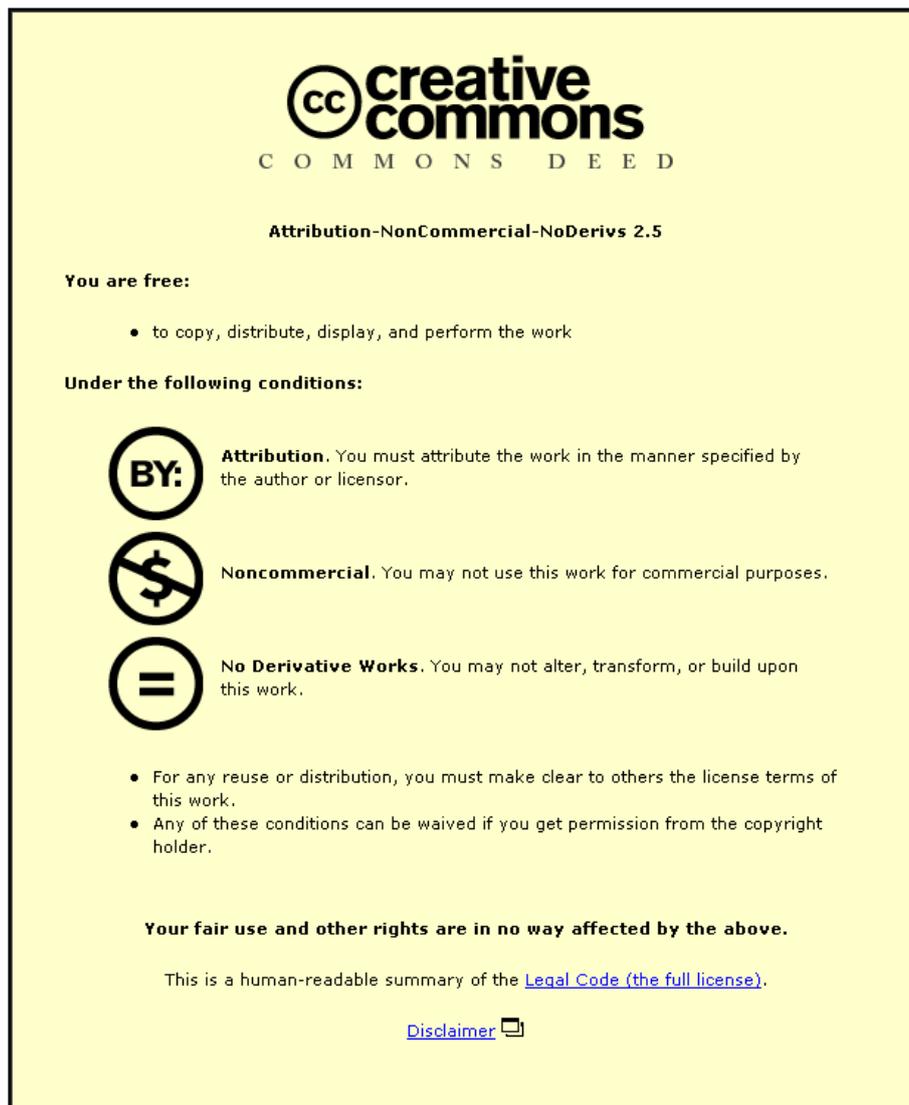


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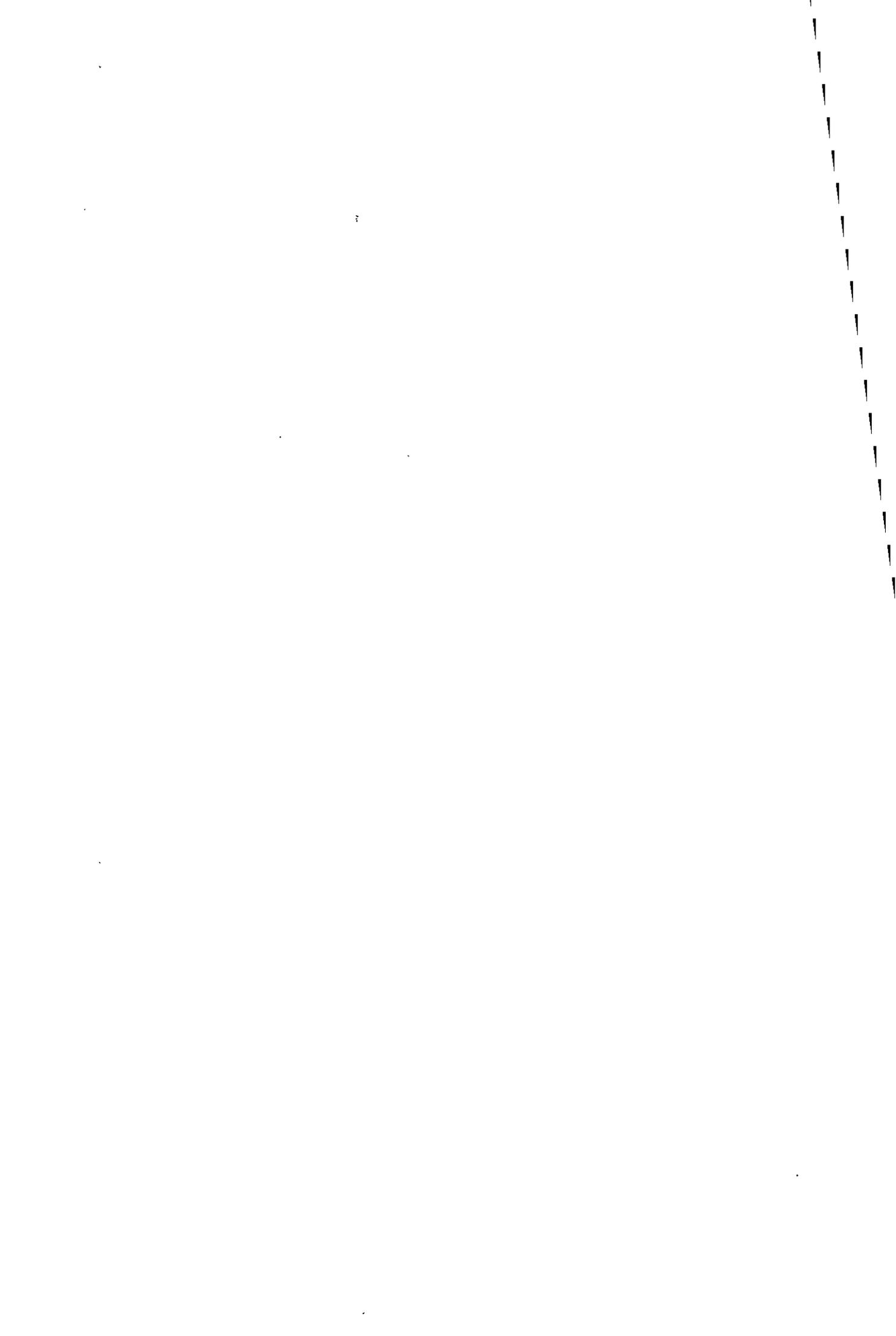
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A NOVEL TENSILE STRESS RELAXATION TEST

**Development and applications to a study of non-rubber
constituents and fillers in natural rubber**

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DEDICATION

To my dear wife, Naimah who has sacrificed her profession, encouraged me to proceed with my research works and endured the hardship together, and my children, Nazrul, Afzal, Fatin, Ana and Era, who have made my three years stay at Loughborough interesting and lively.

ACKNOWLEDGEMENTS

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Last but not least, I would like to thank Dr.Fuad M.Morris of the MRPRA and my colleagues at the RRIM, particularly Puan B. Noraishah, Dr.H.Hasma and Mr.M.N.Shafie as well as the staffs at Physical Testing Laboratory and workshop at RRIM and IPTME for their help, suggestions and assistance.

SYNOPSIS

A novel tensile stress relaxation test has been developed. It measures the residual stress in slender specimens mounted on a simple test frame by creating a small bowstring-like movement and measuring the force required to do so. Unlike the commoner compression tests, it permits a high ratio of exposed surface to volume to be maintained in the specimens, facilitating study of environmental effects. It also avoids suppression of any effects where progress of surface cracking might play an important part. The accuracy of the test is estimated at $\pm 5\%$ and, unlike simple tensile tests, would suffer no further deterioration from friction or adhesion of frame components. The test is cost-effective and the frames can operate in a wide range of temperatures and environments.

Natural rubber contains non-rubber constituents which are mostly proteins and amino-acids. The effects of these upon the properties of the unfilled rubber and a range of filled rubber compounds were investigated. This was done initially by adding these non-rubber constituents, one at a time to carefully purified rubber, to study their individual effects. Later the stress relaxation test was used to study the behaviour of natural rubber specimens containing various fillers: carbon black and coated and uncoated calcium carbonate and clay. The specimen tested had their non-rubber constituents present either individually or in commercially-occurring combination. Their physical and chemical stress relaxation behaviour when interacting with the fillers were studied at different humidities and temperatures, in air and nitrogen.

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LIST OF SYMBOLS

a	A measure of distance
A, B	Constants associated with occluded volume and shape factor of filler
A_0	Cross section area of sample
C_1, C_2	Mooney constants
D	Diffusion coefficient
E, E_0	Young's modulus of filled and unfilled rubbers
F	Force
f	Aspect ratio of filler
f	Tensile force
f_0, f_t	Tensile stress at reference time and time, t
G, G_0	Shear modulus
G_∞	Limiting shear modulus
k	Boltzmann constant
K_E	Einstein's viscosity coefficient
l	sample length
M, M_0	Modulus of filled and unfilled rubbers
M_c	Molecular weight between crosslinks
M_t	Weight of water absorbed at time t
M_∞	Weight of water absorbed at infinite time (i.e equilibrium weight)
n, n_0	Viscosities of suspension and liquid

N_0, N_t	Number of stress supporting network chain at reference time and at time, t
R	Gas constant
S, S_2, S_x	Mono, di and polysulphidic sulphur linkages in rubber vulcanizates
S, S_0	Rates of stress relaxation of filled and unfilled rubbers (% per decade)
T	Absolute temperature
t	Time
V	Molar volume of solvent
V_r	Volume fraction of rubber
W	Stored energy density
x,y,z	Extension ratios
y	Vertical displacement
χ	Polymer-solvent interaction parameter
ρ	Density of rubber
ϕ	Volume fraction of filler
ϕ_{occ}	Occluded volume of rubber
σ	Stress per unit unstrained area (engineering stress)
θ	Angle of deflection

LIST OF PUBLICATIONS

PAPER 1

'Stress Relaxation Measurement of Rubber in Tension: A New Technique'

A.B.Othman and C.Hepburn

Polymer Testing, 11(1992), pp47-59

ABSTRACT

Stress relaxation measurements in tension are potentially an elegant way of assessing the accelerated ageing characteristics of rubber. Extensive work has been carried out to develop a method suitable for an international standard. Generally, the equipment developed has been relatively expensive and this has, perhaps, contributed to the lack of widespread adoption of stress relaxation as a routine measurement. Recently, a new technique for monitoring continuous stress decay in a stretched piece of rubber was developed. This technique uses simple trigonometry to calculate stresses from a three-point bending configuration. The development of the new technique and a comparison of stresses obtained between the conventional ways of monitoring stress decay are reported.

PAPER 2

'Influence of non-rubber constituents on elastic properties of natural rubber'

A.B.Othman, C.Hepburn and H.Hasma(RRIM)

Plastics, Rubber and Composites: Processing and Applications,
19(1993), pp185-194

ABSTRACT

Natural rubber (NR), which is derived from latex of the Hevea brasiliensis tree, contains about 3-5% of non-rubber constituents. These have been found to cause, to some extent, variability of the vulcanizates' properties. Deproteinized NR (DPNR) and technically specified NR were initially produced to minimize this variability.

This investigation was carried out to determine the constituents of the NR latex which cause variability in the properties of the rubber vulcanizates. The constituents of the non-rubber were isolated from NR latex and were incorporated separately into purified NR to determine their effects on the physical properties of the vulcanizates. The effects of some of these non-rubber constituents on the elastic and swelling characteristics of vulcanizates are reported. In particular, the change in modulus with humidity for purified NR doped with non-rubber constituents is discussed.

CHAPTER ONE

GENERAL INTRODUCTION

1.1 INTRODUCTION

Natural rubber(NR) latex is a complex cytoplasmic system consisting of rubber and non-rubber particles suspended in an aqueous serum phase. The rubber is isolated by either coagulating the latex with acid or naturally (i.e by bacterial action) followed by washing and drying. Thus, different grades of NR are available depending on the source materials (*Figure 1.1*). Rubbers obtained using acid coagulation are usually the premium grade rubber such as SMR L, SMR CV50 and SMR CV60. Rubber grades SMR10 and SMR20 are obtained from latex which are coagulated naturally in the fields.

During coagulation of the rubber, some of the non-rubber constituents are lost in the aqueous serum during the washing process, but many of them are retained in the rubber phase. Some of the retained non-rubber constituents may influence properties and cause variation between and within batches and grades of the rubber. This is still a major problem in the rubber industries.

The variability of a rubber vulcanizate is normally assessed by its tensile strength value. The property was chosen because it is easy to measure and fairly sensitive. However, the method is not able to provide data of fundamental significance.

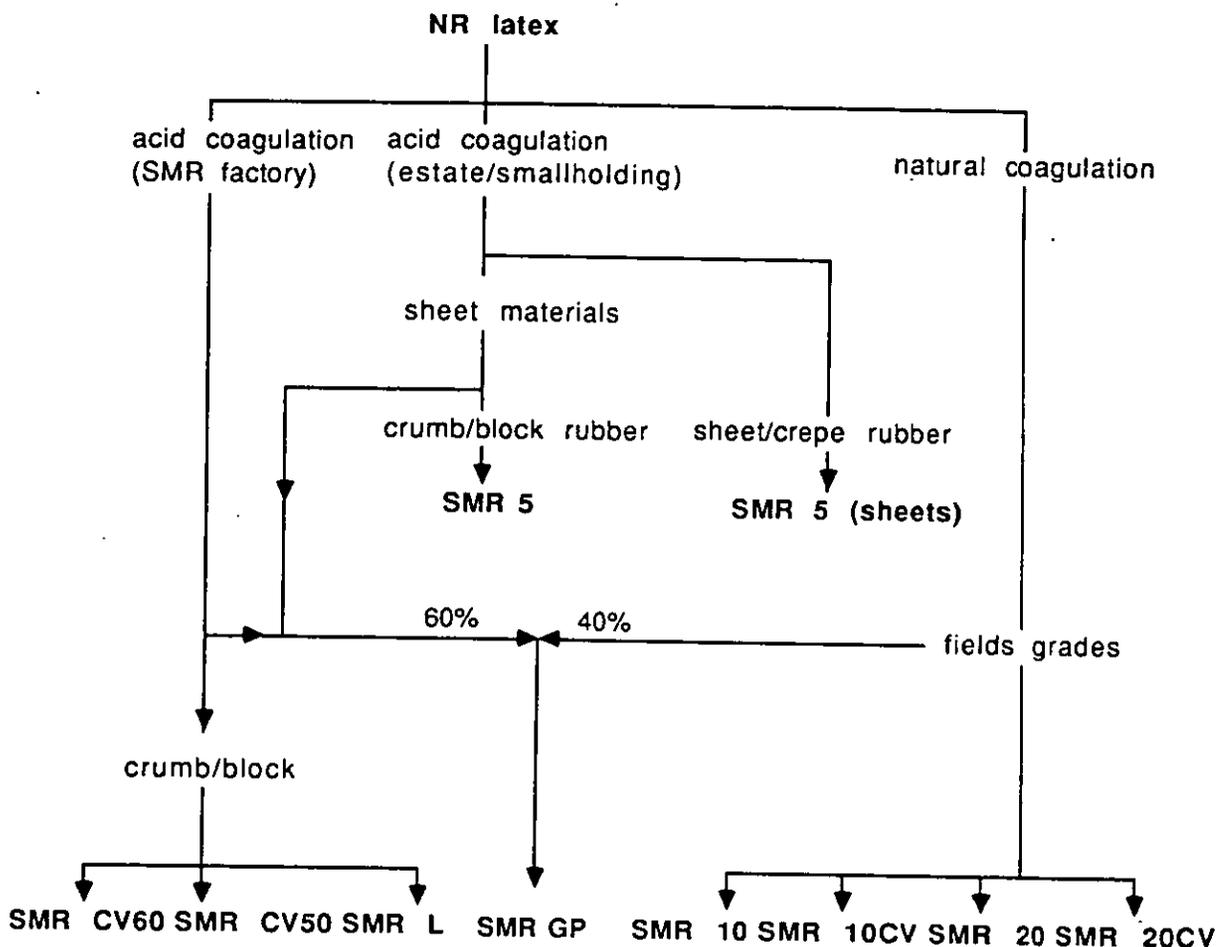


Figure 1.1: Diagram showing the source materials for the various SMR grades

An alternative property which could be used for the assessment of variability of rubber is stress relaxation or the decay in stress at a constant strain. This property gives data of fundamental significance since stress relaxation is related to the movement and breakdown of the rubber molecules within the rubber network. An insight into the changes taking place in the rubber network could be studied by this method.

However, the conventional technique of monitoring stress decay particularly on large number of samples is unattractive. This is due to the elaborate experimental set-up which requires the sample to be permanently attached to the load measuring devices for a considerable length of time. This makes the test unattractive since the set-up itself is expensive and the test is time consuming. Hence monitoring the variability of the rubber using the conventional stress relaxation technique will be out of question. However, if a cheap and simple technique of monitoring stress decay is developed, stress relaxation could be a useful tool for evaluating the consistency of the rubber vulcanizates.

1.2 OBJECTIVES

The main objectives of this study are,

(a) to develop a simple and cheap method of test for stress relaxation under tension,

(b) to explore the effect of naturally occurring non-rubber constituents, particularly proteins and amino-acids on the viscoelastic properties of unfilled natural rubber, and

(c) to evaluate the effect of fillers on the viscoelastic properties of natural rubber containing natural occurring non-rubber constituents.

1.3 RUBBER TECHNOLOGY

1.3.1 Compounding and Vulcanization

Raw or unvulcanized rubber is a long chain flexible material which can be deformed to a high extension before fracture. The high degree of elasticity was produced by weak secondary or Van der Waal forces between the long chain molecules. The effectiveness of these physical linkages is greatly increased by the complex entanglements existing between very long randomly kinked chains.

Unvulcanized rubber will flow under large stresses; in order to prevent flow, chemical linkages are introduced between rubber chains to form a three dimensional network. This is done by a process called vulcanization; i.e heating the mixture of rubber and some chemicals or compounding ingredients. The process of vulcanization transforms the soft plastic-like raw rubber into a strong, elastic engineering materials. Generally, vulcanization is carried out under pressure at high temperature (normally $>100^{\circ}$ C). Vulcanized rubber is referred to simply as "rubber", a practice used in this thesis.

Prior to vulcanization, rubber has to be compounded. This is a process of incorporating and blending the vulcanizing agents and other chemical ingredients with rubber to produce a homogeneous mix.

The compounding ingredients which are incorporated into the rubber may be classified as follows:

- a) vulcanizing agents
- b) accelerators
- c) accelerator modifiers
- d) fillers
- e) processing aids
- f) protective agents
- g) others

Any chemicals which are capable of forming crosslinks between the rubber chains can act as vulcanizing agents, but the preferred and the most important chemical is still sulphur.

When sulphur and rubber are heated together, a very slow crosslinking reaction takes place. Commercially, the process is not attractive since it requires heating the rubber mixture for a long period of time. In order to speed up the reaction, organic accelerators are used.

The organic accelerator used in the sulphur vulcanizing system requires zinc oxide and fatty acid (normally stearic acid) as auxiliary agents or accelerator modifiers. The zinc oxide-fatty acid system is also known as an activator; their function in the crosslinking process is mainly to interact with the accelerator to form an active sulphurating complex prior to the attack on the rubber chain. When dicumyl peroxide is used as the crosslinking agent, no activator is required.

Unfilled rubbers are not suitable for most practical applications because they are too soft. Fillers are therefore added to stiffen the product. Two main categories of filler are available; reinforcing and non-reinforcing types. Carbon black is a common type of reinforcing filler and fillers such as china clay and calcium carbonate are known as non-reinforcing types. Reinforcing fillers are used to give better strength and wear properties to the rubber while the non-reinforcing fillers are normally incorporated to make the product stiffer and cheaper.

When fillers are mixed with rubber, the use of process oil is advantageous. These are hydrocarbon oils and their presence reduces the frictional energy generated during mixing, thus assisting the mixing process.

Protective agents are added to reduce oxidation and cracking of the rubber.

Other chemicals which may be added are ingredients such as colouring pigment for aesthetic value and the deodorant for better smell.

1.3.2 Crosslinks

Different types of vulcanization system produce different types of crosslink. The accelerated sulphur vulcanizing system produces three different types of crosslink, namely the mono-, di- and polysulphidic types (PORTER,1968; BARNARD et. al 1970). Monosulphidic type contains one sulphur atom, disulphidic type contains two sulphur atoms and polysulphidic type contains more than two sulphur atoms per crosslink.

The structural features of the vulcanizate of rubber crosslinked using an accelerated sulphur system may be represented pictorially in *Figure 1.2*. Apart from crosslinks, cyclic mono- and di-sulphides, pendent sulphide groups containing accelerators fragments and conjugated diene and triene units are also present.

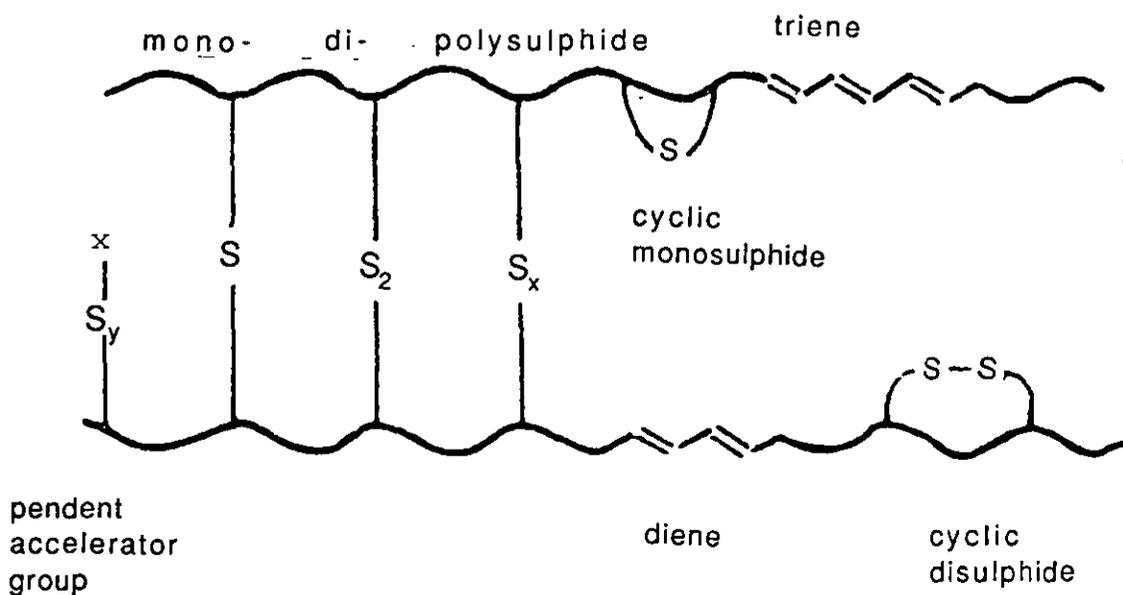


Figure 1.2: Structural features of accelerated sulphur vulcanizates of NR ($x = \text{accelerator fragments}; x \geq 3; y > 1$)

There is an accepted terminology for the accelerated sulphur vulcanizing system. Conventional vulcanizing system contains much higher concentration of sulphur than accelerator, efficient vulcanizing system (EV) contains a much lower concentration of sulphur than accelerator and semi-efficient system (semi-EV) is between those two extremes.

The conventional system gives a higher proportion of di- and polysulphidic crosslinks while the EV system gives a higher monosulphidic crosslinks. Semi-EV system gives about 50% polysulphidic and 50% mono- and disulphidics crosslinks. The proportion of these crosslinks present in the three different systems are given in *Table 1.1*.

Table 1.1: Approximate types of crosslink present in the accelerated sulphur system at optimum cure

Vulcanizing system	Conventional	Semi-EV	EV	Peroxide
Crosslinks				
Poly and di-sulphidic	95%	50%	20%	-
Monosulphidic	5%	50%	80%	-
Carbon-carbon	-	-	-	100%

Organic peroxide, such as dicumyl peroxide form a carbon-carbon crosslink. The crosslinks are formed without the use of any catalyst or accelerators, so normally their formation requires high temperature or long cure time.

Polysulphidic crosslinks are thermally less stable than mono or disulphidic types. The carbon-carbon crosslink is the most stable. The ranking to thermal stability of different types of crosslink is as follows, C-C > C-S-C > C-S-S-C > C-S_x-C (where x=3 or more).

1.3.3 Effect of crosslink density on properties

Vulcanizate properties are influenced by the crosslink density of the network structure. *Figure 1.3* shows the variation of mechanical properties with crosslink density. Modulus of the rubber generally increased with crosslink density while properties such as hysteresis and permanent set decreased. These increase in modulus and decrease in hysteresis and permanent set are due to the extra load bearing linkages holding the network chain together giving higher retractive forces.

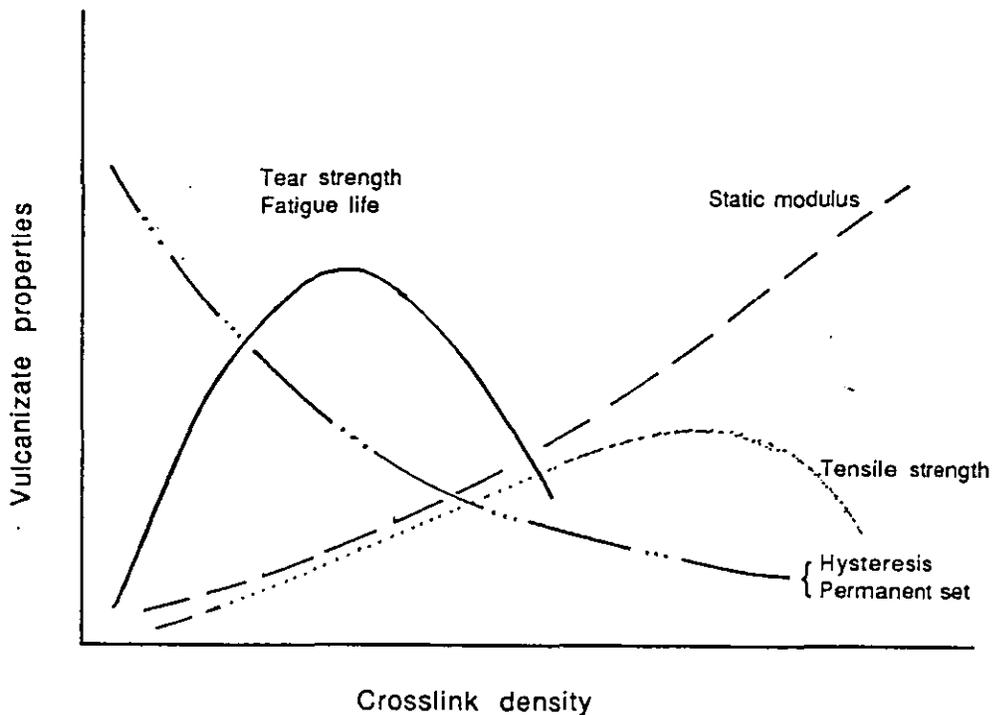


Figure 1.3: Effects of crosslink density on rubber properties

Properties such as tear strength, fatigue life and tensile strength increase and reach a maximum with crosslink density. The maximum is reached due to the inextensibility of the rubber network; too many crosslinks reduce the molecular mobility of the chain, making it brittle.

It should be noted that all these properties are functions not only of crosslink density but also of the types and nature of crosslink, types of rubber and types and amount of filler used. Further details could be found in literature (BATEMAN et., al, 1963(b); HEPBURN AND BLOW, 1982).

1.4 RESEARCH PROGRAMME

Chapter one gives the general introduction and the objective of this work. A brief account of the compounding, vulcanization and the types of crosslink present in natural rubber vulcanizates is given.

The literature review of relevant work carried out by other workers is given in chapter two. This include studies carried out on non-rubber constituents, stress-strain behaviour of unfilled and filled rubbers, diffusion of water and stress relaxation.

Chapter three discusses the development of the novel tensile stress relaxation test. The discussion is preceded with the historical developments and shortcomings of the conventional techniques, followed by the development of the new technique. The advantages and limitations of the new technique are also given.

The experimental methods used during this study are given in chapter four.

Chapter five gives the results of the studies carried out on the effects of non-rubber constituents and fillers on the viscoelastic properties of rubber vulcanizates. This include the work on the effects of water and humidity on the elastic modulus and stress relaxation. The role of non-rubber constituents and fillers on physical and chemical relaxation is also discussed.

The conclusions of the work carried out during this study are summarised in chapter six while the recommendations for further work are given in chapter seven.

CHAPTER TWO

LITERATURE REVIEW

2.1 THE NON-RUBBER CONSTITUENTS OF NATURAL RUBBER LATEX

Freshly tapped natural rubber latex is a complex cytoplasmic system consisting of rubber and non-rubber constituents (SOUTHORN, 1961). The rubber hydrocarbon constitutes about 30-45% weight of the whole latex and the non-rubber constituents account for about 3-5% weight, the rest being water. Many of the non-rubber constituents are dissolved in the aqueous serum of the latex, others are adsorbed at the surface of the rubber particles.

The rubber and non-rubber particles have different densities and they could be separated by centrifuging the latex. Ultracentrifuging the latex will separate the constituents into four main fractions: a white rubber fraction, a yellowish-orange layer containing the Frey-Wyssling particles, the serum fraction and the grey-yellow gelatinous bottom fraction (*Figure 2.1*).

The white rubber fractions are mostly rubber hydrocarbon and they occur as molecular aggregates in the form of discrete particles which are usually spherical with diameter ranging from about 150Å to 3 microns. During coagulation, these rubber particles coalesce together to form rubber network.

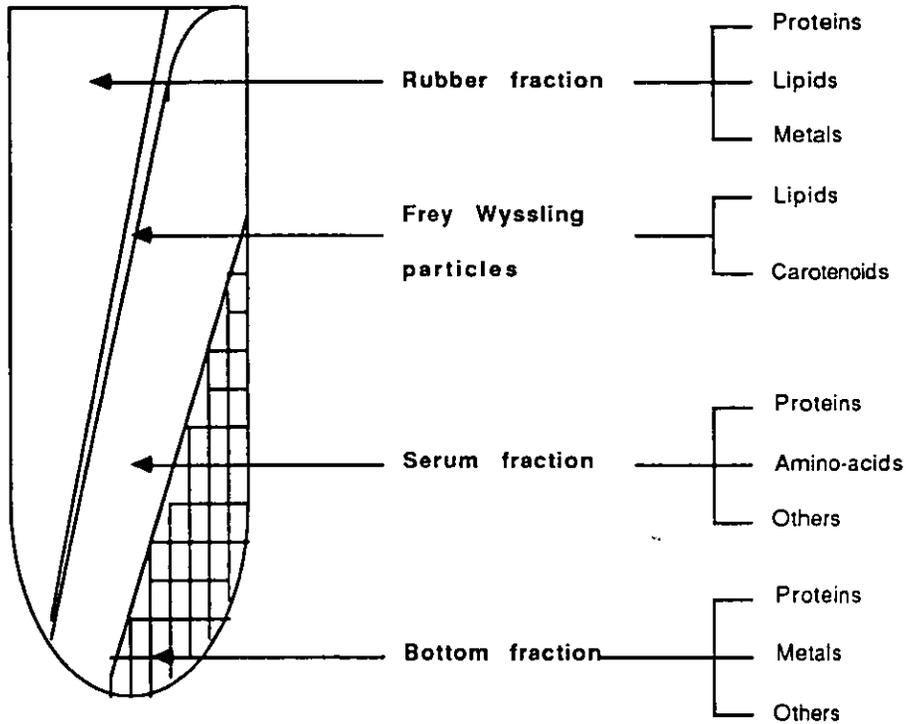


Figure 2.1: Ultracentrifuged fresh natural rubber latex fractions

Frey-Wyssling particles were described as spherical globule, of diameter about 15 times larger than rubber particle and slightly higher density. The yellow-orange colour of these particles is due to the presence of the carotenoid pigments.

The aqueous serum is the major component of latex (about 53% weight). Most of the non-rubber constituents of latex are found in the serum fraction and a large amount are washed away during processing of the rubber:

The bottom fraction is the heavier fraction and constitutes about 10% weight of the latex. About 10% weight of the non-rubber constituents are in the bottom fraction.

2.1.1 Chemical components of fresh latex

The non-rubber constituents of latex comprise proteins, amino-acids, inositols, carbohydrates, lipids, and inorganic substances. A list of the non-rubber constituents so far detected in fresh latex is given in *Figure 2.2* (ARCHER, et. al., 1963). The sub-division of the constituents is made into those associated with the rubber phase, the Frey-Wyssling particles, the aqueous serum and the bottom fraction. The approximate concentration of the constituents in the latex are included in *Figure 2.2*, but considerable differences can occur in latex from different trees due to genetical and environmental factors. Some of the non-rubber constituents which has some technological significance are described below.

a) Proteins

Proteins constitutes about 1.2% weight of latex and this account for about 20-30% of the total non-rubber constituents. About 40% of the protein is adsorbed on the rubber particles and another 20% is found in the bottom fraction. The remainder (about 40%) is dissolved in the serum phase (ARCHER,et. al.,1963). The protein which is associated with the rubber particle, the proteolipids, are hydrphobic while the serum proteins are hydrophilic. The adsorbed proteins, together with adsorbed phospholipids, impart colloidal stability to the latex.

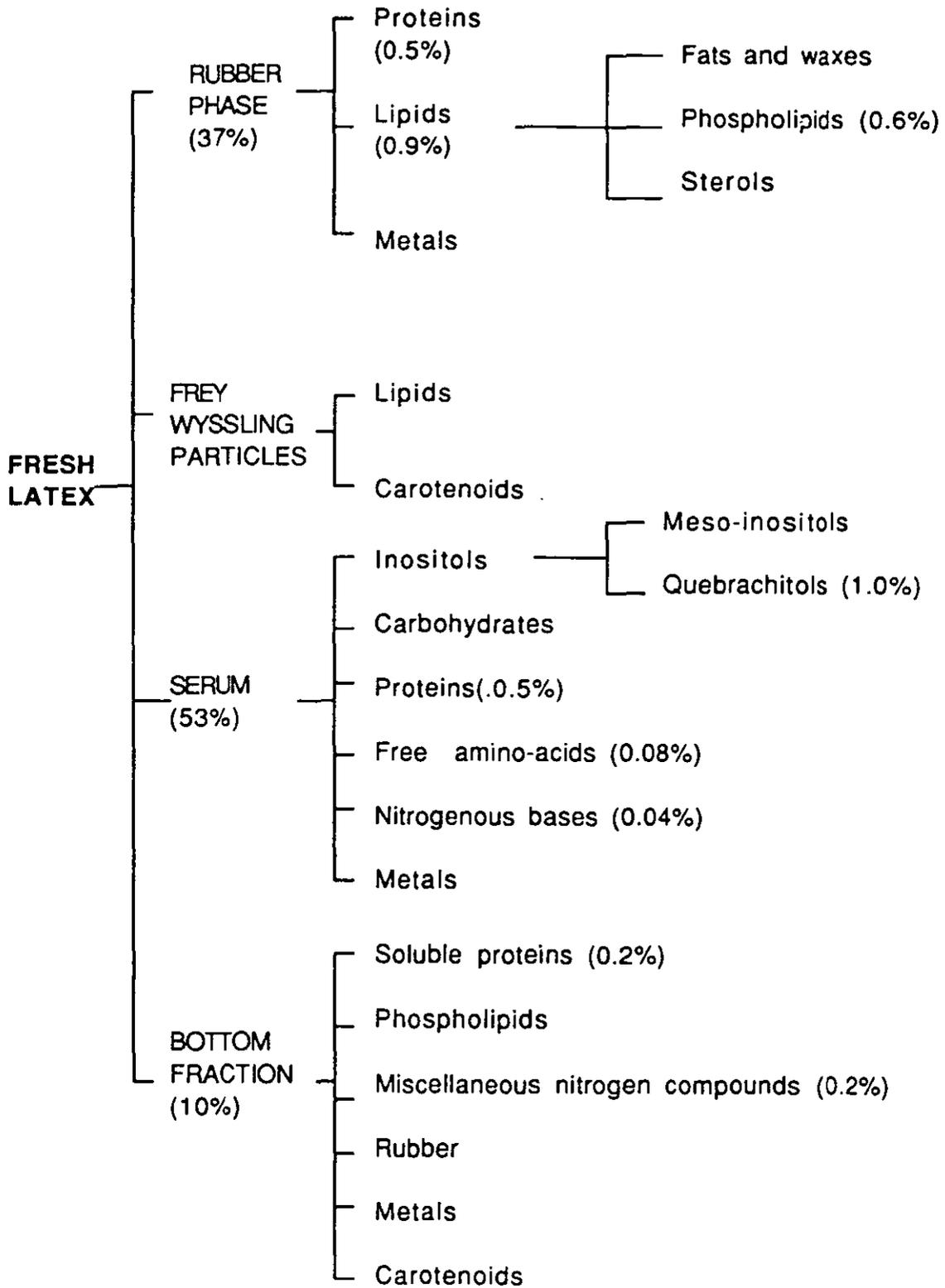
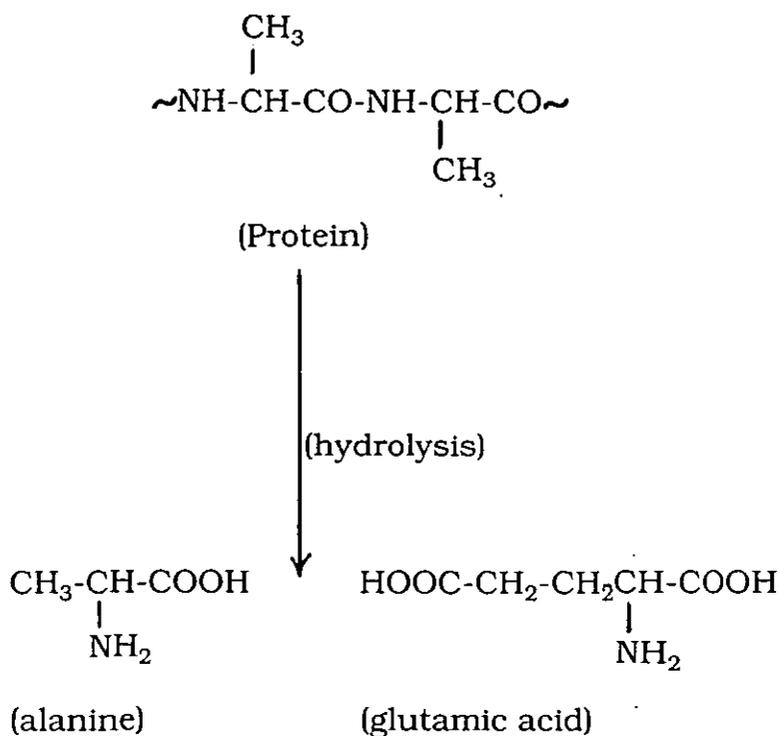


Figure 2.2: The non-rubber constituents of fresh natural rubber latex (Figures in parenthesis indicates approximate concentration in g/100g latex)

During the processing of latex into raw rubber, most of the proteins are removed. However, some of the proteins, particularly the proteolipids are retained in the rubber. These proteins has been reported to influence the properties of rubber. Smith (SMITH, 1974) observed that the removal of proteins reduces the rate of creep and affinity of rubber to water. Knight and Tan (KNIGHT AND TAN, 1975) reported that the presence of proteins caused the modulus of rubber to increase. In a later studies, Metherell showed that the hysterisial and relaxation properties of non-deproteinised rubber were higher than deprotenised rubber (METHERELL, 1980). Protein was said to be chemically inactive and act as a filler in the vulcanizate; the effect of proteins on vulcanizate properties was similar to the effect observed when fillers were added to rubber (see section 2.3.2)

b) Amino-acids

Amino-acids occur as the product of hydrolysis of proteins.



In fresh natural rubber latex, amino-acids constitute about 0.15% weight, of which about 80% are found in the serum phase. Twelve different types of amino-acid have been identified. They include alanine, glutamic acid, glycine, valine, lysine and arginine. Alanine and glutamic acid are the major amino-acids presence.

Few works has been published on the effect of amino-acids on rubber properties. Thus far, amino-acid was reported to have the protective affect on the ageing of raw rubber (BOUCHER AND CARLIER, 1964). No literature is available on the effect of individual amino-acids on vulcanizates properties.

c) Inositols and carbohydrates

Quebrachitol, a methyl inositol, is the most concentrated single non-rubber constituent, in the serum phase, amounting to about 1% of the latex (BEALING,1969). The inositols and carbohydrates together make up about 1.6% of the latex. They occur either in free form in the serum or complexed with other non-rubber constituents in the rubber phase and the bottom fraction (RESING, 1951).

The carbohydrates are metabolized by the bacteria in the commercial latex and converted into volatile fatty acids (LOWE,1960). These acids (mainly acetic,formic and propionic) are not present in fresh latex and their concentration in commercial latex is a measure of the degree of bacterial decomposition which the latex has undergone. A higher volatile fatty acids content indicates unsatisfactory preservation of latex and subsequently lower stability.

The inositols and carbohydrates are not known to have any influence on rubber properties (BOUCHER AND CARLIER, 1964; HASMA, 1993)

d) Inorganic constituents

The total concentration of inorganic ions in fresh latex is approximately 0.5% weight, the main constituents are (ARCHER et. al, 1963)

	<u>% weight of rubber.</u>
Potassium	0.12-0.25
Magnesium	0.01-0.12
Copper	0.0002-0.0005
Iron	0.001-0.012
Sodium	0.001-0.10
Calcium	0.001-0.03
Phosphate	0.25

The distribution of the metallic ions between the different phases in fresh latex has been investigated (BELMAS, 1952; ARCHER et. al, 1963). Some copper, calcium, potassium and iron are associated with the rubber phase and magnesium in the bottom fraction.

Metallic ions such as potassium, magnesium, sodium, calcium and phosphate are not known to give any significant effect on vulcanizate properties but some metallic ions such as iron and copper are pro-oxidants. These pro-oxidant impart deleterious effects on the ageing behaviour of rubber vulcanizates.

e) Lipids

The lipids of fresh latex consist of fats, waxes, sterols, sterol esters and phospholipids. These compounds are all water insoluble and are concentrated in or on the rubber phase with smaller quantities in the bottom fraction and in the Frey-Wyssling particles. The total lipid content of the latex is about 0.9%, most of which (ca.0.6%) consists of phospholipids which are long chain fatty acid esters. The colloidal stability of fresh latex is believed to be due to a mixed film of protein and phospholipid on the surface of the rubber particles (ARCHER, et. al, 1963).

The effect of lipids on natural rubber vulcanizates has been investigated by Hasma (HASMA,1984). The presence of lipids was reported to give large variation in the cure characteristics of the rubber. Some types of lipids such as fatty acids lower the cure rate while hydroxylamines increased the cure rate. However, the presence of lipids was reported to gave small changes to the physical properties of vulcanizates.

Certain types of lipid, such as oleic and linoleic acids (i.e fatty acids) were reported to act as pro-oxidant and promotes autoxidation of rubber (ARNOLD AND EVANS, 1991) However, lipids such as tocotrienols was reported to act as natural antioxidant for both raw and vulcanized natural rubber (HASMA AND OTHMAN, 1990).

2.1.2 Practical relevance of separation by centrifuging

Technologically, nitrogenous materials, are the most important non-rubber constituents of natural rubber; they can strongly influence cure characteristics. This influence varies markedly with the sources and processing techniques of the latex.

Most of these nitrogenous materials are removed during the processing of the latex. The present processing technique of commercial grades SMR retained about half of the nitrogenous materials (ca. 0.4% weight nitrogen). A much larger proportion of nitrogenous materials is removed during the processing of DPNR; only about 10% weight (ca. 0.08% wt. nitrogen) is retained.

These nitrogenous materials could also be separated from the rubber phase by centrifugation. This technique has been used by earlier worker; its simplified the study and identification of these non-rubber constituents (ARCHER, et. al, 1963; HASMA, 1984).

Rubber obtained by centrifugation contained mostly bound proteins and lipids. The level of nitrogenous materials is lower than found in SMR; about 35% (ca. 0.24% wt. of nitrogen) nitrogenous materials is retained. Thus a study of the effect of bound proteins and lipids could be carried out using the centrifuged rubber fraction.

Bound proteins and lipids could be separated from the rubber particles by using surfactants such as sodium dodecyl sulphate. A 'clean' (purified) rubber, which is purer than DPNR and contained about 5% nitrogenous materials (ca. 0.02-0.04% wt. nitrogen) could be obtained.

Centrifugation the latex will give a serum fraction which is rich in non-rubber constituents. This serum fraction could be reintroduced into the rubber where its influence on the vulcanizates could be studied. The serum fraction is also a source of proteins, which could be isolated by precipitation and reintroduced into the rubber.

2.2 STRESS STRAIN BEHAVIOUR OF RUBBER

2.2.1 Theory of rubber elasticity

Rubbery materials are long chain molecules with chemical structures permitting free rotation of segments of molecules about their chemical bonds in many places and sufficiently small intermolecular forces to take up random configurations. The linear distances between the ends of the molecules form a normal distribution about the most probable value (TRELOAR, 1975). Irrecoverable deformation or flow is prevented by some permanent connections between molecules such as the chemical crosslinks introduced during vulcanization. The interlocking of the molecules at few places along the chain length forms a three dimensional network, thus giving rise to its elastic nature.

There are two main approaches in describing the elastic nature of the rubbery materials, namely the statistical and phenomenological. The statistical approach considers the molecular network of rubber subjected to deformation; it is based on the recognition that the flexible rubber molecules take up irregular and statistically random configurations under thermal motion. The phenomenological theory, on the otherhand, is based not on a molecular concept but on an entirely mathematical consideration.

a) The statistical theory

The statistical treatment requires the calculation of the entropy of the whole assembly of the chains as a function of the microscopic state of strain in the sample and the derivation of the free energy or work of deformation. The work done in deforming the rubber elastically is considered to arise from the decrease in entropy when the molecules are forced by deformation to take up the less probable configuration. The work of deformation is given by,

$$W = 1/2 G(x^2 + y^2 + z^2 - 3) \quad 2.1$$

where W represents the elastically stored free energy per unit volume of rubber (or strain energy density), x , y and z are the extension ratios in the three corresponding directions and G , the elastic constant. The elastic constant is related to the number average molecular weight, M_c of the chains (i.e segment of molecules between successive crosslinks) by,

$$G = \rho RT/M_c \quad 2.2$$

where ρ is the density of the rubber, R is the gas constant and T is the absolute temperature.

In simple extension, whereby during the deformation one dimension of the specimen is increased in the ratio x and the other two dimensions are correspondingly reduced by $1/x^{1/2}$ the strain energy function is given by

$$W = 1/2G(x^2+2/x-3) \quad 2.3$$

The force required to extend the network chain in the direction x will be

$$\sigma = dW/dx = G(x-x^2) \quad 2.4$$

where σ is the force per unit cross-section area measured in the unstrained state.

Uniaxial compression is the reverse of simple extension and the compression ratio is less than one. The stress strain relation for rubber under compression is similarly given by equation 2.4

Experimental examination of the stress strain relationships reveals significant deviations between the theoretical and experimental results. In simple extension, there are two distinct deviations. First at moderate strain ($1.5 < x < 4$), the experimental curve falls below the theoretical values, and secondly, at higher strains ($x > 4$), the stresses tend to rise sharply and eventually exceed the theoretical predictions (*Figure 2.3*).

At high strains, the deviation observed has been attributed to the finite maximum extensibility of the network chains (TRELOAR, 1975). It arises because a Gaussian type of probability distribution is used to describe the end-to-end distances between the rubber chains. The use of Gaussian distribution is only justified when the end-to-end distance is ^{much} smaller than the fully extended length of the chain. Hence the departure from the theory is expected to become more prominent at higher strains. much

The deviation at moderate strains, for which the experimental stress is lower than the predictions, could not yet be satisfactorily explained. The deviations of the theoretical prediction suggest that the statistical theory, which only involves a constant G , is inadequate to describe the stress strain behaviour of a real rubber.

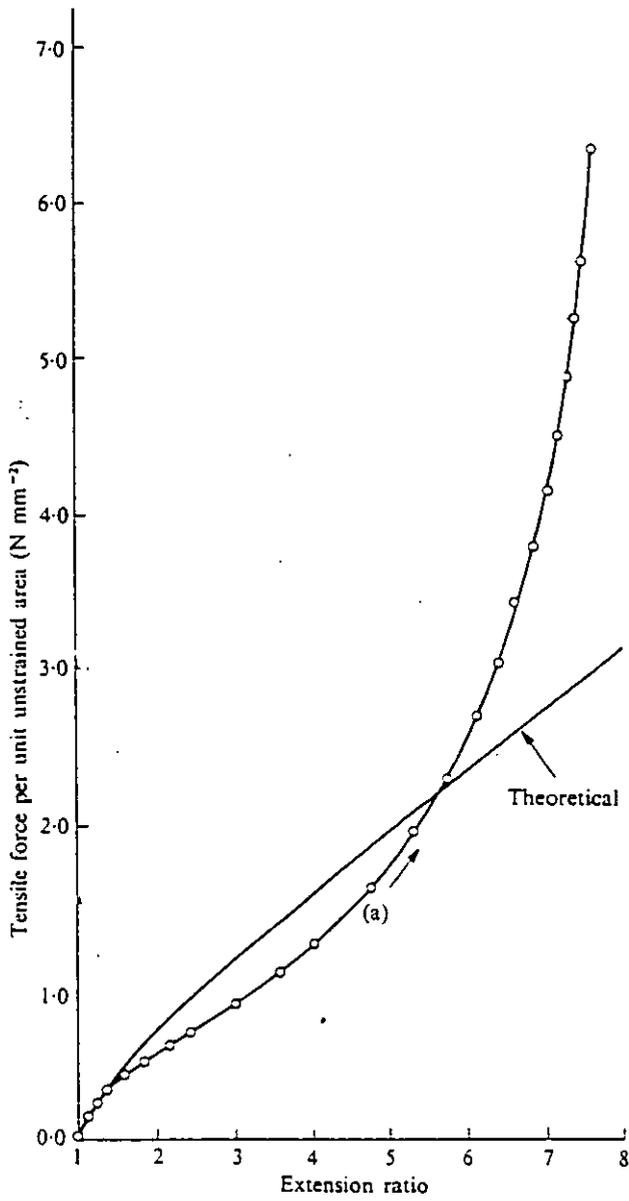


Figure 2.3: Comparison between experimental curve with theoretical prediction for simple extension (TRELOAR, 1975)

b) Phenomenological theory

The phenomenological theory is based on purely mathematical reasoning. Thus it is concerned with the way of describing the property of the material not with their explanation or interpretation in the molecular or physical sense.

There are a number of phenomenological theories available but one of the earliest and the most widely used is the theory of Mooney (MOONEY,1940). This theory appeared some years before the statistical theory and its evolution obviously has no relation to the latter theory. Mooney was concerned with the problem of developing a general theory for large elastic deformations. Making use of the assumptions that a rubber is incompressible and isotropic in the unstrained state and that Hooke's law is obeyed in simple shear, Mooney derived the stored energy function,

$$W=C_1(x^2+y^2+z^2-3)+C_2(1/x^2+1/y^2+1/z^2-3) \quad 2.5$$

which contained two elastic constants, C_1 and C_2 . The first term on the right hand side of equation 2.5 corresponds to the form derived from statistical theory with $2C_1=G$. The statistical theory is therefore a particular case of the Mooney theory corresponding to $C_2=0$.

For simple extension where $y=z=1/x^{1/2}$, equation 2.5 becomes,

$$W = C_1(x^2+2/x-3)+C_2(1/x^2+2x-3) \quad 2.6$$

and the nominal stress, σ , is given by

$$\sigma = 2(x-1/x^2)(C_1+C_2/x) \quad 2.7$$

The term $2C_1$ is equated to the quantity $\rho RT/M_c$ of the statistical theory. The equation has found particular favour in work on unfilled natural rubber vulcanizates because these materials conform quite closely to the relationship over a useful range of crosslink densities for sulphur and non-sulphur vulcanization systems in both dry and swollen states (CAMPBELL, et. al., 1992). Treloar (TRELOAR, 1975) discusses at some length the legitimacy of equating the Mooney constant, $2C_1$ to $\rho RT/M_c$.

The term C_1 was found to be proportional to the crosslink density and was subsequently related to the elastic constant of the statistical theory (GUMBRELL et. al, 1953). The origin of the C_2 term is still obscure, but it can be regarded as a measure of the departure of the observed stress-strain relationship from the form derived from statistical theory.

Numerous experiments under tensile deformation have been carried out which give support to the applicability of the Mooney equation (GUMBRELL et. al, 1953, MARK, 1975). However, when the data of tensile and compressive deformation are considered together marked deviation from the Mooney relationship was observed (RIVLIN AND SAUNDERS, 1951). In extension region, ($1/x < 1$) the Mooney line corresponds to a value of $C_2/C_1 = 0.8$, but in compression ($1/x > 1$), C_2 was found to be about zero (Figure 2.4).

