STUDY ON ACCELERATORS IN RUBBER VULCANIZATION WITH SPECIAL REFERENCE TO THE BINARY SYSTEMS CONTAINING SUBSTITUTED DITHIOBIURETS

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By

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SEPTEMBER 1989

CERTIFICATE

This is to certify that this thesis is a report of the original work carried out by Sri.George Mathew under my supervision and guidance. No part of this work reported in this thesis has been presented for any other degree from any other institution.

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DECLARATION

I hereby declare that the work presented in this thesis is based on the original work done by me under the guidance of Dr.A.P.Kuriakose,Professor, Department of polymer Science and Rubber Technology, Cochin University of Science and Technology and no part of this thesis has been presented for any other degree from any other institution.

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GEORGE MATHEW

CONTENTS

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LIST OF ABBREVATIONS USED IN THIS THESIS

NR	Natural Rubber
SBR	Styrene-butadiene Rubber
TMTD	Tetramethyl thiuram disulphide
CBS	N-cyclohexyl-2-benzthiazyl Sulphenamide
DTB-I	2,4 - Dithiobiuret
DTB-II	1-Phenyl 2,4-dithiobiuret
DTB-III	1,5-Diphenyl 2,4-dithiobiuret
HAF black	High Abrasion Furnace Black
FEF black	Fast Extrusion Furnace Black
NA-22	Ethylene thiourea
DPG	Diphenyl guanidine
DOTG	Di-ortho tolyl guanidine
MBT	2-Mercapto benzothiazole
MBTS	Mercaptobenzthiazyl disulphide
TETD	Tetra ethyl thiuram disulphide
TBBS	N-t-butyl-2-benzothiazole Sulphenamide
phr	Parts per hundred rubber
B.A	Before ageing
A.A	After ageing
% Rtn	Percentage retention
V_r	Volume fraction of rubber network
V_{ro}	Value of V_r for filled vulcanizates
M_c	Number average molecular weight of rubber chains between cross-links.

χ	..	Polymer-solvent interaction parameter
V_s	..	Molar volume of solvent
ρ_r	..	Density of rubber
ρ_s	..	Density of solvent
Z	..	Volume fraction of carbon black
M.mole/Kg RH	..	Millimole per kilogram of rubber hydro carbon
ASTM	..	American Society for Testing and Materials
BS	..	British Standards
BIS	..	Bureau of Indian Standards

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CHAPTER - I

INTRODUCTION

INTRODUCTION

In 1839 Charles Goodyear discovered that rubber heated with sulphur gave products which were far superior to the original material and were not so sensitive to temperature changes. This was the foundation upon which the rubber industry has been built. Goodyear[1] patented the process in 1841, and shortly after that Hancock independently patented a similar process. The word vulcanization had been suggested to this process by William Brockedon, who derived it from Vulcan, the God of fire and volcanoes to signify that both heat and sulphur, which is of volcanic origin, were involved in the reaction. It was in 1894 that Weber, a British Chemist, showed that the sulphur actually combined chemically with the rubber during vulcanization. Not long after the discovery of this process, it was found that the same chemical modification could be brought about by immersing rubber in sulphur monochloride without the application of heat and it is now possible to use materials other than sulphur, but the term vulcanization is still employed. Vulcanization can simply be defined as a process of converting a highly soluble and plastic material to highly insoluble and elastic one. It is now known that the process of vulcanization results in the introduction of a small number of crosslinks between the polymeric chains to give a three-dimensional network structure which is responsible for the enhanced insolubility and high elasticity of the vulcanizates.

Vulcanization is usually effected industrially by heating the mechanically plasticized rubber with sulphur and auxiliary vulcanizing agents such as organic accelerators, zinc oxide, and long chain fatty acids (stearic or lauric acid) or the Zn salts of these acids, and other additional ingredients viz. antioxidants and antiozonants, fillers, reinforcing agents, etc. Normally the temperature of vulcanization of NR is 140°C and is somewhat higher for SBR (upto 150 - 160°C). Lower temperature can be used if specially active accelerators are used. Elemental sulphur can be replaced by certain organic disulphides such as tetraalkyl thiuram disulphides.

Natural rubber and most of the unsaturated synthetic rubbers can also be vulcanized by a wide variety of non-sulphurated agents including organic peroxides, quinones and their oximes and imines, polynitrobenzenes, bis-azodicarboxylic esters, and by means of high energy radiations. Polychloroprene rubbers are usually vulcanized by metallic oxides (generally MgO). Non-olefinic polymers generally require non-sulphurated agents or high energy radiation for effective vulcanization.

The crosslink efficiency of the vulcanizates obtained by heating natural rubber with sulphur alone at 140°C is very low. Considering the chain scission, the crosslinking efficiencies (E) at different stages of cure in the above case show that between 40 and 55 sulphur atoms are combined for each chemical crosslink formed. This poor crosslinking efficiency is attributed to the incorporation of the sulphur in the form of (a) long polysulphide crosslinks, (b) cyclic monosulphides which constitute important modifications of the main chains and (c) vicinal crosslinks, which act physically as a single crosslink. In addition, model experiments indicate that further modifications of the main chains result from the introduction of conjugated triene units. It is thus evident that the natural rubber network obtained by unaccelerated sulphur vulcanization is extremely complex. Structures with C-C crosslinks may also be formed specially in radical cured vulcanizates. C-C bonds develop as a result of interaction among polymer radicals and with the original molecules of rubber. The polymer radicals, in turn, are formed either under physical influence or as a result of interaction with vulcanizing agents and accelerators of vulcanization, such as, in vulcanization with disulphides and sulphenamides and also in peroxide vulcanization. In addition to the above processes, chain scission also occurs to varying degrees during vulcanization. Chain scission decreases the primary chain length, thus affecting the vulcanizate properties.

There are two tendencies towards the interpretation of the general nature of chemical reaction of sulphur with rubber. Farmer and co-workers[2-5] proposed a free radical chain mechanism, whereas Bateman[6-13] and coworkers favoured a polar mechanism, for the structural changes in rubber during vulcanization. Dogadkin and Shershnev[14] suggest that the differences in the points of view regarding the mechanism of vulcanization, are not so much a matter of approach to the interpretation of experimental factors, as the fact that for such a complicated phenomenon as vulcanization it is impossible to support a single mechanism. This may vary depending on the thermodynamic considerations with regard to the reactions, the type of rubber used, and specially on the type of accelerators and activators employed. Such a conclusion has also been made by Shelton and McDonel[15].

ACCELERATED VULCANIZATION

Large proportions of sulphur and relatively long vulcanization times at relatively high temperatures are necessary in order to vulcanize rubber with sulphur alone. This time consuming process leads to a slow and expensive production, and yields vulcanizates of poor physical properties and ageing resistance. The addition of certain basic inorganic compounds or certain organic compounds greatly accelerate the vulcanization reaction. These substances known as 'accelerators' can cut the cure time from days or hours to minutes or seconds at the vulcanization temperature. Use of a small amount of accelerator not only increases the rate of vulcanization but also effects better physical and chemical properties of the finished products. The decrease in cure time is of tremendous economic importance because of increased turnover and consequent reduction in cost of production. Further more, in the presence of an accelerator, a very small amount of sulphur, generally 0.1 to 3 parts per hundred rubber (phr) is sufficient to give a vulcanizate of desired properties. In general, good accelerators give 'flatter' cure, improve tensile strength, set, hysteresis and ageing properties and make possible a wider range in the combination of properties obtainable.

The first accelerators were inorganic compounds. Among the basic salts and metal oxides, which are or have been widely used as accelerators, litharge, lime, magnesium oxide and zinc oxide are the most important ones. Organic vulcanization accelerators were first utilized in the rubber industry in the beginning of the 20th century[16-22]. Oenslager[17] in 1906, first introduced the organic bases aniline and thiocarbanilide as accelerators into rubber compounds to improve the quality of low grade rubbers and to accelerate the rate of vulcanization. Thus, organic bases were the first vulcanization accelerators of rubber[23-25]. Other accelerators such as, diphenyl guanidine (DPG), di-orthotolyl guanidine[26-27] (DOTG) and hexamethylenetetramine (HEXG) came into use around 1910 and were a great relief for the people in the rubber industry because of their relative nontoxic character compared to the former ones.

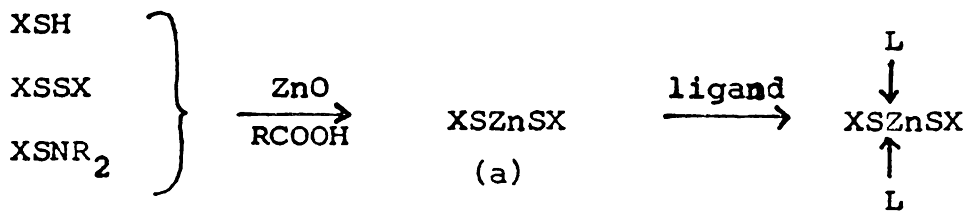
Dithiocarbamates (R_2NCSSR^1) and Xanthates (ROCSSR') were widely used as accelerators. Because of their instability, fast reactivity and poor processing safety they are generally used in low temperature processing and curing and in accelerator combinations. In 1925 Sebrell et.al [28-30] and Bruni et.al[31] discovered independently that 2-mercapto benzothiazole, its homologues, its disulphides[32-33] and its metal salts are very effective accelerators, which yields vulcanizates of improved physical properties. Dibenzothiazyl disulphide (MBTS) was developed to give greater scorch safety at higher processing temperature. With the introduction of synthetic elastomers and the use of fine furnace blacks, delayed action accelerators like sulphenamide type (eg: benzothiazyl derivative of sulphenamide) were developed for long processing safety and satisfactory cure rates. Attempts to modify the extraordinarily fast ammonium dithiocarbamates resulted in the zinc dialkyl dithiocarbamates. Further efforts to substitute the mercaptan sulphur in dithiocarbamate resulted in tetra alkyl thiuram disulphides eg. tetra methyl thiuram disulphide (TMTD), tetra-alkyl thiuram monosulphides and thiuram tetra sulphides[34-36]. All of these products are currently used in a large scale as accelerators. Thus the discovery of various types of accelerators which differ in their effects on the rate of cure, scorching, ageing etc. of rubber compounds and on the structure of the resultant vulcanizates which determines the ultimate property have revolutionised the rubber industry.

Organic accelerators, when used in conjunction with auxiliary agents like zinc oxide and fatty acids, have many physicochemical and technological functions. Abundant literature is available on the subject. Although mechanism of accelerated vulcanization has been extensively studied over last few decades, there is still much disagreement as to its exact mechanism. Craig[9], Dogadkin[10-11] Bevilacqua[37], Scheel[38-39], Blokh Tsurugi and Fukuda[40-41] and their coworkers have advanced free radical mechanism to explain the results of accelerated sulphur vulcanization, whereas Bateman[42] Porter[43] and Allen[44] suggested polar mechanism as a logical extension of their proposed mechanism for unaccelerated sulphur vulcanization. On the other hand Shelton and McDonel[45] and Coran[46] proposed mechanisms involving both free radical and ionic species. In fact it is now believed that in a complex mixture of rubber, ZnO, sulphur, fatty acids and accelerators both free radical and ionic reactions may occur simultaneously at different stages of the overall vulcanization reaction depending on the system used[45-47].

MECHANISM OF ACCELERATED VULCANIZATION

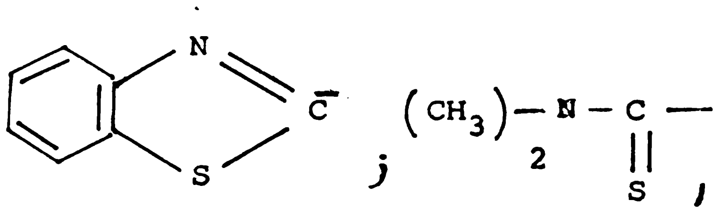
Any mechanism postulated for accelerated sulphur vulcanization must explain the structural and kinetic features effected by the addition of accelerator, zinc oxide and fatty acid. It is now generally accepted that accelerated vulcanization[48] involves the following steps.

Formation of active sulphurating agent[49-51] is the first step. The accelerator and activators first interact to form a species which then react with sulphur to form sulphurating agent. The initial step can be represented as follows:



$$\left.\begin{array}{l} XSH \\ XSSX \\ XSNR_2 \end{array}\right\} \xrightarrow[RCOOH]{ZnO} \underset{(a)}{XSZnSX} \xrightarrow{\text{ligand}} \underset{\underset{\displaystyle L}{\uparrow}}{\overset{\overset{\displaystyle L}{\downarrow}}{XSZnSX}}$$

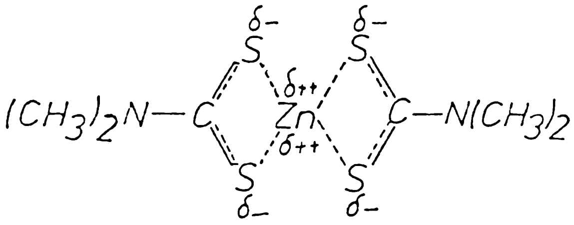
where X =



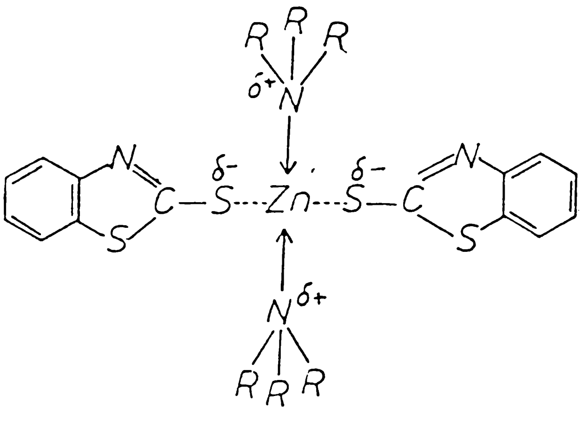
; $(CH_3)_2N-\underset{\underset{\displaystyle S}{\|}}{C}-$, etc.

L = ligand

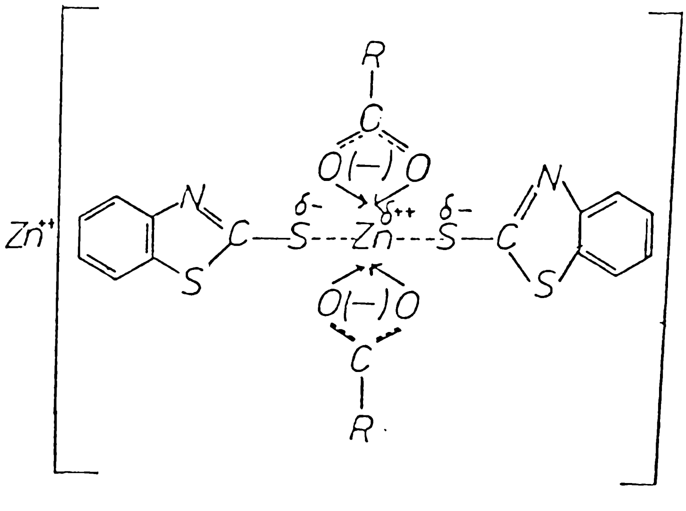
The initial Mercaptide (a) formed may be soluble and internally chelated zinc dimethyl dithio carbomate (A) or insoluble zinc benzothiazolyl mercaptide[52] which is rendered soluble through co-ordination with nitrogen bases (which is either present in the raw natural rubber or added as accelerator) (B), or zinc carboxylates (C)[53-55].



(A)

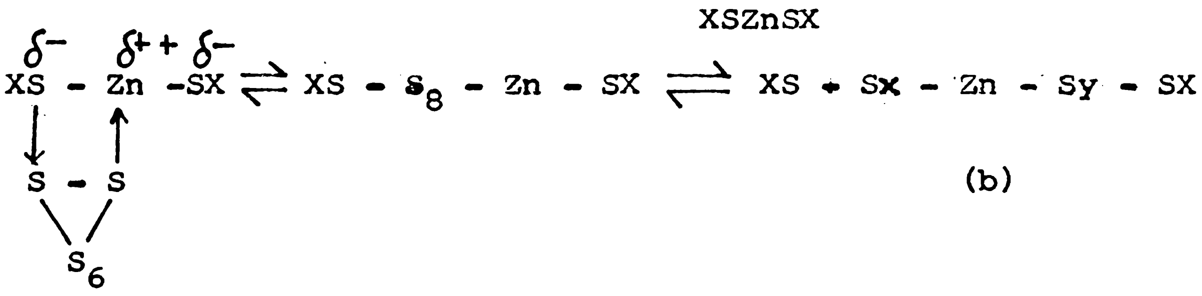


(B)



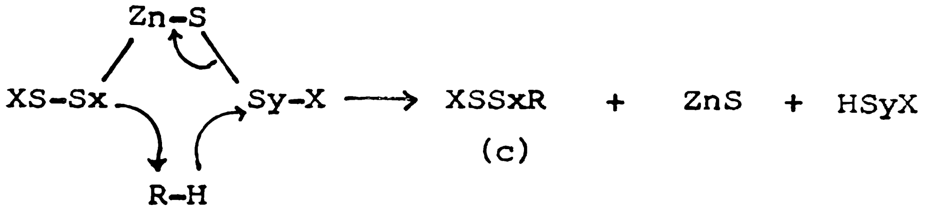
(C)

In the next step the zinc mercaptide complex (represented as XSZnSX without the ligands for simplicity) are thought to react with sulphur to form zinc perthiomercaptide (b) by means of a series of equilibria involving sulphur insertion and interchange.



The relative concentrations of sulphur and zinc mercaptide complex determine the average values of x and y. Zinc perthiomercaptide complexes are believed to be the actual sulphurating agents in the vulcanization reaction.

Formation of rubber-bound intermediate may be considered as the next step. The mechanism of the formation of this intermediate by the reaction of rubber with perthiomercaptide complex is not very clear, but it has been suggested by Bateman and Coworkers that the reaction involves nucleophilic attack of a terminal perthiomercaptide sulphur atom on an α-methylenic or α-methylic carbon atom in the rubber hydrocarbon (RH).



$$2\,H\,Sy\,X \xrightarrow{ZnO} XSyZnSyX + H_2O$$

Rubber chains with pendent polysulphidic groups terminated by accelerator parts (c) are thus formed and zinc perthiomercaptide is regenerated and is available for further reaction.

Raman and ESR spectroscopic studies on the thermal degradation of various vulcanizing systems involving thiuram sulphides by Shelton and coworkers[56] identified the formation of persulphenyl radicals from the accelerator molecules especially in the presence of sulphur and zinc oxide. These persulphenyl radicals react with rubber, forming the rubber-bound intermediates.

$$XSx\,X \xrightarrow{\text{Thermolysis}} X\dot{S} + X\,\dot{S}x$$

$$XS\dot{x}\,(X\dot{s}) + RH \rightleftharpoons \dot{R} + XSxH\,(XSH) \xrightarrow{ZnO} SXZnXS$$

$$\dot{R} + XSxX \longrightarrow RSyX + X\dot{S}x{-}y$$

$$\dot{R} + X\,\dot{S}x(X\dot{S}) \longrightarrow R\,Sx\,X\,(RSX)$$

This result is considered to be compelling evidence for a free radicals mechanism for the formation of the rubber-bound intermediates.

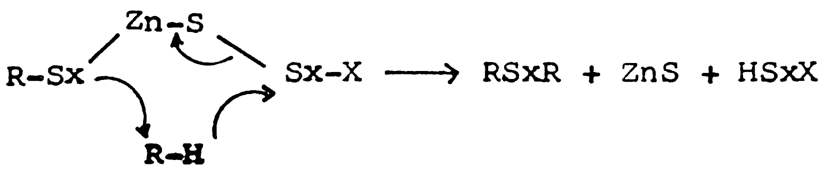
The next step is believed to involve the formation of polysulphidic crosslinks. Disproportionation reactions involving cleavage of S-S bonds are considered to be the most probable route for the conversion of the rubber-bound intermediate into crosslinked polysulphides. These reactions may be initiated by mercaptide ions ($\mathrm{X\bar{S}}$) derived from the zinc mercaptide.

$$\mathrm{RSxSX} + \mathrm{X\bar{S}} \rightleftharpoons \mathrm{R\ S\bar{a}} + \mathrm{XSbX}$$

$$\mathrm{RS\bar{a}} + \mathrm{RSxSX} \rightleftharpoons \mathrm{RSzR} + \mathrm{XS\bar{c}} \quad \text{etc.}$$

A further possibility is the interchange between the rubber-bound intermediate and zinc perthiomercaptide followed by sulphuration at another rubber chain:

$$\mathrm{RSxSX} + \mathrm{XSSx\ ZnSySX} \rightleftharpoons \mathrm{RSxZnSxSX} + \mathrm{XSSySX}$$



In the next step of vulcanization sequence, the initial polysulphidic crosslinks formed, as described above, undergo further transformation or maturing by two competing reactions; desulphuration and decomposition. Desulphuration leads to progressive shortening of the polysulphide crosslinks producing monosulphidic crosslinks in the limit. The desulphuration is effected by the zinc mercaptide complexes.

$$\mathrm{RSx\ R + X\ S\ Zn\ Sx} \longrightarrow \mathrm{RSR + XSSm\ Zn\ Sn\ SX}$$

Zinc perthiomercaptide produced can form further crosslinks by the same reaction sequences.

Decomposition of polysulphide crosslinks is thought to be an uncatalysed thermal process and results in the formation of zinc sulphide, cyclic mono- and disulphides, conjugated dienes and trienes. Though the exact mechanism of these reactions are not known, it is likely that intramolecular hydrogen transfer is involved. The relative extent of desulphuration and decomposition depends on the vulcanization conditions. A high concentration of zinc mercaptide complexes leads to rapid desulphuration of polysulphide crosslinks, effectively preventing their alternative thermal decomposition. Thus a high concentration of accelerators and activators relative to sulphur will favour the formation of monosulphide crosslinked network while a low concentration of it relative to sulphur favours a mainly polysulphide crosslinked network, with the modification of the main chains by cyclic sulphide and olefinic groups. These two types of network linkages are given in Fig.1.1. However, an actual vulcanizate network will possess an intermediate structure having features of both the networks.

After the formal vulcanization process is over, changes may continue to occur in the network structure,

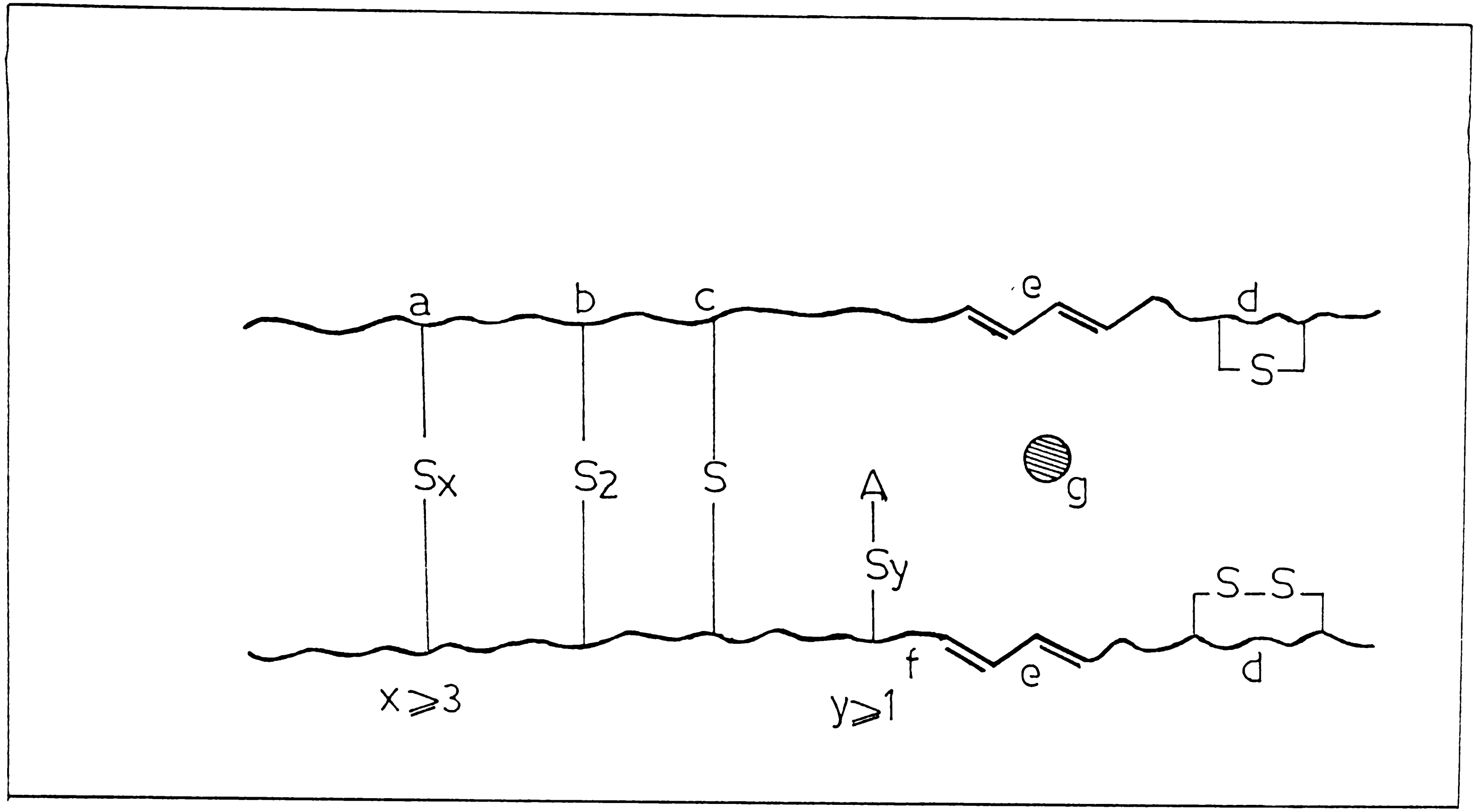


Fig.1.1: Structural Features of a Sulphur-Vulcanized Rubber

Crosslinks

(a) Polysulphidic
(b) Disulphidic
(c) Mono sulphidic

Main-chain Modification

(d) Cyclic sulphide
(e) Conjugated trienes and dienes.
(f) Accelerator-terminated pendent group.

Extra-network Material

(g) Activator and accelerator reaction products.

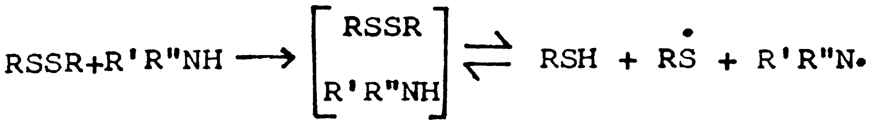
especially if the vulcanizate is in service under elevated temperatures. Monosulphide crosslinks are thermally stable and hence vulcanizates with predominantly monosulphidic linkages are not likely to change much on ageing. On the other hand, polysulphide crosslinks are thermally unstable, and hence the vulcanizates with this type of structure will undergo reversion (loss of crosslink) and main chain modification with corresponding change in physical properties. These results lead to reduced resistance to compression set and creep of the vulcanizate. However, while vulcanizates with predominently monosulphidic crosslinks have excellent heat resistance, those with predominantly polysulphidic crosslinks have better overall physical properties. In addition to the effects described above in the aged vulcanizate, there may also be other effects due to the occurrence of any oxidative reaction.

BINARY ACCELERATOR SYSTEMS IN RUBBER VULCANIZATION

There is no ideal accelerator, ie. one, that is absolutely safe at processing temperature and also cures fast at vulcanizing temperatures. Use of suitable binary accelerator system has been found to approach this ideal behaviour to some extent[57-59]. Consequently binary accelerator systems are being widely used in industry now a days and are becoming increasingly popular due to the fact that such mixed systems (1) prevent prevulcanization, (2) permit the vulcanization to be carried out at lower temperature in lesser time, and (3) produce a vulcanizate with superior physical and mechanical properties compared to those of a stock cured with single accelerator.

Though a great deal of work has been done on elucidating the mechanism of vulcanization by single accelerators, little attention has been paid so far to the chemistry of vulcanization with binary accelerator systems. Minotaya and Aoe[60-62] explained the higher activity of binary system by assuming the formation of either eutectic mixture or salt forming compounds having better solubility in rubber and greater chemical reactivity. It has been known for a long time that amines are powerful activators of thiazole type accelerators. Jones[63] suspected that the action of bases was similar to that of fatty acids, and reported that diphenyl guanidine (DPG), like a fatty acid, could act as a transmitter of zinc by forming a zinc diphenyl guanidine compound. His theory can be applied in principle to all accelerators having amine bases soluble in rubber. It has been observed that very fast rate of vulcanization can be obtained by taking an equimolar mixture of an acidic and basic accelerators. This compels one to assume that the reaction between the accelerators involves a salt or complex formation which is actually responsible for the observed accelerating effect. But this explanation cannot satisfactorily interpret the action of all of the known binary systems used for vulcanization of rubbers.

Dogadkin and collaborators[11] and Skinner and Watson[64-65] investigated a number of popular accelerator combinations and found mutual activation with many of them. Depending on the experimental results obtained in the vulcanization with various combinations of the most generally used accelerators, Dogadkin and collaborators classified the various binary systems into the following three different groups: (1) Systems with synergistically active accelerators; (2) Systems in which the mutual activity of the pair does not exceed the activity of the more active of the accelerator used; and (3) Systems with an additive action of the accelerators. The first group consists of disulphides (eg.MBTS, TMTD, TETD) or mercaptans (eg.MBT) with nitrogen containing organic bases, and disulphides with sulphenamides. The second group consists of sulphemamides with N containing organic bases. The third group exhibiting additive effect involves sulphenamides (and some disulphides) in combination with TMTD, and those containing combination of accelerators belonging to the same class. Based on these observations Dogadkin and collaborators[66-67] suggested that in the initial stage of vulcanization, the accelerators interact with one another to form an active complex, which then disintegrates with the formation of active free radicals responsible for initiating the interaction of rubber with sulphur.



$$RSSR + R'R''NH \longrightarrow \begin{bmatrix} RSSR \\ R'R''NH \end{bmatrix} \rightleftharpoons RSH + R\dot{S} + R'R''N\cdot$$

$$\text{disulphide} + \begin{array}{l}\text{Organic}\\ \text{amine or}\\ \text{sulphena-}\\ \text{mides}\end{array} \longrightarrow \begin{array}{l}\text{intermediate}\\ \text{complex}\end{array} \rightleftharpoons \begin{array}{l}\text{free}\\ \text{radicals}\end{array}$$

Though the above classification of binary accelerator systems is very useful, the mechanism suggested cannot explain all the facts exhibited by the mixed accelerator systems. Further investigations[68-70] with binary accelerator systems have provided more valuable information regarding their mechanism of action. Zamyslov[71]et.al showed that sulphenamide-tetramethyl thiuram accelerator system exhibits synergistic activity. Corinberg[72] et.al found that salts of MBT combined with DPG and piperidine have activities similar to those of the sulphenamides, the activity of the latter being dependent on the basicity of the amine group attached to the sulphenamide N-atom. MBT salts when used along with strong organic bases as accelerators was found to produce high strength vulcanizates.

To determine the synergistic effects and the effectiveness of different binary accelerator systems Kemperman[73] et.al investigated many pairs of vulcanization accelerators in NR and SBR stocks. Out of these,majority of combinations ~~with~~ showed strongly positive, few slightly positive and very few of them did not show observable synergism. Kuzin[74] et.al reported that in vulcanization of chlorosulphonated polyethylene, MBT-DPG system is much more scorchy than MBT-TMTD system. Skinner and Watson[64] observed synergism in the activity of the binary systems like CBS-TMTD, MBT-TMTD, MBT-DPG etc.

SCOPE AND OBJECTIVES OF THE PRESENT WORK

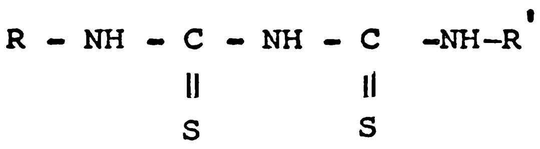
Thiourea and its various derivatives are finding much use in the binary accelerator systems in rubber vulcanization. A number of studies have been reported in the literature on the accelerator activity of thiourea and its derivatives[75-77]. Some of the more common among them are diphenyl thiourea (thiocarbanilide), Sym-di-o-tolyl thiourea, N,N'-di-methyl thiourea, N-butyl thiourea, diethylene thiourea etc. These derivatives in their capacity as accelerators also ensure a fast vulcanization at comparatively lower temperature (eg. around 100°C). They are more popular in the vulcanization systems of natural rubber latex.

Accelerators in which sulphur is combined as S-S, C-S-C or S-N are generally inactive at lower temperatures because of the high thermal stability of their sulphur bonds. In his studies on the vulcanization of natural rubber latex using the TMTD/thiourea binary system, Philpott[68] has shown that, sulphur containing nucleophiles such as thiourea enables accelerators like TMTD to operate at lower vulcanization temperatures. He suggested an ionic mechanism, where the S-S bond in TMTD is cleaved by the nucleophiles (Y^-) produced from thiourea.

$$R\text{-}S\text{-}S\text{-}R^1 + Y^- \longrightarrow RSY + R^1\bar{S}$$

In the case of the sulphenamides ($XS-NR_2$) scission at the S-N centre would take place by the subsequent displacement of nitrogen anion R_2N^-.

A perusal of the literature indicates that eventhough a number of thiourea derivatives have been tried in rubber vulcanization, the accelerating activity of dithiobiuret derivatives of thiourea have not been investigated. We undertook this study assuming that dithiobiuret derivatives of the general formula (I), which will show more nucleophilic activity than simple thiourea derivatives, will be more reactive in the rubber vulcanization reaction with accelerators of the thiuram or sulphenamide type.



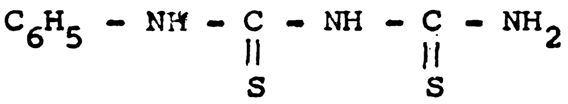
$$R-NH-\underset{\overset{\|}{S}}{C}-NH-\underset{\overset{\|}{S}}{C}-NH-R'$$

I

It has also to be noted that though suggestion has been made of the nucleophilic reactivity of thiourea and its derivatives in binary systems containing these compounds, no conclusive proof has been given in the earlier work to such a postulate. We started our work aiming at synthesising different dithiobiurets of the type DTB-I, DTB-II and DTB-III, varying in their nucleophilic reactivity, and studying them in the accelerated rubber vulcanization systems. One of the aims was also to give proof of the theory of nucleophilic reactivity in such binary systems.

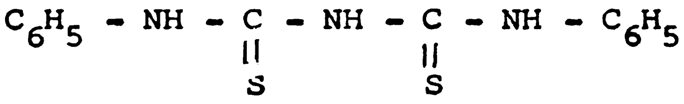
$H_2N - \underset{\underset{S}{\|}}{C} - NH - \underset{\underset{S}{\|}}{C} - NH_2$

DTB-I



$C_6H_5 - NH - \underset{\underset{S}{\|}}{C} - NH - \underset{\underset{S}{\|}}{C} - NH_2$

DTB-II



$C_6H_5 - NH - \underset{\underset{S}{\|}}{C} - NH - \underset{\underset{S}{\|}}{C} - NH - C_6H_5$

DTB-III

We could synthesise 1-phenyl 2,4 dithiobiuret (DTB-II) and 1,5 diphenyl 2,4 dithiobiuret (DTB-III), according to Joshua[78] et. al in sufficient quantities for our experimental work. But 2,4 dithiobiuret (DTB-I) could not be obtained in sufficient quantities because of the very poor yield in its synthesis. In this study, we first used DTB-II and DTB-III in binary systems containing TMTD and CBS in sulphur vulcanization of natural rubber using standard compounding recipes. In all these systems we have studied, it is found that the dithiobiurets act as better nucleophiles and this is evidenced by the significant reduction in cure times in the systems containing DTB-II and DTB-III. Also it was found that the reduction in cure time is more in systems containing DTB-II, which is more nucleophilic than in those containing DTB-III. These facts point to a nucleophilic reactivity in the acceleration of vulcanization in the systems under review.

Moreover these vulcanizates showed definite increase in tensile properties and good retension of these properties after ageing. In the evaluation of some other physical properties also these vulcanizates gave promising results. In view of the significant reduction in curetime along with increase in tensile properties of the vulcanizates containing dithiobiurets, we thought these systems will be of definite technological significance in the rubber product manufacturing industry. The difficulty usually faced by a rubber compounding chemist in choosing the correct accelerator combination to obtain the desired properties of the final product without sacrificing the time of cure was also in mind. This is all the more true when speciality rubber products are to be manufactured using specific compounding recipe. In this context we made a thorough study of the use of dithiobiurets in various binary accelerator systems in rubber vulcanization. The different polymers used, experimental techniques employed, accelerator systems selected, effect of different fillers on these systems, different properties of the vulcanizates evaluated etc, etc. are discussed in the following chapters.

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CHAPTER - II

EXPERIMENTAL TECHNIQUES

EXPERIMENTAL TECHNIQUES

The materials used and the details of the experimental procedures adopted are described in this chapter.

MATERIALS

A. Elastomers:

1. Natural Rubber (NR)

Natural rubber used was solid block rubber conforming to ISNR-5 grade, obtained from Rubber Research Institute of India, Kottayam. The Mooney Viscosity [ML(1+4) at 100°C] of the rubber was 85.43 and $\bar{M}w$ 7.70×10^5. Since it is known that the molecular weight, molecular weight distribution and non-rubber constituents of natural rubber are affected by clonal variations, season, use of yield stimulants and method of preparation[1,2] rubber from the same lot has been used in a particular experiment.

2. Styrene-butadiene Rubber (SBR)

Styrene-butadiene rubber used was synaprene 1502 grade obtained from Synthetics and Chemicals Ltd, Bareilly, U.P. The Mooney Viscosity [ML(1+4) at 100°C] was 52.0

B. OTHER INGRADIENTS

1. Zinc oxide (activator)

Zinc oxide was supplied by M/s Meta Zinc Ltd. Bombay having the specifications given below:

Specific gravity	.. 5-5.70 ± 0.08
Zinc oxide content	.. 98%
Acidity	.. 0.4% Max.
Heat loss (2 hrs at 100°C)	.. 0.5% Max.

2. Stearic acid (Co-activator)

Stearic acid was supplied by Godrej Soap (P) Ltd., Bombay and had the following specifications;

Melting point	.. 50-69°C
Acid number	.. 185-210
Iodine number	.. 9.05 Max.
Specific gravity	.. 0.85 ± 0.01
Ash	.. 0.1% Max.

3. TMTD (Accelerator)

Tetramethyl thiuram disulphide supplied by Rubochem. Industries, Kottayam had the following specifications:

Melting point	.. 138°C
Specific gravity	.. 1.405 ± 0.025
Ash (max.)	.. 0.5%
Moisture (max.)	.. 1%

4. CBS (Accelerator)

N-cyclo hexyl-2 benzthiazyl sulphenamide used in the study was Santocure CBS supplied by Polyolefins Industries, Bombay having the following specifications:

Ash .. 0.5% (max.)
Moisture .. 0.5% (max.)
Specific gravity .. 1.27

5. Sulphur (Crosslinking Agent)

Sulphur was supplied by Standard Chemical Co. Pvt.Ltd., Madras and had the following specifications:

Specific gravity .. 2.05
Acidity .. 0.01%(max.)
Ash .. 0.10% (max.)
Solubility in CS_2 .. 98% (max.)

6. Thiourea (Accelerator)

Thiourea used for this study was of analytical grade supplied by Sisco Research Laboratories, Bombay.

Purity .. 99.5%
Sulphated ash .. 0.1 (max.)

7. Naphthenic oil (Process oil)

Naphthenic oil was supplied by Indian oil Corporation. It had the following specifications:

Pour point (°C)	-40 to -12
Aniline point (°C)	-78
Viscosity gravity constant (VGC)	0.85-0.90
Aromaticity as %	10-30

8. Fillers:

High Abrasion Furnace Black (N 330) used in the experiments was supplied by M/s Carbon and Chemicals (India) Limited, Cochin.

Precipitated silica vulcasil-S was of commercial grade and the China clay was hard clay (rubber grade) both - supplied by Rubochem Industries, Kottayam.

9. Reagents for network structure elucidation:

Propane 2-thiol, 1-hexane thiol and piperidine were of analytical grade supplied by Fluka, Germany. Benzene, n-heptane, petroleum spirit (40-60°C) were of analytical grade.

10. Reagents for estimation of free sulphur:

Sodium sulphite, strontium chloride, cadmium acetate, formaldehyde, glacial acetic acid and iodine were of analytical grade.

11. Reagents for zinc sulphide estimation:

Ether, cadmium chloride, sodium acetate, sodium thiosulphate and hydrochloric acid were of analytical grade.

12. Reagents for preparation of dithiobiurets:

Carbondisulphide, ammonium thiocyanate, aniline, ammonia, lead nitrate, thiourea, sodium hydroxide, acetonitrile and hydrochloric acid were of analytical grade.

EXPERIMENTAL PROCEDURE

1. PREPARATION OF DITHIOBIURETS:[3]

(a) 1-Phenyl, 2,4-dithiobiuret (DTB-II)

Phenyl isothiocyanate was prepared[4] by the interaction of carbon disulphide and aniline in ammoniacal medium. Carbon disulphide (43 ml) and conc. ammonia (90 ml) were mixed with stirring. Aniline (55ml) was added drop -wise. The reaction was carried out in an ice bath (0°C)with vigorous stirring. Ammonium phenyl dithiocarbamate formed on steam distillation with lead nitrate afforded phenyl isothiocyanate. The phenyl isothiocyanate (0.025 mol) was added dropwise during 5 min. to a stirred solution of thiourea (0.025 mol) and powdered sodium hydroxide (0.025 mol) in acetonitrile (15 ml). The reaction mixture was heated to about 60°C and stirred at this temperature for another 30 min., when a clear solution resulted ; the reaction mixture was diluted with water (150ml), filtered, the filterate acidified with con. hydrochloric acid (4 ml, 33%) and the precipitated product collected and redissolved in minimum quantity of 4% aq. sodium hydroxide to remove any unreacted thiourea and filtered. The alkaline filterate on acidification at 0°C afforded 1-phenyl, 2,4-dithiobiuret which recrystallised as needles from ethanol (M.P 180°C)

$$C_6H_5 - NH_2 + CS_2 \xrightarrow{NH_3(H_2O)} C_6H_5NH\ CS_2\ NH_4$$

$$C_6H_5\ NH\ CS_2\ NH_4 + Pb(NO_3)_2 \longrightarrow C_6H_5-NCS+NH_4\ NO_3+HNO_3 + PbS.$$

$$NH_2-CS-NH_2 + C_6H_5-NCS \longrightarrow NH_2-CS-NH-CS-NH-C_6H_5$$

(b) 1,5 diphenyl 2,4-dithiobiuret (DTB-III)

Phenyl thipurea[5] was prepared by the interaction of aniline with ammonium thiocyanate in hydrochloric acid and by the subsequent isomerisation of phenylaminethiocyanate obtained. Phenyl isothiocyanate (.025 mol) was added dropwise during 5 min. to a stirred solution of phenyl thiourea (0.025 mol) and powdered sodium hydroxide (0.25 mol) in acetonitrile (15 ml). The reaction mixture was heated to about 60°C and stirred at this temperature for another 30 minutes when a clear solution resulted. This was diluted with water (150ml) filtered, the filterate acidified with con. hydrochloric acid (4 ml, 33%) and the precipitated product collected and redissolved in minimum quantity of 4% aq. sodium hydroxide to remove any unreacted phenyl thiourea and filtered. The alkaline filterate on acidification with hydrochloric acid at 0°C afforded 1,5-diphenyl 2,4-dithiobiuret which recrystallised as needles from ethanol (M.P.143°C).

$$C_6H_5NH_2 + HCl + NH_4\text{-}NCS \xrightarrow{\Delta} C_6H_5NH\text{-}CS\text{-}NH_2 + NH_4Cl$$

$$C_6H_5NH\text{-}CS\text{-}NH_2 + C_6H_5NCS \longrightarrow C_6H_5NH\text{-}CS\text{-}NH\text{-}CS\text{-}NH\text{-}C_6H_5$$

2. MIXING AND HOMOGENIZATION OF THE RUBBER COMPOUND:

Mixes were prepared on a laboratory size two roll mixing mill (33cm x 15cm) at a friction ratio of 1:1.25 in the case of natural rubber and 1:1.1 in the case of styrene butadiene rubber. Natural rubber was first masticated to attain a Wallace Rapid Plasticity (100°C, 1cm platen; BS 1673, Part 3, 1969) around 20 by careful control of temperature, nip gap, time of mastication and by uniform cutting operation. The compounding ingredients were added as per ASTM Designation D15-62 T in the following order: activators, fillers, accelerators and sulphur. Before the addition of accelerators and sulphur the batch was thoroughly cooled.

In the case of blends, natural rubber was masticated to a Mooney Viscosity of 40 (approx.), comparable to that of SBR. These rubbers were preblended and then the additives were added, unless otherwise stated.

After complete mixing, the stock was sheeted out and passed six times endwise through tight nip and finally sheeted out at a nip gap of 3mm. Mixing time and temperature were controlled during the studies. When sulphur was incorporated, the temperature of the rolls was maintained at 35° - 40°C.

3. DTERMINATION OF CURE CHARACTERISTICS OF RUBBER COMPOUNDS USING MONSANTO RHEOMETER:

The Monsanto Rheometer used in the study for determining the curing behaviour of rubber compounds was model R100. In this instrument, the rubber compound is contained in a cylindrical cavity (50mm x 10mm) and has embedded in it a biconical rotor of diameter 37mm which is oscillated sinusoidally through a small arc amplitude (1 to 3 degree). The cavity and specimen are maintained to within $\pm$ 0.5^{o}C and the force required to oscillate the disc is measured. A typical torque time curve (vulcanization curve) also known as rheograph is shown in Fig.2.1. The relevant data that could be taken from the torque-time curve are:

i. Minimum torque (M_L): This is the torque attained by the mix after homogenizing at the test temperature before the onset of cure.

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

iii. Induction time (t_1): This is the time taken for one unit (0.1 Nm) rise above the minimum torque (about 5% vulcanization).

iv. Scorch time (t_2): This is the time taken for 2 units (0.2 Nm) rise above the minimum torque (about 10% vulcanization).

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

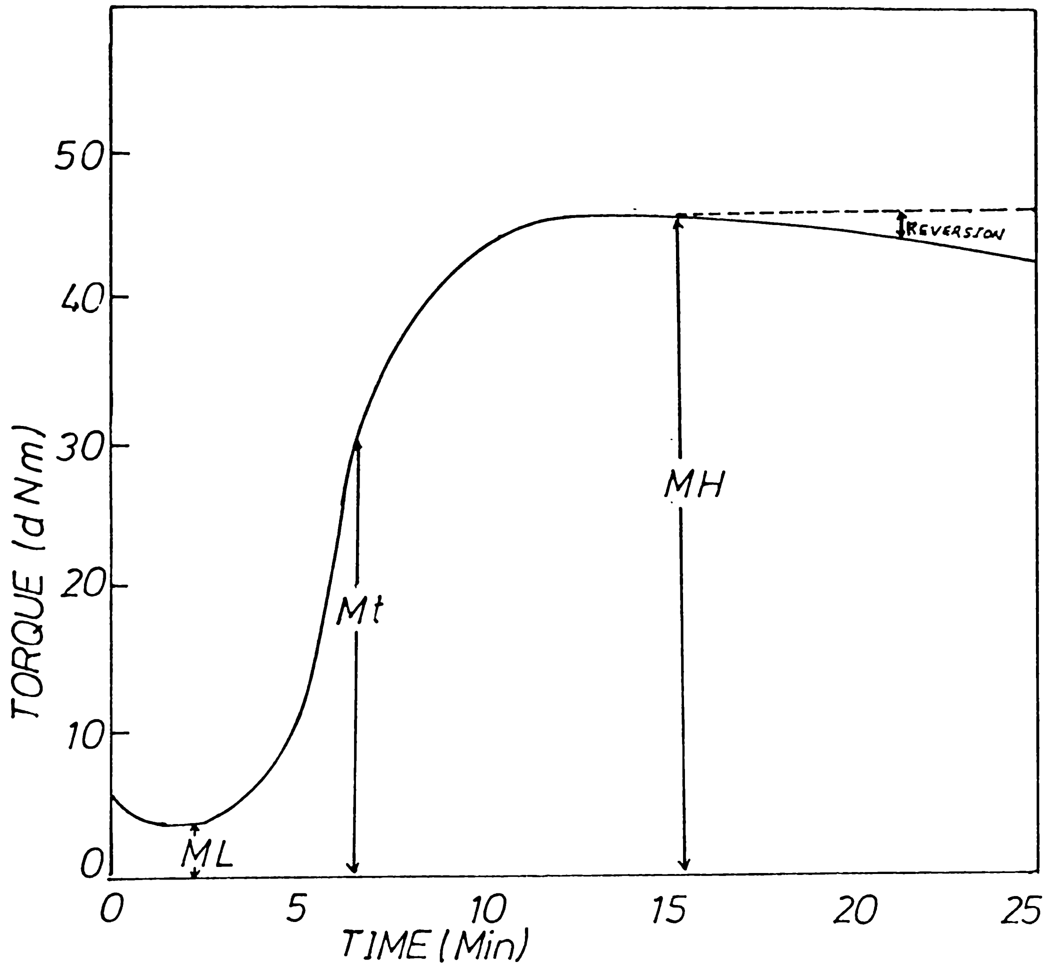

Fig. 2.1: Analysis of a typical rheograph to find out various cure parameters of a rubber mix.

M_H - Maximum torque, M_L - Minimum torque

M_t - Torque at any specified time.

vi. Cure rate index: Cure rate index was determined from the rheographs of the respective mixes.

Cure rate index $= \frac{100}{t_{90} - t_2}$ where t_{90} and t_2 are times corresponding to the optimum cure and two units above minimum torque respectively.

4. MOONEY SCORCH MEASUREMENT:

The Mooney Scorch time of the vulcanizates were measured on the Mooney Viscometer which is designed for measuring the shearing viscosity of rubber and rubber like materials by a disc rotating (2 rev/min) in a cylindrical cavity set at 120°C and filled with rubber under test. In running a scorch test, the sample was allowed to warm up for one minute after the platens were closed and the motor was then started. Time taken for 5 units rise above the minimum is taken as the Mooney Scorch time.

5. VULCANIZATION:

Vulcanization of the samples was carried out in a David Bridge single daylight electrically heated press having 30cm x 30cm platens, at 150°C & 120°C at a pressure of 45 kg/cm^2 on the mould, upto optimum cure time. Mouldings were cooled quickly in water at the end of the curing cycle and stored in a cold and dark place for 24 hours, and were used for subsequent physical tests and chemical analysis. For samples having thickness more than 6mm (like heat build up, compression set, etc.) additional times based on the sample thickness were used to obtain satisfactory mouldings.

6. PHYSICAL TEST METHODS:

At least three specimens per sample were tested for each property as follows and mean values reported.

(a) Modulus, Tensile strength and Elongation at break:

In the present work these tests were carried out according to ASTM designation D412 -51T using dumbbell specimens. All the above tests were carried out at 28 ± 2°C. Samples were punched from vulcanised sheets parallel to the grain direction using a dumbbell die (C-type). The thickness of the narrow portion was measured by bench thickness gauge. Two marks were made 2.5 cm apart in the middle of the narrow portion. The sample was held tight by the two grips in a 'Zwick' tensile testing machine (sensitivity 0.1 kg), the upper grip of which being fixed. The rate of seperation of the power actuated grip was 50cms per minute. The load at 300% elongation and at break were read from the dial. The elongation at break was measured using a scale. From the recorded loads, the stress was calculated on the basis of the original cross-sectional areas of the specimen.

The tensile strength and modulus are reported in MPa (conversion factor: 1kgf $/cm^2$ = 0.098 MPa.

(b) Tear Resistence:

The test was carried out as per ASTM method D624-48; unnicked, 90^{o} angle test pieces were used. The samples were cut from the vulcanised sheets parallel to the grain direction. The test was carried out on a 'Zwick' tensile testing machine. The speed of extension was 50cms per minute and the temperature 28 ± 2^{o}C. Tear resistance has been reported in N/mm.

(c) Hardness:

Shore A type Durometer was employed to find out the hardness of the vulcanizates. The instrument uses a calibrated spring to provide the indenting force. Readings were taken after 15 seconds of the indentation when firm contact has been established with the specimens. The method employed is the same as that in ASTM D676-52 T.

(d) Compression set:

The samples (1.25cm thick and 2.8cm diameter) in duplicate, compressed to constant deflection (25%) were kept for 22 hours in an air oven at 70^{o}C (ASTM D395-61, method B). After the heating period, the samples were taken out, cooled to room temperature for half an hour and the final thickness was measured. The compression set was calculated as follows:

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

where t_0 and t_1 are the initial and final thickness of the specimen and t_s is the thickness of the spacer bar used.

(e) Heat Build up:

The Goodrich Flexometer conforming to ASTM designation D 623-67 method A was used for measuring heat build-up. The test was carried out with the cylindrical samples of 2.5cm in height and 1.9cm in diameter. The oven temperature was kept constant at 50°C. The stroke was adjusted to 4.45mm and the load to 10.9 kg. The sample was preconditioned to the oven temperature for 20 minutes. The heat development at the base of the sample was sensed by a thermocouple and relayed to a digital temperature indicator. The temperature rise ($\Delta T^{o}C$) at the end of 20 minutes was was taken as the heat build up.

(f) Rebound resilience:

Dunlop Tripsometer (BS 903, pt.22, 1950) was used to measure rebound resilience. The sample was held in position by suction. It was conditioned by striking with the indentor six times. The temperature of the specimen holder and sample was kept constant at 35°C. Rebound resilience was calculated as follows:

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

where θ_1 and θ_2 are the initial and rebound angles respectively. θ_1 was 45^{o} in all tests.

(g) Ageing studies:

Dumb-bell samples for evaluation of physical properties were prepared and kept in an air oven at predetermined temperatures (70°C) for specified periods (96 hours). Physical properties like tensile strength, elongation at break, modulus etc. were measured before and after ageing and the percentage retention of these properties was evaluated for assessing the effect of ageing. The procedure given in ASTM D573 was followed.

7. CHEMICAL TEST METHODS:

(a) Free sulphur estimation:

Free sulphur was estimated according to ASTM Designation D297 - 72A. The principle of this method is based on the reaction of free sulphur with sodium sulphite to give sodium thiosulphate which is finally titrated against standard iodine solution.

$$S + Na_2SO_3 \longrightarrow Na_2S_2O_3$$

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

Two grams of finely divided sample was digested gently with 100ml of aqueous sodium sulphite solution (50gm/litre) for 16 hours in the presence of 5ml of sodium stearate suspension in water (1gm/litre) to assist wetting and approximately 1 gm ot paraffin wax to avoid aerial oxidation. 100 ml of strontium chloride (5gm/litre) solution was added to precipitate fatty acids and 10ml of cadmium acetate solution (30gm/litre) to remove accelerators. For the vulcanizates containing higher proportion of accelerators, additional 10ml of cadmium acetate solution was added to ensure complete precipitation of the accelerators. Rubber and the precipitate were seperated by filtration. It was then washed twice with 75ml portions of cadmium acetate ~~was~~ solution (1.2gm/litre). To the filterate 10ml of 40% formaldehyde solution was added with vigorous stirring and subsequently acidified with glacial acetic acid (10ml). The solution was cooled below 15°C by adding enough crushed ice and titrated with 0.02N iodine solution using strach as indicator.

A reagent blank was run and this value was substracted from the titre value of the sample.

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

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

(b) Zinc sulphide estimation:

The procedure is based on the following reactions:

$$ZnS + 2HCl \longrightarrow Zncl_2 + H_2S$$

$$H_2S + CdCl_2 \longrightarrow CdS + 2HCl$$

$$Cds + 2H^+ + I_2 \qquad Cd^{++} + 2HI + S$$

The finely divided sample (2 gm) along with 25ml of freshly obtained peroxide-free ether was placed in the digestion flask of the apparatus as adopted by Adam and Johnson[6]. The reaction flask was immersed in a constant temperature water bath maintained at 37°C. 100ml of absorbing solution (5 gms of $CdCl_2$, 25 gm of sodium acetate and 25ml of glacial acetic acid per litre of the solution) was used for absorbing the gas, generated during digestion. After the sample had become swollen with ether (1 hour), 25ml of concentrated HCl was added to the digestion flask and nitrogen gas was bubbled through the reaction mixture for a period of one hour. The amount of H_2S liberated from the sample by the HCl-ether digestion, which is the measure of ZnS-Sulphur was absorbed as Cadmium sulphide (CdS) in the absorbing solution. A measured excess of 0.05 N iodine solution was added and the excess iodine was back titrated against 0.05N sodium thiosulphate solution using starch as indicator. A blank titration was also conducted. From the two titre values, the volume of iodine reacted with cadmium sulphide was noted. The amount of zinc sulphide sulphur was calculated as follows:

$$\text{Zinc sulphide sulphur, \%} = \frac{(x-y) \times N \times 0.016 \times 100}{W}$$

where x is the volume of thiosulphate required for the blank in ml and y that for the sample in ml and N, the normality of thio sulphate solution and 'W' the weight of the sample taken.

(c) Determination of Concentration of Crosslinks of the vulcanizates:

The concentration of crosslinks (crosslink density) of the vulcanizates was determined from the equilibrium swelling data as follows:

Samples of approximately 1cm diameter, 0.20cm thickness and 0.20gm weight were punched out from the central portion of the vulcanizate and allowed to swell in solvent (benzene) containing 0.1% phenyl-β-Napthylamine (PBN). After 24 hours, the solvent containing PBN was replaced by pure solvent and after another two hours swelling was stopped. The swollen sample was weighed, solvent removed in vacuum and the sample weighed again.

The volume fraction of rubber (Vr) in the swollen network was then calculated by the method reported by Ellis and Welding[7] from the following equation:

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

where T = weight of the test specimen

D = De-swollen weight of the test specimen

F = Weight fraction of insoluble components

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

ρ_r = Density of test specimen

ρ_s = Density of solvent

The value of ρ_r and ρ_s taken were

ρ_r (NR) = 0.92 g/cm^3
ρ_r (SBR) = 0.94 g/cm^3
ρ_s(benzene) = 0.875 g/cm^3

The crosslink density $\frac{1}{2Mc}$ was then determined from Vr using the Flory Rehner[8,9] equation.

$$-\left[\ln(1-Vr) + Vr + \chi V^2 r\right] = \frac{\rho\ Vs\ (Vr)^{1/3}}{Mc}$$

where Vs = molar volume of solvent

Vs (benzene) = 90 c.c/mole

and χ = the parameter characteristic of interaction between rubber and solvent.

Value of parater χ taken for calculations[10,11] were the following

For NR- benzene χ = 0.40
SBR-Benzene χ = 0.31

For NR/SBR blend, χ was found to vary linearly with composition. Hence the average value of χ was taken for 50/50 blend of these polymers.

Although natural rubber gum vulcanizates have received much attention less details are available on network structure of filled vulcanizates, because of the uncertainties introduced by filler-rubber interaction. In the case of vulcanizates containing HAF black, the value of Vr, obtained as above, were converted into V_{ro} (the value Vr would have had in the absence of the black) by means of the following equation which was derived by Porter[12,13].

$$Vro/Vr = 0.56\ e^{-z} + 0.44$$

where Z is the weight fraction of carbon black in the vulcanizate. V_{ro} was then substituted in the Flory-Rehner equation in place of V_r to obtain the crosslink density.

(d) Determination of Concentration of Different Types of Crosslinks[14-16]:

(i) Concentration of Polysulphidic Crosslinks.

The concentration of polysulphidic crosslinks was estimated from the change in the crosslink density of the vulcanizates before and after treatment with propane-2-thiol and piperidine which cleaves the polysulphidic crosslinks in the network. Vulcanizate sample weighing about 0.2 - 0.3gm was allowed to stand in excess of solvent (benzene) containing 0.1% PBN for 24 hours at room temperature. Then the solvent was replaced by a solution (100ml) of 0.4 M propane-2-thiol and piperidine in benzene containing 0.5% PBN for two hours. On completion of reaction, the sample was removed from the reagent solution, washed with petroleum ether (40°C - 60°C) four times, surface dried on filter paper as quickly as possible and dried in vacuum to constant weight at room temperature. The specimen was then kept in excess of the solvent with 0.1% PBN for 24 hours, and finally extracted for two hours in pure solvent. The swollen sample was weighed, solvent removed in vacuum and the sample weighed again. The volume fraction of rubber (V_r) was then determined as before and the crosslink density was determined.

(ii) Concentration of disulphidic and monosulphidic crosslinks:

Both polysulphidic and disulphidic crosslinks in the vulcanizates could be cleaved by treatment with 1-hexane thiol in piperidine. The determination of crosslink density before and after this treatment gives the concentration of monosulphide linkage, assuming carbon-carbon linkages to be negligible. Since the concentration of polysulphudic linkage was determined before, the concentration of disulphidic linkages also could be estimated.

Vulcanizate sample weighing about 0.2 - 0.3gm was allowed to stand in 100ml of 1-hexanethiol in piperidine (1M solution) containing 0.5% PBN for 48 hours at room temperature. The mixture was agitated occasionally. On completion of reaction the sample was removed from the reagent solution, washed with petroleum ether (40° - 60°C) four times, surface dried on filter paper as quickly as possible and dried in vacuum to constant weight at room temperature. Then the specimen was kept in excess solvent (benzene) containing 0.1% PBN for 24 hours. Finally the specimen was kept in pure solvent for 2 hours and weighed. Then the solvent was removed in vacuum and the de-swollen sample was weighed. The volume fraction of rubber in the swollen network (V_r) was then determined as before and the crosslink density was calculated.

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CHAPTER - III

STUDY ON THE BINARY ACCELERATOR SYSTEMS CONTAINING SUBSTITUTED DITHIOBIURETS IN NATURAL RUBBER.

STUDY ON THE BINARY ACCELERATOR SYSTEMS CONTAINING SUBSTITUTED DITHIOBIURETS IN NATURAL RUBBER

INTRODUCTION

Natural rubber which is commonly obtained from the latex of Hevea brasiliensis, contains approx. 94% rubber hydrocarbon, 3% protein and 3% of other materials including fatty acids and resins. Purified natural rubber hydrocarbon is a long chain polymer made up of cis 1,4 polyisoprenoid units and the average molecular weight ranges from 200,000 - 500,000[1].

Due to its high structural regularity, natural rubber tends to crystallise on stretching. The strain induced crystallization gives it the unique high tensile strength in pure gum or in non-reinforcing filler vulcanizates. Natural rubber is the preferred polymer in many areas because of its superior building tack, green stock strength, better processing, high resilience and excellent dynamic properties.

