Stress relaxation testing with a novel machine using rapid application of load

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STRESS RELAXATION TESTING WITH
A NOVEL MACHINE
USING RAPID APPLICATION OF LOAD

by

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A Master’s thesis submitted in partial fulfilment of
the requirements for the award of
Master of Philosophy
of
Loughborough University

August 1998

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THIS THESIS IS GRATEFULLY DEDICATED

TO

MY MOTHER, AND IN MEMORY OF MY FATHER
ACKNOWLEDGEMENTS

I would like to express my sincere regards and appreciation to my kind supervisors Mr. G. A. W. Murray and Prof. A. W. Birley for their invaluable guidance, constructive assistance and encouragement throughout the research programme.

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ABSTRACT

It has long been desirable to conduct Stress Relaxation measurements over shorter test times. The problem has been to achieve a short well-characterised loading phase and to obtain the first stress relaxation reading soon after the completion of loading. Although it is possible to programme a standard computer-controlled mechanical tester to acquire readings down to very short time periods, uncertainty of achieving the correct deformation at very high loading rates restricts its use. The Hounsfied Test Equipment company in collaboration with the Loughborough University has produced a compression tester intended to overcome the problem.

This new machine is capable of giving compressive strain rates from 0.1 mm/min up to 250 mm/min (SLOW MODE) and one extremely high compressive strain rate of 2 m/sec (120,000 mm/min - FAST MODE).

The machine was employed initially to produce sets of stress relaxation curves to investigate possible machine errors. The main error found was incorrect compression produced by the tester; it varied from 20% to 27% instead of the desired 25%. After this and some smaller errors were identified, several precautionary actions were taken to compensate for them.

The compensation techniques permitted progress to a study of three different Natural Rubber compounds at three different temperatures using several different compressive strains in both slow and fast modes.

A clear difference in the residual forces between fast mode test curves and slow mode test curves has been identified and the possible reasons for differences are discussed.

It has been shown that the relaxation curves in slow mode can be represented by two linear portions representing two different relaxation processes. On the each relaxation process the effect of the rate of compressive strain and the temperature of the material is discussed.
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LIST OF SYMBOLS

\( N(t) \) Concentration of load bearing net work chains at time \( t \).
\( R \) Universal gas constant.
\( T \) Temperature.
\( \lambda \) Elongation ratio.
\( \Delta \lambda \) Infinitesimal change in elongation ratio.
\( \sigma(t) \) Stress at time \( t \).
\( \sigma_c(t) \) Stress measured in continuous relaxation method at time \( t \).
\( \sigma_i(t) \) Stress measured in intermittent relaxation method at time \( t \).
\( \sigma_r(t) \) Relative stress at time \( t \).
\( \varepsilon, \varepsilon_1, \varepsilon_2 \) Strains
\( f(t), f_i \) Force at time \( t \) (i.e. \( \sigma(t) \times \text{Area} \))
\( f_e \) Equilibrium force at infinite time.
\( A_0 \) Cross sectional area of undeformed specimen
\( F(t) \) Force at time \( t \).
\( \Delta F(t) \) Change in force at time \( t \).
\( c(t) \) Moles of effective tetrafunctional crosslinking per cubic centimetre.
\( q(t) \) Number of moles of chain cleavage per cubic centimetre.
\( C_1 \) Elastic constant.
\( G_i \) Shear modulus.
\( \tau \) Relaxation time.
\( E(\tau) \) Distribution of relaxation time.
\( \eta \) Viscosity of Maxwell body.
\( k \) Rate constant.
\( c, n \) Constants
\( \varphi, \beta \) Constants.
$E'$ Complex dynamic tensile modulus.

$E'$ Tensile storage modulus

$E''$ Tensile loss modulus.

$S$ Weight of the swollen test specimen

$D$ deswollen weight of the test specimen

$V_r$ Volume fraction of rubber in the swollen specimen

$T$ Weight of the test specimen

$F$ Weight fraction of insoluble components of the specimen

$a_0$ Weight of absorbed solvent at equilibrium

$\rho_r$ Density of the rubber

$\rho_s$ Density of the solvent

$\chi$ Polymer solvent interaction parameter

$V_o$ Molar volume of the solvent

$a$ radius of the sample

$e$ Strain in the vertical direction

$E_o$ Young's modulus of rubber

$F_1$ Force required to compress the rubber sample under perfect lubrication condition

$F_2$ Force required to compress a bonded rubber sample

$t$ Sample thickness

$n_m(0)$ Initial network chain density determined based on statistical theory

$ns(0)$ Initial network chain density determined using swelling measurements

$n_m(0)$ Initial network chain density determined using stress-strain measurements
CHAPTER ONE

GENERAL INTRODUCTION

1.1. INTRODUCTION

Measuring the physical properties of polymers at high deformation rates is becoming more and more important. Data obtained under static conditions or at slow speeds do not satisfactorily evaluate those polymers which are subjected to rapid loading in service. On the other hand high speed testing can drastically reduce the time span of a test and gives an opportunity to predict the properties within a very short period.

The rapid loading (impact loading) is encountered very frequently in service but it is difficult to achieve similar conditions in laboratory.

Advanced apparatus is available today in the field of high speed testing. These apparatus can perform tests at reasonably high speed and can overcome the difficult problems encountered in measuring short time intervals and obtain reasonably detailed and exact information concerning the behaviour during the first few seconds. However having information on stress relaxation behaviour during the first few microsecond or milliseconds with a reasonably low cost instrument is still a problem.

In order to overcoming these difficulties, Hounsfield Test Equipment Company with collaboration from IPTME, has designed a new instrument to measure the stress relaxation behaviour of viscoelastic materials at very short time, after the application of load.

Measurements of stress relaxation of an elastomer is one of the several experiments used in studying viscoelastic properties of a material. Basically, the sample to be tested is deformed to a fixed strain and the stress required to maintain that fixed strain is measured as a function of time at constant temperature. In principle, long term stress relaxation measurements will characterise the viscoelastic behaviour of the material.

Beside the theoretical interest in these measurements, there are instances where stress relaxation is also of direct practical interest. Studies have been made attempting to relate stress relaxation to other physical phenomena, such as impact behaviour\(^{(1)}\). Long term stress relaxation experiments are also often used in investigating the effect of environment on viscoelastic materials. Phenomena such as thermal and oxidative degradation\(^{(2)}\) have been studied using this technique.
The long term properties of elastomers can result from two fundamentally different processes. First, there can be physical relaxation processes such as the flow of chains and the movement of entanglements, etc. Second, there can be chemical processes such as scission of covalent bonds at crosslinks or along the main chain.

Relaxation test at high speed loading is a sensitive indicator of small changes in composition, changes in structure such as degree of crystallinity or extent of branching in the polymer which show up markedly in the early part of the relaxation test\(^3\).

1.2. OBJECTIVES

The objectives of this research can be broadly divided into three groups

A) To investigate the functionality of the newly developed machine

It is necessary to determine the accuracy of the newly developed machine in detail, before it is used to carry out the stress relaxation tests. (However when the machine behaviour was found to be inconsistent, more attention was spent on a study of the machine behaviour.)

B) To study the influence of loading rate on the subsequent physical relaxation process.

In a previous work\(^4\), the stress relaxation curves obtained at a very high loading rate were different to the curves obtained in conventional, low loading rate tests. It is important to establish whether these results were the consequences of an error or if they were directly linked with the high loading rate. However, if additional relaxation phenomena are involved in the test at high loading rates, then such tests will not be fully comparable to tests that have been carried out in the past at low loading rates.

The influence of crosslink density and temperature on the subsequent relaxation process with fast and slow loading rates will also be studied and it is hope to discuss the possible mechanism for relaxation behaviour.

C) To develop a protocol for stress relaxation tests which start with a very high strain rate.

The high speed stress relaxation test is a novel test. Such tests can provide a considerable amount of data within a very short period. Using the newly developed
machine, some six decades of physical relaxation data can be collected in less than seventeen minutes, thus creating an attractive way to obtain relaxation data in fields such as quality control and materials testing. Hence it is important to develop a protocol for relaxation tests which use very high loading rates.

1.3 INTRODUCTION TO STRESS RELAXATION AND RELEVANT TERMINOLOGY

The main intention of this section is to introduce the two important aspects of mechanical properties of polymers and the terminology which will be used extensively to describe the relaxation phenomena of polymers.

The foundation for all the molecular theories of the physical properties of polymers was laid when Guth, Mark and Kuhn(5) first recognised the role of configurational entropy of polymer chains. Macromolecule segments are able to rotate with respect to each other along the chain backbone. They are capable of taking large number of conformations differing in entropy. This provides a link in interpreting the macroscopic physical properties in terms of microscopic molecular dynamics.

MECHANICAL BEHAVIOUR OF RUBBERY MOLECULES

When a cross-linked amorphous polymer is subjected to a deformation, the backbone chains of the molecule have to undergo the necessary conformational changes(6) in order to accommodate the displacement of crosslinks. The rate of change of conformation towards its equilibrium depends on two factors:

1) The inactivity of the chain to change its conformation
2) How far away the actual conformation is from its equilibrium

The conformational change which occurs even after the deformation ceases is termed as Physical Relaxation. As this aspect is very relevant to our studies, it will be considered in detail.

Physical relaxation depends on the chain sluggishness. It is accepted that increase of chain sluggishness increases the physical relaxation. On the other hand chain sluggishness inevitably leads to more damage to network giving more chemical relaxation. The dependence of physical relaxation on the chain sluggishness can be shown by performing the relaxation test at different loading rates. A detailed discussion on the influence of loading rate on subsequent relaxation will be considered in Chapter 2.
High speed loading rates transfer kinetic energy to polymer molecules enhancing the molecular mobility. Similarly, the mobility can be influenced by changing the temperature. The mobility of the molecules can be better understood by considering the thermal energy, as the kinetic energy criteria is more complex to consider. However, in order to incorporate the thermal effect, it is necessary to consider the internal energy variation associated with the molecular movement.

When considering an isolated linear polymer chain, it is capable of assuming many different conformations. Because of thermal energy, such a chain is constantly changing its conformation from one to another, namely it is undergoing Brownian motion\(^7\). However, these changes (rotational) are restricted due to the presence of intermolecular and intramolecular forces.

This phenomena can easily be explained related to n-butane molecule. The rotation potential due to intramolecular forces for the central bond of n-butane is given in Fig. 1.1. In this molecule, at the lowest energy level, the terminal methyl groups are presumed to be fixed in staggered conformation\(^8\). Likewise for any polymer molecule, with respect to a specific bond, such potential energy distribution can be calculated.

![Fig. 1.1: The conformational energy of n-butane as a function of the rotational angle \(\phi\) about the central C-C bond\(^6\).](image1)

![Fig. 1.2: Staggered Position\(^6\)](image2)
At low temperatures, the thermal energy is not sufficient to overcome the potential barriers for rotational motions of segments. The chain segments are essentially frozen in fixed positions.

When increasing the temperature segmental vibration starts and the amplitude of vibrational motion becomes greater, and eventually the thermal energy becomes roughly comparable to the potential energy barriers of segment rotation. This makes the conformational changes virtually unrestricted. Therefore the influence of intermolecular and intramolecular forces of the polymer molecules will be minimal. With further increase of temperature, short-range diffusional motion starts and becomes faster and faster. As a result the physical relaxation of rubber molecules at high temperatures completes within very short period. However at low temperature the short range diffusional motion does not take place. This makes the molecule more sluggish and takes a long time to relax the stress through molecular rearrangements. Hence at low temperature, it takes a longer time to relax the stress through physical relaxation.

Having discussed physical relaxation, all time dependant phenomena subsequently observed can only be explained by considering processes leading to changes in network structure. These processes are collectively known as Chemical Stress Relaxation. In general chemical stress relaxation does not mean the necessary involvement of chemical reactions through electron transfer from one molecular segment to another, but broadly the damage and subsequent rearrangement of molecular structure.

A detailed discussion on physical relaxation and chemical relaxation is given in Chapter Two.
CHAPTER TWO

LITERATURE REVIEW

2.1 INTRODUCTION

Stress relaxation, which is the time dependent stress decay under constant strain condition, is a manifestation of viscoelasticity. This is the cumulative effect of a number of separate physical and chemical processes. Physical processes are due to viscoelastic nature of the elastomer and involve re-orientation of molecular network, the breaking of secondary valency bonds and the movement of entanglements upon the application of stress. Chemical relaxation occurs through chain scissions of a rubber network by thermal and oxidative effects. These both types of processes occur simultaneously, but because of their different nature, the time and the temperature at which one or the other dominates is different.

Both physical and chemical relaxations are sensitive to temperature. Other factors that influence the stress relaxation behaviour of an elastomer include the nature of crosslinks, the presence of fillers and the crosslink density which will be discussed later in detail.

2.2 PHYSICAL STRESS RELAXATION

Physical relaxation can occur for number of reasons including physical movements of chains, aggregates or entanglements. This type of relaxation is dominant in the early stages of stress relaxation, specially at low temperature and consists of an early rapid relaxation with a relaxation time of $10^{-6}$ to $10^{-4}$ seconds followed by a slow decay.

In addition to these two processes a third type of pseudo-physical process takes place through breaking or forming of bonds between segments of rubber chains and carbon black particles. However the mechanisms are not well understood.

Derham has pointed out that physical relaxation of natural rubber and styrene-butadiene rubber is a linear function of the logarithm of time. It was also shown that dicumyl peroxide vulcanised natural rubber has a much lower relaxation rate than sulphur/CBS (N-Cyclohexyl -2-Benzothiazyl Sulphenamide) cured natural rubber. From these experiments, Derham inferred that both the type of crosslinks and the nature of polymer are important factors in determining the relaxation behaviour.
Furthermore he has pointed out that inclusion of a high proportion of carbon black increases the stress relation rate and also increases all the viscoelastic effects. Derham has commented\(^{(19)}\) that stress relaxation measurements are superior to compression set measurements for assessing the service performance of rubber sealing rings, as it gives a measure of how the sealing stress decay with time. Compression set measurements given in the standards for evaluating sealing ring performances measure the ability of a vulcanisate to recover from a lengthy imposed deformation. It does not give an idea about the sealing stress, which is the most important factor in evaluating the sealing performance.

According to Gent's study\(^{(20)}\), the stress relaxation of natural rubber vulcanisates (2-mercapto benzothiazole and sulphur system) at a constant extension has a linear dependence upon log time and also the percentage rate of stress relaxation under moderate deformation is substantially independent of the amount of deformation. The dependence of stress relaxation on the deformation up to 200% is shown in the Fig. 2.1.

![Fig. 2.1: Relationship between percentage rate of stress relaxation and extension\(^{(20)}\)](image)

Cotton and Boonstra\(^{(18)}\) have studied the influence of filler to polymer linkage resulting from polar forces in various filler systems by the use of stress relaxation technique. butadiene rubber (cis 1,4) and SBR-1500 were chosen for their study. In order to avoid the influence of changes in simple polymer-polymer covalent crosslinks and covalent filler polymer linkages on stress relaxation(chemical scission of chains) they did their experiments at room temperature. In this study, they pointed out that reinforcing fillers influence the stress relaxation by two separate mechanisms.
1) In raw rubbers, stress relaxation is a viscous controlled process and its rate decreases in the presence of reinforcing fillers, probably caused by an increase in the viscosity of the compound.

2) In cured swollen rubbers, reinforcing fillers increase the rate of relaxation and this increase is related to the modulus value, i.e. the reinforcing potential of the filler.

The activation energy for the relaxation process of raw compounds with or without filler is in the range of $16\pm 2$ k cal/mole. Since the activation energy for a viscoelastic process would be expected to be 15 - 25 k cal/mole at room temperature, it is suggested that the observed relaxation process is controlled by molecular friction as well as stiffening action of chain entanglements\(^{(21)}\).

The effect of surface activity of fillers has been investigated\(^{(18)}\) by incorporating heat treated ISAF (Intermediate Super Abrasion Furnace) black. The heat treatment of black removes active groups from the surface of carbon black particles without changing their structure. It has been observed that the relaxation rate in the raw styrene butadiene rubbers\(^{(1500)}\), the rate of relaxation increases as the surface activity of the carbon black decreases.

Further in raw styrene-butadiene rubber, the rate of stress relaxation is closely related to the percentage bound rubber, for a number of compounds varying in carbon black loading. The rate of relaxation decreases as the bound rubber percentage increases (i.e. increasing carbon black loading).

The rate of stress relaxation in vulcanised pure butadiene (cis-4) gum stocks decreased significantly with increased crosslink density achieved by increasing the concentration of dicumyl peroxide\(^{(18)}\). A similar trend has been observed for rubbers swollen to constant volume fraction of rubber (i.e. $V_r = 0.25$). The rate of stress relaxation in raw rubbers is related to the fractional resistance of molecular flow and the number of mobile entanglements. The number of mobile entanglements and the final extensibility of molecular chains are, however decreased appreciably as crosslinks are introduced and this is responsible for the decrease in rate of relaxation.

In unswollen, cis-4 polybutadiene compounds, there is no significant change in the rate of relaxation with carbon black loading, although in swollen samples a very large increase in the rate of relaxation occurs as the carbon black loading is increased\(^{(18)}\). The insignificant change in the rate of stress relaxation of unswollen samples may be due to the masking of carbon black and polymer interactions by the viscous flow of the polymer.
In the above study\textsuperscript{(18)} the relaxation measurements were taken after 0.4 min. and 10.0 min. after the deformation is applied. Hence above conclusions are only derived from physical relaxation measurements.

Bartenev\textsuperscript{(16,17)} has studied the stress relaxation in unfilled crosslinked rubber and has shown that relaxation is related to three basic processes.

1) Rapid Stage of Physical Relaxation.
   Orientation and shifting of free segments of the molecular chains, occurring very rapidly, with relaxation times from $10^{-4}$ to $10^{-6}$ sec. at 20°C.

2) Slow Stage of Physical Relaxation\textsuperscript{(22,23)}.
   Regrouping of elements of supermolecular structures with relaxation times ranging from $10^2$ to $10^3$ sec.

3) Chemical Relaxation.
   Rearrangement of crosslinks and backbone chains both from chemical reactions and as a result of stress with relaxation times of the order $10^7$ to $10^9$ sec. at 20°C.

Further study\textsuperscript{(24)} by Bartenev on the mechanism of the slow stage of the physical relaxation process in vulcanisates has suggested three further fundamental processes which are characterised by one and the same activation energy, corresponding to the activation energy of viscous flow in the same rubber. From this it follows that not only the fundamental processes of the slow stage of physical relaxation, but also viscous flow, possess the very same general segmental mechanisms, which are at the same time connected with the reorganisation of supermolecular weight structures in the form of well-ordered microregions of various sizes. The relaxation times for the three fundamental processes will vary and these differences are explained by the fact that in the rubbers the ordered microregions differ in size.

In another publication Bartenev et al.\textsuperscript{(25)} have proposed a multi stage mechanism for stress relaxation of carbon black filled compounds. There it is suggested that the relaxation process consists of five fundamental processes. The first three processes are related to the slow stages of physical relaxation within the bulk of rubber and have no connection with the fillers. Further it is observed that the activation energies for first three processes in the filled and unfilled rubbers take the same value and it is not a function of the deformation up to 200% elongation or the black content of the system.
The fourth process is connected with the relaxation in the black-rubber domains. The activation energy of this process is a function of the deformation and of the filler content. Here the relaxation process takes place through a breaking-away and adhesion of segments of the rubber chains to the black particles. The fifth process involves the chemical relaxation of vulcanisates.

Steiner and Tobolsky\(^{(26)}\) have studied the viscoelastic behaviour of dicumyl peroxide vulcanised natural rubber in air and vacuum at different temperatures. Their results have shown that the relaxation in vacuum is different from that of in air. In vacuum, in the temperature range from 25 °C to 100°C, very little relaxation occurs and equilibrium values are attained within a relatively short period of time. This takes place in the range of $10^3$ to $10^5$ seconds depending upon the temperature. These results indicate that finite equilibrium values exist for stress relaxation of natural rubber in vacuum in the above temperature range.

In contrast to the relaxation behaviour of NR in vacuum, Thirion\(^{(27)}\) has shown that in air, relaxation takes an extremely long time to attain an equilibrium value (i.e. no change in relative stress with time).

Murakami and Tamura\(^{(28)}\) has studied EPT polymers (Ethylene Propylene Terpolymer) which contains crosslinkages of C-C, C-S-C and C-S\(_{1,2}\)-C types. They concluded that the physical relaxation in the initial stages is independent of the kind of crosslinkages at a given crosslink density.

Derham\(^{(19)}\) has reported that the physical relaxation of natural rubber (NR) vulcanisates is directly proportional to the logarithm of time. He also showed\(^{(29)}\) that incorporation of organic filler, for instance carbon black, results in an increase in the relaxation rate. A partial explanation of this follows from the theory of strain amplification, which shows that, due to the inextensibility of the filler, the strain in the polymer phase of the filled material is greater than the overall strain. Stress relaxation rates in general increase with increasing polymer extension, thus filled rubbers would be expected to show higher relaxation rates. Derham has also shown that the stress relaxation rate at 100% extension for natural rubber increases with increasing loading of a semi reinforcing carbon black filler. According to Derham, higher relaxation rates in filled materials may be associated with filler-filler or filler-polymer breakdown.

Murakami et al.\(^{(28)}\) have observed that the physical relaxation caused by entanglements significantly affects the chemical stress relaxation. Then a study\(^{(30)}\) has been carried out to explore the quantity of chain scissions of peroxide vulcanised natural rubber vulcanisates having different amounts of trapped entanglements and to investigate the influence of physical relaxation on chemical relaxation. For this purpose the rubber networks crosslinked in the swollen state and crosslinked conventionally
have been used. The main reason to prepare the samples in the swollen state is, it gives simpler topologies than those prepared by conventional vulcanisation.

The quantity of chain scission for networks prepared in the swollen state and dry state have been evaluated by means of chemical stress relaxation. The degree of degradation for both kinds of networks also have been determined by the degree of equilibrium swelling and by sol fraction determination of degraded networks. By comparing the chemical stress relaxation of both networks with the degree of degradation, the influence of physical relaxation on chemical stress relaxation has been evaluated.

The stress relaxation behaviour of solution cured samples differed significantly from that of the samples crosslinked conventionally. Further they have found that there is little or no influence of the physical relaxation caused by entanglements in the equilibrium swelling. The effect of dangling chains arising from scission on the equilibrium swelling is negligible. Based on their work they have shown that the swelling method can be used as a measure of degree of degradation on chemorheology. Taking into account the influence of physical relaxation on chemical relaxation, a new relationship between the relative stress decay and the relative network chain density has been proposed for conventionally vulcanised samples. The relationship is,

\[ \frac{f(t)}{f(0)} = \left[ A \left[ \frac{n_{sw}(0)}{n_{sw}(t)} - 1 \right] + 1 \right]^{-1} \quad (A \geq 1) \]

Where \( n_{sw}(t) \) and \( n_{sw}(0) \) are the network chain densities of samples at time \( t = t \) and \( t = 0 \). The slope, \( A \) is a constant representing the degree of physical relaxation in chemical stress relaxation. The dependence of value \( A \) on temperature and initial network density is shown as in the Fig.2.2.

The value of \( A \) decreases linearly with increasing \( n_{sw}(0) \) except at lower degrees of crosslinking, where its value increases abruptly. On the other hand, the value of \( A \) varies little with temperature. This can be interpreted in terms of the amounts of trapped entanglements in the network. At the lower degree of crosslinking, there is a lot of trapped entanglements in networks compared with that of the chemical crosslinks. As the degree of crosslinking increases, on the contrary, the portion of chemical crosslinks is predominant in networks, so that the influence of the physical relaxation diminishes.
2.3 CHEMICAL STRESS RELAXATION

Physical relaxation predominantly controls the early part of the relaxation process at low temperatures. But at high temperatures and at long times, chemical relaxation is the dominant way of relaxing the stress. It involves the breaking and rearrangement of crosslinks and backbone chains with relaxation times in the order of $10^7 - 10^9$ seconds at 20°C.(25).

In chemical stress relaxation, the damage on the structure can take place mainly in two ways.

1) Scission of chemical backbone bonds leading to the breakage of elastically effective chains. Each scission will reduce the number of active chains by one.

2) Rupture of chemical crosslinks which hold the molecular segments together, forming a three-dimensional network. Each crosslink that undergoes rupture will affect two molecular segments, reducing the number of active chains by two.

The two factors will lead to a consequent formation of chemically active radicals, which will in turn undergo a series of reactions, leading to further changes in the structure.

Fig. 2.2: Dependence of $A$ on the initial network chain density $n_{sw}(0)$ for conventionally crosslinked sample degraded at various temperatures in air: 373 K (O), 383 K (.), 393 K (\()^{30}\).
A. V. Tobolsky\(^{(3)}\) was the first to study the chemical stress relaxation in rubbers. He studied the stress decay of vulcanised rubbers such as natural rubber, neoprene, butyl, butadiene-styrene copolymers and butadiene-acrylonitrile copolymers. He found that in the temperature range 100°C to 150°C these vulcanised rubbers showed a fairly rapid decay to zero stress at constant extension. Since in principle, a thermoset elastomer in the rubbery range should show little relaxation and certainly no decay to zero stress, the phenomenon was attributed to a chemical rupture of the elastomer network. This rupture was specifically ascribed to the effect of molecular oxygen since under the condition of very low oxygen pressure the stress relaxation rate was markedly diminished.

The kinetic theory of elasticity is a molecular theory concerning the equilibrium elastic properties of rubber materials. So it does not permit one to predict the behaviour of a rubber under non equilibrium situations such as stress relaxation. However, it is possible to apply the methodology of the kinetic theory in certain special cases where the consequences of the degradative processes fall within the scope of the above theory. In the application of statistical theory to the calculation of the entropy of a molecular network, it is necessary that the network remain constant for a long enough time for the chains to assume all accessible configurations sufficient number of times so that their average properties approach those which would be statistically calculated. Thus the statistical theory may be applied to a polymer which relaxes by virtue of chemical scission of its crosslinks.

The basis for much of the discussion of chemical relaxation is the two network theory of Tobolsky\(^{(2)}\). This theory is based on the statistical theory of rubber elasticity.

Tobolsky presented a very basic concept to deal with the simultaneous scission and crosslinking occurring at a state of constant stress. This concept says that the equilibrium stress experienced by a crosslinked rubber is proportional to the number of stress supporting network chains per unit volume. If the crosslinked rubber undergoes a reaction resulting in chain scissions, the number of stress supporting chains will be reduced resulting in a decay of stress. During ageing, chains and crosslinks can be broken and reformed simultaneously, new crosslinks formed are in equilibrium in the stress and do not affect the stress of the sample. If the stress is then removed, they will not contribute to the return of the specimen to its original strain free condition, and thus the original specimen dimensions will not be regained. From these considerations the techniques of continuous and intermittent stress relaxation measurements came into practice as separate methods of measuring the effects of scission and consequent crosslinking.
Scott and Stein\(^{(32)}\) were the first to consider a molecular model in order to explain the effects of simultaneous crosslink rupture and complete recombination. In this work they justified the application of the statistical theory of long chain molecules to the stress relaxation situation. Further they have attempted a fundamental treatment which suggested that when crosslink rupture and formation occur simultaneously, the two-network theory is incorrect. When crosslinking occurs during degradation there arises the possibility that, although the added crosslinks may make no immediate contribution to the tension, they may do so at later stages after other bonds have been broken. Later on, their mathematical treatment has been criticised\(^{(33)}\) and it has been shown that their model gave the same result as the two-network theory for the case of crosslink formation without any degradation reaction.

