The drying of natural rubber. Further studies of the stress relaxation behaviour of rubber in compression

This item was submitted to Loughborough University's Institutional Repository by the/an author.

Additional Information:

- Doctoral Thesis. Submitted in partial fulfillment of the requirements for the award of Doctor of Philosophy of Loughborough University.

Metadata Record: https://dspace.lboro.ac.uk/2134/7300

Publisher: © Mohd Tahir Bin Abdul Rahman

Please cite the published version.
This item is held in Loughborough University’s Institutional Repository (https://dspace.lboro.ac.uk/) and was harvested from the British Library’s EThOS service (http://www.ethos.bl.uk/). It is made available under the following Creative Commons Licence conditions.

For the full text of this licence, please go to: http://creativecommons.org/licenses/by-nc-nd/2.5/
PART 1: THE DRYING OF NATURAL RUBBER

PART 2: FURTHER STUDIES OF THE STRESS RELAXATION BEHAVIOUR OF RUBBER IN COMPRESSION

by

MOHD TAHIR B. AB. RAHMAN
B.Sc.(Mal.), A.N.C.R.T.(Lond.), Grad. P.R.I.(Lond.), Dip. Techno-Econ.(Stirl.)

A Doctoral thesis submitted in partial fulfilment of the requirements for the award of the degree of

DOCTOR OF PHILOSOPHY

at Loughborough University of Technology, U.K.

NOVEMBER 1985

Supervisors: Professor A.W. Birley (former Director of Research and Head of the Institute of Polymer Technology).

Mr. M.J. Stevens (retired Senior Lecturer)

Institute of Polymer Technology
Loughborough University of Technology
Loughborough, Leics. LE11 3TU, England

© MOHD TAHIR BIN ABDUL RAHMAN
In the name of Allah, the Beneficient, the Merciful

By the declining day,
Man is a certain loser,
Save those who have faith and do righteous deeds
and counsel one another to be steadfast.

The Quraan: 103.
DEDICATION

In everlasting memory of my dearest father who has encouraged me in the pursuit of my research programme, but did not live to see the fruit of my endeavour, through his death on 22nd November 1984.

Also my heartiest gratitude and appreciation to my dear wife Muzi who has persevered through the confinement of my Ph.D programme and manifested "stress relaxation" in our family. I am exceedingly thankful to my most wonderful bunch of children; Fazli, Faizal, Asma', Anas and Amal who have always boosted my spirit when times are low.
ACKNOWLEDGEMENT

I wish to express my most sincere gratitude to my supervisor, Professor A.W. Birley for his unrelentless guidance and assistance throughout the research period, and Mr. M.J. Stevens for his supervision of the 'drying programme'.

My appreciation to the Victaulic Co. Ltd. (Huntingdon); Water Research Centre (Swindon); and Engineering Research Station of the British Gas Corporation (Newcastle upon Tyne) for some financial support. My special thanks to the members of the Stress Relaxation Study Group, especially Mr. D. Brister (Victaulic), Mr. B. Gill (Water Research) and Mr. D. Boyes (British Gas) for their useful suggestions and discussions.

I gratefully acknowledge the financial support provided by the Malaysian Government, with my highest regards to all those concerned from the Rubber Research Institute of Malaysia who have granted me a prolonged study-leave.
PART 1  The Drying of Natural Rubber.

This was the initial research programme to be carried out at the Institute of Polymer Technology as a result of renewed interest in the area following information feed-back from the natural rubber consumers indicating a problem of wet rubber contamination. However, due to the difficulty in producing an acceptable starting material, the work had to be terminated with the compilation of what had been achieved including the literature survey, trials to produce a representative field latex coagulum, dewatering, diffusion and absorption experiments.

PART 2  Further Studies of the Stress Relaxation Behaviour of Rubber in Compression.

With the development of stress relaxation measuring equipment at the Institute of Polymer Technology, highly accurate and reproducible results were obtained from the 'ideal curves'. This equipment not only provides measurement of residual force and the instantaneous modulus of a sample but also enables the whole process from 'loading' to the measurement of subsequent relaxed stresses to be made.
It has been found that the stress relaxation behaviour of a rubber not only depends on the type of polymer and/or its formulation as widely accepted, but also on the technique of measurement. One example is the effect of rate of loading which is considered only briefly in the current standard test methods but which affects the subsequent stress relaxation appreciably. Another important variable is temperature, step changes of which contribute to more rapid stress relaxation. It was also found essential to specify the initial stress of a sample since the rate of stress relaxation is most rapid immediately after loading.

An attempt has been made to explain the modulus enhancement factor (MEF) which occurs immediately after loading in the black compound and in the compound with non-reinforcing filler, though at a lower level, but is almost negligible in a gum compound. Its relationship to hysteresis and stress relaxation was investigated. In long term measurements, the role of oxygen in governing the rate of stress relaxation was found to be small at room temperature as well as at higher temperature up to 100°C. The modulus for this same time period remains almost unchanged but increases abruptly when the stress has practically relaxed. Tests carried out in nitrogen have offered an explanation for this behaviour.

The commercial significance of stress relaxation and MEF in the performance of seals and gaskets is also explored.
PART 1

THE DRYING OF NATURAL RUBBER
CONTENTS

CHAPTER 1. INTRODUCTION

1.1 LITERATURE REVIEW 1

1.2 CONSTITUENTS OF NATURAL RUBBER 1

1.2.1 The Rubber Phase 2

1.2.2 The Non-Rubber Phase 2

1.3 DEVELOPMENT IN THE OPERATION PROCESS OF NATURAL RUBBER PRODUCTION 3

1.3.1 Drying of Natural Rubber and its Problem 4

1.4 STAGES INVOLVING REMOVAL OF WATER FROM COAGULUM 7

1.4.1 Dewatering Process 7

   a. Syneresis 7

   b. Mechanical Dewatering 10

   c. Syneresis of Machined Coagulum 11

1.4.2 Drying Stages 11

   a. Drying of Sheet Rubbers 11

   b. Drying of Crumb Rubbers 14

1.5 ALTERNATIVE DRYING METHODS 17

1.5.1 Solar Energy 17

1.5.2 Superheated Steam 18

1.5.3 Microwave 18
CHAPTER 2. EXPERIMENTS

2.1 INTRODUCTION 20

2.2 COAGULATION 20

2.2.1 Stability of Natural Rubber Latex 21

2.2.2 Changes in Chemical Constitution During Ammoniation and Storage 22

a. Effect of Ammoniation 22

b. Effect of Storage 23

2.2.3 Destabilisation of Natural Rubber Latex 24

2.2.4 Experiments to Determine a Method of Coagulating Diluted Latex Concentrate 25

a. Delayed Action Coagulation 26

b. Acid Coagulation 26

2.2.5 Summary 27

2.3 MICROSCOPIC ANALYSIS 27

2.4 DESIGN OF DEWATERING MOULD 28

2.5 SYNERESIS 30

2.6 DEWATERING OF COAGULUM 30

2.7 ABSORPTION BEHAVIOUR OF NATURAL RUBBER 33

2.8 CONCLUSIONS 41

REFERENCES 43
CHAPTER 1

INTRODUCTION

1.1 LITERATURE REVIEW

Studies involving drying of natural rubber were carried out as early as in 1936 at the Rubber Research Institute of Malaysia (RRIM) by Piddlesden, and Gale in 1957 on sheet rubber and later on in 1964 on comminuted or crumb rubber by Sethu. Recently, in 1978/79 there was renewed interest in this area to look into alternative drying methods. The work was carried out at the Malaysian Rubber Producers' Research Association (MRPRA) by Metherrel which includes feasibility studies of drying the rubber by solar energy, super-heated steam and microwave. There are also various other works on coagulation and drying which contain relevant points given in the References.

1.2 CONSTITUENTS OF NATURAL RUBBER (NR)

Commercial NR is obtained from the latex that is tapped from the tree known as Hevea Brasiliensis. The typical constitution of fresh NR latex is known as follows:

<table>
<thead>
<tr>
<th>Component</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>total solid content</td>
<td>36</td>
</tr>
<tr>
<td>dry rubber content</td>
<td>33</td>
</tr>
<tr>
<td>proteinaceous matter</td>
<td>1-1.5</td>
</tr>
<tr>
<td>resinous substances</td>
<td>1-2.5</td>
</tr>
<tr>
<td>ash and sugars</td>
<td>up to 2</td>
</tr>
<tr>
<td>water</td>
<td>ad. 100</td>
</tr>
</tbody>
</table>
They are distributed among 3 phases:

- the rubber phase
- the aqueous phase
- the lutoids and other particulate phases.

1.2.1 The Rubber Phase

About 86% of the rubber phase is made up of rubber hydrocarbon which is predominantly cis-1,4 polyisoprene. The molecular weights range widely with a bimodal distribution showing maxima at $1-2 \times 10^5$ and $1-2.5 \times 10^6$ a.m.u. The particle size ranges from $150\,\text{Å}$ to $3\,\mu\text{m}$ with the mode at $1000\,\text{Å}$.

1% of the rubber phase consists of proteinaceous substances. It occurs as an adsorbed layer which surrounds the external surfaces of the rubber hydrocarbon particles. Though small in amount, the protein determines the charge on the particle, its electrophoretic characteristics, and its coacervative behaviour.

Lipid substances consisting of about 3% of this phase are strongly adsorbed onto the surfaces of the rubber particles as intermediaries by which proteins are anchored onto the rubber particles.

1.2.2 The Non-Rubber Phase

The non-rubber phase i.e the aqueous, the lutoids and other particulate phases is basically a dilute aqueous solution
containing chemical species such as low molecular weight carbohydrates, proteins and amino acids, organic, inorganic and metallic ions, enzymes and others.

1.3 DEVELOPMENT IN THE OPERATION PROCESS OF NATURAL RUBBER PRODUCTION

It is probably convenient here to firstly consider the main types of natural rubber by their sources6:

Field Latex. This is the liquid rubber latex which constitutes the major portion of the crop.

Cuplumps. These are the cup coagula from late dripping after latex collection. Cuplumps constitute 10 to 20% of the total crop depending upon the tapping system, age and clone of the tree, weather conditions, etc.

Tree Lace. This is the coagulum which remains on the tapping cut and is removed as a 'lace' prior to tapping. They represent approximately 2.5% of the total crop.

Prior to the introduction of SMR (Standard Malaysian Rubber), natural rubber was produced as sheets. Field latex were processed to RSS (Ribbed Smoke Sheet) while cuplumps and tree-laces were processed into brown crepe which is of lower grade to RSS.
The 'SMR Scheme' was introduced in 1963 as an effort to keep up natural rubber with the demands of modern polymer technology. Many processes have then been suggested for the preparation of natural rubber in technically specified block-bale form; as a sophisticated raw material and not merely as a purely agricultural product. Since then many types of machinery have been developed and introduced to perform the operation, for example: granulator, hammermill and pelletiser to break up rubber into conveniently small-size crumbs; heat gelation system and extruder drier as a continuous means of coagulating and drying latex, and several others.

Although there have been investigation and research on the dewatering and drying of natural rubber, they are mostly confined to the mechanical and design improvement on the efficiency of driers, and more recently on the different methods of drying and their effect on the technical properties of the rubber produced4.

1.3.1 Drying of Natural Rubber and its Problems

Sheet rubber is often air-dried by natural convection at temperature rarely exceeding 60°C with a total drying period of 3 to 4 days, and a drier throughput of about 1 tonne per day. This method is too slow and not suitable for drying crumb rubber. Crumb rubber is dried using forced-air circulation through the bed at relatively higher temperatures of 110-120°C and low relative humidity to dry the rubber within a few hours.
Crumb rubbers are discrete when wet, but their natural tack return during the drying. Usually, when the drying is complete the entire bed of crumbs becomes a semi-coherent mass which could be lifted and handled as a block.

The drying is achieved by passing hot air through the bed of crumbs and several types of drier are available being either batch, semi-continuous or continuous types. Heat may be supplied either by direct firing i.e. using the products of combustion of diesel fuel diluted with fresh air, or indirectly by the use of heat exchangers. There appears to be little difference in the properties of rubber dried by direct or indirect methods. Indirect firing is approximately 15% less efficient in terms of fuel usage and the resultant rubber may be a little lighter in colour.

Air flow, humidity and temperature are important aspects of drying. In most type of driers, a certain amount of recirculation also occurs. High humidity is particularly important in the early stages of drying in order to prevent the development of a non-porous surface skin.

The structure of the crumb also plays an important part in its drying since drying relies not only on the intrinsic particle size but also on its porosity. If the porosity is destroyed the rubber must be reduced to a far smaller size for effective drying.
Drying of particulate solids such as crumb rubber, is a two-stage process. The first stage is dominated by evaporation of water from the surface and the rate of evaporation is proportional to the surface area and the rate of heat transfer. The second stage is controlled by the rate of transport of water from the centre to the surface and is independent of the velocity of the heat transfer medium. Generally, the overall drying time is substantially controlled by the second process which in rubber is the diffusion of water.

Ever since its introduction, SMR has been produced from crumb rubber and its form receives approval from rubber manufacturers world-wide over. However, one of the problems which still remains with SMR is the presence of wet rubber particles, popularly termed as white-spots, in SMR bales. These wet lumps of rubber are generally considered to be due to poor hammermilling, particularly of cuplumps. Since drying is largely diffusion controlled, the drying time increases with the square of the particle size. Hence the drying time of large lumps will be many times that of smaller crumbs. Increasing the drying time can cause oxidation of the bulk of the fine crumbs before the lumps are dry.

According to a working paper, following the information feedback from the SMR consumers, out of 2453 recurrent irregularities and deficiencies reported, 1507 or 60% consisted of incidents of wet rubber and concentrated white spots.
This finding indicates that the wet rubber still constitutes a major residual problem both at the export and the receiving end, and is included in the priority problem area. It was in the light of this problem that the author undertook the program to study the mechanism involved in the drying of natural rubber.

1.4 STAGES INVOLVING REMOVAL OF WATER FROM NATURAL RUBBER COAGULUM

Since the removal of water from the rubber starts not from the instance it gets into a drier but rather as early as after the rubber coagulates in a process known as 'syneresis', it was decided that the research programme should start from the coagulation process itself.

This whole process of water removal can then be divided into two stages as follows:

1. Dewatering of coagulum which involves:
   a. syneresis
   b. mechanical dewatering
   c. syneresis of machined coagulum.

2. Drying of the dewatered coagulum.

1.4.1 Dewatering Process

a. Syneresis

As described earlier the rubber phase of a fresh NR latex consists of rubber hydrocarbon particles surrounded by amphoteric
proteinaceous substances which acts as intermediaries. In its natural state the rubber phase is stabilised against coalescing by the negatively charged protein layer, and its stability can be extended, usually, by the addition of ammonia as preservative. Addition of acid to the latex will neutralise the negative charge of the protective protein layer and destabilise the latex causing it to gel.

In the gelation process the latex gradually changes from a fluid system to a uniform, semi-rigid gel usually accompanied or followed by spontaneous contraction of the gel in which serum is exuded, the process is known as syneresis.

Gelation seems to depend upon gradual development throughout the latex of a continuous network of aggregated, coalesced particles. The strength and rigidity of the resultant gel being determined partly by the extent to which coalescence has occurred and partly by the concentration of the reticulated structure which is derived from the latex particles. The secondary process of syneresis is to be understood as a spontaneous contraction of this network with consequent relief of stresses which have become built-in during the formation of initial reticulum.

In an experiment, Gale observed the syneresis of natural rubber latex which has been coagulated with formic acid and left to stand overnight. He obtained this average value:
% of dry rubber weight

serum in latex (15% drc) 570
serum in coagulum 350

He further referred to the works of other investigators in this area. Southorn\(^8\) showed that the rate of syneresis of coagulum is affected by the following factors:

- the pH of coagulation
- the preservative used
- the time for which the preserved latex has been stored before acidification.

He found that the pH of maximum syneresis was always in the range of 3.8 to 4.3 which approximately corresponds to the iso-electric point of the latex, i.e. the point at which the forces promoting adhesion between latex particles are at a maximum.

Schoon\(^9\) observed that the latex coagulum reached an equilibrium serum content of 275% after about 4 days when left in its serum; similarly if it was soaked in fresh water. When the coagulum was allowed to stand under the pressure of its own weight, greater exudation occurred to a lower equilibrium serum but was never less than 67%. This value was obtained after 5 days in an atmosphere of 100% relative humidity.

Gale, therefore, concluded that the rate of collapse of coagulum and so the extent of syneresis depends on the relative
values of the applied compressional force and various factors which affect the forces of attraction or repulsion between the latex particles. These factors vary with the type of latex, pH of coagulation, and the presence of additives.

b. Mechanical Dewatering

Gale in another experiment\(^2\) found that reducing the serum content below 15% is extremely difficult by mechanical means of passing the coagulum through a two-roll mill. He then referred to the observation made by Kemp\(^{10}\) who used field latex preserved for three months with 1% ammonia. He determined the loss in weight when the coagulum was subjected to repeated pressing of one minute at high pressure. The effect of varying the pressure from 1400 to 28,400 p.s.i or applying the pressure slowly or rapidly, were without effect on residual water content.

Gale then suggested that between 10 and 15% serum content a very stable structure appears to be built up in the coagulum. In this region of moisture content, it is known that drying rate changes abruptly, and dried sheets which are soaked in water also reach a water content of this level.

The serum content of a machined sheet also seemed to be influenced by the pH of coagulation; coagulation at pH 4.5 consistently giving higher serum content than at pH 4.0.
c. Syneresis of Machined Coagulum

It was also noted by Gale that the syneresis did not stop even after the coagulum had been mechanically dewatered. He observed that the coagulum sheet which had been mechanically dewatered to about 40% serum content would expel serum when placed under water, losing in weight some 10 to 15% in the first hour after machining. He also showed that a higher temperature caused an increase in the rate of exudation.

This exudation process is of interest from the heat economy point-of-view in that if the exuded serum can be removed as liquid, latent heat evaporation does not have to be provided during the drying process.

1.4.2 Drying Stages

The drying of natural rubber in its different forms, i.e., sheet and crumb rubbers has been discussed earlier. However, several other points are discussed in this section.

a. Drying of Sheet Rubbers

Conventional sheet rubbers are dried by suspending them over poles mounted on trolleys and dried either by natural convection or by forced-draught air circulation normally in purpose-built drying sheds. The temperature in the process rarely exceeds 60°C, above which the wet sheets tend to sag under their own stress, and the drying time under such conditions varies between 3 to 4 days. Prior to going into the drying sheds,
trolleys of the wet sheets are left for about 2 hours to allow dripping to occur in the shade since sunlight may tend to cause oxidation.