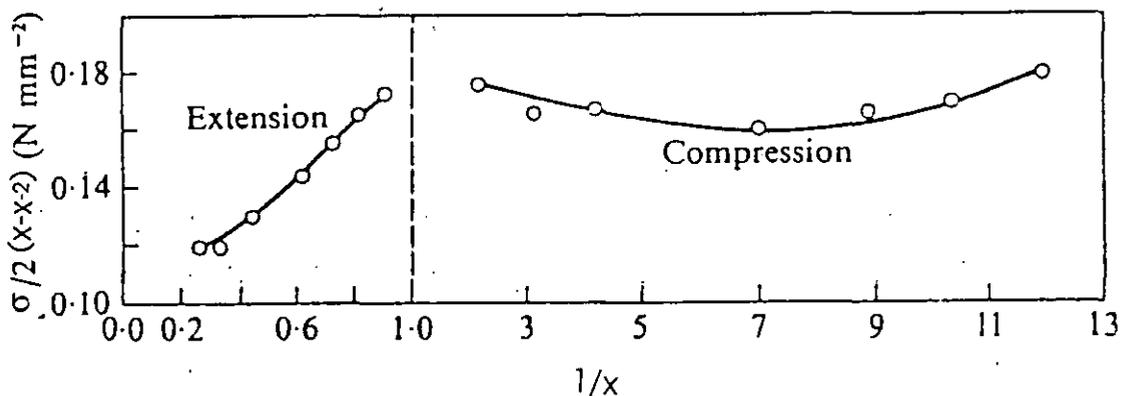


Figure 2.4: Mooney plots for data obtained from simple extension and uniaxial compression (RIVLIN AND SAUNDERS, 1951)

If the Mooney line representing the extension data were extrapolated into the compression region, the force at $1/x=12$ would attain a value of more than ten times the observed value at this point. Thus when considering the extension and compression together, it is clear that the Mooney equation is no improvement over the statistical theory.

2.2.2 Mechanics of rubber/filler systems

The use of fillers in rubber ranks as one of the two most important processes in rubber technology. Only vulcanization could be considered to surpass its usefulness.

Rubber fillers can be broadly classified into two main groups, the reinforcing and non-reinforcing types. Carbon black is the main reinforcing filler while the non-reinforcing fillers include clay and calcium carbonate.

Incorporating the reinforcing fillers into rubber enhances its wear characteristics as well as increasing the stiffness and hardness. The strength quality as measured in the laboratory (tensile and tear strengths) is largely not affected. The presence of non-reinforcing filler, on the otherhand, increases the stiffness and hardness without giving any improvement to the wear properties. Thus it can generally be concluded that the principal effect of incorporating fillers into rubber is to increase its stiffness with no impairment in strength and the mechanisms involved have been attributed to two different phenomena, hydrodynamic effects of fillers and the interaggregate interactions.

a) Hydrodynamic effects

In the hydrodynamic theory, the rubber is regarded as a continuum and the attention is focussed on the effects of filler without concern for the behaviour of the rubber at the molecular level. The mechanism proposed for the effect of fillers on the stiffness of rubbers are derived from formally identical problem of the increase in viscosity

of a liquid caused by a suspension of solid particles. For rigid spherical particles at concentrations sufficiently small for interaction between particles to be neglected, the viscosity of the suspension is given by the Einstein equation (EINSTEIN, 1906)

$$n = n_0 (1 + K_E c) \quad 2.8$$

where n and n_0 are the viscosities of the suspension and liquid respectively, c is the volume concentration of the particles and K_E is the Einstein coefficient. For a system containing dispersed rigid spheres, K_E has a value of 2.5.

The Einstein's equation only holds for suspension of rigid particles in a very dilute concentration. Even so, an analogous equation to describe the elastic behaviour of rubber containing fillers was proposed by Smallwood; the viscosity n of Einstein's equation was replaced by Young's modulus E (SMALLWOOD, 1945), namely

$$E = E_0 (1 + 2.5\phi) \quad 2.9$$

where E and E_0 are the Young's modulus of filled and unfilled rubbers respectively and ϕ is the volume fraction of filler. Smallwood showed that the stress-strain data of several large particle size non-reinforcing and lightly reinforcing fillers at low concentration fitted the above relationship.

Filler particles normally interact with each other to form aggregates. To take into account the hydrodynamic interaction between pairs of particle, Guth (GUTH, 1945) added an extra term involving the square of concentration of fillers to the Smallwood equation, namely

$$E = E_0 (1 + 2.5\phi + 14.1\phi^2) \quad 2.10$$

Guth found that equation 2.10 fitted the behaviour of rubber filled up to about 30% thermal black, which consist essentially of spherical particles. However, the equation could not be used to predict the modulus of rubber containing reinforcing fillers. Guth suggested that the departures observed with reinforcing fillers were due to the asymmetric nature of aggregated chain-like clusters of those fillers. To take into account the asymmetric nature of reinforcing fillers such as carbon black, Guth proposed a modified equation

$$E = E_0 (1+0.67f\phi+1.62f^2\phi^2) \quad 2.11$$

where f is a factor describing the shape of the asymmetric particle as expressed by the ratio of their length to their diameter (or aspect ratio). With a proper choice of the value of f , equation 2.11 was able to account for the variation of the modulus E for several rubber-filler systems. For systems containing up to 30% volume concentration of N330 black, an aspect ratio of 6.5 was required (MULLIN AND TOBIN, 1965). However, later studies of shapes of carbon black particles and aggregates using electron microscope indicate that the aspect ratio of most carbon blacks are less than 6.5; they are usually in the range of 2 to 3 (DANNENBURG et. al.,1970). Thus if the value of the aspect ratio is taken as between 2 to 3, the predicted value of E will be much lower than the experimental values given by Mullins and Tobin.

With rubber filled with reinforcing filler such as carbon black, the void spaces which are present within the filler aggregates/agglomerates are filled with rubber. These rubbers are occluded within the interstices of the filler structures. When subjected to stress, these occluded rubber is shielded to a significant extent from deformation which the bulk of the rubber undergoes and it thus acts as part of filler rather than as part of rubber matrix (MEDALIA, 1970; KRAUS, 1971).

Sambrook (SAMBROOK,1970) proposed that the effective volume fraction of filler, ϕ' , i.e the volume fraction of filler plus volume fraction of occluded rubber, should be used in equation 2.10 instead of ϕ . The value of ϕ' could be calculated from the value of ϕ and DBPA value (dibutyl phthalate absorption value) using the relation (MEDALIA,1970)

$$\phi/\phi' = (46.75+DBPA)/68.26 \quad 2.12$$

Using ϕ' in equation 2.10, Sambrook observed that the values of Young's modulus obtained were about 20% higher than the experimental values, suggesting that the use of equation 2.12 in conjunction with equation 2.10 does not adequately describe the stiffening effects of filler.

Later Medalia (MEDALIA,1972) observed that the effective volume fraction of filler is equal to the volume fraction filler plus half of the occluded rubber, i.e

$$\phi' = \phi + 0.5\phi_{occ} \quad 2.13$$

where ϕ_{occ} is the volume fraction of the occluded rubber. This signifies that only 50% of the total occluded rubber is shielded from deformation and acts as filler. Clarke (CLARKE, 1994) found that about 67% of the occluded acted as filler, a value slightly higher than the value given by Medalia.

Using the new effectiveness factor (equation 2.13), Medalia (MEDALIA,1973) showed that the experimental and calculated values of the shear modulus at 10% strain amplitude for several filled rubbers were in reasonably good agreement.

The concept of effectiveness factor was recently utilised by several authors (WOLF, S AND DONNET, J.B, 1990; WANG, et. al. 1993). Wolf and Donnet showed that the hydrodynamic equation was able to describe the moduli of rubber containing up to 0.22 volume fraction of filler. Wang, however, showed that this modified Guth-Gold equation can only describe the dependence of the elastic modulus on filler concentration up to a certain critical loading. Above the critical loading, the experimental value was found to be higher than those obtained using the modified Guth-Gold equation. This deviation was said to be due to filler networking; filler-filler interaction forming secondary structure which causes the rubber to be trapped and not destroyed during deformation. This trapped rubber give rise to a higher effective volume of filler, and thus higher modulus.

From these studies, it appears that the Guth-Gold type of hydrodynamic equation was found to be inadequate to describe the stiffening of rubber containing fillers, particularly reinforcing fillers. Other factors, apart from the hydrodynamic factors, could be responsible for the stiffening of rubber by fillers. This may include the enhancement of crosslink density by the fillers, a factor which is discussed in section 5.5.1

b) Interaggregate interaction

According to Payne (PAYNE,1962), the shear modulus of filled rubber is maximum at low strain (ca. 1%) but decreases as the strain increases until at a sufficiently high strain when the modulus becomes independent of strain. The idealised form of shear modulus against shear strain plots may be represented by *Figure 2.5*.

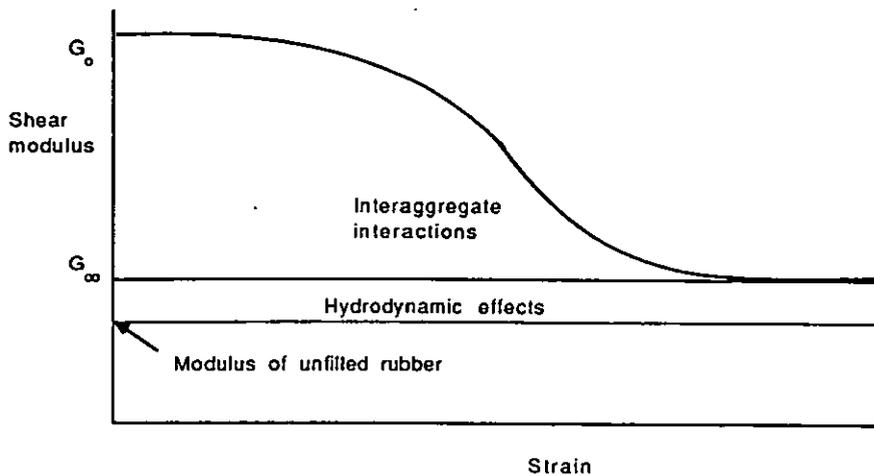


Figure 2.5: Idealised plot of shear modulus as a function of shear strain

The limiting modulus at low strain was referred to as G_0 while that at high strain was referred to as G_∞ . The corresponding modulus for unfilled rubber is represented by the lower horizontal line. According to Payne, the maximum elastic modulus at low strain, G_0 , is caused by a maximum development of the filler agglomerates. At higher strains, the filler agglomerates are broken down and the elastic modulus attains a low value, G_∞ resulting from the contribution of the rubber matrix and the aggregated structure. The value, $G_0 - G_\infty$ therefore characterises the maximum effects of filler agglomeration in rubber. Payne referred to the effects of filler agglomeration as the structural effects, that is the value $G_0 - G_\infty$ arises from the filler agglomerate structures. This constitutes the additional contribution to the modulus at low strain which was not accounted for by the hydrodynamic equations.

Chemical methods have been used to remove the effects of filler agglomeration in rubber (PAYNE, 1965). The chemical used are generally known as chemical promoters, usually organic nitroso compounds. When the chemical promoters such as N-(2-methyl-2-nitro-propyl)-4-nitrosoaniline, are added to filled rubbers, the filler dispersion greatly improved and $G_0 - G_\infty$ values decrease considerably.

The filler agglomeration was observed to be attributed to the mutual particle attraction due to Van der Waals forces (VOET et al,1970). Hence increasing the loading of filler increases the value of G_0-G_∞ since the presence of more filler increases the tendency of agglomeration. The presence of different rubbers has an effect on the value of G_0-G_∞ but it was observed to be independent of crosslink density (PAYNE et. al, 1972). This implies that any change in the rubber matrix does not affect the agglomerate structure of the fillers.

2.3 DIFFUSION OF WATER IN RUBBERS

Diffusion is a transport process by which molecules are transferred from a region of higher concentration to one of lower concentration as a result of random thermal motions. The transport of liquid into rubber is a similar process. The rate of diffusion of a material in a polymer is determined by its concentration gradients and by its mobility in the polymer matrix.

2.3.1 Diffusion theory

The movement of the liquid obeys the law of diffusion. The first law of diffusion (Fick's law) is based on the premise that the flux is proportional to the concentration gradient (dc/dx) of the penetrant, that is,

$$F=-D(dc/dx) \quad 2.14$$

where D is the constant of proportionality called diffusion coefficient (CRANK, 1975). The flux F is defined as the rate of mass transfer per unit area of section, c is the concentration of the diffusing substance and x is the space coordinate normal to the section.

Fick's first law does not consider the mass transfer effects of the penetrant in diffusion processes. The effect was taken into account in Fick's second law and for diffusion in one dimension, it may be written as,

$$dc/dt=D(d^2c)/d^2x \quad 2.15$$

where t is the time and D is a constant.

General solutions to the diffusion equation for a variety of geometrical shapes (e.g sheet, sphere and cylinder) are available (CRANK, 1975). However, each diffusion equation has to be solved subject to its appropriate initial and boundary conditions. Of a particular interest to the work presented in this thesis is a solution for plane sheet.

For a plane sheet of thickness l , the total amount of liquid absorbed at time t is given by

$$M_t/M_\infty = 4/(Dt/\pi)^{1/2} \quad 2.16$$

where M_∞ is the amount of liquid absorbed at equilibrium (MUNIANDY et. al., 1988). Diffusion coefficient can be obtained from the initial slope of the graph of M_t versus $t^{1/2}$. The values for various liquids in natural rubber has been published and they are of the order 10^{-12} to $10^{-14}m^2/s$. The diffusion coefficient of water is approximately $10^{-10} m^2/s$.

2.3.2 Diffusion of water in rubber

Vulcanized rubber is used in a variety of applications and water is perhaps the most common liquid with which it comes into contact. In marine and off-shore engineering applications, for example, the rubber products spend a considerable time under water. Thus

information on the water absorption characteristics of the rubber is useful.

Water diffuses through the rubber matrix to the hydrophilic materials where it then dissolves if it is water soluble, forming droplets. If the hydrophilic materials are not water soluble, it will swell the materials, forming watery domains in the rubber.

Natural rubber has been known to contain naturally occurring non-rubber materials, which are of different molecular weights. The low molecular materials are constituents such as the inorganic salts and the high molecular weight materials are the nitrogenous materials such as proteins. These materials, which is about 3-5% weight, has been claimed to be responsible for the absorption of water by the rubber.

Boggs and Blake (BOGGS AND BLAKE, 1926) suggested that water absorption in natural rubber was due principally to the proteins naturally present in the rubber. Kemp (KEMP, 1937) on the other hand, argued that the effect was mainly due to low molecular weight water soluble substances. Kemp's argument was right and it was later confirmed by Muniandy (MUNIANDY, 1987).

Based on these findings, it appears that the affinity of natural rubber to water is dependent on the low molecular hydrophilic materials, but the nature of these materials is not well understood. The effect of some low molecular weight materials such as amino-acids were investigated in this study.

2.4 STRESS RELAXATION STUDIES

In classical terms, the mechanical properties of an elastic solid can be described by Hooke's Law, which states that an applied stress is proportional to the resultant strain, but independent on the rate of strain. For liquids, the corresponding statement is known as the Newton's law, with the stress proportional to the rate of strain. In many cases, a material may exhibit the characteristics of both liquid

and solid and neither of the limiting laws will adequately describe its behaviour. The system is then said to be in a viscoelastic state. Rubber is an example of a material which exhibit viscoelastic characteristics and this results in the phenomena known as creep, stress relaxation and recovery.

There are two types of relaxation processes which takes place in rubber, physical and chemical relaxations. Physical relaxation has been associated with the nature of the material and its involves physical movement of the rubber matrix. It is dominant at short time at ambient temperature.

Chemical relaxation involves with chemical changes taking place in the rubber. This is due mainly to the breaking up of primary bonds in the rubber network and the effect is dominant at long times and higher temperatures.

2.4.1 Physical relaxation

Physical (or primary) relaxation has been taken to imply the physical movement of chain network of the rubber after it has been subjected to a continuous stress or strain. This concept of physical movement of chain network has not been fully elucidated and hence the precise understanding of the mechanism which causes the slow relaxation of polymers has not been satisfactorily achieved. Mathematical equation which has been put forward to explain the process of stress relaxation has therefore been empirical. Thirion and Chasset (THIRION AND CHASSET, 1963) for instance proposed the equation below to explain the physical relaxation of natural rubber crosslinked using dicumyl peroxide at 30.5°C.

$$s_t = s_e + Ct^{-n} \quad 2.17$$

where s_t is the tensile stress at time t and C , n and s_e are constants with the latter expressing the limiting force for a theoretically infinite time. Cotton and Boonstra (COTTON AND BOONSTRA, 1967) on the other hand suggested that, for all rubbers at room temperature, the stress at time t (s_t) could be expressed as,

$$s_t = s_1 t^{-n} \quad 2.18$$

where s_1 is the stress after one minute of relaxation and n is defined as the relaxation rate of the material. Cotton and Boonstra also investigated the behaviour of both raw and vulcanized rubbers and they observed that the equation was applicable over a period from 0.1 second to about 6 months.

a) Effect of types and concentrations of crosslink

The types of crosslink present affect the rate of physical relaxation of the rubber (SOUTHERN, 1986). Generally, the C-C type of crosslink gives a lower rate of physical relaxation than the urethane or the sulphidic types of crosslink and the polysulphidic crosslink gives a lower relaxation rates than the corresponding monosulphidic crosslink (*Figure 2.6*).

Increasing the crosslink density of the rubber decreases the rate of physical relaxation (SOUTHERN, 1986,; DERHAM et.al., 1970; FARLIE, 1970). For unfilled natural rubber vulcanizates, Farlie (FARLIE, 1970) observed that the relaxation rate was related to the elastic constants (or commonly known as Mooney constants) C_1 and C_2 .

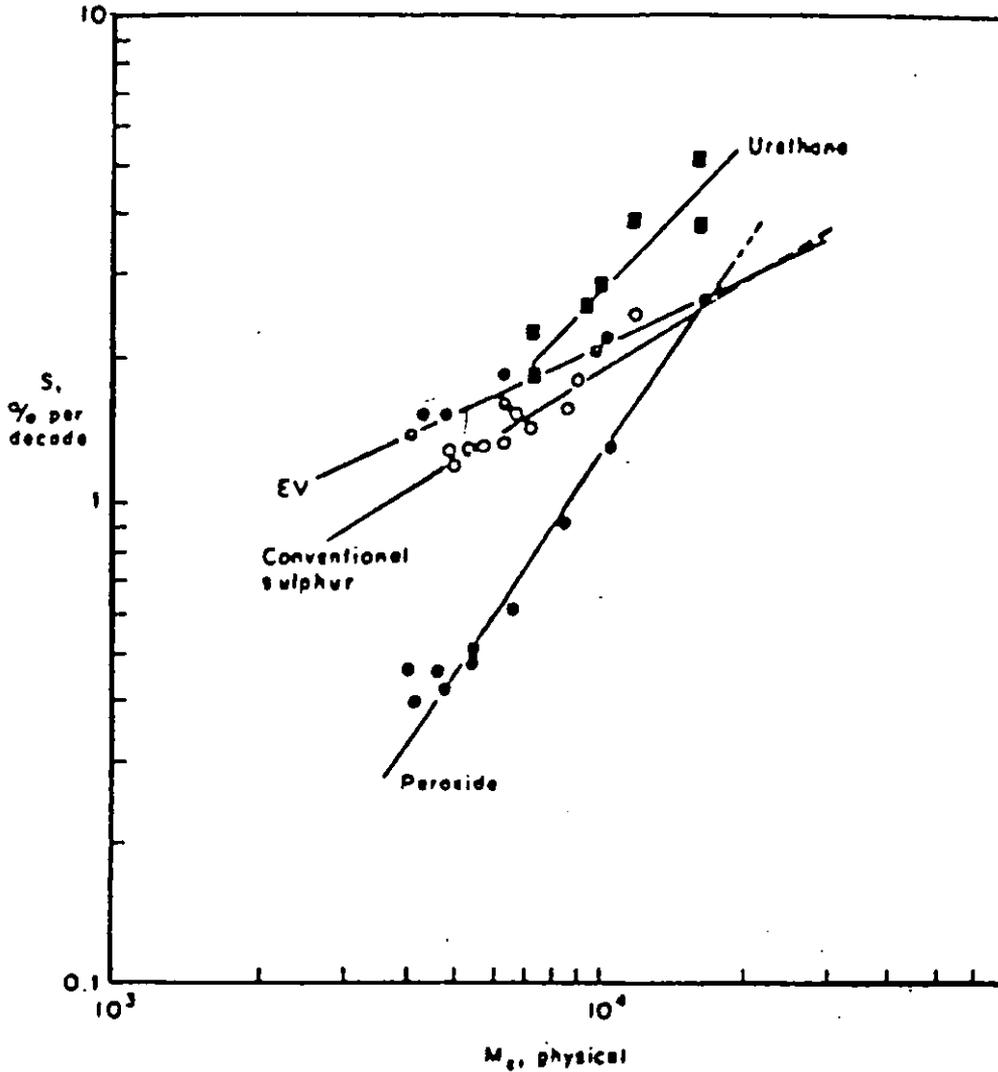


Figure 2.6: Stress relaxation rate, S of unfilled NR as a function of molecular weight between crosslinks, M_c

b) Effect of fillers

The incorporation of fillers into rubber generally improves the mechanical properties of the product and that also resulted with an increase in the rate of relaxation (*Figure 2.7*). The effect is particularly marked with carbon black fillers, where there is an interaction between the rubber and the filler (GREGORY et. al., 1978).

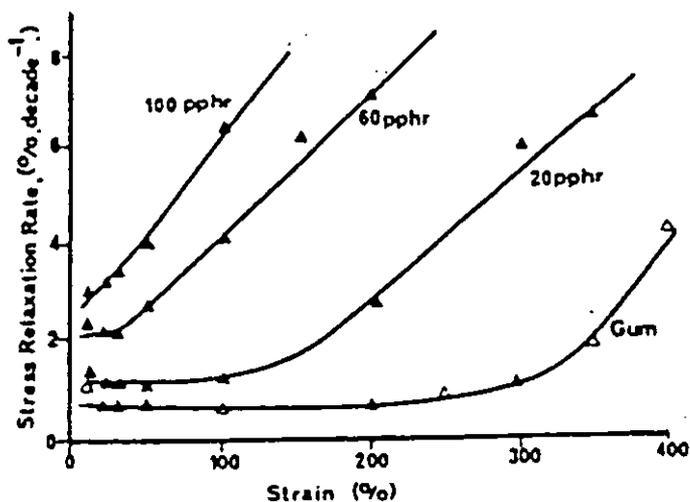


Figure 2.7: Variation of stress relaxation rate with applied strain for carbon black(SRF) filled NR

The factors which contributed to the increase in the physical relaxation rate in the presence of fillers are complex but it may be identified as resulting from two sources : stress softening and strain amplification.

Stress softening is a phenomenon which gives rise to a rubber requiring a greater stress to produce a given elongation on its first extension than during subsequent extensions (MULLINS, 1950). It is exhibited by both filled and unfilled rubbers. In filled rubber, the effect has been attributed mainly to the breakdown of the filler-filler and filler-rubber bonds during deformation. Derham (DERHAM, 1973) observed that prestressing prior to the test resulted with stress softening and subsequently a reduction in creep. The rate of creep decreases with the number of prestressing.

In a filled rubber, the filler particles are considered to be effectively inextensible and their presence alters the extensibility of the polymer phase. Under a stress, generally the polymer phase of the filled rubber will have a much greater strain than the overall or bulk strain. This is known as "strain amplification" and its generally lead to an increase in the relaxation rates. Studies carried out showed that the relaxation rates of the filled rubber resembles that of the unfilled rubber at higher extension, implying that the higher rates of relaxation of the filled rubber cannot be due to the rubber-filler interaction (GENT, 1962).

c) Effect of strain

There are differences in opinion with regard to the effect of strain on the rate of stress relaxation of unfilled rubber. Gent (GENT, 1962) showed that the rate of physical stress relaxation of a conventional unfilled natural rubber vulcanizates was substantially independent of the strain for an extension of up to 200 percent. However, Derham et. al.(DERHAM et al, 1970) showed that, for similar vulcanizates, the rate of the physical relaxation was dependent on the strain of the rubber. The behaviour of the peroxide cured natural rubber was shown to be similar to that of the conventional sulphur cured vulcanizates at low crosslink density, but substantially independent of strain at higher crosslink density.

Holley and Smith (HOLLEY et. al., 1972) and Chan et. al. (CHAN et. al., 1974) showed that the stress relaxation rates of the fully soluble efficient vulcanization system were independent of strain for extensions of 10 to 100 percent. However, when stearic acid was used as cure activator instead of the rubber soluble activator, Zinc Ethyl Hexanoate (ZEH), the stress relaxation rates of those vulcanizates became remarkably strain dependent. The variation of the stress relaxation rate with strain observed with rubber activated with stearic acid was attributed to the effects of insoluble zinc soap presence. The presence of the insoluble zinc soap increases the contribution of the Mooney Rivlin constant C_2 , thus increases the rate of the physical stress relaxation.

The variation of stress relaxation rate with strain for carbon black filled rubber is considerably greater than the corresponding unfilled rubber (GREGORY et. al., 1978). Generally it has been observed that the rates of physical stress relaxation increases with strain (*Figure 2.7*).

d) Effect of environmental changes

Changes in temperature resulted with marked variation in the rates of physical relaxation. Derham (DERHAM, 1973) investigated the effect of a short abrupt temperature cycle on the relaxation behaviour of natural rubber and observed a marked acceleration of the relaxation process when the rubber was subjected to a temperature cycle of 20°C higher for about 20 minutes. The effect has been attributed to the breaking up of weak bonds, probably the Van der Waals types of bonds, which would be fairly stable in the absence of a temperature or the bonds which would otherwise fail at longer time in the absence of the abrupt temperature changes.

Changes in the relative humidity of the environment has also been known to cause variation in the relaxation rates of the rubber. Derham (DERHAM 1972) reported that the relaxation rates of natural and synthetic rubbers increase with increasing relative humidity. The relaxation rate was observed to double when the relative humidity increases from 15 to 80 percent (*Figure 2.8*). This increase in the relaxation rate was attributed to the penetration of the water into the rubber, resulting with a drop in modulus, hence the increase in the relaxation processes.

However, Prabhu (PRABHU, 1991) observed that with 15 different types of rubber tested, immersion in water for 7000 hours did not significantly alter their relaxation rates. Epichlorohydrin, which absorbed about 15% weight water only gave a 2% change in relative stress after 7000 hours.

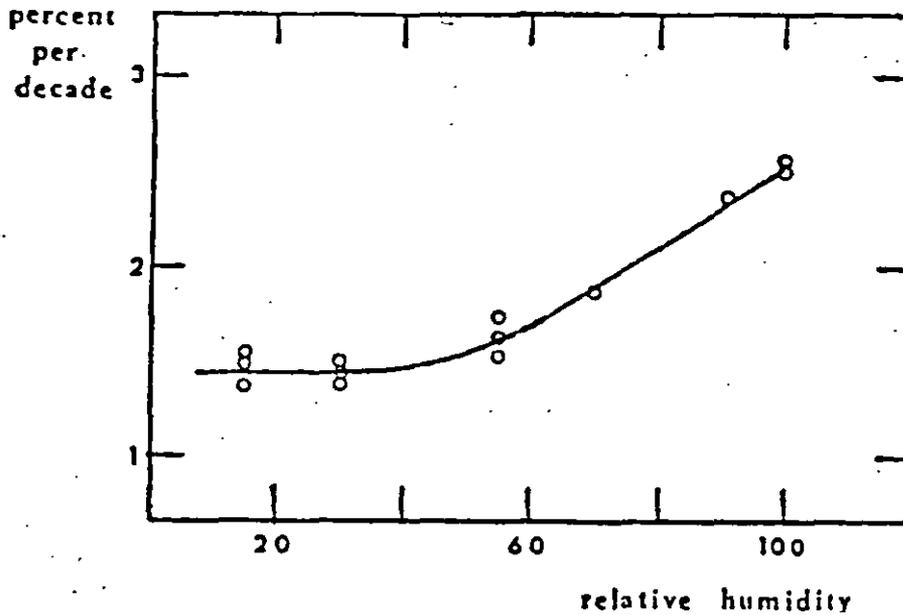


Figure 2.8: Stress relaxation rate as a function of humidity for unfilled natural rubber

The findings of Derham and Prabhu appear contradictory. However those two workers carried out test on sample of different geometries and at two different environments, namely humidity and water. The mode of deformation was also different; Derham tested under tensile load while Prabhu carried out compression relaxation. The differences in the outcome of the finding indicates that a) the effects of humidity and water immersion were different b) the sample geometry played an important role in the stress relaxation studies or c) results of tensile and compressive stress relaxation are not comparable.

e) Effect of types of rubber

The rates of relaxation of different types of rubber are expected to be different because of the structural differences. Derham (DERHAM, 1972) reported that, at the same relative humidity the rates of stress relaxation of natural rubber was much lower than polychloroprene, the difference of which could have been due to the differences in the molecular structure of those rubbers. At higher relative humidity, polychloroprene possesses a higher rate of relaxation than natural rubber since the former has a greater tendency to absorbed water.

Different grades of natural rubber also gives different rates of relaxation. Deproteinised natural rubber (DPNR), a rubber containing a very low nitrogenous material, has been observed to give a lower rate of relaxation than conventional grade natural rubber (SMITH, 1973) . Skim rubber, a rubber containing a very high nitrogenous materials, possesses the highest relaxation rates among natural rubber. The differences in the rates of relaxation observed between different grades of natural rubber has been attributed to the presence of different amount of proteins. Protein was deduced to act as a filler in the rubber matrix, apart from increasing the tendency for the rubber to absorbed water and moisture (METHERELL, 1980).

2.4.2: Chemical relaxation

Chemical stress relaxation of rubber broadly implies the damage and subsequent rearrangement of the molecular structure.

In rubber vulcanizates, the damage on the rubber network structure could be due to the two types breakages, namely,

- (a) scission of the molecular backbone
- (b) rupture of the chemical crosslinks in between the molecular segment.

Both types of bonds failure leads to the breakages of the elastically effective chains. The chains/bonds rupture will consequently leads to the formation of chemically active radicals which will in turn undergo a series of reactions leading to further changes in the network structure.

The chemical (or secondary) relaxation has been used to provide a measure of degradation of the polymer. The technique is based on the kinetic theory of the rubbery material which relates the force f exerted by an extended sample to the number of stress - supporting network chains, N , given by

$$f = NkTA_0 (x-x^{-2}) \quad 2.19$$

where k is the Boltzmann's constant, T is the absolute temperature, A_0 is the unstrained cross-section area and x is the ratio of the extended to the unextended or initial length of the sample. If the extension ratio x and the temperature are kept constant, the stress is proportional to the number of stress-supporting network chains, N_t . Degradation will result in a reduction in the number of stress-supporting chains and if $(N_0 - N)$ of the original N_0 chains are broken due to degradation process, then the ratio of the final tensile force f_t to the initial force f_0 will be

$$f_t / f_0 = N_t / N_0 \quad 2.20$$

Thus this decay in stress at constant extension provides a direct measure of the extent of degradation of a crosslinked rubber and forms a basis for the chemical stress-relaxation technique.

Two types of stress relaxation measurement may be made, namely a continuous stress relaxation, in which the sample is held extended throughout the duration of the experiment and an intermittent stress relaxation, in which the sample is strained only at a time for which the stress is to be measured. The continuous stress relaxation thus provides a measure of the decrease in the network in the extended state while the intermittent measurement gives an indication of the new network formed when the sample is unextended. The difference in the stresses obtained between the continuous and intermittent measurements has been considered to be the contribution to the network due to the formation of crosslinks during ageing.

The extent of the chemical relaxation has been shown to be proportional to the time of deformation; the dependence of the rate of the chemical relaxation on temperature was observed to be high, being similar to the temperature dependence of the chemical reactions (DUNN et. al., 1959; GENT, 1962). At ambient temperature, the rates

of chemical stress relaxation are very low (DERHAM et. al., 1969) . A time must elapse for the chemical reaction to be apparent and the time is dependent on the ratio of the physical to the chemical relaxations. Hence, at ambient temperature, the chemical stress relaxation is only observed after a very long period of time.

a) Chain scission

According to the Tobolsky's theory on chain scission, a dependence of the chemical stress relaxation on the initial crosslink density N_c indicates a main chain scission while the crosslink scission will be indicated by the independence of stress relaxation on the N_c (TOBOLSKY, 1960). Several papers have been written on the subject of main-chain and crosslink scission of rubber and the subject has been summarised by Murakami and Ono (MURAKAMI, et al 1979). A simplified summary for natural rubber vulcanized using different vulcanizing systems is shown in *Figure 2.9*.

The value f_t is the number of chain scission per unit volume after a time t and the ratio f_t/f_0 is the relative stress. The constant k gives the scission rate for the rubber. It was reported that the value of the constant k for natural rubber crosslinked using sulphur was larger than the corresponding rubber crosslinked using peroxide. The sites of scission could either be along the main chain or at the crosslink and the issue has not be universally agreed, as indicated by the differences in opinions expressed by Tobolsky (TOBOLSKY, 1960) and Watson (BERRY AND WATSON, 1955). However, recent findings suggest that, under normal environmental condition, oxidative scission occurs mainly along the main chains. (MURAKAMI AND ONO, 1979) However, under inert environment, scission occurs mainly near the crosslink sites and the present of small amount of oxygen will result with the scission at the crosslink sites in the initial stages, but along the main chain at the later stages (TAMURA AND MURAKAMI, 1980).

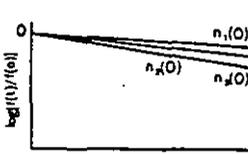
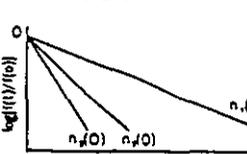
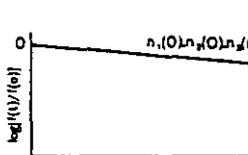
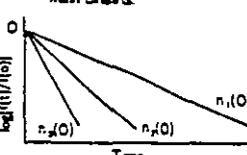
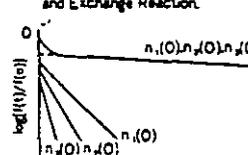
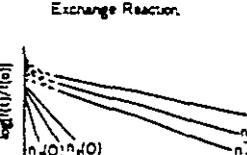
Kind of Polymer	Structure	Thermal Degradation	Oxidative Degradation
Peroxide or Irradiation cured Natural Rubber	$\begin{array}{c} \text{CH}_3 \qquad \text{CH}_3 \\ \qquad \quad \\ -\text{C}-\text{CH}_2-\text{CH}_2-\text{C}-\text{CH}=\text{CH}_2- \\ \qquad \quad \\ -\text{C}-\text{CH}_2-\text{CH}_2-\text{C}-\text{CH}=\text{CH}_2- \\ \qquad \quad \\ \text{CH}_3 \qquad \text{CH}_3 \end{array}$	<p>Random Scission along Main Chains.</p>  $\frac{f(t)}{f(0)} = e^{-\alpha(t) \langle \alpha'(t) \rangle}$	<p>Random Scission along Main Chains</p>  $\frac{f(t)}{f(0)} = e^{-\frac{\alpha'(t)}{N(O)} \text{Time}}$ $k_1 = f(N(O)) \langle \alpha'(t) \rangle$
TMTD cured Natural Rubber	$\begin{array}{c} \text{CH}_3 \qquad \text{CH}_3 \\ \qquad \quad \\ -\text{C}-\text{CH}_2-\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2- \\ \qquad \quad \\ \text{S} \qquad \quad \text{S} \\ \qquad \quad \\ -\text{C}-\text{CH}_2-\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2- \\ \qquad \quad \\ \text{CH}_3 \qquad \text{CH}_3 \end{array}$	<p>Scission at Crosslinks.</p>  $\frac{f(t)}{f(0)} = e^{-k_2 t} \quad k_2 = \text{const.}$	<p>Random Scission along Main Chains</p>  $\frac{f(t)}{f(0)} = e^{-k_1' t}$ $k_1' = g(N(O))$
Sulfur cured Natural Rubber	$\begin{array}{c} \text{CH}_3 \qquad \text{CH}_3 \\ \qquad \quad \\ -\text{C}-\text{CH}_2-\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2- \\ \qquad \quad \\ \text{S}_x \\ \qquad \quad \\ -\text{C}-\text{CH}_2-\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2- \\ \qquad \quad \\ \text{CH}_3 \qquad \text{CH}_3 \end{array}$	<p>Scission at Crosslinks and Exchange Reaction.</p>  $\frac{f(t)}{f(0)} = A e^{-k_1 t} + B e^{-k_2 t} \quad k_2 = \text{const.}$	<p>Random Scission along Main Chains and Exchange Reaction.</p>  $\frac{f(t)}{f(0)} = A e^{-k_1 t} + B e^{-k_2 t}$

Figure 2.9: Degradation mechanisms at high temperature for natural rubber vulcanizates with different crosslink density, $n(o)$

b) Dependence of chemical stress relaxation on strain

The chemical stress relaxation has been observed to be generally independent of strain at low strain, but became dependent of strain at higher strain. Tobolsky (TOBOLSKY, 1960) for instance reported that the relative stress for unfilled natural rubber crosslinked using sulphur at 100°C was independent of strain for up to 200 percent extension, after which it became strain dependent. Murakami (MURAKAMI, 1975) on the other hand observed that the relative stresses obtained by intermittent stress relaxation of rubber in air at 88°C and 100°C were independent of strain for extension of below 50 percent but became strain dependent at higher strains.

With filled rubbers, the effects were observed to be similar to the unfilled rubber : the chemical stress relaxation at temperature below 100°C was independent of strain for up to 200 percent extension (BERTENEV et. al., 1972).

c) Effect of types and concentrations of crosslink

There were conflicting findings on the effects of crosslink density on the chemical stress relaxation. Tamura and Murakami (TAMURA et. al., 1973) for instance reported the existence of two relaxation zones for both sulphur cured and irradiation cured natural rubber, with the overall relaxation rates increasing with the concentration of the curatives. On the other hand, other workers reported that the rate of relaxation decreases with crosslink density (TOBOLSKY, 1960). The steeper initial relaxation rate was attributed to the interchange reactions of the polysulphidic crosslinks, while the long term relaxation was attributed to the random scission of the main chains. Thus, a complete chemical stress relaxation might be described by a sum of two exponential terms with reaction rates corresponding to interchange reaction and random scission reactions.

2.4.3 Stress relaxation tests

Stress relaxation tests are covered in the British Standard specification BS 903: Part A42:1992 and A52:1986. Part A42 (=ISO 3384:1991) described the determination of stress relaxation at ambient and at elevated temperature for rubber under compression while part A52(=ISO 6914) gives the method of testing under tension.

a) Stress relaxation in compression

In BS.903:Part A42, three methods of determination stress relaxation are given. In method A, the test piece is compressed at test temperature and is maintained at this temperature throughout the test period. All measurements of counter force are taken at test temperature. With method B, all measurements are taken at normal laboratory temperature ($23\pm 2^\circ\text{C}$) but the test piece is maintained at any desired testing temperature. In method C, the compression is applied at normal laboratory temperature but all measurements of counter force are made at test temperature.

In all the three methods, the test pieces used may be cylindrical disc or rings. The test pieces are sandwiched between polished metal plates and compressed to 15 ± 2 or $25\pm 2\%$ strain within a period of 30s-120s. The initial reading (f_0) is taken after 30 minutes and the test normally runs for a period of not less than 168 hours. The stress relaxation is expressed as % reduction in counter force

$$\%R_t = (f_0 - f_t) / f_0 \times 100 \quad 2.21$$

where f_t is the force at any given time t . When the sample is subjected to different times of exposure, the reduction in counter force could be plotted as a function of $\log(\text{time})$. This will facilitates the interpretation of the results since continuous data is available.

In ASTM D 1390-76, a similar procedure is adopted with the test carried out at 100°C for 46h. The initial reading is taken 3 minutes after the compression. However, this standard has been discontinued in ASTM publications of 1989 onwards.

The test methods describe in the above British Standard assumes that the stress relaxation is independent of strain rate. Generally, for crosslinked rubber, this assumption is valid but not for thermoplastic rubber (PRABHU, 1991). Since this standard covers test for thermoplastic rubber, the dependent of strain rate on stress relaxation has to be considered.

The test piece used in compression is fairly thick (6.3mm). The effect of oxidative ageing could not be accurately determined using such thick sample due to non-uniform degradation. This arises from different extent of oxygen diffusion into the rubber; diffusion of oxygen and subsequent oxidative degradation is dependent on sample thickness. Thus interpretation of data obtained from aged compression sample may be difficult.

b) Stress relaxation in tension

BS 903:Part A52:1986 describes the stress relaxation test under tension. Two variants of the technique are given. One is the continuous strain technique, in which the test piece is held in extension throughout the ageing period in the oven. The other is the intermittent strains conditions, in which the test piece is aged in the oven in the unstressed state. In this intermittent test, the test piece is periodically removed from the oven and stress measured under normal laboratory conditions. The advantage of this method is that it does not require the use of special apparatus since a standard tensile testing machine can be used for the measurement of stress.

Continuous stress relaxation gives a measure of the total residual stress during ageing. Any networks form during ageing, as suggested by Tobolsky in his 'two network theory' will not contribute to the stress in the rubber (TOBOLSKY, 1960). With intermittent strain

technique, the measurement gives the residual stress of the original network plus the stress due to the new network form. Thus the continuous and intermittent strain techniques may differ considerably; the difference in stress obtained being the contribution to the network of any crosslinks produced during ageing.

This part of the British Standard gives three methods of measurement of the change of stress in an extended test piece. Method A is intended for measurement under continuous strain conditions while Method B is the preferred method for measurement under intermittent strain conditions. In both cases, a stress tester is used to record the stress at the temperature of ageing.

Method C is an alternative to method B for the measurement under intermittent strain conditions but the stress is recorded at standard laboratory temperature, after allowing 30 ± 5 minutes cooling time.

In all three methods, the test piece are parallel sided strips cut from a sheet. The thickness of the sample has to be 1.0 ± 0.05 mm or thinner in order to minimise the effect of non-uniform degradation due to differences in the extent of diffusion of oxygen during ageing. The test piece shall be extended to $50 \pm 5\%$ but a smaller elongation of $20 \pm 2\%$ may be used. The initial force is taken at 5 ± 0.5 min after stretching the test piece for methods A and B. With method C, the initial force is taken immediately after a repeated straining cycle of five times.

The retention of stress is given by the ratio of force at time t (f_t) to the initial force (f_0). The results are presented in the form of graph of f_t/f_0 against time t .

It may be noted that for both compressive and tensile deformation, the results from the three different types of test should not be compared. The test procedure described causes the sample to be subjected to different temperature cycles during measurement of force. This will

lead to a considerable variation in results since stress relaxation is known to be dependent on stress and temperature history (DERHAM, 1973). Further variation in stress relaxation will occur due to the differences in the temperature at which the measurement are taken. This arises because the stress in rubber is proportional to temperature (TRELOAR, 1975).

Thus all the three methods of testing give different results and the test method selected will be dependent on the applications of the product. In cases where the products are to be exposed to elevated temperature continuously, measurement of force should be made at the test temperature. However, if the products involves are to be subjected to variation of temperature cycles, then it is more appropriate for the measurement of force to be made at standard laboratory temperature.

c) Comparison between test in compression and tension

Stress relaxation test in tension has several advantages compared to test in compression and some of them are discussed here. Firstly the large surface to volume ratio of the samples used in tension enables tests at different temperatures and environments to be expedited. Use of thin sample (<1.0 mm) will also minimise the effect of oxygen diffusion and non-uniform degradation. Thus more reliable information could be obtained with test in tension.

Secondly the intermittent strain technique could not be successfully carried out in compressive mode due to experimental difficulties such as ensuring the sample to remain fully lubricated after repeated strain cycles and maintaining sample alignment.

Thirdly most of the theoretical treatment available such as 'two-network theory' has been derived based on rubber subjected to tensile force. Such theory would not be suitable for data obtained in compression.

However, test in compression is, currently more cost effective than in tension due to the types of relaxometer available. Eventhough tensile stress relaxation has some merits compared to test in compression, the economics has discouraged the former to be fully exploited. This justified a need for a more cost effective tensile stress relaxation test and the development of such test is described in chapter three.

2.5 CONCLUSIONS

Stress relaxation involves the movement and breakages of the molecular chain of the rubber. The phenomena are dependent on the types and concentrations of crosslink. Thus any chemicals or constituents which changes the physical and chemical structures of the rubber networks will influence its stress relaxation characteristics.

Some naturally occurring non-rubber constituents, particularly nitrogenous materials, has been reported to have an influence on the raw rubber properties (BOUCHER AND CARLIER, 1964) and sulphur vulcanization of the compound (ALTMAN, 1948; LOO, 1982). Those non-rubber constituents may also give an affect on the relaxation behaviour of the rubber. However, no study has been

undertaken to check these effects. Thus, a study on the effect of non-rubber constituents on the relaxation behaviour of the rubber could be interesting.

Protein is the non-rubber constituents which has been reported to have an influence on the relaxation behaviour of rubber (SMITH, 1974; METHERELL, 1980). The removal of proteins reduces the rate of creep and stress relaxation. Those findings were based on comparative studies carried out between deprotenised and non-deprotenised rubbers. However, such studies could not give conclusive results since deprotenisation process will removed most of the non-rubber materials including proteins. A more conclusive study to check the effect of proteins and its hydrolysed components, by reintroducing them into 'clean' rubbers could be useful.

In the presence of fillers, the effect of the natural occurring non-rubber constituents in natural rubber, if any, has been assumed to have been diluted and masked. Stress relaxation, being a sensitive tools in the study of changes in the rubber network, could be employed to check this assumption.

To be a sensitive tool, the stress relaxation tests has to be carried out in tension. However, the set-up described in BS903: Part A52 (1986) is not versatile and unattractive. It requires a tensile testing machine and the sample has to be permanently attached to the load measuring devices. Thus large number of test could not be carried out simultaneously. A versatile stress relaxation test in tension which has a similar set-up and jigs as described in BS903: Part A42 (1991) for test in compression would be more attractive.

CHAPTER THREE

DEVELOPMENT OF TENSILE STRESS RELAXATION TEST

3.1 INTRODUCTION

Stress relaxation is a method which is often employed for the investigation of the time dependent properties of rubbers. The same technique is frequently employed in ageing studies on rubber as a monitor of the effect of degradation on mechanical properties.

Previously, work has been carried out to develop suitable equipment for stress relaxation (TOBOLSKY et. al,1944; BERRY,1956). Earlier development work on the technique of monitoring continuous stress decay in rubber involved permanent attachment of the sample to the load measuring device, thereby limiting the number of tests which could be carried out at one particular time. This, and perhaps, the relatively expensive equipment which is required, contributed to the lack of widespread adoption of stress relaxation as a routine measurement.

More recently, there has been significant progress in the development of the stress relaxation test. They are the techniques and equipments developed by Loughborough University of Technology (LUT) and Rubber and Plastics Research Association (RAPRA) (FERNANDO,1984; ARMAH et.al.,1986; RAPRA,1986). These newer techniques measure the stress relaxation of rubber in compression and have since been adopted by International Standard Organization as their standard test methods (ISO,1989). The technique involves compressing rubber

cylinder in a specially designed jig, which could be easily dismantled from the load measuring device, but maintaining the forces on the rubber. The stresses in the rubber under compression were taken up by the jig set-up and it could be periodically monitored using the load measurement set-up developed. The RAPRA technique uses an arbitrary sample compression rate while the LUT technique has a fixed compression rate, which could be changed if necessary. A fixed compression rate is preferable due to the variation in relaxation behaviour with compression rate.

Those techniques have the advantage in cases where large numbers of samples are to be tested. The stresses in all the rubber under compression could be periodically and simultaneously monitored since the jigs holding the samples are detachable and the samples are not permanently attached to the load measuring devices. The limit to the number of samples to be tested will be the availability of the sample jigs, not the load measuring device; the former are cheaper and simpler to fabricate than the latter.

The techniques and equipment developed so far, such as those developed by LUT and RAPRA are applicable only to rubber samples subjected to compression deformation. Those developments were made due to the practical need of such testing data, particularly for monitoring products performance of sealing rings and similar materials, which are used in compression.

A similar technique for rubber under tensile load has recently been developed, and this chapter discusses the new developments in the technique for monitoring stress decay for a sample under tensile deformation. The stress-relaxation under tension was considered because of the following:

- i) Effects of the environment could be expedited, and accelerated by using thin strips of samples with high surface area to volume ratio.

ii) Errors in the measurements of strain could be minimised since the sample will be relatively long. In compression, the error in the measurement of strain will be bigger due to shorter sample height.

iii) Effect of extension ratio and rate of strain could be easily studied since the sample is long. In compression, these effects will be comparative more difficult to be investigated due to small working deflection.

iv) The problems associated with surface friction and barrelling which occurs in compression will be absent.

3.2 STRESS RELAXATION MEASUREMENT IN TENSION: CONVENTIONAL TECHNIQUES

The conventional techniques of measuring stress relaxation under tensile load, are mostly based on the principles of either the balance beam or helical spring.

3.2.1 Balance beam relaxometer

The balance beam relaxometer was first used by Tobolsky (TOBOLSKY et al,1944) to study the stress relaxation behaviour of natural and synthetic rubbers and this constitutes a significant development in the stress relaxation test. The relaxometer consisted of a modified beam balanced in an air thermostat with the balanced pans outside the box. A neon light was installed to provide the indication for the point of balance. The set-up gave a direct measurement of stress but it requires a very careful manipulation and was not suitable for tests at low stresses.

Subsequently, based on Tobolsky's principle, an improved balanced beam relaxometer was developed by Robinson and Vodden (ROBINSON et.al.,1955). With this relaxometer, the stress in the rubber was supported by bowed steel strips whose lateral deflections were measured by strain gauges and recorded automatically on a chart. The apparatus has the provision for six measurements to be carried out simultaneously.

A similar relaxometer was also developed by Danjard (DANJARD,1956). The relaxometer essentially constituted a beam scale with asymmetric arms mounted on a ball bearing (Figure 3.1). The test-piece is enclosed in a heating chamber to provide different environment and the stress in the sample is balanced on the opposite side by a counter weight slide on a worm screw. The sensitivity of the apparatus is improved by use of an electric contact compared to visual judgement.

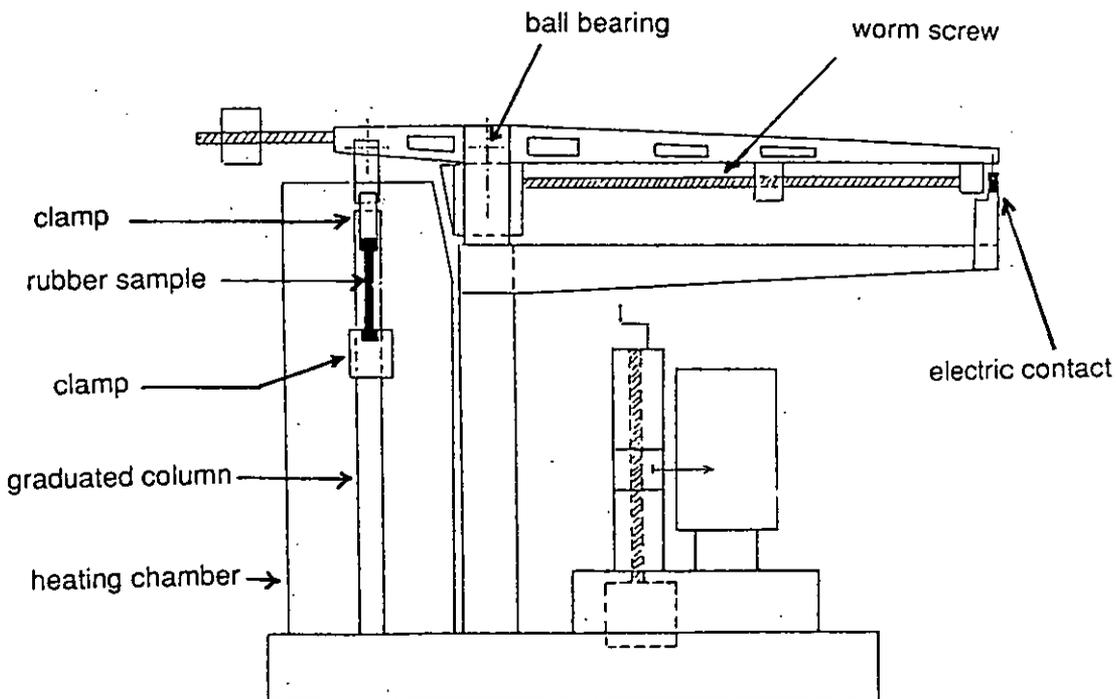


Figure 3.1: Schematic diagram of the balance beam relaxometer (DANJARD, 1956)

3.2.2 Helical spring relaxometer

Helical spring relaxometer was first described by Berry (BERRY,1956) and later improved by Dunn and Scanlan (DUNN et.al, 1960) (Figure 3.2).