An experimental and theoretical study has been made by Berry et al.\(^{(33)}\) on the crosslinking of a stretched network in the absence of degradation and it was suggested that for this case the two-network model provides a satisfactory approximation to the real network.

Subsequently, Scanlan and Watson\(^{(34)}\) have considered the consequence of rupture of crosslinks concurrently with formation of new crosslinks at a fixed state of strain. They were the first to show that the two-network hypothesis was incorrect, where rupture occurs after new crosslinks have been introduced to the network.

In their study, the susceptibility of the following factors for peroxide cured natural rubber vulcanisates and sulphur cured vulcanisates have been verified experimentally. These factors have been deduced from the two-term form of the equation for the strain energy of a aged network. The two-term form of the equation has been formulated with the aid of the two-network theory.

(i) The rate of stress relaxation should be independent of extension if it is the result of a chemical reaction whose rate is not affected by the strain energy.

(ii) The amount of permanent set may be calculated by combining the "continuous" stress relaxation measurements with that of the "intermittent" stress relaxation.

(iii) The behaviour of the elastic constant $C_1$ in interpretation of ageing in terms of network changes.

Elastic constant $C_1$ is found in the two parameter equation\(^{(35)}\),

$$\frac{1}{2}A_0^{-1}(\lambda - \lambda^{-2})^{-1} = C_1 + C_2\lambda^{-1},$$

which closely represents the actual stress-strain behaviour of the rubber.
It has been found that the experimental verification of the above prediction of the two-network theory is reasonably good. However, in the third factor, the results on the variation of 'elastic constant' with initial extension show a trend closer to that predicted by the two-network theory up to extension ratio 2.67 and then falls away.

So, the above experimental results are mainly in accord with the two-term form of the strain energy.

A theoretical treatment of a model network in which one chain is broken and one is formed has been treated in the work of Scanlan and Watson(34). This model is capable of explaining the experimental results, but it is also in agreement with the suggestion(32) that crosslinks at first making no contribution to the tension during the stress relaxation, come when other links are broken, to serve to increase the tension.

This model has indicated a slower rate for stress relaxation than predicted by the two-network hypothesis. So they have expressed their doubtfulness in using the two-network theory in interpretation of stress relaxation measurements.

Later, Thomas(36) discussed the limitations of the two network theory interpretation of stress relaxation data in rubbers. He discussed the equation \( \frac{f_t}{f_0} = \frac{n_t}{n_0} \), where \( f_t \) and \( n_t \) represents the force and network concentration at time \( t \), \( f_0 \) and \( n_0 \) being the original unaged values. \( f_t \) is determined solely by the fraction of initial or first, net work remaining at time \( t \), no account being taken of new network chains formed during ageing. This assumption is embodied in the two network theory. Because of this the above theory can lead to errors in the interpretation of continuous and intermittent stress relaxation in terms of two interpenetrating, but otherwise independent networks. In this analysis he has considered four types of network change mechanisms which can lead to ageing of rubber.

The first case which he considered was 'network chain scissions only' while the second one was 'crosslink formation without network scission'. The two network theory is valid for both cases. The third type was crosslink scission with concurrent crosslink formation, both links being of the same chemical type. Then no change in crosslink density occurs. No actual system behaves like this. Flory(37) has studied this theoretically and has pointed out that stress will decay more slowly than required by the 'two network' theory. The fourth type was 'crosslink scission with concurrent formation, the new crosslink being immune from further scission'. The theory has shown a deviation from the experimental curves, once about 30 percent of the first network has being removed.

Most stress relaxation studies in rubber materials have been made on thin samples, so that the relaxation rate is not diffusion controlled. The oxygen content in
the atmosphere has been found to strongly effect the stress relaxation for thin walled, sulphur cured natural rubber specimens\(^\text{38}\). For thin-walled specimens it has been found that oxygen under increased pressure significantly influence the relaxation rate.

Tamura and Murakami\(^\text{39}\) have studied the initial network densities of peroxide cured natural rubber, based on the statistical theory \((n_m(O))\), stress - strain measurements \((n_{sm}(O))\) and by swelling measurements \((n_s(O))\). The difference between \(n_m(O)\) and \(n_s(O)\) was usually constant and independent of the magnitude of network chain density. That is, it was found that the number of entanglement network chains in the crosslinked natural rubber is usually constant, independent of network chain density. The entanglement network chain density has been found as \(0.7 \times 10^4\) mole/ml. This led to the supposition that the molecular weight between entanglement points would be about 9000. Furthermore they have found that the scission of dicumyl peroxide cured natural rubber occurs only in the main chain.

Arasora and Dogadkin\(^\text{40}\) have studied the stress relaxation of different vulcanisates [natural, polybutadiene, styrene butadiene, poly isoprene, carboxylated rubbers vulcanised with different vulcanising agents (sulphur and metal oxides) using different vulcanising methods (irradiation and thermal)] in vacuum at ambient temperature (130°C). The relaxation taking place in the vacuum should be purely due to thermal degradation of the weak bonds in the three dimensional network. Comparison of kinetic data on stress relaxation produced by thermal degradation yields an indication of the structure and the character of the structural changes in the vulcanizate. Through this experiment they inferred that the rate constants of thermal stress relaxation decrease with network density, and the thermal relaxation of stress in natural rubber vulcanised by radiation is mainly due to rupture of molecular chains. In this case, relaxation is accompanied by a decrease in the network density.

Thermal stress relaxation in rubbers vulcanised with metal oxides is due to rearrangement of the salt crosslinks by exchange. In this case the molecular chains remain intact, and the number of crosslinks is not altered. Thermal relaxation in rubbers vulcanised with sulphur is due to preferential rupture and rearrangement of the weak polysulfide crosslinks. The new crosslinks contain a smaller number of sulphur atoms. In this case the number of crosslinks may either rise or fall, depending on the secondary reactions of the polymer radicals formed.

According to Stenberg and Janson\(^\text{41}\), thermo oxidative relaxation of filled natural rubber (with semi reinforcing blacks (SRF)-N700 series) is diffusion controlled. The diffusion at high temperature can be affected by a very hard oxide skin which is found to be formed on the rubber samples.
A. N. Gent has examined the influence of amount of extension and the presence of reinforcing fillers on stress relaxation in vulcanisates of natural rubber, butyl rubber and SBR (non crystallising). In unfilled natural rubber vulcanisates the rate of stress relaxation has been found to rise sharply for extensions of more than about 200%. The reasons for this has been attributed to the growth of a crystalline phase. Similar rates have been observed at all extensions for carbon black filled natural rubber vulcanisates.

In butyl rubber, the percentage rate of stress relaxation is seen to be substantially independent of the imposed extension for small extensions, up to about 100%. At larger extensions a significant decrease occurs. The relaxation rate at 300% extension being about 30 to 40% lower than that obtained at low extensions. In contrast to NR vulcanisates, butyl rubber does not show significant amounts of crystallinity until the extension reaches 500 to 700%. The reduction probably reflect the behaviour of an oriented amorphous network.

For unfilled SBR vulcanisates, the rate of stress relaxation has found to be substantially constant only at low (i.e. up to about 50%) extensions. At higher extensions it was considerably smaller, becoming about one-half of the original value at 360% extension. In filled SBR, firstly the rate of relaxation decreases sharply as the extension is increased in the range of 0-25%. Secondly the relaxation rate increases at large extensions. The increase was attributed to the progressive failure of rubber-carbon black attachments, either at the surface of the filler particles or by rupture of the rubber molecules attached to them.

K. H. Hillmer and W. Scheele have studied the physical stress relaxation process and the chemical relaxation process, which overlap each other and influence the final result. Measurements of the continuous stress relaxation of thiuram vulcanisates and intermittent stress relaxation of both sulphur and c-c crosslinked vulcanisates of natural rubber have been considered and the following conclusions have been drawn.

1) Determination of the rate of continuous tension loss is not suitable for measuring the oxidative degradation. The reason for this is that rheological processes superimpose themselves on the chemical reactions induced by oxygen, cause a reduction in tension and affect both the form of the relaxation curve and the rate of tension loss. This is particularly noticeable in the case of vulcanisates containing polysulphidic bonds.

2) Using intermittent stress relaxation (section 3.1.1) and by choosing suitable temperatures and frequencies it is possible to eliminate the influence of
rheological processes and thus to measure only the rate of tension loss due to oxidative degradation.

Bell and Cunneen\(^{(44)}\) suggested that the rate of auto-oxidation reaction depends on the structure of the crosslinks. Further they have suggested that polysulphide crosslinks and elemental sulphur inhibit the oxidative mechanism, whereas cyclic sulphur is a weak inhibitor or even may catalyse the oxidation process. In practice the auto-oxidation relaxation is masked by the presence of anti-oxidants in the compound.

Tamura et al.\(^{(38)}\) have studied the stress relaxation mechanism of sulphur-cured natural rubber of different crosslinked structures (mono: mono and di: mono, di and poly) under continuous and intermittent methods in atmospheres containing different concentrations of oxygen and nitrogen. In order to study the scission mechanism three models\(^{(45)}\) have been considered based on the type of network scission namely for the random scission along the main chain, scission of crosslinks and selective scission near the crosslink sites. Stress relaxation of each vulcanisate has been determined using three models in relation to sol fraction and the swelling measurements of samples degraded under the same conditions. Then they have ascertain the concordance of these models with continuous and intermittent relaxation data.

In the above study, they have observed at high temperatures, even very low amount of oxygen strongly affects the degradation of these vulcanisates. Furthermore the scission mechanism of the vulcanisates depends on the quantity of oxygen in the atmosphere. In a nitrogen atmosphere, the scission occurred mainly near the crosslink sites in all samples. However, in the presence of a small amount of oxygen, the scission took place near the crosslink site in the initial stage of degradation and then along the main chain at the later stage. In an atmosphere of comparatively high oxygen content, the degradation seems to result from the oxidative scission along the main chain.

Murakami and Tamura\(^{(46)}\) have studied the mechanism of stress relaxation of TMTD cured vulcanisates in a nitrogen environment. Experimental work has been conducted in the temperature range \(99^\circ C\) to \(230^\circ C\). They have attributed the faster decay in stress during the initial period (approx. 4hrs) of the stress relaxation curve to the scission of crosslinks. In longer time, the stress relaxation occurring in the temperature range \(99^\circ C\) to \(160^\circ C\) has been attributed to physical relaxation while above \(160^\circ C\) it has been attributed to the scission reaction of crosslinks.

According to Lyubchanskaya et al.\(^{(47)}\) the effect of oxygen is negligible if the stress decay is due to break down of polysulphidic crosslinks. They reported a twelve-fold increase in stress relaxation when the primary scission is due to mono, di- sulphide crosslinks. They also showed that the stability of main chains is the factor of interest as the stress relaxation increases with the amount of double bonds in the main chain.
They found a seven fold increase in relaxation in NR having abundant unsaturation compared with sodium catalysed butadiene rubber having 43-49% double bonds.

Thus in chemical stress relaxation mainly two types of reactions are in operation. Firstly, oxidative degradation of molecular chains and secondly the thermal breakdown of the network. The extent of these two reactions may depend on the nature of the main chain and the nature of crosslinks in the structure. From the study of chemical relaxation the following conclusions can be made.

1) Chemical relaxation is independent of the amount of compression\(^{(47)}\) varying from 10-50%. (against 0-250% in tension reported by other workers\(^{(48,49)}\)).

2) During the chemical relaxation process, the change in the equilibrium modulus* may be very small: this indicates that the amount of crosslink scissions is equal to the formation of new crosslinks in the unstressed state\(^{(36,41,44,46,50)}\).

* Modulus obtained when the rubber is elongated to the desired level and allowing the stress to relax to its equilibrium value (i.e. when the stress does not change with time) at a constant temperature\(^{(51)}\).

3) The effect of oxygen on chemical relaxation depends on
   - The type of sulphur crosslinks\(^{(5,10,47)}\).
   - The susceptibility of polymer chains to oxidation\(^{(41,44)}\).

4) The presence of filler is very important on the chemical relaxation as the addition of filler reduces the activation energy of polymer oxidation\(^{(47)}\) and has also been found to increase the resistance to photo-degradation\(^{(31)}\).

2.4. FACTORS AFFECTING STRESS RELAXATION BEHAVIOUR

2.4.1 TYPE OF DEFORMATION

The stress relaxation rate of natural rubber has been studied\(^{(20)}\) under simple extension, simple shear, indentation and in sidewise deflection deformation. Under these deformation modes it has been found that the stress relaxation is virtually independent of the imposed deformation. The stress relaxation rates determined under each mode have given fairly close values. However a difference between relaxation rates in tension and compression has been observed for natural rubber samples\(^{(52)}\). For 16 mm thickness samples the relaxation values were higher in tension than in compression while for 4 mm thickness samples the relaxation values were lower in tension than in compression (Fig.2.3).
This difference may be due to the fact that the exposed area to volume ratio increases with decreasing sample thickness for dumb-bell (under tensile mode) shape samples, but it is constant for the cylindrical samples. Further, thin samples may also have different morphologies from bulk specimens. So thin sections permit more rapid chemical changes than in thick samples.

![Graph](image)

**Fig. 2.3:** Relaxation in compression and in tension versus logarithmic time for materials A and B at 85°C (Numbers indicate the type of the test and the sample thickness)(52)

Material A is natural rubber compound without antioxidant while Material B is with antioxidant.

### 2.4.2 EFFECT OF STRAIN LEVEL

The influence of strain level on the stress relaxation has been studied in various deformation modes. Gent, A.N. et al.\(^{(20)}\) have studied the stress relaxation rate of butadiene-styrene copolymer at various strain levels (<50%). They have employed three deformation modes namely, a series of loading cycles in simple shear, an interrupted tensile load and an uninterrupted tensile load. In each mode samples have been subjected to different levels of strains (initial forces). The percentage rate of relaxation calculated in each level of strain under different modes has been found to be almost the same. According to his study, it has been found that the stress relaxation is substantially independent of the amount of deformation at low deformations (<50%).
The stress relaxation of unfilled natural rubber has been found to be independent of the imposed deformation up to 200%\(^{(42,53)}\). At strains greater than 200\% the rate of relaxation increases. So the stress relaxation at large extensions (>200\%) is less accurately proportional to the logarithm of time than at low extensions (Fig. 2.4a and 2.4b).

At this level of strain it is reported that the strain induced crystallisation of natural rubber vulcanisates affects the chemical stress relaxation behaviour\(^{(10)}\). In contrast to NR, in SBR and BR the fractional stress decay is smaller at high extensions than at low extensions. The reason given for this behaviour is the growth of the crystalline phase at higher extensions. In the compression mode, NR and NBR relaxation rates were independent of the imposed strain between 15 and 25\%.

![Graph](image)

Fig. 2.4a - Effect of elongation on chemical st. relaxation of sulphur cured natural rubber at 100°C\(^{(54)}\).

![Graph](image)

Fig. 2.4b: Experimental relation between the percentage rate of stress relaxation S and the imposed extension for the unfilled natural rubber\(^{(42)}\).

### 2.4.3 EFFECT OF STRAIN RATE (LOADING RATE)

Few studies are available on the effect of the loading rate upon the subsequent stress relaxation. A gum NR compound and a filled NR compound have been subjected to loading rates of 0.3 mm/min and 1.56 mm/min in order to study the subsequent relaxation process\(^{(55)}\). The gum compound of NR have shown to be fairly independent of the rate of loading (Fig.2.5), while the relaxation in filled NR is affected by the loading rate.
Another study\textsuperscript{(55)} carried out on filled natural rubber at the compressive loading rates of 0.1, 1.0, 10.0 mm/min has shown that the rate of loading affects the stress developed and the higher stresses are associated with higher relaxation rate (Fig. 2.6).
MacKenzie and Scanlan\textsuperscript{(57)} have studied the effect of tensile strain rate on the relaxation of natural rubber vulcanisates. They have found that increasing the tensile strain rate of natural rubber specimens from 1 to 596 seconds\textsuperscript{-1} has little effect on the relaxation rate at longer time, but the very early stage of the relaxation has been affected (Fig. 2.7).

![Fig. 2.7: Effect of tensile strain rate on stress relaxation of filled NR compound\textsuperscript{(57)}](image)

Franklin and Chang\textsuperscript{(58)} have applied Boltzmann Superposition Principle on a generalised Maxwell model and have presented a relation between extension, relaxation and hysteresis. In this analysis they have considered the effect of strain rate...
on the relaxation stress of poly-isobutylene. The stress time relation derived from a Maxwell model, which is generally accepted for the interpretation of stress relaxation, predicts that the relaxation stress is directly proportional to the strain rate. In their experiment they have calculated the relaxation modulus at various strains and have shown that the relaxation modulus does not vary with strain rate when the time is measured from the start of extension, except in the early period of relaxation.

Cotton and Boonstra\(^{(18)}\) have studied the applicability of the empirical formulation \(f_t = f_{t_0} \times t^n\) for most of the rubbers and have comment that all the rubbers at room temperature obeyed the above equation. In this formulation \(f_t\) is the force at time \(t\) (in minutes), \(f_{t_0}\) is the force after one minute of relaxation and \(n\) is the relaxation rate of the material. They have studied the relationship between \(\log(f_t)\) and \(\log(t)\) for SBR and BR compounds and have shown that relaxation rate is independent of the speed at which the samples are being compressed. They have been able to reproduce the rate of relaxation \((n)\) within the range of \(\pm 2\%\).

2.4.4 EFFECT OF FILLERS

A wide variety of fillers are commonly employed, such as carbon black, carbonates and silicates of calcium and magnesium and zinc oxide. These fillers are used mainly

1) to bring down the cost of the article.
   eg: non-reinforcing fillers as diluents

2) as a reinforcement to provide high mechanical strength.
   i.e. reinforcing fillers.

With the incorporation of reinforcing fillers the mechanical properties of rubber changes drastically from that of gum rubber.

Among the few investigators who have studied filled rubbers, Mullins occupies a prominent place with his very important observation called Mullins effect\(^{(59)}\). This effect occurs in rubber containing filler: it shows a higher modulus on the first stretch than it does on succeeding stretches. The lower modulus persists in the material even though the material is allowed to relax for many days at room temperature. However, the rubber recovers to its original high modulus if it is allowed to rest at a temperature near 100 °C.

The reduction in modulus is attributed to the breakdown of filler structure. The major portion of the relaxation of stress which occurs in strongly reinforced
vulcanisates held at constant strain at normal temperature is also due to a breakdown of filler structure\(^{(60)}\).

Based on the above observation Blanchard and Parkinson\(^{(61,62)}\) have made an attempt to investigate a possible theoretical treatment for the softening of rubber by an applied stress. The finding of these authors have strongly supported that the softening of reinforced rubber, when it is stressed to moderate extensions, owes little to breakdown of filler chain structure and is due primarily to rupture of attachments between the filler and the rubber molecules. This means that the stiffness of reinforced rubber is influenced greatly by the mode of attachment of rubber to filler. This work has further suggested that the attachment formed through carbon particles are of two kinds. One is a relative weak type linkage due to physical attachments and the other a strong type linkage due to chemisorptive attachments, which remain unbroken by stressing. The strong linkages are relatively few and have not been found with fillers other than carbon black, but the strength distribution of the weaker type does not depend on the chemical nature or type of such relatively weak attachments.

Cotton and Boonstra\(^{(18)}\) have investigated the effect of surface activity of carbon black to stress relaxation under tensile mode. They have incorporated heat treated ISAF black (heat treated to 500°C, 800°C, 1100°C, 1500°C, 2700°C) into SBR 1500. It has been observed that relaxation rate increased as the surface activity of the black was reduced, although the Mooney viscosity values remained nearly constant.

In SBR 1500 the rate of stress relaxation was closely related to the percentage of bound rubber, for a number of compounds varying in carbon black loading. In raw rubbers, reinforcing carbon blacks decrease the rate of relaxation while in cured rubbers the effect of carbon black is very small. Further the stress relaxation test has been carried out at various temperatures in the range of -9°C to 80°C and stress relaxation curves have been plotted. The data so obtained have been transposed to a standard temperature (24°C) by using Leidemans Superposition Principle. An excellent agreement between calculated and observed curves have been obtained.

Ono\(^{(63)}\) studied the tensile stress relaxation of carbon black filled SBR in the linear viscoelastic region as a function of temperature and volume fraction of fillers. He found that time-temperature superposition is valid. Further, he noticed carbon black increases the modulus of the compound, especially in the rubbery region and the time range over which the glass-rubber transition occurs. The shift factor is divided into three regions; an Arrhenius dependence in rubbery and glassy states and WLF (William - Landel-Ferry) dependence in the transition region. The apparent activation energy in the rubbery state increases with the volume fraction of carbon black (or silica) and is unaffected by the structure of the filler. This increase in activation energy is caused by
the attachment of rubber chains to the carbon surface. At 30% elongation, the activation energy of physical relaxation process for carbon black filled rubber has a value of 32 kcal/mole, independent of structure and concentration of the filler.

The effect of carbon black on stress relaxation depend on the amount of filler. In natural rubber the physical stress relaxation rate is highly dependent on the black loading. The relaxation rate at tensile strain of 100% increases from about 1% to 6% per decade, when the SRF carbon black loading increases from 20phr to 100phr. Similar effects have been found in SBR, butyl rubber and polybutadiene.

Other fillers such silica, calcium carbonate, whiting and clay have also been investigated. Silica has been found to affect the relaxation process more than calcium carbonate, but the effect of non-reinforcing fillers are smaller compared with the effects of carbon black.

2.4.5 EFFECT OF CHEMICAL STRUCTURE OF THE ELASTOMER

The chemical structure of the elastomer strongly influences the total relaxation behaviour. Physical as well as chemical relaxation decreases as the crosslink density increases. This relationship is common in peroxide, sulphur and radiation vulcanised systems. Chemical relaxation curves for peroxide vulcanised natural rubber samples of different crosslink densities are given in Fig. 2.8.

![Chemical stress relaxation curves for various conventionally crosslinked (DC) samples at 383K in air: DC-1(O), DC-2(Φ), DC-3(Θ), DC-4(Θ). The extension ratio is 1.2](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>$10 \times n_{sw}$ (mol dm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DC-1</td>
<td>0.19</td>
</tr>
<tr>
<td>DC-2</td>
<td>0.22</td>
</tr>
<tr>
<td>DC-3</td>
<td>0.39</td>
</tr>
<tr>
<td>DC-4</td>
<td>0.58</td>
</tr>
</tbody>
</table>

Fig. 2.8: Chemical stress relaxation curves for various conventionally crosslinked (DC) samples at 383K in air: DC-1(O), DC-2(Φ), DC-3(Θ), DC-4(Θ). The extension ratio is 1.2.
A similar behaviour has been observed in SBR<sup>(69,70)</sup>, peroxide cured EPDM<sup>(7)</sup> and various other elastomers<sup>(68)</sup>. The influence of accelerator systems on the relaxation behaviour of SBR have been studied in detail. In this study a decrease in the rate of relaxation has been observed with accelerator systems which give higher state of cure at a given temperature.

Chemical stress relaxation behaviour depends upon the nature of the crosslinks in the vulcanisate. This has been shown by tests on natural rubber vulcanisates with different curing systems<sup>(68)</sup>, carried out in the absence of oxygen. The thermal relaxation in radiation vulcanised natural rubber is mainly due to rupture of the molecular chains, reducing the network chain density. For the sulphur cured vulcanisate, relaxation is by preferential rupture and rearrangement of weak poly sulphide crosslinks and for natural rubber vulcanised by metal oxides, it is due to rearrangement of crosslinks by exchange reactions.

Thirion<sup>(71)</sup> has extensively studied viscoelastic properties and stress relaxation properties based on natural rubber, Polybutadiene and Styrene butadiene. A study carried out on the above vulcanisates at 10% extension and at 30°C have shown that the stress diminishes faster and relaxation is more marked in a given time interval as the cure time is shortened and hence the degree of crosslinking is reduced.

The incorporation of antioxidants to the vulcanisate influence the chemical stress relaxation<sup>(52,72)</sup> reducing the relaxation rate. When the antioxidant is not incorporated, formation of a hard oxidized surface layer on the material protects the interior of the sample from oxygen, but this is not so effective as incorporation of antioxidants to the compounds.

2.4.6 EFFECT OF TEMPERATURE

Stress relaxation measurements have been made at various temperatures. The range of temperatures which can be covered is however, limited. Above about 60°C the rubber vulcanisates become susceptible to atmospheric oxidation and stress relaxation of chemical origin is started. On the other hand, the glass transition is approached when the temperature is lowered so that additional relaxation processes become important. However for a given curing system, an increase in temperature gives an increase in the degree of relaxation, and the effect is greater when intermolecular bonds are least stable.

For short term stress relaxation in the temperature range from -10 to 60°C, it can be assumed that physical relaxation is the predominant stress relaxation mode<sup>(57)</sup>.
For filled SBR, NR and butadiene rubber, plots of stress against time can be represented by two straight lines\(^{57}\) (Fig.2.9).

![Fig. 2.9: Effect of temperature of stress relaxation in filled SBR vulcanisate\(^{57}\)](image)

The first portion has the greater slope and represents approximately the first minute of relaxation. It has been observed that the relaxation slope difference and the intercept difference of the first portion does not depend upon the nature of the rubber. This suggests that only the fillers influence the relaxation process at this stage. The second portion of the plot is suggested to be due to molecular chain rearrangement. The effect of temperature on the second part is very small which suggests that the physical relaxation is relatively independent of temperature.

The effect of temperature on stress relaxation becomes prominent at higher temperatures (>80°C) and at longer test duration. When the vulcanisate is heated, the drop in stress is caused by rupture of the molecular chains (by oxidation or thermal degradation). Hence, the thermal degradation depends on the nature of the vulcanisate\(^{57}\).
Fig. 2.10: Decrease of relative stress of natural rubber with temperature\(^{(73)}\)

Fig. 2.10 shows the relative stress decay with temperature, in natural rubber vulcanisates having tetramethyl thiuram disulphide (TMTD):sulphur ratio of 1:6.

2.5. MODELS OF STRESS RELAXATION

2.5.1 MATHEMATICAL MODELS OF STRESS RELAXATION

**INTRODUCTION**

In order to predict the long term stress relaxation behaviour, mainly the extrapolation technique and accelerated test methods have been used. As the stress relaxation can be considered as the additive consequence of physical and chemical relaxation, several researchers\(^{(74,75)}\) have suggested that in order to predict the long term behaviour at low temperature, it is necessary to separate the relaxation process into physical and chemical processes. Investigation of the influence of time and temperature on each process and then recombination of the two to give the overall relaxation follows the above mentioned separation.
A) MODELS OF PHYSICAL RELAXATION

Several mathematical expressions for the physical stress relaxation of elastomers have been proposed. Many of them are based on simple models of viscoelastic behaviour, such as the Maxwell model and its variants.

i) The Maxwell Model.