The vulcanization of natural rubber may be effected with the aid of sulphur, organic peroxide, synthetic resins and other polyfunctional reagents and also by ionizing radiation. Sulphur vulcanization of NR forms the subject of numerous publications[2-7]. Natural rubber is usually vulcanized at 140 - 180°C with a combination of sulphur (2 - 3 phr), one or more accelerators (0.5 - 1.0 phr), zinc oxide (3 - 5 phr) and a fatty acid

(1 - 3 phr). The vulcanizates so obtained have the best overall combination of physical properties for many applications. The main deficiency of these vulcanizates is that, although their initial physical properties are very good, they deteriorate with time, even when antidegradents are present. This deficiency is largely due to the low thermal stability of the network and is characterised by a rapid reversion in properties when the vulcanizate is subjected to over cure.

Vulcanizates with very good heat resistance are obtained by using a high ratio of accelerator to sulphur (3 - 6 phr of accelerator to 0.3 - 0.5 phr sulphur). Tetramethyl thiuram disulphide (TMTD), which is an ultra accelerator belonging to thiuram group, can be effectively used for this purpose[8]. It imparts the vulcanizates with relatively high modulus, good mechanical and ageing properties. Compounds containing TMTD are suitable for vulcanization by all methods, press, steam and hot air curing. The onset of vulcanization of compounds containing TMTD can be enhanced by adding small amount of secondary accelerators or boosters, such as DPG, DOTG, dithiocarbamate, thiourea etc[9].

Sulphenamide accelerators like CBS, MBS, TBBS etc. are widely employed in the natural rubber vulcanization. They are characterized by the presence of a certain induction period [10]. This fact is of great importance in the manufacture of monolithic and particularly multi-layered articles such as tyres. The mechanical properties of articles produced with sulphenamide are found to be superior. In low sulphur system if some secondary accelerators like dithiocarbamates, thiuram or thiourea are added along with sulphenamide, the optimum cure time will be reduced and the resulting vulcanizates may possess many advantages, such as low compression set, better heat resistance, less heat build up etc. Thiourea and its various derivatives are finding much use in the binary accelerator systems in natural rubber vulcanization due to their acceleration (boosting) effect and heat resistant property. In his studies on the vulcanization of natural rubber latex, using TMTD/thiourea, CBS/thiourea systems, Philpott suggested an ionic mechanism where the S-S bond or S-N bond of the accelerator is cleaved by the nucleophiles, produced by thiourea. But no conclusive proof for this suggestion has been given. Considering the above facts we have made an attempt to find the accelerating effect of the dithiobiuret derivatives of thiourea which are more nucleophilic than simple thiourea. In this study we have tried 1-phenyl 2,4 dithiobiuret (DTB-II) and 1,5 diphenyl 2,4 dithiobiuret (DTB-III) which are varying in their nucleophilic reactivity as secondary accelerators in the vulcanization of natural rubber using TMTD/sulphur system and CBS/sulphur system. TMTD/thiourea system is taken as a control.

Table 3.1 - 3.4 give the composition of the various mixes. In all the mixes 5 phr zinc oxide, 2 phr stearic acid and 0.5 phr sulphur were incorporated as activator, co-activator and vulcanizing agent, for 100 parts of natural rubber. An attempt was made to find out the optimum concentration of the dithiobiurets in the vulcanization reaction under standard conditions. Mix A_o contain 1.5 pnr TMTD alone while mix B_o contain 1.5 phr TMTD and 0.5 phr thiourea as accelerators. Mix C_o contain CBS alone as accelerator. Mixes A_2 - A_5 contain different concentrations of DTB-II ranging from 0.25 - 1 phr along with 1.5 phr TMTD, while mixes B_2 - B_5 contain same concentrations of DTB-III with 1.5 phr TMTD. Mixes C_1 - C_4 contain different concentrations of DTB-II ranging from 0.25 - 1.5 phr along with 1.5 phr CBS while mixes D_1 - D_4 contain same concentrations of DTB-III with 1.5 phr CBS. Trial mixes were also prepared without TMTD or CBS (mixes A_1 & B_1), but they cured very slowly and hence were not proceeded further.

RESULTS AND DISCUSSION

1. Cure Characteristics

The cure characteristics of various mixes at 150°C and 120°C were evaluated using a Monsanto Rheometer (R 100) and the cure curves obtained are given in Figs.3.1 - 3.8. The cure characteristics are given in Tables 3.5 - 3.12. The scorch time of the mixes at 120°C were evaluated using a Mooney Viscometer. It can be seen from the tables3.5 & 3.7 that the optimum cure time for the system containing TMTD alone at 150°C is 11 mts. It is reduced to 1.5 mts by adding 1 phr DTB-II and to 4.5 mts by adding the same quantity of DTB-III to the above system. A corresponding increase in the cure rate can also be observed. These results clearly indicates the superior acceleration effect of the dithiobiurets in the vulcanization of natural rubber using TMTD/sulphur system. This finding is of quite technological significance because the reduction in optimum cure time will save time and energy and hence effect increased turnover in the rubber product manufacture. The dithiobiurets are better accelerators than thiourea, as indicated by their reduction in optimum cure time. Of the two dithiobiurets studied, DTB-II is more active accelerator than DTB-III. This is an indication of the nucleophilic reaction mechanism in the sulphur vulcanization of natural rubber using TMTD/dithiobiuret systems.

Along with the reduction in optimum cure time the induction time and scorch time will also be reduced. Similarly the maximum torque value of the vulcanizates is also decreasing with the increase in the concentration of dithiobiurets. This will adversely affect the systems. So by reducing the amount of dithiobiurets, a practical cure system can be obtained. A dosage of 0.5 phr of

DTB-II and 0.75 phr of DTB-III are found to be optimum. At these dosages there is appreciable reduction in cure time and at the same time scorch time and maximum torque developed are comparable to TMTD alone or TMTD/thiourea systems. Reversion resistance as noted by the number of units of torque value dropped in 5 mts at 170°C also improved at the optimum concentrations.

At the lower temperature of 120°C the acceleration effect of dithiobiurets are more significant. The optimum cure time is reduced from 57.5 to 15 mts by the addition of 1 phr DTB-II and to 35 mts by that of DTB-III. Here also the optimum concentration is derived at by considering the scorch time and maximum torque. 0.5phr of DTB-II and 0.75 phr of DTB-III are giving sufficient reduction in optimum cure time with out sacrificing much processing safety and maximum torque.

In the sulphur/CBS vulcanization system dithiobiurets are showing better acceleration of vulcanization. Here also DTB-II is more reactive than DTB-III. At 150°C addition of 1.5 phr DTB-II reduces the optimum cure time of NR/CBS/sulphur system from 13.5 to 3.5 mts, where as the DTB-III is reducing it to 4.5 mts. However the scorch time is also considerably reduced. 0.5 phr DTB-II and 1 phr DTB-III can be taken to be the optimum concentrations. The reversion resistance is also improved at these dosages. At 120°C also the dithiobiurets are showing better acceleration action. The optimum concentrations of 0.5 phr of DTB-II and 1 phr of DTB-III are reducing the optimum cure time from 54 mts to 24 mts and 25 mts respectively.

2. Tensile Properties

Rupture can occur in rubbers under various imposed mechanical conditions such as in small cyclic deformations, or stretching to ultimate extension etc. For each of these, there is a corresponding rupture resistance or strength like, fatigue resistance, tensile strength etc. Tensile strength is the simplest for measurement and for this a standard test specimen is subjected to a uniform uniaxial tensile stress.

Natural rubber is a strain induced crystallisible rubber, so it has got good gum strength. The strength of natural rubber can be improved by incorporation of reinforcing fillers. The correct choice of vulcanization system is also important in getting good tensile strength in the rubber vulcanizate. We have evaluated the tensile properties of the vulcanizates obtained from the different systems under review. These properties are shown in Figs. 3.9 - 3.17. In the case of TMTD/dithiobiuret binary systems; 300% modulus, tensile strength and elongation at break are higher compairing to TMTD alone or TMTD/ thiourea systems. Lower dosages are giving better results. At 150°C the optimum dosage of 0.5 phr

DTB-II and 0.75 phr DTB-III are giving appreciable increase in the tensile strength. This can be attributed to the increase in polysulphide linkages[11-13] obtained in the crosslink density study represented in Table 3.21. The higher tensile strength obtained in the DTB-III system compared to that of DTB-II may be due to the higher concentration of polysulphide linkages in that system. The percentage retention of tensile properties is slightly less for the dithiobiuret systems. This is also indicated by the slight decrease in the monosulphide linkage in these systems. At 120°C also the dithiobiurets are giving better tensile properties than that of TMTD alone, but it is slightly less for DTB-II compared to TMTD/thiourea system.

In the case of CBS/dithiobiuret systems the above trend is not followed. The tensile properties are decreasing with the decrease in the concentration of dithiobiurets, but after a level it further enhances. It has been seen from the Table 3.21 that the total crosslink density and the polysulphide linkages are lower for the dithiobiuret systems at the optimum concentrations. After the optimum level further lowering of the concentration of dithiobiuret does not seem to have significant effect on CBS. At 120°C also the same trend is followed but the properties are further enhanced. It may be due to a higher concentration of polysulphide linkages present at this temperature.

3. Other Physical Properties

Other physical properties studied are hardness, compression set, heat build up, resilience and tear strength. These are given in Tables 3.13-3.20. In the case of vulcanizates containing TMTD and dithiobiurets, hardness, resilience and tear strength are increasing as the concentration of dithiobiuret decreases. Compression set and heat build up values are decreasing. At the optimum dosage of 0.75 phr, DTB-III is giving better results than that of TMTD alone or TMTD/thiourea systems. Optimum concentration (o.5 phr) of DTB-II is giving slightly lower value. This may also be seen in the lower total crosslink density value of DTB-II (Table 3.21) than that of TMTD alone and TMTD/thiourea system while DTB-III is having comparable value. At 120°C also the physical properties are better at lower concentration of dithiobiurets. Here also the optimum concentration of 0.5 phr DTB-II is not giving any improvement in hardness, compression set or heat build up, but resilience and tear strength are improved. This is shown in the decrease in monosulphide crosslinks. The increase in polysulphide linkage may be responsible for the higher resilience and tear strength[11]. Optimum concentration of DTB-III is giving better results.

In the case of CBS/dithiobiuret systems, hardness, resilience and tear strength decreases first and then increases as the concentration of dithiobiuret decreases. Compression set and heat build up are showing reverse trend. At the optimum level these properties are lesser than that of CBS alone. This may be due to a decrease in the total crosslink density and different type of linkages in the dithiobiuret systems. When cured at 120°C, these properties are seen to improve. This is also shown by the increase in the total crosslink density and polysulphide linkages of these systems.

4. Chemical Characterization

It is well known that the mechanical properties of rubber vulcanizates depend very strongly on the crosslink density[14]. The nature of the crosslinks and the presence of other rubber-bound side products of vulcanization may also influence physical properties. In order to get more details of the vulcanization reaction of the systems containing dithiobiurets chemical characteristics of the vulcanizates were also evaluated. Total chemical crosslink density, different types of crosslinks like mono,di and polysulphide linkages, free sulphur and zinc sulphide sulphur were estimated. The results of the chemical characterization of systems containing TMTD alone, CBS alone, TMTD/thiourea system and the systems containing optimum concentration of dithiobiurets are given in Table 3.21. The total crosslink density and mono and di sulphidic linkages of the vulcanizates containing dithiobiurets cured at 150°C, are less than that of TMTD alone but the polysulphide linkages are higher. The higher tensile properties and some of the higher physical properties like resilience and tear strength can be due to this higher polysulphidic crosslink density. The crosslink density and concentration of different types of linkages are higher for DTB-III than for DTB-II. This may be the reason for higher physical properties obtained in the system containing DTB-III. Compairing to TMTD/thiourea system; systems containing DTB-II and DTB-III are giving less mono and di sulphidic linkages but the polysulphidic linkages are more. This explains the higher tensile strength obtained with dithiobiurets than with TMTD/thiourea.

Cured at 120°C, the total crosslink density and mono sulphide crosslinks are slightly lesser for DTB-II, compairing to TMTD or TMTD/thiourea system but the di and polysulphidic linkages are higher. For DTB-III total crosslink density is also improved. This accounts for the higher tensile strength obtained with dithiobiurets at 120°C. The free sulphur concentration is lower for DTB-III system indicating the more efficient utilization of sulphur in that system. The zinc sulphide sulphur concentration in systems containing dithiobiurets are lower than that in TMTD system, which indicates lesser concentration of mono sulphide linkage formed by desulphuration processes.

In the CBS/dithiobiuret systems the total crosslink density and different type of linkages like mono, di and poly sulphide crosslinks are lesser than in CBS alone when cured at 150°C,but at 120°C the crosslink densities are higher indicating the efficiency of the system at lower temperature. The free sulphur concentration is also lesser for dithiobiuret systemsindicating the effective utilization of sulphur in these systems at this temperature. However the lower con. of ZnS sulphur indicates the lower rate of desulphuration, indicating a lower concentration of mono and disulphidic linkages.

EFFECT OF FILLERS

Fillers are generally incorporated in rubber compounds for improved processability, reinforcement or cheapness. They are of two classes: reinforcing and non-reinforcing. Reinforcing fillers are used for enhancement of properties like tensile strength, abrasion resistance or tear strength whereas non-reinforcing fillers are incorporated to cheapen and stiffen the final product. Physical properties of the filler like particle size, surface area per unit weight, surface activity, electrical charge on the particle and chemical properties like pH& reactivity with accelerators will affect the vulcanizate properties. In general the best reinforcing fillers are those having the smallest particle size. The fundamental aspects of polymer-filler interaction have been studied in a number of polymers[15-18]. Pure gum natural rubber compounds, although high in physical strength are suitable for relatively few commercial applications. For most type of service, relatively large amounts of fillers are to be incorporated to increase hardness, stiffness, strength and resistance to tear or abrasion. In order to study the effect of various fillers in the sulphur vulcanization of natural rubber containing dithiobiurets, we have taken TMTD / dithiobiuret binary systems and vulcanizates were prepared with carbon black (different concentrations), precipitated silica and china clay. Curing studies were carried out at 150°C and various properties of the vulcanizates were evaluated:

1. Effect of Carbon black.

Carbon blacks are the most effective reinforcing fillers used in rubber industry[19-22]. They are essentially elemental carbon prepared by the partial combustion or thermal decomposition of liquid or gaseous hydro carbons. Depending on the process adopted for the preparation, carbon blacks are grouped as furnace blacks, thermal blacks, channel blacks and lamp blacks. For application where resistance to abrasion and maximum strength are required, fine carbon blacks are almost universally used. With the general purpose elastomers like natural rubber, high abrasion furnace (HAF) blacks with average particle size in the range 24-28 $m\mu$ are most widely used. It is known that carbon black contain active functional groups such as -OH, -COOH, $>C=O$, C=C[23-26] etc. During vulcanization carbon black enters a chemical reaction with sulphur, accelerators etc., participating in the formation of the vulcanized network. The introduction of carbon black into the rubber mixture results in an additional consumption of accelerators because of the adsorption of accelerators on the surface of the carbon black[27-28] particles. So more accelerator or a combination of more active accelerators has to be employed in the vulcanizates containing carbon black. In this context, we have tried TMTD/dithiobiuret systems, which are found to be an active accelerator combination in mixes containing various concentration of HAF black (N.330). Table 3.22 shows the formulation of the mixes. All the mixes contain 1.5 phr of TMTD as the primary accelerator. Mixes IA - ID contain 5, 10, 20 and 50 phr HAF black in which TMTD alone is taken as the accelerator. Mixes IIA - IID contain same sequence of HAF black in which TMTD and 0.5 phr thiourea are taken as accelerator. Mixes IIIA - IIID contain the same sequence of HAF black where TMTD and 0.5 phr DTB-II are taken as the accelerator combination & IVA - IVD contain the same amounts of HAF black where TMTD and 0.5 phr DTB-III forms the accelerator system.

The cure characteristics of the above mixes calculated from the cure curves at 150°C (fig. 3.18 - 3.21) are shown in Table 3.23. It can be seen from the

Table that in all the systems studied there is an increase in the Rheometric Torque with increase in the filler loading. Similarly there is a reduction in the induction time, Rheometric scorch time, and optimum cure time and a corresponding increase in the cure rate index which indicates an effective interaction of HAF black with polymer and vulcanization systems. Compared to the systems containing TMTD alone and TMTD/ thiourea, the systems containing DTB-II and DTB-III reduced the optimum cure time considerably. As in the case of gum vulcanizates, DTB-II is more active than DTB-III in black filled vulcanizates also. At higher filler loading there is substantial reduction in the optimum cure time and corresponding increase in the cure rate index. The reversion resistance of these systems are also quite high.

Table 3.24 shows the tensile properties of these systems. There is an increase in 300% modulus and tensile strength and a corresponding decrease in the elongation at break with increase in filler loading. The tensile properties are higher than that of thiourea system, but slightly lesser than that of TMTD alone. Other physical properties of the vulcanizates evaluated are given in Table 3.25. In all the systems, the general trend is that with increase in concentration of carbon black, hardness ~~and~~, tear strength, compression set, heat build up increases while resilience decreases as expected. In these properties also dithiobiurets give comparable values with that of TMTD alone or TMTD/thiourea systems. The results of the chemical characterisation of mixes containing 50 phr HAF black (N 330) is given in Table 3.21. The total crosslink density and di-and polysulphidic linkages in the systems containing dithiobiurets are lesser than that of TMTD alone but the monosulphidic linkages are higher. Compared to TMTD/thiourea system the monosulphide linkage is less but the di-and poly sulphide linkages are more. DTB-III is giving slightly more crosslink density than DTB-II. The lower free sulphur concentration of DTB-III system than that of DTB-II indicates a more effective utilization of sulphur. The increase in the zinc sulphide sulphur concentration is an indication of increased desulphuration process leading to shorter crosslinks.

2. Precipitated Silica

Precipitated silicas are the best non-black reinforcing fillers so far developed and come closest to carbon black in its reinforcing properties. They have particle size as fine as that of carbon black and they also have an extremely reactive surface. In mill mixing of silica loaded natural rubber compounds, some precautions are necessary to ensure good dispersion. Excessive milling may cause reduction in properties and hence a complete batch should be mixed and cut from the mill as quickly as possible. Precipitated silicas are highly adsorptive. Hence in formulating natural rubber compounds containing them it is necessary to use more than the normal quantity of accelerator or a combination of accelerator system which is more active. Because of this special characteristics of precipitated silica, we thought that the active binary systems containing dithiobiurets and TMTD will be an ideal choice for natural rubber vulcanization containing these fillers.

In our study of the systems 50 phr of precipitated silica is taken as the filler. Table 3.26 gives the composition of the various mixes. Mix VA contain 1.5 phr TMTD alone, VB contain 1.5 phr TMTD and 0.5 phr thiourea, VC contain 1.5 phr TMTD and 0.5 phr DTB-II and VD contain 1.5 phr TMTD and 0.5 phr DTB-III as accelerator. The cure characteristics of the above mixes calculated from the cure curves (Fig. 3.22) are shown in Table 3.28. It can be seen from the table that there is no significant reduction in cure time in the system containing dithiobiurets and we presume it to be due to the highly absorptive nature of the precipitated silica and cure retardation by silica[29-30]. Tensile properties are given in Table 3.30. It is seen that the tensile properties of the vulcanizates containing dithiobiurets are slightly better than that of TMTD/thiourea system, but there is no appreciable enhancement compared to that of TMTD alone. Other physical properties evaluated are given in Table 3.32.

Eventhough there is some improvement in compression set and heat build up, not much change in resilience, tear strength or hardness is recorded.

3. China Clay

Clays represent the largest volume nonblack filler used in rubber. They owe this popularity to a combination of low cost, low-to moderate reinforcement and benefits to processing especially extrusion and calendering. It has a pronounced stiffening effect and imparts hardness and fairly good abrasion resistance. Clays are the natural decomposition products of felspars and other aluminia silica minerals. Clays are known to reduce the cure rate of NR vulcanizates. So we thought it will be ideal to try the TMTD/dithiobiuret systems,which are shown to accelerate the vulcanization considerably;in NR compounds containing china clay.

We tried dithiobiurets DTB-II and DTB-III along with 1.5 phr TMTD as the accelerators. 50 phr of china clay is taken as the filler in all the systems. Table 3.27 gives the composition of mixes. Mix VIA contain TMTD alone, while mix VIB contain TMTD and 0.5 phr thiourea. Mix VIC contain 0.5 phr DTB-II and mix VID contain 0.5 phr DTB-III along with TMTD. The cure characteristics of the above mixes cured at 150°C are given in Table 3.29 and the cure curves in Fig. 3.23. It can be seen from the Table that there is no appreciable change in the Rheometric torque, or optimum cure time of the mixes containing dithiobiuret as is the case with precipitated silica. These results indicate that the system containing china clay is also rather unaffected by the presence of dithiobiurets in the accelerator system. The tensile properties like 300% modulus tensile strength and elongation at break are however seen to be slightly decreased (Table 3.31). Other physical properties are not much affected by these binary systems (Table 3.33).

TABLE 3.1

Formulation of Mixes

Ingredients	A_o	B_o	A_1	A_2	A_3	A_4	A_5
N R	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2
TMTD	1.5	1.5	--	1.5	1.5	1.5	1.5
Thiourea	--	0.5	--	--	--	--	--
DTB II	--	--	0.5	1.0	0.75	0.5	0.25
Sulphur	0.5	0.5	0.5	0.5	0.5	0.5	0.5

TABLE 3.2

Ingredients	A_o	B_o	A_1	A_2	A_3	A_4	A_5
N R	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2
TMTD	1.5	1.5	--	1.5	1.5	1.5	1.5
Thiourea	--	0.5	--	--	--	--	--
DTB-III	--	--	0.5	1.0	0.75	0.50	0.25
Sulphur	0.5	0.5	0.5	0.5	0.5	0.5	0.5

TABLE 3.3

Formulation of Mixes

Ingredients	C_o	C_1	C_2	C_3	C_4
N R	100	100	100	100	100
Zinc oxide	5	5	5	5	5
Stearic acid	2	2	2	2	2
C B S	1.5	1.5	1.5	1.5	1.5
DTB II	--	1.5	1.0	0.5	0.25
Sulphur	0.5	0.5	0.5	0.5	0.5

TABLE 3.4

Ingredients	C_o	D_1	D_2	D_3	D_4
N R	100	100	100	100	100
Zinc oxide	5	5	5	5	5
Stearic acid	2	2	2	2	2
C B S	1.5	1.5	1.5	1.5	1.5
DTB III	--	1.5	1.0	0.5	0.25
Sulphur	0.5	0.5	0.5	0.5	0.5

TABLE 3.5

Cure characteristics of mixes containing TMTD/DTB-II at 150°C

Mix No.	Min. Torque (dN.m)	Max. Torque (dN.m)	Induction time (t_1) (min.)	Rheometric scorch time(t_2) (min.)	Optimum cure time (t_{90}) (min.)	Cure rate index.	Reversion at 170°C (No.of units reverted in five minutes)
A_o	10	50	3.0	3.5	11.0	13.33	3.0
B_o	6	43	3.0	3.5	9.5	16.67	2.0
A_2	9	27	0.5	0.5	1.5	100.00	0.5
A_3	11	40	1.5	2.0	6.0	25.00	0.5
A_4	4	41	2.0	2.5	7.0	25.00	1.5
A_5	6	45	2.0	2.5	7.5	20.00	1.5

TABLE 3.6

Cure characteristics of mixes containing TMTD/DTB-II at 120°C

Mix No.	Min. Torque (dN.m)	Max. Torque (dN.m)	Induction time t_1 (min.)	Optimum cure time (t_{90}) (min.)	Cure rate index	Mooney Scorch time (t_5) (min.)
A_o	7	46	13.0	57.5	2.35	15.0
B_o	9	46	11.5	46.5	3.03	13.5
A_2	9	35	1.0	15.0	9.52	1.5
A_3	6	35	3.5	15.5	7.14	4.5
A_4	10	41	5.0	27.0	4.76	6.0
A_5	7	44	8.0	47.0	2.70	10.0

TABLE 3.7

Cure Characteristics of the Mixes containing TMTD/DTB-III at 150°C

Mix No.	Min. Torque (dN.m)	Max. Torque (dN.m)	Induction time (t_1) (min.)	Rheometric scorch time (t_2) (min.)	Optimum cure time (t_{90}) (min.)	Cure rate index	Reversion at 170°C (No.of units reverted in 5 minutes)
A_o	10	50	3.0	3.5	11.0	13.33	3
B_o	6	43	3.0	3.5	9.5	16.67	2
B_2	13	44	1.5	2.0	4.5	40.00	1
B_3	7	46	1.5	2.0	7.5	18.18	1
B_4	7	47	2.0	2.5	8.0	15.38	2
B_5	7	47	2.0	2.5	9.0	15.38	2

TABLE 3.8

Cure Characteristics of the Mixes containing TMTD/DTB-III at 120°C

Mix No.	Min. Torque (dN.m)	Max. Torque (dN.m)	Induction time,t_1 (min.)	Optimum cure time,t_{90} (min.)	Cure rate index	Mooney Scorch time (t_5) (min.)
A_o	7	46	13.0	57.5	2.35	15.0
B_o	9	46	11.5	46.5	3.03	13.5
B_2	14	47	7.5	35.0	4.00	10.0
B_3	9	44	8.5	46.0	2.94	11.0
B_4	11	46	10.0	54.5	2.32	11.5
B_5	8	46	11.0	56.5	2.30	13.0

TABLE 3.9

Cure Characteristics of the Mixes containing CBS/DTB-II at 150°C

Mix No.	Min. Torque (dN.m)	Max. Torque (dN.m)	Induction time (t_1) (min.)	Rheometric scorch time (t_2) (min.)	Optimum cure time, t_{90} min.	Cure rate index	Reversion at 170°C (No. of units reverted in 5 minutes.)
C_o	7.5	41.5	9.0	10.00	13.5	28.57	2
C_1	8.0	35.0	1.5	1.50	3.5	50.00	1
C_2	4.0	30.0	1.0	1.25	3.5	44.44	1
C_3	3.5	32.0	2.5	3.00	5.5	40.00	1
C_4	4.0	33.0	4.5	5.00	8.0	33.33	1

TABLE 3.10

Cure Characteristics of the Mixes containing CBS/DTB-II at 120°C

Mix No.	Min. Torque (dN.m)	Max. Torque (dN.m)	Induction time t_1 min.	Optimum cure time t_{90} min.	Cure rate index	Mooney scorch time t_5 min.
C_o	9	39	35.0	54.0	5.56	36.0
C_1	9	39	2.5	13.0	10.00	3.0
C_2	5	34	3.0	18.0	7.14	4.0
C_3	5	35	9.0	24.0	6.90	9.5
C_4	5	35	14.0	30.0	6.67	15.0

TABLE 3.11

Cure Characteristics of the Mixes containing CBS/DTB-III at 150°C

Mix No.	Min. Torque (dN.m)	Max. Torque (dN.m)	Induction time (t_1) (min.)	Rheometric scorch time, t_2 min.	Optimum cure time, t_{90} min.	Cure rate index	Reversion at 170°C (No.of units reverted in 5 minutes)
C_o	7.5	41.5	9.0	10.0	13.5	28.57	2.0
D_1	8.0	41.5	1.5	1.5	4.5	33.33	0.5
D_2	4.0	34.0	1.5	2.0	6.0	33.33	0.5
D_3	3.0	29.0	3.5	4.0	7.5	29.41	1.0
D_4	3.0	34.0	4.0	4.5	8.5	25.00	1.0

TABLE 3.12

Cure Characteristics of the Mixes containing CBS/DTB-III at 120°C

Mix No.	Min. Torque (dN.m)	Max. Torque (dN.m)	Induction time, t_1 min.	Optimum cure time, t_{90} min.	Cure rate index	Mooney Scorch time t_5 Min.
C_o	9	39	35.0	54.0	5.56	36.0
D_1	10	43	2.5	22.0	5.40	3.0
D_2	5	36	5.0	25.0	5.26	6.0
D_3	4	35	12.5	33.0	5.13	13.5
D_4	6	35	17.0	38.0	5.00	18.0

TABLE 3.13

Physical properties of the vulcanizates containing TMTD/DTB-II cured at 150°C

Mix No.	Hardness (Shore A)	Compression set (%)	Heat build up (ΔT^oC)	Resilience (%)	Tear strength (N/mm)
A_o	32	17.02	9	75.35	23.24
B_o	30	18.15	10	74.60	21.79
A_3	31	17.20	12	74.20	24.85
A_4	30	17.88	11	75.35	25.35
A_5	33	17.61	11	79.89	28.80

TABLE 3.14

Physical properties of the vulcanizates containing TMTD/DTB-II cured at 120°C

Mix No.	Hardness (Shore A)	Compression set (%)	Heat build up (ΔT^oC)	Resilience (%)	Tear strength (N/mm)
A_o	30	23.50	13	74.50	22.64
B_o	30	22.23	12	75.20	25.10
A_3	28	24.23	14	73.05	25.69
A_4	29	23.15	14	74.80	26.87
A_5	32	19.61	13	76.60	27.03

TABLE 3.15

Physical properties of the vulcanizates containing TMTD/DTB-III cured at 150°C

Mix No.	Hardness (Shore A)	Compression set (%)	Heat build up (ΔT °C)	Resilience (%)	Tear strength (N/mm)
A_o	32	17.02	9	75.35	23.24
B_o	30	18.15	10	74.60	21.79
B_2	34	16.14	12	77.33	31.10
B_3	35	15.90	14	78.60	31.55
B_4	36	15.30	10	81.08	36.75
B_5	36	14.80	9	81.25	42.00

TABLE 3.16

Physical properties of the vulcanizates containing TMTD/DTB-III cured at 120°C

Mix No.	Hardness (Shore A)	Compression set (%)	Heat build up (ΔT °C)	Resilience (%)	Tear strength (N/mm)
A_o	30	23.50	13	74.50	22.64
B_o	30	22.23	12	75.20	25.10
B_2	30	23.60	13	75.42	28.70
B_3	32	22.10	13	76.75	31.30
B_4	34	18.81	12	78.50	38.50
B_5	35	16.35	11	79.25	41.40

TABLE 3.17

Physical properties of the vulcanizates containing CBS/DTB-II cured at 150°C

Mix No.	Hardness (Shore A)	Compression set (%)	Heat build up (ΔT °C)	Resilience (%)	Tear strength (N/mm)
C_o	28	33.82	33	72.38	26.50
C_1	26	42.81	20	70.90	24.40
C_2	24	46.11	24	67.56	22.70
C_3	24	44.85	23	71.66	24.80
C_4	25	39.93	20	72.38	25.40

TABLE 3.18

Physical properties of the vulcanizates containing CBS/DTB-II cured at 120°C

Mix No.	Hardness (Shore A)	Compression set (%)	Heat build up (ΔT °C)	Resilience (%)	Tear strength (N/mm)
C_o	26	45.57	35	70.91	25.70
C_1	27	36.25	18	73.85	26.20
C_2	26	40.18	22	72.50	24.40
C_3	26	38.60	22	71.20	24.60
C_4	27	37.95	21	70.91	25.20

TABLE 3.19

Physical properties of the vulcanizates containing CBS/DTB-III cured at 150°C

Mix No.	Hardness (Shore A)	Compression set (%)	Heat build up (ΔT °C)	Resilience (%)	Tear strength (N/mm)
C_o	28	33.82	33	72.38	26.50
D_1	28	39.26	24	72.04	26.10
D_2	26	43.30	26	70.16	25.50
D_3	25	45.07	28	70.08	25.90
D_4	28	39.86	27	70.99	26.02

TABLE 3.20

Physical properties of the vulcanizates containing CBS/DTB-III cured at 120°C

Mix No.	Hardness (Shore A)	Compression set (%)	Heat build up (ΔT °C)	Resilience (%)	Tear strength (N/mm)
C_o	26	45.57	35	70.51	25.70
D_1	30	34.25	20	73.40	33.50
D_2	27	38.15	23	71.80	28.05
D_3	27	39.46	25	71.35	30.90
D_4	26	40.78	28	70.91	26.80

TABLE 3.21

Chemical Characterization of Vulcanizates.

Cure temperature	Mix No.	Total cross-link density (m.mole/Kg RH)	Mono sulphide linkages (m.mole/Kg RH)	Disulphide linkages (m.mole/Kg RH)	Poly sulphide linkages (m.mole/Kg RH)	Free sulphur con. (m.mole/Kg RH)	Zinc sulphide sulphur con. (m.mole/Kg RH)
150	A_o	60.5	33.8	13.8	12.9	13.50	10.60
	B_o	54.2	34.8	14.2	5.2	19.30	11.50
	A_4	50.9	25.5	11.8	13.6	18.75	6.50
	B_3	58.8	28.5	12.5	17.8	13.10	8.20
120	A_o	57.4	35.6	13.2	8.6	14.40	12.50
	B_o	56.9	28.2	13.0	15.7	14.50	7.60
	A_4	52.0	26.9	14.6	10.5	15.65	7.20
	B_3	62.1	30.1	14.0	17.5	10.90	5.15
150	C_o	50.8	23.1	12.5	15.2	6.00	4.50
	C_3	30.6	16.2	6.2	8.2	7.60	3.20
	D_2	47.4	23.7	13.4	10.3	6.35	4.90
120	C_o	32.4	15.2	6.2	11.0	9.30	3.0
	C_3	35.5	14.9	6.2	14.4	8.40	2.9
	D_2	39.9	13.6	5.9	20.4	7.20	2.5
150	ID	69.7	30.1	22.2	17.4	5.15	4.40
	IID	61.3	32.8	16.1	12.4	6.70	9.40
	IIID	60.3	31.3	15.5	13.5	8.50	6.45
	IVD	62.5	31.6	18.0	12.9	6.30	7.30

TABLE 3.22

Formulation of mixes containing carbon black

Ingredients	IA	IB	IC	ID	IIA	IIB	IIC	IID	IIIA	IIIB	IIIC	IIID	IVA	IVB	IVC	IVD
N R	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
HAF black	5	10	20	50	5	10	20	50	5	10	20	50	5	10	20	50
Naphthenic oil	0.5	1	2	5	0.5	1	2	5	0.5	1	2	5	0.5	1	2	5
T M T D	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Thiourea	-	-	-	-	0.5	0.5	0.5	0.5	-	-	-	-	-	-	-	-
DTB-II	-	-	-	-	-	-	-	-	0.5	0.5	0.5	0.5	-	-	-	-
DTB-III	-	-	-	-	-	-	-	-	-	-	-	-	0.5	0.5	0.5	0.5
Sulphur	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5

TABLE 3.23

Cure characteristics of mixes containing carbon black

Mix No.	Min. Torque (dN.m)	Max. Torque (dN.m)	Induction time (t_1) (min.)	Rheometric scorch time, t_2 (min.)	Optimum cure time t_{90} (min)	Cure rate index	Reversion at 170°C (No. of units reverted in 5 min.)
IA	3.5	44	3.0	3.50	7.0	28.57	1
IB	3.5	46	3.0	3.50	7.0	28.57	2
IC	4.0	50	2.5	2.75	6.0	30.77	2
ID	8.0	67	2.0	2.25	5.0	36.36	2
IIA	4.0	39	2.0	2.50	5.5	33.33	2
IIB	4.0	43	2.0	2.25	5.0	36.36	2
IIC	5.0	48	2.0	2.25	5.0	36.36	3
IID	7.0	61	1.5	2.00	4.0	50.00	3
IIIA	4.0	37	1.3	1.50	3.5	50.00	1
IIIB	5.0	41	1.3	1.50	3.5	50.00	1
IIIC	5.0	46	1.3	1.50	3.0	66.67	1
IIID	8.0	60	1.3	1.50	2.8	80.00	2
IVA	3.0	41	2.0	2.50	5.5	33.33	1
IVB	3.0	44	2.0	2.25	5.0	36.36	1
IVC	4.0	46	2.0	2.25	4.5	44.44	1
IVD	6.5	63	1.5	1.75	4.0	44.44	2

TABLE 3.24

Tensile properties of the vulcanizates containing carbon black

Mix No.	300% Modulus (MPa)			Tensile strength (MPa)			Elongation at break (%)		
	B.A	A.A	% Rtn.	B.A	A.A	% Rtn.	B.A	A.A	% Rtn.
IA	2.14	2.04	95.33	19.2	18.4	95.83	858.29	770.98	89.83
IB	2.93	2.83	96.59	21.2	20.9	98,58	765.57	754.74	98.59
IC	5.60	5.50	98.21	23.6	22.15	93.86	756.42	686.89	90.80
ID	13.87	12.8	92.29	25.6	22.90	89.45	512.29	455.63	88.94
IIA	1.98	1.80	90.91	14.7	13.05	88.78	838.21	744.28	88.79
IIB	2.78	2.55	91.73	17.1	16.4	95.91	765.57	699.18	91.33
IIC	5.00	4.70	94.0	19.4	19.35	99.74	642.48	620.72	96.61
IID	13.55	11.4	84.13	22.20	18.83	84.82	515.55	376.59	73.05
IIIA	2.28	1.89	82.89	18.3	15.2	83.06	865.39	794.50	91.81
IIIB	3.23	2.55	78.95	21.3	20.2	99.84	857.64	791.21	92.25
IIIC	5.25	3.90	74.29	23.1	22.6	97.84	731.43	684.46	93.58
IIID	14.14	10.50	74.26	24.2	23.1	95.45	565.13	399.86	70.76
IVA	2.61	1.82	69.73	14.4	14.01	96.82	810.77	713.41	87.99
IVB	3.51	2.83	80.63	19.2	18.95	98.70	776.67	710.28	91.45
IVC	5.65	5.10	90.26	22.3	19.3	86.55	768.12	670.28	87.24
IVD	13.60	11.80	86.76	23.0	19.3	83.91	498.13	371.31	74.54

TABLE 3.25

Other physical properties of the vulcanizates containing carbon black

Mix No.	Hardness (Shore A)	Compression set (%)	Heat build up (ΔT °C)	Resilience (%)	Tear strength (N/mm)
IA	36	18.56	15	56.40	39.30
IB	37	22.86	15	55.38	43.20
IC	43	23.55	18	55.07	57.80
ID	61	27.93	32	43.97	82.20
IIA	32	27.98	22	55.72	31.70
IIB	35	28.55	22	55.07	42.50
IIC	38	28.97	23	54.42	54.50
IID	58	29.05	23	40.53	72.30
IIIA	32	24,09	20	49.37	37.25
IIIB	35	26.39	21	48.14	42.50
IIIC	38	28.77	26	46.94	57.35
IIID	58	35.45	34	39.98	76.50
IVA	33	22.14	17	53.16	38.20
IVB	36	24.63	17	49.37	42.50
IVC	42	28.47	19	46.94	57.75
IVD	60	29.83	32	38.31	71.70

TABLE 3.26

Formulation of mixes containing precipitated silica

Ingredients	VA	VB	VC	VD
N R	100	100	100	100
Zinc oxide	5	5	5	5
Stearic acid	2	2	2	2
Precipitated silica	50	50	50	50
Naphthenic oil	5	5	5	5
T M T D	1.5	1.5	1.5	1.5
Thiourea	-	0.5	-	-
D T B II	-	-	0.5	-
D T B III	-	-	-	0.5
Sulphur	0.5	0.5	0.5	0.5

TABLE 3.27

Formulation of mixes containing china clay

Ingredients	VIA	VIB	VIC	VID
N R	100	100	100	100
Zinc oxide	5	5	5	5
Stearic acid	2	2	2	2
Clay	50	50	50	50
Naphthenic oil	5	5	5	5
T M T D	1.5	1.5	1.5	1.5
Thiourea	-	0.5	-	-
D T B II	-	-	0.5	-
D T B III	-	-	-	0.5
Sulphur	0.5	0.5	0.5	0.5

TABLE 3.28

Cure characteristics of mixes containing precipitated silica

Mix No.	Min. Torque (dN.m)	Max. Torque (dN.m)	Induction time, t_1 (min)	Rheometric scorch time, t_2 (min)	Optimum cure time, t_{90} min.	Cure rate index	Reversion at 170°C (No. of units reverted in 5 minutes)
VA	3	43	1.5	1.75	3.5	57.14	11
VB	4	36	1.5	1.75	3.5	57.14	9
VC	4	41	1.5	1.75	4.0	44.44	9
VD	5	45	1.5	1.75	4.0	44.44	9

TABLE 3.29

Cure characteristics of mixes containing china clay

Mix No.	Min. Torque (dN.m)	Max. Torque (dN.m)	Induction (min) (t_1)	Rheometric scorch time, t_2 (Min.)	Optimum cure time, t_{90} min.	Cure rate index	Reversion at 170°C (No. of units reverted in 5 minutes)
VIA	2.5	41	2.00	2.5	5.5	33.33	2
VIB	2.0	37	1.50	1.75	5.0	30.77	3
VIC	4.0	38	1.75	2.0	4.5	40.00	1
VID	4.0	41	1.75	2.0	4.5	40.00	2

TABLE 3.30

Tensile properties of the vulcanizates containing precipitated silica

Mix No.	300% Modulus (MPa)			Tensile strength (MPa)			Elongation at break (%)		
	B,A	A.A	%Rtn	B.A	A.A	% Rtn	B.A	A.A	% Rtn
VA	7.63	6.90	90.43	15.93	14.75	92.59	506.79	456.14	90.01
VB	6.50	5.10	78.46	12.60	11.23	89.13	479.24	416.61	86.93
VC	7.00	5.57	79.57	15.20	13.50	88.82	561.05	405.07	72.20
VD	7.70	5.70	87.01	15.40	14.20	92.21	573.23	460.92	80.41

TABLE 3.31

Tensile properties of the vulcanizates containing china clay

Mix No.	300% Modulus (MPa)			Tensile strength (MPa)			Elongation at break (%)		
	B.A	A.A	% Rtn	B.A	A.A	% Rtn	B.A	A.A	% Rtn
VIA	4.26	3.85	90.38	14.80	12.50	84.46	546.85	514.40	94.07
VIB	3.91	3.51	89.77	13,70	11.40	83.21	523.71	482.86	92.20
VIC	3.82	3.71	97.12	12.45	10.70	85.94	471.27	443.42	94.09
VID	4.18	4.12	98.56	14.0	12.40	88.21	531.68	510.21	95.90

TABLE 3.32

Other physical properties of the vulcanizates containing precipitated silica

Mix No.	Hardness (Shore A)	Compression set (%)	Heat build up (ΔT °C)	Resilience (%)	Tear strength (N/mm)
VA	47	16.22	51	56.40	43.65
VB	43	14.41	46	49.98	37.75
VC	41	12.94	48	51.26	41.25
VD	42	12.34	38	51.89	41.60

TABLE 3.33

Other physical properties of the vulcanizates containing china clay

Mix No.	Hardness (Shore A)	Compression set (%)	Heat build up (ΔT °C)	Resilience (%)	Tear strength (N/mm)
VIA	42	13.81	13	64.49	30.20
VIB	39	14.95	19	63.81	29.95
VIC	37	13.19	18	58.38	28.55
VID	38	14.22	20	63.13	32.35

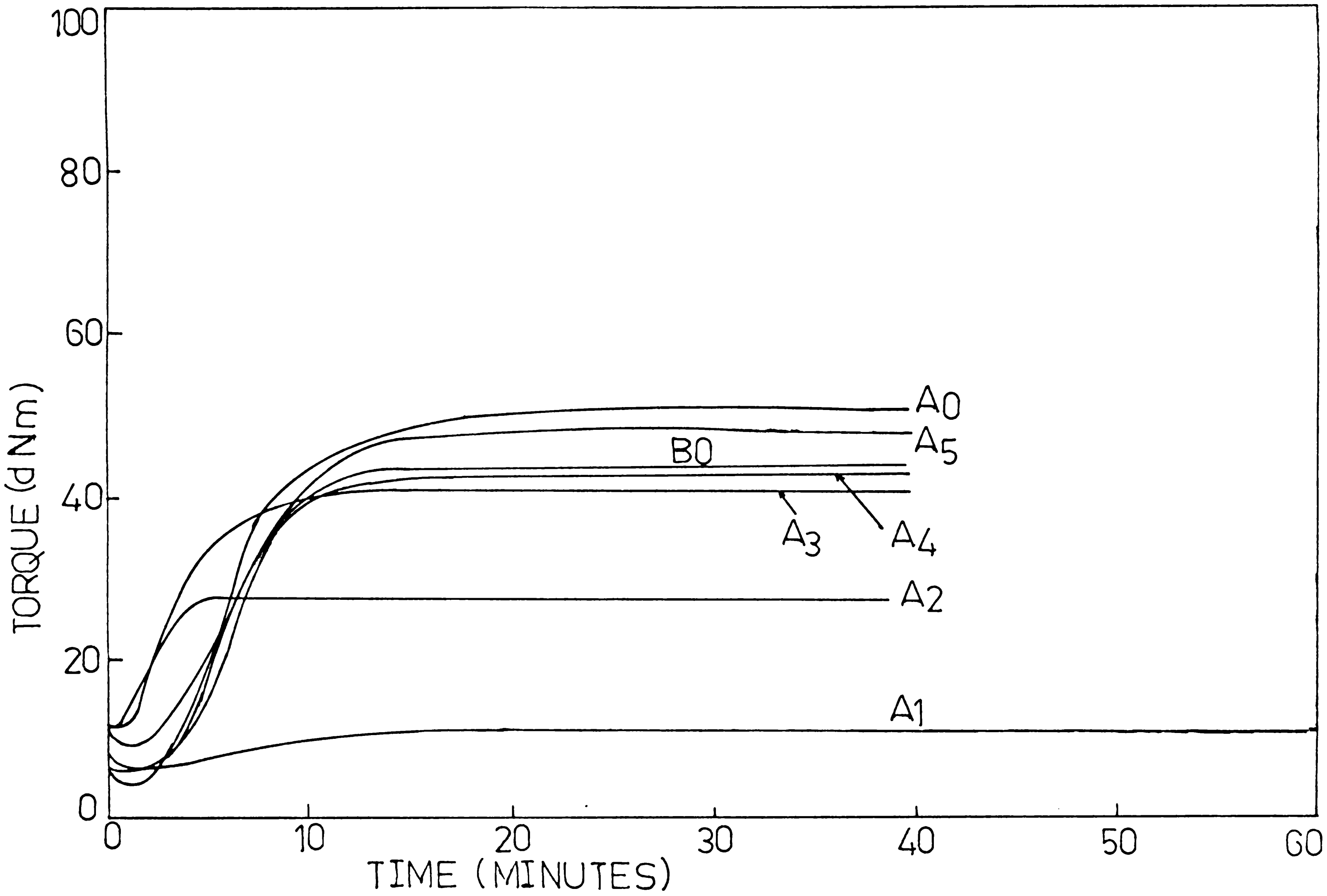

Fig. 3.1 : Rheographs of the mixes containing TMTD/DTB-II at 150°C. (Ref. Tables 3.1 & 3.5)

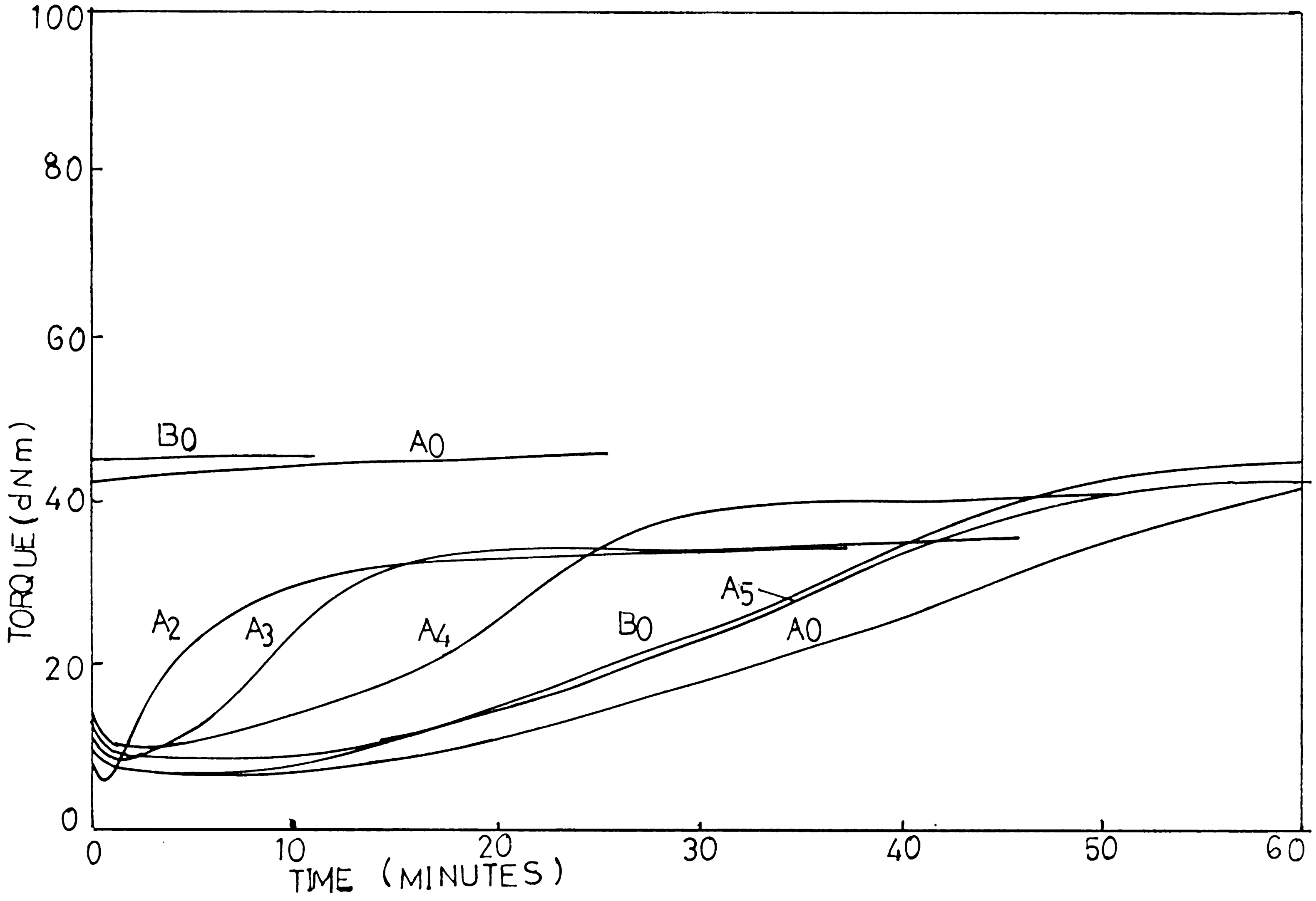

Fig. 3.2 : Rheographs of the mixes containing TMTD/DTB-II at 120°C .
(Ref: Tables 3,1 and 3.6)

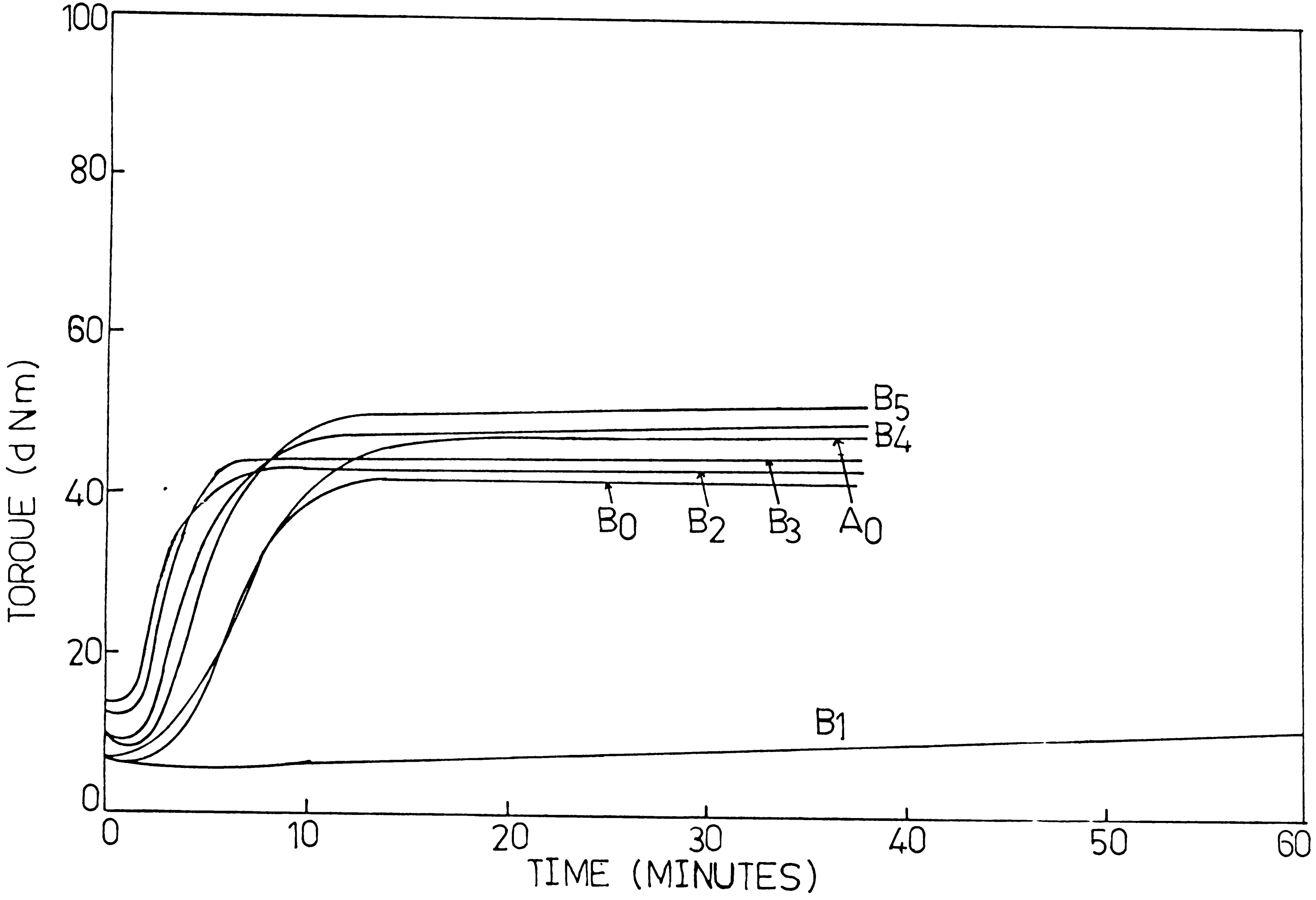

Fig. 3.3 : Rheographs of the mixes containing TMTD/DTB-III at 150°C (Ref: Tables 3.2 & 3.7)

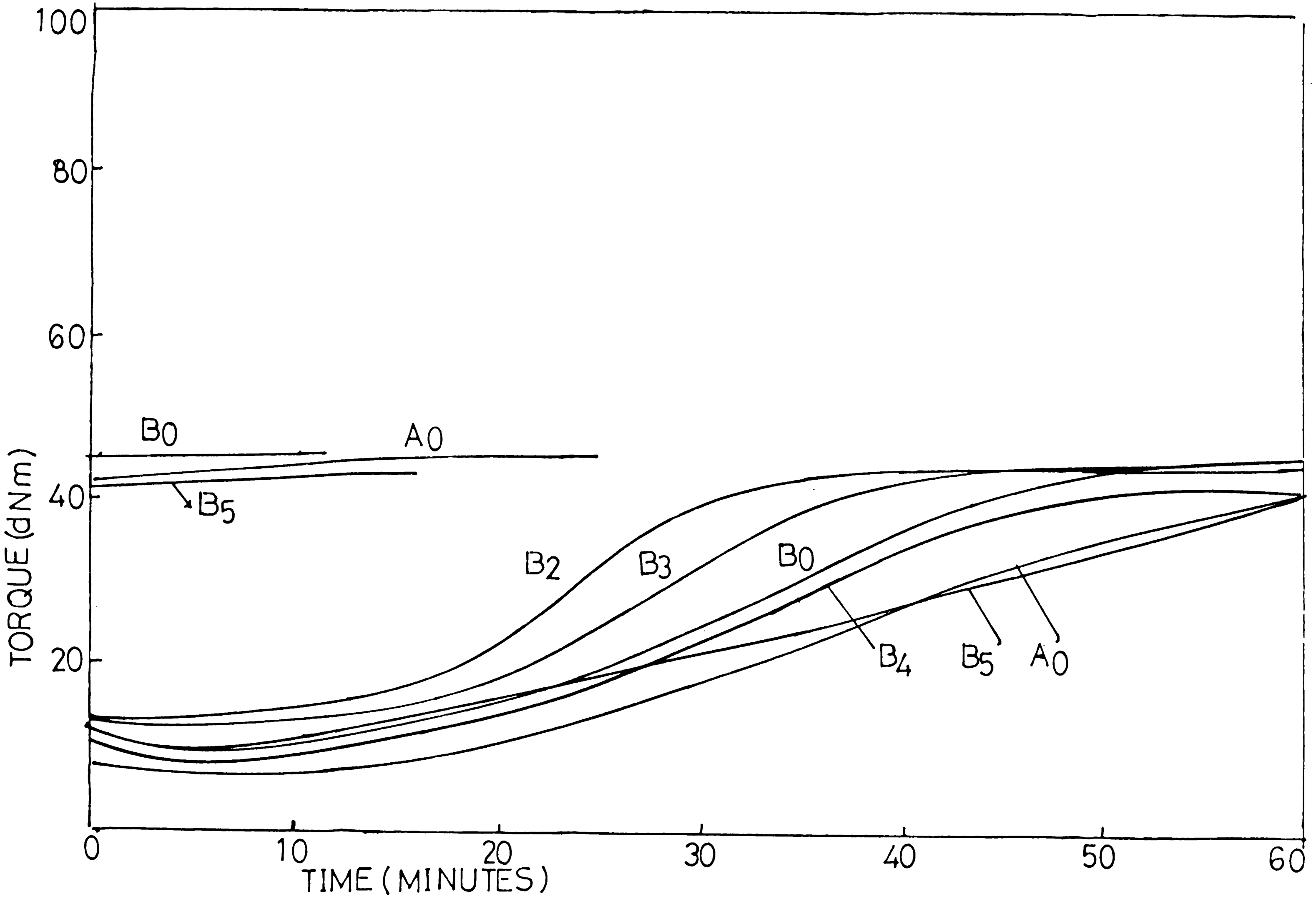

Fig. 3.4 : Rheographs of the mixes containing TMTD/DTB-III at 120°C (Ref: Tables 3.2 and 3.8)

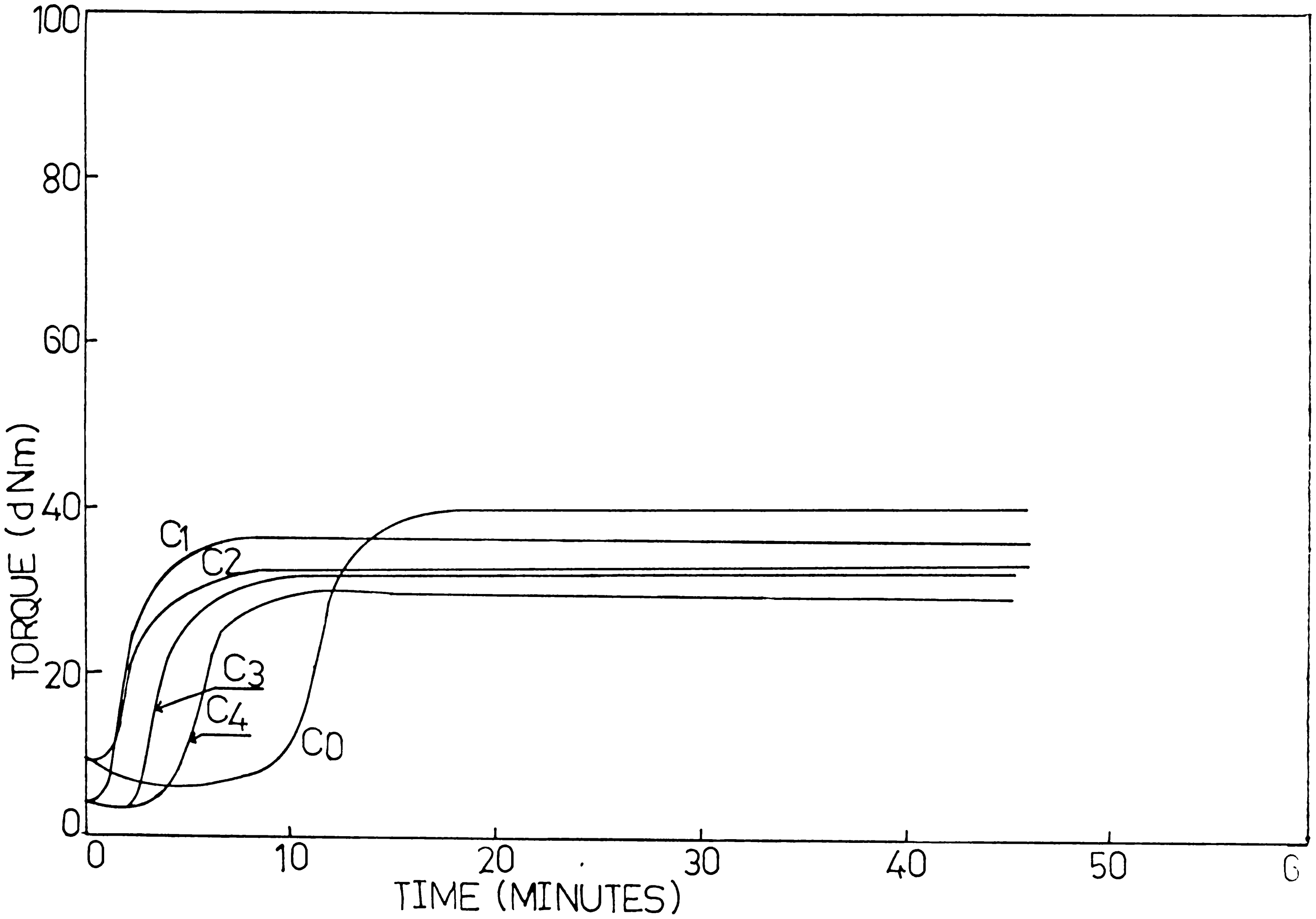

Fig. 3.5 : Rheographs of the mixes containing CBS/DTB-II at 150°C
(Ref: Tables 3.3 & 3.9)