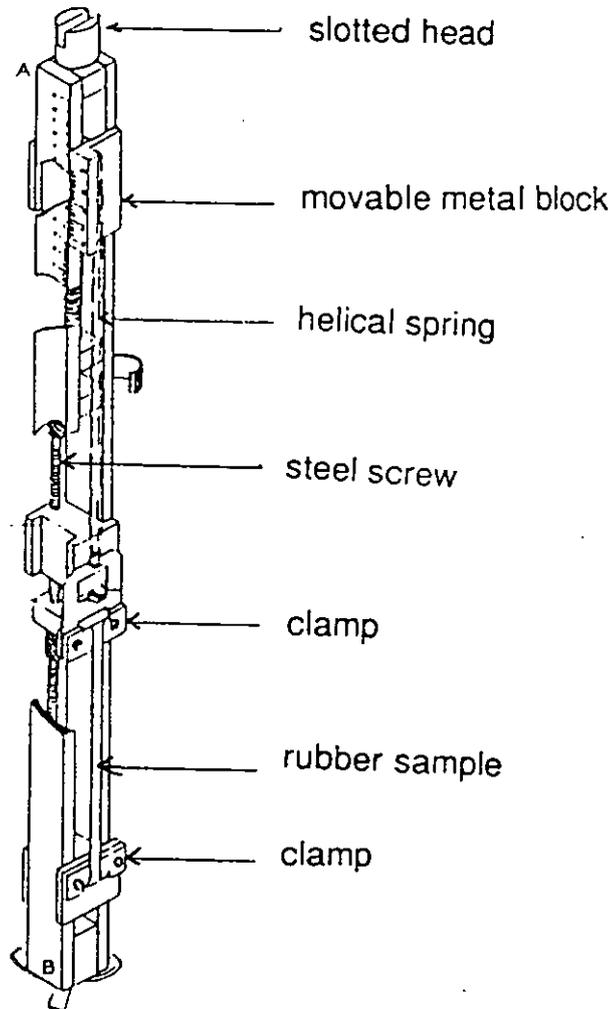


Figure 3.2: Helical spring relaxometer (DUNN AND SCANLAN, 1960)

The rubber sample is stretched between two clamps and the stress in the rubber is balanced by the force in the extended helical spring operating within its Hooke's Law range. The extension of the spring is measured on the vernier, the reading of which is directly proportional to the force. A series of spring is available so that whatever the modulus of the rubber, the initial vernier reading is high on the scale. The apparatus can be placed inside a glass tube in order that measurements may be made in a vacuum or in any desired atmosphere under careful temperature control.

3.2.3 Wallace Shawbury self-recording agestester

Based on the principles and designs put forward by earlier scientists, a commercial tensile stress relaxometer was developed by Wallace (WALLACE,1971) The apparatus called 'Wallace Shawbury Self Recording Agetester' incorporates facilities for stress relaxation and ageing test (*Figure 3.3*). Six tests could be carried out simultaneously using six relaxometers and each test-piece could be housed in different ageing oven-cell.

The test-pieces, in the form of rubber strip or dumb-bell shape samples, are held between two grips in such a manner that they are totally inside the oven-cell. The upper grip is supported by a horizontal beam which is mounted on and balanced about a high grade miniature ball bearing. The downward force exerted by the strained test-piece is balanced by the upward force applied by a vertical helical spring. As the rubber relaxes, the beam tilts. This movement energises a small electric motor which adjusts the position of the spring anchorage to reduce the force applied by the spring until a condition of balance is restored to the beam.

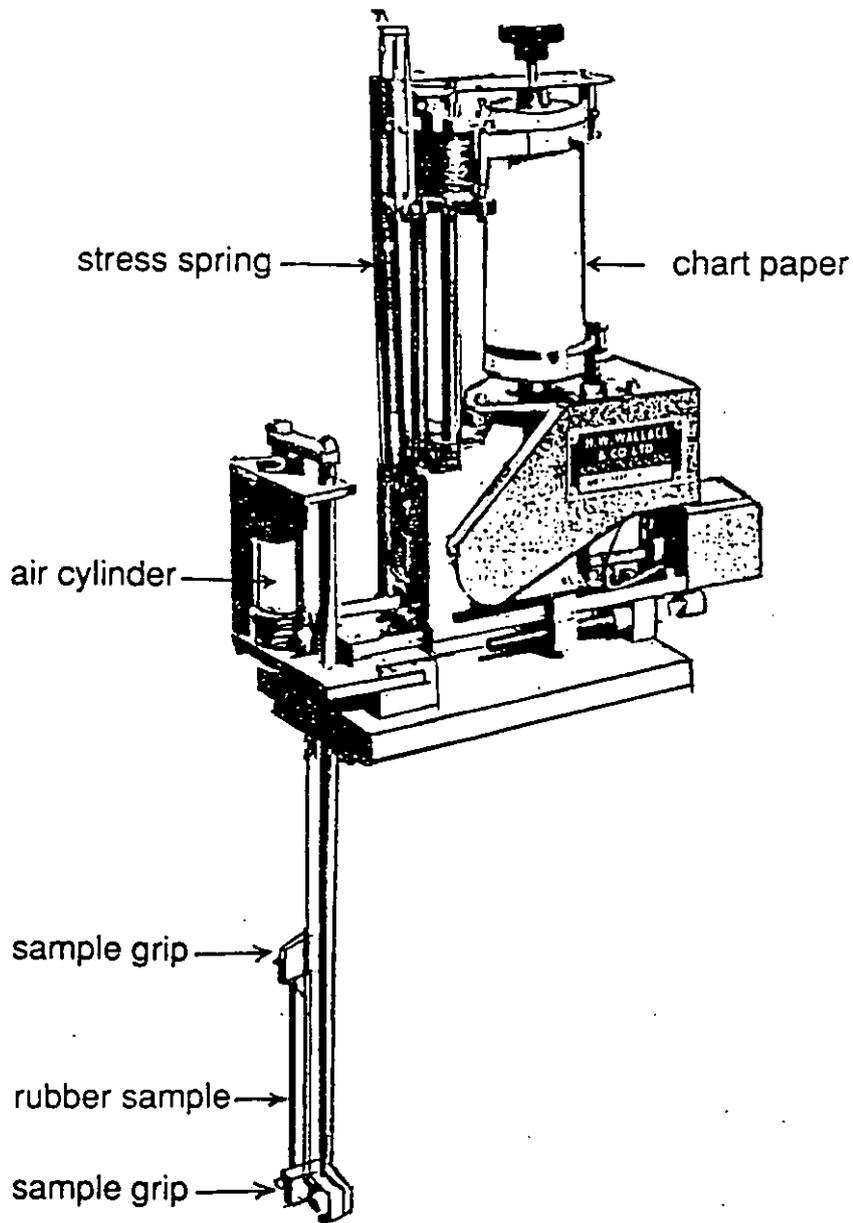


Figure 3.3: The Wallace Shawbury agetester (WALLACE, 1971)

3.2.4 Recent developments

Modern tensile testing machines such as those supplied by Instron model 1122 or Lloyd JJ technically, are ideal equipment for the stress relaxation test. However, those machine are very expensive. Running long term stress relaxation on the testing machine means a major blockage for other tests to be carried out.

To overcome this problem, Loughborough University of Technology (LUT) constructed a jig which could be coupled with the tensile testing machine to carry out stress relaxation test in tension (PRABHU, 1991). The jig was designed so that it could be freed from the testing machine after the test, while leaving the test specimen under tension (Figure 3.4).

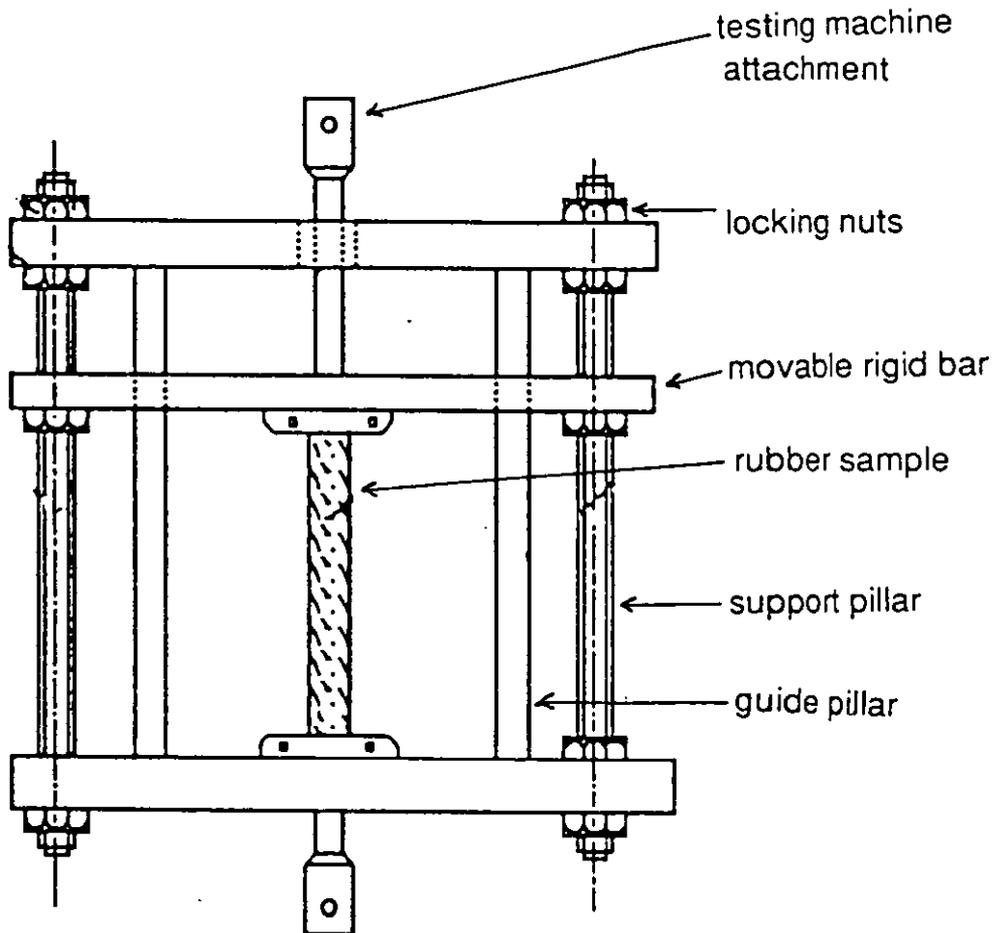


Figure 3.4: Loughborough University of Technology (LUT) modified tensile stress relaxometer jig (PRABHU, 1991)

It consists of two supporting pillars held together by three horizontal rigid bars to form a rectangular frame. A rubber strip is held between the rigid horizontal bars and guided by two pillars during extension. Extension was achieved by pulling the rubber strip via the vertical rod attached to the sample grip and maintained at the extended position using the locking nuts. The stress or load in the rubber strip was monitored at fixed time by applying a load to the extended rubber to break the contact between the movable horizontal bar and the locking nuts and the recorded load was taken as the value of the relaxed load at the time considered. However, the technique was severely limited by the significant amount of friction developing between the supporting pillars and the movable horizontal bars.

Based on the concept of the balanced lever arm, another simple stress relaxometer was developed by LUT (PRABHU,1991). A schematic diagram of the relaxometer is shown in *Figure 3.5*. The relaxometer consists of a balanced lever arm and a slide, supported on a strong, rigid base at the centre of a platform. The wooden base was reinforced with metal to restrict distortion.

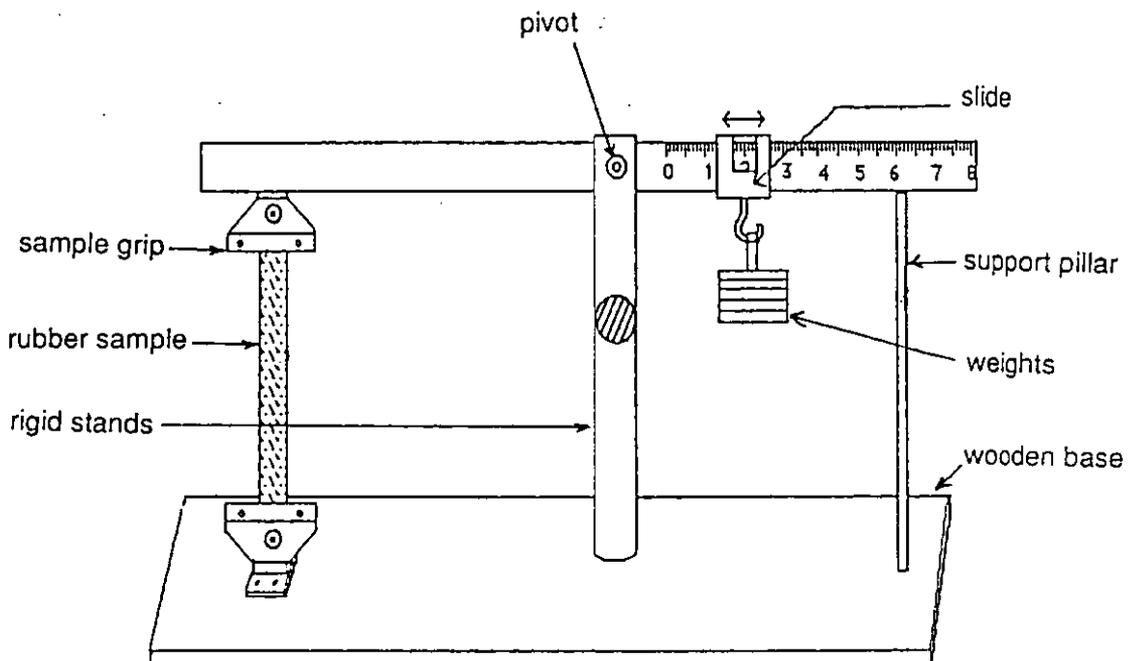


Figure 3.5: Loughborough University of Technology (LUT) pivoted arm balance beam relaxometer (PRABHU,1991)

Rubber strips of 100x10mm were used. It was held between manually tighten grips and the gauge length was selected to ensure the arm to be horizontal when loaded using dead weights. The stress in the rubber was calculated using the principle of moments.

3.2.5 Shortcomings of conventional techniques

The earlier relaxometers, such as the balanced beam type developed by Tobolsky (TOBOLSKY,1944) and the helical spring type developed by Berry (BERRY,1956) were reliable and accurate and could be used under different and adverse environmental conditions. However, their sophistication, relatively expensive price, and the continuous dependence of the sample jigs/holder on the load measuring devices make them unsuitable for long term testing, particularly on large numbers of sample.

The later development such as the modified tensile jig to be coupled to the tensile testing machine is an interesting proposition since the jig was designed to be freed from the load measuring devices and the test could be carried out using modern testing machine. However, the problem of the high frictional forces developing between the vertical pillars and the horizontal movable bars makes it unsuitable to be used for stress relaxation studies. The amount of friction was far too high for any significant amount of relaxation to be traced using the jig.

The LUT balance lever arm technique is simple and the set-up is very cheap to fabricate but the equipment is cumbersome and bulky. It occupies too much space; it measures about 100x30x30cm. Its size makes it unsuitable to be used under different test environments, such as in an oven. The set-up is not suitable to be used for long term testing because large area of space has to be created to keep the sample undergoing testing.

The adjustment of the balance weight on the slide is carried out manually and the balanced point decided based on visual observation. Thus the accuracy of the test is highly dependent on the operator. Small change in stress will not be able to be measured due to the crude nature of the set-up.

3.3 A NEW TECHNIQUE FOR STRESS RELAXATION TESTS

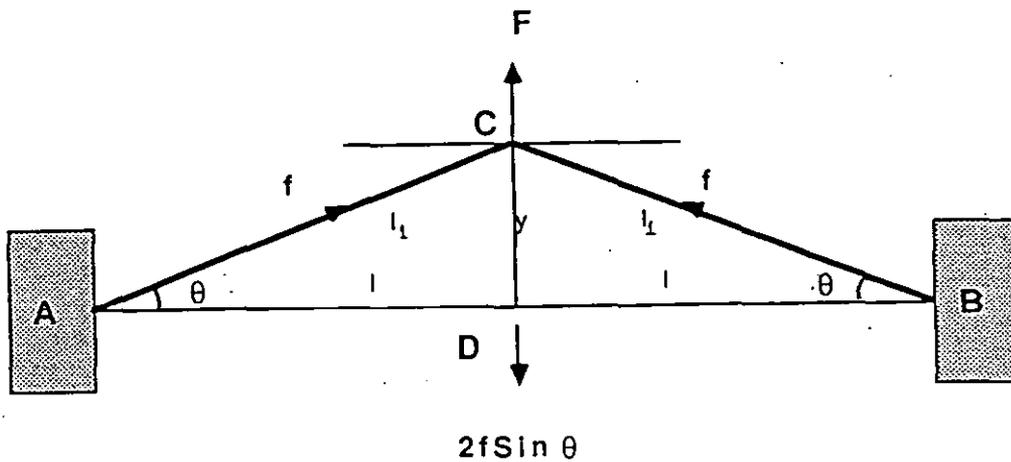
The shortcomings of the present tensile stress relaxometer left the quality control personnel and scientists with no suitable method for long term stress relaxation testing particularly on large number of samples. This makes it desirable for a new simple, relatively cheap and reliable relaxometer to be developed. The new relaxometer should overcome the problems encountered by the earlier equipment.

A new technique of stress relaxation test which utilises a different principle for the measurement of load has been developed and describe below.

3.3.1 Principles of test

The new technique is based on a three point bending or 'bow-string' configuration and utilises a simple principle of trigonometry to resolve the forces/stresses in the extended rubber strip.

Consider a horizontally extended rubber strip which is being pushed, at mid-point vertically (*Figure 3.6*).



- 2l - extended length of sample
- y - vertical displacement
- F - applied force
- θ - angle of deflection
- f - force in the extended sample
- $2l_1$ - extended length of sample under force F

Figure 3.6: Resolution of forces along a stretched piece of rubber strip

When a vertical force F is applied to an extended strip of rubber of length 2l, to give a deflection θ , the new length of the rubber strip will be $2l_1$. If f is the tensile force in the rubber held between A and B, then resolving the forces in the vertical direction will give:

$$F = 2f \sin \theta \tag{3.1}$$

At small angle, $\sin \theta \approx \theta$

Therefore $l_1 \approx l$

Thus equation (3.1) can be written as

$$F = 2fy/l \tag{3.2}$$

where y is the vertical displacement, or

$$f = Fl/2y \tag{3.3}$$

Thus, provided the angle θ is small, the tensile force in a piece of stretched rubber strip could be determined using equation (3.3), with known force F , length l and vertical deflection y .

3.3.2 Effect of test variables

This new technique of measurement stresses in an extended rubber strip is dependent on a number of variables such as a) angle of deflection, b) off-centre application of load, c) sample thickness, and d) plunger dimension. The effect of these variables are discussed below.

a) Angle of deflection

The above technique of measuring a tensile force in a stretched piece of rubber assumes the angle of deflection θ to be small. Only at small θ , does,

$$\sin\theta \approx \theta \quad (3.4)$$

since the other components of the expansion series will be negligible. A simple calculation showed that when the angle of deflection is 10 degrees or less, the differences between $\sin\theta$ and θ is $<0.5\%$. These values are shown in *Table 3.1*, which also lists the change in sample length resulting from the angular displacements.

Table 3.1 : Effect of Angle of Deflection

Deflection θ	$\frac{\sin \theta}{\theta}$	Change in strain %
5	0.999	0.38
10	0.995	1.54
15	0.989	3.56
20	0.980	6.42
30	0.955	15.47

Graphically, the deviation in load for rubber extended to different elongation is shown in *Figure 3.7*. The points refer to the experimental data while the lines are the linear load-deflection plots. Any deviation will be shown by the differences between the lines and the experimental data. However the figure showed the experimental data and the predicted lines to be almost identical. This shows that equation (3.4) is valid for the range of deflection investigated (<10 degrees) and deviation observed from the line is negligible.

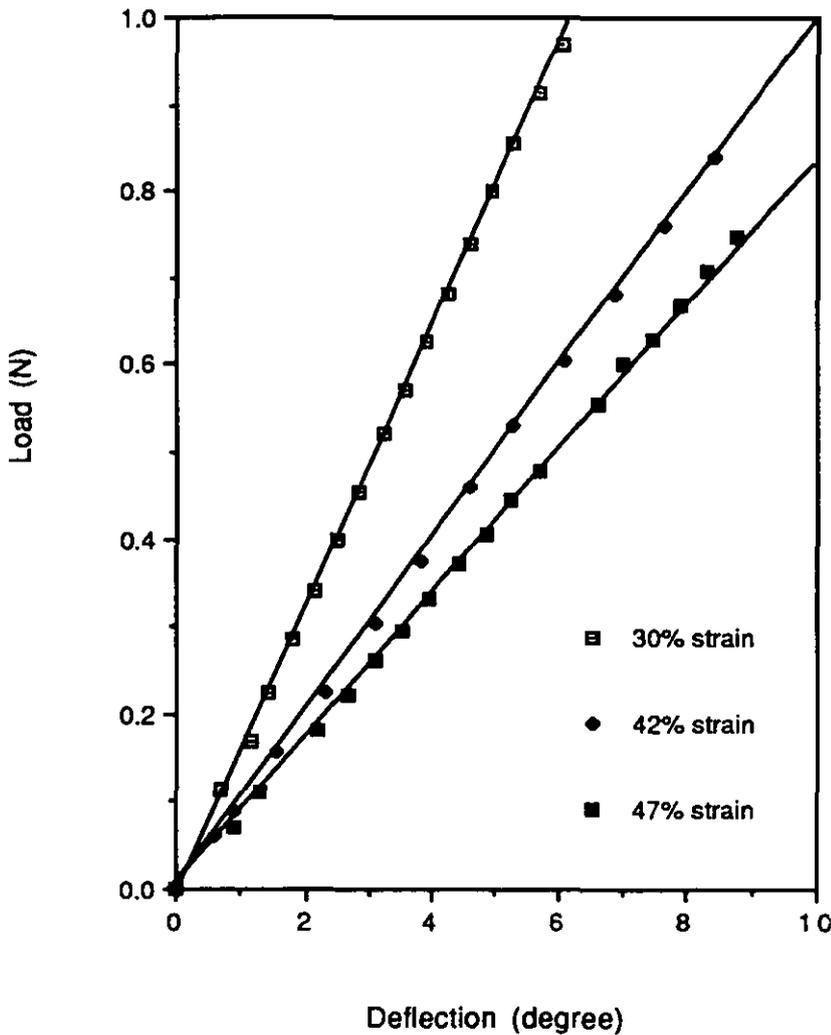


Figure 3.7: Deviation of load from linearity due to the increase in deflection for sample extended at different strains

b) Off-centre application of force

The resolution of forces in an extended rubber strip subjected to a vertical forces at mid-point to form a 'bow-string' configuration is shown in *Figure 3.6*. Point C should be midway between A and B. Practically, locating the mid point of the rubber strip may be difficult, but possible. In the event that the loading is at off-centre position, how much variations in the pushing force will occur?

Consider an off-centre loading shown in *Figure 3.8*.

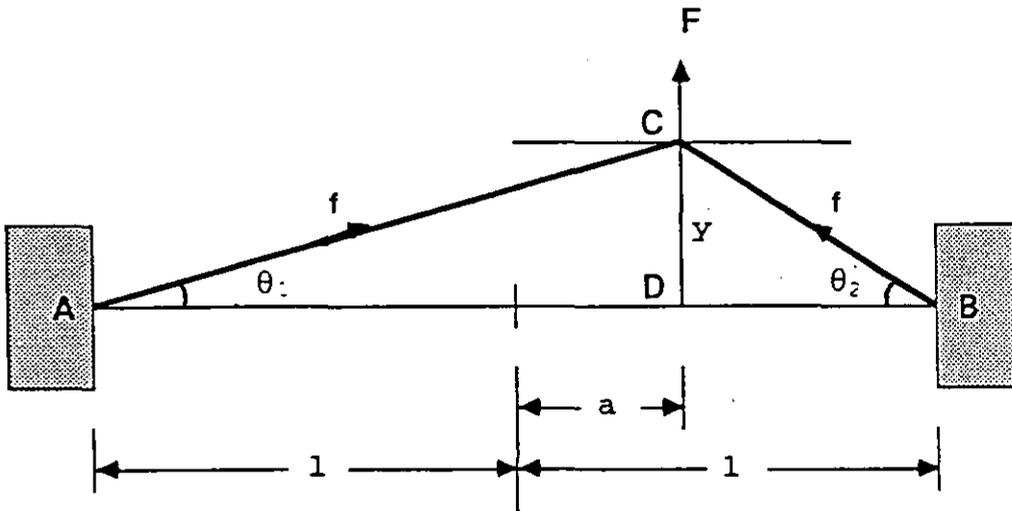


Figure 3.8: An off-centre application of load

If the force F is applied at a point C, where C is a distance away from the midpoint AB, then,

$$F = f\sin \theta_1 + f\sin \theta_2 \tag{3.5}$$

$$\begin{aligned} y &= (l+a)\cos \theta_1 \\ &= (l-a)\cos \theta_2 \end{aligned} \tag{3.6}$$

At small angle,

$$y = (l+a)\theta_1 \approx (l-a)\theta_2 \quad 3.7$$

Then from equation (3.5),

$$\begin{aligned} F &= f(\theta_1 + \theta_2) \\ &= f\{y/(l+a) + y/(l-a)\} \\ &= 2ly/(l^2 - a^2) \end{aligned}$$

or rearranging,

$$f = F(l^2 - a^2)/2ly \quad 3.8$$

Thus the force f changes with the square of the difference between the extended length l , and the off-centre distance a . Theoretically, for any length l , an off-centre distance of 10% gives a 1% change in force f while a 20% off-centre loading gives about 4% change in force (Table 3.2).

Table 3.2 : Effect of an off-centre loading

Off Centre position, a, (% of length, l)	Variation of force (%)
2	0.04
4	0.16
6	0.36
10	1.0
14	1.96
20	4.0
30	9.0

At small (<30%) off centre position, the predicted increase in force due to an off-centre loading was observed to be comparable to the experimental values (Figure 3.9). This shows that the change in force due to the off-centre loading is small, and under normal testing, for which the sample length is long (>100mm), the variation due to a possible off-centre loading will be small.

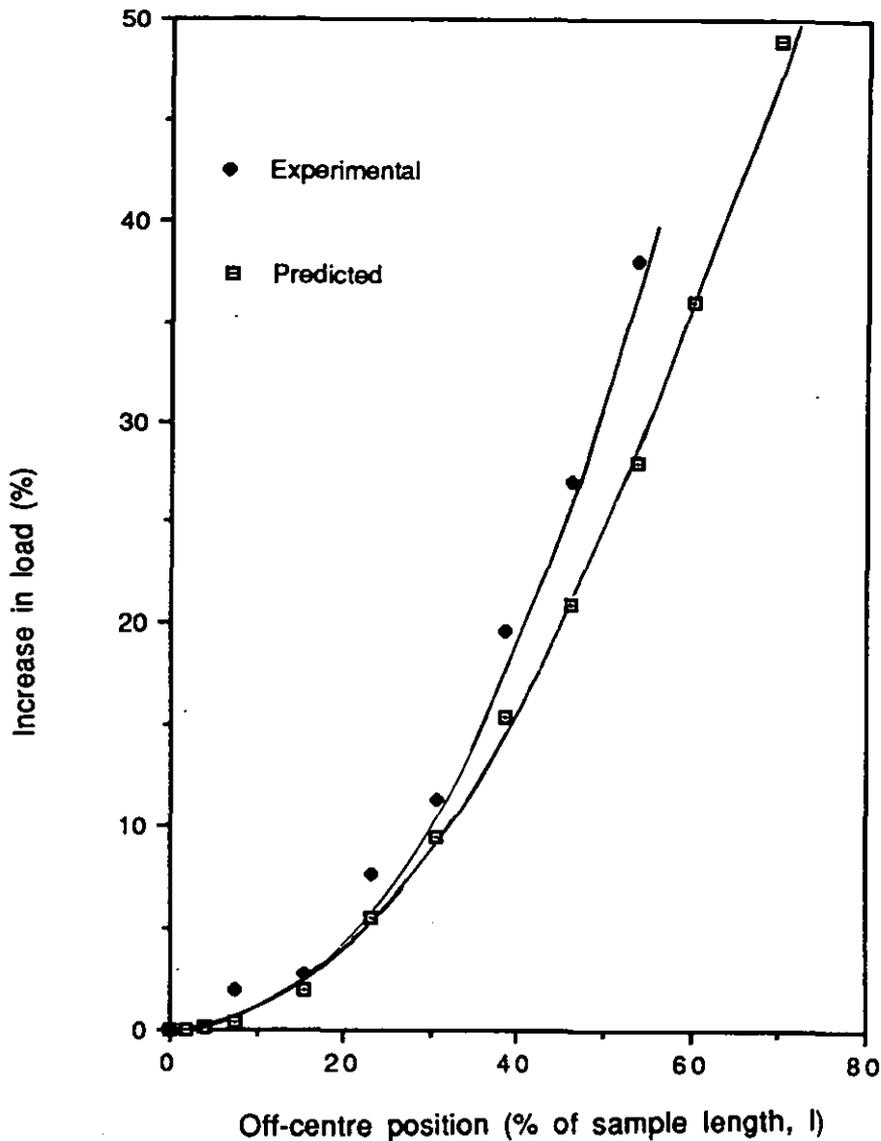


Figure 3.9: Increase in load as a function of the off-centre position

c) Sample thickness

The standard tensile testing of rubber uses test specimen of about 2mm thick. This new relaxometer is designed to utilise the same type of sample dimension. However, to ensure that no significant difference in the stresses due to a possible variation in the sample thickness occur, a study was undertaken. This study involves testing the rubber obtained from the same batch but moulded to different thicknesses (0.5 to 3 mm) using the same state of cure (t_{100}).

Results obtained showed that sample of thickness ranges from 0.5mm to 3.0mm gave a minimal difference to the value of the resolve stresses obtained from the configuration adopted (*Table 3.3*). The results for NR filled with 40phr N550 black which was extended to 30% strain and monitored over a 100 minutes period gave a small variation in the value of stresses obtained (CV<1%). This suggests that when the rubber sample was less than 3.0mm thick, no significant variation in the resolve stresses was observed.

Table 3.3 : Effect of sample thickness on stress

Time (min)	Thickness,mm						Ave (MPa)	CV (%)
	0.5	1.4	1.7	2.0	2.7	3.0		
1	0.769	0.781	0.768	0.762	0.780	0.768	0.771	0.89
2	0.756	0.773	0.761	0.755	0.767	0.756	0.761	0.87
3	0.751	0.765	0.757	0.747	0.761	0.751	0.756	0.84
5	0.747	0.759	0.749	0.742	0.757	0.745	0.750	0.85
7	0.742	0.756	0.747	0.737	0.750	0.742	0.746	0.85
10	0.739	0.752	0.742	0.734	0.746	0.736	0.742	0.81
20	0.730	0.746	0.736	0.728	0.743	0.733	0.736	0.90
30	0.726	0.738	0.733	0.723	0.738	0.728	0.731	0.81
50	0.724	0.735	0.727	0.718	0.735	0.725	0.727	0.81
70	0.722	0.730	0.723	0.715	0.729	0.722	0.723	0.70
100	0.717	0.727	0.719	0.710	0.723	0.717	0.719	0.73

d) Plunger dimensions

A different size plunger used to push the extended rubber strip into a 'bow-string' configuration may give rise to a variation in the resolved forces due to a possible bending or/and penetration of the plunger into the rubber sample. A large plunger may give rise to a large area of contact and hence more significant bending forces than a thinner plunger.

A study was undertaken to investigate the effects of plunger geometry on the value of the resolved forces. Two different types of plunger geometry, namely a flat and spherical end, were used. They are shown in *Figure 3.10*.

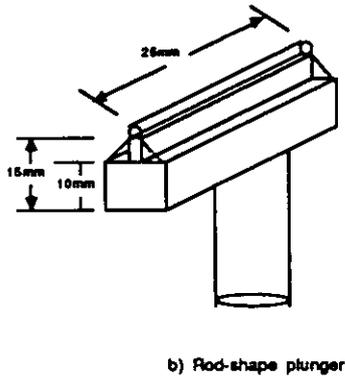
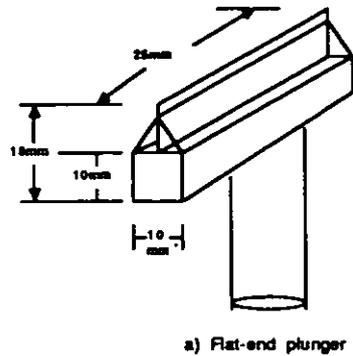


Figure 3.10: Two different types of plunger

With flat-ended plunger, the value of forces obtained progressively increase with the width of the plunger (*Figure 3.11*). A thin plunger (ca 0.1mm thick) gave a significantly lower value of stresses than a comparatively thicker plunger (ca.2.0mm thick). The low value of stresses obtained with thinner plunger may be due to the slight penetration of the plunger tip into the rubber sample during pushing, this giving inaccurate deflection values, while a thicker tip plunger gave a relatively bigger forces due to a possible bending effects (*Figure 3.12*). These values are consistent at all angles of deflection investigated.

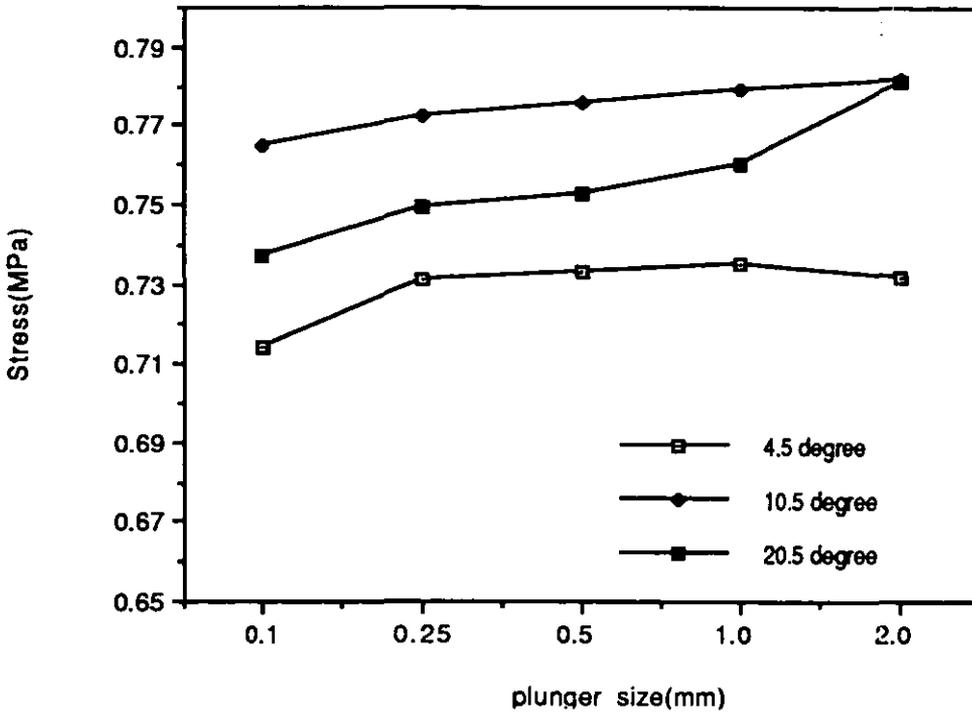


Figure 3.11: Effects of plunger thickness on stresses at different deflections

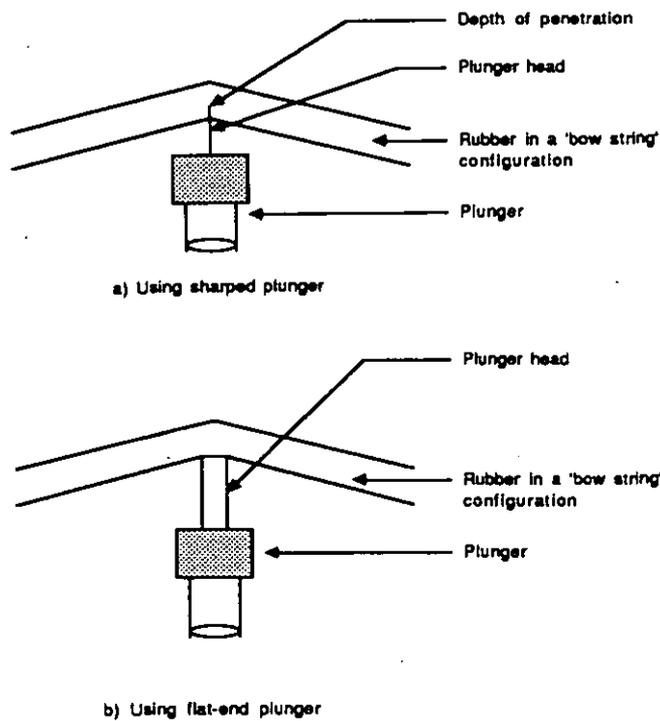


Figure 3.12: Schematic diagram showing the types of indentation made by different plungers (side view)

With spherical or rod shape plunger, the stresses obtained were approximately the same for the range of different diameter investigated (*Figure 3.13*). The result were observed to be the same for up to 20 degree deflection and this suggest that the resolved forces are independent of the plunger diameter over the ranges covered.

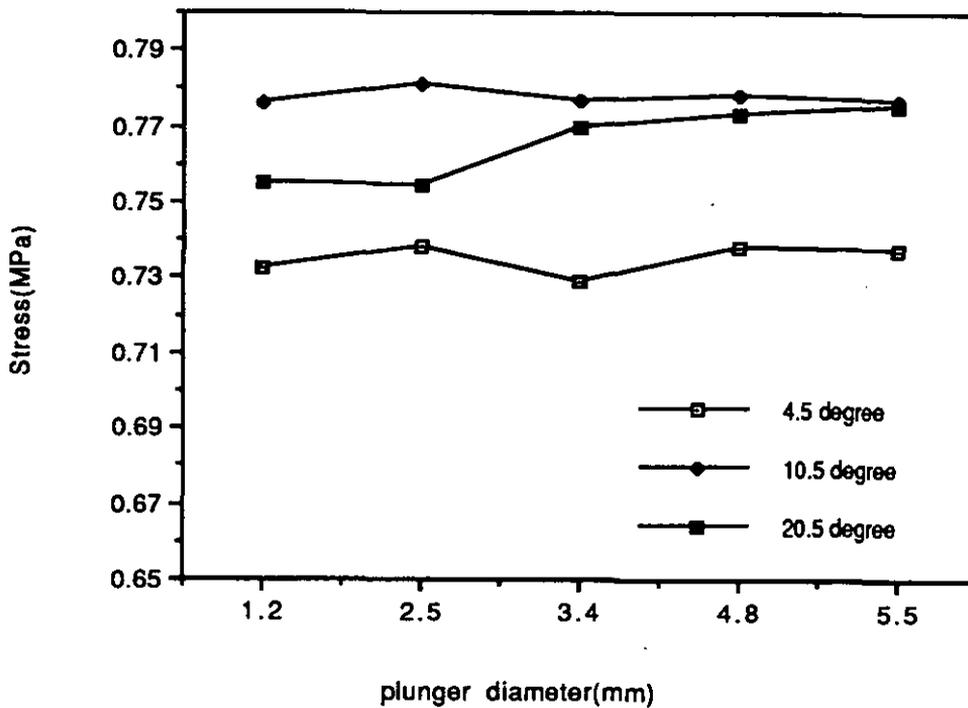


Figure 3.13: Effects of plunger diameter on stresses at different deflections

3.4 THE EQUIPMENT

3.4.1 Practical consideration in the development of the equipment

An important component of this new technique of stress relaxation measurement is the sample frame or jig. The frame should be,

- a) able to grip the sample without any slippage and easily operated,
- b) able to withstand adverse environmental conditions,
- c) cheap, easily fabricated and not bulky,
- d) easily fitted to and dismantled from load measuring devices

These requirements are necessary to overcome the shortcomings encountered by currently available relaxometers.

3.4.2 The sample frame

The sample frame/jig used for this study consist of a rectangular housing onto which the samples are gripped (*Figure 3.14*). The housing structure was constructed from two threaded stainless steel rod of 10mm diameter and 250mm long. The steel rods were held together, at their ends, by two stainless steel housing bars.

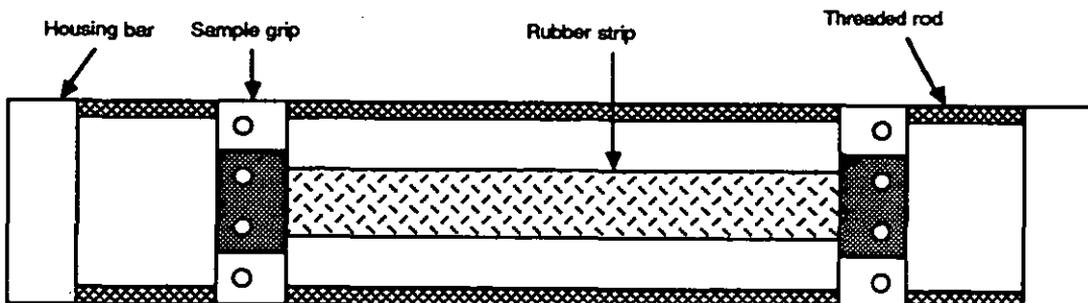


Figure 3.14: Plan view of the sample holder/frame

The sample grips move along the threaded rod, enabling the extension of the sample to be set accordingly. The present sample frame allows a maximum extended length about 150mm. The sample grips are secured onto the threaded rod using locking nuts.

Rubber strips are secured on the grooved sample grips manually using locking nuts. This reduced the possibility of sample slippage.

The sample frame was designed to fit an adapter which could be fitted to the tensile testing machine.

3.4.3 Load measuring devices

The measurements of load in a stretched piece of rubber strip for the new technique of stress relaxation studies could either be carried out using any standard load measuring devices such as Tensile Testing Machine or similar testing equipment.

a) Standard testing machine

Any modern standard tensile testing machine can be utilised as a load measuring device for the new technique of measuring stress decay provided a suitable attachment is available. For the purposes of this study, a simple attachment was constructed to fit the base of a testing machine. A typical test set-up is shown schematically in *Figure 3.15*.

The rubber sample, which was held in the sample jig was rigidly restrained at the base platen of the testing machine. The load was applied at the mid-point of the sample using a metal hook/plunger attached to the moving crosshead which carries a load-cell. Load and deflection values were recorded on the chart paper.

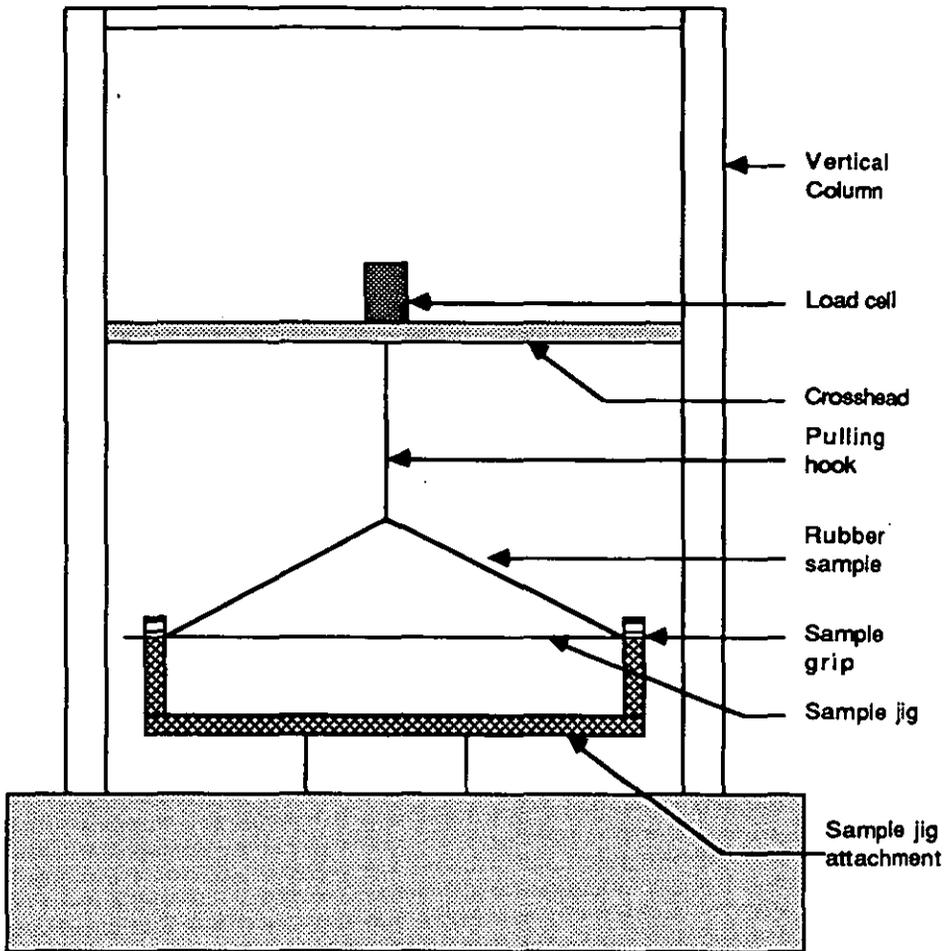


Figure 3.15: Schematic diagram showing the 'bow-string' set-up using modern tensile testing machine

b) Portable testing machine

This new stress relaxation test could be more versatile if a portable load measuring device is available. Thus a prototype portable testing machine was designed and constructed. It consisted of the load frame unit which can hold a sample frame and the electronic control console (Figure 3.16).

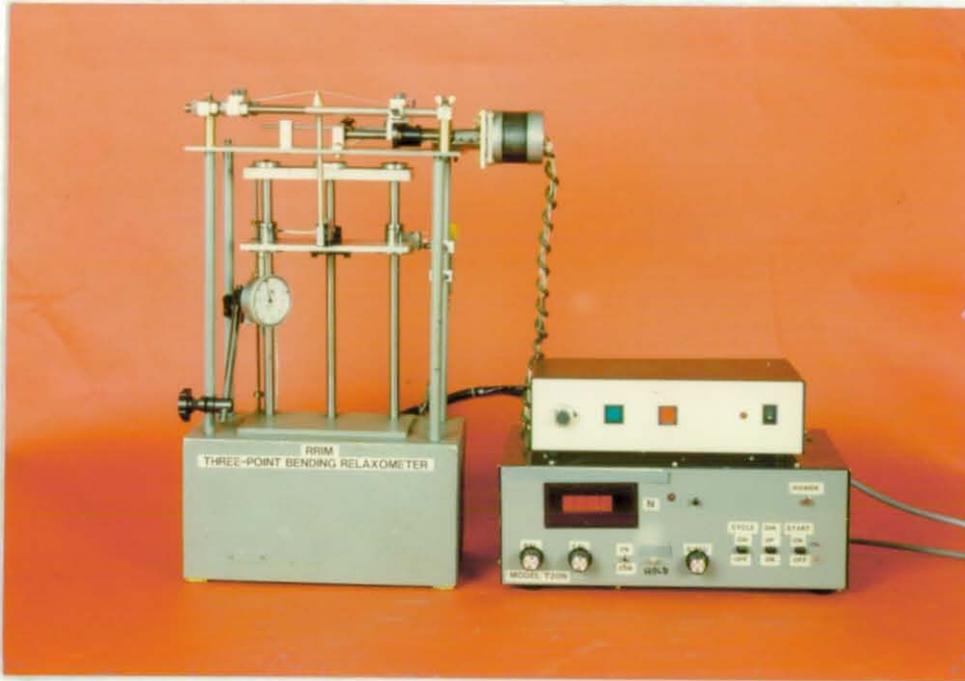


Figure 3.16: Portable (prototype) 'bow-string' tensile stress relaxometer

The rectangular load frame comprises a base unit, seven vertical columns and an upper transverse beam. A base platen is set into the upper section of the base unit. A moving crosshead, guided by two vertical rods, is located between the base unit and the upper transverse beam. The crosshead, to which is attached the mini-beam load cell, is driven by low friction threaded screw.

Specimens to be tested are secured to the sample frame which is held rigidly on the upper transverse beam. The sample vertical deflections are controlled by a preset gauge, having a fixed vertical movement of about 0.5mm per step. The actual vertical displacement is measured using the dial gauge, with an accuracy of 0.01mm.

The electronic control console consists of a load measurement system, crosshead control system and sample extension system.

The load measurement system comprises the load-cell, load-cell amplifier and a digital panel meter. The load-cells are interchangeable and the present model uses a 0-22N load capacity, with an accuracy of 0.01N. A load range switch has been incorporated to cater for different ranges of loading sensitivity. This prototype model has two sensitivity ranges, namely 2N and 20N full scale loading. The loading system is calibrated using standard weights, and the output is displayed on the digital panel meter.

The crosshead system controls the vertical movement via a threaded screw. The movement of the crosshead is set at a fixed distance by an opto-electrical switch.

The sample extension system enables the gripped samples to be extended at a fixed rate. Due to designed constrained, the extension rate could only be varied from between 100mm to 500mm per minute.

3.5 SAMPLE ASSEMBLY AND LOADING PROCEDURE

Rubber strips, about 2mm thick, 10mm wide are used as test-pieces. The test-pieces are secured onto the sample grips, and the jig rigidly mounted onto the top platen of the loading frame. The test-piece is extended after the jig is fixed into position using the sample extension system. The extension ratio of the sample is measured using a cathetometer, based on the gauge length marked on the sample strip prior to loading.

The vertical force is applied approximately mid-point to the extended rubber strip via a wedge-shaped plunger. The vertical movement was set at about 0.5mm per step. The load to push vertically the extended rubber strip at three different displacements are recorded and the stresses at each displacement calculated. The average of the three stresses is taken as the stress in the rubber at a fixed time. For the stress relaxation experiment, the vertical force is applied to the rubber strip at known time intervals, so that a series of stresses at a specified time intervals could be obtained.

3.6 COMPARISON OF DIFFERENT METHODS OF MEASURING STRESS DECAY

A comparative study of stresses obtained using the established conventional technique and the new, 'bow-string' technique was carried out. Sample strips, of 2 ± 0.1 mm thick, die-stamped from the same moulded sheet were used. The samples were extended at the same strain rate (100mm/min), to a different extension at room temperature (23°C). The decay in stresses were monitored for upto 100 minutes and results are given in *Tables 3.4 and 3.5*.

Table 3.4 : Comparison between stresses of unfilled synthetic polyisoprene obtained using two different equipment

Strain (%)	Stress after 100 min relaxation,(MPa)	
	Instron 1122 ^a	New Technique ^b
30	0.401	0.385
42	0.477	0.460
48	0.540	0.530
70	0.688	0.675
100	0.866	0.879

- Note: a) stress in a rubber strip monitored using Standard Tensile Testing Machine.
 b) Stress calculated from the resolution of forces in a 'bow-string' configuration.

Table 3.4 gives the results for unfilled polyisoprene, a synthetic rubber having very small changes in stress with time. The value of stresses were calculated after 100 minutes extension, and for the strain range investigated, the stresses obtained using the two different methods were within experimental variation ($\pm 5\%$).

Table 3.5 : Comparison between stresses of filled NR (65 IRHD) at different time interval (100% extension) obtained using different equipment

Time (min)	INSTRON 1122		NEW STRESS-RELAXOMETER*	
	Average Stress (MPa)	C.V. (%)	Average Stress (MPa)	C.V. (%)
1	2.133	3.27	2.171	4.29
2	2.084	2.43	2.099	4.38
3	2.068	3.12	2.059	3.19
5	2.038	3.04	2.045	3.13
7	2.018	3.01	2.030	2.94
10	1.998	2.97	2.000	2.25
20	1.954	2.66	1.977	2.67
30	1.931	2.68	1.961	3.00
50	1.903	2.59	1.914	2.99
70	1.900	2.56	1.893	2.67
100	1.851	2.41	1.874	2.83
Rates (%/dec)	6.78		6.31	

* - 'Bow String' Stress Relaxometer

Table 3.5 gives the comparative stresses obtained from filled natural rubber vulcanized using sulphur semi-EV system. Five repeat tests were carried out and the average stresses and their coefficient of variation (CV) values are given. The CV for the stresses were within experimental variation ($\pm 5\%$) and the stresses obtained using the two different techniques of measurement were comparable. This shows that the new technique of measuring stresses in an extended rubber strip is accurate and reliable and the stresses values were not significantly different from those obtained using the conventional method.

3.7 ADVANTAGES AND LIMITATIONS OF THE NEW TECHNIQUE

a) Advantages

The new technique of measuring stress relaxation in rubber has several advantages.

- 1) Being tensile in nature, it does permit high surface/volume ratio specimen, good accuracy and ability to study cracking and ageing.
- 2) Problems associated with uniaxial compression relaxation such as surface friction, uneven stress distribution across the sample width and sample bulging were absent.
- 3) Sample under stress is gripped to a simple frame which is detachable from load measuring devices, while maintaining the strain. Thus, the set-up allows large number of sample to be tested simultaneously using a single testing machine.
- 4) The sample frame is handy, strong, durable and fairly small. This make it possible for large number of sample under going long term test to be kept safely in a control environment without taking too much space.

5) Any modern testing machine could be easily adapted to take up the stress relaxation sample frame. Thus the measurement of load could be carried out periodically using any available testing machine. The major cost of employing the new technique will be only the cost of fabricating the sample frames.

6) The problem of electrical drift associated with load measuring devices is eliminated since the load reading is taken at intervals not continuously.

b) Limitations

The limitation which could be encountered with this new testing technique will be as follows.

1) The reference stress could be taken only after about 1 minute. This is due to the time required for the sample to be extended horizontally and subsequently pushed vertically. The whole operation takes about 30 to 45 seconds.

2) During testing, the plunger and the rubber surface should be parallel. This is to ensure that the surface of the plunger facing the rubber could make continuous contact with the rubber when the load readings were taken. Tilting of either the rubber sample or the plunger will give a lower and incorrect readings. This could be overcome by proper alignment of the plunger and the rubber surfaces.

3) Thin samples (<0.5mm) are not suitable to be used with this new technique. This is due to possible cracking and breaking of the sample during the vertical push by the plunger; this is particularly apparent with aged samples.

4) The present sample frame could not be used in saline water or corrosive environment due to the limitations of the materials used for their construction.

5) Load readings were taken at ambient conditions since appropriate test chamber was not constructed. Test could be carried out at different environments if a proper test chamber is available.

CHAPTER FOUR

EXPERIMENTAL METHODS

4.1 INTRODUCTION

Natural rubber containing different types and proportions of naturally occurring non-rubber constituents were used for this study. They were purified rubber(PR) containing different types of non-rubber constituents; total solid rubber(TSR); centrifuged latex fractions; commercial grades Standard Malaysian Rubber(SMR) and Deproteinised natural rubber(DPNR). A schematic illustration of the types of rubber used and the tests sequence undertaken are summarised in a flow diagram shown in *Figure 4.1*. All tests were carried out in duplicate (unless indicated) and the average readings were taken.