Fig. 2.11. A Maxwell element

A single dashpot pair in series, such as those arrayed in Fig.2.11 is called a Maxwell element. The spring represents a linear elastic solid (Shear rigidity $G_i=1/J_i$) and the other linear viscous fluid (viscosity $\eta_i$), thus the model represents a material which combines the characteristics of linear elasticity and a viscous fluid. The mathematical model which represents the Maxwell Body has the same stress in both elements and the deformation of the total model is the sum of the deformations of the spring and the dash pot. It is assumed that the spring obeys Hook's law $\sigma = E \varepsilon_1$ and the dash pot obeys Newton's law $\sigma = \tau = E (d\varepsilon /dt)$. As the total deformation is

$$\varepsilon = \varepsilon_1 + \varepsilon_2$$

$$\frac{d\varepsilon}{dt} = \frac{1}{E} \frac{d\sigma}{dt} + \frac{1}{E} \frac{\sigma}{\tau}$$

If the model is assumed to be held at constant strain, the stress relaxation is given by the following equation:

$$\sigma (t) = \sigma (0) \exp \left( \frac{-Et}{\eta} \right)$$
\[ \frac{\sigma(t)}{\sigma(0)} = \exp\left(\frac{t}{\tau}\right) \]

Where \( \eta/\ell \) is defined as the relaxation time \( \tau \), \( \sigma(t) \) is the stress at time \( t \), \( \sigma(0) \) is the original stress and this expression may be rewritten as
\[ \ln(\sigma_r) = -\frac{t}{\tau} = -kt \]

Where \( \sigma_r \) is the relative stress relaxation at time \( t \) and \( k \) is the rate constant.

This is not an accurate model to represent the relaxation behaviour of the polymeric materials, mainly due to the following reasons:

(a) Real polymers have a large number of relaxation mechanisms and therefore a large number of relaxation times distributed over many decades of time.

(b) This model predicts a linear relaxation between logarithm of stress relaxation and time, not between the stress relaxation and the logarithm of time as found in practice.

To correct the above, a more complex model consisting of a very large (or infinite) number of Maxwell elements in parallel was proposed by Weichart\(^{(77)}\) and is known as Generalized Maxwell model.

ii) **Generalized Maxwell model**

![Generalized Maxwell model](image)

**Fig. 2.12. Generalized Maxwell model\(^{(2)}\)**
In this model each element has its own relaxation time and elastic modulus. For a single element it can be written as

\[
\frac{d\varepsilon}{dt} = \frac{1}{E_i} \left( \frac{d\sigma_i}{dt} \right) + \frac{1}{\tau_i} \left( \frac{\sigma_i}{E_i} \right)
\]

Where \( \varepsilon \) = Tensile strain \( \tau = \) Relaxation time 
\( \sigma = \) Tensile stress \( E = \) Tensile modulus

The equation (2.1) is a suitable model for a non-crosslinked or linear polymer, because at constant strain this model will show a decay to zero stress.

By further processing of this equation, it can be shown that

\[
\sigma(t) = \varepsilon_0 \sum E_i \exp \left( \frac{t}{\tau_i} \right)
\]

and

\[
E_i(t) = \frac{\sigma(t)}{\varepsilon_0} = \sum E_i \exp \left( \frac{t}{\tau_i} \right)
\]

A more generalized equation of the above consisting of a continuous distribution of relaxation times \((E(\tau))\) and the stress relaxation modulus \(E_i(t)\) can be given as

\[
E_i(t) = \int E(\tau) \exp \left( \frac{-t}{\tau} \right) d\tau
\]

Then, a new function \(E_1(\tau)\), which is the first approximation of relaxation distribution is defined by

\[
E_1(\tau) = -\frac{dE(t)}{dt}
\]

Then the distribution of relaxation may be expressed in terms of another function \(H(\tau)\) defined as follows

\[
H(\tau) = \tau E(\tau)
\]

Then,

\[
H_1(\tau) = \tau E_1(\tau) = \left( \frac{dE_1(t)}{d\ln(t)} \right)_{\text{max}}
\]

\[
H_1(\tau) = \frac{1}{2.303} \left[ \frac{dE_1(t)}{d\log(t)} \right]_{\text{max}}
\]

The relationship expressed in equation 2.2 is known in mathematics as the laplace transformation. To use this transformation one must know \(E_i(t)\) over the entire time scale from \(t=0\) to \(t = \infty\) (i.e. covering many decades of time). It is difficult to obtain results through a long period of time at constant temperature by a
single experiment. To overcome this difficulty the master curve concept, which uses
the principle of time- temperature superposition has been developed. This principle will
be discussed under the empirical models of physical relaxation.

2.5.2 EMPIRICAL MODELS

A) EMPIRICAL MODELS OF PHYSICAL RELAXATION

Several empirical models of Physical relaxation are available in the
literature(18,79). According to Thirion and Chasset(79) the relaxation curve at 30°C can be
represented by the following equation

\[ f_t = f_e + c \cdot t^n \] .......................... 2.3

Where, \( f_t \) is the tensile force at time \( t \),

c, \( n \) and \( f_e \) are constants

\( f_e \) is the equilibrium force at infinite time.

\( f_e \) cannot be determined empirically. As its value is unknown, the three coefficients
have to be determined by looking for a \( f_e \) value which gives a straight line, when log(\( f_t - f_e \)) is plotted against logt.

Through this work Thirion et al. investigated the relative effects of network
relaxation and ageing for dicumyl peroxide cured natural rubber in air and found that at
100°C, relaxation is caused by ageing, except in the initial stages. Conversely, at 30°C
the effect of ageing is negligible. At intermediate temperatures both phenomena occur
simultaneously over a time interval ranging from 3 minutes to 150 hours.

Nichols, Kienle and Clifton(80) studied the stress relaxation in pure elastomers
under compression, and postulated that the overall relaxation may be broken into two
components represented by \((f_0-f_{10})\) and \((f_{10})\) where \( f_0 \) and \( f_{10} \) are the forces after 0 and
10 minutes respectively. However, this was not applicable to carbon black filled
stocks.

Another empirical relation has been used by Cotten and Boonstra(18). Their
work showed that all rubbers obey the equation 2.4 at room temperature.

\[ f_t = f_{1.0} \cdot t^n \] .......................... 2.4

Where, \( f_t \) is the force at time \( t \) (in minutes), \( f_{1.0} \) is the force after 1 minute of relaxation,
and \( n \) is defined as the relaxation rate of the material. This equation is in general
agreement with findings of most previous workers(81,82,83,84). The constant \( n \) in the
equation 2.4 is equal to \( (df/f)/\log(t) \), i.e. the percentage decrease in force per unit log
cycle of time, and corresponds to the definition of the rate of stress relaxation used by Gent\textsuperscript{(20)}.

Another empirical model of physical relaxation applied for different polymer systems including SBR is the Nutting equation\textsuperscript{(81,83)}, which is in the form

$$\sigma = e^{\beta} \cdot \psi \cdot t^n$$

Where, $e$ is the imposed strain, $\psi$, $\beta$, and $n$ are material constants.

Buchdahl and Nielsen\textsuperscript{(82)} have applied the Nutting equation to polymers such as plasticized PVC, SBR and polystyrene. They showed that the constant $n$ in equation 2.5 is closely related to the damping coefficient $\delta$, obtained from dynamic mechanical measurements. The parameter $\psi$ is also related to the dynamic modulus.

All the models discussed above show a linear relationship between stress relaxation and $\log$(time). This linear relationship has been the basis for extrapolation techniques. By using this relationship long term physical relaxation at a given temperature may be determined from short term data.

\textit{Time Temperature Superposition and Master Curves}

The time-temperature superposition principle whereby viscoelastic data at one temperature are transformed to another temperature by a simple multiplicative transformation of the time scale\textsuperscript{(85,86,87,88)} has been independently proposed by Tobolsky and Andrews\textsuperscript{(85)} and by Leadermann\textsuperscript{(87)}. The basis of the technique is that; the modulus of a viscoelastic material is a function of both temperature and time. Thus, there are two methods to determine the behaviour of a polymer at longer time. The first method is by directly measuring the response at longer time. The second method is by conducting a series of short time measurements at different temperatures and using these short time tests data can be superpositioned by making a horizontal shift along a logarithmic time axis to give a master curve at a reference temperature, covering several decades of time.

Much work on time temperature superposition has been conducted by Tobolsky\textsuperscript{(2)} and William, Landel and Ferry\textsuperscript{(89)}. Each curve at temperature $T$ is shifted along the horizontal time axis by a factor known as the shift factor $a_T$. The temperature dependence of the shift factor is given by an equation first proposed by William, Landel and Ferry referred as WLF equation\textsuperscript{(89)}. 


Where \( c_1 \) and \( c_2 \) are constants which vary slightly from polymer to polymer. The glass transition temperature is often chosen as the reference temperature \( T_0 \). This equation is valid between \( T_g \) and 100°C above \( T_g \).

The horizontal shift compensates for the change in the time scale brought about by changing temperature. There is also an inherent change in modulus brought about by a change in temperature. The modulus of a rubber network is directly proportional to the absolute temperature. Thus a change in temperature will produce a slight vertical shift in the individual curves. Similarly, since the volume of polymer is a function of temperature, a correction must be made for the changing mass per unit volume. Each curve is therefore multiplied by a correction factor \( k \) given by

\[
k = \frac{T_0 \rho_0}{T \rho}
\]

Where, \( T \) is the temperature and

- \( T_0 \) is the reference temperature for which the master curve is constructed,
- \( \rho \) is the density at temperature \( T \) and
- \( \rho_0 \) is the density at the reference temperature.

The assumptions involved in constructing mastercurves using time temperature superposition principle are as follows

1. The material is assumed to behave as a linear amorphous polymer or a slightly crosslinked polymer.
2. The modulus of the material is a function of both temperature and time.
3. All relaxation mechanisms have the same temperature dependence, so that when the temperature is changed from a standard value \( T_0 \) to \( T \), each point of the curve is multiplied by the same factor \( a_T \).

The use of time-temperature superposition to construct a master curve for crosslinked elastomers has been criticised by Sasaki et al. for attributing the vertical shift in the master curve only to the inherent change in modulus brought by the change in temperature. In their study they have shown that the vertical shift is a function of temperature as well as the level of strain, at high temperatures (above 40°C for NR) or at high strain level (strain > 100%). The vertical shift increases as temperature increases.
as well as strain level increases. Despite the criticisms, time-temperature superpositions have been successfully carried out on natural rubber, nitrile rubber, EPDM and SBR. It has been shown that this method of extrapolation is not satisfactory for elastomers where chemical relaxation might be expected to play an important role. Further, the time-temperature superposition is a possible method of extrapolation for other materials such as thermoplastic elastomers.

B) **Empirical Models for Chemical Stress Relaxation Data**

**Extrapolation of chemical relaxation data**

The rate of most chemical reactions increases as the temperature is raised. The dependence of the rate coefficient of reactions on temperature has been represented by Arrhenius with the following equation

\[ k = A \exp \left( \frac{-E}{RT} \right) \]

Where, \( k \) is the rate constant,

\( E \) is the activation energy

The above equation can be rearranged as

\[ \ln k = \ln A - \frac{E}{RT} \]

Once a reaction is found to show this type of behaviour it is a easy task to predict how the reaction rate responds to a change in temperature. This technique has been used extensively in the time-temperature superposition technique by Tobolsky.

This equation has been used mainly to calculate the activation energy for relaxation of stress at different temperatures. Relaxation curves at different temperatures are plotted as reduced stress vs. logarithmic time and superpositioned by shifting along the time scale. Then the curves at different temperatures can be represented by a single curve plotted as reduced stress vs. the logarithm of \( (k't) \). Where, \( k' \) is a function of temperature alone. Its value determines the position of the relaxation curve along the simple logarithmic time scale. The temperature dependence of \( 'k' \) has been found to be expressible by the Arrhenius equation.
The Arrhenius expression is empirical, but it represents many experimental situations and it is often a fair first approximation to the actual situation. This method of extrapolation has been used in several ways to model both chemical and physical relaxation\cite{74,93} behaviour.

2.5.3 MATHEMATICAL MODELS FOR TOTAL STRESS RELAXATION BEHAVIOUR

The methods available for the extrapolation of chemical and physical relaxation have individually been described previously. The various models used for the separation of physical and chemical relaxation, their extrapolation and subsequent recombinations are described in the following sections.

i) The Aben Technique.

This technique\cite{74} was originally developed for tensile stress relaxation and it is based upon the individual extrapolation of all the components which make up the final relaxation curve. These components include physical relaxation, incubation time for chemical relaxation to initiate and the numerous reactions which are occurring in the network.

In developing this technique, Aben has made the following assumptions.

1) Physical relaxation is assumed to be linear with log time.

2) The rate of physical relaxation is independent of temperature over long periods of time.

3) The point at which the stress relaxation curve rapidly falls away from a linear relation with log(time) is taken as the induction time for chemical stress relaxation to start: before this point chemical relaxation does not occur.

4) Chemical relaxation mechanisms follow a simple first order Arrhenius reaction and therefore the induction time also follows an Arrhenius reaction.

Using a family of stress relaxation curves generated at various temperatures the induction time for chemical relaxation to start is determined. This induction time obeys the rules of the first order Arrhenius relation, from which the induction time at the required temperature is determined. The physical relaxation measured at this temperature is then extrapolated to the induction time.
Then the chemical relaxation is extrapolated. The assumptions made here are

1) Chemical relaxation only occurs after the protection system has been consumed.
   i.e. After the induction time.

2) Generally, numerous degradation mechanisms are involved in chemical relaxation each consisting of their own rate and activation energy.

3) The rate of each individual chemical reaction is linear with time.

In order to extrapolate each mechanism separately, extrapolated physical relaxation is subtracted from the total measured relaxation at each temperature, to give a series of chemical relaxation curves. The different relaxation reactions are separated from the total chemical relaxation using the procedure $X^{(94)}$. Then each reaction is extrapolated using an Arrhenius relationship to give the reaction rate at the required temperature. The total chemical relaxation is then added to the extrapolated physical relaxation at the extrapolated induction time to give the predicted overall stress relaxation behaviour.

The main problem in this technique seems to be the use of 'Procedure X', in order to determine the number of reactions occurring in the chemical relaxation process. The Procedure X can only be applied successfully if the log(relaxation modulus) Vs. time curve shows a linear behaviour within the time period considered. If the relaxation curve is still curving away even at the end of the testing period, then a problem arises on allocating the number of tangents to the relaxation modulus curve. This gives an uncertainty in deciding the actual number of individual reactions occurring in the chemical relaxation process and will affect the estimated value of service life. Hence if a practical method is available to determine the type and number of reactions occurring in during the chemical stress relaxation, it can significantly reduce the application difficulties of the Aben extrapolation technique.

A check on the accuracy of the forecast has not been done by Aben, due to the longer period of time required to obtain the estimated results, practically. However a measure of trust on the accuracy has been derived from the excellent agreement between the calculated curves and the actual tensile relaxation results obtained over a period of three years.

Later an attempt has been made to apply the technique to the compression stress relaxation data of several nitrile rubbers$^{(95)}$. In this study, the technique has been able to apply with a certain degree of success, although the process of separating the chemical mechanism seems to be potentially a source of error. Furthermore in the same study it is concluded that in order to increase the accuracy of the extrapolation for measurements in compression, data at different temperatures should be obtained over a
period of one to two years. However Aben has used data collected during a period of only 70 days in order to apply the technique proposed by him.

The main reasons for the differences in the required length of testing periods can be attributed to the oxidation differences in the samples used in the compression and tensile mode. In the tensile mode, the thickness of the sample is approximately 1.0 mm while in the compression mode the test piece is a cylindrical rubber button of at least 10mm diameter. Hence in the tensile mode the rate of diffusion of atmospheric oxygen is higher than in the compression mode. Thus the tensile relaxation curve attains linearity faster than the relaxation curve obtained under the compression mode. As a result, in the tensile mode the Procedure X can be applied with data obtained during a short period of time. However, with the available literature it is difficult to decide whether both the modes, tensile and compression give the same value for the forecasted service life.

ii) Salazar and Curro Method

Another separation technique for physical and chemical relaxation form the total relaxation behaviour has been proposed by Salazar and Curro (75,96). The published data of this method covers ethylene propylene rubber, butyle rubber and fluoro elastomers

In their analysis they have assumed that in the temperature range of 25°C to 111°C, no chemical relaxation occurs over the time scale of the experiment, which is about 100 hrs. Then the data are analysed using the conventional time-temperature superposition technique and the amount of physical relaxation occurring in each of the high temperature is calculated. These physical relaxation contributions are then subtracted from the total stress relaxation curves at the high temperatures, thus isolating the chemical effect. The kinetics of the chemical processes and the change in crosslink density with time, at high temperatures are calculated using an equation developed in this study. Then the crosslink densities are estimated as a function of time at other arbitrary temperatures. The estimated crosslink density values are used to calculate the long term relaxation modulus at high temperature. There after high temperature modulus values are extrapolated to lower temperature and it is combined with the measured physical data to give the overall long term relaxation. In this procedure it is assumed that the rate constant for reaction kinetics has Arrhenius temperature dependence.
In comparison to the Aben technique, this method of extrapolation is complex, further the technique proposed is based on certain assumptions and the following drawbacks can be listed.

a) Here time-temperature superposition has been used in order to obtain high temperature relaxation values. In this principle the WLF equation is used to calculate the relevant shift factors. It has been pointed out that the accuracy of the WLF equation diminishes at temperatures greater than $T_g+100^\circ C$ (97). However in the present extrapolation technique the relaxation data has been shifted well above this threshold level, giving an uncertainty on the final outcome.

b) The kinetics involved in the reaction of chemical relaxation has been assumed as first order and the rate constant has been assumed as having Arrhenius Temperature dependence. The assumption on the kinetics of the reaction is correct only if random scission at crosslinks occurs(2). Hence this method is not universally applicable to all polymer vulcanisates.

The method employed in the Aben technique in order to determine the chemical relaxation is more accurate than the method proposed by Salazer and Curro as it represents chemical relaxation by a series of first order reactions.

c) Another assumption in this method is ‘there exists a certain temperature range above the glass transition temperature over which the chemical effect can be neglected for the time scale of the experiment’. The temperature range selected for the study of ethylene propylene rubber (EPR) and butyl rubber is 23°C to 77°C while that for the fluoro elastomer is 25°C to 111°C. The time selected in all cases is 100 hrs. The procedure for selecting these temperature ranges are not given. However it is clear that these ranges have been carefully selected to avoid the influence of the chemical relaxation.

The chemical relaxation of a vulcanisate is mainly determined by the stability of the network (network chains and crosslinks). Depending on the stability of the network it can start chemical relaxation at very early stage with a reasonably high temperature (eg. some natural rubber vulcanisates starts to show chemical relaxation at 60 hrs. at 70°C (96)). Hence the temperature range and the time period for the application of this technique cannot be selected arbitrary. A fair knowledge on the relaxation behaviour of the vulcanisate is required before practising this technique.

d) In both Aben and Curro-Slazer techniques, the physical relaxation data obtained in the low temperature range is used to calculate the physical relaxation at high temperatures. But at high temperatures the vulcanisate undergoes network damages and hence a change in the network structure of the original vulcanisate is expected.
Due to this change, the estimated physical relaxation values obtained from low temperature data may not represent the actual physical relaxation at high temperature.

iii) The method proposed by Stenberg and Janson

Stenberg and Janson\(^{(99)}\) have attempted to measure the physical relaxation directly from measurements of the real and imaginary parts of the complex Young’s modulus at different frequencies and at different temperatures. The relationship between relaxation modulus \(E(t)\) and complex modulus \(E^* = E' + iE''\) proposed by Ninomiya and Ferry\(^{(97)}\) has been used in their analysis.

\[
E(t) = E(\omega) - 0.4E''(0.4\omega) + 0.014E''(10\omega)
\]

Where, \(\omega = \frac{1}{t}\) and \(E(t)\) values are calculated from values of \(E'(\omega)\) and \(E''(\omega)\) at different temperatures, and the \(E(t)\) curves are shifted usual way to the long term relaxation temperature.

In their studies they have chosen three nitrile rubber vulcanisates with different crosslink densities. In addition to the dynamic test, a few samples have been tested on a relaxometer under the compression mode for a time period up to 2000 hrs. and more samples at different temperatures in order to determine the total stress relaxation behaviour. The physical relaxation data is obtained by performing dynamic modulus measurements at the same temperature at which the total stress relaxation data were measured. By subtracting the physical relaxation from the total relaxation measurements the chemical relaxation is isolated. These separated chemical relaxation data and measured physical relaxation data are extrapolated separately and then recombined to obtain the long term relaxation modulus.

The major drawbacks and advantages of this methods are as follows.

a) This method needs materials to show linear viscoelasticity. Inclusion of fillers in the compound leads to non-linear viscoelasticity\(^{(100,101)}\). By selecting a compound with a low carbon black loading (less than 15 vol.%) and using a small amplitude to determine the dynamic modulus, Stanberg et al. have assumed linear viscoelastic behaviour in their study. In practice most of the compounds have much higher levels of carbon black than 15%. Hence the above assumption restricts the use of the proposed method in many instances.
b) The major disadvantage in this method over the two methods mentioned previously is the use of an additional test, measurement of the complex modulus in addition to the stress relaxation measurements.

c) The linear viscoelastic behaviour can be expected to be valid for vulcanisates whose basic structure is not changing with time during the experiment\(^{(2)}\). As the time required to determined the dynamic modulus using modern apparatus at different frequencies and at constant temperature is considerably short, the possibility of structural damages occurring during the experiment is minimal. Hence using this method a direct and accurate measurement of the physical relaxation at high temperature can be obtained. This is an advantage over the Aben and Slazer-Curro method.

2.6 **VULCANISATION WITH TETRA METHYL THIURAM DISULPHIDE (TMTD)**\(^{(102,103)}\)

When TMTD is used in the vulcanisation process, depending on the amount of sulphur used, it can act as an accelerator or as a curing agent. In the first case TMTD is used in fairly small quantities. (e.g. 0.5 TMTD accelerator and 2.0\% of sulphur) In the second case the use of sulphur can be dispensed with a larger proportion of TMTD (about 3\% of TMTD). The second case is known as "Thiuram Vulcanisation". In thiuram vulcanisation small proportion of sulphur is often added to raise the degree of vulcanisation. Properties of the vulcanisate can be considerably improved with addition of 0.2 parts of sulphur\(^{(104)}\). Some of the properties can be still further improved by raising the sulphur content to 0.5 parts by weight. However with this addition the heat resistance of the vulcanisate is reduced.

In the present study the vulcanisation system used is TMTD, CBS and S. According to the amount of TMTD and the sulphur used in the compounds (ratio of TMTD:S is 4:1), the TMTD has been used as a curing agent. Hence the vulcanisates have been obtained through the Thiuram Vulcanisation.

When TMTD is used in vulcanisation there is a tendency for the TMTD or the conversion products formed during the vulcanisation to bloom giving a grey coating on the surface of the vulcanisate. To reduce the tendency to bloom it is recommended to add thiazole accelerators such as MBT (Mercaptobenzo thiazole), MBTS (Mercapto dibenzothiazyl disulphide) or CBS (N-cyclohexylbenzthiazyl sulphanamide). The use of these secondary accelerators also results a delay in the onset of vulcanisation. The simultaneous use of TMTD and sulphanamides enables to reduce the proportion of
TMTD at the cost of increasing amount of sulphanamide, giving the advantage of reducing undesirable effects of TMTD\textsuperscript{(105)}. However large amount of sulphanamide accelerators in Nitrile rubbers have shown high tendency to reversion.

In the vulcanisation process the TMTD reacts with ZnO to give tetramethyl thiuram polysulphide which reacts with rubber and more Zinc Oxide to give a rubber bound intermediate compound containing a polysulphide group. This then reacts with more rubber and ZnO to form a vulcanised rubber with polysulphide crosslinks, which as cure proceeds give mainly monosulphidic crosslinks\textsuperscript{(106,107)}. The other intermediate compound form is Zinc diethyl dithiocarbamate.

By treating the thiuram vulcanisates with Lithium aluminium hydride\textsuperscript{(108)} it has been found that the average number of Sulphur atoms per crosslink decreases as the curing time is extended.
CHAPTER THREE

TECHNIQUES AND INSTRUMENTS FOR STRESS RELAXATION MEASUREMENTS

3.1 THE TECHNIQUES FOR RELAXATION MEASUREMENTS

The measuring techniques of relaxation found in literature can be broadly classified into three groups:

3.1.1 Tobolsky's classical techniques\(^{(31,87,109)}\)

A) continuous measurements
B) intermittent measurements

3.1.2 Ore's relaxation measurement method

Intermittent Tangent Modulus Measuring Technique (ITMM) \(^{(110,111)}\)

3.1.3 Simultaneous Measurement of Continuous and Intermittent Relaxation (SMCIR) \(^{(112)}\)

The above techniques will be discussed in detail under the forthcoming sub sections.

3.1.1 TOBOLSKY'S CLASSICAL TECHNIQUES

In the statistical theory of rubber elasticity, it is shown that the stress \((\sigma(t))\) acting on a uniaxially strained rubber item is completely determined by the strain \((\lambda)\), the temperature \((T)\) and the network density \((N(t))\).\(^{(113)}\)

\[
\sigma(t) = N(t) RT(\lambda - \frac{1}{\lambda^2})
\]

When the above equation is applied at the beginning of the stress relaxation experiment, it can be shown that

\[
\sigma(0) = N(0) RT(\lambda - \frac{1}{\lambda^2})
\]

Then,

\[
\frac{\sigma(t)}{\sigma(0)} = \frac{N(t)}{N(0)}
\]

i.e., measurement of the stress at constant temperature and strain in a degrading rubber network provides a measure of the concentration of network chains as a function of time through the above equation.
N(t) in the above equation refers to all the load bearing network chains. If the degradation process involves additional crosslinks as well as chain scission, it is possible that some of the new network chains formed during the degradation to be load-bearing and some not to. If this is the case then the above equation no longer provides a measure of the total concentration of network chains at any time and some additional assumptions must be introduced in order to deal with the situation. It is therefore assumed that any network chains formed during the degradation are non-load bearing numbers of the network and these do not contribute to N(t) in the above equation. This is known as the two-network hypothesis\(^2\).

The application of two-network hypothesis to experimental data leads to two types of relaxation measurements, continuous and intermittent.

**A) CONTINUOUS STRESS RELAXATION MEASUREMENT**

In this technique the sample is deformed (compressed or stretched) to a fixed length as quickly as possible and maintained at the same deformation, at constant temperature while the retractive force is followed as a function of time. The retractive force is usually found to decrease with time.

Directly after applying the deformation, the retractive force usually declines rapidly because of the conformational changes and alignment of polymer chains\(^{115}\). Entanglement effects have an influence on the modulus of rubber at shorter times. After some time these effects no longer dominate the stress relaxation, specially at higher temperatures. A way of minimising these complicating effects is to normalize the data. A typical normalized stress relaxation curve is shown in Fig.3.1.

![Continuous Stress Relaxation curve normalized to time \(t_0\)](image)

Fig 3.1 :A Continuous Stress Relaxation curve normalized to time \(t_0\)\(^{114}\)
From the above relaxation measurements $N(t)$ can be calculated with the help of equation 3.1. The $N(t)$ obtained in this way represents only the load bearing chains in the network, but according to the network theory the new chains formed as a result of degradation will contribute nothing to the stress. As a result $N(t)$ represents the portion of the network that has not undergone chain scission at time 't'.

B) INTERMITTENT STRESS RELAXATION MEASUREMENT

The intermittent stress relaxation measurements reflect the combined effect of scission and crosslinking, whereas crosslinking reactions make no contribution to retractive forces measured by continuous stress relaxation.