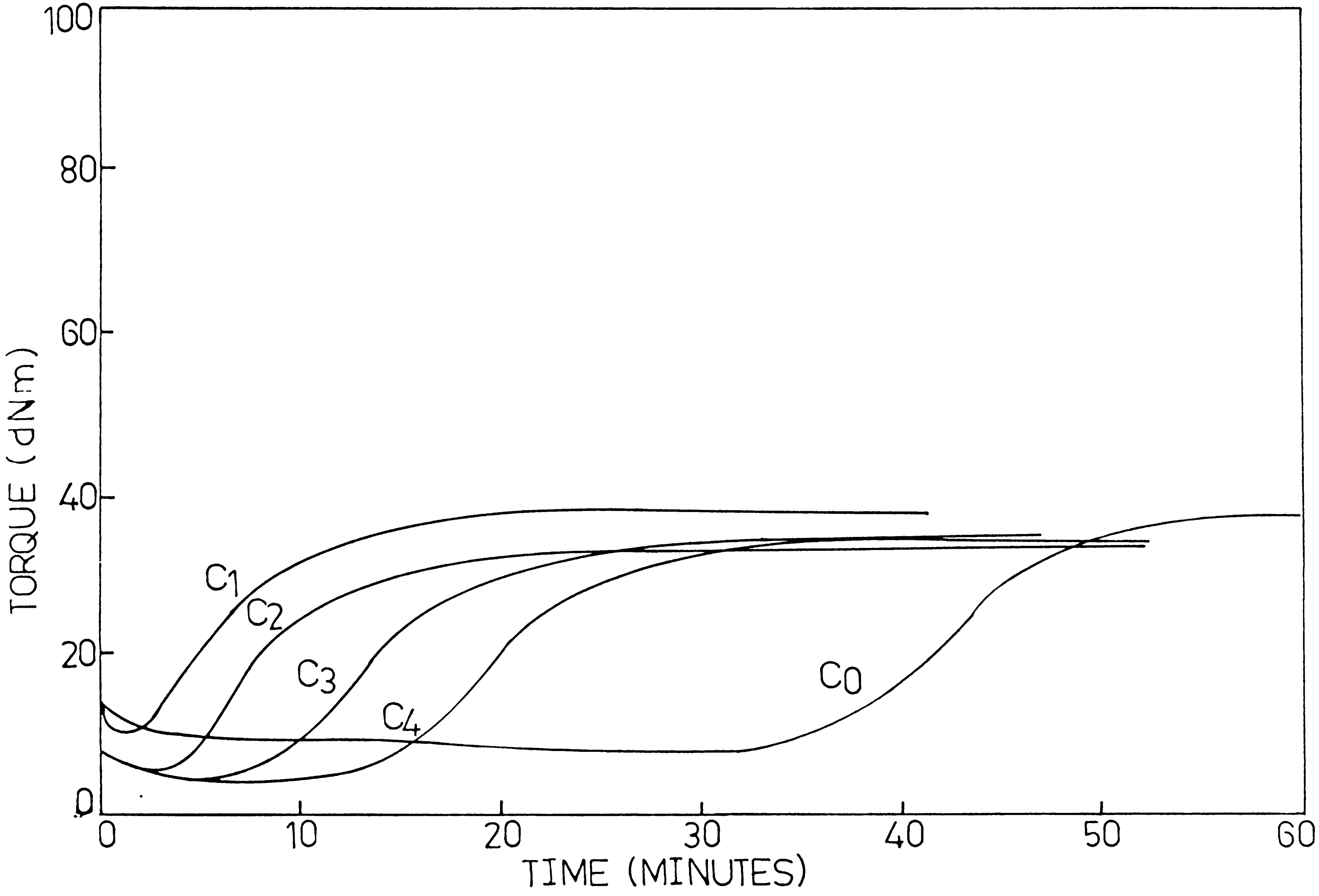

Fig. 3.6 : Rheographs of the mixes containing CBS/DTB-II at 120°C
(Ref: Tables 3.3 & 3.10)

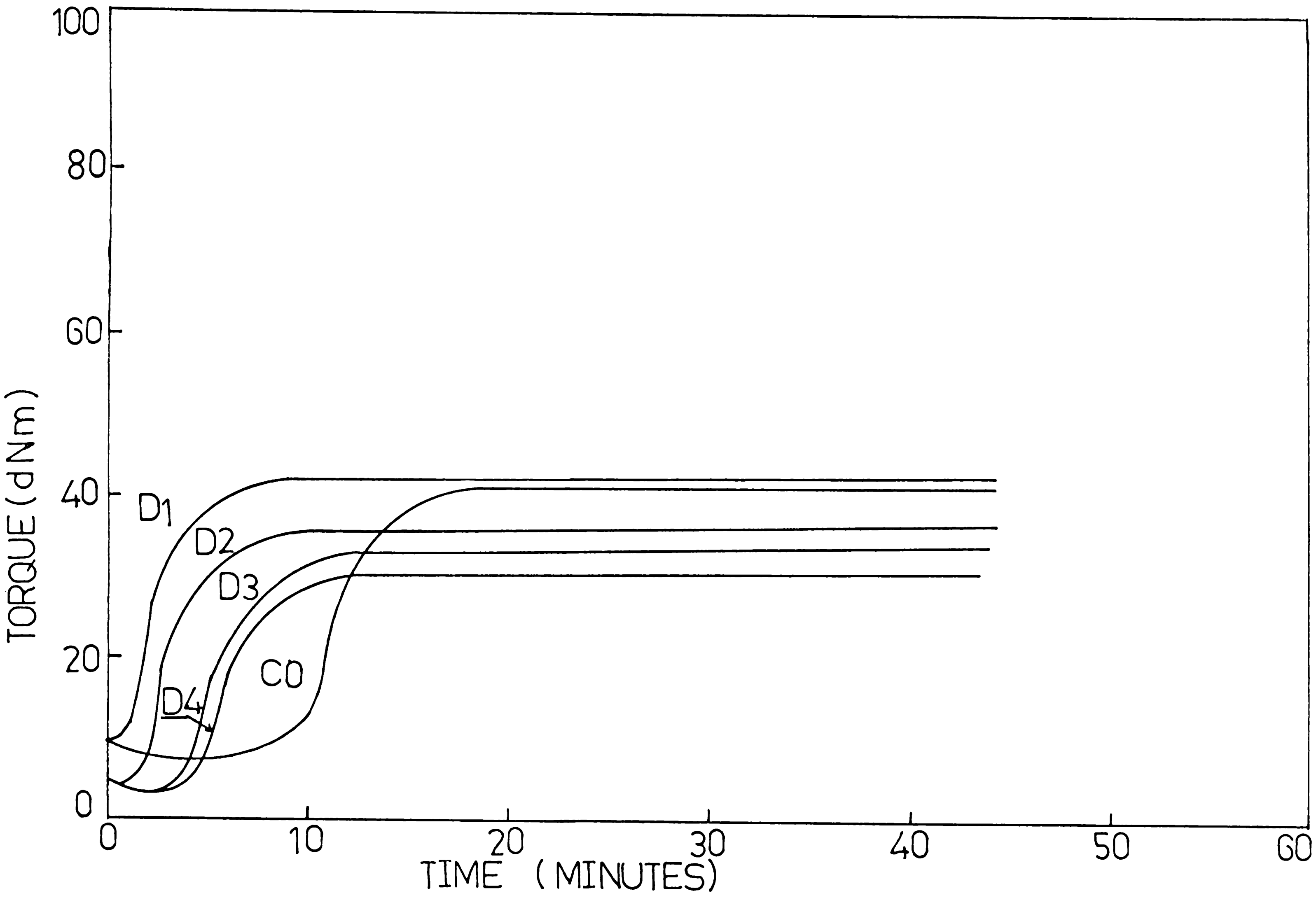

Fig. 3.7 : Rheographs of the mixes containing CBS/DTB-III at 150°C (Ref: Tables 3.4 & 3.11)

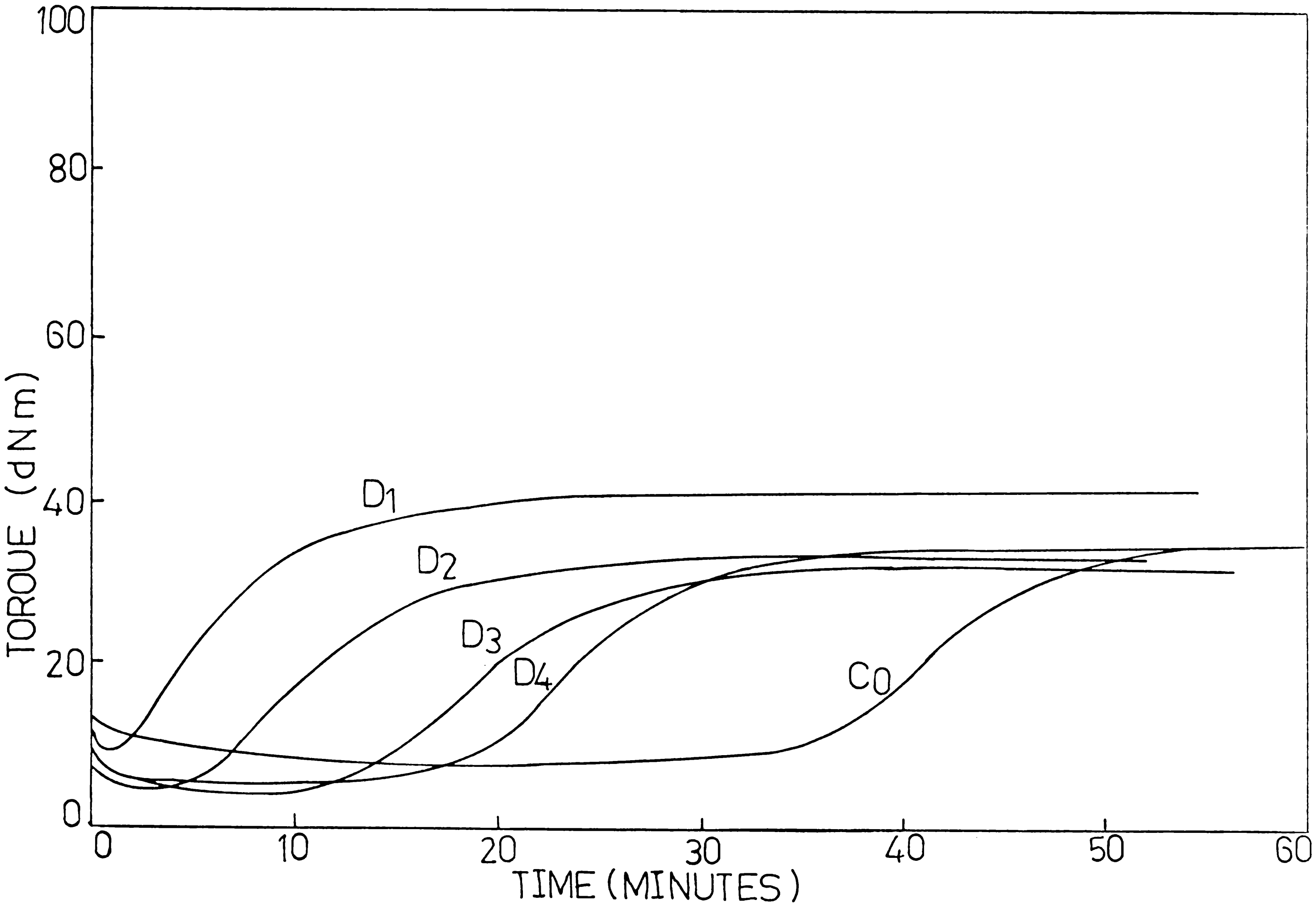

Fig. 3.8 : Rheographs of the mixes containing CBS/DTB-III at 120°C (Ref: Tables 3.4 & 3.12)

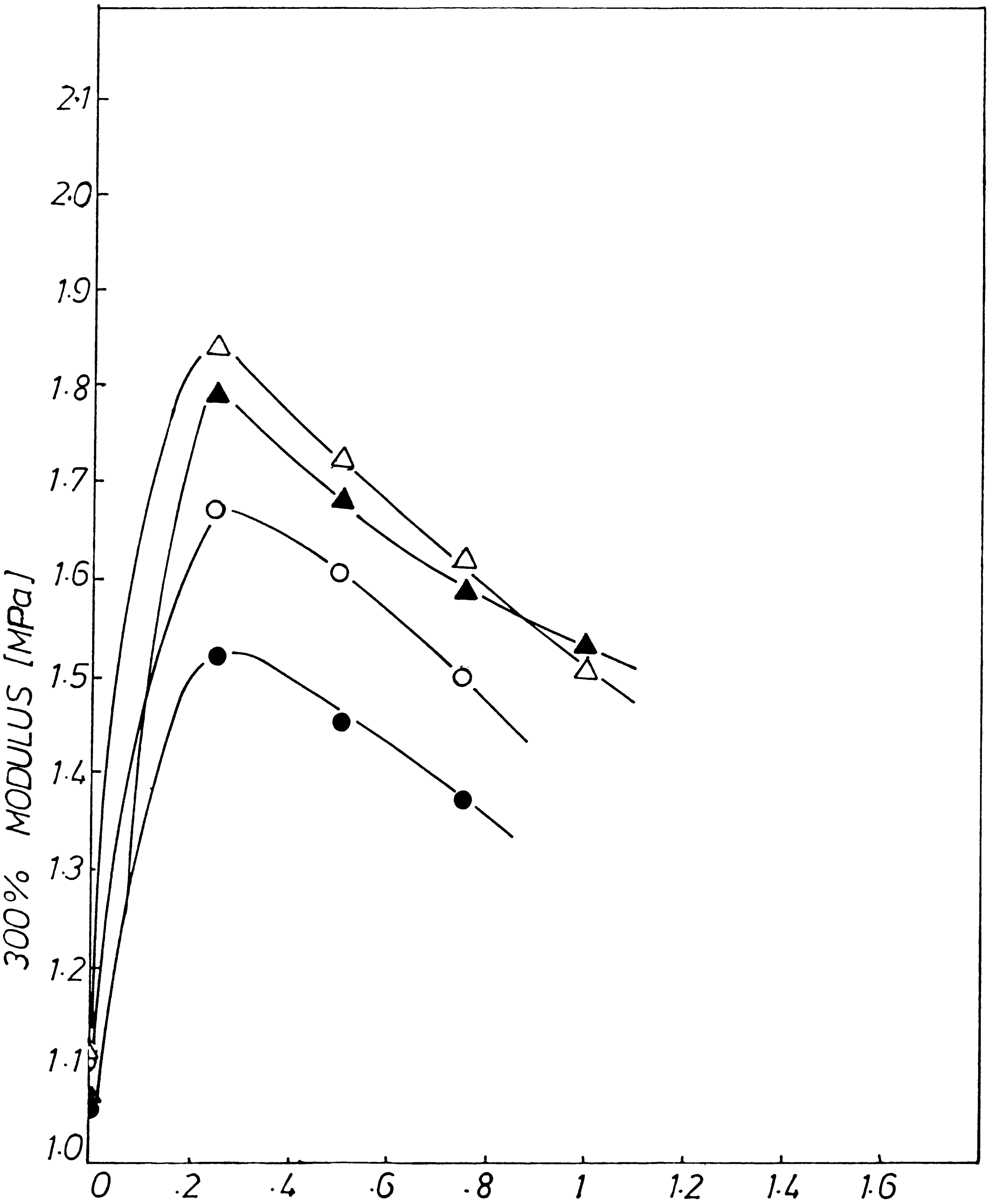

Fig. 3.9 : Variation of 300% modulus of vulcanizates containing TMTD/Dithiobiurets with con. of dithiobiurets; (●) TMTD/DTB-II cured at 120°C; (○) TMTD/DTB-II cured at 150°C; (▲) TMTD/DTB-III cured at 120°C (△) TMTD/DTB-III cured at 150°C.

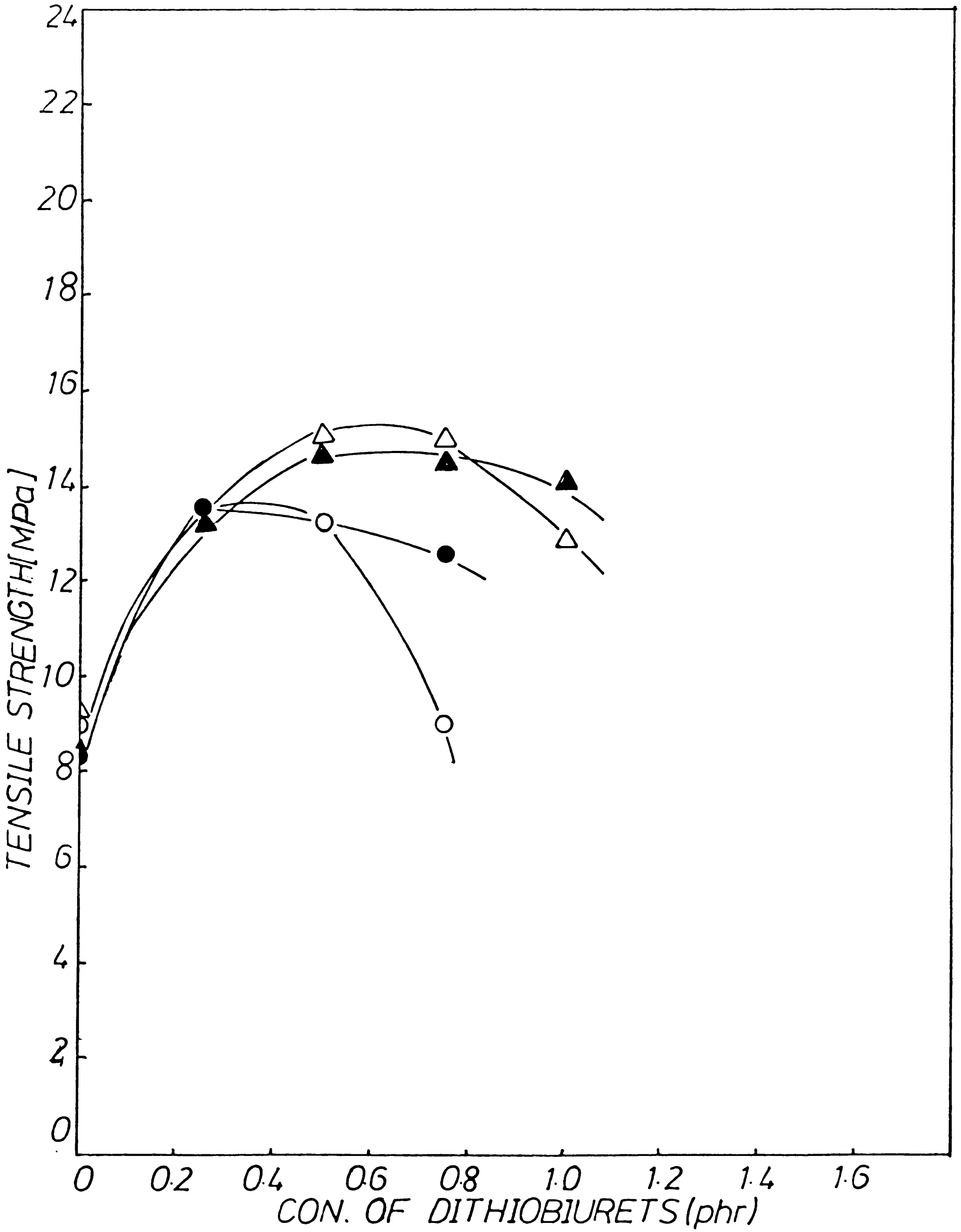

Fig. 3.10: Variation of Tensile strength of vulcanizates containing TMTD/dithiobiurets with con. of dithiobiurets (●) TMTD/DTB-II cured at 120°C; (○) TMTD/DTB-II cured at 150°C; (▲) TMTD/DTB-III cured at 120°C; (△) TMTD/DTB-III cured at 150°C.

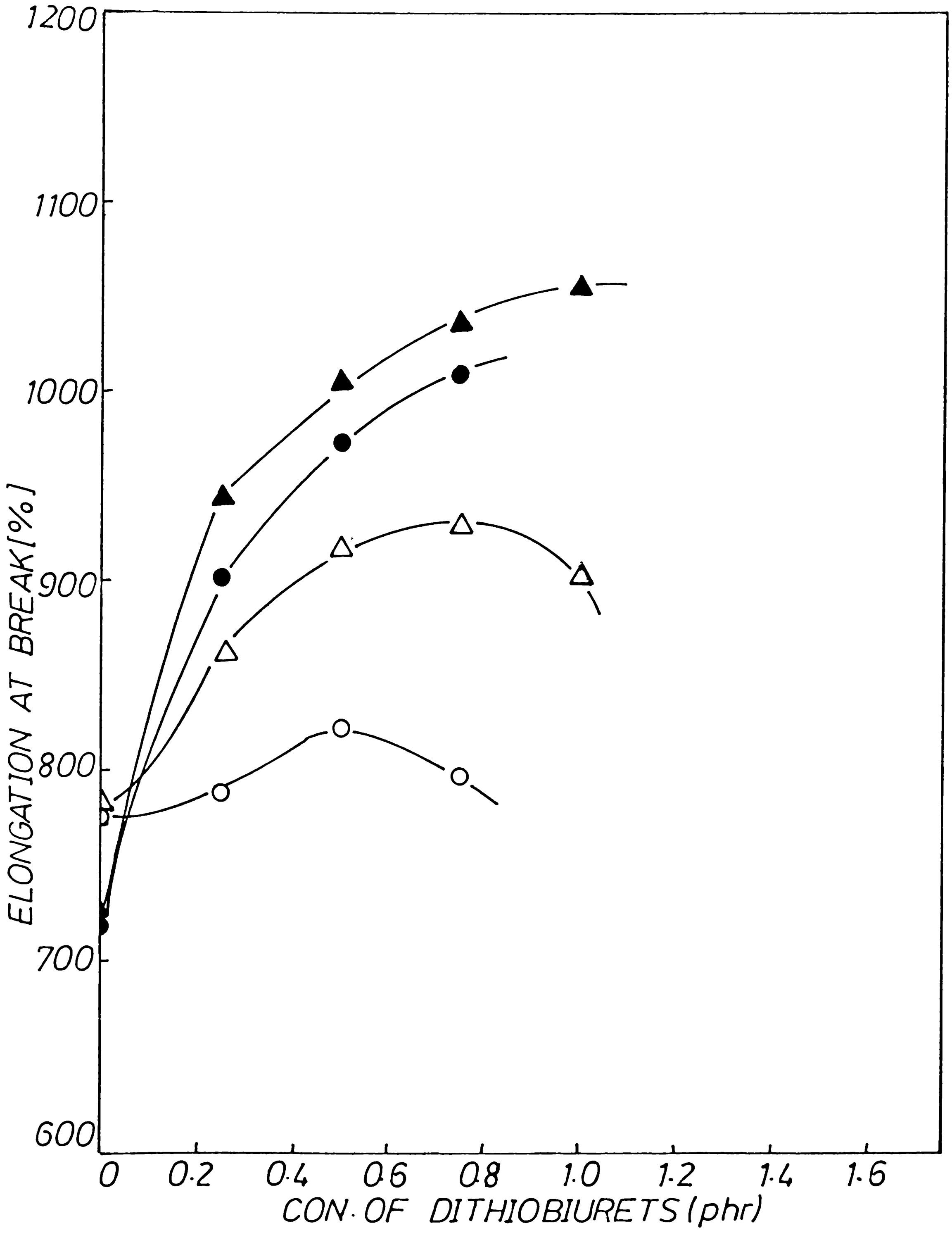

Fig. 3.11: Variation of Elongation at break of vulcanizates containing TMTD/dithiobiurets with con. of dithiobiurets; (●) TMTD/DTB-II cured at 120°C; (○) TMTD DTB-II cured at 150°C; (▲) TMTD/BTB-III cured at 120°C; (△) TMTD/DTB-III cured at 150°C.

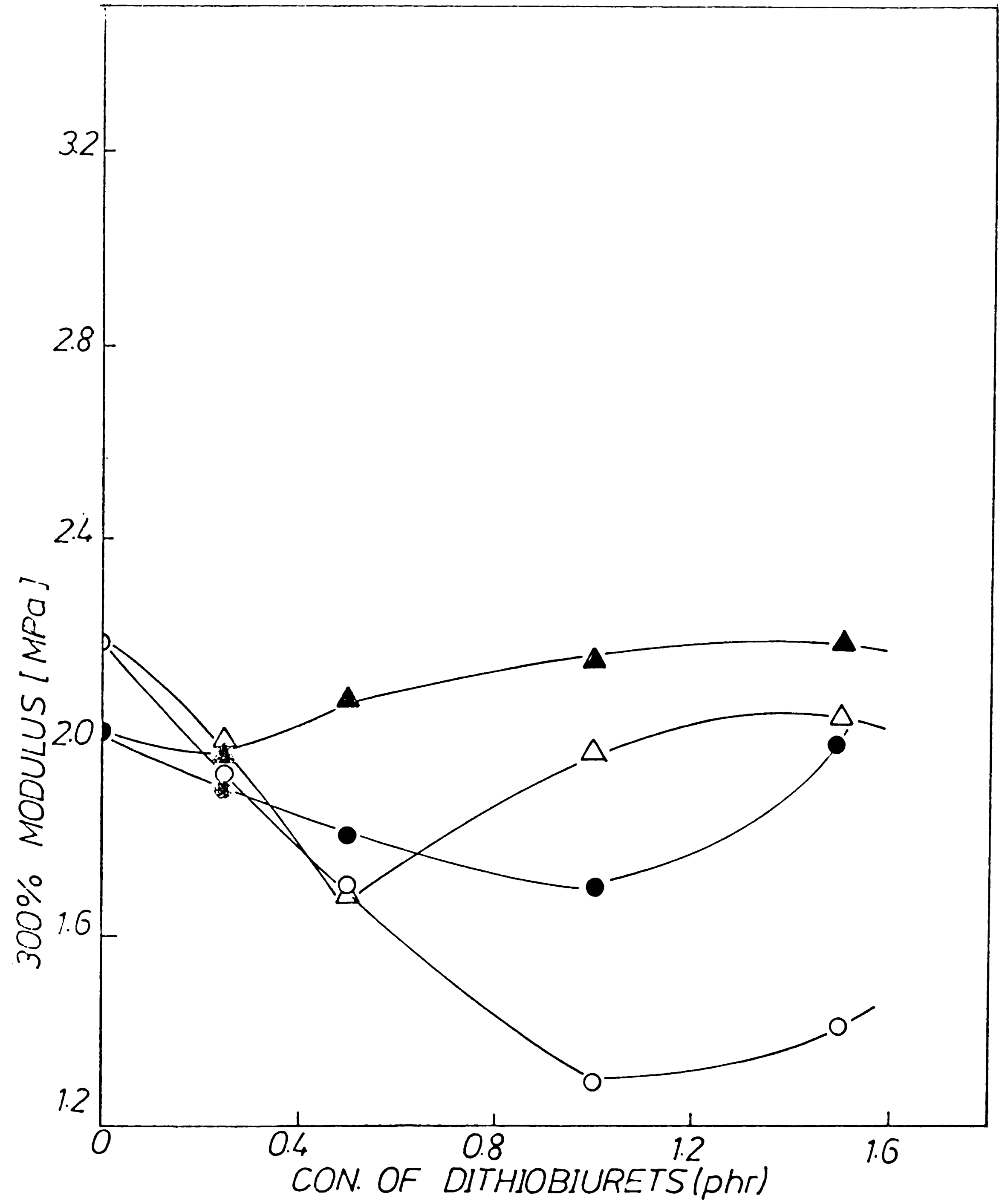

Fig.3.12: Variation of 300% modulus ofvulcanizates containing CBS/dithiobiurets with con. of dithiobiurets. (●) CBS/DTB-II cured at 120°C (○) CBS/DTB-II cured at 150°C; (▲) CBS/DTB-III cured at 120°C; (△) CBS/DTB-III cured at 150°C,

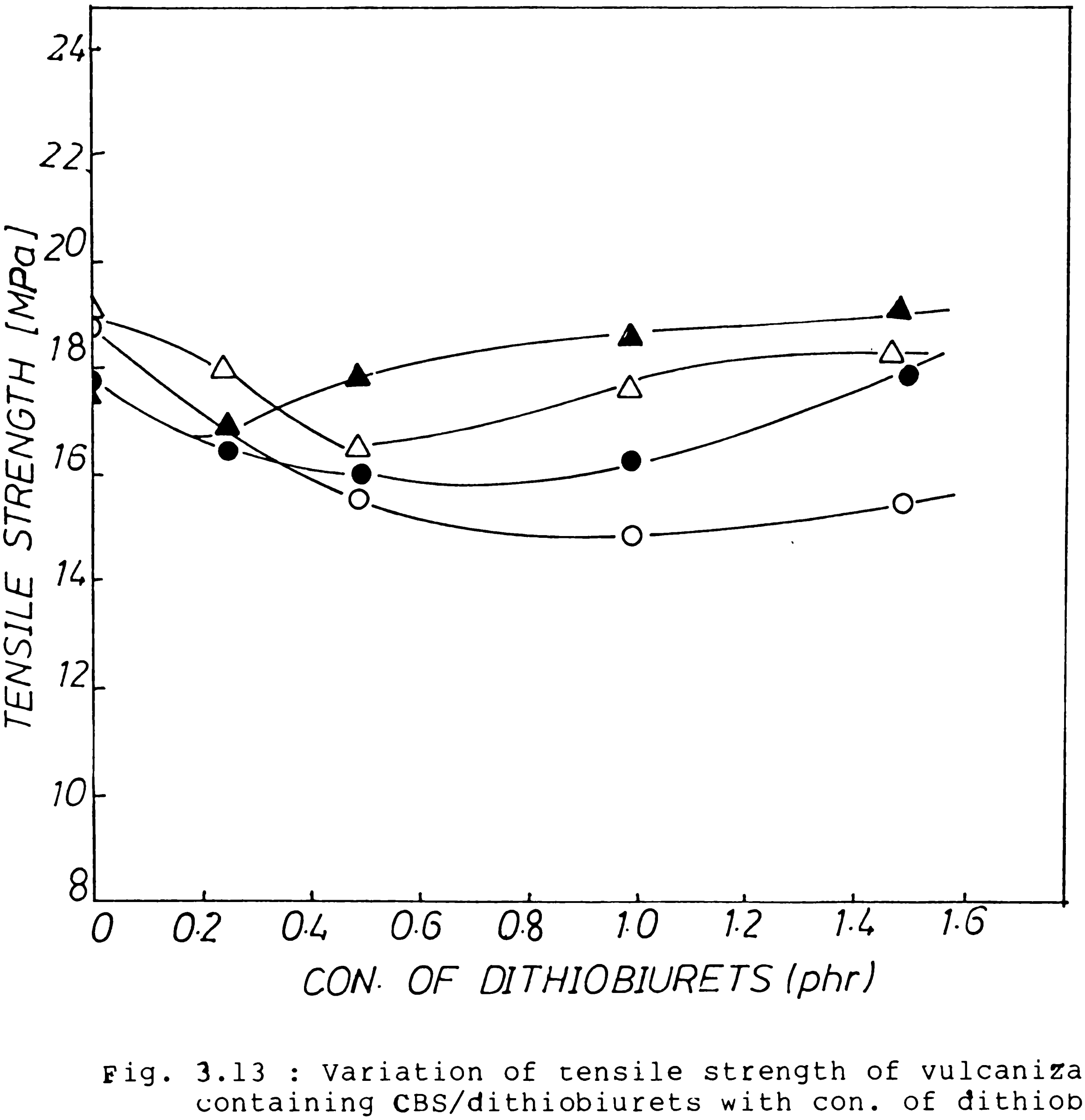

Fig. 3.13 : Variation of tensile strength of vulcanizates containing CBS/dithiobiurets with con. of dithiobiurets (●) CBS/DTB-II cured at 120°C; (○) CBS/DTB-II cured at 150°C; (▲) CBS/DTB-III cured at 120°C; (△) CBS/DTB-III cured at 150°C.

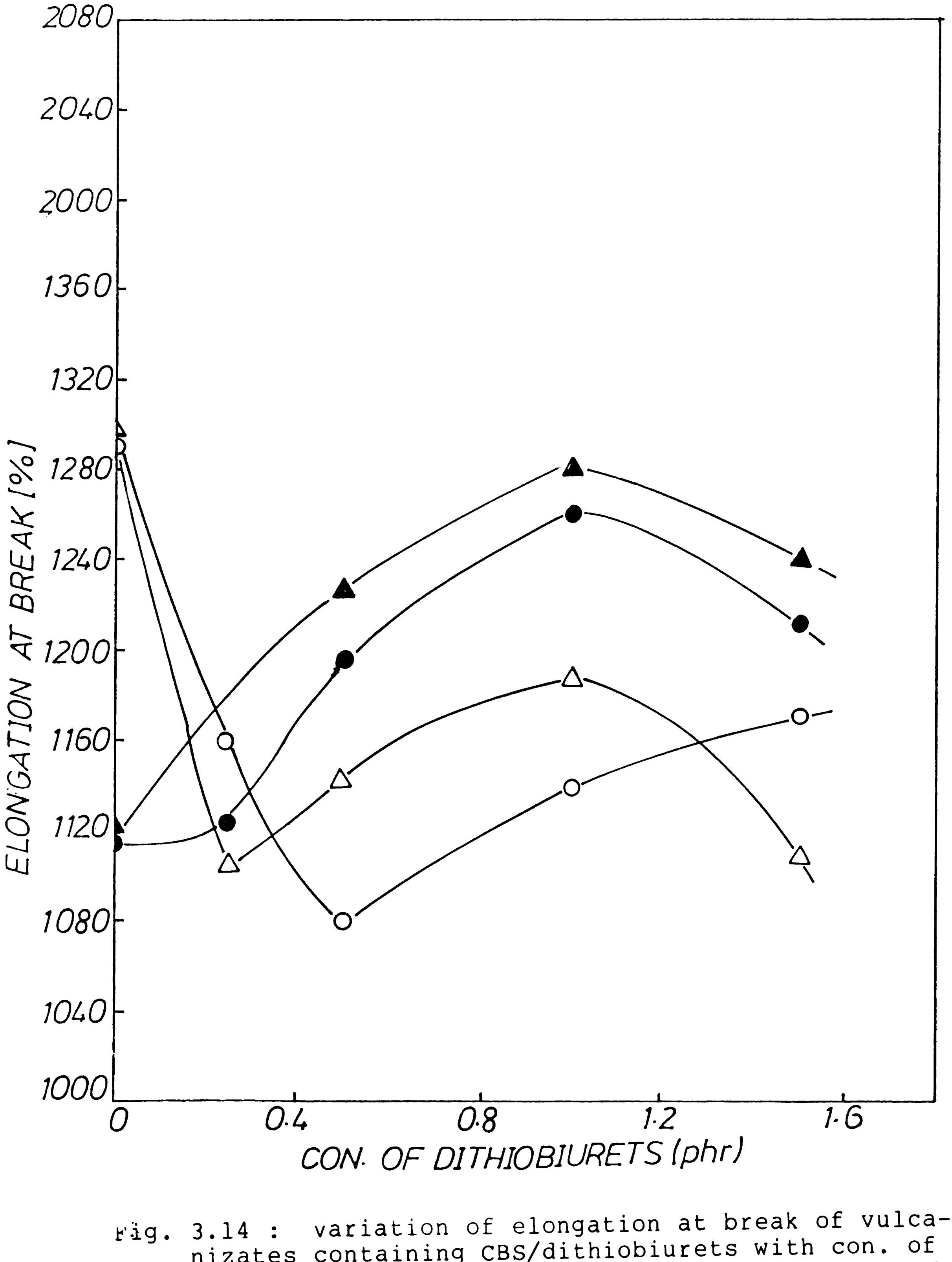

Fig. 3.14 : variation of elongation at break of vulcanizates containing CBS/dithiobiurets with con. of dithiobiurets; (●) CBS/DTB-II cured at 120°C; (○) CBS/DTB-II cured at 150°C; (▲) CBS/DTB-III cured at 120°C and CBS/DTB-III cured at 150°C(△).

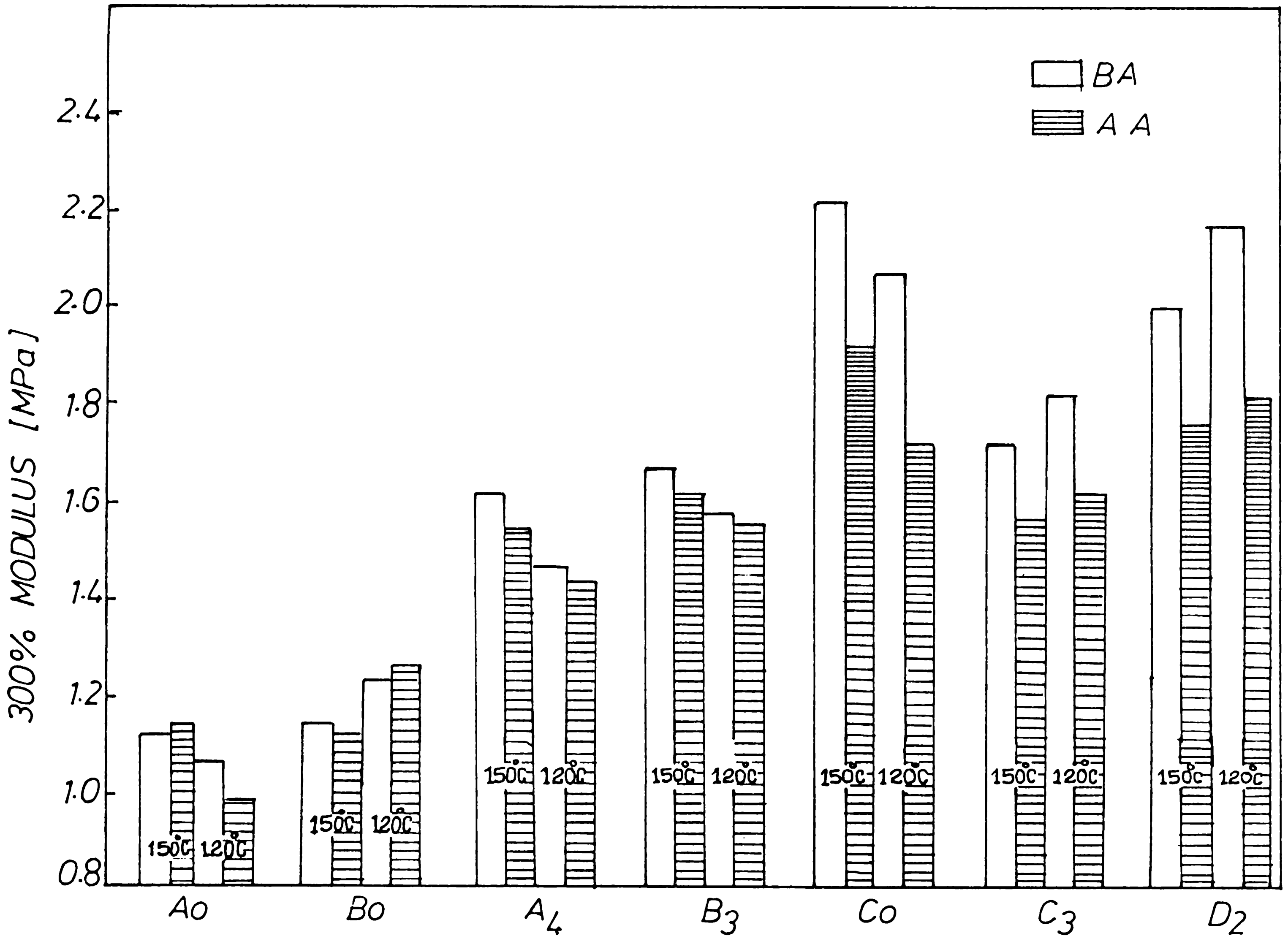

Fig. 3.15: 300% modulus ofthe vulcanizates containing optimum concentrations of dithiobiurets in TMTD and CBS systems.

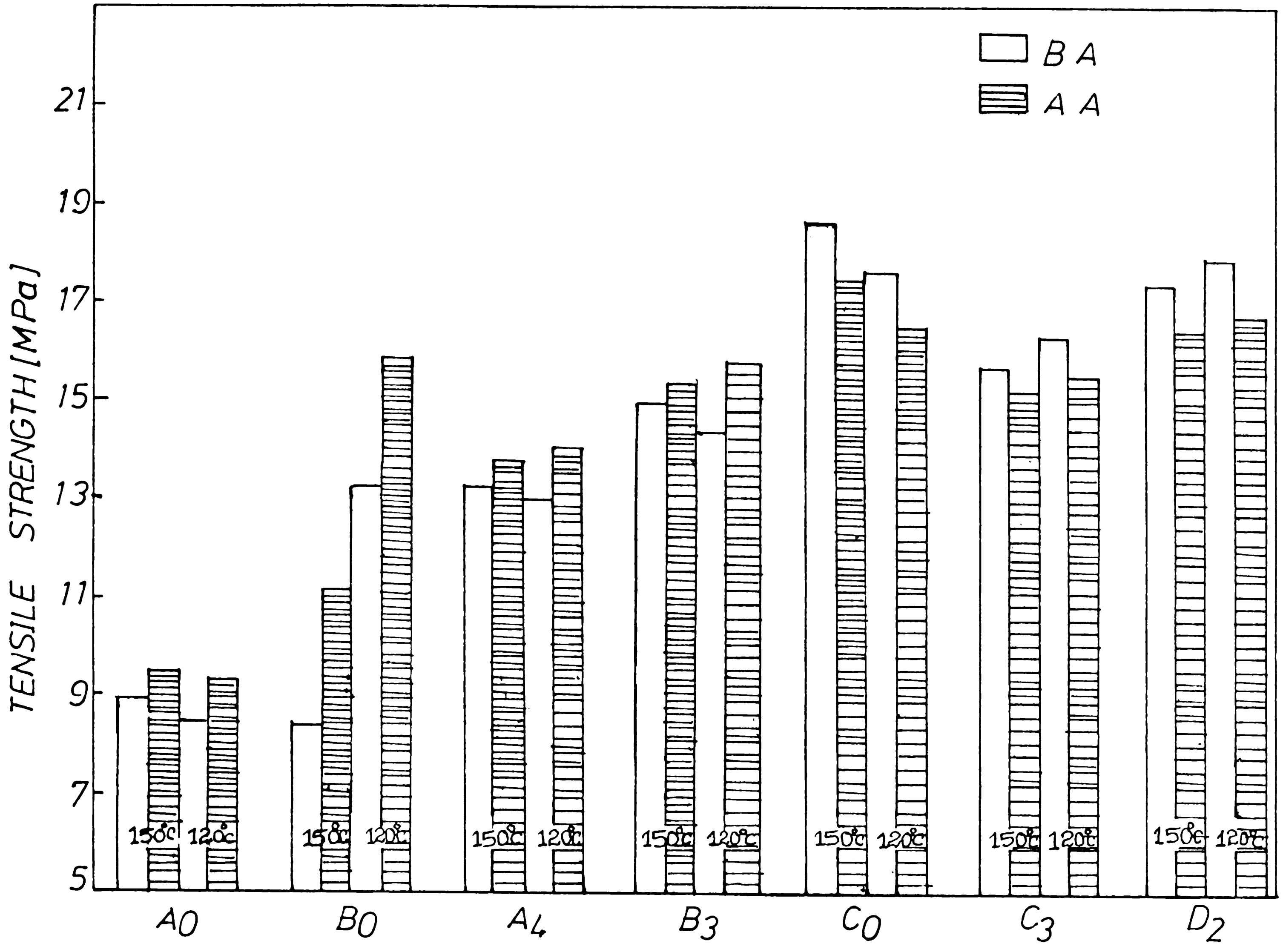

Fig. 3.16 : Tensile strength of the vulcanizates containing optimum concentrations of dithiobiurets in TMTD and CBS systems.

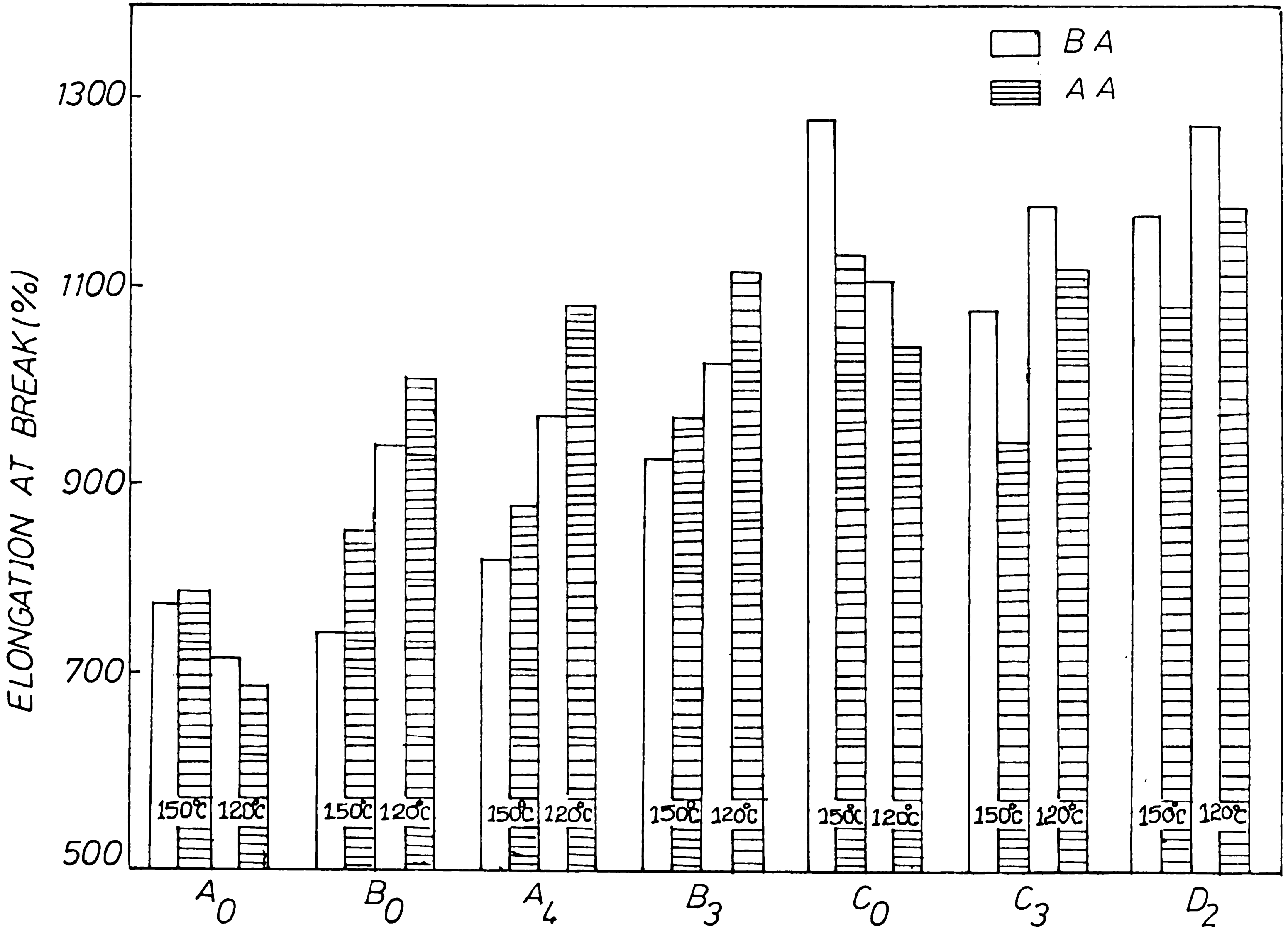

Fig. 3.17 : Elongation at break of the vulcanizates containing optimum concentrations of dithiobiurets in TMTD and CBS systems.

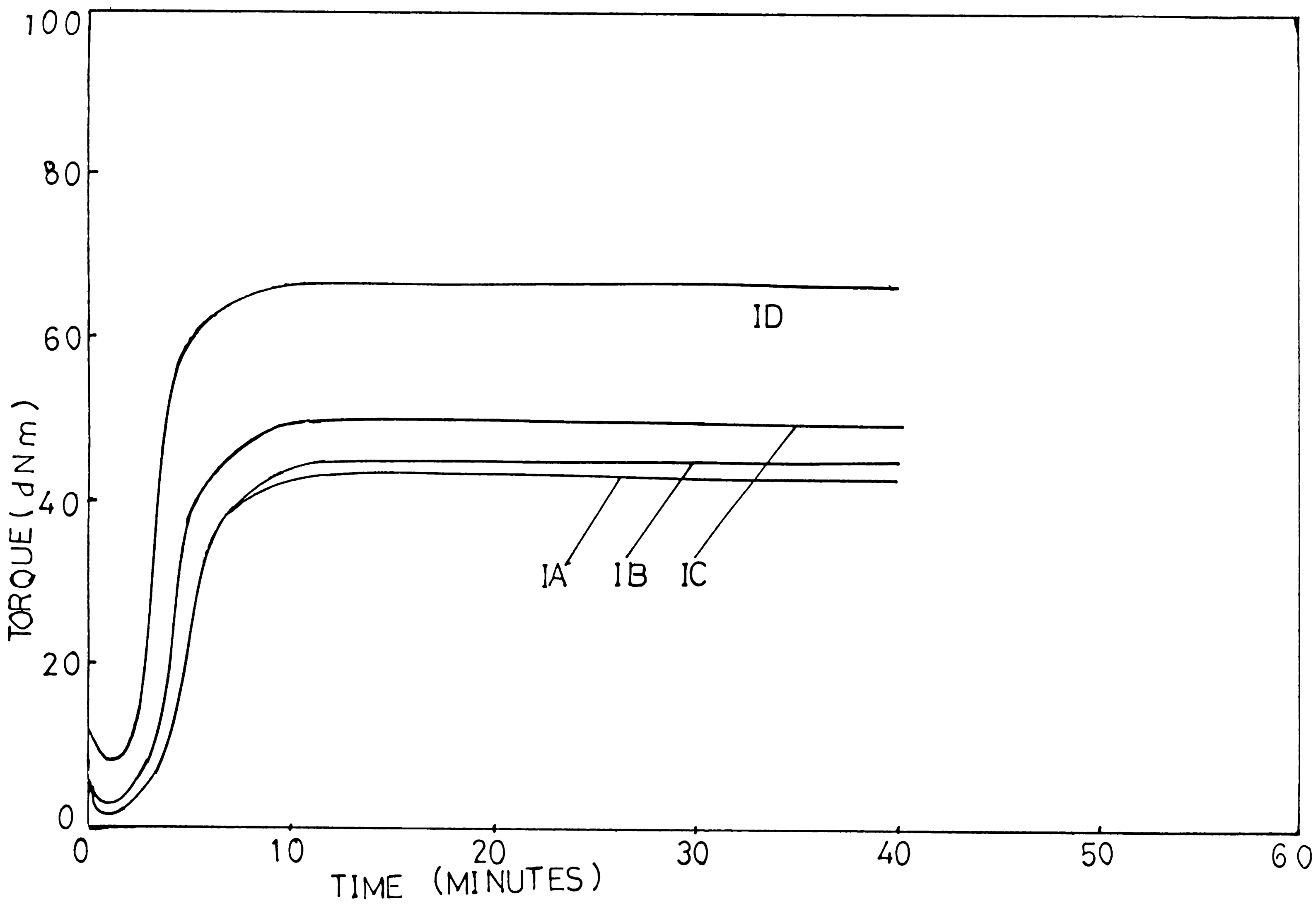

Fig. 3.18 : Rheographs of the mixes containing TMTD alone at 150°C at different loadings of HAF Black. (Ref: Tables 3.22 & 3.23).

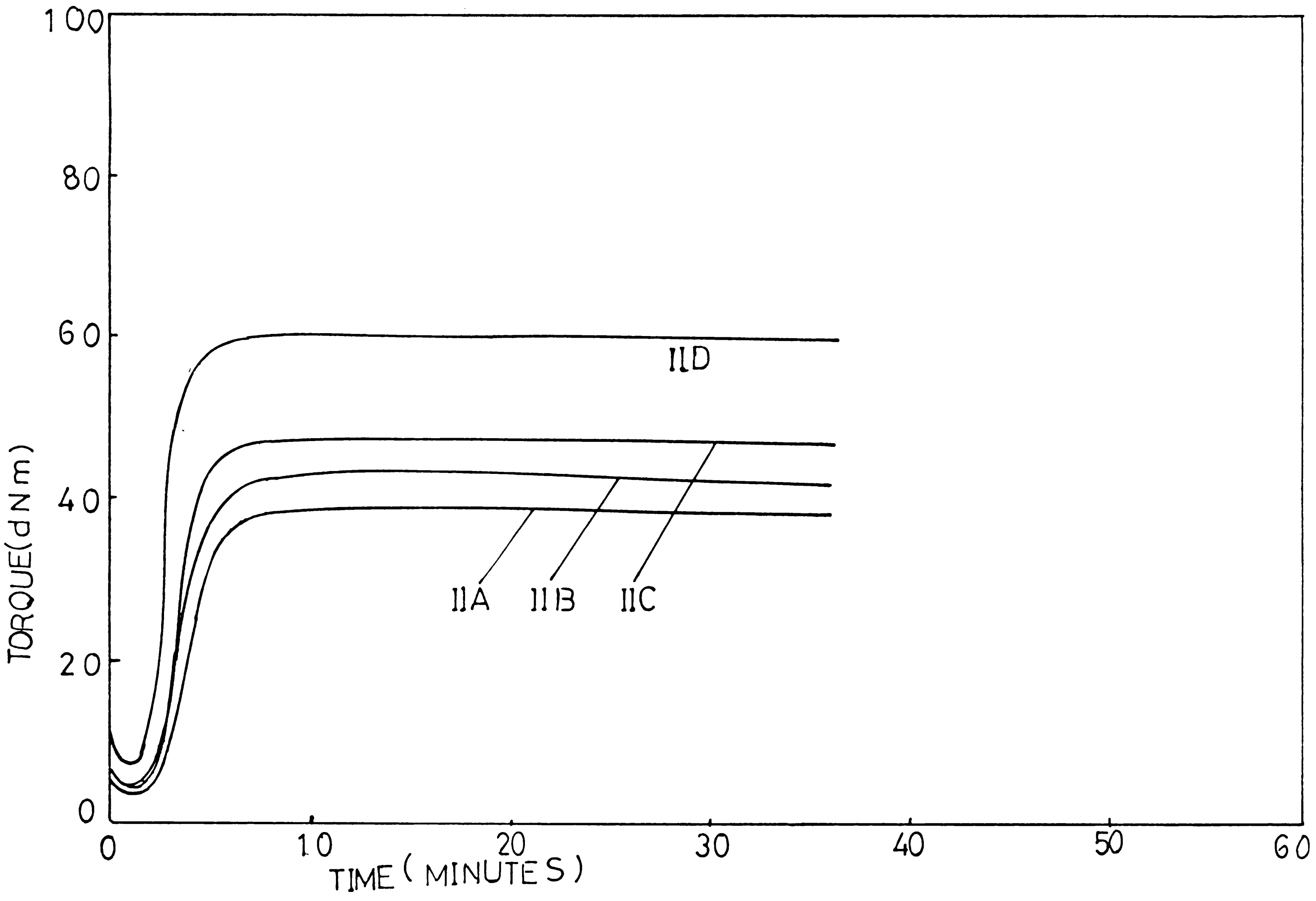

Fig. 3.19 : Rheographs of the mixes containing TMTD/Thiourea at 150°C at different loadings of HAF Black. (Ref: Tables 3.22 & 3.23).

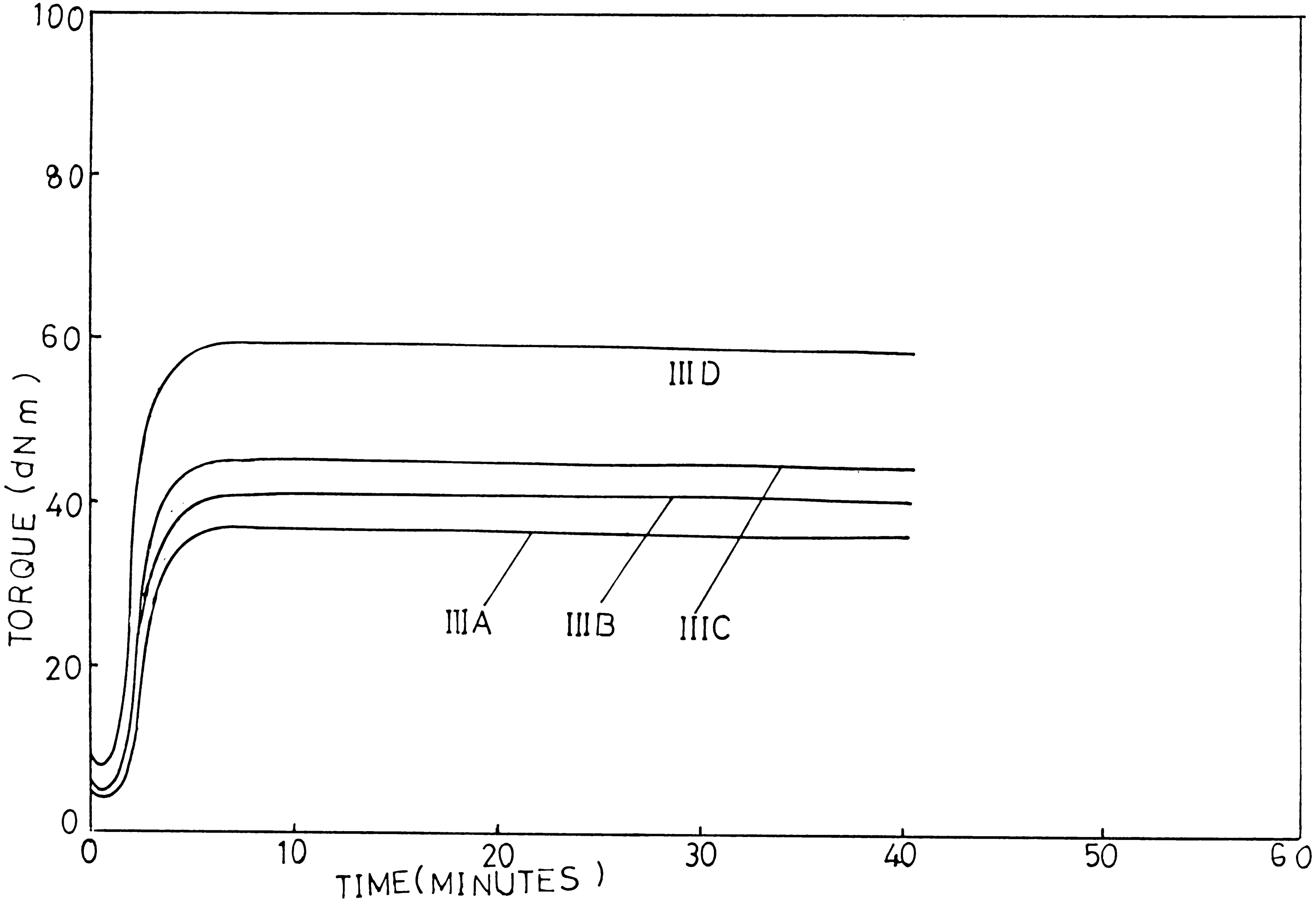

Fig. 3.20 : Rheographs of the mixes containing TMTD/DTB-II at 150°C at different loadings of HAF Black. (Ref: Tables 3.22 & 3.23).

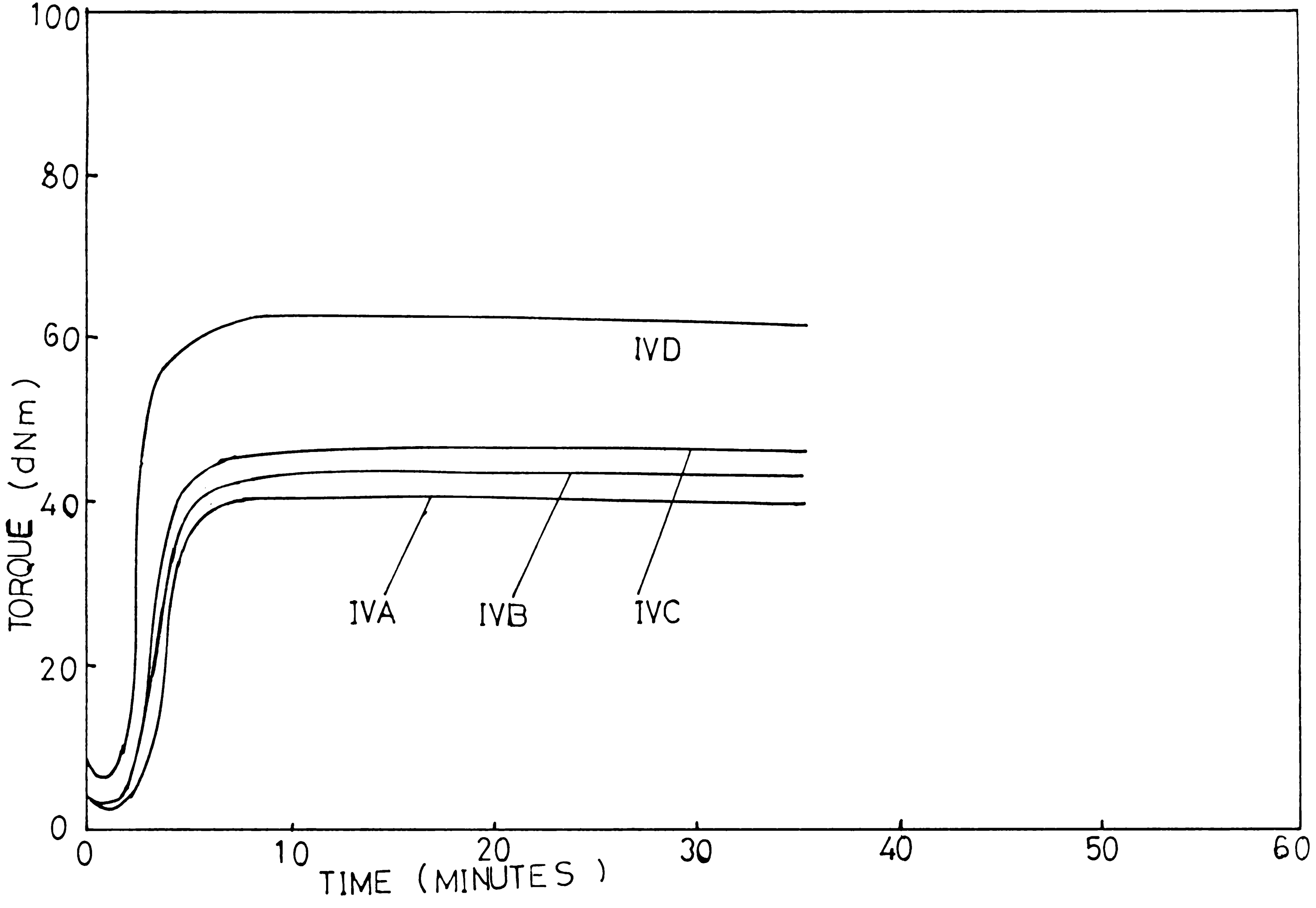

Fig. 3.21: Rheographs of the mixes containing TMTD/DTB-III at 150°C at different loadings of HAF Black. (Ref: Tables 3.22 & 3.23).

