Network defects in vulcanised rubber.

by

GHOLAM-REZA BAKHSHANDEH

A thesis submitted for the degree of Doctor of
Philosophy in the University of Aston in Birmingham.

May 1979

SUMMARY

The molecular weight of natural rubber is very high and must be reduced by mastication so that it has sufficient plasticity to enable the incorporation of compouding ingredients. Such a reduction in molecular weight increases the number of elastically ineffective chain ends which reduces the physical properties of vulcanisate. This thesis describes an attempt made to decrease the number of free chain ends by combining them with radical acceptors that will form vulcanisable end groups. These will form cross-links during the vulcanisation process and tie the free chain ends into the network. Such vulcanisates produce significantly better physical properties. A method to quantitatively assess the reduction in free chain ends has been developed.

It is necessary to carry out the mastication process under nitrogen as competition from oxygen, which acts as a powerful radical acceptor, reduces the yield of reactive end groups. This improves a serious practical limitation on the method.

Rubber

Defects

Mastication

Radical Acceptors

May 1979

DECLARATION

The work described in this thesis was carried out at the University of Aston in Birmingham between January 1976 and May 1979. It has been done independently and submitted for no other degree.

G.R. Bakhshandeh

ACKNOWLEDGEMENTS

I wish to express my special thanks to Mr. J.E.STUCKEY for his unfailing encouragement and supervision throughout the period of this work . I wish also to express my thanks to Mrs. C.SHABANI for her patience whilst typing the manuscript.

Finally, I would like to thank Mr.P.HUGHES for his generous help as the rubber technology laboratory technician.

CONTENTS PAGE

CHAPTER 1

CHAPTER 2 36

PAGE

CHAPTER 1

1-INTRODUCTION

This chapter will cover a brief survey of the present work, and relative studies carried out by researchers in the same field. It summarises relevent experimental work carried out in this project.

1-1-1MASTICATION AND MECHANOCHEMICAL REACTION

Natural rubber is produced from the latex of the rubber trees HEVEA BRASILIENSIS and has the structure of cis-1,4,polyisoprene(1,2). It has initially a very high molecular weight (about 10^6)(3) and because of this it has a very high melt viscosity which makes it difficult to process and difficult to incorporate the numerous compounding ingredients required to produce a vulcanisate of suitable properties.

In 1830, Hancock(4) discovered the process of mastication to increase the plasticity of the rubber and consisted of subjecting the rubber to high mechanical shear This was first achieved by the rotation of a spiked roller within a spiked chamber (Hancock,s pickle) but was later accomplished using two roll-mill or mixer.

It was appreciated that the importance of both mechnical work and heat contributed to the softening and self-adhesion produced in the rubber, but there was no attempt made to explain the chemical reactions involved. This could not take place until the polymeric structure of rubber had been recognized.

Staudinger (5) first demonstrated by osmotic pressure measurements that the mastication of natural rubber caused a degradation of the polymer which produced a great reduction in initial molecular weight, the extent of decrease depending upon the temperature and the shear forces imposed during the mastication process.

1-1-2-EFFECT OF TEMPERATURE ON MASTICATION

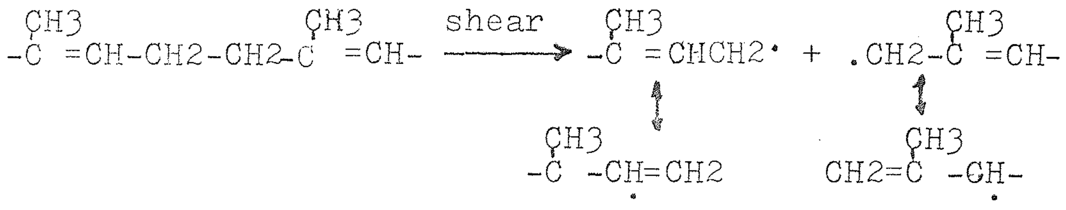
Busse(6) showed that when natural rubber is masticated in an internal mixer at various temperatures for a constant time and rotor speed, the efficiency of degradation was minimal at 115 °C. The positive and negative temperature coefficient of the two degradation processes on either side of the minimum temperature of 115 °C show that two different mechanisms are involved and are referred to as cold and hot mastication respectively. The primary degradation step of cold mastication is the rupture of the rubber molecules by the shearing forces to give polymeric radicals, which after reacting with oxygen or another radical acceptor present in the rubber, are converted to the degraded molecules. Hot mastication on the other hand, is the normal oxidative scission of the rubber(7,8,9).

The rate of degradation is greatest during the early stages of mastication and slows down eventually to zero. Eventhough the rotor speed is constant, the decrease in viscosity due to the reduction in molecular weight causes a decrease in shear rate.

Staudinger and Bondy(10,11) suggested that, cold mastication is not a conventional thermal reaction, but that the required energy is supplied directly as mechanical energy, the molecules being ruptured by the shearing forces imposed during the deformation of the bulk rubber(12).

Mullins and Watson(13), in a comparative study of the viscosity-molecular weight relationship for natural rubber, degraded thin films at 130 °C and 140 °C prepared from hot and cold masticated natural rubber and showed that there is a great resemblence in molecular weight distribution on degradation by hot and cold mastication treatments. They have also pointed out that hot mastication differs from cold mastication by the fact that the former is primarily an oxidative-scission reaction.

The differences in hot and cold mastication were rationalized by Pike and Watson(7) who suggested that rupture occurred at the α-methylene groups in the cis-1,4-polyisoprene molecule as follows:

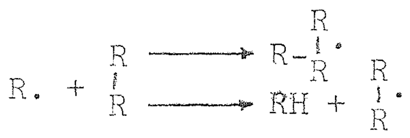


$$-\overset{CH_3}{C}=CH-CH_2-CH_2-\overset{CH_3}{C}=CH-\xrightarrow{\text{shear}}-\overset{CH_3}{C}=CHCH_2\cdot+\cdot CH_2-\overset{CH_3}{C}=CH-$$

$$-\overset{CH_3}{C}-\underset{\cdot}{CH}=CH_2 \qquad CH_2=\overset{CH_3}{C}-\underset{\cdot}{CH}-$$

They further suggested that in the absence of oxygen these radicals would recombine and produce no overall reduction in molecular weight, because of the reaction:

$$R\cdot + R\cdot \longrightarrow R-R$$



$$R\cdot + \begin{matrix}R\\|\\R\end{matrix} \begin{matrix}\longrightarrow R-\overset{R}{\underset{R}{|}}\cdot \\ \longrightarrow RH + \begin{matrix}R\\|\\R\end{matrix}\cdot\end{matrix}$$

In fact an initial icrease in molecular weight due to the branching reaction is often observed. In the presence of oxygen,however,the alkenyl radicals react to produce alkenyl peroxy radicals which decompose to produce inert products. G.Russel(14) later showed that the decomposition proceeded along these lines:

$$RCH_2 \nmid CH_2R \longrightarrow 2\ RCH_2\cdot$$

$$RCH_2\cdot + O_2 \longrightarrow RCH_2OO\cdot$$

$$2RCH_2OO\cdot \longrightarrow RCH_2OH + RCHO + O_2$$

(The alkenyl peroxy radicals must be primery or secondary and have at least one hydrogen atom) . Other reactions of the $RCH_2OO\cdot$ radicals generated by mastication may be inferred from those occuring during autoxidation, including that of rubber itself. In this case peroxy radicals react to form cyclic diperoxide-hydroperoxide groups, during which process α-methylenic hydrogen atoms are abstracted and active sites are generated along the chain at which further peroxy radicals are formed. Alternatively, $RO2.$ radicals can add to the double bonds of chain to produce branched units. Eventually the oxidation chain reaction is terminated either by mutual reaction of peroxy radicals or by their reaction with naturally present or artificially added inhibitors. As a concomitant to all these processes, some chain scission occurs.

This low temperature mastication process became known as mechanochemical degradation.

1-1-3-DESIGN OF EXPERIMENTAL MIXER

Wilson and Watson(15) developed a small mixer which enabled them to study the effect of temperature and shear rate in the presence or absence of radical acceptors using small quantities of elastomers. The shear rate was controlled by the speed of rotation, the viscosity of the rubber, the distance between the mixing faces (which is controlled by the volume of rubber used) and their surface area. Several designs of mixer faces with different surface areas were used.

1-1-4-EFFECT OF RADICAL ACCEPTORS ON MASTICATION

Using this internal mixer (unirotor mixer), Pike and Watson(7) confirmed the work of Busse(16) and Cotton(17) who showed that oxygen was required for efficient breakdown of the rubber. They reasoned that radical acceptors other than oxygen should produce the same result for example thiophenol should react thus:

$$R. + H\text{-}S\text{-}Ph \longrightarrow RH + .S\text{-}Ph$$

The benzenesulphenyl radical subsequently reacting with a second polymeric radical or dimerizing. Purified natural rubber was masticated in an atmosphere of nitrogen with a number of different radical acceptors including thiophenol and in all cases a reduction in molecular weight was observed, although none of them was as efficient as oxygen(7). The presence of thiophenol, or other radical acceptors rather than oxygen, permits degradation induced by mastication to proceed uncomplicated by chemically induced oxidative degradation(7).

This evidence strongly supports the mechanochemical mechanism suggested to explain the mastication process but the more positive analytical evidence that radical acceptor fragments become attached to the rubber during mastication has been definitely demonstrated(8) for 1,1'dinaphthyl disulphide labelled with radioactive sulphur S^{35} and 1,1'- diphenyl-2-picrylhydrazyl (DPPH). Because of the very low concentration of these fragments in the masticated rubber their quantitative estimation relies upon very sensitive detection methods.

The aromatic disulphide, which acts as an efficient radical acceptor during the mastication of an elastomer reacts with free radicals formed by cleavage of the S-S bonds:

$$R\cdot + Ar\text{-}\overset{*}{S}\text{-}S\text{-}Ar \longrightarrow R\text{-}\overset{*}{S}\text{-}Ar + ArS\cdot \qquad Ar = C_{10}H_7$$

$$R\cdot + ArS\cdot \longrightarrow RS\ Ar$$

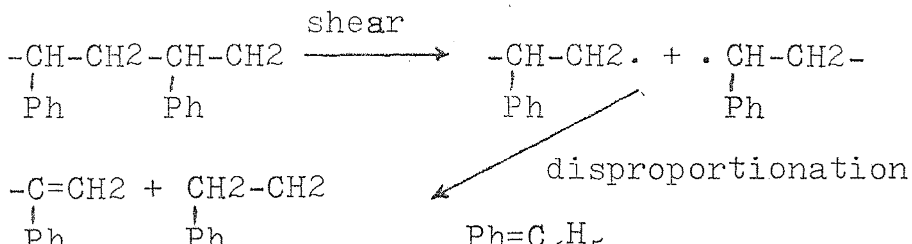
$$ArS\cdot + ArS\cdot \longrightarrow Ar\ SS\ Ar$$

After mastication in an inert atmosphere in the presence of the radioactive disulphide, the rubber was freed from unreacted disulphide by continous extraction with acetone and was then found to possess radioactivity attributable to combined $C_{10}H_7S^*$ groups. The number of sulphenyl groups determined by radio-assay agreed within experimental error with the number of scission events calculated from number average molecular weights determined osmotically, for the condition that two sulphenyl groups become attached to the rubber at each breakage.

The diphenylpicryl hydrazyl, DPPH is unusual in existing as a stable free radical in the solid state and is also stable in the presence of oxygen. The intense purple colour of its solutions in organic solvents offers a ready means of estimating it, even at concentrations of 10^{-5} moles/litre and less. Ayrey, Moore and Watson(8) showed that purified natural rubber containing about 0.1% of free DPPH masticated in an inert atmosphere combined with some of the DPPH. The amount combined was in agreement with that calculated on the basis that each bond rupture involved the combination of two molecules of DPPH. The number of bond ruptures was calculated from the decrease of molecular weight as determined by osmotic pressure measurements.

Bristow(18) showed that cold mastication of natural rubber in oxygen proceeds more rapidly than that in air, and that the thermal oxidation of rubber masticated in oxygen is rather more rapid than that of rubber masticated in nitrogen, in the presence of a radical acceptor. He also showed that gel rubber was produced during mastication under nitrogen produced by the reaction of polymeric free radicals at sites along the polymer chain to yield branched polymeric species(19). He also showed that the initial molecular weight of the rubber controls the extent of gelation, rubber with initial molecular weights of less than 3 x 10^5 showing little or no gelation, while those above 10^6 indicate upto 50% gelation after a few minutes of mastication. Such a dependence on molecular weight of reactions leading to either scission or cross-linking, which is in accord with theoretical prediction, has also been observed(20) in the radiolysis of high polymers. If mastication is carried out in the presence of oxygen, however, then the free radicals are stablised, and recombination prevented.

Further evidence of the production of free radicals during mastication of elastomer included the production of interpolymers when a mixture of purified rubbers were subjected to shear in the absence of other radical acceptor(21) by high shear mixing of an elastomer in the presence of polymerisable monomer(22-28). The mastication of plastomers (i.e.polymers that are below their glass transition temperature (Tg) at room temperature) has been investigated by Ceresa(29) who showed that these degradations were the result of mechanochemical reactions but that they were less influenced by the presence of other radical acceptors(such as oxygen) because disproportionation of the macro radicals was the principle termination process e.g. in the case of polystyrene:



$$-\underset{\text{Ph}}{\text{CH}}-\text{CH2}-\underset{\text{Ph}}{\text{CH}}-\text{CH2} \xrightarrow{\text{shear}} -\underset{\text{Ph}}{\text{CH}}-\text{CH2}\cdot + \cdot\underset{\text{Ph}}{\text{CH}}-\text{CH2}-$$

$$\xrightarrow{\text{disproportionation}} -\underset{\text{Ph}}{\text{C}}=\text{CH2} + \underset{\text{Ph}}{\text{CH2}}-\text{CH2}$$

Ph=C_6H_5

Interpolymerization of vinyl monomer with cross-linked polymers was also accomplished(29) showing that free radicals are produced when polymer networks are subjected to high shear.

The most direct evidence for the formation of free radicals by the mechanical rupture of polymers has been provided by electron spin resonance spectra. Berlin(30) reported a concentration of macro radicals of the order of 10^{-5}-10^{-6} moles/litre formed by masticating natural rubber. Bressler et al (31) obtained the ESR spectra of polystyrene, polytetrafluarethylene, polyisoprene, polymethylmetacrylate, polyethylene and polycaprolactam.

Polymer degradation in solution was first reported by Staudinger(32) who showed that solutions of polystyrene in tetralin were reduced to a limiting molecular weight when repeatedly forced through platinum jets. Thomas et al(33) showed the same effect when viscous solutions of polybutenes were subjected to high speed stirring . Fox and Alexander(34) showed that unextended molecules of polymethacrylic acid in solution were less susceptible to mechano degradation than the extended molecules of the corresponding sodium salts in solution. Very comprehensive investigations have been carried out on the degradation of polymer solutions by ultrasonic vibrations. A literature survey completed by Wilke and Altenberg(26) contains 158 references to published papers.

Much of the Russian work in this field has been of an extremely practical nature covering a wide range of application and a large number of copolymers have been prepared(33-38).

1-2 VULCANISATION

1-2-1-INTRODUCTION

After rubber compounds have been properly mixed, they are then shaped in moulding, calendering, or extruding operations and then vulcanised by the application of heat. During the vulcanisation process the following changes occur:

1) The long chains of the rubber molecules become crosslinked by reactions with the vulcanisation agent to form three dimensional structures. This reaction converts the thermoplastic rubber into a strong elastic three dimensional network.

2) The rubber looses its tackiness and becomes insoluble and is slightly more resistant to deterioration normally caused by heat and light ageing processes.

These changes generally occur with the use of the following vulcanisation systems.

1-2-2 SULPHUR VULCANISATION

Sulphur is the most commonly employed vulcanising agent. It is practically useful for unsaturated rubbers such as natural rubber (NR), butadiene rubber (BR), styrene-butadiene rubber (SBR), nitrile rubber (BNR) etc. although it is often used with the saturated rubbers such as ethylene-propylene terpotymer (EPT) and butyl rubber (IIR).

Reaction of sulphur with rubber as first discovered by Hancock(39) and Goodyear(40) in 1839 and 1843 respectively is very slow and produces very inferior vulcanisates. Basic oxides such as ZnO, PbO, MgO etc. in conjunction with fatty acids such as stearic acid accelerate the process. In 1906 Oenslager(41) noted that aniline produced a very rapid reaction and gave high quality vulcanisates. The aniline was soon replaced by less toxic materials such as thiocarbanilide and a large variety of substances, which became known as organic accelerators, were subsequently produced and are still being discovered. They support a very substantial fine chemicals industry throughout the world.

1-2-3 CONTROL OF THE VULCANISATION PROCESS

With the acid of organic accelerators it has been possible to control the following aspects of the vulcanisation reaction:

I. Induction period (scorch time)

II. Rate of vulcanisation.

III. Number of cross-links introduced (crosslink density)

IV. Type of cross-link.

V. Thermal stability of vulcanisate(reversion charact-ristics).

1-2-3-1 TYPE OF ORGANIC ACCELERATORS

The organic accelerators are normally classified by their speed of reaction and include in order of increasing reactivity the aldehyde amine condensates, thiazoles, sulphenamides, thiurams and dithiocarbamates.

The sulphenamides have a much longer induction period (which can be controlled to some extent by the type of sulphenamides used) and are known as the delayed action accelerators. Many accelerators exhibit synergism and mixtures are often used. The one used in the smaller amount is sometimes referred to as the secondary accelerator or booster. Mixtures of three accelerators are sometimes used. Further increase in the scorch time can be obtained by the use of aromatic acids such as bezoic acid or salicylic acid (retarders) or by the use of N-Cyclo-hexylthiophtalimide which is used in conjunction with sulphenamides and quantitatively interferes with the vulcanisation reaction and gives a very accurately reproducible delay. These are known as prevulcanisation inhibitors.

1-2-3-2 CONTROL OF CROSS-LINK TYPE

The cross-link density and type of cross-link are controlled by the amount of sulphur and ratio of sulphur to accelerator respectively. The most popular sulphur system uses a high ratio of S:accelerator(2.5 sulphur : 0.5 N-Cyclohexylbenzthiazyl-2-sulphenamide (CBS) for natural rubber(NR) vulcanisates) as this produces a high level of cure and a predominance of polysulphide cross-links. These give good tensile and fatigue properties, but produce vulcanisates with poor compression set. This is usually referred to as a conventional system. Reduction of the S:accelerator ratio (S : CBS of 0.5 : 2.5) produces vulcanisates with mainly mono-sulphide cross-links which have good ageing and set properties but the fatigue and tensile performance is inferior. Because of the efficient utilisation of S for the production of cross-links these are usually referred to as efficient vulcanisation (EV) systems. Such EV systems often produce powerful antioxidants"in situ". A CBS:S ratio of 2.5 : 0.5 with NR and with the necessary zinc oxide and stearic acid produces zinc benzolthiazole-2-thiolate and its basic salts and this confers outstanding thermal oxidative stability.

Because of the high price of such formulations a compromise is sometimes made by using semi EV systems with roughly equal S:accelerator ratios. This cost is off set by the higher rate of production achieved by the use of the high vulcanising temperature that the stability of these vulcanisates allows.

1-2-4 NON-SULPHUR-VULCANISATION SYSTEM

No elemental sulphur is used in these systems. Sulphur cross-links maybe produced, however, by using compounds containing an excess of sulphur. Examples of these are the tetra methyl thiuram di, tri and tetrasulphides, dimorpholyl disulphide (DMDS) and the dialkyldithiophosphoryl di,tri and tetrasulphides. As in the case of EV systems powerful anti oxidants are often formed during the vulcanisation process e.g. TMTD produces dithio-carbamates$^{(42)}$ and DIPDIS produces zinc diisopropyldithio phosphate (ZDP)$^{(43)}$.

C-C cross-links are produced when rubbers are vulcanised with peroxides or hydroperoxides. Dicumyl peroxide (DCP)

Cumene hydroperoxide (CH) and ditertiary butyl peroxide are commonly employed. These carbon-carbon cross-links produce vulcanisates which are very similar to the monosulphide network both in ageing and physical properties. They are useful for saturated vulcanisates (eg.Ethylene propylene copolymer EPR) which cannot be vulcanised by sulphur because of their low reactivity or where extremely low compression set is required .

1-2-5 CHEMISTRY OF VULCANISATION

1-2-5-1 IDEALISED NETWORK STRUCTURE

Sulphur is combined in the vulcanisates in many ways (fig.1). It may be present as mono, di or poly sulphide (a), or as pendant accelerator fragments (b), or cyclic mono or polysulphides (c). The original rubber maybe further modified at the cross-link sites (d) by chain scission (e), conjugated unsaturation(f)& cis/trans inversion (g). There maybe carbon-carbon cross-links (h) produced by peroxide vulcanisation or during ageing processes. There is always material associated with but not combined with the vulcanisate (extra network material - E.N.M.). This may be purposely added, be present as impurities in the original rubber or result from decomposition products during vulcanisation. It often has a powerful influence on the properties of the network.

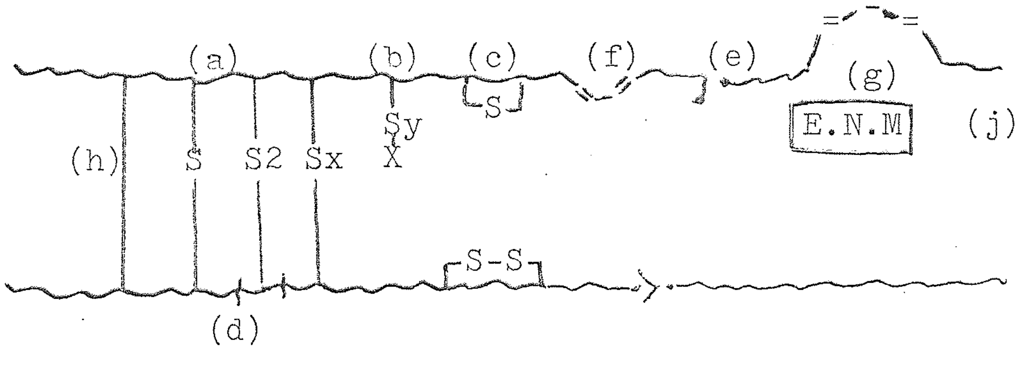


Fig. 1

The identification estimation of these network characteristics is necessary before an understanding of the mechanism of vulcanisation can be obtained.

1-2-5-2 DETERMINATION OF CROSS-LINK DENSITY

The fundamental equation describing the relationship between the force of retraction and extension of an extended rubber vulcanisate is derived from the kinetic theory of rubber elasticity$^{(44)}$.

$$\tau = F/A_o = \nu RT\ (\lambda - \lambda^{-2}) \qquad (1)$$

Where τ = Tension force (F/A_o) to give an extension ratio λ.

F = Force

A_o = Unstrained cross-sectional area

ν = The number of elastically effective network chains per unit volume of rubber.

R = Gas constant

T = Absolute temperature

When swollen with solvent this equation becomes:

$$F/A_o = \nu RT v_r^{1/3}\ (\lambda - \lambda^{-2}) \qquad (2)$$

Where v_r = Volume fraction of rubber in the sample.

This equation only applies to small extensions of unfilled rubber, swollen with solvent. For dry rubbers deviations occur and their behaviour is more accurately represented by the Mooney-Rivlin equation$^{(45,46)}$

$$F = 2A_o[\lambda - \lambda^{-2}][C_1 + \lambda^{-1}C_2] \qquad (3)$$

Where C_1 is related to the effective distance between cross-links by the expression:

$$C_1 = \frac{\rho RT}{2Mc_{phys.}} \qquad (4)$$

Where ρ = Density of rubber hydrocarbon.

$Mc_{phys.}$ = The number average molecular weight between cross-links as calculated from physical measurements (e.g the stress / strain relationship)

C_2 is a constant of uncertain physical significance but perhaps related to the number and influence of chain entanglements or virtual cross-links$^{(47)}$.

1-2-5-3 C_1 BY EXTENSION STRESS STRAIN

It is possible to obtain C_1 from simple stress-strain measurements by applying a technique pioneered by Greensmith$^{(48)}$. Experimentally a series of values of deforming force (F) and extension ratio (λ) are determined and $F/(\lambda - \lambda^{-2})$ plotted against $1/\lambda$ as depicted schematically in Fig.2.

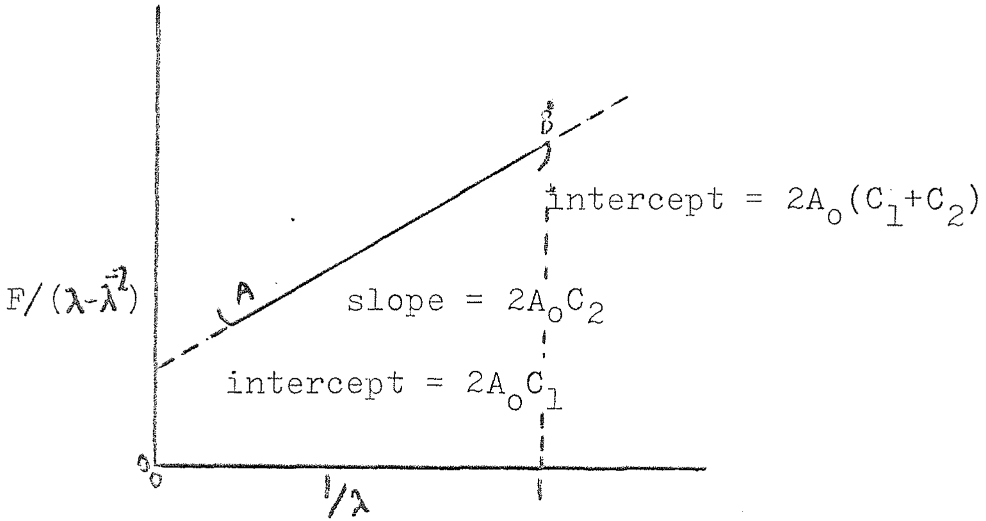


Fig.2. Plot of $F/(\lambda - \lambda^{-2})$ against $1/\lambda$ to determine C_1 for extension stress-strain technique.

Where : $2A_oC_2$ is slope , $2A_oC_1$ is intercept at $1/\lambda = 0$ and $2A_o(C_1 + C_2)$ is intercept at $1/\lambda = 1$

The departures from linearity at A and B are due to the limits of elasticity theory. This technique can also be used with samples swollen to equilibrium when the governing equation becomes (eq. 5)

$$F = 2A_o \nu_r^{-1/3} (\lambda - \lambda^{-2})(C_1 + C_2\lambda^{-1}) \qquad (5)$$

1-2-5-4 C_1 BY COMPRESSION OF SWOLLEN SAMPLES

In the equation (5) the constant C_2 will be effectively zero, at high degree of swelling, then the equation will be:

$$F = 2A_o C_1 \nu_r^{-1/3} (\lambda - \lambda^{-2}) \qquad (6)$$

ν_r values which are required, have been quoted as 0.25 or less$^{(49,50)}$.

For small deformations, further approximations can be made:

$$h_s = h_o \nu_r^{-1/3} \qquad (7)$$

$$\lambda - \lambda^{-2} = 3\Delta h/h_s \qquad (8)$$

Where h_o, h_s, Δh represent the initial height, the swollen height and deformation height of the sample respectively. This results in a much simplified expression for C_1.

$$C_1 = \frac{F}{\Delta h} \cdot \frac{h_o}{6A_o} \qquad (9)$$

The term $F/\Delta h$ is obtained from the slope of the plot of experimental compression stress-strain values of F and the corresponding values of Δh. The term $h_o/6A_o$ is determined solely by the original dimensions of the sample. Later refinents of the approximation to $(\lambda - \lambda^{-2})$ produced a modified expression (eq. 10)$^{(50)}$

$$C_1 = \frac{F}{\Delta h} \cdot \frac{h_o}{A_o} \cdot \frac{1}{1+\nu_r^{1/3}\Delta h\, h_o^{-1}} \qquad (10)$$

Some workers have used results relying on a single load and deformation measurement. This does not involve approximations of the $(\lambda - \lambda^{-2})$ term. A new measurement has been introduced, h_d, The height of swollen, deformed sample$^{(51,52)}$ eq. (11)

$$C_1 = \frac{F \cdot h_o h_d^2}{2A_o(h_d^3 - h_s^3)} \qquad (11)$$

A further exact expression was derived by Stuckey and Melley$^{(53)}$.

$$C_1 = \frac{F\nu_r^{1/3}}{2\ A_o}\left[\frac{3h_s\Delta h^2 - 3h_s^2\Delta h - \Delta h^3}{h_s^3 - 2h_s^2\Delta h + h_s\Delta h^2}\right]^{-1} \qquad (12)$$

Experimental techniques vary mainly in the size of sample tested. Cluff, et al$^{(49)}$ and the "single point" exponents$^{(52,54)}$ used samples 0.75 inches diameter, 0.5 inches thick, and 0.5 inches diameter, 0.25 inches thick. (Compression set buttons being convenient). After developing the reticulometer, Smith$^{(50)}$ used much smaller samples ; 0.4cm^2 by 0.2cm thick, these having the advantage of reaching an equilibrium swell value in a much shorter time.

The determination of C_1 by this method had to be slightly modified for low degrees of cross-linking, i.e. ν_r below

0.09, as compression set was found to occur, as the swollen height, h_s, altered during measurement. If the change in swollen height, Δh_s, causes the unstrained swollen height, h_s, to change to h_s' as Δh changes during the compression cycle, then, h_s'

$$h_s' = h_s - \Delta h_s \qquad (13)$$

The corresponding equations for C_1 are altered by the inclusion of h_s' instead of h_s.(55)

The C_1 values so obtained will vary with condition of measurement and any pretreatment the sample has been subjected to, hence it is necessary to standardise the determination of C_1(56,57).

1-2-5-5 EQUILIBRIUM SWELLING

When cross-linked networks are immersed in liquid they swell to equilibrium. The fundamental equation relating to the degree of equilibrium swelling, is due to Flory and Rehner(58,59)

$$-\left[\ln(1-\nu_r) + \nu_r + \chi\nu_r^2 \right] = \rho V_o \bar{M}_c^{-1} \nu_r^{\frac{1}{3}} \qquad (14)$$

Where χ is an intraction constant characteristic both of the rubber and swelling liquid commonly termed the "Rubber-Solvent interaction parameter"

Vo = Molar volume of the solvent.

It has been modified to

$$-\left[\ln(1-\nu_r) + \nu_r + \chi\nu_r^2 \right] = \rho V_o \bar{M}_c^{-1} \left(\nu_r^{\frac{1}{3}} - \nu_r/2\right) \qquad (15)$$

When using this equation it is necessary to know the value of χ This must be calculated by substituting a value of Mc which has been determined for this vulcanisate by some other independent method (e.g. compression or extension modulus) and then substituted in equation (14,15)(60-65).

Values of X 0.46, 0.42 and 0.50 (in n-decane)at 25°C have been found respectively for natural rubber networks cross-linked by t-butyl peroxide(66), a mercapto benzothiazole (MBT) and sulphur system(65) and sulphur alone(67).

If X is known precisely, equation (16) can be derived from (14) and (15):

$$-[\ln(1-\nu_r) + \nu_r + X\nu_r^2] = 2C_1 V_o \nu_r^{1/3}/RT$$

or

$$-[\ln(1-\nu_r) + \nu_r + X\nu_r^2] = \frac{2C_1 V_o}{RT}(\nu_r^{1/3} - \nu_r/2) \qquad (16)$$

Then it is possible to obtain from ν_r data values of C_1 which can be converted into values of Mc_{chem} by the Mullins treatment(61,66)(section 1-2-5-6)(68).

1-2-5-6 CALCULATION OF THE DEGREE OF CROSS-LINKING

The contribution of the term involving C_1 to the force extending the rubber has been identified with that predicted by statistical theory(61,66,69).

so $C_1 = \frac{1}{2} NkT \qquad (17)$

or $C_1 = \frac{1}{2}\rho RT\, Mc_{phys.}^{-1} \qquad (18)$

Where N = Number of chain per unit volume

k = Boltzmann constant

Therefore

$$C_1 = \frac{1}{2} NkT = \frac{1}{2} RT\, Mc_{phys.}^{-1} \qquad (19)$$

Therefore

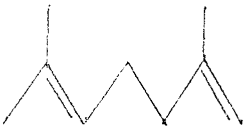
$$Mc_{phys.} = \frac{\rho RT}{2C_1} \qquad (20)$$

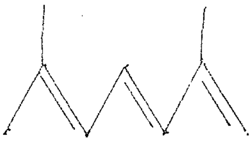
Now the substitution of C_1 in equation 9 (compression modulus) $Mc_{phys.}$ and hence cross-link density can be calculated, but it differs from $Mc_{chem.}$ (the actual molecular weight between chemical cross-links), in that it includes contribution from entanglements and free chain ends. An equation to enable the calculation of $Mc_{chem.}$ from $Mc_{phys.}$ has been derived by Mullins(66), Moore and Watson(71)(eq.21) (see section 1-3).

1-2-5-7 MODEL COMPOUNDS

A standard method of studying the reactions of complicated high molecular weight compounds is to conduct these reactions with simple low molecular weight analogues. In the case of NR, compounds such as 2-methylpentene-2(72) and 2,6-dimethylocta-diene-2,6(73) have been extensively used. The products of the reaction of sulphur with other vulcanising ingredients(accelerator, stearic acid, zinc oxide etc.) are simple enough to be isolated, purified, identified and estimated. The assumption is then made that these reactions of the low molecular weight compounds are typical of the reactions of those of higher molecular weight.

Farmer and Shipley(73), first noted that, in addition to cross-linked polysuphides analogous to those formed by mono-olefins, a substantial portion of the sulphur is combined as cyclic mono-sulphides. The cyclic mono-sulphide obtained from 2,6-dimethylocta-2,6-diene, for example include the thiocyclohexane (2), the thio cyclopentane (3) and the two unsaturated thiocyclopentanes (4) and (5). The conjugated triene (6), is formed concurrently with these compounds.


(1)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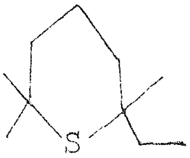
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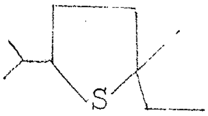
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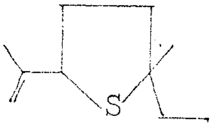
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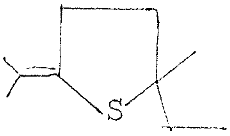
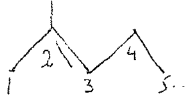

(5)

The precise structure of hydrocarbon sites of the sulphidic cross-links R - S_x- R, can be specified in detail. Thus, the disulphide cross-links are found to be situated almost entirely at the C_1 and C_4 positions in (7), as in (8) and (9), whilst the monosulphide cross-links are based on these structures with their allylically- isomeric counter parts (10) and (11) respectively$^{(72,75,76)}$.



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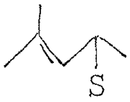

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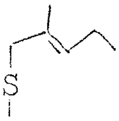

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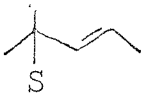

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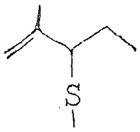
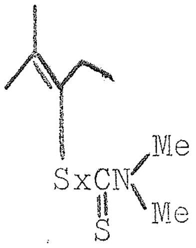


(11)

The existence of pendant accelerator residues as shown in (12,13,14 and 15) resulting from the reaction of 2-methyl-pentene-2 with TMTD, ZnO and Stearic acid suggested that the precursors to the cross-linking reaction



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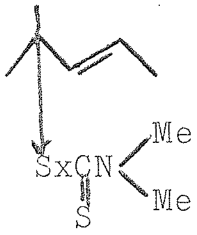

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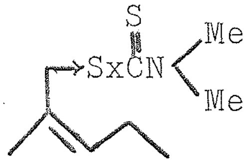

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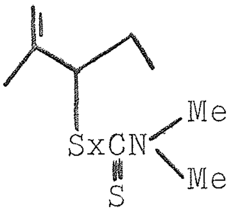


(15)

1-2-5-8 CHEMICAL PROBES

Chemical probes are reagents which quantitatively attack specific cross-links and thereby enable their estimation. They often break these cross-links and it is then possible, by determining the cross-link density due to chemical cross-links before and after probe treatment, to estimate the concentration of a particular cross-link type.

Commonly used chemical probes are:

(a) Methyliodide(77), this will break all sulphide cross-links but leave C - C cross-links unaffected.

(b) Propane-2-thiol/piperidine, cleaves polysulphide cross-links but leaves mono and disulphides unreacted.

(c) n - Hexane thiol/piperidine; which cleaves both S_x and S_2.

(d) Lithium aluminium hydride(78). Cleaves poly and disuphide

(e) Xylol thiol/piperidine(79).Cleaves polysulphide.

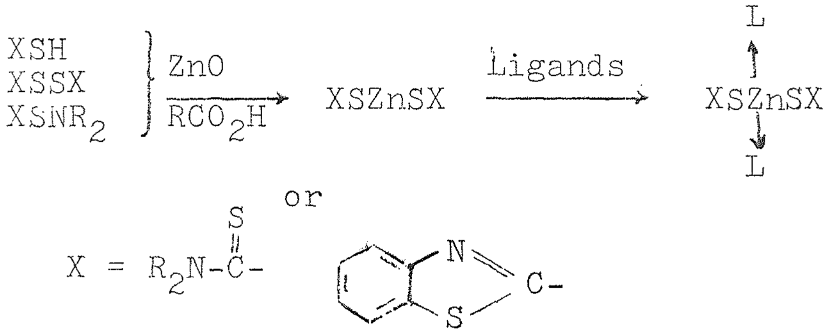
A rather special probe is triphenyl phosphine.(80) This does not break cross-links but converts all di and polysulphides to monosulphides.

Determination of the total sulphur and zinc sulphide content of the vulcanisate enables the concentration of sulphur combined in the network to be calculated. From this the amount of sulphur combined per chemical cross-link formed may be found . This is known as the E value, the efficiency of vulcanisation . Determination of this efficiency after reaction of the network with triphenyl phosphine (E' value) allows an estimate of the sulphurated main chain modification (E'-1).

E - E' represents the concentration of sulphur in the form of di and polysulphidic cross-links and E - (E'-1) is the average sulphur chain length.

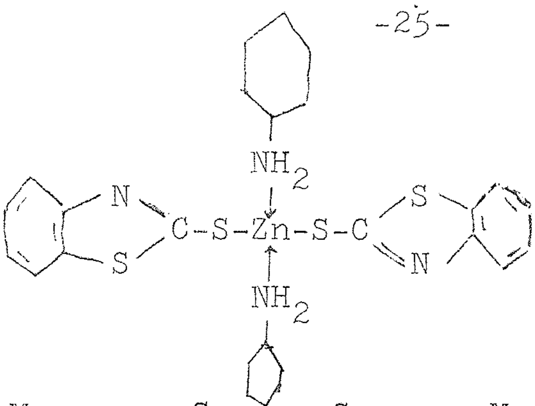
1-2-5-9 FORMATION OF ACTIVE SULPHURATING AGENT

The initial step in sulphur vulcanisation is the reaction of molecular sulphur with a species derived from the accelerator and activators. This species is usually a complex(81) of zinc benzothiazole-2-thiolate (ZMBT) or of a zinc (dialkyl dithio carbamate (ZDC) formed in "situ"(16).

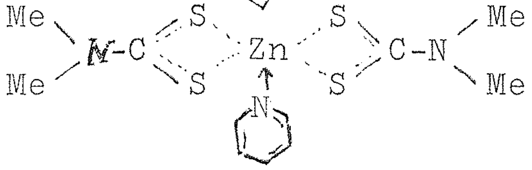


(16)

ZMBT and ZDC are themselves sparingly soluble in rubber but are rendered very soluble through co-ordination with nitrogen bases (either added as accelerator or present in the raw natural rubber or zinc carboxylates). Examples of such complexes are (17) and (18)(82,83), and the less well defined substances formed from ZMBT and zinc carboxylate(84,85), these complexes are for simplicity, collectively represented by X - S - Zn - S - X.

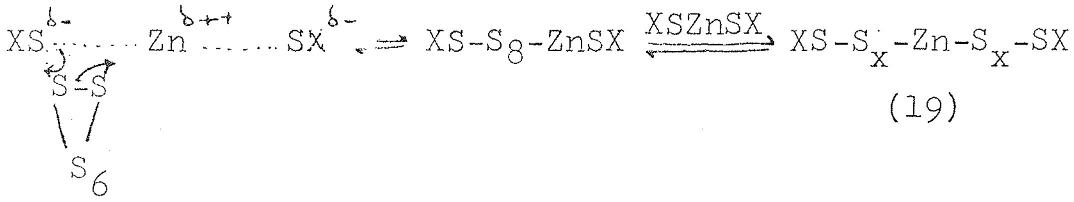


(17)



(18)

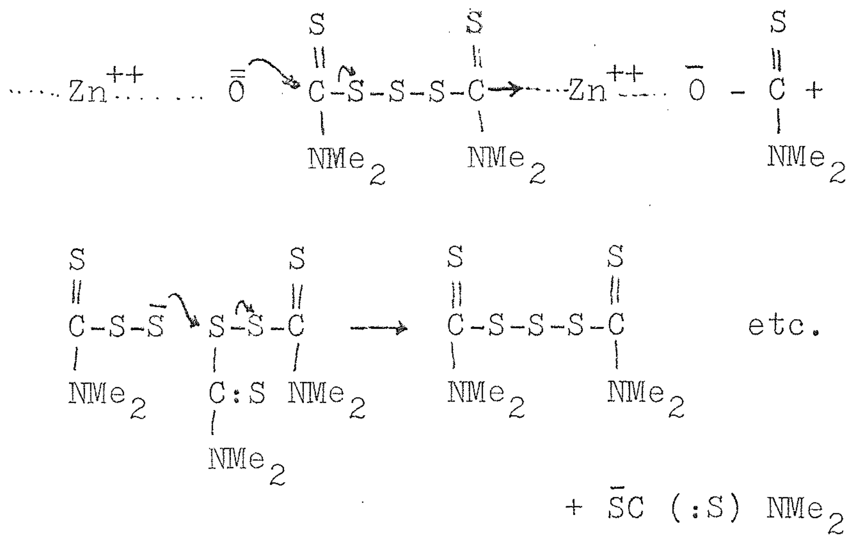
The action of these zinc mercaptide complexes on sulphur is not well understood. It does not give rise to insoluble products, but zinc perthiomercaptides (84) are believed to be formed in a series of equilibria which probably lie well on the side mercaptide complex and free sulphur.



$$XS^{\delta-} \cdots Zn^{\delta++} \cdots SX^{\delta-} \rightleftharpoons XS\text{-}S_8\text{-}ZnSX \xrightleftharpoons{XSZnSX} XS\text{-}S_x\text{-}Zn\text{-}S_x\text{-}SX$$

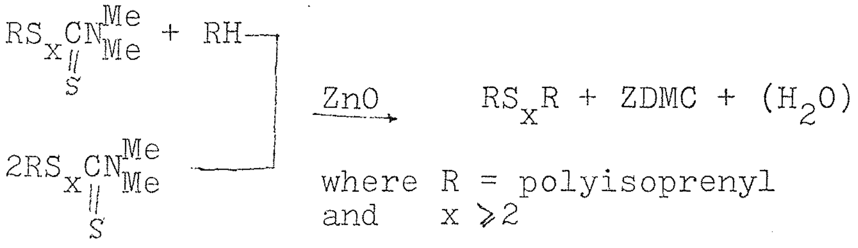
(19)

The nucleophilic activity of amine and zinc carboxylate complexes of ZMBT towards sulphur has been demonstrated in their ability to catalyse disulphide interchange reactions and the insertion of sulphur into diethyl disulphide(85). The average value of x in (19) will be controlled by the relative concentrations of sulphur and soluble zinc mercaptide. Species analogous to (19) may be formed from sulphur donors and zinc oxide (or zinc carboxylates). Tetra-methylthiuram disulphide (TMTD) and zinc oxide for example give a mixture of thiuram polysulphides and zinc dimethydithio carbamate (ZDMC) which may then exchange sulphur to give (14) in which X is specifically $-\overset{S}{\overset{\|}{C}}-NMe_2$ (86,87) in such cases X will always be small.



The zinc perthiomercaptides (19) are believed to be the actual sulphurating agents. Their reaction with rubber hydrocarbon gives rise to the rubber bound intermediate which is the precursor to sulphur cross-linking.

Moore and Watson(88) have shown that reaction of the pendant accelerator groups represented by Et. $\mathrm{SS\underset{\|}{\overset{}{C}}\,N\overset{Me}{\underset{Me}{<}}}$ (where the ethyl groups represent the main chain of the rubber hydrocarbon) with 2-methyl-pentene-2 and zinc oxide at 140°C, forms a cross-link with the liberation of zinc dimethyl-dithiocarbamate (ZDMC). The formation of a cross-link can therefore be shown as:



$$\left.\begin{array}{l}\mathrm{RS_xC({=}S)NMe_2 + RH}\\[1ex] \mathrm{2RS_xC(=S)NMe_2}\end{array}\right] \xrightarrow{ZnO} \mathrm{RS_xR + ZDMC + (H_2O)}$$

where R = polyisoprenyl
and $x \geqslant 2$

1-3 NETWORK DEFECTS

The reasons for the deviation from ideal behaviour described by equation (1) section (1-2-5-2) is thought to be due to departures of the actual network from the theoretical model used for deriving the equation i.e. due to network defects. These defects are illustrated in Fig.3 and include:

(a) Entanglements

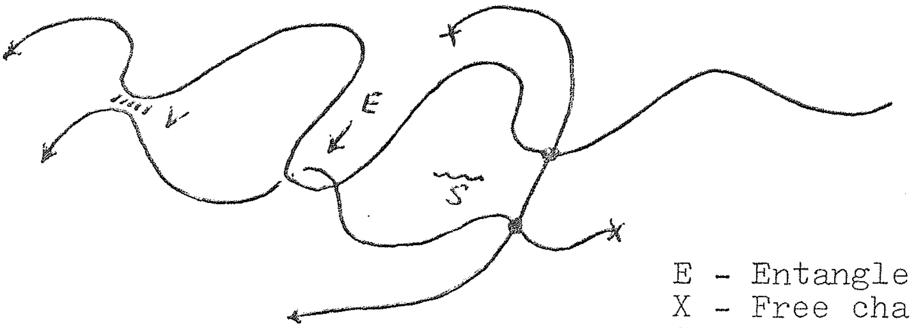
(b) Chain ends

(c) Intra molecular cross-links (loops)

(d) Sol fraction

(e) Intermolecular attraction e.g. Van-der Waals forces, polar-polar interaction (which become greater on orientation) and where appropriate, hydrogen bonding.

For this reason the value of $Mc_{phys.}$ is less than the value of $Mc_{chem.}$ (the actual number of cross-links)



E - Entanglement
X - Free chain end
S - Sol fraction
→ - Network continuation
V - Van-der Waals attraction

P.J.Flory(44) studied the effects of some of these network defects and derived an equation making allowance for entanglements and chain end in the rubber network. He observed that the magnitude of the retractive force at a given elongation is appreciably greater than that calculated from the independently estimated number of chemical cross-linkages in vulcanised Butyl rubber and attributed this to chain entanglements which would increase the effective number of cross-linkages. He also observed that the initial molecular weight of the rubber before cross-linking had an effect upon the elastic properties due to the flaws introduced into the network by the ends of molecules; the lower the initial molecular weight of the rubber, the greater the number of these chain ends resulting in an inferior vulcanisate. Equation (1) was modified to:

$$\Upsilon = (RTgVo/V)\ (1 - \frac{2Mc}{\bar{M}n})\ (\lambda - \lambda^{-2}) \qquad (20)$$

where

g = entanglement factor

$\bar{M}n$ = molecular weight of the raw rubber before vulcanisation

Vo/V = number of chain per unit volume

Mc = molecular weight between cross-links

λ = extension ratio

Υ, R and T have the same meaning

J. Scanlan(70,89,90) has worked on the effect of network flaws on the elastic properties of vulcanisates. In this treatment full allowance is made for elastically inactive material which exists either as sol or as loose ends in the network. The cases of linear primary molecules with either a random distribution of lengths or with uniform lengths are considered, and results are compared with those of earlier theoretical treatments.

Another study has been carried out on the chain entanglements and elastic behaviour of poly-butadiene networks by G. Krans and G.A. Moczvgemba(47). They investigated the role of chain entanglements in determining the stress-strain properties of the polybutadiene network. In this investigation the numberof entanglements was varied by changing the primary molecular weight and chemical cross-link concentration. Networks essentially free of entanglements were prepared by end group coupling of carboxyterminated poly-butadiene with a molecular weight of 5500. Conventional sulphur or peroxide vulcanisates obeyed the Mooney-Rivlin stress-strain relation, the constant C_2 which represents the deviation from simple kinetic theory diminshing with the time allowed for approaching elastic equilibrium. The constant C_2 was found to increase with both the total physical cross-linking and the entanglement contribution . The end group vulcanisates obeyed the simple kinetic theory of rubber elasticity and approached elastic equilibrium much more rapidly than sulphur or peroxide vulcanisates. The evidence presented however suggests that the apparent deviation of elastomeric vulcanisates from the kinetic theory of rubber elasticity resulting in the appearance of the Mooney-Rivlin C_2 term in the stress-strain relation arises from a slow relaxation process involving the entanglement cross-links.

H.C. Baker and H.W. Greensmith(91) considered the effects of the viscosity of the compounded rubber (the lower the viscosity the lower the molecular weight and hence the more chain ends) on the properties of gum and tread vulcanisates. They examined this together with the effects of filler dispersion and small variations in the degree of cross-linking with refrence to the principal properties (tensile strength, modulus and resilience). They showed that the dynamic property of resilience is the most sensitive to the effects of compound viscosity and filler dispersion. The results of an experimental study of the relationship between resilience and heat build up as measured in the Goodrich Flexometer are also presented. In the light of these and the foregoing results, the trends in the resilience and heat build up properties of tread vulcanisates of market grade rubbers are considered, and it is shown that these trends are associated with differences in compound viscosity and therefore the number of chain ends.