In intermittent relaxation too, we can use the equation 3.1 in order to calculate $N(t)$. However, now $N(t)$ refers to both the original network remaining at time 't' and the new network formed by the additional crosslinking during degradation.

When stress relaxation is measured intermittently\(^2\), the specimen is maintained in a relaxed, undeformed condition at a suitable constant temperature. At widely spaced time intervals, the sample is deformed by a fixed amount as quickly as possible and the equilibrium stress is rapidly measured. The specimen is then quickly returned to its original unstrained condition. This is an intermittent measurement of the modulus of the network under conditions in which the duration of stress measurement is very short compared with the time intervals between measurements. Nearly all scission and crosslinking may be considered as occurring when the network is in an undeformed state. The values measured are normalized with respect to the first measured value, so that intermittently measured stress relaxation data are obtained as those shown in Fig. 3.2.

\[\frac{f}{f_0}\]

\[t_0\]

\[\text{time}\]

Fig 3.2: A Normalized Stress Relaxation curve obtained under Intermittent Stress Relaxation\(^{014}\)
The shape of the resulting curves from intermittently and continuously measured stress relaxation for different types of network degradation are shown in Figures 3.3, 3.4 and 3.5, where the continuous curve represents continuous stress relaxation and the peaks represent intermittent stress relaxation.

Fig.3.3: Behaviour of the normalized intermittent and continuous stress relaxation in a system with only reversible network degradation\(^{(114)}\)

Fig.3.4: Behaviour of the normalized intermittent and continuous stress relaxation in a system with only rearrangement reactions\(^{(114)}\)
In a system with only irreversible network degradation (no rearrangement and crosslinking reactions), continuous and intermittent stress relaxation measurements show the same value, as given in Fig. 3.3.

When only reversible network degradation occurs (rearrangement) continuously measured stress shows a decay in stress while the intermittently measured values remain constant, as shown in Fig.3.4. The cause for the behaviour in intermittent relaxation is presumably that network chains rearrange only from one relaxed position to another. When this behaviour is observed, it can also be explained by both irreversible network degradation and crosslinking reactions where the two opposing effects cancel each other when they are of equal amplitude, resulting no change in crosslink density. As the strained molecules are rearranged by moving from strained to unstrained positions during the deformed stage, a decline in restoring force can be observed, given by the continuous measurement.

Fig.3.5: Behaviour of the normalized intermittent and continuous stress relaxation in a system with network degradation and crosslinking reactions (114)
When crosslinking reactions are detected by intermittent stress relaxation as an increase in retractive force (because of increasing network density), the continuous stress relaxation is unaffected. Typical results are shown in Fig. 3.5.

3.1.2 INTERMITTENT TANGENT MODULUS MEASUREMENT (ITMM) METHOD

An Improved Method of Intermittent Measurement by Ore

Svein Ore proposed\(^{(110)}\) a modified continuous stress relaxation method for the purpose of measuring the amount of crosslinkages in the elongated state and at low elongations. The modification consists simply of obtaining the intermittent relaxation values determined during the continuous stress relaxation experiment and the change in apparent tangent modulus (on the same specimen). This is done by subjecting the relaxing specimen to a small additional force (\(\Delta F\)) at various intervals and measuring quickly the corresponding increase in elongation (\(\Delta \lambda\)), which is measured by a microscope. Such added \(\Delta F\) is chosen so that the resulting \(\Delta \lambda\) is about 0.1 times the imposed constant strain (\(\frac{\Delta \lambda}{\lambda} = 0.1\)).

The increase in the extension \(\Delta \lambda\) leads to an increase in the stress due to \(n_\lambda(t)\), the moles of additional new network chains per cubic centimetre, which are formed up to time 't'.

According to the statistical theory of rubber elasticity, the force associated with the remaining chains of the original network of a specimen, relaxing continuously at the extension ratio \(\lambda\) is given by

\[
F_1 = A_0 R T \left(\lambda - \frac{1}{\lambda^2}\right) N_0(t)
\]

\(N_0(t)\) is the number of original network chains (per unit volume) remaining at time 't'.

When an infinitesimal increase in extension ratio is given (\(d\lambda\)) these chains contribute to the increase in force. This will be given by differentiation of the above equation.

\[
dF_1 = A_0 R T \left(1 + \frac{2}{\lambda^3}\right) N_0(t). d\lambda
\]

The increase in extension ratio \(d\lambda\) leads to an increase in force \(dF_2\) due to the number of moles of additional new network chains \(N_\lambda(t)\) per cubic centimetre which are formed up to time 't'. As the sample has such new chains \(N_\lambda(t)\) in the
unstretched state at elongation $\lambda$, the increased stress $dF_2$ due to $N_\lambda(t)$ will be given by the following equation, for a sample with a cross sectional area of $A_0 / \lambda$.

$$dF_2 = A_0 R T \left( \frac{3}{\lambda^2} \right) N_\lambda(t) d\lambda$$

Hence, the total increase in force

$$dF = dF_1 + dF_2 = A_0 k T \left[ \left( \frac{2}{\lambda^2} \right) N_0(t) + \left( \frac{3}{\lambda^2} \right) N_\lambda(t) \right] d\lambda$$

For extension ratios 1.20 and 1.50, the above equation gives

$$\left( \frac{dF}{d\lambda} \right)_{1.20} = A_0 R T [2.16 N_0(t) + 2.08 N_\lambda(t)]$$

$$\left( \frac{dF}{d\lambda} \right)_{1.50} = A_0 R T [1.59 N_0(t) + 1.33 N_\lambda(t)]$$

In the intermittent stress relaxation proposed by Tobolsky, the force is given by

$$F_I = A_0 R T \left[ \frac{1}{\lambda^2} \right] [N_0(t) + N_\lambda(t)]$$

$$F_{I,1.20} = A_0 R T [0.51 N_0(t) + 0.51 N_\lambda(t)]$$

$$F_{I,1.50} = A_0 R T [1.06 N_0(t) + 1.06 N_\lambda(t)]$$

From the above equations, Ore showed that the two quantities representing initial network chains $N_0(t)$ and additional network chains $N_\lambda(t)$ contribute to $F_I$ equally, but not $dF/d\lambda$. The contribution of $N_\lambda(t)$ to $dF/d\lambda$ is very small (4% difference) from that of $N_0(t)$, when deformation is comparatively small ($\lambda = 1.20$). The difference, however becomes higher (16%) when deformation is high ($\lambda = 1.50$).

The chemical stress relaxation curves obtained from continuous and intermittent methods for natural rubber extracted with acetone at 110°C in air at $\lambda = 1.20$ are shown in Fig. 3.6.

The normal intermittent stress is seen to be consistent with the intermittent tangent modulus for the whole range. The chemical stress relaxation curves for unextracted rubber is shown in Fig. 3.7 and again there is an excellent agreement between the two intermittent stress relaxation methods.
Fig. 3.6: Continuous and Intermittent stress relaxation curves for NR vulcanisates (purified) at 100°C (ext. ratio = 1.20)\(^{116}\).

\{ o - Intermittent(ore’s method), x - Intermittent(Tobolsky’s method), • - Continuous \}

The advantage of ITMM method over the conventional intermittent method is, it can be applied to samples which are liable to break after only few percent of elongation.
3.1.3 SIMULTANEOUS MEASUREMENT FOR CONTINUOUS AND INTERMITTENT RELAXATION (SMCIR) METHOD

The ITMM method suggested by Ore, was found to be difficult when applying to stress relaxation apparatus of the strain gauge type; measurements with small loads and small extension ratios were also found to be difficult from experimental point of view. As a result Sobue et al.\(^{(112)}\) proposed another method of determining intermittent stress relaxation using double elongation of the sample.

In this method, the stress relaxation of the sample is measured at a given strain \( \lambda_1 \). Then the sample is again subjected to a further strain (say \( \lambda_2 \)) in order to measure the next phase of stress relaxation. After the equilibrium stress at \( \lambda_1 \) has been rapidly measured, the sample is immediately returned to \( \lambda_1 \). Thus the continuous and intermittent measurement can be measured in this fashion.

The relaxation stress at the strain \( \lambda_1 (t_c) \) and \( \lambda_2 (t_i) \) can then be expressed as

\[
\sigma_{c(t)} = [2c(0) - q(t)]RT \left( \lambda - \frac{1}{\lambda^2} \right)
\]

and

\[
\sigma_{i(t)} = [2c(0) - q(t)]RT \left( \lambda - \frac{1}{\lambda^2} \right) + 2\Delta c(t)RT \left( \frac{\lambda^2_2}{\lambda_1} - \left( \frac{\lambda_1}{\lambda_2} \right)^2 \right)
\]

\(2\Delta c(t)\) - Additional network chains formed after time ‘t’.

However, the two measurements are carried out at two different strains. The stresses at \( \lambda_1 \) and \( \lambda_2 \) for initial crosslink density \( c(0) \) is given by

\[
\sigma_{c(0)} = 2c(0)RT(\lambda_1 - \lambda_1^2) \quad \text{(a)}
\]

\[
\sigma_{i(0)} = 2c(0)RT(\lambda_2 - \lambda_2^2) \quad \text{(b)}
\]

From equations (a) and (b)

\[
\sigma_{i(0)} = \left( \frac{\lambda_2 - \lambda_2^2}{\lambda_1 - \lambda_1^2} \right) \sigma_{c(0)}
\]

The difference between the intermittent stress relaxation curve and the continuous curve is given by

\[
\left[ \left( \frac{\sigma_{i(t)}}{\sigma_{i(0)}} \right) - \left( \frac{\sigma_{c(t)}}{\sigma_{c(0)}} \right) \right]
\]

Using the above equation it can be shown that
The right-hand side of the above equation becomes \( \frac{\Delta c(t)}{\Delta c(0)} \), when \( \lambda_1 = 1 \), which represents the Tobolsky's classical method.

When the above theory is applied, the continuous stress relaxation curve corresponding to \( \lambda_1 \) and the intermittent curve corresponding to \( \lambda_2 \) can be obtained at the same time for a single sample and further the amount of crosslinkages formed can be estimated. The continuous and intermittent curves obtained for a natural rubber vulcanisate is given in Fig. 3.8.

![Fig. 3.8: Continuous and Intermittent stress relaxation curves for natural rubber vulcanisates obtained by SMCIR method](image)

The test method of SMCIR is as follows. The stress relaxation after the sample is compressed to \( h_1 \) from the original height \( h_0 \) is measured and after time \( t_1 \) the sample is compressed to \( h_2 \) from \( h_1 \) to measure the next phase of stress relaxation. After the equilibrium stress at \( h_2 \) has been rapidly measured, the sample is immediately returned.
to $h_1$, and measurement of the continuous stress relaxation is resumed at $h_1$. Thus the continuous and intermittent measurements can be repeated in this manner.

The SMCIR and ITMM methods have the following advantages over Tobolsky's method.

1. SMCIR and ITMM methods can minimize the error as these require only a single sample and a single condition in the measurement, compared to Tobolsky's method, which needs two samples and two test conditions.

2. The measurement of crosslinkages formed in stretched states shows the effects of strain on the crosslinking reaction.

3. The assumption involved in Tobolsky's method, that the total number of network chain scissions is the same in the unstretched and stretched states is unnecessary for these methods as the amount of network chains formed by crosslinking is estimated at $\lambda_1$.

3.2 CURRENTLY AVAILABLE INSTRUMENTS

3.2.1 INTRODUCTION

Since the introduction of the stress relaxation concept about 50 years ago, several instruments have been used by researchers. Despite the extensive use of stress relaxation measurements, the details of the apparatus used by researchers are not readily available. It may be due to the fact that average researchers are mainly concerned about the results and the way they are interpreted, but not the way in which the results are obtained.

3.2.2 INSTRUMENTS THAT WORK IN TENSILE MODE

Typical systems used in the tensile mode are shown in Fig.'s 3.9, 3.10 and 3.11. As the figures show, in all the systems, one end of the sample is attached to a fixed grip whose position determines the strain level, while the other end is fixed to the force measuring device. The whole system is set in a frame, so that the specimen can
be placed in a controlled environment by inserting the lower part of the frame into an ageing cell. The main differences in these systems are the type of load measuring devices used.

A) WEIGHING BALANCE METHOD

This exploits the principle of a laboratory weighing balance in order to ensure the force. This type of instrument has been very common among the early workers\(^{31,86}\). The Fig.3.9 shows the apparatus in unbalanced position.

![Diagram of relaxing mechanism with weighing balance method](image)

**Fig. 3.9 Relaxometer with weighing mechanism\(^{(31)}\)**

When the measurement is taken, the dead weight \(W\) is moved along the lever \(L\), in the appropriate direction, so that the lever is balanced, detected by the matched pointers \(P_1\) and \(P_2\). It can be shown that the distance \(x\) is directly proportional to the force exerted by the specimen. The specified strain is imposed only when the lever is balanced. Since the force exerted by the specimen continuously decays, the specimen mainly exists at a strain other than that specified. Even though the deviation of actual strain from the specified can be minimised (1\%) by two pins \(x_1\) and \(x_2\), still this can lead to erroneous results.

This apparatus is simple, cheap and less liable to damage, but it is bulky. The main disadvantage of this instrument is, manual adjustment of the strain when the measurement is made. So the instrument is suitable only for very short term testing.
B) **Relaxometer with a Load Cell**

A typical example for this type is the tensile testing machine (Fig. 3.10). Here the force measuring device is a ‘strain gauge’ type instrument, which is commonly called a load cell. This type of force measuring devices are highly rigid (in the rated range), therefore constant strain is accurately maintained. Further it is convenient to use, as the signal can be directly fed into a chart recorder.

![Diagram of Relaxometer with a Load Cell](image)

**Fig. 3.10**: Relaxometer with a Load Cell

C) **Automated-Spinning Relaxometer**.

The Fig. 3.11 shows a very common stress relaxation apparatus\(^{117}\) which works in combination with an ageing cell. This apparatus consists of a steel spring with linear force displacement characteristics to balance the retracting force of the rubber specimen. The method of operation of this apparatus is exactly the same as that shown in Fig. 3.10. However here, the former (Fig. 3.10) has been automated in order to maintain the lever L without touching either of the contacts c\(_1\) or c\(_2\). A motor energised by these contacts, drives s\(_2\) in the appropriate direction, so that the specimen force is balanced by the spring force. Since the spring has linear force-displacement characteristics, the height os\(_2\) becomes a measure of the specimen force. In the apparatus a pencil point attached to the slide s\(_2\) makes a trace on a chart wrapped around a drum which rotates at an appropriate rate, generating the force-time curve.
Fig. 3.11: Automated spinning relaxometer for the tensile mode\(^\text{(117)}\)

This instrument is very uneconomical as a stress relaxation apparatus due to the high cost involved in the equipment compared to the number of specimens that can be tested simultaneously.
3.2.3 INSTRUMENTS THAT WORK IN COMPRESSION MODE

The testing machines used in compression mode have taken a different direction to that of the tensile mode. In order to generate the same amount of information the number of samples that should be tested under compression mode is higher than that in the tensile mode. The main reason behind this is the non uniform and irreproducible slippage of rubber at the holding plates. This makes individual load measuring devices for each sample, highly uneconomical, unless the test time is considerably short.

Taking the above factor into consideration, the facility of separation of specimens from the force measuring device has been achieved by the use of jigs to hold the specimens at the required strain level. Then a single force measuring device has been used for force measurement purposes.

A) THE FORCE MEASURING DEVICE AND THE JIGS AVAILABLE

This consists of a load cell, a means of holding the jig and a drive system to provide relative movement between the load cell and the jig. Ancillary equipment such as amplifiers, power suppliers, digital readouts or chart recorders are essential.

The jigs available

The jigs in which the rubber specimens are compressed to a required nominal strain are kept in the environment required. When a measurement is made the jig is transferred to the force measuring frame and the load plunger is fed into the jig so that the force exerted by the specimen can be measured. The jigs currently available can be divided into three groups according to the way of transferring the load to the measuring frame.

i) The jigs employed by ASTM standard(118), Lucas(119), Rapra(120) and British Gas Company (BGC MK11) shown in Fig. 3.12 employ a low voltage electric circuit to detect the load transfer.

ii) The jig proposed by BGC (MK11)(9) shown in Fig. 3.13 uses a positive displacement to ensure the load transfer.

iii) Constant depth jigs proposed by IPTME (Fig. 3.14)(56,121)
i) Low voltage electric circuit jigs

Fig. 3.12: Jigs which employ low voltage electric circuit\textsuperscript{(56)}
In the low voltage electric circuit jigs the metal to metal contact is made only at the thrust plate B with a part of the jig housing. The arrangement in this jig is as follows.

a) The nominal strain is imposed on the specimen by the depth-changing screw D.

b) When the specimen is under compression the load transfer component A is pressed against the thrust plate B, hence the contact C breaks, which can be detected using an electrical current.

This type of jigs has the following disadvantages

a) It is unsuitable for conductive liquid environments (water etc.)

b) As the metal has been used to facilitate the flow of electrical current, the stickiness and friction reduces the reliability of the measurements, especially at high temperature.

c) Very expensive due to the complexity of the system.

ii) Jigs for positive displacement.

Fig 3.13: Jig which employ positive displacement method

Here the specimen is compressed between two glass plates, one of which rests on the thrust plate. The glass plate is given an incremental displacement (~0.4 mm) to measure the force. The main aim of this arrangement is to eliminate the stickiness problem. However, the following drawbacks have come across in this method.
a) Difficulty in detecting the zero displacement position when measuring displacement.

b) Due to the positive sampling displacement, the force measurement does not correspond to the pre-set strain. (additional 0.4mm on 25% compressed, 6.4mm height sample leads to 31.25% compression.)

c) In some cases, in order to maintain the parallelism of the flat surfaces of the specimen, the moving parts may be guided. As a result, friction affects the reliability of the measurement.

iii) The constant depth jig and the W-F force measuring instrument.

![Thrust Plate](image)

![Jig Housing](image)

**Fig. 3.14: Constant depth jig**

This has been developed at IPTME by Birley et al. [56,121]. In the constant depth jig the main attraction is the elimination of the depth adjusting screw of BGC MK 111 jig, which reduces the uncertainty to the final result. The effect of the screw has been considered in detail in the reference number 55. In order to reduce the stickiness problem, a dry lubricant is applied at either sides of the sample and it is placed in between two glass plates before it is placed in the jig cavity.

Here the force exerted by the specimen is sampled in the load measuring frame (Fig. 3.15) by driving the plunger into the jig. When the plunger makes contact with the top glass plate, the force in the rubber is transferred progressively to the load cell, manifested by a steep straight line on the chart recorder. At the point that the load cell force exceeds that exerted by the specimen, the specimen starts to compress further, showing on the recorder a significant change in force/time response. This further compression of the rubber is terminated after a maximum of 15 seconds, adding about 0.07 - 0.08 mm, that is increasing the compressive strain from 25% to maximum of 26.25%.
B) A compression relaxometer for rubber materials

Stenberg et al.\(^{41}\) have developed an instrument to measure the stress relaxation of rubber materials under compression (Fig. 3.16).

Here the sample is placed on a spring (1), which is clamped at one edge (2) and it is rested upon a knife edge. The spring together with the displacement transducer (3)
act as the stress measuring system. (4a) and (4b) are two bars. The core of the transducer is mounted to the upper bar (4a), while the bobbin is fixed to the lower bar. Then the sample (5) is compressed by turning up the screw (6) which is on the threaded movable compression rod against the plate (7), so that the compression is held constant at the required level. When the sample is compressed, the spring together with the displacement transducer measures the stress. During the compression of the sample, the distance $b$ is increased. At the relaxation, the distance ‘$b$’ decreases reflecting how the counter force diminishes with time.

The main disadvantage of this instrument is the significant time taken to compress the test piece; a lot of data is lost during that period.

3.2.4 Instruments that work in shear mode

i) Dynamic Stress Relaxometer (DSR)

This machine\(^{(122)}\) (Fig. 3.17) has been designed by Porter and Karper for use as a B.F.Goodrich internal test instrument for assessment of gum elastomers, compound quality and processability.

![Diagram of Dynamic Stress Relaxometer (DSR)](image)

Fig 3.17: A schematic diagram of Dynamic Stress Relaxometer (DSR)\(^{(123)}\)
The DSR measures the relaxation response of an elastomeric material to a prescribed shear deformation at any chosen temperature from room temperature to 200°C. The instrument consists of a rotor and a stator, which are heated electrically. The sample to be tested is placed inside the cavity of the stator (Fig. 3.18)

![Diagram of DSR sample geometry](image)

Fig. 3.18: Sample geometry of DSR

Then the stator moves up and stops automatically when a conical cavity of specific size is formed between the stator and the rotor assemblies. The excess material is forced out to maintain a specific sample size. Then the sample is heated for a given period of time, usually 60 seconds. The rotor is then rotated in a short time $t_m$ (5 ms) through a very small narrow angle (typically 0.035 rad) giving a shear deformation on the sample which increases within time $t_m$ and then remains constant. The load variation, which results from the sample relaxation is measured as a torque time curve (Fig. 3.19).

![Schematic diagram of torque variation](image)

Fig. 3.19: The time dependent torque schematic diagram
The values of

1. The peak torque ($T_{\text{m}}$)
2. The time constant $t^*$ required for the torque to decay to a pre-selected fractional value of $\lambda$ of the peak torque and
3. The integral $\sum T$ of torque-time curve

over a chosen time $t_A$ (i.e., Area under the curve) are displayed on the screen. The three numbers $T_{\text{m}}, \sum T$ and $t^*$ have proven useful in defining uniformity and processability of elastomeric materials.

In this instrument the loading system is step strain as the step loading methods employed in viscoelastic testing provides the maximum amount of rheological information. This is because no relaxation (or very minimal) of elastomers occurs during the loading phase. However, the equipment required to perform step loading measurements is more complex than some of the alternative loading models, and sample preparation is more demanding since residual stress from the sample preparation itself must be carefully removed before performing the measurement.

ii) Dynalyser

A machine called Dynalyser (Fig 3.20) has been introduced to the market by Bergougnan Benelux for the purpose of characterisation of the mechanical properties of rubber materials by measuring the dynamic moduli. It characterises the mechanical properties of rubber materials with a time dependent relaxation modulus $E(t)$, measured by means of an indentation test.

Instead of measuring the transfer function of a rubber material in the frequency domain, as dynamic testing devices do (output = dynamic moduli), the Dynalyser measures the very same transfer function in the time domain (output = relaxation modulus). The Dynalyser calculates the dynamic moduli analytically out of the relaxation modulus $E(t)$.

The dynalyser consists of three functional units.

a) Measuring Unit: Frame with indentation mechanism and force sensor.
b) Calculation Unit: Computer.
c) Printing Unit.
Here the sample (2) is put upon an anvil (1), which can be adjusted in height by means of a setting screw. The spherical indenter (3) is mounted so as to load a piezo-electrical cell, which is fixed in the hollow shaft (5), sliding in a sleeve (6). The pneumatic cylinder (7) actuates the movement of the indenter. It turns an eccentrically mounted bearing (9) which acts upon the hollow shaft in which the indenter is mounted and causes a cosine displacement of it. The indentation time is 30ms. The total loading time is 15 seconds. The analogue force during and after the motion is sampled in 256 points. The relaxation moduli $E(t)$ and the dynamic moduli $E'(f)$ and $E''(f)$ are consequently calculated out of these 256 points.
Determination of Mooney viscosity is not new to the rubber industry. But Mooney viscosity alone is insufficient to guarantee that other rheological properties are well controlled. In order to overcome this situation, most of the manufacturers use tests like strain recovery or stress relaxation to ensure control over their process. Such tests provide information on the elastic response of the elastomer. So in order to measure the Mooney viscosity and stress relaxation (elastic response), the Monsanto company has developed a new viscometer with better control (reduced rotor friction and computer control for frictional correction). Here the microprocessor automatically calculates the 4 or 8 minute viscosity values at the end of the test and also notes the stress decay (MLR) or the stress relaxation curve. After viscosity has been determined with the rotor turning at 2 cpm, the rotor stops and the relaxation is recorded automatically for whatever time period we choose. This test involves measuring the area under the curve for a fixed percentage of stress decay following a complex shear strain loading. Fig. 3.21 shows the Mooney relaxation curve obtained using this instrument.

![Mooney relaxation curve](image)

Out of the parameters, slope of the graph (M), intercept, MLR area and $\tau_r$, the MLR area has been identified as the best parameter as it gives a good repeatability and high degree of correlation to a proprietary stress relaxation, which is used for process control purposes.

The main drawbacks of this instruments are

1) Even the best parameter identified (MLR area) has a reproducible standard deviation (SR) of about 4%.
2) The machine has no facility to acquire relaxation data below one second.

3) The relaxation test has to be carried out always at elevated temperatures as it is always followed by the Mooney viscosity test. So one carrying out this test has to assume that the Mooney viscosity test temperatures and times are compatible with the relaxation measurements.

4) The test must be done in the uncrosslinked state
CHAPTER FOUR

THE NOVEL INSTRUMENT AND THE PROPOSED EXPERIMENTAL TECHNIQUE

4.1. INTRODUCTION

It is possible with mechanical test machines controlled and monitored by PCs, to carry out relaxation measurements at short times. However, existing machines are not set up to begin a relaxation test with a rapidly applied load.

According to Dietz(1) some high speed deformation tests are sensitive indicators of small changes in composition of the test material. Relaxation tests, for example, have been found to be good indicators of small changes in polymeric materials, if the first few milliseconds of a test can be accurately recorded. Small changes in composition, changes in structure such as degree of crystallinity or extent of branching in the polymer, show up markedly in the early part of the relaxation test. Hence can be a useful tool in evaluating and determining the structure of such materials.

Two important measurements in such stress relaxation tests are load and deformation. Since load cannot often be measured directly it has to be determined by the deformation of a load-sensing device, such as a load cell. Furthermore since the relaxation data during the early stage of the test is important, priority should be given to speed up the loading process, so that the relaxation during the loading process is negligible. Subsequently, attention should be given to stop the piston (plunger) at a predetermined compression accurately, which is essential in order to compare the results at different test runs.

The Hounsfie1d Test Equipment company in collaboration with the IPTME has produced an equipment which was intended to overcome the above problems.

This chapter discuss the detail on this instrument, experimental techniques used and the methods used to determine the properties of compounds used in the test programme.

4.2. THE NOVEL INSTRUMENT

The equipment depicted in Fig. 4.1 comprises a piston which is driven pneumatically (5-10 bar), and a platen, which houses the load cell and traverses up and
down mechanically. These correspond to the two ways of operating the equipment: the mechanical drive gives the rate of movement from 0.01 to 250 mm/min., whilst the pneumatic drive provides the speed of 2m/sec. This latter value is a very high loading rate and one needs to consider whether this will result in some of the phenomena normally met in impact tests.

Fig. 4.1: Hounsfield Stress Relaxometer.

4.2.1 DEFINITION OF IMPACT LOADING AND NON IMPACT LOADING

When the test piece is loaded from the pneumatically driven plunger, a stress wave travels along the specimen with a velocity equal to the velocity of sound for the material of which the specimen is made. In general, depending on the attenuation in the material and the nature of the support, the wave will be reflected from the bottom end and may travel along the specimen several times. Eventually, the stress wave dies out and the specimen comes to uniform compression from one end to the other. When the waves are travelling, the specimen will not be under uniform compression along its length. Depending on the rate at which the load is applied, the compressive force can
be anything from the full value of the load at one end and without any force at the other, to a value where the difference cannot be detected along the length of the specimen. The former would be impact loading, the latter is non impact loading\(^{(118)}\).