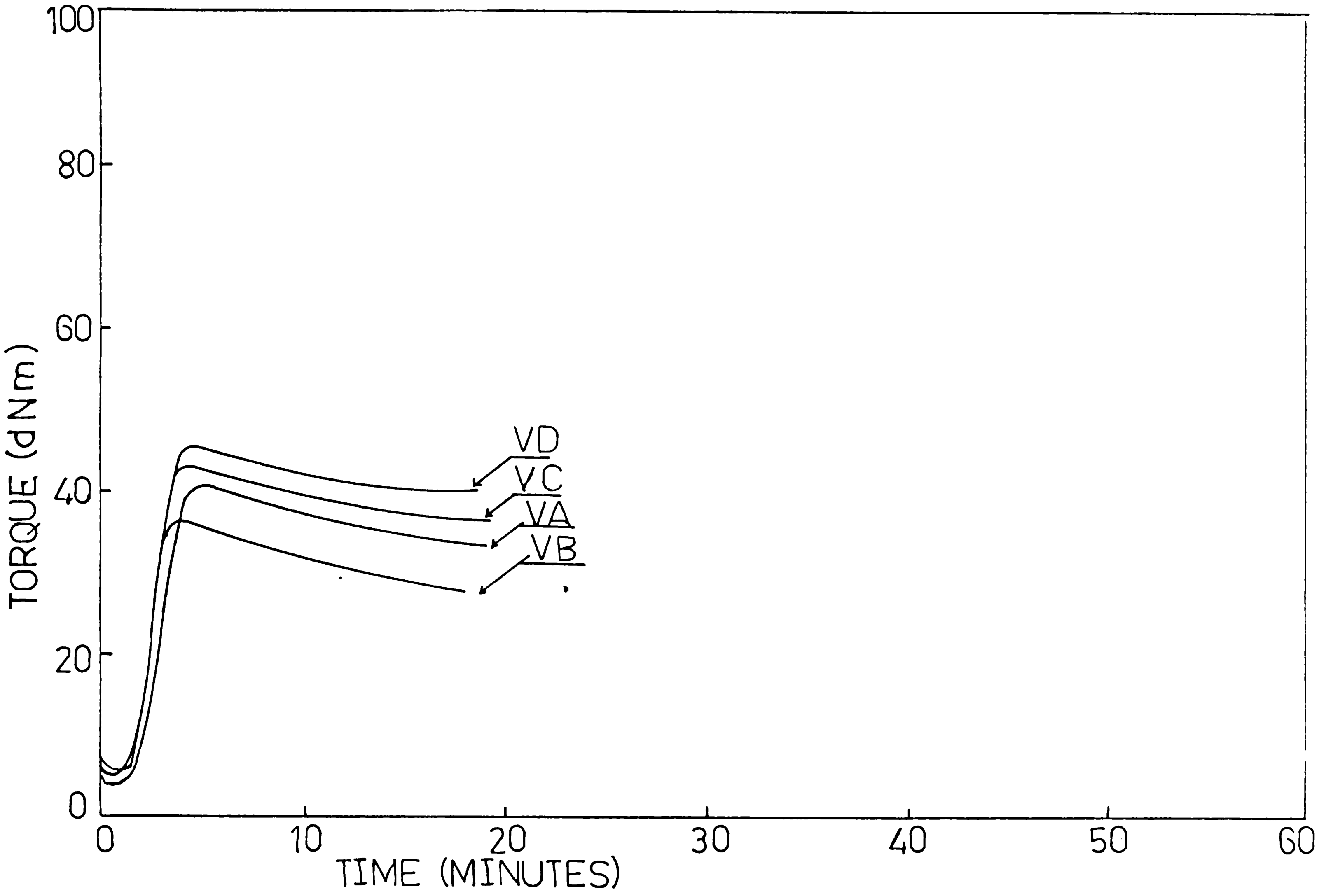

Fig. 3.22 : Rheographs of the mixes at 150°C at 50 phr loading of precipitated Silica. (Ref: Tables 3.26 & 3.28)

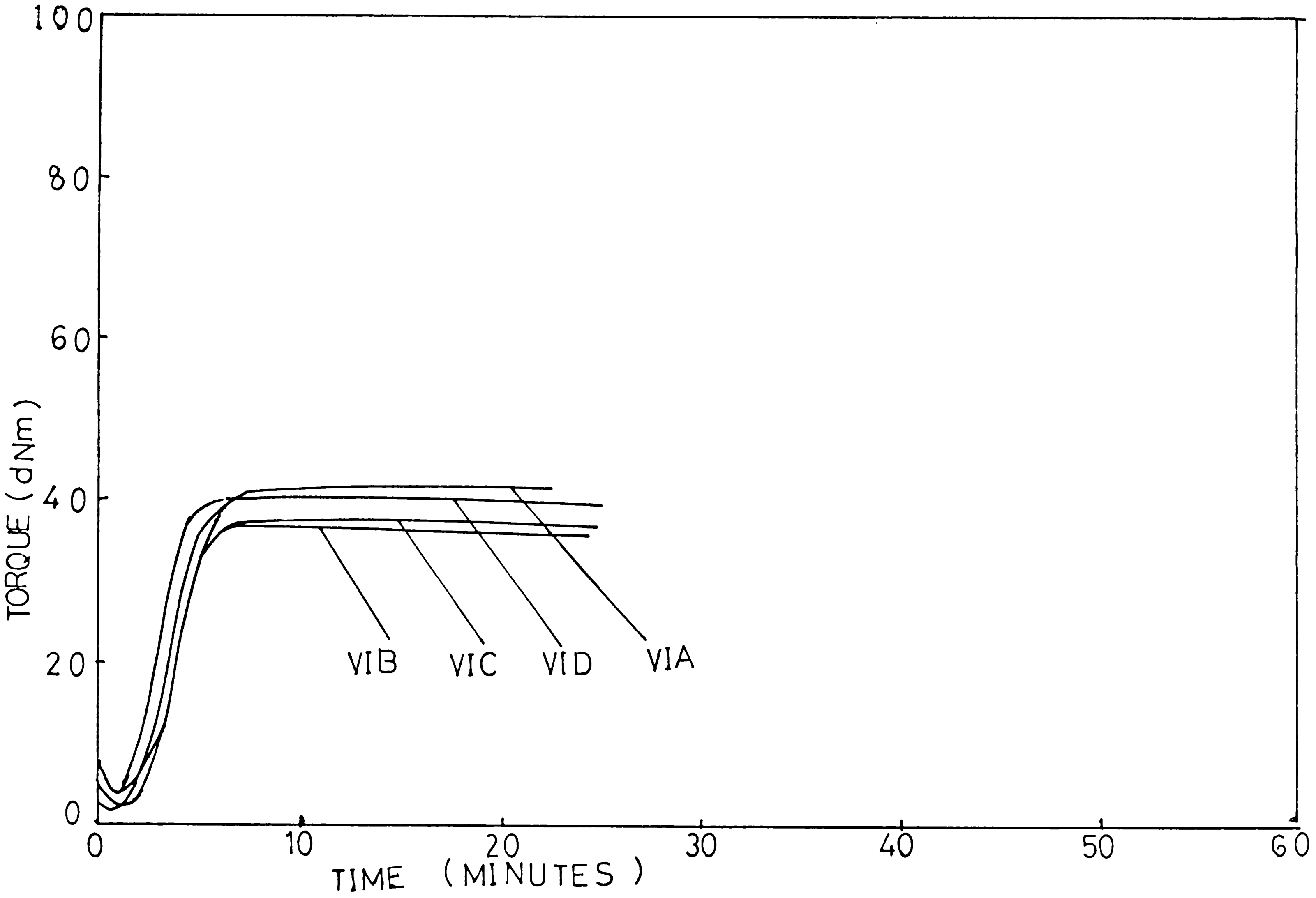

Fig. 3.23 : Rheographs of the mixes at 150°C at 50 phr loading of China Clay (Ref: Tables 3.27 & 3.29)

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CHAPTER - IV

STUDIES ON BINARY ACCELERATOR SYSTEMS CONTAINING SUBSTITUTED DITHIOBIURETS IN NR LATEX

STUDIES ON BINARY ACCELERATOR SYSTEMS CONTAINING DITHIOBIURETS IN NR LATEX

INTRODUCTION

Natural rubber latex is a negatively charged colloidal dispersion of rubber particles suspended in an aqueous serum. It has specific gravity in the range of 0.96 to 0.98 and having a variable viscosity. Its pH ranges from 6.5 to 7.0 and surface free energy from 40 to 45 ergs cm^{-2}. The size of the rubber particles ranges from 0.025 to 0.3 microns. These rubber particles are surrounded by a layer of protein and phospholipids. Latex contains a variety of other non rubber constituents which varies according to season, soil, atmospheric conditions, clone, stimulation practices, tapping systems etc. The size of the rubber particles varies between wide limits, (the range 200 to 20,000 A^{o}). For higher wetgel strength, to avoid unnecessary transportation of water content and for better uniformity in composition, the normal latex is concentrated, whereby a large portion of the serum and small rubber particles are removed . Centrifuging is the main technique adopted for this.

The processing of latex requires only relatively light and simple machinery. Capital outlay and power requirements are relatively low compared with the requirements for the heavy, expensive equipments which are used for the processing of dry rubber. The absence of any polymer degradation step such as mastication in the processing of latex not only saves time and energy but also gives a vulcanizate which will display inherently greater resistance to deteriorative influences.

Natural rubber latex is now-a-days extensively employed in the manufacture of various dipped articles, foam and cellular rubbers, impregnation of coir, fabric etc.[1] Latex articles such as gloves, weather balloons, thread etc. give service performance superior to that of articles made of rubber solutions[2-4].

The vulcanization of latex is the result of colloidal chemical reactions taking place in the heterogeneous system. For this reason, in order to produce high quality latex articles, it is necessary to have the ingradients introduced into the latex as solution, emulsions or dispersion in water. The preparation of aqueous dispersions of ingradients using a ball mill and their incorporation in latex has been described in the literature[5-8].

The use of accelerators in latex is basically different from their use in dry rubber[9-11]. The accelerators introduced into the latex mixture should become evenly distributed without causing the mixture to coagulate or to thicken[12-14]. Ultra accelerators are frequently employed in latex mixtures, since there is no danger of scorching[15-18].

TMTD may be used to cure natural rubber latex without the addition of sulphur or with the addition of a small amount of sulphur, to prepare heat resistant article[19-22]. It may also be used to prepare vulcanizates which can prevent copper catalysed oxidative degradation. The vulcanization of latex using TMTD proceeds only at relatively high temperature. At low temperature (100°C or below) the reaction is too slow to be of any technical interest. It has been shown by Philpott[23], that certain sulphur containing nucleophiles like thiourea, are able to activate vulcanization by TMTD, so that well cured natural rubber vulcanizates may be produced rapidly at 100°C. In line with the above observation we have tried dithiobiuret derivatives such as DTB-II and DTB-III which are more nucleophilic than thiourea,in the sulphur vulcanization of natural rubber latex along with TMTD.

Philpott[23] has also observed that sulphenamide accelerators, which do not vulcanize natural rubber latex in absence of added sulphur or at very low dosages of sulphur are also activated by thiourea to such an extent that the combination will effect cure at technologically useful rates. He found that a combination of CBS and thiourea, with or without the addition of elemental sulphur allows the formulation of latex compound which are resistant to copper staining. We have made a detailed study of the reaction using

DTB-II and DTB-III where thiourea is taken as a control.

EXPERIMENTAL

a) Preparation of Dispersions.

For the present study the following dispersions were prepared using a ball mill. Sodium salt of a sulphonic acid (Dispersol F) manufactured by M/s Indian Explosives Ltd, is used as the dispersing agent.

1. 50% Zinc oxide dispersion:

Zinc oxide	..	100.00
Dispersol F	..	2.00
Water (de-ionised)	..	98.00
Ball milled for		48 hrs.

2. 33% TMTD dispersion:

TMTD	..	100.00
Dispersol F	..	2.50
Water (de-ionised)	..	197.50
Ball milled for		48 hrs.

3. 33% CBS dispersion:

CBS	..	100.00
Dispersol F	..	2.50
Water (de-ionised)	..	197.50
Ball milled for		48 hrs.

4. 50% Sulphur Dispersion:

Sulphur	100.00
Dispersol F	3.00
Water (de-ionised)	97.00
Ball milled for	72 hrs.

5. 50% Clay Dispersion:

Clay	250
Dispersol F	5
Water (de-ionised)	245
Ball milled for	48 hrs.

6. 25% Carbon black Dispersion:

H A F black	250
Dispersol F	5
Water (de-ionised)	745
Ball milled for	48 hrs.

7. 25% Precipitated Silica Dispersion:

Precipitated silica	250
Dispersol F	5
Water (de-ionised)	745
Ball milled for	48 hrs.

b) <u>Compounding of Latex</u>

Centrifuged latex conforming to Bureau of Indian Standards (BIS)5430 - 1981 was used for this study. Other compounding ingradients were of commercial grade. 2gms of 10% potassium hydroxide solution was added to maintain the latex stock throughout the compounding and processing stages. Dispersions of zinc oxide, accelerators, sulphur and fillers were added according to formulation given in the Table (4.1 - 4.4, 4.14, 4.16 and 4.17). Thiourea was added as 10% solution in water and DTB-II and DTB-III were added as 10% aqueous alkaline solutions. All the ingradients were added with slow and thorough stirring. After the addition of ingredients the compounds were kept for maturation at room temperature for 48 hours.

c) Vulcanization and Testing

Latex films were prepared by casting the matured compound in shallow glass dishes. The film thickness was controlled in the range of 1 to 1.25 mm and the films were then vulcanized at 120 and 100°C for specific time periods in an air oven. The tensile properties of the vulcanized latex film were then determined both before and after ageing as per ASTM D 412 (83) using a Zwick Universal Testing Machine. The chemical crosslink density by equilibrium swelling method, the polysulphidic linkages, free sulphur and zinc sulphidic sulphur concentrations were also found out for the vulcanizates at the optimum conditions. For a latex compound the optimum cure time can be found out from the tensile properties - time graph. Tensile properties viz. modulus, tensile strength, elongation at break are plotted against time taken for vulcanization. From the graph the time taken for attaining the optimum properties is taken as the optimum cure time.

RESULTS AND DISCUSSION.

1. Cure Characteristics

The tensile properties-time graphs at 120° and 100°C, for TMTD/dithiobiuret systems are given in Figs. 4.1 - 4.3 and 4.4 - 4.6. The tensile-time graphs were drawn for the systems containing TMTD alone (Mix A_o), TMTD/thiourea (Mix B_o), TMTD/DTB-II (Mix A_3) and TMTD/DTB-III (Mix B_3) ~~systems~~. It can be seen from the Figs. 4.1 - 4.3 that DTB-II system is taking 20 minutes, to attain optimum tensile properties while DTB-III system is taking 30 minutes. The TMTD/thiourea system is taking 45 minutes and the system containing TMTD alone has taken 60 minutes. At 100°C the time required were found to be 40, 50, 60 & 70 minutes respectively. These results are indication of the efficient acceleration activity of the dithiobiurets in the vulcanization of natural rubber latex containing TMTD. DTB-II is showing more accelerating activity than that of DTB-III pointing to the nucleophilic reactivity in the vulcanization reaction meachanism. The tensile properties-time graphs for CBS/dithiobiurets systems at 120° and 100°C are given in Figs. 4.7 - 4.9 and 4.10 - 4.12. Time-tensile graph were drawn for CBS/thiourea (Mix D_o) CBS/DTB-II (Mix C_3) and CBS/DTB-III (Mix D_3) systems. The mix containing CBS alone as accelerator did not cure satisfactorily. So it was not taken in our study. At 120°C the system containing DTB-II took 40 minutes only to attain optimum tensile properties while the system containing DTB-III and that containing thiourea took 60 and 80 minutes respectively. At 100°C these systems have taken 60, 80, 90 minutes respectively to attain optimum tensile properties. From this it is quite clear that dithiobiurets can give a very active accelerator system in the vulcanization of natural rubber latex. In the CBS systems also DTB-II is superior to DTB-III as expected.

2. Tensile properties

In order to find the optimum concentration of dithiobiurets vulcanizates were prepared with various con. of DTB-II and DTB-III in both TMTD and CBS systems according to the formulation **shown** in Table 4.1 - 4.4. The tensile properties of the vulcanizates are given in Tables 4.5 to 4.12. In the case of TMTD/dithiobiuret systems, the tensile strength and 300% modulus increases as the dosage of dithiobiuret decreases and after the optimum stage, it decreases. The elongation at break is showing reverse trend. It decreases first and then increases. At 100°C also the same trend is followed but the tensile properties are better than those at 120°C. 0.5 phr of DTB-II (Mix A_3) and 1.0 phr of DTB-III are giving the optimum tensile properties and are taken as the optimum dosage s. In the case of CBS/dithiobiuret systems also the same trend is followed ie. first the tensile properties increase and after the optimum level it decreases. In this case 1 phr of DTB-II (Mix C_2

and 1.5 phr DTB-III (Mix D_1) are found to be the optimum dosages.

3. Chemical Characterization

For chemical characterization, samples of the mixes containing optimum concentrations of dithiobiurets were prepared as described in IVC. Table 4.13 shows the chemical characterisation of the vulcanizates. It can be seen from the table that both at 120 and 100°C the total crosslink density and polysulphidic linkagesof the vulcanizates containing dithiobiuret are more than that containing TMTD alone or TMTD/thiourea system s. The increase in the tensile properties can be attributed to the higher concentration of polysulphidic linkages in DTB systems.

In the case of CBS systems dithiobiurets are having a lesser concentration of total crosslink density and polysulphidic linkages at 120°C compairing to that of thiourea, but at 100°C these values are improved. The lower tensile strength values of dithiobiurets at 120°C may be attributed to the lower polysulphidic concentration and the enhancement of tensile strength at 100°C may be due to the increases in the polysulphidic crosslinks compaired to CBS/thiourea system.

EFFECT OF FILLERS

Fillers are added to natural rubber latex in order to modify its properties and to reduce cost[24]. Generally, they will weaken the rubber films, rather than improve its strength. Some studies have already been conducted in this line and the poor rubber-filler interaction in latex vulcanization is attributed to various factors such as insufficient distribution of fillers, non-simultaneous deposition of fillers and rubber particles and the presence of protective layer of stabilizers around the rubber and filler particles in latex[25].

Clay is the chief filler added to the latex compound, mainly for stiffening purposes. It is readily dispersed in water with the aid of small amounts of dispersing agent. At low proportions soft vulcanizates are obtained. Carbon black and precipitated silica are added in small quantities as pigments but they do not reinforce latex deposits. In order to study the effect of dithiobiurets in filled latex systems, TMTD/dithiobiurets systems were studied at 120°C with fillers such as clay, HAF black and precipitated silica.

The formulation of the vulcanizates containing clay is given in Table 4.14. 1.25, 2.5 & 5 phr of clay is added into the system containing TMTD alone, TMTD/thiourea, TMTD/DTB-II and TMTD/DTB-III and vulcanized at 120°C for the optimum time. The tensile properties are given in Table 4.15. It can be seen from the table that the tensile strength and elongation at break decreases while the modulus increases with the increase in the concentration of clay. Comparing to TMTD alone or TMTD/thiourea systems, dithiobiurets are giving higher tensile strength and modulus. DTB-III is giving higher values than DTB-II. This is indicative of the fact that dithiobiurets can act as effective accelerators in clay filled latex compounds also.

Tables 4.16 and 4.17 give the formulation of vulcanizates containing carbon black and precipitated silica respectively. 0.25 phr carbon black/silica was added to systems containing TMTD alone, TMTD/thiourea, TMTD/DTB-II, TMTD/DTB-III and vulcanized at 120°C at optimum time. Tensile properties of the samples are given in Tables 4.18 and 4.19. In these filler systems also dithiobiurets show a similar trend as in the previous one.

TABLE 4.1

Formulation of the mixes

Ingradients	A_o	B_o	A_1	A_2	A_3	A_4
60% centrifu - ged latex	167.0	167.0	167.0	167.0	167.0	167.0
10% potassium hydroxide soln.	2.0	2.0	2.0	2.0	2.0	2.0
50% zinc oxide dispersion	1.0	1.0	1.0	1.0	1.0	1.0
33% T M T D dispersion	6.0	6.0	6.0	6.0	6.0	6.0
10% thiourea solution	--	5.0	--	--	--	--
10% DTB-II solution	--	--	15.0	10.0	5.0	2.5
50% sulphur dispersion	1.0	1.0	1.0	1.0	1.0	1.0

TABLE 4.2

Ingredients	A_o	B_o	B_1	B_2	B_3	B_4
60% centrifuged latex	167.0	167.0	167.0	167.0	167.0	167.0
10% potassium hydroxide soln.	2.0	2.0	2.0	2.0	2.0	2.0
50% zinc oxide dispersion	1.0	1.0	1.0	1.0	1.0	1.0
33% T M T D dispersion	6.0	6.0	6.0	6.0	6.0	6.0
10% thiourea solution	--	5.0	--	--	--	--
10% DTB III soln.	--	--	15.0	10.0	5.0	2.5
50% sulphur dispersion	1.0	1.0	1.0	1.0	1.0	1.0

TABLE 4.3

Formulation of the mixes

Ingradients	C_o	D_o	C_1	C_2	C_3	C_4
60% centrifuged latex	167.0	167.0	167.0	167.0	167.0	167.0
10% potassium hydroxide soln.	2.0	2.0	2.0	2.0	2.0	2.0
50% zinc oxide dispersion	1.0	1.0	1.0	1.0	1.0	1.0
33% C B S dispersion	6.0	6.0	6.0	6.0	6.0	6.0
10% thiourea solution	--	5.0	--	--	--	--
10% DTB-II solution	--	--	15.0	10.0	5.0	2.5
50% sulphur dispersion	1.0	1.0	1.0	1.0	1.0	1.0

TABLE 4.4

Ingradients	C_o	D_o	D_1	D_2	D_3	D_4
60% centrifuged latex	167.0	167.0	167.0	167.0	167.0	167.0
10% potassium hydroxide soln.	2.0	2.0	2.0	2.0	2.0	2.0
50% zinc oxide dispersion	1.0	1.0	1.0	1.0	1.0	1.0
33% C B S dispersion	6.0	6.0	6.0	6.0	6.0	6.0
10% thiourea solution	--	5.0	--	--	--	--
10% DTB-III soln.	--	--	15.0	10.0	5.0	2.5
50% sulphur dispersion	1.0	1.0	1.0	1.0	1.0	1.0

TABLE 4.5

Tensile properties of vulcanizates containing TMTD/DTB-II cured at 120°C

Mix No.	300% Modulus (MPa)			Tensile strength (MPa)			Elongation at break (%)		
	B.A	A.A	% Rtn.	B.A	A.A	% Rtn	B.A	A.A	% Rtn.
A_o	1.12	0.98	87.50	20.7	17.9	86.47	1025.0	915.0	89.27
B_o	1.22	1.12	91.80	23.0	21.9	95.22	1120.0	1040.0	92.86
A_1	1.26	1.22	96.83	23.1	22.4	96.97	1230.5	1170.1	95.09
A_2	1.28	1.25	97.66	23.4	22.8	97.64	1172.7	1120.7	95.57
A_3	1.36	1.34	98.53	24.3	23.9	98.35	1074.5	1040.5	96.84
A_4	1.25	1.21	96.80	20.6	19.8	95.75	1391.6	1330.1	95.58

TABLE 4.6

Tensile properties of the vulcanizates containing TMTD/DTB-II cured at 100°C

Mix No.	300% Modulus (MPa)			Tensile Strength (MPa)			Elongation at break (%)		
	B.A	A.A	%Rtn.	B.A	A.A	% Rtn.	B.A	A.A	% Rtn.
A_o	1.05	0.90	85.71	22.1	20.1	90.95	980.0	845.5	86.28
B_o	1.42	1.36	95.77	23.3	22.2	95.28	1015.5	960.2	94.55
A_1	1.37	1.33	97.08	23.30	22.7	97.42	1190.3	1145.7	96,25
A_2	1.40	1.37	97.86	23.70	23.2	97.89	1160.3	1123.5	96.83
A_3	1.42	1.40	98.59	24.30	24.1	98.97	1122.5	1092.1	97.29
A_4	1.30	1.26	96.92	24.15	23.4	96.89	1220.6	1176.3	96.37

TABLE 4.7

Tensile properties of vulcanizates containing TMTD/DTB-III cured at 120°C

Mix No.	300% Modulus (MPa)			Tensile Strength (MPa)			Elongation at break (%)		
	B.A	A.A	% Rtn.	B.A	A.A	% Rtn.	B.A	A.A	% Rtn.
A_o	1.12	0.98	87.5	20.7	17.9	86.47	1025.0	915.0	89.27
B_o	1.22	1.12	91.8	23.0	21.9	95.22	1120.0	1040.0	92.86
B_1	1.55	1.44	92.9	24.8	23.8	96.29	1038.7	965.5	92.95
B_2	1.48	1.38	93.2	25.3	24.7	97.63	1020.2	960.0	94.10
B_3	1.39	1.32	94.8	24.5	23.6	96.30	1085.0	1020.5	94.06
B_4	1.38	1.30	94.2	22.3	21.4	96.18	1187.4	1080.2	90.97

TABLE 4.8

Tensile properties of the vulcanizates containing TMTD/DTB-III cured at 100°C

Mix No.	300% Modulus (MPa)			Tensile Strength (MPa)			Elongation at break (%)		
	B.A	A.A	% Rtn.	B.A	A.A	% Rtn.	B.A	A.A	% Rtn.
A_o	1.05	0.90	85.71	22.1	20.1	90.95	980.00	845.5	86.28
B_o	1.42	1.36	95.77	23.3	22.2	95.28	1015.50	960.2	94.55
B_1	1.60	1.53	95.63	25.8	25.1	97.29	1010.10	964.8	95.52
B_2	1.90	1.84	96.84	26.2	25.8	98.47	995.30	960.0	96.45
B_3	1.47	1.41	95.92	25.4	24.6	96.85	1035.50	985.5	95.17
B_4	1.38	1.32	95.65	24.8	23.9	96.37	1120.45	1060.0	94.60

TABLE 4.9

Tensile properties of vulcanizates containing CBS/DTB-II cured at 120°C

Mix No.	300% Modulus (MPa)			Tensile Strength (MPa)			Elongation at break (%)		
	B.A	A.A	%Rtn.	B.A	A.A	%Rtn.	B.A	A.A	%Rtn
D_o	.83	.63	75.90	12.10	10.70	88.43	780	660	84.62
C_1	.90	.80	88.89	10.90	10.01	91.83	860	790	91.86
C_2	.96	.88	91.67	11.20	10.52	93.93	870	805	92.59
C_3	.79	.71	84.97	10.75	10.03	93.30	915	830	90.71
C_4	.52	.45	86.54	9.30	8.55	91.94	940	840	89.41

TABLE 4.10

Tensile properties of vulcanizates containing CBS/DTB-II cured at 100°C

Mix No.	300% Modulus (MPa)			Tensile Strength (MPa)			Elongation at break (%)		
	B.A	A.A	% Rtn.	B.A	A.A	%Rtn	B.A	A.A	% Rtn.
D_o	.60	.53	88.33	10.50	9.08	86.47	810	730.0	90.12
C_1	.92	.84	91.30	11.60	10.90	93.97	825	770.5	93.39
C_2	.99	.92	92.93	11.80	11.20	94.92	842	794.0	94.30
C_3	.81	.73	90.12	11.50	10.75	93.48	845	770.5	91.18
C_4	.64	.56	87.50	9.90	9.20	92.93	915	830.0	90.71

TABLE 4.11

Tensile properties of vulcanizates containing
CBS/DTB-III cured at 120°C

Mix No.	300% Modulus (MPa)			Tensile strength (MPa)			Elongation at break (%)		
	B.A	A.A	% Rtn.	B.A	A.A	% Rtn.	B.A	A.A	% Rtn.
D_o	0.83	0.63	75.90	12.1	10.7	88.43	780.0	660.0	84.62
D_1	1.10	0.98	89.09	12.05	11.3	93.77	810.5	750.0	92.59
D_2	0.95	0.86	90.53	11.80	11.1	94.07	850.0	792.0	93.18
D_3	0.82	0.74	90.24	11.60	10.7	92.24	890.0	810.5	91.07
D_4	0.60	0.53	88.33	10.80	9.60	88.89	915.5	810.0	88.48

TABLE 4.12

Tensile properties of the vulcanizates containing
CBS/DTB-III cured at 130°C

Mix No.	300% Modulus(MPa)			Tensile Strength (MPa)			Elongation at break (%)		
	B.A	A.A	% Rtn.	B.A	A.A	% Rtn.	B.A	A.A	% Rtn.
D_o	0.60	0.53	88.33	10.50	9.08	86.47	810.0	730.0	90.12
D_1	1.12	1.01	90.18	12.10	11.40	94.21	802.5	752.0	93.71
D_2	1.03	0.95	92.23	11.90	11.32	95.12	825.0	780.5	94.61
D_3	0.85	0.78	91.76	11.75	10.96	93.28	837.5	790.0	94.33
D_4	0.68	0.61	89.71	11.20	10.15	90.06	870.0	802.5	92.24

TABLE 4.13

Chemical Characterization of the Vulcanizates

Cure temp.	Mix No.	Total cross link density (m.mole/ Kg RH)	Poly sulphide linkages (m.mole/ Kg RH)	Free Sulphur concentration (m.mole/ Kg RH)	Zinc Sulphide concentration. (m.mole/ (Kg RH)
120	A_0	51.5	20.6	20.5	8.10
	B_0	57.8	21.6	24.2	6.50
	A_3	60.2	23.7	19.3	11.50
	B_2	66.4	26.4	17.5	12.40
100	A_0	51.8	20.9	20.8	8.20
	B_0	60.2	22.5	23.3	6.20
	A_3	61.6	25.4	18.4	11.80
	B_2	70.5	29.8	15.2	13.20
120	D_0	29.5	12.8	10.2	7.40
	C_2	27.4	10.5	12.5	5.50
	D_1	29.0	12.1	11.4	6.20
100	D_0	22.4	10.8	12.8	4.80
	C_2	28.0	11.2	9.4	6.80
	D_1	30.4	13.4	8.2	8.50

TABLE 4.14

Formulation of the mixes containing china clay.

Ingredients	IA	IB	IC	IIA	IIB	IIC	IIIA	IIIB	IIIC	IVA	IVB	IVC
60% centrifuged latex.	167	167	167	167	167	167	167	167	167	167	167	167
10% Potassium hydroxide solution	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
50% Zinc oxide dispersion	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
50% Clay dispersion	2.5	5	10	2.5	5	10	2.5	5	10	2.5	5	10
33% T.M.T.D dispersion	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
10% Thiourea solution	-	-	-	5.0	5.0	5.0	-	-	-	-	-	-
10% D.T.B-II solution	-	-	-	-	-	-	5.0	5.0	5.0	-	-	-
10% D.T.B-III solution	-	-	-	-	-	-	-	-	-	5.0	5.0	5.0
50% Sulphur dispersion	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0

TABLE 4.15

Tensile properties of the vulcanizates containing china clay

Mix No.	300% Modulus (MPa)			Tensile strength (MPa)			Elongation at break (%)		
	B.A	A.A	% Rtn	B.A	A.A	% Rtn.	B.A	A.A	% Rtn.
IA	1.02	0.84	82.35	9.50	8.12	88.74	1020.00	950.2	93.16
IB	1.05	0.86	81.90	9.40	8.05	85.64	960.50	880.0	91.62
IC	1.10	0.90	81.82	9.20	7.90	85.87	948.86	820.5	86.47
IIA	0.88	0.84	95.45	8.80	8.60	97.73	963.33	935.0	97.06
IIB	0.92	0.87	94.57	8.55	8.29	96.96	960.30	930.0	96.84
IIC	0.99	0.92	92.93	8.50	8.08	95.06	955.40	920.4	96.34
IIIA	2.16	2.05	94.90	15.10	14.50	96.03	820.50	790.2	96.31
IIIB	2.20	2.10	95.45	15.00	14.30	95.33	800.01	768.7	96.09
IIIC	2.24	2.12	94.64	14.93	14.06	94.17	782.20	710.0	90.77
IVA	2.20	2.10	95.45	16.90	16.30	96.45	915.20	870.5	95.12
IVB	2.25	2.15	95.56	16.70	16.05	96.11	885.63	850.2	95.68
IVC	2.30	2.18	94.78	16.38	15.58	95.29	867.60	820.0	94.58

TABLE 4.16

Formulation of the mixes containing carbon black

Ingredients	VA	VB	VC	VD
60% centrifuged latex	167	167	167	167
10% potassium hydroxide solution	2.0	2.0	2.20	2,0
50% zinc oxide dispersion	1.0	1.0	1.0	1.0
25% HAF black dispersion	5.0	5.0	5.0	5.0
33% TMTD dispersion	6.0	6.0	6.0	6.0
10% Thiourea soln.	--	5.0	--	--
10% DTB-II solution	--	--	5.0	--
10% DTB-III soln.	--	--	--	5.0
50% sulphur dispersion	1.0	1.0	1.0	1.0

TABLE 4.17

Formulation of the mixes containing precipitated silica

Ingredients	VA	VB	VC	VD
60% centrifuged latex	167	167	167	167
10% potassium hydroxide soln.	2.0	2.0	2.0	2.0
50% Zincoxide dispersion	1.0	1.0	1.0	1.0
25% precipitated silica dispersion	5.0	5.0	5.0	5.0
33% TMTD dispersion	6.0	6.0	6.0	6.0
10% Thiourea soln.	--	5.0	--	--
10% DTB-II soln.	--	--	5.0	--
10% DTB-III soln.	--	--	--	5.0
50% sulphur dispersn.	1.0	1.0	1.0	1.0

TABLE 4.18

Tensile properties of vulcanizates containing carbon black

Mix No.	300% Modulus (MPa)			Tensile strength (MPa)			Elongation at break (%)		
	B.A	A.A	% Rtn.	B.A	A.A	% Rtn.	B.A	A.A	% Rtn.
VA	1.34	1.15	85.82	11.01	9.64	87.56	905.51	780.91	86.24
VB	1.34	1.29	96.27	12.07	10.84	89.81	840.10	763.83	90.92
VC	1.36	1.32	97.06	11.94	10.84	90.79	886.54	816.00	92.04
VD	1.38	1.37	98.53	12.46	11.40	91.49	780.50	720.38	92.30

TABLE 4.19

Tensile properties of the vulcanizates containing precipitated silica

Mix No.	300% Modulus (MPa)			Tensile strength (MPa)			Elongation at break (%)		
	B.A	A.A	% Rtn.	B.A	A.A	% Rtn.	B.A	A.A	% Rtn.
VIA	0.97	0.88	90.72	7.98	6.65	83.33	965.04	815.47	84.50
VIB	1.40	1.47	98.00	14.12	13.88	98.30	900.26	843.23	93.67
VIC	1.20	1.17	97.50	10.12	9.95	98.32	970.01	930.50	95.93
VID	1.63	1.60	98.16	14.68	14.50	98.77	851.50	820.60	96.37

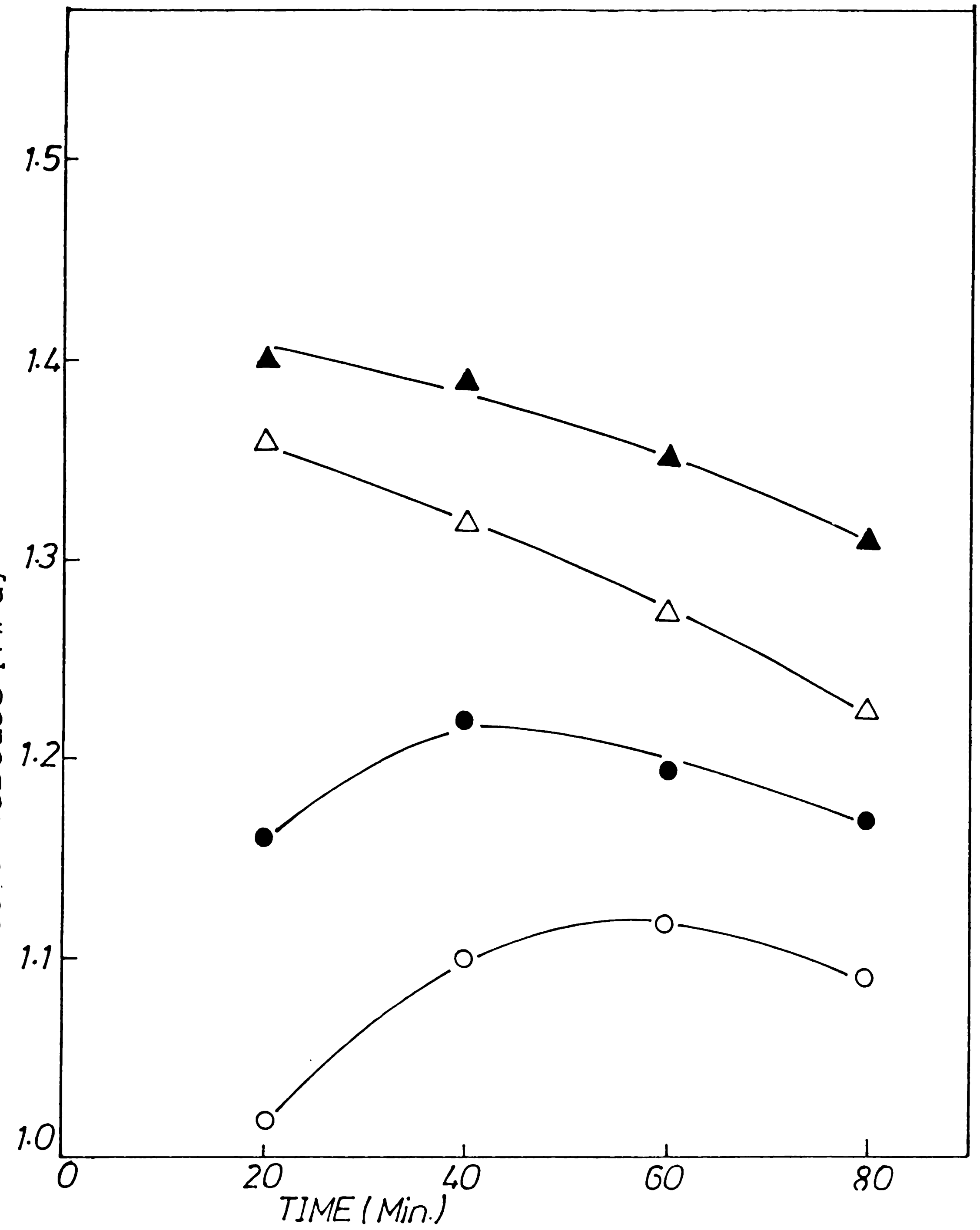

Fig. 4.1 : Variation of 300% modulus of vulcanizates with vulcanization time at 120°C for (○) TMTD alone; (●) TMTD/thiourea; (△) TMTD/DTB-II; (▲) TMTD/DTB-III.

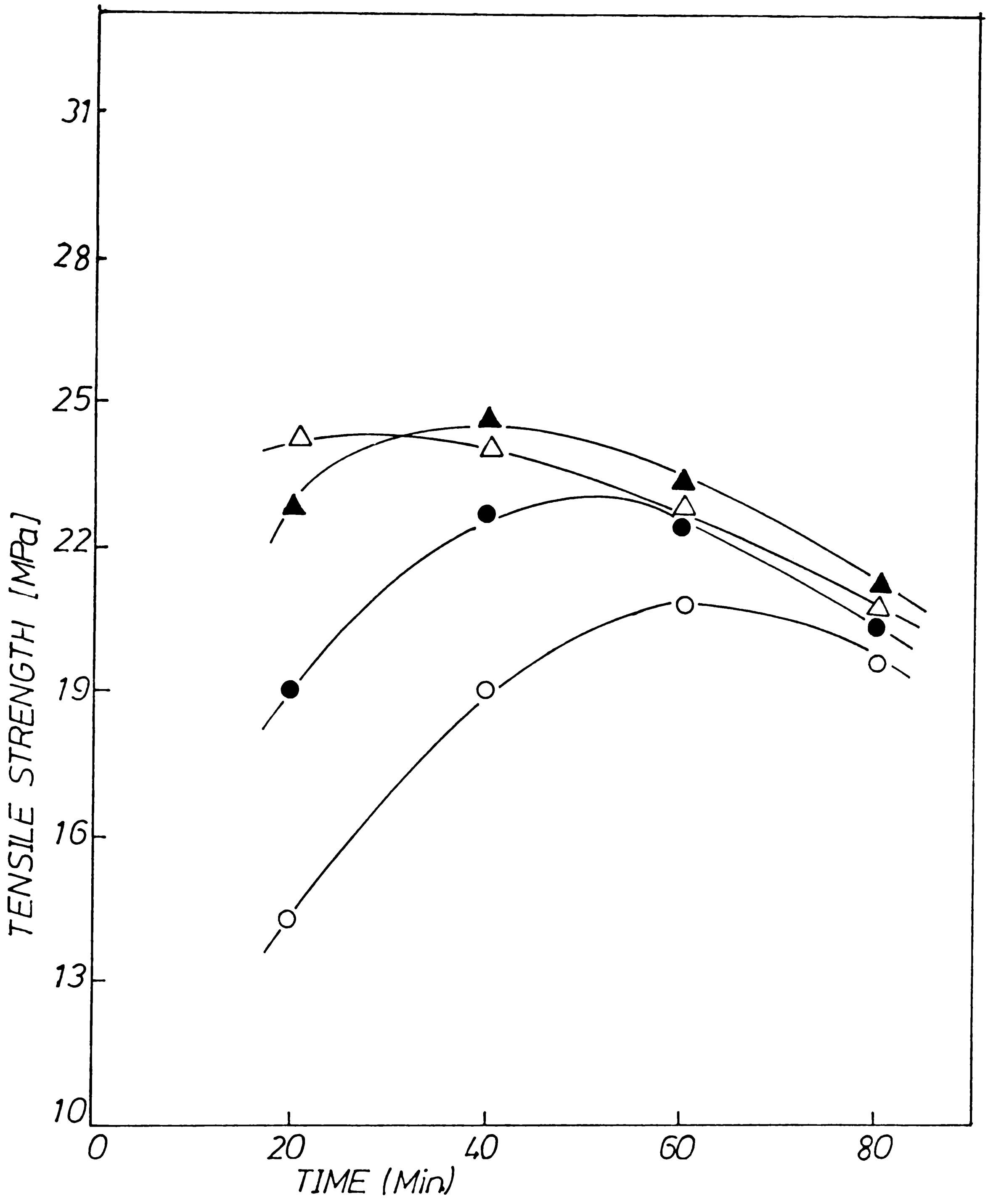

Fig.4.2 : Variation of Tensile Strength of vulcanizates with vulcanization time at 120°C for; (○) TMTD alone; (●) TMTD/thiourea; (△) TMTD/DTB-II; (▲) TMTD/DTB-III.

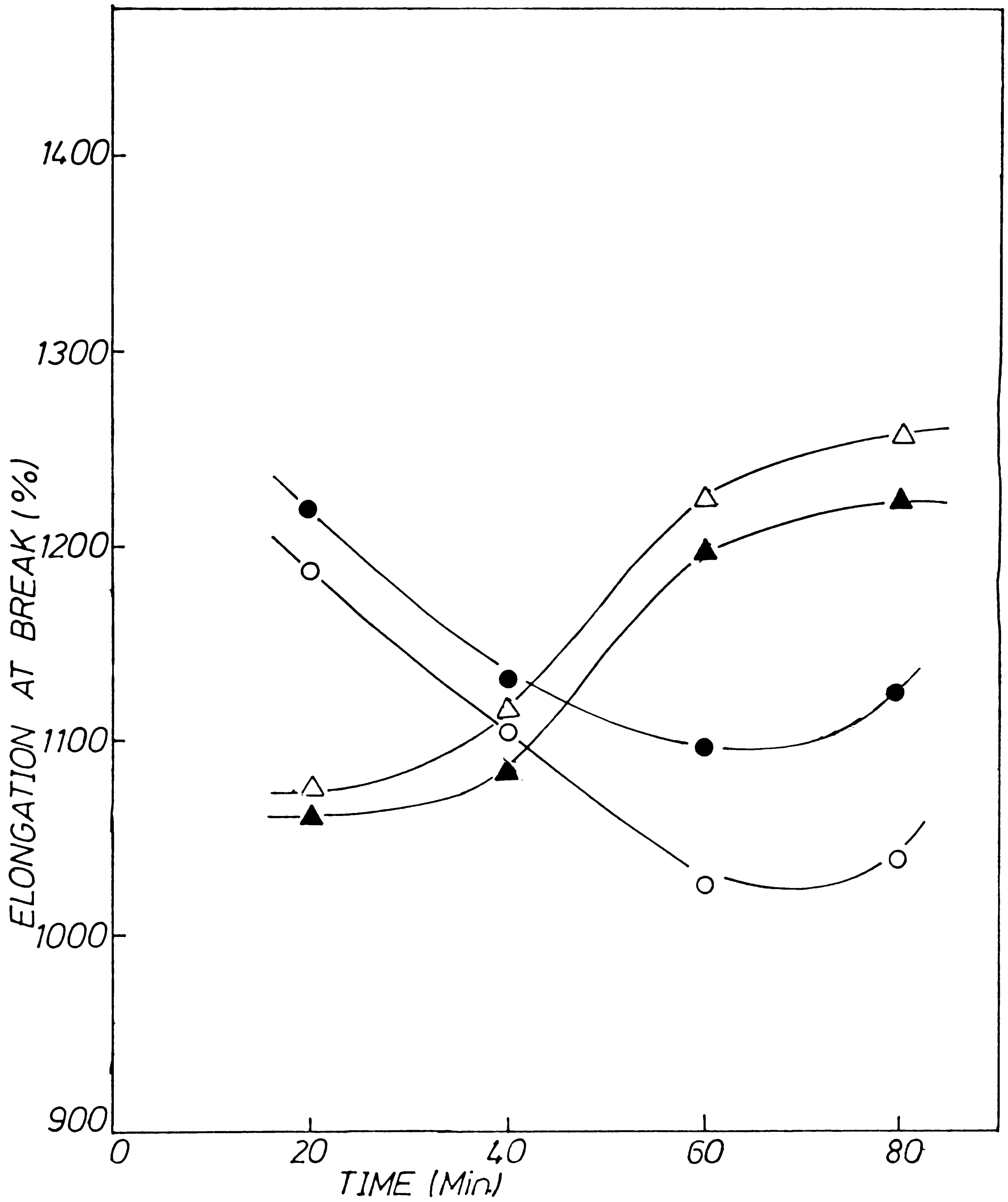

Fig. 4.3 : Variation of elongation at break ofvulcanizates with vulcanization time at 120°C for (○) TMTD/alone; (●) TMTD/thiourea; (△) TMTD/DTB-II; (▲) TMTD/DTB-III.

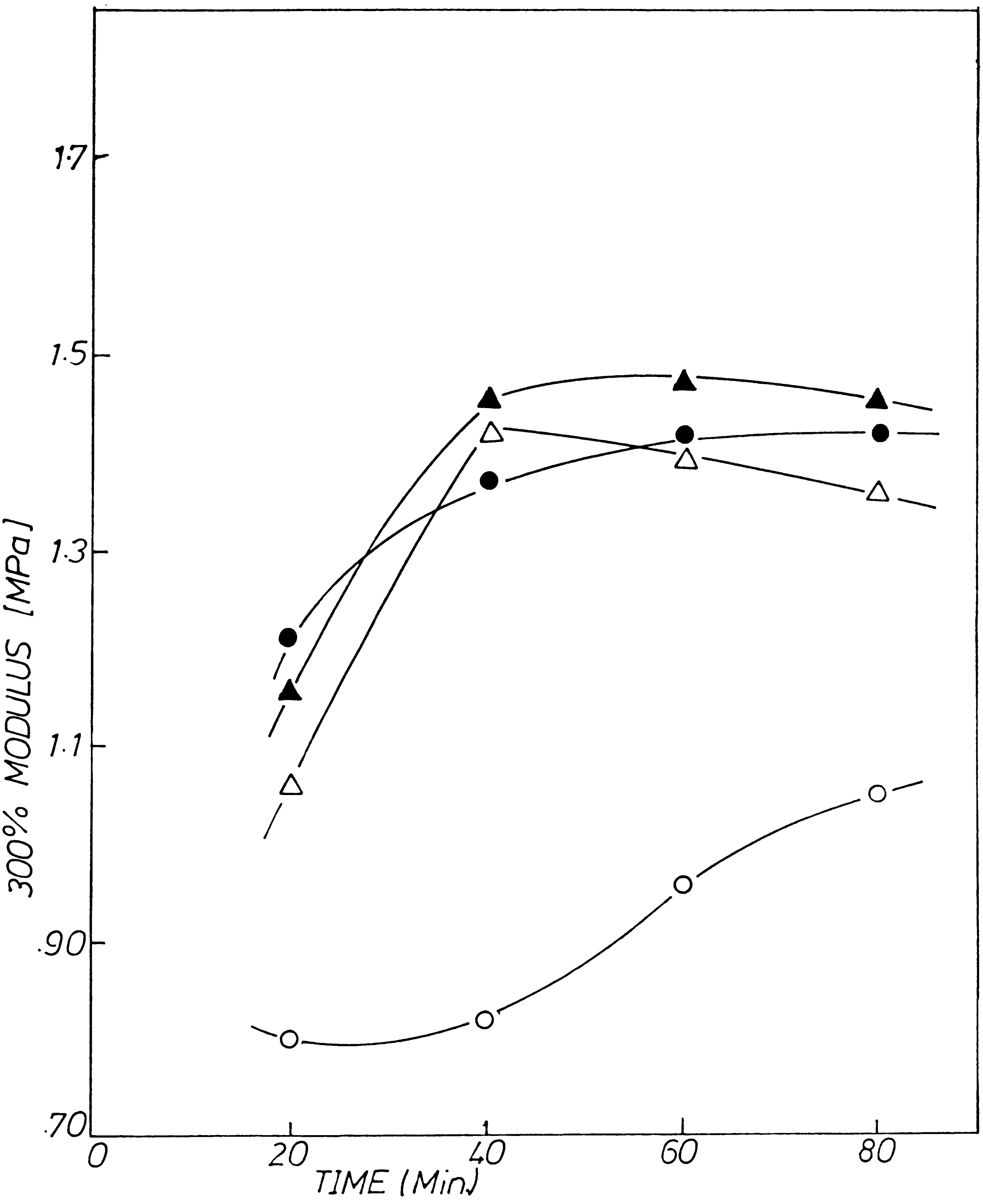

Fig. 4.4 : Variation of 300% modulus of vulcanizates with vulcanization time at 100°C for (○) TMTD alone; (●)TMTD/thiourea; (△) TMTD/DTB-II; (▲) TMTD/DTB-III.

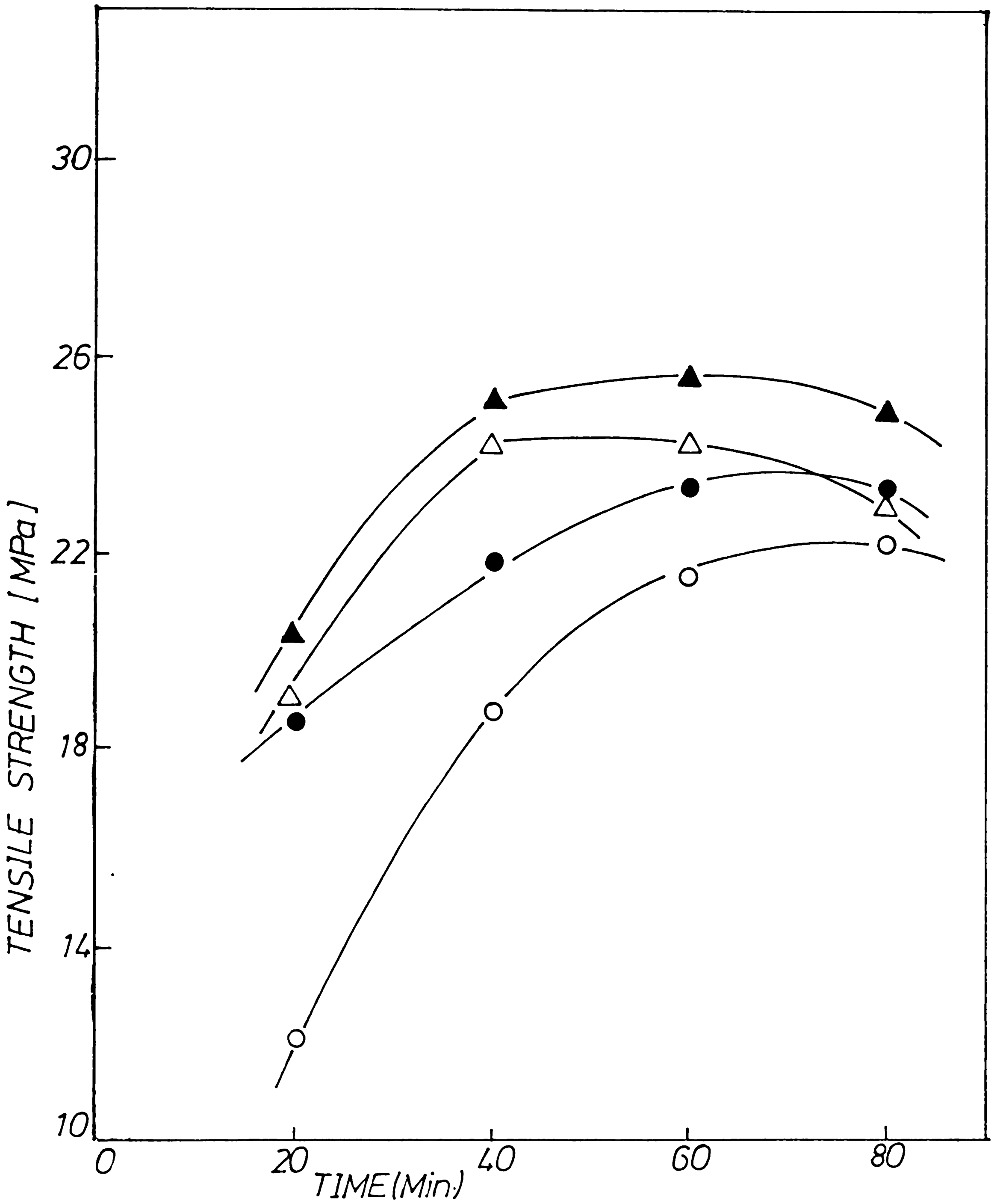

Fig.4.5 : Variation of Tensile Strength of vulcanizates with vulcanization time at 100°C for (○) TMTD alone; (●) TMTD/thiourea; (△) TMTD/DTB-II; (▲) TMTD/DTB-III.

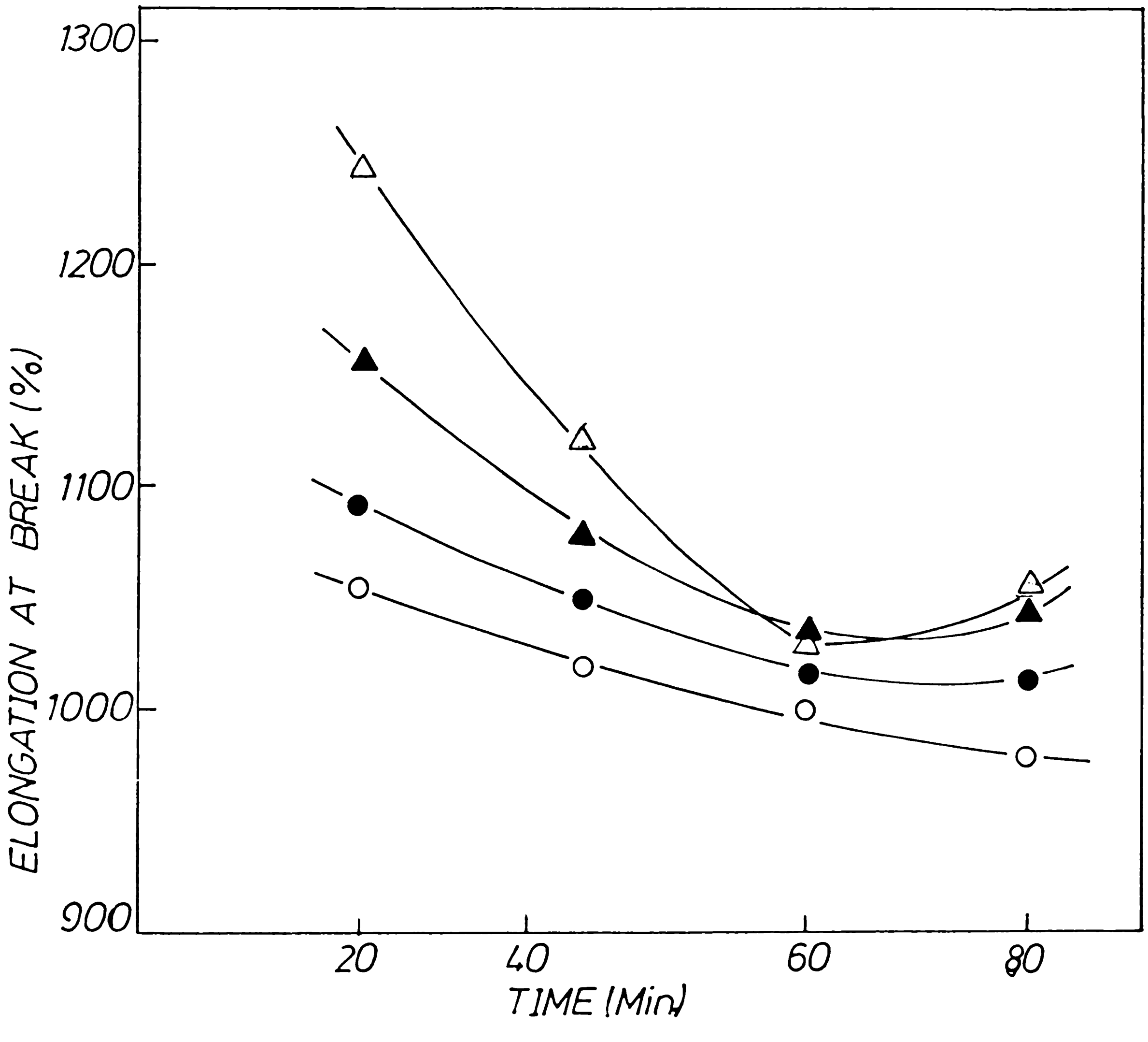

Fig. 4.6 : Variation of Elongation at break of vulcanizates withvulcanization time at 100°C for (○) TMTD alone; (●) TMTD/thiourea; (△) TMTD/DTB-II; (▲) TMTD/DTB-III.

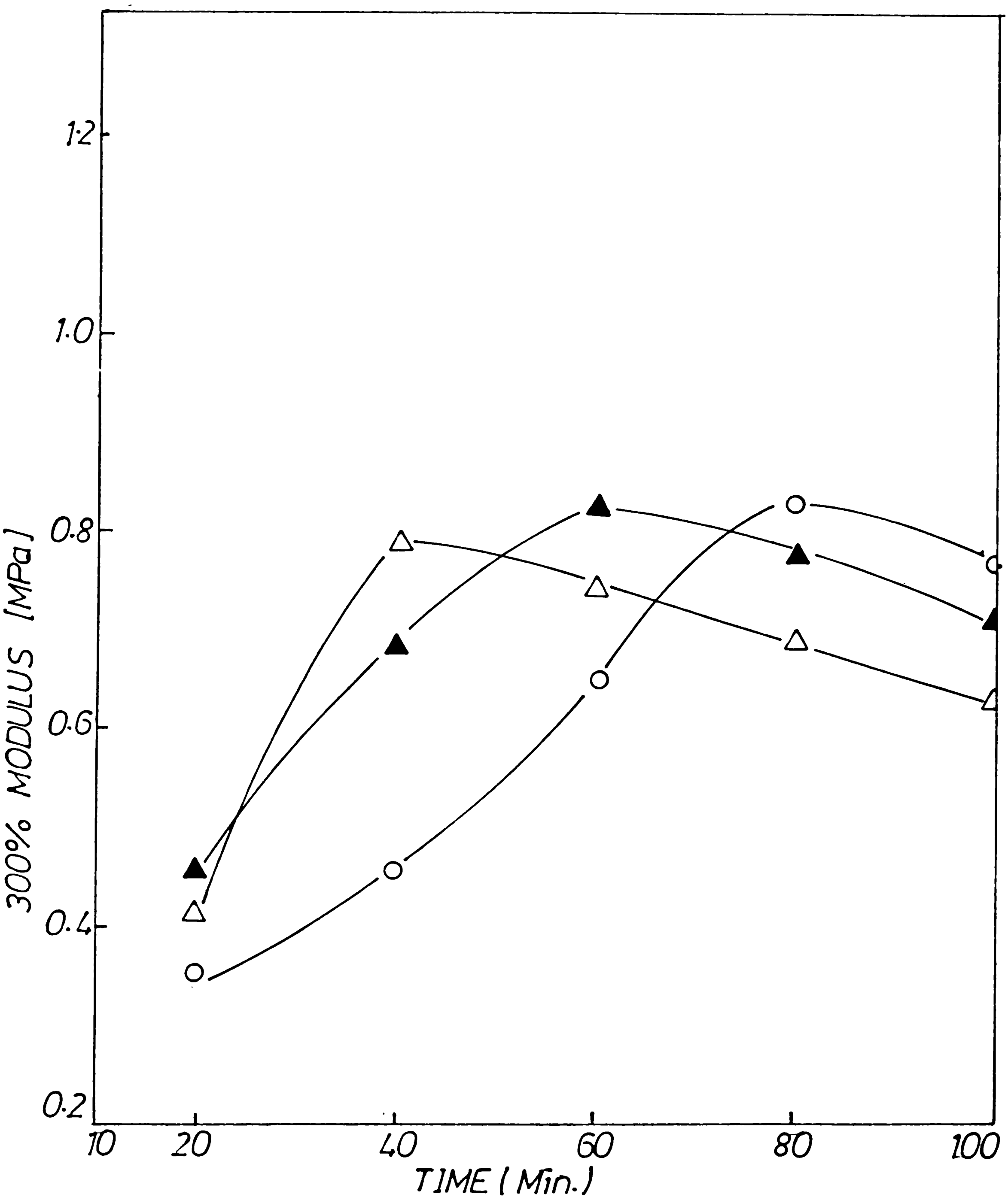

Fig.4.7 : Variation of 300% modulus of vulcanizates with vulcanization time at 120°C for (○) CBS/thiourea; (△) CBS/DTB-II; (▲) CBS/DTB-III.