The effect and detection of loose chain ends in cross-linked polyurethane elastomers was studied by A.E. Oberth(92). As in plasticized elastomers, tensile strength and elastic modulus are reduced approximately by a factor $(1\text{-VE.P})^2$, where VE.P is the volume fraction of loose chain ends, plasticizer or both. This effect is much larger than predicted by present theory. Also the equilibrium volume swelling ratio Vo/V, of rubbers having terminal chains or an equal volume of plasticizer is the same, provided they do not differ in cross-link density. However, the volume fraction of "network rubber" in the equilibrium swollen specimen differs owing to the non-extractability of terminal chains. On this basis a method is proposed for the experimental determination of the volume fraction of loose ends.

Elastomers containing a high proportion of loose chain ends show markedly less long term stress relaxation.

This effect is not clearly understood but is useful to detect the presence of a non load-bearing network.

Edward(93) showed that a three dimensional network containing no free chain ends produced from α,ω - Dibromo- polybutadiene had superior physical properties.

Hoffman and Gobran(94) achieved the same results by preparing end free network from α,ω- Dicarboxyl-polybutadiene.

J.E. Fellers and M.R. Semanani(95) have carried out some work on dynamic mechanical studies of end group modified polystyrene. They synthesized polystyrene having both modified and unmodified end group structures. These polystyrenes were then subjected to dynamic mechanical testing below their glass transion temperature. The modified structures were shown to influence the β transion of polystyrene, while the mechanism of this secondary transion has been speculated but never unequivocally substantiated in the past, the evidence presented strongly support the idea that the β transition of polystyrene arises from chain end motions.

Moore, Mullins and Watson(71,61) cross-linked NR with di-tertiary butyl peroxide (DTBP) and on the assumption the reaction sequence was quantitative as shown below:

$$(CH_3)_3CO\text{-}OC(CH_3)_3 \longrightarrow 2(CH_3)_3CO\cdot$$

$$(CH_3)_3CO\cdot + HR \longrightarrow (CH_3)_3COH + R\cdot$$

$$(CH_3)_3CO\cdot \longrightarrow (CH_3)_2C{:}O + CH_3\cdot$$

$$CH_3\cdot + HR \longrightarrow CH_4 + R\cdot$$

$$R\cdot + R\cdot \longrightarrow R - R$$

The decomposition products were quantitatively estimated and hence the number of actual cross-links calculated.

The corresponding C_1 values were calculated from estimation of stress-strain data(48) and an equation relating $Mc_{phys.}$ to $Mc_{chem.}$ developed(71,61)

$$C_1 = \left(\frac{\rho RT}{2Mc_{chem}} + 0.78 \times 10^6\right)\left(1 - \frac{2.3\ Mc_{chem}}{\bar{M}n}\right) \quad (21)$$

where $\bar{M}n$ is the number average molecular weight before vulcanisation.

The quantity 0.78×10^6 is based on a statistical calculation and represents maximum entanglement contribution.

A precise knowledge of Mc_{chem} from measurements of $Mc_{phys.}$ is essential for network structure analysis, where the actual number of chemical cross-links is required (e.g. where using chemical probes) and it was probably this requirement that stimulated Moore, Mullins and Watson at NRPRA to produce the semi-empirical equation relating the two values.

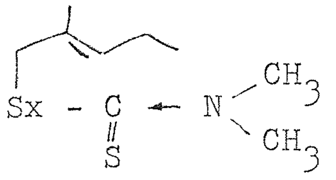
A demonstration of the practical consequences of the chain end defect was produced by Helfland and Tonelli(96) who showed that when cis-1,4-polyisoprene is randomly cross-linked to produce a cross-link density of one cross-link per 100 monomer units that 26.3% of the polymer is wasted as free elastically ineffective chain ends and that when the cross-linking reduces to one cross-link for every 133 monomer units the ineffective concentration of polymer increased to 35.1%. Roussel(97) who was suggesting a study of chain end defects as a fruitfull research area for the future commented on Tonelli's work and pointed out that the implication is that the performance of the compound with 100 parts of rubber randomly cross-linked might be matched by a compound Of 74 parts of rubber and 26 parts of a plasticiser if the rubber could be cross-linked to a perfect network, with the obvious savings. This assumption neglects the formation of virtual cross-links by entanglements with the loose chain ends and by absorption onto the surfaces of filler particles

1-4 PURPOSE OF THE PRESENT WORK

In view of the numerous examples that have been given to illustrate the wastage of polymer in rubber networks due to the existence of chain ends it was proposed to investigate practical methods of tying loose chain ends into the network and thereby make them elastically effective. As the molecular weight of natural rubber has to be drastically reduced by mastication to make it soft enough to incorporate other compounding ingredients and then further reduced by the shear forces exerted during the compounding operation, it was decided to try to make use of the mechanochemical reaction described in section (1-1-4)

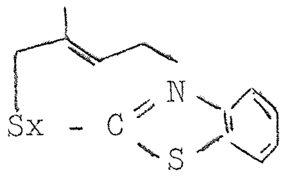
Model compound work on 2-methyl pentene-2 and 2,6-dimethyloctadiene-2,6$^{(72,73)}$have shown the existence of pendent accelerator (or sulphur donor) groups and these are believed to be the precursor to the cross-links.

e.g. tetramethyl thiuram disulphide yields:



(See section 1-1-5-7)

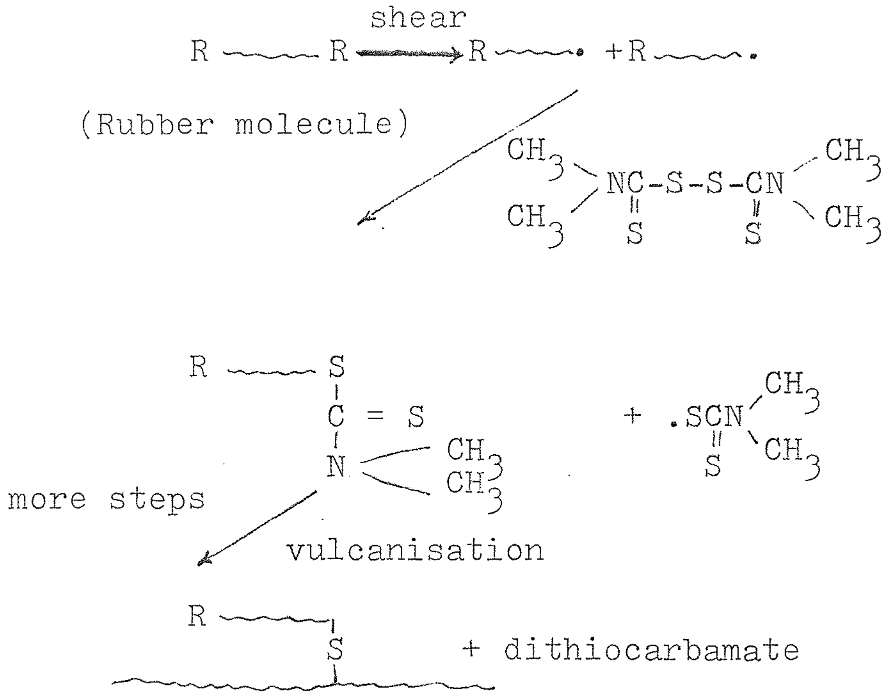
and 2 - mercapto benzthiazol yields



etc.

If during the mastication stage of the NR, radical acceptors which would produce similar types of pendent groups, are added, then these would form at the ends of chains broken by the shear action and they should be capable of producing cross-links during the subsequent vulcanisation reaction. Fortunately many of the accelerators and sulphur donors used in practical vulcanising systems are radical acceptors and there are large ranges of compounds to try.

An example of the reaction sequence expected with, say, TMTD would be



It was proposed to assess the efficiency of this reaction first under ideal conditions with purified natural rubber and then conduct the "mastication" under an atmosphere of nitrogen to reduce the competion from indigenous free radical acceptors and oxygen respectively. The application of the method to a more practical situation would also be assessed.

This [illegible] used [illegible] experimental work. In [illegible]

[illegible]

[illegible] Natural Rubber grade [illegible] supplied [illegible] throughout this work. As the rubber was [illegible] acetone [illegible]

[illegible] necessary, however, [illegible] laboratory two-roll mill so that it [illegible] efficiently and this did [illegible] involve a small [illegible] weight reduction but this was kept to the very minimum. After extraction the rubber was dried under vacuum at 40°C for 12 hours by which time it had reached constant weight.

2-1-2 ZINC OXIDE (ZnO). (Amalgamated Oxides Ltd. Zinc Oxide was used without further purification.

2-1-3 STEARIC ACID (SA) supplied by [illegible] Co.

CHAPTER 2

2-1 INTRODUCTION

This chapter is divided into three sections materials used, description of apparatus and experimental work. In the first section materials and their synthesis , where required, have been stated, the second section gives a brief description of equipment and machines, the third section covers the experimental work and procedures by which it is carried out.

2-1-1 NATURAL RUBBER (NR)

Standard Malaysian Natural Rubber grade 5 (SMR-5 supplied by Dunlop) was used throughout this work. As the rubber was to be used for mechanochemical reactions it was all acetone extracted for 48 hours under an atmosphere of nitrogen to remove any indigenous radical acceptors.

It was necessary, however, to sheet it on a 12" water cooled, laboratory, two- roll mill so that it could be extracted efficiently and this did involve a small molecular weight reduction but this was kept to the very minimum. After extraction the rubber was dried under vacuum at 40°C for 12 hours by which time it had reached constant weight.

2-1-2 ZINC OXIDE (ZnO), (Amalgamated oxides Ltd.)

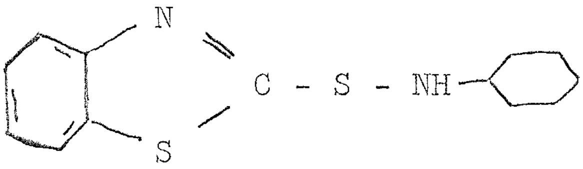
Zinc Oxide was used without further purification.

2-1-3 STEARIC ACID (SA), Supplied by Anchor Chemical Co.

It was used without purification.

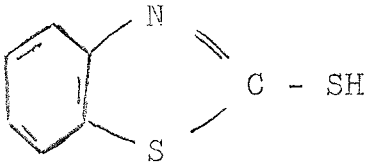
2-1-4 SULPHUR (S), Supplied by Anchor Chemical Co. Sulphur type D was used without further purification.

2-1-5 N-CYCLOHEXYLBENZTHIAZYL-2-SULPHENAMIDE (CBS)



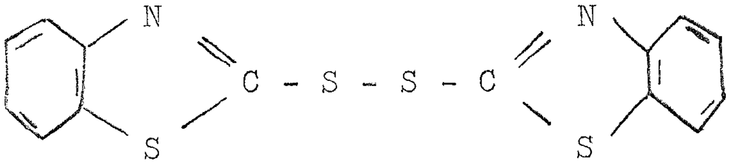
Supplied by Monsanto Chemical Ltd. as "Santocure" and used without furthur purification.

2-1-6 2-MERCAPTO BENZTHIAZOLE (MBT)



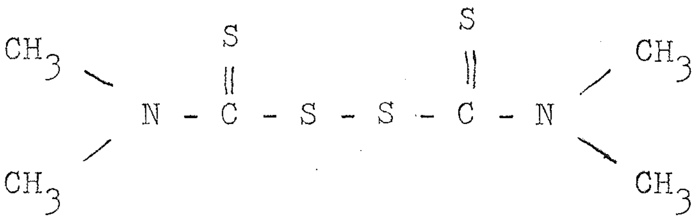
Supplied by Monsanto Chemical Ltd. as "thiotax" and used as recieved from the manufacturers .

2-1-7 DIBENZTHIAZYLDISULPHIDE (MBTS)



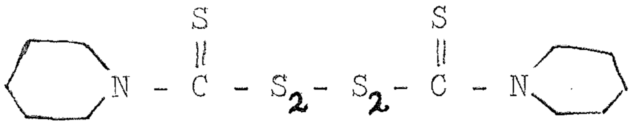
Commercial material from Monsanto Chemical Ltd. "Thiofide"

2-1-8 TETRAMETHYLTHIURAMDISULPHIDE (TMTD)



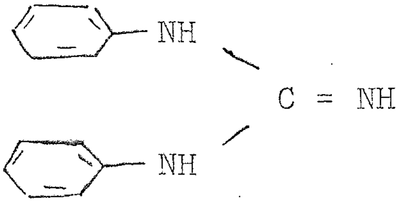
Supplied by Monsanto Chemical Ltd. as "thiurad" and used without further purification.

2-1-9 DIPENTAMETHYLENETHIURAMTETRASULPHIDE (P25)



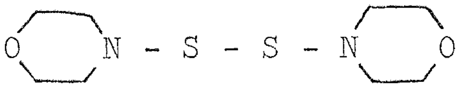
Used as supplied by Robinson Bros. Ltd. as "thiuram P_{25}"

2-1-10 DIPHENYLGUANIDINE (DPG)



Supplied by Monsanto Chemical Ltd. as "1.3 Diphenylguanidine"

2-1-11 DIMORPHOLINODISULPHIDE (DMDS)

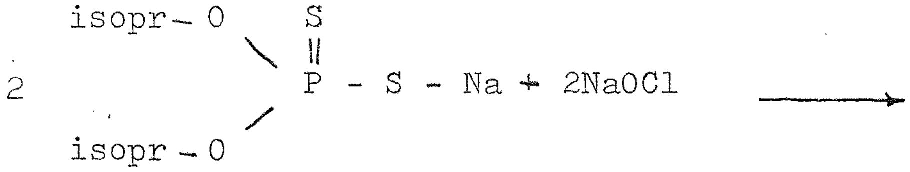


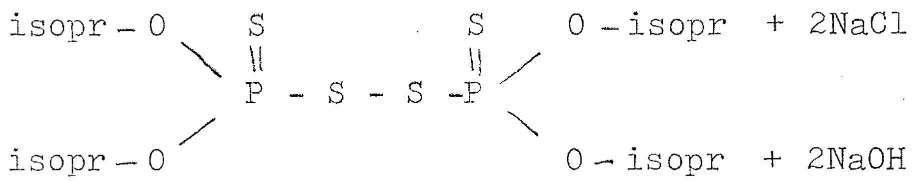
Supplied by Monsanto Chemical Ltd. as "sulphasan R" and used without further purification.

2-1-12 BIS (DIISOPROPYL) THIOPHOSPHORYLDISULPHIDE(DIPDIS)

This was prepared by oxidation of sodiumdiisopropyldithiophosphate(NaDIS)Supplied by Albright and Wilson Ltd. The procedure finally adopted was that described by Mikeska(98,99) using sodium hypchlorite and modified by Pimblott(55).

The use of Nitrous acid(100-104) and Hydrogen peroxide(1o5,106 as oxidizing agent was tried but abandonded because of the better yield obtained by the sodium hypochlorite oxidation. The reaction can be represented as follows:





Sodium diisopropyldithiophosphate (100g) was dissolved in distilled water (200ml) and cooled to 10°C and sodium hypochlorite solution(12% available chlorine) added until slight excess was present. The pale yellow precipitate was extracted by ether and separated from the residue and then evaporated in a rotary evaporator. It was crystallized from ethanol (melting point 89°C) and then recrystallized in the same solvent (melting point 91°C). 54g (60% yield) of yellow crystals was obtained. The sulphur percentage was 37.8 (theoretical 30%).

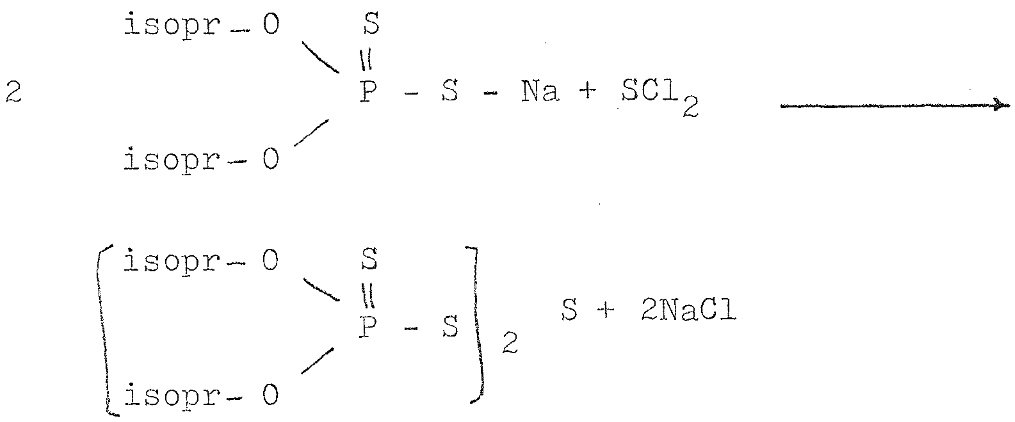
The following abbreviations are used in the description of the I.R Spectra:

M = Medium
S = Strong
W = Weak
St = Stretching

The I.R absorption using a Perkin-Elmer 457 grating spectrophotometer, (4000-250 cm^{-1}) with a KI cell is as follows: Maxima (cm^{-1}) at 2990M-2920W (CH St.); 1630M (CH St.); doublet 1450 W-1370 M (isopr); doublet 1170M-1100M (isopr); doublet 9505-870(CH_2O-P); doublet 750-650S ($-O\overset{S}{P},\overset{S}{P}-$); 560-530W ($S_2$).

2-1-13 BIS(DIISOPROPPYL)THIOPHOSPHORYLTRISULPHIDE(DIPTRI)

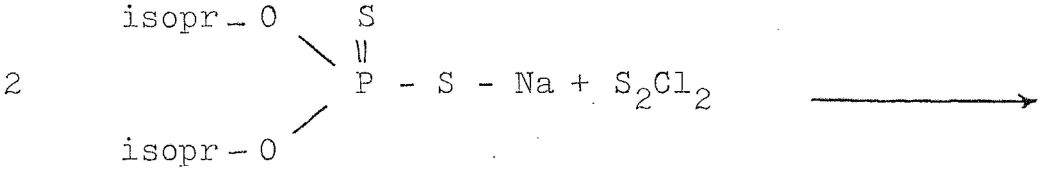
This was prepared as described by Romieux(107-110) by the reaction of NaDIS with sulphur dichloride i.e.

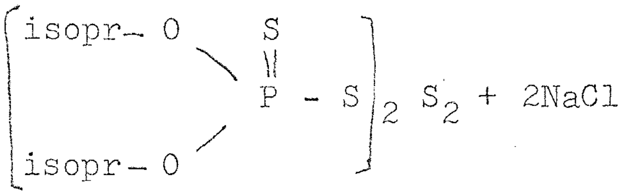


NaDIS (236g) was dissolved in distilled water (472) and cooled to 5°C,sulphur dichloride (31.4 ml) was then added to the stirred solution at such a rate that the temperature remained below 10°C. The resulting yellow oil, mixed with a milky liquid, was dissolved in ether, separated from the aqueous layer, dried and the ether removed in a rotary evaporator. A light green oil remained (yield 136g, 60% of theoretical). The sulphur percentage was 38 (theoretical 35%).
The refractive index and I.R spectrum were obtained. Refractive index (d20) is 1.5565, I.R absorption showed peaks at 2990M -2920W (CH St.); doublet 1450W-1370M (isopr); doublet 1170M -1100M (isopr); doublet 950S - 870 (CH_2O-P); doublet 750M-650S ($-O\overset{S}{\overset{\|}{p}}.\overset{S}{\overset{\|}{P}}-$); doublet 595W-540W ($S_3$)

2-1-14 BIS(DIISOPROPYL)THIOPHOSPHORYLTETRASULPHIDE (DIPTET)

This was prepared as described by previous workers(98,107, 108,111) by reacting NaDIS with sulphur monochloride

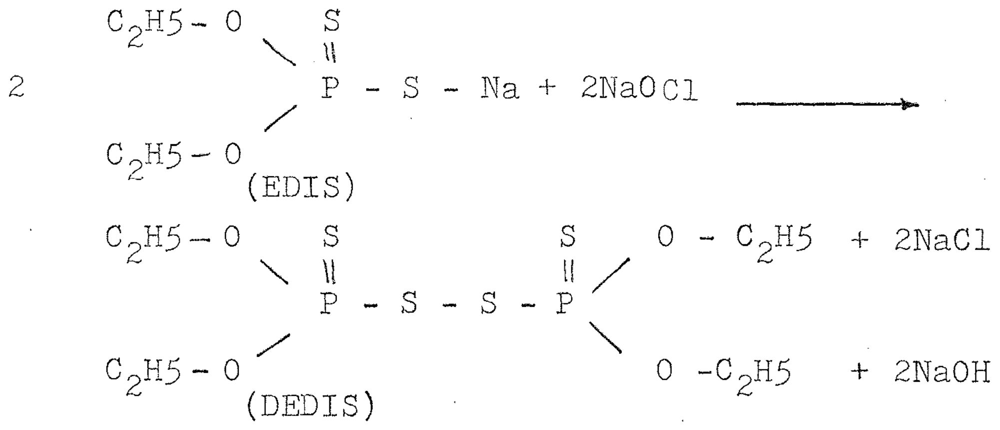




NaDIS (236g) was dissolved in warm distilled water (472ml) and cooled to 5°C. 40 ml of sulphur mono chloride was slowly added. The reaction temperature maintained below 10°C, the resulting oil (yellow) which was emulsified with the aqueous layer, was extracted with ether, and dried with sodium sulphate. Ether was then removed by means of a rotary evaporator. The yellow viscous oil (180g yield 73%) had a sulphur percentage of 46.5 (30% theoretical)the refractive index (d20) of 1.5940 and I.R absorptions as follows: 2990M-2920W (CH St.); 1630M (CH.St.); doublet 1450W-1370M (isopr); doublet 1170M-1100M (isopr); doublet 950S-870 (CH_2-)O doublet 750M-650S (-O$\overset{S}{P}$,$\overset{S}{P}$-); triplet 590W,554W,510W (S4).

2-1-15 BIS(DIETHYL)THIOPHOSPHORYLDISULPHIDE (DEDIS)*

The preparation of DEDIS was based on the method used for DIPDIS (2-1-12)using sodiumdiethyldithiophosphate (EDIS)

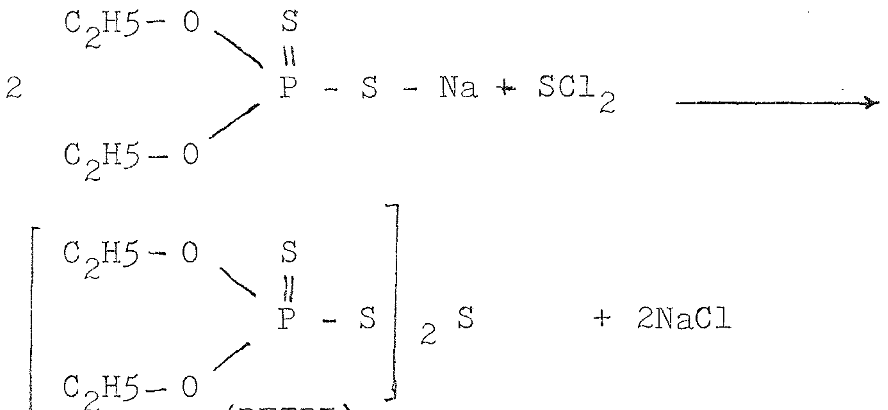


* The ethyl derivatives described in 2-1-15,16 and 17 were not used because of their objectionable smell but the information on synthesis and characterisation is included for further workers .

Ether extraction yielded a yellow oil (52g 58% of theoretical and sulphur percentage was 33.8, theoretical is 34.6) with a refractive index (d20) of 1.5225 and I.R absorptions at 2990M-2920M (CH St.); doublet 1700S-1630M (CH St.); doublet 1430M-1370S (CH_3C); 1230S-1152W($(RO)_2\text{=}\overset{O}{\underset{O}{P}}$); doublet 1030S-930S (CH_2-O-P); doublet 770M-680S (O-$\overset{O}{P}$,P=S); 570-530W(S_2).

2-1-16 BIS(DIETHYL)THIOPHOSPHORYLTRISULPHIDE (DETRI)

It was prepared in a similar manner to that described for DIPTRI (2-1-13) using EDIS

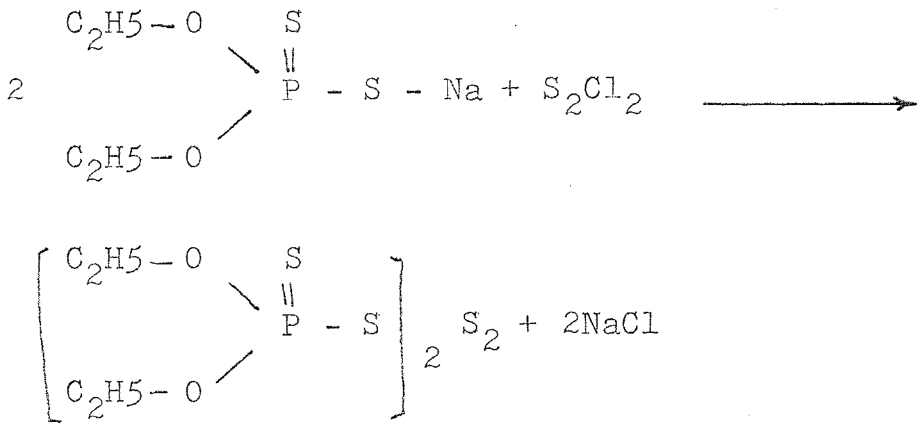


(DETRI)

Ether extraction yielded a yellow oil (110g 55% of theoretical) and sulphur percentage was 30.9 (theoretical 39.8), refractive index (d20) is 1.5625. The I.R spectrum showed peaks at 2990M-2920W (CH St.); doublet 1700S-1630M (CH St.); doublet 1430M-1370S (CH_3C); 1230S-1152W($(RO)_2\overset{O}{\underset{O}{P}}$) doublet 1030S-930S (CH_2-O-P); doublet 770M-680S(O-P=S,P=S); doublet 600W-550W (S_3).

2-1-17 BIS(DIETHYL)THIOPHOSPHORYLTETRASULPHIDE (DETET)

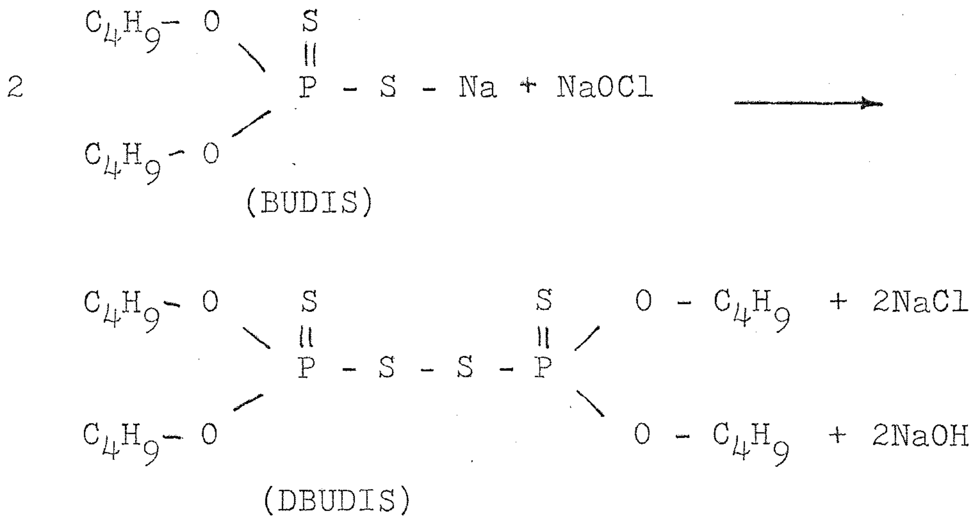
The preparation of DETET was carried out exactly as described for DIPTET (2-1-14) using EDIS.



Crystallisation from ethanol to constant melting point (66°C) yielded a yellow powder (136g 63% yield sulphur percentage was 50.8 and the theoretical is 44.2). I.R characterisation: maximum at 2990M-2920W (CH St.);doublet 1700S-1630M (CH St.); doublet 1430M-1370S (CH_3C), 1230S-1152W ($(RO)_2P{<}^{O}_{O}$); doublet 1030S-930S (CH_2-O-P); doublet 770M-680S (O-P=S,P=S); triplet 600W,550W,550W(S_4).

2-1-18 BIS(DIBUTYL)THIOPHOSPHORYLDISULPHIDE (DBUDIS)

This was prepared from sodium dibutyldithiophosphate (BUDIS) by hypochlorite oxidation as described for DIPDIS (2-1-12)



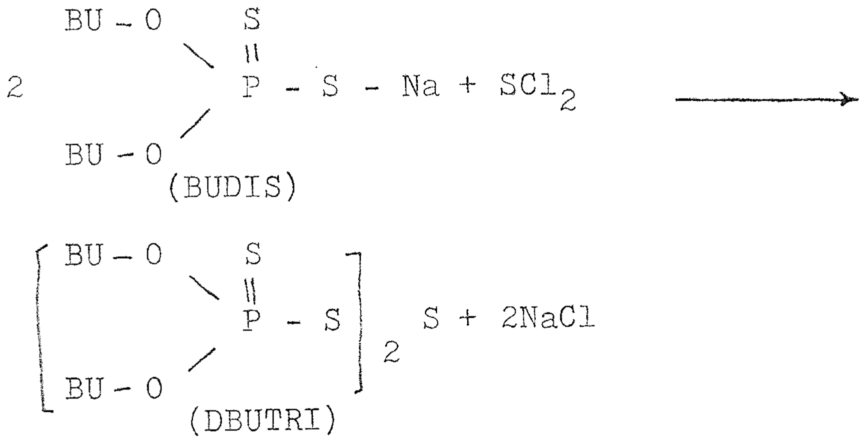
(BUDIS)

(DBUDIS)

Ether extraction yielded a yellow oil (70g 64% of theoretical, and sulphur percentage was 30.2, theoretical is 26.5) with a refractive index (d20) of 1.5190 and I.R spectrum showing the following characteristic: triplet peaks (cm^{-1}) at 2980S, 2960S, 2880M (CH St.); 1620M (CH St.); doublet 1450M-1370M (CH_3C); doublet 1020W, 920M (CH_2-O-P); triplet 880M, 850M, 800M (-O-P=S); 670(P=S),560,520(S_2).

2-1-19 BIS(DIBUTYL)THIOPHOSPHORYLTRISULPHIDE (DBUTRI)

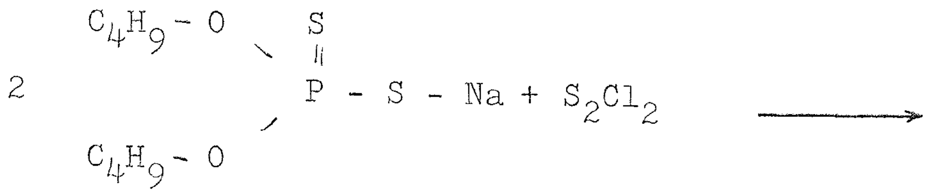
Preparation as described for DIPTRI (2-1-13) by reaction of BUDIS with sulphur dichloride



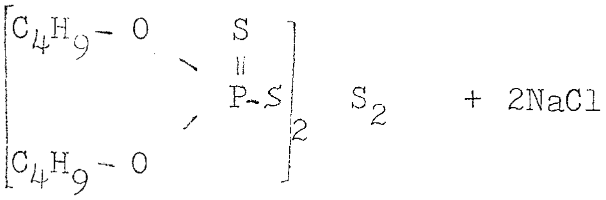
After purification a yellow oil was obtained 120g,47% of theoretical containing 39.0 percent of sulphur,theoretical 31.1 with refractive index (d20) of 1.5550 and I.R characteristic I.R absorption peaks at 2980S, 2960S,2880M triplet (CH St.); 1620M (CH St.); doublet 1450M-1370M (CH_3C);doublet 1020W, 920M(CH_2-O-P); triplet 880M, 850M, 800M (-OP=S); 670(P=S), doublet 580W-540W (S_3).

2-1-20 BIS(DIBUTYL)THIOPHOSPHORYLTETRASULPHIDE (DBUTET)

It was prepared in the similar manner to that described for DIPTET (2-1-14) using BUDIS and Sulphur monochloride:



(BUDIS)



(DBUTET)

Ether extraction yielded a yellow oil (210g 77% of theory containing 39.9 percent sulphur, theoretical is 35.2) refractive index (d20 = 1.5660), I.R characteristics: triplet at 2980S, 2960S, 2880M (CH St.); 1620M (CH St.); doublet 1450M-1370M (CH_3C); doublet 1020W, 920M (CH_2-O-P); triplet 880M, 850M, 800M(O-P=S); 670(P=S), triplet 590W, 560W, 520 (S_4).

2-1-21 THE I.R ABSORPTION SPECTRUM OF THE EDIS

(Used in the preparation of DEDIS, DETRI and DETET)

Peaks (cm^{-1}) at 3300-3550S (OH single bridge) as impurity, 2990M-2920W (CH St.); doublet 1700S-1630M(CH St.) doublet 1430M-1370S (CH_3C); 1230S-1152W ($(RO)_2\overset{O}{\underset{S\quad O}{P}}$); doublet 1030S-930S (CH_2-O-P); doublet 770M-680S (O-P,P=S).

2-1-22 THE I.R ABSORPTION SPECTRUM OF THE NaDIS

(Used in the preparation of DIPDIS, DIPTRI and DIPTET)

Peaks (cm^{-1}) at 3500-3300S (OH single bridge) as impurity, 2990M-2920W (CH St.); 1630M (CH St.); doublet 1450W-1370M (isopr); doublet 1170M-1100M (isopr); doublet 950S-870 (CH_2O-P); doublet 750M-650S ($-O\overset{\overset{S}{\|}}{P},\overset{\overset{S}{\|}}{P}-$).

2-1-23 THE I.R ABSORPTION SPECTRUM OF THE BUDIS

(Used in the preparation of DBUDIS, DBUTRI and DBUTET

Peaks (cm^{-1}) at 3500-3400S (OH single bridge) as impurity, triplet 2980S,2960S,2880M (CH St.); 1620M (CH St.); doublet 1450M-1370M (CH_3C); doublet 1170W-1120W ($(CH_3)_2C$) small amount of as impurity; doublet 1020W, 920M (CH_2-O-P); triplet 880M,850M,800M ($-O\overset{\overset{S}{\|}}{P}$); 670 (P=S).

2-2 DESCRIPTION OF APPARATUS

2-2-1 UNIROTOR MIXER

The unirotor mixer was developed from a small mixer designed by Watson and Wilson(15) and manufactured on a limited scale by Baker Perkin Ltd. It consists of a vertical rotor which can turn at a variable speed inside a fixed mixing chamber. The rotor and stator are clamped together by means of a collar which is closed by a nut and bolt. An O - ring of silicone rubber hermetically seals the chamber. A variety of designs of mixing faces on the rotor and stator are available. A "plough shaped" rotor was used for the present work. The distance between the mixing faces is controlled by a capstan operated screw with left and right hand screw threads so that the shell casing around the rotor can be raised or lowered depending on the direction of the rotation of the capstan. The rotor is powered by an electric motor which is connected to the shaft through a worm-gear and a variable drive V-belt pulley; the latter is used to control the shaft speed. The temperature is recorded by means of a thermocouple located within about two millimeters of the hardened steel face of the mixer and some measure of temperature control is achieved by raising a bath of thermostatted liquid so that the head of the mixer is completely immersed. In this work, where the lowest practical temperature was required (to achieve maximum mechanochemical efficiency from the shear action(16)) a mixture of ice and water was used. Either air, or nitrogen were circulated through the mixing chamber and in the case of the latter, traces of air were removed by degassing the chamber at a reduced pressure(7) for a few minutes and then flooding with white spot nitrogen (passed through alkaline pyrogallol solution). This degassing was repeated three times. During mixing a positive gas pressure of 10-15 mm of mercury was maintained. The shear rate exerted on the polymer in the mixing chamber is a function of:

(a) The distance between the mixing faces
(b) The relative speed of movement of the faces
(c) The surface area of the faces

(d) The viscosity of the polymer

In this work the shear rate was kept constant by using the same mixing chamber, the same amount of polymer (10g); the faces were pulled tightly together by the capstan and the amount of polymer between them controlled their distance apart. The speed of rotation was (40rpm) as this was the maximum speed that could be used without a measurable rise in temperature of the polymer above 25°C. The time of mastication was dependent upon the extent of degradation required and was determined by the time necessary to reach the desired molecular weight.

2-2-2 TWO ROLL-MILL

All rubber compounds were mixed on a water cooled laboratory 12", two roll-mill using a nip setting of 2-3mm.

2-2-3 WALLACE RAPID PLASTIMETER

The plasticity of a rubber stock is important for two reasons:

(a) It gives a measure of the processability of the rubber and

(b) It gives a measure of the initial molecular weight of the raw rubber which has an influence on the physical properties of vulcanisate produced(91).

In the present investigation plasticity is measured by the Wallace rapid plastimeter manufactured by H.W. Wallace Ltd. This is a compression type plastimeter in which a thin test-piece (disc 3-4 mm thick) is placed between steam heated platens at 100°C and first subjected to a pre-compression for 1-2 sec. which automatically stops when the thickness of the test-piece is reduced to 1 mm ten seconds after the start of the pre compression. The proper test starts with the application of a 10 kg load. The test-piece is subjected to this load for 15 seconds and the thickness of sample then measured using a dial micrometer. This thickness is recorded and quoted as the plasticity number. The greater the plasticity of the rubber, the lower the plasticity number.

By using a calibration graph plotted from the results obtained by Mullins and Wastson(13) and also recalibrated by the author from solution viscosity measurements, it is possible to obtain the number average molecular weight of rubber. (Section 2-3-8).

2-2-4 MONSANTO RHEOMETER (MODEL 100)

The monsanto rheometer was developed by Decker and Wise(112). It consists of a biconical disc embedded in the elastomeric sample contained in a circular cavity under a pressure of 600 P.S.I. and subjected to shear by the biconical disc oscillating within the sample at a constant amplitude of 1^{o}, 2^{o} or 3^{0} and at constant rate of 750 RPM. The reason for the different amplitude of oscillation is to accommodate rubbers having a wide range of viscosities. For the compounds used in this study an amplitude of 1^{o} was found to be ideal. The rotor system is connected to a transducer which converts the torque exerted on the rotor to an electrical impulse, which in turn is transferred to a mechanical pen recorder. Thus, a visual trace of torque (in inch-Ib) as a function of time is obtained. A typical monsanto rheograph consists of an initial decrease in torque due to the thermal plasticization of the stock which becomes constant for the induction period of the vulcanisation reaction (scorch time) followed by a rise in torque, as the cross-linking reaction proceeds upto a maximum value, and finally, a gradual decrease in torque as reversion occurs. From such a rheograph all the usual curing parameters are measured continuously during vulcanisation, (eg. scorch time, curing rate, cure time, degree of cure and reversion characteristics).

A typical torque-time curve produced on the Monsanto Rheometer during the cure of rubber stock is shown in Fig. 4 .

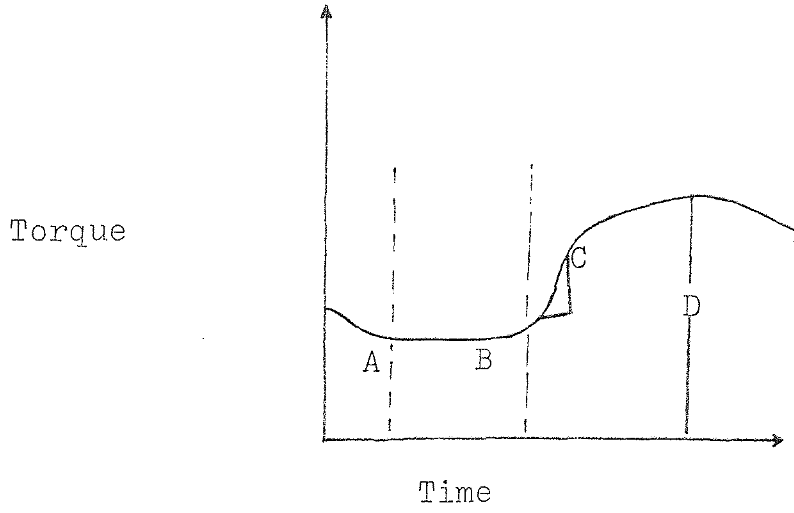


Fig.4

There is an initial decrease in the viscosity of the stock (A) due to the increasing temperature, which then flattens out until the onset of cross-linking produces a sharp rise in viscosity (B), and therefore, in the torque exerted by the oscillating rotor embedded in the specimen. This torque increases until the cross-linking is complete. The curve may show a decrease in torque with time if chain scission takes place on extended heating or there may be a continual increase if a slow cross-linking reaction takes place.

It is possible to obtain roughly quantitative figures for the scorch time B based on an arbitary number of units of torque increase above the minimum value, and for the rate of cure as assessed from the slope of the curve.

A more accurate kinetic interpretation of this curve suggested by Coran(113,114) is as follows:-

Assuming that cross-link formation is a first order reaction after an induction period t_i.

$$\frac{dv}{dt} = k(V_\infty - V_t)$$

where k = the overall first order rate constant

V_t = the cross-link density at time t

V_∞ = the maximum cross-link density

t = the time in minutes

t_i = the induction time in minutes.

On integration :-

$$\int_{V_o}^{V_t} \frac{dv}{V_\infty - Vt} = k \int_{t_i}^{t} dt$$

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

$$\therefore \quad \ln \frac{V_\infty - V_t}{V_\infty} = k(t - t_i)$$

It has been shown that $V_t \infty R_t$

where $R_t \equiv$ the torque developed at time t

$\therefore \quad V_t = kR_t$

and similarly $V_\infty \equiv R_{max}$

$\therefore \quad V_\infty = kR_{max}$

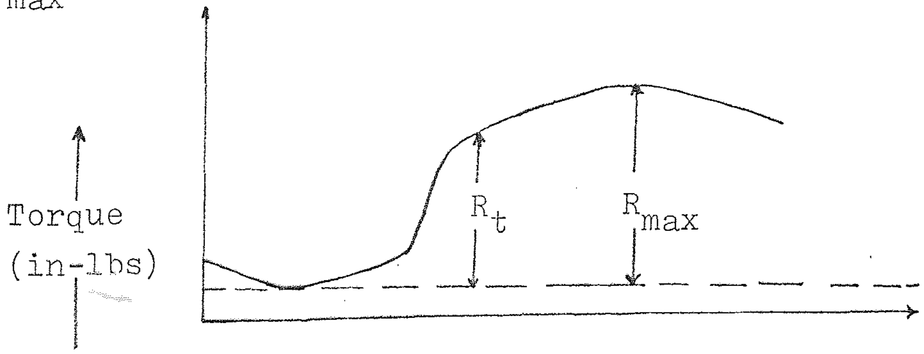
where R_{max} = the maximum torque developed and is taken as a direct reading from the rheographs.

Substituting these values in the last equation :

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

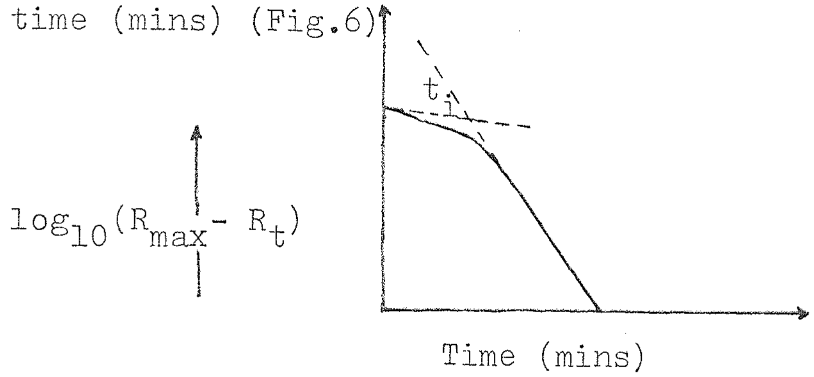
$$\therefore \log_{10}(R_{max} - R_t) = \log_{10} R_{max} + \frac{k(t - t_i)}{2.303}$$

R_t and R_{max} can be directly read from the rheometer curve (Fig.5)



(Fig 5)

To obtain k, values of $\log_{10}(R_{max} - R_t)$ can be plotted against time (mins) (Fig.6)



$$\text{Slope} = \frac{k}{2.303}$$

$$k = \text{slope} \times 2.303 \ \text{min}^{-1}$$

t_i is the time necessary for the reaction to become 1st order.

The vulcanisation system thus becomes characterised by three parameters.

t_i - the induction period which is a measure of the time for the formation of an active sulphurating agent and the reaction of this with the hydrocarbon to form a rubber- bound intermediate which is the precursor to cross-link formation.

k - the overall first-order rate constant.

R_{max} - the maximum torque developed during the vulcanisation process which is a measure of the cross-link density.

2-2-5 RUBBER HARDNESS TESTER

The hardness of a rubber is a useful property which is measured by determining the depth of penetration of a needle of specified dimensions which is pressed into the rubber for a defined time with a defined force. As it is a reversible deformation it gives a measurement which is related to a modulus (eg. compression modulus) and is, therefore a function of cross-linking density for an unfilled vulcanisate. This test measures therefore, a fundamental property yet it is probably one of the simplest test that could be performed.

The instrument used in this case is the wallace hardness-tester, manufactured by W.H. Wallace Ltd. It consists of a vertical plunger, the indentor, terminating in a rigid ball of 2.44 mm diameter that is capable of substantially frictionless vertical movement, the part of the plunger immediately above the ball is reduced in diameter to avoid contacting with the rubber. A dial guage indicates the movement of the plunger and is calibrated directly in international rubber hardness degrees (I.R.H.D) Loads of 30± 1g and 570± 5g can be applied to the indentor as described. A annular foot forming part of the position measuring guage, rests on the test-piece and exerts a pressure of between 200 and 300 g/cm^2. An electrically operated buzzer gently vibrates the apparatus to overcome slight frictional force(115).

2-2-6 RESILIENCE TESTER

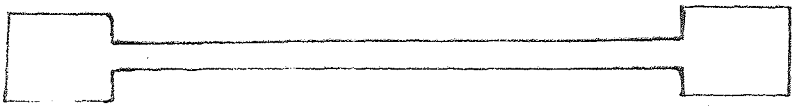
Craig(116) defines resilience as the ratio of the energy given upon recovery from deformation to the energy required to produce the deformation expressed as a percentage. There are many methods of determining this quantity eg. the lupke pendulum, the Dunlop tripsometer, the Dunlop pendulum (B.S. 903 part A8, 1963) the Schob pendulum (DIN 53512) and the Goodyear Healey pendulum (ASTM D 1054). In all these cases the percentage rebound of a striker of given dimensions from the rubber test-piece is measured. In this work the Dunlop tripsometer(117,118) was used. It has a steel ball indentor, which can be set at desired angle (45° in this work). A test-piece is placed in a test-piece holder and the swinging pendulum is then released. The steel ball hits the rubber sample and rebounds back along the scale from which the maximum reading is observed.

2-2-7 MR 100 APPARATUS

The Modulus at 100% elongation represents a modulus at a relatively small extension and as such gives for non-filled vulcanisates a measurement that is a function of the cross-link density, the apparatus is described in British standard(119).

A test piece of the dimensions shown in fig.7 below

Fig.7



is held by two grips that can be accurately extended by 100%. The force exerted by this extension is measured by a beam balance with sliding weights giving a maximum load of 1kg and capable of being read to 0.5g, an upper grip is attached to the underside of a normal balance pan support by means of an extension rod projecting downwards through a clearance gap in the base casting. The base casting carries a fixed and vertically aligned rod. A lower grip, similar in construction to the upper is provided with a fixed projecting cylindrical peg which slides into one of two drilled and bushed holes in the vertical rod. In either position, when the lower and the upper grips are vertically opposed. When the lower grip is supported in the higher position, its distance from the upper grip is such that the test-piece is elongated 100 percent. The balance is fitted with a device for counter-poising the weight of the assembly attached to the balance pan support, with stops to restrict the swing of the beam, so that the corresponding change in extension of the test piece is within ±1 percent.

2-2-8 STRESS RELAXATION

The stress relaxation theory is based upon the kinetic theory of rubber elasticity which relates the tension force "F" exerted by a stretched piece of rubber and the number "N" of stress supporting chains.

i.e. $F = NkTA_0 (\lambda - \lambda^{-2})$ (120)

where k = Boltzmann constant

T = Absolute temperature

A_0 = Original cross-section area

λ = Extension ratio

If λ and T are constant the $F/F_0 = \frac{N}{N_0}$

where F_0 and F are the original tension force and the tension force after $(N - N_0)$ chains are broken respectively and where

N_o equals the original number of chains and N the number of chains broken when the tension force is F.

Thus the decay in stress at constant extension during ageing is a measure of the chains broken$^{(12)}$.

It is essential that the test pieces are thin enough for the surface oxygen attack to represent the oxidation of the whole sample. If they are too thick, the process becomes diffusion controlled. It was found necessary to use samples with a thickness of less than 1 mm. Convenient specimens for this test were cut by a test piece cutter designed for the MR 100 test shown in Fig.(7).

Ageing studies were carried out using the Wallace stress relaxameter which has been developed from a simple helical spring relaxameter$^{(66,122-125)}$. The stress in the rubber stretched between clamps is balanced by the force in an extended helical spring operating within its Hooke'S law range. The extension of the spring is measured on a recorder, the reading of which is directly proportional to the force thus, if the recorder reading is l,

$$l/l_o = f/f_o = N/N_o$$

A series of springs is available so that whatever the modulus of the rubber, the initial reading is high on the scale. The apparatus is placed inside an oven tube in a Wallace oven and the measurement made at an elavated temperature in any desired atmosphere. In this case a temperature of 70°C ±2°C was used with an air flow of $2ft^3/$ hour. Although the equipment can be used to measure intermittent relaxation it was only used for measuring continuous stress relaxation in this case.