In the case of Ribbed Smoked Sheet (RSS) it is dried in 'smokehouse' by the convection of smoke-and-air mixture at 60°C. During the first 4 to 5 hours of smoking, the wet sheets will attain a temperature approaching 60°C and a considerable quantity of water will be lost due to further syneresis at this elevated temperature.

Gale in his paper\textsuperscript{11} reached several conclusions based on his observations in his study involving drying of sheet rubber. In one of his calculations he showed that if contraction of width and length of a rubber sheet could be restricted, the thickness of the sheet would be reduced by 20\% compared to a sheet which is not restricted, and that the drying rates of these restricted sheets were correspondingly greater.

The measurement of shrinkage due to water removal has enabled the effect of machining and weight stresses to be assessed. From the results he suggested that since no voids were left in the rubber during water removal, capillarity is not much concerned in the mechanism of water transport from the centre to the surface of the sheet.
In studying the drying behaviour at below 10% water content he observed that minor variations in serum composition or changes in method of coagulation were unlikely to affect the rates of drying in the constant rate period and that the effect would mainly be noticed in the diffusion controlled period, i.e below the 10% water content.

Raising the temperature from 60 to 80°C at constant absolute humidity was found to reduce the drying time by a factor of 2.65 which is of the order expected; but reducing the relative humidity from 70 to 15% at 60°C which reduced drying time by a factor of 2.7 was unexpected and contrary to previously held views. Piddlesden\(^1\) anticipated, on the basis of diffusion theory, that there would be no effect of relative humidity on the drying; while in another view held by other workers was that increasing the relative humidity would prevent the formation of an impermeable skin on the surface of the rubber and thus increase the rate of drying.

However, Gale in his calculations indicated in terms of thermal efficiency, that high temperatures are likely to be more economic and that there would be an optimum humidity.

Gale had also referred to the works carried out by other contributors in this area which includes Piddlesden\(^1\) as mentioned earlier who found two distinct phases of drying, i.e a rapid reduction in water content down to about 10% followed by a very
slow rate of drying. He postulated that this second phase was controlled by a diffusion mechanism since the drying time was found to be roughly proportional to the square of the sheet thickness. Then there were Newman and Sherwood\textsuperscript{12,13,14} who observed fairly wide variations from the average relationship between thickness and drying time, and consistent departures from the theoretical drying rate curve, which was attributed to dimensional changes and characteristics of the drying apparatus; Stevens\textsuperscript{15} who expressed the view that the porosity of coagulum is reduced by compression during machining and that the drying rate of unmachined coagulum might be greater than that of machined sheet in spite of the former's greater thickness and initial water content; Philpott and Walker\textsuperscript{16} who found that the inclusion in sheet of protein precipitants or tanning agents accelerated drying coupled with the fact that drying is retarded both by removal of protein and the addition of sodium sulphite to latex.

b. Drying of Crumb Rubbers

Crumb rubber is the product from the process of size reduction of coagulum by mechanical means, such as granulation, shredding, pelletising and hammermilling usually in various combinations and often include crepeing. The size reduction mechanisms involve various degrees and rates of deformation in compression and shear of the coagulum.

Rubber, whether wet or dry, when subjected to a high shear force, ruptures to produce a large exposed area of fresh
surfaces. These fresh surfaces, especially of natural rubber, have very strong tack-property which tend to stick together the pieces of crumb rubber. To overcome this undesirable effect during the size reduction process as well as during the drying, a non-compatible lubricant, usually castor oil is either introduced or applied to the coagulum to reduce the tack.  

From RRIM the main contribution on drying of crumb rubber is from Sethu. In one of his earlier papers on this subject he provided information on drying characteristics of rubber granules and the effect of coagulation conditions, particle size, etc., on the drying time. In determining a method of drying crumb rubber, it was found that through-bed air circulation drying is a more efficient method compared to hot chamber drying with slight air movement and so the former method was chosen for subsequent work. In this aspect Sethu made the following observations:

1. From the drying curve three phases of drying were distinct, i.e. the constant rate, the first and second falling-rate periods. The first critical moisture content appears around 10% and the second around 1.5%.

2. The following have no obvious or significant effect on time:

   - dry rubber content
   - pH of coagulation
   - age of coagulum.
3. There was a rapid reduction in the drying time when the temperature is increased from 85 to 100°C.

4. Unlike sheet rubber where the drying time is proportional to the square of the thickness, the drying time of granulated rubber varies only slightly with the particle size. An observation which suggests that rapid drying of crumb rubber is not only due to the increase in surface area, but also to its porous structure.

5. By dripping the wet crumbs, in spite of reducing the initial moisture content by 10 to 15%, it increases the overall drying time considerably and so darkens the colour of the dried rubber as well. It was thus expected that during dripping, most of the porous structure in the freshly cut rubber crumbs collapse, probably due to relaxation of machining stress, which influence the release of serum by syneresis.

In his other paper Sethu\textsuperscript{19} indicated his observation during the constant rate period that the rate of drying of crumb rubber varies,

- directly with the humidity gradient
- exponentially with air velocity
- inversely with the loading depths of the crumbs.

With this observation he confirmed the theory that gas-film mass transfer is the controlling mechanism in this period.
During the falling rate period, Sethu suggested that the rate of drying, as with the sheet rubber, is controlled by an activated diffusion mechanism. In this aspect he referred to Gale\textsuperscript{20} who studied the internal water movement in sheet rubber and suggested that the movement occurs by activated diffusion under the influence of differences in moisture concentration.

1.5 ALTERNATIVE DRYING METHODS

Based on the MRPRA Reports\textsuperscript{4}, three alternative methods of drying natural rubber have been considered namely:

- solar energy
- superheated steam
- microwave.

1.5.1 Solar Energy

Two possible approaches of utilising solar energy to produce the heat required for drying were studied. The first approach looked into the use of conventional solar panels. Having considered the solar radiation that might be received in Malaysia; the expected efficiency of a solar drier; and the amount of water to be removed from crumb rubber it was found that as a result of the cost of the large solar collection area required, the depreciation figure of the solar panel alone is in the same range as the running costs of the present method of drying by fuel heating. This method is, therefore, economically unjustifiable unless the three factors mentioned above can be improved.
The other approach is to use 'solar sheds' in place of the expensive solar panels. The roof of the solar shed is used as the solar collector to heat the air between the solar roof and an inner roof. This heated air can then be circulated through drying chamber. Even though the cost is reduced, the major disadvantage which remains with this system as with the solar panel drying, is the large shed area required for solar collection, i.e 350m per tonne rubber dried per day.

1.5.2 Superheated Steam

The principle of using superheated steam is because it is 'dry', i.e below its saturation-point and can, therefore, take up more water until it reaches saturation. The rubbers which were steam dried were claimed to have lesser amount of storage hardening compared to those which were air dried and also the amount of storage hardening decreases with the temperature of drying; a desirable property for natural rubber.

1.5.3 Microwave

Microwave energy is a form of electromagnetic radiation of frequency around 1000 MHz, which will penetrate about 1 foot of rubber or about 2 feet of crumbs. With microwave, the heating does not depend on the conduction of heat through the solid such as rubber, but rather on the ability of the material to absorb the microwave energy; and only polar materials absorb microwave energy. The uniformity of heating in a solid by microwave depends on the symmetry of the material, provided the attenuation of
microwave field by the substance is low. The low attenuation of microwave energy in rubber enables large samples to be heated fairly uniformly.

Three ways of applying microwave heating to dry crumb rubber were attempted:

1. complete drying with microwave energy
2. microwave heating at initial drying stage
3. microwave heating at final drying stage.

In the first application, an estimate indicates that it is very capital intensive, costing about three times more compared to conventional hot-air circulation drying for a similar output. The second application, i.e to use microwave heating in the initial drying stage should be more advantageous over conventional drying. However, the power requirement is too high making it incredibly expensive. Similarly, in the third application microwave heating becomes too expensive in order to have any advantage over hot-air drying. Furthermore, it requires supplementary hot-air circulation to dry the rubber at the surfaces of the bed.

In this investigation, microwave drying was thus concluded as not very attractive.
CHAPTER 2

EXPERIMENTS

2.1 INTRODUCTION

At the beginning of the programme the main concentration was to obtain an acceptable method of coagulating diluted latex concentrate. However, as the time taken by this exercise alone became unexpectedly long, other experiments were carried out with the coagula which were obtained from the various coagulation trials even though they were not in the most satisfactory form. The intention was that when a 'representative' coagulum has been obtained, the experiments can be carried out with more experience behind them. Such experiments include syneresis investigation, microscopic work, effect of dewatering, etc.

The result obtained from the experiments should, therefore, be treated with caution bearing in mind that it is not the outcome of a fresh field latex coagulum or which is representative of it.

2.2 COAGULATION

Coagulation in natural rubber latex can be considered as a process of destabilising the latex to an extent that the particles agglomerate and coalesce in large numbers.
Since it had been decided that coagulation should be the starting point of this research programme with the first objective of establishing a method of coagulating diluted latex concentrate closest in mechanism to coagulating fresh field latex and producing coagulum closest, physically and chemically, to that of field latex coagulum it is probably appropriate to understand how a latex maintains its stability and what is the effect of long-term preservation for storage purposes on the latex before looking into how latex is destabilised during coagulation.

It should also be noted at this juncture, that it is the inability to achieve the objective in the coagulation exercise above which resulted in the decision to abandon this programme after almost 2 years of trial-and-hope to a time when the situation is more favourable.

2.2.1 Stability of Natural Rubber Latex

One of the factors which promotes the stability of any latex is the presence on the rubber particle surfaces of electric charges of similar polarity causing mutual coulombic repulsions between the particles\(^5\). As mentioned in the previous chapter, natural rubber particles in latex have two protective envelopes of lipid and protein which provide a negatively charged surface resulting in its stability.
The presence around the rubber particles of a layer of tightly-bound water molecules which acts as a mechanical barrier against the coalescence of two rubber particles also supplements the stability of the latex. Adsorption of the water molecules in a specific manner occurs since water is a polar material; its polarity leading to the formation of a near-regular three-dimensional honeycomb-like configuration strongly attracted to the surface of the rubber particles, and the anionic surface characteristics are preserved. This hydration layer provides a physical buffering to the rubber particles.

2.2.2 Changes in Chemical Constitution During Ammoniation and Storage

Chemical composition of ammonia-preserved latex after storage differs somewhat from that of fresh, unammoniated latex. Quantities of proteins and resinous substances tend to fall while overall concentration of ions present in the serum tends to increase particularly fatty acids, phosphate, low molecular-weight carboxylic acid and amino acid anions.

a. Effect of Ammoniation

Ammonia is the most widely used preservative for natural rubber latex. Ammoniation promotes the following hydrolysis reactions:

- Proteins $\rightarrow$ polypeptides and amino acids
- Lipids $\rightarrow$ glycerol, fatty acid anions, phosphate anions and organic bases.
The liberated fatty acid anions are adsorbed at the rubber particle interface thus enhancing the stability of the latex. This is why the stability of the ammonia preserved latex tends to increase during storage. Lutoid, Frey-Wyssling particles and other particulate phases too dissolve in serum when fresh latex is ammoniated.

b. Effect of Storage

Volatile fatty acids (VFA i.e formic, acetic and propionic acids) are present in the ammonia-preserved latex as ammonium salts. Their effects is to reduce the mechanical and chemical stabilities of the latex. The mechanical/chemical stability of ammonia preserved latex stored for a length of time is thus a product of several factors. The most important being:

- VFA formation, which tends to reduce latex stability
- Lipid hydrolysis to give long-chain fatty acid anions, which tends to enhance stability.

The final stability of a latex, therefore, is largely determined by the balance of these two factors.

Both the above effects, i.e ammoniation and storage of ammonia-preserved latex occurs whether the latex is concentrated or not. Centrifugation by itself has little effect on coagulation behaviour; its effect is in fact an improvement in the colloid stability due to sedimentation of the lutoid fraction, which contains destabilising entities, during centrifugation.
2.2.3 Destabilisation of Natural Rubber Latex

Destabilisation of natural rubber latex can be affected either by:

- chemical coacervants, or
- physical destabilising agencies.

A chemical coacervant functions mainly by reducing the zeta-potential associated with the electrical double layer surrounding the latex particles. This is achieved either by direct interaction between the coacervant and one of the adsorbed components of the double layer described as 'insolublisation' of the adsorbed stabiliser; or by indirect interaction in the form of swamping or 'compression' of the double layer by ions of opposite polarity, or indirect interaction such as when the coacervant causes a fine precipitate of high specific surface area to form in the aqueous phase and successfully compete with the polymer particles for the colloid stabilisers in the system.

The chemical coacervants can be divided into 3 groups:

- direct or contact coacervants
- heat-sensitising coacervants
- delayed action coacervants.

Physical destabilising agencies brought about destabilisation in latex by increasing either the frequency or the violence of the collisions between particles, or both. And this can be done by:
2.2.4 Experiments to Determine a Method of Coagulating Diluted Latex Concentrate

The aim of this experiment was to find a reproducible method of preparing natural rubber coagulum from latex concentrate which can closely represent fresh field latex coagulum, chemically and physically. Three types of natural rubber latex were considered:

- High Ammonia (HA) latex concentrate
- Low Ammonia (LATZ) latex concentrate
- High Ammonia field latex.

All these latex were obtained from MRPRA. When using them they were first diluted with distilled water to 30% d.r.c (dry rubber content) which is typical of field latex. The different methods of coagulation that were attempted can be classified as follows:

- delayed-action coagulation
- acid coagulation.

In the course of the coagulation-trial it was decided not to use LATZ concentrate because it was considered as being not chemically representative of field latex; whilst between the High-Ammonia latex concentrate and field latex there was no
significant difference in their coagulation behaviour so the former was chosen as the starting material because of its availability. Before coagulating, the ammonia level of the latex was first reduced by chemically deammoniating it with calculated amount of formaldehyde solution.

a. Delayed Action Coagulation

This method was attempted mainly to overcome 'point coagulation' which occurred when acid is added directly to the latex and also to achieve gradual coagulation to obtain uniform coagulum. The coacervant used was sodium silica fluoride and even though gradual coagulation was achieved it did not give a firm and coherent coagulum even after a long period of standing, or at elevated temperature unless some other chemicals were added such as zinc oxide. Since, from the main objective of this exercise, any other addition of chemicals to the latex is not desirable and also because the coagulum obtained was not in the satisfactory form, the method became unacceptable.

b. Acid Coagulation

Coagulation using formic acid is the established method of coagulating fresh field latex, and so it was decided to investigate the possible techniques of using formic acid to coagulate the diluted latex concentrate. These include using different acid concentrations from 5% down to 0.1%, various ways of adding the acid to latex such as drops, in jets and others. All these methods end up in point coagulation. The technique that
was finally adopted was applying the acid in mist spray form (aerosol) which in actuality coagulates the latex in layers. This was the best form of coagulum that can be achieved to meet the objective of this exercise even though it might still be remote from representing a fresh field latex coagulum.

2.2.5 Summary

An ammonia preserved latex is predominantly a two-phase system comprising rubber particles and serum only. The rubber particles are stabilised by fatty acid anions and proteinate ions instead of the latter only as in the case of fresh latex. This accounts for some of the observed differences in colloid behaviour between fresh and ammonia-preserved latex; e.g. addition of dilute acids to fresh latex does not cause immediate coacervation, but rather a slow gelation. On the other hand, ammonia-preserved latex when acidified causes immediate formation of coagulum at pH values as high as 7.05.

2.3 MICROSCOPIC ANALYSIS

An approach which was being considered to investigate the mechanism involved in drying natural rubber is by the microscopic analysis of its structure at different stages of dewatering and drying. Unfortunately, the difficulty in getting thin sections of the coagulum by microtoming and preserving its structure for microscopic observation have made this approach impractical.
Among the methods tried out to produce thin sections of coagulum but without much success were by deep-freezing the sample in liquid nitrogen in order to 'solidify' the coagulum prior to cutting. However, this method has the disadvantage of rupturing any micro-structures in the sample by the water present during freezing thus defeating the purpose of this exercise. Another method tried was by freezing the sample in-situ with carbon dioxide before microtoming. In both cases the main problem was the rolling or curling up of the thin sections as soon as they were cut before mounting them on glass slides. Adjusting the angle of the microtome blade in order to reduce the tendency of the sample to curl up did not prove to be successful.

2.4 DESIGN OF DEWATERING MOULD

A mould was designed which was to be used for mechanical dewatering of the coagulum samples by pressure. The physical effect of pressure on the coagulum and its subsequent effect on drying was then to be investigated.

Some of the features and concept in the design of the mould includes the following:

1. The mould is made up of aluminium block and aluminium plated steel so as to prevent any possible corrosion by the acidic nature of the serum from the coagulum.
2. To maximise dewatering, grooves were cut through the mould and separated from the coagulum sample by a perforated plate.
3. To prevent the expelled serum from going back into the
dewatered coagulum, drainage was provided for it which
could be collected for analysis if necessary.

The dewatering mould was basically designed as of a semi-
positive mould, see Fig 1.

2.5 SYNERESIS

The effect of environment on syneresis was investigated
in this exercise by placing coagulum in water, air and water-
saturated atmosphere. The percentage weight on dry rubber basis
of serum left in the coagulum against time indicates the extent
of syneresis that has taken place. The results are given in Table
1 and plotted in Fig 2.

2.6 DEWATERING OF COAGULUM

The method of dewatering coagulum is very important not
only on its own as a processing unit but also towards subsequent
process of drying the dewatered coagulum. Too much water left in
the material after the dewatering process would mean a higher
energy required to evaporate the water during drying, while too
much work on the coagulum to maximise the removal of water has
the possibility of changing or destroying the porosity of the
coagulum thus making the movement of water in the material more
difficult during drying.
Table 1
Syneresis in Various Environments

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>% Weight of water on dry rubber in:</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Water</td>
<td>Air</td>
<td>Saturated Atm.</td>
</tr>
<tr>
<td>0</td>
<td>500.9</td>
<td>497.6</td>
<td>455.9</td>
</tr>
<tr>
<td>1</td>
<td>477.6</td>
<td>465.8</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>467.5</td>
<td>450.8</td>
<td>-</td>
</tr>
<tr>
<td>2.5</td>
<td>-</td>
<td>-</td>
<td>415.9</td>
</tr>
<tr>
<td>5</td>
<td>-</td>
<td>-</td>
<td>399.4</td>
</tr>
<tr>
<td>16</td>
<td>443.9</td>
<td>426.1</td>
<td>-</td>
</tr>
<tr>
<td>19</td>
<td>429.1</td>
<td>408.1</td>
<td>-</td>
</tr>
<tr>
<td>21</td>
<td>425.0</td>
<td>402.7</td>
<td>-</td>
</tr>
<tr>
<td>22</td>
<td>-</td>
<td>-</td>
<td>381.4</td>
</tr>
<tr>
<td>23</td>
<td>421.5</td>
<td>396.9</td>
<td>-</td>
</tr>
<tr>
<td>24</td>
<td>-</td>
<td>-</td>
<td>377.0</td>
</tr>
<tr>
<td>27</td>
<td>-</td>
<td>-</td>
<td>374.2</td>
</tr>
<tr>
<td>30</td>
<td>-</td>
<td>-</td>
<td>371.6</td>
</tr>
<tr>
<td>41</td>
<td>413.9</td>
<td>376.4</td>
<td>-</td>
</tr>
<tr>
<td>46</td>
<td>410.1</td>
<td>367.4</td>
<td>368.5</td>
</tr>
</tbody>
</table>
To avoid or at least minimise any destruction to the structure of the coagulum during dewatering, the water is removed by centrifuging the samples at different speeds. The drying behaviour of these samples was then compared with those which were dewatered using the dewatering mould under different pressures.

