcanization". Rubber Chem. Technol. 1960, 33, 373.

33. Dogadkin, B.A., Belyatskaya, O.N., Dobromyslova, A.V. and Feldstein, M.S.
"Vulcanization of rubber in the presence of N,N-diethyl-2-benzothiazolylsulphenamide as accelerator". Rubber Chem. Technol. 1960, 33, 361.

34. Bevilacqua, E.M.
"Vulcanization with TMTD". Rubber Chem. Technol. 1959, 32, 721.

35. Dogadkin, B.A. and Shershnev, N.A.
"The interaction of tetramethylthiuram disulphide with rubber and with compounds containing a labile hydrogen atom". Rubber Chem. Technol. 1960, 33, 401.

36. Krebs, H.
"The mechanism of accelerator action". Rubber Chem. Technol. 1957, 30, 962.

37. Shelton, J.R. and McDonel, E.T.
"Investigation of radical and polar mechanisms in vulcanization reactions". Rubber Chem. Technol. 1960, 33, 342.

38. Sibley, R.L.
"Organic sulphides as vulcanizing agents of rubber". Rubber Chem. Technol. 1951, 24, 211.

39. Throdahl, M.C. and Harman, M.W.
"Vulcanization characteristics of N,N'-dithioamines in furnace black stocks". Ind. Eng. Chem. 1951, 43, 421.

40. Alliger, G. and Sjothun, I.J. (eds).
"Vulcanization of elastomers". Chapman and Hall, London, 1964.

41. Craig, D., Juve, A.E. and Davidson, W.L.
Tetramethylthiuram disulphide vulcanization of extracted rubber I. Introduction and compounding". J. Polym. Sci., 1950, 5, 709.

42. Scheele, W., Graseman, H., Mau, G. and Stange, P.
"Vulcanization of elastomers. 19. The function of oxides in thiuram vulcanization". Rubber Chem. Technol. 1959, 32, 150.

43. Fletcher, W.P. and Fogg, S.G.
"Natural rubber compounds for high temperature service". Rubber Age 1959, 84, 632.

44. Moore, C.G.
"The nature of the crosslinks in tetramethylthiuram disulphide - zinc oxide-natural rubber vulcanizates". J. Polym. Sci. 1958, 32, 503.

45. Gee, G.
"Tensile strengths of pure gum natural rubber compounds".
J. Polym. Sci. 1947, 2, 451.

46. Scheele, W. and Hummel, K.
"Vulcanization of elastomers. 21. Vulcanization of natural rubber with thiuram disulphides. VI". Rubber Chem. Technol. 1959, 32, 566.

47. Scheele, W., Lorenz, O. and Dummer, W.
"Studies of the vulcanization of high elastic polymers. 1. The vulcanization of natural rubber with thiuram disulphides".
Rubber Chem. Technol. 1956, 29, 1.

48. Scheele, W., Lorenz, O. and Dummer, W.
"Vulcanization of natural rubber with thiuram disulphides Part 2".
Rubber Chem. Technol. 1956, 29, 15.

49. Scheele, W. and Stange, P.
"The vulcanization of elastomers. VII. The vulcanization of natural rubber with thiuram disulphides. Part IV". Rubber Chem. Technol. 1957, 30, 69.

50. Scheele, W. and Toussaint, H.E.
"Studies of the vulcanization of elastomers. VIII. The vulcanization of synthetic rubbers with thiuram disulphides (1)". Rubber Chem. Technol. 1957, 30, 77.

51. Scheele, W., Grasemann, H. and Mau, G.
"The vulcanization of elastomers. 17. The role of the oxide in vulcanization with thiuram compounds. II". Rubber Chem. Technol. 1958, 31, 315.

52. Scheele, W., Lorenz, O. and Dummer, W.
"Vulcanization of natural rubber with thiuram disulphides Part 3". Rubber Chem. Technol. 1956, 29, 29.

53. Lorenz, O., Scheele, W. and Redetzky, W.
"The vulcanization of elastomers. X. The vulcanization of natural rubber with thiuram disulphides". Rubber Chem, Technol. 1957, 30, 903.