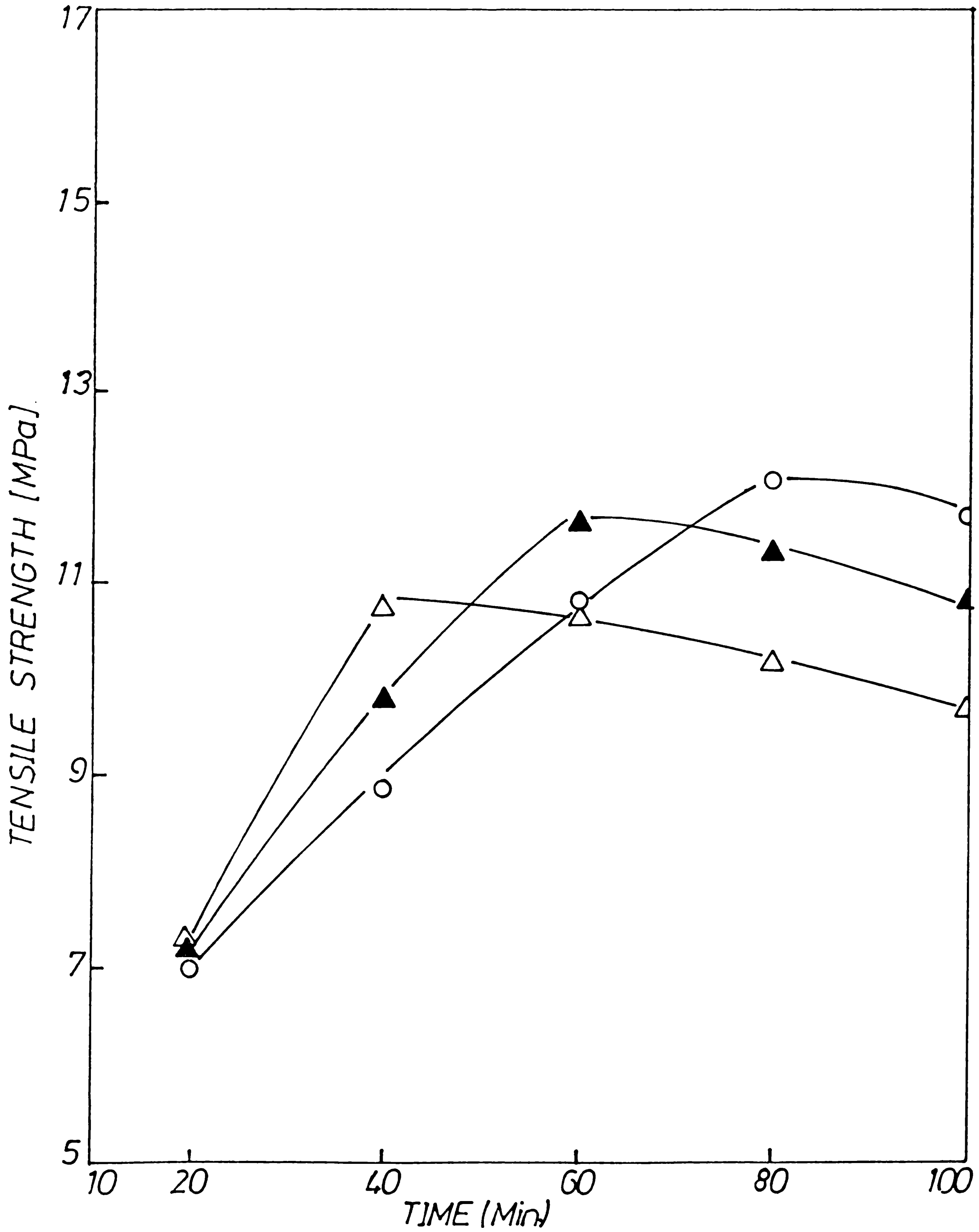

Fig. 4.8 : Variation of Tensile Strength of the vulcanizates with vulcanization time at 120°C for (○) CBS/thiourea; (△)CBS/DTB-II; (▲) CBS/DTB-III.

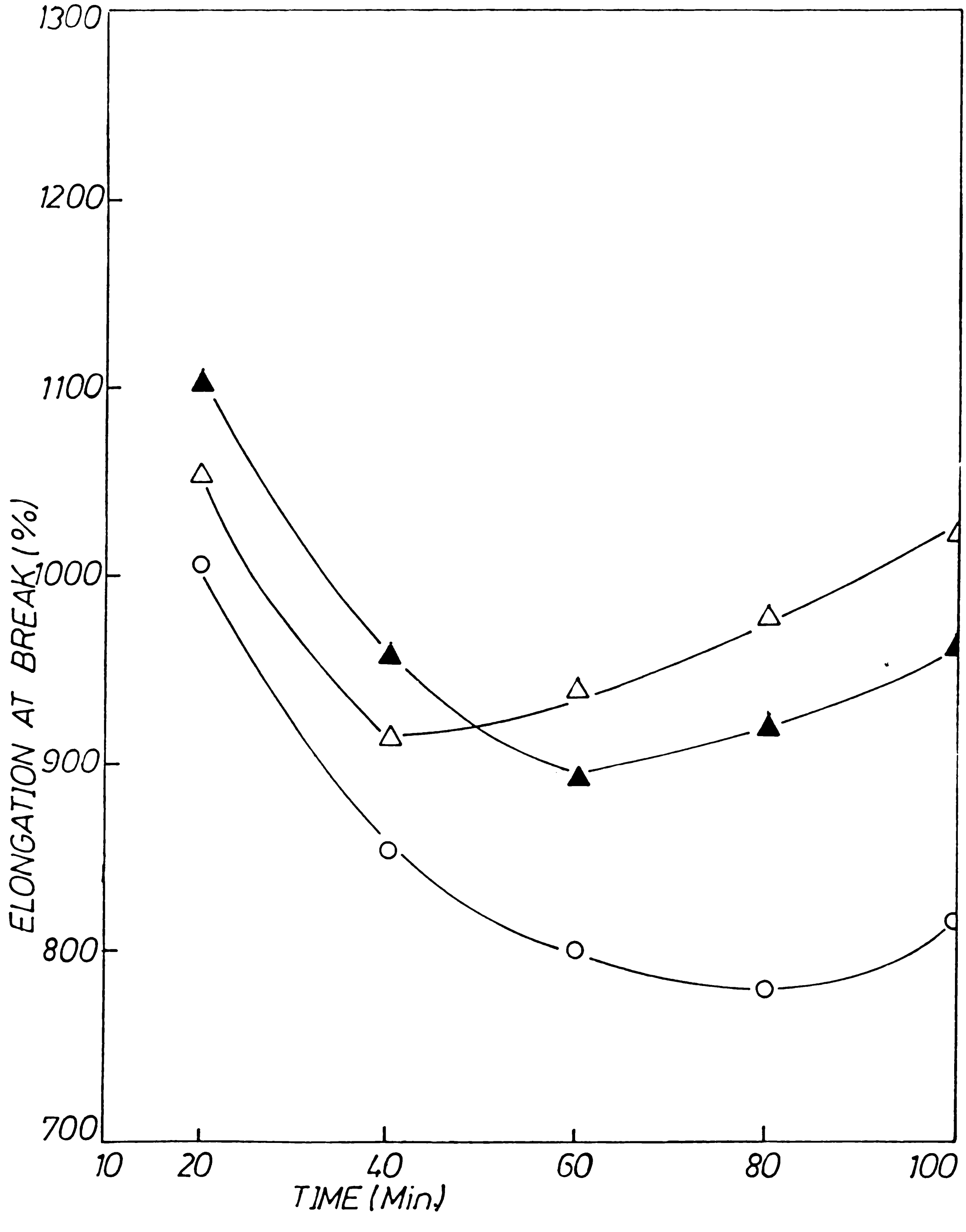

Fig. 4.9 : Variation of elongation at break of vulcanizates with vulcanization time at 120°C for (○) CBS/thiourea; (△) CBS/DTB-II; (▲) CBS/DTB-III.

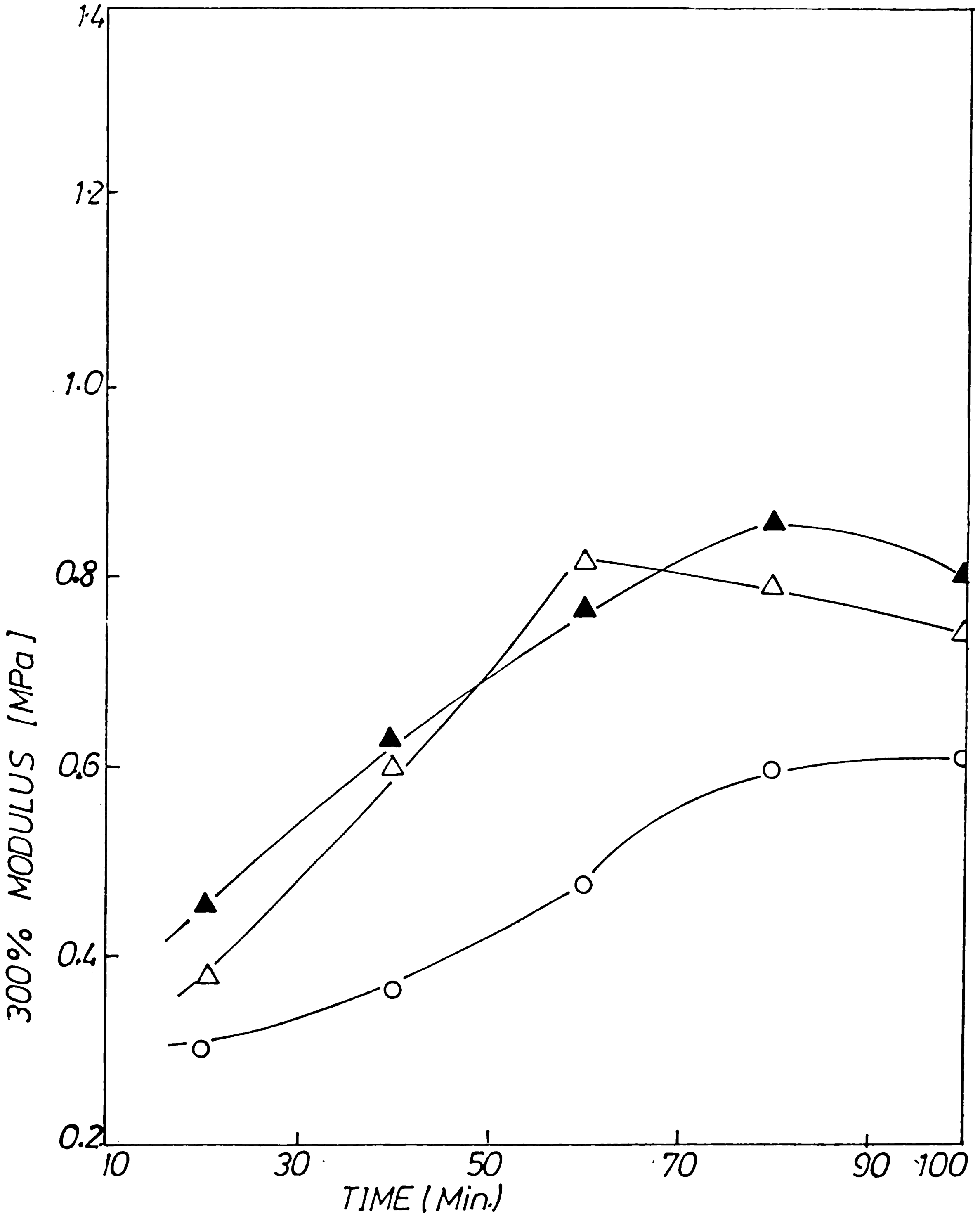

Fig.4.10 : Variation of 300% modulus of the vulcanizates with vulcanization time at 100°C for (○) CBS/thiourea; (△) CBS/DTB-II; (▲) CBS/DTB-III.

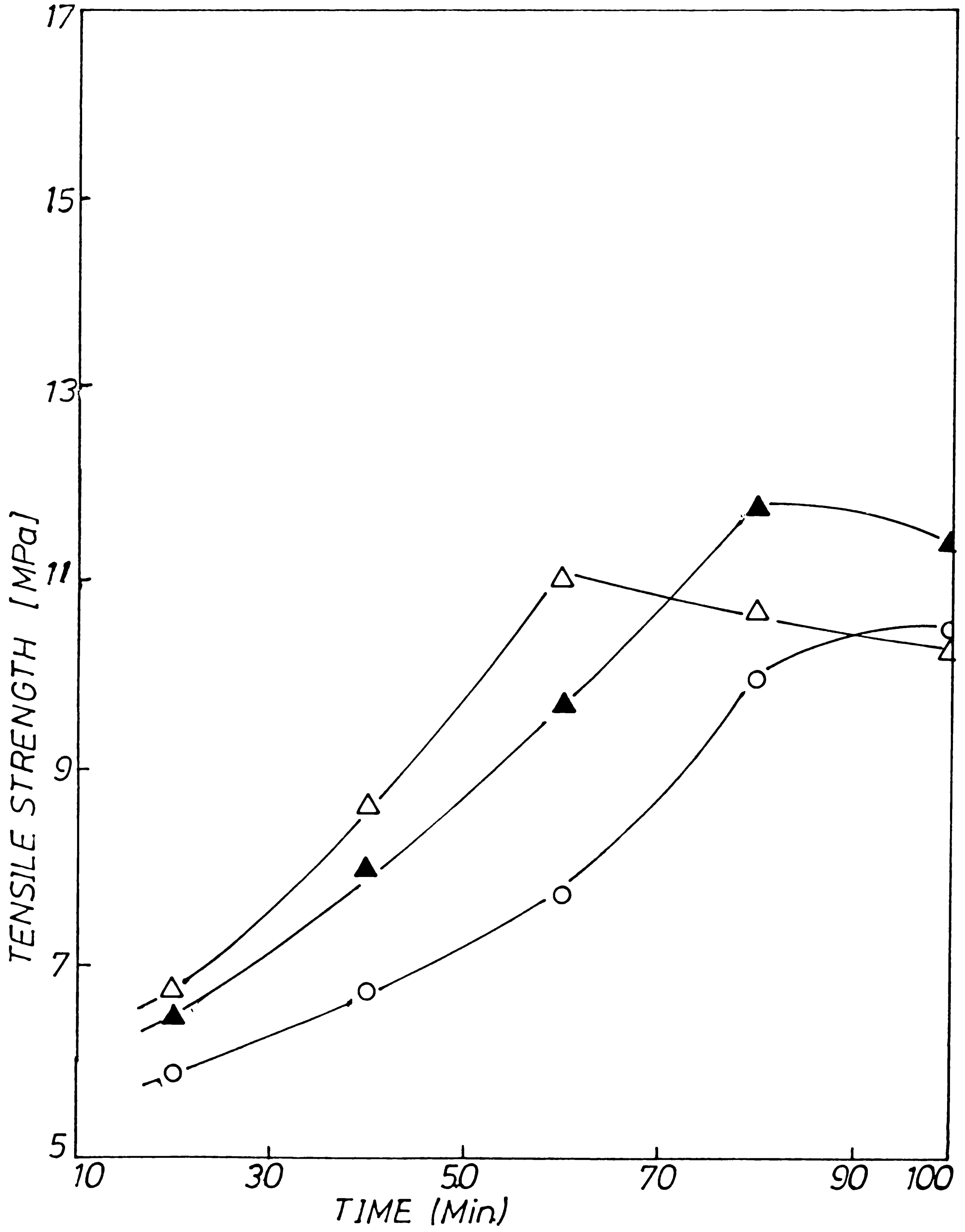

Fig. 4.11 : Variation of Tensile Strength of the vulcanizates with vulcanization time at 100°C for (O) CBS/thiourea; (△) CBS/DTB-II; (▲)CBS/DTB-III.

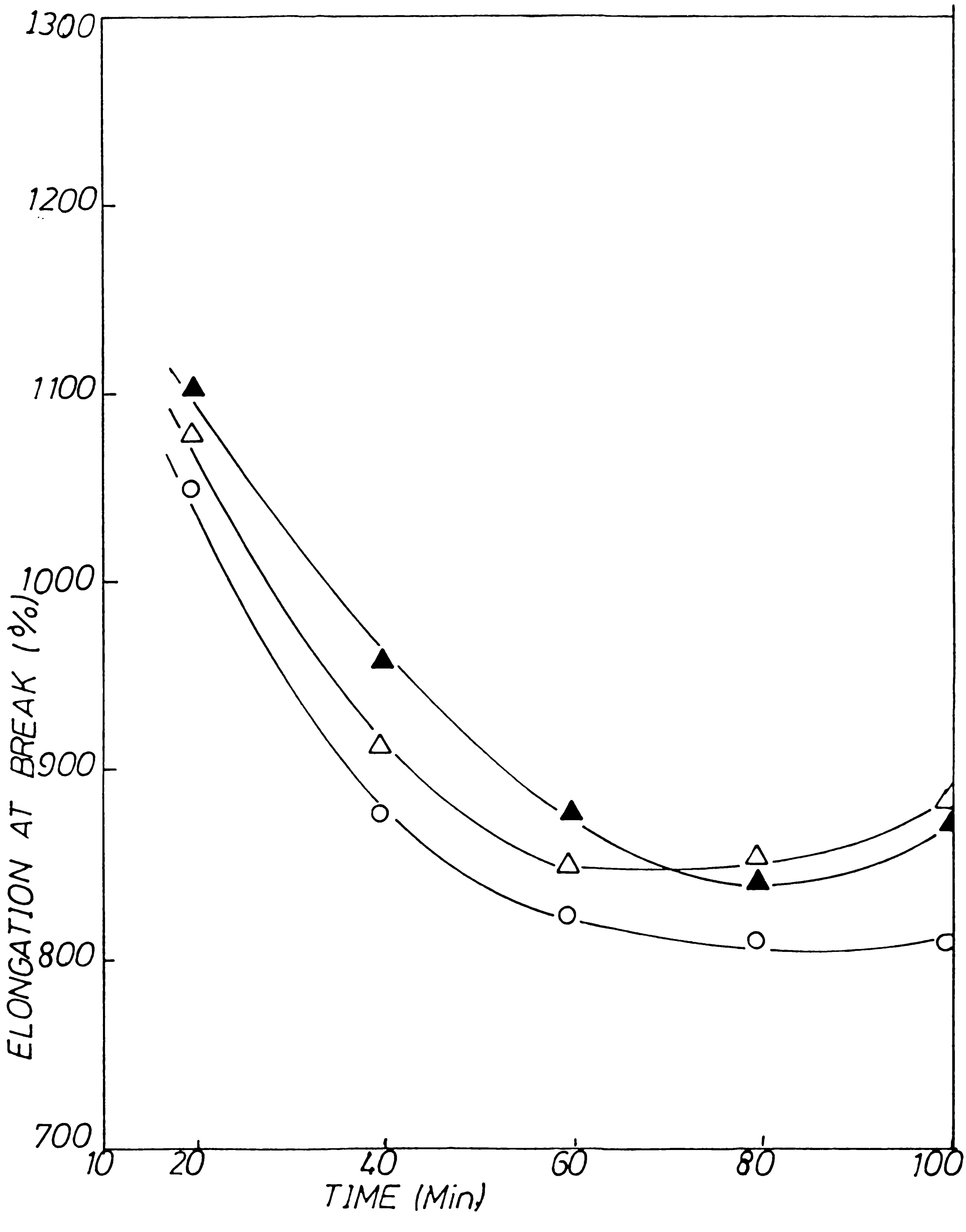

Fig.4.12 : Variation of elongation at break of the vulcanizates with vulcanization time at 100°C for (○) CBS/thiourea; (△) CBS/DTB-II; (▲) CBS/DTB-III.

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CHAPTER - V

STUDY OF DITHIOBIURETS IN SBR VULCANIZATION SYSTEMS

STUDY OF DITHIOBIURETS IN SBR VULCANIZATION SYSTEMS

INTRODUCTION

The study of dithiobiurets in natural rubber and NR latex revealed that they are having definite accelerating effect in these systems. So we thought of trying them in synthetic rubbers also. First we tried these systems in styrene butadiene rubber, which is a general purpose synthetic rubber of large tonnage use. It is a copolymer of styrene and butadiene, manufactured by polymerising them under strictly controlled conditions of reaction and temperature using emulsion polymerisation technique. At present cold and hot polymerised SBR, are marketed in numerous varieties under various trade names[1]. These brands differ from one another in the relative proportions of butadiene and styrene, their content of different initiating agents, emulsifiers, oil, fillers, temperature of polymerisation etc.

For this study we have selected SBR 1502. It is a non-staining non-discolouring cold rubber. It produces good physical properties in either black or light coloured products. It has high loading capacity and is applied in the manufacture of tyre parts, sports goods, moulded and extruded products, footwear, sheetings, sponge, coated fabric etc.

The unsaturation of SBR is less than that of natural rubber and the double bonds are less active chemically than the double bonds of the isoprenoid unit in natural rubber. Hence SBR rubbers are slower curing than natural rubber, and either more accelerator or a more active accelerator system is required[2]. Scorch problems are less likely with SBR than with natural rubber stocks. In SBR, plasticization before mixing with other ingradients is not necessary.

TMTD can be used as a primary accelerator, in the normal sulphur vulcanization of SBR. It imparts the vulcanizates, relatively high modulus, good mechanical and ageing properties. Large proportion of TMTD with small quantity of sulphur improves heat resistance. The onset of vulcanization of compounds containing TMTD can be increased by adding small amounts of accelerators, such as DPG, DOTG, Dithiocarbamate, thiourea etc. In the present study we have tried to increase the rate of vulcanization of SBR containing TMTD by adding DTB-II & DTB-III as secondary accelerators using thiourea as a control.

Sulphenamide accelerators like, CBS, sulphenamide BT etc. are also widely employed in SBR, especially so in the manufacture of tyres[3,4]. The mechanical properties of articles produced using sulphenamides are found to be superior. The activity of sulphenamide accelerators in SBR is some what lower than in Natural rubber, with the result that secondary accelerators can be employed without danger of scorching to increase the rate of vulcanization. In this study we have used DTB-II and DTB-III as secondary accelerators in the sulphur vulcanization of SBR, using CBS also as the primary accelerator. Tables 5.1 - 5.4 give the composition of the various mixes. An attempt was made to find out the optimum concentration of the dithiobiuret in the vulcanization reaction under standard conditions. Mix A_o contains 1.5 phr TMTD alone while mix B_o contain 1.5 phr TMTD and 0.5 phr thiourea as accelerators. Mix C_o contain only CBS as accelerator. Mixes A_2 - A_5 contain different concentrations of DTB-II with 1.5 phr TMTD. Mixes B_2 - B_5 contain different concentrations of DTB-III with 1.5 phr TMTD. Mixes C_1 - C_4 contain different concentrations of DTB-II with 1.5 phr CBS while mixes D_1 - D_4 contain different concentrationsof DTB-III with 1.5 phr CBS. Trial mixes were also prepared without TMTD/CBS (mixes A_1 and B_1), but they cured very slowly and hence were not proceeded further.

In order to study the effect of dithiobiurets in special purpose synthetic rubbers, we have taken polychloroprene (neoprene W type) for our study. Mixes were prepared according to the formulation ; Neoprene 100, stearic acid 0.5, FEF black 40, naphthenic oil 5.0, NA-22 0.5, MgO 4.0 and zinc oxide 5.0. DTB-II (0.5 phr) was added into the system to replace ethylenethiourea (NA-22).

The cure curves obtained are given in Fig.5.1. From these curves it is evident that the dithiobiuret has shown only slight acceleration in the vulcanization of neoprene. It can be explained to be due to the difference in the vulcanization mechanism of neoprene with sulphur bearing accelerators[5] compared to the other diene rubbers. Based on this, we have not further gone into these systems in detail.

RESULTS AND DISCUSSION

1. Cure Characteristics

The cure characteristics of various mixes at 150°C and 120°C were evaluated using a Monsanto Rheometer (R.100) and the cure curves obtained are given in Figs.5.2 - 5.9. The cure characteristics are given in Tables 5.5 - 5.12. The scorch time of the mixes at 120°C were evaluated using a Mooney Viscometer. The results clearly indicate the acceleration effect of the dithiobiurets in the vulcanization of SBR. Of the two dithiobiurets studied, the vulcanization system containing TMTD and DTB-II is found to be more effective. This is indicative of a nucleophilic reaction mechanism in sulphur vulcanization of SBR also. The addition of 1.5 phr of DTB-II reduces the optimum cure time to almost half and the cure rate is almost doubled. However, the very low scorch time of this mix (A_2) is likely to cause processing problems. As the concentration of dithiobiurets increases there is appreciable reduction in maximum torque value of the vulcanizates. By reducing the amount of DTB-II a practical cure system can be obtained. A dosage of 0.5 phr of DTB-II can be taken as optimum. At this level there is appreciable reduction in cure time and at the same time scorch time and maximum torque developed are not very low. Compared to DTB-II, DTB-III is found to be less active. Although there is some reduction in optimum cure time and corresponding increase in cure rate, the effects are less significant at the dosage of 0.5 phr DTB-III. A dosage of 1.0 phr of DTB-III is found to give optimum cure characteristics. The reversion studies of systems were carried out at 170°C to see the stability of the system. The number of units of torque value dropped in 5 minutes at 170°C is nil showing the excellent reversion resistance of these systems. For a long time period the cure curve shows plateau. At the lower temperature of 120°C also both DTB-II and DTB-III are showing reduction in optimum cure time compared to TMTD alone or TMTD and thiourea. But the cure rate is not appreciably increased as indicated by the cure rate index. So the cure characteristics of the systems containing lower concentration of dithiobiurets were not further studied.

The effect of DTB-II is found to be more pronounced in the CBS-sulphur system. Here also the optimum dosage is found to be 0.5 phr. At this level the optimum cure time is brought down to 28 min from 47.5 min., while maintaining the scorch time and the maximum torque developed in the desirable range. In this system also, DTB-III is found to be less active than DTB-II. However, the effect of DTB-III is more significant here than in TMTD - sulphur system. It is also found that to get almost the same effect as that obtained with 0.5 phr of DTB-II a dosage of 1.0 phr of DTB-III is required. Here also the number of units of torque dropped in 5 minutes at 170°C is nil, showing the excellent reversion resistance in this system. At 120°C mix C_o took much higher time to start curing and hence the cure characteristics of the systems containing CBS alone as accelerator was not further studied.

2. Tensile Properties

SBR is a nonstrain crystallising rubber and hence has poor gum strength. However, even at this level the new accelerators DTB-II and DTB-III are found to improve many of the tensile properties of both TMTD and CBS systems. The tensile properties are given in Figs.5.10 - 5.15. In the case of TMTD/dithiobiuret binary systems 200% modulus and tensile strength are improving at the lower dosages of dithiobiurets and the elongation at break is decreasing. At the optimum dosage of 0.5 phr DTB-II and 1 phr DTB-III there is appreciable increase in the tensile properties when compared to vulcanizate containing

TMTD/thiourea accelerator system. This may be due to the increase in polysulphidic linkages, as evidenced by the crosslink density studies (Table 5.21). The total crosslink density and polysulphidic linkages are higher for vulcanizates containing DTB-III than that of DTB-II. This may be the reason for higher tensile properties of the system containing DTB-III. As expected the percentage retention of tensile properties are also quite high. It may be due to the presence of a higher concentration of mono and disulphidic linkages in the system.

In the case of CBS/dithiobiurets binary systems there is a slight change in the behaviour of dithiobiurets. In the case of DTB-II 200% modulus and tensile strength are increasing first and then it decreases; the elongation at break is first decreasing and then increasing as the dosage of dithiobiuret decreases. At the optimum dosage of 0.5 phr DTB-II, it shows maximum tensile strength and modulus. In the case of DTB-III, tensile strength and modulus are decreasing and elongation at break increases with decrease in the dosage of dithiobiuret. At the optimum dosage of 1 phr the tensile properties are superior to that of the system containing CBS alone. DTB-III is giving better tensile properties than DTB-II; this may be due to a higher concentration of polysulphidic crosslinks in the system containing DTB-III. In these systems also the percentage retention of tensile properties after ageing is quite high and this may be attributed to the presence of higher concentration of mono and disulphidic linkages in these systems.

3. Other Physical Properties

Other physical properties studied are hardness, compression set, heat build up, resilience, and tear strength. These are given in Tables 5.13 - 5.20 • In the case of vulcanizates containing TMTD/dithiobiuret systems hardness, resilience and tear strength are generally increasing as the concentration of dithiobiuret decreases. Compression set and heat build up values are decreasing. At the optimum dosage of 0.5 phr and 1.0 phr of DTB-II and DTB-III respectively, these properties are higher than that of TMTD/thiourea system. This may be attributed to the fact that total crosslink density and polysulphidic linkages are more in the vulcanizates containing TMTD/dithiobiuret systems. This is in agreement with results obtained in the study of tensile properties. Cured at 120°C, hardness, tear strength and resilience are lower while compression set and heat build up are higher than that at 150°C. Here also the values are better than that of TMTD/thiourea system. In all these physical properties DTB-III is showing higher values than DTB-II.

In the case of CBS/dithiobiuret systems, hardness, resilience and tear strength are increasing with decrease in concentration of dithiobiuret, but after a stage it decreases. The compression set and heat build up are decreasing first and then increases. At the optimum levels the properties are quite higher than that of the vulcanizate containing CBS alone and after that level the systems show decrease in theseproperties. The increase in these properties is reflected in the total crosslink density and polysulphide linkages.

4. Chemical Characterization

The total chemical crosslink densities and different types of crosslinks like mono, di and polysulphidic linkages, free sulphur and zinc sulphide sulphur were evaluated for vulcanizates containing TMTD alone, CBS alone, TMTD/thiourea systems, and the systems containing optimum concentration of dithiobiurets. The results are given in Table 5.21. The total crosslink density and polysulphidic linkages of TMTD/DTB-II system cured at 150°C is slightly less than that of TMTD alone but it is higher than TMTD/thiourea systems. This may be one of the reasons for the decrease in tensile strength of TMTD/DTB-II system compared to TMTD alone. DTB-III is showing highest values of total crosslink density and polysulphidic linkages. These systems show better modulus, tensile strength, hardness and resilience values than those of DTB-II. The higher amount of monosulphide linkages in the systems containing dithiobiurets explain its better ageing properties. The free sulphur concentration is lower for dithiobiuret systems indicating the more efficient utilization of sulphur for vulcanization. The zinc sulphide sulphur concentration is also higher which favours the formation of more mono and di sulphidic linkages by the desulphuration process in the dithiobiuret systems in comparison to the system containing TMTD alone.

In the CBS/dithiobiuret systems also the total crosslink density and polysulphidic linkages are higher than that of CBS alone, which supports the higher modulus, tensile strength, hardness, resilience and lower compression set and heat build up of the vulcanizates containing dithiobiurets. In this case also DTB-III is giving higher values of chemical crosslinks which favours its superior physical properties than DTB-II. The free sulphur concentration is lower for dithiobiuret systems than that of CBS alone at 150°C, which indicates the efficiency of vulcanization of dithiobiuret system. The zinc sulphide sulphur concentration is lower at 150°C. This probably accounts for the lower concentration of mono sulphidic linkages in these systems.

EFFECT OF FILLERS.

The molecular irregularity and large pendant group in SBR prevent crystallization on stretching. This will result in lower green strength and gum tensile strength. To overcome this type of behaviour of SBR, incorporation of fine reinforcing fillers is required. Dinsmore[6] reported that the ratio of tensile strength of black filled to that of gum vulcanizate is 10 to 5 for vulcanizates of SBR. SBR has some optimum filler loadings for particular properties such as wear and tear resistance[7]. In order to study the effect of various fillers on the sulphur vulcanization of SBR containing dithiobiurets we have taken TMTD/dithiobiuret binary systems and vulcanizates were prepared with carbon black (in varying concentrations), precipitated silica and china clay. Curing studies were carried out at 150°C & various properties of the vulcanizates were evaluated.

i) Carbon black

Carbon black improves the tensile properties and resistance to failure of the SBR vulcanizates. A pure gum vulcanizate of SBR has a tensile strength of only about 2.20 MPa, but by mixing 50 phr of a reinforcing black, the value can easily be raised upto 16 MPa. This is the result of interaction between the surface of the carbon black and the elastomer. Carbon black has a significant effect on the vulcanization reaction of SBR. It appears to adsorb accelerator from the compound and there is an increase in the crosslinking efficiency. Porter[8] as well as Bhowmick and De[9] have discussed the role of reinforcing black in the sulphuration process in vulcanization. With the general purpose elastomers like SBR, HAF black with average particle size in the range 24 - 28 $m\mu$ are most widely used. The optimum black level vary from 30 to 60 phr, although, if more oil are added considerably larger quantities can be employed. In the present study HAF black (N 330) is used. Table 5.22 shows the formulation of the mixes. All the mixes contain 1.5 phr of TMTD as the primary accelerator. Mixes IA - ID contain 5, 10, 20 and 50 phr HAF black in which TMTD alone is taken as the accelerator. mixes IIA - IID contain a definite sequence of HAF black in which TMTD and 0.5 phr thiourea are taken as the accelerators. Mixes IIIA - IIID contain the same sequence of HAF black where TMTD and 0.5 phr DTB-II are taken as the accelerator combination: IVA - IVD contain the same amounts of HAF black where TMTD and 0.5 phr DTB-III forms the accelerator system.

The cure characteristics of the above mixes calculated at 150°C (Figs.5.16 - 5.19) are shown in Table 5.23. It can be seen from the table that in all the systems studied there is an increase in the Rheometric torque with increase in the filler loading. Similarly there is a reduction in the induction time, Rheometric scorch time and optimum cure time and a corresponding increase in the cure rate index which indicates an effective interaction of HAF black with polymer and vulcanization systems. Compared to the system containing TMTD alone and TMTD/thiourea, the system containing DTB-II and DTB-III reduced the optimum cure time considerably. As in the case of natural rubber, DTB-II is more active than DTB-III. At higher filler loading there is substantial reduction in the optimum cure time.

Table 5.24 shows the tensile properties of the vulcanizates. There is an increase in 300% modulus tensile strength and elongation at break with increase in filler loading. The tensile properties of the vulcanizates containing dithiobiurets are higher than that containing TMTD alone and TMTD/thiourea systems. Other physical properties of the vulcanizates evaluated are given in Table 5.25. In all the systems, with increase in the concentration of carbon black, hardness, compression set, heat buildup and tear strength are increasing while resilience decreases. In these properties dithiobiurets give comparable values with that of TMTD alone or TMTD thiourea systems. The results of the chemical characterisation of mixes containing 50 phr HAF black is given in table 5.21. The total crosslink density and polysulphide linkages in the system containing DTB-III are higher while monosulphide linkages are slightly lesser than that of TMTD alone. In the case of DTB-II also, the polysulphide linkages are higher but monosulphide linkages are slightly lesser than that of TMTD alone. Both the dithiobiuret systems are giving better results in crosslink density than that of TMTD/thiourea system. Free sulphur concentration in DTB-III is lower than that of other system. In DTB-II it is lower than that of thiourea system but slightly higher than TMTD alone. So it can be concluded that the incorporation of the secondary accelerators DTB-II and DTB-III in these systems has the significant effect of reducing the optimum cure time considerably without adversely affecting the desired physical properties.

ii) Precipitated silica

Non-black fillers like precipitated silica are used in SBR to improve processing and to reinforce the polymer in the production of white or coloured compounds[10]. Good strength and abrasion resistance can be achieved with precipitated silica, although they are some what inferior in this respect to blacks and are more expensive. Due to the highly absorptive nature of precipitated silica, more accelerators or a combination of accelerators which is more active is necessary. In this study we tried TMTD/ dithiobiuret systems in the vulcanization of SBR where precipitated silica is used as a filler. As in the case of NR, in SBR also there is no significant reduction in cure time in the silica filled systems, which may be due to the higher absorption of the accelerators by the filler. So we have not investigated this system further.

iii) China clay

Clay is used in SBR when highest value of physical properties are not essential and reduction in cost is more important. Clays are highly absorptive and hence reduce the cure rate of SBR vulcanizates also. We have tried dithiobiuret systems in the sulphur vulcanization of SBR where china clay is also used as the filler. It was observed that there is no significant effect for dithiobiurets in the china clay filled SBR also. So we have not proceeded further with these systems.

TABLE 5.1

Formulation of the Mixes

Ingredients	A_o	B_o	A_1	A_2	A_3	A_4	A_5
S B R 1502	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2
T M T D	1.5	1.5	--	1.5	1.5	1.5	1.5
Thiourea	--	0.5	--	--	--	--	--
DTB-II	--	--	0.5	1.5	1.0	0.5	0.25
Sulphur	0.5	0.5	0.5	0.5	0.5	0.5	0.5

TABLE 5.2

Ingredients	A_o	B_o	B_1	B_2	B_3	B_4	B_5
S B R 1502	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2
T M T D	1.5	1.5	--	1.5	1.5	1.5	1.5
Thiourea	--	0.5	--	--	--	--	--
DTB-III	--	--	0.5	1.5	1.0	0.5	0.25
Sulphur	0.5	0.5	0.5	0.5	0.5	0.5	0.5

TABLE 5.3

Formulation of the Mixes

Ingredients	C_o	C_1	C_2	C_3	C_4
S B R 1502	100	100	100	100	100
Zinc oxide	5	5	5	5	5
Stearic acid	2	2	2	2	2
C B S	1.5	1.5	1.5	1.5	1.5
DTB-II	--	1.5	1.0	0.5	0.25
Sulphur	0.5	0.5	0.5	0.5	0.5

TABLE 5.4

Ingredients	C_o	D_1	D_2	D_3	D_4
S B R 1502	100	100	100	100	100
Zinc oxide	5	5	5	5	5
Stearic acid	2	2	2	2	2
C B S	1.5	1.5	1.5	1.5	1.5
DTB-III	--	1.5	1.0	0.5	0.25
Sulphur	0.5	0.5	0.5	0.5	0.5

TABLE 5.5

Cure characteristics of the mixes containing TMTD/DTB-II at 150°C

Mix No.	Min. Torque (dN.m)	Max. Torque (dN.m)	Induction time(t_1) (min.)	Rheometric scorch time (t_2) (min.)	Optimum cure time(t_{90}) (min.)	Cure rate index	Reversion at 170°C (No.of units reverted in 5 mnts.
A_o	10.5	65.0	3.0	3.5	18.5	6.67	--
B_o	11.0	56.0	2.0	2.5	11.5	11.11	--
A_2	14.0	61.0	0.5	1.0	9.5	11.11	--
A_3	13.0	63.0	0.75	1.25	11.5	9.76	--
A_4	10.5	61.5	2.0	2.5	12.5	10.0	--
A_5	10.0	65.0	2.5	3.0	15.5	8.0	--

TABLE 5.6

Cure characteristics of the mixes containing TMTD/DTB-II at 120°C

Mix No.	Minimum Torque (dN.m)	Maximum Torque (dN.m)	Induction time(t_1) (min.)	Optimum cure time(t_{90}) (min.)	Cure rate index	Mooney scorch time (t_5) (min.)
A_o	15	55	15.0	70.0	1.89	17.0
B_o	15	56	11.0	64.0	1.96	13.0
A_2	16	58	2.5	42.0	2.56	3.0
A_3	16	58	6.0	63.0	1.80	7.5

TABLE 5.7

Cure Characteristics of the Mixes containing TMTD/DTB-III at 150°C

Mix No.	Min. Torque (dN.m)	Max. Torque (dN.m)	Induction time(t_1) (min.)	Rheometric scorch time(t_2) (min.)	Optimum cure time (t_{90}) (min)	Cure rate index	Reversion at 170°C (no.of units reverted in 5 min.
A_o	10.5	65	3.0	3.5	18.5	6.67	--
B_o	11.0	56	2.0	2.5	11.5	11.11	--
B_2	13.0	65	1.5	2.0	15.5	6.78	--
B_3	11.0	64	2.0	2.5	17.5	6.67	--
B_4	11.0	66	2.0	2.5	18.0	6.45	--
B_5	10.5	66	2.5	3.0	18.5	6.45	--

TABLE 5.8

Cure Characteristics of the Mixes containing TMTD/DTB-III at 120°C

Mix. No.	Min. Torque (dN.m)	Max. Torque (dN.m)	Induction time(t_1) (min.)	Optimum cure time(t_{90}) (min.)	Cure rate index	Mooney scorch time t_5 (min.)
A_o	15	55	15.0	70.0	1.89	17.0
B_o	15	56	11.0	64.0	1.96	13.0
B_2	19	55	1.5	55.5	1.87	2.0
B_3	15	57	7.0	77.5	1.46	9.0

TABLE 5.9

Cure Characteristics of the Mixes containing CBS/DTB-II at 150°C

Mix No.	Min. Torque (dN.m)	Max. Torque (dN.m)	Induction time(t_2) (min.)	Rheometric scorch time(t_2) (min.)	Optimum cure time (t_{90}) (min.)	Cure rate index	Reversion at 170°C (No.of units reverted in 5 min.)
C_o	10.0	37	16.0	17.5	47.5	3.30	--
C_1	11.0	44	1.5	2.0	19.0	5.88	--
C_2	10.0	44	2.0	2.5	25.5	4.35	--
C_3	10.0	45	4.0	5.0	28.0	4.33	--
C_4	10.0	42	7.0	8.5	32.0	4.25	--

TABLE 5.10

Cure Characteristics of the Mixes containing CBS/DTB-II at 120°C

Mix No.	Min. Torque (dN.m)	Max. Torque (dN.m)	Induction time(t_1) (min.)	Optimum cure time(t_{90}) (min.)	Cure rate index	Mooney scorch time(t_5) (min.)
C_o	--	--	--	--	--	--
C_1	14.5	45	4.5	62.0	1.80	6
C_2	15.0	46	6.0	95.0	1.14	7

TABLE 5.11

Cure Characteristics of the Mixes containing CBS/DTB-III at 150°C

Mix No.	Min. Torque (dN.m)	Max. Torque (dN.m)	induction time(t_1) (min.)	Rheometric scorch time(t_2) (min.)	Optimum cure time (t_{90}) (min.)	Cure rate index	Reversion at 170°C (No.of units reverted in 5 min.)
C_o	10.0	37.0	16.0	17.5	47.5	3.30	--
D_1	10.0	48.0	2.5	3.0	22.5	5.13	--
D_2	10.0	46.5	4.0	5.0	29.5	4.08	--
D_3	11.0	47.0	9.0	10.5	38.5	3.57	--
D_4	10.5	40.0	9.0	11.5	45.0	2.99	--

TABLE 5.12

Cure Characteristics of the Mixes containing CBS/DTB-III at 120°C

Mix No.	Min. Torque (dN.m)	Max. Torque (dN.m)	Induction time (t_1) (min.)	Optimum cure time(t_{90}) (min.)	Cure rate index	Mooney scorch time (t_5) (min.)
C_o	--	--	--	--	--	--
D_1	16	47	10	68.5	1.79	13
D_2	9	45	18	119.0	1.03	22

TABLE 5.13

Physical properties of the vulcanizates containing TMTD/DTB-II cured at 150°C

Mix No.	Hardness (Shore A)	Compression set (%)	Heat build up ($\Delta T^{o}C$)	Resilience (%)	Tear strength (N/mm)
A_o	43	15.05	15	65.50	14.06
B_o	32	19.20	26	63.90	12.08
A_2	38	17.40	22	63.47	10.46
A_3	41	16.70	20	64.15	11.55
A_4	43	15.25	19	65.85	12.53
A_5	45	14.80	17	66.50	14.15

TABLE 5.14

Physical properties of the vulcanizates containing TMTD/DTB-II cured at 120°C

Mix No.	Hardness (Shore A)	Compression set (%)	Heat build up ($\Delta T^{o}C$)	Resilience (%)	Tear strength (N/mm)
A_o	29	28.35	15	50.15	10.25
B_o	30	22.10	24	51.30	11.40
A_2	32	18.75	20	60.38	11.86
A_3	32	17.90	18	62.70	11.90

TABLE 5.15

Physical properties of the vulcanizates containing TMTD/DTB-III cured at 150°C

Mix No.	Hardness (Shore A)	Compression set (%)	Heat build up (ΔT°C)	Resilience (%)	Tear strength (N/mm)
A_o	43	15.05	15.0	65.50	14.06
B_o	32	19.20	26.0	63.90	12.08
B_2	40	16.80	24.0	64.15	11.85
B_3	42	15.53	22.0	65.68	12.59
B_4	44	14.90	19.0	66.90	14.41
B_5	46	14.43	18.0	67.00	14.85

TABLE 5.16

Physical properties of the vulcanizates containing TMTD/DTB-III cured at 120°C

Mix No.	Hardness (Shore A)	Compression set (%)	Heat build up (ΔT°C)	Resilience (%)	Tear strength (N/mm)
A_o	29	28.35	15	50.15	10.25
B_o	30	22.10	24	51.30	11.40
B_2	31	20.25	22	63.40	10.30
B_3	32	19.40	20	63.90	12.32

TABLE 5.17

Physical properties of the vulcanizates containing CBS/DTB-II cured at 150^{o}C

Mix No.	Hardness (Shore A)	Compression set (%)	Heat build up (ΔT^{o}C)	Resilience (%)	Tear strength (N/mm)
C_o	34.0	51.12	37	46.94	10.72
C_1	43.0	26.12	34	53.81	12.59
C_2	45.0	25.30	30	55.41	14.41
C_3	45.0	24.90	30	55.77	14.85
C_4	40.0	34.30	33	50.63	11.85

TABLE 5.18

Physical properties of the vulcanizates containing CBS/DTB-II cured at 120^{o}C

Mix No.	Hardness (Shore A)	Compression set (%)	Heat build up (ΔT^{o}C)	Resilience (%)	Tear strength (N/mm)
C_o	--	--	--	--	--
C_1	35	38.60	32	51.70	10.30
C_2	36	36.20	31	53.40	12.35

TABLE 5.19

Physical properties of the vulcanizates containing CBS/DTB-III cured at 150°C

Mix No.	Hardness (Shore A)	Compression set (%)	Heat build up (Δ T°C)	Resilience (%)	Tear strength (N/mm)
C_o	34.0	51.12	37.0	46.94	10.72
D_1	48.0	27.96	32.0	63.13	19.87
D_2	46.0	35.69	28.0	61.08	16.91
D_3	44.0	41.38	29.0	60.63	10.78
D_4	35.0	44.12	31.0	54.20	10.28

TABLE 5.20

Physical properties of the vulcanizates containing CBS/DTB-III cured at 120°C

Mix No.	Hardness (Shore A)	Compression set (%)	Heat build up (Δ T°C)	Resiliience (%)	Tear strength (N/mm)
C_o	--	--	--	--	--
D_1	36	34.50	30	59.58	12.50
D_2	38	32.25	26	61.40	14.20

TABLE 5.21

Chemical characterization of vulcanizates cured at 150°C

Mix No.	Total cross link density (M.mole/ Kg RH)	Monosulphide linkages (M.mole/ Kg RH)	Disulphide linkages (M.mole/ Kg RH)	Polysulphide linkages (M.mole/ Kg RH)	Free sulphur con. (M.mole/ Kg RH)	Zinc sulphide sulphur con. (M.mole/ Kg RH)
A_o	81.0	52.4	17.5	11.1	6.28	14.36
B_o	75.6	56.6	12.8	8.2	9.10	16.60
A_4	77.8	54.5	13.4	9.9	7.90	15.80
B_3	86.4	55.5	15.8	15.1	5.99	16.20
C_o	37.7	20.4	6.1	11.2	14.71	4.25
C_3	45.8	18.9	13.2	13.7	12.40	3.80
D_2	50.9	16.9	16.4	17.6	11.90	3.25
ID	81.6	39.2	30.8	11.6	3.43	14.50
IID	74.4	30.8	33.4	10.2	4.55	4.39
IIID	80.2	35.6	32.7	11.9	4.10	8.36
IVD	83.3	37.5	31.7	14.1	2.50	12.13

TABLE 5.22

Formulation of the mixes containing carbon black

Ingredients	IA	IB	IC	ID	IIA	IIB	IIC	IID	IIIA	IIIB	IIIC	IIID	IVA	IVB	IVC	IVD
SBR 1502	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
HAF Black	5	10	20	50	5	10	20	50	5	10	20	50	5	10	20	50
Naphthenic oil	0.5	1	2	5	0.5	1	2	5	0.5	1	2	5	0.5	1	2	5
TMTD	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Thiourea	--	--	--	--	0.5	0.5	0.5	0.5	--	--	--	--	--	--	--	--
DTB-II	--	--	--	--	--	--	--	--	0.5	0.5	0.5	0.5	--	--	--	--
DTB-III	--	--	--	--	--	--	--	--	--	--	--	--	0.5	0.5	0.5	0.5
Sulphur	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5

TABLE 5.23

Cure Characteristics of the vulcanizates containing carbon black

Mix No.	Min. Torque (dN.m)	Max. Torque (dN.m)	Induction time(t_1) (min.)	Rheometric scorch time(t_2) (min.)	Optimum cure time(t_{90}) (min.)	Cure rate index	Reversion at 170°C (No.of units reverted in 5 mts
IA	12.0	72	2.5	3.0	17.5	6.90	--
IB	12.0	74	2.5	3.0	15.0	8.33	--
IC	14.0	77	2.5	3.0	15.0	8.33	--
ID	17.5	90	2.0	2.5	13.0	9.52	--
IIA	13.0	64	3.0	3.5	14.5	9.09	--
IIB	14.0	71	2.5	3.0	13.5	10.53	--
IIC	14.0	75	2.5	3.0	12.5	11.11	--
IID	18.0	85	2.0	2.25	12.0	10.0	--
IIIA	12.0	66	2.0	2.5	13.5	9.09	--
IIIB	13.0	69	1.5	2.0	12.5	9.52	--
IIIC	14.0	78	1.5	2.0	11.0	11.11	--
IIID	18.0	93	1.0	1.5	10.0	11.76	--
IVA	12.0	70	2.5	3.0	14.0	7.14	--
IVB	13.0	72	2.5	3.0	13.0	7.14	--
IVC	14.0	76	2.5	2.75	12.0	8.16	--
IVD	18.0	90	2.0	2.25	11.5	8.89	--

TABLE 5.24

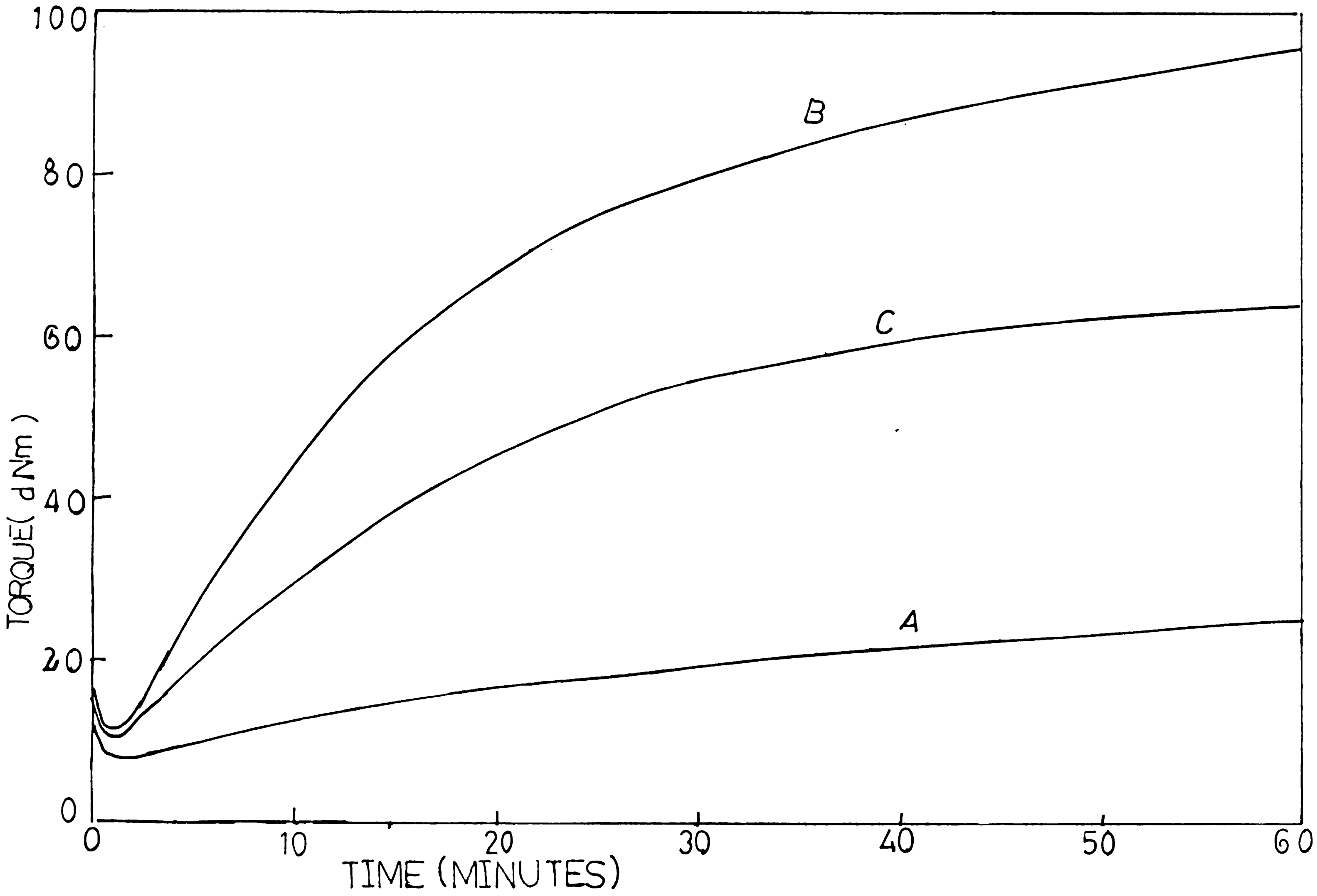
Tensile properties of the vulcanizates containing carbon black.

Mix No.	300% Modulus (MPa)			Tensile strength(MPa)			Elongation at break		
	B.A	A.A	% Rtn	B.A	A.A	% Rtn	B.A	A.A	% Rtn
IA	2.87	2.48	86.41	3.12	2.98	95.51	363.52	311.17	85.60
IB	3.19	3.07	96.24	4.34	4.18	96.31	366.09	355.59	97.13
IC	4,85	4,75	97.94	6,20	6.10	98.39	394.86	385.54	97.64
ID	9.70	9.35	96.39	16.40	14.60	89.02	483.86	403.13	83.32
IIA	2.46	2.26	91.87	2.58	2.08	80.62	292.97	227.19	77.55
IIB	2.78	2.68	96.40	3.90	3.38	86.67	304.61	261.82	85.95
IIC	3.72	3.35	90.05	5.57	4.80	86.18	388.15	300.50	77.42
IID	7.30	6,55	89.73	14.2	12.00	84.51	494.09	342.84	69.39
IIIA	2.54	2.20	86.61	2.70	2.22	82.22	319.28	260.38	81.55
IIIB	2.89	2,63	91.00	3.32	3.20	96.39	335.61	290.90	86.68
IIIC	5.13	4.83	94.15	7.16	6.80	94.97	395.47	323.32	81.76
IIID	9.93	9.92	92.55	17.68	16.19	91.57	490.20	361.22	73.69
IVA	2.59	3.30	88.80	2.73	2.67	97.80	308.82	284.79	92.22
IVB	3.00	2.69	89.67	3.56	3.06	85.96	374.59	319.47	85.29
IVC	5.85	5,42	92.65	8.10	7.27	89.75	505.31	449.54	88.96
IVD	10.80	9.08	84.07	18.20	16.95	93.13	577.12	514.23	89.10

TABLE 5.25

Other physical properties of the vulcanizates containing carbon black

Mix No.	Hardness (Shore A)	Compression set (%)	Heat build up ($\Delta T^{o}C$)	Resilience (%)	Tear strength (N/mm)
IA	45	17.73	13	59.71	22.51
IB	47	17.93	15	57.70	26.14
IC	50	18.43	18	56.40	46.30
ID	65	20.46	29	48.75	73.35
IIA	48	18.87	11	57.73	19.66
IIB	50	19.33	13	56.40	22.88
IIC	54	20.14	16	55.07	30.88
IID	63	21.76	25	49.37	58.50
IIIA	45	15.35	14	59.03	17.42
IIIB	51	16.32	16	56.46	18.35
IIIC	53	18.10	20	55.72	40.70
IIID	65	21.16	29	50.63	59.70
IVA	45	15.56	16	62.35	15.21
IVB	48	17.05	18	59.71	16.74
IVC	50	18.33	22	56.40	31.40
IVD	61	21.75	31	50.63	68.40



5.1 : Rheographs of Neoprene mixes at 150°C (A) without accelerator (B) NA-22 as accelerator (C) DTB-II as accelerator.