4.2 PREPARATION OF RUBBER

a) Total solid rubber (TSR)

Total solid rubber was obtained by film drying the fresh latex onto glass plates at room temperature (21°C). The latex film was about 1 to 2mm thick and the drying process took about 24-48 hours. A fan was used to speed up the drying process to overcome the problem of bacterial action that would occur in the latices if they were exposed unnecessarily long in an open environment.

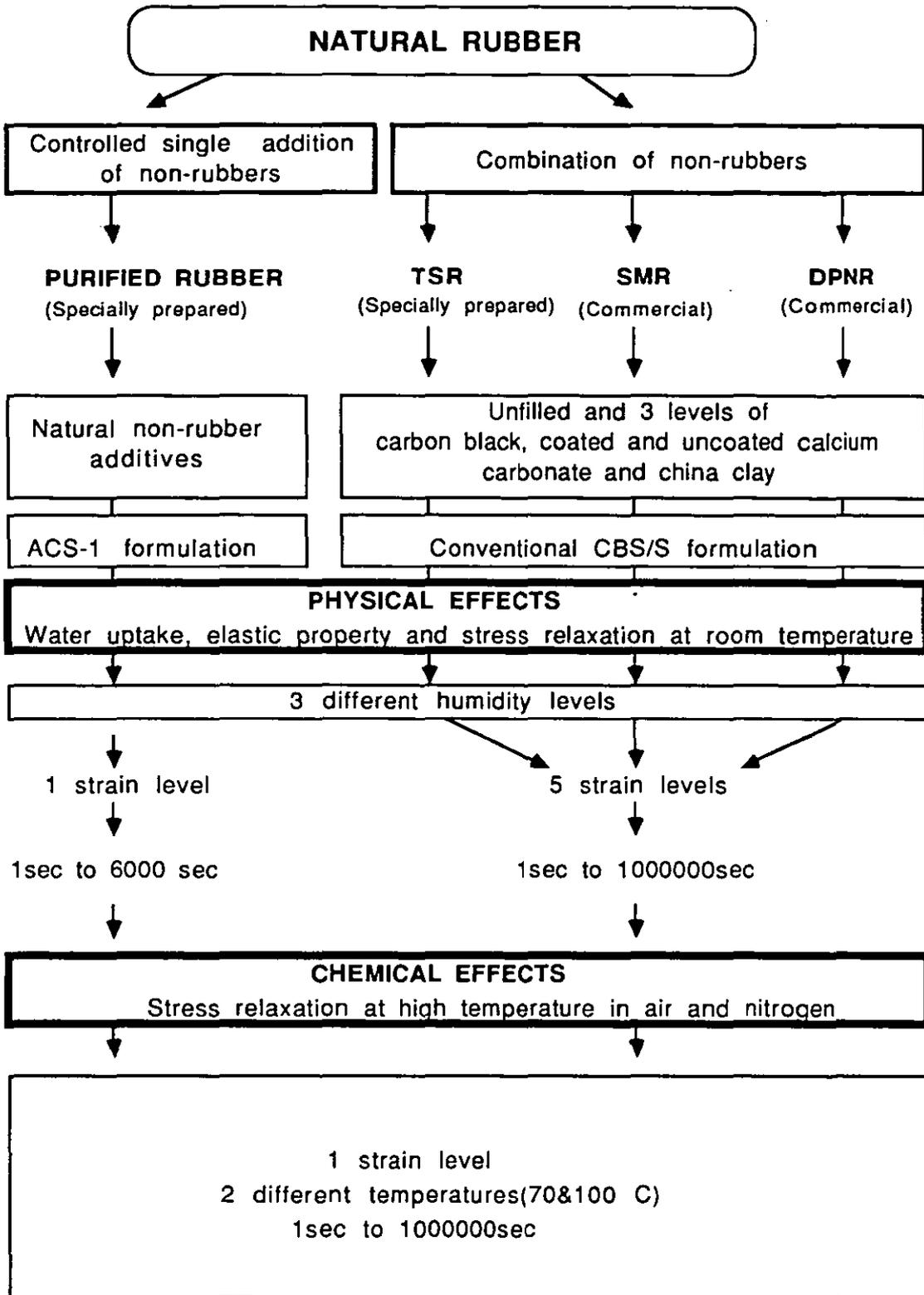


Figure 4.1: Flow diagram of the experiment

b) Centrifuged fractions

Fresh latex (i.e TSR) was ultracentrifuged at 19500 r.p.m for about an hour in a Beckman centrifuge: its fractionates into four main fractions :a white rubber fraction (i.e. rubber phase), a yellowish-orange layer containing the Frey Wyssling particles, a serum fraction and a grey-yellow gelatinous bottom fraction (*see Figure 2.1*). They were manually separated to give fractions containing different types and proportions of non-rubber constituents (see section 2.1)

The rubber phase (RP) was redispersed in distilled water and film dried at room temperature in a similar manner as the TSR.

Rubber phase containing bottom and serum fractions were prepared by mixing it with those fractions before the filming and drying process.

c) Purified rubber

The purified rubber was obtained from the rubber fraction. The rubber phase (or the rubber fraction) was first manually isolated and redispersed in a 5% aqueous sodium dodecyl sulphate solution for about 24 hours before being recentrifuged to remove the remnants of the serum fractions. The treated rubber phase was rewashed with aqueous sodium dodecyl sulphate solution followed by water before it was finally redispersed in water to give a purified latex. The purified latex was subsequently film dried on glass plates at room temperature (21°C) to give the purified rubber (PR).

d) SMRL and DPNR

Standard Malaysian Rubber grade L (SMRL) and deprotenised natural rubber(DPNR) used were commercial grades rubber obtained from Malaysian Rubber Producers' Research Association.

4.3 ISOLATION OF NON RUBBER CONSTITUENTS

a) Isolation of bottom protein (i.e bottom serum protein)

The bottom serum protein (later termed bottom protein) was obtained from the bottom fraction of the ultracentrifuged fresh latex. The bottom fraction was first freeze-thawed three times, recentrifuged and the clear serum collected. Ammonium sulphate was added to the serum to a saturation level and the mixture was left in the refrigerator for overnight. The precipitated protein was collected from the recentrifuged mixture, redissolved in water and dialysed against water to remove any ammonium sulphate remnants. The dialysed mixture was then freeze-dried to give a powdered form of ammonium sulphate precipitated bottom protein.

b) Isolation of serum protein

The serum protein was obtained from the serum fraction of the ultracentrifuged latex in a similar manner as the bottom protein through precipitation with the ammonium sulphate.

c) Isolation of proteolipid

The proteolipid was obtained from the rubber phase of the NR latex according to the procedure reported by Hasma (HASMA, 1987).

The rubber phase was redispersed in water, filtered and added dropwise to about five volumes of a continuously stirred chloroform/methanol (2:1, volume/volume) mixture. The extract was separated from the rubber coagulum and washed with salt solution. A lower layer of the chloroform fraction and a thin whitish interfacial layer were isolated. The chloroform layer was concentrated on a rotatory evaporator. The insoluble portion containing proteolipids was collected.

d) Amino-acids and natural rubber serum powder (NRSP)

Amino-acids used were of commercial grades and the NRSP was obtained from the Rubber Research Institute of Malaysia (RRIM) pilot plant.

4.4 INCORPORATION OF PROTEINS AND AMINO ACIDS

Proteins and amino-acids were added in aqueous form to the purified latex. They were first dissolved in water and then added to the purified latex. The mixture was thoroughly mixed before film drying on glass plates at room temperature. Dried latex films were then blended using a two-roll mill to give rubbers containing the required proportion of the non-rubber constituents.

4.5 COMPOUNDING AND VULCANIZATION

Dried films of purified rubber containing non-rubber constituents, total solid rubber, different fractions of centrifuged latex and commercially processed rubbers (SMRL and DPNR) were mixed in accordance with the formulation given in *Table 4.1*.

Two different types of filler were used. They were reinforcing and non-reinforcing fillers.

Reinforcing filler consist of high structure carbon black filler(N330) of mean particle size of about 29 nm. The amount of carbon black varied from 5 to 40 phr.

The non-reinforcing fillers were calcium carbonate and china clay. Two different types of calcium carbonate fillers were used: coated and uncoated. The coated calcium carbonate was in the form of ground chalk whiting specially treated with surface coating (stearate) while the uncoated calcium carbonate is the standard ground whiting. Both types of calcium carbonate has similar particle size distribution (ca. 10-25 micron).

The china clay, (which are essentially aluminium silicates) used consisted of hard clay of particle size less than 2 microns. The amount of calcium carbonate and clay varied from 40 to 120 phr.

Table 4.1: Rubber formulation (in parts per hundred rubber, phr)

Vulcanizing systems	ACS-1	Conventional	Semi-EV	EV
Rubber ^a	100	100	100	100
Zinc oxide	6.0	5	5	5
Stearic acid	0.5	2	2	2
Sulphur	3.5	2.5	1.5	0.6
MBT ^b	0.5	-	-	-
CBS ^c	-	0.6	1.5	2.5
N330	-	variable	→	→
Clay	-	variable	→	→
Uncoated CaCO ₃	-	variable	→	→
Coated CaCO ₃	-	variable	→	→
Processing oil ^d	-	variable	→	→

- Note: a The non-rubber constituents were added at 1%wt. of NR. The nitrogen and ash contents were determined in accordance with ISO 1656(1988) and ISO 247(1980) respectively
- b 2-Mercaptobenzothiazole
- c N-cyclohexyl benzothiazole-2-sulphenamide
- d The processing oil (dutrex R) was added at 10% wt. of filler

All unfilled purified rubbers were mixed in accordance with ACS-1 formula while the unfilled and filled commercial grade and total solid rubbers were mixed using semi-EV (CBS/S) systems (unless indicated otherwise).

The mixing process was carried out using a laboratory two-roll mill and the Banbury internal mixer. The laboratory two roll mill was used to mix the purified rubber, centrifuged rubber fraction and total solid rubber with the rubber additives. Commercial grade rubbers were mixed using internal mixer according to the following mixing cycle,

<u>Time(min)</u>	<u>Addition sequence</u>
0	Rubber
1	Zinc oxide, stearic acid
2	Half of filler, processing oil
3.5	Remaining half of filler
7	Dump

Vulcanizing agents and accelerators were added to a 200g batch of the compound using the laboratory two-roll mill. To reduce losses of chemicals during the mill mixing of small batches of rubber, the compounding ingredients were added in the form of master batches.

Moulding of rubber test pieces was carried out using a steam-heated press at 150°C for a period required to fully vulcanize the rubber (i.e t_{100}).

4.6 PHYSICAL TESTS

a) Relax modulus test

The relaxed modulus test (MR 100) was carried out by extending a square-end dumb-bell test piece to 100% extension and monitoring the load after one minute. The test was carried out on the rubber conditioned under different environments, namely at room temperature humidity ($55\pm 5\%RH$), in a dry atmosphere (7% to $25\pm 5\%RH$) and immersed in water. The relative humidity of water was taken to be $100\pm 5\%RH$.

The water immersion procedure was in accordance with the immersion test described below (section 4.7a), and the weight changes due to the water imbibed by the rubber was determined by weighing the MR 100 test pieces before and after the immersion test. In a dry environment, the conditioning process was as described for stress relaxation test (section 4.8.1).

b) Stress strain test

Stress strain test was carried out using modern standard tensile testing machine (JJ Lloyds). Samples consist of strip of 10x120x1.5 mm which were die-stamped from moulded sheet. The samples were grip using screw tighten sample holder to prevent slippages during testing.

The separation of the sample grip was taken as the gauge length during the test. It was set at 100mm apart. Zero strain was taken at a point at the zero load position.

The sample was extended at 100% per minute; this gives a reasonably good reproducibility ($\pm 5\%$). The output of the test was fed directly onto a computer. All tests were carried out at room temperature (21°C)

4.7 SWELLING TEST**a) Water immersion test**

The water swelling test of the rubber was carried out using distilled water containing 5% by weight sodium chloride. The salt was added to accelerate the uptake of water by the rubber (SOUTHERN AND THOMAS, 1980; MUNIANDY, 1987). Square sample of 25x25x1.5mm was immersed in about 500cm³ water and the weight changes was monitored until equilibrium weight was obtained.

The test-pieces which were used for physical tests were also immersed in water and the changes in weight monitored in a similar manner.

b) Solvent swelling and crosslink density measurements

The crosslink density of the rubber was determined from the equilibrium swelling data using the Flory-Rehner equation (FLORY AND REHNER, 1943).

Samples of about 1.5 mm thick were cut into 25 mm squares and swollen in toluene in the dark for several days, during which their weights were regularly monitored. At equilibrium swelling, the weights of the swollen rubber were recorded and samples were subsequently dried in a vacuum oven at 60°C. The difference between the weight of the swollen and dried samples was taken as the true weight of the solvent imbibed for the calculation of the volume fraction and crosslink density.

Specimens which were subjected to high temperature ageing test were also swollen in a similar manner.

4.8 STRESS RELAXATION MEASUREMENT

Stress relaxation tests were carried out under tensile deformation. Sample strips which were die-stamped from moulded sheet were used. Two techniques were employed for this study; a conventional technique and the 'bow string' technique.

The conventional technique uses modern tensile testing. Samples were held firmly in screw tighten grips and pulled to a required extension at 100% per minute. The change in stress at constant strain was monitored using the output facilities available (i.e a portable computer).

The 'bow string' technique is a new technique developed during this study. The development of this new stress relaxation technique has been explained in detailed in chapter three. This technique allows the change in stress, under different environments, to be monitored for longer period of time (3 months).

A wedge shape plunger with a rod tip of diameter about 2.5mm was used and the plunger was driven at 50mm per minute. In this study, the sample was pushed vertically at mid-point along the extended rubber strip to three different angular displacements, namely (about) 4, 6, 8 degrees. The stresses at those angular displacements were calculated and the average value taken.

The sample used were die-stamped from moulded sheet of about 1 to 1.5 ± 0.2 mm thick and 10 mm wide. Thinner samples (< 1.0 mm) were used for test at high temperature to reduce the effects of non-uniform degradation. Most of the relaxation tests were performed at 30% extension and extension rate was 100% per minute, unless otherwise stated. At low strain ($< 50\%$), the rubber is within the so called 'affine deformation' region, where the bulk deformation of the sample is considered to be a good approximation of the infinitesimal deformation of the rubber network. Thus, at this low extension, the possible effects due to non-affine deformation will be minimised.

The relaxation study was carried at different humidities and temperatures under air and nitrogen. Due to machine limitation, test at different environments were only carried out using 'bow string' technique.

All results were either presented as a plot of relative stress, which is the ratio of stress to the reference stress, against time or as relaxation rate. The rate was calculated from the load/stress-log(time) plot and expressed as percent per decade of time.

4.8.1 Test at different relative humidities

The relaxation test was carried out at three different relative humidities, namely low humidity (7% to $25\% \pm 5$ RH), room humidity ($55 \pm 5\%$ RH) and high humidity ($100 \pm 5\%$ RH). Prior to the test, the sample strips which were die-stamped from moulded sheet, were conditioned at the respective humidity for about 14 days.

The low humidity environment was achieved by placing phosphorous pentoxide (P_2O_5) in a desiccator. Samples were continuously placed in the desiccator were taken out only during testing.

The higher humidity condition was obtained by immersing the sample in water. It was carried out by placing the sample in water for between 14-30 days. The change in weight of the sample due to absorption of water into the rubber was measured prior to testing.

Equilibration of samples at room humidity was carried out by placing the rubber strip in dark cupboard. The relative humidity at room humidity varied from about 48%RH to about 60%RH, depending on the outside weather.

Tests at different humidity environments were only restricted to physical relaxation due to limitation of the test set-up.. Physical relaxation ($t < 10^4$ min. @ 23°C) is known to give a linear stress/load versus $\log(\text{time})$ plot (see section 2.4). Initial test shows that linear plots were obtained for samples which were equilibrated at room and high humidity, but not at low humidity (*Figure 4.2*).

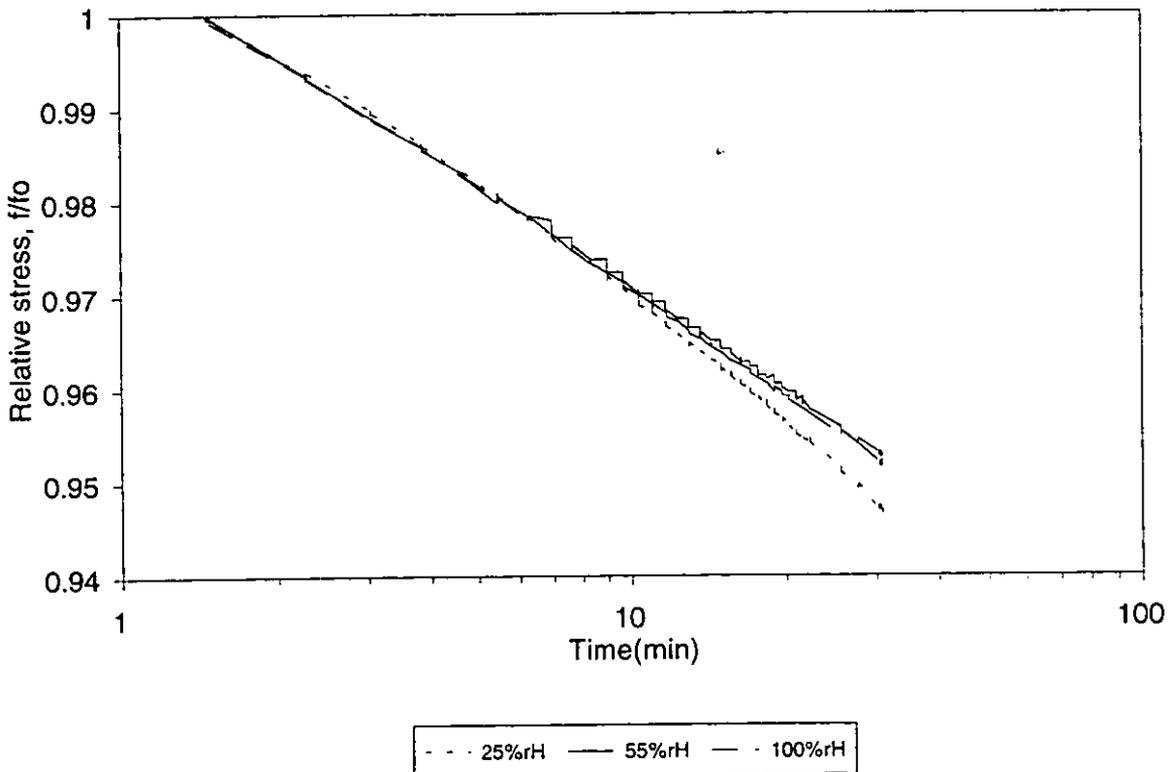


Figure 4.2: Stress relaxation of purified rubber at different relative humidities

At low humidity, the plot of stress versus $\log(\text{time})$ showed an initial straight line, after which it deviates. This deviation was due to the changes in the humidity of the sample while the test was being carried out. The changes in humidity affects the stress in the rubber, thus causing the deviation from linearity. This occurred because the environment around the testing equipment was not under humidity control. Thus the rate of relaxation of sample equilibrated at low relative humidity was calculated either based on data at linear portion of the stress- $\log(\text{time})$ plot obtained using modern testing machine or from data obtained using the bow string technique. The latter technique was able to give continuous data at different relative humidity since the sample frame was always kept in a desiccator having a constant relative humidity.

4.8.2 Test at high temperature in conventional air oven

The air ageing test was carried out at $70\pm 2^\circ\text{C}$ and $100\pm 2^\circ\text{C}$. The test were carried out by extending the sample strip to a set extension (30%) on the bow string sample frame at room temperature. The extended sample was then placed on the bow string set-up for the measurement of load after one minute (i.e reference load at 1 min. relaxation)

Immediately after the load was measured, the sample frame, with the extended sample was placed in an air oven at $70\pm 2^\circ\text{C}$ or $100\pm 2^\circ\text{C}$. At a prescribed time interval the sample frame was taken out and the load immediately measured. The same sample was left for about 30 minutes at room temperature before another load reading was taken. The sample frame was returned to the oven for further relaxation test and the test sequence was repeated at another prescribed time interval. The process continued for about 2 weeks or until the stress was reduced by more than 50%.

Test carried out on several samples revealed that there were large differences between load/stress of the rubber measured immediately after taken out of oven (<1 minute) and 30 minutes later. The stress progressively decrease as the temperature of the rubber reduces once the sample was outside the oven. This is due to the dependence of stress on temperature (TRELOAR,1975) At oven temperature of 70°C, for instance, the stress measured immediately after the sample was taken out of the oven was about 5% higher than at 30 minute later (Figure 4.3). Generally, it was observed that the stress remained fairly constant after about 20-30 minutes out of hot oven (Figure 4.4). Thus it can assumed that after 20-30 minute out of oven, the temperature of the sample has attained the room temperature condition. Hence all load measurements were carried out after 30 minutes cooling time.

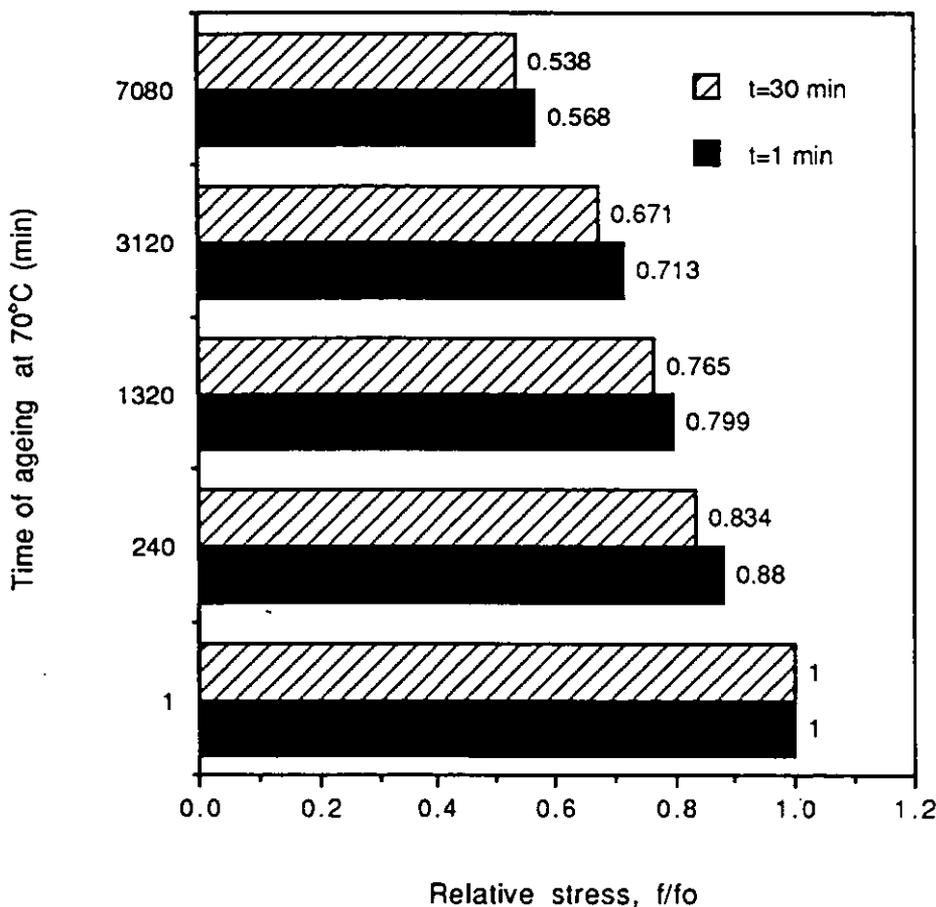


Figure 4.3: Stresses obtained from a rubber strip (1.5mm thick) after 1 and 30 minutes cooling at room temperature

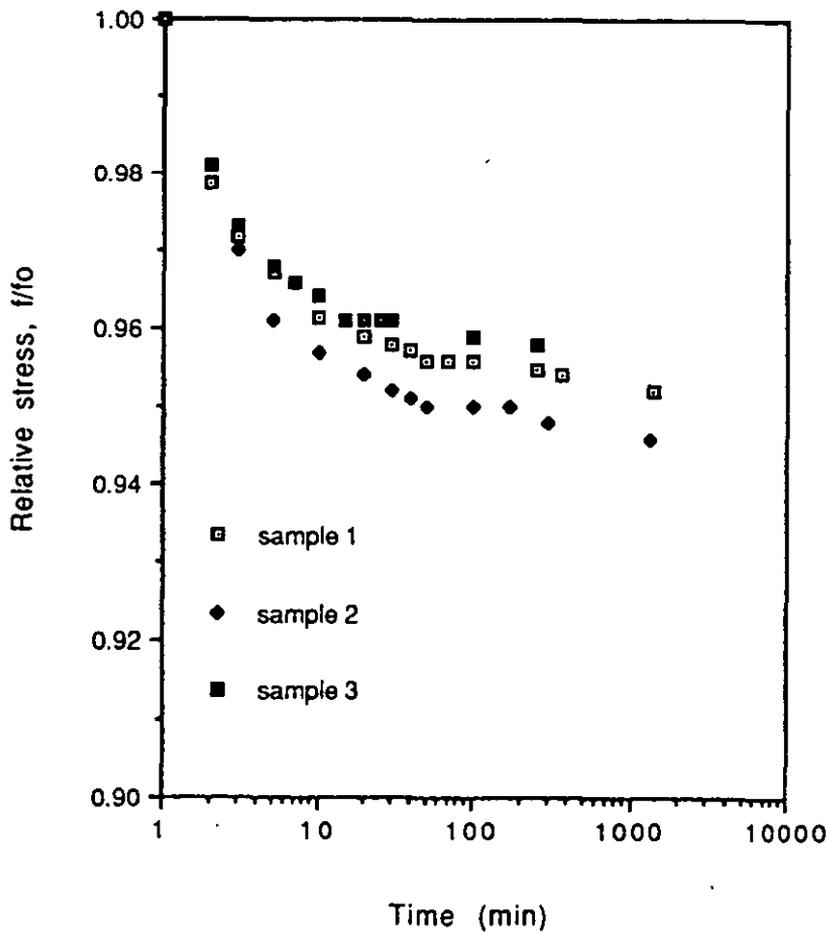


Figure 4.4: Change in stress with cooling time at ambient temperature for NR strip conditioned for 24h at 70°C

4.8.3 Test at high temperature under nitrogen

Test under inert environment was carried out in a similar manner as in air oven. The sample was first strained by extending the sample on the sample frame under normal room environment. Load measurement was taken at 1 minute and the sample frame was immediately placed in a desiccator. The air in the desiccator was evacuated and replaced with nitrogen.

A schematic diagram of the set-up for the displacement of air with nitrogen in a desiccator is shown in *Figure 4.5*. The air in the desiccator containing test sample was first evacuated using a vacuum pump. The pumping of the air out was carried out until the pressure gauge indicates all the air was evacuated, that is when the pressure reaches zero mm Hg. Nitrogen was immediately fed into the desiccator via a reservoir to fill the vacuum. The process of evacuation of air was repeated twice for each test cycle to ensure complete displacement of air with nitrogen before the desiccator and content was placed in the oven.

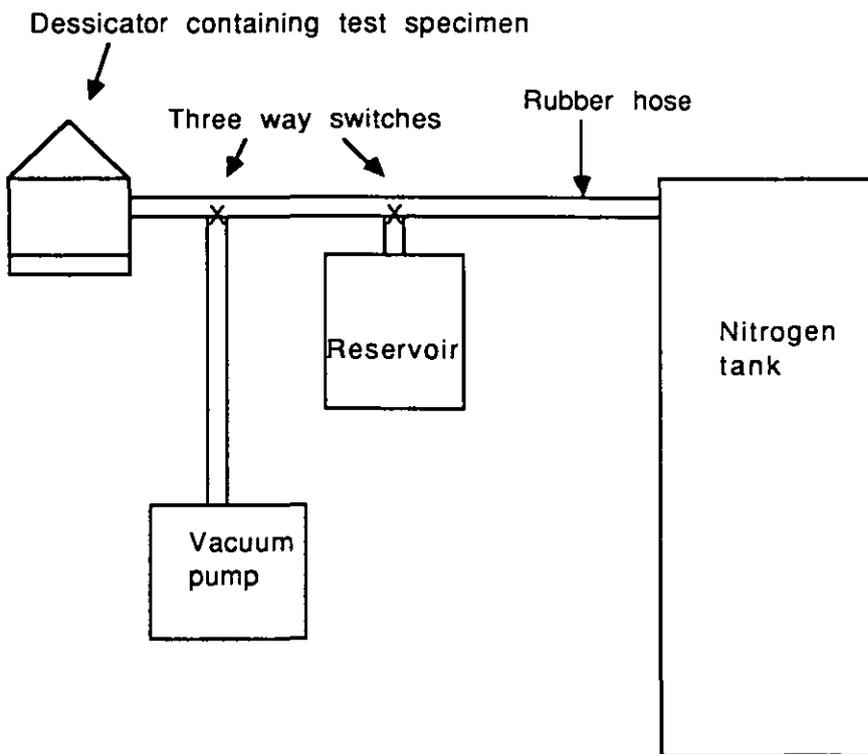


Figure 4.5: A schematic diagram showing a set-up for the displacement of air with nitrogen

After a specified ageing time, the sample frame was taken out for the measurement of load. All load was taken after 30 minute cooling period.

The process of evacuation of air and subsequent filling-up of the empty spaces in the desiccator with nitrogen was repeated after each measurement of load until the end of the relaxation test.

CHAPTER FIVE

RESULTS AND DISCUSSION

5.1 INTRODUCTION

Commercial natural rubber is produced in different grades; it arises from the different sources of latex coagulum and different methods of handling rubber (*see Figure 1.1*). Conventional grades (e.g Standard Malaysian Rubber, SMR grades) are processed by coagulating the latex using acids followed by washing and drying the rubber, whilst the processing of deproteinised rubber (DPNR) involves an extra step whereby the naturally occurring proteins are removed prior to coagulation (CHIN, et. al.,1974; KHOO et. al 1988). Hence, DPNR contains lower amount of nitrogenous non-rubber constituents than conventional grades.

It has been reported that rubber which has been processed in different ways showed a marked variation in properties due to the presence of different types of non-rubber constituents. For instance, proteins are believed to affect creep; Smith observed that the removal of proteins in DPNR reduces the rate of creep (SMITH,1974). Tan and Knight reported that the presence of proteins caused the modulus of rubber to increase (KNIGHT AND TAN,1975), while amino-acids affect the storage hardening of the raw rubber (BOUCHER AND CARLIER,1964). Storage hardening is also affected by inorganic materials (BATEMAN & SEKHAR,1966). Certain nitrogenous bases and fatty acids take part in the sulphur vulcanization reaction which

subsequently affects the properties of rubber vulcanizates (ALTMAN 1948,;LOO,1982). The presence of non-rubber constituents also affects the sensitivity of the rubber to water, thereby affecting related properties such as elastic modulus and stress relaxation (DERHAM,1972).

This chapter gives experimental results and discusses the effect of some non-rubber constituents, particularly proteins and hydrolysed components (amino-acids) on the stress relaxation of unfilled and filled rubber vulcanizates. The discussion of the effect of water and humidity on the elastic modulus preceded stress relaxation because the latter is known to be strongly influenced by water and humidity (SOUTHERN, 1979).

5.2 PHYSICAL PROPERTIES

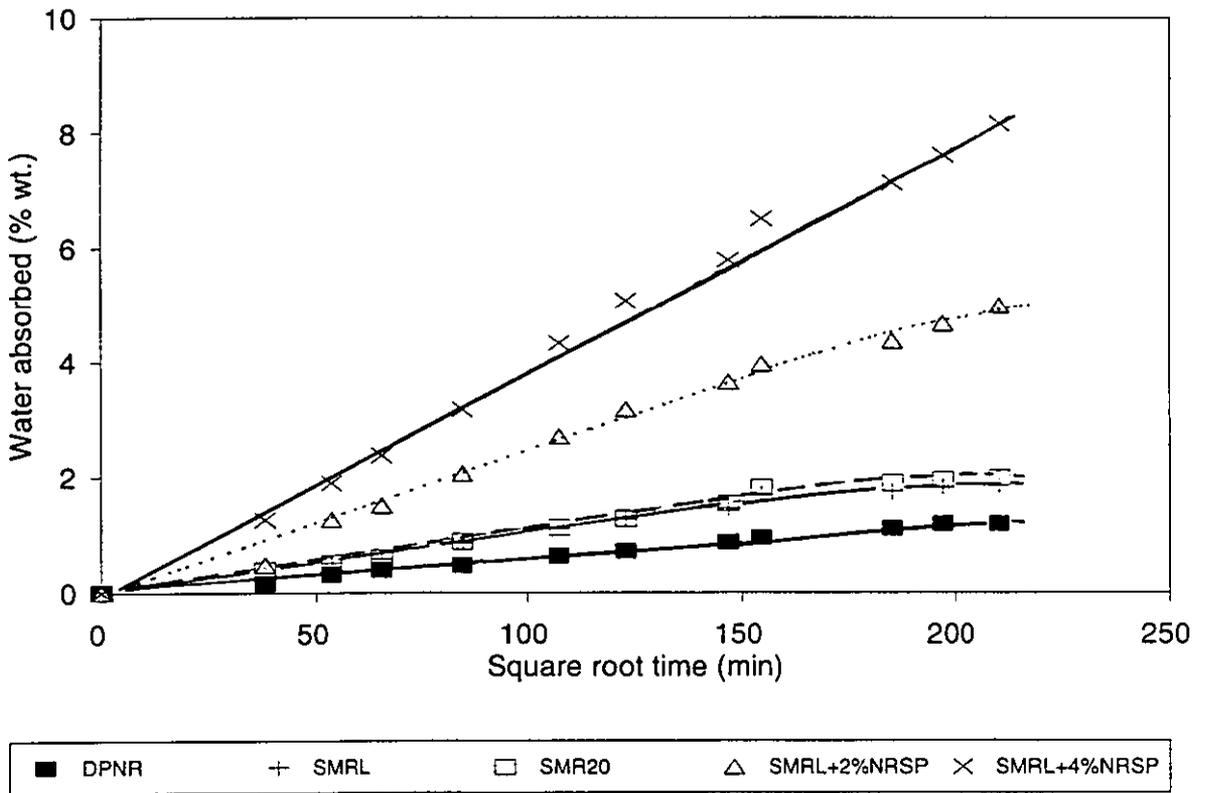
5.2.1: Water uptake

a) Effects of non-rubber constituents on water uptake

Rubbers containing different types of non-rubber constituents were used for this study. They were commercial grade rubbers containing different amount of nitrogenous materials (i.e DPNR and SMRL), centrifuged fresh latex fractions (see section 2.1.2) as well as purified rubber to which has been added different types of non-rubber constituents.

The results of water absorption of commercial grade rubbers, presented as a plot water absorbed (% wt.) versus $t^{1/2}$, are shown in *Figure 5.1*. After about 30 days ($t^{1/2}=208$) immersion in water, Standard Malaysian Rubber grades L (SMR L) and 20 (SMR 20) absorbed approximately the same amount of water. Deproteinised Natural Rubber (DPNR) absorbed about 50% lower amount of water than SMRL. When some impurities containing a high level of natural nitrogenous matter (i.e natural impurities obtained from NR latex serum=NRSP) were added to the SMRL, the water uptake by the

Figure 5.1
Water uptake characteristics of different types
of natural rubber



rubber increased considerably. For instance, after 30 days in water, the presence of 2 pphr NRSP increased the water uptake of SMRL by more than 100% and the incorporation of 4 pphr NRSP resulted with more than 400% increase in the water uptake.

It may be noted that after 30 days in water, rubber containing NRSP has not reached an equilibrium state of swelling; SMRL, SMR20 and DPNR have attained an equilibrium value, during which no change in the weight of water absorbed occur. The equilibrium water uptake of rubbers containing NRSP could be higher than the values at 30 days swelling.

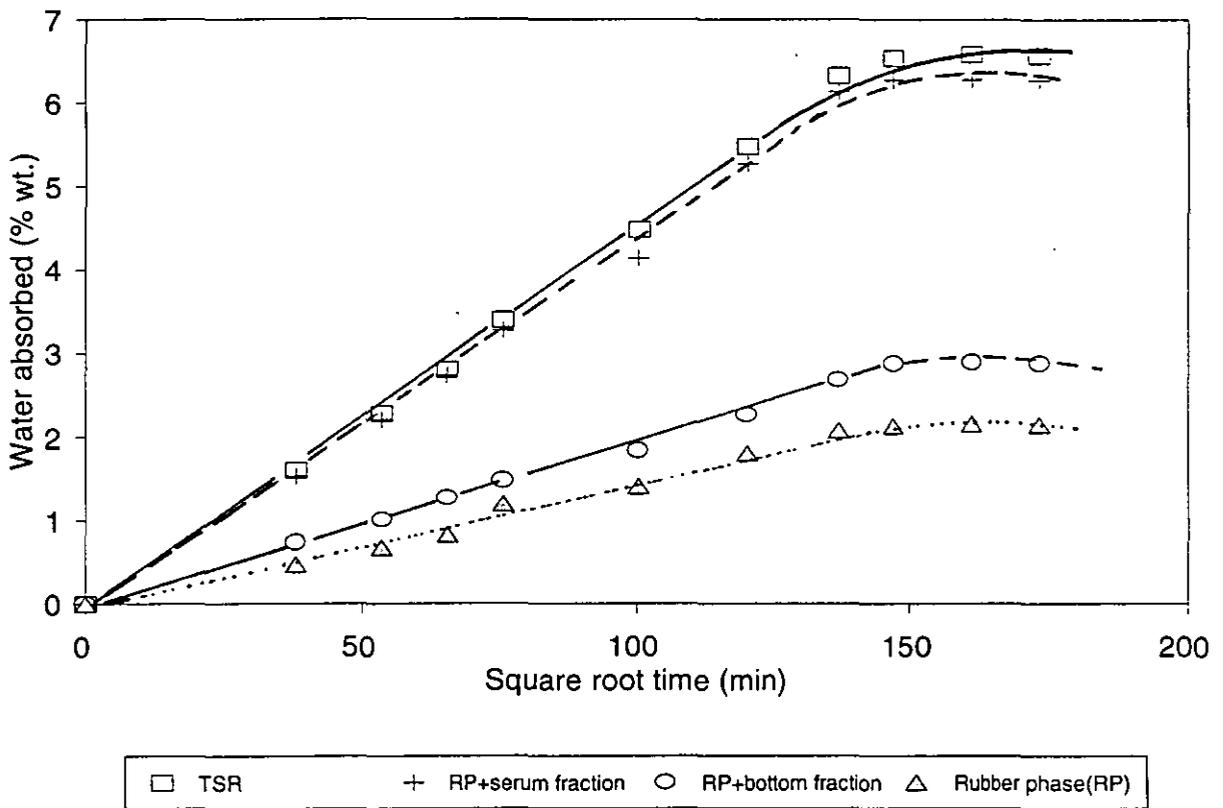
The slope of linear portion of the plot of water absorbed vs $t^{1/2}$ gives the rates of water uptake per unit volume of rubber. With commercial grades rubbers, the calculated rates of water uptake are given in *Table 5.1*. The presence of nitrogenous material (NRSP) increases the rate of water uptake of SMRL considerably. Conversely, when the nitrogenous materials were extracted from the rubber, as in DPNR, the rate of water uptake decreases. This shows that the presence of nitrogenous materials in rubber influences the uptake of water.

Table 5.1: Equilibrium water uptake by commercial grade rubber

Rubber	Water uptake (% wt.)	Rates (mg/cc/min ^{1/2})	Corr. coeff.
DPNR	1.19	0.05	0.9967
SMRL	1.86	0.09	0.9979
SMR20	1.99	0.10	0.9981
SMRL+2%NRSP	4.99	0.24	0.9927
SMRL+4%NRSP	8.17	0.38	0.9972

Some of the nitrogenous materials in the latex were separated from the rubber particles by centrifuge (see section 2.1.2) and water absorption tests were carried out on these centrifuged fractions; results obtained are given in *Figure 5.2*.

Figure 5.2
Water uptake characteristics of centrifuged
NR latex fractions



The equilibrium water uptake was observed to vary with the types of centrifuged fraction. At equilibrium swelling, the amount of water absorbed by rubber fraction/phase (RP) is about 70% lower than total solid rubber (TSR); TSR and RP containing serum fraction absorbed about the same amount of water. Similar pattern was observed with the rates of water absorbed by these centrifuged rubber fractions (Table 5.2). This demonstrates that the majority of the water absorbed is associated with the non-rubber constituents in the serum fraction.

Table 5.2: Equilibrium water uptake by different centrifuged latex fractions

Rubber	Water uptake (% wt.)	Rate (mg/cc/min ^{1/2})	Corr. coeff.
Rubber phase(RP)	2.20	0.14	0.9935
RP+bottom fraction	2.90	0.17	0.9962
RP+serum fraction	6.33	0.41	0.9982
Total solid(TSR)	6.57	0.42	0.9990

It may be noted that the rates and values of equilibrium water uptake given for different types of natural rubber in Tables 5.1 and 5.2 varied considerably. These were due to the different types of non-rubber constituents present in the rubber. The non-rubber constituents found in the rubber phase were approximately of the similar order present in the SMR grades rubber (see section 2.1.2).

The serum fraction is known to contain proteins, amino-acids, carbohydrates, nitrogenous bases, nucleic acid, inorganic ions and some metallic ions (ARCHER, et. al., 1963). Protein is a major constituent of the non-rubber contents (ca.20-30% wt.) with about half of the proteins are in the serum fraction. The presence of proteins has been reported to increase the affinity of rubber to water (SMITH, 1974).

A study of the water uptake by the purified rubber containing added proteins (1% wt.) was carried out. Three types of protein which are present in the latex were used; they were the hydrophilic bottom fraction and serum proteins and the hydrophobic membrane protein (proteolipid). The water absorption results are given in *Figure 5.3*. At equilibrium swelling, those three different types of protein gave approximately the same amount of water uptake as the purified rubber (rubber containing low nitrogen content, about 0.02% weight). This shows that the present of 1% wt. added proteins in purified rubber did not induce the uptake of water by the rubber.

If proteins themselves are not causing the water uptake, it could be that the water uptake seen by previous investigators was caused by the amino-acids (which may be regarded as products of proteins hydrolysis-see section 2.1.1). The effect of these amino-acids on the water uptake by purified rubber was also determined. Certain types of amino-acid which are known to act as cure activators for the rubber, were incorporated into the purified rubber for this test. They include amino-acid such alanine and arginine; the results are given in *Figure 5.4*.

The amount of water absorbed, at equilibrium swelling by rubber containing different types of amino-acid were about the same. However, these are significantly lower than the values obtained with total solid rubber (*Figure 5.4*). Similar pattern was observed with the rates of water uptake by the rubber (*Table 5.3*).

Table 5.3: Equilibrium water uptake by rubber containing proteins and amino-acids

Rubber	Water uptake (% wt.)	Rate (mg/cc/min ^{1/2})	Corr. coeff.
Purified rubber, PR	1.40	0.08	0.9934
PR+serum proteins	1.41	0.09	0.9813
PR+proteolipids	1.33	0.08	0.9963
PR+bottom proteins	1.33	0.08	0.9933
PR+glutamic acid	1.80	0.11	0.9992
PR+alanine	2.21	0.14	0.9990
PR+arginine	2.33	0.15	0.9990

Figure 5.3
Water uptake characteristics of purified rubber
containing proteins

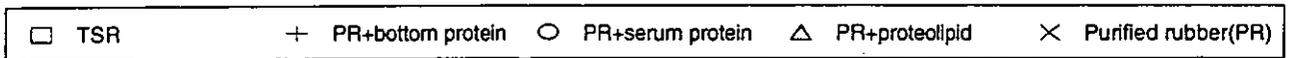
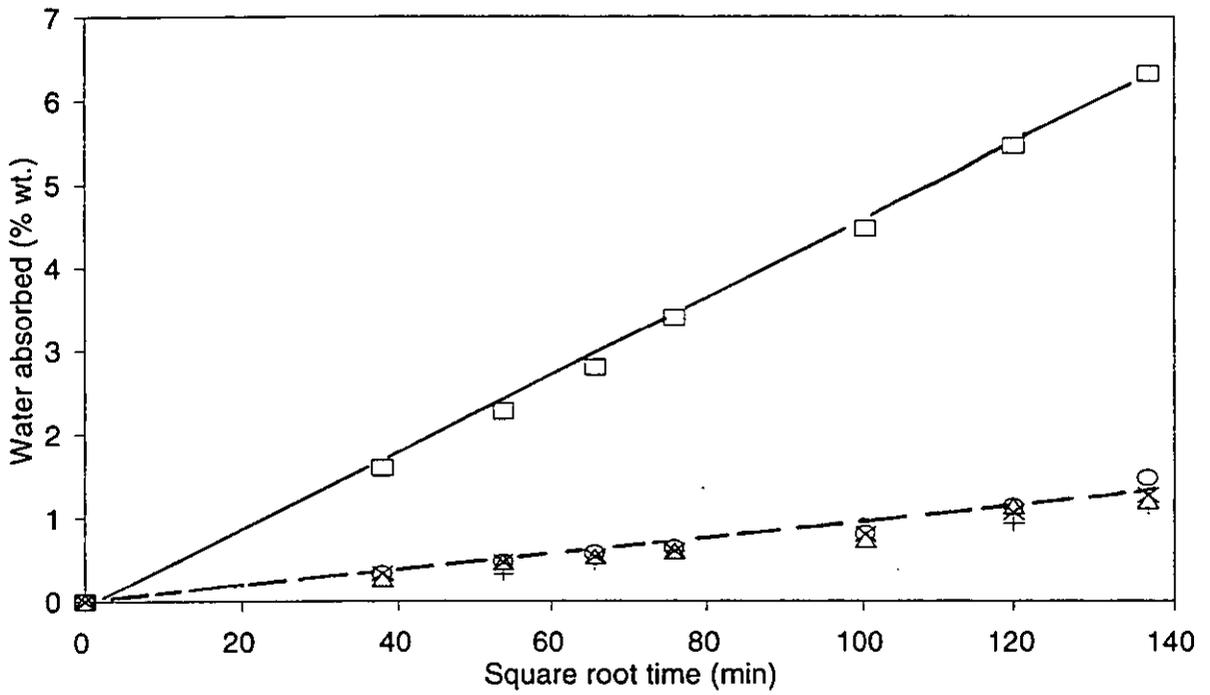
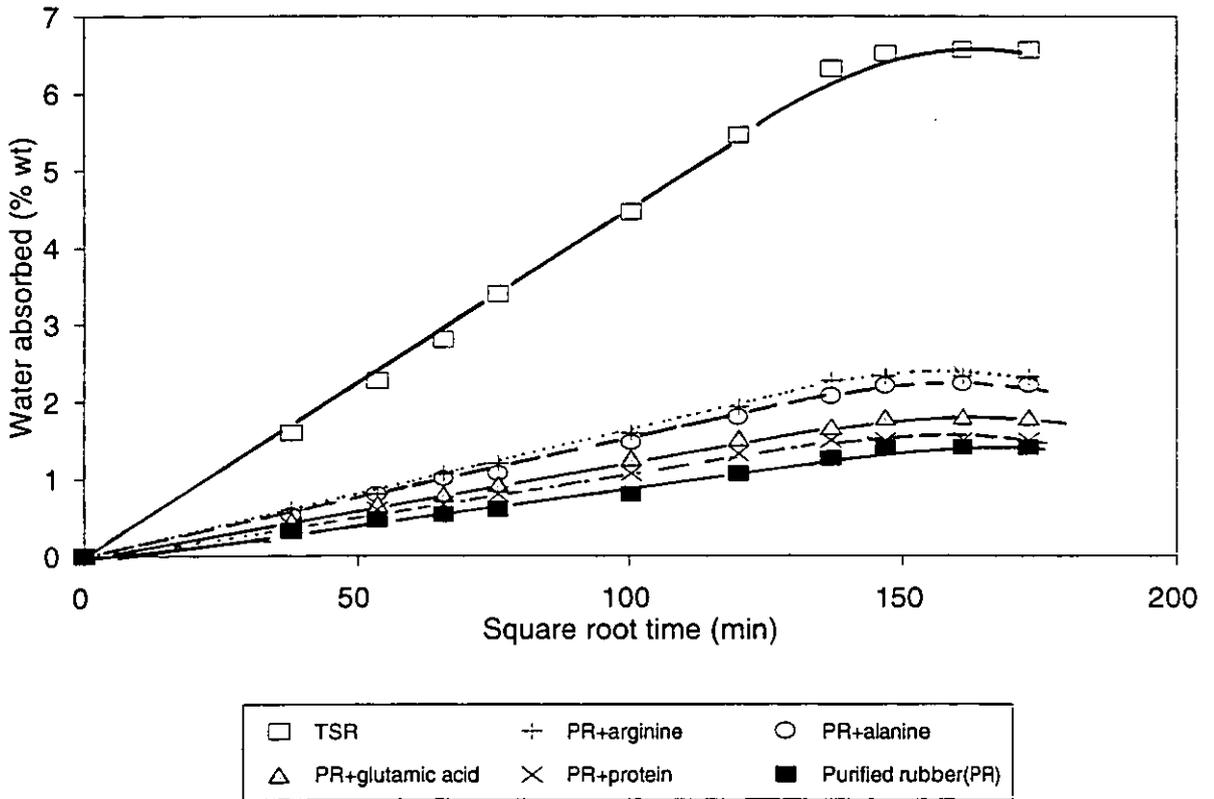


Figure 5.4
Water uptake characteristics of purified rubber
containing non-rubbers



Both proteins and amino-acids are nitrogenous materials and the small variation in rates and equilibrium water uptake obtained appears to indicate their presence had little influence on water absorption characteristics of the rubber. This is clearly indicated by the plots of rates and amount of water uptake versus nitrogenous materials (*Figures 5.5 and 5.6*). There is an upward trends, but a great deal of scatter is present. Thus, it could be concluded that factors other than the presence of nitrogenous materials are responsible for the high water uptake by the TSR and serum fraction.

Low molecular weight materials were shown by Thomas and Muniandy (MUNIANDY & THOMAS, 1988), to be responsible for the higher water uptake by the rubber. The serum fraction as tested here, is known to contain both low and high molecular weight materials. The extracts from the serum were dialysed to separate the high molecular weight materials, such as proteins, from the low molecular weight materials (M.W<14000), such as amino-acids and inorganic materials. These dialysed fractions were incorporated into the purified rubber and their water absorption characteristics measured.

Dialysed fractions of low molecular weight were observed to induce a higher water uptake than the high molecular weight fraction (*Figure 5.7*). This is in agreement with a published finding (MUNIANDY & THOMAS, 1988), which shows that the low molecular weight materials induced a higher water uptake by the rubber.

The low molecular materials^{which} could induced water into rubber are amino-acids and inorganic materials. Amino-acids has be found not to be responsible for the high water uptake by natural rubber (*Table 5.3*). Thus the other low molecular weight materials which are present in natural rubber are the inorganic materials. These inorganic materials are usually related to the ash content of the rubber. The ash content of several rubbers were determined. The equilibrium water absorbed was presented as a function of ash content (*Figure 5.8*). A linear relationship was obtained. This shows that the low molecular weight inorganic materials are responsible for affinity of rubber to water.