The above distinction between impact and non impact loading depends on the length of the specimen as well as the rate of loading. For the specimens used in these tests the following calculation can be performed to decide whether the loading is impact or non-impact.

The height of the specimen used in this test is approximately 6.4 mm. An average value for the velocity of sound in rubber with 50 phr carbon black\(^{(127)}\) is approximately 141 m/sec. Then the time required for a stress wave to travel from one end of the specimen to another is \(4.5 \times 10^{-5}\) seconds \((6.4 \times 10^{-3} \text{ m} / 141 \text{ m/sec})\). If the specimen is loaded in \(4.5 \times 10^{-5}\) seconds or less than that, then one would classify the loading as impact.

The maximum loading rate that can be attained in the Hounsfield test instrument is 2 m/sec. At this speed, the time required to compress the sample by 25% of its height is \(0.8 \times 10^{-3}\) seconds, which is more than the time required for impact loading. So, the loading at 2 m/sec. speed is technically not an impact loading. For our convenience, in order to distinguish the main two speed levels of the instrument, we will call loading at 2 m/sec. as fast loading mode, while the 0.01-250 mm/min. speed range as slow loading mode.

4.2.2 THE FAST LOADING MODE

The main special feature of the test machine is its ability to carry out high speed tests, where the shortest time taken for a measurement of force is 50 \(\mu\)s and up to 1200 data points are available for each run, packaged into blocks of 200. The first 200 points are achieved in 10 ms and the five remaining packages are deployed in geometric progression to 1000 seconds. The 1200 data points are stored in the memory of the relaxometer until they are transferred, on demand to MS-DOS computer for analysis purposes.

A schematic diagram of the plunger and platen movements in the fast loading mode is given in Fig. 4.3, while a photo showing the relaxometer in capturing mode is given in the Fig. 4.3.
In the fast mode test

Stage 1 - Before the test is started. The platen and load cell is at any arbitrary position. The plunger is at its maximum height.

After instruction is given to start the test;

Stage 2 - Plunger is still at the same position while the Load cell and the platen move down maximum allowed (by X) and stops.

Stage 3 - Plunger comes down and stops just before meets the sample. Then the load cell and the platen starts to move up until the load cell experiences a force of 1 Newton. The load cell initialized this position.

Stage 4 - The plunger goes back by the maximum allowed and meantime the load cell and the platen moves up by the amount of requested compression (e.g. by 1.6 mm).

Stage 5 - The plunger comes down at 2 m/sec speed to the same position as it was in the Stage 4. This process compresses the sample by the requested amount.
As soon as the compression starts, the load cell sends a string of load values to its memory. At the end of the test, the data (time and corresponding force values) is transferred to an external computer and the ‘decay in force’ is plotted against the ‘time’. In order to show the short term behaviour of the force decaying process exaggerate the logarithm value of time has been selected as the X-axis of the graph. A typical graph obtained in this manner is shown in Fig. 4.4.
The instrument starts to collect data as soon as the plunger starts to compress the sample. The initial rising part of the graph represents the force measured during the period plunger attains to reach the specified compression. Up to approximately $10^{-2}$ seconds the measured force shows a harmonic behaviour. This behaviour is believed to be arising from the vibrational motion of the rubber sample and the plunger which has no damping mechanism. Actually, during the time period from $10^{-4}$ to $10^{-2}$ seconds the force is trying to come to an equilibrium level, beyond which the graph represents the relaxation behaviour of the material.

4.2.3 THE SLOW LOADING MODE

In addition to the fast loading mode test, this machine is designed to give slow loading rates from 0.01 mm/min. to 250 mm/min. At the maximum speed of the slow mode test, it takes approximately 0.384 seconds to compress a sample of 6.4 mm height by 25%. During the test, the force values experienced by the load cell is directly downloaded to an external computer and the loading graph and the subsequent relaxation graph is plotted. A typical graph obtained under the slow loading mode for filled natural rubber is given in Fig.4.5. The test duration can be selected from 0.01 min. to 99 hrs.
4.2.4 THE INACCESSIBLE RANGE

As mentioned earlier, the fast loading mode test can be carried out only at the speed of 2 metres/second (i.e. 120,000 mm/min). The slow loading mode test can be carried out in the speed range of 0.01 mm/min. to 250 mm/min. The loading rates between these two modes are inaccessible with this instrument.

4.3. EXPERIMENTAL TECHNIQUES

It was decided to carry out the testing programme in two phases. The first phase was to evaluate the machine performances and its limitations. The second phase was to identify the behaviour of test curves produced by the machine and to investigate structural influences on stress relaxation at different loading rates and at different temperatures.
The rubber compound formulation used by an early researcher\textsuperscript{(56)} to study the long term effect of stress relaxation was taken as the basic formula in this test programme too. The idea behind selecting the same formula was to have both earlier very long time and newly created short time data for comparison purposes.

In addition to the basic formula another two compounds were prepared at different crosslink densities by changing the curative levels. The basic formula is designated as NR1 with lower crosslink densities designated as NR2 and NR3.

4.3.1 COMPOUNDING INGREDIENTS AND FORMULATIONS

A) THE COMPOUNDING INGREDIENTS

\textit{Rubber}

SMR 10 rubber was used throughout the research programme. The dirt content of SMR 10 rubber is approximately 0.08\%\textsuperscript{(128)} while the Mooney viscosity value (ML(1+4)100\degree C) found in the laboratory was 63.5.

\textit{Carbon Black}

High-Abrasion Furnace black (HAF) classified as N330 (ASTM) with an average particle diameter of 26-30 nm was used as the reinforcing filler.

\textit{Vulcanising Agents}

The curatives used in the rubber compounds are Sulphur, TMTD (TetraMethyl Thiuram Disulphide) and CBS (1-N-cyclohexyl-2-Benzothiazyl sulphenamide). The main cross-linking agent is TMTD, while small amount of sulphur was used to improve the properties of vulcanisates such as modulus and degree of cross-linking. The secondary accelerator CBS was incorporated in order to reduce the tendency of blooming and to delay the onset of cross-linking.

\textit{Antioxidant}

The antioxidant incorporated was polymerised 1,2-dihydro -2,2,4 - trimethyl quinoline (Flectol H)

\textit{Activators}

Zinc oxide (ZnO) was used as the inorganic activator while stearic acid (fatty acid) was used as the organic activator.
This combination produces the fatty acid salt which gives better stability than ZnO alone and a more uniform dispersion of the accelerators and fillers in the rubber compound.

B) COMPOUND FORMULATIONS

It was decided to obtain three different levels of cross link densities in order to determine the machine performances and the relaxation behaviour. Having this in mind, only the curative level of the original formulation was changed in the case of the second and third compounds.

Table 4.1: Compound formulations

<table>
<thead>
<tr>
<th></th>
<th>NR1</th>
<th>NR 2</th>
<th>NR 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>S</td>
<td>0.5</td>
<td>0.250</td>
<td>0.125</td>
</tr>
<tr>
<td>St. Acid</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>CBS</td>
<td>3.0</td>
<td>1.50</td>
<td>0.75</td>
</tr>
<tr>
<td>ZnO</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>TMTD</td>
<td>2.0</td>
<td>1.0</td>
<td>0.5</td>
</tr>
<tr>
<td>Fl. H</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>C. Black</td>
<td>50.0</td>
<td>50.0</td>
<td>50.0</td>
</tr>
</tbody>
</table>

Curative ratio - NR 1:NR 2:NR 3 = 4:2:1

4.3.2 MIXING OF THE INGREDIENTS

All the compounds were mixed in the Francis Shaw K1 internal mixer consisting of specially designed (interlocking) rotor blades. The capacity of the intermix is 5.5 litres. The circulating water temperature was adjusted to 40°C and the rotor speed used was 35 rpm.
The Mixing Cycle

The mixing cycle used for the above compound was

1st Addition  Rubber @ 0 Sec.
             ZnO, St. Acid, Flec.H

2nd Addition  C. Black @ 120 Sec

3rd Addition  CBS, TMTD @ 180 Sec.

4th Addition  Sulphur @ 240 Sec.
             Discharge @ 320 Sec.

See notes below, regarding total mixing time.

Initially, the mixing cycle used in phase one was adopted. Subsequently, the cure characteristics were determined at 150°C using the Wallace Shawbury Precision Cure Analyser. The frequency and the strain applied for all compounds were 1.7 Hz and 0.4 respectively.

The 90% cure times of the samples, obtained from different places of the same batch were found to be inconsistent. As this is a sign of a poorly mixed batch (especially the curatives), the above batches were passed through the K1 mixer again for 180 seconds. Then they proved to be adequately uniform.

4.4 THE SPECIMEN

Vulcanised rubber sheets having an approximate thickness of 6.4 mm were prepared using the compression moulding method at 150 °C. Then the cylindrical test buttons having a diameter of 12.5 mm were prepared using a sample cutter.

4.5 TEST CONDITIONS

Machine performances were evaluated only at room temperature. To investigate the relaxation behaviour of the prepared compounds, the room temperature as well as two elevated temperatures (80°C and 100°C) were used.
4.6 PHYSICAL PROPERTIES OF VULCANISATES

Under the Physical properties only the Young's modulus and hardness were determined.

4.6.1 DETERMINATION OF YOUNG'S MODULUS.

It is uncommon to measure the modulus values for rubbers. Hence in practice, the stress at various percentage of elongations, commonly at 100%, 200%, 300% etc. are given (This is incorrectly called as modulus at 100% etc.). If a value for Young's modulus is required then this could be obtained from a more sensitive measurement of stress and strain and by considering the very early part of the stress/strain curve\(^{129}\).

In this study the stress and strain values for vulcanisates, were obtained in accordance with B.S. 903. PART A2 (1971)(Determination of Tensile Stress/Strain properties). For each compound at least six dumb-bell shaped specimen were tested. The samples were elongated to 100% at a speed of 500 mm/min and the relevant stress was obtained. Then using the equation given below the Young's modulus value was calculated (assumed linear relationship between stress and strain)

\[
\text{Young Modulus} = \frac{(F/A)}{\delta L/L}
\]

Where:

- \(F\) - force required to give specific strain
- \(A\) - cross sectional area.
- \(L\) - Unstrained length between the two marks of the specimen
- \(\delta L\) - increase in the original unstrained length

4.6.2 DETERMINATION OF HARDNESS.

The Hardness of the compounds were tested using the Shore A Micro Hardness Tester, in accordance with B.S. 903: Part A26(1969)((Determination of Hardness)

Briefly the hardness test is conducted as follows. A standard semi-spherical indentor is allowed to penetrate the surface of a standard rubber specimen under a specific load in a given time, normally 30 sec. The amount of penetration is then read on dial gauge as a hardness degree.
4.7 SWELLING MEASUREMENTS

The samples were then reimmersed in the solvent and the process was repeated until a constant swollen weight \( (S_i) \) was obtained. Then the samples were de-swollen in vacuum at room temperature to a constant weight \( (D) \) in order to find the volume fraction of solvent absorbed in the rubber.

From the above data, the volume fraction of rubber in swollen vulcanisate \( (V_r) \) was calculated using the equation given below:

\[
V_r = \frac{(D - FT)}{(D - FT)\rho_r^{-1} + a_o\rho_s^{-1}}
\]

where

- \( T \) - Sample weight
- \( D \) - Deswollen weight of the sample
- \( F \) - Fraction of the insoluble components*
- \( a_o \) - weight fraction of the absorbed solvent at equilibrium \( (S_i - D) \)
- \( \rho_r \) & \( \rho_s \) - Densities of rubber and solvent respectively

* In this study ZnO, S, TMTD and CBS were considered as insoluble components.

Then the \( V_r \) value obtained from the above calculation was used to estimate the cross-link densities of the compounds. In order to calculate the cross-link density of the compounds modified Flory-Rhener equation, which is given below was used.

\[
v = \frac{-\ln(1-V_r) - V_r - \chi V_r^2}{V_o(V_r^{3/2} - V_r/2)}
\]

where

- \( V_r \) - Volume fraction of rubber in swollen vulcanisate
- \( \chi \) - Polymer - Solvent interaction parameter \( (NR- Toluene = 0.391) \)
- \( V_o \) - Molar volume of the solvent - ie. \( (\text{Molecular wt./Density}) \)

The above calculation gives the total density of physical cross-links and chemical cross-links.

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4.8 MEASUREMENT TECHNIQUES USED WITH THE NOVEL INSTRUMENT

4.8.1 THE MEASURING METHOD OF CORRECT COMPRESSION

As it was discovered that the machine does not give the specified compression accurately, in all the tests an external measuring device was used to obtain the correct compression. The external measuring device used was a Travelling Microscope, where the minimum reading of the instrument was 0.01 mm. The equipment arrangement used to take the measurement is shown in Fig. 4.6.

![Image](image_url)

**Fig. 4.6**: The Equipment arrangement used to measure the actual compression.

In order to measure the correct compression, one line was marked on the plunger while another line was marked on the platen. Then the position of these lines were noted before and after compression.

4.8.2 THE ARRANGEMENTS FOR HIGH TEMPERATURE TESTS.

In high temperature tests, before the sample is transferred to the machine, the sample was heated for 30 min. at the required temperature. To maintain the temperature of the sample approximately constant during the test period, the platen
was heated to the required temperature with the aid of a band heater, which is fixed to the top part of the platen (Fig. 4.7). In this arrangement the temperature of the top surface of the platen was monitored by a temperature control device externally, and the power was supplied or cut off accordingly by the temperature control device to the band heater. With this arrangement it was possible to maintain the required temperature with a good accuracy (variation approximately ±1.5 °C.).

Fig. 4.7: Platen arrangement for high temperature tests.
In order to minimise the effect of the conduction of heat to the load cell, cool water was passed through the lower part of the platen. A schematic diagram of the modified platen with water cooling facility is given below.

Fig. 4.8 : Schematic diagram of the platen

While high temperature tests were carried out, the temperature between the platen and load cell was measured to check whether the heat is conducting to the load cell. In this exercise it was found that no heat conduction to the load cell takes place even at 100°C, if tap water (temperature around 16°C) is used for cooling.
5.1 FACTORS RELATING TO THE TESTING METHODS AND HARDWARE

5.1.1. INTRODUCTION

At the beginning of the research programme an evaluation of the performances of the new machine in both modes was carried out. In this evaluation it was revealed that the slow mode test is not functioning as expected. All the shortcomings observed and the suggestions for further improvements are listed in the annex 1. In order to use the slow mode test in the research programme, later the software of the slow mode test was replaced by a more developed version which gives better controllability and more flexibility.

With the newly installed programme, the relaxation test in the Slow mode can be carried out at different compressive strain rates starting from 0.01 mm/min. to 250 mm/min. for different time durations. In both the slow and fast modes, the required compression on the test samples needs to be input at the beginning. Then at the start of the test, the plunger compresses the sample by the amount of compression specified.

Further investigation on both the modes showed that the machine is unable to give the required compression accurately and also has poor test repeatability.

As a result the machine was examined again by the manufacturer in order to rectify the above problems. After careful investigation, it was decided that it would be necessary to have extensive modifications on the mechanical system and the software of the machine. As that would be a time consuming task, it was decided to use the machine in the test programme with the following precautionary actions.

The actual compression value was measured with an external measuring device without depending on the input compression values. To avoid the poor test repeatability, only the tests whose actual compression value lie in the range (25% ± 5%) were selected for further analysis. In few tests it was possible to observe disproportionate force values compared to the amount of compression. To analyse
results in such cases a set of compensation procedures for processing data was developed.

The forthcoming sections explain the machine performance, remedial actions taken, test data analysis criteria in detail and also the effect of strain rate on rate of relaxation for materials with different crosslink densities at different temperatures.

5.1.2 ERRORS IN THE SLOW LOADING MODE

A typical set of graphs obtained for a filled natural rubber compound (NR1 compound) under seven different loading rates is shown in Fig. 5.1.

![Graph showing relaxation curves](image)

**Fig. 5.1:** A set of relaxation curves obtained for the NR1 compound at different strain rates under the slow mode test

Other than the relaxation curves corresponding to two slowest compression rates, almost all other curves give approximately linear graphs. These linear graphs are not perfectly parallel to each other.

A) TEST REPEATABILITY UNDER THE SLOW MODE TEST

In order to discuss the test repeatability, test curves obtained for a filled natural rubber compound specimen at the loading rate of 10 mm/min. were selected. In each
case the compression assigned was 25%. A set of graphs so obtained is shown in Fig. 5.2. Ideally the graphs in Fig. 5.2 should represent a set of relaxation curves obtained at the same rate of strain and at the same level of compression.

As the material, strain rate and amount of compression are the same for the curves obtained at 10 mm/min. compressive strain rate, similar relaxation curves were expected with approximately the same force values. Contrary to this, the test results obtained at 10 mm/min., range from 388 N to 409 N at 1 second.

![Graph showing stress relaxation curves for the NR1 compound at the speed of 10 mm/min.](image)

**Fig. 5.2:** Stress Relaxation curves for the NR1 compound at the speed of 10 mm/min.

Since the samples had been uniformly prepared, the observed variation i.e. 21 N was considered too large in order to attribute only to a sample variation. Furthermore at other strain rates, similar variations could be observed. Hence the following work is centred on possible machine variations.

i) *The Specified and Actual Compression*

After the above experiments, it was suspected that inaccurate levels of compression produced by the machine have caused the scatter of the relaxation curves. To investigate this, a series of tests were conducted in order to determine the actual level of compression. These tests were repeated at different loading rates.
During these tests, the machine was set to give a compression equal to 25% of the sample height. Then the actual compression was measured externally using a travelling microscope. In addition to the microscope reading, the amount of compression shown in the display unit of the machine (the LCD reading) was also noted. The compression values obtained under both measuring systems at different speeds are tabulated in Table 5.1. The blocks of tests are grouped under the various testing rates at which the experiments were repeated.

The first column of Table 5.1 represents the compressive strain rate and the second column gives sample thickness. The third and the fourth columns represent the percentage compression calculated using a travelling microscope and the LCD reading respectively.

**Table 5.1: Compression percentages for the NR1 compound at different speeds**

<table>
<thead>
<tr>
<th>Speed</th>
<th>Sample Thickness (mm)</th>
<th>MEASURED BY MICROSCOPE</th>
<th>INDICATED ON LCD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>COMP. %</td>
<td>AVG.</td>
</tr>
<tr>
<td>0.1 mm/min.</td>
<td>6.46</td>
<td>23.1</td>
<td>24.9</td>
</tr>
<tr>
<td></td>
<td>6.46</td>
<td>22.6</td>
<td>24.9</td>
</tr>
<tr>
<td></td>
<td>6.48</td>
<td>23.5 23.2</td>
<td>24.9 24.9</td>
</tr>
<tr>
<td></td>
<td>6.50</td>
<td>23.2</td>
<td>24.9</td>
</tr>
<tr>
<td></td>
<td>6.47</td>
<td>23.5</td>
<td>25.0</td>
</tr>
<tr>
<td>1.0 mm/min.</td>
<td>6.43</td>
<td>24.0</td>
<td>25.0</td>
</tr>
<tr>
<td></td>
<td>6.43</td>
<td>22.5</td>
<td>25.0</td>
</tr>
<tr>
<td></td>
<td>6.45</td>
<td>23.5 23.5</td>
<td>25.0 25.0</td>
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<td></td>
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<td>23.5</td>
<td>25.0</td>
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<td></td>
<td>6.48</td>
<td>24.0</td>
<td>25.0</td>
</tr>
<tr>
<td>10.0 mm/min.</td>
<td>6.38</td>
<td>22.5</td>
<td>25.0</td>
</tr>
<tr>
<td></td>
<td>6.35</td>
<td>23.3 23.2</td>
<td>25.0 25.1</td>
</tr>
<tr>
<td></td>
<td>6.42</td>
<td>23.1</td>
<td>25.0</td>
</tr>
<tr>
<td></td>
<td>6.41</td>
<td>23.4</td>
<td>25.1</td>
</tr>
<tr>
<td></td>
<td>6.43</td>
<td>23.8</td>
<td>25.1</td>
</tr>
<tr>
<td>Strain Rate (mm/min)</td>
<td>Compression (%)</td>
<td>Residual Force (%)</td>
<td>Readings</td>
</tr>
<tr>
<td>----------------------</td>
<td>-----------------</td>
<td>--------------------</td>
<td>----------</td>
</tr>
<tr>
<td>20 mm/min.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.38</td>
<td>23.4</td>
<td>25.0</td>
</tr>
<tr>
<td></td>
<td>6.40</td>
<td>23.4</td>
<td>25.2</td>
</tr>
<tr>
<td></td>
<td>6.35</td>
<td>24.1</td>
<td>23.6</td>
</tr>
<tr>
<td></td>
<td>6.35</td>
<td>23.5</td>
<td>25.1</td>
</tr>
<tr>
<td></td>
<td>6.36</td>
<td>23.4</td>
<td>25.3</td>
</tr>
<tr>
<td>50 mm/min.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.35</td>
<td>22.6</td>
<td>24.7</td>
</tr>
<tr>
<td></td>
<td>6.40</td>
<td>24.0</td>
<td>25.4</td>
</tr>
<tr>
<td></td>
<td>6.43</td>
<td>23.6</td>
<td>23.7</td>
</tr>
<tr>
<td></td>
<td>6.42</td>
<td>24.1</td>
<td>25.3</td>
</tr>
<tr>
<td></td>
<td>6.34</td>
<td>24.0</td>
<td>25.3</td>
</tr>
<tr>
<td>150 mm/min.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.44</td>
<td>25.3</td>
<td>26.7</td>
</tr>
<tr>
<td></td>
<td>6.34</td>
<td>24.2</td>
<td>26.8</td>
</tr>
<tr>
<td></td>
<td>6.40</td>
<td>23.6</td>
<td>24.5</td>
</tr>
<tr>
<td></td>
<td>6.44</td>
<td>23.7</td>
<td>26.2</td>
</tr>
<tr>
<td></td>
<td>6.42</td>
<td>25.5</td>
<td>26.7</td>
</tr>
<tr>
<td>250 mm/min.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.44</td>
<td>26.8</td>
<td>24.3</td>
</tr>
<tr>
<td></td>
<td>6.44</td>
<td>26.4</td>
<td>28.7</td>
</tr>
<tr>
<td></td>
<td>6.39</td>
<td>23.5</td>
<td>25.9</td>
</tr>
<tr>
<td></td>
<td>6.44</td>
<td>26.4</td>
<td>28.5</td>
</tr>
<tr>
<td></td>
<td>6.44</td>
<td>26.4</td>
<td>28.6</td>
</tr>
</tbody>
</table>

When comparing the microscope and the LCD readings, the LCD reading always gives a higher average value, but the deviation observed in the microscope method is larger than that of the LCD reading. That is, there are variations between the intended compression (25%), the compression that the relaxometer displays (24.7% to 28.7%) and the compression actually achieved (22.5% to 26.8%).

If one uses the compression values and the residual force values obtained at any of the above strain rates, it is possible to verify whether the microscope or LCD readings better represent the scatter shown in the graphs. In this study 10 mm/min. strain rate was arbitrarily selected to continue the analysis. The relaxation curves corresponding to the tests carried out at 10 mm/min. are given in Fig. 5.2. The corresponding compressions for the curves given in the Fig. 5.2 are Test 1- 22.5%, Test 2- 23.3%, Test 3- 23.8%, Test 4- 23.1%, Test 5- 23.4%.
ii) Forces Represented by Microscope and LCD Readings

At the rate of 10 mm/min. compressive strain, the variation in the compression percentage observed through the microscope method is 1.37%, while that of the machine LCD readings is 0.11%. The magnitude of the force difference between the curve having the maximum force value and the minimum force value at the end of 1 second. (log(t)=0) is 20.61N (i.e. 388 N to 408.61 N).

Thus if the microscope reading is correct then the force value 20.61N is represented by the compression difference of 1.37%. On the other hand if the LCD reading is correct then 20.61N is represented by a compression difference of 0.11%. If a linear behaviour in force and compression up to the compression level of 25% is assumed, then based on the above two compression and force values, the force required in each case to achieve a 25% compression can be calculated.

If the Microscope Reading is correct.

A compression of 1.37% is represented by 20.61 N
Thus a compression of 25% should be represented by (20.61/1.37) x 25 N
The force required to compress by 25% is 376.09 N

If the LCD Reading is correct.

A compression of 0.11% is represented by 20.61 N
Thus a compression of 25% should be represented by (20.61/0.11) x 25 N
The force required to compress by 25% is 4684 N

It is seen clearly from the curves given in Fig. 5.2 that the force required to compress the rubber sample by 25% is in the range 388 - 408 N. So the values obtained through the microscope is more closer to the real situation, while the readings obtained through the LCD represent an exaggerated situation.

A similar behaviour is observed in the other strain rates too. The calculated force values which give 25% compression for the above two cases are given in Table 5.2.
Table 5.2: Calculated force values for the NR1 compound (25% compression)

<table>
<thead>
<tr>
<th>Strain rate (mm/min.)</th>
<th>If the Microscope reading is correct (N)</th>
<th>If the LCD reading is correct (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>358</td>
<td>1815</td>
</tr>
<tr>
<td>1.0</td>
<td>369</td>
<td>2188</td>
</tr>
<tr>
<td>10.0</td>
<td>376</td>
<td>4684</td>
</tr>
<tr>
<td>20.0</td>
<td>408</td>
<td>673</td>
</tr>
<tr>
<td>50.0</td>
<td>347</td>
<td>633</td>
</tr>
<tr>
<td>150.0</td>
<td>396</td>
<td>491</td>
</tr>
<tr>
<td>250.0</td>
<td>494</td>
<td>537</td>
</tr>
</tbody>
</table>

The above results confirm that the microscope reading represents the real situation. Hence for further analysis purposes only the compression percentages obtained through microscope readings will be considered.

iii) Scatter in Measured Compression

The measured compression varies with the rate of compressive strain and there is a tendency for the amount of compression to increase with the increase of compression rate. The Fig 5.3 shows the behaviour of average compression values given in Table 5.1 with strain rate. The standard deviation value values of the tests carried out at each strain rate are also given in the same plot.

This graph shows clearly that the average percentage compression increases with the strain rate. Further the scatter of the compression values also increases with strain rate. This implies that the machine has poor test repeatability at high strain rates.
5.1.3. ERRORS IN THE FAST LOADING MODE

A typical graph obtained in this mode is given in Fig. 4.4 of Chapter 4. Even though the graph commences at $10^4$ seconds, up to approximately $10^{-2}$ seconds, no relaxation process can be observed. This part of the graph represents a complex harmonic motion, which may be the resultant behaviour of damped vibrational motions of the rubber specimen under impact and/or the load sensing mechanism of the load cell of the instrument.

In order to check the influence of the sample height on the resonant frequency, samples with half of the original height were subjected to the same test. The graphs so obtained are given in Fig. 5.4.

From these graphs it is noticed clearly that the frequency and the amplitude of the damped vibration does not significantly depend on the sample height, as it would if
the oscillation were coming from the test piece. Hence the main contributory factor for the fluctuations observed in the early part of the relaxation curve can be due to the vibrations taking place in the measuring device.