The samples were centrifuged for forty minutes at the set speeds while those dewatered by pressure were pressed for one minute under the set pressures. The moisture contents of the samples before and after dewatering were recorded. After dewatering the samples were placed in a dessicator for 'drying' and their moisture contents calculated at intervals until they were almost unchanged. The results are given in Tables 2, 3, 4 and 5 and plotted in Figures 3 and 4.

2.7 ABSORPTION BEHAVIOUR OF NATURAL RUBBER

A series of experiments which were meant to be a preliminary investigation on the structure of rubber were carried out. In the experiments dry rubber samples were placed in salt solutions of different concentrations as well as in water with wetting agent added to it.

RSS rubber of about one inch square were used as the test samples. They were placed in distilled water and salt solutions, and their weights were taken at intervals. At the same time their volumes were calculated using Archimedes principle. The
Table 2
Dewatering by Centrifugation

<table>
<thead>
<tr>
<th></th>
<th>Centrifuge speed (rpm)</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>2000</td>
<td>3000</td>
<td>4000</td>
<td>5000</td>
</tr>
<tr>
<td>Initial wt.</td>
<td>6.455</td>
<td>16.218</td>
<td>19.000</td>
<td>16.041</td>
<td>20.410</td>
</tr>
<tr>
<td>Dewatered wt.</td>
<td>12.230</td>
<td>12.552</td>
<td>10.493</td>
<td>11.080</td>
<td></td>
</tr>
<tr>
<td>Dry wt.</td>
<td>2.528</td>
<td>6.065</td>
<td>6.357</td>
<td>5.837</td>
<td>7.166</td>
</tr>
<tr>
<td>Total water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>content</td>
<td>3.927</td>
<td>10.153</td>
<td>12.643</td>
<td>10.204</td>
<td>13.244</td>
</tr>
<tr>
<td>Water removed</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>removed</td>
<td>-</td>
<td>39.3</td>
<td>51.0</td>
<td>54.4</td>
<td>70.4</td>
</tr>
</tbody>
</table>

Table 3
Drying of Centrifuged Samples

<table>
<thead>
<tr>
<th>Hours</th>
<th>% Moisture content at centrifuge speed (rpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>155.3</td>
</tr>
<tr>
<td>5</td>
<td>101.7</td>
</tr>
<tr>
<td>6</td>
<td>96.1</td>
</tr>
<tr>
<td>23</td>
<td>14.0</td>
</tr>
<tr>
<td>29</td>
<td>11.4</td>
</tr>
<tr>
<td>48</td>
<td>9.4</td>
</tr>
<tr>
<td>54</td>
<td>9.1</td>
</tr>
<tr>
<td>72</td>
<td>8.4</td>
</tr>
<tr>
<td>96</td>
<td>7.8</td>
</tr>
</tbody>
</table>
### Table 4
**Dewatering by Pressing**

<table>
<thead>
<tr>
<th>Pressure (Kg on 10.16 cm diameter ram)</th>
<th>50</th>
<th>100</th>
<th>300</th>
<th>500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial wt.</td>
<td>148.63</td>
<td>142.73</td>
<td>131.97</td>
<td>137.24</td>
</tr>
<tr>
<td>Dewatered wt.</td>
<td>40.04</td>
<td>35.81</td>
<td>32.10</td>
<td>31.30</td>
</tr>
<tr>
<td>Dry weight</td>
<td>28.71</td>
<td>28.45</td>
<td>26.57</td>
<td>25.55</td>
</tr>
<tr>
<td>Total water content</td>
<td>119.92</td>
<td>114.28</td>
<td>105.40</td>
<td>111.69</td>
</tr>
<tr>
<td>Water removed</td>
<td>108.59</td>
<td>106.92</td>
<td>99.87</td>
<td>105.94</td>
</tr>
<tr>
<td>% water removal</td>
<td>90.5</td>
<td>93.6</td>
<td>94.8</td>
<td>94.9</td>
</tr>
</tbody>
</table>

### Table 5
**Drying of Pressed Samples**

| Hours | % Moisture content of sample pressed at*:
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50</td>
</tr>
<tr>
<td>0</td>
<td>38.5</td>
</tr>
<tr>
<td>3</td>
<td>35.6</td>
</tr>
<tr>
<td>18</td>
<td>25.6</td>
</tr>
<tr>
<td>26</td>
<td>20.8</td>
</tr>
<tr>
<td>47</td>
<td>10.7</td>
</tr>
<tr>
<td>115</td>
<td>7.7</td>
</tr>
</tbody>
</table>

* Kg on 10.16 cm diameter ram.
Figures denote pressure on ram.

**NOTE:**

---

**FIG 4**

PRESSED SAMPLES

% MOISTURE CONTENT

HOURS

0 20 40 60 80 100

50 100 200 300

30 20 10
### Table 6
Absorption in Different Concentration of Salt Solutions

<table>
<thead>
<tr>
<th>Hours</th>
<th>0% soln.</th>
<th>5% soln.</th>
<th>15% soln.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>water</td>
<td>rubber</td>
<td>water</td>
</tr>
<tr>
<td>2</td>
<td>0.004</td>
<td>0.012</td>
<td>0.000</td>
</tr>
<tr>
<td>3</td>
<td>0.007</td>
<td>0.016</td>
<td>0.001</td>
</tr>
<tr>
<td>5</td>
<td>0.017</td>
<td>0.017</td>
<td>0.003</td>
</tr>
<tr>
<td>22</td>
<td>0.043</td>
<td>0.027</td>
<td>0.027</td>
</tr>
<tr>
<td>28</td>
<td>0.038</td>
<td>0.023</td>
<td>0.027</td>
</tr>
<tr>
<td>45</td>
<td>0.053</td>
<td>0.031</td>
<td>0.033</td>
</tr>
<tr>
<td>53</td>
<td>0.055</td>
<td>0.030</td>
<td>0.034</td>
</tr>
<tr>
<td>118</td>
<td>0.083</td>
<td>0.051</td>
<td>0.048</td>
</tr>
<tr>
<td>170</td>
<td>0.108</td>
<td>0.067</td>
<td>0.069</td>
</tr>
</tbody>
</table>

### Table 7
Effect of Wetting Agent on Absorption

<table>
<thead>
<tr>
<th>Hours</th>
<th>In water</th>
<th>In water + wetting agent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>2.5</td>
<td>0.4</td>
<td>0.7</td>
</tr>
<tr>
<td>19</td>
<td>0.8</td>
<td>2.1</td>
</tr>
<tr>
<td>44</td>
<td>1.7</td>
<td>3.4</td>
</tr>
<tr>
<td>70</td>
<td>1.8</td>
<td>4.0</td>
</tr>
<tr>
<td>140</td>
<td>2.0</td>
<td>5.5</td>
</tr>
<tr>
<td>165</td>
<td>2.4</td>
<td>6.1</td>
</tr>
<tr>
<td>189</td>
<td>2.9</td>
<td>6.5</td>
</tr>
<tr>
<td>242</td>
<td>3.7</td>
<td>7.1</td>
</tr>
<tr>
<td>311</td>
<td>4.8</td>
<td>9.2</td>
</tr>
<tr>
<td>411</td>
<td>5.4</td>
<td>10.2</td>
</tr>
<tr>
<td>472</td>
<td>6.1</td>
<td>11.1</td>
</tr>
<tr>
<td>542</td>
<td>5.4</td>
<td>11.2</td>
</tr>
<tr>
<td>662</td>
<td>5.9</td>
<td>12.1</td>
</tr>
<tr>
<td>740</td>
<td>6.1</td>
<td>11.9</td>
</tr>
</tbody>
</table>
FIG 5

ABSORPTION IN SALT SOLUTIONS

- Volume of water absorbed
- Increase in volume of rubber

VOLUME (mm$^3 \times 10^{-3}$)

HOURS

0%

5%

15%

40 80 120 160
FIG 6
ABSORPTION

% MOISTURE CONTENT

Water + Wetting agent

Water

HOURS

200 400 600
experiment was carried out in constant temperature bath at 40°C for a period of 170 hours.

In the experiment involving wetting agent a similar procedure was carried out except that it was run for a longer period of 740 hours, however, the volume changes in the rubber during the course of the experiment were not followed. The results are given in Tables 6 and 7 and the values plotted in Figures 5 and 6.

2.8 CONCLUSIONS

From this limited work it is possible to arrive at several conclusions as follows:

1. Even though a number of investigations have been done in the drying of natural rubber, they are mostly confined to engineering and designing aspect of dewatering machinery and driers. Little emphasis has been placed towards understanding the mechanism and process involved in the drying of the material, i.e water moisture and the rubber, which is again different from that involved in the non-polymeric materials.

2. Although the experiments in this exercise were carried out from 'trial' coagula, the results are informative as a preliminary investigation. This is discussed below.
3. Syneresis is a natural dewatering process, however, it is not a significant contributor to the drying process as a whole.

4. Coagulum dewatered by centrifugation does not display any improvement on the drying behaviour compared to the compressed coagulum. The conventional method of dewatering by crepeing and hammermilling is, therefore, a suitable dewatering process for natural rubber coagulum prior to drying. Furthermore, the methods of dewatering examined, i.e. pressing and centrifuging, do not influence the subsequent drying behaviour.

5. In the absorption experiments, the increase in volume of rubber samples do not correspond to the volume of water absorbed by them; the volume of the samples increases less than the volume of the water absorbed. It is an indication that the water possibly occupies voids present in the samples. This argument is supported by the evidence of the increase in the absorption when a wetting agent is added to the water to reduce surface tension.
REFERENCES


9. Schoon., Archief voor de Rubbercultuur, Extra No.2


OTHER REFERENCES


PART 2

FURTHER STUDIES OF THE STRESS RELAXATION BEHAVIOUR

OF RUBBER IN COMPRESSION
# CONTENTS

<table>
<thead>
<tr>
<th>CHAPTER 1. HISTORY OF STRESS RELAXATION</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1 INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.2 DEVELOPMENT IN THE STUDY OF STRESS RELAXATION IN COMPRESSION</td>
<td>3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CHAPTER 2. APPRAISAL OF THE CURRENT RELEVANT STANDARDS</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 INTRODUCTION</td>
<td>15</td>
</tr>
<tr>
<td>2.2 ASTM STANDARDS</td>
<td>17</td>
</tr>
<tr>
<td>2.3 BSI STANDARDS</td>
<td>20</td>
</tr>
<tr>
<td>2.4 THE IPT METHOD OF DETERMINING STRESS RELAXATION</td>
<td>23</td>
</tr>
<tr>
<td>2.4.1 Preparation of Test Specimen</td>
<td>24</td>
</tr>
<tr>
<td>2.4.2 Loading of Specimen</td>
<td>24</td>
</tr>
<tr>
<td>2.4.3 The Initial Measurement and the Total Relaxation Behaviour</td>
<td>25</td>
</tr>
<tr>
<td>2.4.4 Step Changes in Temperature</td>
<td>26</td>
</tr>
<tr>
<td>2.4.5 Subsequent Relaxation Measurement</td>
<td>29</td>
</tr>
<tr>
<td>2.5 CONCLUSION</td>
<td>29</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CHAPTER 3. EQUIPMENT AND EXPERIMENTAL PROCEDURES</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1 INTRODUCTION</td>
<td>31</td>
</tr>
<tr>
<td>3.2 EQUIPMENT</td>
<td>32</td>
</tr>
<tr>
<td>3.2.1 The Jigs</td>
<td>34</td>
</tr>
<tr>
<td>3.2.2 The Force Measuring Device</td>
<td>35</td>
</tr>
<tr>
<td>3.3 SPECIMEN PREPARATION AND ASSEMBLY</td>
<td>37</td>
</tr>
<tr>
<td>3.4 EQUIPMENT SETTING UP</td>
<td>41</td>
</tr>
<tr>
<td>3.5 LOADING PROCEDURE</td>
<td>42</td>
</tr>
</tbody>
</table>
3.6 TYPES OF EXPERIMENT

3.6.1 Experiments at Elevated Temperatures
3.6.2 Experiment in Water
3.6.3 Experiments in Nitrogen

3.7 MEASUREMENT AND INTERPRETATION OF RESULTS

3.7.1 Measurements
3.7.2 Long Term Stress Relaxation
3.7.3 Modulus Enhancement Factor (MEF)

3.8 SHORTCOMINGS OF THE EQUIPMENT

CHAPTER 4. THEORETICAL ASPECTS OF STRESS RELAXATION

4.1 STRESS RELAXATION: VISCOELASTIC BEHAVIOUR

4.1.1 INTRODUCTION
4.1.2 THE MAXWELL MODEL FOR STRESS RELAXATION
4.1.3 NON-LINEAR VISCOELASTICITY OF RUBBER
4.1.4 THEORY OF RUBBER ELASTICITY

4.2 STRESS RELAXATION: DEGRADATION

4.2.1 INTRODUCTION
4.2.2 THE TWO-NETWORK THEORY

CHAPTER 5. INFLUENCE OF MECHANICAL VARIABLES
ON STRESS RELAXATION

5.1 INTRODUCTION

5.2 RATE OF LOADING

5.2.1 Experimental
5.2.2 Comparison of Stress Relaxation and MEF at Different Rates of Loading
5.3 MECHANICAL CONDITIONING
  5.3.1 Experimental
  5.3.2 Effect of Mechanical Conditioning on Stress Relaxation and MEF

5.4 STRAIN AMPLIFICATION
  5.4.1 Experimental
  5.4.2 Strain Amplification Effect on Stress Relaxation and MEF of Black and Gum Vulcanisates

CHAPTER 6. INFLUENCE OF OTHER TEST VARIABLES ON STRESS RELAXATION

6.1 INTRODUCTION

6.2 TEMPERATURE
  6.2.1 Experimental
  6.2.2 Stress Relaxation and MEF at Elevated Temperature

6.3 STEP CHANGES IN TEMPERATURE
  6.3.1 Experimental
  6.3.2 Effect of Step Changes in Temperature

6.4 ENVIRONMENTS: AIR, NITROGEN AND WATER
  6.4.1 Experimental
  6.4.2 Effect of Environment

6.5 TEST SPECIMEN: LUBRICATED AND BONDED
  6.5.1 Experimental
  6.5.2 Effect of Slippage on Stress Relaxation
CHAPTER 7. EFFECT OF FORMULATION VARIABLES ON STRESS RELAXATION

7.1 INTRODUCTION 121
7.2 ANTIOXIDANTS 122
  7.2.1 Experimental 122
  7.2.2 Effect of Antioxidants on Stress Relaxation 123
7.3 FILLERS 138
  7.3.1 Experimental 139
  7.3.2 Effect of Fillers on Stress Relaxation 141
7.4 CURING SYSTEM AND RUBBER TYPE 150
  7.4.1 Experimental 151
  7.4.2 Effect of Curing System and Choice of Rubber on Stress Relaxation 152

CHAPTER 8. MODULUS ENHANCEMENT OF RUBBERS IN COMPRESSION

8.1 INTRODUCTION 158
8.2 THE MODULUS ENHANCEMENT FACTOR (MEF) 159
8.3 MEF AND STRESS RELAXATION 162
8.4 MEF AND HYSTERESIS 167
8.5 MEF AND SWELLING MEASUREMENTS 171
8.6 MEF AND AGEING 177
8.7 DISCUSSION AND CONCLUSIONS 179

CHAPTER 9. GENERAL DISCUSSION AND CONCLUSIONS

9.1 GENERAL DISCUSSION 183
9.2 RECOMMENDATIONS FOR FURTHER WORK 191
CHAPTER 1

HISTORY OF STRESS RELAXATION IN COMPRESSION

1.1 INTRODUCTION

Rubbers are widely employed in seals and gaskets, in which applications they are usually subjected to constant compressive strains and are expected to operate satisfactorily over timescales of 50 to 100 years. It is, therefore, not surprising that stress relaxation tests have been standardised, ostensibly to support this market, but sometimes included as a part of a more general investigation of ageing. Research in the Institute of Polymer Technology has been concerned with developing equipment and methods for monitoring stress relaxation in compression, based on a detailed analysis of the loading and subsequent behaviour of a small rubber disc specimen subjected to a compressive strain of 25%.

Measurement of stress relaxation of a polymer is one of the several experiments used in studying viscoelastic properties of the material. Basically, the sample to be tested is deformed to a fixed strain and the stress required to maintain that fixed strain is measured as a function of time at constant temperature. In principle, long term stress relaxation measurement will characterise the viscoelastic behaviour of the polymer and it can be related to other properties such as creep and dynamic properties of the material.
Besides the theoretical interest in these measurements, there are instances where stress relaxation is also of direct practical interest. Studies have been made attempting to relate stress relaxation to other physical phenomena, such as impact behaviour\(^1\). Stress relaxation experiments are also often used in investigating the effect of environment: phenomena such as thermal and oxidative degradation\(^2\) have been studied by stress relaxation techniques.

Stress relaxation tests can be carried out under conditions of tension, compression, flexure, shear or biaxial loading. However, despite the fact that most of the applications of rubber, especially in engineering, involve deformations in compression and shear, and that non-linearity of the elastic properties of rubber does not allow accurate prediction or correlation of the behaviour at low to moderate strain in compression from values obtained at high strains in tension, the majority of stress relaxation work found in the literature has been in tension.

Probably one of the most important factors deterring stress relaxation tests is the lack of a simple, inexpensive machine for maintaining samples under constant strain and for making periodic stress measurements. This problem has been solved by using jigs to maintain the sample at a fixed deformation rather than tying down an instrument with one test. The jig is independent of the stress measurement apparatus such that it can be removed and
stored in the desired environmental condition. In this way, periodic measurements can be made over several years.

1.2 DEVELOPMENT IN THE STUDY OF STRESS RELAXATION IN COMPRESSION

As far as history is concerned it is not definitely known when and by whom the stress relaxation test in compression was first performed. The purpose of this section is to give an indication of what has been done and found in developing the knowledge of stress relaxation of rubber in compression. Most of the publications are only briefly described here; however, they will be described in more detail in later sections.