Figure 5.5
Equilibrium water uptake as a function of
nitrogenous materials

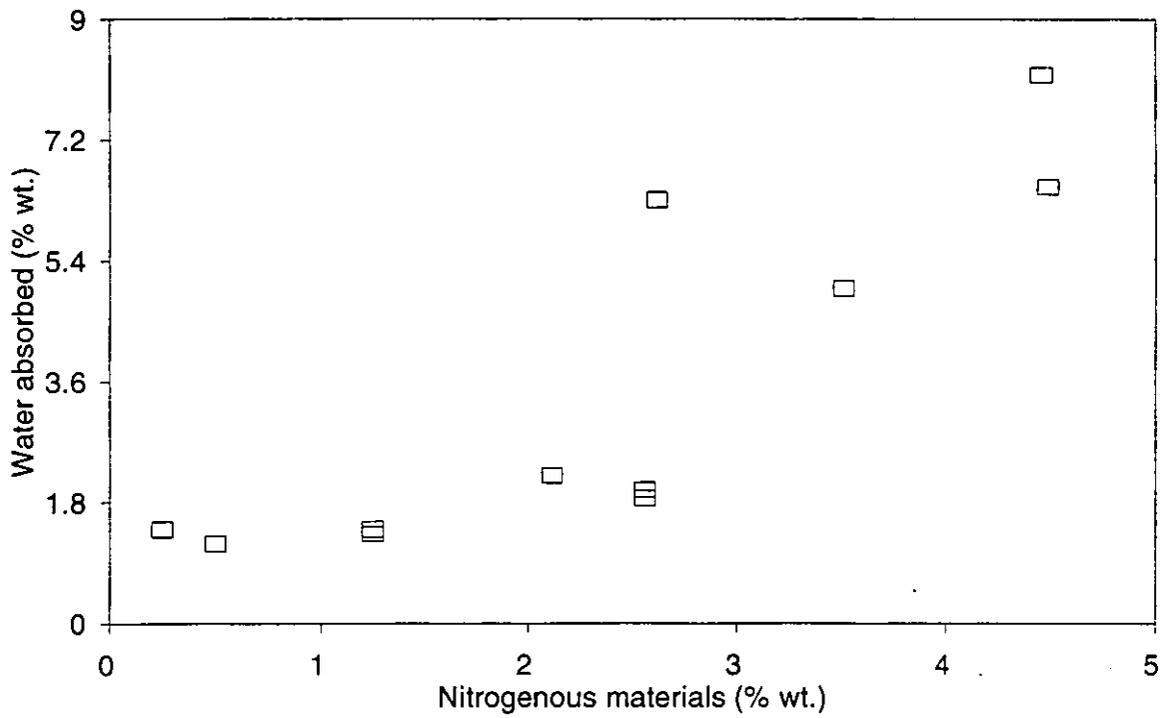


Figure 5.6
Rates of water uptake as a function of
nitrogenous materials

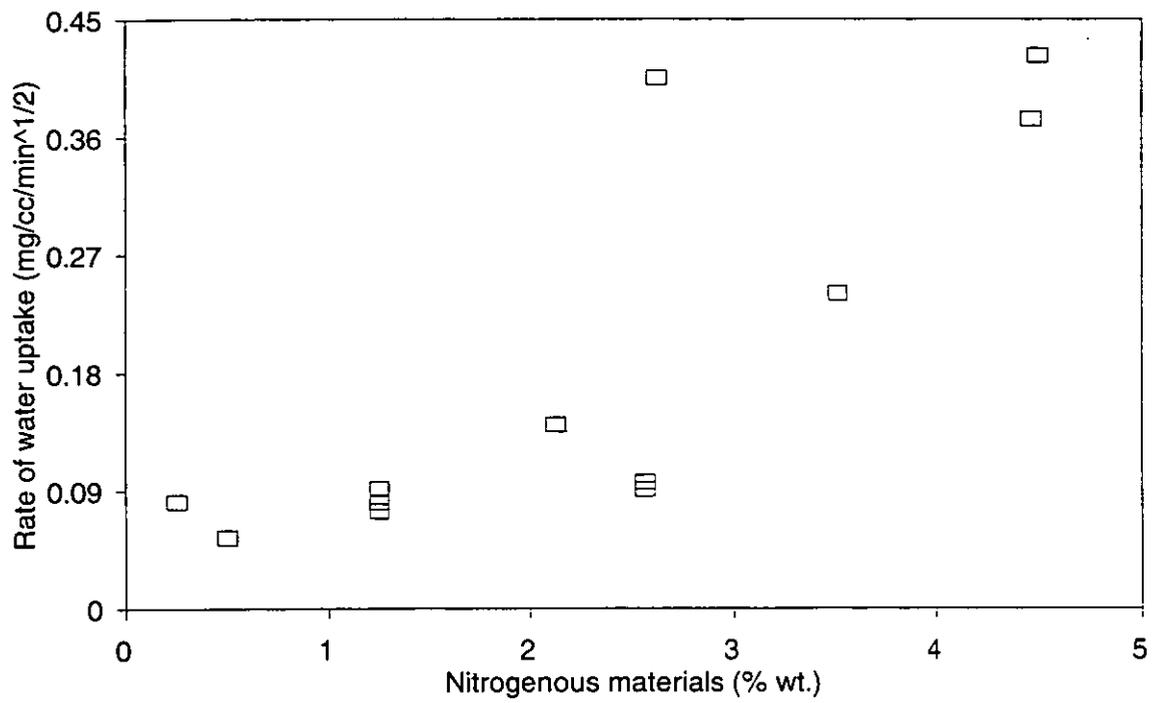


Figure 5.7
Water uptake characteristics of purified rubber
containing dialysed serum fractions

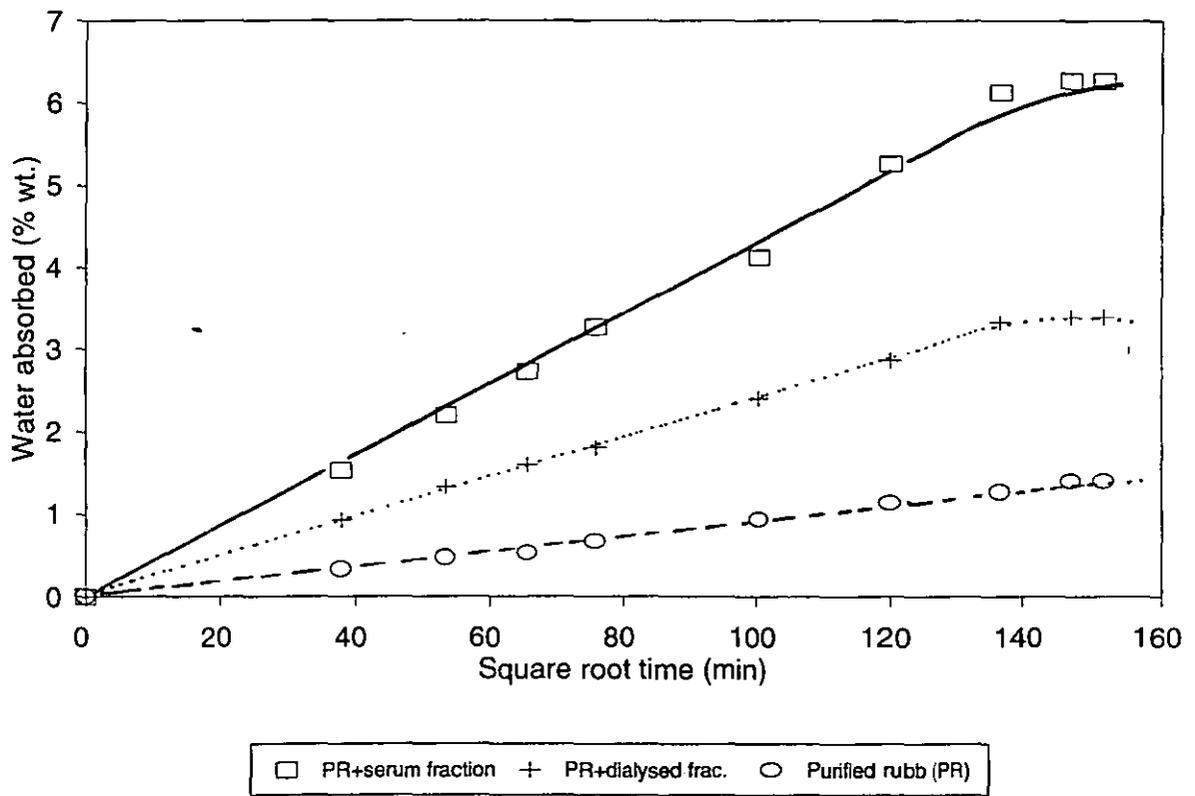
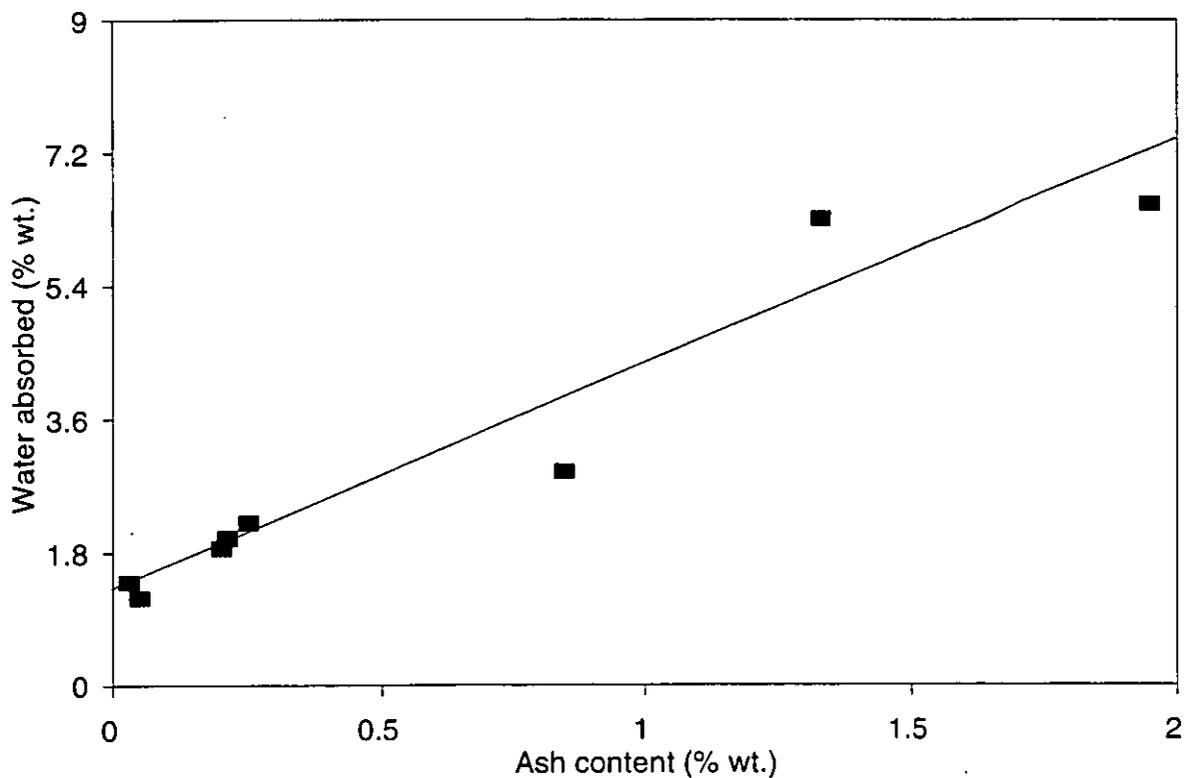


Figure 5.8
Equilibrium water uptake as a function of ash contents



These results together with those above clearly showed that the presence of proteins, which are high molecular weight materials, does not significantly induce the water uptake by the rubber. The low water uptake showed by DPNR could not be entirely due to the removal of proteins. Low molecular inorganic materials, which were also removed during the processing of DPNR, are responsible for the low water uptake.

b) Effect of fillers on water uptake

The water uptake by DPNR, TSR and SMR containing three types of filler, namely carbon black (N330), coated and uncoated calcium carbonate were investigated. Swelling tests were carried out at room temperature for up to 45 days ($t^{1/2}=250$ min).

Equilibrium swelling was reached after immersing the rubber for about 14 to 30 days, depending on the types of rubber used. For instance, unfilled DPNR takes about 14 days to reach equilibrium swelling weight while TSR takes a longer time (ca.30 days) (*Figures 5.9-5.11*)

Generally it was observed that the rates and equilibrium water uptake by both unfilled and filled TSR were higher than SMRL and DPNR. The rates and amount of water absorbed are summarised in *Table 5.4*.

Table 5.4: Equilibrium water uptake by DPNR, SMRL and TSR

Rubber	Water uptake (% wt.)	Rates (mg/cc/ $t^{1/2}$)	Corr. coeff
DPNR unfilled	0.81	0.05	0.9937
SMRL unfilled	1.44	0.11	0.9867
TSR unfilled	3.96	0.21	0.9958
DPNR+carbon black	0.93	0.06	0.9907
SMRL+carbon black	1.44	0.09	0.9892
TSR+carbon black	3.00	0.16	0.9960
DPNR+calcium carbonate	0.66	0.05	0.9930
SMRL+calcium carbonate	1.04	0.07	0.9930
TSR+calcium carbonate	2.83	0.13	0.9918

Figure 5.9
Water uptake by different types of unfilled natural rubber

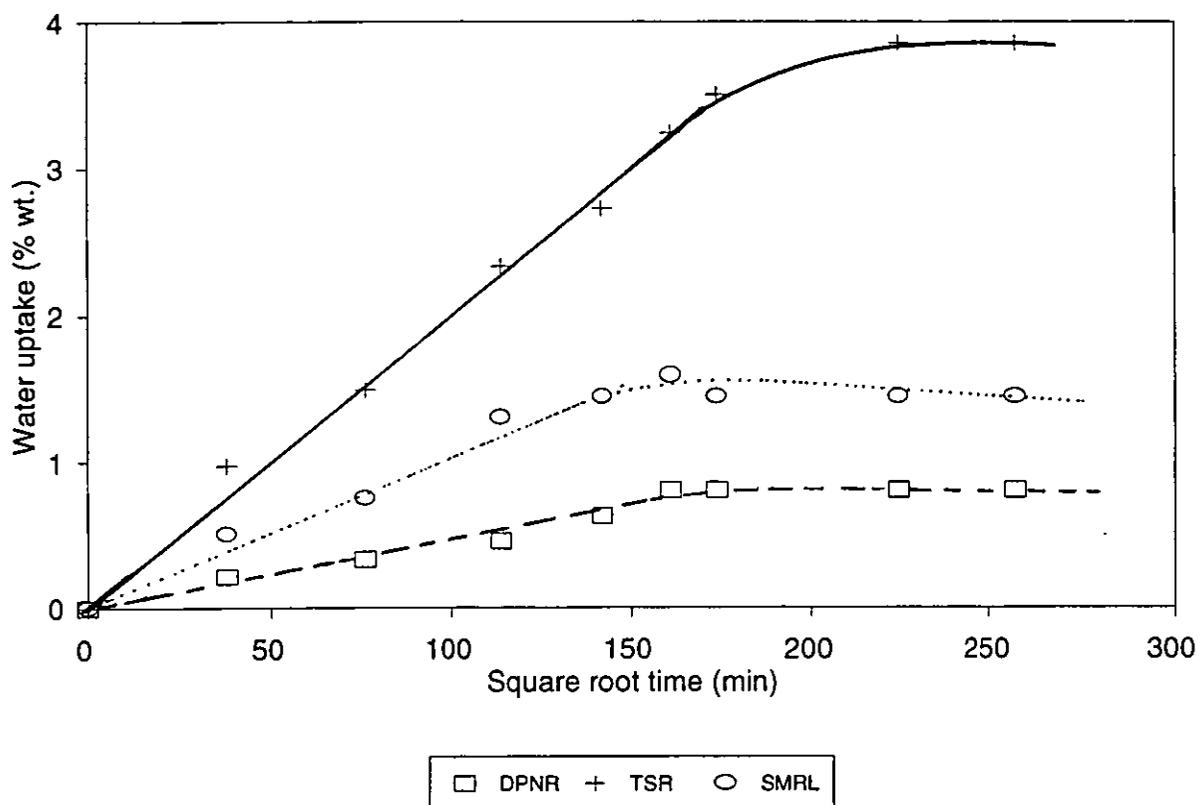


Figure 5.10
Water uptake by different types of natural rubber
filled with carbon black

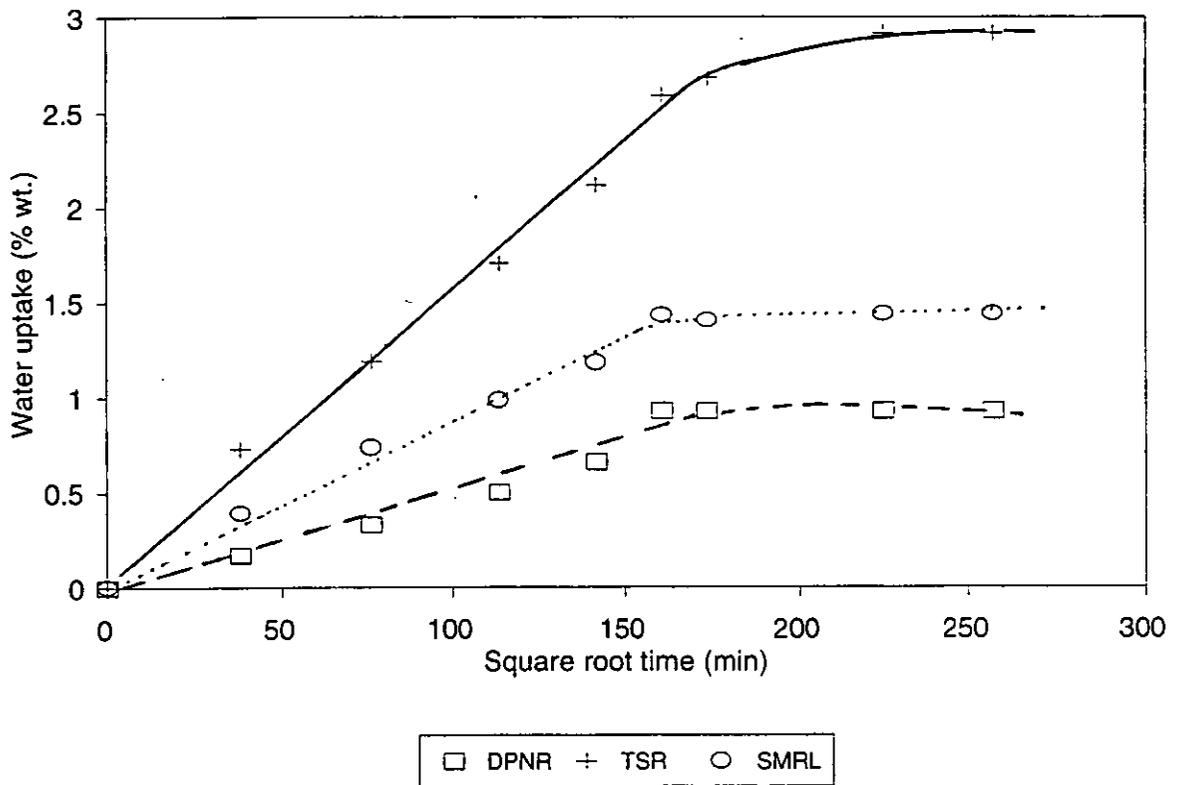
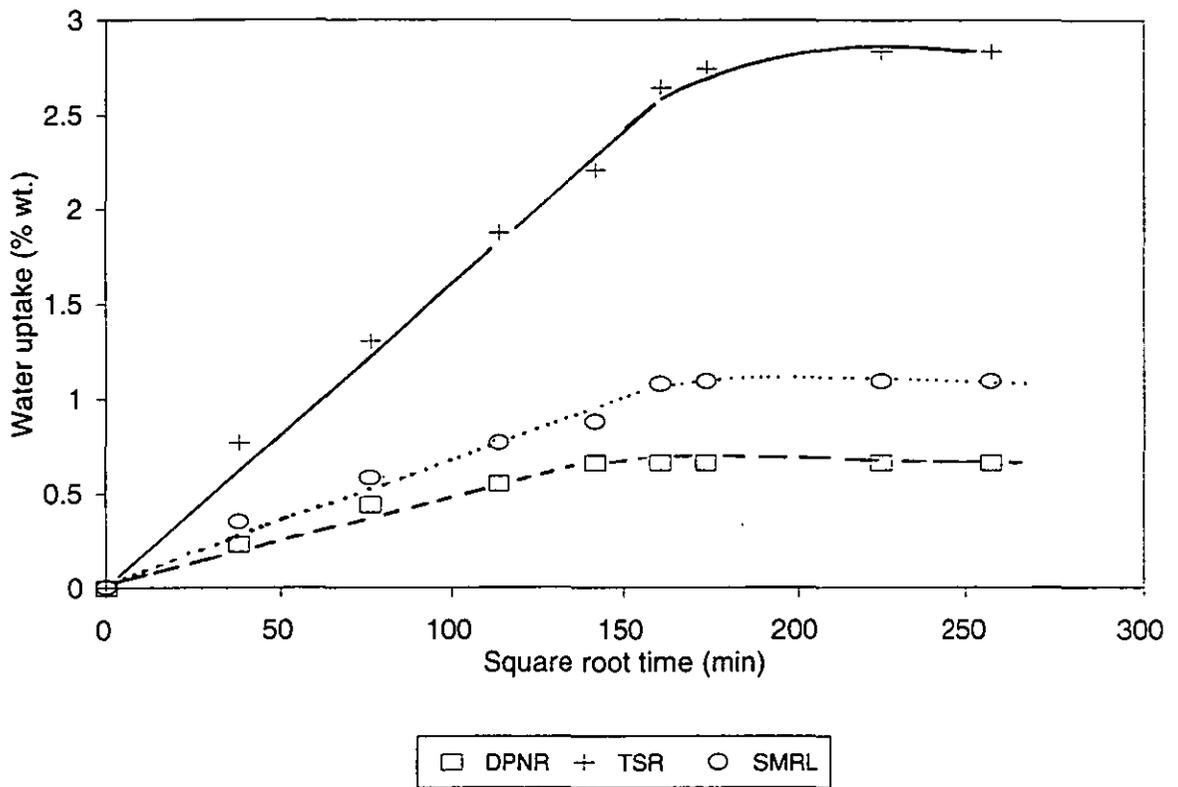


Figure 5.11
Water uptake by different types of natural rubber
filled with CaCO_3



According to the present understanding of water absorption phenomena, water is induced into the rubber due to the presence of hydrophilic sites such as non-rubber materials. The higher proportion of non-rubber constituents in TSR than DPNR provides more sites in the former for the water to diffuse. As water diffuses into the rubber to swell the non-rubber materials, watery domains are formed. This resulted in a higher osmotic pressure gradient between the swollen domains and the external solution. In TSR, more watery domains are formed than in DPNR. This results in a higher pressure gradient, hence higher rates and amount of water uptake by TSR than DPNR. This also leads to a longer time for the equilibrium swelling to be achieved.

The presence of filler in rubbers gave a similar pattern of results. Rubber containing higher natural non-rubber constituents such as TSR absorbed more water than the rubber containing lower quantity of non-rubber constituents such as DPNR.

At equilibrium swelling, filled rubber was observed to absorb less water than unfilled rubber. This could be due to the presence of lower quantity of the rubber in filled compared with unfilled compound. By assuming that the water absorbed by rubber is linearly related to the total volume of rubber present, a calculation of the amount of water imbibed by the filled TSR was made. The calculation was based on the value of water imbibed by the unfilled TSR; the results obtained are given in *Table 5.5*.

Table 5.5: Experimental and predicted equilibrium weight of water imbibed by filled rubbers

Rubber	Relative volume of rubber	Water imbibed (%wt.)	
		experimental	predicted
TSR unfilled	1.0	4.0	-
TSR+black	0.745	3.0	2.98
TSR+CaCO ₃	0.718	2.8	2.87

The experimental values were found to be approximately the same as the predicted values. This shows that the total amount of water imbibed is dependent on the volume of rubber present and diffusion takes place only in the rubber phase. The presence of fillers will reduced the amount of water absorbed by the rubber.

5.2.2: Elastic properties

a) Effects of non-rubber constituents on elastic properties

The stress-strain behaviour, which is one of the important characteristics of rubber, depends on factors such as types of rubber, vulcanizing systems and reinforcing agents. For natural rubber, the tensile modulus has also been reported to be influenced by the presence of the naturally occurring non-rubber constituents (ALTMAN, 1948; SMITH, 1974).

The variability of the raw NR within and between different grades as a result of the differences in the processing of the rubber has been investigated (FULLER, 1988). These variations in properties often cause processing difficulties and frequently lead to complaints by the users.

Tensile modulus is the common parameter used for the assessment of the variability of different rubber grades. Test carried out during this study on rubbers having the same formulation showed that the relaxed modulus at 100% strain (MR 100) of the SMR 20 is approximately 30% higher than the SMR L, and the latter has a similar modulus to the DPNR, a rubber which contained a small quantity of nitrogenous materials (Table 5.6). This difference may be due to the variation in the methods of processing the raw rubber and consequently gives rise

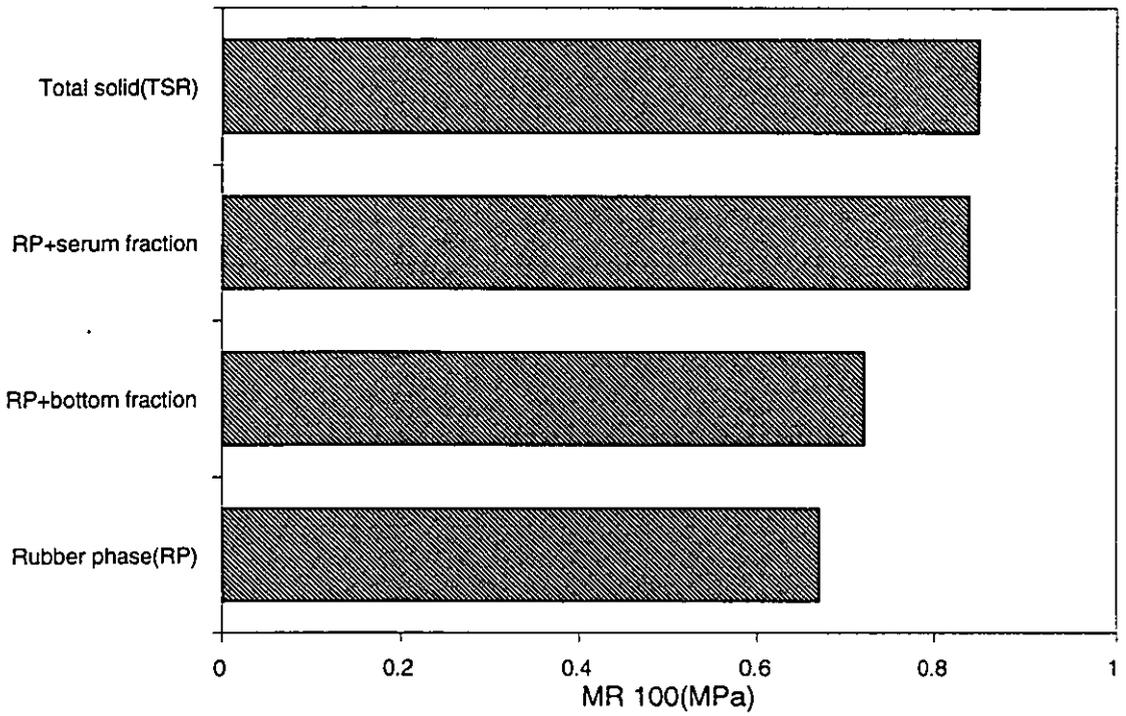
to different types of non-rubber constituents present; SMR 20, though contained about the same quantity of nitrogenous materials as the SMR L, has a longer maturation time prior to the natural coagulation process. The long maturation time allows the bacteria in the NR latex and wet rubber to consume the proteinaceous non-rubber constituents. This causes the breakdown of the non-rubber constituents, giving rise to different types of nitrogenous degradation products. The presence of these nitrogenous products contributed to the variable modulus observed with different grades of NR.

Table 5.6 : Physical properties of commercial grades natural rubber

Rubber	Hardness (IRHD)	MR 100 (MPa)	Nitrogen content (% wt.)
SMR L	35	0.62	0.41
SMR 20	41	0.81	0.41
DPNR	36	0.66	0.08

The variability of the modulus of rubber was initially investigated using rubber latex which was separated from the non-rubber constituents by centrifuge. The moduli of different fractions of the centrifuged rubber latex were measured. A wide variation in the values of modulus was observed; results obtained showed that the rubber phase containing the serum fraction gave a markedly higher modulus than the corresponding rubber phase containing the bottom fraction (*Figure 5.12*). The modulus of the rubber phase containing serum fraction is approximately the same as the modulus of the total solid rubber. This clearly shows that the serum fraction contained the non-rubber constituents which influences the modulus of the vulcanizates.

Figure 5.12
Modulus of centrifuged natural rubber latex fractions



The non-rubber constituents which are present in the serum fraction includes proteins and its hydrolysed components (amino-acids). Incorporation of 3% weight proteins into the purified rubber, (namely the hydrophilic bottom and serum proteins and the hydrophobic proteolipids), did not give any significant difference in the modulus of the vulcanizates (*Figure 5.13*).

However, tests carried out using rubber containing amino-acids gave markedly different results. The presence of certain types of amino-acid gave a marked increase in the modulus of the rubber. For instance, the incorporation of 1% weight of arginine gave about 60% increase in modulus of the purified rubber. However, the presence of amino-acids such as the glutamic acid did not give any effects on the modulus of the rubber.

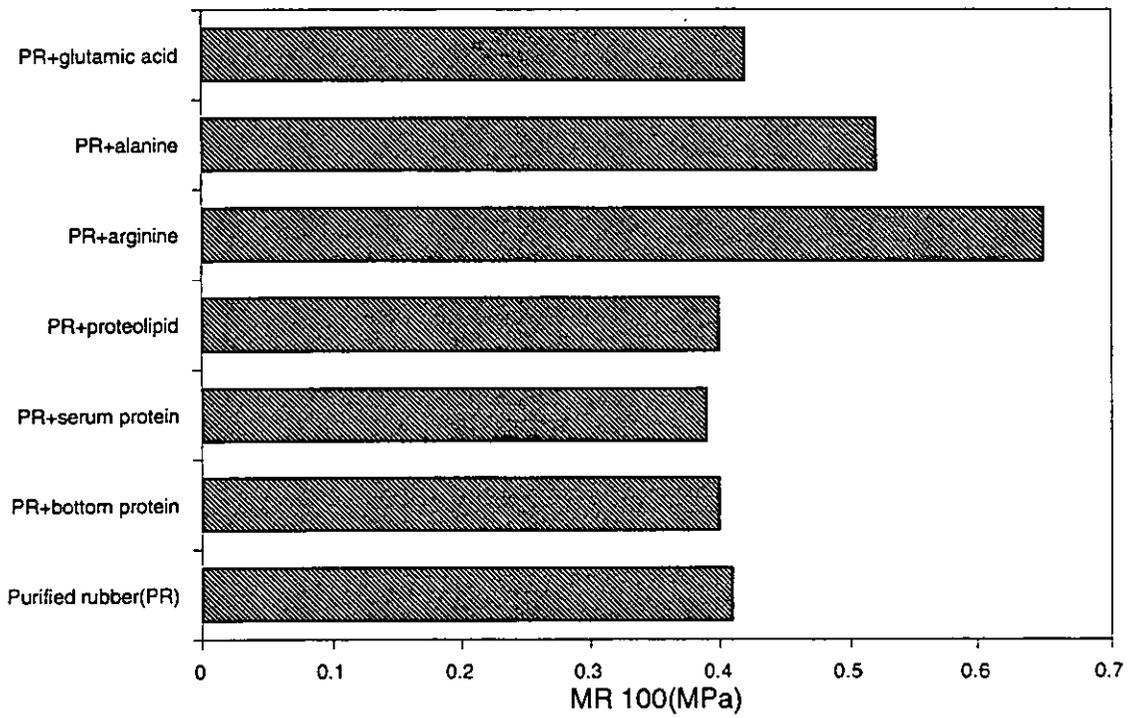
The effects of non-rubber constituents on purified rubber are summarised in *Table 5.7*.

Table 5.7: Change in modulus due to the presence of non-rubbers constituents

Non-rubbers	Change in modulus (MR100)
proteins (3% wt.)	no effect
glutamic acid(1% wt.)	no effect
alanine (1% wt.)	27% increase
arginine (1% wt.)	60% increase

The absence of any effect with the incorporation of proteins suggests that no chemical reaction takes place between protein molecules and the rubber network. The proteins molecules probably acted as inert fillers, as suggested by Metherell (METHERELL, 1980). At this low level of loading (1-3 phr), the stiffening effects imparted by proteins will be marginal.

Figure 5.13
Modulus of purified rubber containing proteins
and amino-acids



The presence of protein in the rubber vulcanizates was studied using scanning electron microscopy (SEM). The SEM micrographs taken from purified rubber containing proteins showed large lumps of undispersed particles (*Figure 5.14*). They are most probably proteins particles since they are absent in the vulcanizates of purified rubber without non-rubber additives or those containing amino-acids. These micrographs confirmed the suggestion that proteins are not soluble in rubber and acted as inert fillers.

The marked increase in modulus of rubber containing amino-acids such as alanine and arginine could be due to an increase in the crosslink density of the rubber network. In order to check this possibility, the crosslink density of the rubber was calculated using both the equilibrium swelling technique and stress-strain measurement. The equilibrium swelling measurement yields the number of chemical crosslinks between the molecular chain. The stress strain data, on the otherhand, give the total number of crosslinks, which includes both chemical crosslinks and physical linkages due to chain entanglements.

The swelling technique involves immersing the rubber in toluene until its weight reaches equilibrium and calculating the crosslink density using the Flory-Rehner equation (FLORY & REHNER, 1943). The equation relates the molecular weight between crosslink, M_c , to the volume fraction of rubber, V_r , by the following,

$$(\rho V/M_c)V_r^{1/3} = -\ln(1-V_r) - V_r \chi V_r^2 \quad 5.1$$

where ρ is the density of rubber, V is the molar volume of the solvent and χ is the rubber-solvent interaction parameter.

(a)



(b)



(c)

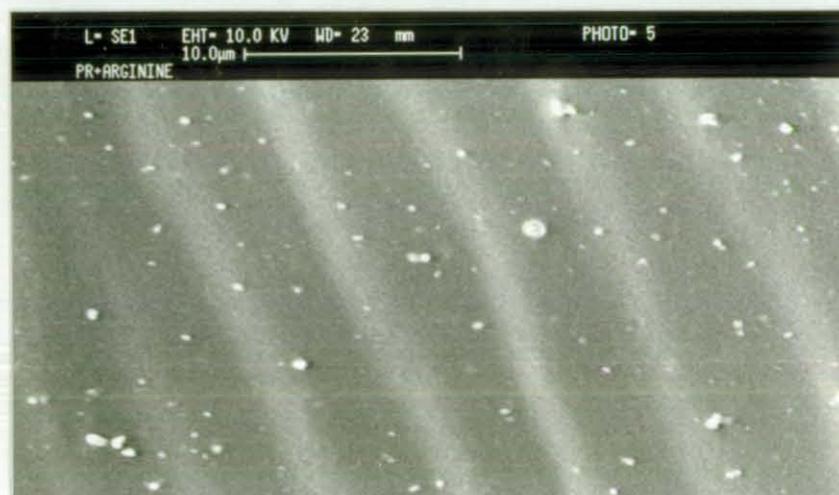


Figure 5.14
Micrographs of rubber surface containing proteins and amino-acids (a) purified rubber (PR) (b) PR+protein (c) PR+amino-acid (arginine)

For NR-toulene system, the interaction parameter was taken as 0.41. Knowing the interaction parameter and the volume fraction of rubber, the molecular weight between crosslink, M_c , which is inversely related to the crosslink density, can be calculated.

The crosslink density of purified rubber containing alanine and arginine was calculated from the equilibrium swelling data. Results obtained showed an increase in the chemical crosslink density of these rubbers; the presence of alanine and arginine increased the crosslink density of the purified rubber by about 17% and 55% respectively (*Table 5.8*).

Table 5.8 : Properties of purified rubber containing alanine and arginine

Rubber	MR 100 (MPa)	$(1/M_c) \times 10^5$ (mole/g)	Compression set (72h @ 70°C. %)
Purified Rubber(PR)	0.42	2.44	51.4
PR+alanine	0.52	2.86	43.0
PR+arginine	0.65	3.80	24.0

The crosslink density of the rubber could also calculated from the stress-strain data using the Mooney-Rivlin equation (MULLINS & THOMAS, 1963; CAMPBELL et. al. 1992). The equation relates the nominal stress, σ , with extension ratio, x , by

$$\sigma/(x-1/x^2) = 2C_1 + 2C_2/x \quad 5.2$$

where C_1 and C_2 are the Mooney constants (see section 3.2.1). Plotting the values of $\sigma/(x-1/x^2)$ against $1/x$ gives a linear line of slope C_2 and intercept C_1 . The constant, C_1 , is related to the molecular weight between crosslink, M_c , by

$$C_1 = \rho RT / 2M_c \quad 5.3$$

where ρ is the density, R is the gas constant and T is the absolute temperature. With known C_1 , the value of M_c is calculated.

For the series of rubber studied, the crosslink densities obtained are given in *Table 5.9*. The presence of amino-acid such as arginine in purified rubber resulted with about 100% higher physical crosslink density (i.e $1/M_c$); this is higher than TSR.

Table 5.9 : Crosslink density of purified rubber(PR) containing proteins and amino-acids

Rubber	$(1/M_c) \times 10^5$ (mole/g)	Corr. coeff.
Purified rubb.(PR)	7.67	0.9992
PR+protein	8.88	0.9994
PR+glutamic acid	7.00	0.9994
PR+alanine	10.04	0.9997
PR+arginine	17.00	0.9999
Total solid(TSR)	13.52	0.9996
SMRL	8.08	0.9995

It may be noted that the values of the crosslinks obtained from the stress strain data were about three times higher than the chemical crosslinks obtained from swelling data. These differences could possibly be attributed to the introduction into the network of physical entanglements as an indirect consequence of the formation of the chemical crosslink. Such entanglements would serve as additional crosslinks and hence the divergence between the two different methods of determination of the crosslink density (BATEMAN et. al, 1963).

The above results, which gave differences in crosslink density of rubber due to the presence of amino-acids, showed that some types of amino-acid such as alanine and arginine take part in the chemical reaction of the rubber. This chemical reaction occurs during the vulcanization process (*Figure 5.15*).

During the vulcanization process, the reactions has been demonstrated to be accelerated by a complex of zinc accelerator thiolate, either catalytically or with the formation of zinc sulphide (CHAPMAN AND PORTER, 1988). To be effective, the zinc thiolate must be soluble in rubber. The presence of amino acids such as arginine and arginine assist the formation of a rubber-soluble complexes; a high concentration of this complex is desirable. These soluble complexes react with sulphur to form zinc perthiomercaptides, the active sulphurating agent which is defined as the species which reacts with the rubber hydrocarbon to form the C-S bonds (BATEMAN et. al.,1963).

In a vulcanization reaction, if a high concentration of zinc perthiomercaptide complexes is available, two reactions are possible. Firstly, since zinc perthiomercaptides complex is a catalyst responsible for the reaction of sulphur with rubber, the efficiency of the sulphur vulcanization could increase. Thus, in the presence of amino-acids, where more rubber-soluble complexes are formed, a more efficient vulcanization reaction could take place. This could lead to rubber having higher crosslink density, as can be seen with purified rubber containing arginine and alanine.

Secondly, a high concentration of zinc perthiomercaptide complexes could lead to a faster rate of desulphuration of the polysulphide crosslinks. This occurs during the network maturing reactions, at the expense of crosslink decomposition and thus more crosslinks of lower sulphur rank (i.e mono- and disulphidic types) are formed. This is in accord with the low compression set values obtained using the rubber containing these amino-acids (*see Table 5.8*).

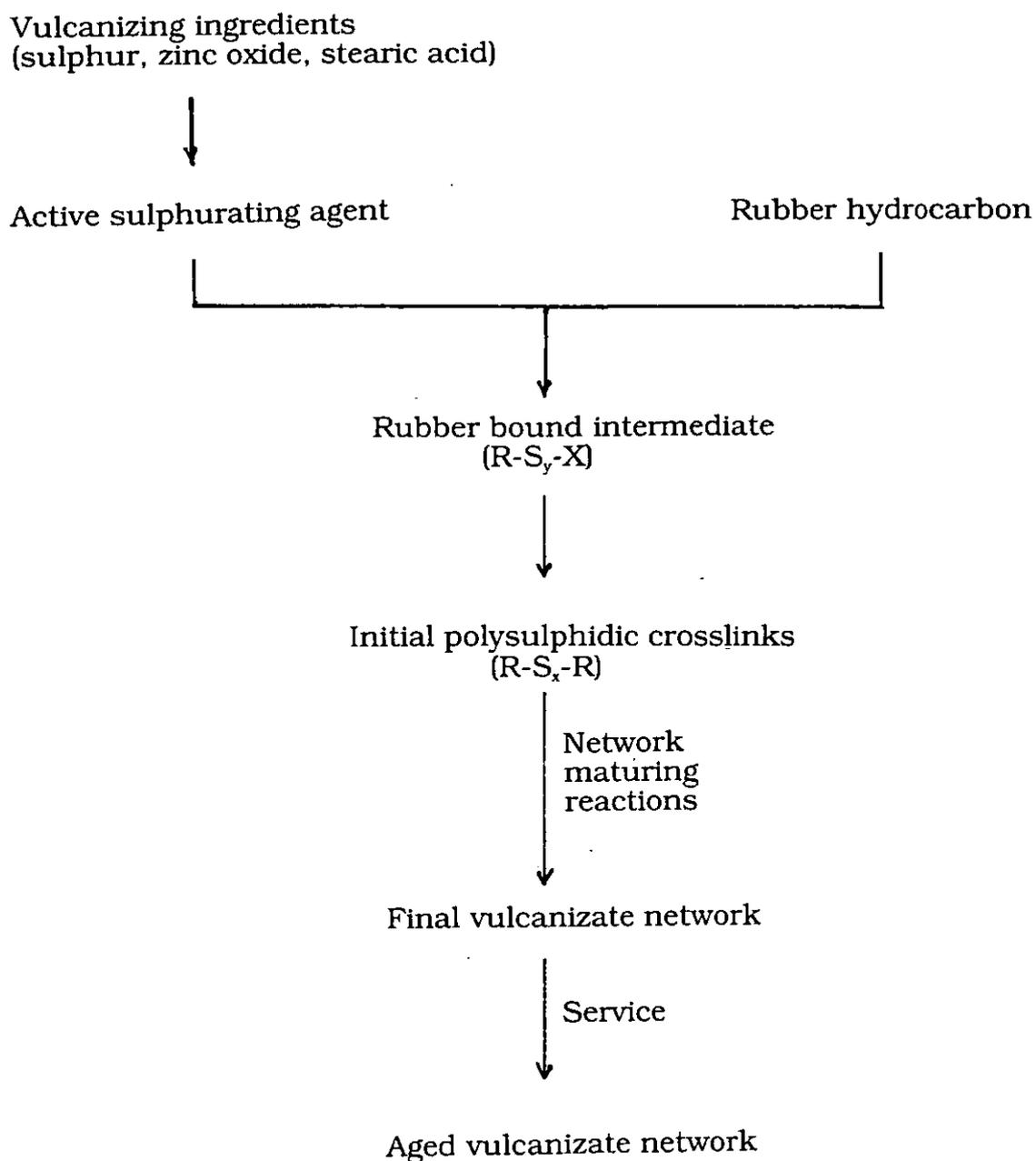


Figure 5.15
Overall course of accelerated sulphur vulcanization

b) Effect of fillers on elastic properties

The chemical activities of non-rubber constituents in filled systems were investigated using total solid rubber (TSR) vis-a-vis DPNR. Both reinforcing carbon black and non-reinforcing calcium carbonate fillers were used and the rubbers were compounded using the same formula.

Results obtained showed that, generally, filled TSR has higher modulus than filled DPNR. For instance, at 100% strain, the difference in stresses between TSR and DPNR varies from about 13% for carbon black filled rubber to about 32% for calcium carbonate filled rubber (*Table 5.10*). Since comparisons are made between different rubbers, with all other variables the same, these variations in stress are presumably due to the differences in the non-rubber constituents present; TSR contained higher non-rubber constituents than DPNR. The higher modulus obtained with TSR suggest that the non-rubber constituents present in the vulcanizates take part in the vulcanization reaction of filled rubber, similar to unfilled rubber.

It may be noted that the change in modulus between carbon black and calcium carbonate filled rubbers is more than double. This difference is due to factors which are discussed in section 5.5.1

Table 5.10 : Difference in modulus between unfilled and filled TSR and DPNR at 100% extension

Rubber	Modulus (MR 100) (MPa)	Modulus increase (%)
DPNR unfilled	0.6031	
TSR unfilled	0.7432	23
DPNR + black	1.4637	
TSR + black	1.6541	13
DPNR + CaCO ₃	0.8916	
TSR + CaCO ₃	1.1736	32

5.2.3: Change in elastic modulus with humidity

a) Unfilled rubber

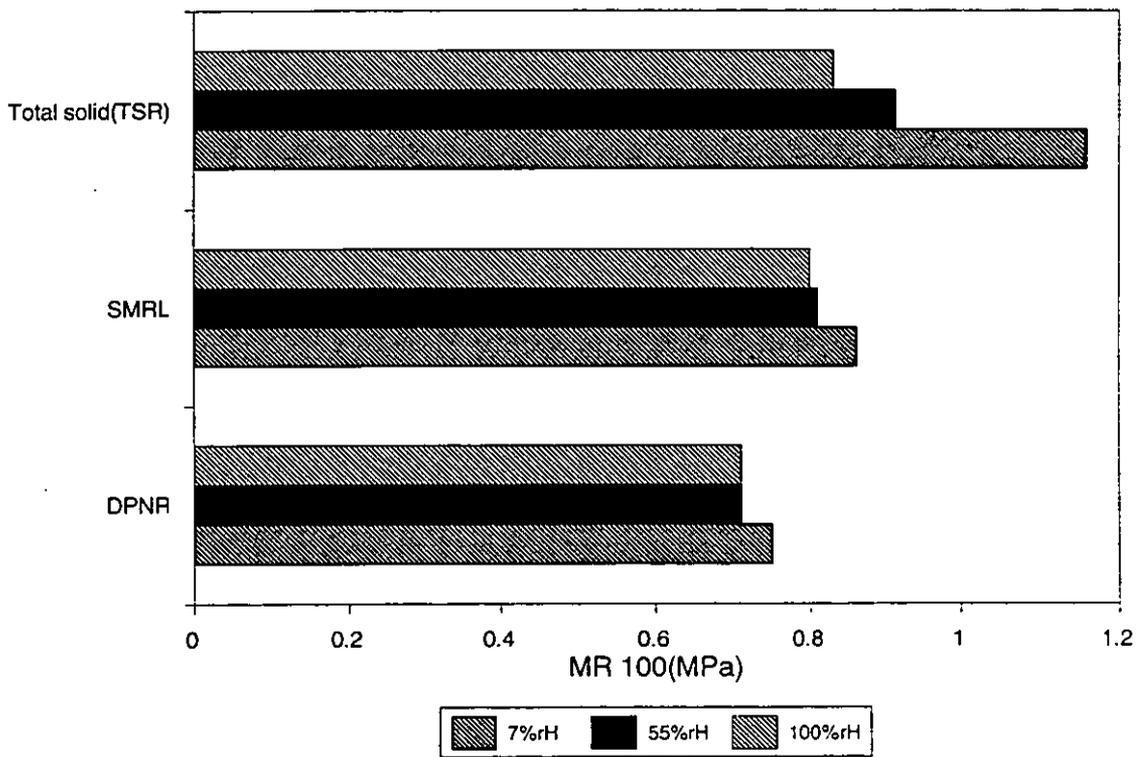
Various authors have demonstrated changes in modulus with humidity (DERHAM, 1972; LAKE AND POND, 1989). It was reported that by changing the relative humidity from about 20% to 80% reduces the modulus of the conventional sulphur cured unfilled SBR by about 3-5% while the equivalent NR vulcanizates gave about 6% reduction. When rubber was immersed in water, it was reported that the modulus decrease linearly with the amount of the water imbibed.

The present work undertook a study to show how the presence of natural occurring non-rubber constituents and fillers would modify these relationships.

The tests were carried out by equilibrating the test specimen to fixed humidity levels, namely two low humidity (7% and 25%RH), room humidity (about 55%RH) and high humidity (100%RH.). Modulus values obtained on tests carried out using different types of unfilled NR, having different proportions of non-rubber constituents are given in *Figure 5.16*.

Variation of up to 30% in the modulus was observed when the rubbers were subjected to an environment of different relative humidity. The total solid rubber (TSR) gave about 21% decrease in modulus when the relative humidity changes from 7% to 55% and a further 9% reduction in modulus occurred when the sample was immersed in water for 14 days at room temperature. DPNR is least affected (ca.5%) by the changes in relative humidities and immersion in water, followed by SMR (ca. 7%).

Figure 5.16
Change of modulus with humidity for different
types of natural rubber



Stress strain tests on unfilled DPNR, TSR and SMR which were equilibrated at different relative humidities were carried out and the results are given in *Figures 5.17-5.19*. Using the Mooney-Rivlin equation, crosslink densities of the rubber were calculated from the stress-strain data and the results are given in *Table 5.11*. The results obtained showed that there was an apparent decrease in the crosslink density of the rubber when the sample was equilibrated from a lower to a higher relative humidities. The unfilled TSR gave about 5% decrease in crosslink density when the humidity was increased from 25% to 55%. About 12% drop in modulus was observed when the humidity was increased from 25% to 100% These changes are of similar magnitude to the changes in modulus. No significant decrease in crosslink density was observed with DPNR and SMR.

Table 5.11: Crosslink density of rubber equilibrated at different relative humidities.

Rubber	Humidity (RH,%)	$(1/M_c) \times 10^5$ (mole/g)	Corr. coeff.
DPNR	25	11.26	0.999
	55	11.12	0.999
	100	11.26	0.999
TSR	25	14.42	0.999
	55	13.62	0.998
	100	12.67	0.999
SMR	25	12.50	0.999
	55	12.37	0.999
	100	11.49	0.999

The preceding results showed that rubber having higher amount of non-rubber constituents (TSR) gave bigger change in modulus/crosslink density with humidity than 'cleaner' rubber (DPNR). Tests were carried to determine the types of non-rubbers which are responsible for the variation in modulus with humidity. Total solid rubber, centrifuged rubber fractions (see section 2.1.2) and purified rubber containing added non-rubber constituents were used.

Figure 5.17
Stress-strain behaviour of unfilled DPNR
at different humidities

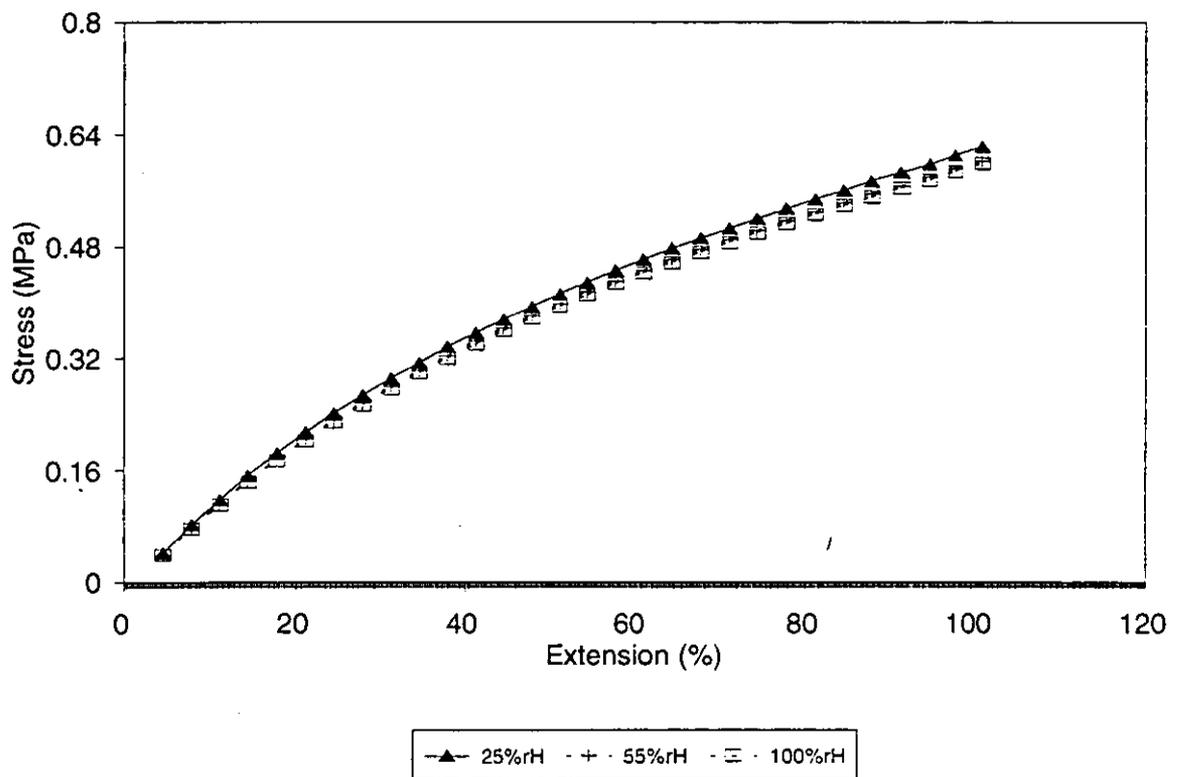


Figure 5.18
Stress strain behaviour of unfilled TSR
at different humidities

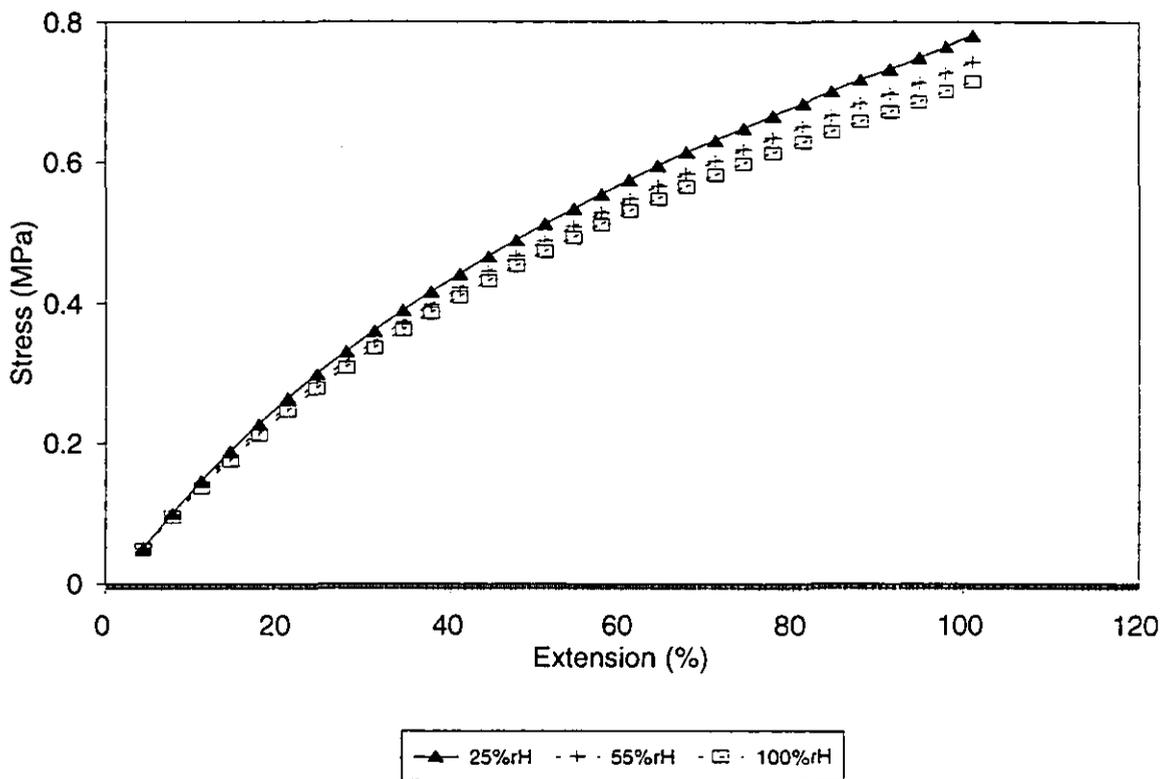
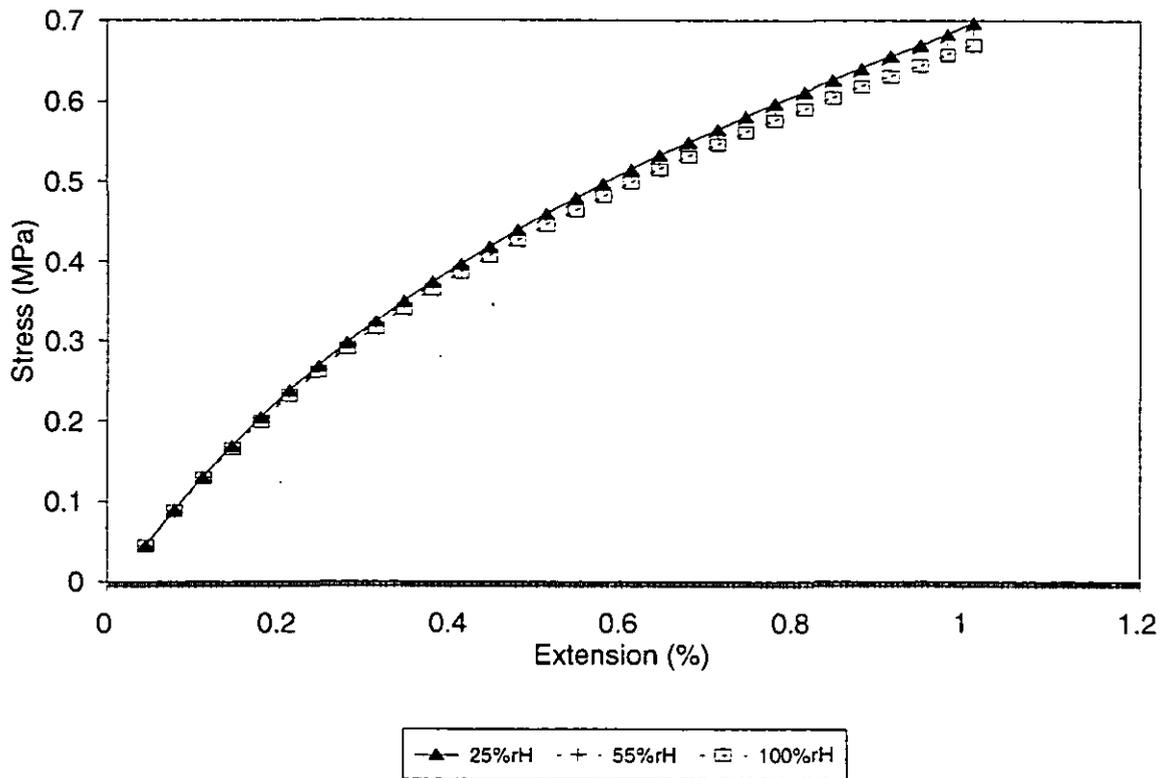


Figure 5.19
Stress strain behaviour of unfilled SMRL
at different humidities



Results obtained from rubbers prepared by centrifugation of the latex (TSR) are shown in *Figure 5.20*. The rubber phase(RP) gave a relatively small (ca.8%) decrease in modulus when the relative humidity was increased from 7% to 100%. However, the corresponding vulcanizates obtained from RP containing added serum fraction gave a marked reduction (ca 28%) in modulus; they are similar to the total solid rubber.