54. Scheele, W., Toussaint, H.E. and Stange, P.
"Vulcanization of elastomers. 14. Role of the oxide in vulcanization with compounds of the thiuram series. 1". Rubber Chem. Technol. 1958, 31, 539.

55. Moore, C.G., Saville, B. and Watson, A.A.
"An interpretation of acceleration by thiourea and related compounds of the tetramethylthiuram disulphide vulcanization of natural rubber". J. Appl. Polym. Sci. 1960, 3, 373.

56. Ostromyslenski, I.I.
"New method for the hot vulcanization of caoutchouc by means of peroxides or per acids in absence of sulphur". India Rubber J. 1916, p.470.

57. Fisher, H.L. and Gray, A.E.
"Chemical unsaturation of rubbers vulcanized with polynitro compounds and benzoyl peroxide, and its possible bearing on vulcanization". Ind. Eng. Chem. 1928, 20, 294.

58. Braden, M. and Fletcher, W.P.
"Vulcanization of rubber with organic peroxides. Part II". Trans. Inst. Rubber Ind. 1955, 31, 155.

59. Chow, Y.W. and Knight, G.T.
"Delayed action peroxide vulcanization systems". Paper presented to the International Rubber Conference, Brighton, England (May, 1977).

60. Dunn, J.R. and Scanlan, J.
"Ageing of natural rubber vulcanizates in the presence of dithiocarbamates". Trans. Inst. Rubber Ind. 1958, 34, 228.

61. Braden, M., Fletcher, W.P. and McSweeney, G.P.
"Vulcanization of rubber by organic peroxides". Trans. Inst. Rubber Ind. 1954, 30, 144.

62. Parks, C.R. and Lorenz, O.
"Crosslinking efficiency in the reaction of dicumyl peroxide with dimethyloctadiene". J. Polym. Sci. 1961, 50, 287.

63. Thomas, D.K.
"Crosslinking efficiency of dicumyl peroxide in natural rubber". J. Appl. Polym. Sci. 1962, 6, 613.

64. Lorenz, O. and Scheele, W.
"Studies of the vulcanization of elastic high polymers. The vulcanization of natural rubber with benzoyl peroxide". Rubber Chem. Technol. 1956, 29, 901.

65. Hercules Technical Bulletin, *"Peroxides".*

66. Luperox Technical Bulletin, *"Organic peroxides for crosslinking polyolefins and elastomers".*

67. Akzo Chemie Technical Bulletin, *"Rubber chemicals"*.

68. Blow, C.M. and Hepburn, C. (eds).
"Rubber technology and manufacture". 2nd ed. Newnes-Butterworths London, 1982.

69. Loan, L.D.
"Mechanism of peroxide vulcanization of elastomers". Rubber Chem. Technol. 1967, 40, 149.

70. Baker, C.S.L.
"Vulcanization of natural rubber with Novor and peroxides". Malaysian Rubber Producers' Research Association, Technical Report No. 946.

71. Bristow, G.M.
"Vulcanization time with peroxide cure systems". NR Technology (MRPRA), 1976, 7, 61.

72. van Rossem, A., Dekker, P. and Prawirodipoero, R.S.
"Vulcanization with benzoyl peroxide". Rubber Chem. Technol. 1932, 5, 97.

73. Farmer, E.H. and Michael, S.E.
"Rubber, polyisoprenes and allied compounds. Part II. The molecule-linking capacity of free radicals and its bearing on the mechanism of vulcanization and photo-gelling reactions". J.Chem. Soc. 1942, p.513.

74. Moore, C.G. and Watson, W.F.
"Determination of degree of crosslinking in natural rubber vulcanizates. Part II". J. Polym. Sci. 1956, 19, 237.

75. Moore, C.G. and Scanlan, J.
"Determination of degree of crosslinking in natural rubber vulcanizates Part VI. Evidence for chain scission during the crosslinking of natural rubber with organic peroxides". J.Polym. Sci. 1960, 43, 23.

76. Hummel, K. and Kaiser, G.
"Vulcanization of elastomers. 44. Vulcanization of polybutadiene with cumyl peroxide 1". Rubber Chem. Technol. 1965, 38, 581.