2-2-9 COMPRESSION MODULUS APPARATUS (RETICULOMETER)

The apparatus marketed under the name "Wallace Smith Reticulometer" is produced by W.H. Wallace of Croydon and was developed by D.A. Smith(50). It was developed for a Wallace rubber micro hardness tester(126) with a wedge factor of 6:1 modified in the following respects. a) The I.R.H.D. dial guage is replaced by a dial micrometer graduated in 0.01 mm dimensions.

b) A jacketed reticulometer test cup is substituted for the flat base of the test bed and a flat circular stainless steel disc (1.9 cm diameter), replaces the indentor.

c) A larger weight pan is fitted

Thermostatted water at the test temperature is circulated through the reticulometer pot.

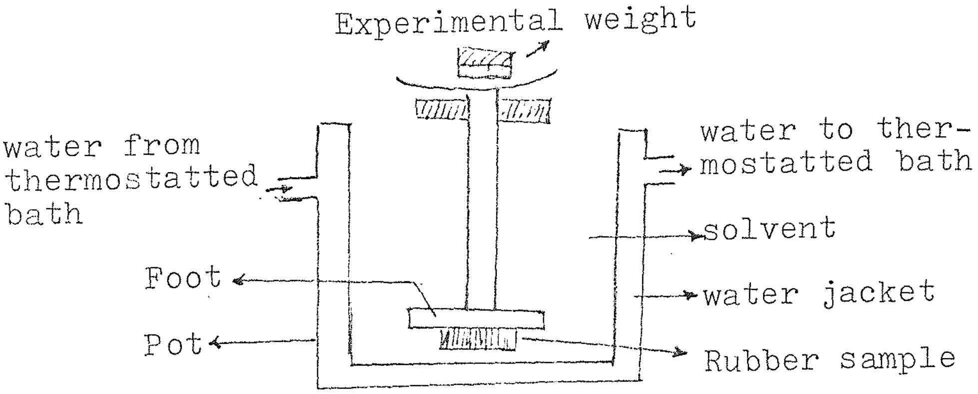
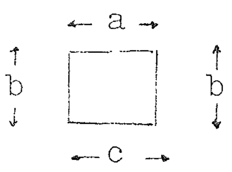


Fig.8

The pot is filled with solvent before testing and allowed to equilibrate to the test temperature (25°C); loss of solvent by evaporation was overcome by periodic addition of fresh solvent also at 25°C.

Samples were cut with a scalpel from the central part of vulcanised sheets. This method was preferred because it avoided the concave edges produced by the punching operation(13).

A vernier microscope with a accuracy of ±0.001 cm was used to measure the length of the specimen. For compression modulus determination, the values required were A_o, h_o (the original cross-section area and height respectively) h_o was obtained by taking the average of three readings of height. A_o was computed from the values of lengths of the four sides of the specimen and the same for the other side as shown in Fig.



$$A_o = \frac{(a + c)}{2} \cdot \frac{(b + d)}{2}$$

A circular cutter was later found to be more convenient.

Values of C_1 were calculated as described in appendix (1). It was also found useful to determine the polymer-solvent intraction coefficient (χ) of the Flory Rhener equation(58,59) at the same time. The volume swelling was determined by weighing the swollen compression modulus specimen and again after deswelling to constant weight under a vacuum for about 48 hours at 50°C. The computer program in basic language is shown in appendix (1).

2-3- EXPERIMENTAL WORK

2-3-1- ACETONE EXTRACTION

All the rubber (NR) used was purified by acetone extraction, as previously described,(2-1-1),except for a limited amount of work which was carried out to determine the competition offered by indigenous radical acceptor present in the rubber . The latter was necessary to assess the large scale practicallity of the work as large scale modification would be too expensive if acetone extraction was required as one of the production steps.

2-3-2- MASTICATION OF NON-EXTRACTED NR IN AIR

NR was masticated in air in both the Uni-rotor mixer and a two-roll mill for different times (0,1,2,5,10,15, 20 minutes) at approximately 25°C. Only 10 gram quantities of NR could be masticated in one operation in the Uni-rotor mixer and 20 gram on the 6" two-roll mill. It was therefore necessary to prepare a number of batches under identical conditions to obtain sufficient compound for vulcanisation.

Mastication was also carried out in air on the two-roll mill in the presence of 1phr of the radical acceptor(MBT) .

In all cases a plot of plasticity versus time was constructed and it was observed that the rate of mechanochemical degradation was much greater on the two-roll mill than the Uni-rotor mixer because of the more effective shear rate of the former .

The rate of degradation produced by mastication in the presence of MBT after 20 minutes was slightly greater than that produced in air only, although it was obvious that they would ultimately converge. In each case mastication was carried on until a wallace plasticity of 38-40 units was obtained ($\overline{M}_n \cong 265\text{-}275$ Kg mole^{-1}).

2-3-3- MASTICATION OF NON-EXTRACTED NR IN THE PRESENCE OF NITROGEN (N_2)

Mastication of rubber in an inert atmosphere of N_2 was carried out in the Uni-rotor mixer . 10 gram of non-extracted NR was masticated for different periods of time ranging from 0-20 minutes (0,1,2,5,10,15,20) using a rotor speed of 40 rpm and temperature of approximately 25°C. The temperature was measured using a thermocouple positioned about 1mm from the face of the mixing surface of the stator and controlled by immersing the stator in an ice-water mixture. Nitrogen was freed from oxygen using alkaline pyrogallol solution and passed through the mixer at least 5 minutes before switching the motor on to remove all the oxygen and this was continued throughout the mixing period.

As expected a plot of plasticity versus time showed that the efficiency of mastication was much lower in N_2 than that in air either in the Uni-rotor mixer or two-roll mill This could be due to the recombination of radicals by themselves rather than by the free radical acceptors.

2-3-4- RADICAL ACCEPTOR ACTIVITY

A- MASTICATION OF EXTRACTED NR IN AIR

To establish the best condition, the mastication of extracted NR was carried out in the Uni-rotor mixer under a variety of conditions. These included the amount of rubber used (which controls the distance between the mixing faces), the speed of rotation, the temperature and the time. It was finally decided to use a batch weight of 10 gram at 25°C using a rotor speed of 40 rpm. The reduction of molecular weight was almost completed within 20 minutes.

Extracted NR was also masticated on a two-roll mill in air and in the presence of (1phr) of the following radical acceptors: (MBT, MBTS, TMTD, P25, DIPDIS, DIPTRI, DIPTET) (table 4)

A plot of plasticity versus mastication time which was also converted to a molecular weight versus mastication time graph (using the Mullins and Watson calibration)(13) was plotted. Results are shown in tables (5,6) and figs. 10,11 .

B-MASTICATION OF EXTRACTED NR IN N_2

Extracted NR was masticated with and without radical acceptors in the Uni-rotor mixer using the procedure described in (2-3-3) under a nitrogen atmosphere. The radical acceptors used were : MBT, MBTS, TMTD, P25, DIPDIS, DIPTRI, DIPTET and the amount of radical acceptor used was 1phr in each case (table 4) .

10 gram batches of rubber were first sheeted on a two-roll mill in the shortest possible period of time and the radical acceptor was then distributed over the sheet which was then folded and sealed . These "packages" were

then added to the Uni-rotor mixer and the loss of the powder thus avoided.

Mastications were carried out for 0,1,2,5,10,15 and 20 minute at 40 rpm. The temperature being maintained at 25°C . Results are shown in table (6) and fig.(12).

2-3-5- PREPARATION OF NR GUM MASTERBATCH IN N_2

300 gram quantities of extracted NR were masticated in 10 gram batches in the Uni-rotor mixer in an atmosphere of N_2 at 40 rpm and 25°C in the presence of 1phr of the following radical acceptors:MBT,MBTS,TMTD,P25,DIPDIS, DIPTRI,DIPTET,DBUDIS,DBUTRI,DBUTET. These radical acceptors were used in the formulation 1 and 2 as indicated in tables 1 and 2 .

300 gram quantities of extracted NR were masticated as above in the Uni-rotor mixer using the whole quantities of radical acceptor required in the formulation i.e. TMTD (3.5phr),P25 (3.5phr),DIPDIS (3phr) and DIPTET (6phr) as shown in table 3.

Mastication was carried out to a wallace plasticity of 38-40 units ($\overline{M}n$ =265-275 Kg mole^{-1}). The batches obtained from the same radical acceptors were then blended on a two-roll mill and each masterbatch was compounded with the appropriate formulation to wallace plasticity of 20 (formulation 1) and 10 (formulations 2 and 3). The molecular weights of a selection of the compounded rubbers were also determined by viscosity measurements.

In the case of DIPDIS used in formulation 3 a further quantity of masterbatch was prepared in the Uni-rotor mixer (N_2 atmosphere,40 rpm,25^oC) to a wallace plasticity of 15 and after compounding the wallace plasticity was further reduced to 5 .

A comparison of the mastication efficiencies of the Uni-rotor mixer and two-roll mill with TMTD is shown in fig.13 (table 7) .

2-3-6- PREPARATION OF NR MASTERBATCH IN AIR

Sufficient batches (300) of extracted NR were masticated on a two-roll mill (12") to a wallace plasticity of 38-40 units to prepare (formulations 1,2 and 3) shown in tables 1,2 and 3 .

The wallce plasticities after compounding were 20 and 10 as described in section (2-3-5). The molecular weights of a selection of these compounded rubbers were also determined by viscosity measurements. Another 300 g of rubber was masticated to a wallace plasticity 38 and after compounding to wallace plasticities of 27,19.5,14.5 and 9 units. The intrinsic viscosities of these were also determined (table 8) .

3 x 300 gram batches of extracted NR were masticated as above ,containing 1phr MBT, 3.5phr TMTD, and 3phr DIPDIS respectively. These were used for the preparation of the formulations shown in table 3 .

2-3-7- FORMULATIONS

The formulations used are divided into three sections and are shown in tables 1,2 and 3 .

In the formulations shown in table (1) using 1phr of radical acceptor (the accelerator) in combination with 2.5phr of sulphur , no attempt was made to optimise the sulphur:accelerator ratio. In each formulation extracted NR was used but modified by adding the 1phr of radical acceptor at the mastication stage. The mastication was carried out under a N_2 atmosphere as already described in section (2-3-5) . When the NR is modified in this manner the formulation number is given a "+" sign . In one case where MBT is used, the mastication with the 1phr of MBT is also carried out in air (to assess the competition of oxygen as a radical acceptor)and this formulation number is marked with sign "a" .

Formulations shown in table (2) have been optimised to give practical S:accelerator or NR:S-donor ratios . Once again a comparison of unmodified extracted NR with the rubber modified by mastication with 1phr of the radical acceptor in N_2 is made and indicated by "+" .

The formulations in table (3) differ from the other two in that all the radical acceptor (the accelerator or S-donor) has been added at the mastication stage. Mastication in N_2 is shown by "n" with the formulation number and mastication in air is shown by "a" .

Table 1 : Formulation (1):(High Sulphur Compounds)

Formulation (1)	1A, $1A_a$ $1A_+$	1B, $1B_+$	1C, $1C_+$	1D, $1D_+$	1E, $1E_+$	1F, $1F_+$	1G, $1G_+$	P
Rubber	100	100	100	100	100	100	100	100
S	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
ZnO	5	5	5	5	5	5	5	5
Stearic acid	3	3	3	3	3	3	3	3
MBT	1	-	-	-	-	-	-	-
MBTS	-	1	-	-	-	-	-	-
TMTD	-	-	1	-	-	-	-	-
P25	-	-	-	1	-	-	-	-
DIPDIS	-	-	-	-	1	-	-	-
DIPTRI	-	-	-	-	-	1	-	-
DIPTET	-	-	-	-	-	-	1	-
CBS	-	-	-	-	-	-	-	0.5

Index(a) : 1g of radical acceptor added at the mastication stage under air.

Index(+) : 1g of radical acceptor added at the mastication stage under N_2

Table 2 : Formulation (2):(Optimized)

Formulation (2)	2B, $2B_+$	2C, $2C_+$	2E, $2E_+$	2F, $2F_+$	2G, $2G_+$	2H, $2H_+$	2M, $2M_+$	2N, $2N_+$
Rubber	100	100	100	100	100	100	100	100
S	3	-	0.5	-	-	0.5	-	-
ZnO	5	5	5	5	5	5	5	5
Stearic acid	2	1	3	1	1	3	1	1
DPG	0.2	-	-	-	-	-	-	-
DMDS	-	-	1.63	-	-	1.63	-	-
MBTS	5	-	-	-	-	-	-	-
TMTD	-	3.5	-	-	-	-	-	-
DIPDIS	-	-	3	-	-	-	-	-
DIPTRI	-	-	-	6	-	-	-	-
DIPTET	-	-	-	-	6	-	-	-
DBUDIS	-	-	-	-	-	4	-	-
DBUTRI	-	-	-	-	-	-	7	-
DBUTET	-	-	-	-	-	-	-	7

Index (+) 1g radical acceptor added at the mastication stage under N_2

Table 3 : Formulation (3) ; (Optimized)

Formulation (3)	3C, $3C_a$, $3C_n$	3D, $3D_a$, $3D_n$	3E, $3E_a$, $3E_n$	3G, $3G_a$, $3G_n$
Rubber	100	100	100	100
ZnO	5	5	5	5
Stearic acid	1	1	3	1
S	-	-	0.5	-
DMDS	-	-	1.63	-
TMTD	3.5	-	-	-
P25	-	3.5	-	-
DIPDIS	-	-	3	-
DIPTET	-	-	-	6

Index (a) : total amount of radical acceptor added at the mastication stage under air.

Index (n) : total amount of radical acceptor added at the mastication stage under N_2.

The compounds were all prepared on a water cooled laboratory, 12" two-roll mill using rubber that had been previously masticated with or without added radical acceptor to a wallace plasticity of 38-40 . The ingredients were added in the same order in all cases, the sulphur or S-donor was added last. Mixing was carried on until a wallace plasticity of 10 was obtained . The wallace plastimeter readings were carried out in triplicate and agreed within ± 1 wallace plasticity unit. The calibration of Mullins and Watson(13) was used to convert the results to the number average molecular weight ($\bar{M}n$) .

2-3-8- SOLUTION VISCOSITY MEASUREMENTS

Solution viscosity measurements were carried out using an Ubblehode suspended level viscometer which was immersed in a water bath maintained at 25°C ± ·1°C . The viscometer is shown diagramatically in fig.(9) . A 1% solution of the rubber compound in benzene was prepared, making allowance for the non-rubber constituents, filtered and then centrifuged. Five consecutive flow times using 5ml of the solution (agreeing to within ± 0.2 sec.) were determined. Five mls. of the pure benzene were then added to the solution in the viscometer and mixed by blowing filtered air through the tube "D" . It was then allowed to reach temperature equilibrium and the flow time redetermined . This process was repeated after the addition of a further two 5ml portions of benzene . The flow time for pure benzene

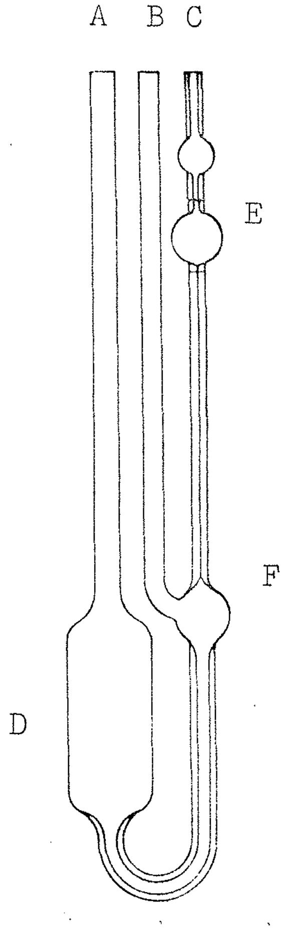


Fig.9 UBBLEHODE VISCOMETER

at 25°C was also determined . The ratio of the flow time of the solvent and solution is known as the relative viscosity ηr . (ηr -1) is known as specific viscosity and the plot of(η r -1)/conc. versus concentration gives a straight line. When extrapolated to zero concentration it gives the viscosity of the solution which is known as the intrinsic viscosity $[\eta]$ and is related to the number average molecular weight by the well known Mark-Houwink(127) equation.

$$[\eta] = K.Mn^{\alpha}$$

where K and α are constants. For NR in benzene at 25°C these constants are :

$K = 2.29 \times 10^{-7}$

$\alpha = 1.33$

A typical (η r - 1)/conc. versus concentration is shown in fig.(13).

The viscosities of dilute solutions of compound 2C (TMTD) at wallace plasticity values of 27,19.5,14.5,9 were determined by the above method to confirm the Mullins and Watson plasticity calibration curve . The values obtained are shown in tables(8,9). Fig.(14) shows the agreements of this calibration with the values obtained by Mullins and Watson (13).

The calibration was,therefore,used for much of the subsequent work.

Where accurate values of $\overline{M}n$ were required e.g. for calculation of the number of free chain ends, the solution viscosity was still used . This was, therefore, used for formulations in tables 2 and 3 .

A curve relating intrinsic viscosity to $\overline{M}n$ was constructed (fig. 16) and used to simplify $\overline{M}n$ calculations .

2-3-9- MONSANTO RHEOGRAPH

All formulations under investigation were examined on the Monsanto Rheometer at cure temperature of 140°C . The maximum degree of cure (Rmax) and optimum cure time were calculated . This was carried out for two reasons: to obtain an estimate of the time required for optimum cure when pressing sheets in the laboratory and to assess any chage in Rmax and cure rate that might have resulted from a reduction in chain ends due to mastication in the presence of a vulcanisable radical acceptor. The latter comparison of modified and unmodified vulcanisates was carried out in all cases. A specimen rheograph is shown in fig. (9a) but all the results are quoted in table (10).

In certain cases the first order rate constants were included. These are shown in table (10). The Monsanto rheometer was also used to establish the fact that a sufficient dispersion of compounding ingredients had been achieved when preparing the formulation used. This was done simply by comparing the rheographs obtained from pieces of stock taken from different parts of the sheet from the mill. Identical curves were produced when good dispersion was obtained .

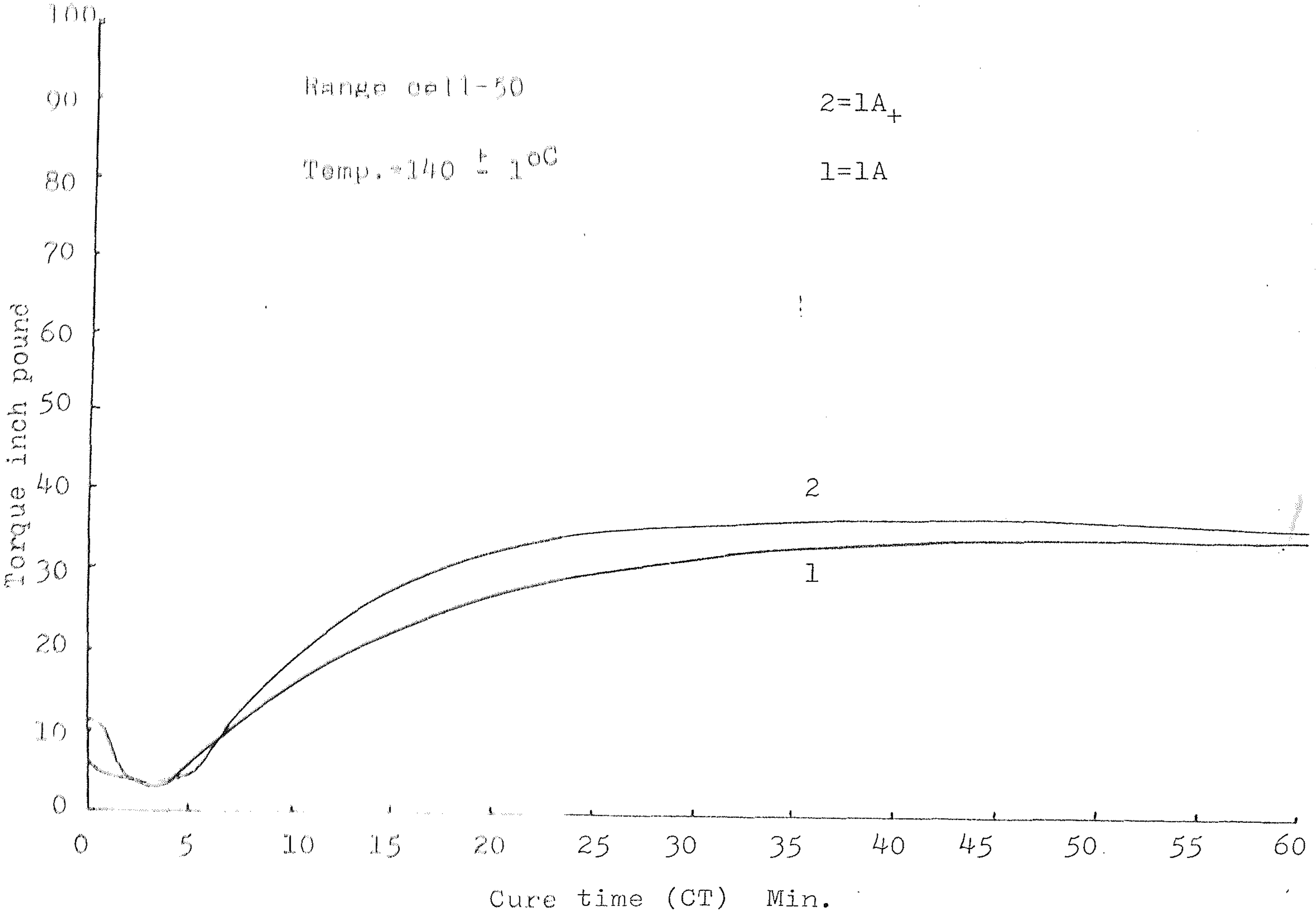


Fig.(04): Monsanto Rheograph for ME1

2-3-10- PREPARATION OF VULCANISATES

Vulcanisation of the formulations shown in tables (1,2 and 3) section(2-3-7)was carried out using a Bradley and Turton hydraulic press with induction heated platens . A temperature of 140°C ± 2°C was used . The time of vulcanisation was varied according to the compound used and the state of cure required . In all cases the moulds were carefully cleaned,treated with a silicone release agent(except where stress relaxation tests were to be carried out) and preheated before use . A weighed quantity of rubber calculated to produce a 10% excess over that required by the mould cavity was used . A pressure of 456 MN m^{-2} (30 ton in^{-2}) was applied during the whole of the cure cycle although this was momentarily released at the beginning of the operation to prevent the formation of air bubbles .

Stocks of formulations 1 and 2 were cured to optimum cure time but stocks of formulation 3 were cured for four different cure times . After vulcanisation the sheets taken out of the press were immediately immersed in cold water to quench further curing reaction and then dried and placed in the deep freeze at -20°C until required for evaluation . These sheets were removed from the deep freeze and kept at room temperature for 24 hours before using them for the assessment of physical properties .

Vulcanisates were prepared for the following tests .

(a) Hardness. : 2.5 cm diameter and 1 cm thickness, specimens were used .

(b) Compression modulus, swelling and resilience sheets of dimensions 2.5 x 7.5 x 0.3 cms were used for these tests. The specimens used for compression modulus determinations and swelling tests were cut from the sheets by means of a dumbell test piece cutter (B.S S6/1/1A) and then again at right angles across the parallel-sided section of the specimen to produce a square . Later on in this work it was found more convenient to use a cork-borer of 0.6 cm diameter

(c)Stress relaxation

For this work very thin specimens are required otherwise the rate of oxidation becomes diffusion controlled .A cavity mould giving sheets of 12 x 22 x 0.05 cms was used .

No silicone release agent was employed as it was found to retard the rate of oxidation . Test specimens were produced using a cutter designed for the MR100 apparatus which gives rectangular specimens as shown in fig.(7) .

(d) Stress strain properties

Sheets of nominal dimensions 12 x 22 x 0.1 cm were moulded. Specimens for tensile strergth were cut by means of a dumbell test piece cutter (B.S S6/1/3C). MR100 specimens were cut with a special cutter which was also used for stress relaxation determination .

2-3-11- SWELLING TEST

Three test pieces were cut from each vulcanisate as described in section (2-3-10) . The samples were then weighed ,placed in sample-bottles and immersed in dry n-hexane at 25°C± 0.2°C. They were then left for 24 hours by which time they had reached constant weight.

The samples were then taken out individually, the excess surface solvent removed with filter paper, placed in a tared, stopped weighing bottle and reweighed to ± 0.1 mg. The transferance to the weighing bottle had to be done quickly to prevent loss of the solvent by evaporation. The samples were then returned to the bottles containing the solvent and kept in the water bath at 25°C for compression modulus determinations which will be described in section (2-3-12). After compression modulus had been determined the samples were dried in a vacuum oven at 40°C to constant weight (48 hours) and the volume of solvent absorbed calculated.

It is necessary to deswell the samples in vacuum to obtain the weight of the unswollen rubber as the original weight of the dry specimen could not be used because the solvent leaches out the soluble material and a false result would be obtained.

The equilibrium swelling ratio was calculated as :

$$\nu r = \frac{V_R}{(V_R + V_S)}$$

where V_R is the volume of the deswollen rubber and V_S is the volume of the solvent absorbed.

These values of νr, together with the value of Mc_{phys} which was determined from compression modulus data (2-3-12) were substituted in the Flory-Rhener equation$^{(58,59)}$ and the values of the polymer solvent intraction coefficient (χ) calculated. The computer program for the calculation together with that for solving the compression modulus data is given in appendix 1 .

This procedure was adopted for all formulations in tables 1 and 2 at optimum cure time and the values of χ obtained were then used for the direct determination of Mc_{phys} from swelling data for vulcanisates prepared from formulation 3 over a range of cure times . Results are shown in tables(11,12,13,14,15) and figs.(17-28).

2-3-12- COMPRESSION MODULUS

2-3-12-1- COMPRESSION MODULUS ON SWOLLEN SAMPLES USING THE WALLACE RETICULOMETER

The wallce reticulometer has been described in section (2-2-10). The following procedure was used .

The reticulometer was switched on and the pot filled with n-hexane (the same solvent used for the swelling determination),thermostatted water at 25°C was passed through the jacket surrounding the pot using a water pump. When temperature equilibrium had been obtained the test-piece was transferred to the pot . The foot of reticulometer was lowered until the sample was well immersed in the hexane . The instrument was then zeroed using the small back knob at the back on the left side of the instrument .

The foot was then lowered onto the surface of the sample and a small pressure was applied by the wheel until a positive reading was produced by turning on the C.R.G. The pressre was then released to zero . the column was locked using the chrome lever on the left side of the instrument . The test was then carried out as follows:

(a) 500 g(excess load) was placed on the pan for 20 sec.

(b) The excess load was then removed and the sample was allowed to relax for 5 minutes .

(c)After relaxation 25 g weight (dead load) was put on the pan for 1 minute .

(d) The dead load was removed and the first experimental load was added . The chrome wheel was turned until the C.R.G. read zero and the dial gauge reading was read and the chrome wheel was turned to returned dial gauge to zero .

(f) After 20 sec the dead load was put on the pan for 1 minute .

(g) For each experimental(weight load) step (d) to (f) were repeated .

The series of experimental loads used (gram) were as follows:

→

50 100 150 200 250 300

50 100 150 200 250 300

←

The wedge factor ofthe instrument was 1/6 . Therefore all reading have to be divided by 6 . The approximation due to D.A.Smith(50) (1-2-5-4) was used i.e.

$$C_1 = \frac{F}{\Delta h} \cdot \frac{h_o}{6A_o}$$

Mc_{phys} was then calculated from the relationship :-

$$C_1 = \frac{\rho RT}{2Mc_{phys}}$$

Mc_{chem} was calculated from the Moore,Mullins and Watson equation(61,66,71) in section (1-3) .

The value of $\overline{M}n$ was either obtained from the wallace plasticity number of the stock immediately before vulcanisation using the calibration curve (fig. 14) or for more accurate determinations(e.g. when trying to obtain numerical values of the chain ends tied during the modification and vulcanisation process) .. determined directly from intrinsic viscosity $[\eta]$ as described in section (2-3-8) . The value of Mc_{phys} obtained was used as described in section (2-3-11) to calculate the value of χ for formulation 1 and 2 from the Flory-Rhener equation(58,59) . Results are shown in tables (11,12,13,14,15)and figs.(17-28) .

2-3-12-2- COMPRESSION MODULUS ON UNSWOLLEN SAMPLES

The same procedure as above was carried out on dry samples prepared from formulations P,2C and $2C_+$.

From this experiment the values of F/A_0 and $\Delta h/h_0$ were plotted for different cure times and the slopes (the compression moduli) determined . The variation of compression modulus with cure time was also determined . Results are shown in table (16) and figs.(56- 58).

2-3-13- HARDNESS MEASUREMENTS

This measurement was carried out with the wallace hardness tester previously described in (2-2-5) using the disc specimen (2-3-10) . The samples were pre-loaded with a weight of 30 g for 5 sec.,the dial micrometer adjusted to a value of 100 and then loaded with the full test weight of 540 g . The depth of penetration of the indentor (which was electrically vibrated during the test) was measured on the dial gauge . As this is time dependent the reading was taken after 30 secs.

An average of 6 readings (3 reading from different points of each side) were taken . The test was carried out at ambient temperature .

Hardness tests were determined for vulcanisates from formulations 1,2 and 3 . The results are shown in tables (17, 18,19,20) and figs.(35,36,37,44,49,55,61) .

2-3-14- RESILIENCE TEST

The instrument used in the determination of this physical property was Dunlop tripsometer described in section (2-2-6). Two square test pieces were fitted tightly into the holder and left for a period of 5 minutes . The disc was rotated in an anti-clock wise direction through an angle of 45° and clamped . The clamp was released and the rebound angle measured .

The test was subjected to a number of impacts until a constant reading was obtained for three consecutive impacts.

This experiment was performed for formulations 1,2 and 3 at 20°C ± 1°C and results were simply expressed as below:

Rebound Resilience% = (reading /45) x 100

The results are shown in tables (17,18,19,20) and figs. (41,42,46,52,53,59,62)

2-3-15- MR100 MEASUREMENT

This property was determined using the MR100 apparatus described in section (2-2-7) .

Five test pieces were cut ,as described in section (2-3-10) from each vulcanisate .

The test pieces was placed in the grips with the lower grip in the upper position,the lower grip then moved down to the lower position to give a 100 percent elongation of the test piece and the tension in the rubber was balanced by sliding the weights on the balance arm until it equalled the tension of the test piece . The equilibrium point of the balance was determined by the completion of an electrical circuit which energises a neon bulb . The balancing load was read and recorded and corrected for the initial weight of the test piece and grips which had previously been determined .

This experiment was carried out for vulcanisates prepared from formulations 1A,1A+,1Aa,3E,3Ea and 3En at four different cure times . The results are shown as modulus at 100% elongation (MN m^{-2}) in tables(19,20) and figs.(38,39,50). The thickness and width of test pieces were measured using a dial micrometer.

2-3-16- TENSLE STRENGTH AND MODULI AT GIVEN ELONGATION

These tests were carried out as specified in British standard, 903:part A2:1971 using a tensometer type "E" with an instron test piece holder attached . The test was performed using a motor speed of 3750 rpm . A 50 lb load cell which produced a full scale chart deflection was found most convenient .

The width and thickness of the central part of the dumbell shape samples, which were previously cut using the smallest dumbell cutter, (type B.S.S6/1/3C), were measured and the cross section area calculated . The test piece was clamped to the holders and extended . The loads required to produce an elongation of 100% and in some cases 200%, 300%, 600% and further to break the specimen were measured . The ultimate tensile strength was calculated in MN m^{-2} using the original cross sectional area of the test pieces .

This experiment was carried out for formulations 1A, $1A_4$ and formulations in table 3 at different cure times and an average of results of five test pieces in each cases was calculated . The results are shown in tables(17,18, 19,20) and figs.(32,33,34,40,43,45,47,48,51,54,60) . Any obviously low results were dismissed(as they were produced by flawed test pieces) and new test pieces substituted .

2-3-17- STRESS RELAXATION USING THE WALLACE AGE TESTER

This was determined using the wallace age tester described in section (2-2-9) .

Half of the samples (section 2-3-10) were acetone extracted for 48 hours and vacuum dried to a constant weight . The remaining samples were tested without extraction .

The samples were fitted in the test piece holder and left in the oven cell at a temperature 70°C ± 2°C and flow of 2 ft^3 hr^{-1} until equilibrium temperature was achieved . The instrument was used at maximum sensitivity and each recorder zeroed at 100 .

The continuous relaxation of stress was recorded for periods of between 24 and 48 hours .

The logarithm of the ratio of initial stress strain after a given time (Log F/F_0) was plotted as a function of time .

Three separate determinations(using different samples) were made for each vulcanisate .

This experiment was carried out for formulations in table 2 with extracted and non-extracted vulcanisates . A selection of the more important results are shown in figs.(30,31) .

CHAPTER 3

3- Results and discussion

3-1 MEASUREMENTS OF RADICAL ACCEPTOR ACTIVITY

The radical acceptor efficiecies of DIPDIS, TMTD, DIPTRI, MBT ,MBTS ,P25 andDIPTET have been assessed by mastication under different conditions. Figs.(10,11) show the decrease in molecular weight of acetone extracted NR when masticated for 0,1,2,5,10,15 and 20 minute intervals in air on the two-roll mill. It can be seen that they all increase in the rate of mechanochemical degradation although it seems that oxygen is playing a predominant role. The reduction in molecular weight due to the mastication of the rubber in a nitrogen atmosphere in the Uni-rotor mixer (Fig.12) enables one to list the radical acceptors in order of their acceptor efficiencies i.e $N_2 < \text{MBTS} < \text{DIPDIS} < \text{DIPTET} < \text{DIPTRI} < \text{P25} < \text{TMTD} < \text{MBT} < O_2$

This method of comparing relative efficiencies was originated by Pike and Watson(7) with referance to (Fig. 13) which compares. The mastication of NR under various conditions the reduction in molecular weight of the rubber when masticated in air on the two-roll mill and in the Uni-rotor mixer is very similar,i.e they must have similar rates. It can be seen that TMTD with air is the most effective radical acceptor combination.

3-2- INTERDEPENDANCE OF WALLACE PLASTICITY AND NUMBER AVERAGE MOLECULAR WEIGHT

The determination of the $[\eta]$ by solution viscosity measurements of the natural rubber compound(2C), reduced to different plasticities by mastication, has been described in section 2-3-8. Table (8) gives detailed results of these determinations and fig.15 shows the extrapolation. The $\overline{M}n$ and $[\eta]$ values for a range of compounds is shown in fig. 16 and was used for determining the $\overline{M}n$ of their compounds of known $[\eta]$ by inspection. $\overline{M}n$ values were determined from the Mullins, Watson calibration graph of $\overline{M}n$ versus plasticity as described in section 2-3-8 and shown in fig.14.

3-3-QUANTITATIVE ASSESSMENT OF FREE CHAIN ENDS

When natural rubber is masticated to a molecular weight of $\overline{M}n$ and then cross-linked, the elastic constant of the Mooney, Rivlin equation$^{(45,46)}$ (C_1) can be calculated from the equation $^{(61,71)}$:

$$C_1 = (\rho RT/2Mc_{chem} \quad +0.78\text{x}10^6)(\ 1-2.3\ Mc_{chem}/\overline{M}n\ )\ \frac{\text{dynes}}{\text{cm}^2}$$

where ρ = density of the rubber hydrocarbon

R= gas constant

T= absolute temperature

Mc_{chem}= number average molecular weight between cross-links

$(\rho RT/ 2Mc_{chem})$ represents the contribution due to chemical cross-links.

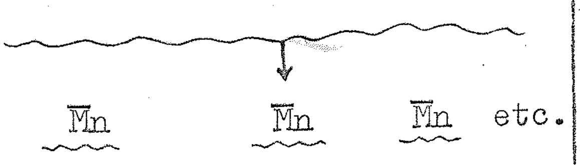
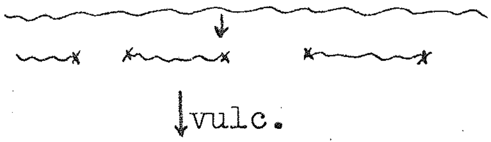
(0.78×10^6) is the maximum calculated entaglements contribution.

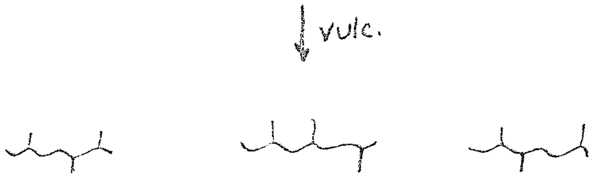
$(1- 2.3Mc_{chem}/ \overline{Mn})$ is a reduction due to free chain ends.

When natural rubber is masticated to the same $\overline{Mn}$ value but in the presence of a radical acceptor that will produce terminal groups that will combine with the network during vulcanisation then the value of C_1 obtained (C_{1mod}) is different eventhough the value of Mc_{chem} is kept constant.(The constant Mc_{chem} is maintained by using the same formulation in the same mould with strict control of the time and temperature). This change in $C_{1\,mod}$ must be due to the only remaining variable, $\overline{Mn}$, which changes to an apparent value of $\overline{Mn}'$ when the reactive end of the molecule combines with the network.

If the chain end modification is 100% effective then the value of $\overline{Mn}'$ becomes very large and the number of free chain ends becomes very small.

This is illustrated as follows:

MASTICATE IN AIR WITHOUT ADDITIONAL RADICAL ACCEPTOR	MASTICATE IN N_2 WITH A VULCANISABLE RADICAL ACCEPTOR TO THE SAME $\overline{Mn}$
	

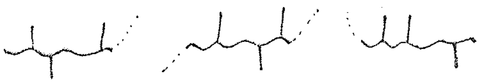


i.e 2 chain ends per $\overline{Mn}$

Total No. of molecules* = M-S/ $\overline{Mn}$

where M = overall molecular weight of network

S = molecular weight of additional sulphur used in cross-linking.



value of $\overline{Mn}$ now becomes $\overline{Mn}'$

Similarly:

Total No. of molecules*

= M-S/ $\overline{Mn}'$

∴ The % chain ends remaining after modification

$$= 2(M-S/\overline{Mn}')\,/\,2(M-S/\overline{Mn})$$

$$= \overline{Mn}\,/\,\overline{Mn}' \times 100$$

∴ The % chain ends combined is $= (1-\overline{Mn}/\overline{Mn}') \times 100$

The value of $\overline{Mn}'$ can be calculated as follows:

$$\frac{C_1}{C_{1mod}} = \frac{(\rho RT/2Mc_{chem} + 0.78\times10^6)(1-2.3Mc_{chem}/\overline{Mn})}{(\rho RT/2Mc_{chem} + 0.78\times10^6)(1-2.3Mc_{chem}/\overline{Mn}')}$$

$$\therefore \frac{C_1}{(1-2.3Mc_{chem}/\overline{Mn})} = \frac{C_{1mod}}{(1-2.3Mc_{chem}/\overline{Mn}')}$$

$$\therefore 1-2.3Mc_{chem}/\overline{Mn}' = C_{1mod}/C_1\,(1-2.3Mc_{chem}/\overline{Mn})$$

$$\therefore 2.3Mc_{chem}/\overline{Mn}' = 1-C_{1mod}/C_1(1-2.3Mc_{chem}/\overline{Mn})$$

$$\therefore \overline{Mn}' = \frac{2.3Mc_{chem}}{1-C_{1mod}/C_1(1-2.3Mc_{chem}/\overline{Mn})}$$

$$= \frac{2.3\overline{Mn}C_1Mc_{chem}}{\overline{Mn}(C_1-C_{1mod}) + 2.3C_{1mod}Mc_{chem}}$$

∴ % Chain ends combined after modification :

$$\%C.E.C. = \frac{(2.3Mc_{chem} - \overline{M}n)(C_1 - C_{1mod})}{2.3C_1Mc_{chem}}$$

3-3-1- DETERMINATION OF C_1,Mc_{phys},Mc_{chem},νr AND χ

Table(11)shows the value of Mc_{phys} and Mc_{chem} for compounds of formulation 1 and 2 masticated to initial molecular weights of $\overline{M}n$=175 and $\overline{M}n$=128 respectively(Kg mole^{-1}). The formulations were vulcanised to optimum cure time and the compression moduli of the swollen vulcanisates determined as described in section 2-3-12-1 . In all cases the Mc_{phys} value of the vulcanisates prepared from rubber masticated in the presence of radical acceptors in nitrogen (shown with a + sign after the formulation number) are less than those for rubber masticated in air eventhough great care has been taken to maintain to a constant cross-link density by using the same formulation and strictly controlling the vulcanisation conditions. Many preliminary experiments were carried out to make sure that it was possible to obtain consistent cross-link densities from a given formulation . This reduction in Mc_{phys} is what would be expected if there was a reduction in chain ends .

Table(12)shows the values of Mc_{phys}, νr and χ obtained from compression modulus and swelling determinations on optimum cure time vulcanisates swollen in n-hexane at 25°C (sections 2-3-11,12) . The χ values obtained were different for different formulations and it was necessary to use these specific χ values for the determination of Mc_{phys} for vulcanisates prepared from formulations shown in table 3 . The reduction of chain ends by masticating with radical acceptor produced no detectable difference in the value of χ .

Table(15) shows the values of C_1 obtained from compression modulus determination of swollen vulcanisates prepared from rubber masticated in air ($C_{1 \cdot or}$) with those obtained from rubber masticated with radical acceptors ($C_{1 \cdot mod}$) for all formulation in table 3. The corresponding values of Mc_{chem} and the $\overline{Mn}$ value of the rubber immediately before vulcanisation (determined from $[\eta]$ results) enables us to calculate the apparent value that this molecular weight would have when cross-linked into the network to produce this reduced number of chain ends (i.e $\overline{Mn}'$) see section 3-3 .

3-3-2- REDUCTION OF CHAIN ENDS BY MASTICATION WITH RADICAL ACCEPTORS UNDER N_2

Figs. 15-26 show the variation of $\overline{Mn}'$ with cure time and percentage of chain ends combined versus cure time for all formulations in table 3 and formulation 1A and $1A_+$ (MBT) for short cure times at 140°C the value of $\overline{Mn}'$ and the value of chain ends combined increases. For longer cure times these reach a limiting value exept in the case of the TMTD vulcanisates where the number of chain ends cleaves and then increases with increasing cure time. This is unexpected in view of the stability of the TMTD specific χ values for the determination of Mc_{phys} for vulcanisates prepared from formulations shown in table 3 . The reduction of chain ends by masticating with radical acceptor produced no detectable difference in the value of χ .

Table(15) shows the values of C_1 obtained from compression modulus determination of swollen vulcanisates prepared from rubber masticated in air ($C_{1\cdot or}$) with those obtained from rubber masticated with radical acceptors ($C_{1\cdot mod}$) for all formulation in table 3. The corresponding values of Mc_{chem} and the $\overline{Mn}$ value of the rubber immediately before vulcanisation (determined from $[\eta]$ results) enables us to calculate the apparent value that this molecular weight would have when cross-linked into the network to produce this reduced number of chain ends (i.e $\overline{Mn}'$) see section 3-3 .

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The percentage reduction in chain ends produced by the various radical acceptors when the rubber is masticated in the Uni-rotor mixer under nitrogen to an $\overline{M}n$ value of 128 Kg mole^{-1} is :

MBT-25%
DIPDIS-30%
P25 -35%
DIPTET-40%
TMTD -50%

The fact that TMTD is the most efficient chain end reducer is an agreement with the fact that it is a very efficient radical acceptor (figs 10,11) although MBT is even more efficient as a radical acceptor it is the least efficient chain ends reducer and we must conclude that although a large number of the polymer free radicals produced on mastication are terminated by MBT their reaction with sulphur to tie them into the network must be very inefficient .

When the rubber was masticated for 45 minutes under N_2 to an exceptionally low molecular weight with DIPDIS ($3E_n$),$\overline{M}n$ =100 Kg mole^{-1}, its apparent molecular weight in the vulcanisate $\overline{M}n'$ increased after 50 minutes cure at 140°C to 2.2×10^3 Kg mole^{-1} which corresponds to a reduction in the number of free chain ends of 95% .

Fig.29 shows how $\overline{Mn}'$ varies with the percentage of chain ends combined (p) using the expression deduced in section 3-3 ,i.e.

$$p = (1 - \overline{Mn}/ \overline{Mn}') \times 100$$

$$\therefore \overline{Mn}' = \overline{Mn} / (1- p/100)$$

At small values of p $\overline{Mn}' \cong \overline{Mn}$ but at high values of p a small change in p causes a very large change in $\overline{Mn}'$ and the value of $\overline{Mn}$ is difficult to estimate with accuracy e.g. the change in $\overline{Mn}'$ when p increases from 90-95% is about 600 Kg mole^{-1} .

3-3-3- ATTEMPTED REDUCTION OF FREE CHAIN ENDS BY MASTICATION WITH VULCANISABLE RADICAL ACCEPTORS IN AIR

The results are shown in table (13, 15) formulations in tables(1,2,3) and futher illustrated in figs.(17-29). It can be seen that NR with both MBT and DIPDIS produces an increase rather than a decrease in chain ends (table 15) . This is presumably due to the very effective competition by oxygen which is the most efficient radical acceptor (fig. 12). Even with prolonged mastication with DIPDIS the chain ends increses.

3-4-PHYSICAL PROPERTIES

With decreasing number of chain ends we would expect an improvement in physical properties . This has been confirmed in all cases as shown in tables(16-20) and figs.(32-62). This includes the vulcanisates prepared with DIPDIS,DIPTET,MBT,TMTDand P25 the physical properties measured being ultimate tensile strength (U.T.S), hardness ,modulus at 100%elongation ($MR100_s$ using MR100 apparatus) ,moduli at 100%,200%,300% and 600% elongation (MR100,MR200, MR300 and MR600 respectively)and resilience. The most dramatic improvements take place in the case of the DIPDIS vulcanisates (formulation $3E_n$). When the chain ends reduction is very high due to prolonged mastication of the rubber with DIPDIS the optimum U.T.S increases by 30% (fig. 33) , the hardness by 10% (fig. 36) and the modulus at 100% elongation by 2%(fig.39)when a chain end reduction in the order of 95% occurs (fig.28).

Mastication with the radical acceptors DIPDIS and MBT on a two-roll mill in air produced a slight decrease in all physical properties assessed. Hardness,Ultimate tensile strength ,Moduli at 100%and 300% elongation and resilience (figs.33,35,36,37,38,39,40,41,42,47,49,50,51, 53)(tables 19,20). Because of the large number of variables during mastication, compounding , vulcanisation and testing to obtain the preceeding results they were confirmed by repeating experiments from the mastication stage (figs,37,42,48,53). These results are in accord with the fact that the mastication in air results in an increase rather than a decrease in free chain ends in the final vulcanisate.

Table(4) :

List of radical acceptors which were used in the present work.

NO.	RADICAL ACCEPTOR	SHOWN BY
1	MBT	A
2	MBTS	B
3	TMTD	C
4	P25	D
5	DIPDIS	E
6	DIPTRI	F
7	DIPTET	G
8	DBUDIS	H
9	DBUTRI	M
10	DBUTET	N
11	CBS	P

Table(5)Mastication of 20 grams extracted natural rubber in Micro-two roll mill at room temperature and thickness of 1 mm.

CONDITION	TIME Min	$\overline{W.P}$	$\overline{Mn}$ Kg mole^{-1}	
Air	0	75	450	
"	1	64	395	
"	2	57	360	
"	5	42	285	
"	10	27	210	
"	15	15	150	
"	20	9	120	
MBT in Air	5	25	200	
"	10	11	130	
"	15	8	115	
"	20	7	110	
MBTS in Air	5	40	275	
"	10	21	180	
"	15	11	130	
"	20	7	110	
TMTD in Air	5	37	260	
"	10	20	175	
"	15	12	135	
"	20	7	110	
P25 in Air	5	38	265	
"	10	18	165	
"	15	12	135	
"	20	8	115	

Cond.

Table(5):Continued:

CONDITION	TIME Min	$\overline{W}$.P	$\overline{M}$n Kg $mole^{-1}$	
DIPDIS in Air	5	38	265	
"	10	22	185	
"	15	13	140	
"	20	8	115	
DIPTRI in Air	5	35	250	
"	10	19	170	
"	15	11	130	
"	20	6	105	
DIPTET in Air	5	28	215	
"	10	20	175	
"	15	14	145	
"	20	9	120	

Fig.(10):Mastication of extracted NR in Air on a two roll-mill with different radical acceptors.