With purified rubber and purified rubber containing added proteins, a small reduction in modulus was obtained. A change in relative humidity from 7% to 100% only gave about 4% to 8% reduction in modulus (*Figure 5.21*). A similar change in modulus was observed with purified rubber containing certain types of amino-acid such as glutamic acid.

However, when certain types of amino-acid, such as arginine, or alanine, were present in the purified rubber, there were marked reductions in modulus with humidity. For instance, when arginine was incorporated into purified rubber, there was about 13% reduction in modulus when the humidity increased from 7% to 55%. When the humidity was increased from 55% to 100%, a further 3% reduction in modulus was observed.

The change in modulus with humidity for purified rubber(PR) containing proteins and amino-acids as well as centrifuged latex fractions are summarised *Table 5.12*.

Table 5.12: Effect of relative humidity on modulus

Rubber	Reduction in modulus(%)	
	7% to 55%RH	55% to 100%RH
PR	4	2
PR+proteins	4	2
PR+glutamic acid	3	2
PR+alanine	11	2
PR+arginine	13	3
Rubber phase(RP)	6	3
RP+bottom fraction	10	7
RP+serum fraction	22	7
Total solid(TSR)	22	9

Figure 5.20
Change of modulus with humidity for
centrifuged latex fractions

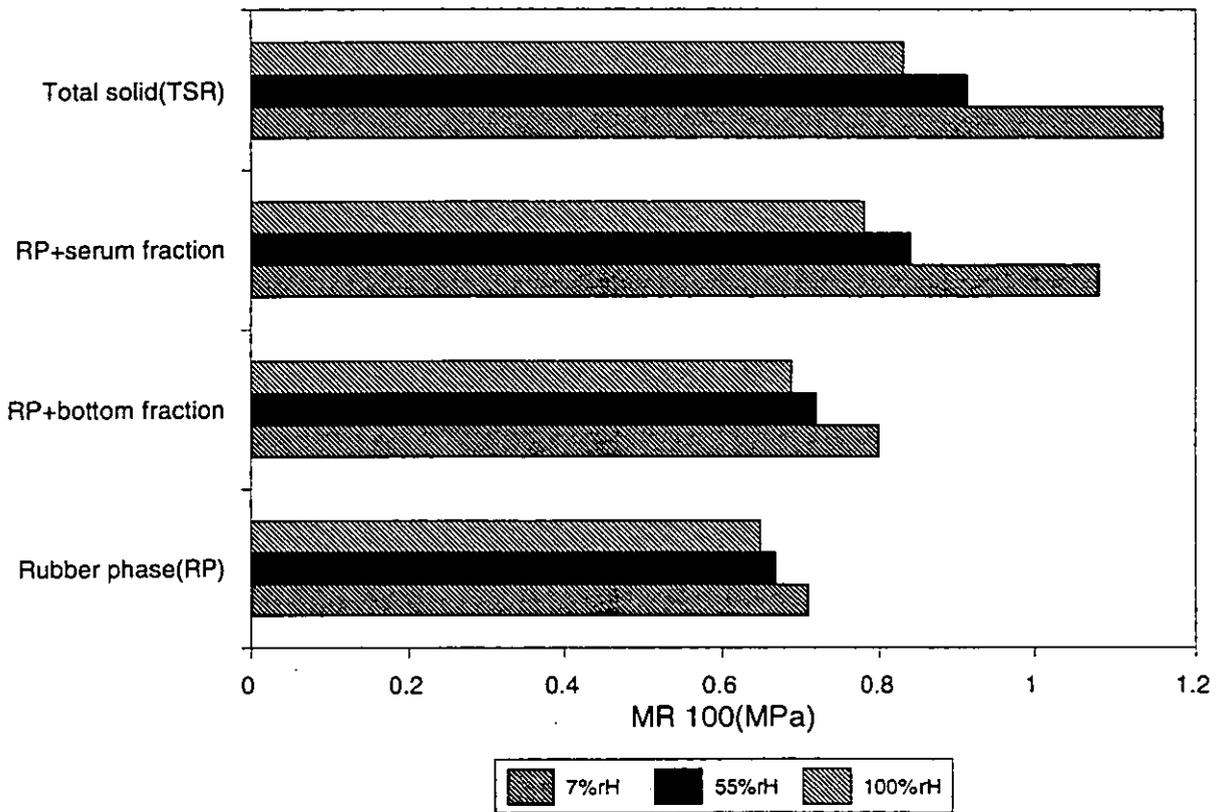
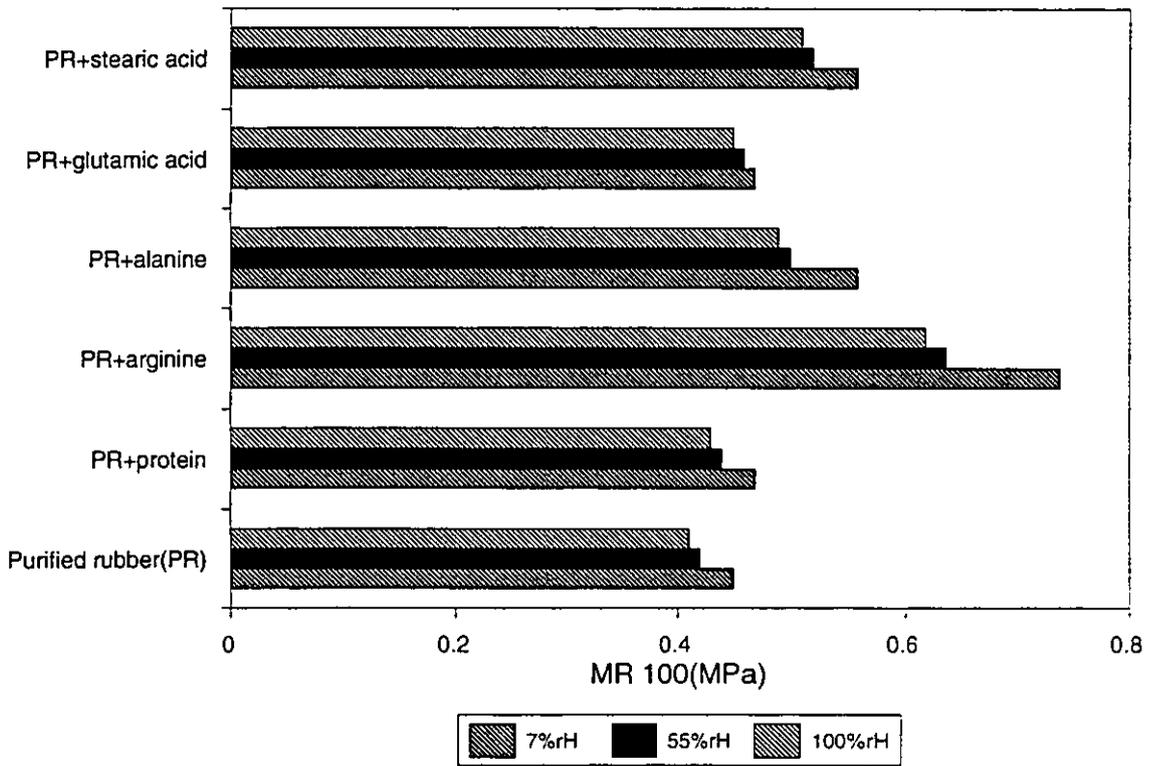


Figure 5.21
Change of modulus with humidity for
purified rubber containing non-rubbers



An increase in relative humidity gave a significant reduction in modulus particularly with purified rubber containing amino-acids such as arginine and alanine. The rubber phase which contained proteins and lipids gave small reduction in modulus with humidity; purified rubber containing proteins gave similar results. Thus it is likely that the large reduction in modulus with humidity observed with TSR and RP containing added serum fraction is not due to the presence of proteins but amino-acids. These amino-acids, such as alanine and arginine, are known to be present in the serum fraction of the latex (ARCHER et. al., 1963).

b) Filled rubber

The study on the effect of relative humidity was extended to filled rubbers. Two different types of filler were used; reinforcing carbon black and non-reinforcing calcium carbonate (CaCO_3). They were incorporated into rubber containing different amounts of non-rubber constituents and the vulcanizates equilibrated at different relative humidities.

Results obtained showed that, even with filled system, equilibrating the rubber at different relative humidities gave variation in modulus. Generally, the rubber which was equilibrated at lower humidity gave a higher modulus (or stress) than those equilibrated at higher humidities, similar to unfilled system. These are shown by plots of stress against extension for DPNR and TSR filled with calcium carbonate (*Figures 5.22-5.23*)

The reduction in stress with humidity was bigger for rubber filled with non-reinforcing filler than reinforcing fillers. These are shown in *Figure 5.24* where the change in stress for filled rubbers equilibrated between 25 to 55%RH and 25 to 100%RH are given.

Figure 5.22
Stress strain behaviour of DPNR filled with calcium carbonate

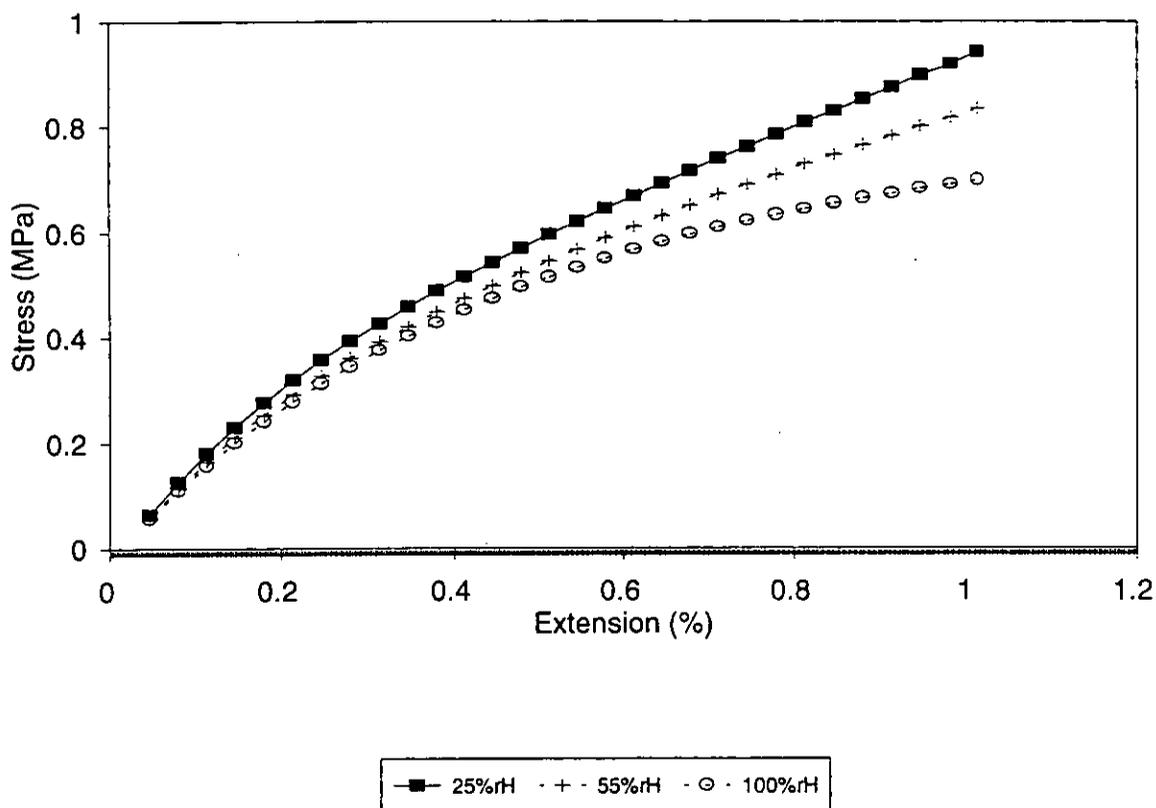


Figure 5.23
Stress strain behaviour of TSR filled with calcium carbonate

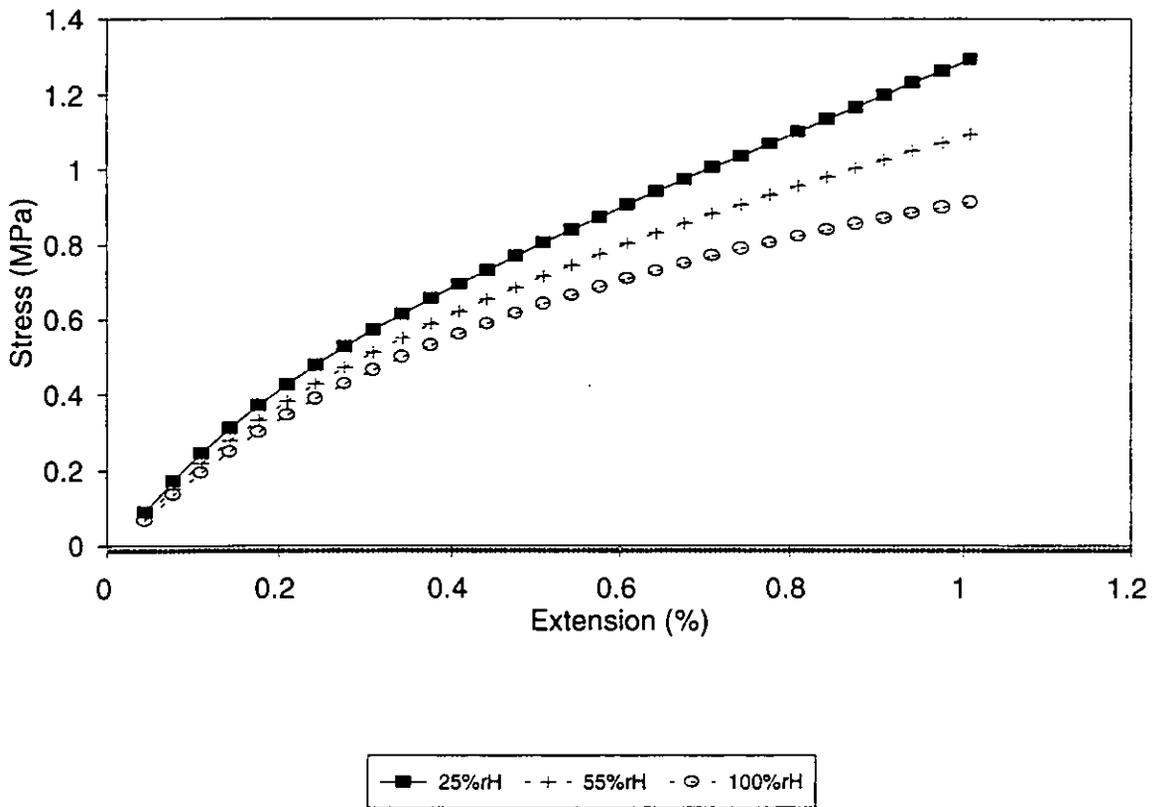
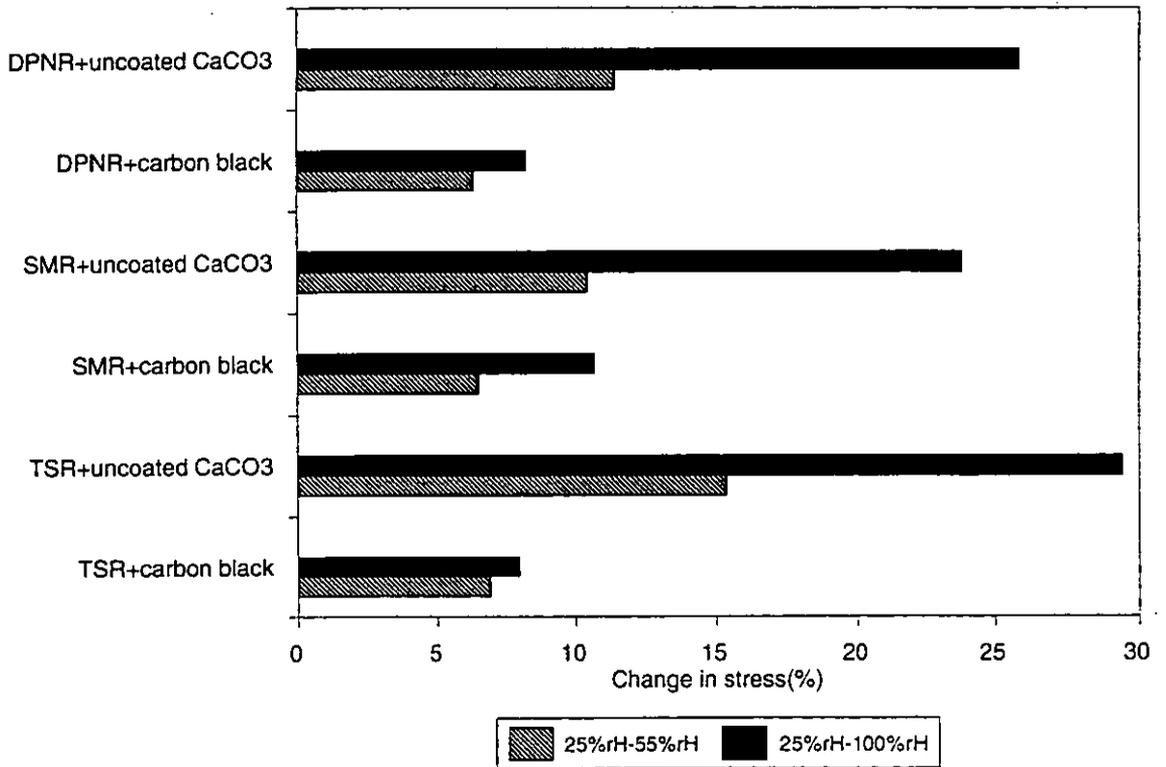


Figure 5.24
Reduction in stress after equilibration at
different humidities



It may be noted from *Figure 5.24* that with a filled system the effects of filler are more important than the amount of non-rubber constituents present. The reductions in stress with humidity for TSR and DPNR are about the same, indicating that the presence of about 5% wt. of non-rubber constituents in filled rubber gave no effect to the vulcanizates. The effect of humidity on the modulus due to the presence of non-rubber constituents has been masked by the fillers.

A possible mechanism responsible for the change in modulus with humidity is discussed in section 5.5.2.

5.3 PHYSICAL RELAXATION

Physical (or primary) relaxation has been associated with movement taking place amongst the following : rubber network; the side groups on the rubber chain; chain entanglements; filler structures/particles. This type of relaxation is dominant in the early stages of the relaxation process ($<10^4$ min.), particularly at ambient or low temperatures and the changes in stress has been observed to be linear with $\log(\text{time})$ (COTTEN AND BOONSTRA, 1967; DERHAM, 1973). The slope of the stress- $\log(\text{time})$ plot gives the rate of relaxation of the rubber. The rate of relaxation is often expressed in percent per decade of time.

5.3.1: Effect of non-rubber constituents on physical stress relaxation

It has been reported that DPNR has greater resistance to relaxation than conventional grades of SMR (SMITH, 1974). The current work which was carried out using three different types of rubber containing different proportions of natural non-rubber constituents is in agreement with those results. They were the unfilled DPNR, a conventional grade NR (SMRL) and the total solid rubber(TSR); TSR has a higher proportion of non-rubber constituents than SMRL and DPNR has the lowest content.

The results, presented as a plot of relative stress, f/f_0 against $\log t$ are given in *Figure 5.25*. DPNR was observed to have a higher relative stress than SMRL or TSR. This shows that DPNR has a lower rate of physical stress relaxation than SMRL or TSR. The relaxation rate of unfilled DPNR, expressed as percent per decade of time, was about 0.8% while the rate for SMRL was about 1.4%. The stress relaxation rate for TSR was marginally higher than SMR.

The reduction of the rate of stress relaxation of DPNR compared to SMR and TSR is presumably due to the removal of non-rubber constituents during deproteinisation process.

The non-rubber constituents removed during the production of DPNR includes proteins and amino-acids. A study was carried out to relate the presence of these individual non-rubber constituents to the relaxation rates of the rubber. Initially, tests were carried out using the three different centrifuged fractions of latex, namely the rubber phase(RP), the bottom fraction and the serum fraction. Results showed that the rates of relaxation of those rubber are as follows (*Figure 5.26*),

$$(RP=RP+\text{bottom fraction}) < (RP+\text{serum fraction}=TSR)$$

The relaxation rate of the RP containing added serum fraction is about 2.7% per decade, which is approximately the same as the total solid rubber(TSR), a rubber containing all naturally occurring non-rubber constituents. This shows that most of the non-rubber constituents which increased the stress relaxation of the rubber are in the serum rather than the bottom fraction.

The serum fraction contains several types of non-rubber including proteins and amino-acids. Proteins are the major component of the non-rubbers and amino-acids are their hydrolysis products. Accordingly, the effects of proteins and the amino-acids, on stress relaxation, were investigated.

Figure 5.25
Stress relaxation of different types of
unfilled natural rubber

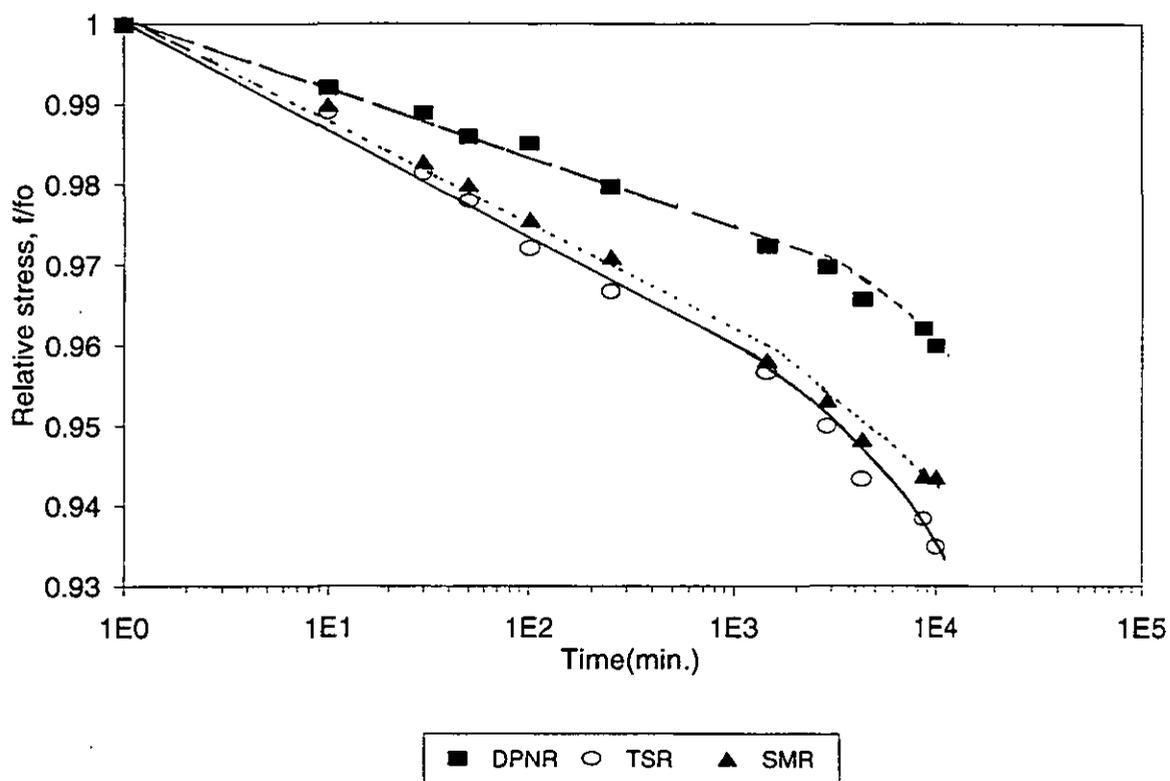
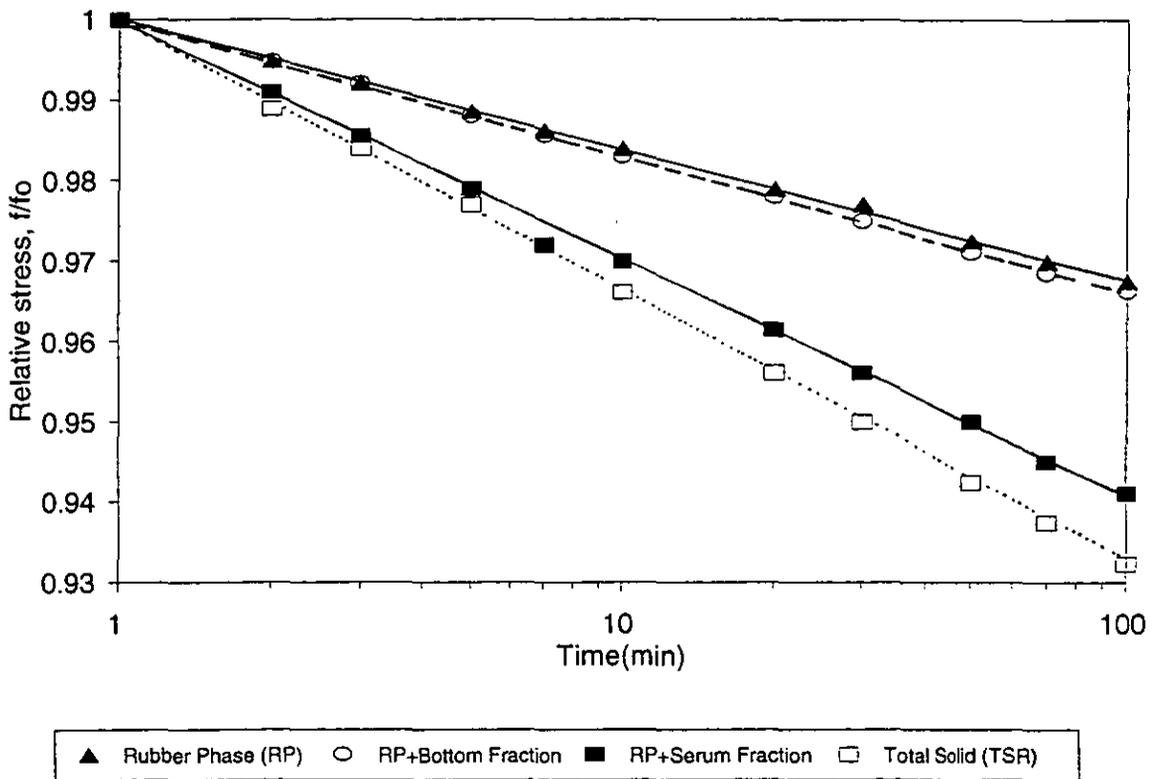


Figure 5.26
Stress relaxation of centrifuged NR latex fractions



The stress relaxation results, presented as a plot of relative stress against time for purified rubber containing proteins and amino-acids are shown in *Figure 5.27*.

The incorporation of 1% protein into the purified rubber did not give any significant change to the relaxation behaviour of the NR vulcanizates. The relative stress of purified rubber containing proteins was approximately the same as for purified rubber. A similar value was obtained with amino-acids such as glutamic acid.

However, the incorporation of amino-acids such as alanine and arginine, gave a different result; their relaxation rates were markedly lower. The presence of 1% alanine and arginine reduces the relaxation rate of purified rubber by about 30% and 60% respectively.

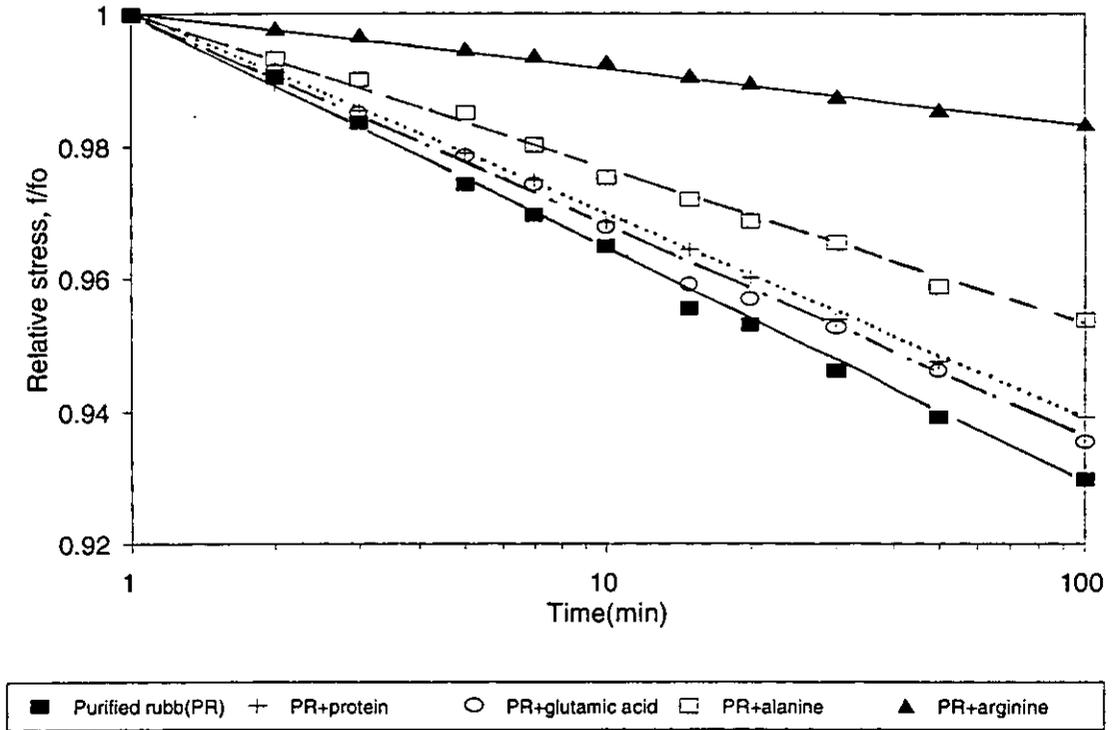
It may be noted that there are differences in the rate of relaxation between two 'clean' rubbers, purified rubber (ca. 0.04% wt. nitrogen) and DPNR (ca. 0.08% wt. nitrogen). It would be expected that these two rubbers have approximately similar relaxation rates due to the low amount of nitrogenous materials. However, direct comparisons of the results in *Figures 5.25 and 5.27* show the rate of relaxation of DPNR is lower than the rate for purified rubber.

These differences could be due to three possible reasons. Firstly, the two rubbers were processed by different methods, resulting with rubber having different average molecular weight. Purified rubber possesses lower molecular weight than DPNR as reflected by the lower Mooney viscosity values (*Table 5.13*). This will lead to purified rubber having comparatively higher relaxation rate than DPNR.

Table 5.13: Mooney viscosity of raw rubber

Rubber	Mooney viscosity [ML(1+4)@100°C]
Purified rubber	64
DPNR	81

Figure 5.27
Stress relaxation of purified rubber containing
proteins and amino-acids



Secondly, the two rubbers were compounded using different formulation; DPNR using a semi-EV and purified rubber with ACS-1 formulation. This will give rubber having different types of crosslink and give rise to differences in the relaxation rate.

Thirdly, commercial grade DPNR is treated with thiourea after the coagulation and washing processes. The thiourea treatment was carried out to increase the plasticity retention index of the raw rubber; an index giving a measure of the oxidisability of the rubber. This occurs by the chelation of the pro-oxidants present in the rubber and with the introduction of small amount of crosslinks to the rubber network. This treatment will results with DPNR having higher resistance to physical relaxation. No thiourea treatment was given to purified rubber.

These three different processes give two different types of rubber which could not be compared directly and the differences in the relaxation properties between DPNR and purified rubber is possibly be due to these factors.

Physical stress relaxation is due to physical realignment and chain slippages. Any factor which influences chain mobility will affect the rates of physical relaxation. This includes internal lubricants, molecular chain modifications or/and changes in the crosslink density.

Previously, (see section 5.2.2) it was shown that the presence of alanine and arginine increases the crosslink density of rubber. The presence of these amino-acids was shown earlier to give rise to rubber having a good resistance to physical relaxation. Thus it is likely that the good resistance to stress relaxation of these rubbers could be due to the increase in the crosslink density. That is, the presence of those non-rubber constituents resulted with rubber having a higher crosslink density, thus better resistance to relaxation.

The dependence of relaxation rates on crosslink density was checked by presenting the rates as a function of molecular weight between crosslinks, M_c , which is inversely proportional to crosslink density. The values of M_c were calculated from stress-strain data as explained earlier (section 5.2.2).

Results showed that the relaxation rates of several purified rubbers containing proteins and amino-acids were linearly related to the M_c (Figure 5.28). This linear relationship shows that the relaxation rate decreases as the crosslink density of the rubber increases. This is consistent with published results which showed a linear decrease in relaxation rates as the crosslink density increases (SOUTHERN, 1979).

Thus, it is most likely that the improvement in the relaxation behaviour of the purified rubber is due to the increase in the crosslink density. The extra crosslinks were introduced, possibly, during the vulcanization reaction due to the presence of amino-acids such as alanine and arginine. The presence of these extra crosslinks reduces the ability of the chain movement and slippages, thus lowering the relaxation rates.

5.3.2 Effect of fillers on physical stress relaxation

The incorporation of fillers has been shown to increase the stress relaxation rates of the rubber. The effect was reported to be large when reinforcing filler such as carbon black was used (GREGORY, et. al, 1978).

In this current work, stress relaxation rates were measured for a number of filled and unfilled rubber compounds. The relaxation rates, (expressed as % per decade), presented as a function of strain are given in (Figures 5.29-5.31). These showed rather complex relationship, depending on the nature of rubber compounds used. The stress relaxation rates in the filled rubber were much higher than in the unfilled rubber. The differences were most marked at low strains.

Figure 5.28
Stress relaxation rates of purified rubber
containing non-rubbers

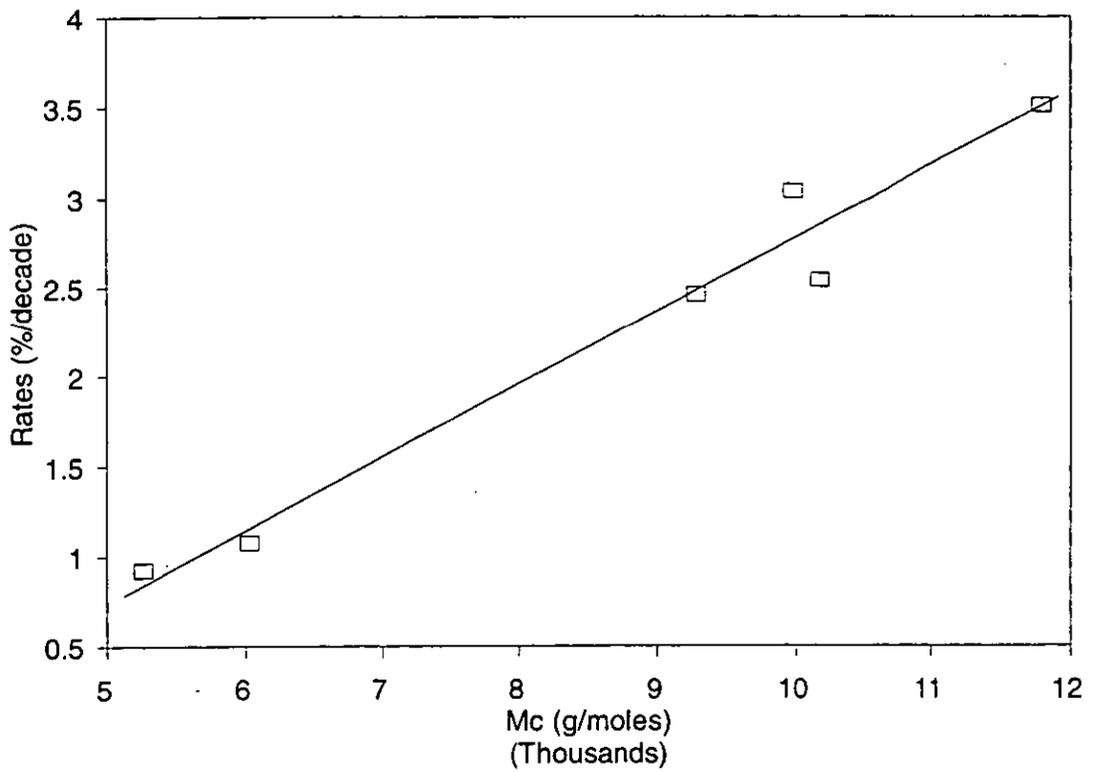


Figure 5.29
Stress relaxation rates of natural rubber
filled with carbon black

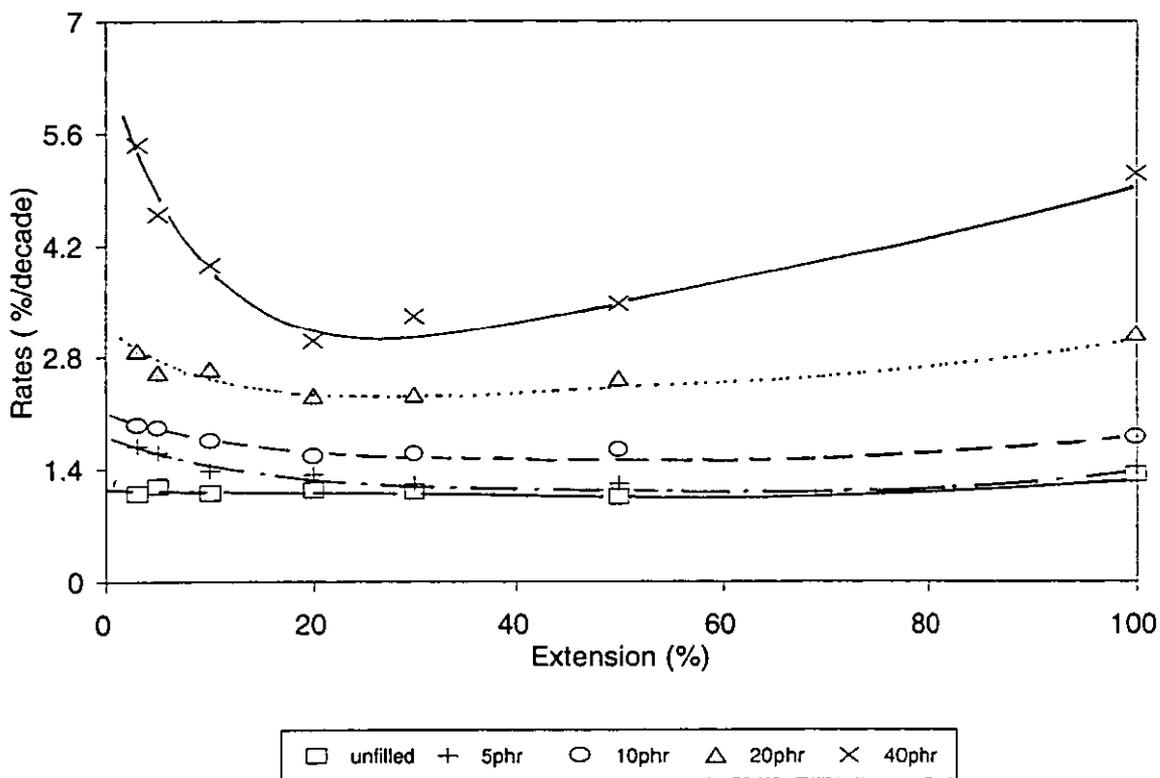


Figure 5.30
Stress relaxation rates of natural rubber
filled with clay

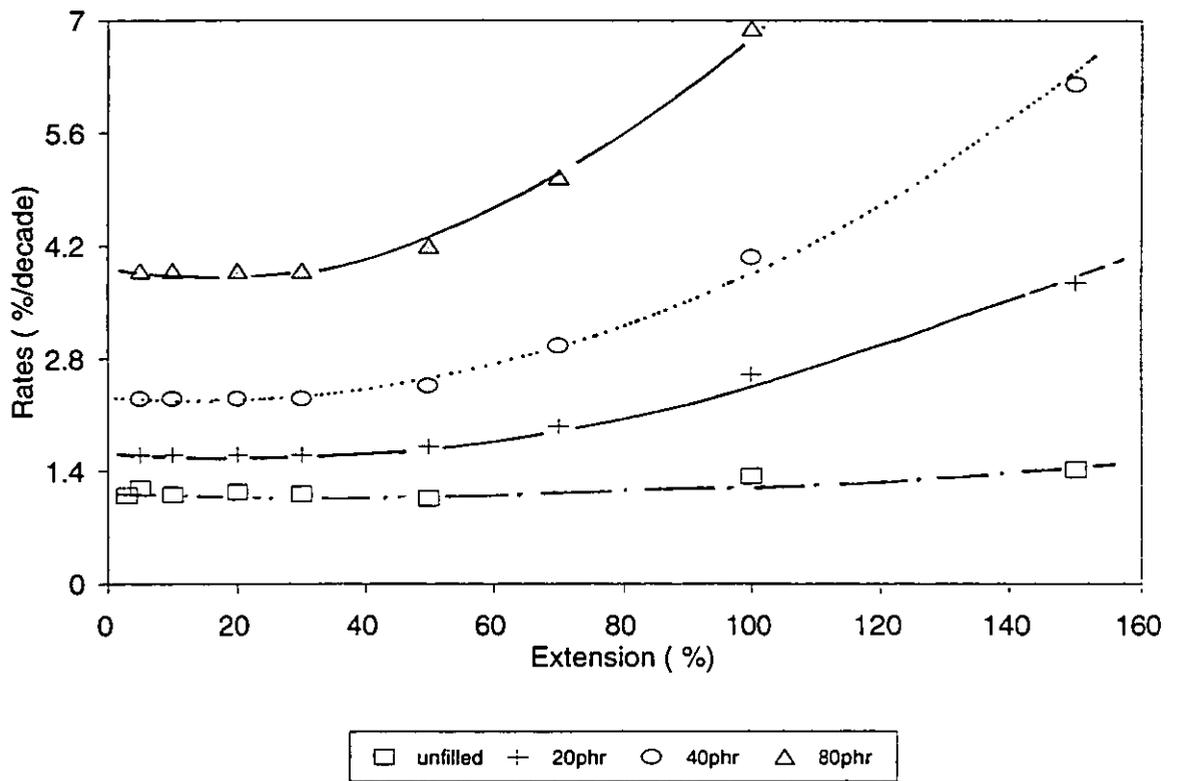
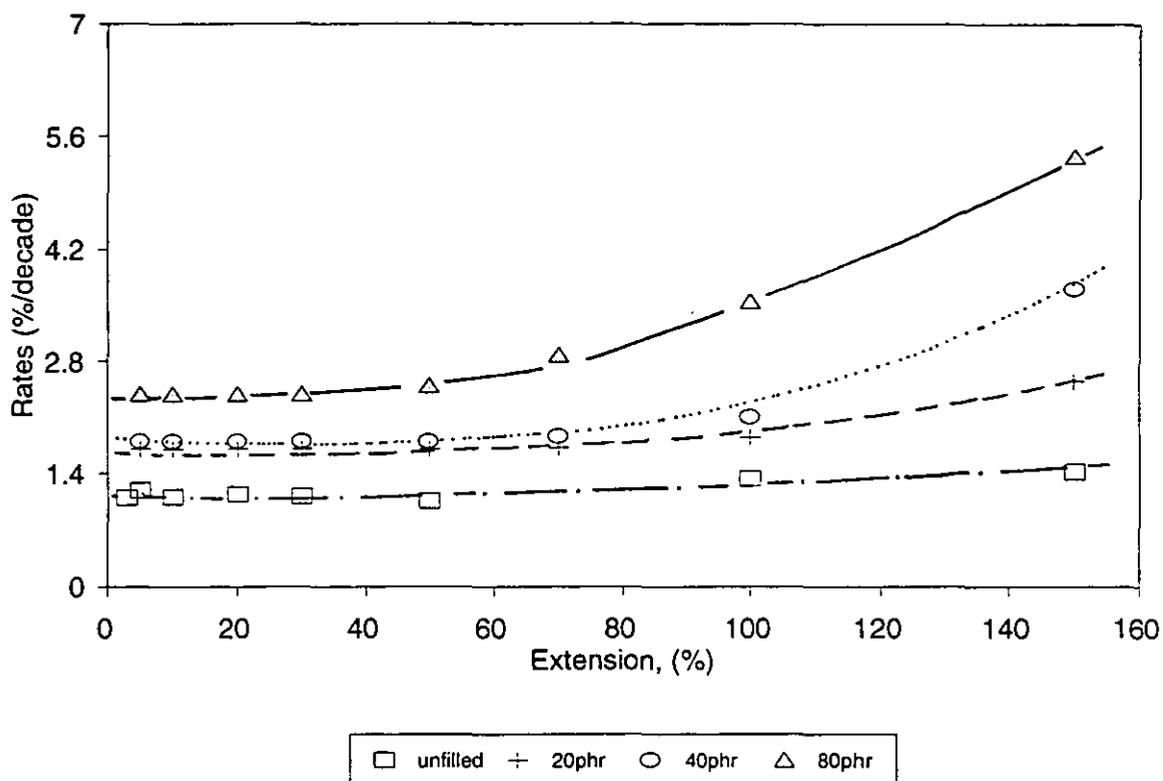


Figure 5.31
Stress relaxation rates of natural rubber
filled with calcium carbonate



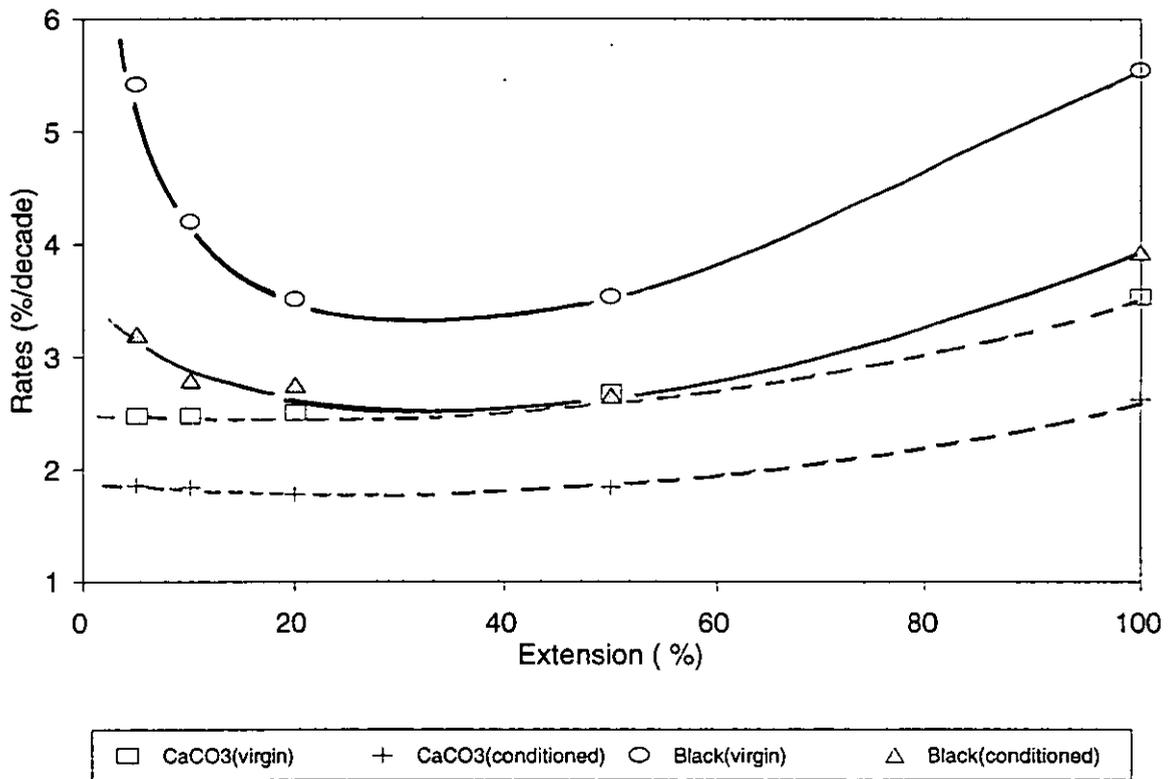
With unfilled compound, the relaxation rate was observed to be substantially independent of strain for up to about 200% extension. At higher strains (>200%), the rate increases considerably. These results are consistent with published findings (GREGORY, et. al., 1978).

With rubber filled with reinforcing carbon black, the stress relaxation rate is a function of strain (*Figure 5.29*). At the lowest strain, relaxation rate is high. At increased strains, relaxation rate goes through a minimum at about 30% strain. Beyond that the increase is always present but varies with the amount of fillers (see section 5.5.1).

When non-reinforcing fillers, such as clay and calcium carbonate were used, the relaxation rate was independent of strain at below about 30%. Above that, the rate increases with strain (*Figures 5.30-5.31*).

There could be two different phenomena taking place in the stress relaxation of filled rubber at low and at high strain. At low strain, the reduction in relaxation rate with strain could be due to the rubber/filler structure. The reinforcing filler which gave a high relaxation rates at low strain has many linkages with rubber molecules of types that may readily be broken. This labile nature was demonstrated by taking some samples and 'scragging' them in 10 cycles each to magnitude equal to the strain for the subsequent stress relaxation test. The 'scragging' rate was 100% per minute. This drastically decreased the stress relaxation rates (*Figure 5.32*). In contrast, the non-reinforcing fillers showed smaller effects in a similar test. Hence we may say that the high rate of relaxation of 'unscragged' rubber containing reinforcing fillers comes directly from the labile bonds.

Figure 5.32
Effects of scragging on relaxation rates of
filled natural rubber



At higher strain, the increase in relaxation rates may be associated with the non-affine deformation of the rubber. The rubber matrix in a filled compound were subjected to a strain higher than the bulk strain of the test sample due to the presence of inextensible filler particles. This difference in the extent of deformation experienced by the rubber matrix and the bulk of the sample, which is termed 'non-affine deformation' causes the increase in the relaxation rates of filled rubber as the strain increases. Thus, the rate of relaxation will be higher with higher filler concentrations since the effects due to non-affine deformation will be greater.