77. van der Hoff, B.M.E.
"Reactions between peroxide and polydiolefins". Ind. Eng. Chem. Prod. Res. Develop. 1963, 2, 273.

78. Kraus, G.
"Quantitative characterization of polybutadiene networks". J. Appl. Polym. Sci. 1963, 7, 1257.

79. Loan, L.D.
"Crosslinking efficiencies of dicumyl peroxide in unsaturated synthetic rubbers". J. Appl. Polym. Sci. 1963, 7, 2259.

80. Makowski, H.S., Cain, W.P. and Wei, P.E.
"Readily curable chlorinated poly-α-olefins and ethylene-α-olefin copolymers". Ind. Eng. Chem. Prod. Res. Develop. 1964, 3, 282.

81. Wei, P.E. and Rehner, J.
"New vulcanizing systems for ethylene-propylene elastomers". Rubber Chem. Technol. 1962, 35, 133.

82. Harpell, G.A. and Walrod, D.H.
"Organic peroxides for cure of ethylene-propylene rubbers". Rubber Chem. Technol. 1973, 46, 1007.

83. Loan, L.D.
"Peroxide crosslinking of ethylene-propylene rubber". J. Polym. Sci. 1964, A2, 3053.

84. Warrick, E.L., Pierce, O.R., Polmanteer, K.E. and Saam, J.C. *"Silicone elastomer developments".* Rubber Chem. Technol. 1979, 52, 437.

85. Weisfeld, L.B., Little, J.R. and Wolstenholme, W.E. *"Bonding in urethane elastomers".* J. Polym. Sci. 1962, 56, 455.

86. Urs, S.V. *"Rapid curing of urethane elastomers".* Ind. Eng. Chem. Prod. Res. Develop. 1962, 1, 199.

87. Loan, L.D. *"The reaction between dicumyl peroxide and butyl rubbers".* J. Polym. Sci. 1964, A2, 2127.

88. Hoffmann,W. *"Vulcanization and vulcanizing agents".* Maclaren and Sons Ltd., London, 1967.

89. Kovacic, P. *"Bisalkylation theory of neoprene vulcanization".* Ind. Eng. Chem. 1955, 47, 1090.

90. Kato, H. and Fujita, H. *"Some novel systems for crosslinking polychloroprene".* Rubber Chem. Technol. 1975, 48, 19.

91. Tawney, P.O., Little J.R. and Viohl, P. *"The vulcanization of butyl rubber with phenol formaldehyde derivatives".* Rubber Age 1958, 83, 101.

92. Thelamon, C. *"Vulcanization of rubber by means of resins".* Rubber Chem. Technol. 1963, 36, 268.

93. Nikitin, Y.N., Epshtein, V.G. and Polyak, M.A.
"Infrared spectra of reaction products of natural rubber with alkylphenol formaldehyde resins". Rubber Chem. Technol. 1968, 41, 621.

94. Cunneen, J.I., Farmer, E.H. and Koch, H.P.
"Rubber, polyisoprenes and allied compounds. Part V. The chemical linking of rubber and of other olefins with phenol-formaldehyde resins". J. Chem. Soc. 1943, 472.

95. Elliot, D.J. and Tidd, B.K.
"Developments in curing systems for natural rubber". Progress Rubber Technol. 1973/4, 37, 83.

96. van der Meer, S.
"The vulcanization of rubber with phenol formaldehyde derivatives. 1". Rubber Chem. Technol. 1945, 18, 853.

97. Bruni, G. and Geiger, E.
"New derivatives of rubber". Rubber Age 1927, 22, 187.

98. Pummerer, R. and Gündel, W.
"The preparation and molecular size of isorubber nitrone". Rubber Chem. Technol. 1929, 2, 373.

99. Rehner, J. and Flory, P.J.
"Vulcanization reactions in butyl rubber - action of dinitroso, dioxime and related compounds". Rubber Chem. Technol. 1946, 19, 900.

100. Martel, R.F. and Smith, D.E.
"Structure-property relationships of N,N'-dinitroso-p-phenylenebis(hydroxylamine) salts. Vulcanization of non-halogenated elastomers". Rubber Chem. Technol. 1962, 35, 141.