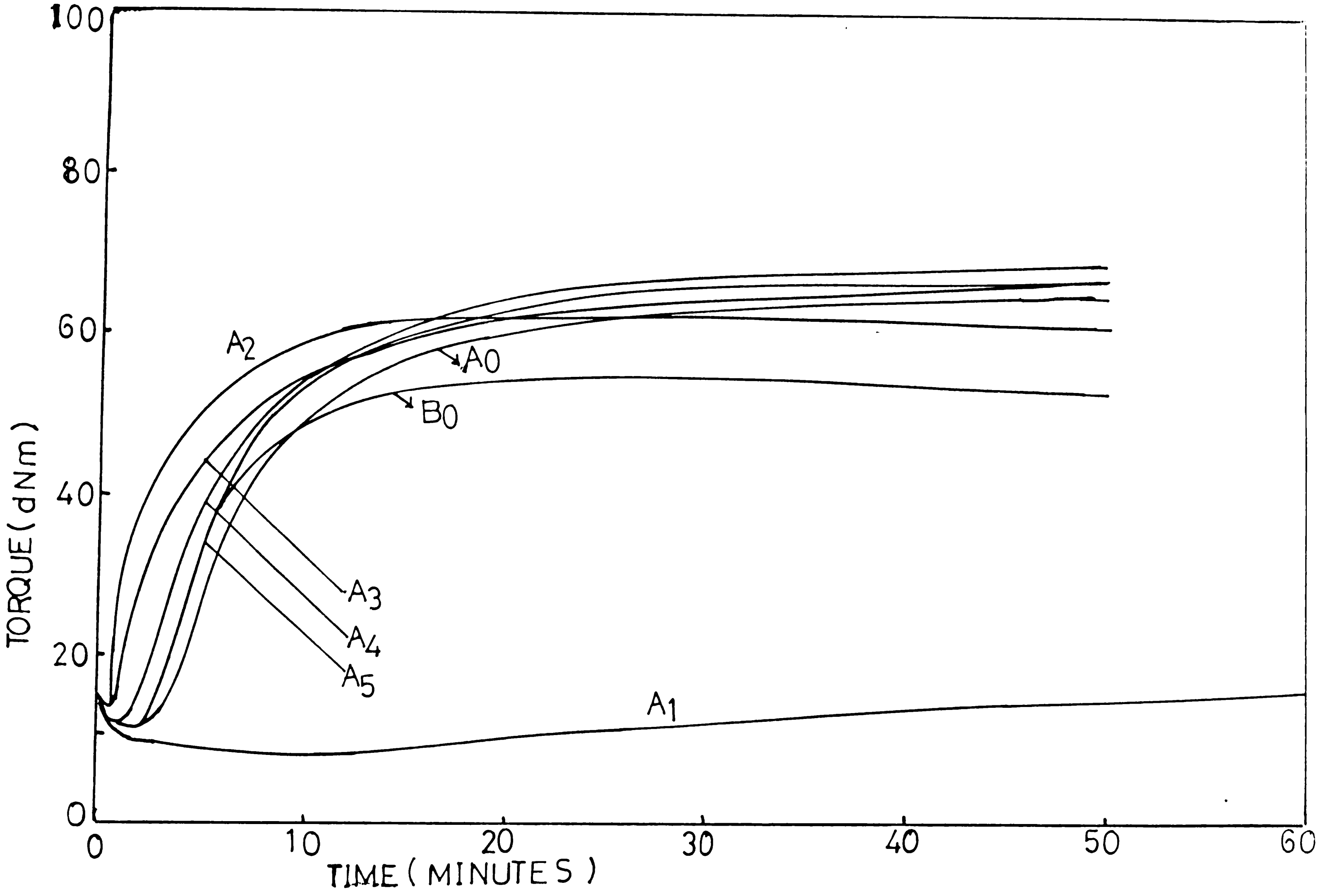


Fig. 5.2 : Rheographs of mixes containing TMTD/DTB-II at 150°C (Ref: Tables 5.1 & 5.5)

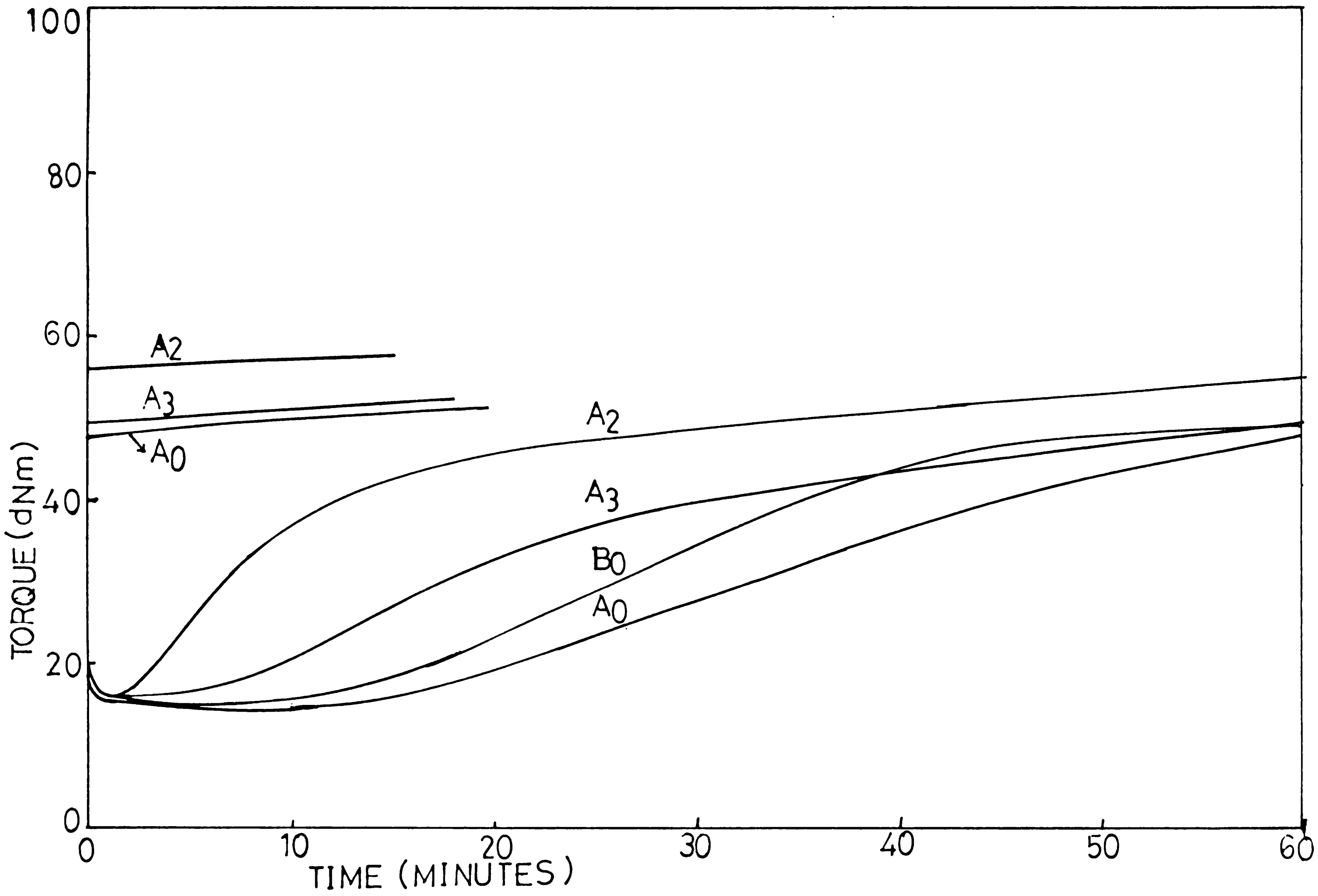


Fig. 5.3 : Rheographs of the mixes containing TMTD/DTB-II at 120°C (Refer Tables 5.1 & 5.6)

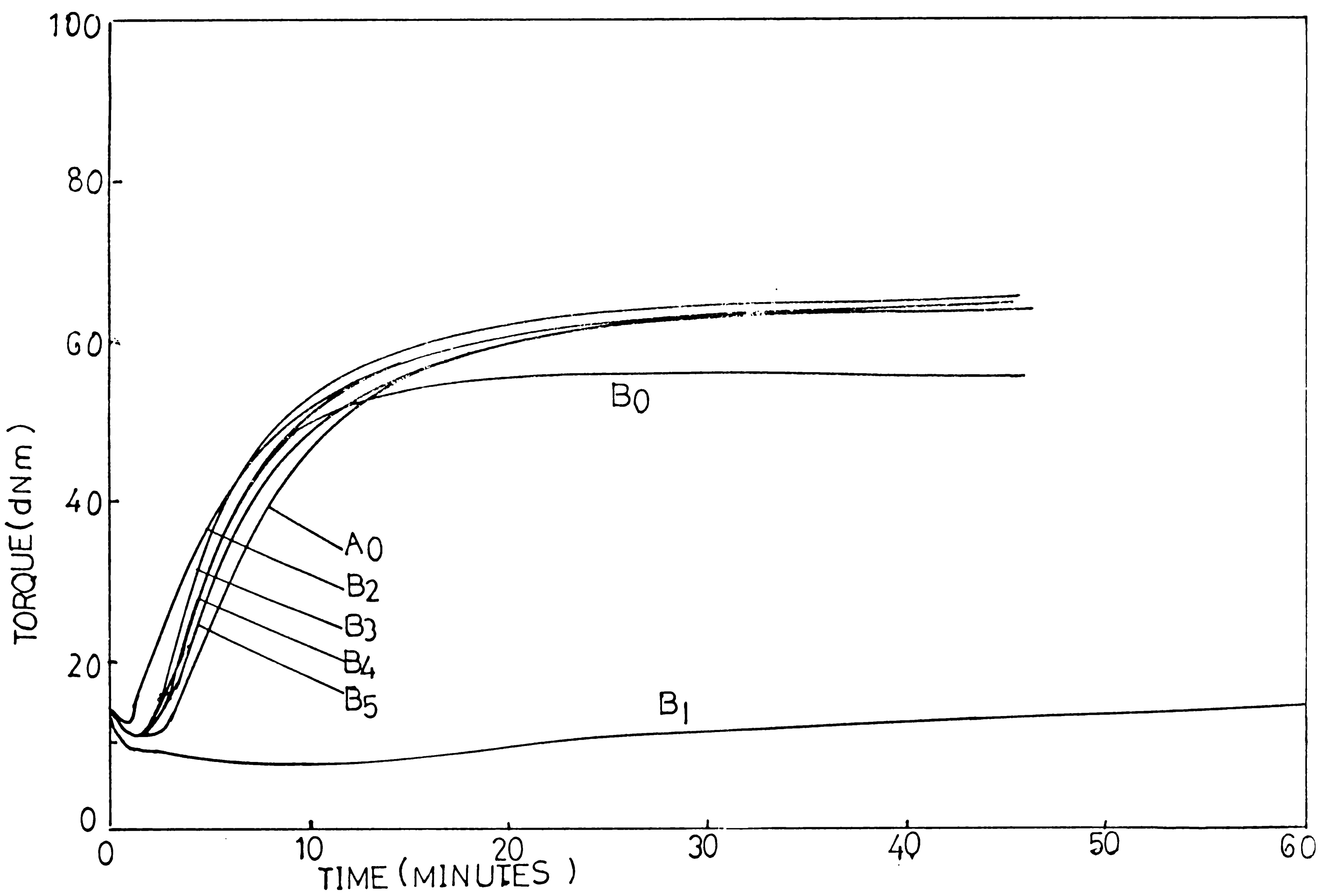


Fig. 5.4 : Rheographs of the mixes containing TMTD/DTB-III at 150°C (Ref: Tables 5.2 & 5.7)

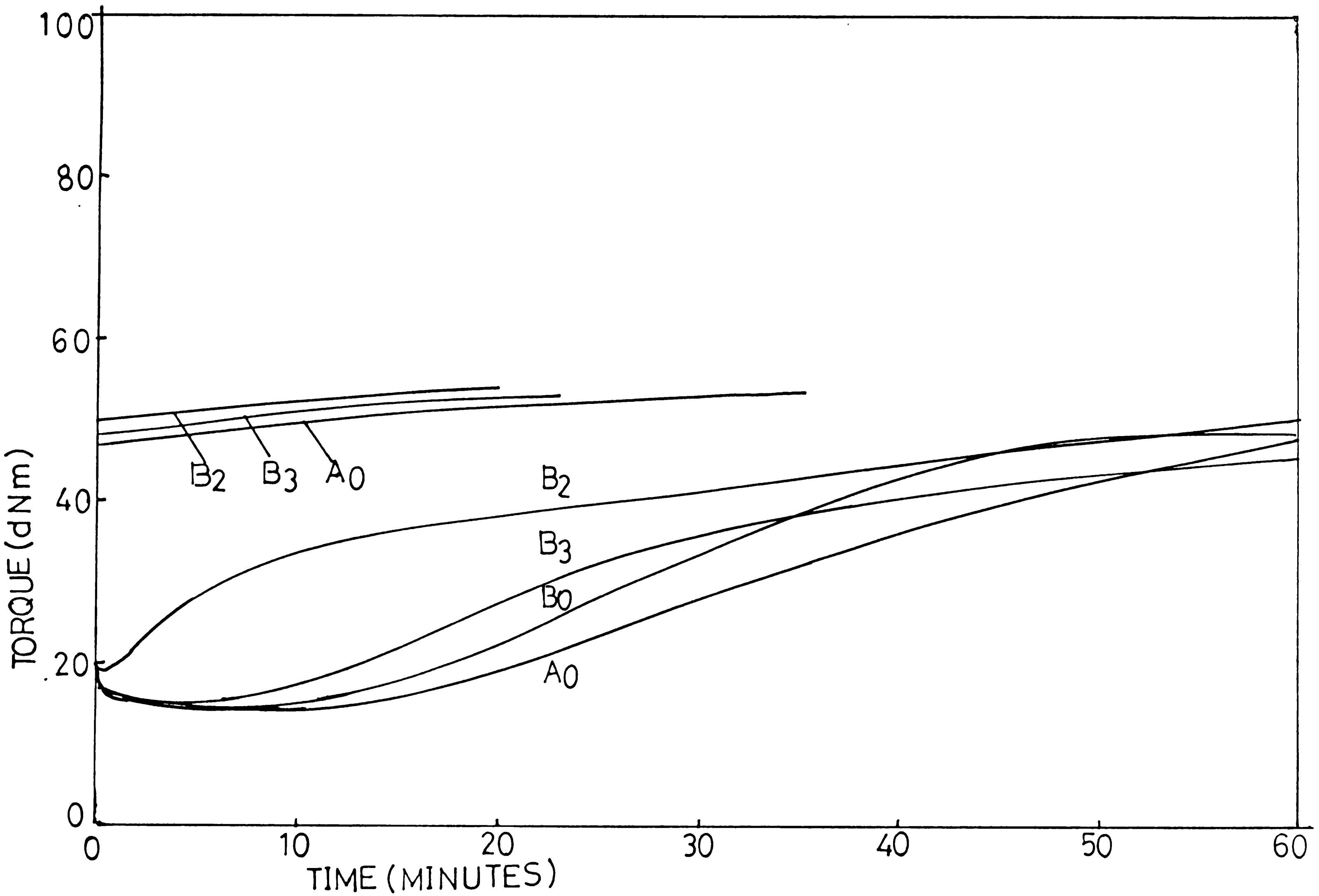


Fig. 5.5 : Rheographs of the mixes containing TMTD/DTB-III at 120°C (Ref: Tables 5.2 & 5.8)

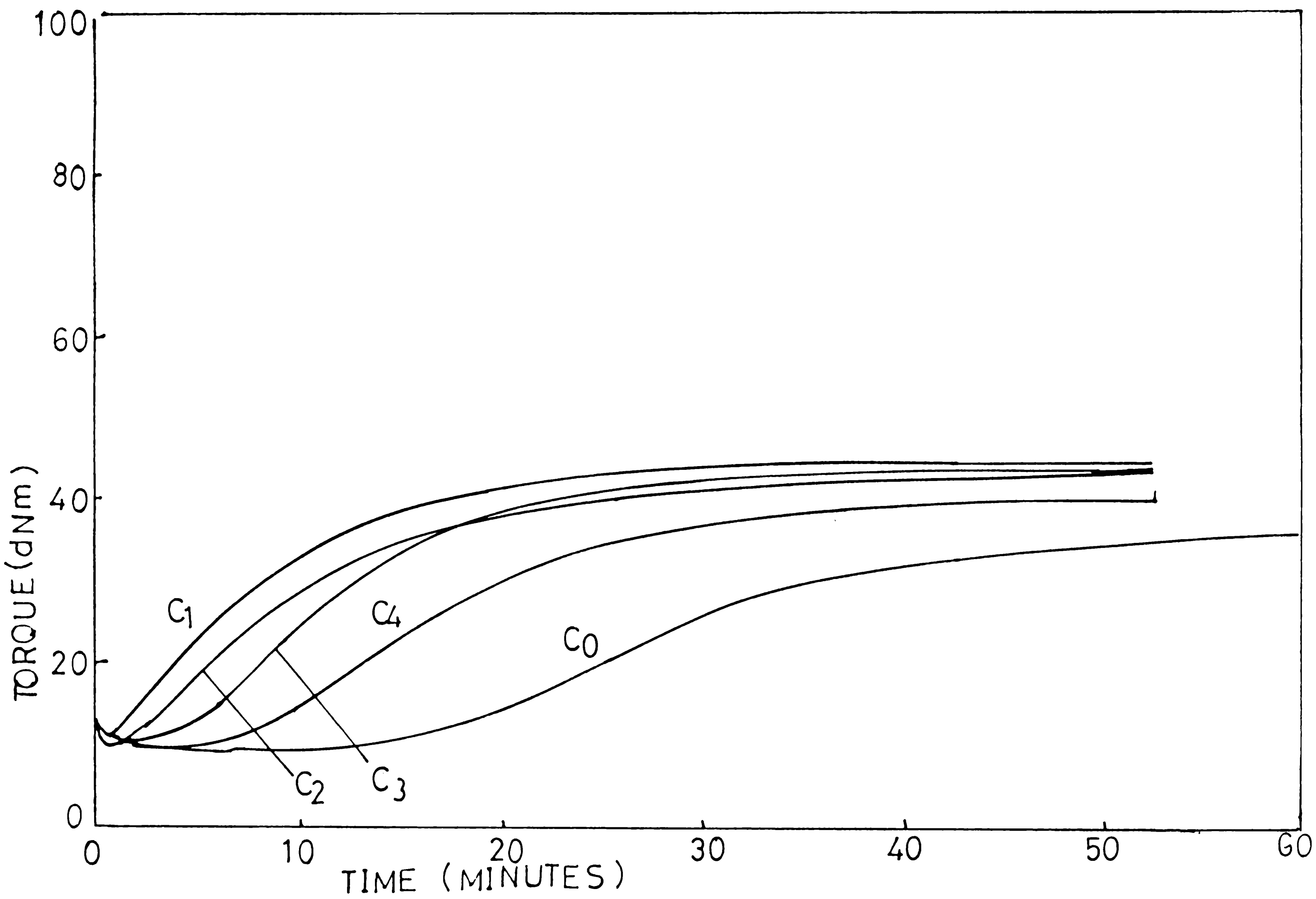


Fig. 5.6: Rheographs of the mixes containing CBS/DTB-II at 150°C (Ref. Tables 5.3 & 5.9)

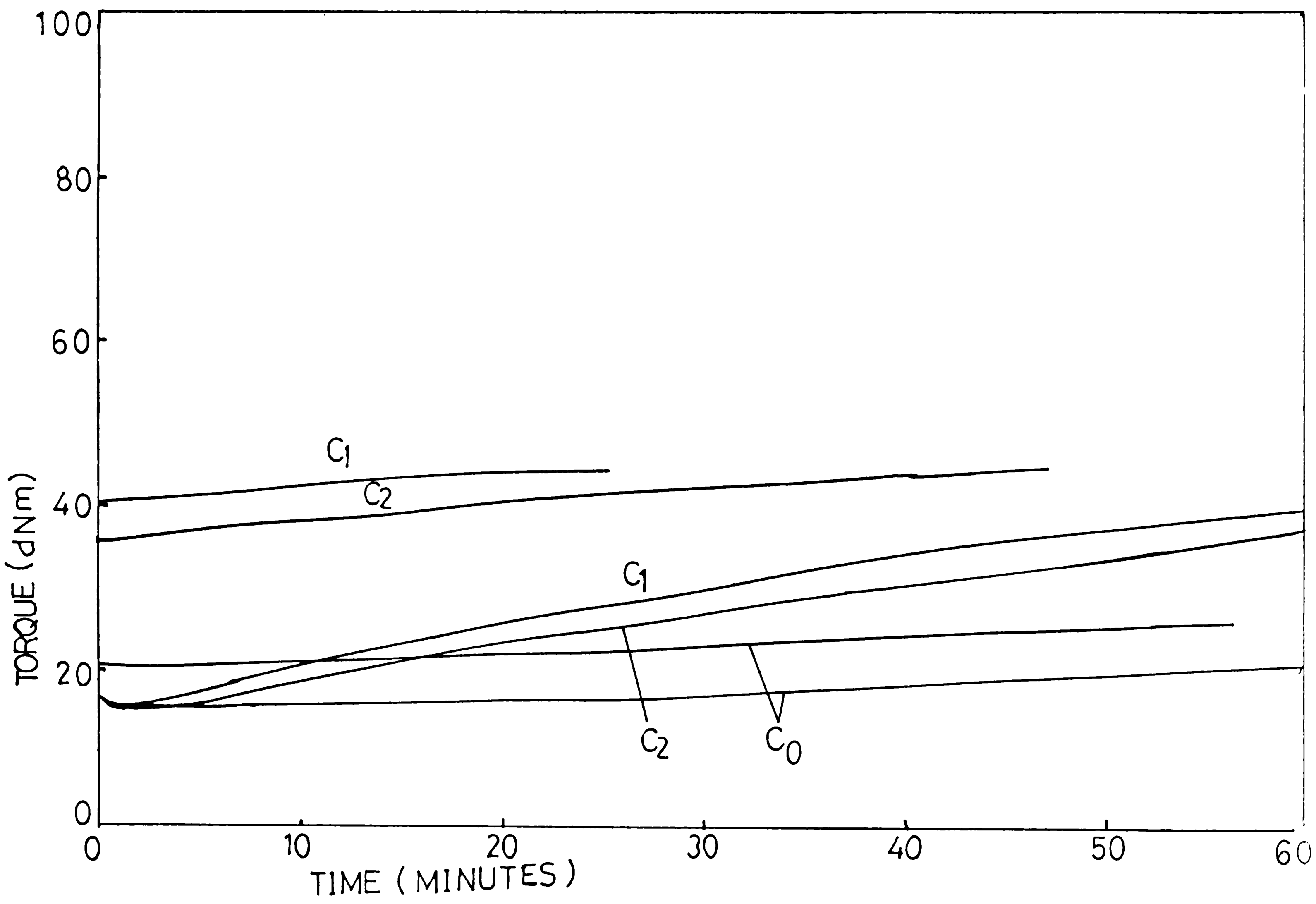


Fig. 5.7: Rheographs of the mixes containing CBS/DTB-II at 120°C (Ref: Tables 5.3 & 5.10).

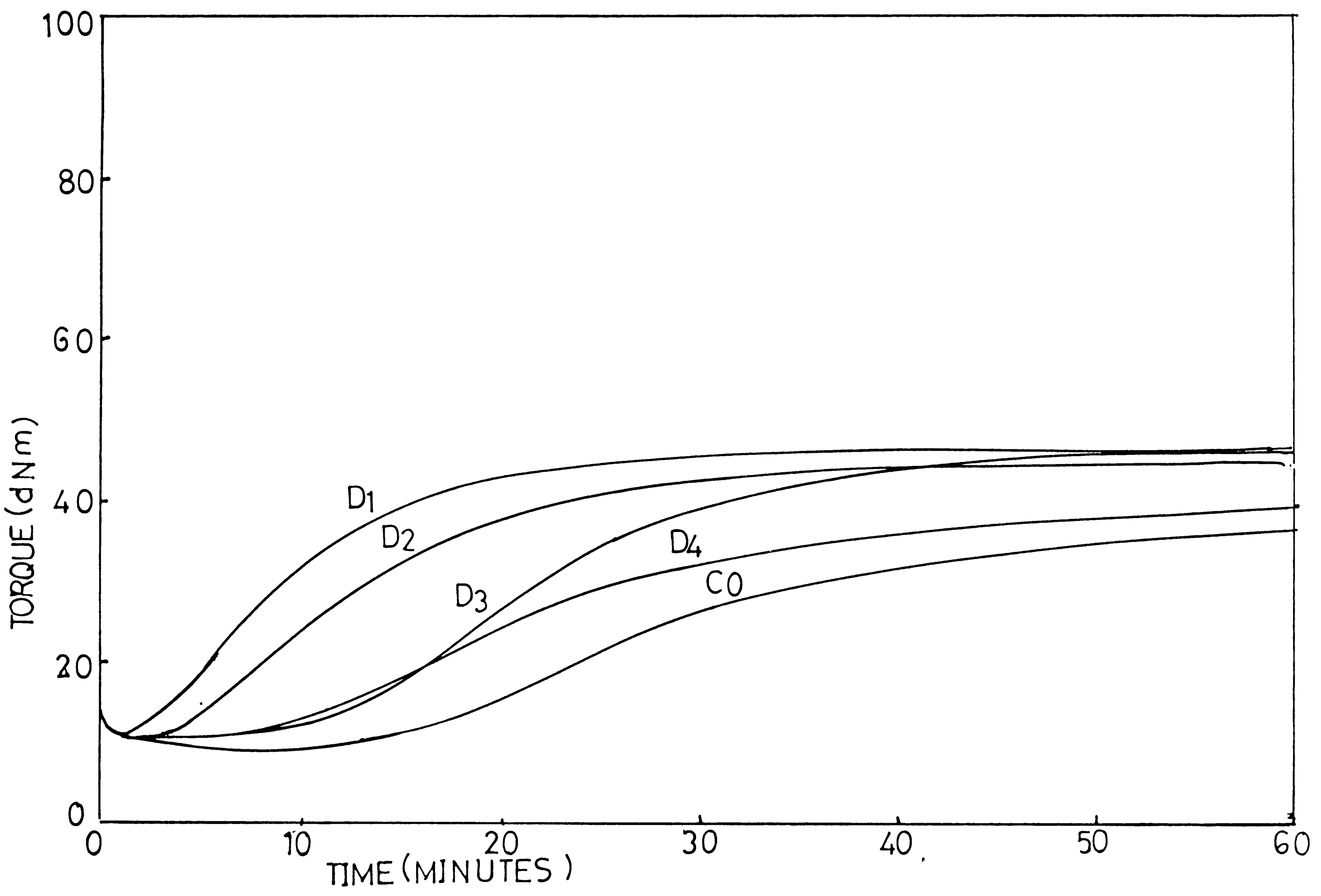


Fig. 5.8: Rheographs of the mixes containing CBS/DTB-III at 150°C (Refer Tables 5.4 & 5.11)

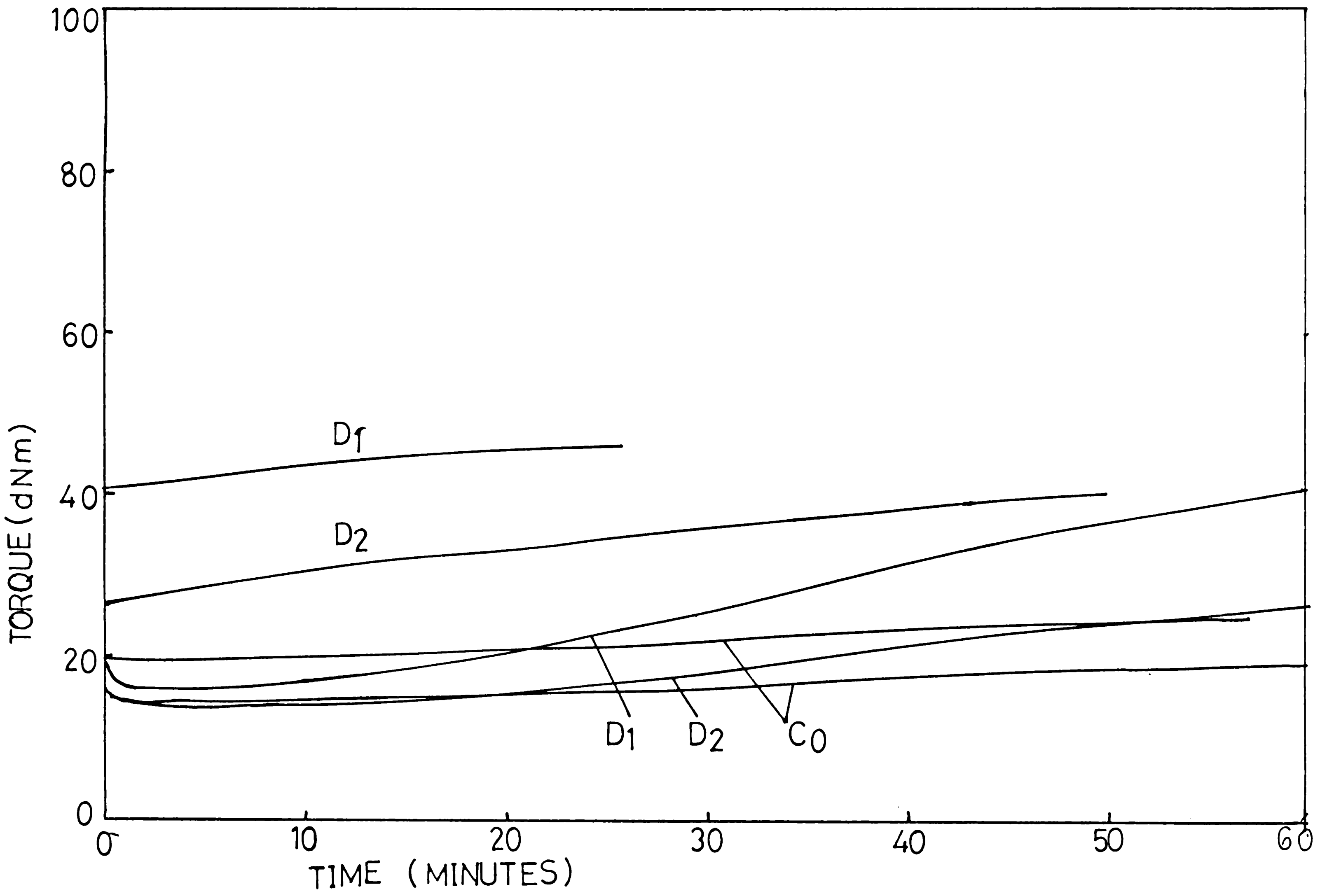


Fig. 5.9: Rheographs of the mixes containing CBS/DTB-III at 120°C
(Ref: Tables 5.4 & 5.12)

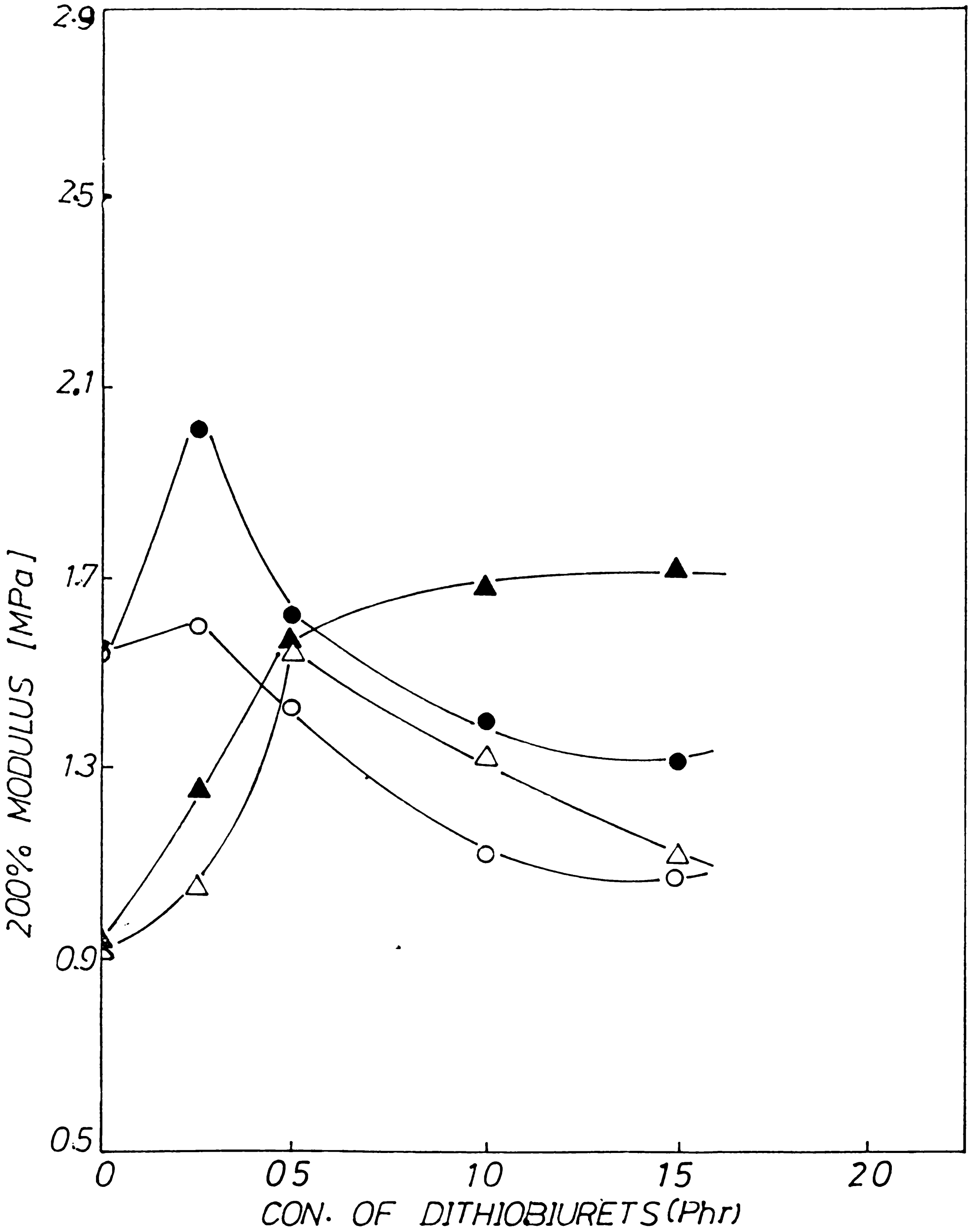


Fig. 5.10 : Variation of 200% modulus of vulcanizates cured at 150°C with con. of dithiobiurets (○) TMTD/DTB-II; (●) TMTD/DTB-III; (△) CBS/DTB-II; (▲) CBS/DTB-III.

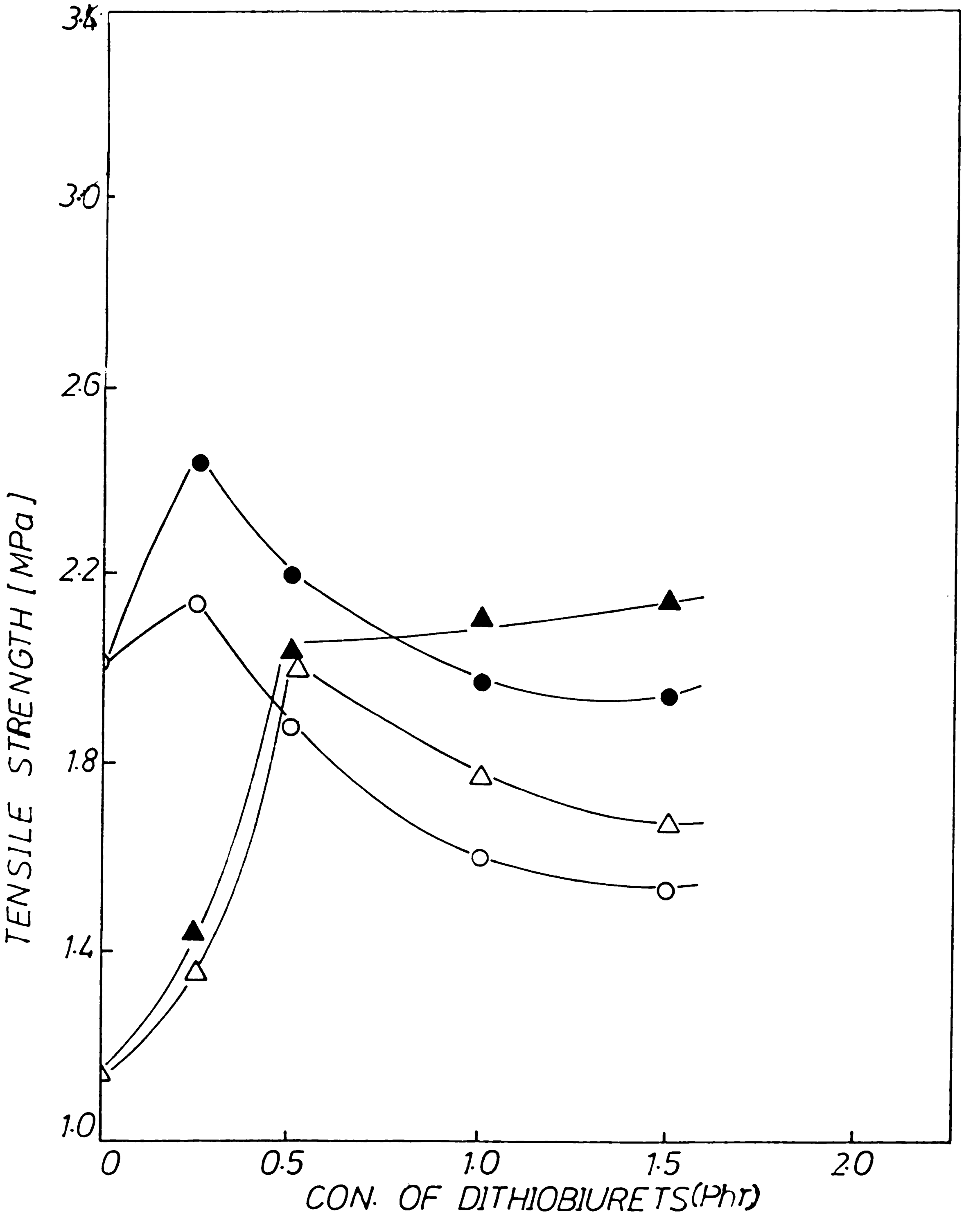


Fig. 5.11 : Variation of tensile strength of vulcanizates cured at 150°C with con. of dithiobiurets; (○) TMTD/DTB-II; (●) TMTD/DTB-III (△) CBS/DTB-II; (▲) CBS/DTB-III.

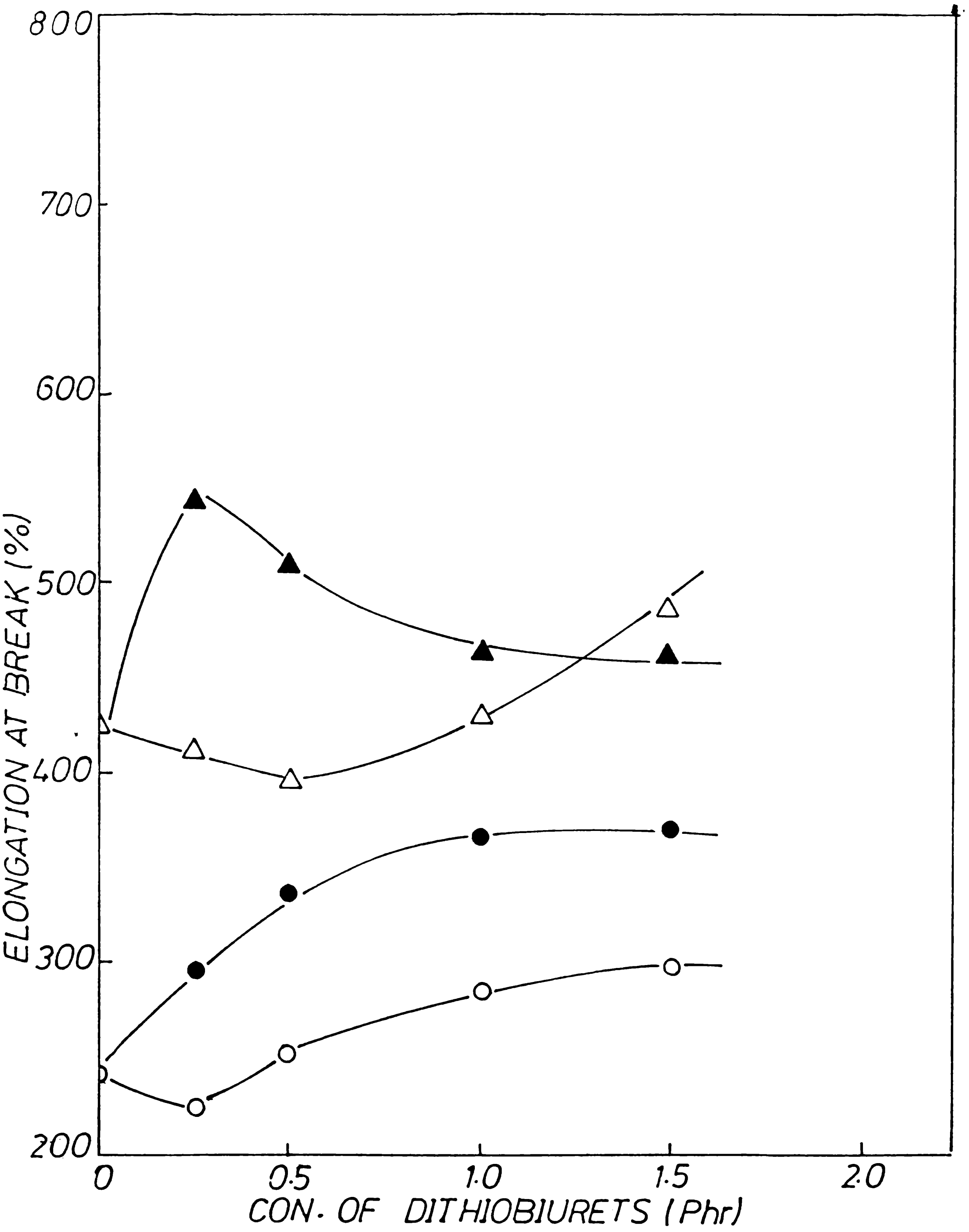


Fig. 5.12: Variation of elongation at break of the vulcanizates cured at 150°C with con. of dithiobiurets (○)TMTD/DTB-II; (●) TMTD/DTB-III; (△) CBS/DTB-II; (▲) CBS/DTB-III.

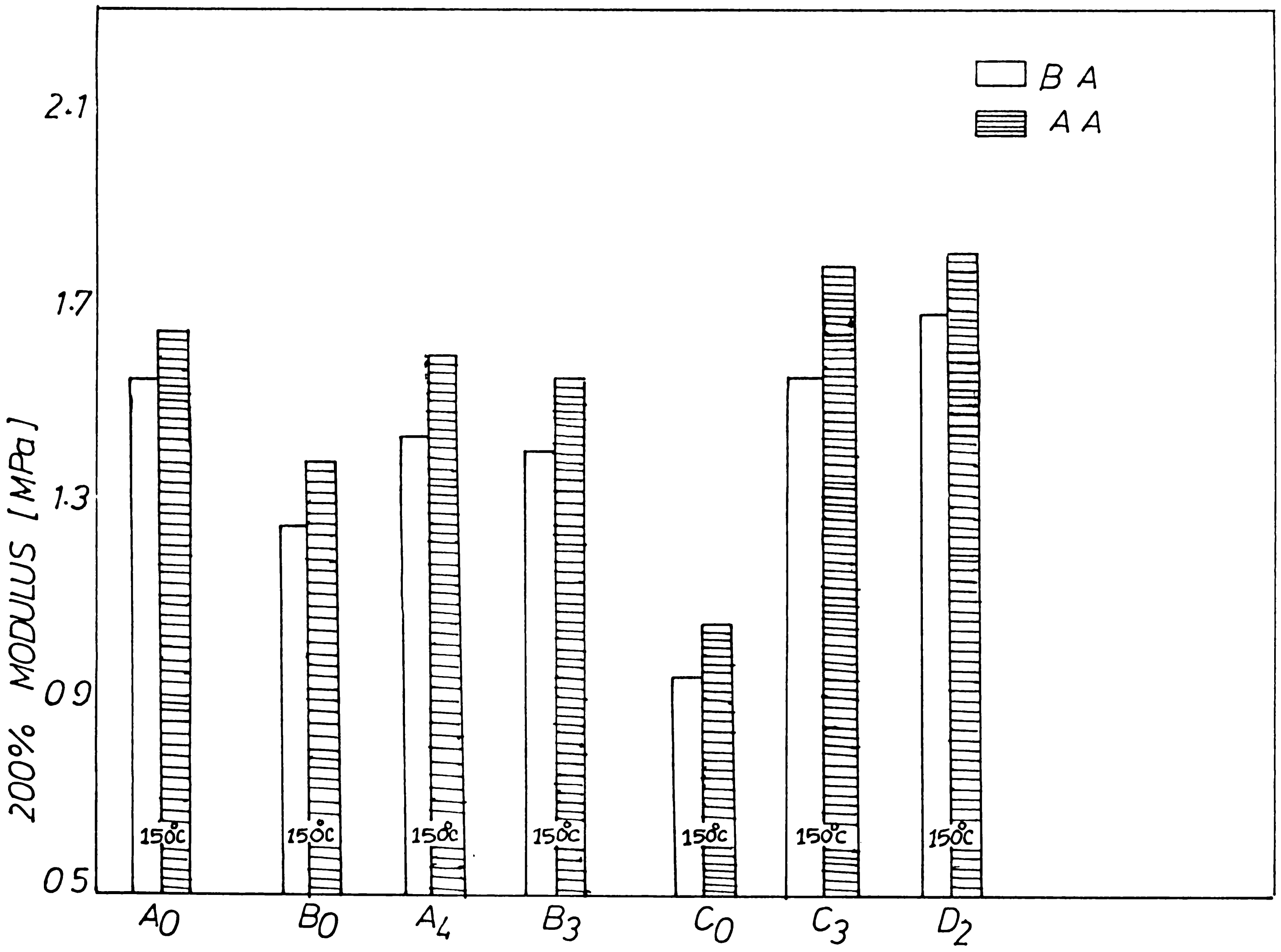


Fig. 5.13 : 200% modulus of the vulcanizates containing optimum concentrations of dithiobiurets in TMTD and CBS systems.

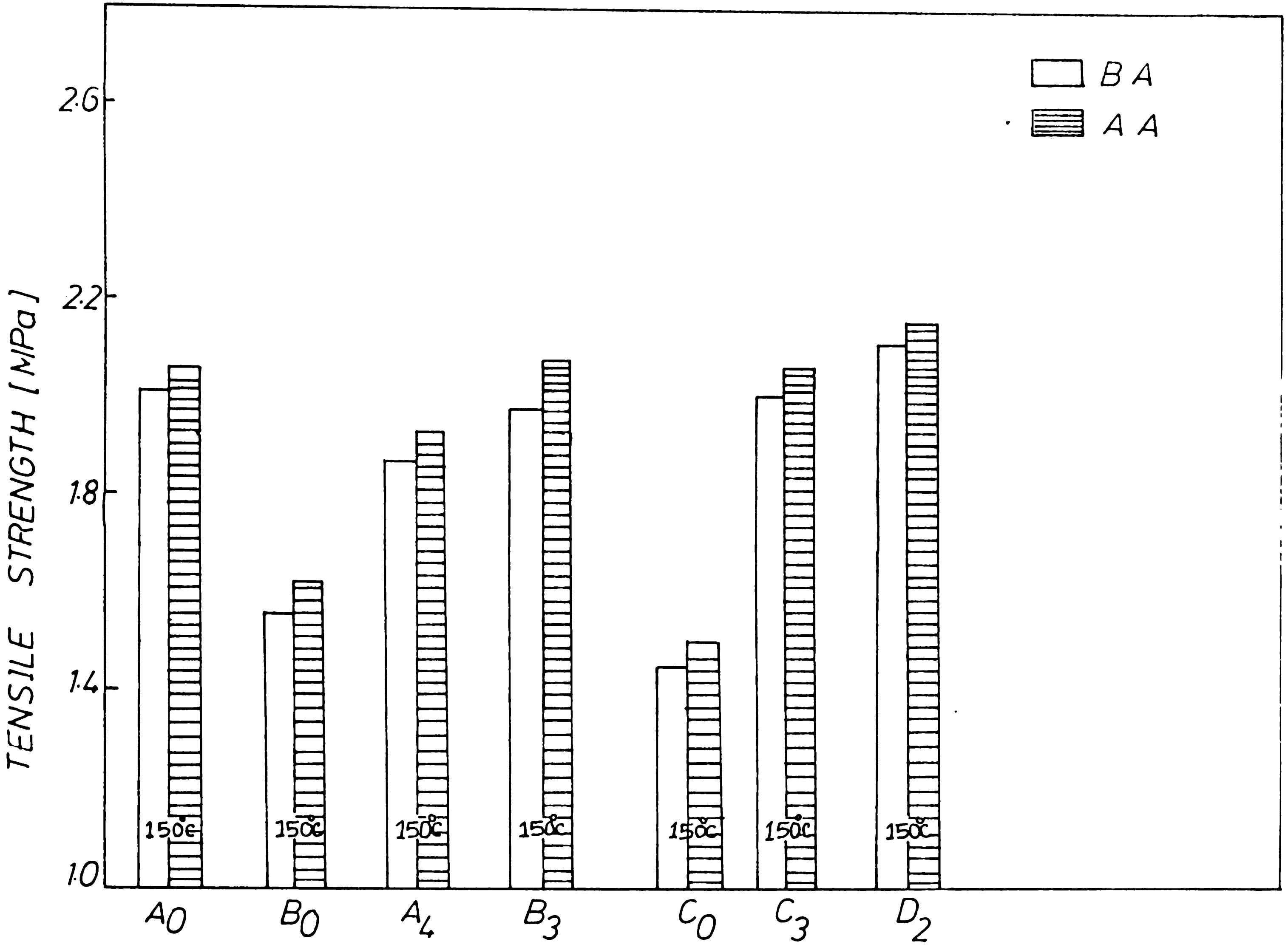


Fig. 5.14 : Tensile Strength of vulcanizates containing optimum concentrations of dithiobiurets in TMTD and CBS systems.

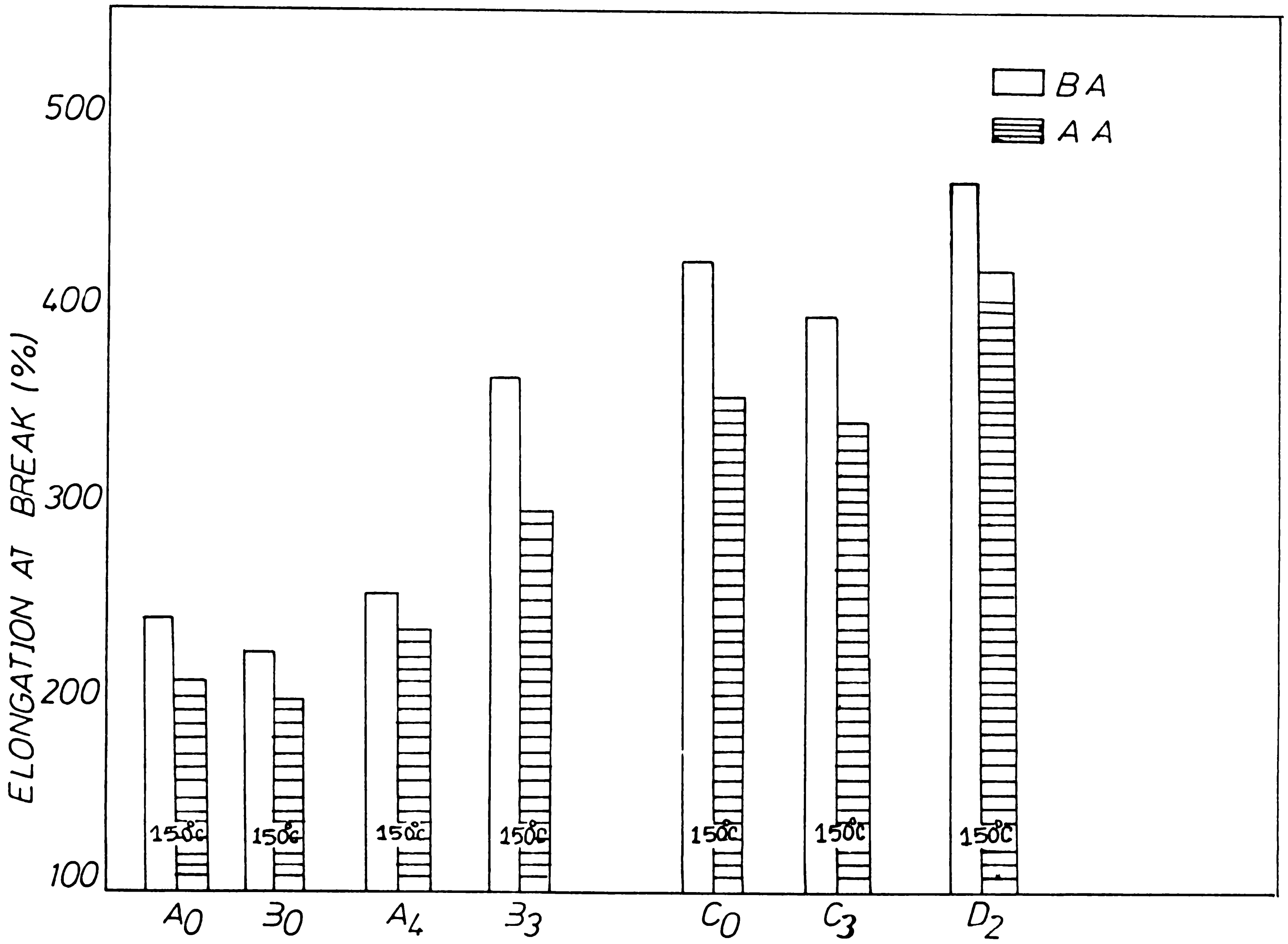


Fig. 5.15 : Elongation at break of vulcanizates containing optimum concentrations of dithiobiurets in TMTD andCBS systems.

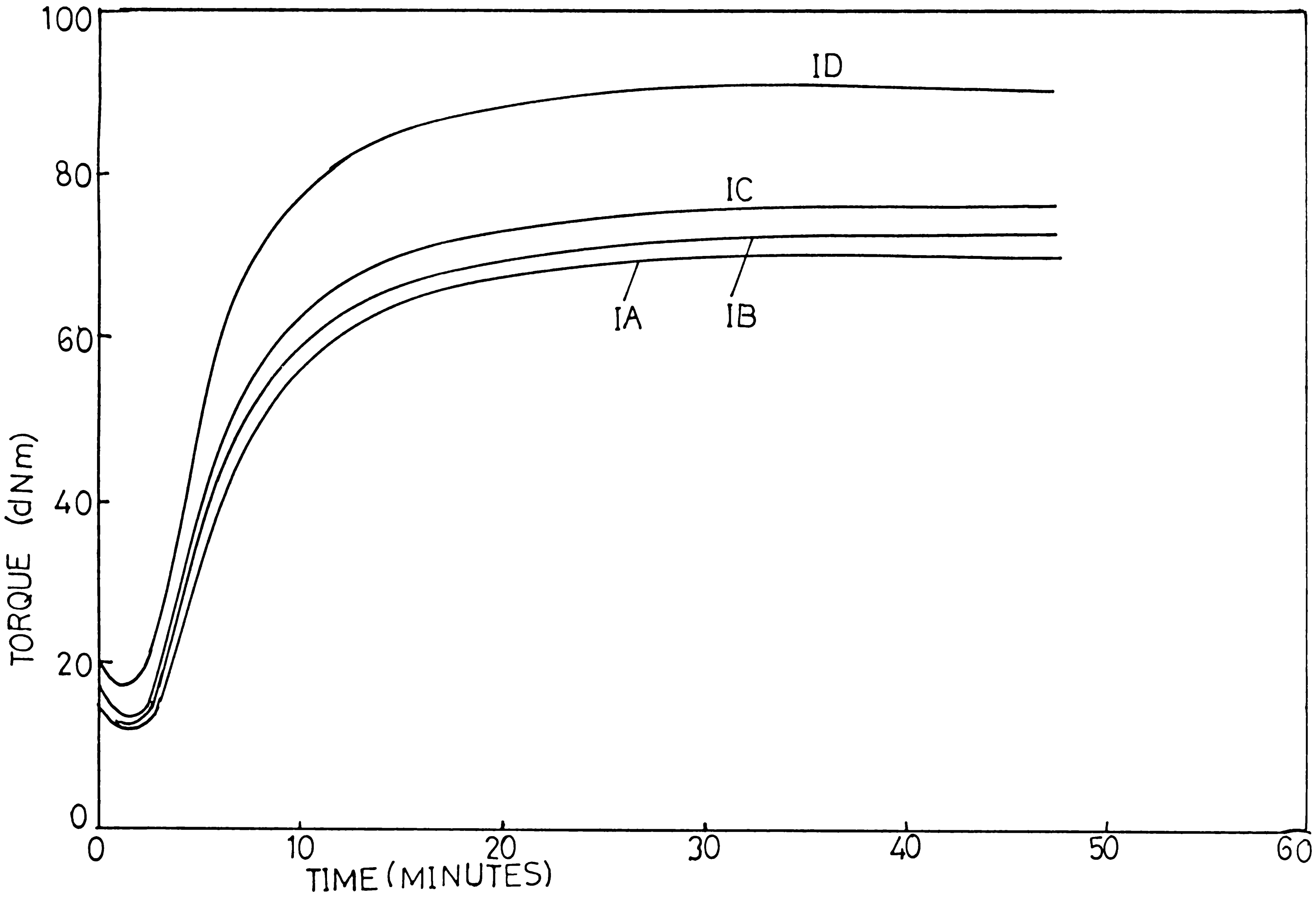


Fig. 5.16 : Rheographs of the mixes containing TMTD alone at 150°C at different loadings of HAF Black (Ref. Tables 3.22 & 3.23)

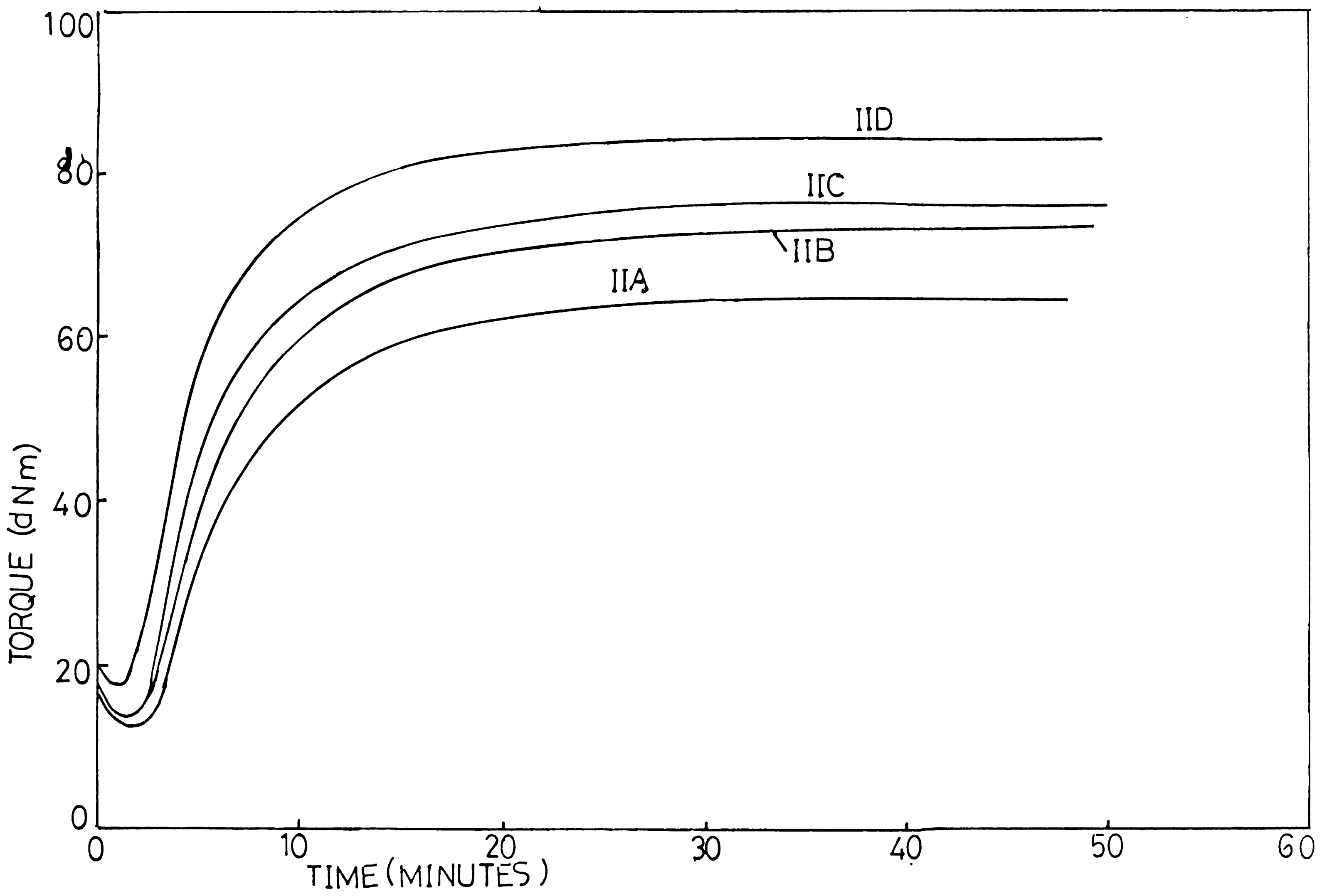


Fig. 5.17 : Rheographs of the mixes containing TMTD/thiourea at 150°C at different loadings of HAF Black(Ref. Tables 3.22 and 3.23)

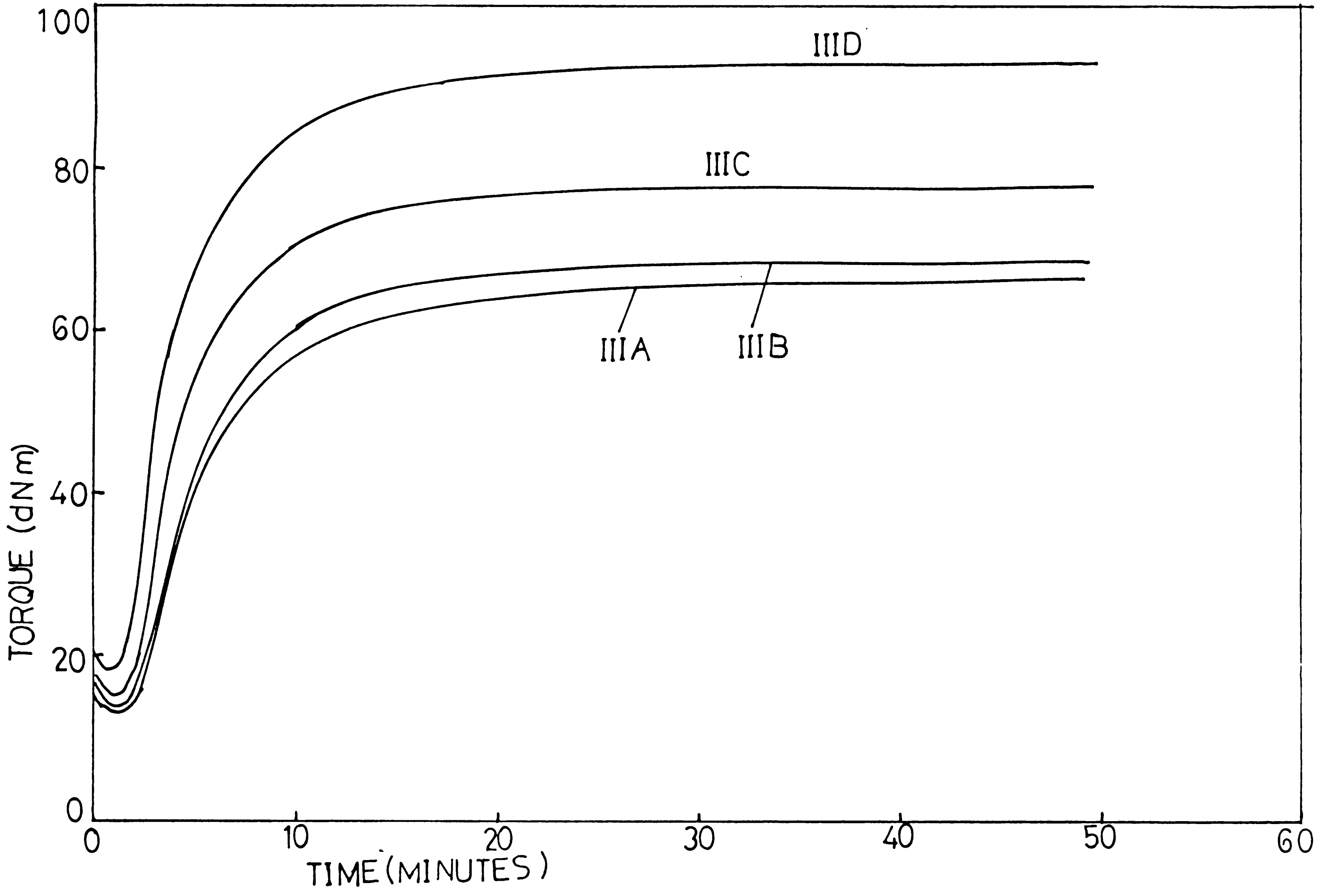


Fig. 5.18 : Rheographs of the mixes containing TMTD/DTB-II at 150°C at different loadings of HAF Black (Ref. Tables 3.22 & 3.23)

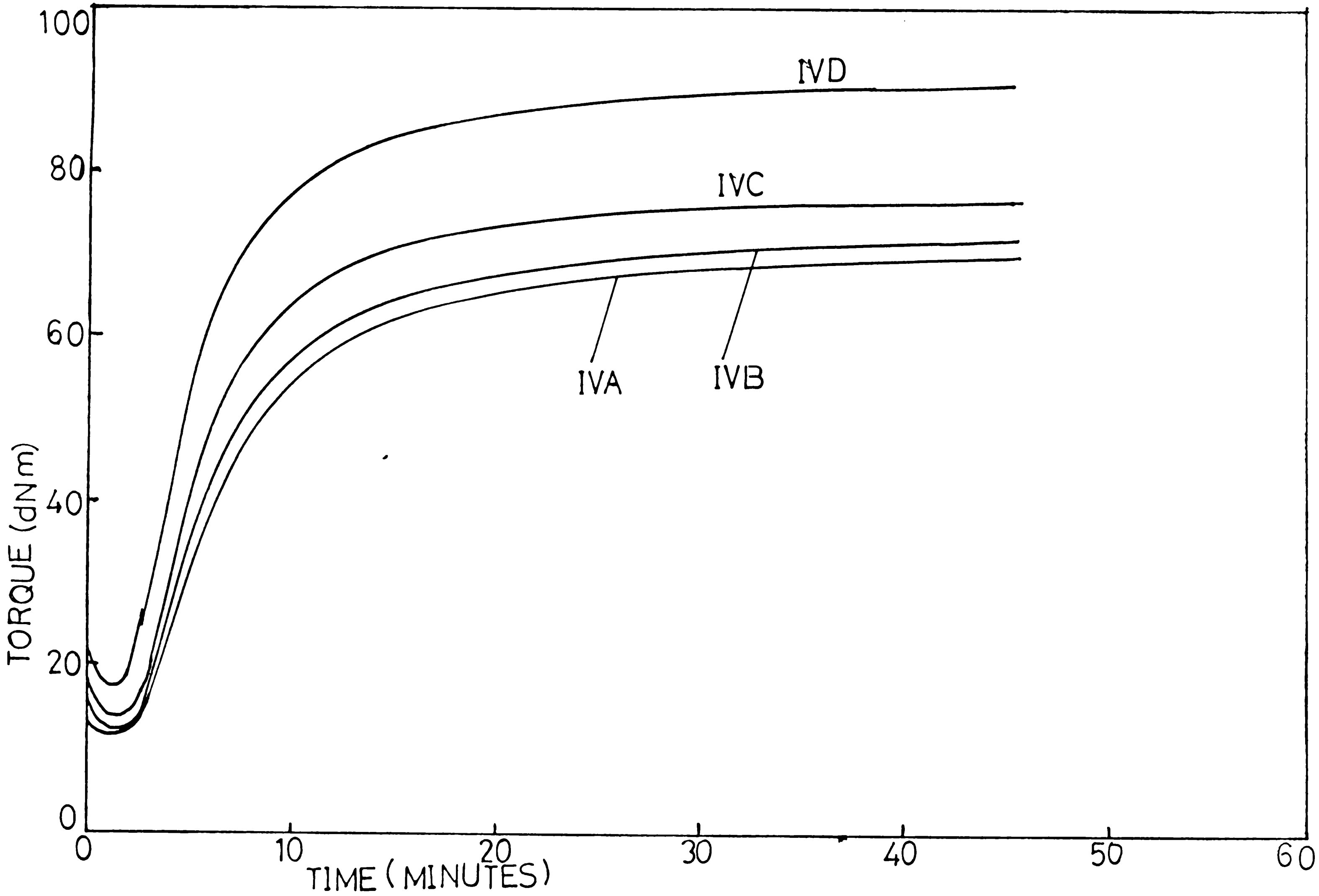


Fig. 5.19 : Rheographs of the mixes containing TMTD/DTB-III at 150°C at different loadings of HAF Black. (Ref. Tables 3.22 & 3.23)

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CHAPTER - VI

STUDY OF DITHIOBIURETS IN VULCANIZATION SYSTEMS OF NR-SBR BLENDS

STUDY OF DITHIOBIURETS IN VULCANIZATION SYSTEMS OF NR-SBR BLENDS

INTRODUCTION

It is recognised that a single elastomer cannot meet all the requirements like oil and chemical resistance, dynamic properties, weathering resistance etc. of a rubber product. Blends of rubbers are widely used for obtaining a balance of properties including cost, which one elastomer alone cannot give and to overcome processing difficulties. SBR and NR belong to the general purpose Rubbers' group. They can be usefully blended if the fundamental differences and similarities between them is recognised. NR and SBR are unsaturated hydrocarbon polymers and hence unvulcanized compounds will dissolve in most hydrocarbon solvents and other liquids of similar solubility parameters, while cured stocks will swell extensively[1]. Both rubbers may be reinforced by carbon black and neither can be classed as a heat resistant rubber.