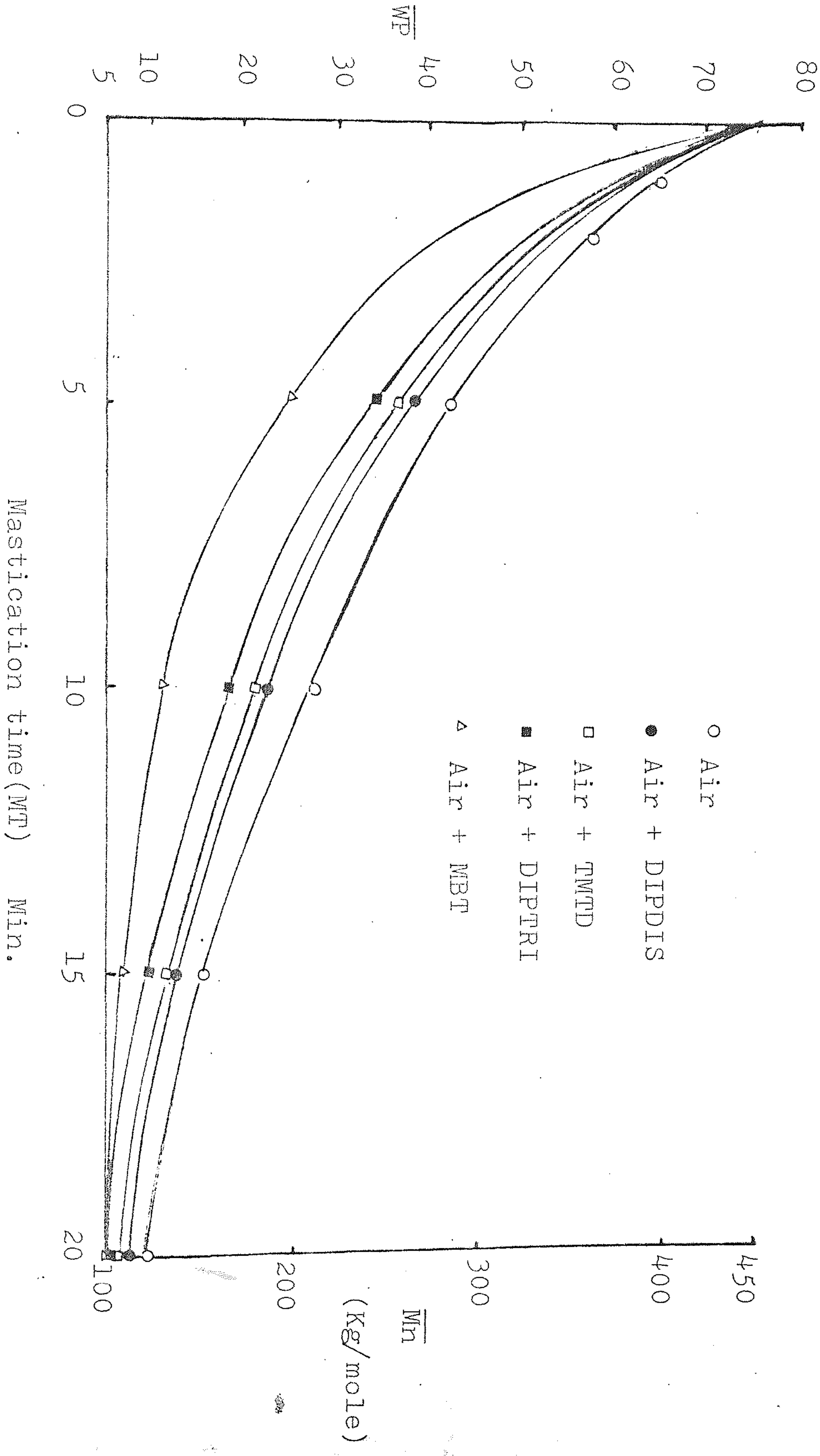
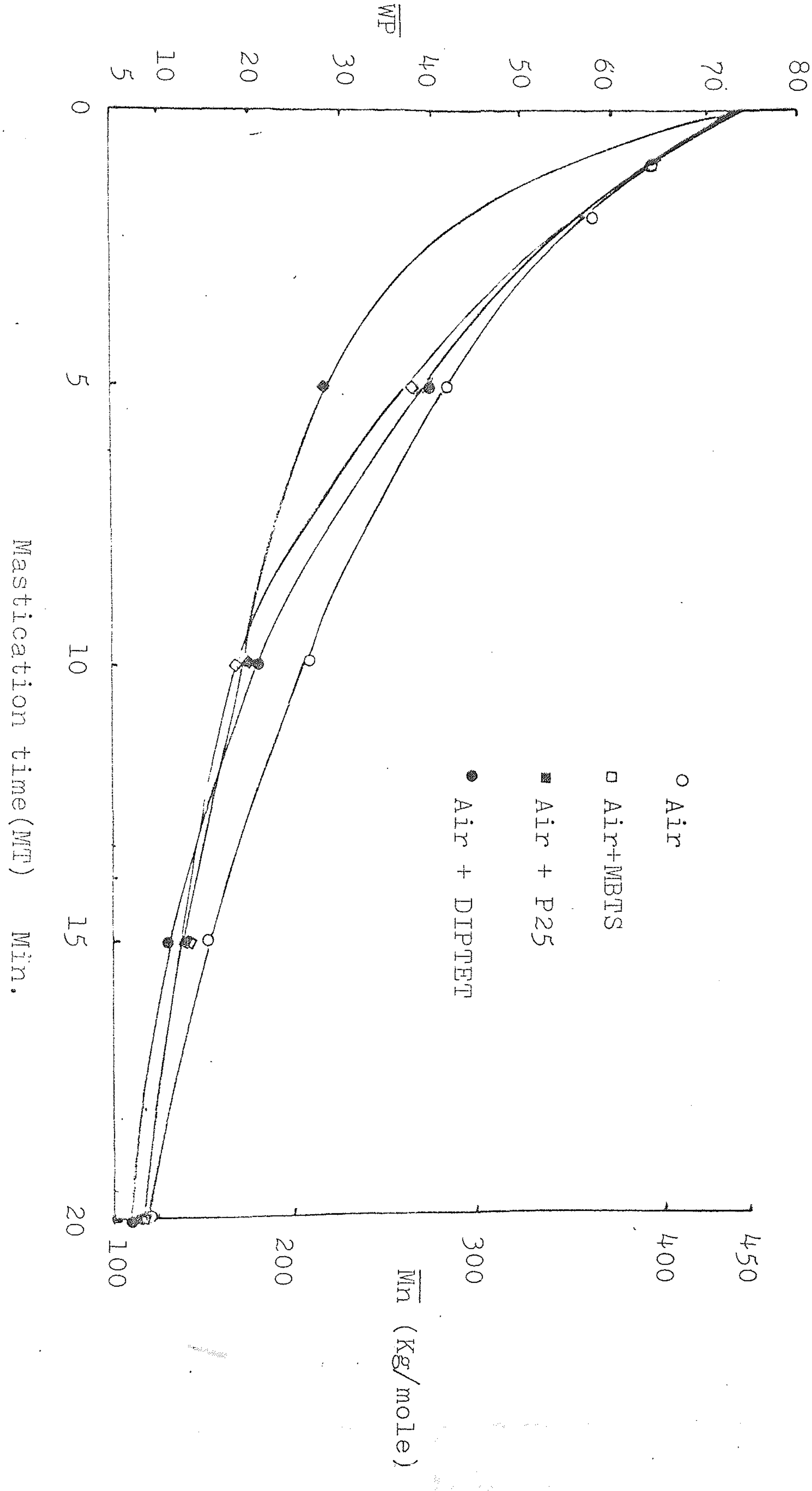


Fig.(11):Mastication of extracted NR in Air on a two roll-mill with different radical acceptors.



Table(6):Mastication of 10 grams extracted rubber in unirotor mixer at 25°C and 40 RPM rotor speed.

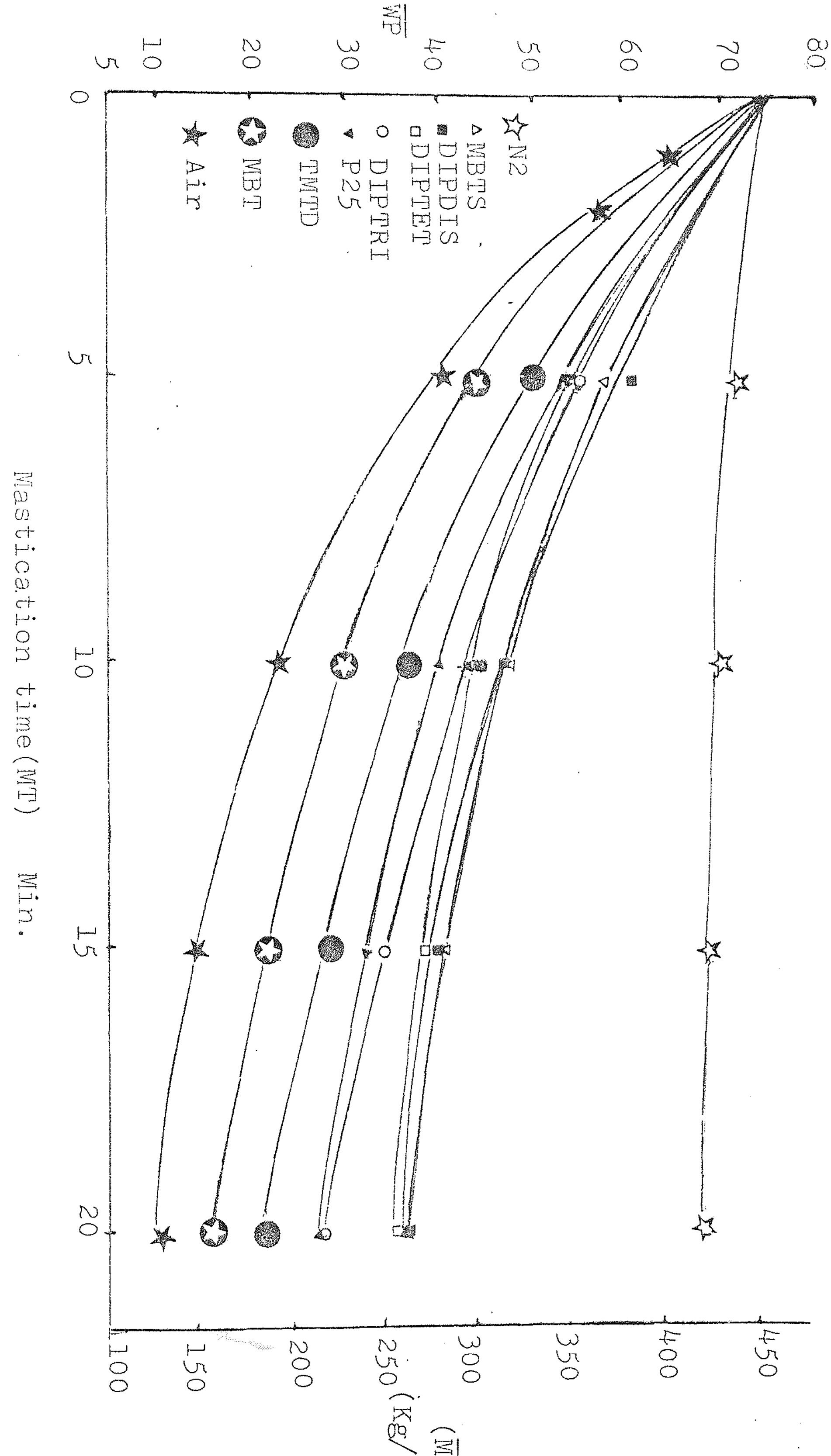
CONDITION	TIME Min	$\overline{W.P}$	$\overline{Mn}$ Kg mole^{-1}	
Air	0	75	450	
"	1	66	405	
"	2	58	365	
"	5	41	280	
"	10	23	190	
"	15	16	155	
"	20	11.5	133	
N2	5	73	440	
"	10	71	430	
"	15	70	425	
"	20	69	420	
MBT in N2	5	45	300	
"	10	31	230	
"	15	22	185	
"	20	18	165	
MBTS in N2	5	59	370	
"	10	48	315	
"	15	42	285	
"	20	37	260	

Cond.

Table (6) Continued:

CONDITION	TIME Min	$\overline{W.P}$	$\overline{Mn}$ Kg mole^{-1}	
TMTD in N2	5	51	330	
"	10	38	265	
"	15	29	220	
"	20	23	190	
P25 in N2	5	54	345	
"	10	41	280	
"	15	33	240	
"	20	28	215	
DIPDIS in N2	5	61	380	
"	10	48	315	
"	15	40.5	273	
"	20	37	260	
DIPTRI in N2	5	55	350	
"	10	45	300	
"	15	35	250	
"	20	29	220	
DIPTET in N2	5	54	345	
"	10	45	300	
"	15	39	270	
"	20	36	255	

Fig.(12):Mastication of extracted NR under N2 in unirotormixer with different radical acceptors.



Table(7):

Mastication efficiency:NO.1,2&3 in unirotor mixer(at 25°C and 40 RPM rotor speed) NO.4&5 in micro two roll mill(at room temperature)

NO.	CONDITION	TIME Min	$\overline{W.P}$	$\overline{M}_n$ Kg mole^{-1}
1	N2	0	75	450
	"	5	73	440
	"	10	71	430
	"	15	70	425
	"	20	69	420
2	TMTD in N2	5	51	330
	"	10	38	265
	"	15	29	220
	"	20	23	190
3	Air in unirotor mixer	1	66	405
	"	2	58	365
	"	5	41	280
	"	10	23	190
	"	15	16	155
	"	20	11	133
4	Air in micro two roll mill	1	64	395
	"	2	57	360
	"	5	42	285
	"	10	27	210
	"	15	15	150
	"	20	9	120
5	TMTD in Air	5	37	260
	"	10	20	175
	"	15	12	135
	"	20	7	110

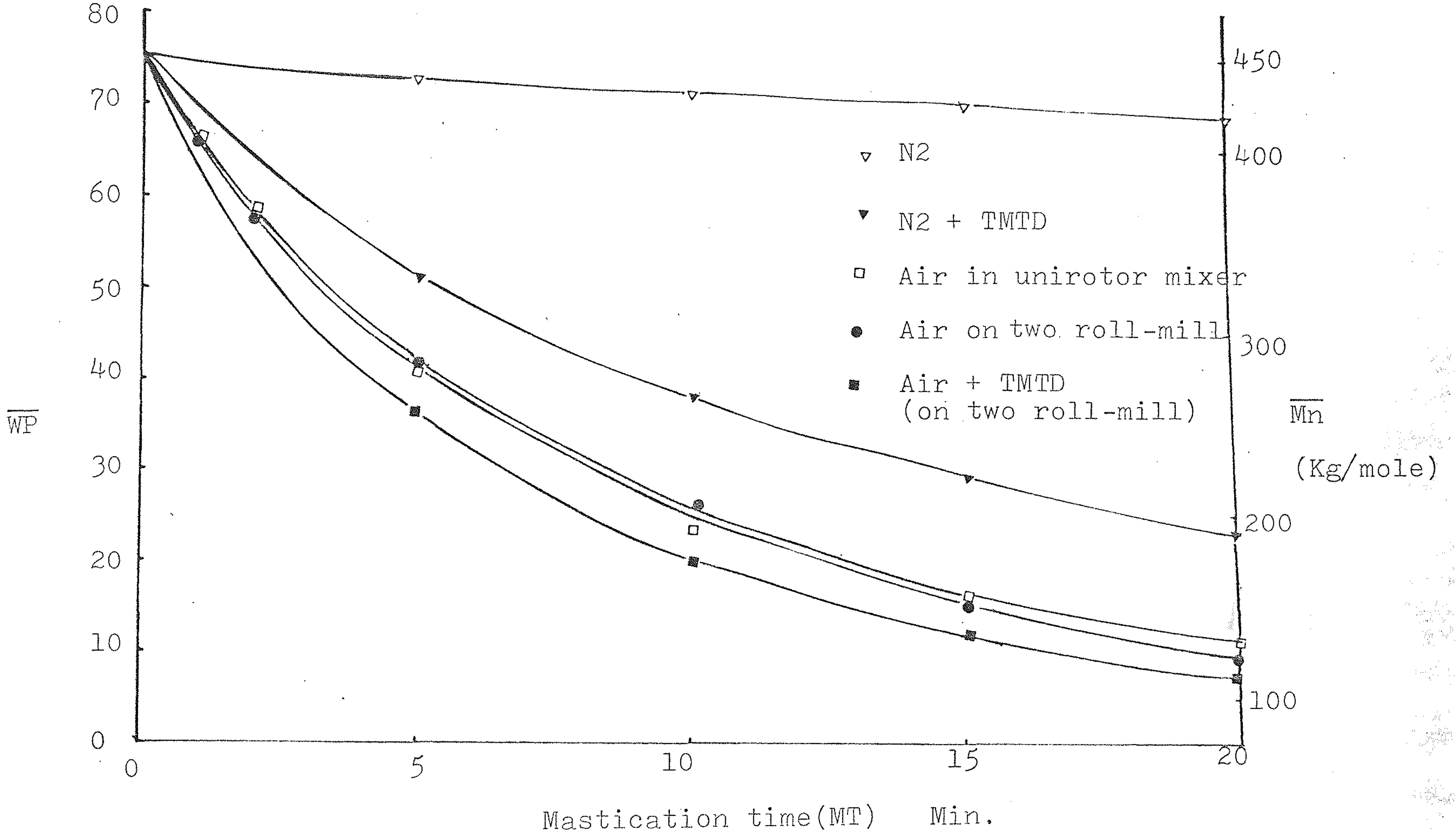


Fig.(13): Mastication efficiency.

Table(8) :

Viscosity measurements at 25°C .

SAMPLE	$\overline{W.P}$	C Gram/100ml	η_{sp}	$[\eta]$	$\overline{M_n}$ Kg mole^{-1}
2C	27	0.304	4.37	2.60	210
		0.457	4.75		
		0.913	7.16		
2C	19.5	0.304	2.90	1.90	160
		0.457	3.25		
		0.913	4.60		
2C	14.5	0.304	2.10	1.50	133
		0.457	2.37		
		0.913	3.18		
2C	9	0.304	1.62	1.13	108
		0.457	1.82		
		0.913	2.56		

Table(9) :

$\overline{Mn}$ values from viscosity measurements .

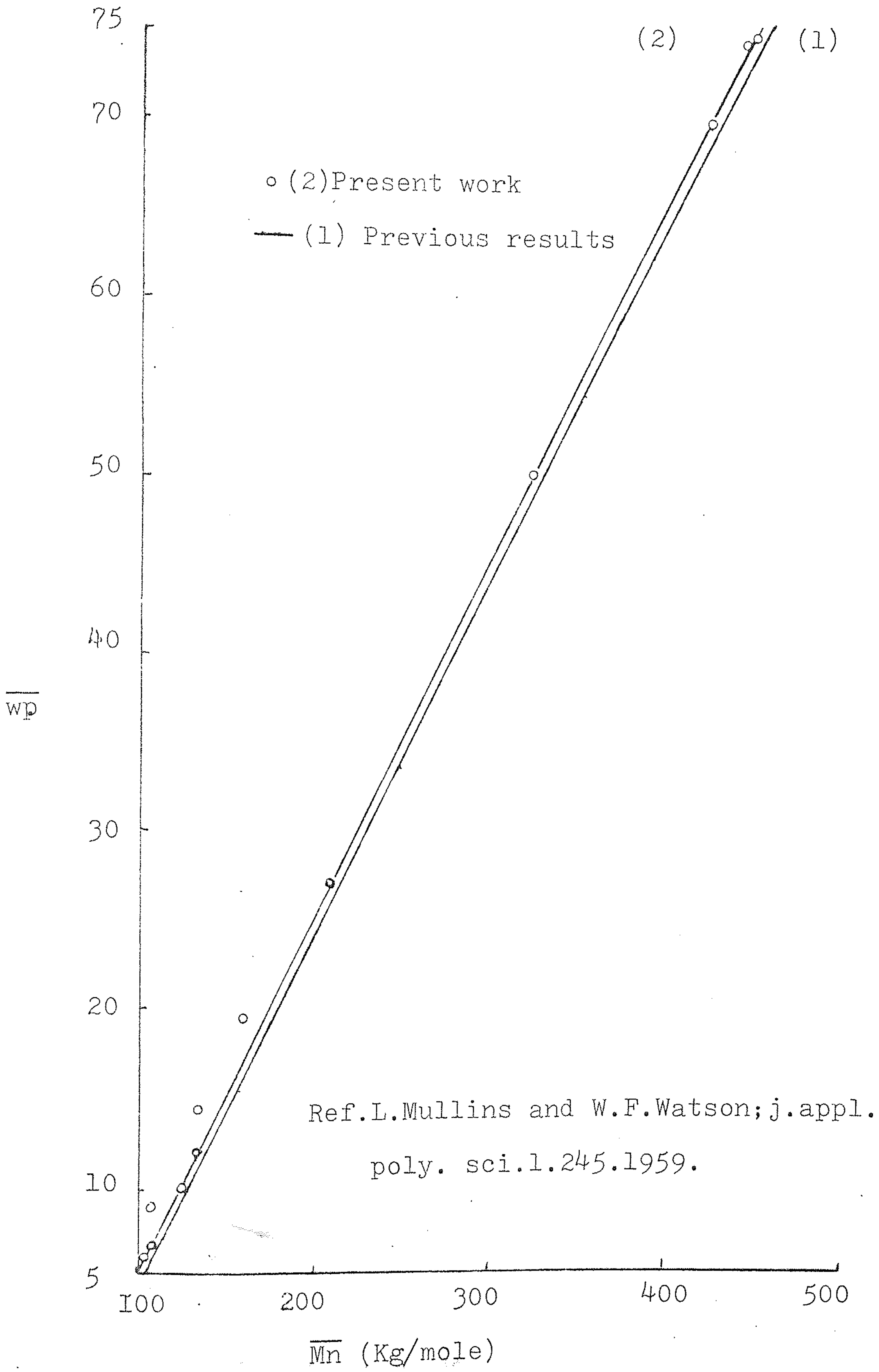
SAMPLE	$\overline{W.P}$	$[\eta]$	$\overline{Mn}$ Kg mole^{-1}
1A	7.5	1.22	114
1A$_+$	11	1.52	135
2B	11.5	1.45	130
2B$_+$	12	1.53	135
2C	10	1.46	131
2C$_+$	12	1.59	139
1D	11	1.51	134
1D$_+$	11	1.51	134
2E	9.5	1.39	126
2E$_+$	10.5	1.47	131
2G	9	1.35	123
2G$_+$	10	1.36	125
2 H	8	1.10	117
2 H$_+$	10	1.46	131
2 M	11	1.52	135
2 M$_+$	12	1.60	140
2 N	7	1.10	110
2 N$_+$	4.5	0.90	91

Cond.

Table(9)Continued:

SAMPLE	$\overline{W.P}$	$[\eta]$	$\bar{M}n$ Kg $mole^{-1}$
2C	10	1.32	121
$2C_+$	10	1.32	121
2C	10	1.35	123
$2C_a$	10	1.32	121
2C	27	2.60	210
2C	19.5	1.90	160
2C	14.5	1.50	133
2C	9	1.13	108

Fig.(14):Wallace plasticity($\overline{wp}$)versus number average molecular weight($\overline{Mn}$)for natural rubber . Verification of previous results.



Ref.L.Mullins and W.F.Watson;j.appl. poly. sci.1.245.1959.

Fig.(15):Specific viscosity(η_{sp})versus concentration (C)for natural rubber formulation 2C at various plasticities.

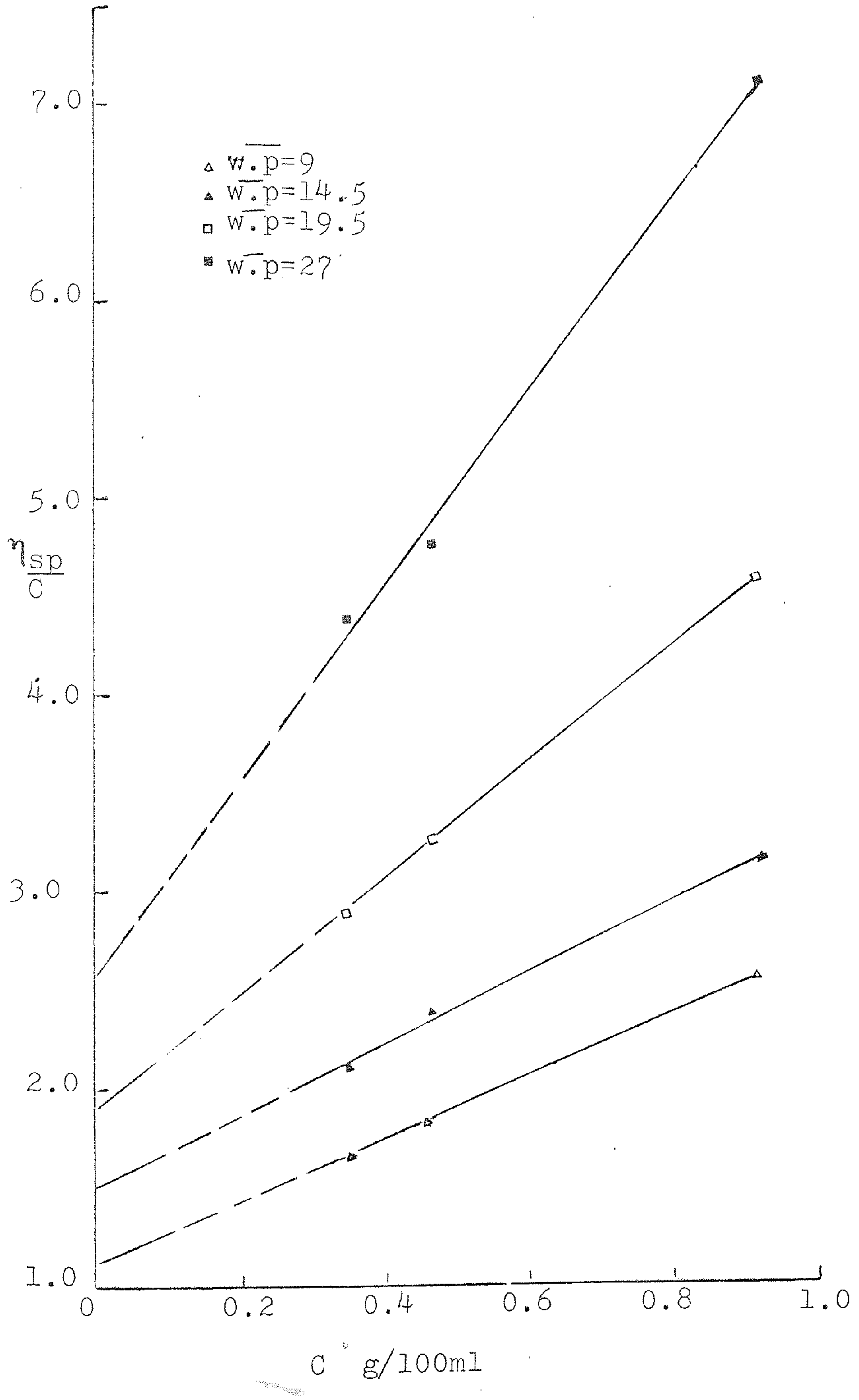
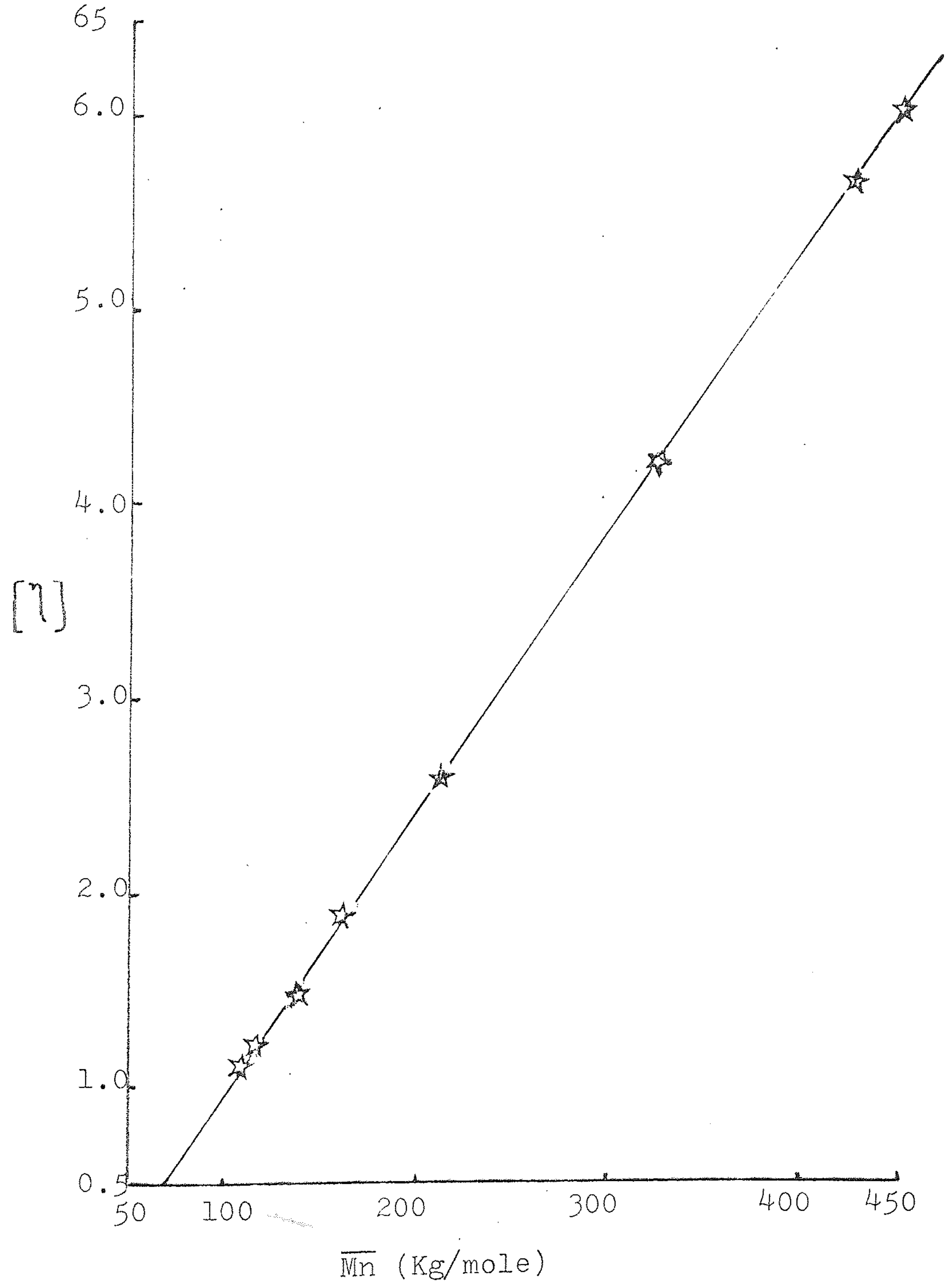


Fig.(16); Intrinsic viscosity[η] versus number average molecular weight($\overline{Mn}$).



Table(10): Comparison of Rmax values for rubbers containig radical acceptor which are added at the mastication stage under nitrogen or at the compoundig stage under air .

RADICAL ACCEPTOR	OPTIMUM CURE TIME AT 140^{oc} (Min)	Rmax (Air)	Rmax (N2)
MBT(1)*	40	31	34
MBTS (2)*	20	59	59
TMTD (2)*	40	31	35
P25 (3)*	15	41	46
DIPDIS(2)*	45	38	40
DIPTET(2)*	30	38	45
DBUDIS (2)*	20	29	35
DBUTRI (2)*	25	45	52
D BUTET (2)*	25	36	51
CBS (1)*	35	38	–

* Number of formulation.

Table(11): Values of Mc_{phys} & Mc_{chem} (Kg $mole^{-1}$) for rubber masticated to an initial molecular weight of $\overline{M}n$=175(Kg $mole^{-1}$) at optimum cure time at 140°C:

SAMPLE	CURE TIME Min	$C_1 \times 10^5$ N m^{-2}	AVERAGE	Mc_{phys} Kg $mole^{-1}$	AVERAGE	Mc_{chem} Kg $mole^{-1}$	AVERAGE
1A	40	1.08		10.49		18.05	
"	"	1.12	1.12	10.19	10.19	17.36	17.36
"	"	1.17		9.98		16.60	
$1A_+$	40	1.22		9.36		18.05	
"	"	1.22	1.22	9.37	9.16	17.36	17.36
"	"	1.30		8.76		16.60	
1B	30	1.02		10.89		19.00	
"	"	1.04	1.02	10.60	10.89	18.51	19.01
"	"	1.00		11.21		19.53	
$1B_+$	30	1.12		10.18		19.00	
"	"	1.17	1.12	10.07	10.18	18.51	19.01
"	"	1.09		10.25		19.53	
1C	11	1.90		6.01		8.40	
"	"	1.88	1.90	6.20	6.01	8.55	8.45
"	"	1.90		6.01		8.41	
$1C_+$	11	1.95		5.85		8.40	
"	"	1.92	1.95	5.92	5.85	8.55	8.45
"	"	1.99		5.75		8.41	

$C1 = F.\Delta h/6A_o.h_o$ N m^{-2}

$C1 = \rho.R.T/2MC_{phys}$ hence MC_{phys}=

$C1 = (\rho.R.T/2MC_{chem} + 0.78\times10^5)(1 - 2.3MC_{chem}/Mn)$ hence MC_{chem}=......

Table(11): Cond.

SAMPLE	CURE TIME Min	C_1x10^5 N m^{-2}	AVERAGE	Mc_{phys} Kg $mole^{-1}$	AVERAGE	Mc_{chem} Kg $mole^{-1}$	AVERAGE
1D	11	1.45		7.81		12.12	
"	"	1.44	1.45	7.92	7.84	12.20	12.12
"	"	1.47		7.61		12.01	
$1D_+$	11	1.57		7.06		12.12	
"	"	1.68	1.57	6.75	7.05	12.20	12.12
"	"	1.46		7.84		12.01	
1E	40	0.55		18.01		34.00	
"	"	0.60	0.59	17.30	17.43	32.51	32.80
"	"	0.63		17.02		32.01	
$1E_+$	40	0.71		16.01		34.00	
"	"	0.68	0.72	16.68	15.86	32.51	32.80
"	"	0.77		15.10		32.01	
1F	40	0.70		15.50		28.50	
"	"	0.72	0.69	15.31	15.60	28.21	28.45
"	"	0.65		16.01		29.02	
$1F_+$	40	0.90		12.62		28.50	
"	"	0.88	0.89	12.74	12.74	28.21	28.45
"	"	0.89		12.88		29.02	

Table(11):Cond.

SAMPLE	CURE TIME Min	$C_1 \times 10^5$ N m^{-2}	AVERAGE	Mc_{phys} Kg $mole^{-1}$	AVERAGE	Mc_{chem} Kg $mole^{-1}$	AVERAGE
1G	40	0.75		15.00		27.00	
"	"	0.70	0.73	15.70	15.30	28.01	27.51
"	"	0.73		15.21		27.51	
$1G_4$	40	1.01		11.32		27.00	
"	"	0.98	0.98	11.60	11.60	28.01	27.51
"	"	0.95		11.91		27.51	

Cond.

Cond.

Table(11): Values of Mc_{phys} & Mc_{chem} for rubber masticated to an initial molecular weight of $\overline{M}n$=128(Kg mole^{-1})at optimum cure time at 140°C . (averaged results)

SAMPLE	CURE TIME Min.	$C_1 \times 10^5$ N m^{-2}	Mc_{phys} Kg mole^{-1}	Mc_{chem} Kg mole^{-1}
1A	30	1.17	9.84	13.80
$1A_+$	30	1.36	8.36	13.80
2B	30	2.59	4.40	5.46
$2B_+$	30	2.82	4.04	5.46
2C	60	1.41	8.12	11.59
$2C_+$	60	1.47	7.77	11.59
1D	12	1.69	6.75	9.28
$1D_+$	12	1.93	5.93	9.28
2E	45	1.63	6.97	9.50
$2E_+$	45	1.69	6.79	9.50
2G	30	3.15	3.62	4.32
$2G_+$	30	3.30	3.46	4.32
2H	30	1.16	9.83	13.94
$2H_+$	30	1.50	7.60	13.94
2M	30	2.16	5.26	6.80
$2M_+$	30	2.42	4.70	6.80
2N	30	2.31	5.51	6.03
$2N_+$	30	2.51	4.54	6.03

Cond.

Cond.

Table(11): Values of Mc_{phys} & Mc_{chem} for rubber masticated to an initial molecular weight of $\bar{M}n=128$(Kg mole^{-1}) at optimum cure time at 140°C . (averaged results)

SAMPLE		CURE TIME Min.	$C_1 \times 10^5$ N m^{-2}		Mc_{phys} Kg mole^{-1}		Mc_{chem} Kg mole^{-1}	
2C	I II III	60	1.36 1.37 1.37	1.37	8.40 8.16 8.30	8.30	12 11.6 11.82	11.88
$2C_+$	I II III	60	1.42 1.41 1.40	1.41	8.05 8.05 8.06	8.05	12 11.60 11.82	11.88
2E	I II III	45	1.62 1.63 1.60	1.62	7.05 7.00 7.14	7.05	9.63 9.50 9.72	9.63
$2E_+$	I II III	45	1.70 1.70 1.71	1.70	6.68 6.69 6.67	6.68	9.63 9.50 9.72	9.63
$3C_a$	I II	60	1.37 1.37	1.37	8.28 8.36	8.32	11.60 11.72	11.66
3C	I II	60	1.44 1.45	1.44	7.94 7.87	7.91	10.96 10.99	11.07
$3C_n$	I II	60	1.51 1.49	1.50	7.51 7.63	7.57	10.52 10.62	10.57

Cond.

Table(12): Values of ν_r, M_{phys} and χ for rubber masticated to an initial molecular weight of $\bar{M}_n$=175(kg mole^{-1})at optimum cure time at 140°C . (averaged results)

SAMPLE	CURE TIME Min	M_{phys} Kg mole^{-1}	ν_r	χ	AVERAGED χ
1A	40	10.19	0.285	0.545	0.550
$1A_+$	40	9.16	0.300	0.555	
1B	30	10.89	0.275	0.551	0.551
$1B_+$	30	10.18	0.291	0.552	
1C	11	6.01	0.340	0.572	0.571
$1C_+$	11	5.85	0.347	0.570	
1D	11	7.48	0.330	0.570	0.569
$1D_+$	11	7.05	0.334	0.568	
1E	40	17.43	0.262	0.572	0.569
$1E_+$	40	15.68	0.280	0.567	
1F	40	15.60	0.269	0.569	0.567
$1F_+$	40	12.74	0.289	0.564	
1G	40	15.30	0.274	0.561	0.561
$1G_+$	40	11.60	0.285	0.561	

Cond.

Cond.

Table(12): Values of ν_r,$M_{c\,phys}$ and χ for rubber masticated to an initial molecular weight of $\bar{M}n$=128(Kg mole^{-1}) at optimum cure time at 140°C . (averaged results)

SAMPLE	CURE TIME Min	$M_{c\,phys}$ Kg mole^{-1}	ν_r	χ	AVERAGED χ
1A	30	9.84	0.285	0.548	0.548
1A$_+$	30	8.36	0.290	0.548	
2B	30	4.40	0.381	0.589	0.589
2B$_+$	30	4.04	0.397	0.589	
2C	60	8.12	0.267	0.509	0.510
2C$_+$	60	7.77	0.273	0.510	
1D	12	6.75	0.333	0.569	0.570
1D$_+$	12	5.93	0.350	0.570	
2E	45	6.97	0.302	0.532	0.533
2E$_+$	45	6.79	0.305	0.533	
2G	30	3.62	0.375	0.548	0.560
2G$_+$	30	3.46	0.398	0.569	
2H	30	9.83	0.264	0.521	0.525
2H$_+$	30	7.60	0.292	0.529	
2M	30	5.26	0.332	0.545	0.553
2M$_+$	30	4.70	0.366	0.561	
2N	30	5.51	0.335	0.557	0.560
2N$_+$	30	4.54	0.366	0.563	

Cond.

Cond.

Table (12): Values of ν_r, Mc_{phys} and χ for rubber masticated to an initial molecular weight of $\overline{M}n$=128(Kg mole^{-1}) at optimum cure time at 140°C . (averaged results)

SAMPLE		CURE TIME Min.	Mc_{phys} Kg mole^{-1}		ν_r		χ		χ AVERAGED
2C	I	60	8.40	8.30	0.262	0.260	0.513	0.513	0.506
	II		8.15		0.259		0.514		
	III		8.30		0.258		0.511		
$2C_+$	I	60	8.05	8.05	0.273	0.272	0.498	0.496	
	II		8.05		0.272		0.496		
	III		8.06		0.271		0.494		
2E	I	45	7.05	7.05	0.302	0.302	0.532	0.533	0.533
	II		7.00		0.302		0.533		
	III		7.14		0.301		0.535		
$2E_+$	I	45	6.68	6.68	0.304	0.305	0.531	0.533	
	II		6.69		0.305		0.538		
	III		6.67		0.306		0.532		
$3C_a$	I	60	8.28	8.32	0.266	0.265	0.507	0.506	0.504
	II		8.36		0.267		0.505		
3C	I	60	7.94	7.91	0.271	0.267	0.510	0.506	
	II		7.87		0.262		0.502		
$3C_n$	I	60	7.51	7.57	0.267	0.272	0.497	0.499	
	II		7.61		0.277		0.501		

Table(13): %of chain ends combined in rubber masticated with and without vulcanisable free radical acceptor .

SAMPLE	$C_{1or} \times 10^5$ N m^{-2}	$C_{1mod} \times 10^5$ N m^{-2}	$M_{c\,chem}$ Kg mole^{-1}	$\bar{M}n$, Kg mole^{-1}	C_{1or}/C_{1mod}	$\bar{M}n'$ Kg mole^{-1}	%C.E.C
1A $1A_+$	1.12	1.22	17.36	175	0.92	251	30.28
1B $1B_+$	1.02	1.12	19.01	175	0.91	248	29.43
1C $1C_+$	1.90	1.95	8.45	175	0.97	222	21.17
1D $1D_+$	1.45	1.57	12.12	175	0.92	311	43.73
1E $1E_+$	0.59	0.72	32.80	175	0.82	239	26.78
1F $1F_+$	0.69	0.89	28.45	175	0.77	320	45.31
1G $1G_+$	0.73	0.98	27,51	175	0.75	443	60.50

Cond.

Table(13): % of chain ends combined in rubber masticated with and without vulcanisable free radical acceptor .

SAMPLE	$C_{1or} \times 10^5$ N m^{-2}	$C_{1mod} \times 10^5$ N m^{-2}	$M_{c\,chem}$ Kg $mole^{-1}$	$\bar{M}n$ Kg $mole^{-1}$	C_{1or}/C_{1mod}	$\bar{M}n'$ Kg $mole^{-1}$	%C.E.C
1A $1A_+$	1.17	1.36	13.80	128	0.86	278	53.96
2B $2B_+$	2.95	2.82	5.46	128	0.92	693	81.53
2C $2C_+$	1.41	1.47	11.59	128	0.96	163	21.47
1D $1D_+$	1.69	1.93	9.28	128	0.87	441	70.97
2E $2E_+$	1.63	1.69	9.50	128	0.96	156	18.99
2G $2G_+$	3.15	3.30	4.32	128	0.95	296	56.76
2H $2H_+$	1.16	1.50	13.94	128	0.77	588	78.23
2M $2M_+$	2.16	2.42	6.80	128	0.89	1240	89.68
2N $2N_+$	2.31	2.51	6.03	128	0.92	446	71.30

Table (13): %of chain ends combined in rubber masticated with and without vulcanisable free radical acceptor .

SAMPLE	$C_{1or} \times 10^5$ N m^{-2}	$C_{1mod} \times 10^5$ N m^{-2}	Mc_{chem} Kg $mole^{-1}$	$\bar{M}n$ Kg $mole^{-1}$	C_{1or}/C_{1mod}	m $\bar{M}n'$ Kg $mole^{-1}$	%C.E.C
2C $2C_+$	1.37	1.41	11.82	128	0.97	149	14.1
2E $2E_+$	1.62	1.70	9.63	128	0.95	168	23.81
$3C_a$ 3C $3C_n$	1.44 1.44	1.37 1.50	11.07 11.07	128 128	1.05 0.96	103 145	-24.27 15.86

Table(14): Variation of C_1, Mc_{phys} ,Mc_{chem} , νr and χ with different molecular weight at optimum cure time at 140°C .

SAMPLE	$\bar{Mn}$ Kg $mole^{-1}$	C_1 x10^5 N m^{-2}	Mc_{phys} Kg $mole^{-1}$	Mc_{chem} Kg $mole^{-1}$	νr	AVERAGED χ
2C	210	1.62	7.02	10.69	0.284	0.506
2C	160	1.54	7.39	10.87	0.280	
2C	133	1.47	7.73	10.98	0.275	
2C	108	1.42	8.04	10.74	0.261	

Table (15): Values of ν_r, Mc_{phys}, Mc_{chem}, C_1 , $\bar{M}n'$ and %C.E.C for rubber masticated to an initial molecular weight of $\bar{M}n$=128 (Kg mole^{-1}) at different cure times at 140°C .

SAMPLE	CURE TIME Min.	ν_r	Mc_{phys} Kg mole^{-1}	$C_1 \times 10^5$ N m^{-2}	Mc_{chem} Kg mole^{-1}	$\bar{M}n'$ Kg mole^{-1}	% C.E.C
$1A_a$	20	0.249	18.02	0.64	26.67	132	3.03
1A	20	0.249	18.08	0.63	26.56		
$1A_a$	30	0.264	14.05	0.81	21.52	123	-4.06
1A	30	0.267	13.69	0.83	21.61		
$1A_a$	40	0.274	11.22	0.93	18.57	120	-6.66
1A	40	0.275	11.90	0.96	17.97		
$1A_a$	60	0.281	11.13	1.02	16.52	116	-10.34
1A	60	0.282	10.86	1.05	16.30		
$3E_a$	25	0.294	7.80	1.46	10.97	121	-5.78
3E	25	0.295	7.68	1.48	10.75		
$3E_a$	30	0.296	7.61	1.49	10.63	101	-26.73
3E	30	0.297	7.22	1.58	9.98		
$3E_a$	40	0.298	7.35	1.55	10.20	94	-36.17
3E	40	0.306	6.66	1.71	9.03		
$3E_a$	60	0.297	7.48	1.52	10.43	86	-48.83
3E	60	0.302	6.97	1.64	9.46		

Cond.

Cond.

Table(15): Values of ν_r, Mc_{phys}, Mc_{chem}, C_1, $\bar{M}n'$ and % C.E.C for rubber masticated to an initial molecular weight of $\bar{M}n$=128(Kg mole^{-1}) at different cure times at 140°C .

SAMPLE	CURE TIME Min.	ν_r	Mc_{phys} Kg mole^{-1}	$C_1 \times 10^5$ N m^{-2}	Mc_{chem} Kg mole^{-1}	$\bar{M}n'$ Kg mole^{-1}	% C.E.C
$3E_a$	20	0.251	13.31	0.86	20.13	125	-2.40
3E	20	0.252	13.10	0.87	19.87	136	6.21
$3E_n$	20	0.257	12.70	0.90	19.87		
$3E_a$	23	0.272	10.05	1.13	14.86	125	-2.40
3E	23	0.274	9.99	1.14	14.76	138	7.29
$3E_n$	23	0.276	9.73	1.17	14.76		
$3E_a$	26	0.285	8.64	1.32	12.42	128	0.0
3E	26	0.285	8.60	1.32	12.35	168	23.91
$3E_n$	26	0.290	8.40	1.41	12.35		
$3E_a$	50	0.300	7.18	1.59	9.90	128	0.0
3E	50	0.300	7.19	1.59	9.92	196	34.79
$3E_n$	50	0.306	6.66	1.71	9.92		
1A	10	0.261	14.79	0.77	22.57	165	22.42
$1A_+$	10	0.270	12.79	0.88	22.57		
1A	15	0.280	11.16	1.02	16.77	167	23.35
$1A_+$	15	0.287	10.13	1.12	16.77		
1A	20	0.279	11.36	1.00	17.10	168	23.81
$1A_+$	20	0.285	10.46	1.09	17.10		
1A	30	0.271	12.70	0.90	19.25	171	25.15
$1A_+$	30	0.279	11.21	1.01	19.25		

Cond.

Table (15): Values of ν_r ,Mc_{phys}, Mc_{chem},C_1,$\overline{M}n'$ and % C.E.C for rubber masticated to an initial molecular weight of $\overline{M}n$=128(Kg $mole^{-1}$) at different cure times at 140°C

SAMPLE	CURE TIME Min.	ν_r	Mc_{phys} Kg $mole^{-1}$	$C_1 \times 10^5$ N m^{-2}	Mc_{chem} Kg $mole^{-1}$	$\overline{M}n'$ Kg $mole^{-1}$	% C.E.C
3C	12	0.217	12.30	0.93	18.65	154	16.88
$3C_n$	12	0.225	11.43	0.99	18.65		
3C	25	0.259	9.35	1.19	13.95	254	47.97
$3C_n$	25	0.266	8.24	1.38	13.95		
3C	40	0.260	8.41	1.34	12.20	246	49.61
$3C_n$	40	0.267	7.57	1.51	12.20		
3C	120	0.251	8.15	1.40	11.61	207	38.16
$3C_n$	120	0.264	7.44	1.53	11.61		
3D	3	0.256	25.45	0.45	33.44	134	4.48
$3D_n$	3	0.260	24.48	0.48	33.44		
3D	4	0.288	14.18	0.80	21.53	164	21.95
$3D_n$	4	0.295	12.50	0.91	21.53		
3D	5	0.295	12.58	0.91	20.00	181	29.28
$3D_n$	5	0.304	10.98	1.04	20.00		
3D	15	0.299	11.93	0.96	17.99	196	32.98
$3D_n$	15	0.309	10.15	1.12	17.99		

Cond.

Cond.

Table(15): Values of ν_r, Mc_{phys}, Mc_{chem}, C_1, $\bar{M}n'$ and % C.E.C for rubber masticated to an initial molecular weight of $\bar{M}n$=128(Kg mole^{-1}) at different cure times at 140°C .