101. Sullivan, A.B.
"Electron spin resonance studies of a stable arylnitroso-olefin adduct free radical". J. Org. Chem. 1966, 31, 2811.

102. Kovacic, P. and Hein, R.W.
"Crosslinking of polymers with dimaleimides". J. Am. Chem. Soc. 1959, 81, 1187.

103. Tawney, P.O., Wenisch, W.J., van der Burg, S. and Relyea, D.I.
"Vulcanization with maleimides". J. Appl. Polym. Sci. 1964, 8, 2281.

104. Miller, S.M., Roberts, R. and Vale, R.L.
"Use of dimaleimides as accelerators for the radiation-induced vulcanization of hydrocarbon polymers". J. Polym. Sci. 1962, 58, 737.

105. Kovacic, P. and Hein, R.W.
"Crosslinking of unsaturated polymers with dimaleimides II". Rubber Chem. Technol. 1962, 35, 528.

106. Hill, R.K. and Rabinovitz, M.
"Stereochemistry of 'no-mechanism' reactions: transfer of asymmetry in the reaction of olefins with dienophiles". J. Am. Chem. Soc. 1964, 86, 965.

107. Baker, C.S.L.
"Vulcanization with urethane agents". Malaysian Rubber Producers Research Association Technical Bulletin.

108. Sun, K.H.
'Effects of atomic radiation on high polymers". Mod. Plastics, Sept. 1954, p.141.

109. Dobo, J., Takacs, E. and Csato, P.
"Radiation crosslinking of PVC with polyfunctional monomers". Paper presented to International Conference on Radiation Processing for Plastics and Rubber II. Canterbury, England, March, 1984.

110. Nojiri, A. and Sawasaki, T.
"Radiation crosslinking of polypropylene" paper presented to International Conference on Radiation Processing for Plastics and Rubber II. Canterbury, England, March, 1984.

111. Weiss, J.
"Chemical effects in the irradiation of polymers in the solid state". J. Polym. Sci. 1958, 29, 425.

112. Wexler, S. and Marshall, R.
"Consecutive ion-molecule reactions in ethylene". J. Am. Chem. Soc. 1964, 86, 781.

113. Böhm, G.G.A. and Tveekrem, J.O.
"The radiation chemistry of elastomers and its industrial applications". Rubber Chem. Technol. 1982, 55, 575.

114. Harrington, R.
"Elastomers for use in radiation fields. Part V: Effect of gamma radiation on nitrile elastomers". Rubber Age, 1959, 85, 963.

115. Harmon, D.J.
"Radiation vulcanization of elastomers". Rubber Age 1959, 86, 251.

116. Gehman, S.D. and Auerbach, I.
"Gamma-ray vulcanization of rubber". Rubber Chem. Technol. 1957, 30, 380.

117. Lyons, B.J.
"The crosslinking of fluoropolymers with ionizing radiation: a Review". paper presented to International Conference on Radiation Processing for Plastics and Rubber II, Canterbury, England, March 1984.

118. Lyall, D.J.
"Hard facts for radiation curing of elastomers". paper presented to International Conference on Radiation Processing for Plastics and Rubber II, Canterbury, England, March 1984.

119. Jackson, W.W. and Hale, D.
"Vulcanization of rubber with high-intensity gamma radiation". Rubber Age 1955, 77, 865.

120. Sturgis, B.M., Baum, A.A. and Trepagnier, J.H.
"Vulcanization of GR-S with halogen compounds". Ind. Eng. Chem. 1947, 39, 64.

121. Strecker, R.A.H.
"Vulcanization of liquid polydienes with dithiols and peroxides". Rubber Chem. Technol. 1971, 44, 675.

122. Kirkham, M.C.
"Current status of elastomer vulcanization". Progress Rubber Technol. 1978, 41, 61.

123. Baker, C.S.L., Barnard, D. and Porter, M.
"New reactions for the vulcanization ofnatural rubber". Rubber Chem.Technol. 1970, 43, 501.

124. Minoura, Y. and Tsukasa, M.
"Crosslinking reaction of rubber with aldehydes". J. Appl. Polym. Sci. 1968, 12, 2509.

125. Hepburn, C.
"Bisperoxycarbamates: vulcanizing agents that possess bound antioxidant properties". Rubber World 1984, 190, 49.