For this section the work of Kimmich³ in 1940 is chosen as the beginning of major contributions in this field. Using a Shore durometer scale of hardness he studied the load-deflection characteristics of rubber samples with different surface conditions and specimen shape-factors under different speeds of load application. He did not progress to study the stress relaxation behaviour of his samples.

Blow and Fletcher⁴ in 1944 possibly developed one of the earliest equipments to study stress relaxation as a function of time. They devised an apparatus of very simple construction to observe the decay of stress in rubber sample compressed to a constant strain to study the behaviour and properties of oil seals.
MacDonald and Ushakoff\textsuperscript{5} in 1948 introduced the use of measuring jig in which the sample can be maintained at essentially constant strain in order to solve the problem of carrying out tests in compression over long periods of time. They carried out tests over 1800 hours and plotted the curve of stress ratios against log time. In the same year Phillips and Labbe\textsuperscript{6} developed an instrument which could determine the rate of relaxation of rubbers under compression or shear as well as their recovery after partial or complete release of the load at temperatures from -70 to 158°C. The rubber specimen was compressed by a hand crank whilst its stress was measured by a load cell and recorded on a Foxboro Dynalog.

In a study of the effect of accelerators on the properties of nitrile rubber vulcanisates, Morris et al\textsuperscript{7} in 1949 devised an instrument which they called a compressometer to evaluate stress relaxation of the vulcanisates. The instrument contained an air-operated piston which compressed the specimen to the required deformation and its strain was maintained in the apparatus by means of a knurled nut. The stress exerted by the compressed specimen was determined by the application of air pressure until the piston showed a downward movement. Each specimen to be tested required one compressometer, and for the tests carried out for 14 days at 194°F, the whole instrument containing the specimen had to be placed in the oven.
Beatty and Juve\textsuperscript{8} set up an experiment to obtain information on factors which can influence the stress relaxation behaviour of rubber vulcanisates. These included the effect of sample shape and size, slippage, degree of deformation, temperature and types of polymer. An apparatus was designed and built similar to that of Blow and Fletcher mentioned earlier with modification to facilitate the use of jigs in order to increase the number of tests which could be run simultaneously. Later, they extended the work to investigate the stress relaxation of different types of polymer immersed in different types of oil at various temperatures\textsuperscript{9}.

In 1951 Farnam\textsuperscript{10} studied the relaxation characteristics of rubber-bonded asbestos material used in gaskets. Using a relaxometer of his own design he was able to measure the extent of relaxation of the material under conditions of heating and cooling cycles for different temperatures and cycles. The effect of reapplication of the original load on the specimen after prescribed periods during which relaxation was allowed to occur was examined, also on the effects of flange pressure and humidity.

In 1952 Schay and Szor\textsuperscript{11} carried out an experiment to test the validity of an equation relating the stress-strain behaviour of rubber blocks, cylindrical and quadratic prisms, under compression. The stress-strain curves of the rubber samples were determined using Hoppler's consistometer at room temperature. In
the same year Gehman\textsuperscript{12} of Wingfoot Corporation in America invented and patented an apparatus for measuring stress relaxation of elastomeric materials under compression. The instrument used a hydraulic system consisting of a pneumatic chamber and valves to load a sample to predetermined deformation and to maintain the strain. The stress decay was measured by a pressure-indicating device on the pneumatic chamber.

In 1955 Foster\textsuperscript{13} devised a way of eliminating friction at the faces of a sample under compression test by a method of lubrication. It was achieved by forcing a liquid between the sample faces and the compression plates at any strain. The sample was compressed in steps of 2 to 3\% up to about 32\% and the lubricant was 'applied' at each step by means of a valve control. The stress-strain curves were obtained after considering lateral expansion of the sample and showed very good agreement with the theoretical curve. He thus considered the lubricating method a success and the deviation of experimental curves from the theoretical curve obtained by previous workers as a result of poor lubrication of their samples or failure to eliminate sample surface friction.

In the ASTM Bulletin of 1955\textsuperscript{14} a number of articles on stress relaxation were published. Eller in his paper 'Stress relaxation of vulcanised rubber in compression and tension' described tests carried out to determine the relationship between stress relaxation after a fixed ageing period in compression and
in tension with respect to different amounts of deformation. He also determined the behaviour of the stress relaxation as a function of time at room and elevated temperatures. The experiment was done with apparatus similar to that described in Method B of ASTM Methods D395-53T. Lem and Reynar in their paper 'Stress relaxation of non-metallic gasket materials' described their finding in the stress relaxation after a fixed ageing period of 6 hours for various types of non-metallic gasket materials using the Farnam-Cole relaxometer, despite the conclusion that the instrument did not seem to be very reliable. In another article of a joint discussion of papers by the above three authors a suggestion of using removable jigs based on the Hopkins-Farnam jig for stress relaxation and other similar work was put forward. In 1956, Thorn proceeded with yet another simplified and inexpensive jig which was referred to as 'center-locked' jig.

In 1956, Eller by using similar material, made a comparison between stress relaxation property and the sealing qualities of the material. For stress relaxation he used the apparatus described in ASTM D395-53T while for sealability a seal ageing apparatus was developed from which the sealing pressure was determined against 'indentation'. It was found that the stress relaxation has a good correlation with sealability; thus he considered it a suitable method for determining the sealability of a gasket material. Payne using pure gum natural rubber vulcanisate studied the effect of specimen shape and size
on the static and dynamic stress-strain relationship of bonded rubber in compression. A similar study on bonded rubber was carried out by Gent and Lindley\textsuperscript{18} which included vulcanisates containing various quantities of carbon black.

Khruslov and Bartenev\textsuperscript{19} from their experiment in 1961 claimed that preliminary heat treatment of rubber gaskets at 150°C in swelling fluids can reduce the rate of stress relaxation thus preserving the contact pressure of the gasket; Gorelik and Bukhina\textsuperscript{20} on studying the effect of degree of compression found that the contact pressure and the permanent set do not depend on the degree of compression in the range between 15 and 70% at room temperature, at elevated temperatures up to 90°C and at reduced temperatures down to -55°C.

In 1962 Lyubchanskaya et al\textsuperscript{21} studied some features of stress relaxation of rubber in compression, including the degree of compression, types of vulcanising system, environment, fillers and antioxidants. The study was done on an axial compression relaxometer.

At about the same time, several instruments for measuring stress relaxation in compression were developed in the USSR. In 1963 Popov and Shlyapina\textsuperscript{22} devised one such apparatus. They used different types of vulcanisates and studied the effect of shape factor and deformation on stress relaxation. Another instrument called 'Relaks' was developed by Zakharenko et al\textsuperscript{23} intended for
assessing the quality of mixes and rubbers by determining the stress relaxation of the material in compression. The device was improved and modernised in 1971 by Fedyukin et al\textsuperscript{24}. Using an apparatus called the Polanyi dynamometer, Babitskii\textsuperscript{25} in 1967 designed a compression attachment which enabled him to determine the compression modulus of rubber vulcanisates.

Wolstenholme\textsuperscript{26} in 1967 used high-speed testing to simulate dynamic compression of press-rolls on paper-making machines and measured the compression modulus at various loading rates and temperatures. He observed at a particular loading rate that the compression modulus decreased with increasing temperature but above a certain temperature, some compounds showed inversion in modulus, which increased with temperature. He also found that the modulus-temperature curves shifted upwards with increasing loading rates.

In 1974 Schaetz et al\textsuperscript{27} designed an instrument for measuring stress relaxation of rubber samples in compression up to a temperature of 250°C. The instrument consisted of a weighing beam with automatically adjusted balance weights as the compressive force changed. At about the same time Stenberg and Jansson\textsuperscript{28} devised another instrument which they called a "compression relaxometer" for a similar purpose. The instrument which used a removable rod to compress the rubber sample and a displacement transducer to measure the force, enabled experiments to be carried out at elevated temperatures and measurements to be
continued for more than 1000 hours.

In 1975, Aston of Lucas Aerospace Ltd. investigated the stress relaxation behaviour of rubber seals for aircraft fuel systems which require a service temperature range of -54 to 150°C with occasional peak to 182°C. Using fluorocarbon and fluorosilicone 0-rings for his tests in air and kerosene (aircraft fuel), he suggested that stress relaxation tests in compression were more indicative of the performance of rubber seals than the low-temperature compression set and flexibility measurements.

A testing device complete with test chamber designed to measure changes in sealing force and long term compression stress relaxation performance of rubber under simulated conditions of temperature and environment was introduced by Testing Machine Inc. in 1978. The apparatus used compression jigs which were separate from the load measuring instrument. It used electrical contact in measuring the force and enabled continuous or intermittent stress relaxation measurement to be made.

In 1977 Stenberg and Jansson made use of the instrument they developed earlier to investigate stress relaxation of rubbers in compression. In one investigation they made an attempt to distinguish between the physical and the chemical processes in the stress relaxation of nitrile rubber. The physical relaxation behaviour was determined from dynamic data on the
rubber, and by comparing them with the stress relaxation under static compression it was shown that physical mechanisms of stress relaxation dominate around room temperature whilst at higher temperature the relaxation is dominated by chemical mechanisms. In another investigation they studied the isochronous stress-strain relation in compression of rubbers at room temperature based on stress relaxation measurement using lubricated and bonded specimens. The behaviour observed in the samples, and the differences between them were then explained in terms of the linearity of deformation processes and the strain amplification theory.

In 1980 Porter and Meinecke determined the response of rubber in shear with a superimposed compression using a Tinius-Olsen static stress-strain tester at a compressive strain between 15 to 36%. After considering the reduction in specimen thickness due to compression, a larger surface area due to bulging and the force stored in the rubber, it was concluded that shear stress-strain of rubber is the same irrespective whether it was compressed or uncompressed.

Muniandy and Mook Sang in 1979 investigated some of the factors that affect compression set of natural rubber vulcanisates at constant strain and explained the results observed. The investigation included the effect of test duration, state of cure, degree of compression, and shape and size of the test pieces.
In 1980 Lowman\textsuperscript{35} undertook an investigation to determine whether oxygen under pressure would diffuse into compressed rubber and affect its dimensions. The test was performed in a Scott Tester LGP Aluminium Block Pressure Ageing Oven under oxygen and nitrogen at 300 psi and 70°C, and measurements were taken up to 168 hours. He chose to use natural rubber, SBR and Butyl rubber and concluded that oxygen is a factor in compression set especially with the two former rubbers.

In a similar area, Stenberg and his colleagues\textsuperscript{36,37,38} carried out a series of experiments to determine the role of oxygen and antioxidants in the degradation process associated with compression stress relaxation. It was concluded that the relaxation was not caused by the oxygen in the atmosphere, which was only responsible in the formation of oxidised skin, but rather by the oxygen incorporated in the rubber and that the antioxidant was effective only in preventing the rapid stress decay in the initial stage whilst at later stages it is either ineffective or has been lost.

In 1981, Mathew et al\textsuperscript{39} investigated the changes occurring in natural rubber vulcanisates under compression in order to determine whether the network changes were either due to compression or ageing. From the result it was concluded that the network changes were due to ageing accelerated by the compressive strain.
In a short communication Yeoh\textsuperscript{40} in 1984 described a method for determining the compression modulus of rubber vulcanisates. The apparatus introduced a pneumatic cylinder to compress the test piece and a load cell to measure the force, whence the modulus is calculated. It can also be operated as a stress relaxometer and is said to be readily automated.

At the Institute of Polymer Technology, Fernando\textsuperscript{41,42} introduced a new concept for stress relaxation measurements of rubber in compression and on this basis designed a compressive stress relaxation instrument. A commercial version of this instrument called the 'Wykeham-Farrance' machine is being used by the writer for the experimental work of this thesis.

Meier et al\textsuperscript{43} in 1983 applied the method of reduced variables to predict long-term stress relaxation in compression of natural and nitrile rubbers using short-term relaxation data from tests carried out between room temperature and 100°C for a duration between 4 to 64 weeks. The predicted results were found to be in good agreement with the actual stress relaxation at 20°C over a period of 16 years: but a word of caution was given for longer periods of 20 to 50 years!

In a recent paper, Ellul and Southern\textsuperscript{44} determined the correlation between stress relaxation and compression set using cylindrical and O-ring test pieces. The investigation included effect of initial strain, compound formulations and temperature.
It was concluded that the compression set gave a reasonable correlation with stress relaxation but only so for the purpose of ranking and in quality control.

These are some of the papers published on stress relaxation of rubber in compression or related to it from around 1940 to the present time, that is for a period of 45 years. However, the list is by no means exhaustive, nevertheless, one can roughly appreciate what has been covered in this field compared to the vast amount of work in tension, whereas in service especially in engineering, compression is more\ common and relevant than tension. There is, therefore, a large potential and scope to widen and deepen the knowledge in the behaviour of rubber under compression given an economic, reliable instrument and other necessary facilities.
CHAPTER 2

APPRAISAL OF THE CURRENT RELEVANT STANDARDS

2.1 INTRODUCTION

The objective of a standard test is the attainment of unique, reproducible test results when the procedural details are strictly followed, independent of the skill of the operator. The current British and American Standards for stress relaxation measurements in compression for rubbers are discussed and assessed in the light of results which have been obtained with the new equipment, which has been developed in the Institute of Polymer Technology; hereafter termed the 'IPT method'. The work covers the development of equipment of satisfactory performance, which is suitable for commercial exploitation, and the investigation of meaningful tests for industrial use.

Specifications BS 903-A42 (1983)\textsuperscript{45} and ASTM-D 1390 (1976)\textsuperscript{46} are typical standard tests for stress relaxation in the compression mode; the former is a refinement of the International Standard ISO 3384-1979. Using a compression 'jig', a cylindrical rubber button is compressed to a specified strain, 25\% in the British Standard, which is held constant during the test. This is carried out at a standard temperature, not necessarily high, and the stress is sampled shortly after loading, and thereafter at suitable time intervals. The British Standard covers two methods A and B; in the former, both the loading and the stress
measurement are carried out at the test temperature, whilst in the latter, loading and stress measurement are at room temperature, and the specimen is subjected to intermittent treatment at high temperatures. The American method follows the second procedure, but the heat treatment is specified, 46 hours at 100°C.

There is significant—informative comment in the introduction to the British Standard: "The processes responsible for stress relaxation may be either physical or chemical in nature, and under all normal conditions both processes will occur simultaneously. However, at normal or low temperatures and/or short times, stress relaxation is dominated by physical processes, whilst at high temperatures and/or long times, chemical processes are dominant. Hence it is neither safe to extrapolate time/stress relaxation curves in order to predict stress relaxation after periods considerably longer than those covered by the test, nor to use tests at higher temperatures as accelerated tests to give information on stress relaxation at lower temperatures".

The same standard continues: "In addition to the need to specify the temperature and time intervals in a stress relaxation test, it is also necessary to specify the initial stress and the previous mechanical history of the test piece since these may also influence the measured stress relaxation, particularly in rubbers containing fillers". The importance of these remarks will
be discussed later in this Chapter as well as in Chapters 5, 6, 7 and 8.

The limitations of current standards for the measurement of stress relaxation in the compression mode include:

1. few recommendations on the apparatus performance required to ensure reproducible results;
2. lack of precision in defining the size and geometry of the specimen;
3. little agreement on what constitutes the 'initial measurement';
4. poor definition and high level of the loading rate;
5. allowance of, or requirement for, step changes in temperature; and
6. inclusion of mechanical conditioning prior to test in the British Standard.

In the following sections a survey is made on the two main standards, ASTM and BSI; they are then compared with the procedures and results of the IPT method, and comment made on them.

2.2 ASTM STANDARDS

Standard procedures related to the stress relaxation behaviour of polymers have been covered in the following ASTM standards:
i. ASTM D1390-76 Rubber Property - Stress Relaxation in Compression

ii. ASTM F38-80 Standard Test Methods for Creep Relaxation of a Gasket Material

iii. ASTM D2991-71 Standard Recommended Practice for Testing Stress Relaxation of Plastics.

ASTM D2991-71 recommends a practice which covers the determination of the stress relaxation of plastics resisting long-duration constant strains at conditions of constant temperature and relative humidity and negligible vibration.

Methods in ASTM F38-80 provide a means of measuring the amount of creep relaxation of a gasket material at a stated time after a compressive 'initial stress' has been applied. The test specimen is subjected to a stress between two platens, with the stress being applied by a bolt and nut. The stress is applied at a uniform rate such that at the end of 10 ± 2 seconds the specified stress is reached which is considered as the initial stress. In experiments at elevated temperatures the specimen unit is first removed from the oven and cooled to room temperature before any measurement is taken.

ASTM D1390-76 is concerned with the stress relaxation of rubber in compression involving static loading or constant deformation. The stress relaxation is considered as the decrease in the back or residual stress exerted by a specimen which has
been compressed to a constant deformation under specified conditions of time and temperature. This standard recommends a compression testing machine having a speed of approximately 1.0 mm/min with a hand-operated screw to apply the load. The test specimen is compressed between steel plates of sufficient thickness to withstand the compressive stresses without bending, and the surfaces in contact with the specimen are of highly polished chromium-plated finish.

The recommended dimension of the test specimen is 28.68 ± 0.13 mm diameter and 12.5 ± 0.5 mm thickness. The compression on the specimen is limited by metal space bars and the percentage strain can be altered using an adjustable base plug. A deformation of 25% compression is recommended. The load-applicator which actually compresses the specimen slides with minimum friction in vertical ball bushings. The back stress is then measured by means of an electrical system.

The stress relaxation time is counted at the completion of loading the specimen which is then maintained at constant strain by bolting the device. The initial back stress is then determined after 3 minutes ± 10 sec.

For high temperature tests the stress relaxation device is placed in the ageing oven after 60 ± 5 minutes at room temperature after loading. After a specified ageing period, 46 hours at 100 ± 1°C is recommended, the apparatus is allowed to
cool to room temperature for 5 ± 0.5 hours before the back stress of the aged specimen is again determined.

The stress relaxation in the specimen is then calculated as follows:

\[
\text{stress relaxation, percent} = \frac{S_I - S_F}{S_I} \times 100
\]

where, \( S_I \) = initial back stress in appropriate units in the specimen 3 minutes after being compressed, and \( S_F \) = final or back stress in the aged specimen.

2.3 BSI STANDARDS

BSI has also published procedures related to the determination of stress relaxation behaviour of rubber. The standards referred to in this work are Parts from BS 903 - Methods of Testing Vulcanised Rubber as follows:

i. Part A34. Determination of Stress Relaxation of Rubber Rings in Compression

ii. Part A42. Determination of Stress Relaxation.