A) **TEST REPEATABILITY UNDER THE FAST MODE TEST**

Similar to the slow mode, a scatter is observed among the relaxation curves. As the loading rate was constant and the samples were obtained from the same vulcanisate, the suspected cause of the scatter is incorrect compression.

A set of samples was tested in order to verify whether the sample is being compressed by 25% of its height. Again a travelling microscope was used to measure the compression externally. In the fast mode, as the machine does not show the amount of compression on the LCD, only the compression measurements obtained through the microscope is available this time. The results so obtained are tabulated in Table 5.3.
Table 5.3: Compression values of the NR1 compound measured during the Fast Mode Test

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Sample Thickness (mm)</th>
<th>Measured compression</th>
<th>Compression, set in the Machine</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.45</td>
<td>19.8%</td>
<td>25%</td>
</tr>
<tr>
<td>2</td>
<td>6.39</td>
<td>21.9%</td>
<td>25%</td>
</tr>
<tr>
<td>3</td>
<td>6.34</td>
<td>22.1%</td>
<td>25%</td>
</tr>
<tr>
<td>4</td>
<td>6.43</td>
<td>23.3%</td>
<td>25%</td>
</tr>
<tr>
<td>5</td>
<td>6.40</td>
<td>23.4%</td>
<td>25%</td>
</tr>
<tr>
<td>6</td>
<td>6.42</td>
<td>24.9%</td>
<td>25%</td>
</tr>
</tbody>
</table>

The relaxation curves obtained for the above tests are given in Fig. 5.5.

As the compressive force should increase with increasing compression, ideally the curve of test number 6 should be at the highest level followed by the curves obtained for the test numbers 5, 4, 3, 2, and 1 respectively. But, the curves obtained experimentally have not followed the above sequence.

![Fig 5.5: Stress Relaxation curves obtained for the NR1 compound in six Fast Mode Tests](image-url)
Two types of reasons can be contributed for this random behaviour: those associated with the external measuring system and those associated with the test machine.

5.1.4 THE CONTRIBUTORY FACTORS FOR TEST REPEATABILITY

A) ERRORS ASSOCIATED WITH THE EXTERNAL MEASURING SYSTEM

To measure the compression given during the test, a travelling microscope was used. The minimum reading of this measuring system was 0.1 mm. When this instrument is used to measure the compression of a sample with a height of 6.4 mm, one can expect an error of ±0.6% on the compression of 25%, which indicates that the scatter in the range of 25.0% ± 0.6% is within the experimental limitations. One out of the six tests given in Table 5.3 lie within this range. The worst deviation is -5.16%.

The deviation in compression values met in five tests is too large to attribute for a measurement error. If it is due to a measuring error then the percentages such as 19.84% and 21.90% should be due to an error of 0.33 mm and 0.2 mm respectively, which is unlikely to be read mistakenly from the repetitive measurements of a travelling microscope.

B) ERRORS ASSOCIATED WITH THE MACHINE

Having proved that uncertainty of the measurements, which have been made externally is too small to explain the deviation of compression from 25%, the only other factors one can expect are;

i) Displacements in the plunger due to the force experienced by it, when the compression is given.

ii) Movement of the platen.

iii) Compression/Compression Rates: any differences between specified and actual compression rates.

The above three factors will be considered here individually to assess their influence on the deviation observed.
i) *Displacements of the Plunger*

Out of the above three factors the first was tested only in the slow mode as the movement of the plunger is too complicated in the fast mode test. In order to do this an arbitrary position was marked on the plunger and the movement of that mark was observed with the aid of a travelling microscope while the load is been applied. The loading rate selected was 250 mm/min. as it gives the maximum force to the plunger. Test results are tabulated in Table 5.4.

These results show that if no displacement is enforced by the test then the plunger has the ability of staying stationary even in the load range 400 - 500N.

Table 5.4: Displacement of the Plunger under the load

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Microscope Reading</th>
<th>Movement of the mark (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before the Load</td>
<td>After the Load</td>
</tr>
<tr>
<td>1</td>
<td>63.41</td>
<td>63.41</td>
</tr>
<tr>
<td>2</td>
<td>63.33</td>
<td>63.33</td>
</tr>
<tr>
<td>3</td>
<td>63.47</td>
<td>63.47</td>
</tr>
<tr>
<td>4</td>
<td>63.42</td>
<td>63.42</td>
</tr>
<tr>
<td>5</td>
<td>63.55</td>
<td>63.60</td>
</tr>
<tr>
<td>6</td>
<td>63.19</td>
<td>63.19</td>
</tr>
<tr>
<td>7</td>
<td>63.17</td>
<td>63.17</td>
</tr>
<tr>
<td>8</td>
<td>63.13</td>
<td>63.15</td>
</tr>
<tr>
<td>9</td>
<td>63.14</td>
<td>63.14</td>
</tr>
<tr>
<td>10</td>
<td>63.22</td>
<td>63.22</td>
</tr>
</tbody>
</table>

ii) *Accuracy of the movement of the platen*

The accuracy of the movement of the platen has been checked at the Hounsfield Company. The test has been carried out by measuring the actual displacement of the platen in the range 0.01 - 10.0 mm. The displacement has been given in three stages as follows.
<table>
<thead>
<tr>
<th>Stage No.</th>
<th>Test Nos.</th>
<th>Displacement Range (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 to 19</td>
<td>0.010 to 0.0950 in steps of 0.005</td>
</tr>
<tr>
<td>2</td>
<td>20 to 38</td>
<td>0.1 to 0.950 in steps of 0.05</td>
</tr>
<tr>
<td>3</td>
<td>38 to 56</td>
<td>1.000 to 10.000 in steps of 0.500</td>
</tr>
</tbody>
</table>

The graphical representation of the results is given in Fig. 5.6

![Graph](image)

**Fig. 5.6: Deviation in the platen movement during first 10 mm of the movement**

The maximum error observed is 0.03 mm over 10.00 mm. This is quite acceptable in the stress relaxation measurements. The above graph shows larger deviations for larger displacements. At larger displacements, the deviation is negative resulting an under compression in the sample.

In the slow mode test the anvil displacement is very short (depends on the sample thickness: approximately 2.0 mm). Hence the above result is an adequate representation of the platen movement in the slow mode at no load condition.

However in the fast mode, the anvil displacement is higher than 10.0 mm, usually it is around 10-17 mm. Hence the above graph does not provide an idea on the deviation encountered in the fast mode test.
iii) Inconsistent Compression/compression Rates

In both slow and fast modes, the compression values achieved in the tests have a random behaviour. This could be due to the random calculation errors in the distance calculation step of the software, which would lead to a different strain rate than the requested or to a different compression than requested. Such calculation errors could for example, be caused by truncating errors or jumping out loops at the wrong stage. This of course would affect both modes.

In the present experiment only the compression was checked by travelling microscope, as the techniques involved in measuring the speed of the plunger/anvil are not as easy as the measurement of displacement. Hence the variations in the strain rate could not be quantified.

In the slow mode test, a stepper motor is used to apply the requested compression/compression rates. The use of stepper motor should ensure the repeatability of strain rates, if software issues correct instructions to the stepper motor. However, as the software may possibly generate random calculation errors, the instruction issued to the stepper motor will not be consistent and this will lead to inconsistent compression/compression rate.

In the fast mode test the compression rate is supposed to be a fixed value of 2 m/s. It does not depend on the calculations of the software, but the anvil movement is determined by the software. Hence the software problems discussed previously still influence and lead to incorrect positioning of the anvil, thus giving incorrect compressions.

Another, but mostly less important factor may influence the compression rate. In the fast mode test, the machine uses a pneumatically driven mechanism to achieve the compression rate of 2 m/s. The required air pressure is obtained by connecting to a common compressed air line. As the air pressure of the compressed air line varies, the force exerted on the piston of the machine will not be a fixed value. This will also lead to inconsistent compression rates in the fast mode.

The discussion above shows the possibility of random deviation of the strain rates from the intended values. As the initial force varies with the rate of compression^{65}, the random behaviour of strain rates discussed above can be used to explain the disorderliness of the stress relaxation curves in slow mode tests and fast mode tests.
5.1.5 Influence of Test Parameters on the Actual Compression.

In this section the possible factors affecting the specified compression (25%) is discussed. The influence of strain rate, sample temperature, material hardness and the height unevenness of the sample on the specified compression will be discussed under the forthcoming sub-sections.

A) Influence of the Compressive Strain Rates

An important facility in the Hounsfield relaxometer is the possibility of applying different loading rates ranging from 0.01 mm/min. to 250 mm/min. in the Slow mode or 2 m/second in the fast mode. If the machine is working properly then irrespective of the rate of strain, the machine should give the specified compression and if any deviation is present then it should be a random deviation.

As discussed in section 5.1.1 and 5.1.2 the experimental results indicate the inability of achieving the specified compression. Hence investigations were carried out to see whether this deviation from the specified compression had a random behaviour or a systematic behaviour.

Figures 5.7, 5.8, and 5.9 show how the amount of compression varies with the rate of compressive strain, at room temperature and two other elevated temperatures.

![Graph showing variation in percentage compression with strain rate at room temperature](image)

**Fig. 5.7**: Variation in percentage compression with strain rate at room temperature
When increasing the rate of compressive strain, the compression in the above three graphs behave in a similar pattern. In each case the set compression was 25%. At lower strain rates the compression attained is less than 25%. At higher strain rates the actual compression is higher than the required compression of 25%.
In the fast mode, the machine does not attain the 25% compression. It is usually less than the lowest compression attained in the Slow mode.

Almost all three graphs show overshoot compression values approximately beyond 100 mm/min in the slow mode. After the strain rate of 100 mm/min., the measured compression value increases until the rate of strain reaches 250 mm/min., which is the highest rate available in the slow mode. This overshoot indicates that the machine over compresses the sample at higher strain rates. The range of compressive strain rates above which the machine achieves 25% compression, varies with the sample temperature. Higher the sample temperature, lower the strain rate at which the machine attains 25% compression. The range of strain rate which starts the overshooting decreases with the increasing sample temperature. The three ranges for the three temperatures are as follows.

At room temperature (20°C) - 120 to 170 mm/min.
At 80 °C - 65 to 120 mm/min.
At 100 °C - 55 to 90 mm/min.

Even though the machine over compresses the sample at the strain rates beyond 100 mm/min. in the slow mode, the same tendency cannot be seen in the fast mode. In the fast mode the machine is unable to achieve the required compression of 25%. It is always less than the compression achieved at 250 mm/min. strain rate of the slow mode.

B) INFLUENCE OF THE SAMPLE TEMPERATURE

In the test programme, tests were carried out at three different temperatures namely room temperature (about 20°C), 80°C and 100°C. Prior to carrying out the tests at 80°C and 100°C the samples were preheated for 30 minutes at the respective temperatures. As a result when the samples are transferred to the testing machine for high temperature tests, the samples have been subjected to the same heating time but at different temperatures.

The compression values obtained at different temperatures at different strain rates are given in the appendix 2. There is no significant change in compression values of the slow mode tests and fast mode tests with the temperature. This means compression values are independent of the sample temperature.
C) Influence of Material Hardness on the Amount of Compression at Constant Temperature

In order to determine the influence, the comparison was made among the samples with same pre heating history. The results so obtained are given in the appendix 3. From these results it can be seen that there is no significant change in the compression with the hardness. This indicates that if the samples are subjected to same conditioning prior to the test, then the percentage compression values are independent of the material hardness.

D) Influence of the Thickness Unevenness of Samples

The compression moulding method which was used to prepare vulcanised rubber sheets gave a vulcanisate with a fairly uniform thickness. But the subsequent sample preparation method (cutting of compression buttons using a die) has made a height unevenness in the samples. This sample height unevenness was compared with the compression deviation observed during the test. The values given in Table 5.5 show that the unevenness is very much smaller than the deviations observed during the test.

Table 5.5: Influence of the uneven height of samples

<table>
<thead>
<tr>
<th>Individual height measurements at five different points (mm)</th>
<th>(Max. - Min.) of individual measurements (mm)</th>
<th>Possible error contribution due to height difference</th>
<th>Compression deviations observed during the test</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.12, 7.15, 7.14, 7.14, 7.12</td>
<td>0.03</td>
<td>0.4%</td>
<td>-7.95%</td>
</tr>
<tr>
<td>7.16, 7.17, 7.15, 7.17, 7.15</td>
<td>0.02</td>
<td>0.2%</td>
<td>-2.1%</td>
</tr>
<tr>
<td>7.14, 7.16, 7.16, 7.16, 7.16</td>
<td>0.02</td>
<td>0.2%</td>
<td>-0.7%</td>
</tr>
<tr>
<td>7.30, 7.30, 7.31, 7.30, 7.30</td>
<td>0.01</td>
<td>0.1%</td>
<td>-0.59%</td>
</tr>
<tr>
<td>7.10, 7.14, 7.10, 7.13, 7.14</td>
<td>0.04</td>
<td>0.56%</td>
<td>+1.76%</td>
</tr>
<tr>
<td>7.07, 7.10, 7.08, 7.08, 7.13</td>
<td>0.06</td>
<td>0.85%</td>
<td>+2.86%</td>
</tr>
</tbody>
</table>
Hence, it cannot significantly influence the final result. The sample thickness and the compression values given in Table 5.5 are specifically used to find the influence of the thickness unevenness only.

5.1.6 CONCLUSIONS ON THE MACHINE BEHAVIOUR

a) The compression given in the slow mode depends on the loading rate. Generally the higher the strain rate the higher will be the compression.

b) The fast mode test always under-compress the sample in relative to the value assigned by the machine.

c) The compression given by the machine does not depend on the sample temperature and the material hardness.

d) The compression variation arising from the height unevenness of the samples is too small to explain the compression deviation given by the machine.

5.1.7 STRATEGY FOR USING THE TEST MACHINE

A) VALIDITY OF THE COMPRESSION VALUES ACHIEVED BY THE MACHINE

According to the British Standard (BS903:PART A42:1992)\(^{(13)}\), the allowable deviation on the compression of a test sample for stress relaxation measurements is ±2%. As a result if the aimed compression is 25%, then all the compressions should lie in between 23% and 27%.

The tables given below show the numerical values of the deviation of compression from the specified value of 25%. Each reading represents average value of five tests.
Table 5.6: Deviations of actual compressions at Room Temperature (20 °C)

<table>
<thead>
<tr>
<th>LOADING RATE (mm/min.)</th>
<th>NR 1 dev.%</th>
<th>NR 2 dev.%</th>
<th>NR 3 dev.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>-1.83</td>
<td>-1.18</td>
<td>-1.29</td>
</tr>
<tr>
<td>1</td>
<td>-1.52</td>
<td>-1.75</td>
<td>-0.83</td>
</tr>
<tr>
<td>10</td>
<td>-1.78</td>
<td>-0.61</td>
<td>-0.53</td>
</tr>
<tr>
<td>20</td>
<td>-1.44</td>
<td>-1.07</td>
<td>-0.74</td>
</tr>
<tr>
<td>50</td>
<td>-1.37</td>
<td>-0.50</td>
<td>-1.57</td>
</tr>
<tr>
<td>150</td>
<td>-0.55</td>
<td>0.06</td>
<td>0.18</td>
</tr>
<tr>
<td>250</td>
<td>0.90</td>
<td>2.51</td>
<td>2.62</td>
</tr>
<tr>
<td>120000</td>
<td>-1.87</td>
<td>-1.29</td>
<td>-1.57</td>
</tr>
</tbody>
</table>

Table 5.7: Deviations of actual compressions at 80 °C

<table>
<thead>
<tr>
<th>LOADING RATE (mm/min.)</th>
<th>NR 1 (dev.%)</th>
<th>NR 2 (dev.%)</th>
<th>NR 3 (dev.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>-0.39</td>
<td>-1.005</td>
<td>-0.76</td>
</tr>
<tr>
<td>1</td>
<td>-0.96</td>
<td>-0.81</td>
<td>-1.11</td>
</tr>
<tr>
<td>10</td>
<td>-0.47</td>
<td>-1.06</td>
<td>-1.2</td>
</tr>
<tr>
<td>20</td>
<td>-0.68</td>
<td>-0.99</td>
<td>-0.55</td>
</tr>
<tr>
<td>50</td>
<td>-0.32</td>
<td>-0.95</td>
<td>-0.35</td>
</tr>
<tr>
<td>150</td>
<td>0.59</td>
<td>0.23</td>
<td>0.44</td>
</tr>
<tr>
<td>250</td>
<td>1.76</td>
<td>2.05</td>
<td>2.27</td>
</tr>
<tr>
<td>120000</td>
<td>-3.9</td>
<td>-4.81</td>
<td>-3.78</td>
</tr>
</tbody>
</table>

Table 5.8: Deviations of actual compressions at 100 °C

<table>
<thead>
<tr>
<th>LOADING RATE (mm/min.)</th>
<th>NR 1 (dev.%)</th>
<th>NR 2 (dev.%)</th>
<th>NR 3 (dev.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>-0.76</td>
<td>-0.61</td>
<td>-0.12</td>
</tr>
<tr>
<td>1</td>
<td>-0.89</td>
<td>-0.40</td>
<td>-0.48</td>
</tr>
<tr>
<td>10</td>
<td>-1.09</td>
<td>-0.63</td>
<td>-0.37</td>
</tr>
<tr>
<td>20</td>
<td>-0.87</td>
<td>-0.33</td>
<td>-0.54</td>
</tr>
<tr>
<td>50</td>
<td>-0.41</td>
<td>-0.22</td>
<td>0.03</td>
</tr>
<tr>
<td>150</td>
<td>0.39</td>
<td>0.52</td>
<td>0.71</td>
</tr>
<tr>
<td>250</td>
<td>1.86</td>
<td>2.64</td>
<td>2.68</td>
</tr>
<tr>
<td>120000</td>
<td>-3.41</td>
<td>-2.88</td>
<td>-2.70</td>
</tr>
</tbody>
</table>

When the compression values of the above three cases are considered it can be noticed clearly that the compression values obtained in the fast mode and at the rate of 250 mm/min. of the slow mode do not agree with the relevant British Standard. Furthermore some of the values obtained with the room temperature test are marginal values of the standard specification.
B) MACHINE GENERATED FORCE ERRORS AND THE DATA ANALYSIS CRITERIA

i) A possibility of machine generated force errors in addition to the strain errors

When a rubber specimen is compressed at a constant rate then the compressive force is proportional to the amount of compression. But when the results obtained from the Hounsfield Relaxometer are analysed, in few cases the proportionality between the compression and the force values could not be observed. When a number of samples are tested, giving the same compression at a constant strain rate, then some of the tests which have less compression (actual) show larger force values than the samples with higher compression. Some tests have the same compression (actual) but the force values are considerably different in magnitudes.

Table 5.9 shows the number of such deviant tests for the NR1 compound at room temperature, 80°C and 100°C.

Table 5.9: Number of deviant tests for the NR1 compound.

<table>
<thead>
<tr>
<th>Test speed (mm/min.)</th>
<th>At Room Temp.</th>
<th>At 80 °C</th>
<th>At 100 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total No. of Tests</td>
<td>No. of deviant tests</td>
<td>Total No. of Tests</td>
</tr>
<tr>
<td>0.1</td>
<td>5</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>1.0</td>
<td>5</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>10.0</td>
<td>5</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>20.0</td>
<td>5</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>50.0</td>
<td>5</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>150.0</td>
<td>5</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>250.0</td>
<td>5</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>120,000</td>
<td>7</td>
<td>0</td>
<td>8</td>
</tr>
<tr>
<td>Total No. of tests</td>
<td>42</td>
<td>6</td>
<td>44</td>
</tr>
</tbody>
</table>

Out of 137 tests only 18 tests have shown disproportionate force values. Tables 5.10 and 5.11 explain the method employed to find such deviant tests.

In order to find the number of deviant tests the force values of the individual tests were compared with the measured compression values. Table 5.10 shows such
force values at every 0.5 second during the first 10 seconds of a test, for the NR 1 compound at the loading rate of 10 mm/min. and at room temperature.

**Table 5.10**: Uncorrected force values at every 0.5 second during the first 10 second of a test (NR1 compound, 10 mm/min. loading rate at room temp.)

<table>
<thead>
<tr>
<th>TIME (s)</th>
<th>TEST 1</th>
<th>TEST 2</th>
<th>TEST 3</th>
<th>TEST 4</th>
<th>TEST 5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>COMP:→</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>22.57%</td>
<td>23.30%</td>
<td>23.05%</td>
<td>23.35%</td>
<td>23.64%</td>
</tr>
<tr>
<td></td>
<td>372.78</td>
<td>381.97</td>
<td>393.99</td>
<td>395.5</td>
<td>386.26</td>
</tr>
<tr>
<td>1</td>
<td>368</td>
<td>377.66</td>
<td>388.61</td>
<td>390.27</td>
<td>381.34</td>
</tr>
<tr>
<td>1.5</td>
<td>365.14</td>
<td>374.69</td>
<td>365.53</td>
<td>387.06</td>
<td>378.29</td>
</tr>
<tr>
<td>2</td>
<td>362.84</td>
<td>372.33</td>
<td>362.76</td>
<td>384.42</td>
<td>375.41</td>
</tr>
<tr>
<td>2.5</td>
<td>360.94</td>
<td>370.46</td>
<td>360.93</td>
<td>382.69</td>
<td>373.39</td>
</tr>
<tr>
<td>3</td>
<td>359.21</td>
<td>368.7</td>
<td>379.15</td>
<td>380.76</td>
<td>371.7</td>
</tr>
<tr>
<td>3.5</td>
<td>357.95</td>
<td>367.3</td>
<td>377.7</td>
<td>379.42</td>
<td>370.27</td>
</tr>
<tr>
<td>4</td>
<td>356.75</td>
<td>366.17</td>
<td>376.55</td>
<td>378.09</td>
<td>368.96</td>
</tr>
<tr>
<td>4.5</td>
<td>355.7</td>
<td>365.04</td>
<td>375.34</td>
<td>377.02</td>
<td>367.82</td>
</tr>
<tr>
<td>5</td>
<td>354.88</td>
<td>364.04</td>
<td>374.3</td>
<td>376.03</td>
<td>366.79</td>
</tr>
<tr>
<td>5.5</td>
<td>353.9</td>
<td>363.2</td>
<td>373.45</td>
<td>375.11</td>
<td>365.86</td>
</tr>
<tr>
<td>6</td>
<td>353.09</td>
<td>362.33</td>
<td>372.53</td>
<td>374.22</td>
<td>365.01</td>
</tr>
<tr>
<td>6.5</td>
<td>352.4</td>
<td>361.54</td>
<td>371.69</td>
<td>373.41</td>
<td>364.15</td>
</tr>
<tr>
<td>7</td>
<td>351.61</td>
<td>360.76</td>
<td>370.88</td>
<td>372.6</td>
<td>363.3</td>
</tr>
<tr>
<td>7.5</td>
<td>351.03</td>
<td>360.17</td>
<td>370.24</td>
<td>372</td>
<td>362.62</td>
</tr>
<tr>
<td>8</td>
<td>350.39</td>
<td>359.48</td>
<td>369.57</td>
<td>371.25</td>
<td>361.95</td>
</tr>
<tr>
<td>8.5</td>
<td>349.83</td>
<td>358.87</td>
<td>368.94</td>
<td>370.65</td>
<td>361.32</td>
</tr>
<tr>
<td>9</td>
<td>349.27</td>
<td>358.32</td>
<td>368.35</td>
<td>370.06</td>
<td>360.73</td>
</tr>
<tr>
<td>9.5</td>
<td>348.82</td>
<td>357.77</td>
<td>367.79</td>
<td>369.5</td>
<td>360.17</td>
</tr>
<tr>
<td>10</td>
<td>348.28</td>
<td>357.28</td>
<td>367.27</td>
<td>368.97</td>
<td>359.64</td>
</tr>
</tbody>
</table>
Out of the above five tests the test given in Table 5.10, numbers 3 and 4 seems to be not in proportionate with the other three tests. This can be seen clearly when the above force values are adjusted for 25% compression. The adjusted values are given in Table 5.11.

Table 5.11: The force values of Table 5.10 after adjusting for 25% compression

<table>
<thead>
<tr>
<th>TIME (s)</th>
<th>TEST 1</th>
<th>TEST 2</th>
<th>TEST 3</th>
<th>TEST 4</th>
<th>TEST 5</th>
<th>AVERAGE OF 1,2 &amp; 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>412.92</td>
<td>409.84</td>
<td>427.32</td>
<td>423.45</td>
<td>408.48</td>
<td>410.41</td>
</tr>
<tr>
<td>1.0</td>
<td>407.62</td>
<td>405.21</td>
<td>421.49</td>
<td>417.85</td>
<td>403.28</td>
<td>405.37</td>
</tr>
<tr>
<td>1.5</td>
<td>404.45</td>
<td>402.03</td>
<td>418.15</td>
<td>414.41</td>
<td>400.05</td>
<td>402.18</td>
</tr>
<tr>
<td>2.0</td>
<td>401.91</td>
<td>399.50</td>
<td>415.14</td>
<td>411.58</td>
<td>397.01</td>
<td>399.47</td>
</tr>
<tr>
<td>2.5</td>
<td>399.80</td>
<td>397.49</td>
<td>413.17</td>
<td>409.73</td>
<td>394.87</td>
<td>397.39</td>
</tr>
<tr>
<td>3.0</td>
<td>397.88</td>
<td>395.60</td>
<td>411.23</td>
<td>407.67</td>
<td>393.08</td>
<td>395.52</td>
</tr>
<tr>
<td>3.5</td>
<td>396.49</td>
<td>394.10</td>
<td>409.65</td>
<td>406.23</td>
<td>391.57</td>
<td>394.05</td>
</tr>
<tr>
<td>4.0</td>
<td>395.16</td>
<td>392.89</td>
<td>408.41</td>
<td>404.81</td>
<td>390.19</td>
<td>392.74</td>
</tr>
<tr>
<td>4.5</td>
<td>394.00</td>
<td>391.67</td>
<td>407.09</td>
<td>403.66</td>
<td>388.98</td>
<td>391.55</td>
</tr>
<tr>
<td>5.0</td>
<td>393.09</td>
<td>390.60</td>
<td>405.97</td>
<td>402.60</td>
<td>387.89</td>
<td>390.53</td>
</tr>
<tr>
<td>5.5</td>
<td>392.00</td>
<td>389.70</td>
<td>405.04</td>
<td>401.62</td>
<td>386.91</td>
<td>389.55</td>
</tr>
<tr>
<td>6.0</td>
<td>391.11</td>
<td>388.77</td>
<td>404.05</td>
<td>400.66</td>
<td>386.01</td>
<td>388.63</td>
</tr>
<tr>
<td>6.5</td>
<td>390.34</td>
<td>387.92</td>
<td>403.13</td>
<td>399.80</td>
<td>385.10</td>
<td>387.79</td>
</tr>
<tr>
<td>7.0</td>
<td>389.47</td>
<td>387.08</td>
<td>402.25</td>
<td>398.93</td>
<td>384.20</td>
<td>386.92</td>
</tr>
<tr>
<td>7.5</td>
<td>388.82</td>
<td>386.45</td>
<td>401.56</td>
<td>398.29</td>
<td>383.48</td>
<td>386.25</td>
</tr>
<tr>
<td>8.0</td>
<td>388.12</td>
<td>385.71</td>
<td>400.84</td>
<td>397.48</td>
<td>382.77</td>
<td>385.53</td>
</tr>
<tr>
<td>8.5</td>
<td>387.49</td>
<td>385.05</td>
<td>400.15</td>
<td>396.84</td>
<td>382.11</td>
<td>384.88</td>
</tr>
<tr>
<td>9.0</td>
<td>386.87</td>
<td>384.46</td>
<td>399.51</td>
<td>396.21</td>
<td>381.48</td>
<td>384.27</td>
</tr>
<tr>
<td>9.5</td>
<td>386.38</td>
<td>383.87</td>
<td>398.90</td>
<td>395.61</td>
<td>380.89</td>
<td>383.71</td>
</tr>
<tr>
<td>10.0</td>
<td>385.78</td>
<td>383.35</td>
<td>398.34</td>
<td>395.04</td>
<td>380.33</td>
<td>383.15</td>
</tr>
</tbody>
</table>

The graphical representation of the above five tests is given in Figure 5.10.
Fig. 5.10: Relaxation curves after the compression adjustment is made

It can be seen clearly that test numbers 3 and 4 are not in the same range of the rest. Hence for calculation purposes the test numbers 3 and 4 have to be omitted. This sort of deviant results could be observed in several tests. Hence a set of rules was eventually established in order to remove the deviated tests.

ii) Data analysis criteria

Criterion used to remove deviant tests

The rules given below were established and applied to all the tests carried out in order to remove the deviant tests. It was not necessary to apply all the rules to one set of tests (e.g. tests carried out for a material at a particular speed in a certain temperature) in order to identify the correct tests. Some sets of data could be streamlined with one rule, while some needed two or more.
Rules established

1) In the slow mode tests only the tests with compression in the range \((25 \pm 2\%)\) were selected for analysis purposes. For the fast mode the \((25 \pm 2\%)\) range was used.