126. Abu bin Amu.
"Bisperoxycarbamates as crosslinking agents for natural and polyisoprene rubbers". PhD Thesis, Loughborough University of Technology, 1981.

127. Thaler, W.A. and Franzus, B.
"The reaction of ethyl azodicarboxylate with monoolefins". J. Org. Chem. 1964, 29, 2226.

128. Rabjohn, N.
"The synthesis and reactions of disazodicarboxylates". J. Am. Chem. Soc. 1948, 70, 1181.

129. Flory, P.J., Rabjohn, N. and Schaffer, M.C.
"Dependence of elastic properties of vulcanized rubber on the degree of crosslinking". J. Polym. Sci. 1949, 4, 225.

130. Breslow, D.S., Willis, W.D. and Amberg, L.O.
"A new type of crosslinking agent for elastomers". Rubber Chem. Technol. 1970, 43, 605.

131. Levi, T.G.
"The vulcanization of rubber by diazoamino compounds". Rubber Chem. Technol. 1937, 10, 471.

132. McPherson, A.T.
"Vulcanization of GR-S by the Peachey Process". Rubber Age, 1946, 59, 323.

133. Davis, A.G. and Hunter, K.J.
"Organic peroxides. Part II. Esters of the monopercarbonic acids". J. Chem. Soc. 1953, p.1808.

134a. Pedersen, C.J.
"Preparation and properties of esters of N-substituted peroxycarbamic acids". J. Org. Chem. 1958, 23, 252.

134b. Pedersen, C.J.
"Thermal decomposition of crystalline tert-butyl-N-methyl-N-(p-nitrophenyl) peroxycarbamate". J. Org. Chem. 1958, 23, 255.

135. O'Brien, E.L., Beringer, F.M. and Mesrobian, R.B.
"The decomposition of peroxycarbamates and their efficiency as initiators in vinyl polymerization". J. Am. Chem. Soc. 1957, 79, 6238.

136. O'Brien, E.L., Beringer, F.M. and Mesrobian, R.B.
"The thermal decomposition of substituted t-butyl n-phenylperoxycarbamates". J. Am. Chem. Soc. 1959, 81, 1506.

137. Tobolsky, A.V. and Rembaum, A.
"A new class of block polymers". J. Appl. Polym. Sci. 1964, 8, 307.

138. Lederer, M. and Fuchs, O.
German Patent 1 028 818.

139. Goldberg, E.J.
US Patent 2958672.

140. Stagg, H.E.
"A method for the determination of isocyanates". Analyst 1946, 71, 557.

141. Potts, Jr. W.J.
"Chemical infrared spectroscopy". Vol. 1 Techniques, John Wiley and Sons Inc. 1963.

142. Lee Smith, A.
"Applied infrared spectroscopy: Fundamentals, techniques and analytical problem solving". John Wiley and Sons Inc. 1979.

143. Cross, A.D. and Jones, R.A.
"An introduction to practical infrared spectroscopy". Butterworths, London, 1969.

144. Arnold, R.G., Barney, A.L. and Thompson, D.C.
"Fluoroelastomers". Rubber Chem. Technol. 1973, 46, 619.

145. Pierce, O.R., McBee, E.T. and Cline, R.E.
"The synthesis of fluorine-containing organosilanes". J. Am. Chem. Soc. 1953, 75, 5618.

146. McBee, E.T., Roberts, C.W. and Puerckhauer, G.W.R.
"The addition of trichlorosilane and methyldichlorosilane to fluorine- and chlorine-containing olefins". J. Am. Chem. Soc. 1957, 79, 2329.

147. Tarrant, P., Dyckes, G.W., Dunmire, R. and Butler, G.B.
"The preparation of some fluoroalkylmethyldichlorosilanes and their hydrolysis products". J. Am. Chem. Soc. 1957, 79, 6536.

148. Kojima, G., Kojima, H. and Tabata, Y.
"A new fluoroelastomer derived from tetrafluoroethylene and propylene". Rubber Chem. Technol. 1977, 50, 403.