For both standards a similar specification for compression and force measuring devices is suggested except for Part A34 the plates between which the test piece is to be compressed require two holes about 2 mm diameter on each side of the plate centre to allow free circulation of fluid or air within the volume enclosed by the test piece.
The compression device consists of two parallel flat plates of highly polished chromium-plated steel or stainless steel, sufficiently rigid to withstand the stress without bending, between the faces of which the test piece is compressed. Further, this device should be capable of loading the test piece to the specified compression within 30 seconds and of maintaining the compression for the duration of the test.

Two types of test piece for Part A34 are allowed, either an annular ring of \(2.0 \pm 0.2\) mm square section and \(15.0 \pm 0.5\) mm internal diameter prepared by moulding or by cutting from a sheet or a toroidal ring with the preferred size of \(2.4 \pm 0.08\) mm cross-section and internal diameter \(14.6 \pm 0.2\) mm.

For Part A42 the suggested test piece is a cylindrical disc also prepared either by moulding or by cutting from a flat sheet. Two different test piece dimensions are allowed; either \(13.0 \pm 0.5\) mm diameter and \(6.3 \pm 0.3\) mm thickness or \(29.0 \pm 0.5\) mm diameter and \(12.5 \pm 0.5\) mm thickness.

3 methods of determining stress relaxation of rubber rings are described for Part A34. Briefly, they are:

**Method A**

The test piece and the compression device are brought to the test temperature for about 10 minutes before applying the compression at an even rate to reach the specified strain. All readings are taken at the test temperature.
Method B

The test piece is compressed at 23 ± 2°C. It is brought to the test temperature either in the oven or liquid bath only after the first measurement has been taken 30 ± 1 minutes after the loading. All subsequent measurements are taken after the apparatus has been cooled to 23 ± 2°C for 2 hours, after which it is returned to the test environment.

Method C

The loading compression is applied at 23 ± 2°C before the apparatus is brought to the environmental condition. The first measurement is taken 30 ± 1 minutes after placing the apparatus in the oven or liquid bath and subsequent measurements are made at the test temperature.

Unlike Part A34, Part A42 recommends mechanical preconditioning of the test piece by compressing it to about 25% and then returning it to zero deflection, repeating the operation to give a total of five deformations. The test piece is then allowed to stand between 16 to 48 hours at 23 ± 2°C before carrying out the test. It is claimed that the conditioning improves the reproducibility of results obtained.

Two methods are described in Part A42 for determining stress relaxation in rubber using cylindrical disc test piece which has been mechanically pre-conditioned:
Method A

In this first method the test piece and compression device are preheated to the test temperature before the compression is applied. All the measurements are then taken at the test temperature.

Method B

There is no preheating in this method. The test piece is compressed at 23 ± 2°C and is then stored at the test temperature only after the first reading has been taken at 23 ± 2°C, 30 ±2, -0 minutes after loading. Subsequent measurements are taken after the apparatus is cooled to 23 ± 2°C for 2 hours, after which it is again returned to the test temperature.

2.4 THE IPT METHOD OF DETERMINING STRESS RELAXATION

The IPT method of determining stress relaxation is discussed in the next chapter; the present section only compares the IPT method and the current available standards and briefly reports on the work carried out in examining the test parameters which are required by the standards, in particular, to question the specified values of some of them. This includes factors such as loading rate, mechanical conditioning and temperature of measurement in determining the pattern of stress relaxation and the need for establishing a closer definition of initial stress.
2.4.1 Preparation of Test Specimen

To ensure high structural and geometrical uniformity, the IPT method uses only transfer moulded test specimens, with a diameter of 12.7 ± 0.2 mm and a thickness of 6.2 ± 0.2 mm. They are not subjected to mechanical conditioning prior to loading (as is recommended by the British Standard).

The specimen is compressed between ground glass plates. The surfaces of the test piece and the glass plates which are in contact are lubricated using a dry lubricant, molybdenum disulphide, instead of a silicone or a fluorosilicone fluid as in the BSI procedure. The lubricated specimen sandwiched between the two glass plates is then placed in a compression jig.

The loading is done on a compression-force measuring instrument, the Wykeham-Farrance machine, and the strain is maintained by bolting the jig. Subsequent measurements are again made on the compression machine. Since the jig is independent of the machine except for the force measurement, the machine is thus not tied down with a particular test or experiment and the test jig can be subjected to any environmental condition; air, gas or liquid at different temperatures.

2.4.2 Loading of Specimen

With the finding that the rate of compression affects the consequent stress relaxation behaviour of the test specimen, for the IPT method a manageable compression speed of 0.3 mm/minute
has been fixed, which is also set for the subsequent measurements during stress decay. A higher rate of stress relaxation was found to cause a cross-over effect for the filled rubber (Chap. 5). Neither the ASTM nor the BSI procedures standardise any particular speed at which the compression and subsequent measurement should be set. The ASTM suggests a compression speed of approximately 1.0 mm/minute whilst the BSI requires the compression to be completed within 30 seconds.

In the ASTM method, the force in a test piece is measured by the load applicator which slides in vertical ball bushings thus involving additional frictional force, however minimal, to the back stress in the test piece. With the IPT method, no friction is at all involved since the only contact the load applicator experiences is with the glass plate holding the test piece, such that the force registered is the actual force of the test piece.

2.4.3 The initial measurement and the total relaxation behaviour

The IPT method considers the force in a test specimen when the compression to the specified strain is completed as the initial stress of the specimen. This is achieved as a result of the critical parallelism requirements of the IPT method. On the other hand, BSI suggests the first measurement to be made 30 +2, -0 minutes after the compression to allow physical relaxation; while for the ASTM the initial stress is determined after 3 minutes ± 10 seconds. At high temperatures, and especially for filled rubbers, the initial stress relaxation is rapid, and many
phenomena take place during a short period after loading. Therefore, ideally the initial measurement should be taken as the specimen attains the strain set by the jig which is achieved by the IPT method as mentioned earlier. Valuable information is available in this region of initial stress relaxation especially the occurrence of modulus enhancement, and also the so-called physical relaxation for different type of test specimens, i.e. gum-stock, black-filled and plastic reinforced rubbers. It is wasteful if this information is lost or undetected, simply because of the deficiencies in the equipment or methodology.

Utilising the parallelism and accuracy of various surfaces, the specimen is compressed between the glass plates by the thrust plate of the jig, and the force vs. displacement curve recorded. The curve so generated, \( \ldots \), is shown schematically in Fig. 2.1; this relationship, followed by the relaxation measurements is termed the total relaxation behaviour, as shown in Fig. 2.2. The initial measurement is the force corresponding to point A in Fig. 2.1.

### 2.4.4 Step Changes in Temperature

The American Standard and Method B of the British Standard require that the loading and all measurements of residual force be made at room temperature, whilst the specimen treatment is carried out at elevated temperature. Thus the specimen is subjected to step changes in temperature, which has a deleterious effect on the stress relaxation behaviour (Chap. 6).
FIG 21 INVERSE IDEAL CURVE PRODUCED BY LOADING

FORCE (DISPLACEMENT)

TIME (DISPLACEMENT)

Compression of the specimen

Initial Force Displacement

Initial Modulus

High stiffness metal-to-metal contact
FIG 2.2 TOTAL RELAXATION BEHAVIOUR

LOADING

23°C

100°C

RELAXATION

23°C

100°C

FORCE (N)

200

150

100

50

0

% STRAIN

0 1 2 4 25

HOURS

1 10 100 1000
2.4.5 Subsequent Relaxation Measurement

Results using the ASTM standard, only indicates stress relaxation as a percentage drop of the back stress of a specimen under compression after it has been aged for a specified time and temperature. It provides no information on the relaxation behaviour of the specimen which is undergoing the ageing process. Hence the ASTM method is probably sufficient as a comparative test method on the quality of the specimens from different compounds, e.g. in quality control work, depending on its reproducibility. However, for work involving deeper understanding of the mechanism of stress relaxation in compression, a more comprehensive test is necessary.

The IPT method has not only enabled measurement of reproducible and accurate result to be made but has also uncovered new information concerning stress relaxation behaviour.

2.5 CONCLUSIONS

The conclusions reached concerning the requirements of the relevant British and American Standards are as below:

1. The test procedures which involve loading and measurement at room temperature, with intervening exposure to high temperatures, results in inferior performance apparently due to the imposition of step changes in temperature.
2. The loading rates specified in both standards are high and may lead to irreproducibility of stress relaxation,
especially if different rates are employed. It is essential that the loading process be strictly controlled.

3. There has to be a better definition and agreement on 'initial stress'.

4. Neither standard deals satisfactorily with the reliability of the results. The adoption of a requirement for an ideal curve would reduce the need for multiple measurements.

5. Observations on mechanical conditioning prior to stress relaxation tests show that it only has a marginal effect.
3.1 INTRODUCTION

When rubber is deformed, stress is developed in it. If the deformation is a constant strain, say under compression, the stress, which is the restoring force in the rubber required to maintain the strain, gradually decreases with time. This phenomenon is called 'stress relaxation'. Following the British Standard BS 903-A42 (1983) these terms are defined:

- **stress**: the time-dependent force necessary to maintain a constant compressive strain, divided by the original cross-sectional area over which the force is applied;
- **stress relaxation**: the decrease in stress which has occurred after a specified time interval, during the application of a constant deformation, expressed as a percentage of the stress at the commencement of that time interval.

In this research programme the underlying principle in the calculation of stress relaxation involves the measurement of the restoring force exerted by a specimen when it is being subjected to a small displacement while under deformation, at intervals of time during the process of stress decay.
3.2 EQUIPMENT

The apparatus for stress relaxation measurements in compression consists of 'jigs', to hold the specimens, and the 'force measuring device', to monitor the force exerted by the specimen. In practice, one force measuring device can be used with a large number of jigs, therefore, jigs should be inexpensive, as well as being capable of making accurate measurements, thereby reducing the need for replicate measurements (e.g. 3 specimens, recommended in BS 903-A42). Jigs hold the rubber specimens at the required 'strain' levels, and can be fed with inert or active environments and stored at different temperatures. Thus the jigs must be corrosion-resistant, with the main objective, however, to ensure accurate and reproducible measurements of the stress relaxation behaviour.

The concept of 'ideal curve' has been adopted not only to ensure an accurate measurement, but also enables one to assess the reliability. Further, the amount of information obtained in a single measurement is increased.

Discussion of the ideal curve concept and the practical considerations are reported in the literature\(^\text{41,42}\). In summary, the ideal curve, which is the force/displacement characteristic of the jig/force measuring frame, Fig 3.1, reflects the way the apparatus should behave to ensure an accurate measurement. Therefore, the criterion for standardisation should be, not necessarily the form of the jigs or the force measuring frame,
FIG 3.1

INSTANTANEOUS MODULUS MEASUREMENT

0.07 mm incremental strain

FORCE

TIME (DISPLACEMENT)
but the ideal curve concept. In other words, any set of apparatus (jigs and force measuring device) which gives the ideal curve ensures reliability of the measurement. The various defects found in much of the equipment currently available, which lead to erroneous results, and the design features of the Loughborough (Polymer Institute) equipment have been discussed elsewhere\textsuperscript{41,42}.

3.2.1 The Jigs

The jigs are made up of:
- jig housing,
- thrust plate,
- 3 bolts, and
- 2 glass plates.

To withstand corrosion the metal components of the jig are made of stainless steel, BS 970-321 S12, and to meet the critical criterion of parallelism the horizontal faces of the jig housing and thrust plate are ground\textsuperscript{d} to a smooth finish. Fig 3.2.

![FIG 3.2](image-url)
3.2.2 The Force Measuring Device

The commercial version of this equipment, manufactured by Wykeham-Farrance (Engineering) Ltd., Slough, is capable of making stress relaxation measurements of the quality discussed in this chapter. Fig 3.3 shows the apparatus in schematic form. The main features of the force measuring device is given in detail by Fernando. Essentially, the equipment consists of:

1. A Wykeham-Farrance compression machine, consisting of:
   a. a smooth constant-speed drive system with a range of speeds. A speed of 0.3 mm/min is mainly used in this programme, especially when measuring the stress relaxation force,
   b. a load cell having a relative stiffness of approximately 10 times that of the specimen with a plunger/heat shield attached to it,
   c. a rigid frame which holds the load cell from a crosshead and houses the drive system, with facilities for parallelism adjustment and load cell calibration.

2. A power supply and an amplifier for the load cell. The power supply is capable of maintaining a constant D.C. voltage to the amplifier and thus to the load cell. At the power supply of 24.0 volts the amplifier is supplying 10.0 volts to the strain gauge transducer of the load cell. The signal from the load cell ranging from 0 to 10.00mV is then amplified and received by the chart recorder.
FIG 3.3

- SPRING
- CROSS HEAD
- ADJUSTING PLATES
- LOAD CELL
- JIG
- PLATFORM
- GEAR BOX
- MOTOR DRIVE
- COARSE WHEEL
- FINE WHEEL
- MAINS
- LOAD CELL POWER SUPPLY AMPLIFIER
- CHART RECORDER
3. A strip chart recorder; which is used instead of a more expensive X-Y plotter since the Wykeham-Farrance machine operates at a constant speed drive system such that the displacement of the sample is proportional to the time and the running of the chart.

3.3 SPECIMEN PREPARATION AND ASSEMBLY

Except for commercial specimens, all the specimens used throughout this programme are compounded from very simple formulations with the following basic ingredients:

- rubber
- activator
- accelerator
- filler
- antioxidant
- curing agent

For the natural rubber compounds the mixing was done on a water-cooled two-roll mill whilst for the polyolefine-filled EPDM compounds the blending and mixing were achieved at a higher temperature (up to 160°C), on a steam-heated two-roll mill. The cure times and temperatures were determined by the Monsanto Oscillating Disc Curometer. Detailed formulations, and the cure times and temperatures of the various compounds are given in Appendix 1.
Small rubber disc specimens, 12.7 mm in diameter and 6.25 mm high were produced by transfer moulding. Bonded specimens were produced by using a specially designed transfer mould with facilities for specimen-to-metal bonding. Transfer-moulded specimens are preferred over specimens cut out from rubber sheets since the former is known to produce higher structural and geometrical uniformity.

To improve the reproducibility of the measurements, the variability contributed by the specimen should be eliminated, or minimised. Variability can be associated with the specimen in either the unstrained or strained states. In the unstrained state, principally, the variability is due to geometrical defects of the moulding or cutting technique adopted to prepare the specimen. In some cases structural defects are involved at both the molecular scale (unsatisfactory state of cure), and at the macro scale (voids and variable packing). These contribute to poor reproducibility. Transfer moulding is strongly recommended to reduce the incidence of these defects.

Variability associated with the specimen in the strained state is mainly a consequence of variable slipping at the contact surfaces. One way of eliminating this is to use bonded specimens which, however, complicates the moulding technique. The experience is that dry lubrication of the specimen by graphite powder or molybdenum disulphide, and the use of ground glass plates as the holding or compression plates, reduce this type of
variability. Work with a large number of specimens has proved that this lubrication method is convenient and gives reproducible results. In accordance with most test standards, the specimen is ready for test after resting overnight following vulcanisation.

Although transfer moulded specimens have high structural and geometrical uniformity, this is confined to those of the same formulation. Due to different mould shrinkages, a gum specimen has a mean thickness of 6.10 mm while a black-filled specimen containing 50 phr HAF has a mean thickness of 6.20 mm.

The jigs and glass plates available are of within a fixed range of depths and thicknesses. The jig depths are between 10.720 to 10.740 mm, while the glass plates have thicknesses from 3.00 to 3.06 mm. To apply a strain of 25 ± 1% to a rubber specimen a jig of a specific depth is selected; a thinner specimen will require a shallower jig. The glass plates needed are then calculated using a simple formula:

\[
\text{thickness of paired glass plate} = J - 0.75S
\]

where, \( J \) is the depth of the jig and \( S \) is the thickness of the specimen.

**E.g:** For a gum specimen of thickness \( S = 6.16 \text{ mm} \), a shallow jig of depth \( J = 10.720 \text{ mm} \) is selected. The total thickness of the glass plates needed to strain the specimen to 25% then is

\[
10.720 - (0.75 \times 6.16) = 6.1 \text{ mm}.
\]
So either a pair of glass plates each 3.05 mm thick or two of them of 3.04 and 3.06 mm can be used. A check on the applied strain can be carried out during the loading and will be discussed in the section concerning loading procedure.

Except for the experiment to investigate the effect of bonded specimen on stress relaxation behaviour, all other experiments throughout this programme have been carried out with dry-lubricated specimens. The lubricant used is molybdenum disulphide and is applied both to the specimen and to the surfaces of the glass plates which are in contact with it.

Having selected the jig, the lubricated specimen is sandwiched between the glass plates by first placing one glass plate in the jig cavity, followed by the specimen, making sure at this point that both are positioned centrally in the cavity. This can be checked by placing the thrust plate in position and viewing from the top. The second glass plate is then carefully placed on top of the specimen without displacing it. The thrust plate is then bolted loosely into place without compressing the specimen.

Centrally positioning the specimen and the glass plates in the jig cavity is an important procedural precaution to avoid breakage of the glass plates and tilting of the specimen, which will affect the test results.
The specimen is then ready for loading. Using the Wykeham-Farrance machine, the loading procedure described in detail by Fernando\textsuperscript{41,42} is closely followed with further refinement and modification whenever needed.

### 3.4 EQUIPMENT SETTING UP

There are 3 procedures to be carried out on the setting up of the equipment before the loading and subsequent stress relaxation measurements can be made:

1. **Electrical connections**

   Each of the 3 components of the equipment, namely, the Wykeham-Farrance machine, the load-cell power supply/amplifier, and the chart recorder are separately connected to the power mains. The load cell is directly connected to the power supply/amplifier unit and its output fed to the chart recorder.

2. **Parallelism Adjustment**

   This is a very important procedure in order to obtain the critical condition of perfect parallelism between the load-cell plunger and the surface of the top glass plate in the jig; without which the 'ideal curve' cannot be obtained.

   The requirement to achieve parallelism goes back to the design and production of the plunger/heat shield and the jig themselves which has been discussed in detail by Fernando\textsuperscript{42}. Assuming this requirement has been met, the plunger/heat shield
is attached to the load cell which is fixed to the crosshead of the Wykeham-Farrance main frame. The adjustment is then carried out as described\textsuperscript{42}, see Fig 3.4; and once this is done the load cell can be calibrated.

3. Load Cell Calibration

In order to read out the restoring force of the specimen in conventional units, e.g. Newtons, from the chart recorder, the load cell has first to be calibrated against dead weights using a pivot block at set amplifications, Fig 3.5\textsuperscript{42}. The calibration graphs at different amplifications can then be plotted out. However, from experience it is found better to maintain the equipment at a single amplification for a particular experiment, unless it becomes necessary to change it.