2) The force values recorded by the machine was checked against the measured compression and compared with the force and compression values of other tests. If unmatched tests were found such data were omitted from further calculations.

3) The linear behaviour between force and compression was assumed up to \(27\%\) of compression. Then all the force values in the range \(22\%\) to \(27\%\) compression were adjusted for \(25\%\) compression.

4) After adjusting for \(25\%\) compression the maximum number of tests within a range of \(10\)N were selected for further calculations.

   e.g. Consider the following initial force values of five tests

   \[
   440.39, \quad 442.08, \quad 419.63, \quad 427.70, \quad 450.3
   \]

   According to the rule number 4 only three values can be considered for further calculations. These values are highlighted above for easy identification.

5) After adjusting for \(25\%\), if two sets of tests having the same number of tests are found then the average values of two sets were compared with the force values of the next lower and higher compression rate and the most appropriate average was selected for the calculation purposes.

   e.g. Test 1    Test 2    Test 3    Test 4    Test 5

   \[
   433.93, \quad 428.11, \quad 436.97, \quad 445.99, \quad 440.17
   \]

   set 1(Avg. = 433)          set 2(Avg. = 441.04)

   Then the averages 433 and 441.04 were compared with the force values of the next higher and lower strain rate.

6) After applying the appropriate rule/s, at least three tests from each level of loading rates were selected for calculation purposes.
5.2 FACTORS RELATING TO THE MATERIALS BEING TESTED

5.2.1 INTRODUCTION

Murphy et al.\(^{(4)}\) have reported the use of the Hounsfield relaxometer in fast mode tests in order to study the relaxation behaviour of rubbers, up to the first 1000 seconds. This testing was done in parallel with long term testing with a Wykeham-Farrance (W-F) machine. The stress relaxation plots of the NR-50phr carbon black compound obtained from the two types of tests overlap only in approximately the \(10^2\) to \(10^3\) second range (Fig.5.11). When this range is considered, a mis-match has been observed between the residual forces of the two relaxation curves.

![Figure 5.11](image)

**Fig 5.11 : Relaxation curves obtained through the Relaxometer and Wykeham-Farrance machine for NR-50 carbon black compound\(^{(4)}\)**

For the natural rubber compound the mis-match has been approximately 30% of the force value measured through the W-F machine. The curves obtained through the W-F machine show higher forces than that obtained through the Hounsfield machine. No explanation for this mis-match is given in the above literature.

In the present study, instead of the W-F machine the slow mode of the Hounsfield relaxometer was used. This mode allows loading rates from 0.1 mm/min. to
250 mm/min. Obviously, it allows all the testing to be done on one machine with advantages when comparing the results. The drawback is that an independent check of the magnitudes of measurements is no longer available.

The results obtained through the Hounsfield machine also show similar residual force differences encountered by Murphy et al. In the present study the force observed in the fast mode test is approximately 84% of the force observed at 250 mm/min. compressive strain rate of the slow mode mis-match (Fig. 5.12).

![Stress Relaxation curves](image)

**Fig. 5.12: Stress Relaxation curves obtained at 250 mm/min. and 2 m/second for the NR1 compound**

The 16% difference between these two curves is possibly due to either one or more of the reasons given below.

A). The incorrect compression given in one or both of the two loading rates.
B). Differences in the relaxation taking place during the loading period.
C). Re-seating of the test pieces during the vibrations.
D). Damages taking place in the filled vulcanisate due to very high loading rates.

Out of the above four factors the effect of incorrect compression was quantified in each test and the effect was removed from the results. The second factor comes from a totally different force-time relationship between the tests in the 1/100 seconds. The third factor would affect only the high speed test. The fourth factor would occur mainly in the fast mode test.
5.2.2. FACTORS AFFECTING THE DEPRESSED FORCE VALUES OF THE FAST MODE TEST.

The four factors mentioned in section 5.2.1, which may be responsible for the lower residual force values of the fast mode test is individually discussed in this subsection.

A) THE INCORRECT COMPRESSION

Out of the above four possible factors, the effect of incorrect compression can be removed using the compression values measured with the travelling microscope. The two curves for the NR1 compound after removing this effect is given in Fig.5.13. After adjusting for the 25% compression using simple linear correction, the gap between the curves has been reduced. However about 70% of the original mismatch still remains.

For the NR2 and NR3 compounds the correction made for the incorrect compression reduces the gap of the two curves by 46% and 42% respectively. The force mis-match between the two curves in Newton, after the compression adjustment is made are given in Table 5.12.

Fig 5.13: Relaxation curves obtained at 250 mm/min., 2 m/second strain rates and the corrected curves for compression
Table 5.12: Curve mis-match at one second, after the compression adjustment is made

<table>
<thead>
<tr>
<th>Compound</th>
<th>mis-match after the correction (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR1 (High)</td>
<td>44.8</td>
</tr>
<tr>
<td>NR2 (Medium)</td>
<td>39.9</td>
</tr>
<tr>
<td>NR3 (Low)</td>
<td>35.8</td>
</tr>
</tbody>
</table>

The above mis-match is due to the other factors other than the incorrect compression. The magnitude of the mis-match decreases with decreasing crosslink density of the compounds.

As mentioned earlier this force difference represents the effect of one or more of the three factors (B,C and D) given in section 5.2.1. The contribution of these three factors is impossible to isolate and measure using the simple techniques available. So, no effort was made in this respect. Hence the possible influence will be considered theoretically.

B) DIFFERENCES IN THE RELAXATION PROCESS.

If the start of compression is considered as zero time, then the loading graphs and subsequent relaxation graphs for strain rate 2 m/sec and 250 mm/min. can be drawn as given in Fig. 5.14. The sample thickness is assumed as 1.6x 4 = 6.4 mm.

The time taken by the fast mode test to compress the sample is $8 \times 10^{-4}$ sec., while that for the slow mode test is 0.384 sec. Hence at the beginning of the relaxation test, the test sample of the fast mode test has already relaxed for 0.0008 seconds while that of the slow mode test has relaxed for 0.384 seconds, leaving a difference in the amount of relaxation at the beginning of the relaxation tests.

In the fast mode test as the sample is compressed at very high rate, segments, molecules, etc., have much less time to rearrange than in the slow mode test. However once the compression is seized in the fast mode, initially these rearrangements take place. As these rearrangements are very fast, the initial part of the relaxation curve shows a sharp fall in the residual force within a short time period. This reason coupled with possible damages in the structure leads to show a lower residual force in the fast mode tests than in the slow mode test as time increases.
* By the time of compression taking place in the slow mode test has stopped, the test piece in the fast mode test has already relaxed for 0.3832 seconds under constant compression.

Fig. 5.14: Loading and relaxation curves of the NR1 compound at the strain rates of 2 m/second and 250 mm/min.

The above trend is impossible to see among the slow mode test curves even though the loading time difference between most of the slow tests are higher than those discussed above. In the slow mode tests during the long loading time, relaxation takes place. However it is not possible to observe this relaxation due to the progressively increasing compression force. Consequently by the time of beginning the relaxation curves, there is no significant difference in rate of relaxation. So, once the compression is finished a sharp fall in the residual force among the slow mode tests cannot be observed.

When crosslink density decreases the force required to give a specific compression decreases. As a result the rate of relaxation in both the modes decreases as the crosslink density decreases. The decrease in the rate of relaxation at the beginning of the fast mode test becomes less significant with decrease of crosslink density due to reduced possibility of damages. As a result the gap between slow mode curves and the fast mode curve decreases in the sequence NR1, NR2, NR3.
C) THE RE-SEATING EFFECT

In the fast mode test the relaxometer compresses the sample at the speed of 2 m/sec. This movement stops when the specified compression is achieved. The sudden reduction in speed makes the system vibrate. This is possibly due to the poor damping of the machine or oscillations in the specimen (investigated in the section 5.1.2). As a result the early part of the relaxation curve (time < 10^2 sec.) includes the vibration taking place in the system. While the vibration is taking place, in some instances the recorded value of the compressive force is zero or near zero (Fig. 5.14 - 2 m/sec curve). This implies that there are instances where the sample is applying a reduced force on the machine platen and the plunger. In such instances the two contacting surfaces of the sample are almost free to move horizontally as would be the case of perfectly lubricated situations.

In slow mode tests no vibration is observed even at 250 mm/min. speed and at 100°C. As a result a frictional resistance to horizontal deformation is always applied at the contacting face of the specimen. In such a situation, although there is some lubrication, the contacting surfaces are not totally free move. Because of the movement restrictions at the two contacting surfaces, the free surface of the sample bulge outwards. So this situation can be approximately represented by a bonded sample.

The perfectly lubricated situation and firmly bonded situation can be explained theoretically for the deformation less than 10%. The theoretical consideration is given below.

Case 1: Consider a pure uniaxial compression with perfect lubrication. This explains the sample movements more closely in fast mode tests. The force required to compress the sample in this case is given by

\[ F_1 = E_0 \pi a^2 e \]

where, \( a \) - is the radius of the sample.
\( e \) - is the strain in vertical direction
\( E_0 \) - Young's modulus of rubber.

Case 2: When there is a restriction to move at the contacting surfaces of the sample, as in the slow mode test an additional force is required to compress the sample to the same extent as in the case 1. This can be given by

\[ F_2 = E_0 \pi e a^4/t^2 \]

where, \( t \) - is the sample thickness
In the slow mode test as there is a resistance to horizontal deformation, the compressive force measured in slow mode is approximately the total of \( F_1 \) and \( F_2 \), while the same in the fast mode test is approximately \( F_1 \). Even though the above theoretical calculations represent the ideal situations for the deformations less than 10\%, the same phenomena is taking place in the present test too, but greater in magnitude.

As a result the fast mode test curve is always associated with lower force and this may be a contributory factor for the observed clear gap between the slow mode test curve and the fast mode test curve.

The formulae available to calculate the forces for larger deformations can be used to determine the approximate magnitude of the effect. If perfectly bonded and firmly bonded conditions are assumed for the NR1 compound, then the calculated force difference between these two extremes at 25\% compression level is approximately 35 N, whereas the actual value between the slow mode test and the fast mode test is approximately 50 N.

According to the formulae used above, the force responsible for re-seating of the test sample is a direct measurement of Young’s modulus. The modulus values of three compounds are as follows:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Young’s Modulus (MNm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR1</td>
<td>5.09</td>
</tr>
<tr>
<td>NR2</td>
<td>3.01</td>
</tr>
<tr>
<td>NR3</td>
<td>1.91</td>
</tr>
</tbody>
</table>

The Young’s modulus of the three compounds considered is in the order NR1 > NR2 > NR3. Hence the force depression due to the re-seating effect also follows the same order.

D) DAMAGE TAKING PLACE IN THE FILLED VULCANISATE

This depends mainly on the crosslink density. When the crosslink density increases the force required to give a specific compression increase\(^{(134)}\). As a result the number of filler-filler, filler-polymer bond damages increase with crosslink density.

On the other hand at very high compressive strain rates the molecules have no time to rearrange themselves and thus the rubber acts as a more rigid solid. Consequently the force required to compress the sample increases\(^{(135)}\). When a high
force is applied to a rubber sample, in addition to large scale filler-filler, filler-polymer bond destruction, damage is also possible in network chains and crosslinks (136). A similar behaviour can be expected in the samples subjected to the fast mode test due to very high compressive force experienced by the samples at the beginning of the test.

The above mentioned factors may lead to faster decay in stress initially and subsequently to a lower compressive force in the fast mode test than in the slow mode tests as evident from figure 5.12.

As the force required to compress the sample increases with crosslink density the amount of damage taking place in the vulcanisate is also expected to increase in the sequence NR3, NR2, NR1. This is evident from the widening of the gap between slow mode and fast mode test curves of compounds in the same sequence (Table 5.12).

Overall, the contribution of factors A), B), C), and D) on the three NR compounds has decreased in the order NR1, NR2, NR3 resulting a reduced gap between the fast mode test curve and the slow mode test curve, in the same sequence.

5.2.3 DETAILED ANALYSIS OF THE SLOW MODE AND THE FAST MODE RELAXATION CURVES

All graphs which are referred in forthcoming sections have been corrected for incorrect compression, leaving only the other three factors (difference in the relaxation at the beginning, re-seating effect, structural damage) which might account for the unexpected deviation.

In this section firstly the general behaviour of the stress relaxation curves at room temperature will be discussed. Secondly two relaxation processes involved in slow mode test behaviour and their possible mechanism will be discussed.

A) GENERAL BEHAVIOUR OF STRESS RELAXATION CURVES OF NR1, NR2 AND NR3 AT ROOM TEMPERATURE

In order to study the relaxation behaviour of NR1, NR2 and NR3 compounds at different compressive strain rates, seven slow mode strain rates and the fast mode test were selected. The relaxation curves obtained at these strain rates for three compounds are shown in Figs. 5.15, 5.16 and 5.17. The curves obtained under the slow mode test have shown an increase in the initial compressive force with the increase of compressive strain rate. The initial force value of the fast mode also behaves in the same manner confirming that a higher strain rate gives a higher initial stress.
Fig. 5.15: Relaxation curves of the NR1 compound (high crosslink density) at different loading rates, at room temperature

Fig. 5.16: Relaxation curves of the NR2 compound (medium crosslink density) at different loading rates at room temperature
Fig. 5.17: Relaxation curves of the NR3 compound (low crosslink density) at different loading rates at room temperature

The fast mode test curve is able to show the relaxation behaviour during one more decade at the beginning of the test, than the slow mode test. In the fast mode test, during the first two decades (10² sec. to 1 sec.) the residual force decays much faster than the slow mode test and later shows a much lower residual force than the slow mode test.

After a certain time period, the curves corresponding to different strain rates show approximately linear behaviour with logarithmic time. The time period taken to arrive at linearity depends upon the rate of compressive strain given and the crosslink density of the compound. At higher crosslink densities, the time taken to start linearity is shorter and the same relationship can be seen with strain rates. When compared with the others, the curve for 0.1 mm/min. takes a much longer time to show linear behaviour in the relaxation curve. Other than the curve corresponding to strain rates 0.1 mm/min. and 2 m/second, all curves of each compound have more or less the same gradient for the time period beyond 100 seconds. Depending on the crosslink density the gradient varies from one compound to another. The gradient values of the relaxation curves of three compounds at room temperature are given in Table 5.13.
Table 5.13: Gradient of the linear part of the stress relaxation curves (N/seconds)

<table>
<thead>
<tr>
<th>Strain Rate</th>
<th>Gradient of NR 1 curve</th>
<th>Gradient of NR 2 curve</th>
<th>Gradient of NR 3 curve</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 mm/min.</td>
<td>-10.81</td>
<td>-6.29</td>
<td>-4.93</td>
</tr>
<tr>
<td>1.0 mm/min.</td>
<td>-10.80</td>
<td>-6.11</td>
<td>-5.76</td>
</tr>
<tr>
<td>10.0 mm/min.</td>
<td>-11.29</td>
<td>-6.49</td>
<td>-6.10</td>
</tr>
<tr>
<td>20.0 mm/min.</td>
<td>-11.29</td>
<td>-6.80</td>
<td>-6.08</td>
</tr>
<tr>
<td>50.0 mm/min.</td>
<td>-11.55</td>
<td>-6.78</td>
<td>-6.60</td>
</tr>
<tr>
<td>150.0 mm/min.</td>
<td>-11.86</td>
<td>-7.04</td>
<td>-6.81</td>
</tr>
<tr>
<td>250.0 mm/min.</td>
<td>-11.91</td>
<td>-7.28</td>
<td>-6.76</td>
</tr>
<tr>
<td>2 m/sec</td>
<td>-9.06</td>
<td>-5.52</td>
<td>-5.59</td>
</tr>
</tbody>
</table>

Crosslink density NR1 > NR2 > NR3

In calculating the gradients, there was still significant curvature in the graph corresponding to the strain rate of 0.1 mm/min. Thus the value for this strain rate can mis-represent the real situation. However the value was included in the table in order to give a general idea about the magnitude. The above results (excluding 0.1 mm/min.) show that the fast mode test has the lowest rate of relaxation in the time range considered.

B) THE NATURE OF THE STRESS RELAXATION CURVES

A prominent feature in these relaxation curves is the change in curvature of the curves during the first 10 seconds and this depends on the strain rates. The curvature (convex relative to X-axis) of the relaxation curves of slow mode tests increases with the increase of strain rate. The initial part of the curves for strain rates above 20 mm/min. in the slow mode tests has become approximately linear. So one can represent the stress relaxation by two linear parts with different gradients. This dual linear behaviour is more prominent and lasts for a longer time as the crosslink density of the compound decreases. The initial part of the high speed test is a curve and cannot be treated as dual linear.

Figures 5.18 and 5.19 given in the forthcoming sub-sections show the variation in behaviour of dual linear parts of stress relaxation curves in the slow mode.
test with strain rates. The curve corresponding to the strain rate of 0.1 mm/min. was omitted from the consideration because of inability to calculate the correct gradient at a longer time (specially in the compound NR3).

(i) The behaviour of the stress relaxation curves at long time (10 s < Time <= 1000 s)

Figure 5.18 represents the behaviour of the gradient (rate of stress relaxation) of relaxation curves with strain rate in the time range 10 to 1000 seconds. For the three compounds considered, the behaviour of rate of relaxation (the gradient) is a linear function of the logarithmic value of strain rate. The three materials studied here have three different crosslink densities leaving the network associated with each compound different from the other. Further the three parallel straight lines shown by three different materials imply that the behaviour is independent of the nature of the vulcanisate. This might suggest that within the time period considered the relaxation curves represent a common relaxation process in all three compounds, and it is independent of the nature of the network of the vulcanisate.

![Graph showing the effect of strain rate on the rate of relaxation at room temperature (10 s. < Time <= 1000 s.).](image)

Fig. 5.18: Effect of strain rate on the rate of relaxation at room temperature (10 s. < Time <= 1000 s.)
A mechanism can be suggested for this relaxation behaviour based on the finding on filler relaxation by G. M. Bartenev et al.\textsuperscript{(22)}. According to Bartenev the mechanism of relaxation behaviour of filled vulcanisate consists of five multi-stage mechanisms. Out of these five, the first three relaxation processes are collectively called as the Slow Stage of Physical Relaxation. The fourth process corresponds to the relaxation taking place due to the filler and the fifth process corresponds to the chemical relaxation.

In their study it has been shown that the fourth relaxation is dependent on the presence of bound rubber layers in the rubber, resulting from adsorption reactions between carbon black and rubber. The relaxation process takes place through breaking away and adhesion of segments of rubber chains to the carbon black particles and has been termed as filler relaxation. Furthermore it has been shown that the rate of relaxation is a function of the deformation, the carbon black loading and the initial stress.

In the present study the samples have been made with the same elastomer (NR) and with the same loading level of carbon black (50 phr). However the initial strain is always 25%. Hence in this study the rate of relaxation is a function only of stress and strain rate. As the initial stress increases with the increase of strain rate, the rate of relaxation too should increase with strain rate. The three linear curves shown in Figure 5.18 confirm this behaviour. This, Bartenev suggests, is mainly due to the filler/rubber relaxation. Hence it can be suggested that the relaxation process taking place during the time period 10 sec. to 1000 sec. in all three compounds considered are dominated by filler relaxation.

When a stress is applied to a filled rubber vulcanisate the main stress is exerted upon the carbon black-rubber structure, which is the harder domain of the vulcanisate. This harder domain consists of carbon black aggregates with adsorption of the rubber molecules on the particles of carbon black. When a stress is applied on the sample there is a chance of breaking away of rubber molecules from carbon black aggregates. With the increase of the applied stress, the chance of breaking away will be higher, resulting higher rate of relaxation.
(ii.) *The short time behaviour of the stress relaxation curves (time < 1.0 second)*

This behaviour is shown in Figure 5.19. The gradient of the relaxation curves increases as the strain rate increases. That is, the relaxation process involved up to the 1 second depends on the strain rate, and the rate of relaxation increases as the strain rate increases.

![Graph showing the effect of strain rate on the rate of relaxation](image)

**Fig. 5.19 : Effect of strain rate on the rate of relaxation at room temperature (time < 1.0 second)**

Furthermore the rate of relaxation increases as the crosslink density increases. The NR1 compound, which has the highest crosslink density shows the highest rate of relaxation. There is a crossover of NR2 and NR3 curves, which breaks the relationship between crosslink density and relaxation rate. However, further inspection of the graphs shows a strong similarity in the shapes of NR1 and NR2 graphs. This suggests that different mechanisms are operating in the two high crosslink specimens, compared to low crosslink one, although the results of NR2 and NR3 are quantitatively similar.

A mechanism can be suggested for this relaxation behaviour too based on the observations made by G. M. Bartenev et al. According to them, the relaxation process preceding filler relaxation is the Slow Stage of Physical Relaxation. This stage
represents the relaxation taking place in the ordered micro blocks\textsuperscript{(23,24)} of the vulcanisate. In these micro blocks, the macro molecules or their portions are found to be in a more ordered state than in the remaining portion of the vulcanisate. The degradation and the recombination of ordered micro blocks is accomplished by breaking off and by attachment of the segments.

In filled vulcanisates, as the initial stress increases the rate of the Slow Stage of Physical Relaxation increases. This is probably due to the break down of micro blocks due to the effect of compressive stresses\textsuperscript{(23,24)} and is in agreement with the present observations.

Usually ordered large micro blocks have a reduced probability of degradation than the small ones\textsuperscript{(22)}. The tendency to have larger ordered micro blocks increases as the crosslink density decreases. As a result a lower relaxation rate is expected with decrease of crosslink density. This is also in agreement with the present observations made for the time range $0.1$ to $1.0$ second.

Based on the above inferences it can be suggested that the initial part of the stress relaxation curves obtained through the Hounsfield relaxometer represents the Slow Stage of the Physical Relaxation of the material tested.

C) Behaviour of the Fast Mode Test

In the fast mode test due to rapid compression there is a high chance of breaking chemical crosslinks in addition to the filler-filler, filler-polymer interactions. In the results obtained approximately up to one second, a sharp fall in the residual force is shown. At longer times, the fast mode curves also show linear behaviour; probably representing filler relaxation.

The gradient of this linear part of the relaxation curve is smaller than the gradient observed for slow mode tests. This difference may be a consequence of the very high compressive strain applied, which may lead to convert large number of ordered microblocks to a mainly disordered and unstable state, and also to break other type of bonds. This makes the early part of the relaxation very fast and consequently the residual force is quickly reduced. So, when the filler relaxation starts, the initial force for the filler relaxation is lower than that of the slow mode test. Hence the linear part of the stress relaxation curve, which probably represents the filler relaxation has a lower gradient than that of the slow mode test.
In the slow mode test, the gradient of filler relaxation decreases in the sequence NR1, NR2, NR3. But in the fast mode test the NR2 compound has the lowest gradient (Table 5.13). By considering the gradients at different points along the fast mode relaxation curve, the value of the NR2 can be explained. The Fig. 5.20 shows how the gradient along the fast mode relaxation curve varies with logarithmic time.

Fig. 5.20: Variation in gradient of high speed test curves for NR1, NR2 and NR3 compounds with time at room temperature

It is evident from the Figure 5.20 that the gradient of the NR3 compound is still decreasing even after 500 sec. The other two compounds have an approximately constant relaxation rate after 1 second. Because of the variable gradient in the NR3 compound the gradient calculation method has given a false value for its rate of relaxation.
5.2.4 THE TEMPERATURE EFFECT ON STRESS RELAXATION

To investigate the effect of compressive strain rates on stress relaxation at higher temperatures, tests were carried out at 80°C and 100°C. Figs. 5.21 to 5.23 show the relaxation behaviour at 80°C, while Figures 5.24 to 5.26 show the same at 100°C for the three different compounds. The graphs corresponding to both temperatures follow the same pattern as at room temperature.

In this section, under different subheadings the behaviour of the relaxation curves (excluding the rate of relaxation) will be discussed and the possible mechanisms will be suggested. The behaviour will be discussed mainly in relation to the residual forces measured in three materials at three different temperatures and the relative behaviour of the high speed test curve under different conditions.

![Diagram of relaxation curves](image)

**Fig. 5.21 : Relaxation curves for the NR1 compound (high crosslink density) at different loading rates at 80°C**
Fig. 5.22: Relaxation curves for the NR2 compound (medium crosslink density) at different loading rates at 80°C

Fig. 5.23: Relaxation curves for the NR3 compound (low crosslink density) at different loading rates at 80°C
Fig. 5.24: Relaxation curves for the NR1 compound (high crosslink density) at different loading rates at 100°C

Fig. 5.25: Relaxation curves for the NR2 compound (medium crosslink density) at different loading rates at 100°C
Fig. 5.26: Relaxation curves for the NR3 compound (Low crosslink density) at different loading rates at 100°C

A) RESIDUAL FORCES AT DIFFERENT TEMPERATURES AND CROSSLINK DENSITIES

It can be seen that the behaviour of the NR1 compound is different from that of the NR2 and NR3 compounds with regard to the residual force at different temperatures. In the NR1 compound the magnitude of the residual force of the sample at 100°C is higher (Fig. 5.24) than that at 80°C (Fig. 5.21), whereas in the NR2 and NR3 compounds the magnitude of residual force decreases with the increase of sample temperature (Figs. 5.22, 5.23, and Figs. 5.25, 5.26 respectively).

As the residual force represents the properties of the vulcanisate, the unexpected behaviour in the residual force of the NR1 at 100°C may be due to the changes taking place in the vulcanisate at higher temperatures.

To check the possible changes in the vulcanisate caused by heating, hardness values and the crosslink densities of the vulcanisates at room temperature and after conditioning at high temperature were measured. In preparation for the determination of hardness and crosslink densities at 80°C and 100°C, the vulcanisate was conditioned at the respective temperature for 30 minutes and left to cool to room temperature. This
vulcanisate was then used to prepare the samples for the tests. The average results (each represents average of 7 results) so obtained are given in Tables 5.14 and 5.15.