149. Kojima, G., Yamabe, M., Wachi, H. and Kodama, S.
"A new fluoroelastomer with outstanding chemical resistance and improved properties". Rubber World 1984, 190, 38.

150. Spain, R.G.
"Behaviour of some elastomers in petroleum-based fluids at elevated temperature" paper presented to Division of Rubber Chemistry, ACS meeting, Cincinnati, May 15, 1958.

151. Apotheker, D., Finlay, J.B., Krusic, P.J. and Logothetis, A.L.
"Curing of fluoroelastomers by peroxides". Rubber Chem. Technol. 1982, 55, 1004.

152. Rugg, J.S. and Stevenson, A.C.
"Viton-A: A new fluorine-containing rubber". Rubber Age 1957, 82, 102.

153. Kojima, G. and Wachi, H.
"Vulcanization of a fluoroelastomer derived from tetrafluoroethylene and propylene". Rubber Chem. Technol. 1978, 51, 940.

154. Paciorek, K.J.L.
"Chemical crosslinking of fluoroelastomers" chapter in "Fluoropolymers" (High Polymers, Volume XXV) (ed) L.A. Wall Wiley Interscience, 1972.

155. Moran, A.L. and Pattison, D.P.
"Compression set resistance". Rubber Age 1971, 103(7), 37.

156. Smith, J.F.
"Dithiol curing agents for 'Viton' A fluoroelastomer". Rubber World 1959, 140(2), 263.

157. Dixon, S., Rexford, D.R. and Rugg, J.S.
"Vinylidene fluoride-hexafluoropropylene copolymer". Ind. Eng. Chem. 1957, 49, 1687.

158. Smith, J.F. and Albin, J.R.
"Vulcanization of fluoroelastomers with difluorodiazine".
Ind. Eng. Chem. Prod. Res. Develop. 1963, 2, 284.

159. Du Pont Technical Literature,
"Viton".

160. Paciorek, K.L., Lajiness, W.G. and Lenk, C.T.
"Differential thermal analysis of fluoroelastomer systems".

161. Schroeder, H.E.
"Facets of innovation". Rubber Chem. Technol. 1984, 57, G86.

162. Paciorek, K.L., Mitchell, L.C. and Lenk, C.T.
"Mechanism of amine crosslinking of fluoroelastomers. 1. Solution studies". J. Polym. Sci. 1960, 45, 405.

163. Smith, J.F.
"The chemistry of vulcanization of Viton-A fluorocarbon elastomer". Rubber World 1960, 142(3), 102.

164. Mark, J.E.
"Experimental determinations of crosslink densities". Rubber Chem. Technol. 1982, 55, 762.

165. Neppel, A., Kuzenko, M.V. and Guttenberger, J.
"Swelling of fluoroelastomers in synthetic lubricants". Rubber Chem. Technol. 1983, 56, 12.

168. Flory, P.J.
"Principles of polymer chemistry". Cornell University Press, Ithaca, NY 1953, Chap. xiii.

167. Fogiel, A.W.
"Network characterization of Viton-AHV fluoroelastomer". J. Polym. Sci. 1975, Symposium No. 53, 333.

168. Smith, J.F. and Perkins, G.T.
"The mechanism of post-cure of Viton A fluorocarbon elastomer".
J. Appl. Polym. Sci. 1961, 5, 460.

169. Tobolsky, A.V., Prettyman, I.B. and Dillon, J.H.
"Stress relaxation of natural and synthetic rubber stocks".
J. Appl. Phys. 1944, 15, 380.

170. Andrews, R.D., Tobolsky, A.V. and Hanson, E.E.
"The theory of permanent set at elevated temperatures in natural and synthetic rubber vulcanizates". J. Appl. Phys. 1946, 17, 352.

171. Tobolsky, A.V.
"Properties and structure of polymers". John Wiley and Sons Inc. New York 1960.

172. Thomas, D.K.
"Limitations of the Tobolsky 'Two Network' theory in interpretation of stress relaxation data in rubbers". Polymer 1966, 7, 125.

173. Murakami, K. and Ono, K.
"Chemorheology of polymers" (ed) A.D. Jenkins, Elsevier Scientific Publishing Company, Amsterdam, 1979.