5.3.3 Change in physical stress relaxation with humidity

a) Unfilled rubber

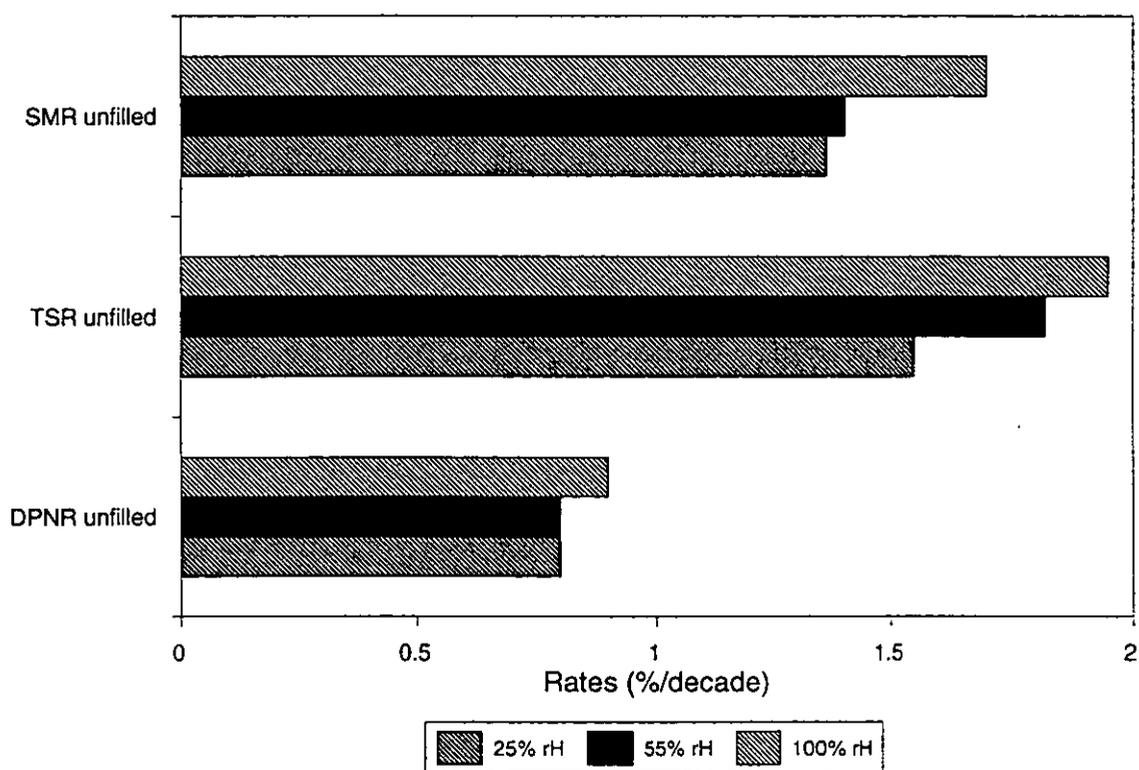
In this studies, the effect of humidity on the stress relaxation of different types of unfilled and filled NR was undertaken. Rubber containing different amounts and types of non-rubber constituents were used. They include TSR, SMR, DPNR and purified rubbers containing added proteins and amino-acids.

Results obtained on tests carried out using the various rubbers are given in *Figure 5.33*. Generally, it was observed that rubber containing higher non-rubber constituents (TSR) gave larger changes in relaxation rates than 'cleaner' rubber (DPNR) (*Table 5.14*). Hence, the presence of non-rubber constituents will cause the larger variability in the relaxation rate of TSR compared to DPNR

Table 5.14: Change in relaxation rates with relative humidity for unfilled DPNR, SMRL and total solid rubber(TSR)

Humidity change	25% to 55%	25% to 100%
Rubbers	Increase in rates (%)	
DPNR	-	10
SMRL	4	10
TSR	17	25

Figure 5.33
Stress relaxation rates of different types of unfilled natural rubbers



When the effects of proteins and amino-acids were studied, small variation (<8%) in the relaxation rates was observed (*Figure 5.34*). For instance, with purified rubber containing 1% wt. arginine, the relaxation rate varies from about 1.26% to 1.33% per decade when the relative humidity was changed from 25% to 100%. The presence of proteins gave a slightly bigger change in relaxation rates with humidity (*Table 5.15*)

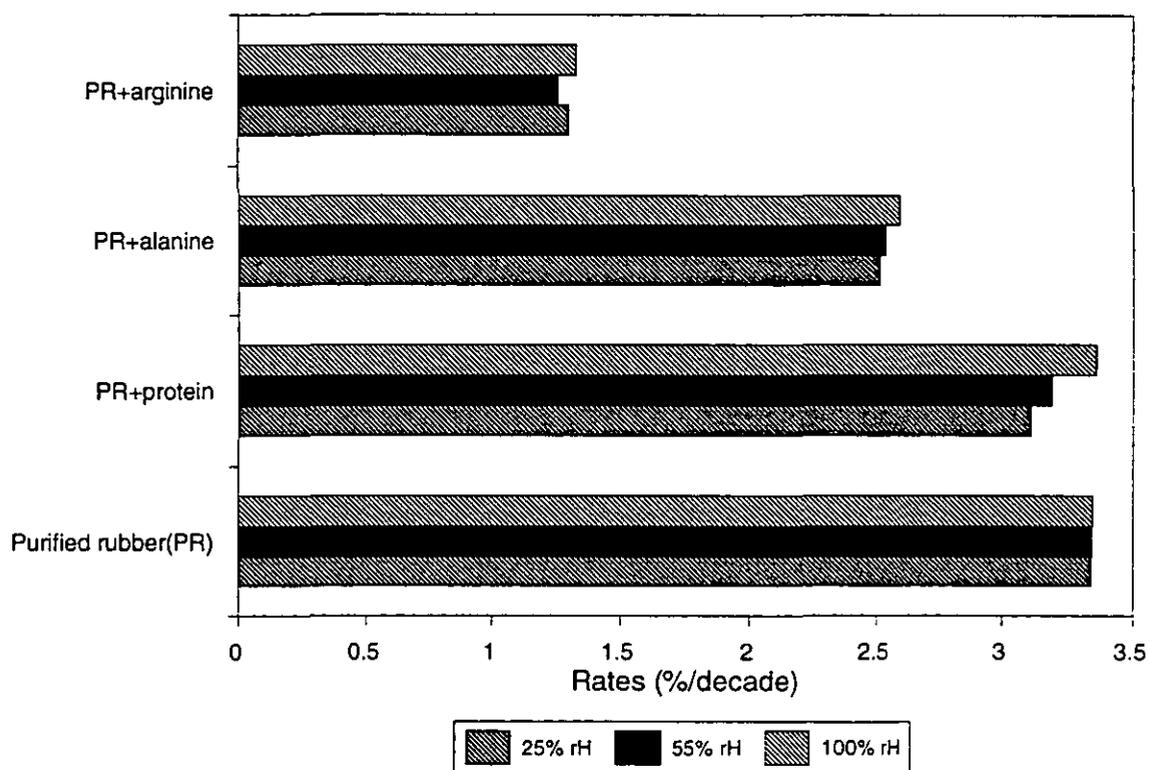
Table 5.15: Change in relaxation rates with relative humidity for purified rubber containing proteins and amino-acids

Humidity change	25% to 55%	25% to 100%
Rubbers	Increase in rates (%)	
Purified rubber(PR)	<1.0	<1.0
PR+protein(1%)	1.5	4.0
PR+protein(3%)	2.5	7.0
PR+alanine(1%)	1.0	3.2
PR+arginine(1%)	<1.0	2.0

These results suggest that the non-rubber constituents which gave a large variation in relaxation rates with humidity were not amino-acids; amino-acids increased the crosslink density (see section 5.2.2), and improves the resistance to physical relaxation, thus reducing the variability at different humidities. So some other factors must be causing the changes.

It is possible that the non-rubber constituents in TSR which caused the large variation in relaxation rates are the materials which are chemically inactive and behave as inert fillers. Protein is one such material. In this study, the variation observed with purified rubber containing proteins was small; though larger than the change observed with the presence of amino-acids. The amount of proteins

Figure 5.34
Stress relaxation rates of purified rubber
containing non-rubbers



added (1% wt.) may be too low to give a more significant variation. If we were to assume that the increase in rates with humidity is linearly related to the amount of proteins, then when the humidity changes from 25%RH to 100%RH, we would obtain about 21% increase in rates when the protein content is increased to 3% wt., the approximate amount present in TSR. Thus it is possible that the increase in relaxation rates observed with TSR when the humidity was increased could simply be due to the presence of non-rubber constituents such as proteins. However, we do not have any evidence for linearity to date so it would be wise to consider what else could have caused the changes in relaxation due to moisture uptake.

The findings reported in section 5.2.1 showed that the presence of low molecular weight inorganic materials increased the affinity to water. These low molecular materials, which are inorganic salts, are present in TSR and commercial grades rubber, but not the purified rubber. Thus it is likely that the large changes in relaxation rates obtained with those rubbers are due to the presence of those inorganic materials.

b) Filled rubber

With filled rubber, the nature of the filler can change the way in which the relaxation responds to changes in relative humidity. When a reinforcing filler was used, the rate of relaxation changed very little with humidity. This is clearly shown by both DPNR and TSR filled with carbon black (*Figures 5.35-5.36*). For both compounds, the rate varies from about 5.2% per decade at 25% humidity to about 5.5% at 100% humidity.

In contrast to this, the non-reinforcing calcium carbonate (CaCO_3) filled rubber showed large variation in the rates of relaxation as the humidity was varied from 25% to 100% (*Table 5.16*).

Table 5.16: Change in relaxation rates with relative humidity for filled rubbers

Humidity change		25% to 55%	25% to 100%
Rubbers	Fillers(phr)	Increase in rates (%)	
DPNR	40 black	-	2
TSR		5	4
DPNR	80 CaCO ₃	11	48
TSR		28	63

With carbon black filled rubber, the filler has diluted and masked the contribution of non-rubber constituents in TSR. But with rubber filled with calcium carbonate, the non-rubber constituents in TSR may have contributed to the large increase in modulus with humidity. This could happen, possibly, by the non-rubbers acting as additional filler to calcium carbonate or interacting with it. The former argument is more likely since the difference in values between DPNR and TSR filled with calcium carbonate is approximately of similar magnitude to that of unfilled rubbers.

Thus it appears that the variation in the rates of stress relaxation of NR depends on both the presence of the non-rubber constituents as well as the types of filler used. These factors which influence the variation of stress relaxation rate with humidity are similar to those which cause the change in modulus with humidity discussed earlier. A possible explanation is given in section 5.5.2.

Figure 5.35
Stress relaxation rates of DPNR

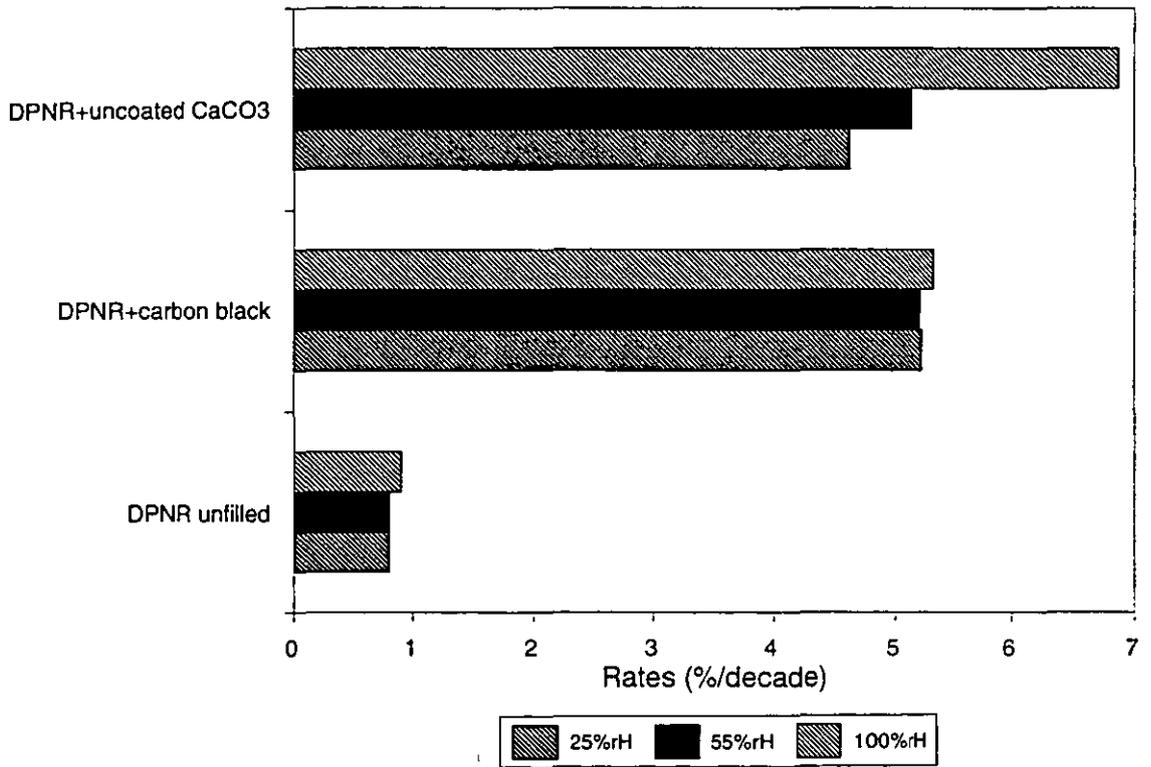
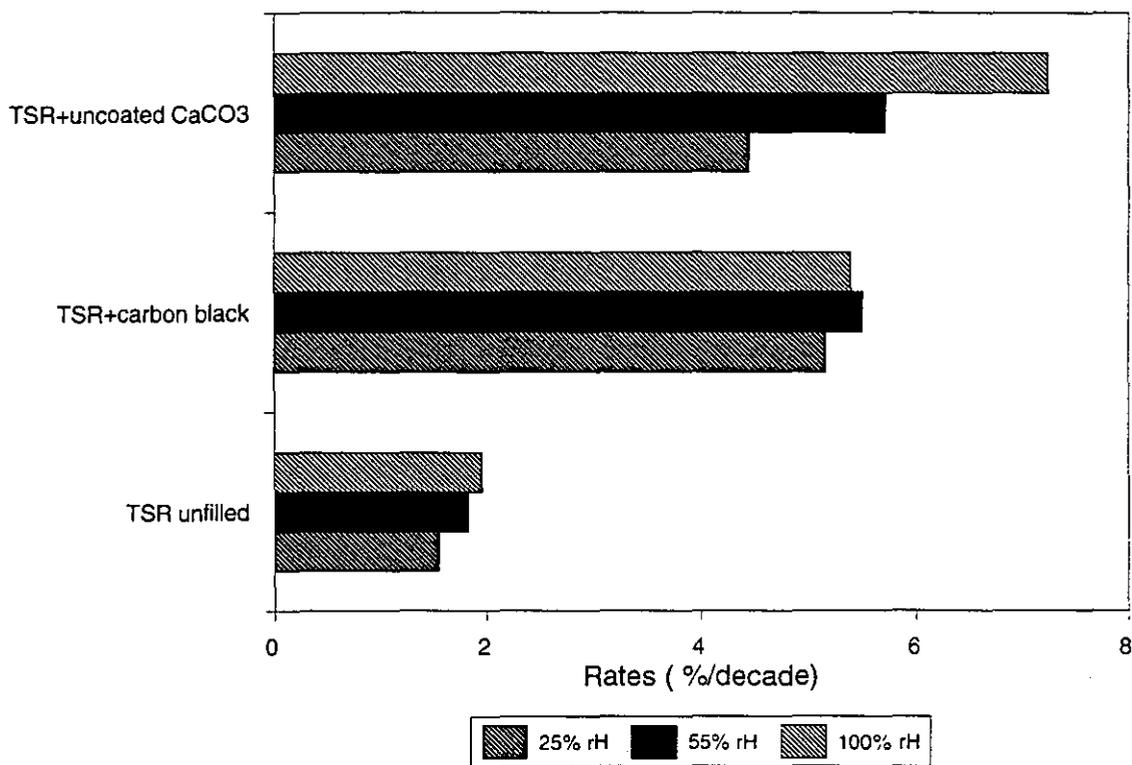


Figure 5.36
Stress relaxation rates of total solid rubber(TSR)



5.4 CHEMICAL STRESS RELAXATION

Chemical stress relaxation has been generally associated with chemical changes taking place within the rubber network. This involves the breaking up and/or formation and subsequent rearrangement of the molecular chain. This type of relaxation is dominant at longer times and high temperatures (*Figure 5.37*). At ambient temperature, the chemical relaxation of a typical rubber becomes important after 10^3 - 10^4 minutes. The change in stress is non-linearly related to $\log(\text{time})$.

5.4.1 Effect of non-rubber constituents on chemical stress relaxation

Any chemicals or constituents which are able to influence the breaking and formation of crosslinks/molecular chains could affect the relaxation characteristics of the rubber. Natural occurring non-rubber constituents has been shown to have an influence on the physical relaxation. The effect of added non-rubber constituents on the chemical relaxation of unfilled natural rubber was investigated at 70°C and 100°C in air.

The chemical stress relaxation at 70°C was initially carried out using centrifuged NR latex fractions. Results obtained are given in *Figure 5.38*. The relaxation behaviour of different centrifuged fractions was observed to vary considerably. For instance, the presence of the bottom fraction in the rubber phase improved their resistance to chemical relaxation. On the other hand, the serum fraction caused the chemical relaxation to deteriorate. The chemical relaxation behaviour of TSR and rubber phase were approximately the same; they are lower than the serum fraction.

Figure 5.37
Stress relaxation of unfilled TSR
at 23°C and 70°C

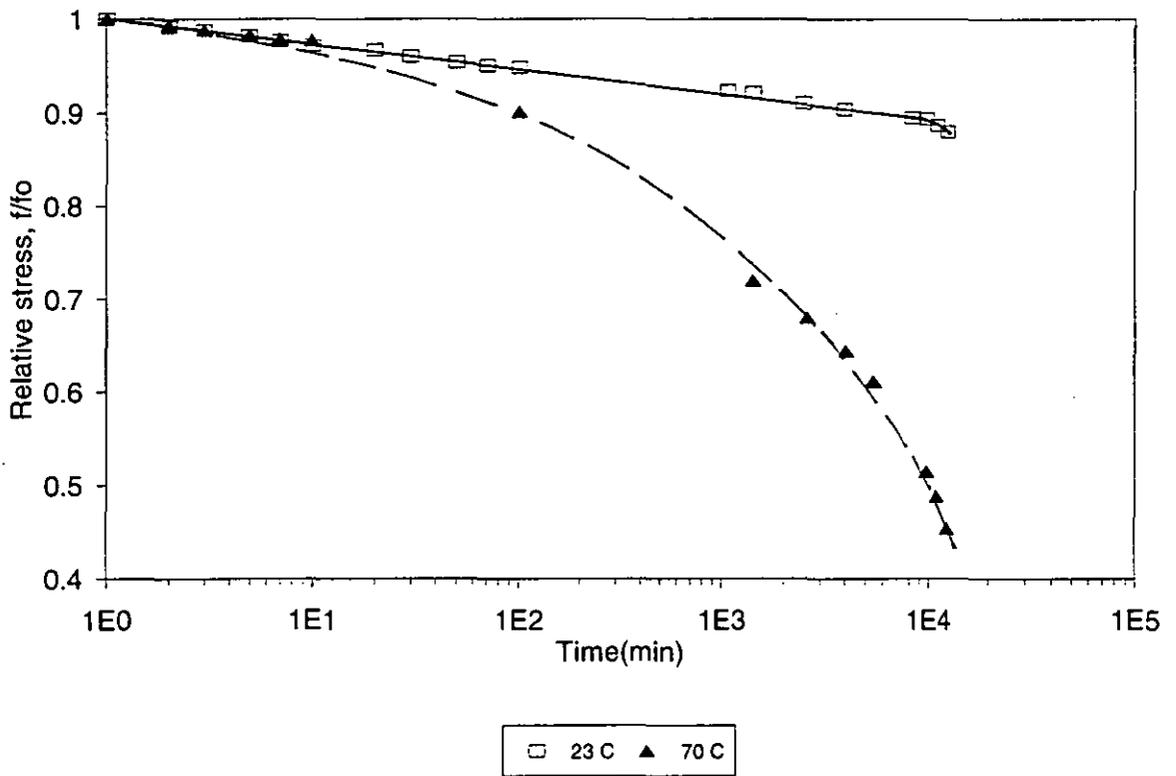
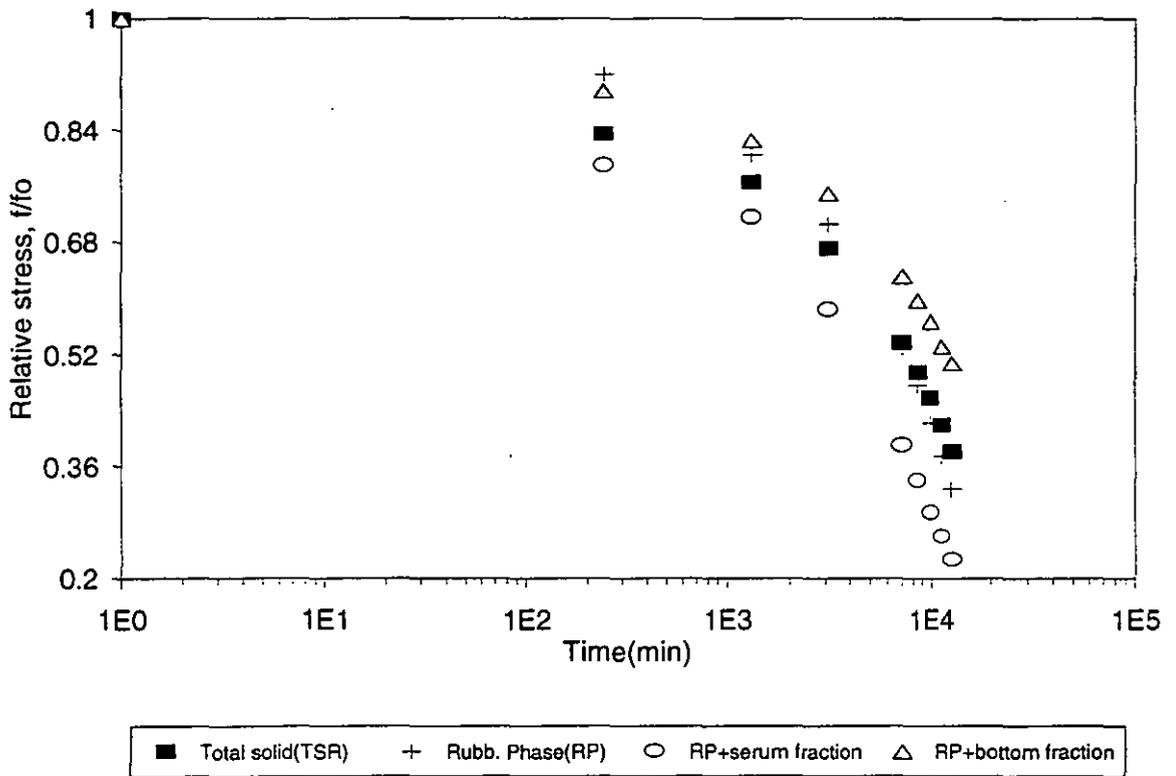


Figure 5.38
Stress relaxation of centrifuged latex fractions
(@ 70°C in air)



The effects of added proteins and amino-acids on the chemical stress relaxation of purified rubber are shown in *Figure 5.39*. The relative stress of rubber containing proteins and amino-acids (alanine and arginine) were observed to be lower than the relative stress of TSR. Similar pattern was obtained when the test was carried out at 100°C. After 1 day (1440 min.) @ 100°C, the relative stress of purified rubber containing proteins and arginine were only about 5% and 12% respectively compared to TSR, which has a relative stress of about 24% (*Figure 5.40*).

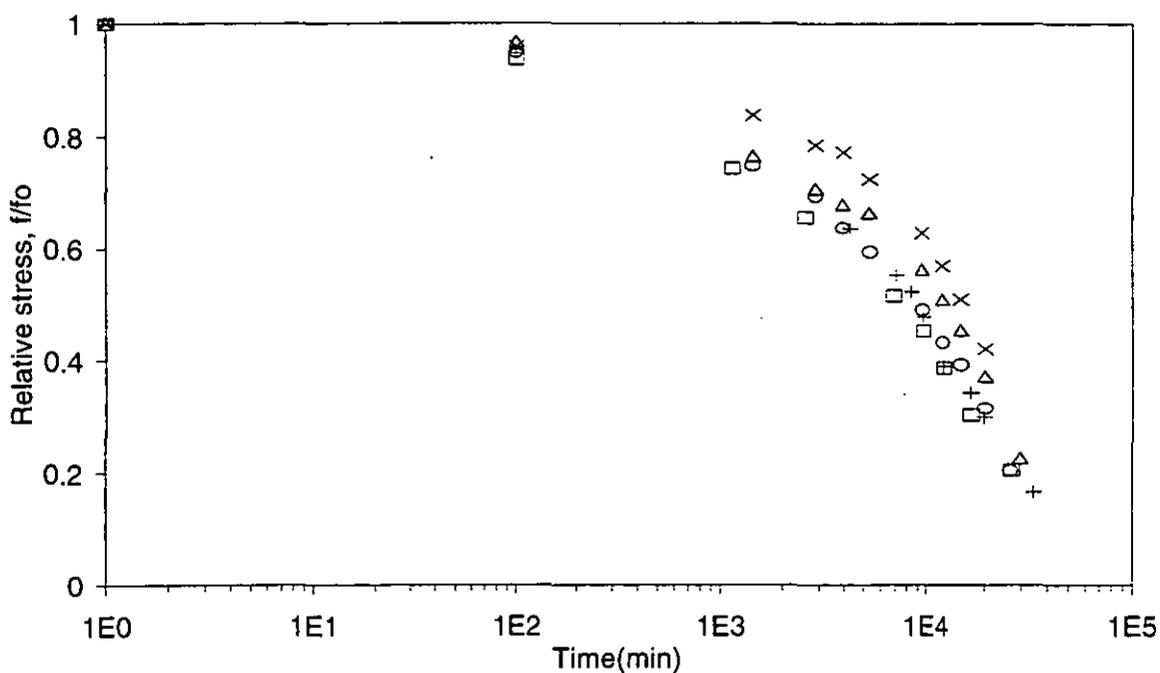
These results showed that (a) the presence of proteins cannot improve the resistance of the chemical relaxation of the purified rubber (b) the serum fraction causes deterioration to the chemical relaxation of the rubber (c) the bottom fraction provides a better resistance to chemical relaxation.

In latex (i.e TSR), both pro-oxidants (metals) and natural antioxidant (lipids) are present (HASMA, 1984). During centrifugation, these non-rubber constituents are separated into bottom fraction, serum fraction and the rubber phase. The differences in the chemical stress relaxation behaviour of those rubber fractions were likely due to the present of these pro- and antioxidants.

The serum fraction does not contained lipids which are the natural antioxidant. Thus the resistance to chemical relaxation were poor. The bottom fraction contained these useful natural antioxidants, which provides some protection to thermal degradation of the rubber.

It may be noted that most of the natural antioxidants which are present in the bottom fraction are usually removed during the processing of commercial grades rubber. This results with commercial grades rubber having poorer resistance to chemical relaxation than TSR (*Figure 5.41*).

Figure 5.39
Stress relaxation of purified rubber
containing non-rubbers (@ 70°C in air)



□ Purified rubber(PR) + PR+protein ○ PR+alanine △ PR+arginine × Total solid(TSR)

Figure 5.40
Stress relaxation of purified rubber
containing non-rubbers (@ 100°C in air)

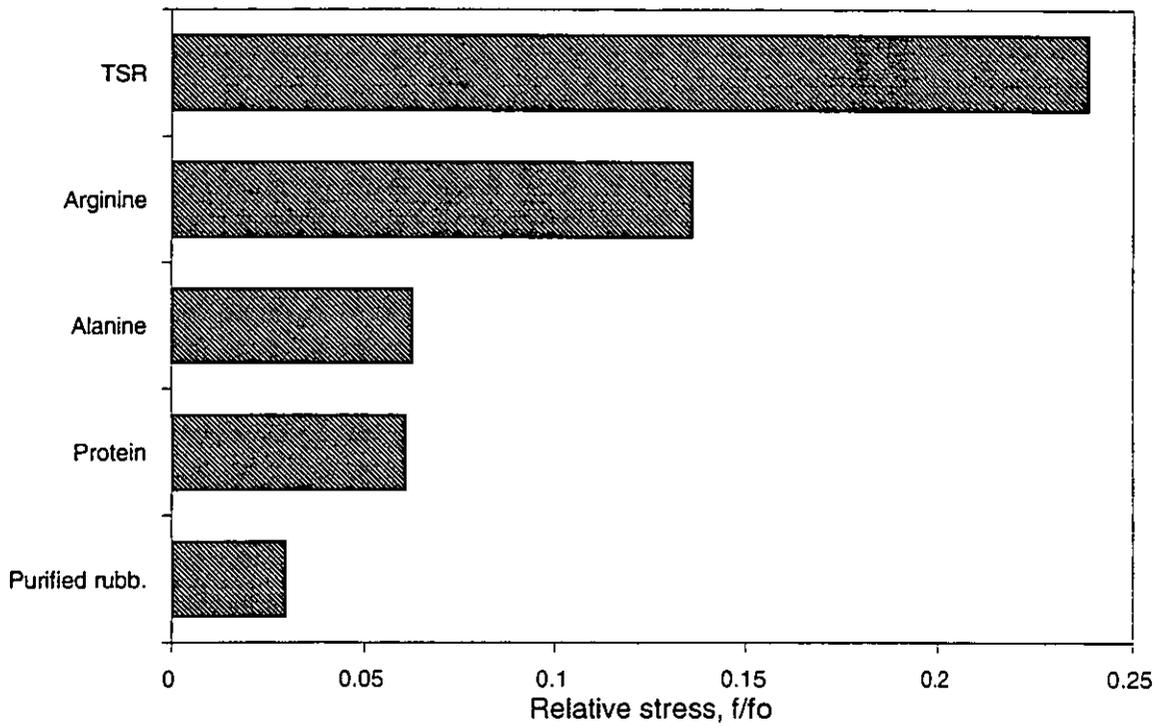
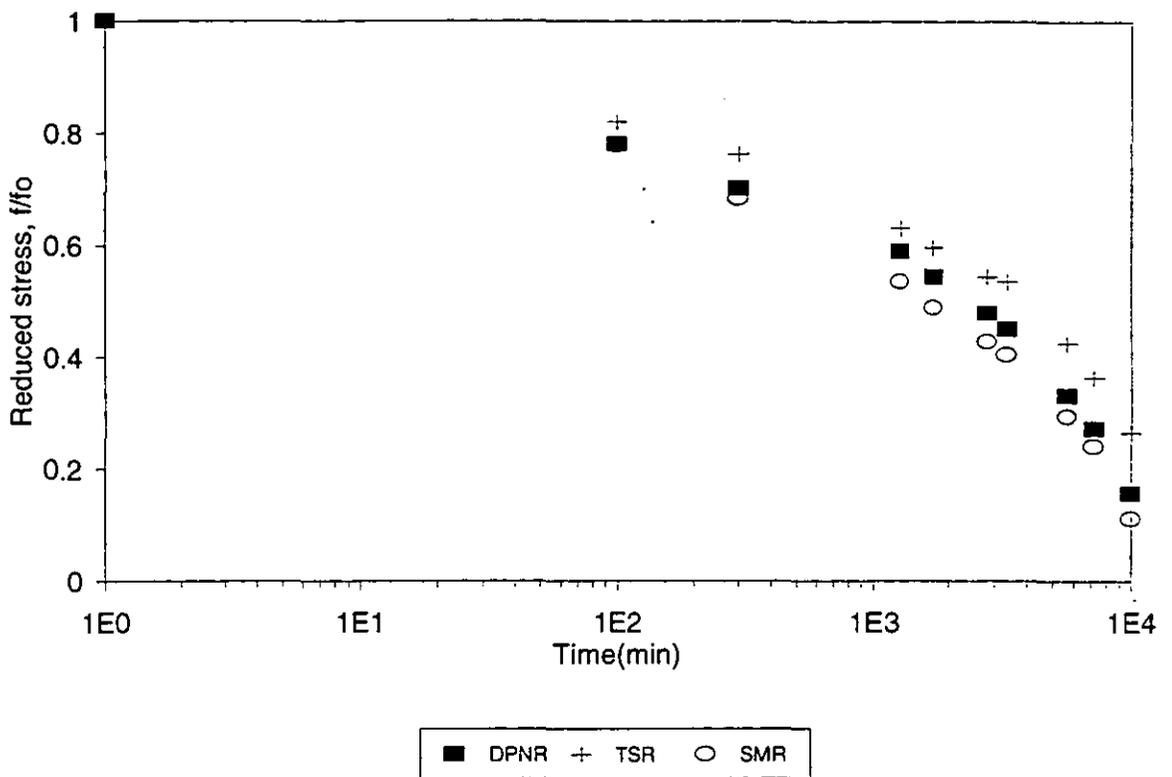


Figure 5.41
Stress relaxation of unfilled natural rubber
(@ 100°C in air)



5.4.2 Effect of fillers on chemical stress relaxation

Generally, the presence of fillers alters the physical and chemical properties of rubber. The obvious effect of fillers is the stiffening effect conferred to the bulk rubber and this has been dealt earlier. The effects of filler with and without the presence of natural occurring non-rubber constituents in the rubber on the chemical relaxation were investigated.

The chemical relaxation behaviour of rubber filled with reinforcing and non-reinforcing fillers are shown in *Figures 5.42 to 5.43*. No difference was observed with the three different types of rubber used. The relative stresses of TSR and DPNR were about the same. This shows that the effects of non-rubber constituents has been diluted by the fillers. The chemical activities of natural antioxidants which were found to be important in the unfilled TSR has been masked by the fillers.

Figure 5.42
Stress relaxation of natural rubber filled
with carbon black (@ 70°C in air)

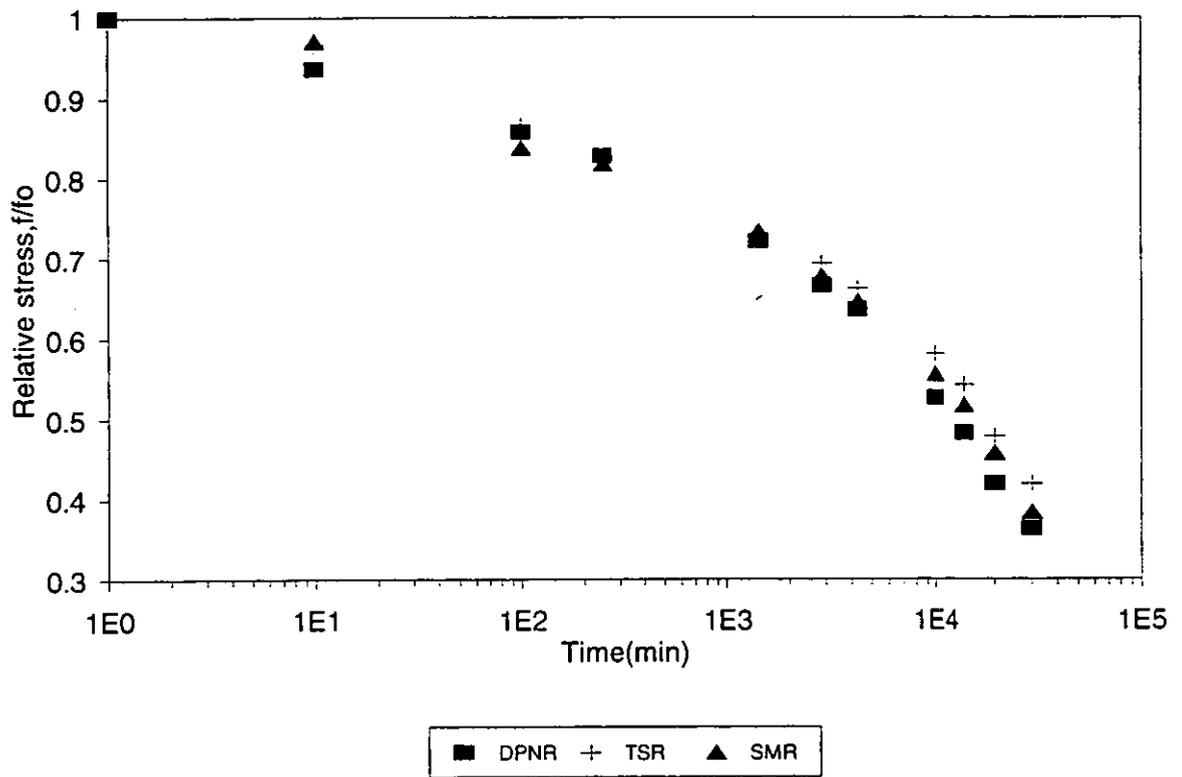
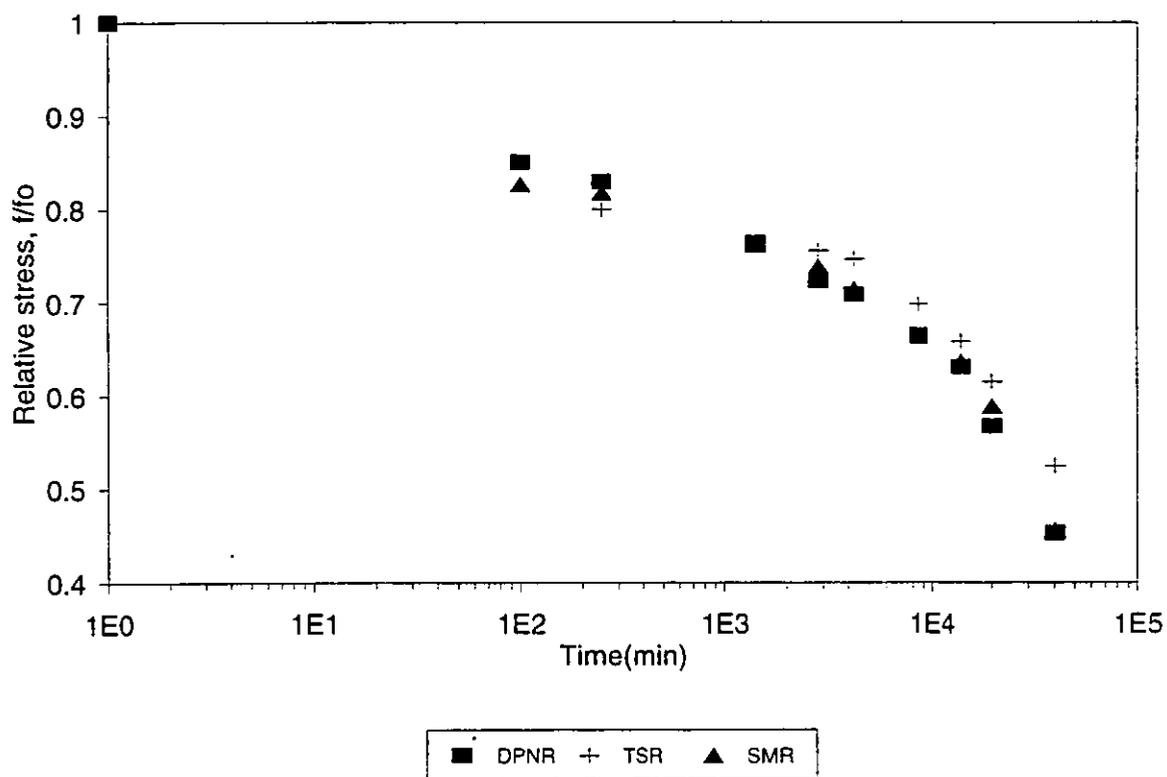


Figure 5.43
Stress relaxation of natural rubber filled
with CaCO₃ (@ 70°C in air)



5.5 DISCUSSION

5.5.1 Change in modulus and stress relaxation of filled rubber

The increase in modulus and relaxation of filled rubber depends, in part, on the amount of filler used. This study revealed that the presence of filler gave a non-linear increase in modulus and rate of relaxation with increasing concentration of filler used. This is clearly shown in *Figures 5.44 to 5.45*.

This non-linear increase in modulus is usually described by the Guth-Gold type of hydrodynamic equation (GUTH-GOLD, 1938). The equation relates the modulus of filled rubber, E , to that of the unfilled rubber, E_0 , by

$$E = E_0 (1 + A\phi + B\phi^2) \quad 5.4$$

where ϕ is the volume fraction of filler and A and B are constants associated with the shape factor and occluded volume effects. Rearranging equation 5.4 gives

$$(E/E_0 - 1)/\phi = A + B\phi \quad 5.5$$

If equation 5.5 is valid, then a plot of $(E/E_0 - 1)/\phi$ against ϕ should be a straight line of slope B and intercept A , the constants of which should be the same for rubber filled with same type of filler. That is to say, the linear plot indicates the validity of the Guth-Gold model.

Figure 5.44
Modulus (@100% ext.) of natural rubber filled
with different types of filler

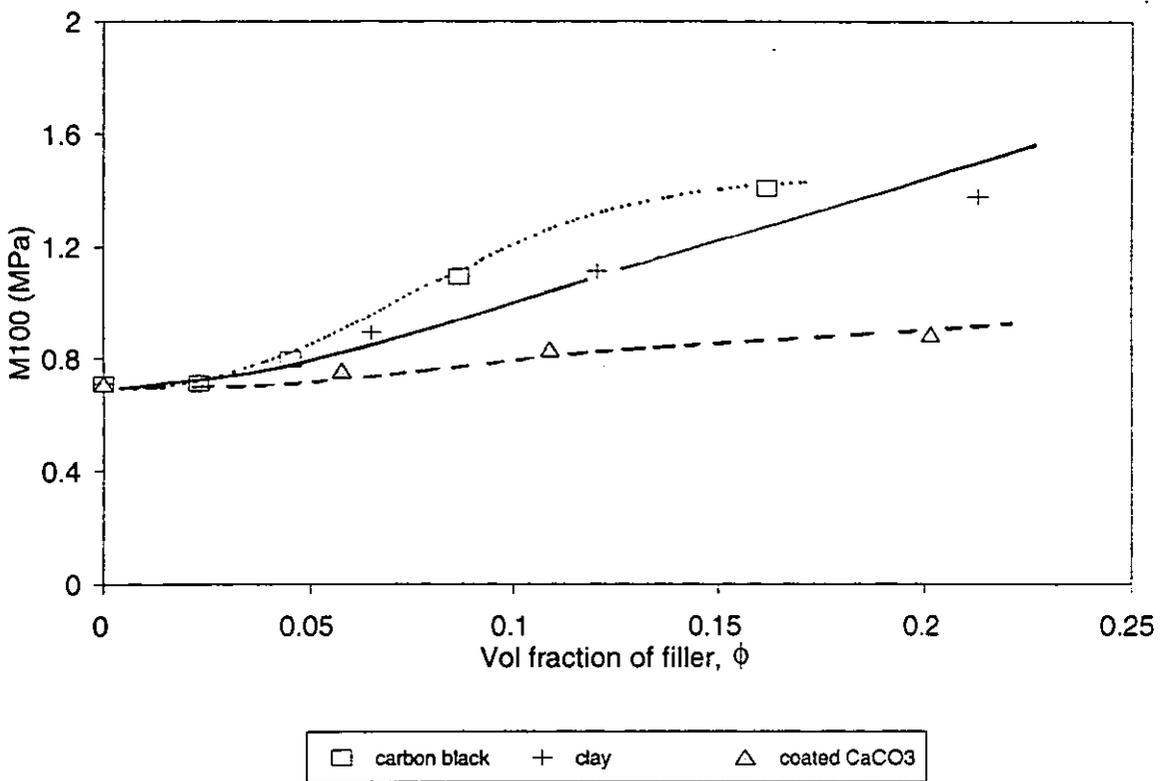
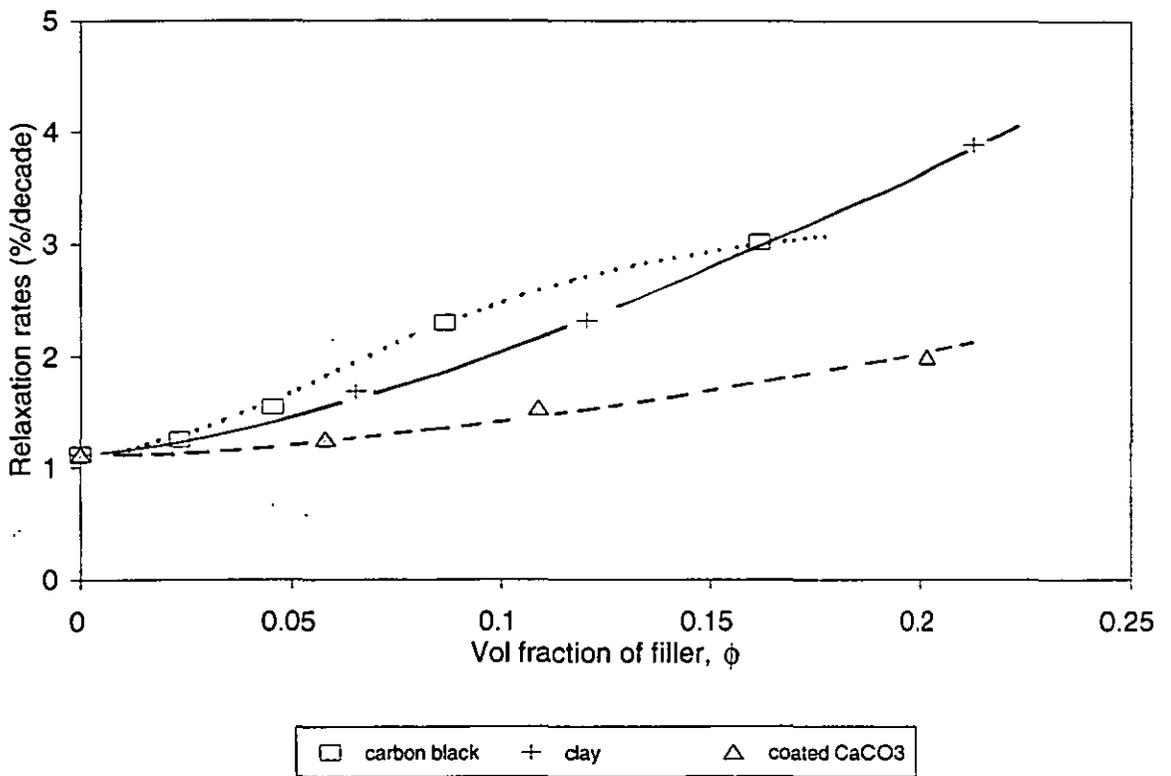


Figure 5.45
Stress relaxation rates of natural rubber filled
with different types of filler



The non-linear increase in modulus with filler concentration was analysed using the Guth-Gold/Guth equation. The value of modulus at 3% extension, which was taken to be the Young's modulus of the rubber, was used. Plots of $(E/E_0-1)/\phi$ against ϕ were made (Figure 5.46). Results showed that straight lines were obtained for rubber filled with non-reinforcing filler such as calcium carbonate and clay, but not for NR filled with reinforcing carbon black filler. The carbon black filled rubber gave a non-linear relation between $(E/E_0-1)/\phi$ and ϕ . Similar results were obtained when the stress at 100% extension, M_{100} , were used in the treatment; the non-reinforcing filler gave a linear plot of $(M/M_0-1)/\phi$ against ϕ but reinforcing carbon black filler gave a non-linear plot (Figure 5.47).

The application of Guth-Gold model was extended to the effect of filler concentration on the relaxation rate of rubber. The analysis was carried out using the values of relaxation rate of filled rubber, S , and unfilled rubber, S_0 , obtained at 30% and 100% extension. Plots of $(S/S_0-1)/\phi$ versus ϕ were made.

When the results of rubber filled with non-reinforcing clay or calcium carbonate were analysed, a linear relationship was observed (Figures 5.48-5.49). However with rubber filled with reinforcing carbon black filler, a non-linear relationship was obtained.

Thus, the trend for the change in modulus and relaxation with filler concentration was similar. With rubber filled with non-reinforcing fillers, linear relations were obtained when plots of $(E/E_0-1)/\phi$ or $(S/S_0-1)/\phi$ versus ϕ were made. Similar plots for rubber filled with reinforcing carbon black filler gave non-linear relationship.

Figure 5.46
Modulus (@3% ext.) of natural rubber filled
with different types of filler

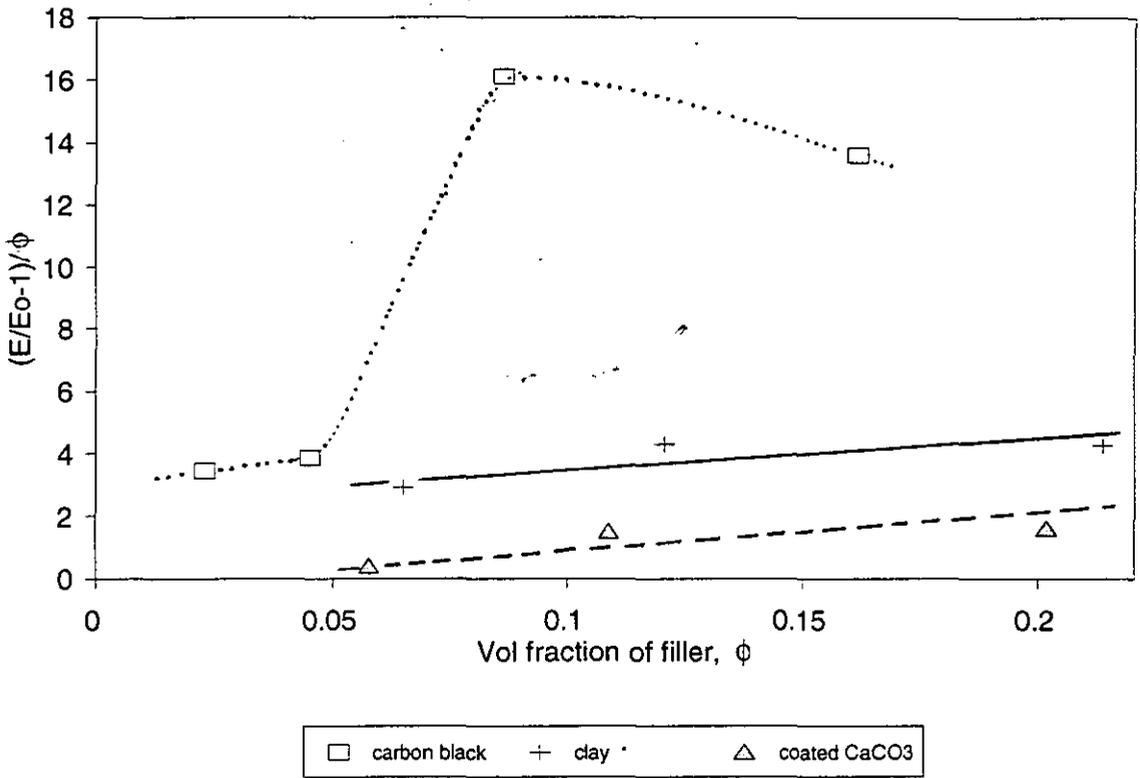


Figure 5.47
Modulus (@100% ext.) of natural rubber filled
with different types of filler

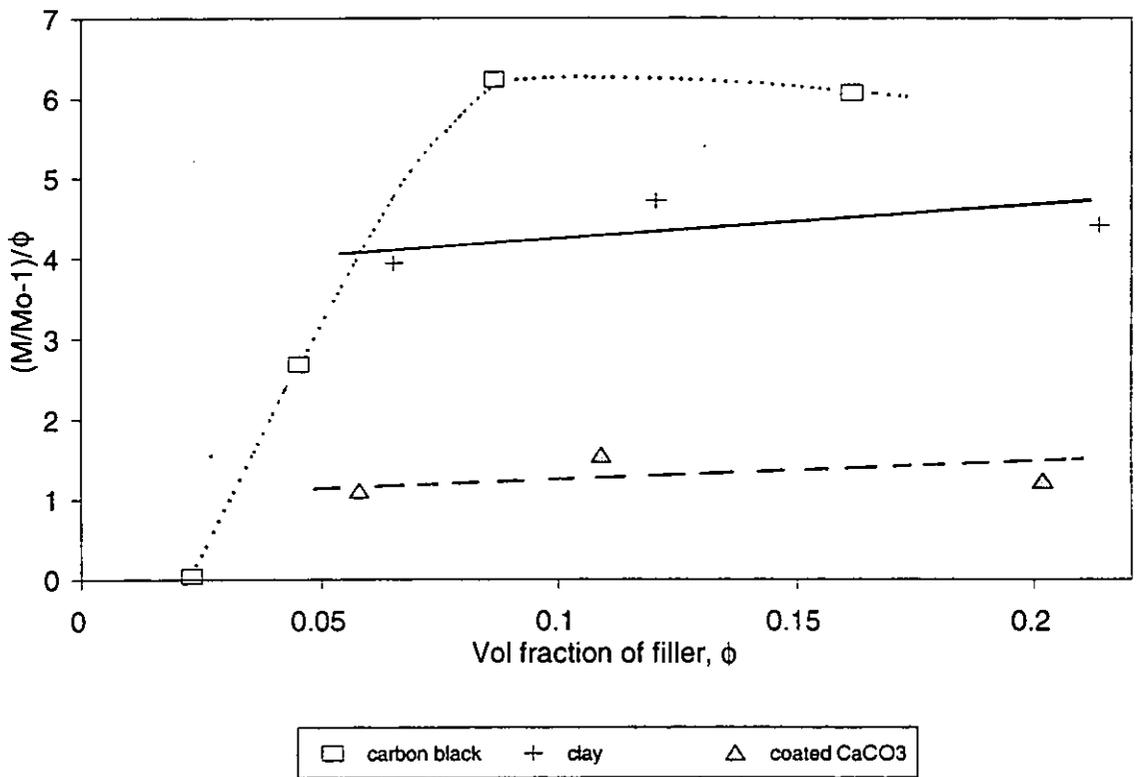


Figure 5.48
Relaxation rates of natural rubber filled
with different types of filler (@30% ext.)