SAMPLE	CURE TIME Min.	ν_r	Mc_{phys} Kg mole^{-1}	$C_1 \times 10^5$ N m^{-2}	Mc_{chem} Kg mole^{-1}	$\bar{M}n'$ Kg mole^{-1}	% C.E.C
3E	20	0.273	10.09	1.13	14.93	137	6.57
$3E_n$	20	0.275	9.80	1.16	14.93		
3E	23	0.275	9.86	1.16	14.53	138	7.25
$3E_n$	23	0.277	9.60	1.19	14.53		
3E	26	0.271	10.43	1.10	15.36	182	29.67
$3E_n$	26	0.281	9.15	1.24	15.36		
3E	50	0.273	10.03	1.13	14.82	179	28.49
$3E_n$	50	0.280	9.23	1.24	14.82		
3G	10	0.260	18.94	0.60	27.49	136	5.88
$3G_n$	10	0.264	17.36	0.65	27.49		
3G	12	0.285	12.42	0.92	18.68	140	8.57
$3G_n$	12	0.288	11.88	0.96	18.68		
3G	15	0.296	10.57	1.08	15.57	192	33.33
$3G_n$	15	0.304	9.34	1.22	15.57		
3G	30	0.296	10.48	1.09	15.60	210	39.05
$3G_n$	30	0.306	9.11	1.25	15.60		

Cond.

Cond.

Table(15): Values of V_r, Mc_{phys}, Mc_{chem}, C_1, $\bar{M}n'$ and % C.E.C for rubber masticated to an initial molecular weight of $\bar{M}n$=100(Kg mole^{-1}) at different cure times at 140°C .

SAMPLE	CURE TIME Min.	V_r	Mc_{phys} Kg mole^{-1}	$C_1 \times 10^5$ N m^{-2}	Mc_{chem} Kg mole^{-1}	$\bar{M}n'$ Kg mole^{-1}	% C.E.C
3E	20	0.252	13.54	0.84	20.56	549	81.78
$3E_n$	20	0.293	7.80	1.46	20.56		
3E	23	0.253	13.28	0.86	20.16	837	88.05
$3E_n$	23	0.296	7.54	1.51	20.16		
3E	26	0.256	12.72	0.89	19.29	1072	90.67
$3E_n$	26	0.297	7.38	1.54	19.29		
3E	50	0.256	12.73	0.90	19.30	2364	95.77
$3E_n$	50	0.299	7.23	1.58	19.30		

Fig.(17): Variation of $\overline{M}n'$ with cure time for formulation with MBT(1A & $1A_+$)

$\overline{M}n$=128

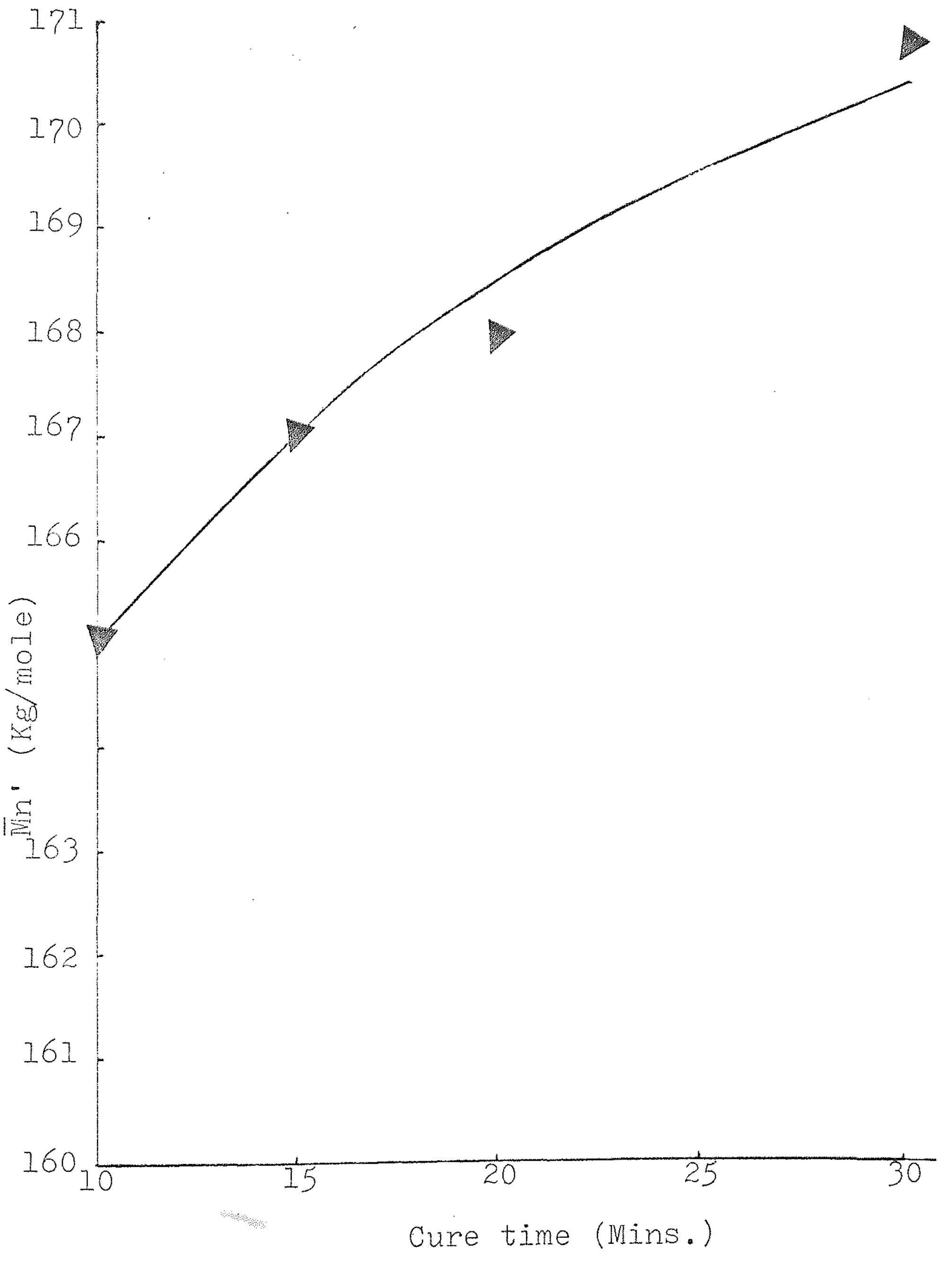


Fig.(18): Percentage of chain ends combined versus cure time for formulation with MBT(1A &1A_+) .

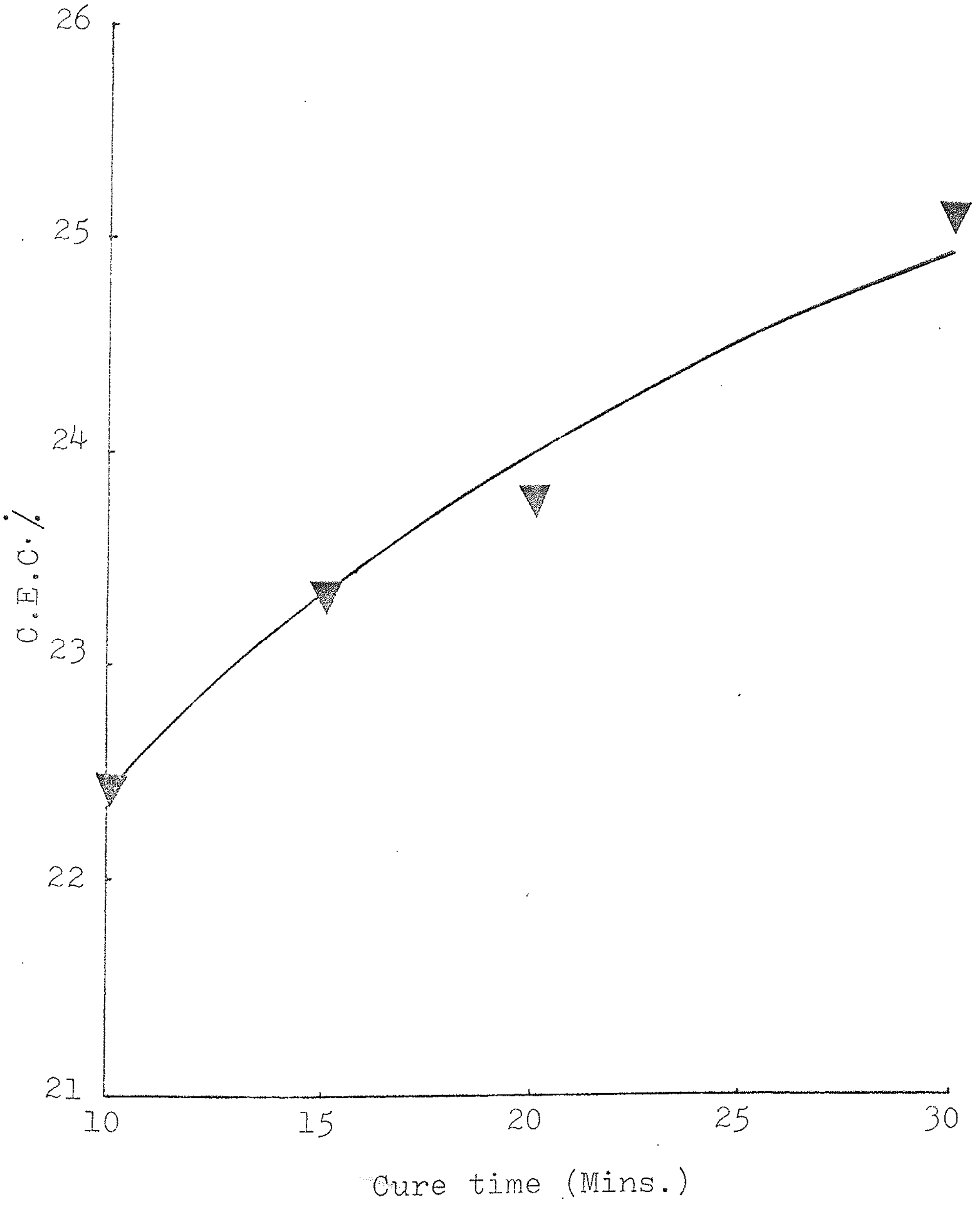


Fig.(19): Variation of $\overline{M}n'$ with cure time for formulation with TMTD (3C &3C$_n$) .

$\overline{M}n=128$

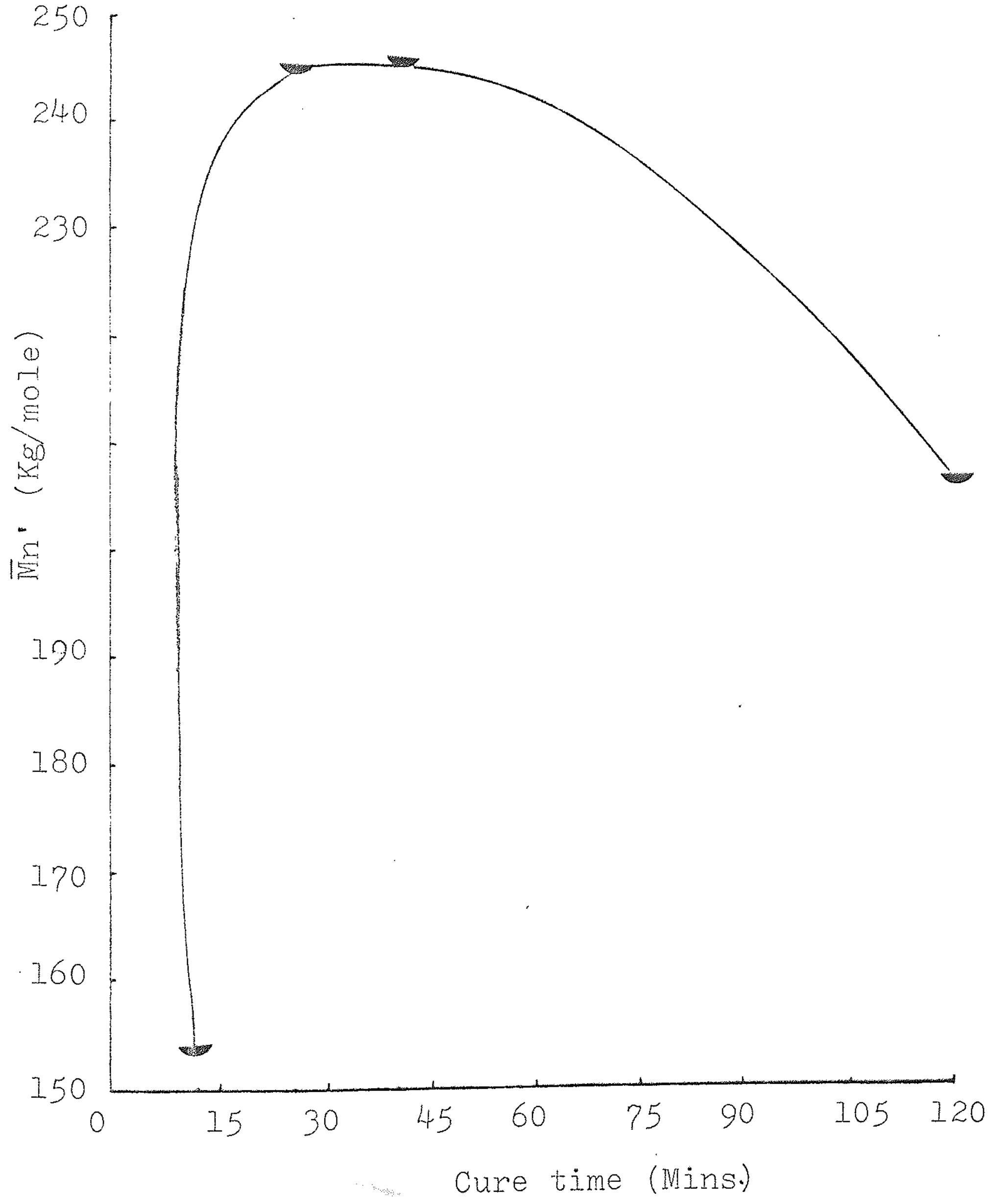


Fig.(20):Percentage of chain ends combined versus cure time for formulation with TMTD(3C & $3C_n$) . $\overline{M}n=128$

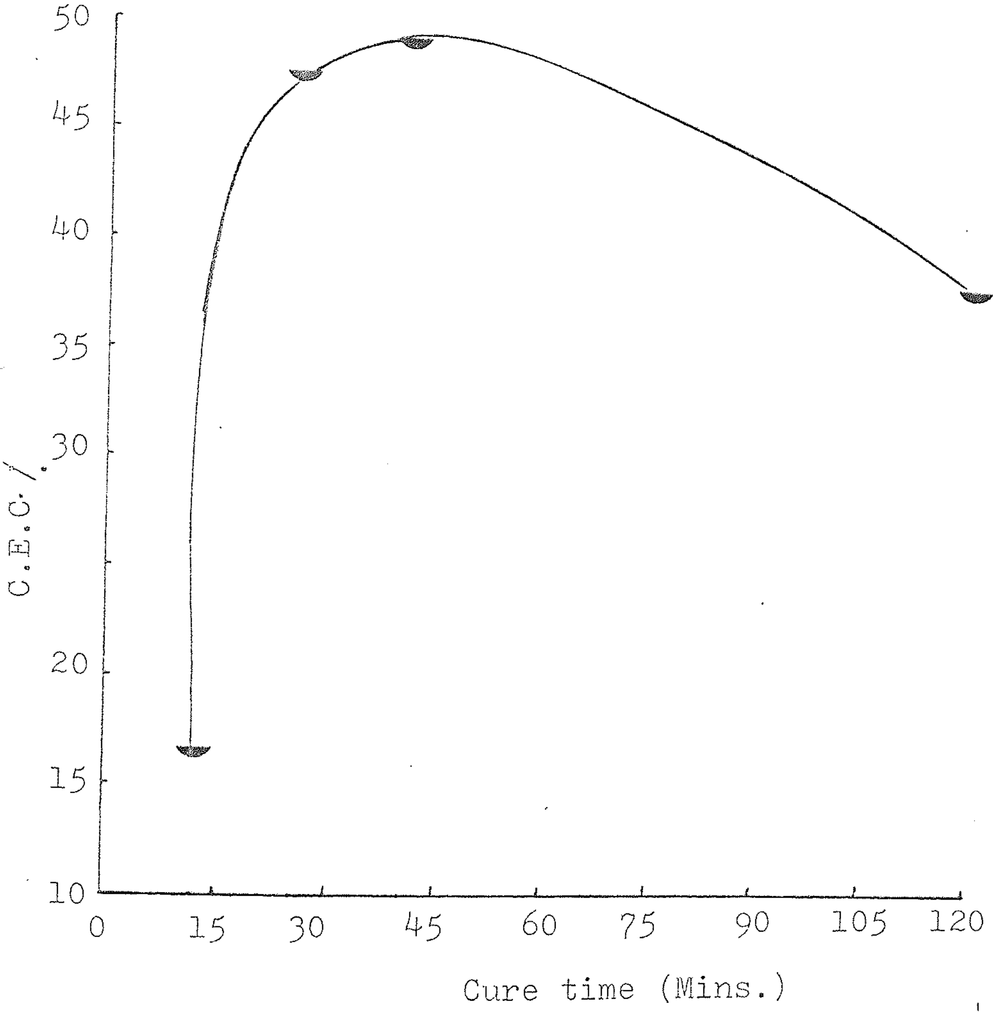


Fig.(21):Variation of $\overline{M}n'$ against cure time for formulation with P25 (3D & $3D_n$) .

$\overline{M}n=128$

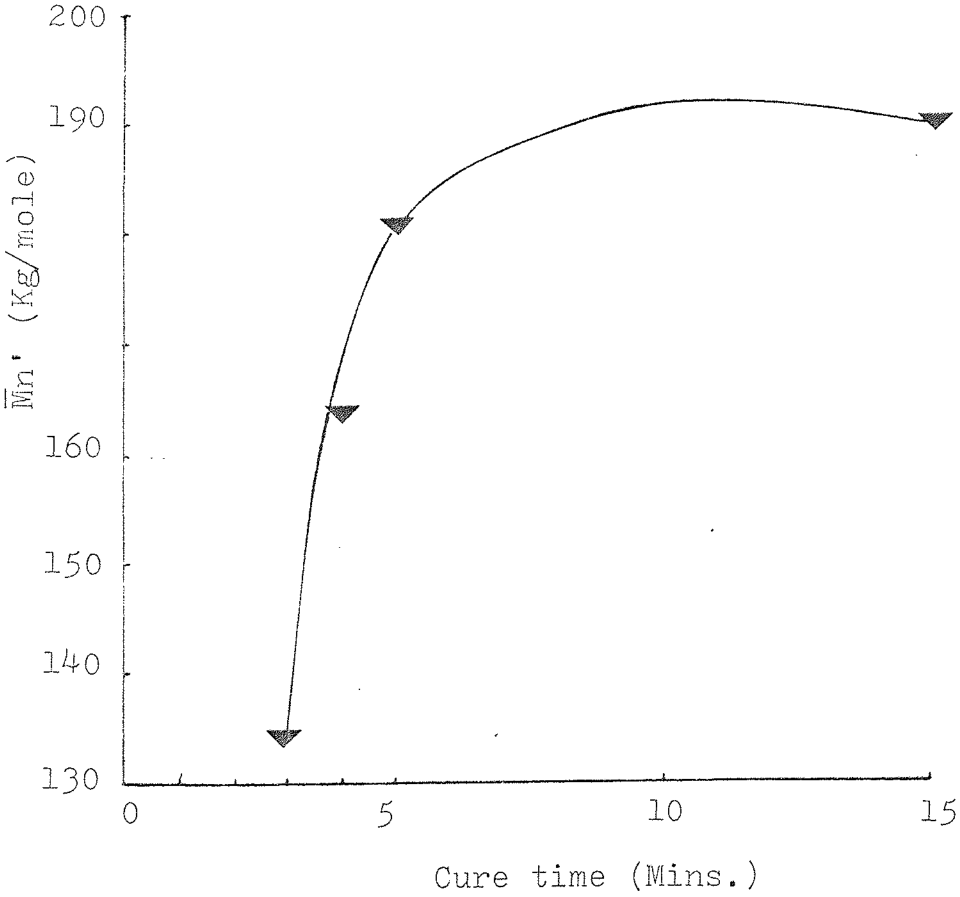


Fig.(22):Percentage of chain ends combined versus cure time for formulation with P25(3D &$3D_n$).

$\overline{M}n=128$

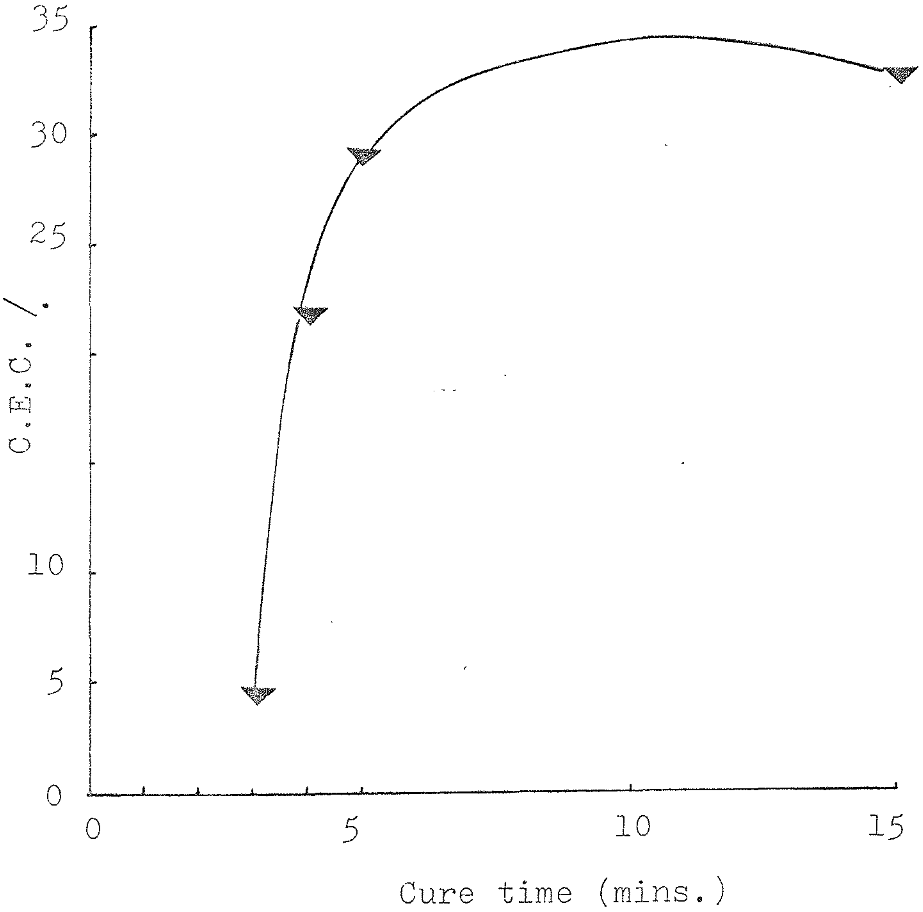


Fig.(23): Variation of $\overline{M}n'$ against cure time for formulation with DIPDIS(3E &$3E_n$).

$\overline{M}n$=128

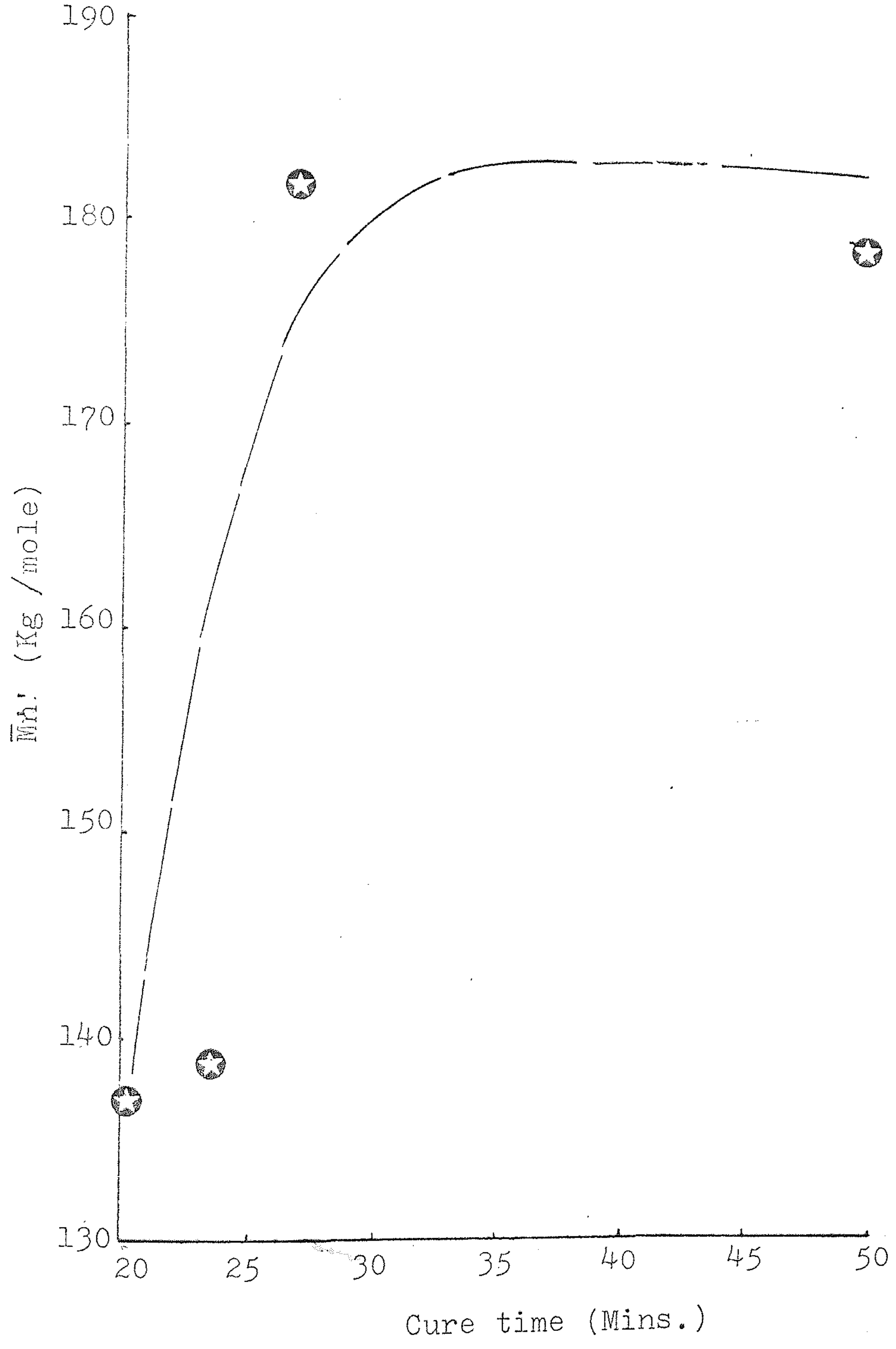


Fig.(24): Percentage of chain ends combined versus cure time for formulation with DIPDIS (3E & $3E_n$).

$\overline{M}n$=128

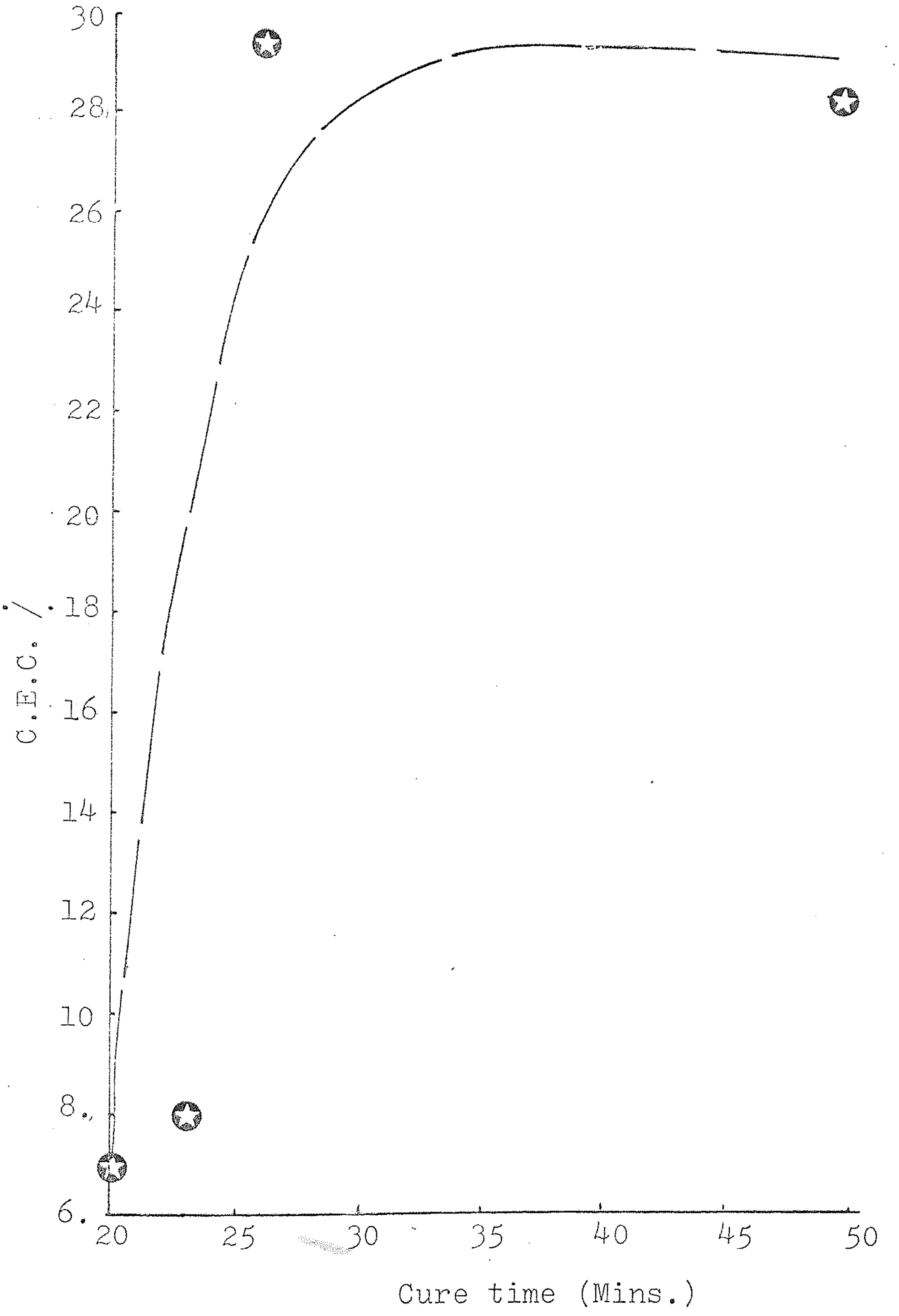


Fig.(25):Variation of $\overline{M}n'$ against cure time for formulation with DIPTET(3G & $3G_n$) .

$\overline{M}n=128$

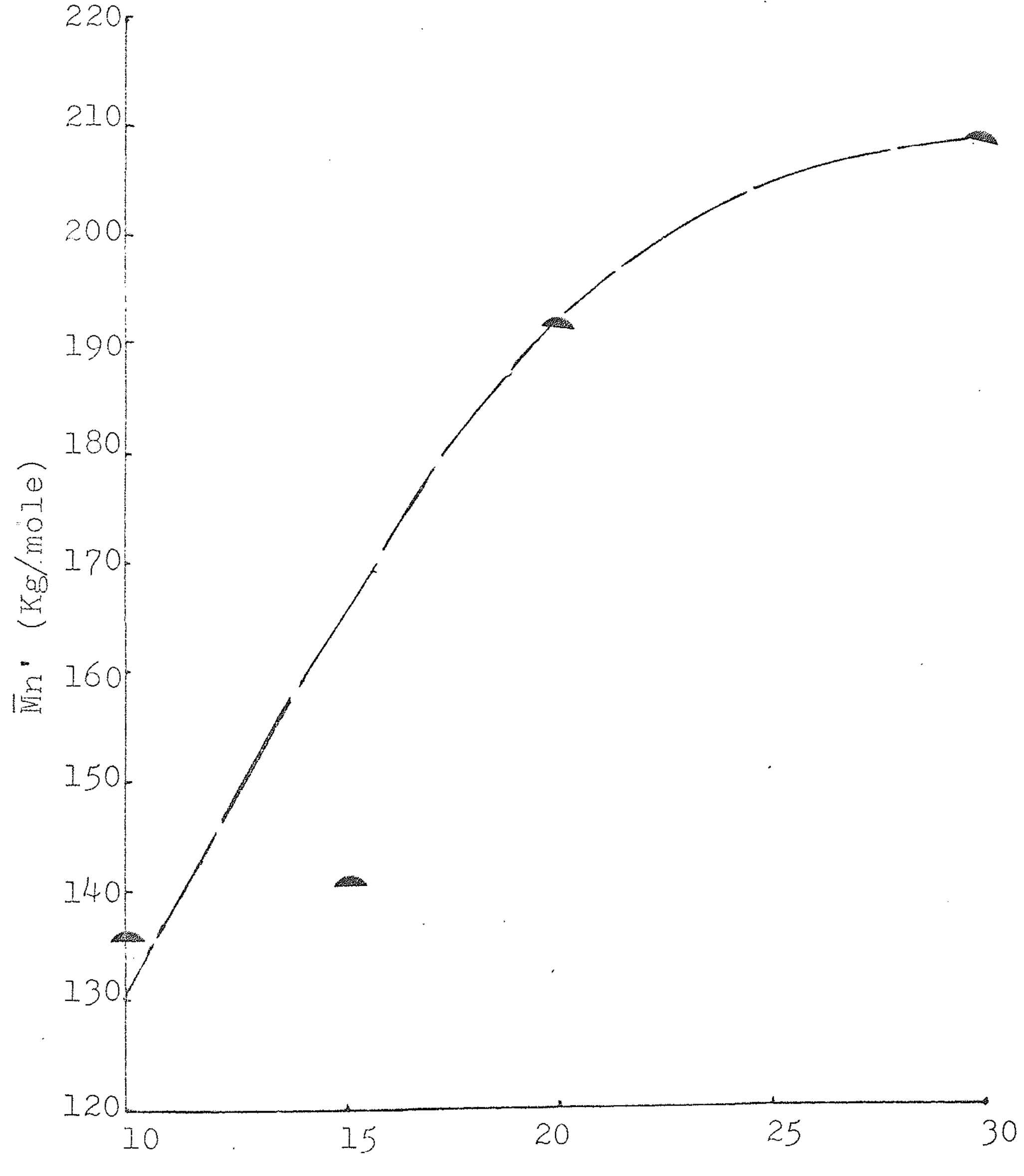


Fig.(26): Percentage of chain ends combined versus cure time for formulation with DIPTET($3G$ & $3G_n$) .
$\overline{M}n=128$

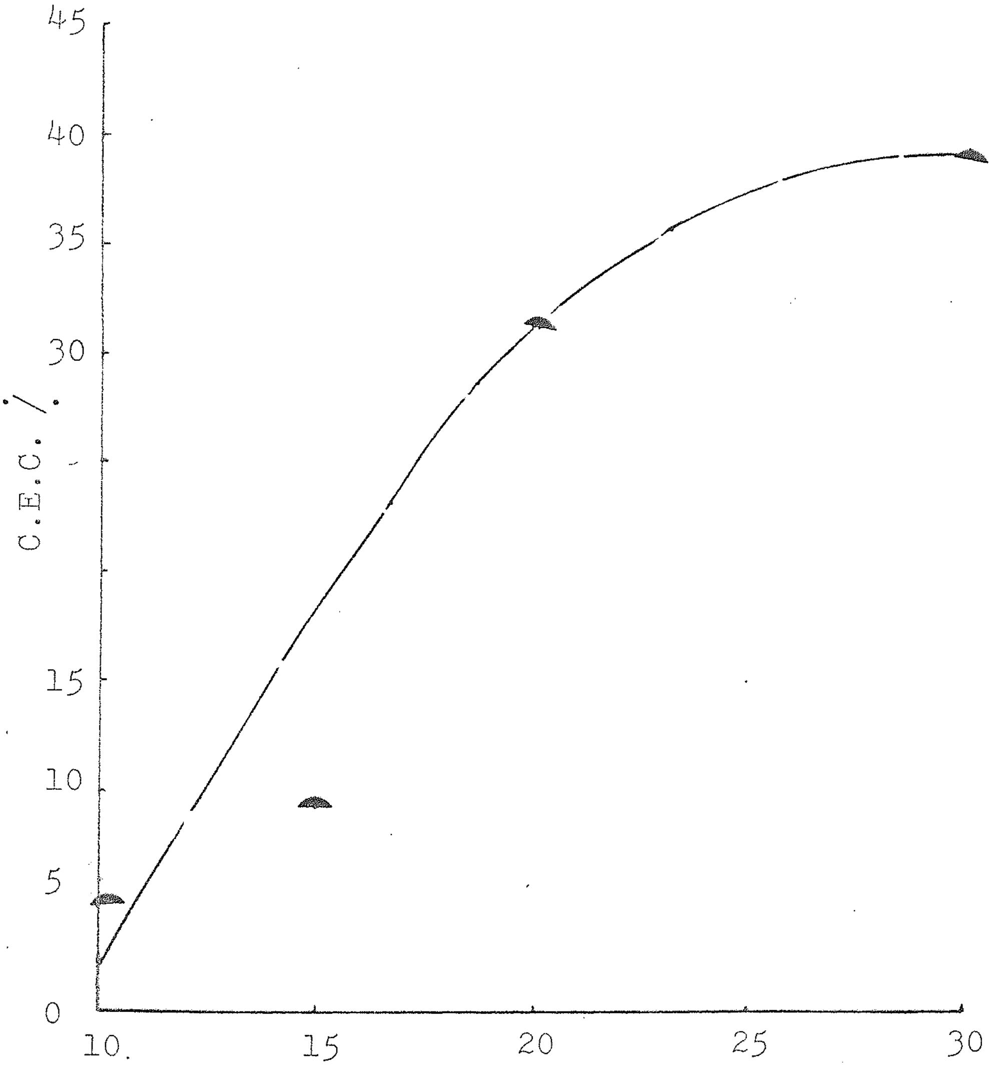


Fig.(27): Variation of $\overline{M}n'$ versus cure time for formulation with DIPDIS (3E &3E_n) .

$\overline{M}n$=100

(Repeat of experiment for prolonged mastication time)

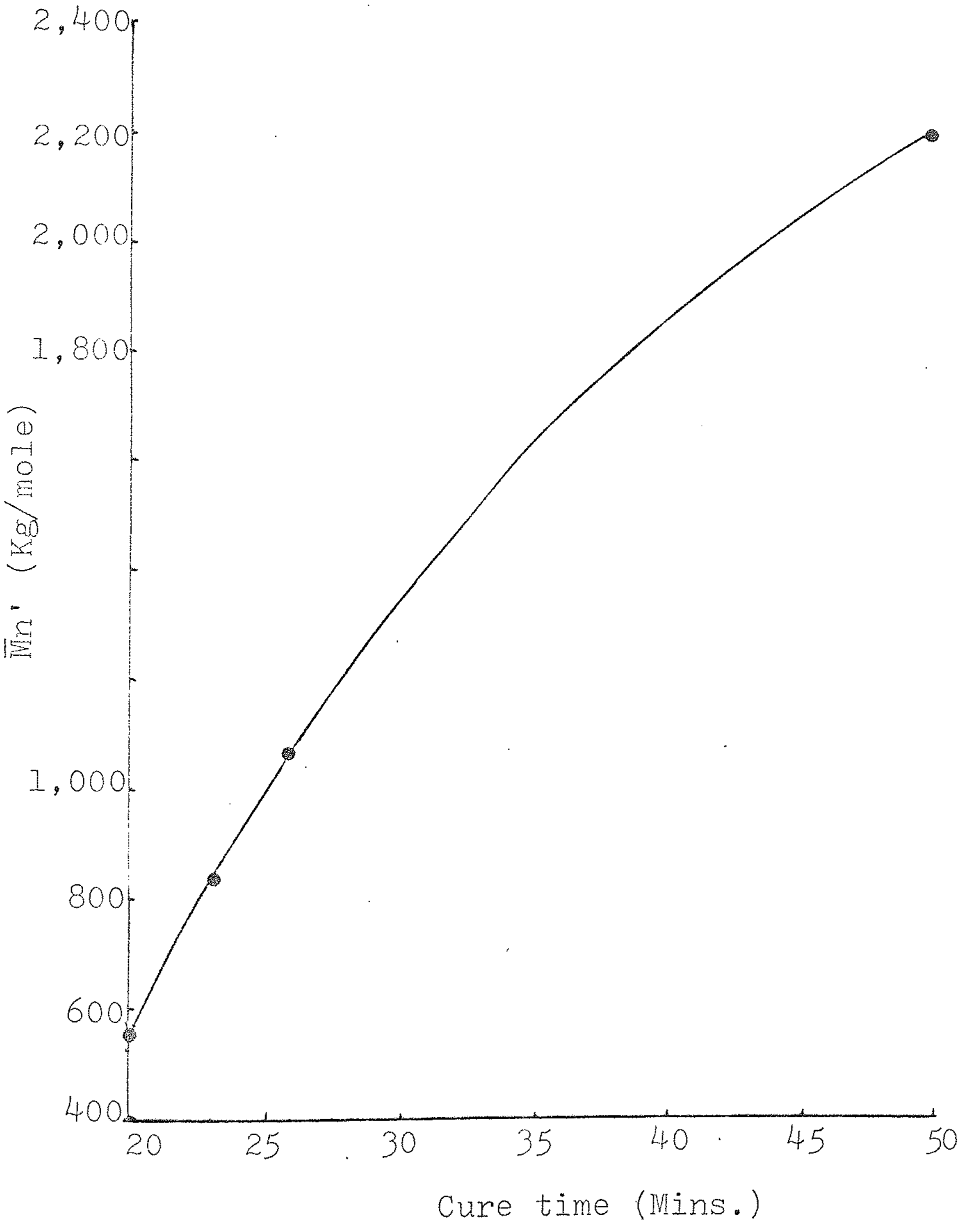


Fig.(28): Percentage of chain ends combined versus cure time for formulatiom with DIPDIS ($3E$ & $3E_n$) . $\overline{M}n=100$

(Repeat of experiment for prolonged mastication time)

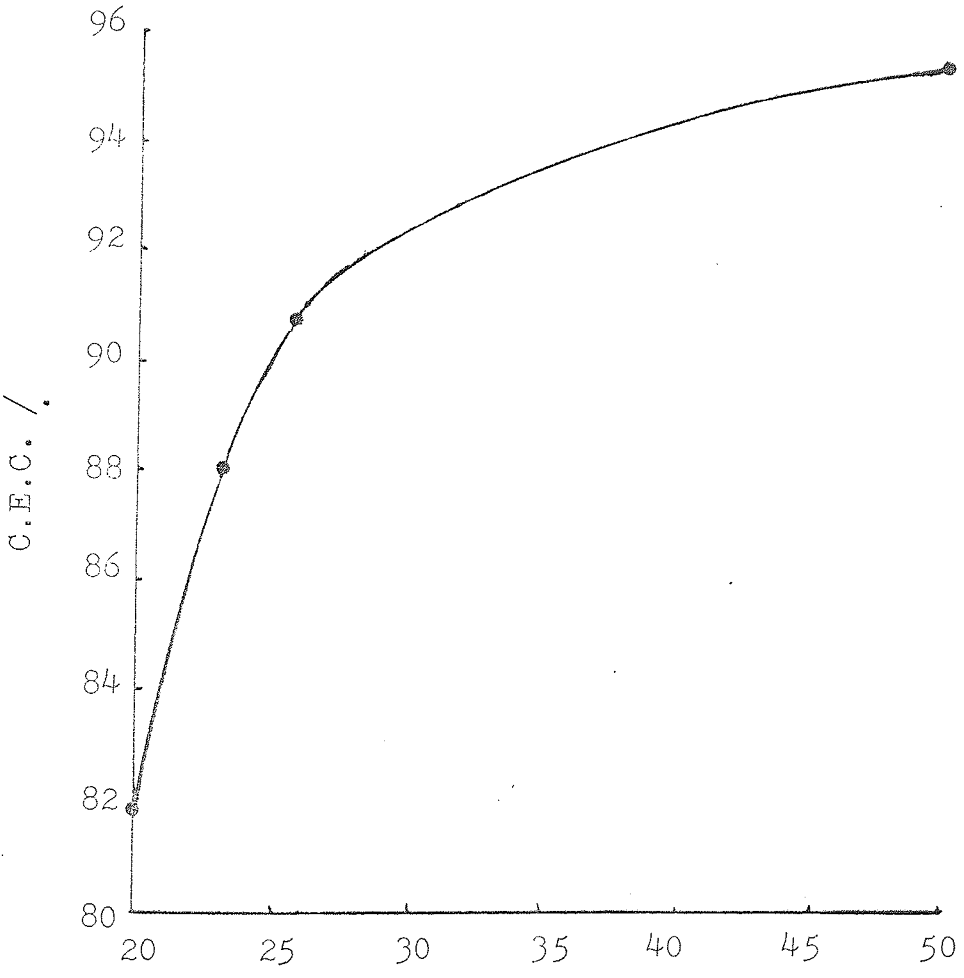


Fig.(29): Variation of $\overline{M}n'$ versus percentage of chain ends combined (C.E.C.%).

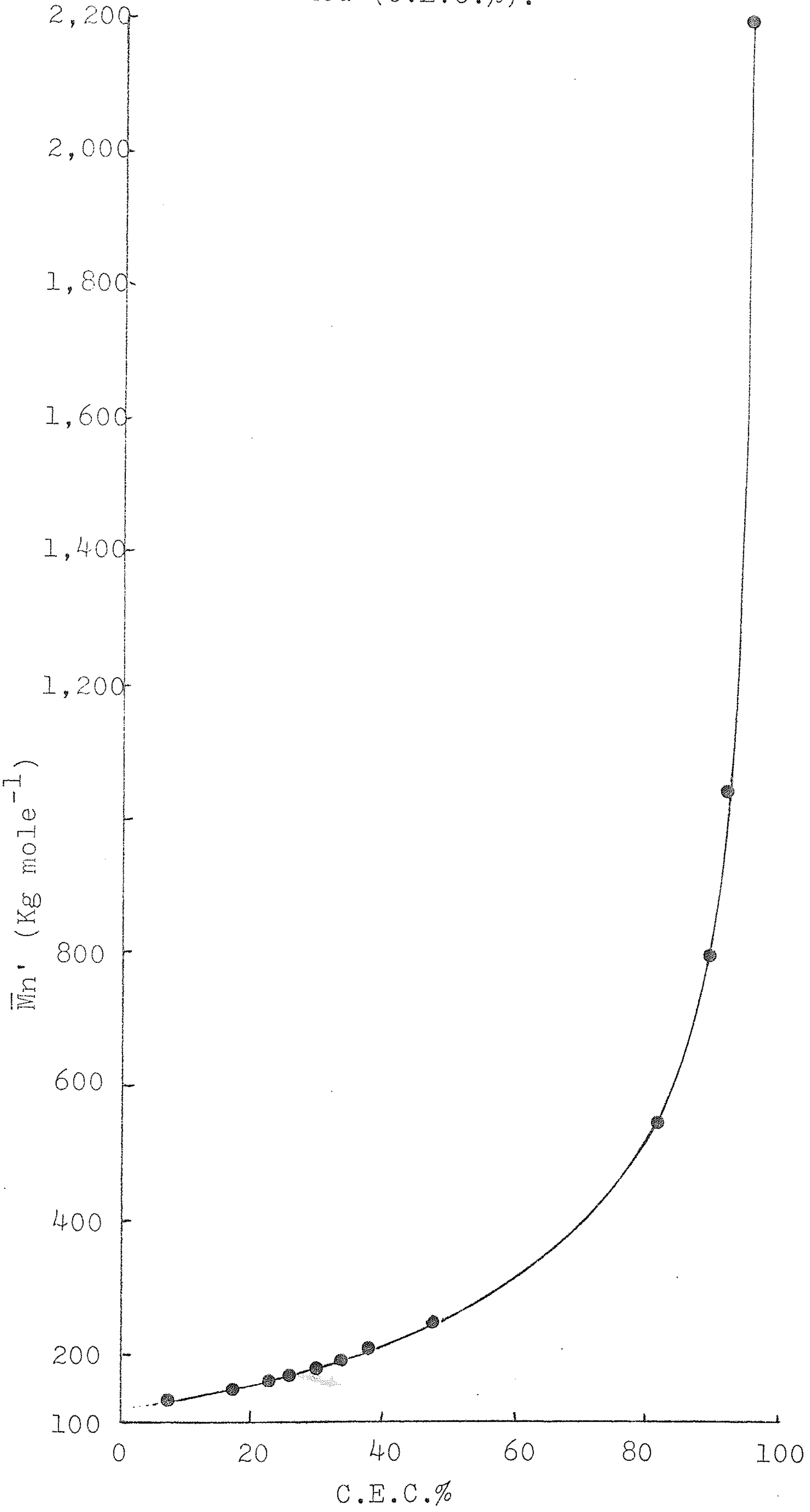


Fig.(30):

Continuous stress relaxation of TMTD, DIPDIS and DBUDIS vulcanisates in air at 70°C.