Table 5.14 : Hardness values (Shore A) at different temperatures

<table>
<thead>
<tr>
<th></th>
<th>20°C (Room Temp.)</th>
<th>80°C</th>
<th>100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR 1</td>
<td>64.7</td>
<td>72.3</td>
<td>74.8</td>
</tr>
<tr>
<td>NR 2</td>
<td>58.3</td>
<td>63.8</td>
<td>63.2</td>
</tr>
<tr>
<td>NR 3</td>
<td>50.9</td>
<td>58.0</td>
<td>56.7</td>
</tr>
</tbody>
</table>

Table 5.15 : Crosslink density values at different temperatures. (10^2 x moles m^-3)

<table>
<thead>
<tr>
<th></th>
<th>20°C (Room Temp.)</th>
<th>80°C</th>
<th>100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR 1</td>
<td>2.98</td>
<td>3.11</td>
<td>3.43</td>
</tr>
<tr>
<td>NR 2</td>
<td>1.61</td>
<td>1.73</td>
<td>1.63</td>
</tr>
<tr>
<td>NR 3</td>
<td>1.32</td>
<td>1.03</td>
<td>1.02</td>
</tr>
</tbody>
</table>

It can be seen from Table 5.14 that the hardness values after conditioning at 80°C is always higher than that at room temperature. This indicates new crosslink formation in all three compounds. At 100°C the hardness value of the NR1 compound has further been increased, again indicating additional crosslink formation. The crosslink density values of the NR1 compound in Table 5.15 confirm this trend although the numeric changes are small.

In the light of these results, one may consider the implications for the relaxation curves of high temperature tests. In the NR1 compound the decrease in residual force value, which would have been taken place due to the increase in temperature has been compensated by the newly formed crosslinks. This has lead to a higher initial force for the NR 1 compound at 100°C than at 80°C and subsequently a higher residual force in the relaxation curve as well.

An increase in the crosslink density of the NR2 compound can be seen with increasing of temperature up to 80°C and it decreases at 100°C. There is a small reduction in hardness values too at 100°C when compared to that at 80°C. This indicates a possible structural damage in the NR2 compound at 100°C. The NR3
compound shows a very clear reduction in both crosslink density and hardness values at 100°C, when compared with that at room temperature. This is clear evidence of a structural damage in the NR3 at 100°C. These factors for NR2 and NR3 compounds together with reduction in viscosity in the compounds as temperature increases, explain the lower residual forces at 100°C compared to that at 80°C.

b) Behaviour of the Fast Mode Test Curve

In room temperature tests, oscillations have ceased by 0.01s. In contrast at high temperature, oscillations persist beyond 0.01 seconds. In high temperature tests these oscillations result in loss of data for analysis purposes in the first 0.04 seconds. Even though a little oscillation is observed after 0.04 seconds, the shape of the relaxation curve beyond 0.04 seconds can be established. In both 80°C and 100°C the time taken to come to an equilibrium through oscillation is more or less the same.

The time taken for oscillation at room temperature is different from that at high temperature. This implies that the test pieces are damping the machine vibration.

The figures relevant to the discussion over the next few pages are summarised in miniature on page 131. In these figures only the curves corresponding to 2 m/second and 250 mm/min strain rates have been given. The reader may find this summary progressively useful as the components of the arguments are developed.

i) The relative positions of the high speed test curves at different temperatures.

In all three compounds, the force difference between the slow mode test curve (e.g. 250 mm/min curve) and the fast mode test curve increases from 20°C to 80°C and then reduces at 100°C. The absolute force differences are given in Table 5.16.

Table 5.16: The absolute force difference between 2 m/second curve and 250 mm/min curve at 1 second (all values are in Newton)

<table>
<thead>
<tr>
<th></th>
<th>ROOM TEMP. 20°C</th>
<th>80°C</th>
<th>100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR 1</td>
<td>48</td>
<td>68</td>
<td>60</td>
</tr>
<tr>
<td>NR 2</td>
<td>40</td>
<td>46</td>
<td>24</td>
</tr>
<tr>
<td>NR 3</td>
<td>34</td>
<td>36</td>
<td>8</td>
</tr>
</tbody>
</table>

crosslink density NR1 > NR2 > NR3
For all the above graphs, Y-axis is Force in Newton; X-axis is Time in seconds.

NOTE: In each figure, the difference between the maximum and minimum values of the Y-Axis is 200 Newtons.
As mentioned in section 5.2.2 there are three possible reasons which individually or collectively may contribute to the high depression at 80°C. Each will be briefly discussed below.

When the effect of re-seating is considered, there is no special reason to show a high force depression value due to the re-seating effect only at 80°C. So this is unlikely to be the major factor contributing to the higher depression at 80°C.

It has been proved\(^\text{(22)}\) that the slow stage of physical relaxation is an inverse function of temperature \([1/T(K)]\). As a result the early stage of relaxation (before 0.04 sec.) should be fastest at room temperature followed by 80°C and 100°C respectively. The difference in the residual force in the early stage of relaxation also should be in the same order. This disagrees with the results given in Table 5.16.

Having dismissed the first two factors as the explanation for the highest depression at 80°C, the only factor to be considered is the network damage in the vulcanisates. The effect due to the structural damage at different temperatures can be explained reasonably using the extent of vulcanisation of thiuram vulcanisates and the progressive increase of monosulphide crosslinkages with increasing cure/post cure time.

The samples at room temperature have not been subjected to any conditioning after the sample is cured. The samples of other two test temperatures have been subjected to additional heat treatment for 30 minutes at 80°C and 100°C, while bringing the samples to the required temperature. When the thiuram vulcanisates are kept at elevated temperatures structural changes take place due to the post curing and crosslink destruction. The special feature of this vulcanisate is the destruction of crosslinks, which are mainly polysulphide in nature leading to monosulphide crosslinks with heat\(^\text{(125)}\). Crosslinks are more easily broken at 100°C than at 80°C. Hence the vulcanisates conditioned at 100°C have more monosulphide crosslinks than at the other two temperatures. Monosulphide crosslinks are stronger than polysulphide crosslinks\(^\text{(127)}\). As a result the crosslinks in the network conditioned at 100°C likely to be more difficult to break by the impact force in the fast mode. This may be the reason for the NR2 and NR3 compounds to have smaller gaps between the fast mode curve and curves of 250 mm/min., at 100°C than at the other two temperatures. In contrast to that in NR2 and NR3, the NR1 compound shows a higher force difference at 100°C than that at room temperature. The reason for this behaviour may be the increase in crosslink density as the sample is heated to 100°C.

At 80°C the samples have also been conditioned for 30 minutes before the test. In this case the force difference between the curves at 250 mm/min. and the fast mode
is always higher than that of the other two temperatures, indicating highest structural damage at 80°C. At this temperature the energy supplied by heating is still not sufficient to convert polysulphide crosslinks into monosulphide crosslinks. As a result, at 80°C still the vulcanisate largely consists of polysulphide crosslinks. Furthermore due to already supplied thermal energy, the energy required to break these polysulphide crosslinks is less than that at room temperature. Hence when the same amount of energy is given through an impact force as in other cases, the extent of structural damage taking place 80°C is higher than that at the other two temperatures. This would lead to the highest depression in the residual force values of the high speed test at 80°C.

ii. The behaviour of the fast mode test curve for compounds with varying crosslink density at fixed temperatures.

The relaxation curves corresponding to compounds of varying crosslink density at room temperature, 80°C and 100°C are as follows: Figs. 5.15, 5.16, 5.17 represents curves for the NR1, NR2, NR3 at room temperature, while Figs. 5.21, 5.22, 5.23 and Figs. 5.24, 5.25, 5.26 represent the curves at 80°C and 100°C respectively.

It can be observed from these graphs that the gap between the 250 mm/min curve and the fast mode curve decreases with decreasing crosslink density (Table 5.16). This behaviour is independent of the sample temperature and the thermal history of the sample. Three reasons can be suggested for such behaviour.

The first reason for this behaviour is the amount of polysulphide crosslinks available in the vulcanisate. As all three vulcanisates are subjected to similar conditions, vulcanisates with higher crosslink density would be expected to have more polysulphide crosslinks than the vulcanisates with lower crosslink density. The higher the poly-sulphide crosslinks the higher will be the damage taking place under the fast mode test and consequently higher will be the depression.

The second reason is the re-seating effect. Young’s modulus is an indicator of the magnitude of this effect if it were to happen. The Young’s modulus of the filled compound decreases as the crosslink density of the compound decreases (see Table 5.17).
Table 5.17: Young's modulus values of three compounds after conditioning at different temperatures ( MNm⁻²)

<table>
<thead>
<tr>
<th>Compound (crosslink density)</th>
<th>Room Temp. 20°C</th>
<th>80°C*</th>
<th>100°C*</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR1 (high)</td>
<td>5.09</td>
<td>4.92</td>
<td>4.69</td>
</tr>
<tr>
<td>NR2 (medium)</td>
<td>3.01</td>
<td>3.10</td>
<td>3.20</td>
</tr>
<tr>
<td>NR3 (low)</td>
<td>1.96</td>
<td>1.99</td>
<td>1.95</td>
</tr>
</tbody>
</table>

* conditioned at the respective temperature and tested in the room temperature.

Hence the force difference between the fast mode curve and the slow mode curve (250 mm/min) decreases as the crosslink density decreases.

The third reason is the extent of relaxation taking place at the initial stage of the test. Earlier it was shown (in the section 5.2.3) that during a given time period, the extent of relaxation taking place increases as the crosslink density increases. Furthermore, due to higher initial stress the extent of relaxation taking place in the fast mode test is higher than that in the slow mode tests. These reasons increase the force difference between the fast mode curve and the slow mode curve (here 250 mm/min) as the crosslink density increases.

5.2.5 THE NATURE OF THE RELAXATION PROCESS IN THE SLOW MODE TEST AT HIGH TEMPERATURES

In high temperature test curves too, the two-linear behaviour can be identified as in the case of room temperature. To study the effect of strain rate at high temperature, the data up to 1 second was considered as the one linear part and the data beyond 10 seconds was considered as the other. This division of data is identical to that used for room temperature tests.

A) THE BEHAVIOUR OF RATE OF RELAXATION WITH STRAIN RATES DURING THE PERIOD 0.1 TO 1 SECOND

The change in rate of relaxation with strain rate during this period at 80°C and 100°C is shown in Fig.5.27. In order to have a broad picture on the behaviour of rate of relaxation at a wide temperature range, the room temperature curves also have been included in the same figure.
Fig. 5.27: Effect of strain rate on the rate of stress relaxation at different temperatures (for time < 1.0 second)

From this figure it can be seen that the rate of relaxation increases with the increase of strain rate. This increase becomes less significant with the increase of temperature.

The reason for the decrease in rate of relaxation as the temperature increases might be as follows.

The compressive force required in rubber compounds to attain a specific compression (in this study, 25%) decreases with the increase of temperature. This would exert lower forces on the micro blocks as the temperature increases. The lower the force applied on ordered micro blocks the lower would be the rate of breaking away of macro molecules from the micro blocks. On the other hand number of ordered micro blocks may be less in the heated vulcanisate compared to that at room temperature. These reasons would result in a lower rate of relaxation as the temperature increases.

B) THE BEHAVIOUR OF RATE OF RELAXATION WITH STRAIN RATE FOR TIME GREATER THAN 10 SECONDS

The curves obtained for high temperature tests are not as smooth as the curves obtained for the room temperature test. This has lead to the exclusion of the uneven portions of the curves for gradient calculations.

In the case of high temperature tests, as the strain rate increases the curves for force vs. log(time) show another dual-linear behaviour during the above period. This
dual-linear behaviour was not studied in this research work; information can be found elsewhere\(^{(54)}\). However due to the effect of this additional dual-linear behaviour it was very difficult to calculate the gradient, specially at high strain rates. In such cases the linear portions at the higher time values were selected for gradient calculations.

The curves so obtained are given in Fig. 5.28. (for easy comparison again the room temperature test results were included in the same figure.)

The curves obtained at higher temperature show that the rate of relaxation at higher temperature is independent of the strain rate. However this is not true for the room temperature tests. In the case of room temperature tests, the rate of relaxation increases as the strain rate increases.

![Fig. 5.28: Effect of strain rate on the rate of stress relaxation at different temperatures (time >10 seconds)](image)

The Fig. 5.28 shows that the rate of relaxation decreases as the temperature increases. This behaviour is completely opposite to the behaviour of chemical stress relaxation, which can be observed at still higher temperatures during the same time range.

Broadly it is possible to say that the best fit lines for each compound obtained at room temperature are parallel to each other. The parallelism can be observed in most of the curves obtained for high temperature tests too. The non parallelism in a
few curves may be a consequence of the difficulty in calculating the correct gradient in force- log(time) curve.

5.2.6 THE EFFECT OF VERY HIGH STRAIN RATE ON THE RATE OF RELAXATION

In this section we wish to study the two linear sections of the fast mode relaxation curves. The time range 1s to 10s has not been studied, since it is a transition region. Also the first range has been mainly confined to 0.1 - 1 second in order to make it possible to cross compare the results of slow mode tests and fast mode test.

A) RESULTS OBTAINED DURING THE 0.1 TO 1 SECOND PERIOD OF THE RELAXATION CURVES

Fig. 5.29, Fig. 5.30 and Fig. 5.31 represent the behaviour of rate of relaxation of fast mode test curve and slow mode test curves and slow mode test curve with strain rate. This has been done at room temp. (20°C), 80°C and 100°C.

![Graph](image)

**Fig. 5.29 : Effect of very high strain rate on the rate of relaxation of NR1 compound at different temperatures (time< 1.0 seconds)**
Fig. 5.30: Effect of very high strain rate on the rate of relaxation of NR2 compound at different temperatures (time < 1.0 second)

Fig. 5.31: Effect of very high strain rate on the rate of relaxation of NR3 compound at different temperatures (time < 1.0 second)
In the range of strain rates values from 0.1 to 250 mm/min., the rate of relaxation of all three compounds follow a similar pattern. This pattern is altered when 120,000 mm/min results are considered.

This may be due to selection of the same time period in the slow mode test and fast mode tests for gradient calculations. The relaxation curves may represent two different stages in the relaxation processes during the time period considered, due to the very large difference in the strain rates of the fast mode and the slow mode tests.

B) RESULTS OBTAINED DURING THE 10 TO 1000 SECONDS PERIOD OF THE RELAXATION CURVES.

Figure 5.32 represents the stress relaxation for the time period beyond 10 seconds for strain rate up to 2 m/second.

Fig. 5.32: Effect of very high strain rate on the rate of stress relaxation at different temperatures (time >10 seconds)

Here the gradient of the curves may not consist with the same uncertainty (representing two different relaxation processes) suffered for the short time analysis as the time period is considerably large. The rate of relaxation calculated for fast mode
test at room temperature is considerably deviated from the trend found in the low strain rates. In the Fig. 5.32, the three trend lines established for room temperature tests have been extrapolated up to 120,000 mm/min in order to show the deviation of fast mode test clearly.

The curves obtained at high temperature are almost parallel to each other and the rate of relaxation is lower than that at room temperature. The parallelism implies that at higher temperatures the rate of filler relaxation is independent of rate of strain.

Even at higher temperatures, the initial stress increases as the strain rate increases. According to the findings of Bartenev(22) the rate of filler relaxation should increase with increase of initial stress. As a result, even at high temperatures, the rate of relaxation should increase as the strain rate increases. In contrary, the fast mode test has shown approximately the same (at higher temp.) or lower values (at room temperature) for filler relaxation. The reason for the lower value at room temperature was discussed in section 5.2.3-C.

A reasonable explanation for the behaviour of the relaxation rates at high temperature can be given as follows. At higher temperatures, due to the supplied thermal energy most of the molecules are able to overcome the intramolecular, intermolecular, filler-polymer attractions and move easily. Hence when an external force is applied to the heated vulcanisate, it can relax very quickly as the disturbed molecules can come to an equilibrium state within a very short time. Hence in the time range considered, the filler relaxation shows a very low value for the rate of relaxation. Further, as the weak filler-polymer interactions are less active at high temperatures, the rate of relaxation does not depend on the initial stress. As a result at high temperatures, the rate of relaxation is independent of the rate of strain. This behaviour is confirmed by the straight lines parallel to the X-axis in Figures 5.28 and 5.32.

Hence the mechanisms so far discussed to explain the filler relaxation process in the room temperature cannot be used to explain the mechanism at high temperature. However for a same vulcanisate the rate of filler relaxation at higher temperatures is always lower than that at room temperature.
CHAPTER SIX

CONCLUSIONS

A) MACHINE BEHAVIOUR

1) The current machine produces incorrect compressions in the test specimens. These machine errors are ones of insufficient compression in fast mode tests. In slow mode tests they vary from insufficient compression to excessive compression as the strain rate rises. The worst error seen was a test producing 81% of the desired compression.

2) The compression applied in the slow mode depends on the loading rate. The higher the strain rate the higher will be the compression.

3) The fast mode test always compresses the sample less than the value assigned by the machine.

4) The compression variation arising from the height unevenness of the samples is too small to explain the compression deviation given by the machine.

B) INFLUENCE OF LOADING RATE ON RELAXATION BEHAVIOUR

5) After correction of test results for machine error, about two-thirds of the mismatch between stress relaxation results obtained in fast and slow modes still remains.

It would now appear that this part of the mismatch is a real effect. The reasons for this have been discussed, for example differences in the relaxation taking place in the loading process, crosslink destruction in fast mode tests, etc. However more detail work is needed to quantify each effect.

6) After compensating for incorrect compression, the fast mode tests show residual stresses which are about 90% of those in the slow mode tests.(was 85% before correction)

At low level of crosslink density the mismatch between relaxation curves is reduced. The mismatch of fast/slow tests was greatest in the tests conditioned at 80°C.
7) There is evidence to say that the initial part of the relaxation curve (up to one second) represents the Slow Stage of Physical Relaxation (SSPR) and the second part as Filler Relaxation as defined by Bartenev.

**Influence of strain rate**

8) The slow mode test graphs may be viewed as having at least two linear parts representing two different relaxation processes. At room temperature, the gradient of the initial part of the curve depends on the rate of strain, while the gradient of the second linear part shows a very weak dependence on rate of strain.

9) At higher temperatures filler relaxation is independent of rate of strain.

10) The rate of the SSPR increases with the increase of strain rate up to 250 mm/min. However the marked trend is altered when the 120,000 mm/min. test results are included.

11) At room temperature, the rate of filler relaxation increases with strain rate up to 250 mm/min. However the rate of relaxation at the strain rate of 120,000 mm/min. (2 m/second) is lower than the rate corresponding to 250 mm/min. This is possibly due to the damage taking place in the vulcanisate, caused by the very high strain rate.

**Influence of crosslink density**

12) The rate of filler relaxation decreases as crosslink density decreases.

13) In the filler relaxation, the change in the rate of stress relaxation with respect to strain rate is independent of crosslink density of the compound.

14) There is a tendency of SSPR to decrease with decreasing crosslink density. However further testing is required to confirm this behaviour.

**Influence of temperature**

15) The rate of filler Relaxation decreases as the temperature increases.

16) The rate of the SSPR decreases as the temperature increases.
C) PROTOCOL FOR TESTS WITH FAST LOADING RATES

17) No protocol has been developed for the high loading rate test.

Relaxation taking place after a very high strain rate is different from that of slow strain rates, perhaps due to damage taking place in the vulcanisate. However the progression of stress relaxation behaviour from slow strain rates to very high strain rates could not be studied in detail as the strain rates between 250 mm/min and 120,000 mm/min. were inaccessible with the available facilities.
CHAPTER SEVEN

RECOMMENDATIONS FOR FURTHER WORK

1) Avoiding the re-seating effect

This effect has been discussed in detail in section 5.2.2-C. The origin of this effect is due to the possible movements of the two contacting surfaces (the loaded surfaces) of the sample during the vibration of the machine. The horizontal movement of these two surfaces can be avoided if the two surfaces are bonded to two light metal plates. If this was done for a limited series of tests, the influence of re-seating in the fast mode test can be removed. So the possible influence could be checked.

2) The new machine is capable to produce strain rates up to 250 mm/min in its slow mode and 2 m/second (120,000 mm/min.) in the fast mode test. The range from 250 mm/min. to 120,000 mm/min. is inaccessible.

It would be useful to have few more strain rates in this range, at least until the mechanism at 2 m/second test is understood.

3) Use of the machine for long term tests

This machine can be easily employed to carry out long term stress relaxation tests with minor modifications in the software. The ability to perform long term tests as well as the facility of short term tests will definitely increase the flexibility of usage and the commercial value of the machine.

In order to carry out the long term tests, the same jigs (constant depth jigs) used in the Wykam-Farrance machine can be used. So the test piece need not to be placed in the machine throughout the test. The proposed method and the necessary modifications are given below.

The method and the modifications necessary

The jig and the sample adjustments can be performed as in the W-F machine. In this instrument a circular metal plate can be used instead of a cylindrical metal tube which was used to compress the sample in the W-F machine. The metal
plate can be placed on the top part of the jig and whole jig with the sample can be placed between the platen and the plunger. Then the sample can be compressed by moving the platen up. The loading graph will appear on the screen. A similar one is given in Fig.7.1.

![Graph showing force vs. compression](image)

**Fig. 7.1: The loading curve of the rubber specimen when a constant depth jig is used**

Once the upper and the lower part of the jig is properly in contact, the force starts to increase steeply. At this instant further compression must be stopped and the bolts of the jig must be tighten. Then the sample will be at the required compression.

A software modification is required to keep the platen and the plunger stationary once the compression is achieved.

Subsequent stress relaxation measurements can be obtained as in the W-F instrument by giving a very small further compression on the sample. The relaxation curve can be observe on the screen while the data can be obtain in a spread sheet for analysis purposes.
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APPENDIX 1

HOUNSFIELD RELAXOMETER

SHORT COMINGS AND DEVELOPMENTS NEEDED

The Slow Mode Test

1) FORCE - EXTENSION DISPLAY

It is impossible to start a test until the FORCE & EXTENSION are displayed on the digital display of the machine. This needs prompting.

If the display is changed into ‘FORCE _ EXTENSION’ after the test is started (pressing the space bar on the computer) still the platform starts to move, but the machine does not obey the load range entered previously into the computer.

2) MONITORING THE COMPRESSION

The machine is unable to give an exact compression since it works by monitoring the load.

3) ABANDONING THE TEST BY THE ESCAPE BUTTON

If the escape button is pressed before the sample is being compressed, then the platform stops giving false Max. compression (N) and Extension values. Some times it gives the following ERROR message.

TRANSMISSION TIME-OUT ERROR ON LASER RS-232!! COMMAND RESUMING.

If the escape button is pressed while the sample is being compressed then the platform stops giving values for Maximum compression (N) and Extension. In some cases it gives the above mentioned ERROR MESSAGE.
4) **OVERSHOOTING OF COMPRESSION FORCE VALUE**

With increasing platform speed, the force value indicated in the machine digital display unit shows an increasing overshoot.

The table given below shows the force value for various speeds at the load range 250N.

<table>
<thead>
<tr>
<th>SPEED (mm/min)</th>
<th>1st TIME (N)</th>
<th>2nd TIME (N)</th>
<th>3rd TIME (N)</th>
<th>4th TIME (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>261*</td>
<td>251</td>
<td>257*</td>
<td>256</td>
</tr>
<tr>
<td>10</td>
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<td>270</td>
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<td>314</td>
<td>349</td>
<td>363</td>
<td>439**</td>
</tr>
<tr>
<td>80</td>
<td>328</td>
<td>309</td>
<td>329</td>
<td>368</td>
</tr>
<tr>
<td>90</td>
<td>324</td>
<td>332</td>
<td>345</td>
<td>350</td>
</tr>
<tr>
<td>100</td>
<td>507</td>
<td>507</td>
<td>505</td>
<td>**</td>
</tr>
</tbody>
</table>

(same specimen throughout a line: new specimen for next line)

* : Graphs did not start at (0,0)

** : An error message appeared (i.e. the same error message given in No. 3)

In some tests when the compression force exceeded 500N, no graphs appeared on the computer. In such cases the platform was brought down using the up/stop/down buttons. Then it was necessary to switch off both the machine and the computer and start again.

5) **THE RELAXATION TEST**

After the force rising phase (compression) the machine does not monitor the force falling phase (relaxation). It would be useful to down load all data points for subsequent processing.
6) THE PLATFORM

If the platform is moved with up/stop/down buttons of the machine then it is unable to carry out the test unless both the computer and the machine are switched off and started again. The symptom is disobedience of instruction.

7) AUTO REVERSE

In the compression test, the plunger does not rise automatically at the end of the test period, i.e. the Auto Reverse is not functioning.

8) REPEATING THE TEST

At the end of a test, if the test conditions are to be changed then it is necessary to press the F6 key three times.

It is suggested to reprogramme the software as follows.

- <F3> - Delete latest results.
- <F4> - Modify break position.
- <F6> - Results screen
- <F7> - Dump graph on printer.
- <F8> - Changing the testing conditions
- <F9> - Exit the peak compression test

9) CROSSHEAD

At the beginning of the compression test, the computer instructs to move the CROSSHEAD* to the operating position. As the manual operation may not be precise, could the software do this automatically like in the Fast Loading mode test?

* Surely PLATFORM not CROSSHEAD

The Fast Mode Test

The time taken in the data capturing mode is always greater than 1000 seconds (Approx.: 1200 seconds)
APPENDIX 2

Influence of temperature on the percentage compression at different strain rates.

NR1 compound

<table>
<thead>
<tr>
<th>Rate (mm/min)</th>
<th>20°C</th>
<th>80°C</th>
<th>100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>23.2</td>
<td>24.6</td>
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<tr>
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<td>23.1</td>
<td>24.7</td>
<td>24.6</td>
</tr>
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<td>24.5</td>
<td>25.6</td>
<td>25.4</td>
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<td>250</td>
<td>27.5</td>
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<tr>
<td>120000</td>
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<td>21.1</td>
<td>21.6</td>
</tr>
</tbody>
</table>

NR2 compound

<table>
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<th>80°C</th>
<th>100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
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<tr>
<td>120000</td>
<td>23.7</td>
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<td>22.1</td>
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</table>

NR3 compound

<table>
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<tr>
<th>Rate (mm/min)</th>
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<th>100°C</th>
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<tbody>
<tr>
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<td>23.4</td>
<td>21.2</td>
<td>22.3</td>
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</table>
APPENDIX 3

Influence of material hardness on the actual compression (percentage) at different strain rates and at different temperatures.

At 20°C (room temperature)

<table>
<thead>
<tr>
<th>Rate (mm/min)</th>
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<th>58 (shore A)</th>
<th>51 (shore A)</th>
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<tr>
<td>1</td>
<td>23.5</td>
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<td>120,000</td>
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</table>

At 80°C

<table>
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<th>51 (shore A)</th>
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</thead>
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<tr>
<td>120,000</td>
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</table>

At 100°C

<table>
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<th>58 (shore A)</th>
<th>51 (shore A)</th>
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<td>21.6</td>
<td>22.1</td>
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The hardness values at high temperature have been represented by the hardness values measured at room temperature after conditioning at the respective temperatures.