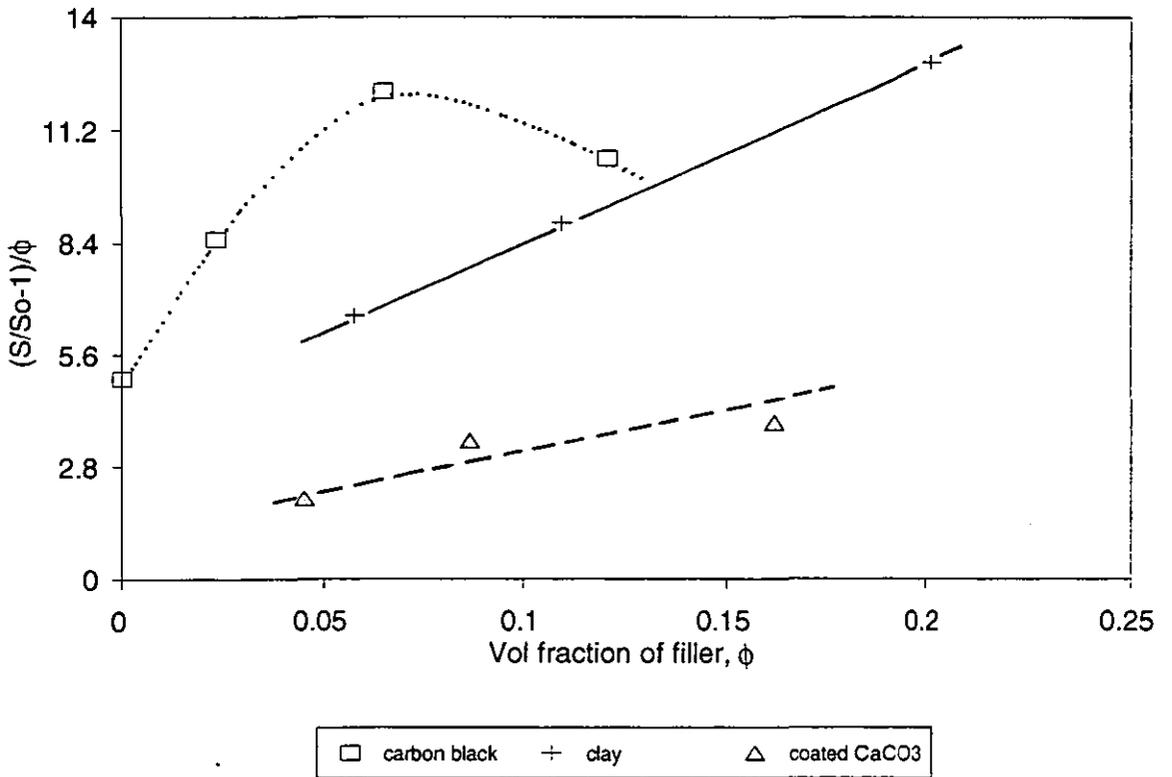
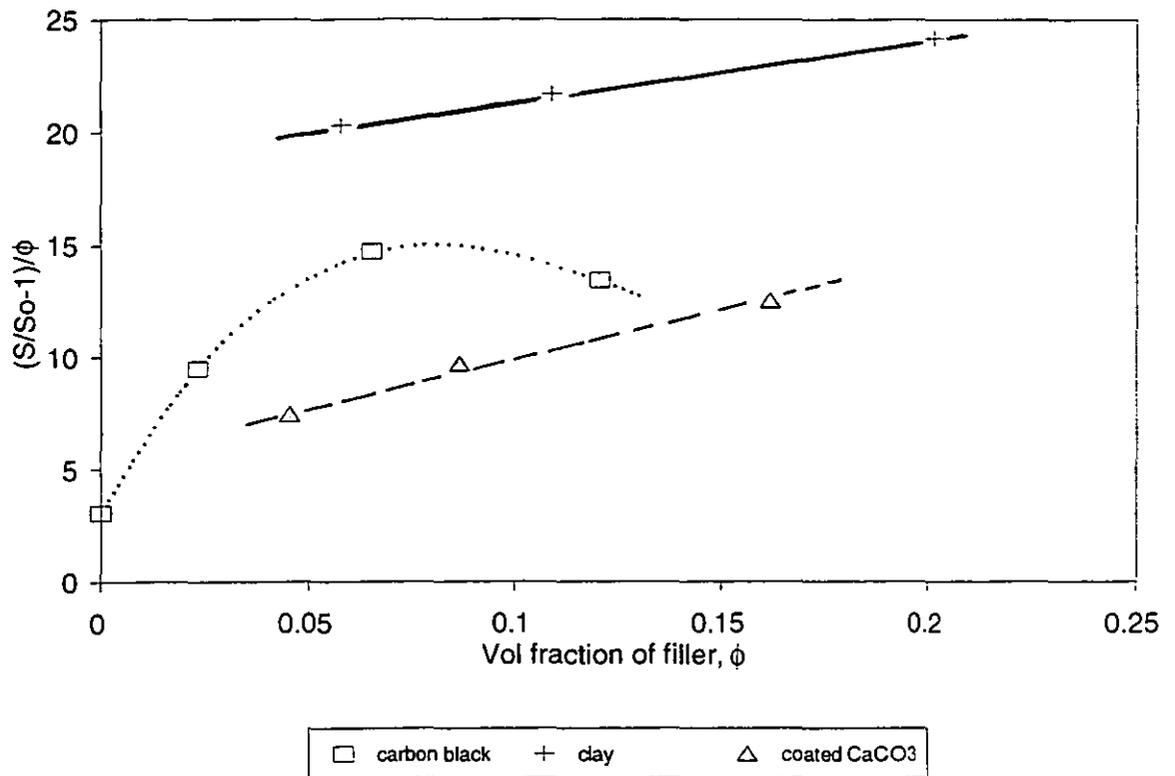


Figure 5.49
Relaxation rates of natural rubber filled
with different types of filler (@100% ext.)



These linear plots showed that the stiffening effects of non-reinforcing fillers could be explained using the volume filling effects of the Guth-Gold equation. Differences in the slope and intercept of the line obtained for those rubbers could be due to the differences in the shape factor of the filler as explained by Guth (GUTH, 1945) in his equation,

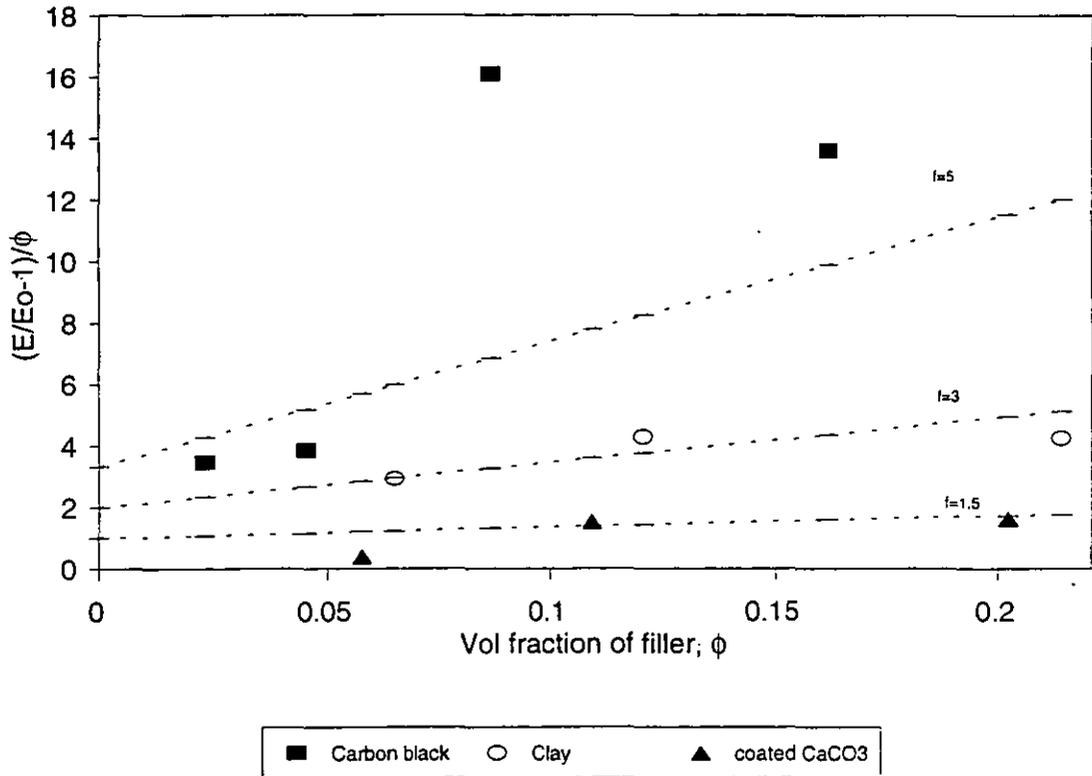
$$E = E_0 (1 + 0.67f\phi + 1.62f^2\phi^2) \quad 5.6$$

where f is a factor describing the shape of the asymmetric filler particle as expressed by the ratio of their length to diameter (aspect ratio).

Since the plots of $(E/E_0 - 1)/\phi$ against ϕ for clay and calcium carbonate filled NR are linear, then the use of proper value of f could shift the graph to fit the Guth-Gold/Guth model. For clay filled NR, a good agreement between the experimental and the predicted values was obtained with a used of shape factor, $f=3$ (*Figure 5.50*). With calcium carbonate filled NR, a value of $f=1.5$ gave a good agreement with the experimental values.

With carbon black filled NR, the use of any numerical values of shape factor, f , may not describe adequately the result since plot of the experimental values of $(E/E_0 - 1)/\phi$ Vs ϕ is not linear. The inclusion of a constant factor, f in the Guth-Gold/Guth equation would still predict a linear plot of $(E/E_0 - 1)/\phi$ versus ϕ .

Figure 5.50
Comparison between predicted and experimental
modulus values (@3% ext.)



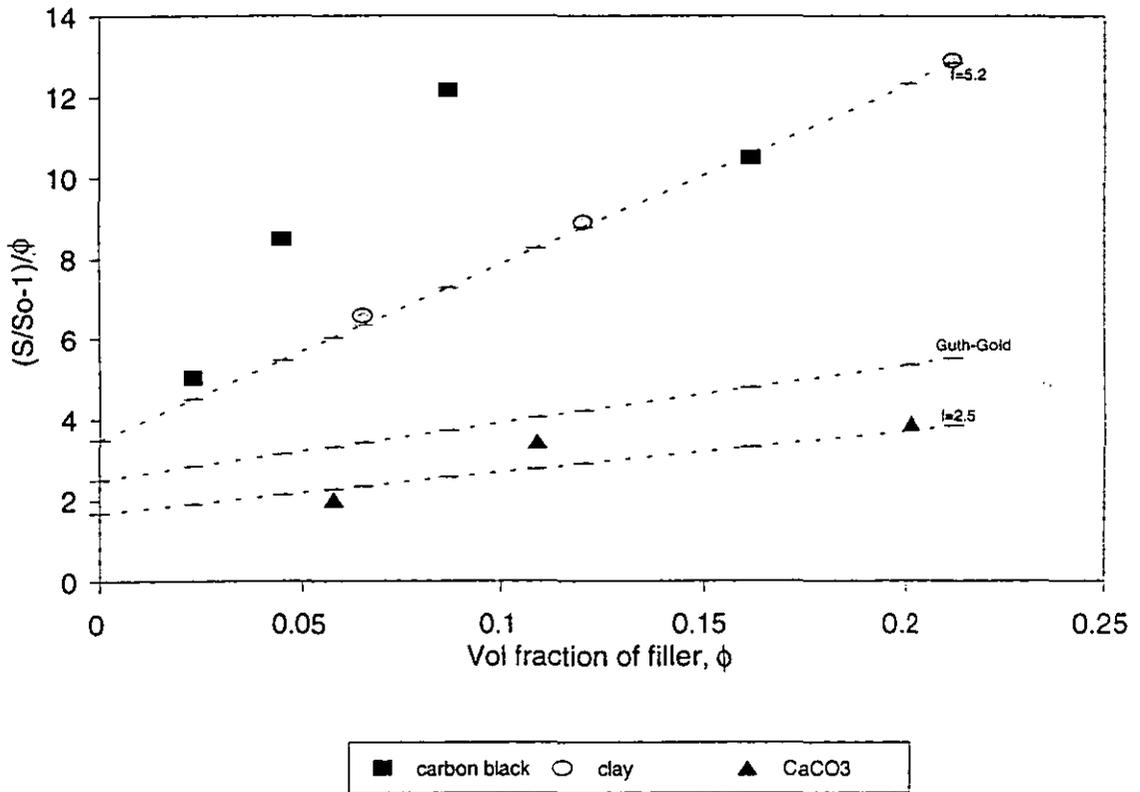
A similar effect was observed with the relaxation rate data. The non-reinforcing filler gave values of the relaxation rate which are in good agreement with the prediction given by the Guth-Gold/Guth model. Clay and calcium carbonate filled rubbers require shape factors of 5.5 and 2.5 respectively to give a good fit to the predicted model (*Figure 5.51*). However, results obtained with rubber filled with reinforcing filler such as carbon black, could not be fitted to the hydrodynamic model because the experimental values of $(S/S_0-1)/\phi$ versus ϕ are not linear.

Medalia (MEDALIA,1972) argued that the presence of carbon black filler gave rise to occluded volume, the volume of rubber trapped within the interstices of carbon black particles or structures. During deformation, part of the occluded rubber is shielded and acted as fillers. Medalia showed that the effective volume of carbon black filler ϕ' is higher than the volume of filler ϕ by

$$\phi' = \phi + 0.5\phi_{occ} \quad 5.7$$

The use of the occluded volume will only increase the effective volume of the filler by a fixed value. The overall shape of the curve for the black filled rubber will not be changed. That is to say, the plot of $(E/E_0-1)/\phi'$ Vs ϕ' for carbon black filled rubber will still be non-linear. Hence it must be assumed that the volume filling effects could not adequately explained the stiffening effects of carbon black.

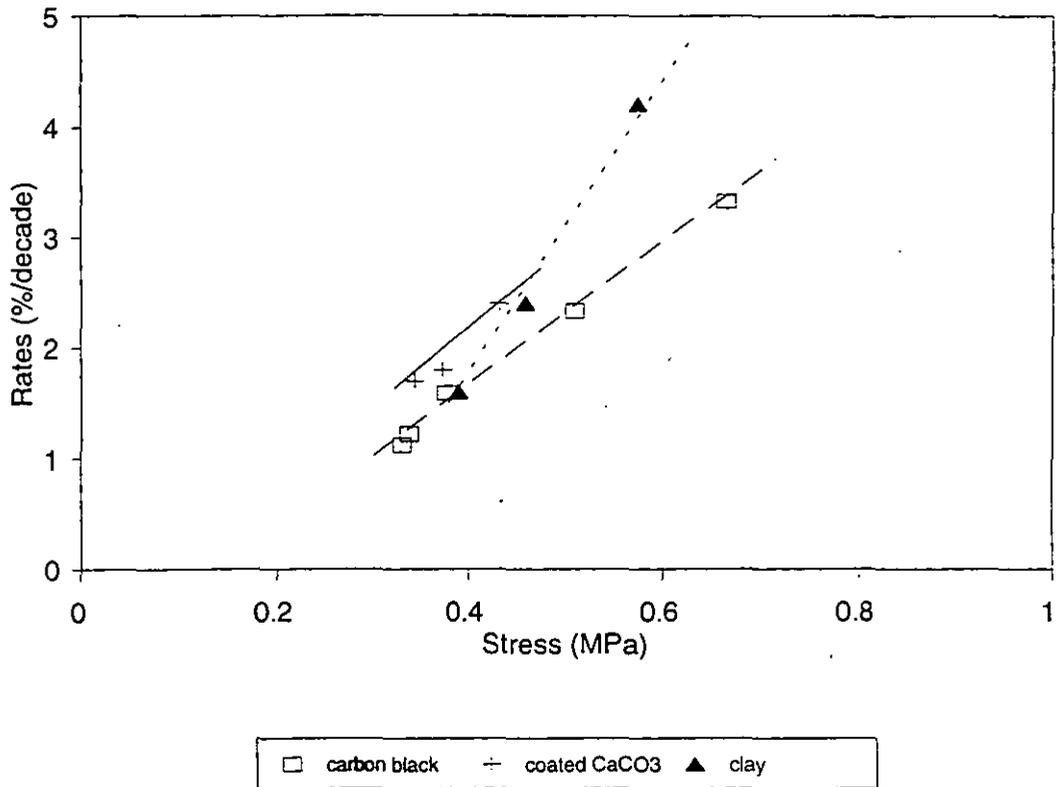
Figure 5.51
Comparison between predicted and experimental relaxation rates (@30% ext.)



Several authors (KRAUS, 1957; PORTER, 1967; OTHMAN & GREGORY, 1987) have reported that there were differences between the cure efficiency of carbon black filled peroxide and sulphur cured NR. Kraus for instance stated that the incorporation of 50 phr N330 carbon black resulted in about 40% increase in the crosslinking efficiency for the sulphur cured rubbers. Similar increase in the the crosslinking efficiency of rubber was reported by Porter and Othman & Gregory when carbon black was used in the N-cyclohexyl benzothiazole-2-sulphenamide (CBS) accelerated sulphur vulcanizing system. Hence based on these reports, it is likely that the discrepancies between the results for NR filled with carbon black and the Guth-Gold model may be due to changes in the crosslink density of the rubber matrix due to the presence of carbon black filler. In order to adequately describe the stiffening effects of carbon black, another factor which may be able to account for the change in the crosslink density of the rubber matrix has to be introduced in the Guth-Gold equation.

The differences in crosslink density between carbon black filled and calcium carbonate filled rubber is confirmed by the stress relaxation results. Here, the results clearly showed a strong dependence of rates on stress (hence crosslink density) (*Figure 5.52*). The presence of different lines for rubber filled with different fillers indicates the differences in crosslink density of the rubber matrix. Since the formulations used for the compound were the same, then any increased in crosslink density must be due to other factors such as the presence of fillers. That is, the presence of fillers alter the crosslink density, hence the relaxation rate of the rubber.

Figure 5.52
Stress relaxation rates as a function
of stress at 30% strain



5.5.2 Effect of moisture on modulus and physical relaxation

All the results presented above indicate that the presence of the non-rubber constituents, either deliberately added or naturally present (i.e. in TSR) in natural rubber influences the change in modulus of the rubber when the humidity changes. Most of the non-rubber constituents which causes the reduction in modulus when the humidity changes were observed to be present in the serum fraction of the latex.

The change in modulus with humidity was found to be independent of the types of crosslink present. These are shown by TSR vulcanized using conventional, semi-EV, EV and peroxide systems, in which the modulus of the rubber consistently decreased by about 22% when the relative humidity was changed from 7% to 55% (*Figure 5.53*).

Correlation was observed between the increase in crosslink density and the changes in modulus with humidity. That is to say, the presence of the non-rubber constituents which causes the enhancement of the crosslink density of the vulcanizates gave the biggest change in the modulus with the change in the relative humidity. Thus, certain types of amino-acids such as the arginine and alanine gave a larger reduction in modulus with humidity changes compared to the presence of other non-rubber constituents. These amino-acids are present in the serum fraction of the NR latex (ARCHER et. al., 1963).

The reduction in modulus when the rubber is being equilibrated at higher relative humidities is reversible. This is clearly shown by unfilled TSR which was subjected to a series of humidity cycles from 55% through 7%, 100% and back to 100% (*Figure 5.54*). The initial modulus obtained at 55%RH was observed to remain approximately the same at the end of the humidity cycles.

Figure 5.53
Change in modulus with humidity for unfilled total solid rubber(TSR)

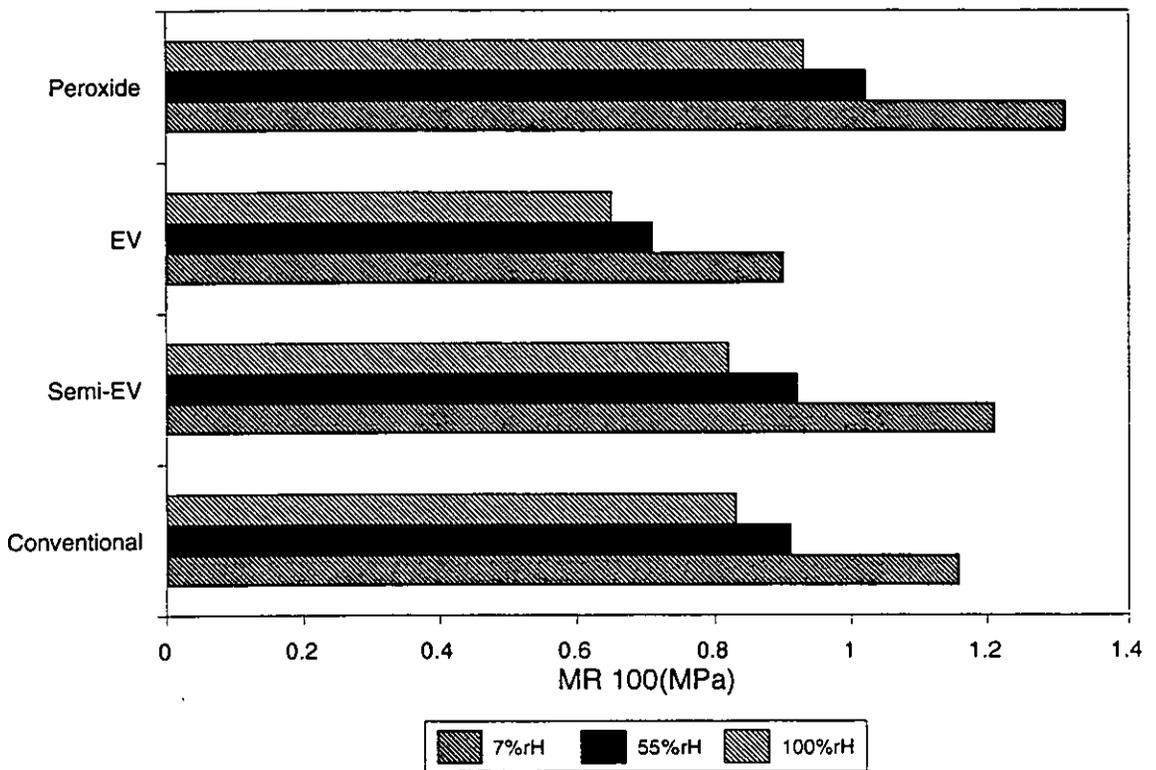
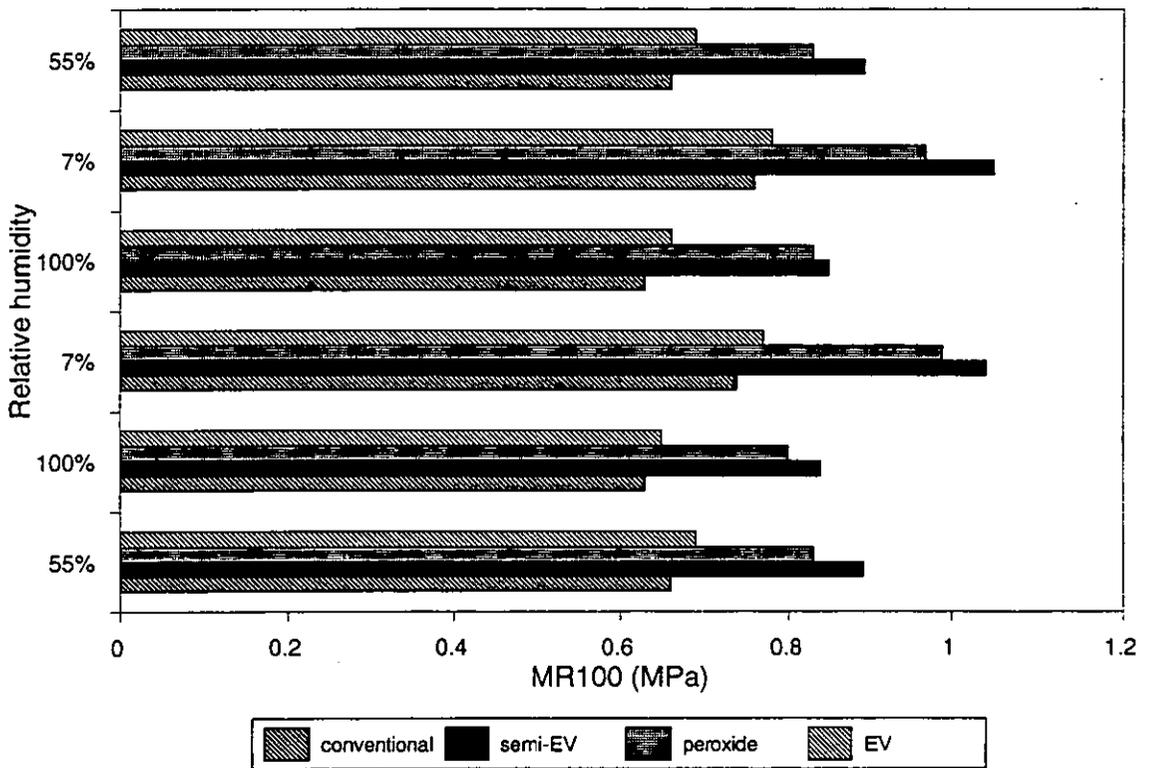


Figure 5.54
Change in modulus of TSR after a series
of humidity cycles



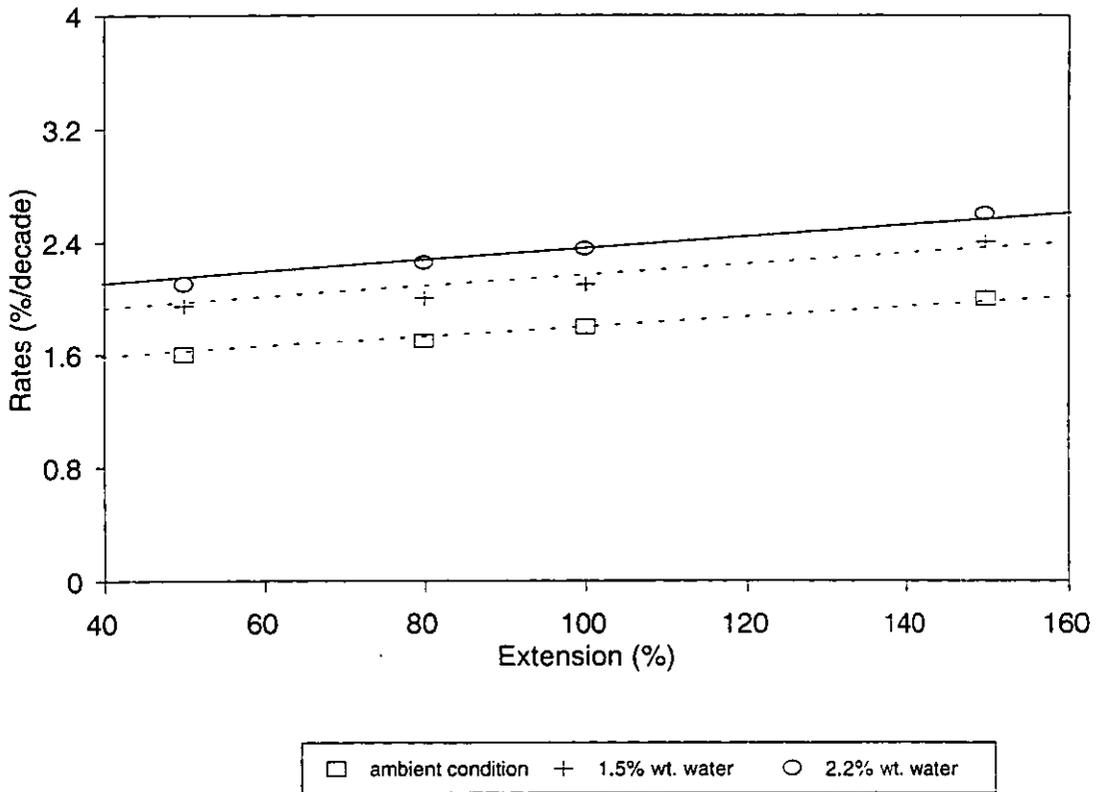
The change in modulus was observed to be very marked when the sample was exposed to moisture. With unfilled rubber, variation was observed to be significant in the presence of alanine and arginine, the two amino-acids present in the serum fraction of the NR latex. When fillers were used, a bigger change was observed with the presence of a non-reinforcing filler such as calcium carbonate compared to a reinforcing filler, carbon black. There was no change in the mass water uptake between rubber equilibrated at low (RH 7% or 25%) and room humidity (55%RH).

A similar effect was observed with the physical stress relaxation behaviour of the rubber equilibrated at different relative humidities. The effect was negligible with unfilled rubber, but fairly large with filled rubber.

The reduction in modulus and increase in rates of relaxation due to the presence of water could be explained by the plasticizing effect of the water, an effect similar to the presence of the oily plasticizer in the rubber (LAKE & POND, 1989). The plasticizing effect of the water lowers the modulus because the rubber network structure approaches a more nearly equilibrium configuration. This being so, it would be expected that the subsequent relaxation rate of the 'wet' rubber would be lower. However, it was observed that the rate of relaxation of unfilled NR increases as the amount of water imbibed increases. This is shown in *Figure 5.55* where the relaxation rates of unfilled NR (SMRL) swollen in water is presented as a function of applied strain. The rates of relaxation clearly increased as the water content in the rubber increases.

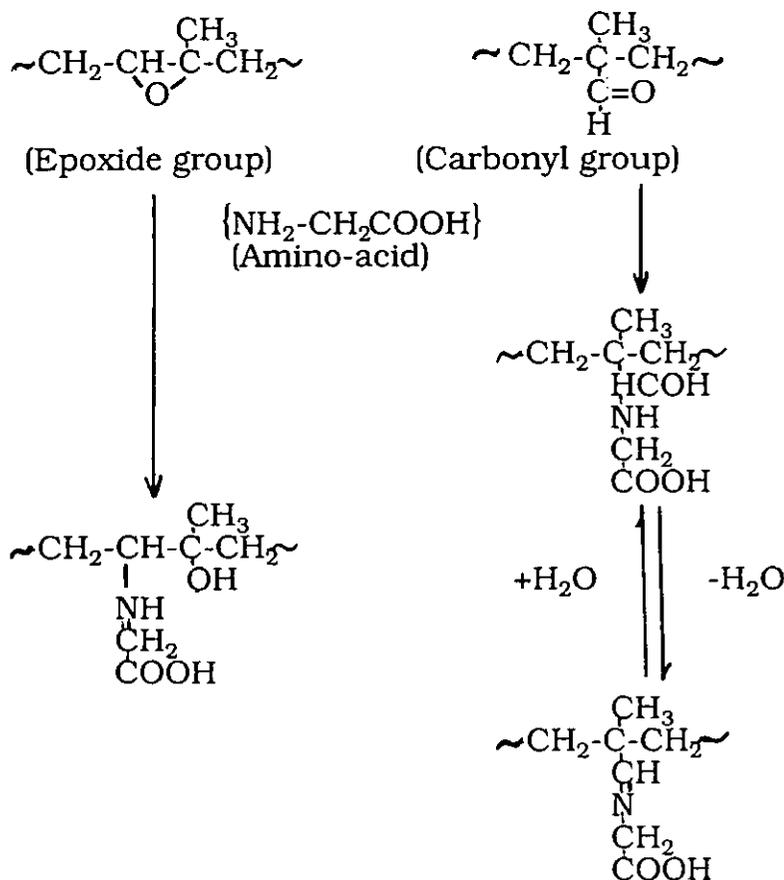
These results indicate that the explanation for the reduction in modulus and the increase in relaxation rates with increasing relative humidity is more complicated than the 'plasticization' theory which suggests that the presence of water 'plasticizes' the rubber network. If the 'plasticization' theory is valid, we would expect the differences in

Figure 5.55
Stress relaxation rates of unfilled
natural rubber containing water



modulus and relaxation at humidities between 7%RH and 55%RH to be negligible since there was no difference in the uptake of water by the rubber at those humidities. However the above results showed a much bigger effects could be obtained when the humidity was reduced from 55%RH to 7%RH; increasing the relative humidity to 100%RH gave a comparatively smaller effect.

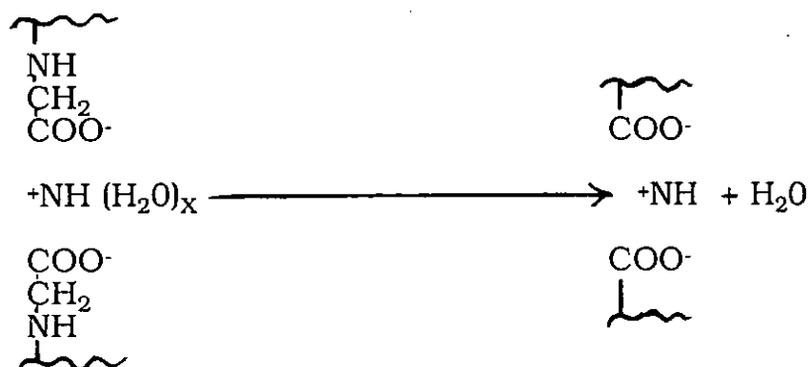
Thus the 'plasticization' theory could not adequately explain the phenomena observed in this study. A possible and more likely process which has taken place is a reaction similar to the phenomena of the storage hardening of the unvulcanized raw rubber (GREGORY & TAN, 1975; BURFIELD, 1986). The presence of certain types of amino-acid may catalyse the formation of the active functional groups from the available side or abnormal groups on the rubber chains, namely the epoxide or the carbonyl groups.



The presence of the -OH group and the -COOH groups may result with the following crosslinking esterification reaction (BURFIELD, 1986).



However, the above esterification process is not reversible and this is not consistent with the current observation whereby the effect of the modulus on humidity is reversible. Thus, a plausible reaction which may give a reversible effect and yet provide a strong linkage may be the ionic crosslink. The crosslink may be catalysed by metal ions (which are present in the rubber) or the amino-acid zwitter ions.



Such systems are known to be sensitive to moisture. The sensitivity to moisture is explicable since a strong hydrated ion reduces the strength of the crosslink. Conversely, drying the rubber reduces the solvation by water, intensifies the ionic interactions and hence effectively increases the apparent crosslink density and reduces the relaxation rates.

5.5.3 Effect of non-rubber constituents on network degradation

Studies on network degradation using stress relaxation had been carried out by several researchers (DUNN AND SCANLAN, 1963; MURAKAMI AND ONO, 1979). It has been established that during relaxation at high temperature in air, both thermal and oxidative degradation take place; network scission occurs both along the main chains and at the crosslinks. Under inert condition, thermal degradation takes place; network scission occurs mainly at the crosslinks (TAMURA AND MURAKAMI, 1980).

Results obtained from the test carried out on unfilled rubbers in air and nitrogen are in agreement with the present understanding of network degradation (*Figures 5.56-5.57*). All the rubbers tested gave large amount of chemical relaxation both in air and nitrogen; the extent of relaxation is bigger in air than nitrogen. This shows that scission takes place both in air and under inert environment.

The resistance to chemical relaxation will be strongly dependent on the bond strength of the linkages within the rubber matrix. A weak bond will break at lower activation energy, giving poor resistance to chemical relaxation.

All the above rubbers were vulcanized using an accelerated sulphur vulcanizing system. With this type of vulcanizing system, the structural features of the vulcanizates will be as depicted in *Figure 1.2* (see chapter 1). The bond dissociation energies of the crosslink are given in *Table 5.17* (TAMURA AND MURAKAMI, 1980),

Table 5.17: Bond dissociation energies in a typical rubber network

Type of bond	Dissociation energy(kcal/mol)
S-S	25-40
C-S	50-60
C-C	90-93

Figure 5.56
Stress relaxation of purified rubber and TSR
in air and nitrogen (@100°C/ACS-1 mix)

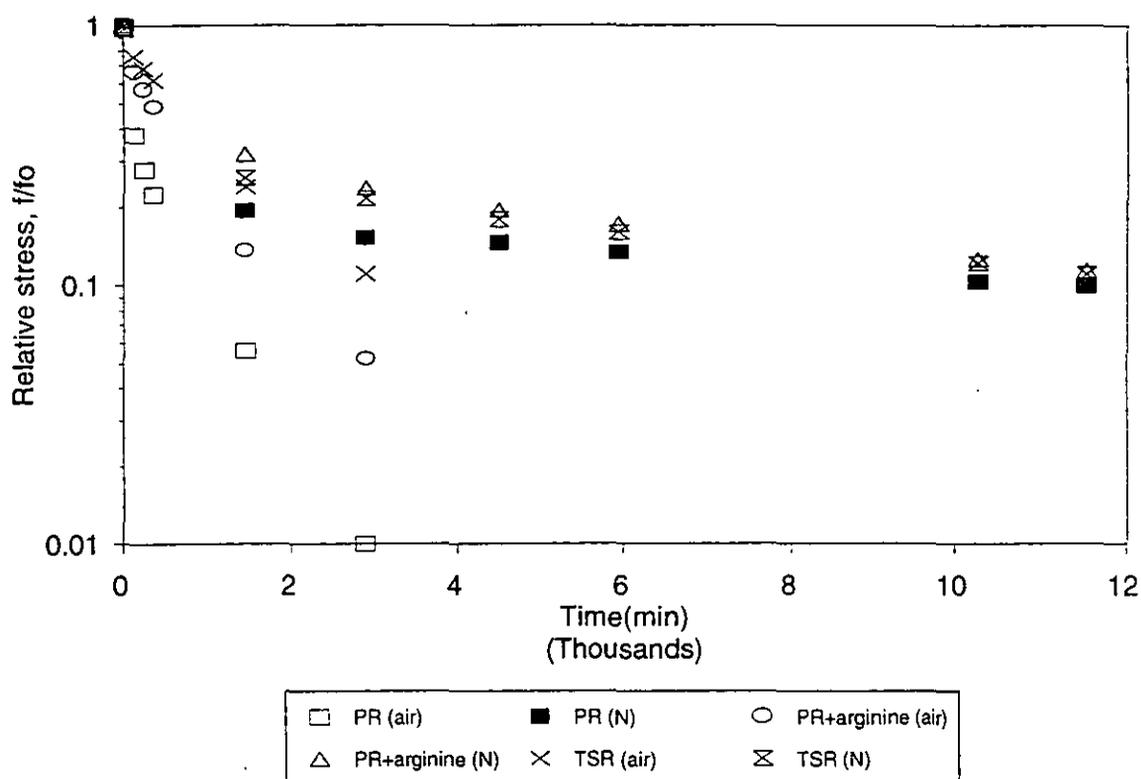
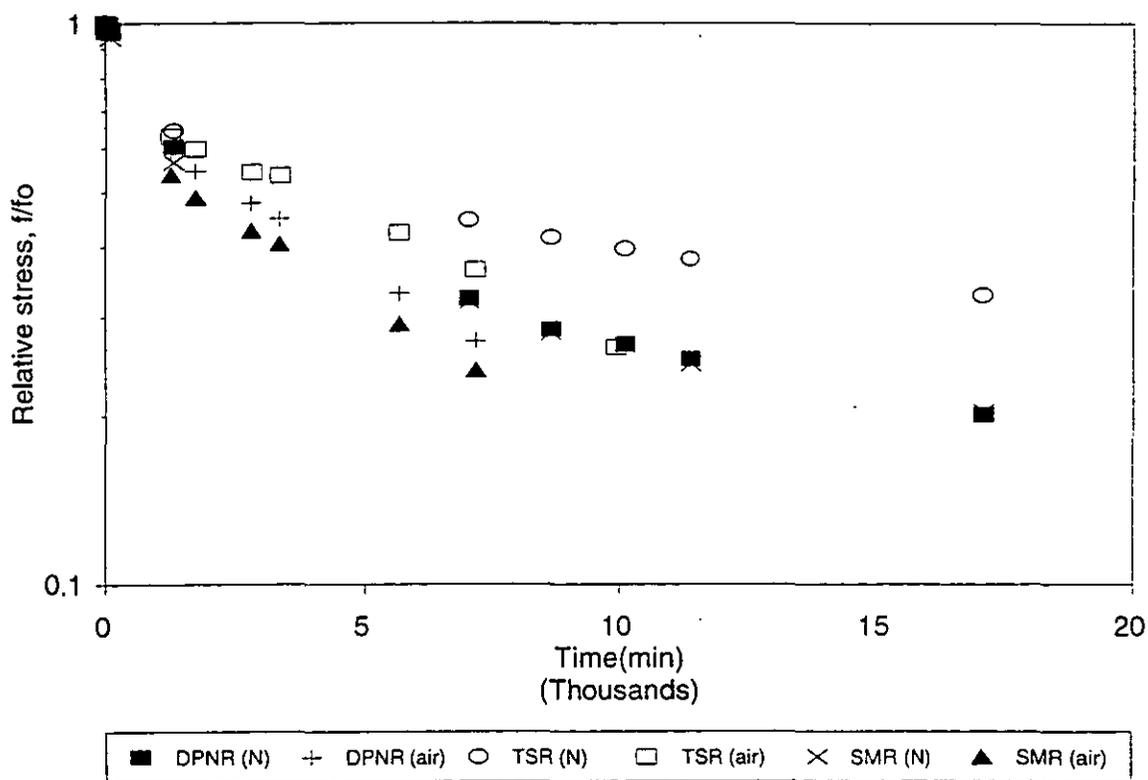


Figure 5.57
Stress relaxation of unfilled natural rubber
in air and nitrogen (@100°C/Semi-EV mix)



Any vulcanizates having comparatively more S-S bond, which are from the polysulphidic crosslinks, will fail at comparatively lower energy. Polysulphidic crosslinks break even in inert environment.

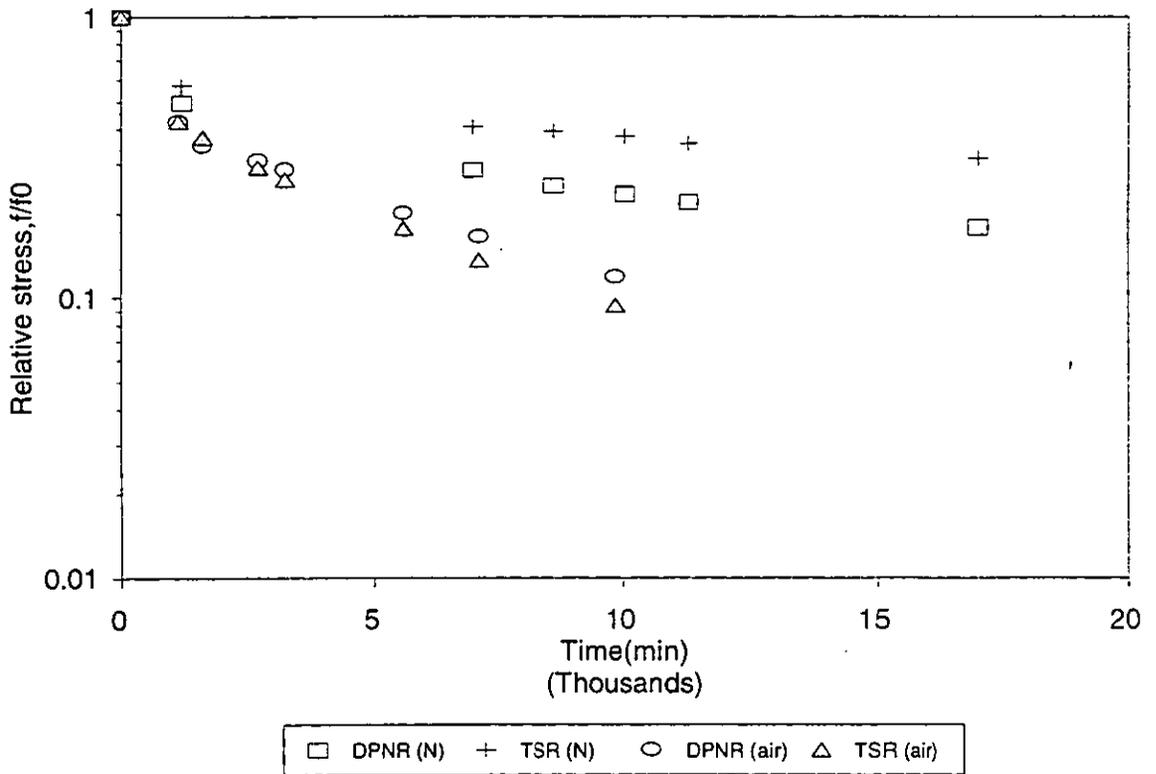
Based on the above results, it can be deduced that the differences in the resistance to chemical relaxation was due to the presence of difference amount of the polysulphidic linkages in the vulcanizates. PR+arginine and TSR have better resistance to chemical relaxation due, possibly to present of lower amount of polysulphidic crosslinks. PR without any non-rubber constituents has poorer resistance to chemical relaxation because of the presence of larger amount of the weaker polysulphidic linkages.

The occurrence of different amounts and types of crosslink in those vulcanizates was due to the presence the non-rubber constituents, such as arginine which has been shown to play a part in the vulcanization reaction (see section 5.2.2).

The premiss that stress relaxation occurs due to the breaking up of the polysulphidic linkages rather than oxidative main chain scission is supported by the relaxation results obtained under nitrogen. In the absence of oxygen, scission will not take place and the plots of $\log(f/f_0)$ versus time will be the same as those obtained at ambient temperature; due to physical relaxation. However, the substantial stress relaxation observed at high temperature in nitrogen and the linear plots $\log(f/f_0)$ versus time suggest that degradation of the network takes place; the weak S-S bonds of the polysulphidic linkages were converted into a stronger mono and disulphidic linkages due to thermal degradation.

The presence of fillers such as carbon black did not change the relaxation characteristics of the rubber (*Figure 5.58*). Similarly large amount of relaxation takes place both in air and nitrogen.

Figure 5.58
Stress relaxation of natural rubber filled
with N330 black (@100°C/Semi-EV mix)



Chemical relaxation involving polysulphides is generally reversible scission (TOBOLSKY, 1966). Thus, polysulphidic crosslinks will break and reform. If the degradation process involves additional crosslinking as well as chain scission, it is possible that some of the new network chains formed during stress relaxation may be load bearing and some may not. The stress relaxation data could no longer provides a measure of the total concentration of network chains at any time.

If the degradation and reformation of network takes place when the sample is not under strain, the new network form will contribute to the stress. However, if the networks are formed when the sample is under strain, then the new network form will be non-load-bearing members of the network. This is known as the 'two-network theory', which was first introduced by Tobolsky (TOBOLSKY, 1960)

Results obtained are in agreement with this theory. Eventhough the stress of the rubber reduced considerably during the ageing process, crosslinking was taking place simultaneously. This is shown by the data obtained from swelling of both degraded rubber samples (*Figure 5.59*).

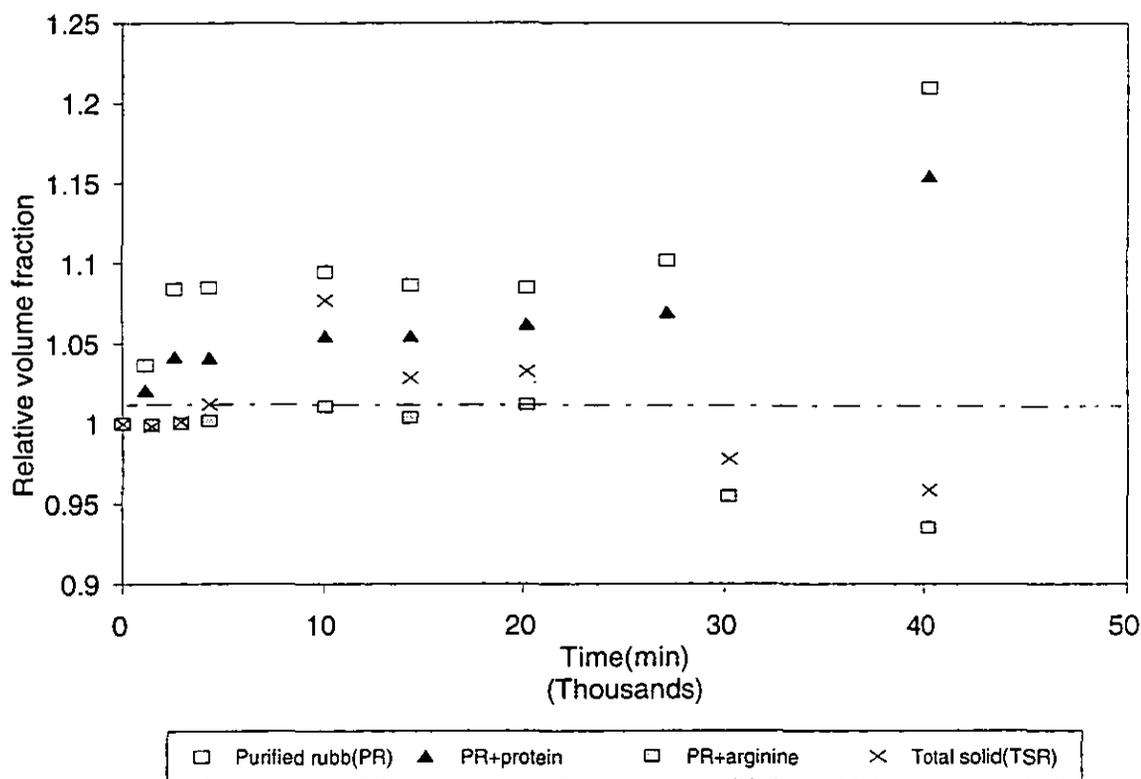
Initially, with all sample tested, the total concentration of crosslink increases with ageing time. However, as the ageing time continued,(>20000 minutes at 70°C), the relative volume fraction of PR and PR+protein continue to increase but the values for PR+arginine and TSR decreased.

These results suggest that at early stages of the ageing (<20000 minutes) network scission was taking place. The rate of network formation, if any, was lower than the rate of network scission

At longer ageing time, two different mechanisms were taking place, depending on the types of rubber used. The progressive increased in relative volume fraction observed with PR and PR+protein suggest that the rate of network scission was faster than network reformation. With PR+arginine and TSR, the decreased in the relative volume fraction with time of ageing shows that the rate of network formation was greater than the rate of network scission.

Generally, it can be concluded that the presence of different types of non-rubber constituents play a part in the chemical degradation of natural rubber vulcanizates. The presence of non-rubber constituents give rise to lower amount of polysulphidic linkages in the vulcanizate, resulting with rubber having better resistance to chemical relaxation.

Figure 5.59
Swelling of purified rubber containing
non-rubbers after ageing in air at 70°C



CHAPTER SIX

CONCLUSIONS

a) Stress relaxation test

1) A tensile stress relaxation test has been developed, which is accurate ($\pm 5\%$), cost effective and can operate in a wide range of temperatures and environments. Being tensile in nature, it does permit high surface/volume ratio specimen, good accuracy and ability to study cracking.

2) With this new stress relaxation test, the sample is gripped to a sample frame which is detachable from load measuring devices, while maintaining the strain. Thus, the set-up allows large number of sample to be tested simultaneously.

3) The problem of electrical drift associated with load measuring devices is eliminated since the load reading is taken intermittently.

4) Existing modern testing machine could be easily adapted to take up the stress relaxation sample frame.

5) The test has been optimised. A suitable sample to use is a strip of standard thickness (1-3 mm), with a length of more than 100mm.

b) Effect of non-rubber constituents and fillers

1) A study of the effect of non-rubbers and fillers were carried out. At ambient condition, wide variation in the modulus and relaxation was observed when non-rubbers were presence. Much relates to the presence of amino-acids, particularly, alanine and arginine, which resulted with an increased in modulus and reduction in relaxation rates. Proteins did not significantly affect these properties; its acted as inert fillers.

2) Further variation in modulus and relaxation was observed at different humidities. It is highest in the grades containing most non-rubbers i.e TSR>SMRL>DPNR.

3) At lower humidity, the relaxation rate is lower than at higher humidity. The modulus is higher at lower humidity. These variations were not observed under compressive deformation.

4) The largest variation properties was caused by the presence of non-rubber, amino-acid. It was reasoned that these variation were due to the formation of ionic crosslinks.

5) The uptake of water by the rubber was not induced by neither the hydrophilic and hydrophobic proteins or amino-acids. It appears to be related to the ash contents of the rubber.

6) Non-reinforcing fillers increase the rate of relaxation; the effect is most marked when strain are high.

7) Reinforcing filler, such as carbon black gave a high relaxation rates at lower strain. The rate decreases as the strain increases until it reaches a 'minimum' at about 20-30% strain, after which it increases.

8) The Guth-Gold model works for non-reinforcing filler but not for reinforcing filler. This shows that the volume filling effect is inadequate to describe the stiffening effects of reinforcing fillers.

9) At higher temperatures(70°C & 100°C), the presence of amino-acids give marginal improvement in the ageing characteristics of the rubber.

10) Higher temperatures reduces the relative stress of the rubber but the total crosslinks presence were unchanged. This suggest that crosslinks were broken up and reformed during the ageing process, rather than simply breaking.

11) Chemical stress relaxation takes place under all circumstances of filler and non-rubber presence. Current thinking ascribe this to the breaking-up of polysulphidic crosslinks.

CHAPTER SEVEN

RECOMMENDATIONS FOR FURTHER WORK

1) The present set-up for the new tensile stress relaxation test is a prototype version. The sample frame was made of stainless steel to be rigid and resistant to rusting. It can be used in test environments which are corrosive. The test is more flexible when the sample frame is made from materials which are able to withstand all environmental conditions.

2) Currently, the data collection is being done manually via a digital output. The test will be more attractive if the output could be interface with a computer terminal. This will facilitates data collection and analysis.

3) This new stress relaxation test has the advantage of the large surface area/volume ratio. Thus, the technique could be used in the study where large surface area of the sample is important. This includes:

a) Cracking of rubber due to ozone. This test is currently still qualitative in nature. A systematic study on the effect of ozone cracking using this new technique could lead to a quantification of the current standard ozone test.

- b) Effects of a short (few minutes) temperature jump. This effect accelerates the physical relaxation markedly and the extent of the increase depends on the types of rubber and temperature used. Valuable fundamental information on relaxation processes could be obtained from such studies. Previously, the test was difficult to be carried out because the set-up was not suitable; special set-up which include a test chamber capable of changing temperature in a matter of minutes was required. This new technique will not need such elaborate set-up.

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