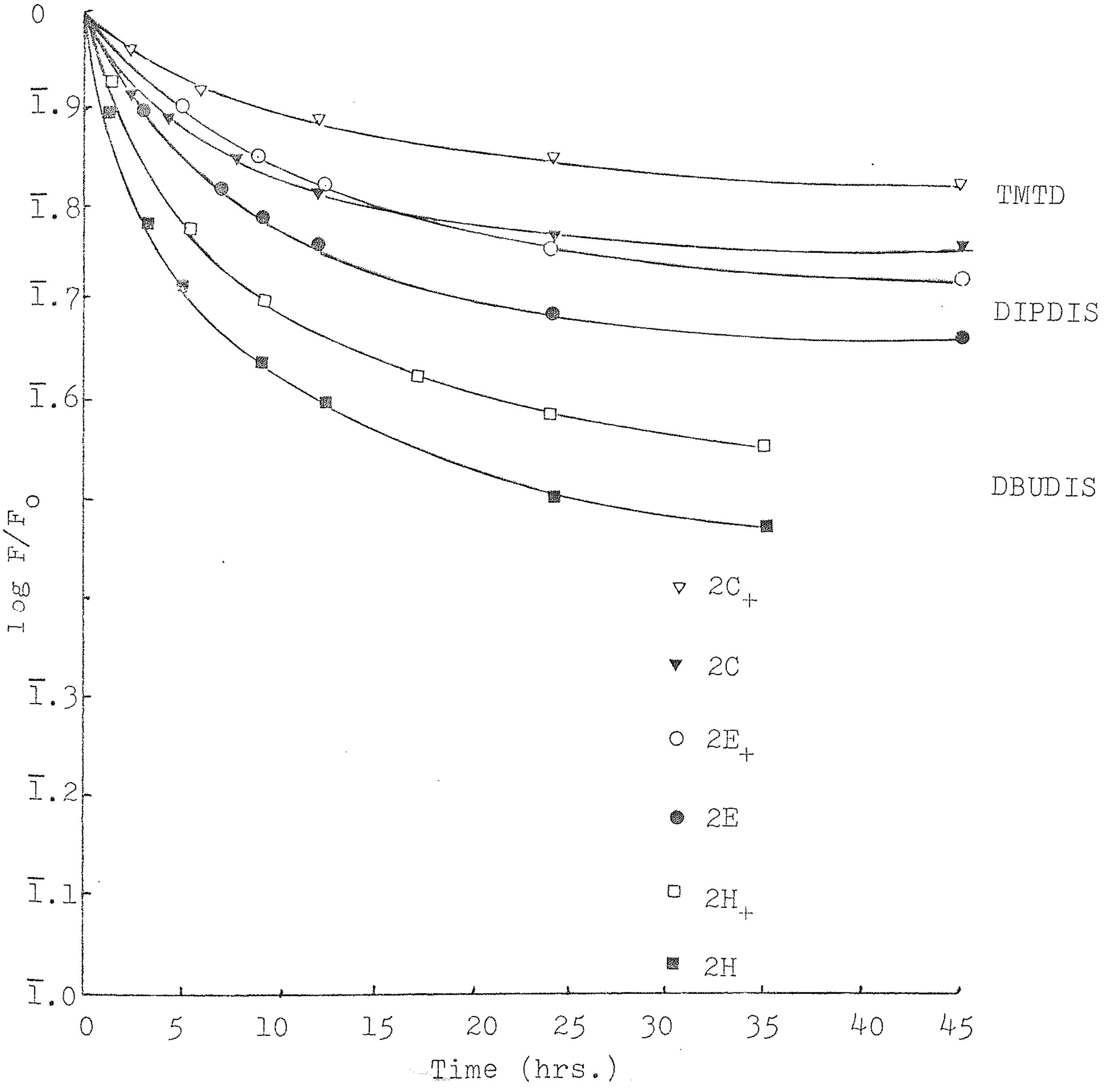
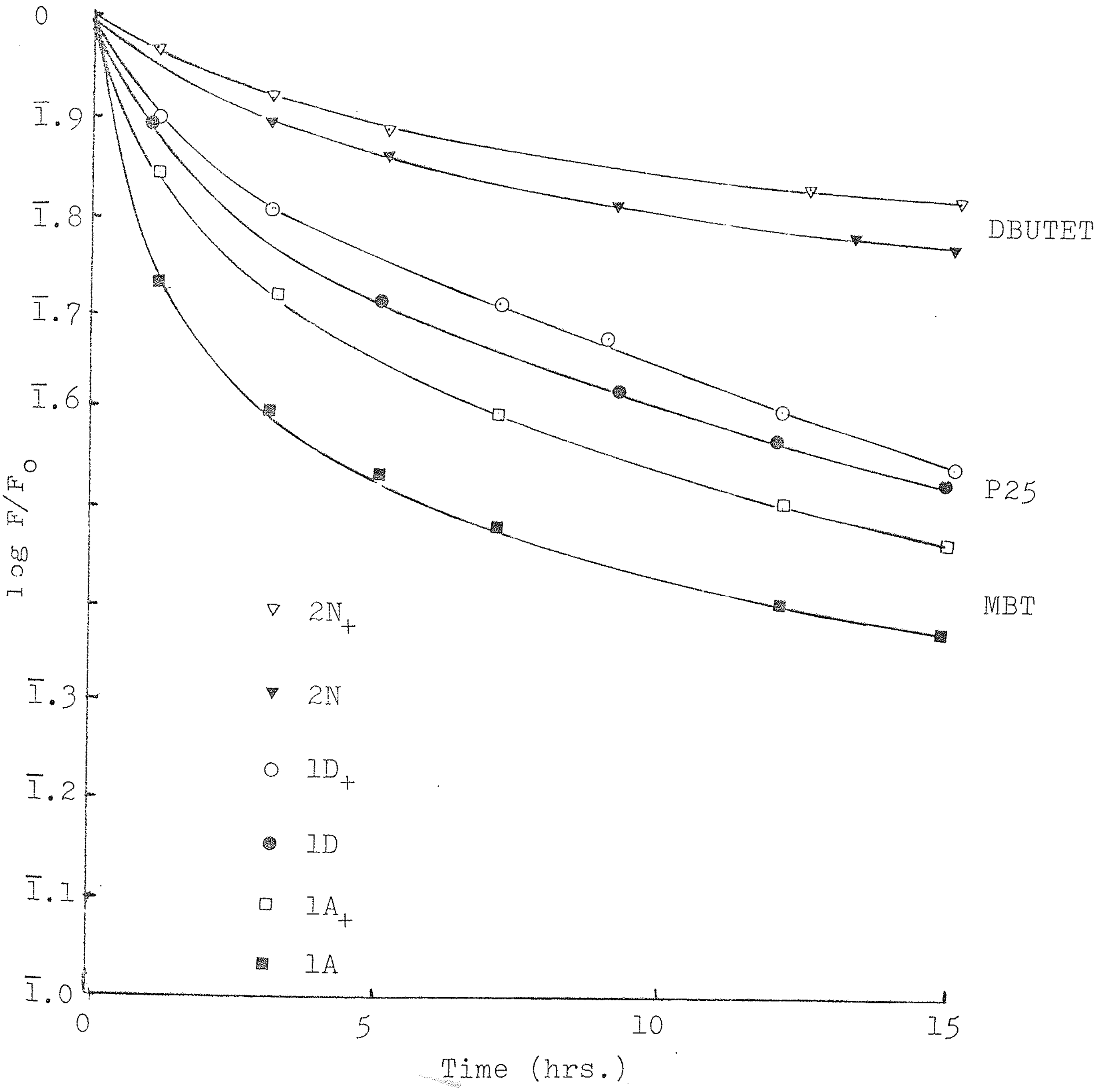


Fig.(31): Continuous stress relaxation of DBUTET, P25 and MBT vulcanisates in air at 70°C.



Table(16): Slope values from compression modulus data on unswollen TMTD vulcanisates .

SAMPLE	CURE TIME Min.at 140°C	F/A_o x10^{-3} MN m^{-2}	$\Delta h/h_o$ x10^{-3}	SLOPE
2C	25	30.9	13.0	1.66
		46.4	23.9	
		61.9	30.4	
		77.4	42.6	
		92.8	50.0	
		185.6	87.4	
$2C_+$	25	30.9	15.3	1.80
		46.4	25.6	
		61.9	34.3	
		77.4	42.6	
		92.8	51.6	
		185.6	93.8	
2C	40	30.9	13.5	1.86
		46.4	22.8	
		61.9	31.2	
		77.4	40.0	
		92.8	47.2	
		185.6	86.0	
$2C_+$	40	30.9	13.0	2.06
		46.4	21.1	
		61.9	28.4	
		77.4	35.4	
		92.8	42.7	
		185.6	76.8	

Cond.

Table(16) Continued:

SAMPLE	CURE TIME Min. at 140°C	$F/A_o \times 10^{-3}$ $MN\ m^{-2}$	$\Delta h/h_o \times 10^{-3}$	SLOPE
2C	60	30.9 46.4 61.9 77.4 92.8 185.6	10.6 19.7 27.2 34.2 41.3 78.3	2.13
$2C_+$	60	30.9 46.9 61.4 77.4 92.8 185.6	12.1 21.4 28.7 37.6 44.9 84.2	2.20
2C	120	30.9 46.4 61.9 77.4 92.8 185.6	12.1 20.8 28.5 35.9 43.3 80.8	1.93
$2C_+$	120	30.9 46.4 61.9 77.4 92.8 185.6	12.6 21.5 29.9 37.1 43.9 84.4	2.00

Table(17): Values of hardness and resilience for rubber masticated to an initial molecular weight of $\bar{M}n$=175(Kg mole^{-1}) at optimum cure time at 140°C .

SAMPLE	CURE TIME Min. at 140°C	HARDNESS I.R.H.D	RESILIENCE	% RES.
1A	40	34	36.3	80.59
$1A_+$	40	36	37.3	82.81
1B	30	34.5	34.5	76.59
$1B_+$	30	36	35.2	78.14
1C	11	34.5	37.1	82.36
$1C_+$	11	36.5	38	84.36
1D	11	35	31.5	69.93
$1D_+$	11	36.5	32.4	71.93
1E	40	35	32.5	72.15
$1E_+$	40	37	33.8	75.04
1F	40	31.5	30.7	68.15
$1F_+$	40	33	32	71.04
1G	40	35	32.5	72.15
$1G_+$	40	37	33.6	74.59

Table(18): Values of hardness and resilience for rubber masticated to an initial molecular weight of $\overline{M}n=128$(Kg mole^{-1}) at optimum cure time at 140°C .

SAMPLE	CURE TIME Min. at 140°C	HARDNESS I.R.H.D	RESILIENCE	%RES.
1A	30	32	35.5	78.81
$1A_+$	30	33.5	36.2	80.36
2B	30	33.5	38.5	85.47
$2B_+$	30	35.5	40.2	89.24
2C	60	33	38.8	86.13
$2C_+$	60	35	39.6	87.91
1D	12	34	37	82.14
$1D_+$	12	35.5	37.9	84.14
2E	45	32.5	37.6	83.47
$2E_+$	45	34	40.2	89.24
2G	30	38.5	40.5	89.91
$2G_+$	30	40	41.2	91.46
2H	30	37.5	37.5	83.25
$2H_+$	30	40	38.7	85.91
2M	30	37	42	93.24
$2M_+$	30	39	43.1	95.68
2N	30	38	40	88.80
$2N_+$	30	40.5	41.5	92.13

Table(19): Values of physical properties for rubber masticated to an initial molecular weight of $\overline{M}n=128$(Kg mole^{-1}) for different cure times at 140°C .

SAMPLE	CURE TIME Min.at 140°C	MR200 MN m^{-2}	MR600 MN m^{-2}	U.T.S MN m^{-2}	HARDNESS I.R.H.D	RESILIENCE at 45°	%RES.	MR100 S* MN m^{-2}
$1A_a$	10							0.454
1A	10	0.80	1.56	8.90	28	38.6	85.69	0.454
$1A_+$	10	0.83	1.63	9.91	32	39.4	87.47	0.458
$1A_a$	15							0.458
1A	15	0.84	1.70	9.95	32	39	86.59	0.459
$1A_+$	15	0.88	1.79	10.95	33	39.6	87.91	0.463
$1A_a$	20							0.463
1A	20	0.88	1.75	11.10	32.5	38.7	85.91	0.463
$1A_+$	20	0.95	1.83	12	34	39.5	87.69	0.469
$1A_a$	40							0.465
1A	40	0.85	1.75	10.49	32.5	36.9	81.92	0.466
$1A_+$	40	0.90	1.79	11.45	34	38.2	84.80	0.470
3C	12	0.57	1.10	7.80	28	36	79.92	
$3C_n$	12	0.61	1.13	8.50	30.5	37	82.14	
3C	25	0.71	1.48	8.53	33	36.5	81.03	
$3C_n$	25	0.79	1.57	9.74	35.5	37.4	83.03	

*= Modulus at 100% elongation using MR100 apparatus .

Cond.

Table(19): Continued.

SAMPLE	CURE TIME Min.at 140°C	MR200 MN m^{-2}	MR600 MN m^{-2}	U.T.S MN m^{-2}	HARDNESS I.R.H.D	RESILIENCE at 45°	%RES.	MR100s* MN m^{-2}
3C	40	0.75	1.50	9.22	34	36.8	81.70	
$3C_n$	40	0.90	1.65	10.66	36.5	37.7	83.69	
3C	120	0.78	1.52	8.7	34	37	82.14	
$3C_n$	120	0.89	1.65	10.61	36.5	38	84.36	
3D	3	1.04	2.35	20.44	28	39.7	88.13	
$3D_n$	3	1.21	2.57	21.75	30	40.6	90.13	
3D	4	1.17	2.55	22.50	31	40.4	89.69	
$3D_n$	4	1.32	2.74	23.92	32	41.4	91.91	
3D	5	1.26	2.65	24.36	42	41	91.02	
$3D_n$	5	1.39	2.82	26.10	44	41.8	92.80	
3D	15	1.22	2.56	22.70	40	41	91.02	
$3D_n$	15	1.34	2.74	24.0	41	42	93.24	
$3E_a$	20				31	39.3	87.22	0.543
3E	20	0.83	1.90	15.66	31.5	39.5	87.69	0.544
$3E_n$	20	0.91	2.04	19.14	33	40	88.80	0.550

Cond.

Table(19):Continued

SAMPLE	CURE TIME Min.at 140°C	MR200 MNm $^{-2}$	MR600 MN m $^{-2}$	U.T.S MN m $^{-2}$	HARDENESS I.R.H.D	RESILIENCE at 45°	%RES.	MR100 $_{s}$* Mn m $^{-2}$
$3E_a$	23				32	40	88.80	0.565
3E	23	0.90	1.96	20.0	32.5	40.2	89.24	0.567
$3E_n$	23	1.00	2.11	23.5	33.5	40.8	90.58	0.572
$3E_a$	26				32.5	40.3	89.46	0.568
3E	26	0.92	2.08	22.10	33.0	40.5	89.91	0.569
$3E_n$	26	1.09	2.22	25.70	34.0	41	91.02	0.575
$3E_a$	50				33.0	40	88.80	0.569
3E	50	0.87	2.04	19.14	33.0	40	88.80	0.570
$3E_n$	50	0.97	2.15	21.31	34.0	40.5	89.91	0.576
3G	10	0.87	1.87	12.6	34.0	37.5	83.25	
$3G_n$	10	1.04	2.38	13.92	35.0	39.5	87.69	
3G	12	1.00	2.35	13.05	35.0	38.5	38.47	
$3G_n$	12	1.16	2.52	14.75	39.0	40.5	89.91	
3G	15	1.22	2.65	14.79	36.0	39.5	87.69	
$3G_n$	15	1.31	2.83	16.53	41.0	41.0	91.02	
3G	30	1.04	2.30	13.05	38.0	39.5	87.69	
$3G_n$	30	1.26	2.78	15.79	42.0	41.0	91.02	

Cond.

Table(19): Continued.

SAMPLE	CURE TIME Min.at 140^{o}C	MR100 MN m^{-2}	MR300 MN m^{-2}	U.T.S MN m^{-2}	HARDNESS I.R.H.D	RESILIENCE at 45^{o}	%RES.	MR100s* MN m^{-2}
$1A_a$	20	0.38	1.02	8.75	32.0	38.9	86.36	
1A	20	0.40	1.01	8.92	32.5	39.0	86.58	
$1A_+$	20	0.47	1.05	9.97	34.0	39.6	87.91	
$1A_a$	30	0.46	1.13	10.20	32.5	39.3	87.25	
1A	30	0.48	1.15	10.50	33.0	39.4	87.47	
$1A_+$	30	0.52	1.22	12.0	34.5	40.0	88.80	
$1A_a$	40	0.54	1.30	9.80	33.0	39.0	86.58	
1A	40	0.54	1.30	10.11	33.0	39 0	86.80	
$1A_+$	40	0.58	1.35	11.72	34.5	39.6	87.91	
$1A_a$	60	0.53	1.26	9.07	32.5	37.8	83.92	
1A	60	0.52	1.24	9.07	32.5	37.5	84.04	
$1A_+$	60	0.56	1.30	9.27	34.0	38.6	85.69	
$3E_a$	25	0.44	1.30	20.88	32.0	40.01	39.02	
3E	25	0.52	1.43	22.02	32.5	40.30	89.47	
$3E_n$	25	0.65	1.59	25.66	33.5	40.90	90.80	
$3E_a$	30	0.52	1.70	22.40	33.0	40.40	89.67	
3E	30	0.62	1.80	23.02	33.5	40.6	90.13	
$3E_n$	30	0.78	1.95	26.84	34.5	41.2	91.46	

Cond.

Table(19): Continued.

SAMPLE	CURE TIME Min.at 140°C	MR100 MN m^{-2}	MR300 MN m^{-2}	U.T.S MN m^{-2}	HARDNESS I.R.H.D	RESILIENCE at 45°	%RES.	$MR100_s$ MN m^{-2}
$3E_a$	40	0.65	1.74	22.05	33	40.3	89.47	
3E	40	0.70	1.85	22.72	33	40.4	89.67	
$3E_n$	40	0.85	2.00	26.20	34.5	41.0	91.02	
$3E_a$	60	0.65	1.70	19.20	32.5	40.0	88.80	
3E	60	0.65	1.74	19.57	33.0	40.0	88.80	
$3E_n$	60	0.80	1.90	22.70	34.0	40.5	89.91	

Table(20): Values of physical properties for rubber masticated to an initial molecular weight of $\bar{M}n$=100(Kg mole^{-1}) for different cure times at 140°C .

SAMPLE	CURE TIME Min.at 140°C	HARDNESS I.R.H.D	MR100$_s$* MN m^{-2}	MR200 MN m^{-2}	MR600 MN m^{-2}	U.T.S MN m^{-2}
3E$_a$	20	30	0.54	0.78	1.78	14.66
3E	20	30.5	0.543	0.80	1.85	15.11
3E$_n$	20	32	0.555	0.91	2.04	19.08
3E$_a$	23	32	0.552	0.83	1.90	18.50
3E	23	32.5	0.554	0.86	1.96	18.92
3E$_n$	23	34	0.57	1.04	2.17	24.50
3E$_a$	26	32.5	0.566	0.90	2.01	21.20
3E	26	33	0.568	0.92	2.06	21.57
3E$_n$	26	36	0.581	1.13	2.26	28.0
3E$_a$	50	33	0.568	0.88	1.99	20.11
3E	50	33	0.569	0.91	2.03	20.45
3E$_n$	50	36	0.582	1.09	2.22	26.82

Fig.(32): Ultimate tensile strength (U.T.S.)of DIPDIS vulcanisates.

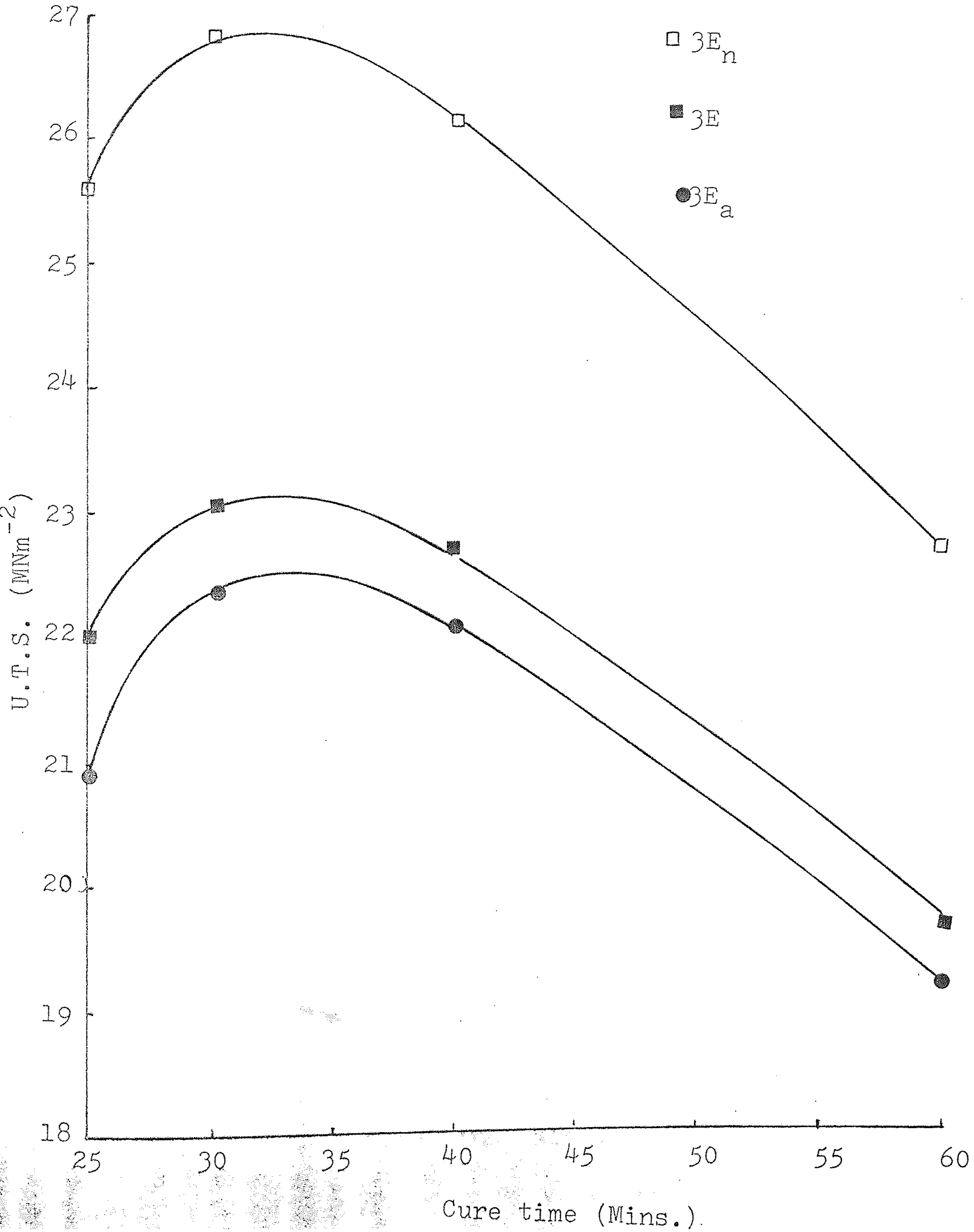
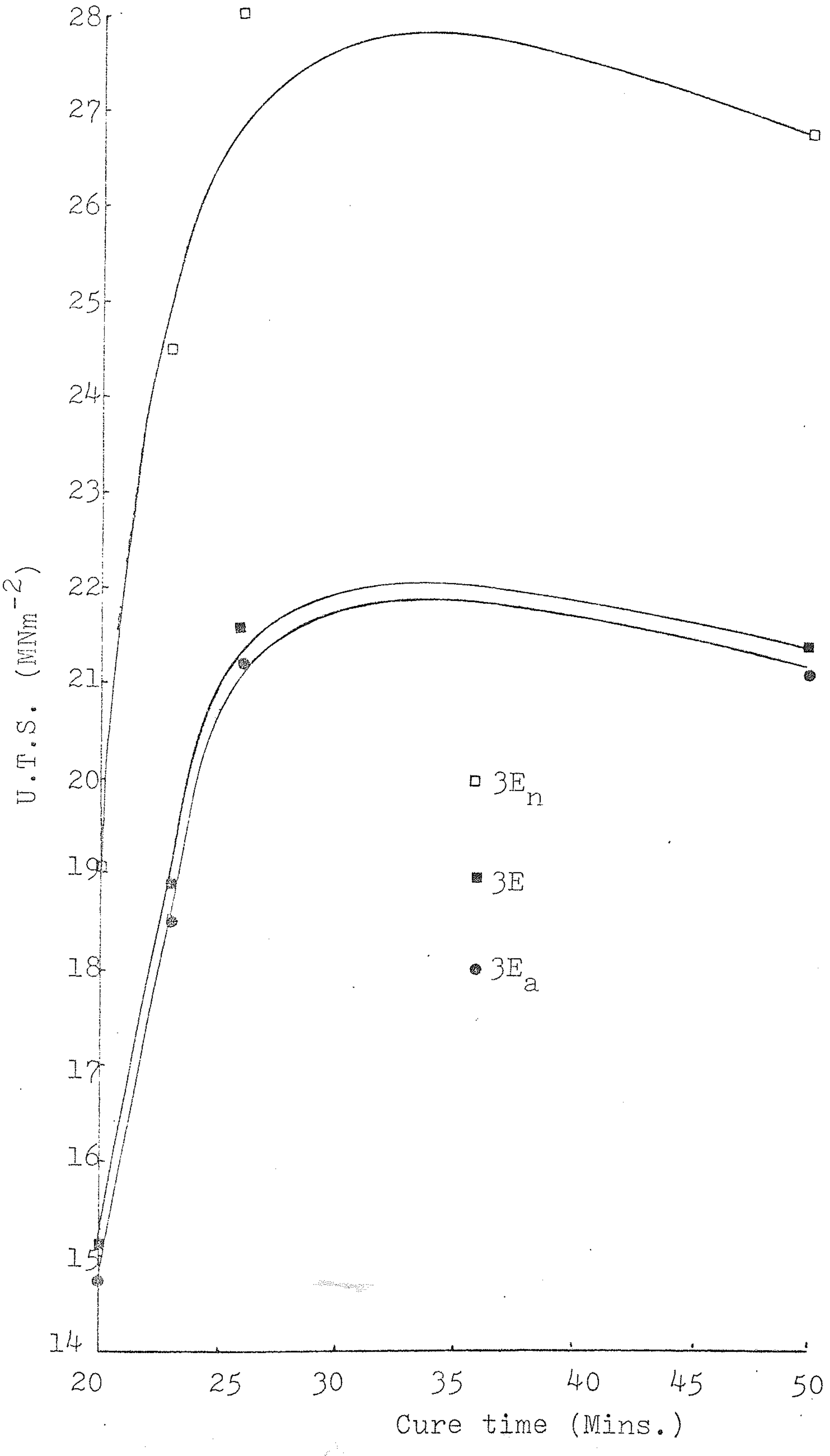


Fig.(33): Ultimate tensile strength (U.T.S.) of DIPDIS(prolonged mastication)vulcanisates.

$\overline{M}n$ before vulcanisation=100 Kg mole^{-1}



Confirmation of results.

Fig.(34): Ultimate tensile strength (U.T.S.) of DIPDIS vulcanisates.

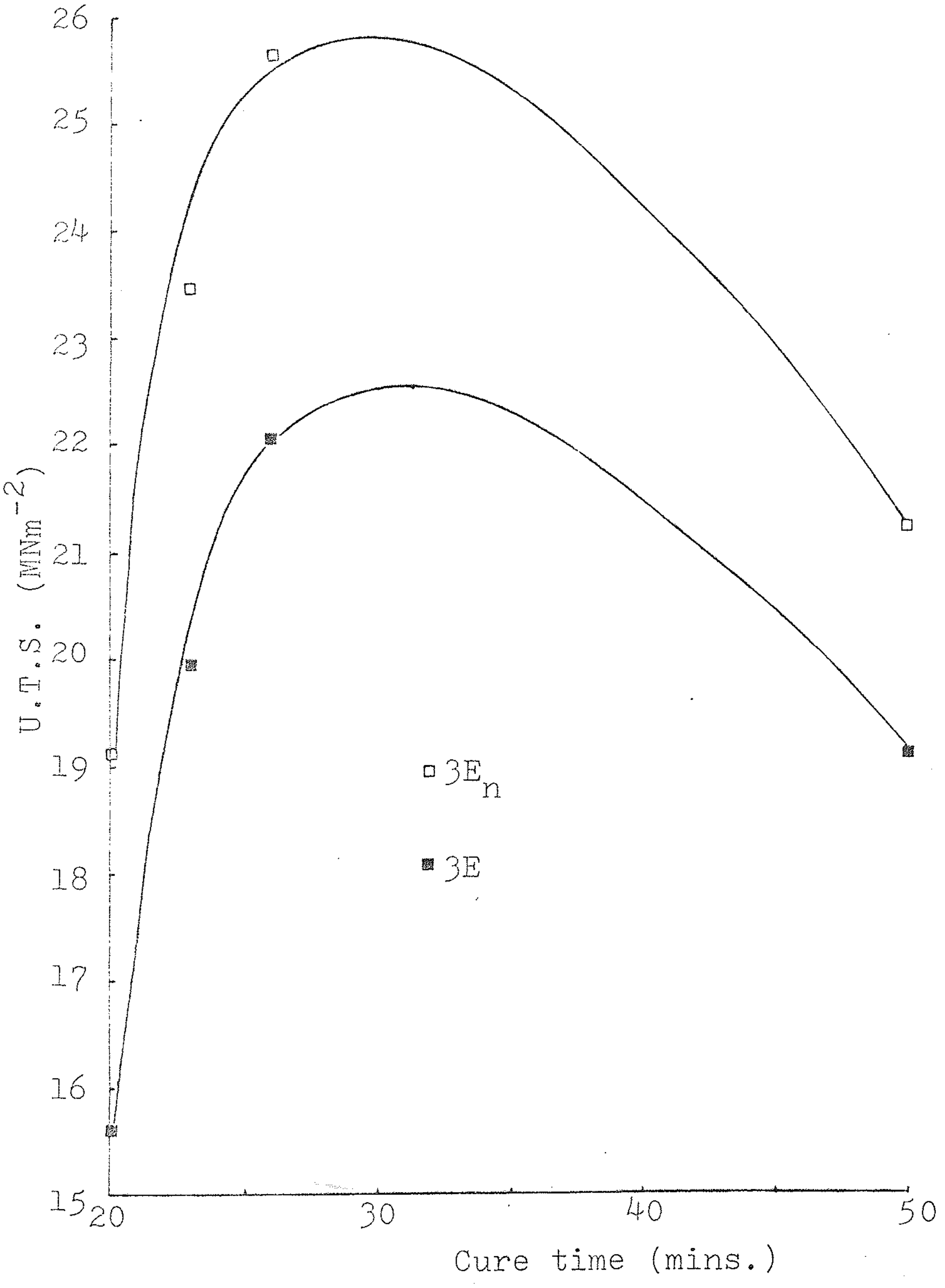


Fig.(35): Hardness of DIPDIS vulcanisates.

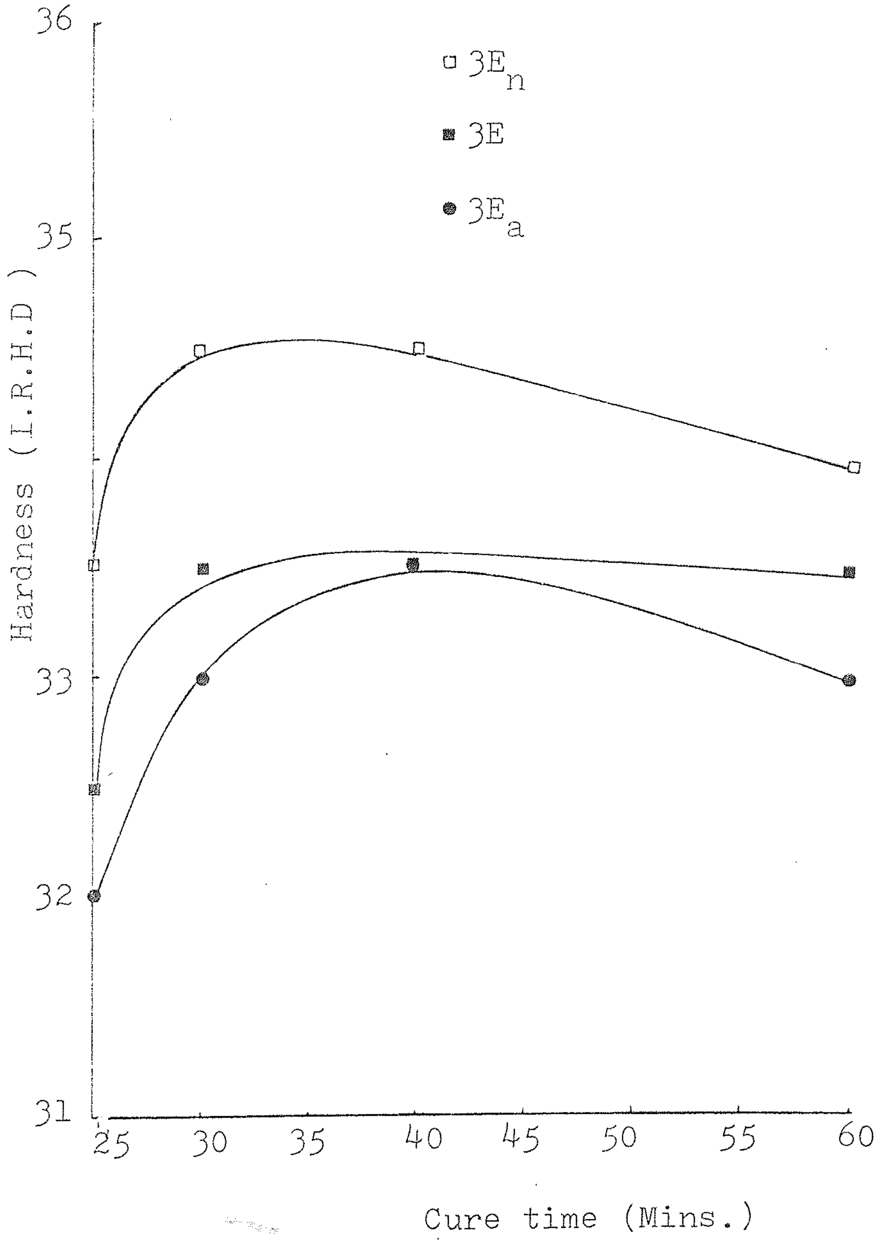
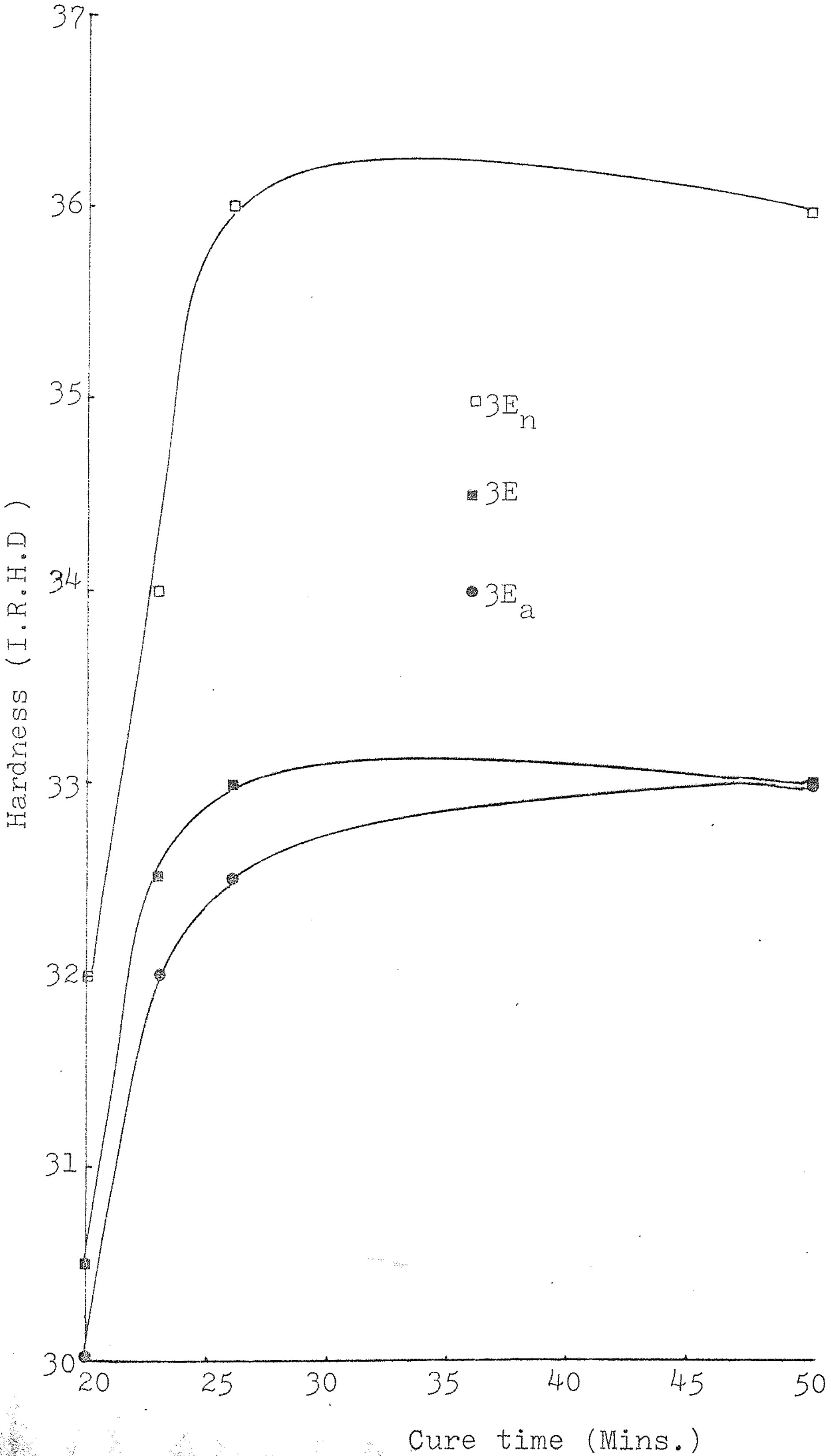


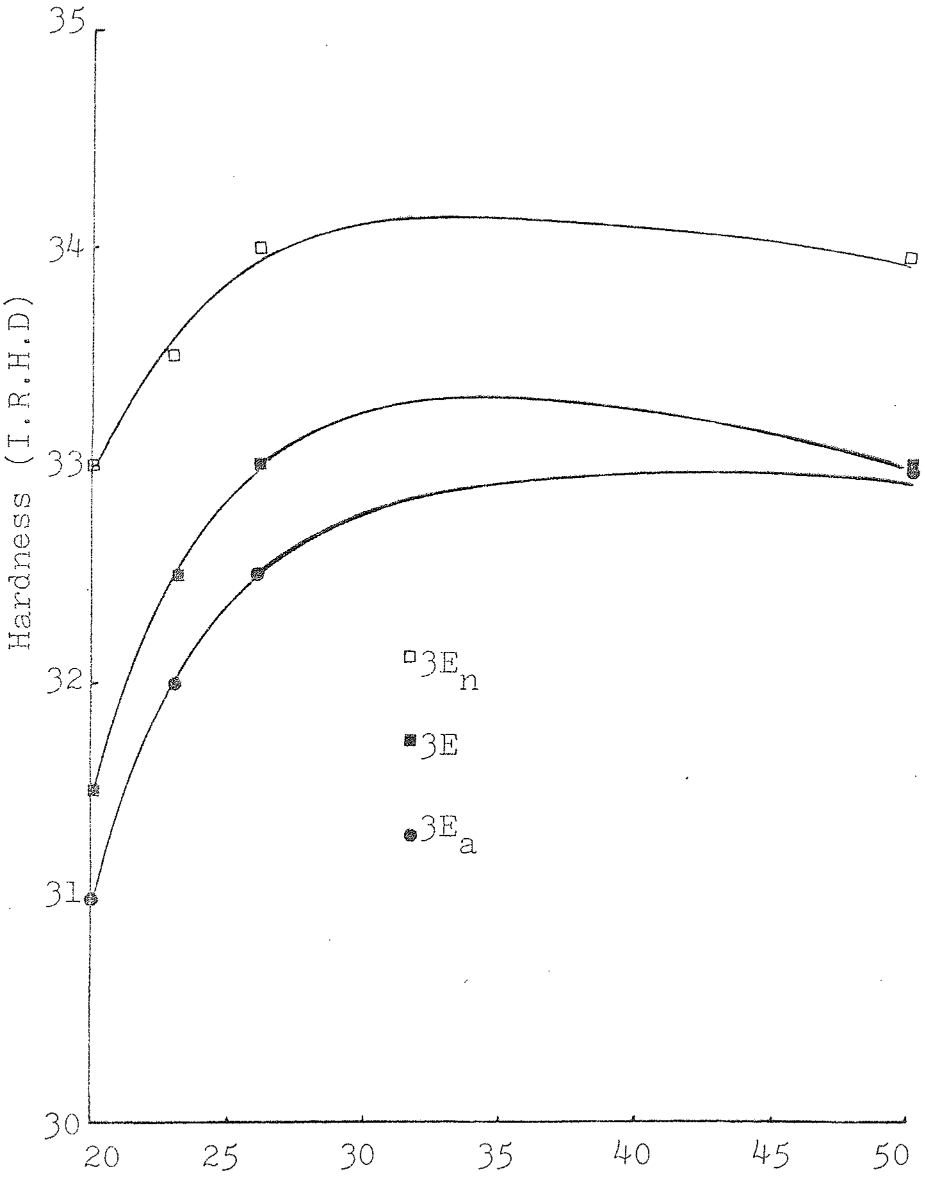
Fig.(36): Hardness of DIPDIS (prolonged mastication) vulcanisates.

$\bar{M}n$=100 (before vulcanisation) Kg mole^{-1}



Confirmation of results.

Fig.(37): Hardness of DIPDIS vulcanisates.



Cure time (Mins.)

Fig.(38): Modulus at hundred percent elongation of DIPDIS vulcanisates (using MR100 apparatus).

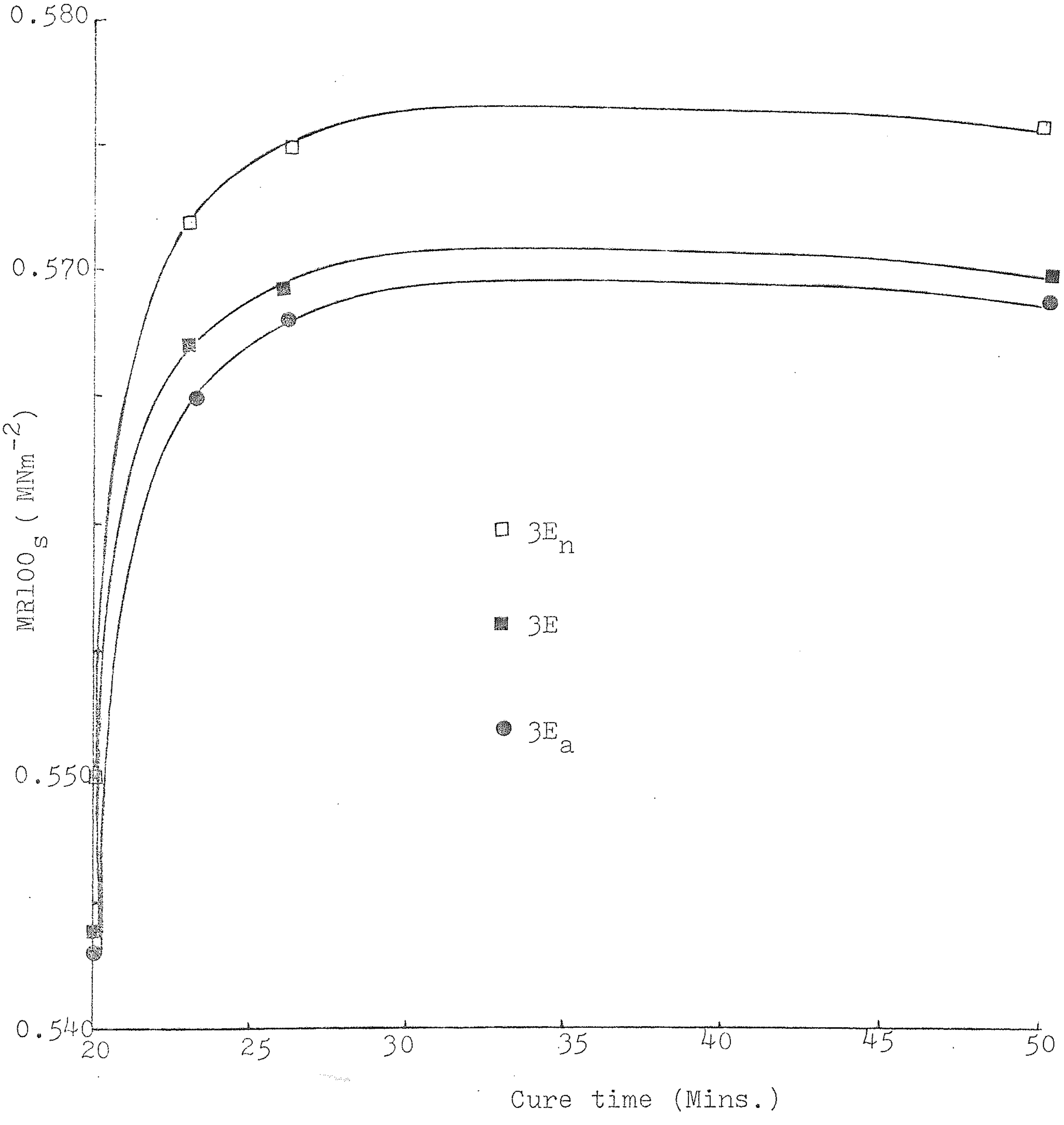


Fig.(39): Modulus at hundred percent elongation (using MR100 apparatus) of DIPDIS (prolonged mastication). $\bar{M}n$=100 Kg mole^{-1} (before vulcanisation).

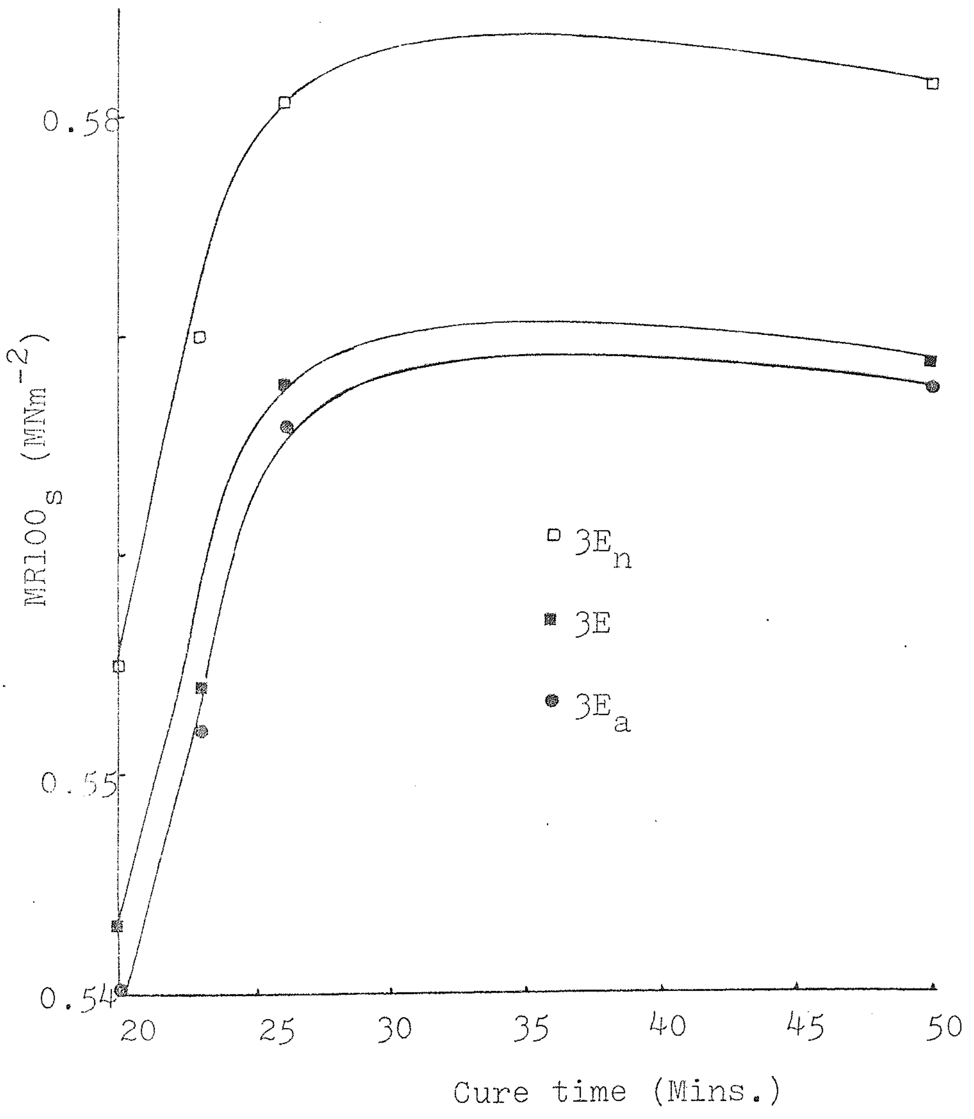


Fig.(40): Modulus at hundred and three hundred percent elongation (MR100,MR300)of DIPDIS vulcanisates.