3.5 Loading Procedure

After carrying out the above procedure on the equipment, the jig containing the specimen is placed on the platform of the machine. The platform is raised and the jig adjusted so that the plunger is in line with the thrust plate hole. It is very important to maintain the jig at a fixed position from loading to taking all subsequent measurements, in order to avoid any variation. This can be easily achieved by making a mark both on the platform and on all the jigs such that during subsequent measurements these markings are always brought in line.
FIG 3.4  PARALLELISM ADJUSTMENT
FIG 3.5 LOAD CELL CALIBRATION
The platform is then lowered in order to insert the 'loading sleeve' around the plunger and then finally raised again to a stand-by position for loading. All these operations are done manually.

Before switching on the machine for loading the following final check is recommended as an experimental routine:

1. the amplifier is at the right setting,
2. the power supply is at 24.0 Volts,
3. the coarse-gear of the machine has been properly disengaged and the fine-gear engaged to the motorised drive system at the correct speed setting, and
4. the chart recorder pen is at zero setting.

The loading can then be started and its performance traced out by simultaneously switching on the machine and the chart recorder.

During loading, the 25 ± 1% compression on the specimen could be checked in 2 ways in the following manner:

1. The instant the pen recorder starts to move from zero load is considered as the 0% strain on the specimen. This is marked on the chart and at the same time the reading on the dial gauge, which is attached to the platform, is noted.
2. At the end of the loading when the thrust plate meets the jig-housing, the recorder pen will move steeply up the chart and the dial gauge reading should again be noted.

Hence, after having set the 25% compression during the specimen assembly, this can further be determined and checked during loading from the dial gauge and the recorder chart. Using a black specimen of original thickness 6.18 mm as an example, the method used are as follows:

1. During Assembly

The specimen is assembled with the following components:

\[
jig = 10.735 \text{ mm in depth}
\]
\[
glass \text{ plate} = 6.08 \text{ mm total thickness (a pair)}.
\]

\[\therefore \text{ the thickness of the loaded specimen will be} \]
\[10.735 - 6.08 = 4.655 \text{ mm}.\]

\[\therefore \% \text{ compression on the specimen} \]
\[= \frac{6.18 - 4.655}{6.18} \times 100 = 24.8\% .\]

2. From Dial Gauge

Initial reading = 15.09 mm

Final reading = 13.57 mm

\[\therefore \text{ the total displacement of the specimen during loading} \]
\[= 15.09 - 13.57 = 1.52 \text{ mm} \]

\[\therefore \% \text{ compression on the specimen} \]
\[= \frac{1.52}{6.18} \times 100 = 24.6\% .\]
3. From The Chart

Initial reading = 48 mm
Final reading = 341 mm
i.e the total distance on the chart = 293 mm.

The chart speed is 1 mm/sec
i.e 293 mm on chart = 293 sec of loading.

The loading rate is 0.31 mm/min = 0.00517 mm/sec
:. the specimen displacement during 293 sec of loading
\[ = 0.00517 \times 293 = 1.515 \text{mm} \]
:. % compression on the specimen
\[ = \frac{1.515}{6.18} \times 100 = 24.5\% . \]

Thus, from these 3 sources of information the percentage compression on the specimen is within the 25 ± 1% strain.

The end of the loading is indicated by a sharp rise in the loading curve as the thrust plate meets the jig housing. After switching off the drive system and the chart recorder the thrust plate is firmly bolted down. The compression on the specimen is thus maintained at 25% and is ready for subsequent measurement. This is the basic procedure being followed for the stress relaxation experiment in air at room temperature. For experiments at other temperatures, or under different environments, experiments involving other than stress relaxation measurement, the procedure is modified accordingly.
3.6 TYPES OF EXPERIMENT

Using the equipment described above a number of experiments other than in air at room temperature have been made, including experiments at elevated temperatures, in gaseous and aqueous environments.

3.6.1 Experiments at Elevated Temperature

For these experiments the test specimen is first preheated to the required temperature prior to loading. The preheating is done by using an insulated heat-band wrapped around the jig. From the calibration carried out, using a thermocouple inserted into the specimen cavity of the jig, it has been found that a one-hour preheating is necessary to bring the temperature of the specimen to equilibrium with the set temperature of the heater. After loading, and about 2 hours of subsequent measurement, the heat-band is removed and the jig is placed in an oven of similar temperature which has been set at least overnight. Further measurements are taken at the same temperature within one minute of taking the jig out from the oven to prevent any temperature drop in the specimen which can affect the accuracy of the reading.

3.6.2 Experiments in Water

Since the experiment has been carried out at room temperature, a similar loading procedure at room temperature was followed before immersing the jigs in a water bath.
3.6.3 Experiment in Nitrogen

This experiment has been performed at 100°C. Oxygen-free nitrogen is supplied direct from a gas cylinder into the jig cavity containing the specimen via a purpose-built hole, after passing through a copper pipe and then a coiled plastic tubing. The heat-band is used for preheating and nitrogen is fed at a rate of 0.1 litre/min. After turning on the gas and switching on the heater, the whole set is placed in a 100°C oven for one hour before loading. After loading the heat-band is removed and the jig replaced into the oven for subsequent measurements. The flow of nitrogen gas in the specimen cavity is regularly checked throughout the experiment (see 6.4 of Chap.6).

3.7 MEASUREMENT AND INTERPRETATION OF RESULTS

3.7.1 Measurements

Essentially, results are extracted from the two curves obtained during:

1. the loading of the specimen, and
2. the subsequent stress relaxation measurements.

1. The Loading Curve

The loading curve for a rubber in compression approximates to a straight line, Fig 3.6, at least to 25% compressive strain, which is the deformation specified by the British Standard. The main contributor to this curve is the rubber specimen, although there is a small contribution from the deflection of the load
FIG 3.6

High stiffness metal-to-metal contact

Force

Displacement

Compression of the specimen
cell and other parts of the equipment. This, however, is such an insignificant part of the total deformation that it can usually be ignored. Briefly, the deflection of the load cell will be the first response when the loading begins. The deflection is related to the stiffness of the load cell which varies proportionally to the reaction force of the specimen. A 'hard' specimen with a force of 250N will deflect the cell by 0.025 mm while a 'soft' specimen of 50N will deflect it by 0.0075 mm before the force exerted by the specimen is registered. This compares with a deflection of approximately 1.5 mm in the specimen, and can safely be ignored.

During loading, the force acting against the load cell is the force of the specimen undergoing compression until the thrust plate comes into contact with the jig which was constructed to correspond to 25% compression on the specimen. From this instant any further compression involves the reaction force of the jig against the load cell. Due to the different hardesses of the rubber specimen and the metal jig, the loading curve comprises two separate responses as is shown in Fig. 3.6.

The loading curve is obtained as an important feature of the total relaxation behaviour when measurements are made with the equipment developed in the Institute. The sharp change in slope at point A in the Figure occurs as the imposed strain reaches 25% and represents the initial stress to which all subsequent (relaxed) stresses are normalised and the gradient
prior to this point is considered the initial modulus of the specimen at 25% compression. By bolting down the thrust plate after loading, the specimen is maintained at 25% compression.

2. Subsequent Stress Relaxation Measurement

The relaxed stress measurements are made by applying a small incremental strain in the force measuring frame, recording the force versus displacement curve. The slope of the second part of the 'ideal curve' obtained is related to the modulus of the rubber at 25% compression for the appropriate time under load, Fig 3.1. The slope can be compared with that of the loading curve at 25%, since similar rates of loading are employed. In practice a total additional displacement of approximately 0.07 mm is imposed on the specimen for measurement purposes.

Although the method is simple, a good deal of care and precaution is needed to produce accurate results. All the surfaces of the parts which are in series between the moving platform on which the jig is placed to the heat shield of the load cell have to be smoothly ground and perfectly parallel to one another as discussed earlier.

The results obtained are plotted as residual stress (normalised to the initial force) versus logarithmic time.
3.7.2 Long Term Stress Relaxation

With the availability of reproducible data obtained at a variety of elevated temperatures, there is a strong temptation to attempt the prediction of the behaviour under service conditions, in spite of the warning sounded in the British Standard.

Stress relaxation is the consequence of a number of responses to the stimulus of the applied strain. Classically, they have been described as 'physical' or 'chemical' with reference to the supposed origins; within the former category were the time-dependent adjustment of entanglements and cross links, whilst the latter included the breaking of cross links and of main chains. These phenomena all contribute in varying degrees to the observed stress relaxation and to the modulus enhancement factor, MEF. Results for the MEF provide information additional to the stress relaxation data on the state of the rubber network at any particular time at the specified strain.

Stress relaxation and MEF data of long term tests at a number of temperatures for commercially available compounds based on natural rubber and ethylene/propylene rubber, have been obtained in an earlier work by Fernando. Arrhenius plots for retained force values of 80% down to 20% were constructed and by extrapolation, predicted life-times for service at 20°C are derived. The results give pessimistic prediction compared with observed performance. Further, at very high temperatures, there are departures from the linear Arrhenius plot which may be due to
oxygen diffusion control of reaction (for unexpectedly long lives), or volatility of one of the components (for unexpectedly short lives).

One may speculate on the better-than-might-be-expected performance at room temperature. The fact that the observed behaviour is superior to that predicted from high temperature data precludes an explanation that other modes of relaxation, possibly physical in nature, are active at low temperature, but not restrictive at higher temperatures; this would adjust the results in the wrong direction.

The observation poses a question on the importance of high temperature stress relaxation measurements, other than their obvious relevance to seals and gaskets applications at these temperatures. Those results indicate that the prediction of service life from high temperature stress relaxation data is likely to be unsatisfactory, confirming the comments in the British Standard. With the high accuracy and reproducibility of the new equipment and the associated method of measurement, it is perhaps more realistic, for standards purposes, to consider specifying relaxation limits at 20 - 23°C over a standard time, say 336 hours (2 weeks), as a basis of a quality control test.

3.7.3 Modulus Enhancement Factor (MEF)

A feature of the ideal curve discussed earlier is that it contains information concerning two independent factors
associated with the specimen: the abrupt change in the slope occurs at the force still exerted by the specimen, the relaxed stress, whilst the slope of the later part of the ideal curve is related to the instantaneous incremental modulus of the rubber at the specified strain/time conditions. Whilst results for the relaxed stress as a function of time have been commonly available for some time, the modulus data have not been obtained previously, but are now derived directly from the ideal curve, and must provide a basis for further comment on the behaviour of the rubber.

It is observed that, for black specimens, the instantaneous incremental modulus increases immediately after loading by a significant factor and that this level is maintained as relaxation proceeds. The factor by which the modulus associated with the relaxing specimen exceeds the modulus at 25% strain during the loading phase is the modulus enhancement, MEF. Experience indicates that MEF and stress relaxation are independent properties, in particular MEF remains unchanged as the stress relaxes, and the sudden increase in MEF at 500 hours at 100°C has no counterpart in the stress relaxation. Chapter 8 deals with this subject in greater detail.

3.8 SHORTCOMINGS OF THE EQUIPMENT

On completion of loading a specimen, a relaxation or drift is observed when the machine is switched off, followed by a further reduction in the force on the load cell as the bolts of
the jig are tightened down, Fig 3.7. In the experiment involving slow stress relaxation such as in the gum specimen, where the stress at 6 minutes after loading, \( F_{0.1} \), is found to be greater than the initial stress \( F_0 \). These observations are thought to be inter-related.

Note on Fig 3.7:

\[ F_{0.1} > F_0 \] for this NR gum specimen.

a is the slow relaxation which was mentioned above,

b is a bedding down of the thrust plate as the retaining bolts are brought to "finger tightness".

c_1, c_2, c_3 record the sequential tightening by Allen key of the retaining bolts.

The total magnitude of b + c_1, c_2 and c_3 may be small or approaching 100% depending on the quality of the jig. It is believed that this explains why, for slowly relaxing rubbers \( F_{0.1} > F_0 \).

Various explanations of the slow drift in the force level (such as in region 'a' of Fig 3.7) have been examined. The possibility that it is due to distortion of the thrust plate or the glass plates holding the specimen, under a loading stress of around 200N was investigated. Using a low-powered laser beam reflected on the surface of the suspected components did not provide a positive indication of significant distortion on them during loading.
FIG 3.7
TIGHTENING EFFECT

FORCE

DISPLACEMENT

F₀₁

F₀
It was perplexing why the drift from the new loading sleeve was inferior to that associated with the older sleeve. It was then realised that the methods of handling the new sleeve were not identical with those developed for the old, the former having much more personal contact which, it was argued, would result in a higher temperature. The effect of preheating the sleeve to 50°C and to 38°C was examined. The system was then reassembled and loaded to about 500N force. Fig 3.8(a) shows the record of residual force vs time for the preheated sleeve. There is a highly significant change in force as the system cools.

A further example of the effect of temperature is afforded by Fig 3.8(b), which is for a system of plunger and load cell, and moving platform in series. This 'hard' response system is affected by the temperature increase associated with touching the plunger causing the system to drift appreciably. It is important, therefore, that the handling of components in the measurement region should be kept to a minimum.

Repeating the experiment illustrated in Fig 3.6 with a compressed metal spring in series provided a 'soft' system which did not respond to temperature change. Further there was no drift in this system or in a similar series which had been loaded slowly over the course of 5-6 minutes, see Fig 3.9.

Having disposed of temperature as a potential contributor to apparent relaxation it appears that regions such as in Fig 3.7...
FIG 3.8

TEMPERATURE EFFECT

(b) Finger heat

(a) Preheated 38°C
FIG 3.9
COMPRESSION OF A SPRING

air-cooled

Loading

FORCE

DISPLACEMENT
genuinely exist; they may appear as a consequence of the gear train which determines the position of the moving platen and is inevitable in the equipment we have adopted.

However, in another series of experiments using gum specimens, the relaxation did not occur when the loading was stopped short just before the metal-to-metal contact of the thrust plate and the jig took place (compared to the immediate relaxation of a black-filled specimen); on completing the loading, i.e. when the thrust plate had come into contact with the jig, the drift was again observed. This was similarly observed when a metal spring was used to represent a soft non-relaxing specimen, in place of the gum specimen. These experiments are most conclusive in pointing the cause of the drift and tightening effect to the jig: the nature of the surfaces in contact and probably the material type of the jig too. Using a jig where the surfaces have been manually smoothened with a diamond paste indicates improvement in these discrepancies, though not entirely eliminated.

The importance of the many of the components showing relaxation behaviour has to be assessed in the light of the technique of measurement. Both the loading curve and the resulting ideal curve, involve 'soft' components, in this case the rubber specimens themselves. There is no uncertainty over the residual stress, obtained from the ideal curve, but there is doubt about the initial force since the thrust plate for some
jigs only beds down to a stable level when the retaining bolts have been well and truly tightened. The best solution is only to use jigs which are relatively free of the tightening irregularity, and aim to bring all the jigs to this state.
4.1 STRESS RELAXATION: VISCOELASTIC BEHAVIOUR

4.1.1 INTRODUCTION

A material is generally classified either as a viscous fluid or an elastic solid. However, these categories represent only the extreme of a broad spectrum of material response and polymers fall somewhere inside the region. To represent the viscoelastic behaviour of rubber under deformation, mechanical models have been proposed (though not to everyone's approval), and theories developed to provide explanation for the observed properties and behaviour.

It is appropriate to note here that almost all the equations derived and the theories described in this Chapter are to explain the behaviour and response of rubber under tension whilst the work for this thesis is being done in compression. However, irrespective of whether the rubber is under tension or compression it is in a state of strain; the theories developed for rubber under tension are thus considered to be relevant to rubber in compression.
4.1.2 THE MAXWELL MODEL FOR STRESS RELAXATION

Rubber does not behave either as an elastic solid or a viscous fluid, in other words it can be considered to have a combined behaviour of an elastic solid and a viscous fluid. The mechanical models which are used to represent the material are based on combinations of springs as the elastic element, and dashpots as the viscous element. There is a wide literature coverage of this subject, so the models will not be discussed in detail here. It is sufficient to mention that the models are basically derived from two arrangements; the parallel arrangement of spring and dashpot which originated from Maxwell and the series arrangement from Voigt. It was found that a differential formulation of linear viscoelastic behaviour particularly suitable for describing creep experiments is based on the Voigt-Kelvin model, where units of spring/dashpot in parallel are joined in series, whilst for the stress relaxation experiments the suitable formulation is based on the Maxwell-Wiechert model, where units of spring/dashpot in series are joined in parallel.

Maxwell in 1867 was among the first to discuss quantitatively the viscoelasticity of matter for substances which could be regarded neither as ideal elastic solids nor as viscous liquids, but having the character of both. Maxwell attempted to describe this viscoelastic behaviour with an equation in which he incorporated Hooke's law and Newton's law as follows

\[
\frac{ds}{dt} = \frac{1}{G} \frac{df}{dt} + \frac{1}{T} f
\]
where $s$ is the shear strain, $f$ the shear stress, $G$ the shear modulus and $\eta$ is a quantity called the relaxation time. He then developed a model named after him, which was made of a spring and a dashpot to behave according to his equation.

The stress decay of a viscoelastic material as represented by the Maxwell model when subjected to a constant strain is obtained from the above equation after considering the boundary condition when $\frac{ds}{dt} = 0$, i.e.

$$0 = \frac{1}{G} \frac{df}{dt} + \frac{1}{\eta} f$$

where on integration, the stress decay becomes

$$f = s_0 G \exp\left(\frac{-t}{\eta}\right)$$

4.1.3 NON-LINEAR VISCOELASTICITY OF RUBBER

An ideal elastic material obeying Hooke's law when subjected to a series of strain $s_0$, $s_1$, $s_2$, $\ldots$, $s_{n-1}$, $s_n$ at times $t_0$, $t_1$, $t_2$, $\ldots$, $t_{n-1}$, $t_n$ will experience at the end of the loading history a stress of,

$$f = E s_0 + E(s_1-s_0) + E(s_2-s_1) + \ldots + E(s_n-s_{n-1})$$

$$= E s_n$$

i.e. the equilibrium force required to maintain the deformation remains constant with time. Whilst for a material which will undergo a linear viscoelastic behaviour when subjected to the
same loading history, the stress produced will show a time
dependence as expressed by the Boltzmann principle
\[ f(t) = E_r(t)(s_0) + E_r(t-t_1)(s_1-s_0) + E_r(t-t_2)(s_2-s_1) + \ldots \]
\[ \ldots + E_r(t-t_n)(s_n-s_{n-1}) \]
or for a continuous strain history, it can be expressed as an
integral equation,
\[ f(t) = \int_0^t E_r(t-\theta)\dot{\varepsilon}(\theta)d\theta \]
where \( E_r(t) \) is the time dependent relaxation modulus and \( \dot{\varepsilon}(\theta) \) is
written for \( \frac{ds(\theta)}{d\theta} \).