SBR is more uniform in quality than NR. It retains its plasticity during mastication while NR decreases in plasticity during processing. SBR compounds tend to be less scorchy than NR compounds and thus allow safer processing. While NR has good gum tensile strength, SBR requires reinforcing fillers such as carbon black or precipitated silica for developing comparable modulus and tensile strength. SBR possess better abrasion resistance and tear resistance than NR while hysterisis and resilience characteristics are inferior to those of NR. Making use of these characteristics blends of NR and SBR can be prepared which will give better processing, strength, ageing and resilience properties.

Information on the practical aspects of NR-SBR blends like processing and vulcanization were reported by Springer[2], Mastication of NR[3] is necessary prior to blending with SBR. Shundo[4] has compared the use of roll mill and Banbury mixer in the preparation of NR-SBR blends and found that mill mixing furnish more uniform compounds. In the vulcanization of NR-SBR blends NR phase takes a larger share of curatives leaving the SBR phase slightly under crosslinked[5]. This necessitate more active accelerator or binary accelerator system to obtain uniform curing. In our studies of dithiobiurets in NR and SBR compounds we have found that these accelerators can form an active accelerator combination with TMTD or CBS. Considering the requirement of special binary combinations of accelerators in NR-SBR blends, we thought of utilising these systems in a 50 : 50 blend of NR and SBR 1502. From this study we have found that TMTD/dithiobiuret systems and CBS/dithiobiuret systems are very active accelerator combinations compared to TMTD or CBS alone or with thiourea.

Also studied was the effect of these systems on the physical properties and crosslinked structures of the vulcanizates. Effect of these accelerator combinations on different fillers in NR-SBR blends was also investigated.

Table 6.1 - 6.4 give the composition of the various mixes. An attempt was made to find out the optimum concentration of the dithiobiurets required in the vulcanization reaction under standard conditions. Mix A_o contain 1.5 phr TMTD alone while mix B_o contain 1.5 phr TMTD and 0.5 phr thiourea as accelerators. Mix C_o contains CBS alone. Mixes A_2 - A_5 contain different concentrations of DTB-II ranging from 1.5 to 0.25 phr with 1.5 phr TMTD while mixes B_2 - B_5 contain that of DTB-III ranging from 1.5 to 0.25 phr., with 1.5 phr TMTD.Mixes C_1 - C_4 contain different concentrations of DTB-II ranging from 1.5 to 0.25 phr with 1.5 phr CBS, while D_1 - D_4 contain that of DTB-III ranging from 1.5 phr to 0.25 phr with 1.5 phr CBS. Trial mixes were also prepared without TMTD/CBS (Mixes A_1 & B_1), but they cured so slowly that they were not proceeded further.

RESULTS AND DISCUSSION

1. Cure Characteristics

The cure characteristics of various mixes at 150°C and 120°C were evaluated using a Monsanto Rheometer (R-100) and the cure curves obtained are given in Figs.6.1 - 6.8. The cure characteristics evaluated are given in Tables 6.5 - 6.12. The scorch time of the mixes at 120°C were evaluated using a Mooney Viscometer. The results clearly indicates the acceleration effect of the dithiobiurets in the vulcanization of NR-SBR blends under review. Of the two dithiobiurets studied, DTB-II is more powerful accelerator both in TMTD and CBS systems indicating a nucleophilic reaction mechanism in the sulphur vulcanization of NR-SBR blends.

In the TMTD systems, the optimum cure time for 1.5 phr TMTD alone is 12 minutes. It is reduced to 5.5 minutes by adding 1.5 phr DTB-II. A corresponding increase in the cure rate can also be observed (Table 6.5). However, the decrease in the induction time and scorch time at higher dosagesof the dithiobiurets will have adverse effect. Similarly the maximum torque value of the vulcanizates decreases with the increase in the concentration of dithiobiurets. So as reported earlier in the studies of NR and SBR, (Chapter III and V) by reducing the amount of DTB-II a practical cure system can be obtained. A dosage 0.5 phr can be taken as the optimum dosage. At this dosage there is definite reduction in the optimum cure time and at the same time, scorch time and maximum torque developed are comparable. The system shows better cure characteristics than that of TMTD/thiourea system at this dosage. DTB-III is found to be less active than DTB-II, but it is also showing definite reduction in optimum cure time. Reversion study at 170°C shows that both DTB-II and DTB-III are showing superior reversion resistance to that of TMTD alone or TMTD/thiourea systems. At the lower temperature of 120°C the acceleration effect of dithiobiurets are more significant. The optimum cure time is reduced from 72.5 to 20 minutes by the addition of 1.5 phr DTB-II and to 22.5 minutes by that of DTB-III.

In the CBS systems, the optimum cure time for CBS alone is 25.5. The addition of 1.5 phr DTB-II is bringing it down to 11 minutes, while DTB-III reduces it to 13.5 minutes. Here also 0.5 phr DTB-II and 1 phr DTB-III are found to give comparable torque values with considerable reduction in optimum cure time. These systems are also showing better reversion resistance than when CBS is used alone. At 120°C, with increase in the concentration of dithiobiurets there is appreciable reduction in the optimum cure time but the compound containing CBS alone cures so slowly that a comparison was not possible.

2. Tensile & other physical properties

The tensile properties such as 300% modulus, tensile strength and elongation at break are shown in figures 6.9 - 6.17. In the case of TMTD/dithiobiuret binary systems 300% modulus and tensile strength are decreasing and elongation at break is increasing as the concentration of dithiobiuret increases. Lower dosages are giving better modulus and tensile strength values. The tensile properties of the sample containing DTB-III is better than that of DTB-II. This may be attributed to the higher concentration of polysulphidic linkages in this system (Table 6.21). These systems are giving better tensile properties compared to that of TMTD/thiourea combination. At 120°C also the same trend is followed and there is a slight decrease in the tensile properties compared to those cured at 150°C.

In the case of CBS/dithiobiuret systems also a decrease in tensile strength and 300% modulus can be observed with increase in the concentration of dithiobiurets. The elongation at break is increasing with increase in the concentration of dithiobiurets. Here the optimum dosage of 0.5 phr of DTB-II is giving slightly lesser values and 1 phr of DTB-III is giving better values than that of CBS alone. The percentage retention in tensile properties is higher for both dithiobiurets. At 120°C also the same trend is followed, but here the tensile properties are higher than that at

150°C. This may be attributed to the formation of more polysulphide linkages at lower temperature.

Other physical properties evaluated are given in Table 6.13 - 6.20. In the vulcanizates containing TMTD/dithiobiuret as well as CBS/dithiobiuret systems the physical properties such as hardness, resilience, tear strength, compression set and heat build up are improving with decrease in the concentration of dithiobiurets. Samples containing DTB-III are giving better results than that of DTB-II. The vulcanizates containing optimum concentration of dithiobiurets are giving comparable values to that of TMTD or CBS alone. But the results are better than those of the samples from the TMTD/thiourea system. At 120°C also the same trend is followed and these values from the samples containing CBS/dithiobiurets are better compared to that at 150°C.

3. Chemical Characterization

The total chemical crosslink densities and different types of crosslinks like mono, di and polysulphide linkages, free sulphur and zinc sulphide sulphur were evaluated for the vulcanizates containing TMTD and CBS alone, TMTD/thiourea systems and the systems containing optimum concentrations of dithiobiurets. The results are given in Table 6.21. The total crosslink density and mono and di sulphide linkages of dithiobiuret systems cured at 150°C are less than that of TMTD alone. But the polysulphide linkages in the vulcanizates containing

DTB-III are higher than that of TMTD alone. The lower values of hardness, compression set, heat build up etc. can be attributed to the lower values of total crosslink density and mono sulphide linkages. The higher tensile strength obtained in the DTB-III may be due to the higher polysulphide linkages observed in that system. The total crosslink density and concentration of different types of linkages are higher for DTB-III, than that of DTB-II. This may be the reason why these vulcanizates show higher physical properties. The total crosslink density and di and poly sulphide linkages of TMTD/dithiobiuret systems are more than that of TMTD/thiourea system . Cured at 120°C also the total crosslink density and different types of linkages of dithiobiuret systems are lesser than that of TMTD alone. The free sulphur concentration of DTB-III system is lower than that of DTB-II indicating higher degree of crosslinking in the former. Similarly the higher concentration of zinc sulphide sulphur in DTB-III system indicates more desulphuration, resulting in the formation of more mono sulphidic linkages.

In the CBS/dithiobiuret systems, vulcanizates containing DTB-II is giving lower crosslink density than that of CBS alone, while that containing DTB-III is giving higher values. At 120°C the crosslink density is higher than that at 150°C. This may be the reason for the improved physical properties of the samples containing dithiobiurets when cured at 120°C.

EFFECT OF FILLERS

As in the case of individual elastomers, fillers are incorporated into the blends also for improved processability, reinforcement or cost reduction. Detailed studies had been carried out on the particle distribution in each polymer phase and the effects of their distribution in compound properties[6-9]. Dismore[10] reported that ratio of tensile strength of black filled to that of gum vulcanizates is 1.5 to 1.0 for NR vulcanizates and 10 to 5 for vulcanizates of SBR and similar elastomers. As different rubbers have different responses to filler loadings for specified properties, control of filler distribution in elastomer blends could have corresponding specific effects. When filler is added to a binary elastomer blend it goes to the less viscous polymer and when the viscosity becomes equal to that of the highly viscous polymer it would be taken up by both the polymers[11]. The factors that dominate the partitioning of carbon black are the degree of saturation of the polymer, their viscosities, polarities and the method of mixing[12]. Since we have studied the effect of binary accelerator systems containing dithiobiurets in the filled NR and SBR vulcanizates we thought it will be useful to study their effect in filled NR/SBR blends also. HAF black, precipitated silica and china clay were used as the fillers for this study.

1. Effect of Carbon Black

Table 6.22 shows the formulation of mixes containing various concentrations of HAF black. All the mixes contain 1.5 phr TMTD as the primary accelerator. Mixes IA - ID contain 5, 10, 20 and 50 phr HAF black in which TMTD alone is taken as the accelerator. Mixes IIA - IID contain same amounts of carbon black while TMTD and 0.5 phr thiourea are taken as the accelerator combination. Mixes IIIA - IIID contain same amounts of carbon black but TMTD and 0.5 phr DTB-II are the accelerators. Mixes IVA - IVD also contain similar amounts of ingradients with TMTD and 0.5 phr of DTB-III forming the accelerator system.

The cure characteristics of the above mixes calculated from the cure curves at 150°C (Figs.6.18 - 6.21) are shown in Table 6.23. It can be seen from the table that in the vulcanizates containing dithiobiurets there is an increase in the rheometric torque, reduction in the induction time, rheometric scorch time and optimum cure time and a corresponding increase in the cure rate index. It is also noted that these favourable properties increase with increase in filler loading, which indicates an effective interaction of HAF black with polymers and vulcanization system. Here also DTB-II is found to be more active than DTB-III. The dithiobiuret systems are showing better reversion resistance also as seen from the table.

Table 6.24 shows the tensile properties of the vulcanized samples. In all these systems there is an increase in 300% modulus and tensile strength and a corresponding decrease in the elongation at break with the increase in the filler loading. Vulcanizates containing dithiobiurets are giving better tensile properties. Tensile properties of samples containing DTB-II are slightly less than that of DTB-III. Other physical properties of the mixes are given in Table 6.25. In all the systems, with the increase in the concentration of carbon black, hardness and tear strength are improving while compression set, heat build up and resilience shows the reverse trend as expected. In some of these properties like resilience and tear strength dithiobiurets are giving better values. The results of the chemical characterisation of the mixes containing 50 phr of HAF black is given in Table 6.21. The total chemical crosslink density of the compounds containing the dithiobiurets are higher than that of TMTD alone or TMTD/thiourea systems. The lower concentration of free sulphur in the dithiobiuret systems indicates a more effective utilization of sulphur in their vulcanization. The zinc sulphide sulphur concentration is higher in DTB-III compared to other systems indicating more efficient utilisation of sulphur.

2. Effect of precipitated silica and china clay.

As in the case of NR and SBR, we have tried TMTD/dithiobiuret systems in the vulcanization of silica and clay filled NR-SBR blend also. No significant changes in the optimum cure times has been observed. So we have not studied these systems further.

TABLE 6.1

Formulation of Mixes

Ingradients	A_o	B_o	A_1	A_2	A_3	A_4	A_5
N R	50	50	50	50	50	50	50
S B R 1502	50	50	50	50	50	50	50
Zinc oxide	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2
T M T D	1.5	1.5	-	1.5	1.5	1.5	1.5
Thiourea	-	0.5	-	-	-	-	-
DTB-II	-	-	0.5	1.5	1.0	0.5	0.25
Sulphur	0.5	0.5	0.5	0.5	0.5	0.5	0.5

TABLE 6.2

Ingradients	A_o	B_o	B_1	B_2	B_3	B_4	B_5
N R	50	50	50	50	50	50	50
S B R 1502	50	50	50	50	50	50	50
Zinc oxide	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2
T M T D	1.5	1.5	-	1.5	1.5	1.5	1.5
Thiourea	-	0.5	-	-	-	-	-
DTB-III	-	-	0.5	1.5	1.0	0.5	0.25
Sulphur	0.5	0.5	0.5	0.5	0.5	0.5	0.5

TABLE 6.3

Formulation of Mixes

Ingredients	C_o	C_1	C_2	C_3	C_4
N R	50	50	50	50	50
S B R 1502	50	50	50	50	50
Zinc oxide	5	5	5	5	5
Stearic acid	2	2	2	2	2
C B [illegible]	1.5	1.5	1,5	1.5	1.5
DTB-II	--	1.5	1.0	0.5	0.25
Sulphur	0.5	0.5	0.5	0.5	0.5

TABLE 6.4

Ingredients	C_o	D_1	D_2	D_3	D_4
N R	50	50	50	50	50
S B R 1502	50	50	50	50	50
Zinc oxide	5	5	5	5	5
Stearic acid	2	2	2	2	2
C B S	1.5	1.5	1.5	1.5	1.5
DTB-III	--	1.5	1.0	0.5	0.25
Sulphur	0.5	0.5	0.5	0.5	0.5

TABLE 6.5

Cure characteristics of the mixes containing TMTD/DTB-II at 150°C

Mix No.	Min. Torque (dN.m)	Max. Torque (dN.m)	Induction time(t_1) (min.)	Rheometric scorch time(t_2) (min.)	Optimum cure time(t_{90}) (min.)	Cure rate index	Reversion at 170°C (No.of units reverted in 5 minutes.
A_o	7.5	57	3.0	3.5	12.0	11.76	2.0
B_o	8.0	44	3.0	3.5	9.0	18.18	1.0
A_2	8.0	44	1.0	1.5	5.5	25.00	--
A_3	8.5	46	2.0	2.5	6.5	25.00	--
A_4	8.0	50	2.5	3.0	7.0	26.00	0.5
A_5	8.0	54	2.5	3.0	9.0	16.67	0.5

TABLE 6.6

Cure characteristics of the mixes containing TMTD/DTB-II at 120°C

Mix No.	Min. Torque (dN.m)	Max. Torque (dN.m)	Induction time(t_1) (min.)	Optimum cure time(t_{90}) (min.)	Cure rate index	Mooney scorch time(t_5) (min.)
A_o	10	55	13.0	72.5	1.77	16.0
B_o	10	47	12.0	50.0	2.74	13.5
A_2	12	42	2.0	20.0	5.71	2.5
A_3	10	44	3.0	30.0	3.85	4.0
A_4	8	43	8.5	39.5	3.39	10.0
A_5	11	51	9.5	53.0	2.38	11.0

TABLE 6.7

Cure characteristics of the mixes containing TMTD/DTB-III at 150°C

Mix No.	Min. Torque (dN.m)	Max. Torque (dN.m)	Induction time(t_1) (min)	Rheometric scorch time(t_2) (min)	Optimum cure time(t_{90}) (min)	Cure rate index	Reversion at 170°C (No.of units reverted in 5 mts.)
A_o	7.5	57	3.0	3.5	12.0	11.76	2.0
B_o	8.0	44	3.0	3.5	9.0	18.18	1.0
B_2	7.0	47	1.5	2.0	6.0	25.00	0.5
B_3	7.0	49	2.0	2.5	8.0	18.18	0.5
B_4	6.0	50	2.5	3.0	8.5	18.18	0.5
B_5	8.0	55	2.5	3.0	11.0	12.50	1.0

TABLE 6.8

Cure characteristics of the mixes containing TMTB/DTB-III at 120°C

Mix No.	Min. Torque (dN.m)	Max. Torque (dN.m)	Induction time(t_1) (min.)	Optimum cure time(t_{90}) (min.)	Cure rate index	Mooney scorch time (t_5) (min.)
A_o	10	55	13.0	72.5	1.77	16.0
B_o	10	47	12.0	50.0	2.74	13.5
B_2	8	41	4.0	22.5	5.71	5.0
B_3	9	49	5.5	35.0	3.57	7.0
B_4	8	48	10.0	45.0	2.99	11.5
B_5	10	53	10.5	59.0	2.17	13.0

TABLE 6.9

Cure characteristics of the mixes containing CBS/DTB-II at 150°C

Mix No.	Min. Torque (dN.m)	Max. Torque (dN.m)	Induction time(t_1) (min.)	Rheometric scorch time(t_2) (min.)	Optimum cure time(t_{90}) (min.)	Cure rate index	Reversion at 170°C (No. of units reverted in 5 minutes)
C_o	7.0	39	11.5	12.5	25.5	7.69	1
C_1	7.5	36	1.5	2.0	11.0	11.11	-
C_2	8.0	38	2.0	2.5	12.0	10.53	-
C_3	6.0	37	3.5	4.0	14.0	10.00	0.5
C_4	7.0	39	6.0	6.5	17.0	9.52	1

TABLE 6.10

Cure characteristics of the mixes containing CBS/DTB-II at 120°C

Mix No.	Min. Torque (dN.m)	Max. Torque (dN.m)	Induction time(t_1) (min.)	Optimum cure time(t_{90}) (min.)	Cure rate index	Mooney scorch time (t_5) (min.)
C_o	--	--	--	--	--	--
C_1	9	38	3.5	35.0	3.28	4.5
C_2	8	39	5.5	39.5	2.99	6.0
C_3	8	41	16.0	56.0	2.67	18.5
C_4	10	43	29.5	75.0	2.44	34.0

TABLE 6.11

Cure characteristics of the mixes containing CBS/DTB-III at 150°C

Mix No.	Min. Torque (dN.m)	Max. Torque (dN.m)	Induction time (t_1) (min.)	Rheometric scorch time (t_2) (min.)	Optimum cure time (t_{90}) (min.)	cure rate index	Reversion at 170°C (No. of units reverted in 5 minutes
C_o	7	39	11.5	12.5	25.5	7.69	1
D_1	6	37	2.5	3.0	13.5	9.52	-
D_2	7	40	2.5	3.0	14.0	9.09	-
D_3	5	37	5.5	6.0	17.5	8.70	0.5
D_4	7	39	7.5	8.5	20.5	8.33	1

TABLE 6.12

Cure characteristics of the mixes containing CBS/DTB-III at 120°C

Mix No.	Min. Torque (dN.m)	Max. Torque (dN.m)	Induction time (t_1) (min.)	Optimum cure time(t_{90}) (min.)	Cure rate index	Mooney scorch time (t_5) (min.)
C_o	-	-	-	-	-	-
D_1	6	42	6	44.5	2.74	8.0
D_2	8	44	10	56.0	2.25	11.5
D_3	6	42	25	83.0	2.15	36.5
D_4	9	44	43	106.0	1.92	54.0

TABLE 6.13

Physical properties of the vulcanizates containing TMTD/DTB-II cured at 150°C

Mix No.	Hardness (Shore A)	Compression set (%)	Heat build up ($\Delta T\,^{\circ}C$)	Resilience (%)	Tear strength (N/mm)
A_o	38	12.32	14	66.44	27.20
B_o	32	18.08	21	65.38	20.83
A_2	33	17.25	21	64.80	21.48
A_3	35	15.60	20	66.25	22.22
A_4	36	15.20	18	69.45	23.97
A_5	37	12.70	15	70.85	26.55

TABLE 6.14

Physical properties of the vulcanizates containing TMTD/DTB-II cured at 120°C

Mix No.	Hardness (Shore A)	Compression set (%)	Heat build up ($\Delta T\,^{\circ}C$)	Resilience (%)	Tear strength (N/mm)
A_o	36	14.48	14	62.70	21.75
B_o	33	17.90	19	58.85	20.83
A_2	30	18.85	18	62.40	20.14
A_3	32	16.25	17	64.40	21.19
A_4	33	15.30	14	68.35	22.40
A_5	35	14.40	13	69.25	22.80

TABLE 6.15

Physical properties of the vulcanizates containing TMTD/DTB-III cured at 150°C

Mix No.	Hardness (Shore A)	Compression set (%)	Heat build up ($\Delta T^{o}C$)	Resilience (%)	Tear strength (N/mm)
A_o	38	12.32	14	66.44	27.20
B_o	32	18.08	21	65.38	20.83
B_2	34	16.00	19	65.30	24.36
B_3	36	14.90	17	67.50	26,82
B_4	37	14.33	15	70.05	28.68
B_5	38	11.68	14	71.25	29.00

TABLE 6.16

Physical properties of the vulcanizates containing TMTD/DTB-III cured at 120°C

Mix No.	Hardness (Shore A)	Compression set (%)	Heat build up ($\Delta T^{o}C$)	Resilience (%)	Tear strength (N/mm)
A_o	36	14.48	14	62.70	21.75
B_o	33	17.90	19	58.85	20.83
B_2	31	19.90	17	63.75	23.04
B_3	33	17.40	16	65.30	24.73
B_4	34	15.90	14	69.12	26.30
B_5	36	14.80	14	70.35	28.12

TABLE 6.17

Physical properties of the vulcanizates containing CBS/DTB-II cured at 150°C

Mix No.	Hardness (Shore A)	Compression set (%)	Heat build up ($\Delta T^{o}C$)	Resilience (%)	Tear strength (N/mm)
C_o	31	22.70	28	58.14	22.79
C_1	28	28.17	34	55.07	21.06
C_2	29	24.65	31	59.42	21.76
C_3	30	23.20	28	63.13	22.05
C_4	31	22.10	25	65.53	22.35

TABLE 6.18

Physical properties of the vulcanizates containing CBS/DTB-II cured at 120°C

Mix No.	Hardness (Shore A)	Compression set (%)	Heat build up ($\Delta T^{o}C$)	Resilience (%)	Tear strength (N/mm)
C_o	--	--	--	--	--
C_1	30	22.80	30	53.16	21.53
C_2	31	21.50	28	56.15	21.95
C_3	33	18.26	24	62.70	22.45
C_4	33	19.09	22	64.40	23.85

TABLE 6.19

Physical properties of the vulcanizates containing CBS/DTB-III cured at 150°C

Mix No.	Hardness (Shore A)	Compression set (%)	Heat build up (ΔT°C)	Resilience (%)	Tear strength (N/mm)
C_o	31	22.70	28	58.14	22.79
D_1	30	23.54	29	65.45	25.15
D_2	33	19.34	27	67.38	24.81
D_3	32	20.20	33	61.40	24.32
D_4	32	21.98	36	53.77	23.92

TABLE 6.20

Physical properties of the vulcanizates containing CBS/DTB-III cured at 120°C

Mix No.	Hardness (Shore A)	Compressionset (%)	Heat build up (ΔT°C)	Resilience (%)	Tear strength (N/mm)
Co	--	--	--	--	--
D_1	34	18.50	26	64.25	26.30
D_2	36	17.40	24	66.40	26.51
D_3	36	17.80	28	62.10	26.22
D_4	34	18.40	32	53.40	25.82

TABLE 6.21

Chemical Characterization of the Vulcanizates

Cure Temp.	Mix No.	Total cross-link density (m.mole/ Kg RH)	Mono sulphide linkages (m.mole/ Kg RH)	Disulphide linkages (m.mole/ Kg RH)	Poly sulphide linkages (m.mole/ Kg RH)	Free sulphur con. (m.mole/ Kg RH)	Zinc sulphide sulphur con. (m.mole/ Kg RH)
150	A_0	70.0	43.10	15.60	11.30	9.46	12.54
	B_0	64.0	44.50	13.30	6.20	12.76	14.30
	A_4	64.4	38.70	14.80	10.90	12.03	13.00
	B_3	68.6	39.60	16.50	12.50	10.76	13.28
120	A_0	69.1	41.90	17.00	10.20	11.05	15.00
	B_0	64.8	41.60	15.20	8.00	12.30	12.50
	A_4	60.9	38.00	14.80	8.10	14.20	9.00
	B_3	64.3	39.00	15.70	9.60	12.80	9.60
150	C_0	40.5	22.20	5.90	12.40	9.46	4.30
	C_3	38.2	15.90	8.70	13.60	10.68	3.60
	D_2	43.2	22.80	6.20	14.20	8.80	4.00
120	C_0	--	--	--	--	--	--
	C_3	39.7	18.40	6.90	14.40	9.20	3.88
	D_2	45.6	23.70	6.20	15.70	8.90	4.25
150	ID	76.4	34.20	29.60	12.60	4.84	8.70
	IID	68.3	31.40	25.60	11.30	5.94	6.28
	IIID	76.5	33.20	29.50	13.80	4.50	7.90
	IVD	78.9	34.80	31.80	12.30	3.90	8.90

TABLE 6.22

Formulation of the mixes containing carbon black

Ingredients	IA	IB	IC	ID	IIA	IIB	IIC	IID	IIIA	IIIB	IIIC	IIID	IVA	IVB	IVC	IVD
N R	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50
SBR 1502	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50
Zinc oxide	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
HAF Black	5	10	20	50	5	10	20	50	5	10	20	50	5	10	20	50
Naphthenic oil	0.5	1	2	5	0.5	1	2	5	0.5	1	2	5	0.5	1	2	5
T M T D	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Thiourea	--	--	--	--	0.5	0.5	0.5	0.5	--	--	--	--	--	--	--	--
DTB-II	--	--	--	--	--	--	--	--	0.5	0.5	0.5	0.5	--	--	--	--
DTB-III	--	--	--	--	--	--	--	--	--	--	--	--	0.5	0.5	0.5	0.5
Sulphur	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5

TABLE 6.23

Cure characteristics of the mixes containing Carbon black

Mix No.	Min. Torque (dN.m)	Max. Torque (dN.m)	Induction time(t_1) (min.)	Rheometric scorch time(t_2) (min.)	Optimum cure time(t_{90}) (min.)	Cure rate index	Reversion at 170°C (No.of units reverted in 5 mnts.
IA	8.0	57	3.00	3.5	11.5	12.50	--
IB	11.0	63	2.50	3.00	11.0	12.50	--
IC	14.0	82	2.50	2.75	9.5	14.81	--
ID	13.0	89	2.0	2.25	8.5	16.00	--
IIA	8.0	51	3.00	3.50	9.5	16.67	1.0
IIB	11.0	58	2.00	2.50	9.0	15.38	1.0
IIC	14.5	66	2.00	2.50	7.5	20.00	0.5
IID	13.0	78	1.75	2.00	7.5	18.18	0.5
IIIA	14.0	58	1.00	1.50	9.0	13.33	--
IIIB	14.0	60	1.50	2.00	8.0	16.67	--
IIIC	18.0	72	1.00	1.50	7.5	16.67	--
IIID	15.0	83	0.75	1.00	6.5	18.18	--
IVA	11.0	59	2.00	2.50	10.0	13.33	--
IVB	11.5	64	2.00	2.50	9.5	14.29	--
IVC	15.0	80	1.50	2.00	8.0	16.67	--
IVD	13.5	86	1.50	2.00	7.0	20.00	--

TABLE 6.24

Tensile Properties of the Vulcanizates Containing Carbon black

Mix No.	300% Modulus (MPa)			Tensile strength (MPa)			Elongation at break (%)		
	B.A	A.A	% Rtn	B.A	A.A	%Rtn	B.A	A.A	% Rtn.
IA	2.46	2.30	93.50	8.55	7.57	88.54	709.28	659.79	93.02
IB	4.25	3.98	93.65	11.83	11.15	94.25	632.52	619.99	98.01
IC	7.07	6.65	94.06	12.63	11.45	90.66	438.19	333.64	76.14
ID	12.57	11.40	90.69	18.57	16.35	88.05	403.39	294.11	72.91
IIA	2.43	2.22	91.36	6.04	4.52	74.83	560.10	471.85	84.24
IIB	3.49	3.25	93.12	8.30	6.50	78.31	531.69	424.78	79.89
IIC	6.0	5.75	95.83	10.13	8.40	82.92	429.36	325.07	75.71
IID	11.97	10.80	90.23	15.57	12.80	82.21	366.04	259.12	70.80
IIIA	5.07	3.80	74.95	8.95	7.35	82.12	837.87	735.47	87.78
IIIB	5.36	4.60	85.82	12.25	11.20	91.43	747.76	682.71	91.30
IIIC	9.89	8.75	88.47	12.85	12.30	95.72	591.63	456.15	77.10
IIID	13.05	11.20	85.82	19.20	17.98	93.65	428.85	303.97	70.88
IVA	3.40	2.85	83.82	7.50	5.44	72.53	668.23	520.47	77.89
IVB	4.74	4.13	87.13	11.40	10.15	89.04	585.24	498.65	85.20
IVC	7.20	6.75	93.75	13.10	12.30	93.89	470.78	385.36	81.86
IVD	15.10	13.57	89.87	16.33	14.85	90.94	398.51	308.19	77.34

TABLE 6.25

Other physical properties of the vulcanizates containing carbon black

Mix No.	Hardness (Shore A)	Compression set (%)	Heat build up ($\Delta T^{o}C$)	Resilience (%)	Tear strength (N/mm)
IA	40	14.63	16	66.61	35.30
IB	43	16.94	16	66.61	46.15
IC	48	18.06	20	65.21	51.35
ID	63	21.59	35	53.16	60.75
IIA	40	17.23	19	65.21	23.70
IIB	41	18.86	20	63.81	32.20
IIC	49	20.06	22	61.08	43.10
IID	62	22.82	38	49.16	57.65
IIIA	44	14.32	17	63.13	34.40
IIIB	47	16.54	18	64.45	35.30
IIIC	51	19.21	22	61.45	50.50
IIID	63	22.86	35	53.77	67.30
IVA	44	13.13	16	67.49	33.20
IVB	48	14.43	17	66.61	44.75
IVC	51	18.03	20	65.21	51.20
IVD	64	19.61	34	60.25	75.95

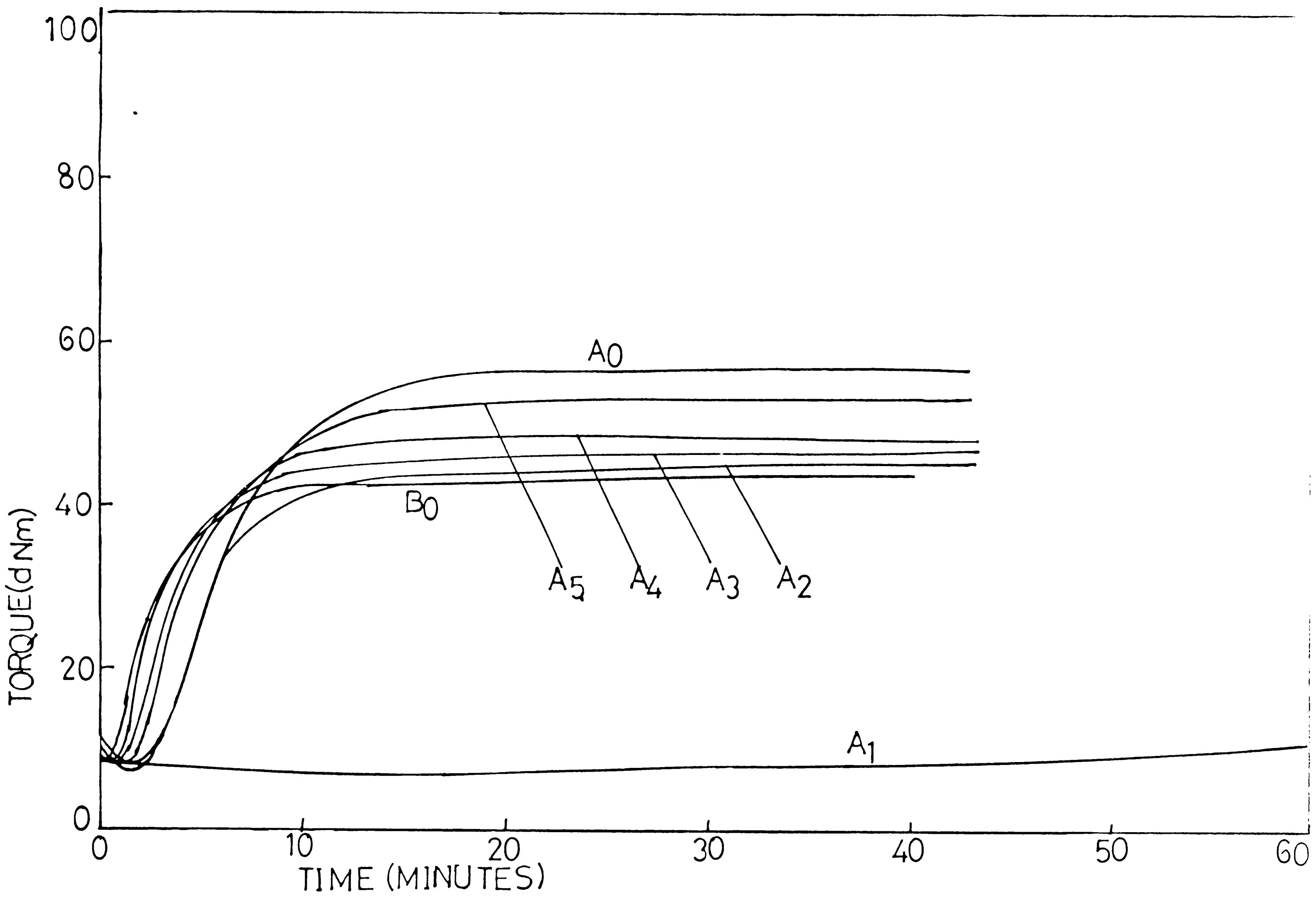

Fig. 6.1 Rheographs of the mixes containing TMTD/DTB-II at 150°C
(Ref: Tables 6.1& 6.5)

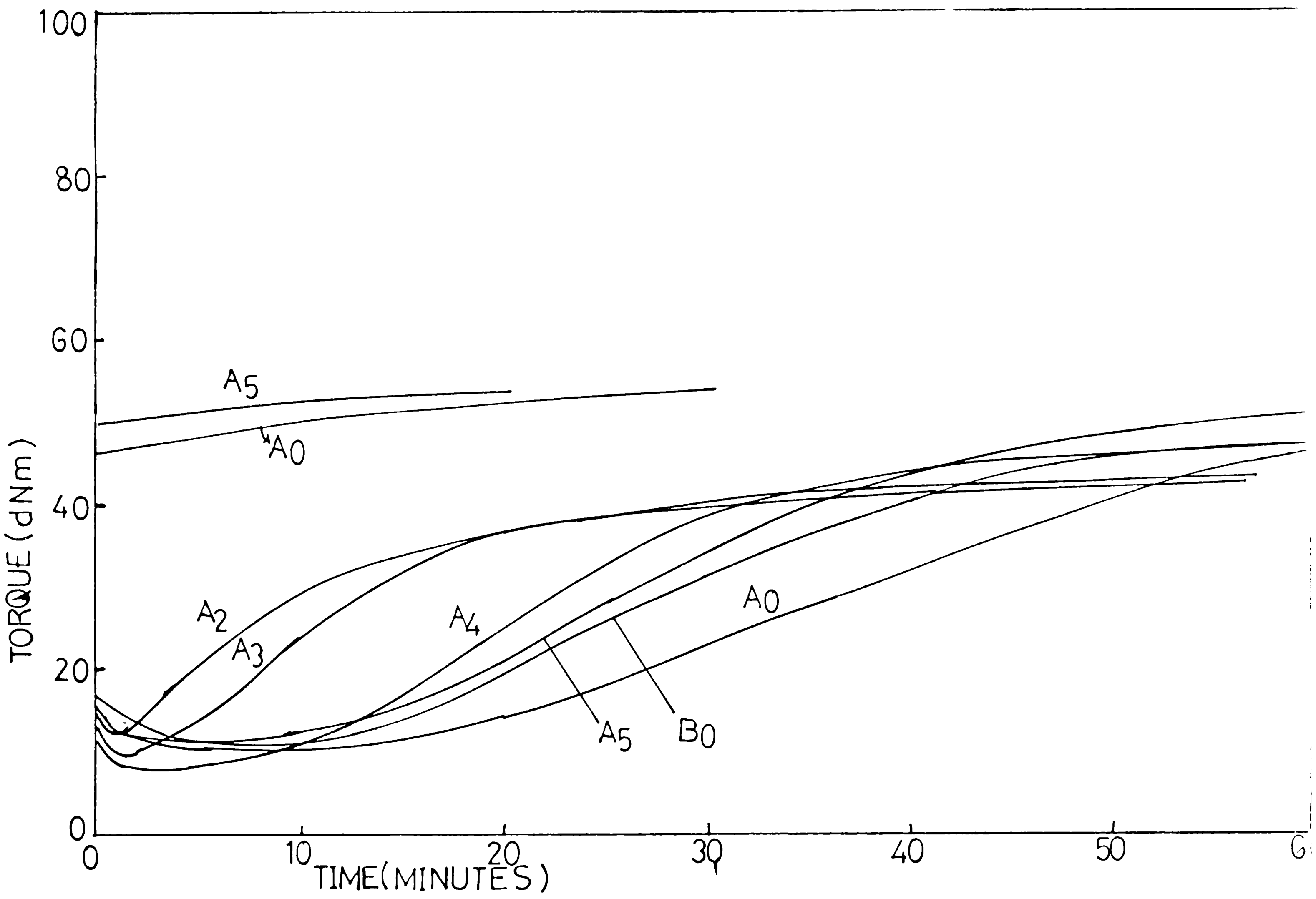

Fig. . 6.2: Rheographs of the mixes containing TMTD/DTB-II at 120°C
(Ref: Tables 6.1 & 6.6)

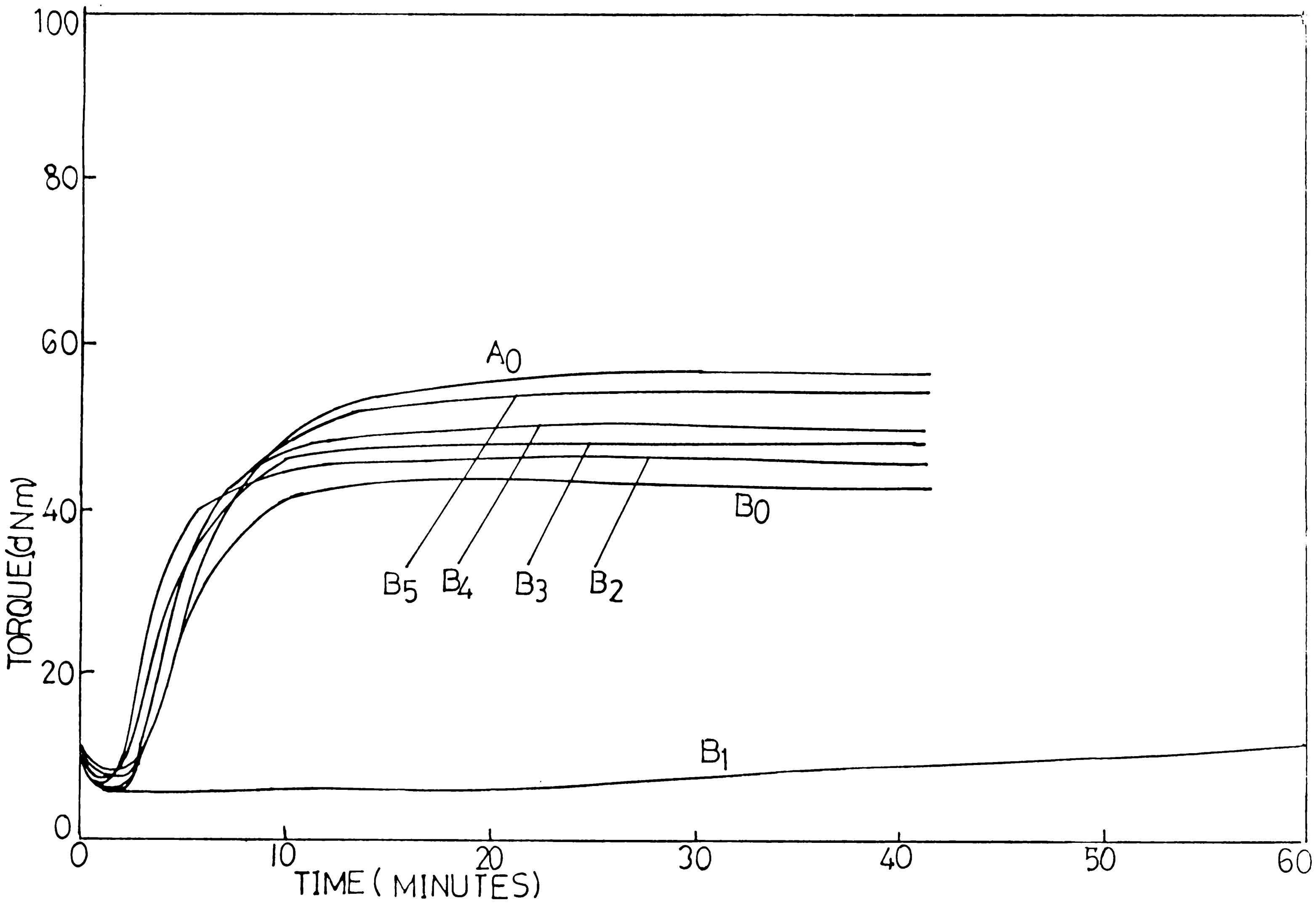

Fig. 6.3: Rheographs of the mixes containing TMTD/DTB-III at 150°C (Refer Tables 6.2 & 6.7)

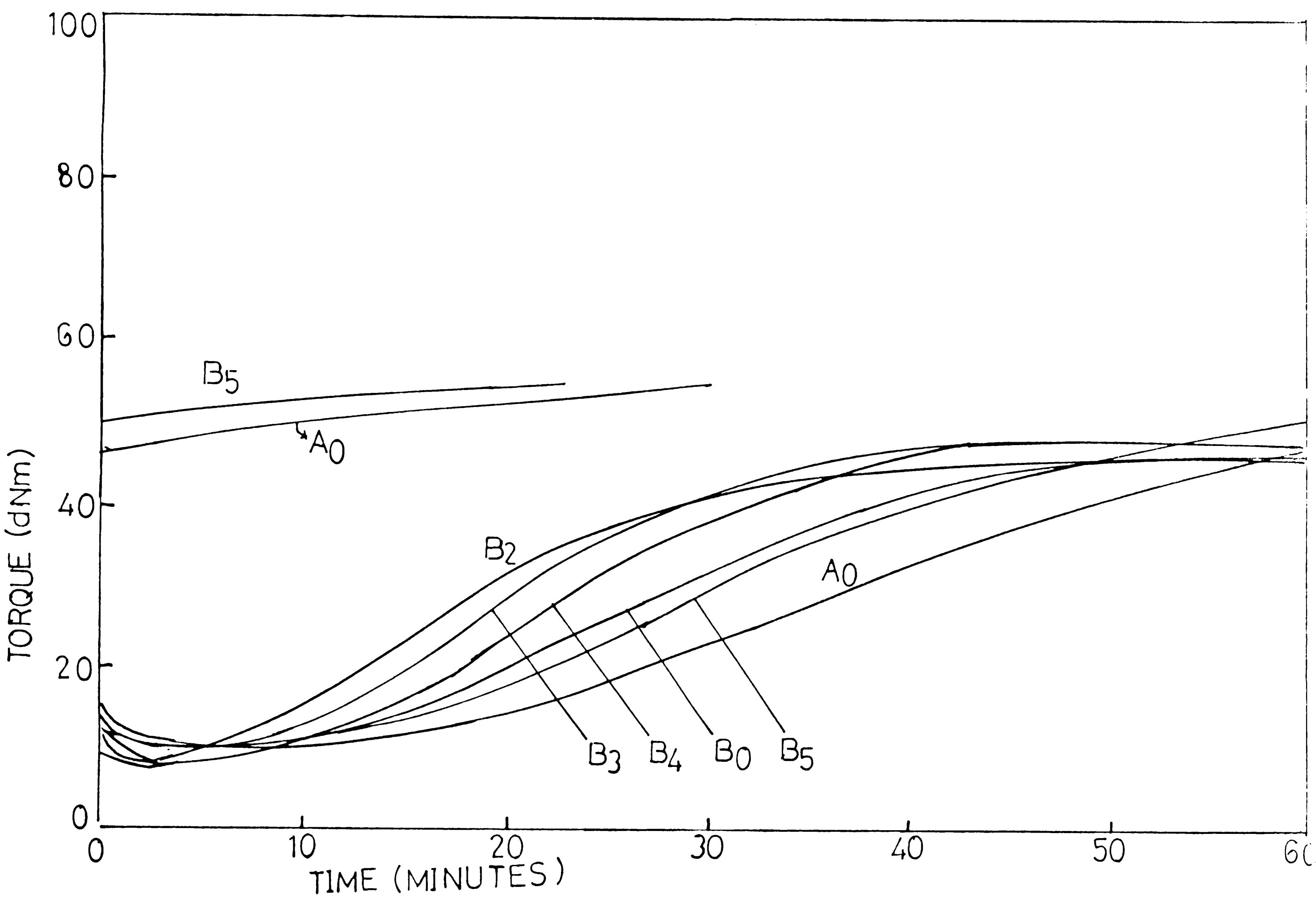

Fig. 6.4 : Rheographs of the mixes containing TMTD/DTB-III at 120°C (Ref: Tables 6.2 & 6.8)

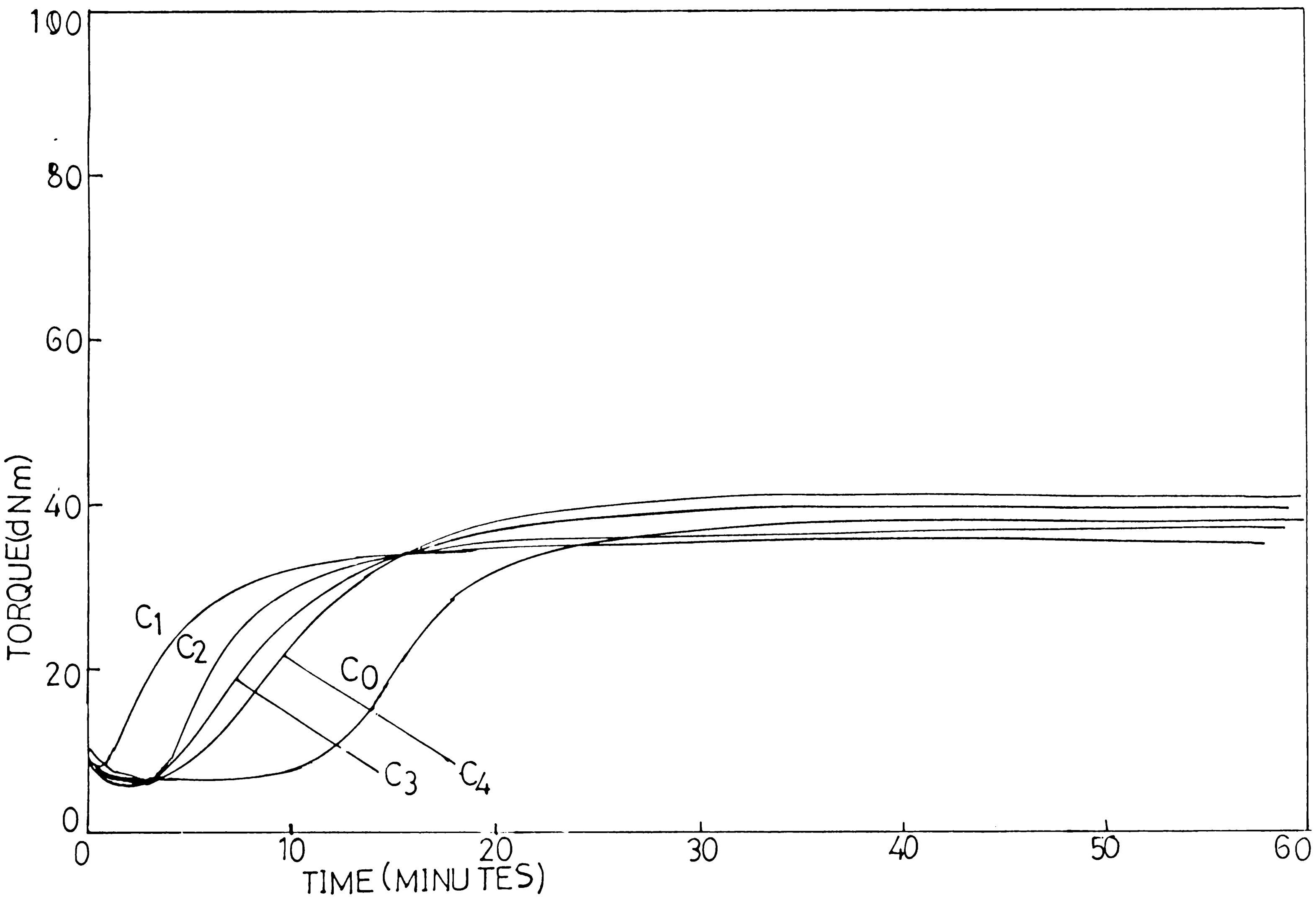

Fig. 6.5 : Rheographs of the mixes containing CBS/DTB-II at 150°C
(Ref: Tables 6.3 & 6.9)

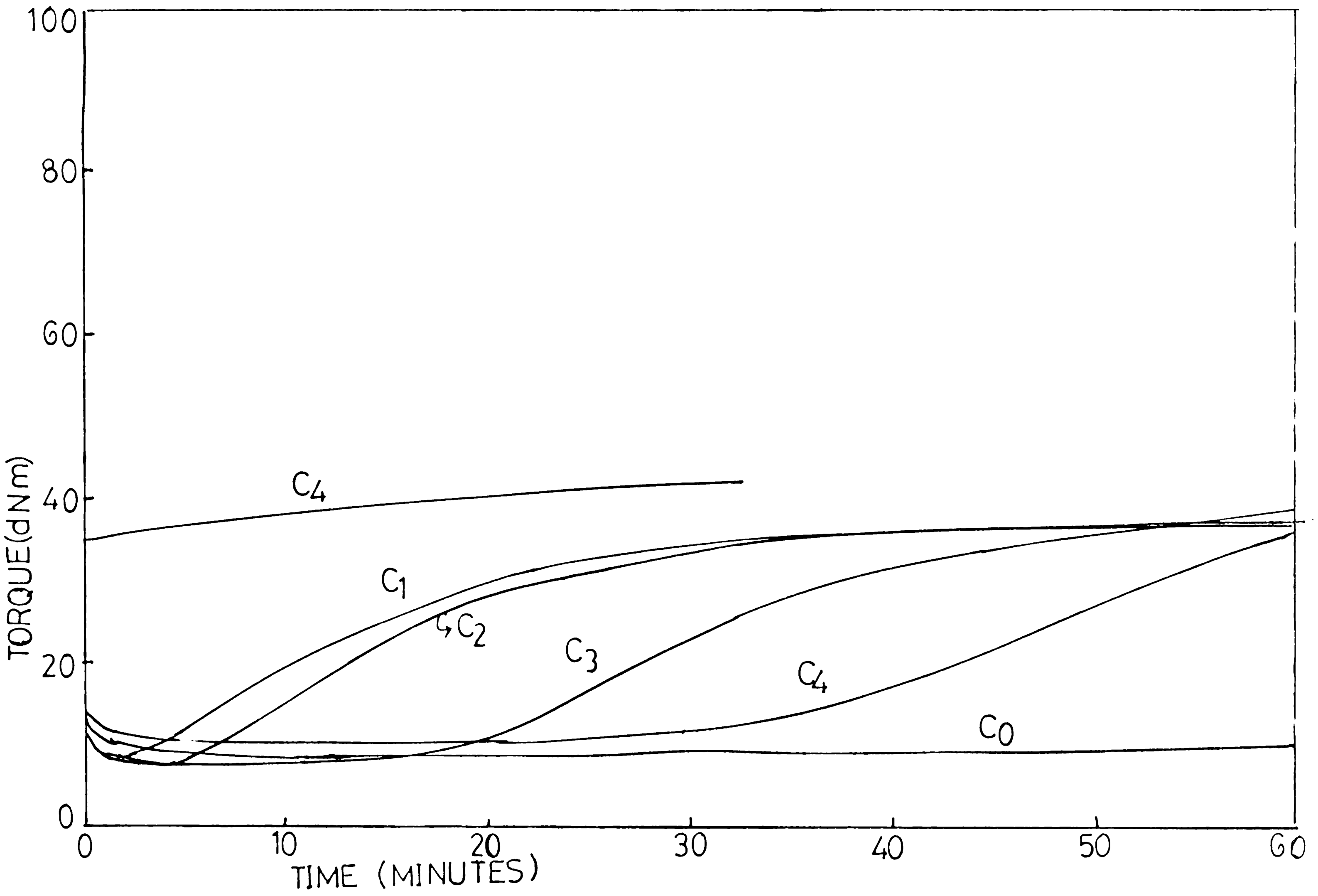

Fig. 6.6: Rheographs of the mixes containing CBS/DTB-II at 120°C
(Ref: Tables 6.3 & 6.10)

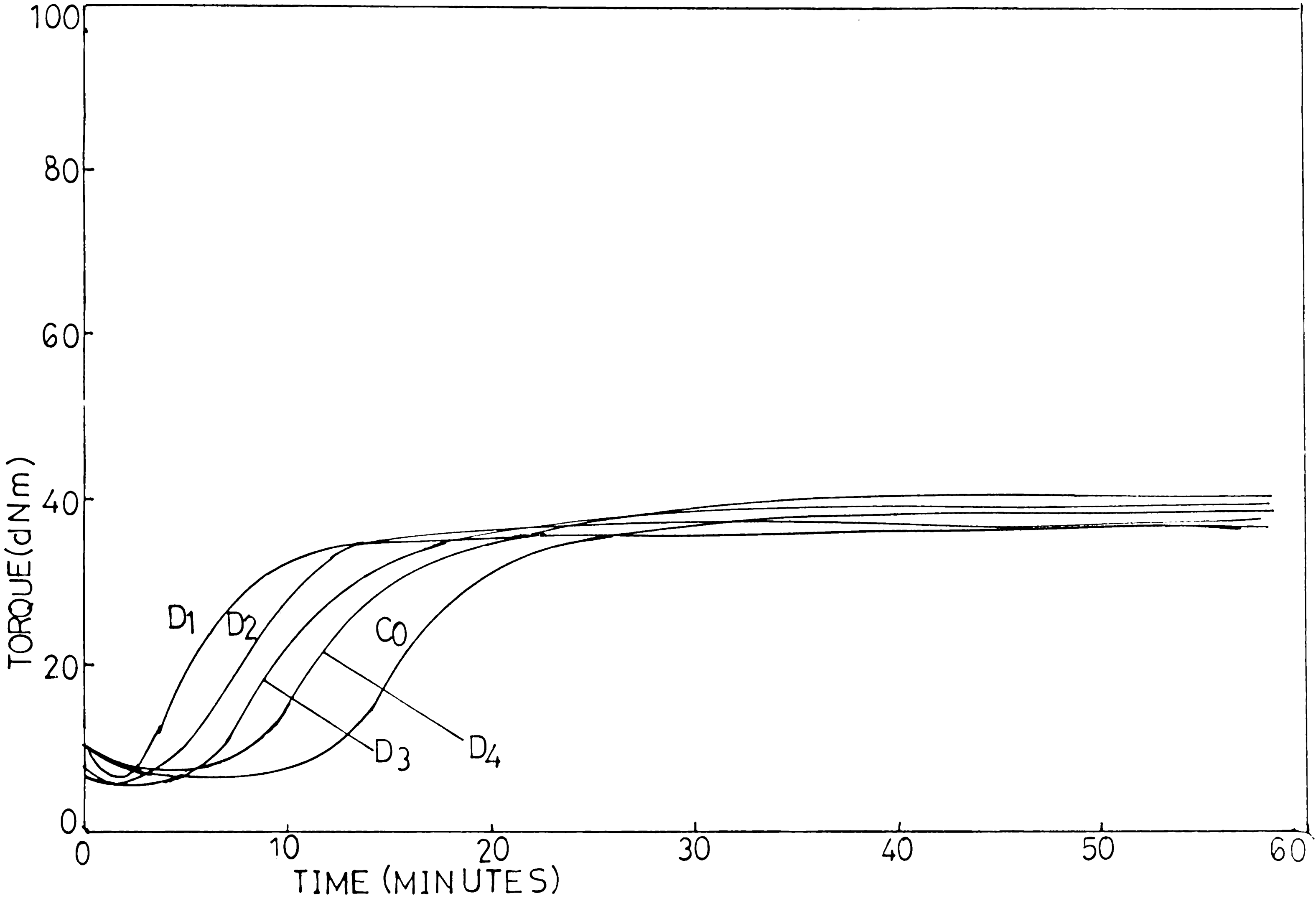

Fig.6.7 : Rheographs of the mixes containing CBS/DTB-III at 150°C
(Ref: Tables 6.4& 6.11)

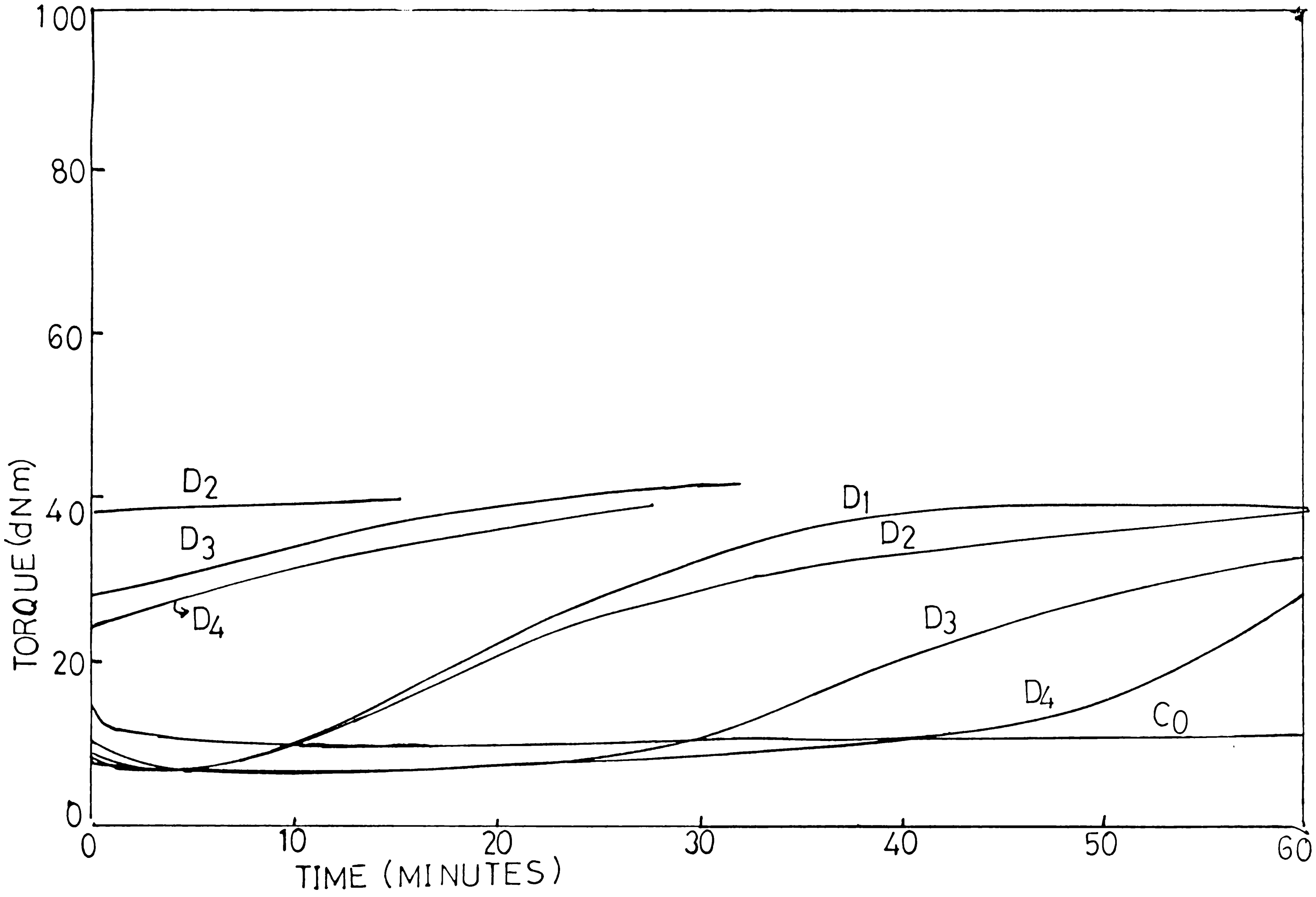

Fig. 6.8 : Rheographs of the mixes containing CBS/DTB-III at 120°C (Ref: Tables 6 4 and 6.12)

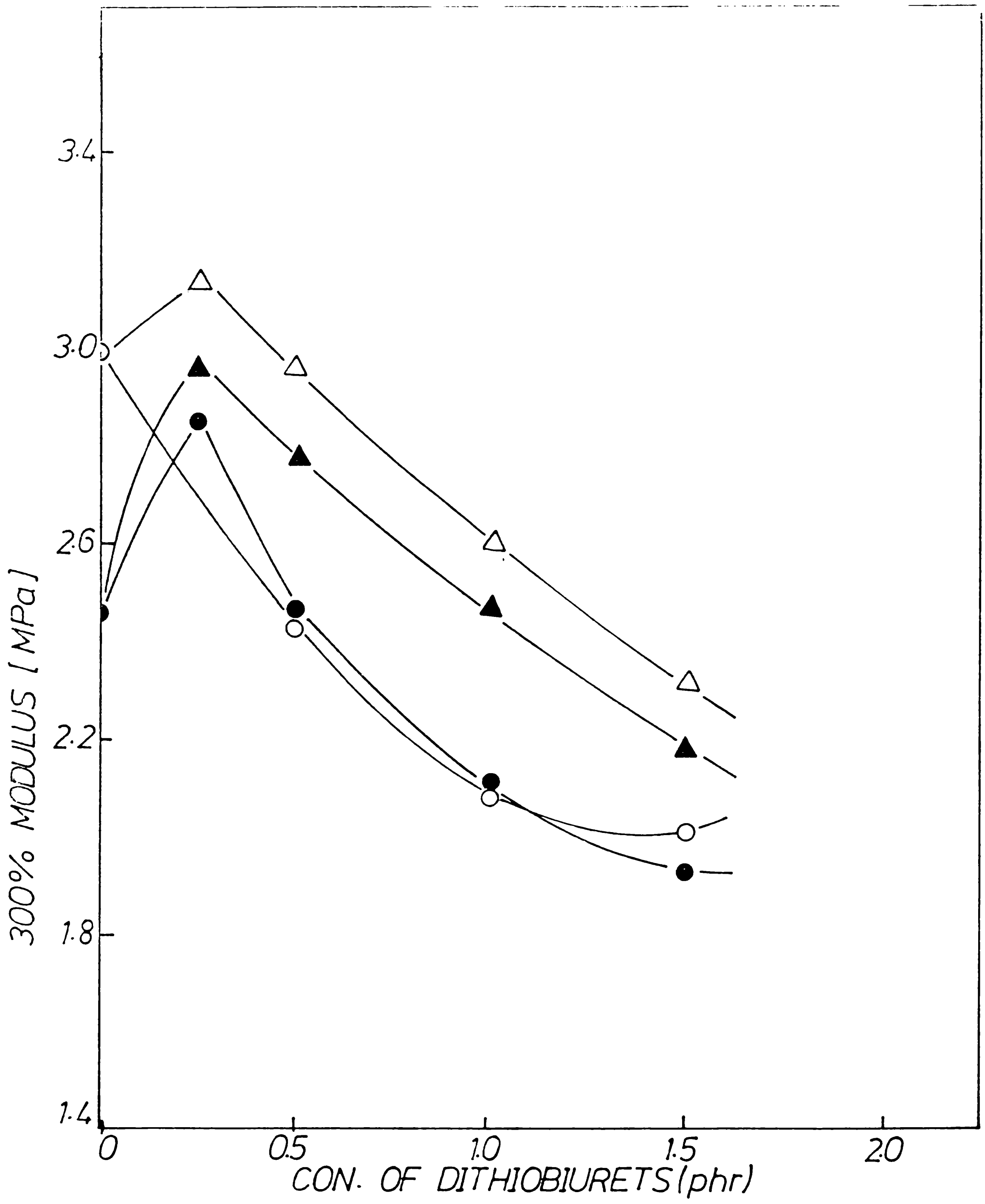

Fig. 6.9 : Variation of 300% modulus of vulcanizates containing TMTD/dithiobiurets with concentration of dithiobiurets; (●) TMTD/DTB-II; cured at 120°C; (○) TMTD/DTB-II cured at 150°C; (▲) TMTD/DTB-III cured at 120°C; (△) TMTD/DTB-III cured at 150°C.