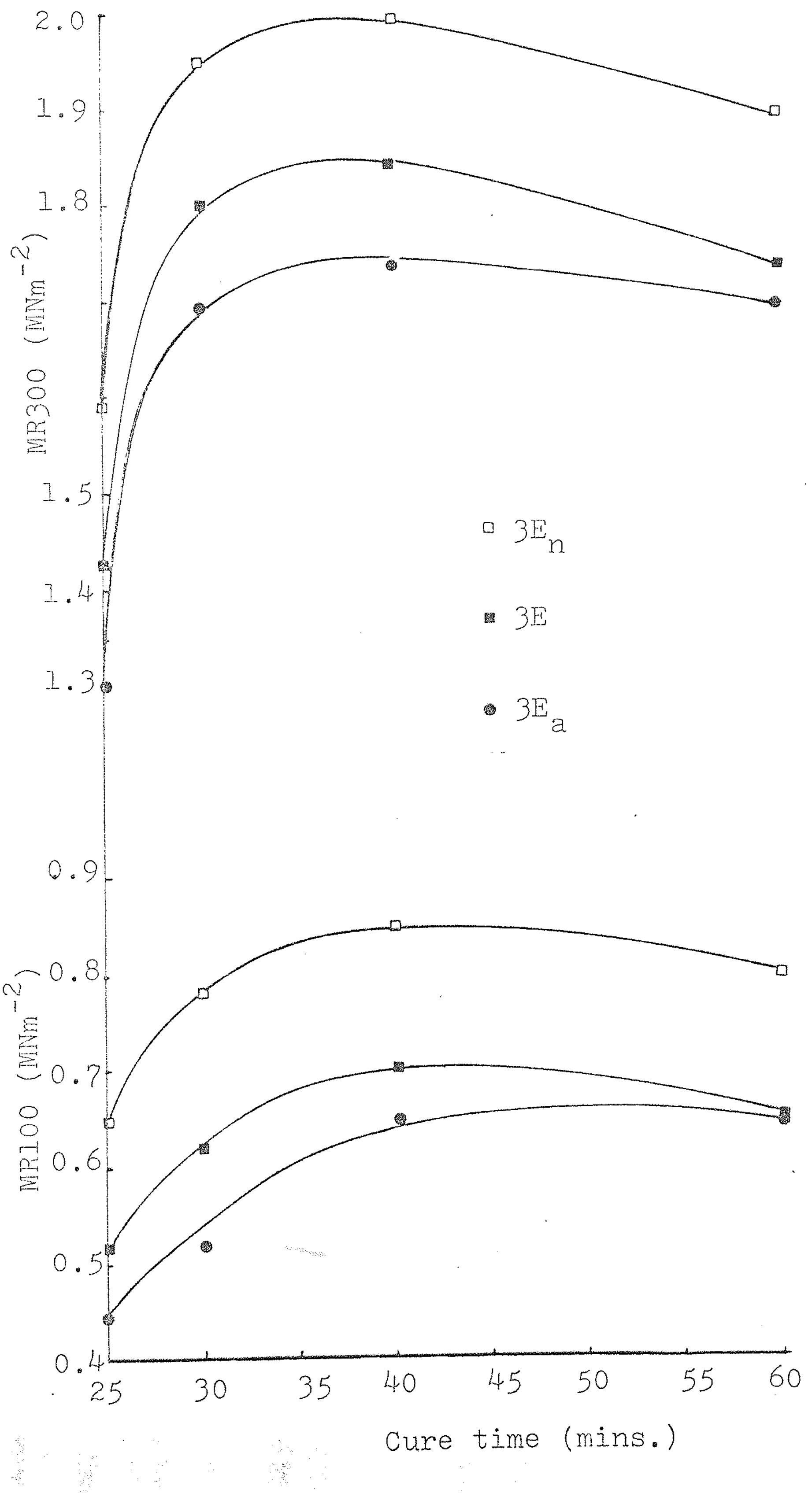
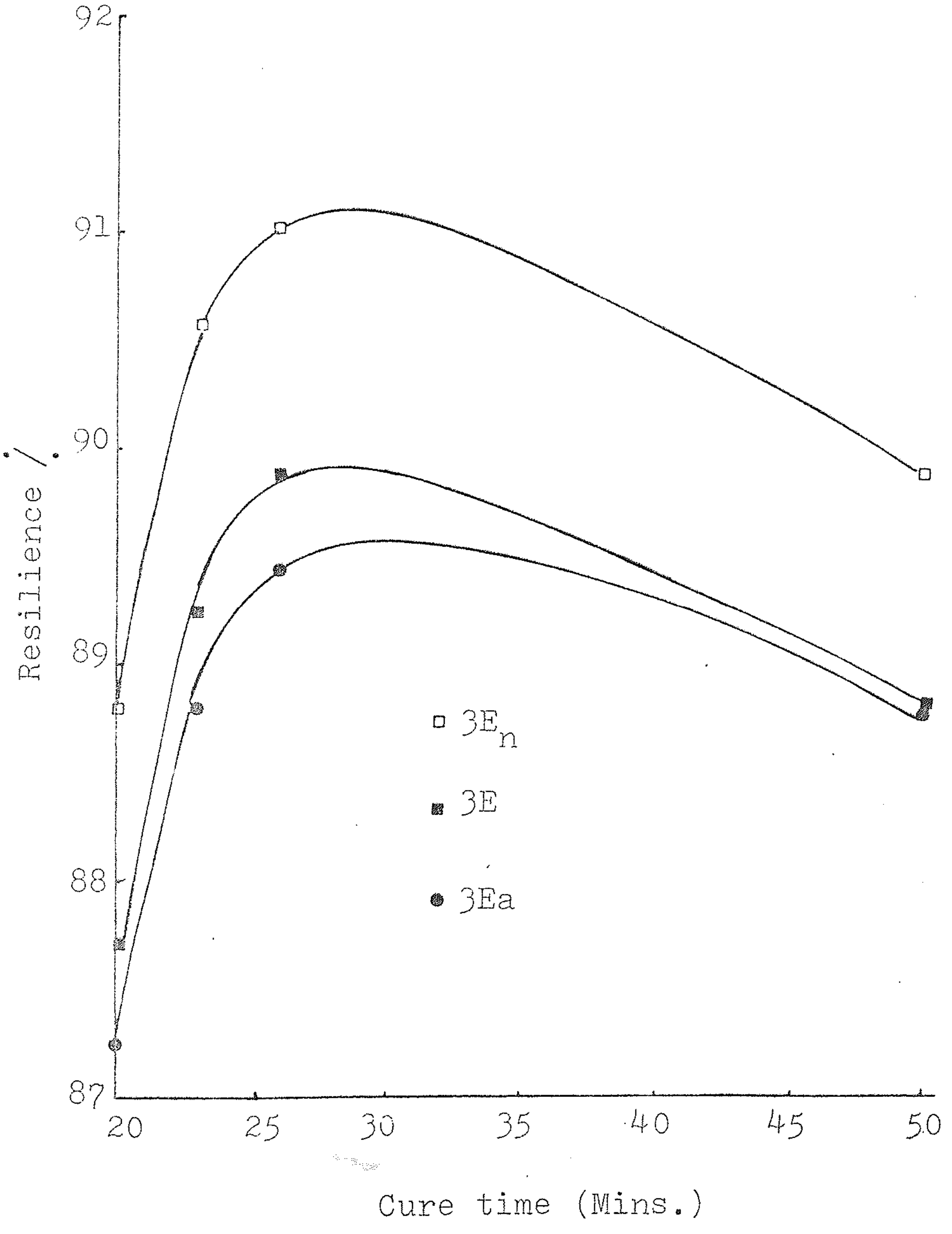


Fig.(41): Resilience of DIPDIS vulcanisates.



Confirmation of results.

Fig.(42): Resilience of DIPDIS vulcanisates.

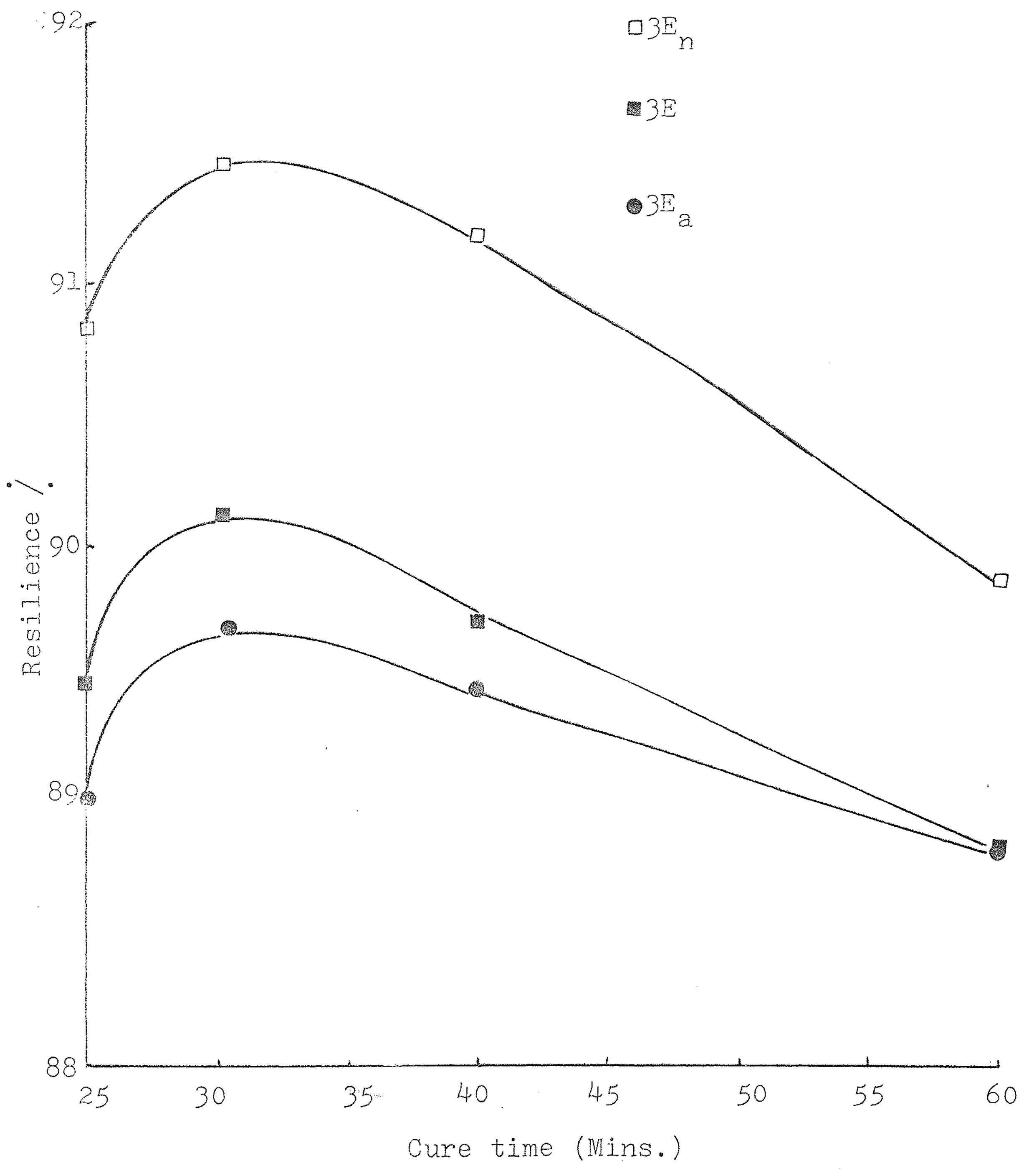


Fig.(43): Ultimate tensile strength (U.T.S.) of DIPTET vulcanisates.

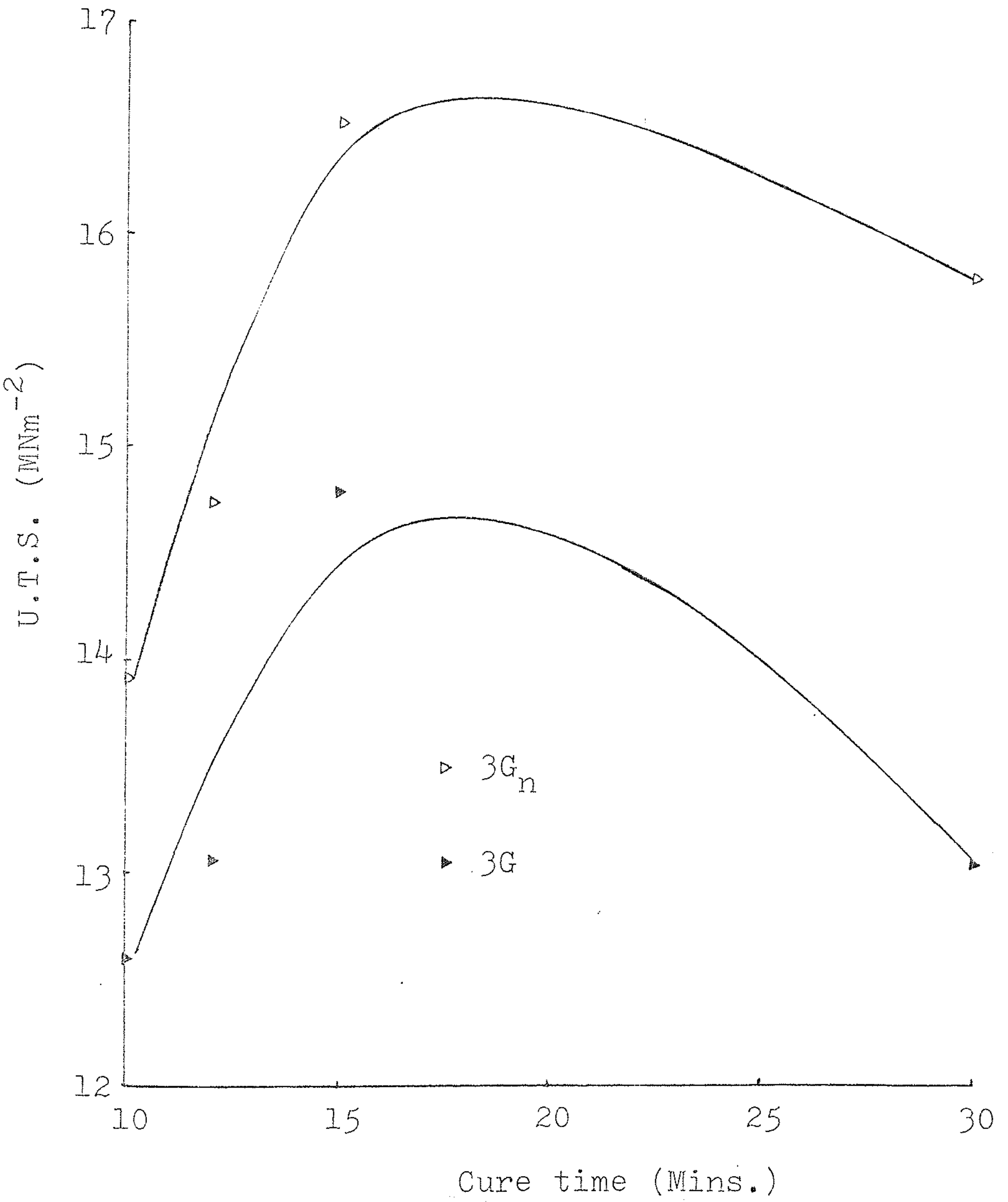


Fig.(44): Hardness of DIPTET vulcanisates.

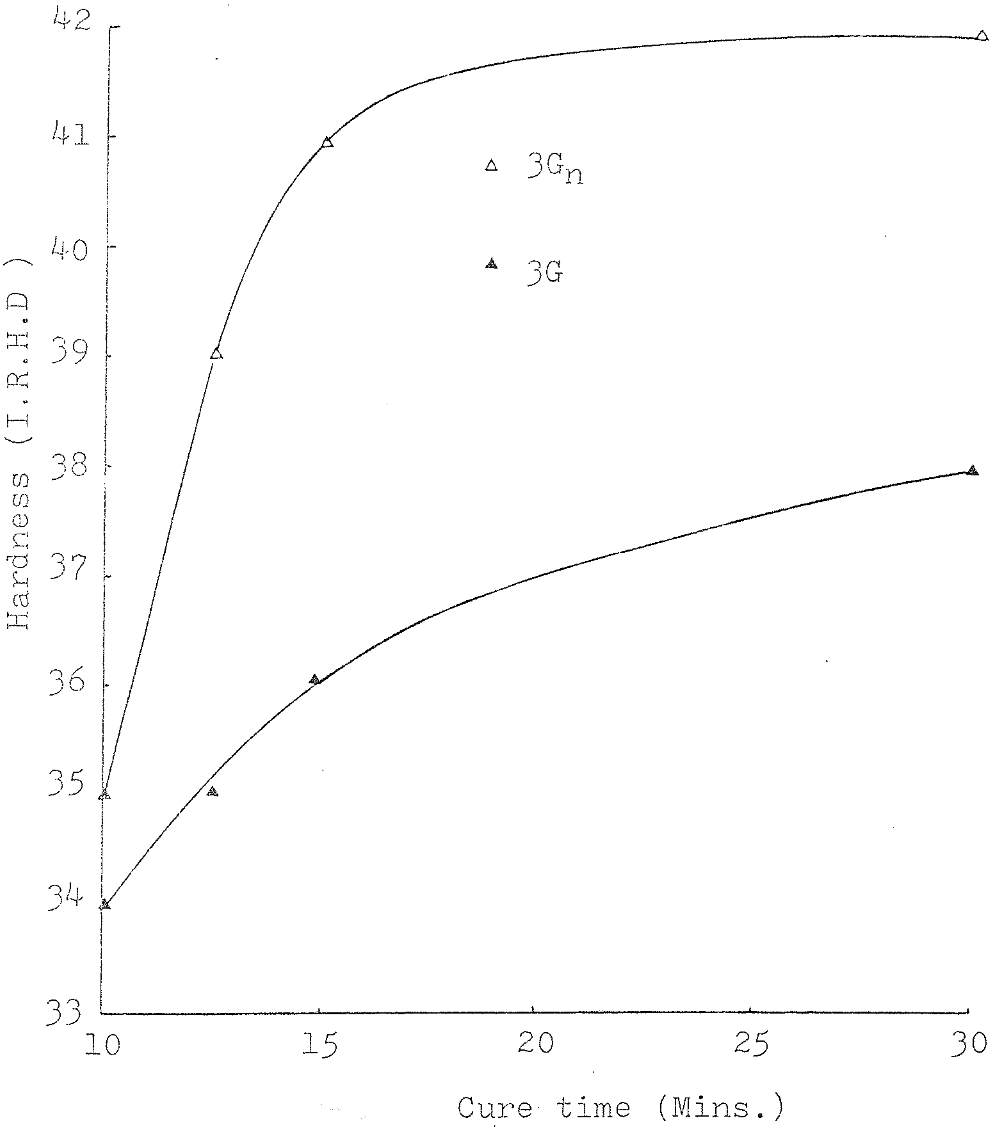


Fig.(45): Modulus at two hundred and six hundred percent elongation (MR200,MR600) of DIPTET vulcanisates.

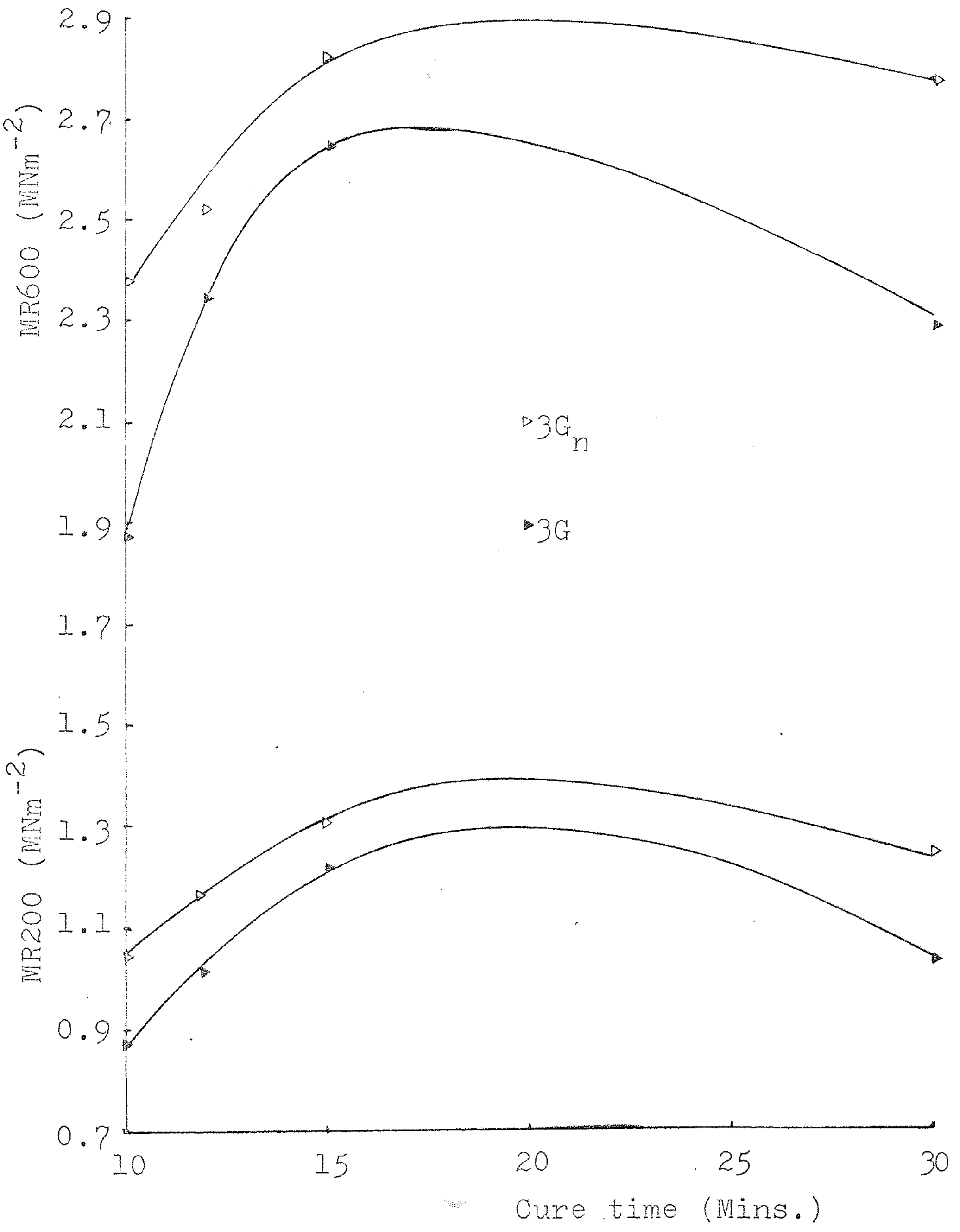


Fig.(46):Resilience of DIPTET vulcanisates.

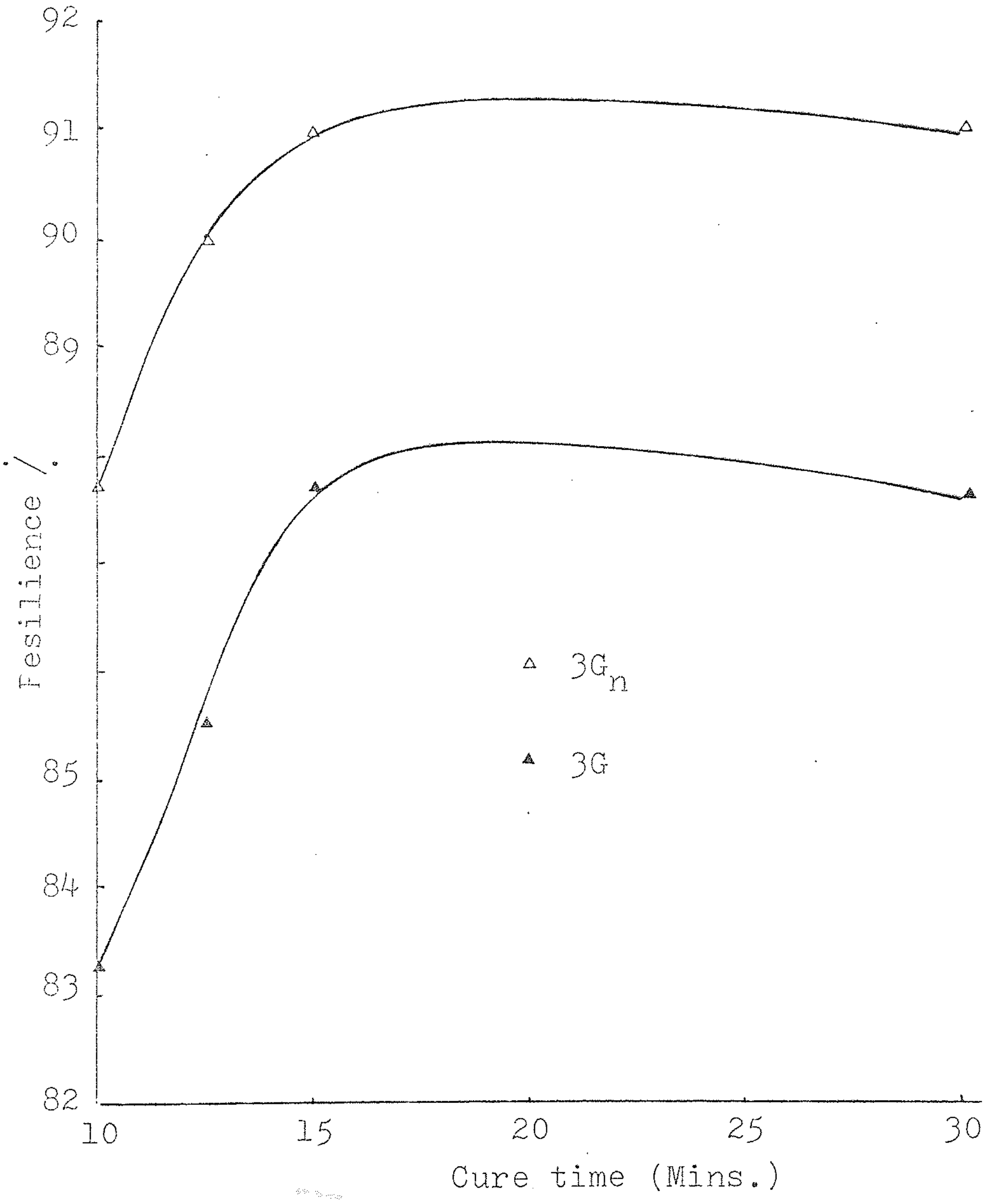
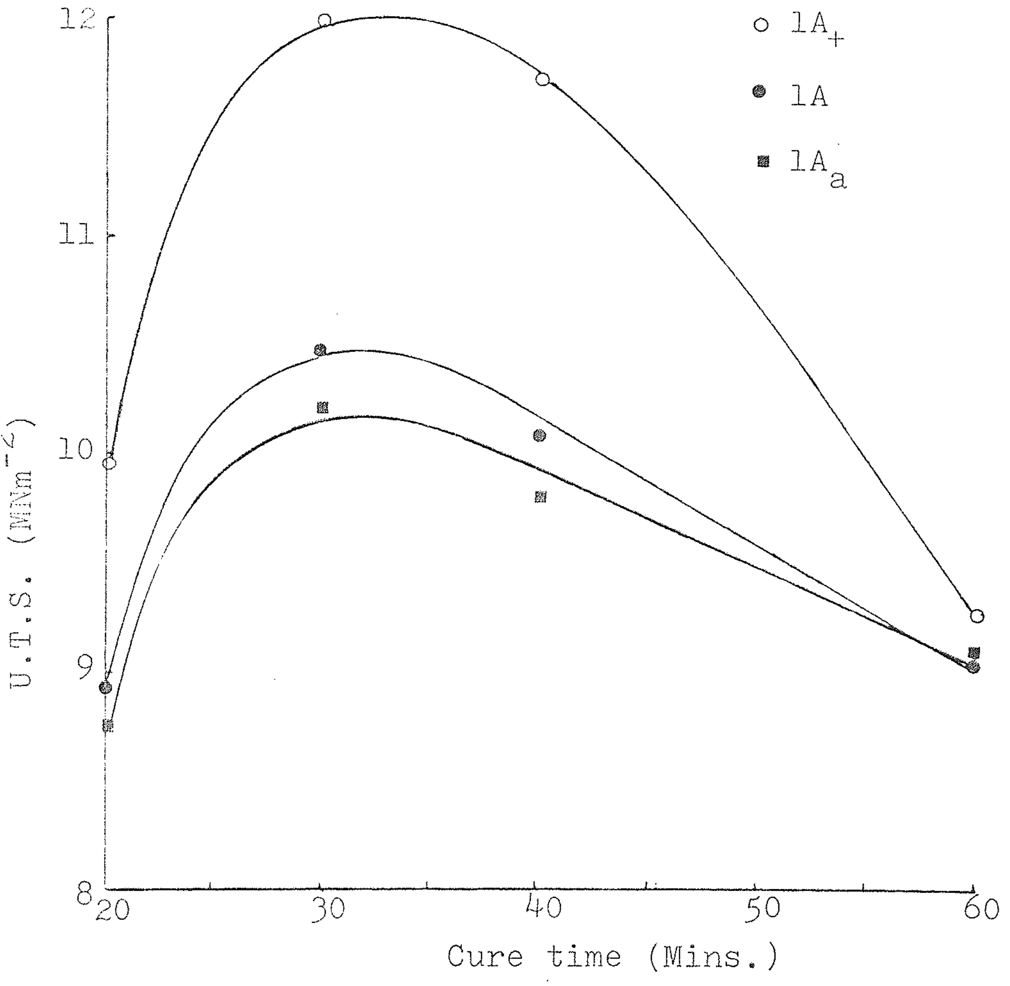


Fig. (47): Ultimate tensile strength (U.T.S.)of MBT vulcanisates.



Confirmation of results.

Fig.(48): Ultimate tensile strength (U.T.S.) of MBT vulcanisates.

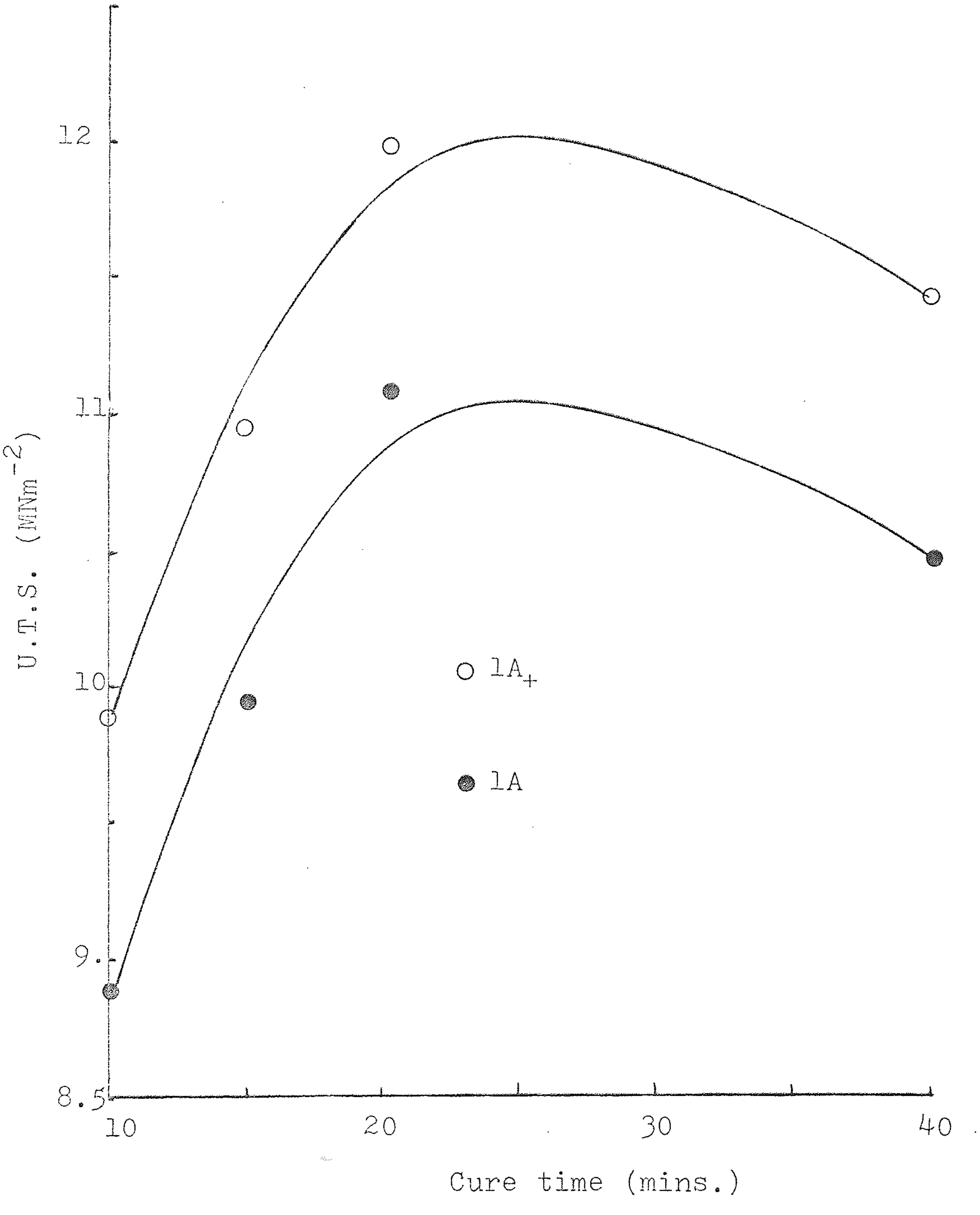


Fig.(49): Hardness of MBT vulcanisates.

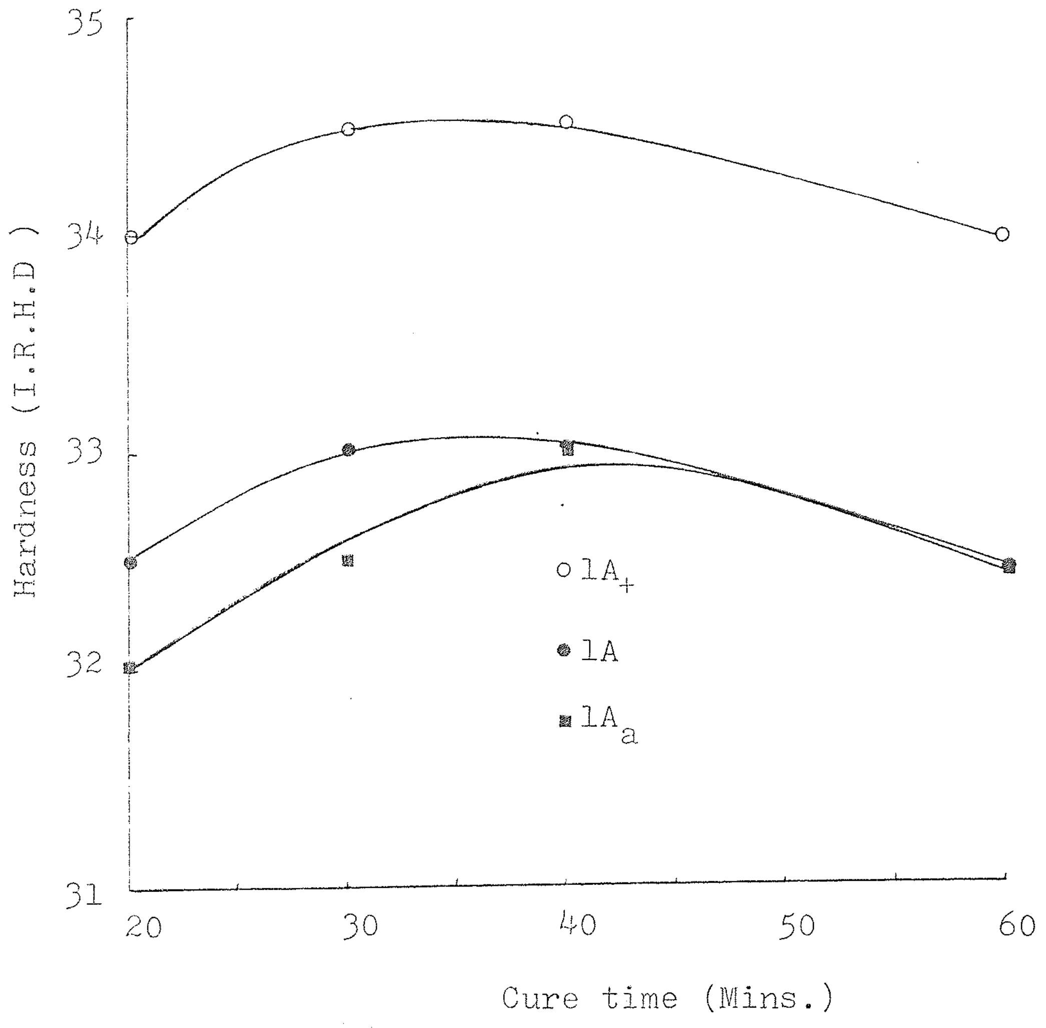


Fig.(50): Modulus at hundred percent elongation of MBT vulcanisates (using MR100 apparatus).

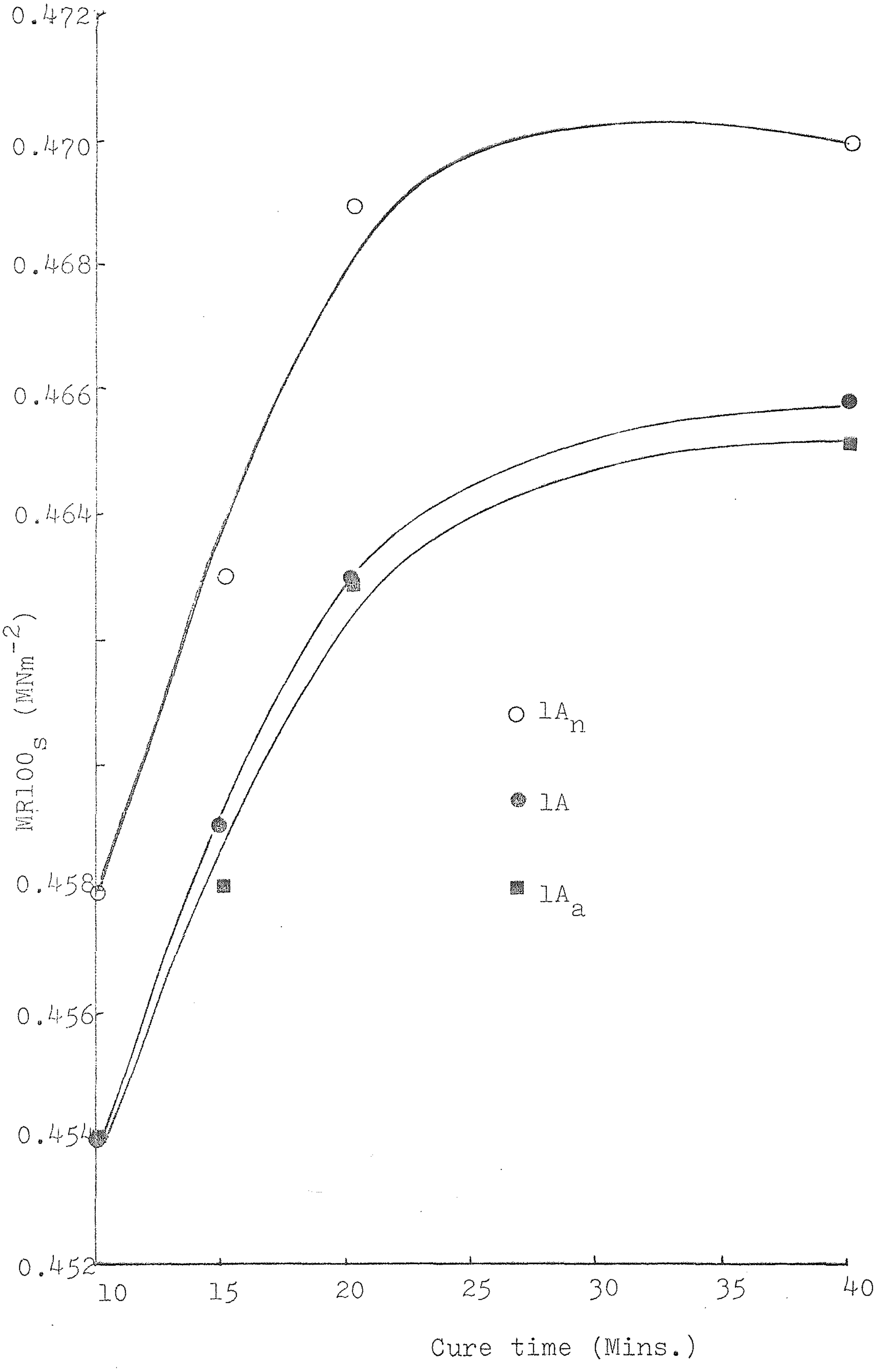


Fig.(51):Modulus at hundred and three hundred percent elongation (MR100,MR300) of MBT vulcanisates.

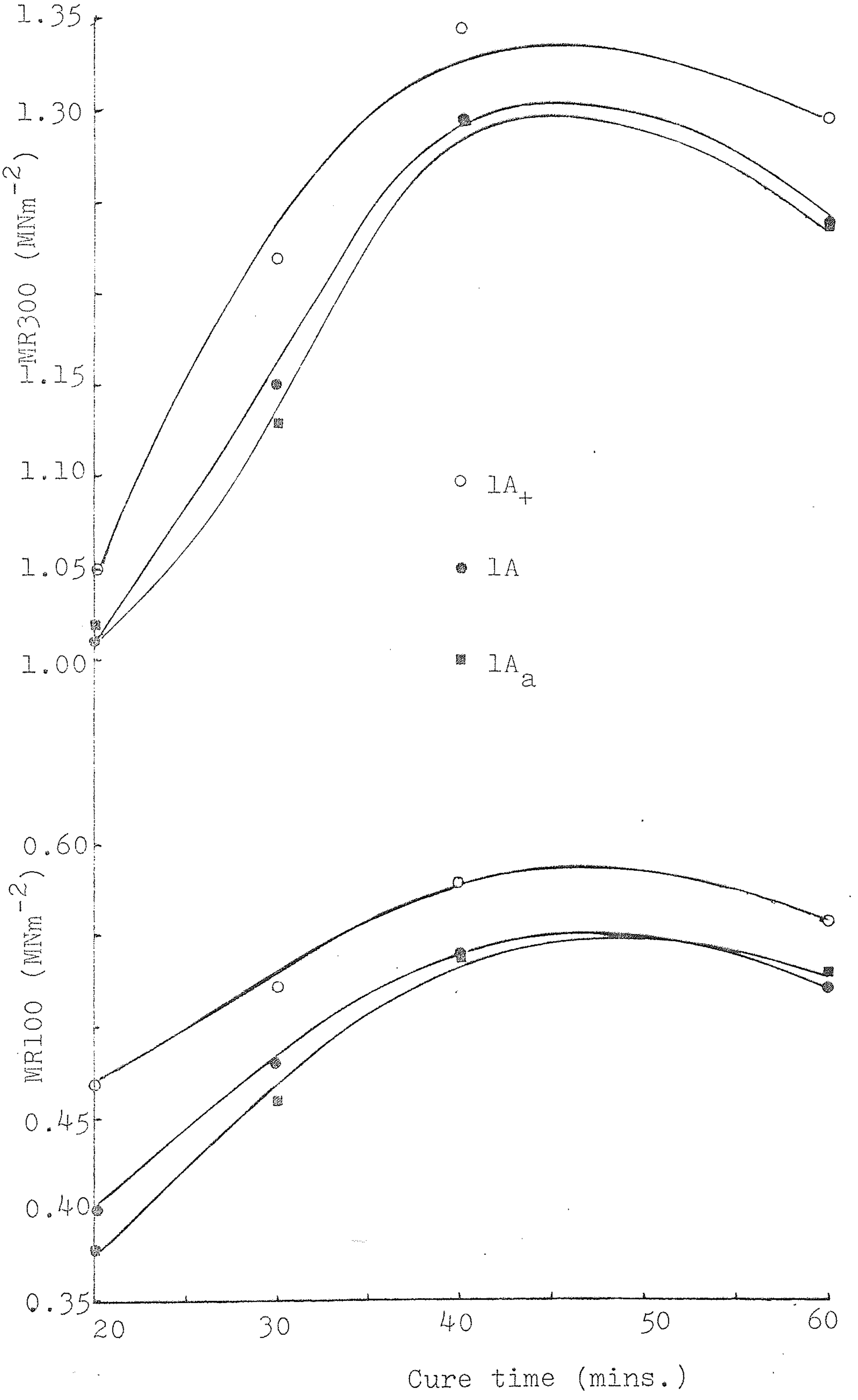
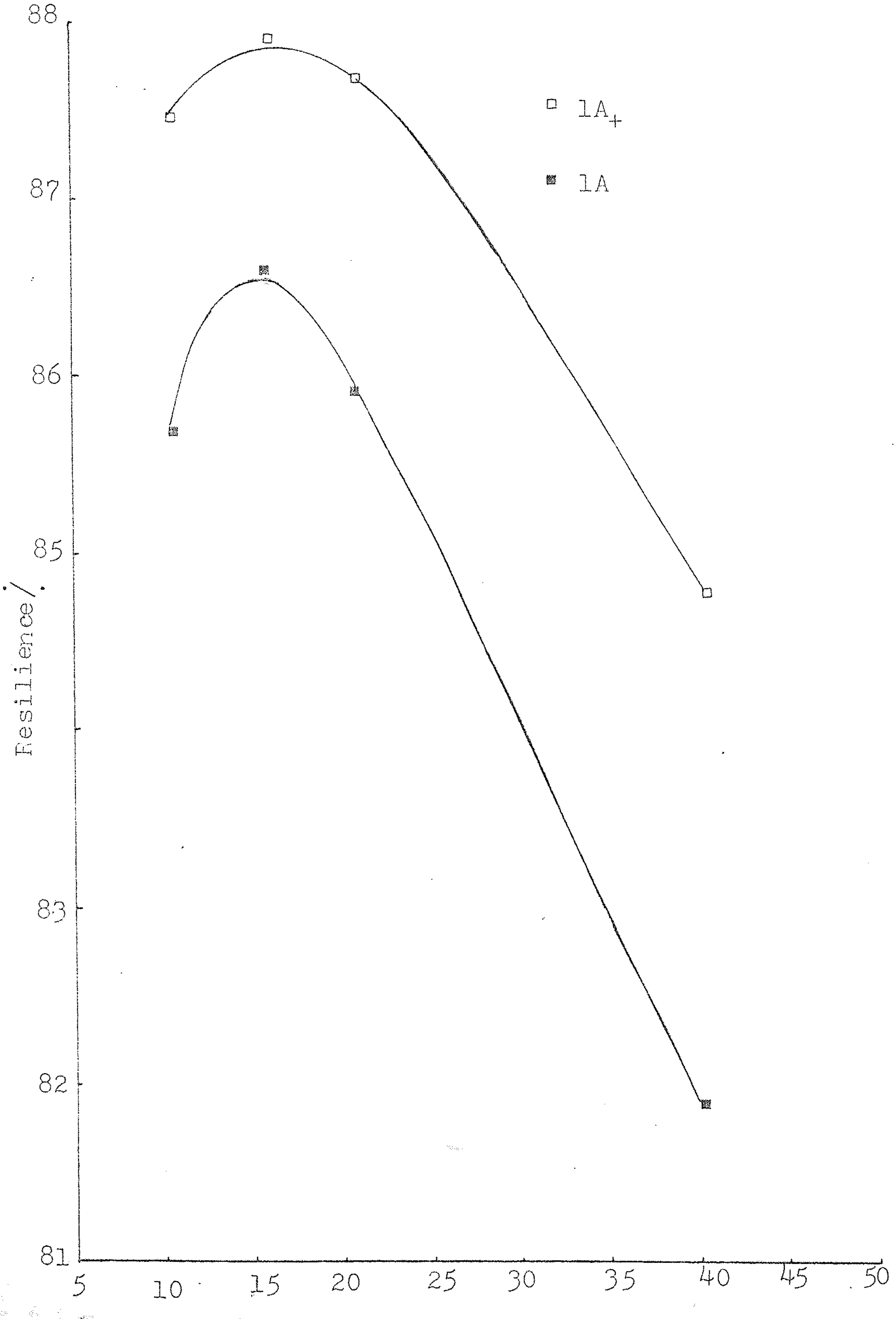


Fig.(52): Resilience Of MBT vulcanisates.



Confirmation of results.

Fig.(53): Resilience of MBT vulcanisates.

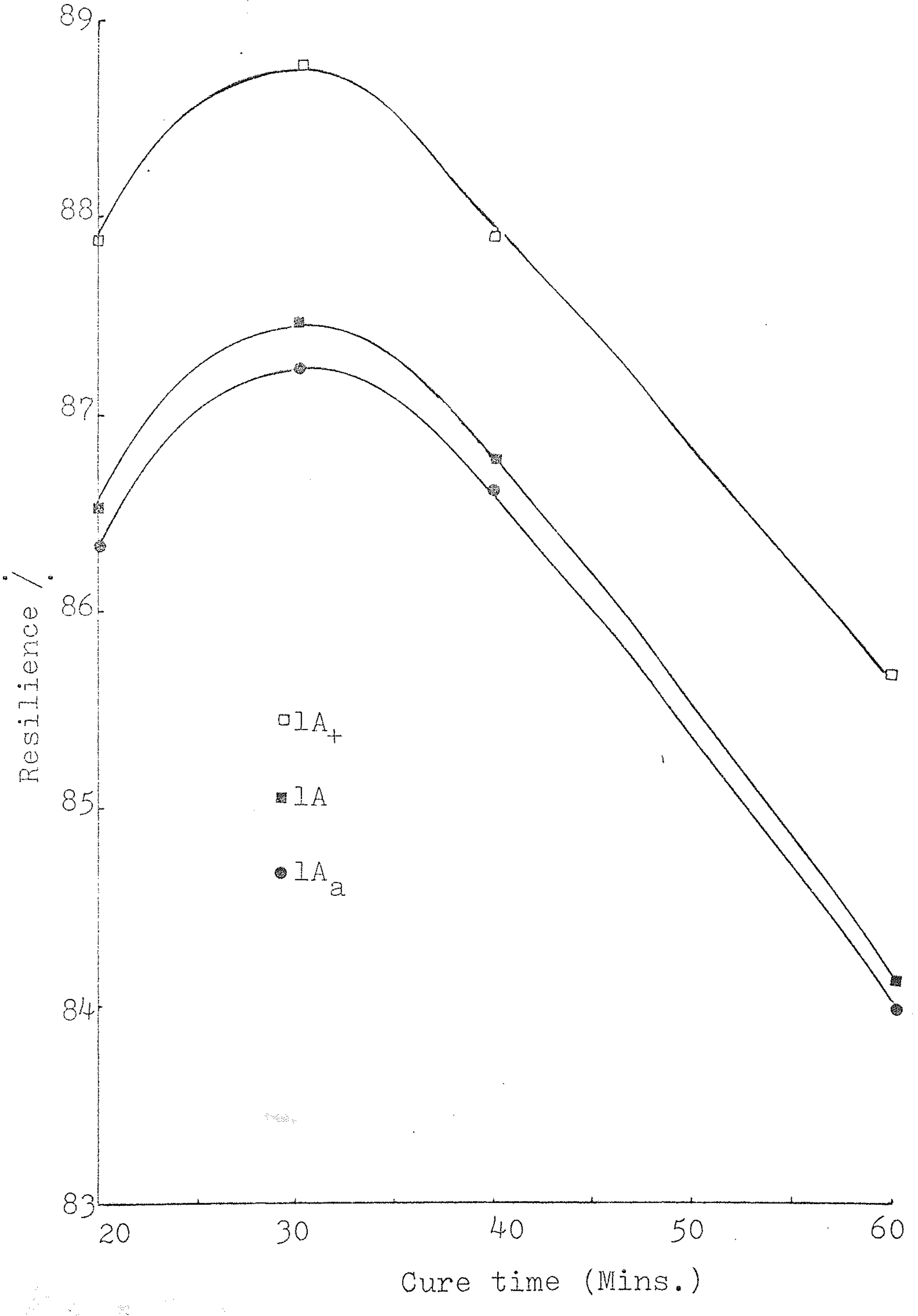


Fig.(54): Ultimate tensile strength (U.T.S.) of TMTD vulcanisates.