Linear viscoelastic behaviour is expected to be valid for
substances whose basic structure does not change with time during
the experiments. However, Leardmen\(^{50}\) found a number of materials
such as rayon, silk, nylon 66 and mohair which are oriented
crystalline fibres, under many experimental conditions showed
marked deviations from the Boltzmann principle of linear
viscoelastic behaviour. The Boltzmann principle is, therefore,
applicable only under special conditions of extremely small loads
and at temperatures where crystallisation does not occur, and
also holds true for all amorphous polymers.

4.1.4 THEORY OF RUBBER ELASTICITY

The development of stress in rubber following its
deformation is due to its elasticity which is the driving force
to recover its original form or shape. Even though the theory of
rubber elasticity is concerned with the equilibrium elastic properties and is not capable by itself of explaining the non-equilibrium situations such as creep or stress relaxation, nevertheless it is of relevance to understand its concept. Coupled with the concept of degradation of rubber network structure under a state of strain in the two-network theory, the elasticity theory would help towards understanding the mechanism of stress relaxation of rubber under deformation. Thus the elasticity theory is briefly considered.

rubber-like

For a material to exhibit elasticity, three molecular conditions must be met:\textsuperscript{51,52}:

1. The material must consist of polymeric chains able to alter their arrangement and extension in space, in response to an imposed stress.

2. The chains are joined into a network structure to obtain recoverability and prevent irreversibility due to sliding of chains over another. This is achieved by cross linking either chemically or physically.

3. The chain must have a high degree of flexibility so that changes in spatial arrangements are not hindered by constraints of inherent rigidity of the chains, extensive chain crystallization or very high viscosity characteristics of the glassy state.
The theory of rubberlike elasticity is based on a Gaussian distribution function \( w(r) \) for the end-to-end separations, \( r \), of the network chains from one crosslink to another.

The function, \( w(r) = \left( \frac{3}{2\pi\langle r^2 \rangle_o} \right)^{3/2} \exp \left( -\frac{3r^2}{2\langle r^2 \rangle_o} \right) \)

where \( \langle r^2 \rangle_o \) represents the dimensions of the free chains as unperturbed by excluded volume effects, is applied to the network chains in both the stretched and unstretched states.

The Helmholtz or elastic free energy of such a chain is given by a variant of the Boltzmann equation

\[
F(t) = -kT \ln w(r) = C(T) + \left( \frac{3kT}{2\langle r^2 \rangle_o} \right) r^2
\]

where \( C(T) \) is a constant at a specified absolute temperature \( T \).

Considering the chain is being stretched from its random undeformed state with \( r = r_o \) components of \( x, y, z \) to the deformed state with \( r \) components of \( \alpha_x x, \alpha_y y, \alpha_z z \) (where \( \alpha \)'s are molecular deformation ratios), the free energy change for a single chain is

\[
\Delta F = \frac{3kT}{2\langle r^2 \rangle_o} [\left( \frac{\alpha_x^2 x^2 + \alpha_y^2 y^2 + \alpha_z^2 z^2}{2} \right) - (x^2 + y^2 + z^2)]
\]
To simplify the theory, the following assumptions were made:

1. The elastic response is essentially entirely intramolecular, such that the free energy change for $N$ network chains with average components $<x^2>$, $<y^2>$, $<z^2>$ is

$$\Delta F = \left( \frac{3NkT}{2<r^2>_<o>} \right) \left[ (\alpha_x^2 - 1)<x^2> + (\alpha_y^2 - 1)<y^2> + (\alpha_z^2 - 1)<z^2> \right].$$

2. The strain-induced displacements of the crosslinks are affine, i.e. the crosslinks experience similar deformation to that of the bulk sample, in which case the deformation ratios are obtained directly from the dimensions of the sample in the strained and unstrained states,

$$\alpha_x = \frac{L_x}{L_{x_i}}, \quad \alpha_y = \frac{L_y}{L_{y_i}}, \quad \alpha_z = \frac{L_z}{L_{z_i}};$$

3. The dimensions of the crosslinked chains in the undeformed state $<r^2>_i = <x^2> + <y^2> + <z^2>$, is identical to $<r^2>_o$, i.e. it is assumed that the crosslinks do not significantly change the chain dimensions from their unperturbed values. Also the isotropy of the undeformed state requires that $<x^2> = <y^2> = <z^2>$

thus, $<r^2>_o = 3<x^2> = 3<y^2> = 3<z^2>$
The expression for the elastic free energy of deformation of a network chain is then simply
\[ \Delta F = \frac{1}{2}(NkT)(\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3) \]

This is the basic equation of the molecular theories of rubberlike elasticity which can be used to obtain the elastic equations of state for any type of deformation. As in the case of elongation where the deformation is assumed to occur at essentially constant volume and that
\[ \alpha_x = \alpha > 1, \text{ and} \]
\[ \alpha_y = \alpha_z = \alpha^{-\frac{1}{2}} < 1, \] the equation then becomes
\[ \Delta F = \frac{1}{2}(NkT)(\alpha^2 + 2/\alpha - 3) \]

Since the free energy equation is a work function and work of deformation is \( f.d\alpha \), the stress \( f \) in the rubber is obtained by differentiating the energy equation such that,
\[ f = NkT(\alpha - \alpha^{-2}) \]

In plain terms, the elasticity theory described above assumed that all conformations of a polymer chain have equal energy. The stress developed in a deformed rubber arises from the kinetic tension in the chain which is mainly due to the change in conformational entropy with negligible effect from the internal energy.

In the unstretched state, the network chain is randomly coiled and is rapidly changing its conformation between fixed
crosslinks. When stretched, the number of possible conformations for the chain is reduced, thus reducing its entropy. The force or stress developed due to this change in entropy resulted with the elastic behaviour of rubber.

Much work related to this theory is still progressing especially in determining the contribution of effective and ineffective crosslinks and the role of entanglements towards elasticity. Active workers in this area include J.E. Mark, K. Murakami, B. Erman, P.J. Flory, and W.W. Graessley. Their recent publications are given in Reference 53.

4.2 STRESS RELAXATION : DEGRADATION

4.2.1 INTRODUCTION

When a polymer degrades its properties deteriorate or its external appearance becomes unacceptable. In most applications it is an unwanted and harmful process which is reduced by stabilisation. To do this with maximum efficiency, the mechanism of the degradation must first be understood. There are various schemes to classify polymer degradation. One popular classification is based on the main factors responsible for the degradation such as thermal, photo, oxidative, mechanical, chemical, biological, etc. Another possible classification is based on the main processes taking place as dominating events during degradation such as depolymerisation, chain scission, crosslinking, substitution, etc.
The measurement of stress relaxation as a function of time in polymers held at constant deformation (usually elongation) has been widely used as a tool to investigate chemical degradation besides using it to study viscoelastic behaviour. In principle, a crosslinked rubber network in the range of rubbery behaviour should experience little stress relaxation and should not decay to zero stress under deformation. However, the phenomenon of chemical stress relaxation has been observed in crosslinked natural rubber, styrene-butadiene rubber, chloroprene rubber, butyl and nitrile rubbers. This phenomenon is attributed to chemical rupture of the rubber network.

4.2.2 THE TWO-NETWORK THEORY

There are various methods of analysing stress relaxation data of rubbers which can be found in the literature. Most of them commonly considered that the relaxation process consists of two contributions, namely:

1. physical relaxation due to the changing of molecular conformations, and
2. chemical relaxation due to structural damage to the network.

The former is said to be dominant at the early stages of the relaxation and at lower temperatures whilst the latter is dominant at the later stages and at higher temperatures.
Damage to the network structure can be of two different kinds:

1. scission of chemical bonds such as $-\text{C}-\text{C}-$ or $-\text{C-S}_x\text{-C}-$, in which case chemical reaction will take place increasing the complexity of the secondary scission and crosslinking reactions,

2. scission of physical bonds such as weak links between polymer chains and filler particles, or removal of physical restrictions such as chain entanglements.

As mentioned earlier, the kinetic theory of rubber elasticity concerns only the equilibrium elastic properties of rubbery materials and cannot account for the behaviour of rubber under non-equilibrium situations such as stress relaxation. Tobolsky and his co-workers\textsuperscript{55,56,57} were among the earliest to explain the stress relaxation phenomenon in terms of breakdown of network structure. The well-known 'two-network' theory proposed by Tobolsky et al\textsuperscript{56,57} introduced the concept of simultaneous scission and crosslinking occurring in a rubber under a state of constant strain.

Flory\textsuperscript{58} further developed the theory by introducing an expression for the elastic energy of a polymer system in which original crosslinks are ruptured and secondary crosslinks are
being introduced in a state of strain different from that when the original crosslinks were formed. The theory considers that when a piece of rubber is subjected to a deformation the original crosslinks present at the beginning of the straining will resist the deformation thus giving rise to a resisting force. However, the scission of crosslinks or chains reduces the number of original crosslinks which contribute to the force whilst the secondary crosslinks formed at the state of strain do not give any contribution to the force since they are formed at that particular state. On the other hand, if the system is then brought to another state of strain, both networks, the original and the newly formed secondary crosslinks, will contribute to the new restoring force though to different degrees.

According to the theory of rubber elasticity, when an ideal rubber is subjected to a deformation of extension ratio $\alpha$, the restoring force or stress developed in the rubber obeys the equation of state,

$$ f_1 = N k T (\alpha - \alpha^{-2}) $$

where $N$ is the number of network chains.

The equation is derived on the basis that the stress in a stretched rubber arises from a decrease in entropy during stretching which in turn is related to the configurational possibilities of the randomly coiled molecular chains. It might thus be expected that the stress of a chemically crosslinked rubber in the region of rubbery behaviour should remain constant.
with time. However, the stress decays with time and this decay, as discussed above, is attributed to the chemical reactions such as chain scission, oxidative-cleavage, etc.

The equation of state, therefore, has to be made time and network dependent by replacing \( N \), a constant, with \( N_{o,t} \) the number of original network chains per unit volume remaining unbroken at time \( t \) such that,

\[
f_1 = A_0 kT (\alpha - \alpha^{-2}) N_{o,t}
\]

where \( A_0 \) is the original cross-sectional area of the specimen measured in the unstrained state.

If the extension ratio is infinitesimally increased by \( d\alpha \), the increase in force contributed by the remaining original network is

\[
df_1 = A_0 kT [1 + (2/\alpha^2)] N_{o,t} \ d\alpha.
\]

In addition, following the two-network theory the presence of a certain number \( N_{s,t} \) of new secondary bonds, formed though not contributive at extension ratio \( \alpha \), increases the net force by an amount of

\[
df_2 = (A_0/\alpha) kT \left[ 1 + \frac{d\alpha}{\alpha} - \frac{1}{(1 + \frac{d\alpha}{\alpha})^2} \right] N_{s,t}
\]

where \( A_0/\alpha \) is the cross-sectional area of the secondary network in its unstrained state such that

\[
df_2 = A_0 kT (3/\alpha^3) N_{s,t} \ d\alpha.
\]
Hence the total increase in force is given by

\[ dF = df_1 + df_2 \]
\[ = A_0 k T \left[ 1 + \frac{2}{\alpha^2} N_{o,t} + \frac{3}{\alpha^2} N_{s,t} \right] d\alpha. \]

Even though the theory has been generally accepted and considered well established, it is still a subject of much discussion with consequent modifications and improvements. There are many areas which are not fully understood and still under investigation; such as the role of fillers and the effect of crystallisation, the choice for the site of scission and re-crosslinking and the role of oxygen in it, the contribution of chain entanglements, etc. The theory will be applied to explain some of the results of the experiments in this thesis.
5.1 INTRODUCTION

In the British Standard\textsuperscript{45} it is said that a mechanically conditioned specimen gives better reproducibility of results. It also defines, rather poorly, the rate of loading. Elsewhere\textsuperscript{61}, it is said that incorporation of fillers have a 'strain amplification' effect on the actual deformation of a rubber compound. These three factors have been investigated and the findings are reported in this chapter.

5.2 RATE OF LOADING

It is well known that the rate of straining of a polymer specimen affects the stress developed, with higher stresses associated with higher rates.

For the British Standard\textsuperscript{45} where the compression is to be applied "within 30 seconds", the minimum loading rate to accomplish 25\% compression for Type 1 test piece of thickness 6.3 mm will be 3.15 mm/min. Whilst for Type 2 test piece of thickness 12.5 mm, the loading rate is increased, by the requirement of the standard, to at least 6.25 mm/min. For the American Standard\textsuperscript{3} the load is to be applied at a speed "approximately 1 mm/min" to a 12.5 mm thick specimen which will take about 3 minutes to achieve a 25\% compression.
These loading rates specified by both standards are, therefore, poorly defined and as we shall see, too high, especially the British Standard, which may lead to irreproducibility of stress relaxation when different rates are employed or different types of specimens are used. It is thus essential that the loading process be strictly controlled.

5.2.1 Experimental

A gumstock (sample G) and carbon black-filled (sample B) natural rubber vulcanisates were used in this programme. Following the procedure described previously, the experiment was performed at 100°C. The speeds of loading chosen were the normal speed used at 0.31 mm/min and a higher one at 1.56 mm/min. In order to be able to make direct comparison of the result from the recorder chart, the chart speed was also synchronised to run at proportionate speed. That is, at the loading rate of 0.31 mm/min the chart speed was set at 1 mm/sec, whilst for the 1.56 mm/min loading the chart speed was set at 5 mm/sec. Subsequent readings after loading were then made at normal speed both for the machine and the recorder.

5.2.2 Comparison of stress relaxation and MEF at different rates of loading

As mentioned earlier, a higher rate of loading is expected to result in a higher initial stress. An explanation for this is that at a higher rate, the relaxation period during loading is reduced; for the present case from 5 minutes to 1 minute. Whilst
at a slower loading rate the specimen has been gradually relaxing during its five times longer loading period, thus the different initial stresses with different loading rates.

In this programme it was found that besides having a higher initial stress, a highly stressed black-filled specimen also experienced a higher rate of stress relaxation resulting in a cross-over effect of relaxation curves as shown in Fig 5.1a. This effect, however, is not observed for the gum rubber the response of which is far less dependent on the rate of loading as shown in Fig 5.1b.

As expected the MEF of gum specimen remains almost unaffected by the change in loading rate in similar response to its stress relaxation as shown in Table 5.1.

**TABLE 5.1**

Effect of Rate of Loading on MEF

<table>
<thead>
<tr>
<th>Loading Rate Specimen</th>
<th>Initial Force (N)</th>
<th>MEF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gum</td>
<td>0.31</td>
<td>124</td>
</tr>
<tr>
<td></td>
<td>1.56</td>
<td>126</td>
</tr>
<tr>
<td>Black</td>
<td>0.31</td>
<td>225</td>
</tr>
<tr>
<td></td>
<td>1.56</td>
<td>254</td>
</tr>
</tbody>
</table>
FIG 5.1b

<table>
<thead>
<tr>
<th>FORCE (N)</th>
<th>1.56 mm/min</th>
<th>0.31 mm/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>150</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Gum specimen

HOURS
The slightly lower MEF of the black specimen at higher loading rate is negligible with no significant consequence, although it does not conform to the observation of high MEF associated with high stress relaxation rate.

A possible explanation for this behaviour is that the higher stress developed causes more damage to the network structure with consequent greater relaxation of stress. The higher rate of straining probably allows lesser opportunity for the bonds and crosslinks to reorientate or bring gradual disentanglement leaving the only alternative of bond-rupture especially at the weaker bonds of polymer-filler interface such that greater effect is observed with filled rubber.

Since the rate of loading can affect the stress relaxation of a rubber specimen, it is important to specifically define this testing parameter. With the equipment at the Institute of Polymer Technology a loading rate of 0.31 mm/min is found to be an acceptable compromise between high rates which needs special precaution especially when reaching the end of compression as well as the effect on subsequent relaxation whilst loading is prolonged unduly if the loading time is in excess of 5 minutes.

This effect may be of industrial significance, for example in the assembly of seals at pipe-joints where a high rate of compression of seal can have an adverse effect on its service-life and sealing performance.
5.3 MECHANICAL CONDITIONING

It is mandatory in the British Standard\textsuperscript{45} that, prior to a stress relaxation test, the specimen should be mechanically conditioned as noted, "It is known that the reproducibility of results may be improved by previous mechanical strain, which is achieved by conditioning as described: compress the test piece by about 25\% and then return it to approximately zero deflection. Maintain the test piece at 23 \pm 2\,^\circ\text{C} during this operation. Repeat the operation to give a total of five deformations. Allow a minimum of not less than 16 hours and a maximum of 48 hours at 23 \pm 2\,^\circ\text{C} to elapse between mechanical conditioning and testing ". The American Standard has no such requirement.

The effect of mechanical conditioning on rubber has been investigated by Derham et al\textsuperscript{62,63,64} and they found that the conditioning has permanent effect on subsequent stress relaxation of the material.

5.3.1 Experimental

Black filled natural rubber compounds (samples B and BP) were used in this experiment. The test specimens were prestrained five times that is each time straining it to 25\% at a rate of 0.31 mm/min and relaxing it back to 0\% strain at the same rate, the process being repeated five times. The experiment was carried out at room temperature and at 100\,^\circ\text{C}. For the room temperature test the specimen was loaded 16 hours after the mechanical conditioning, whilst for the high temperature test the specimen
was first heated for one hour to 100°C before the conditioning was carried out which was also done at the test temperature, and then immediately loaded.

5.3.2 Effect of Mechanical Conditioning on Stress Relaxation and MEF

Fig 5.2 compares the stress relaxation of the specimens which have, and have not, been subjected to mechanical conditioning at room temperature and 100°C. From this Figure, the effect of mechanical conditioning on stress relaxation appears to be somewhat less than has been suggested by other authors\(^{62,63,64}\) and so neither would it have affected its reproducibility as noted by the British Standard\(^{45}\). The only effect, if any, observed is the 'short term' reduction in relaxation for the specimen conditioned at 100°C, which lasted for about 2 hours after loading compared to the observations by Derham et al\(^{63,64,65}\) in which he considers\(^{63}\) "... the change in network arrangement responsible for the reduction in relaxation rate after pre-stressing, is essentially irrecoverable under ordinary conditions ....," and that this preconditioning ".... can have quite a large and usually permanent influence on the subsequent relaxation behaviour."\(^{64}\).

In this exercise, the MEF of the specimen did not appear to have been changed appreciably by the mechanical conditioning as shown in the Table 5.2, if comparison is made with the sample in its initial state:
### TABLE 5.2
Effect of Mechanical Conditioning on MEF

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>Specimen</th>
<th>Overall MEF</th>
<th>MEF after condition</th>
<th>MEF at final loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>23 (B)</td>
<td>normal</td>
<td>2.77</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>conditioned</td>
<td>2.88</td>
<td>1.53</td>
<td>2.13</td>
</tr>
<tr>
<td>100 (BP)</td>
<td>normal</td>
<td>2.02</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>conditioned</td>
<td>1.95</td>
<td>1.15</td>
<td>1.71</td>
</tr>
</tbody>
</table>

*a Overall MEF: Modulus at beginning of stress relaxation Modulus at end of first loading cycle*

*b MEF after cond: Modulus at end of 5th loading cycle Modulus at end of first loading cycle*

*c MEF final load: Modulus at beginning of stress relaxation Modulus at end of final loading*

(B): sample B
(BP): sample BP

If the MEF is related to some feature of the network, as presumably it is, then the indication is that mechanical working has little effect on this feature.