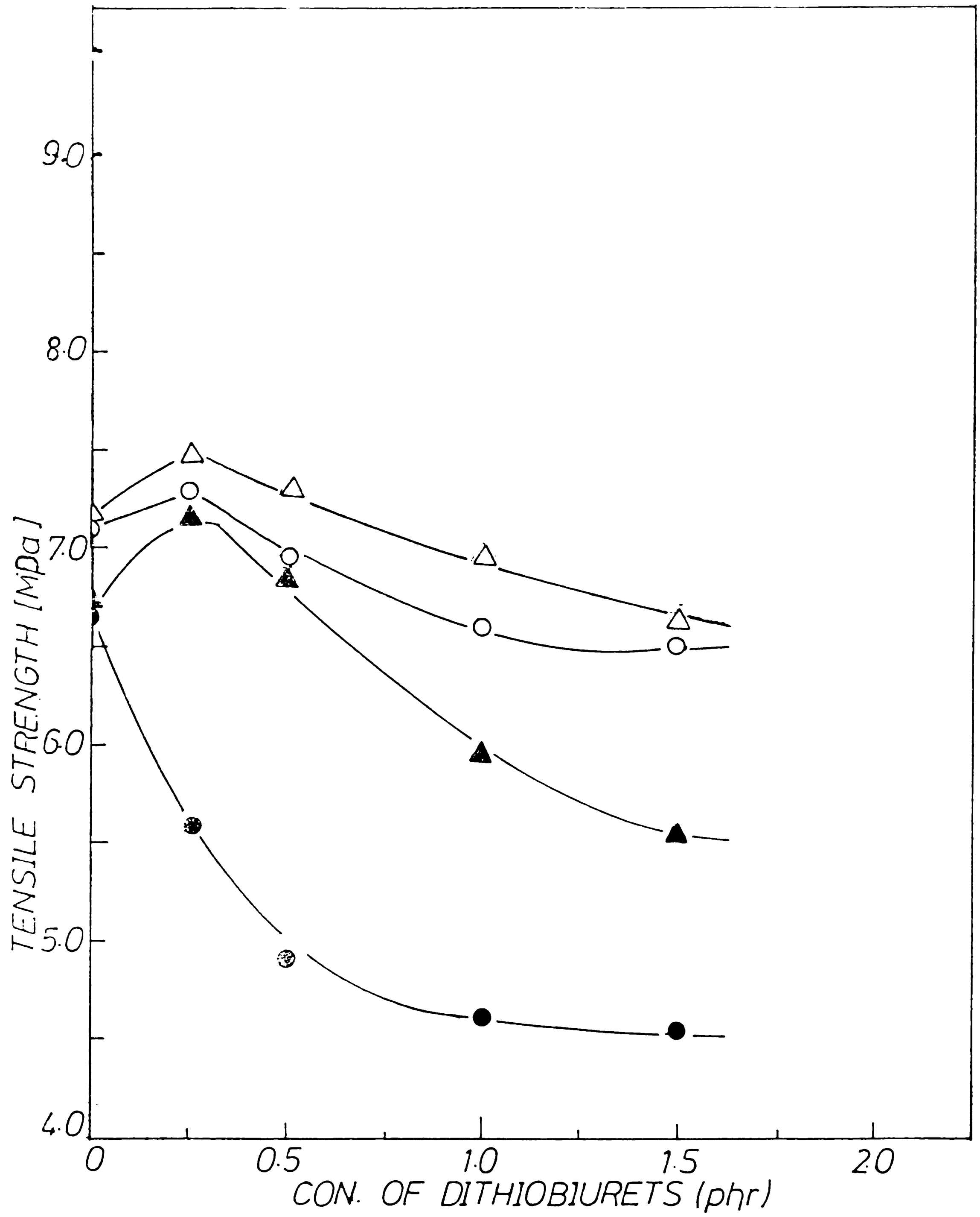

Fig. 6.10: Variation of tensile strength of vulcanizates containing TMTD/dithiourets with con. of dithiobiurets (●) TMTD/DTB-II cured at 120°C (○) TMTD/DTB-II cured at 150°C, (▲) TMTD/DTB-III cured at 120°C(△) TMTD/DTB-III cured at 150°C.

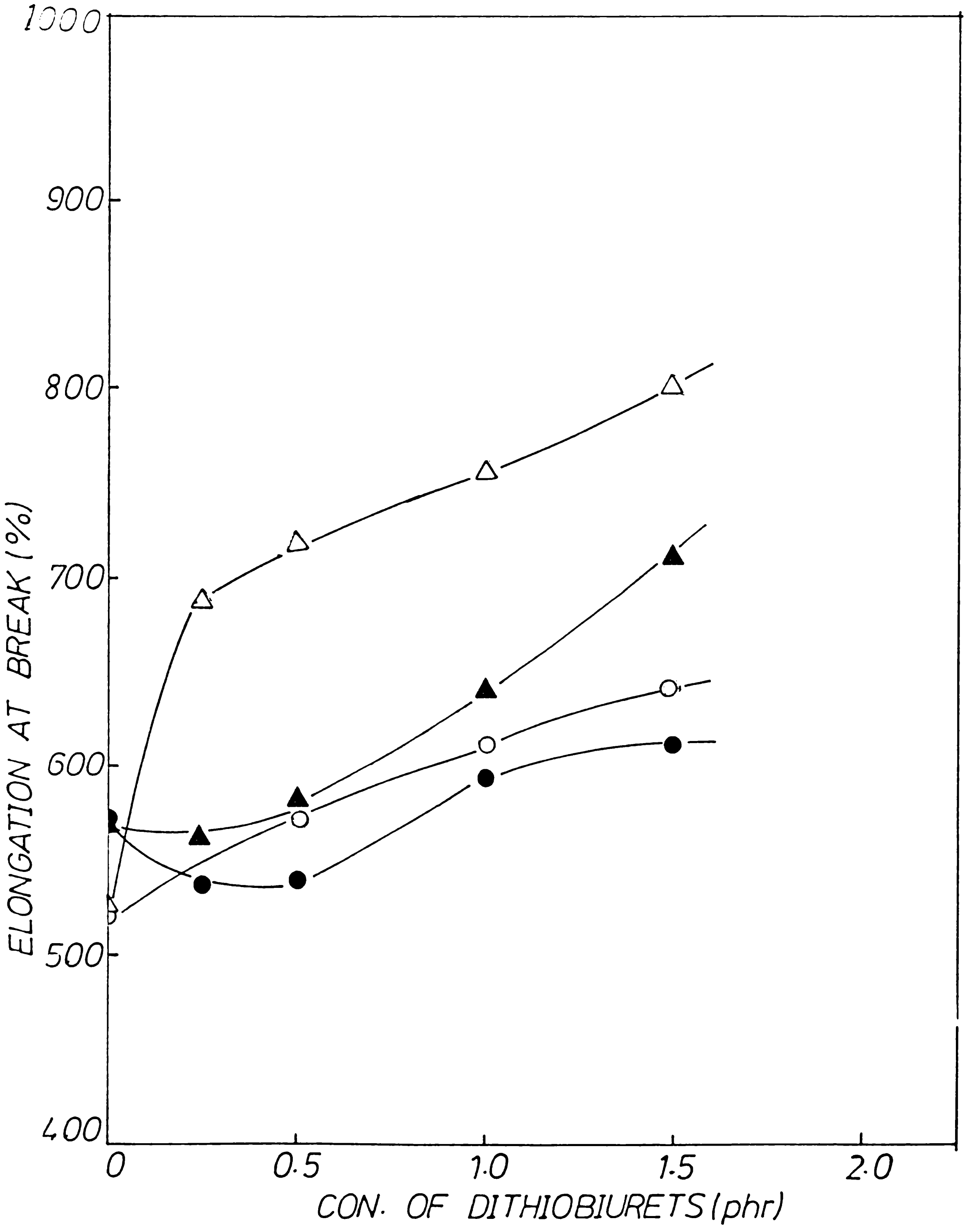

Fig. 6.11; Variation of elongation at break of vulcanizates containing TMTD/dithiobiurets with concentration of dithiobiurets; (●) TMTD/DTB-II cured at 120°C, (○) TMTD/DTB-IIcured at 150°C; (▲) TMTD/DTB-III cured at 120°C; (△) TMTD/DTB-III cured at 150°C.

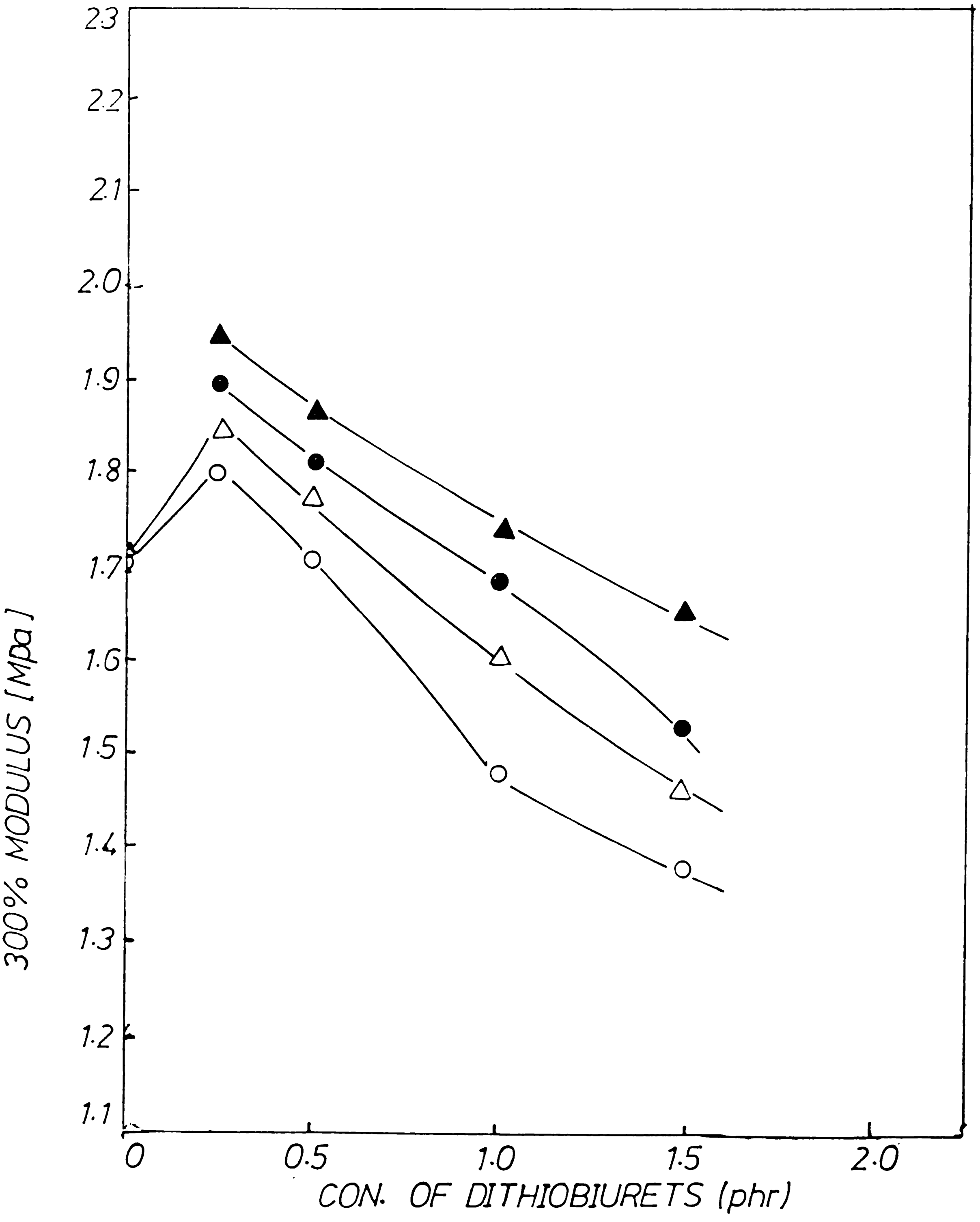

Fig. 6.12 : Variation of 300% modulus of vulcanizates containing CBS/dithiobiurets with concentration of dithiobiurets; (●) CBS/DTB-II cured at 120°C; (○) CBS/DTB-II cured at 150°C; (▲) CBS/DTB-III cured at 120°C (△) CBS/DTB-III cured at 150°C.

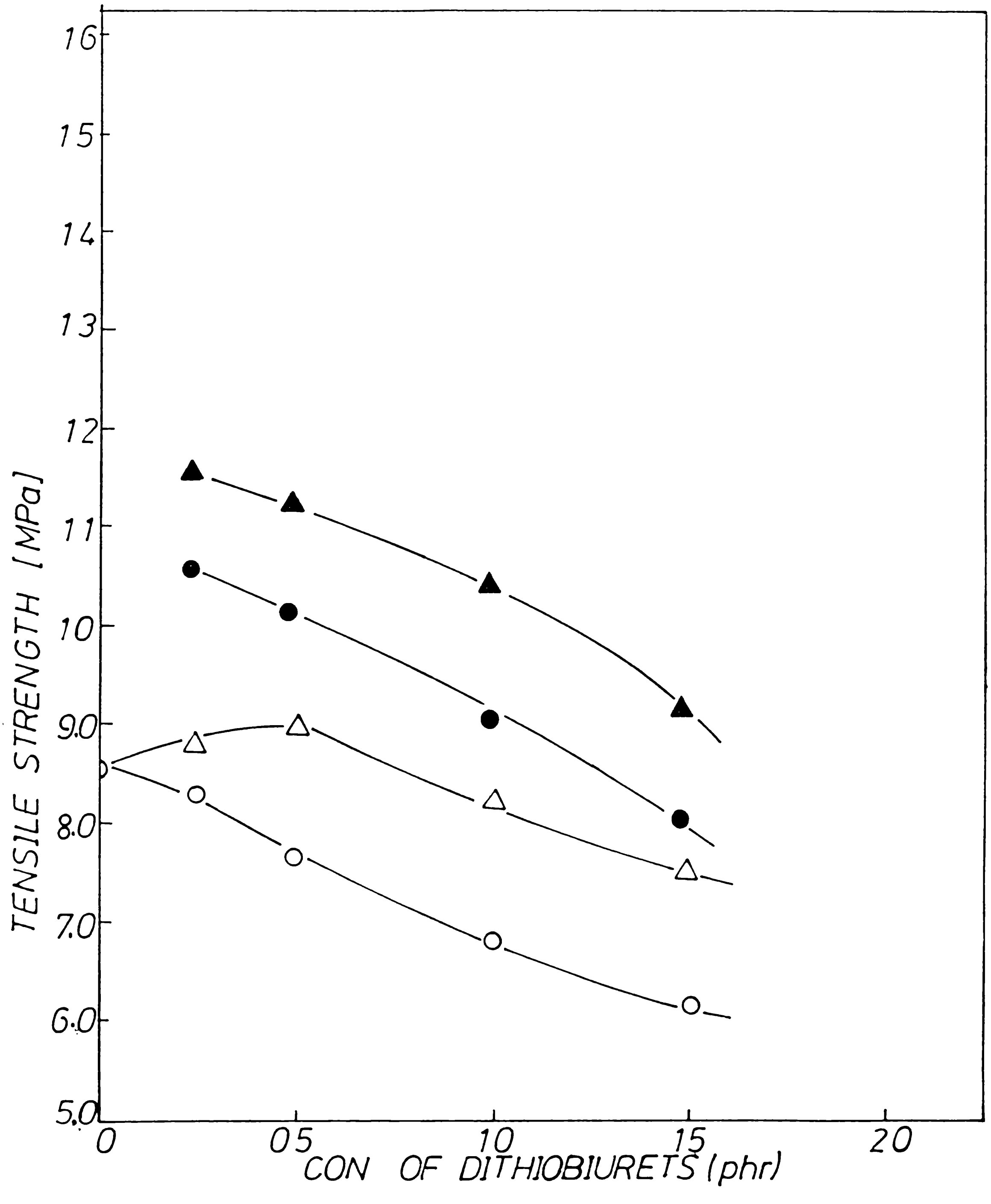

Fig. 6.13 : Variation of tensile strength of vulcanizates containing CBS/dithiobiurets with concentration of dithiobiurets; (●) CBS/DTB-II cured at 120°C; (○) CBS/DTB-II cured at 150°C, (▲) CBS/DTB-III cured at120°C; (△) CBS/DTB-III cured at 150°C.

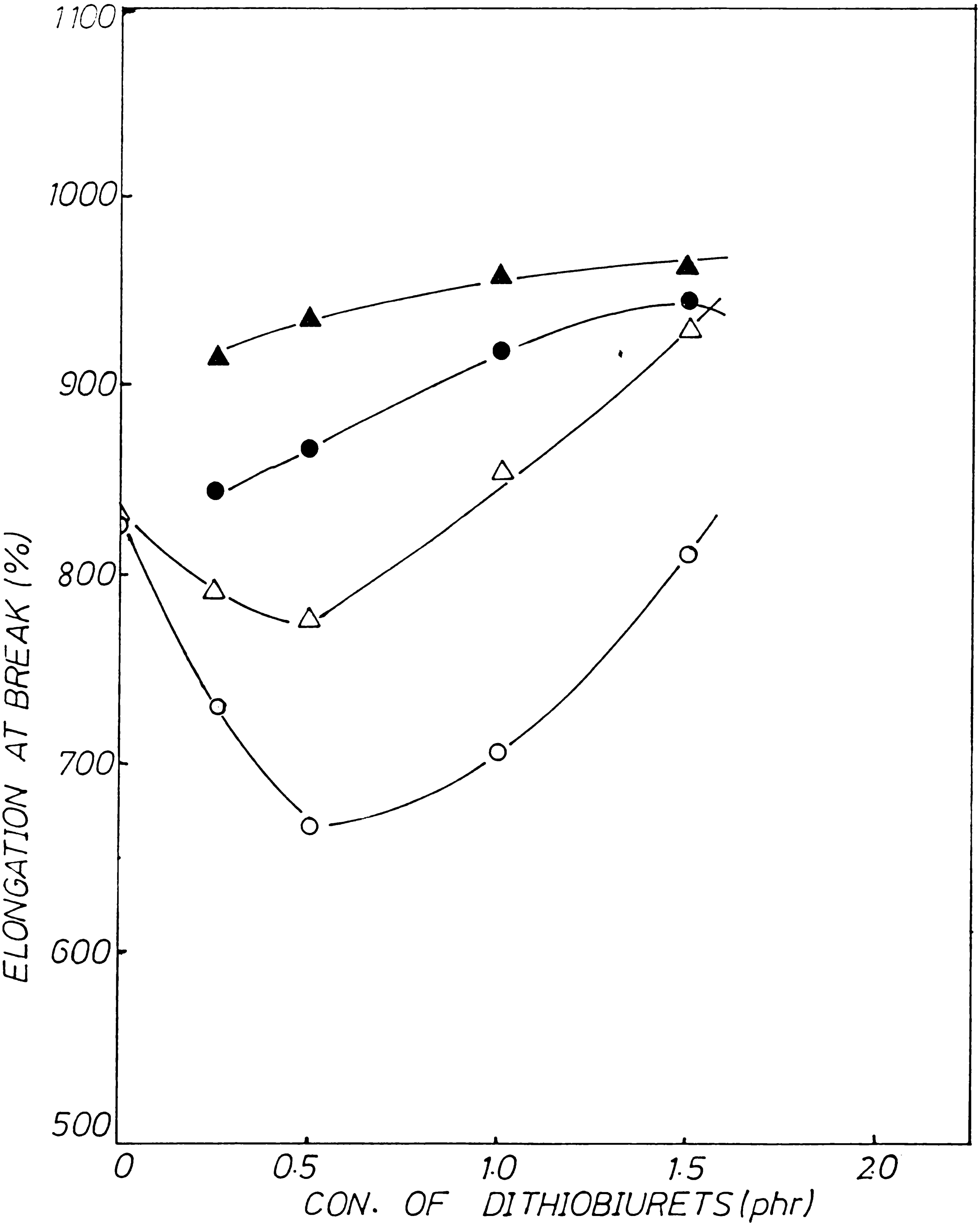

Fig. 6.14: Variation of elongation at break of vulcanizates containing CBS/dithiobiurets with concentration of dithiobiurets; (●) CBS/DTB-II cured at 120°C; (○) CBS/DTB-II cured at 150°C; (▲) CBS/DTB-III cured 120°C; (△) CBS/DTB-III cured at 150°C.

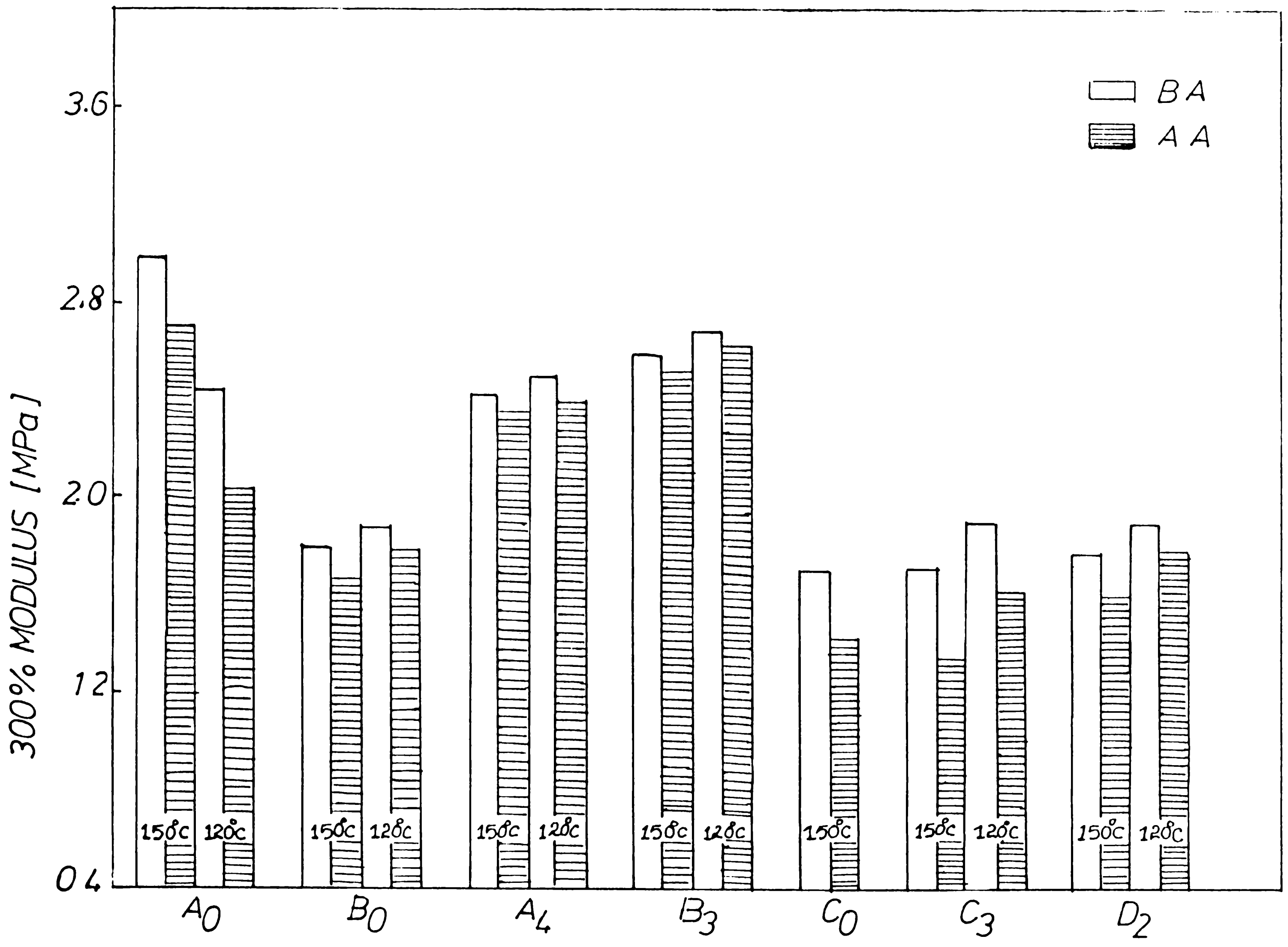

Fig. 6.15: 300% modulus of the vulcanizates containing optimum concentrations of dithiobiurets in TMTD and CBS systems.

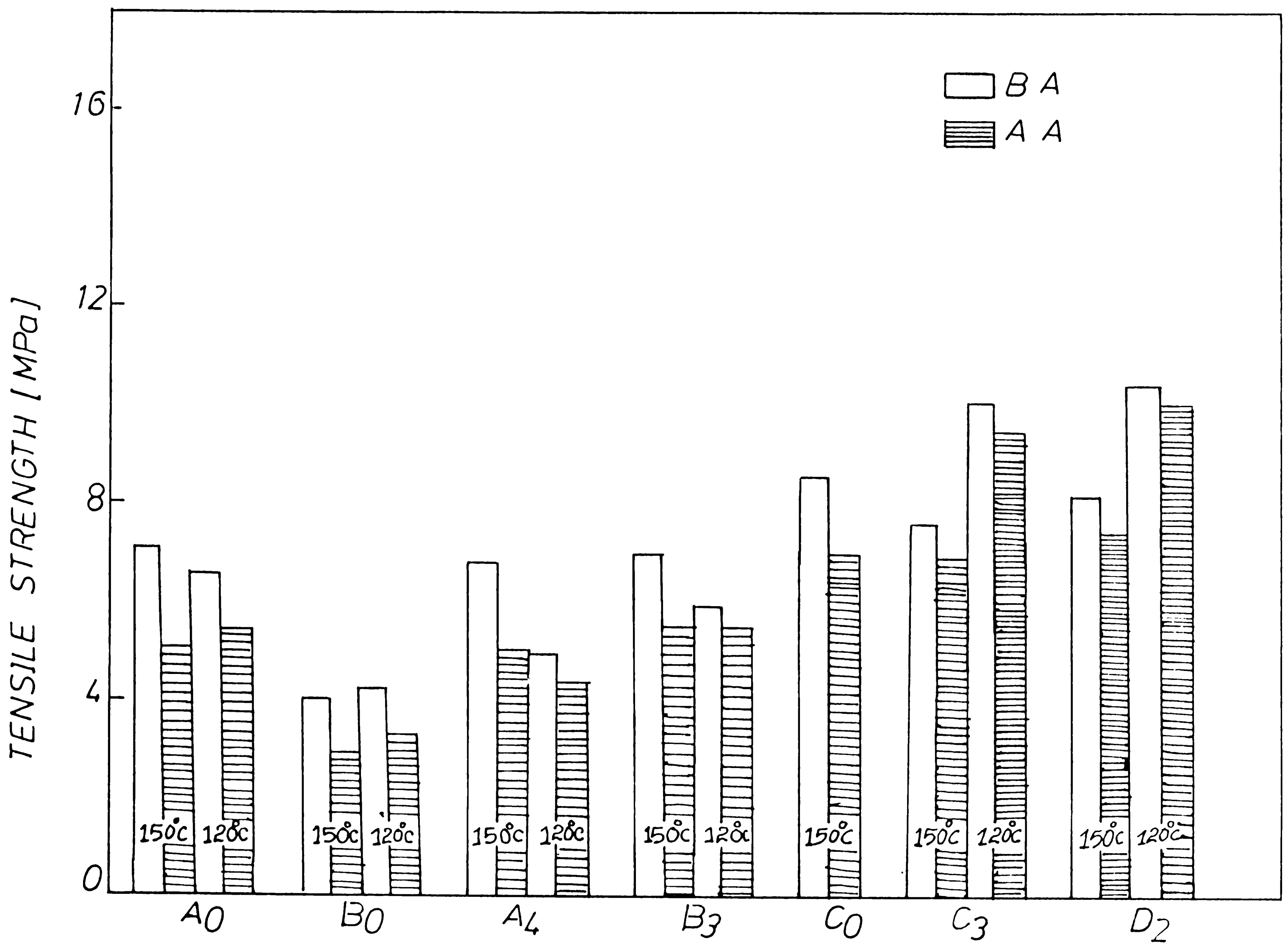

Fig. 6.16 : Tensile strength of the vulcanizates containing optimum concentrations of dithiobiurets in TMTD and CBS systems.

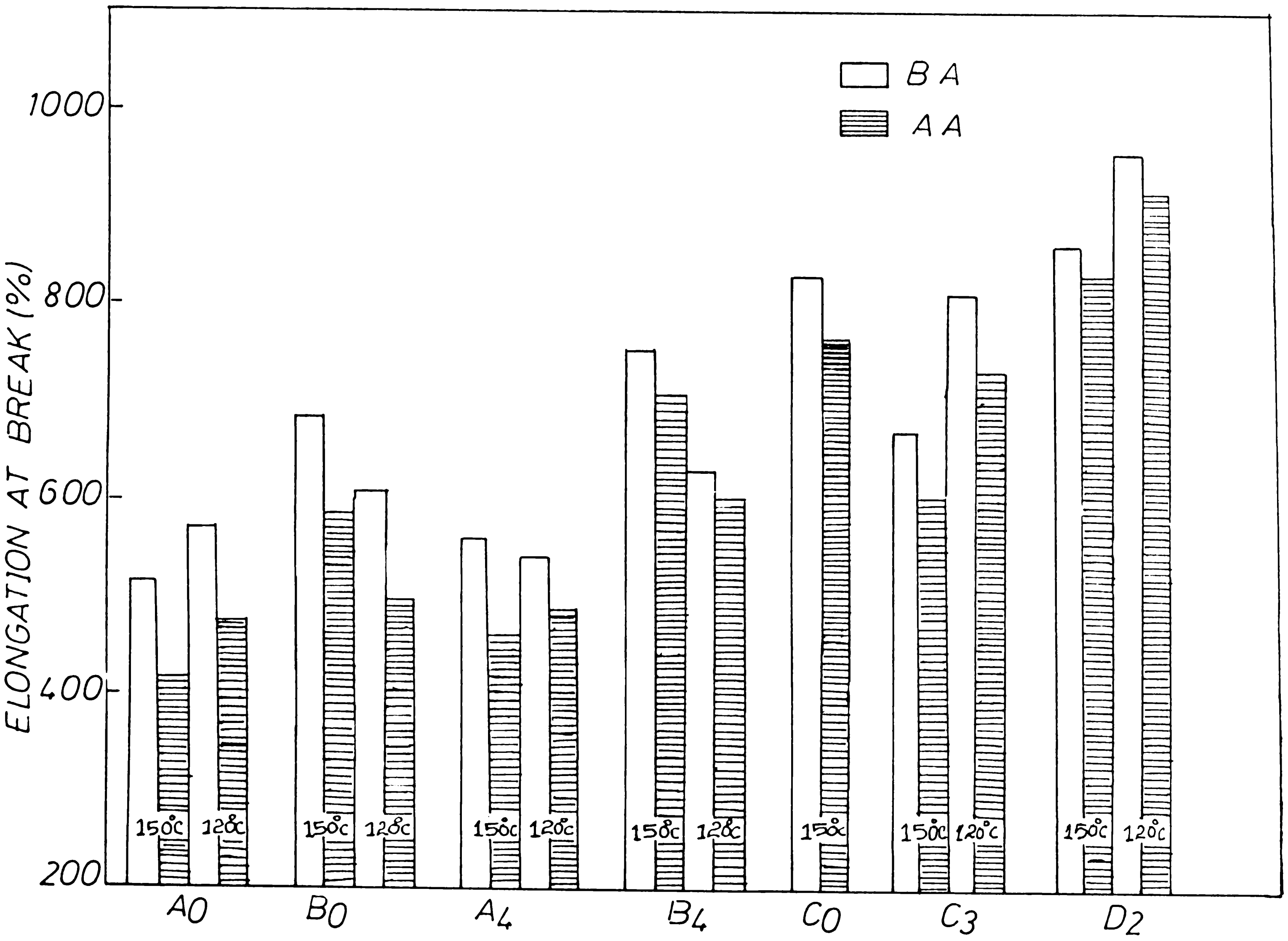

Fig. 6.17 : Elongation at break of the vulcanizates containing optimum concentrations of dithiobiurets in TMTD and CBS systems.

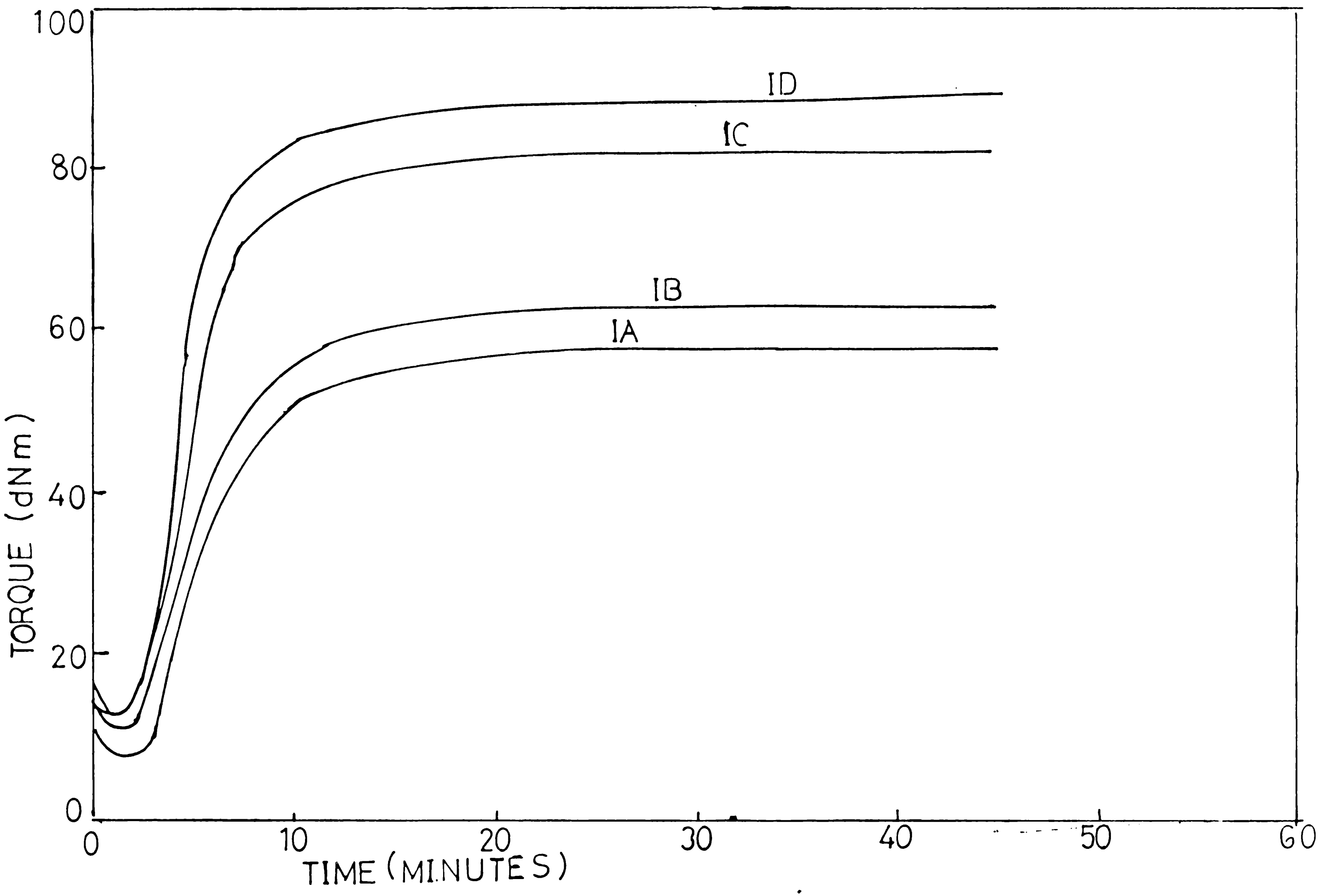

Fig. 6.18 : Rheographs of the mixes containing TMTD alone at 150°C at different loadings of HAF black (Ref: Tables 6.22 and 6.23)

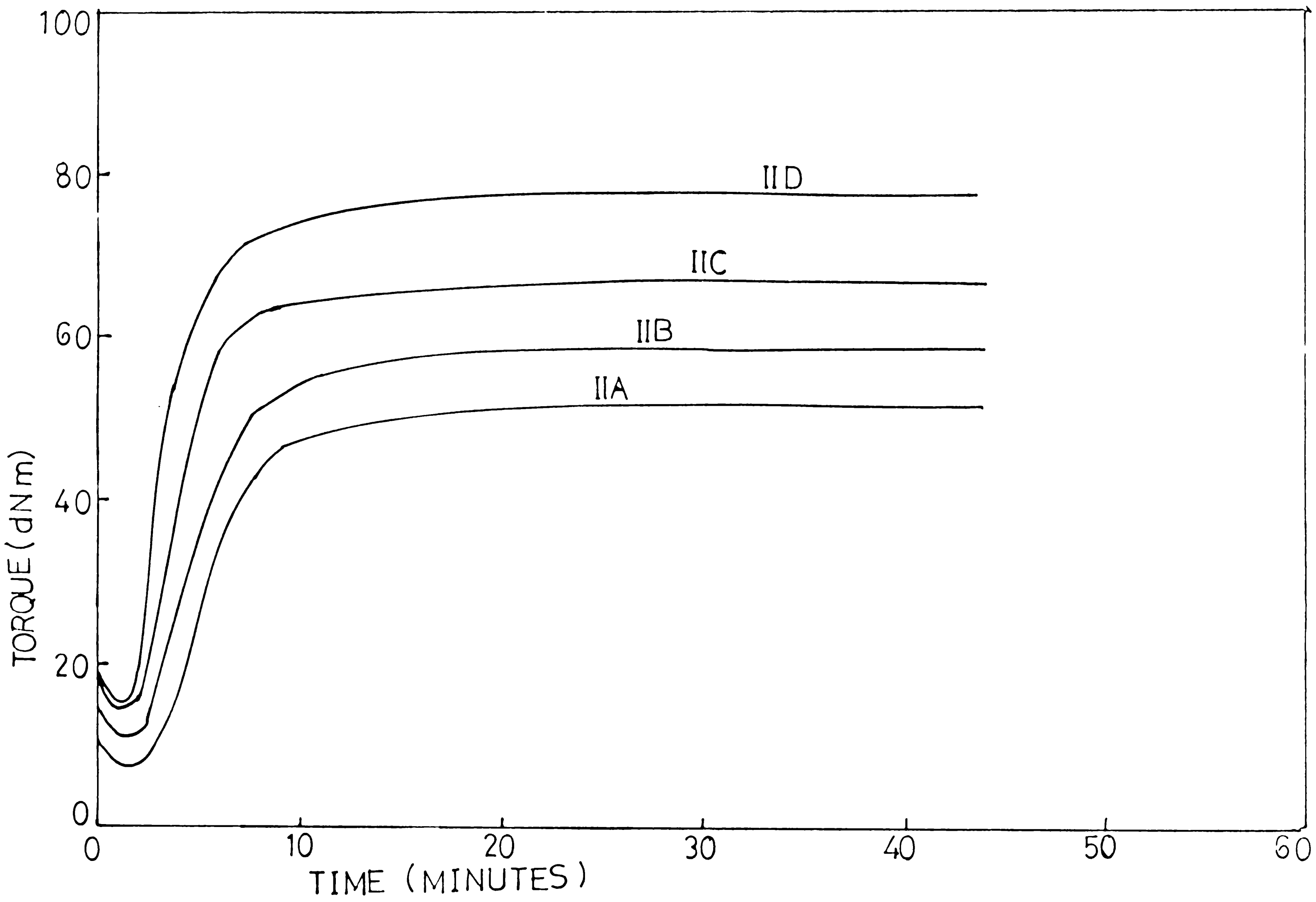

Fig. 6.19; Rheographs of the mixes containing TMTD/thiourea at 150°C at different loadings of HAF Black (Ref:Tables 6.22 & 6.23)

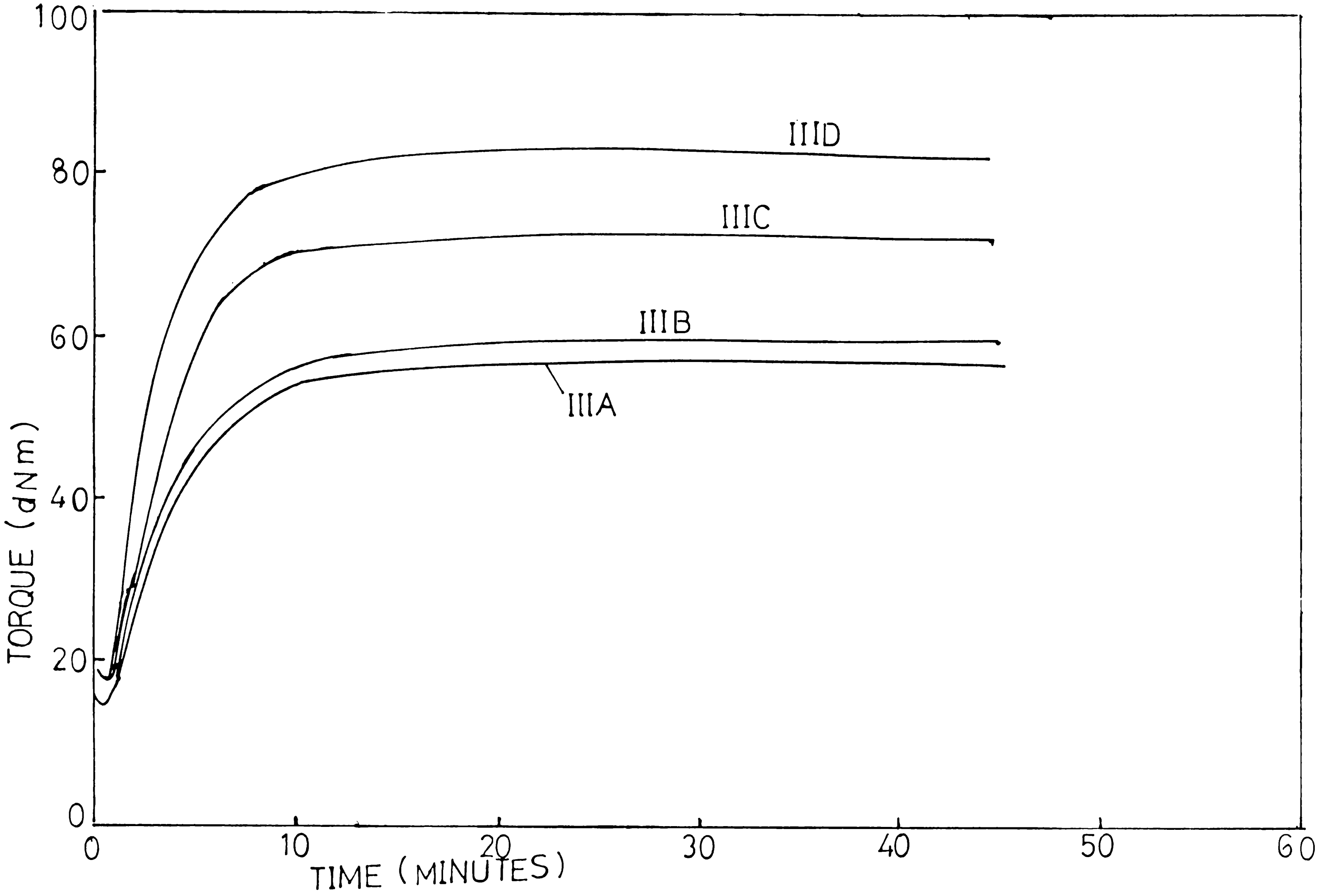

Fig. 6.20: Rheographs of the mixes containing TMTD/DTB-II at 150°C at different loadings of HAF black (Ref: Tables 6.22 and 6.23)

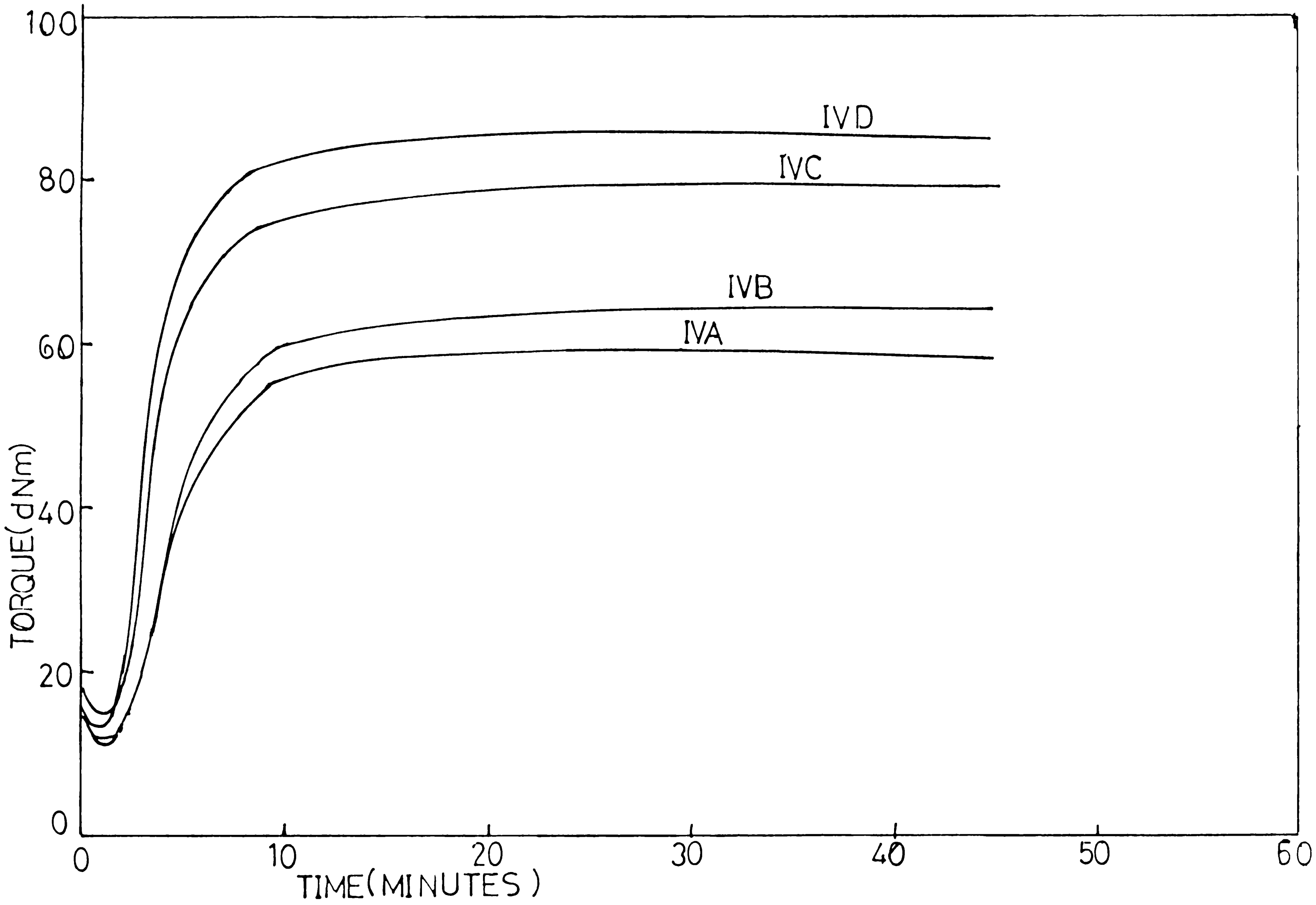

Fig. 6.21: Rheographs of the mixes containing TMTD/DTB-III at 150°C at different loadings of HAF Black (Ref:Tables 6.22 & 6.23)

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CHAPTER - VII

SUMMARY AND CONCLUSIONS

SUMMARY AND CONCLUSIONS

The First Chapter gives an introduction to the rubber vulcanization - the role of accelerators in the process, the mechanism of the vulcanization reaction and the importance of binary accelerator systems. It also includes the scope and objectives of the present work.

The physical and chemical properties of vulcanized rubber are dependent upon the fine structure of the rubber vulcanizates, which in turn is greatly affected by the type of accelerator used, the nature of the curing agent and the conditions of vulcanization. The use of binary system of accelerators have become increasingly popular now-a-days, since they generally provide efficient vulcanization resulting in improved physical and chemical properties of the finished products. It has been suggested that sulphur containing nucleophiles such as thiourea enhance the activity of accelerators, such as TMTD, CBS etc., in which sulphur is combined as S-S, C-S-C or S-N. Eventhough a number of thiourea derivatives have been tried in rubber vulcanization, there is no mention in the literature on the study of the accelerator activity of dithiobiuret derivatives of thiourea which are more nucleophilic than simple thiourea. We synthesised 1,phenyl 2,4 dithiobiuret and 1,5 diphenyl 2,4 dithiobiuret and tried these compounds as secondary accelerators in the binary systems containing TMTD and CBS in sulphur vulcanization of NR. These nucleophiles showed very good acceleration activity in the systems under review. Also there was much improvement in many of the physical properties of the vulcanizates. So we extended this study to NR latex, synthetic rubbers like neoprene and SBR and to NR-SBR blends. In view of the significant reduction in optimum cure time and definite improvement in many of the physical properties of the vulcanizates containing dithiobiurets, we considered these systems to be of practical significance in the rubber product manufacturing industry and hence made a detailed investigation as discussed in the different chapters.

The Second Chapter deals with the experimental procedure adopted for the preparation of DTB-II and DTB-III; the procedure for compounding and vulcanization and determination of physical properties like modulus, tensile strength, elongation at break, hardness, compression set, heat build up etc. Determination of chemical crosslink density, the concentration of mono, di and polysulphidic crosslinks, free sulphur and zinc sulphide sulphur present in the vulcanizates is also included in this chapter.

Study of the accelerator activity of the binary systems containing DTB-II and DTB-III with TMTD;

and with CBS in the sulphur vulcanization of natural rubber using standard procedure for compounding and vulcanization is described in the third chapter. Being S-reactive nucleophiles, these organic compounds accelerated the activity of TMTD and CBS considerably. Different concentrations of the above dithiobiurets were used in different mixes for vulcanization of natural rubber at 150°C and 120°C where thiourea was used as a control. The cure characteristics were evaluated, using standard practices. Significant reduction in the optimum cure time was observed in the mixes containing the dithiobiurets. DTB-II being more nucleophilic in nature is found to be more active than DTB-III. The optimum concentration of the dithiobiurets required was also derived at; 0.05 phr of DTB-II and 0.75 phr of DTB-III (1 phr in CBS system) can be taken as the optimum concentrations. Tensile strength, elongation at break and modulus of the vulcanizates were evaluated. Definite increase in tensile properties of the vulcanizates was observed in most of the mixes containing the dithiobiurets. These vulcanizates also showed better retention in tensile properties after ageing. Other physical properties like, hardness, compression set, heat buildup, resilience and tear strength were also estimated. There is found to be significant improvement in many of these properties also. In these physical properties DTB-III is giving better results than DTB-II. The chemical crosslink density, concentration of different types of crosslinks like, mono, di and polysulphide, free sulphur and zinc sulphide sulphur concentrations were determined for the vulcanizates containing optimum concentrations of dithiobiurets and they gave comparable values to those of systems containing TMTD or CBS alone and better results than that of TMTD/thiourea system.

The effect of fillers in the vulcanization of NR with TMTD/dithiobiuret binary systems was studied. Various concentrations of HAF black were incorporated into standard compounds and the cure characteristics were evaluated. The physical properties of these vulcanizates were compared with samples from mixes containing TMTD alone and TMTD/thiourea systems. Significant reduction in optimum cure time and definite advantage in various physical properties was observed in the systems containing dithiobiurets. The effect of other nonblack fillers like precipitated silica and china clay was also studied but they did not show much effect in cure characteristics or in the various physical properties evaluated, probably due to the highly absorptive nature of these fillers.

Chapter Four deals with the studies on the effect of TMTD/dithiobiuret and CBS/dithiobiuret systems in the natural rubber latex compounds. Mixes containing dithiobiurets were prepared and representative samples were cured at

120° and 100°C for the optimum period. The tensile properties of these samples were plotted against time and from the time-tensile graph, the optimum cure time was found out. It was found that vulcanizates containing dithiobiurets attained the maximum tensile strength and modulus at a shorter period than that of samples containing TMTD or CBS alone or TMTD/thiourea system which indicates the better acceleration effect of the dithiobiurets in latex systems. Here also DTB-II is found to be more active than DTB-III. The tensile properties of the samples prepared with various concentrations of dithiobiurets were evaluated both before and after ageing and the optimum concentrations were also found out. These properties were compared with those obtained from samples prepared under standard recipe containing TMTD/thiourea and CBS/thiourea systems. Deinite increase in tensile properties and better retension of these properties after ageing was observed in the mixes containing DTB-II and DTB-III. The chemical crosslinks were also estimated for the samples containing optimum concentrations of dithiobiurets. The effect of fillers like china clay, precipitated silica and HAF black on TMTD/dithiobiuret systems were evaluated at 120°C and the vulcanizates containing dithiobiurets showed better tensile properties in presence of these fillers.

Chapter five deals with the effect of dithiobiurets in the accelerated sulphur vulcanization of styrene-butadiene rubber and neoprene. As in the above cases standard mixes were prepared with DTB-II and DTB-III along with TMTD and CBS in SBR-1502. The cure characteristics were evaluated at 150°C and 120°C. Definite reduction in optimum cure time was observed in the vulcanizates containing dithiobiurets. Here also DTB-II is found to be a more active accelerator than DTB-III. A dosage of 0.5 phr of DTB-II and 1 phr of DTB-III were found to be optimum. Tensile and other physical properties were evaluated for samples cured at 150°C and at 120°C and definite improvement in many of the physical properties were observed in the mixes containing dithiobiurets. Study of the tensile properties after ageing showed better retention in these properties. Crosslink density studies on these samples were also carried out at the optimum concentration. It is found that the improvement of physical properties in these different vulcanizates is reflected in the increase in total crosslink density and the different types of linkages. The effect of fillers in these binary systems containing DTB-II and DTB-III along with TMTD were also evaluated. The cure characteristics, physical properties and percentage retention of these properties after ageing were evaluated for the mixes containing various concentrations of HAF black. It was found that the samples containing dithiobiurets gave better results in many of these parameters. The effect of nonblack fillers like precipitated silica and clay were also studied in mixes containing dithiobiurets as secondary accelerators. It was found that as in the case of NR vulcanization systems, there is no reduction in cure time in this case also. In the case of neoprene, standard mixes were prepared with DTB-II as accelerator and the cure characteristics were evaluated at 150°C. It was found that DTB-II is having only lesser activity than NA-22; so the dithiobiuret systems were not further studied in neoprene.

Study of the effect of dithiobiurets in the vulcanization of NR-SBR blends is given in the Sixth Chapter. The TMTD/dithiobiuret and CBS/dithiobiuret binary systems were studied in the above blends. Cure characteristics were studied at 150 and 120°C and in this case also dithiobiurets were found to give appreciable reduction in optimum cure time. DTB-II is found to be more active than DTB-III. The optimum dosages of dithiobiurets required were also derived at. The mechanical properties of the samples were studied after curing at 150°C and 120°C. Chemical crosslinks were also evaluated at the optimum concentration. In these studies also improvement in physical properties were observed in the mixes containing dithiobiurets. The effect of fillers in TMTD/dithiobiuret accelerator systems in the above blends were also studied using HAF black (various concentrations), precipitated silica and china clay. Dithiobiurets showed acceleration effect in the case of carbon black filled compounds without affecting the physical properties of the vulcanizates. In the case of other fillers it was found that there is not much variation in the optimum cure time with the introduction of dithiobiurets.

LIST OF PUBLICATIONS

Part of the outcome of these studies has been published/ presented in the following forms:

1. A.P.Kuriakose and George Mathew
   A New Binary Acceleration System for Rubber Vulcanization; Indian Journal of Technology
   Vol.26, pp 344 - 347, July 1988.

2. A.P.Kuriakose and George Mathew
   Studies on a New Binary Accelerator System in Rubber Vulcanization - part II; paper presented in the Fourth Annual Meeting of International Polymer Processing Society;
   May 8 - 11, 1988, Florida, U.S.A

3. George Mathew
   1-Substituted and 1,5 Disubstituted 2,4 dithiobiurets in the Vulcanization of Styrene-butadiene rubber; Paper presented in the Kerala Science Congress,
   February 20 - 28, 1989, Cochin.

4. A.P.Kuriakose, George Mathew and P.Viswanathan Pillai, (RRII, Kottayam)
   Effect of 1 substituted and 1,5 Disubstituted 2,4 dithiobiurets/CBS Binary Accelerator System in the Vulcanization of Styrene-butadiene rubber; Paper presented in the All India Seminar on Mechanism of polymerization processes, University of Madras, Madras, March, 1989.