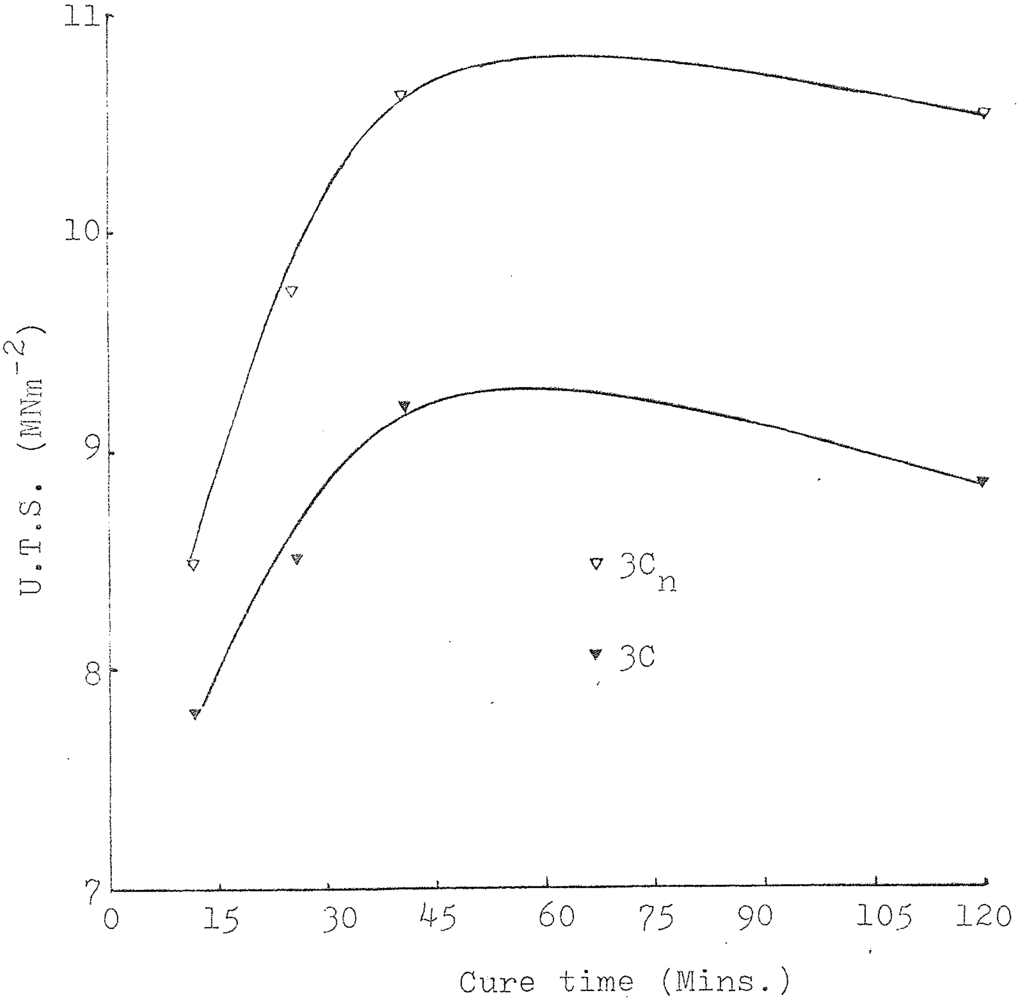


Fig.(55): Hardness of TMTD vulcanisates.

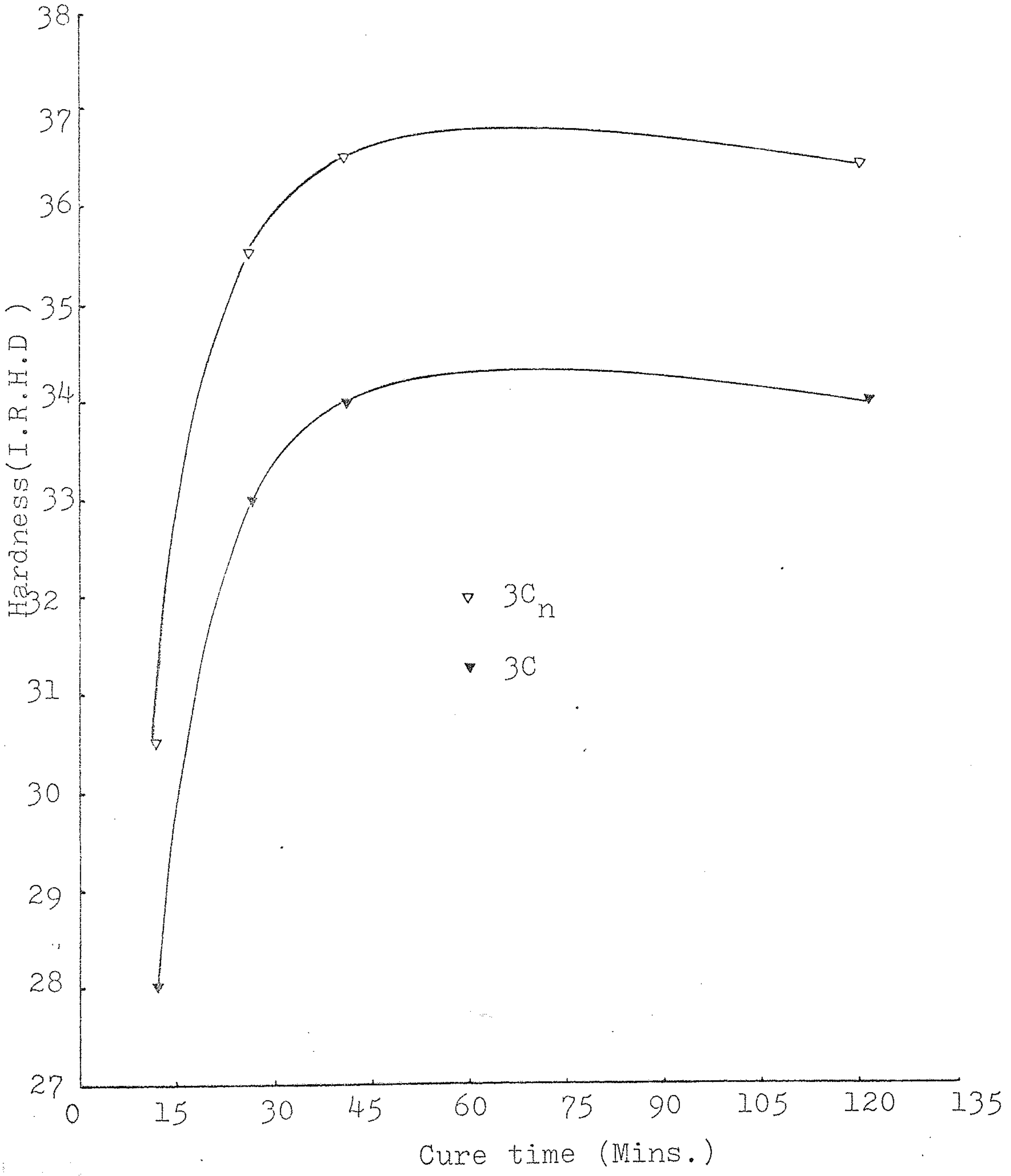


Fig.(56): Compression stress-strain curves for NR/TMTD vulcanisates (formulation $2C_+$) masticated in N2 with the TMTD.

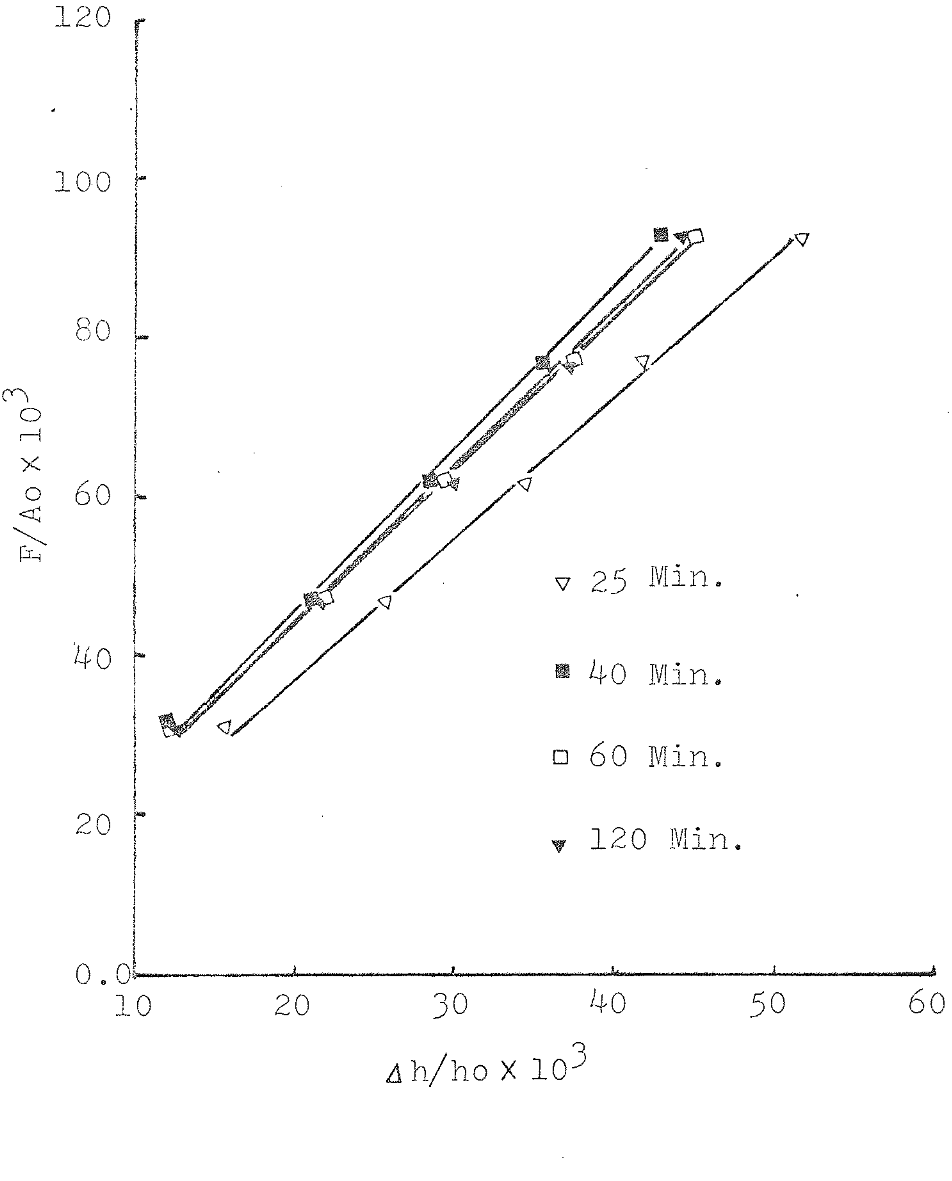


Fig.(57): Compression stress-strain curves for NR/TMTD vulcanisates (formulation 2C) masticated in Air without the TMTD.

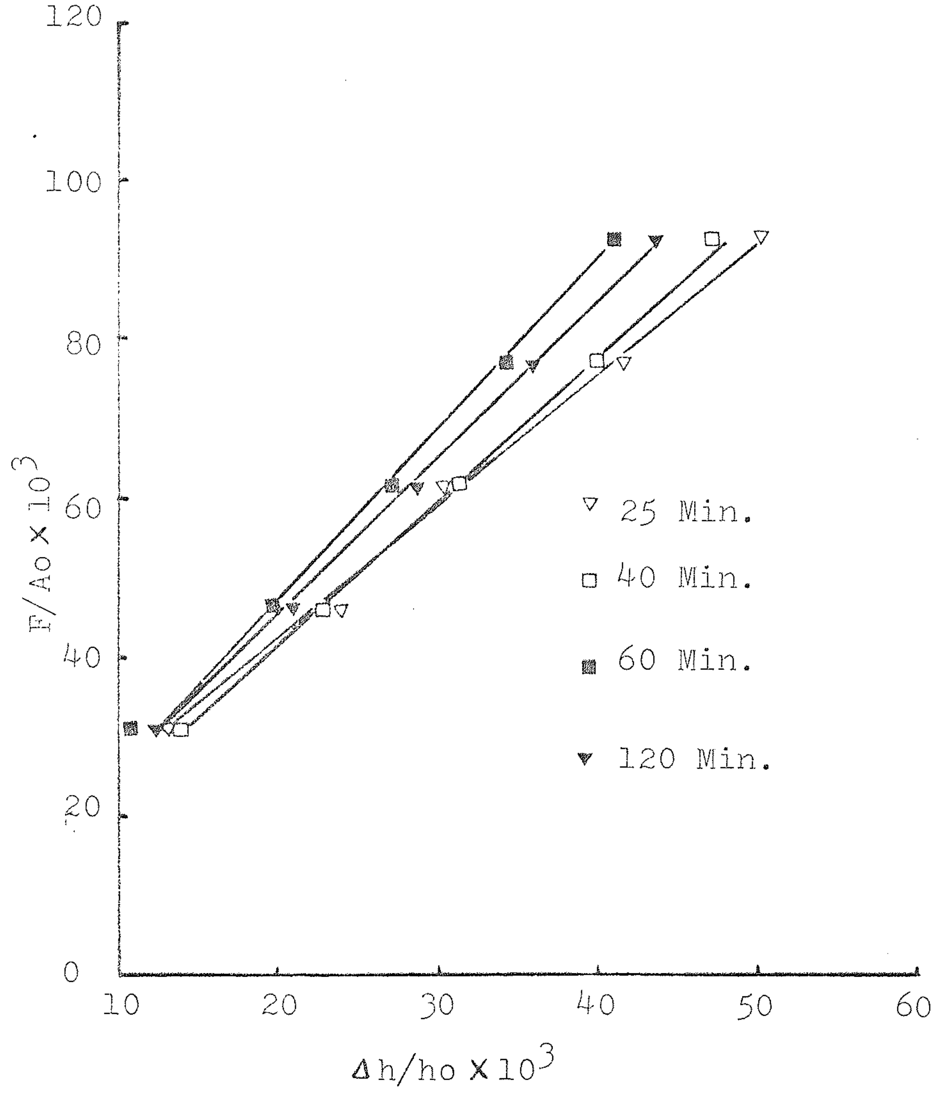


Fig.(58):Variation of compression modulus with cure time for NR/TMTD vulcanisates(formulation 2C,$2C_+$).

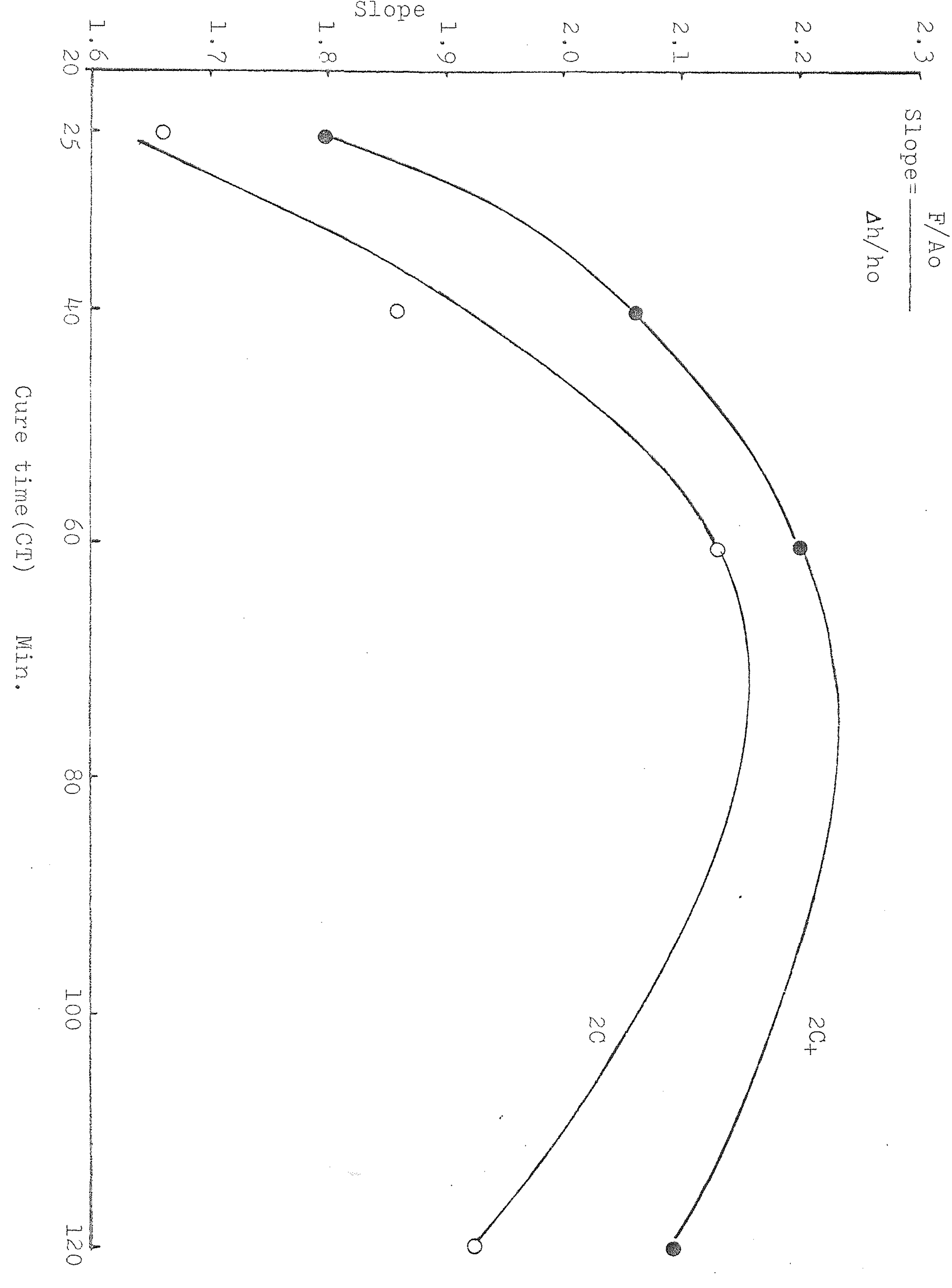


Fig.(59): Resilience of TMTD vulcanisates.

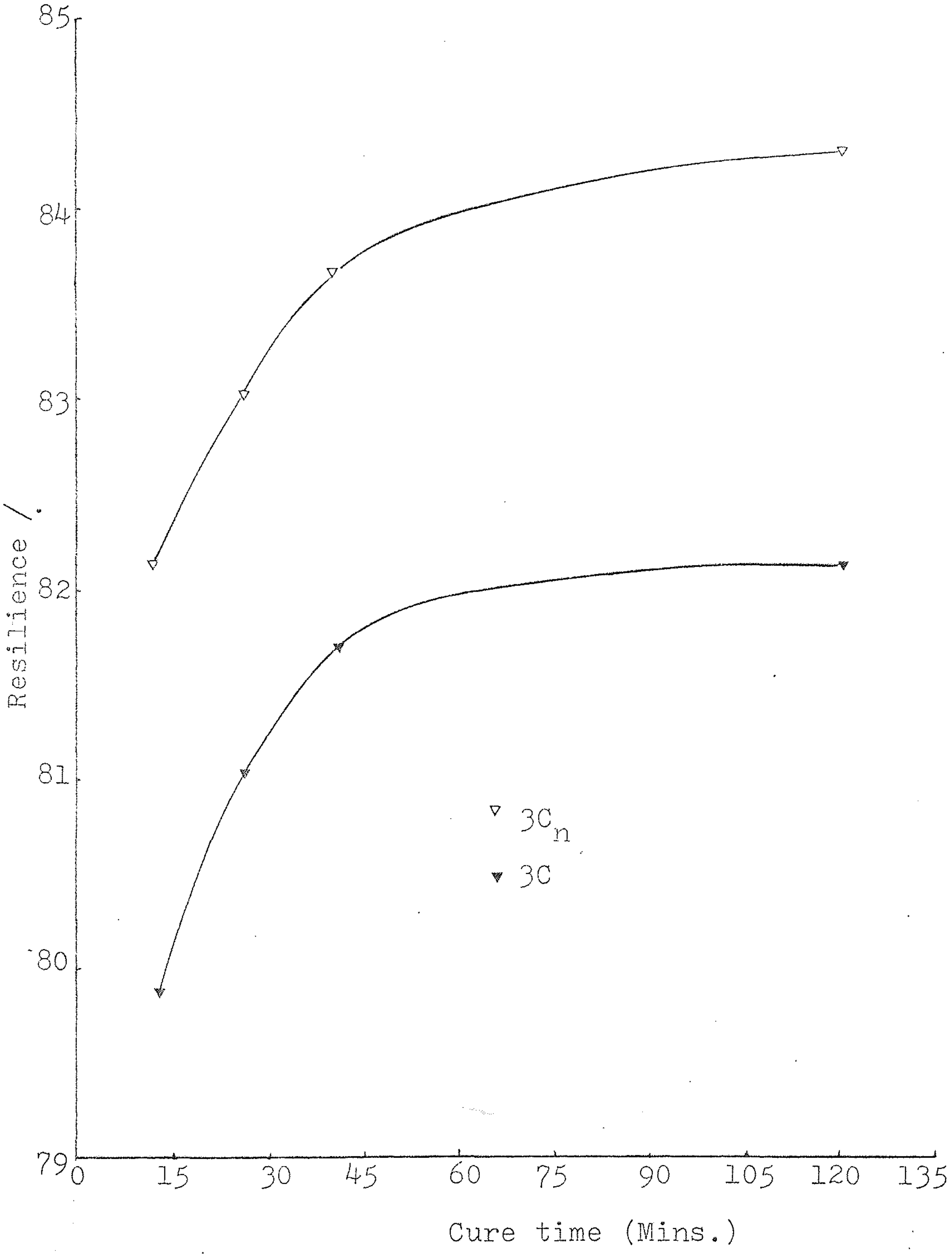


Fig.(60): Ultimate tensile strength (U.T.S.) of P25 vulcanisates.

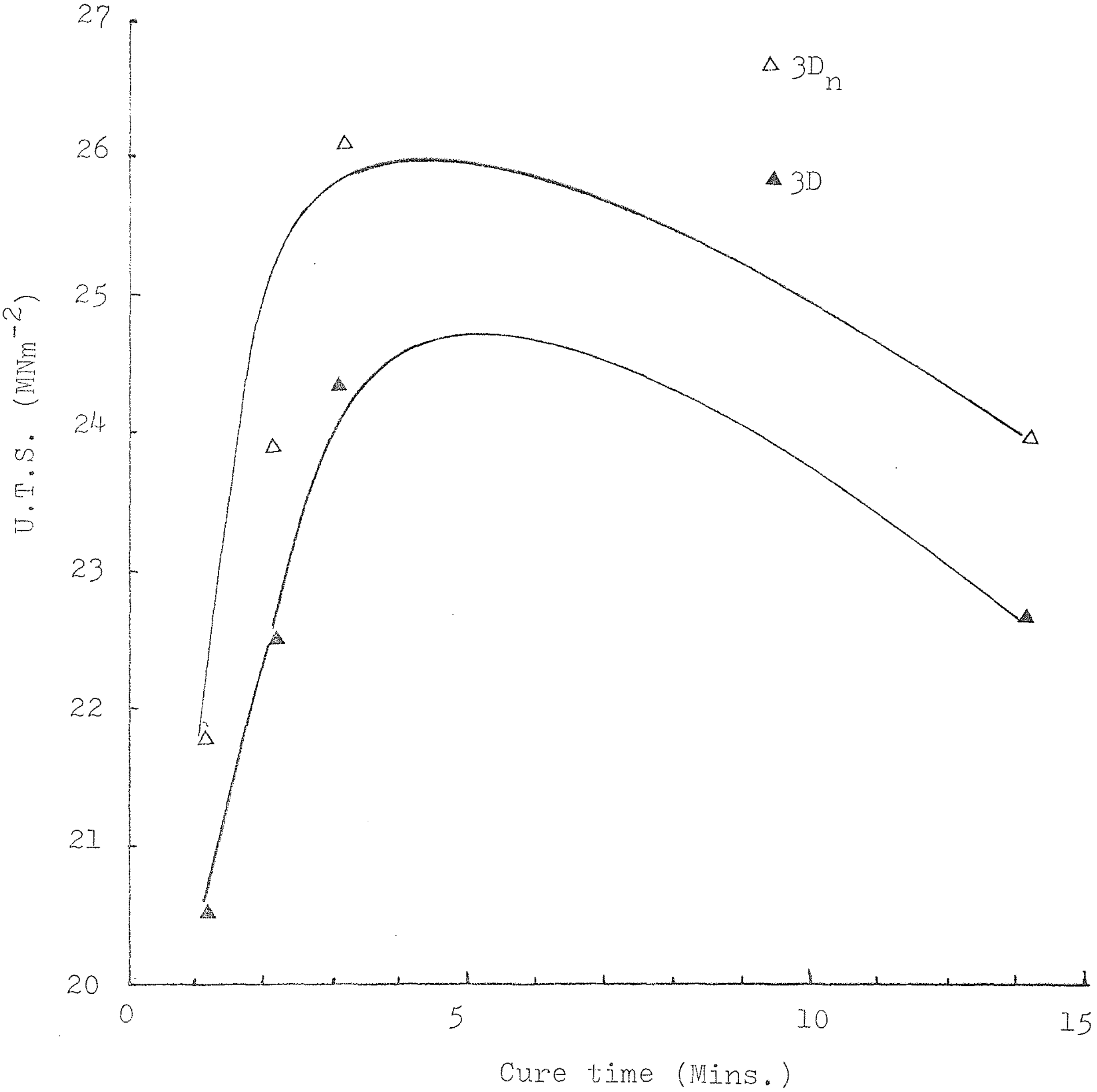


Fig.(61): Hardness of P25 vulcanisates.

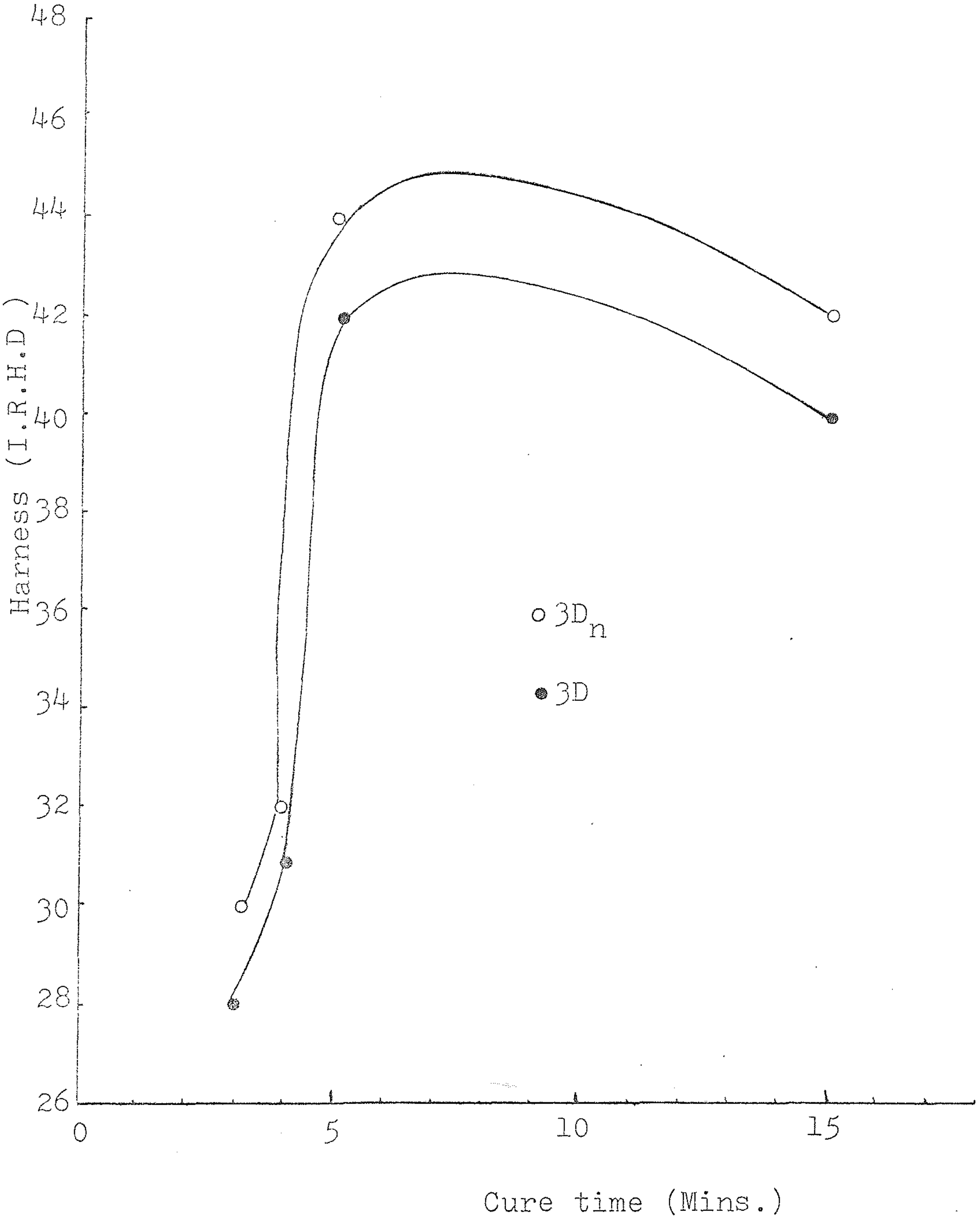
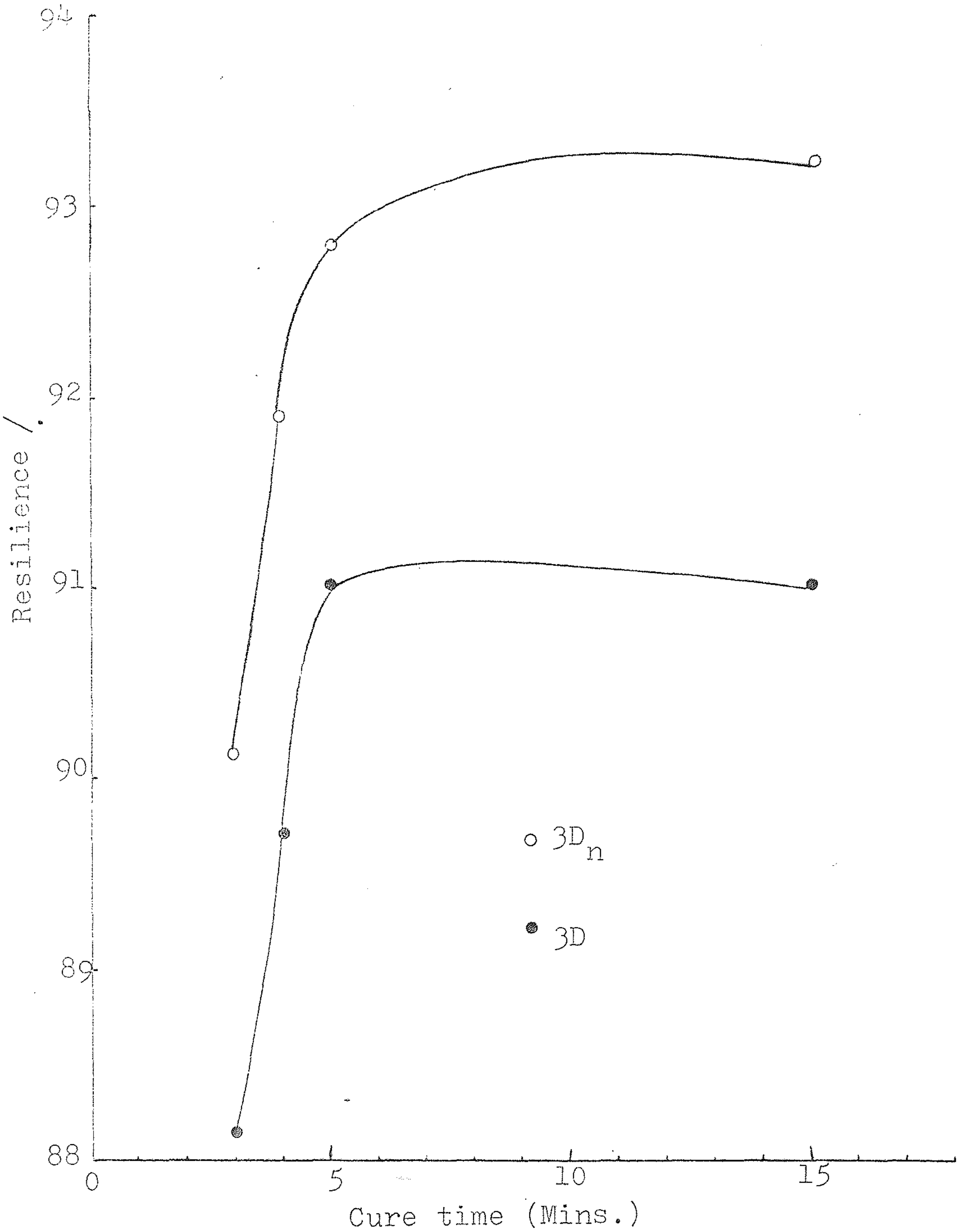


Fig.(62): Resilience of P25 vulcanisates.



CHAPTER 4

4- CONCLUSION

The investigation has been successfull in that we have shown that it is possible to terminate the polymeric free radicals produced during mastication of rubber under N_2 with free radical acceptors that are capable of further reaction during the vulcanisation process to form cross-links.

The reduction in free chain ends decreases during vulcanisation and reaches a minimum. On extended vulcanisation the normal reversion characteristics of the particular vulcanisation system will presumably take place but in the case of TMTD there is a much faster reversion than would be expected . TMTD produces vulcanisates of a very high thermal stability and no explanation can be offered for this degradation. The quantitative assessment based on the apparent increase in $\overline{M}n'$ calculated from the Moore, Mullins and Watson equation is suspect(see fig.29) when there is a concentration of chain ends and this particular result may be due to inaccuracies in the calculation. The reduction in chain ends by the use of the other radical acceptors is very definite however and this is further confirmed by the improvements noted in the physical properties of the vulcanisates especially those produced by prolonged mastication reactions.

Unfortunately these mastication reactions have to conducted in an inert atmosphere (N_2). When oxygen is present ,it is such a good radical acceptor that it reacts to the apparent exclusion of the other radical acceptors and chain end reduction in the corresponding vulcanisates is observed . Infact there is an increase in the number of chain ends accompanied by a slight decrease in physical properties. This is probably due to reaction of oxygen with double bonds to produce hydroperoxide groups which decompose during the high temperature vulcanisation process to produce free radicals which cause network degradation and increase network defects. This means that any practical application of this process must involve anaerobic mastication procedures. This cannot be carried out on a two roll mill and is difficult with an internal Banbury mixer. Angier and Watson (21),however, have successfully carried out anaerobic mechanochemical reactions on a large scale using an extruder . If the improvement in properties obtained by this process warranted a modification of the mastication process this would be a practical way of doing it. Fortunately the radical acceptors used can be the normal accelerators or sulphur donors used in typical formulations and no further recipe modification would be necessary.

The maximum improvements in properties are of the order of 30% for ultimate tensile strength ,12% increase in hardness and 4% increase in resilience . This,however, represents the best results obtained for nonfilled vulcanisates. The improvements in properties due to reinforcing filler may well mask the improvements due to chain end reductions.

The filler itself may have reduced the number of free chain ends because of the carbon gel effect which Watson has shown to be due to the acceptance of polymeric free radicals by the carbon black(128). It is difficult to see how one could prove that carbon black produces a reduction in chain ends because of the difficulties of determining cross-link densities in filled vulcanisates although Porter (129)has made progress in this field. The reduction in chain ends produced by mastication with vulcanisable radical acceptors results in marginally better thermal-oxidative stability but this is too small to be of practical significance .

It would appear ,therefore,that the reduction in chain ends described in this thesis is of very limited applicability . It may be useful where the very maximum properties are required for unfilled rubbers .

CHAPTER 5

5- SUGGESTIONS FOR FURTHER WORK

1- Try using an extruder as an anaerobic mixer to carry out radical acceptor reactions.

2- Assess the improvements in properties of filled vulcanisates and attempt free chain end calculations.

3- Try hot mastication reactions with radical acceptors.

4- Investigation into the reason for the inferior vulcanisates produced when the radical acceptor is masticated with rubber in air.

5- Investigate the possibility of producing vulcanisates with reduced entanglement contribution.

APPENDIX 1

1- TREATMENT OF EXPRESSON USED

$$C_1 = \frac{F}{6A_o} \cdot \frac{h_o}{\Delta h}$$

C_1 was determined from compression modulus data and from C_1 , Mc_{phys} was calculated using Mooney Rivlin eq.

$$C_1 = \frac{\rho RT}{2Mc_{phys}} \Longrightarrow Mc_{phys} = \frac{\rho RT}{2C_1}$$

From C_1 again Mc_{chem} was calculated using Moore ,Mullins and Watson eq.

$$C_1 = \left(\frac{\rho RT}{2Mc_{chem}} + 0.78 \times 10^6 \right)\left(1- \frac{2.3Mc_{chem}}{\overline{M}n} \right)$$

$$C_1 = \left(\frac{\rho RT + 1.56 \times 10^6 Mc_{chem}}{2Mc_{chem}}\right)\left(\frac{\overline{M}n - 2.3Mc_{chem}}{\overline{M}n}\right)$$

$$(\rho RT + 1.56 \times 10^6 Mc_{chem})(\overline{M}n - 2.3Mc_{chem}) = 2C_1\overline{M}nMc_{chem}$$

$$\rho RT\overline{M}n - 2.3\rho RTMc_{chem} + 1.56 \times 10^6 \overline{M}nMc_{chem} -$$

$$3.588 \times 10^6 \ Mc^2_{chem} = 2C_1\overline{M}nMc_{chem}$$

$$3.588 \times 10^6 Mc^2_{chem} + (2C_1\overline{M}n - 1.56 \times 10^6 \ \overline{M}n + 2.3\rho RT)Mc_{chem} -$$

$$\rho RT\overline{M}n = 0$$

$A = 3.588 \times 10^6$

$B = (2C_1\overline{M}n - 1.56 \times 10^6 + 2.3\rho RT)$

$C = -\rho RT\overline{M}n$

$$Ax^2 + Bx - C = 0$$

$$x = \frac{-B \pm \sqrt{B^2 - 4AC}}{2A} \qquad \text{where } x \text{ is } Mc_{chem}$$

χ was calculated from Flory and Rehner equation having Mc_{phys} from compression modulus and ν_r from swelling measurements .

$$-\left[\ln(1-\nu_r) + \nu_r + \chi\nu_r^2\right] = \rho V_o Mc^{-1}(\nu_r^{\frac{1}{3}} - \nu_r/2)$$

$$\text{or} \quad -\left[\ln(1-\nu_r) + \nu_r + \chi\nu_r^2\right] = \frac{2C_1V_o}{RT}(\nu_r^{\frac{1}{3}} - \nu_r/2)$$

$$\therefore \quad \chi = \frac{-\left[\ln(1-\nu_r) + \nu_r + \frac{2C_1V_o}{RT}(\nu_r^{\frac{1}{3}} - \nu_r/2)\right]}{\nu_r^2}$$

$$\text{where} \quad \nu_r = \frac{V_R}{(V_R + V_S)}$$

All these variables were obtained using a computer program under the name of G REZA and in order to have the values of these variables both compression modulus and swelling measurements had to be done . Later another computer program was used (REZA10), in which a known χ value for any specific accelerator (obtained from the other computer program) was used to obtain the rest of variables by doing swelling measuements only .

2- COMPUTER PROGRAMS

There are two computer programs (written by the author) for calculation of the swelling and the compression modulus results that are shown in the next two pages .

COMPUTER PROGRAM NUMBER 1

```
GREZA

20  INPUT R1,R2,R3,R4,R5,R6,M,A0,H0,W0,W1,W2
30  READ D1,D2,V0,R,T
40  DATA .92,.559,130.8,8.314E+07,298
45  H1=((R2-R1)+(R3-R2)+(R4-R3)+(R5-R4)+(R6-R5))
50  C=(2.4525E+06*H0)/(H1*A0)
55  A1=D1*R*T
60  M1=A1/(2*C)
65  C1=1/(2*M1)
70  X=3.588E+06
75  Y=((2*M*C)+(2.3*A1)-(1.56E+06*M))
80  Z=-(A1*M)
85  U=SQR((Y ** 2)-(4*X*Z))
90  M2=(-(Y)+(U))/(2*X)
95  C2=1/(2*M2)
100  D0=C1-C2
110  V1=W2/D1
115  W5=W1-W2
120  V5=W5/D2
125  W3=W0-W2
130  S=V1/(V1+V5)
135  A=(2*C*V0)/(R*T)
140  B=(((S ** .333)-(S/2)))*A
145  K=-(B+LOG(1-S)+S)/(S ** 2)
150  PRINT "c=";C;"m1=";M1
155  PRINT "c1=";C1;"m2=";M2
160  PRINT "c2=";C2;"d0=";D0
165  PRINT "w3=";W3;"s=";S;"k=";K
170  END
```

COMPUTER PROGRAM NUMBER 2

```
REZA10

10  INPUT W0,W1,W2,N
30  READ D1,D2,V0,R,T,K
40  DATA .32,.659,130.8,8.314E+07,293,.513
45  V1=W2/D1
50  W5=W1-W2
55  V5=W5/D2
60  W3=W0-W2
65  S=V1/(V1+V5)
70  A=D1*V0*((S ** .333)-(S/2))
75  B=-(LOG(1-S)+S+(S **.2)*K)
80  M1=A/B
85  A1=D1*R*T
90  C=A1/(2*M1)
95  C1=1/(2*M1)
100  X=3.538E+06
110  Y=((2*M*C)+(2.3*A1)-(1.56E+05*N))
115  Z=-(A1*N)
120  J=SQR((Y ** 2)-(4*X*Z))
125  M2=(-(Y)+(J))/(2*X)
130  C2=1/(2*M2)
135  D0=C1-C2
140  PRINT "w3=";W3;"s=";S
145  PRINT "m1=";M1;"c=";C
150  PRINT "c1=";C1;"m2=";M2
155  PRINT "c2=";C2;"d0=";D0
160  END
```

where R_1 , R_2 , R_3 , R_4 ,R_5 and R_6 are average of 12 readings (2for each) from reticulometer i.e

	1.22	1.52	1.80	2.05	2.31	2.55
	1.23	1.56	1.80	2.05	2.32	2.56
	↓	↓	↓	↓	↓	↓
averge	1.23	1.54	1.80	2.05	2.32	2.56

W_o, W_1 and W_2 are the weight of sample before swelling, swollen and deswollen sample respectively in gram . i.e 0.0778 , 0.2208 and 0.0774

h_o is the original height of the sample in cm i.e 0.265

A_o is the original cross-section area of the sample in cm^2 i.e 0.317

$M=\overline{M}n$

D_1 and D_2 are the density of natural rubber and solvent (hexane) respectively .

V_o is molar volume of solvent

$C = C_1$

$M_1 = Mc_{phys}$

$M_2 = Mc_{chem}$

V_1 and V_5 are the volumes of the rubber and solvent respectively .

$S = \nu r$

$K = \chi$

3- CALCULATION AND DISCUSSION OF CONFIDENCE LIMITS OF TENSILE STRENGTH

Assuming that the tensile strength values follow a normal distribution function, considering a 95% confidence limit , the limits within this specification would be given by $\bar{x} \pm 1.96\sigma$ where $\bar{x}$ is the mean values obtained and σ is the standard deviation of the same values(130). Calculation of the limits could be done as follows, (a sample of the MBT vulcanised for 10 minutes were taken as an example) .

OBSERVED VALUES

9.91	10.47	10.79	7.1	9.8

$\bar{x} = 9.61$

$$\sigma = \sqrt{\frac{\Sigma x_i^2 - \frac{(\Sigma x_i)^2}{n}}{n-1}}$$

where $\Sigma x_i^2 = 470.7$

$(\Sigma x_i)^2/n = 462$

$n = 5$

$\therefore \quad \sigma = 1.4627$

Substituting the values into $\bar{x} \pm 1.96\sigma$, the upper limit would be 12.48 and the lower limit as 6.7 . As it could be seen the observed values are within the range or rather within a better specification .

Hence the observations could be considered as reliable values within the 95% confidence limits .

APPENDIX 2

1-SYMBOLS USED IN THESIS

τ= Tension force

F= Force

A_o= Original cross-section area

ν= The number of elastically effective network per unit volume of rubber

R= Gas constant

T= Absolute temperature

λ= Extension ratio

C_1= Elastic constant

C_2= Elastic constant of uncertain physical significance

ρ= Density of rubber hydrocarbon

Mc_{phys}= The number average molecular weight between physical cross-links

Mc_{chem}= Number average molecular weight between chemical cross-links

$\overline{M}n$= Number average molecular weight

$\overline{M}n'$=Apparent molecular weight (after vulcanisation)

h_s= Unstrained swollen height

h_o= Initial height

Δh= Deformation height

h_s'= Strained swollen height

Δh_s= Change in swollen height

h_d= Height of swollen deformed sample

χ= Interaction coefficient

νr= Equilibrium swelling ratio

V_o= Molar volume of solvent

k= Boltzmann constant

N= Number of chains per unit volume

ηr= Relative viscosity

ηsp= Specific viscosity

$[\eta]$ = Intrinsic viscosity

α = Constant

K= Constant

E= The number of combined sulphur atoms per cross-link in network before treatment

E'= The number of combined sulphur atoms per cross-link in network after treatment

g= Entanglement factor

V_o/V= Number of chains per unit volume of network

p=C.E.C%= Percentage of chain ends combined

2- ABBREVIATION USED IN THESIS

Ph= Phenyl group

Ar= Aromatic group

DPPH= 2,6-diphenyl picryl hydrazyl

T_g= Glass transition temperature

NR= Natural rubber

BR= Butadiene rubber

SBR=Styrene -butadiene rubber

BNR= Nitrile butadiene rubber (nitrile rubber)

EPT= Ethylene-propylene terpolymer

IIR= Isobutylene-isoprene rubber (butyl rubber)

ZnO= Zinc oxide

PbO= Lead oxide

MgO= Magnesium oxide

CBS= N-cyclohexyl benzthiazyl-2-sulphenamide

S= Sulphur

SA= Stearic acid

EV= Efficient vulcanisation system

Semi-EV= Semi efficient vulcanisation system

TMTD= Tetra methylthiuramdisulphide

DMDS= Dimorpholinodisulphide

ZDP= Zinc diisopropyldithiophosphate

DCP= Dicumyl peroxide

CH=Cumene hydroperoxide

EPR= Ethylene propylene copolymer

E.N.M= Extra network material (extra means outside)

MBT= Mercaptobenzthiazole

ZMBT= Zinc benzothiazole-2-thiol (zinc mercaptobenzthiazole)

ZDC= Zinc(diethyldithiocarbamate)

ZDMC= Zinc(dimethyldithiocarbamate)

DTBP= Di-tertiarybutylperoxide

NRPRA= Natural Rubber Producers' Research Association

MBTS= Dibenzthiazyldisulphide

P_{25}= Dipentamethylenethiuramtetrasulphide

DPG= Diphenylguanidine

DIPDIS= Bis(diisopropyl)thiophosphoryldisulphide

DIPTRI= Bis(diisopropyl)thiophosphoryltrisulphide

DIPTET= Bis(diisopropyl)thiophosphoryltetrasulphide

DEDIS= Bis(diethyl)thiophosphoryldisulphide

DETRI= Bis(diethyl)thiophosphoryltrisulphide

DETET= Bis(diethyl)thiophosphoryltetrasulphide

DBUDIS= Bis(dibutyl)thiophosphoryldisulphide

DBUTRI= Bis(dibutyl)thiophosphoryltrisulphide

DBUTET= Bis(dibutyl)thiophosphoryltetrasulphide

EDIS= Sodiumdiethylthiophosphate

NaDIS= Sodiumdiisopropylthiophosphate

BUDIS= Sodiumdibutylthiophosphate

I.R.H.D= International rubber hardness degrees

$MR100_s$= Modulus at one hundred percent elongation (using MR100 apparatus)

U.T.S = Ultimate tensile strength

MR100,MR200,MR300 and MR600 = Modulus at 100%,200%, 300% and 600% elongation respectively

C.R.G = Constant reading gauge

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