Since the observations on mechanical conditioning prior to tests show that it only has marginal effect both on stress relaxation and the MEF the necessity to perform it in order to improve the reproducibility of results as suggested by the British Standard, and to offer a permanent benefit to rubber.
components before they are put into service\textsuperscript{65} especially in compression, requires reconsideration.

5.4 STRAIN AMPLIFICATION

The generally increased stress relaxation rates of rubber containing fillers such as carbon black is explained by the theory of 'strain amplification'\textsuperscript{61}. According to this theory, due to the inextensibility and/or incompressibility of the filler, the rubber matrix is prevented from deforming uniformly by adhesion of the rubber to the surface of the filler particles and thus the strain occurring locally in the rubber phase is greater than the overall apparent strain. As such the ratio of stress to strain is increased by a certain factor\textsuperscript{66} which takes into account both the disturbance of the strain distribution and the absence of deformation in the filler.

Effectively, the strain amplification factor assumes that the strain in the rubber phase of a filled vulcanisate at any stress is, to a first approximation, equal to the strain in a corresponding gum vulcanisate at the same stress\textsuperscript{67}, which means that all vulcanisates subjected to the same initial stress are, therefore, of the same effective strain\textsuperscript{68}. And so it has been suggested\textsuperscript{66} that comparison of stress-strain behaviour of filled and gum rubbers should be carried out on the basis of equal stresses rather than equal strains since the stresses are a better measure of the relative deformation in the polymer itself.
5.4.1 Experimental

Natural rubber gumstock (sample G) and black filled vulcanisate (sample B) were used in this experiment. The aim was:

1. to strain a gum specimen such that its stress is similar to that of a black specimen at 25% compression, and
2. to strain a black specimen such that its stress is similar to that of a gum specimen at 25%.

Since the jigs used were of fixed depth, to achieve (1), an additional metal plate had to be placed at the bottom of the jig cavity, whilst for (2) 3 metal washers had to be positioned at the bolt holes between the jig housing and the thrust plate. The thickness of the metal plate and washers were respectively determined by calculating the extra deformation required by the gum specimen and the extra gap to be left by the thrust plate to reduce the deformation on the black specimen. In order not to affect the 'ideal curves' the parallelism in the system has to be maintained. To assure this, the metal plates and washers were precisely ground to give the required thickness. The experiment was performed at 100°C following the normal procedure of loading and measurement at elevated temperature.

5.4.2 Strain Amplification Effect on Stress Relaxation and MEF of Black and Gum Vulcanisates

In absolute residual force value (Newtons), Fig 5.3a indicates that a gum which has been strained to a similar stress
of a black specimen displays almost a similar stress relaxation behaviour of the black specimen. But for the black specimen which has been strained to a lower initial stress comparable to that of a gum, the similarity is not clearly observed as shown in Fig 5.3b.

However, in the normalised force \( \frac{F_t}{F_0} \), the effect of strain amplification on stress relaxation seemed to be diminished as in Fig 5.3c. If the strain amplification is effective, the stress relaxation of the gum and black specimens strained to a similar initial stresses are expected to be similar, in this case the curves should be closer to one another. But as observed in Fig 5.3c the stress relaxation curves of the gum were closer to each other than they were to the corresponding similarly stressed black specimens; the same is true for the case of the black specimens except that they are a little further apart.

As shown in the Table 5.3 below, strain amplification only slightly affected the MEF of the gum specimen; an increase of about 8% in response to 14% increase in strain. For the black specimen the change in MEF is a little greater; a reduction of 18% in response to 10% decrease in strain. Far from showing any similarity in MEF at equal initial stresses of the gum and the black specimens, the MEF's remain at their typical values for the particular specimen. An indication, possibly, of the relationship of the MEF to some feature of the network, especially those
FIG 5.3c

$\frac{F_t}{F_0}$ vs. HOURS

Key:
- 39% Gum
- 25% Black
- 25% Black
- 15% Black

Legend:
- Squares
- Circles
- Triangles
- Squares
involving fillers. These changes in MEF are comparable with the differences in their normalised stress relaxations.

### TABLE 5.3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial Stress(N)</th>
<th>% Deformation</th>
<th>MEF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gum</td>
<td>124</td>
<td>25</td>
<td>1.06</td>
</tr>
<tr>
<td></td>
<td>239</td>
<td>39</td>
<td>1.15</td>
</tr>
<tr>
<td>Black</td>
<td>225</td>
<td>25</td>
<td>1.95</td>
</tr>
<tr>
<td></td>
<td>119</td>
<td>15</td>
<td>1.60</td>
</tr>
</tbody>
</table>

The strain amplification theory is probably true in its assumptions about the distribution of stress in gum and filled rubber vulcanisates, but the manner in which it affects stress relaxation cannot be fully established. Its effect is only observed in the absolute value of the stress relaxation but when normalised the effect is not well defined. Therefore, the suggestion that, for all tests involving stress-strain behaviour, deformation should be carried out on the basis of equal stresses rather than equal strains cannot be generally justified.

From Figs 5.3a and 5.3b it can also be seen that a particular specimen with greater deformation has higher residual force at any given time even though it has a faster rate of
relaxation (Newtons/decade). Since the usefulness of a seal is its ability to exert and maintain a certain magnitude of residual force, it is of practical importance to find an optimum method of achieving high initial force which compromises between the residual force and its rate of relaxation rather than just considering the latter.
CHAPTER 6

INFLUENCE OF OTHER TEST VARIABLES ON STRESS RELAXATION

6.1 INTRODUCTION

Temperature and environmental effects are among the important test variables in the investigation of the properties of various materials including rubber. High-temperature experiments are often conducted as accelerated performance tests (though with precaution). The effect of temperature-changes during test was studied as well as relaxation behaviour in water and nitrogen. In addition, the effect of slippage was examined from bonded and lubricated specimens.

6.2 TEMPERATURE

The deviation of stress relaxation from the almost linear relaxation at low temperature to shorter times with increasing test-temperature is expected and observed by many workers \cite{8,44,69}. In this programme, stress relaxation tests of black specimens, with and without antioxidants (samples B, BP and BF) at 23, 38, 50, 70 and 100°C were performed.

Several attempts have been made to utilise relaxation data at elevated temperatures for prediction of lower or room temperature relaxation behaviour, unfortunately, without much consistent success \cite{42,43,70}.
6.2.1 Experimental

The experiment was designed to study the effect of antioxidant on stress relaxation (which will be discussed in the next chapter). However, the results are used here to show the effect of temperature on the relaxation of the black specimens. For the tests above room temperature, the specimen which had been assembled in the jig was preheated for 1 hour before loading. All subsequent measurements were then made at the test temperature and the jigs were kept in the appropriate ovens throughout the test period.

6.2.2 Stress Relaxation and MEF at Elevated Temperature

Results shown in Fig 6.1 for sample B (without antioxidant) are much as expected; increasing rate of stress relaxation and earlier deviation from initial relaxation with increasing temperature. The 38°C curve indicates that at this temperature of only 15°C above room temperature the change is already prominent. Therefore, the deterioration in the relaxation is probably affected at a temperature just above room temperature for an unprotected specimen. The residual stress and MEF are summarised in the Table 6.1a.

MEF data have also been obtained at the various temperatures for carbon black-filled natural rubber specimens; they are given in Table 6.1b.
TABLE 6.1a
Stress Relaxation and MEF at Different Temperature

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>Residual Stress Factor at: 10hrs</th>
<th>100hrs</th>
<th>1000hrs</th>
<th>MEF</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>81.4</td>
<td>77.8</td>
<td>67.4</td>
<td>2.60</td>
</tr>
<tr>
<td>38</td>
<td>81.4</td>
<td>73.4</td>
<td>54.5</td>
<td>2.29</td>
</tr>
<tr>
<td>50</td>
<td>81.7</td>
<td>72.8</td>
<td>42.1</td>
<td>2.09</td>
</tr>
<tr>
<td>70</td>
<td>68.7</td>
<td>38.6</td>
<td>10.3</td>
<td>2.03</td>
</tr>
<tr>
<td>100</td>
<td>37.8</td>
<td>18.2</td>
<td>8.9</td>
<td>1.91</td>
</tr>
</tbody>
</table>

Note: MEF values remain constant to at least 1000 hours except at 100°C when the MEF rapidly increases after about 300 hours.

TABLE 6.1b
Effect of Temperature on MEF

<table>
<thead>
<tr>
<th>Specimen</th>
<th>MEF values at temperatures: °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>23</td>
</tr>
<tr>
<td>B</td>
<td>2.60</td>
</tr>
<tr>
<td>BP</td>
<td>2.66</td>
</tr>
<tr>
<td>BF</td>
<td>2.66</td>
</tr>
</tbody>
</table>

There is a suggestion in these data that MEF shows a decreasing trend with increasing temperature, a trend not at variance with the results of Fernando for a commercial natural rubber specimen. However, his data for ethylene-propylene and
epichlorhydrin rubbers indicate some increase in MEF with increasing temperature, whilst nitrile rubber shows little change in MEF with temperature. Fernando reports\(^{42}\) that in the timescale 100 to 10,000 hours, most rubbers have MEF increasing with time, the increase being greater at higher temperatures.

Temperature has a role in accelerating the mechanism of stress relaxation whether 'physically' or 'chemically' as classically described. Physically, the temperature may affect the rate of flow and adjustment of entanglements and crosslinks, whilst chemically, the breaking and reforming of crosslinks; and main chains will be increasingly affected. This subject will be more fully discussed in Chapter 7 where the effect of antioxidants is considered.

6.3 STEP CHANGES IN TEMPERATURE

An investigation to determine the effect of step changes in temperature (T-step) has been carried out, in the light of the procedure described by the American Standard\(^{46}\) and method B of the British Standard\(^{45}\) which require that the loading and all measurements of residual force be made at room temperature, whilst the specimen treatment is carried out at elevated temperatures. Thus the specimen is subjected to step changes in temperature which might affect the stress relaxation behaviour, a possibility which has been investigated practically. This follow earlier work by Derham on the effect of T-jumps on creep behaviour\(^{63}\).
The procedures described by the Standards are as follows:

1. The American Standard.

Quoted from ASTM D1390: "Allow the assembled apparatus to remain at room temperature for 60 ± 5 min, and then place it in the ageing oven. Following the completion of the specified ageing period, permit the apparatus to cool at room temperature for 5 ± ½ hour and then determine the back stress of the aged specimen in the compression testing machine as before."

2. The British Standard.

From BSI 903 A42, Method B:

8.4.1 Compress the test piece by 25 ± 2% at 23 ± 2°C ......
8.4.2 30 ±2, -0 minutes after applying the compression measure the counterforce to an accuracy of ±1%, still at 23 ± 2°C.
8.4.3 Store the compressed test piece in the temperature controlled chamber at the test temperature.
8.4.4 When making measurements of counterforce after the times specified, remove the apparatus from the chamber into an atmosphere at 23 ± 2°C and allow to cool. Determine the counterforce and then return the apparatus to the test environment for a further time, if required.
6.3.1 Experimental

Four separate series of experiments were carried out to explore the importance of step changes in temperature in their effect on the stress relaxation behaviour and the MEF.

Series 1.
Using sample BP, the specimen was loaded at 23°C. Its initial stress and all subsequent stresses were measured at 23°C. One hour after loading, the jig and the specimen were exposed to 50°C for 6 hours. This temperature exposure was repeated daily for 5 days. Measurements were taken at least 3 hours after cooling to room temperature.

Series 2.
Sample B was used. The specimen was loaded at 70°C, its initial stress and all subsequent stresses were measured at 70°C. One hour after loading, the jig and specimen were transferred to a 50°C oven for 6 hours which was repeated daily for 5 days.

Series 3.
Using sample BP, the sample was loaded at 23°C and its initial measurement made at that temperature. One hour after loading the jig and specimen were stored in a 70°C oven. Its subsequent stresses were measured after allowing it to cool for 3 hours at room temperature.
Series 4.

Using sample BP, and following the similar procedure as in Series 1, the jig and specimen were treated to a temperature excursion at 5°C for 6 hours per day.

6.3.2 Effect of Step Changes in Temperature

The effect of step changes in temperature is compared to the corresponding continuous temperature runs as shown in Figs 6.2a - 6.2d. They are summarised in Table 6.2; the data quoted are the residual stress levels as percentages of the initial stresses (termed the residual stress factor, RSF).

Note on Table 6.2
1. Sample BP was used except for Series 2 which used sample B, which is unprotected by antioxidant and shows faster relaxation than BP (in Series 1 and 3).
2. All MEF values remain constant to at least 1000 hours.
<table>
<thead>
<tr>
<th>Treatment</th>
<th>Residual Stress Factor (MEF)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30hrs</td>
</tr>
<tr>
<td><strong>Series 1</strong></td>
<td></td>
</tr>
<tr>
<td>23 - 50 - 23°C</td>
<td>67.7</td>
</tr>
<tr>
<td>23°C continuous</td>
<td>79.7</td>
</tr>
<tr>
<td>50°C continuous</td>
<td>79.3</td>
</tr>
<tr>
<td><strong>Series 2</strong></td>
<td></td>
</tr>
<tr>
<td>70 - 50 - 70°C</td>
<td>46.9</td>
</tr>
<tr>
<td>50°C continuous</td>
<td>78.7</td>
</tr>
<tr>
<td>70°C continuous</td>
<td>54.9</td>
</tr>
<tr>
<td><strong>Series 3</strong></td>
<td></td>
</tr>
<tr>
<td>23 - 70 - 23°C</td>
<td>56.2</td>
</tr>
<tr>
<td>23°C continuous</td>
<td>79.7</td>
</tr>
<tr>
<td>70°C continuous</td>
<td>72.8</td>
</tr>
<tr>
<td><strong>Series 4</strong></td>
<td></td>
</tr>
<tr>
<td>23 - 5 - 23°C</td>
<td>83.1</td>
</tr>
<tr>
<td>23°C continuous</td>
<td>79.7</td>
</tr>
</tbody>
</table>
FIG 6.2c (Series 3)

\[ \frac{F_t}{F_0} \]

- 23°C
- 70°C
- 70 - 23 - 70°C

HOURS
The results given for Series 1 to 3 indicate that the step changes in temperature are deleterious to stress relaxation behaviour, for example, the results in Series 2 show that although the T-step change specimen spends a quarter of its time at 50°C, at least for the first 120 hours, nevertheless it relaxes more than a specimen maintained continuously at 70°C. Similar results are recorded for Series 1 and 3 where, however, it might be argued that the differences which indicate inferiority in the T-step specimen could be associated with different temperatures of measurements.

Series 4 does not follow this trend and it is difficult to explain the difference, although the result should reassure those with pipeline systems involving rubber seals. A possible explanation of this behaviour might be found in the temperatures involved in the different experiments: for Series 4 specimens the temperature never exceeded 23°C, at which temperature chemical relaxation might be considered negligible, whereas Series 1 to 3 involve temperatures of 50°C and higher, where chemical effects might be expected. If this argument is developed, the deleterious effect of the T-step might be associated with increased damage to the rubber network resulting from stresses developed during heating and cooling adding to the applied stress. At low temperatures the total stress is accommodated by the network without failure.
The results obtained for Series 1 to 3 support the earlier work of Derham\textsuperscript{63}, who reported that creep behaviour is deteriorated by step changes in temperature and the study made by Hutchinson et al\textsuperscript{71,72} on the effect of thermal fluctuation on creep of polyethylene in which they attributed the enhancement of the creep rate to thermoelastic stresses generated by the anisotropic thermal expansion of the polymer crystals.

The test procedures described by the British and American Standards which involve loading and measurement at room temperature with intervening exposure to high temperatures, obviously result in inferior performance apparently due to the imposition of step changes in temperature, indicating that a review of these procedures is desirable. To industry, the effect of T-step should caution involvement of temperature fluctuation especially in pipeline systems with rubber seals, such as in the method of steam-cleaning the system and the intermittent use of pipe lines which convey hot liquids.

6.4 ENVIRONMENT: AIR, NITROGEN AND WATER

Like many other properties of rubber, stress relaxation and MEF are expected to be affected by the environment. Rubber specimens with and without antioxidant at 100°C in air show little difference in their stress relaxation (see Chap.7). To determine whether the ineffectiveness of antioxidant is due to its loss from the system, because of its volatility at high temperature, or otherwise, tests under inert atmosphere of
nitrogen were conducted. Stress relaxation of specimens immersed in water were also investigated to simulate seals employed in aqueous conditions.

6.4.1 Experimental

In nitrogen

Sample BP was used and a through-flow nitrogen system was set up. Loading and all measurements were made at 100°C.

Oxygen-free nitrogen from a cylinder was first passed through a copper tubing of internal diameter 30.0 mm and effective length 0.45 m, then through a helical plastic tube of internal diameter 8.0 mm and effective length 10.0 m, all in the oven at 100°C, before finally reaching the specimen to ensure that the nitrogen had reached the 100°C test temperature. This was checked by a thermocouple inserted in the specimen housing cavity. The schematic diagram of the system is shown in Fig 6.3. The arrangement consisting of copper and plastic tubings of different dimensions not only provides extra dwell time and distance for the nitrogen to travel at 100°C to achieve the test temperature but the flexible pipe facilitates subsequent stress measurement to be made without having to discontinue the flow of nitrogen.

Until the loading was completed the temperature was 'further' maintained by a heater band around the jig which was then removed and the jig placed in a 100°C oven. During this same
period, nitrogen was fed at a rate of 350 cm$^3$/min to accommodate the larger outlet openings. After loading, with consequent reduction in the outlet openings, the gas flow was reduced and maintained at 100 cm$^3$/min throughout the test period lasting about 1350 hours. The through-flow of the gas was regularly checked at the outlet openings of the specimen cavity.

\textbf{In water}

No special set up was required. Immediately after loading, the jig and the specimen were placed in a water bath. Samples B, BF, BN and EP53 (an EPDM based commercial sample) were used. After loading the subsequent measurements were taken beginning one hour later, all at room temperature.

\textbf{6.4.2 Effect of Environment}

\textbf{In nitrogen}

Fig 6.4 shows that the stress relaxation is affected, if at all, only slightly by testing under nitrogen. Within this test period lasting 1350 hours the MEF of the specimen had, if anything, decreased marginally, showing a very different behaviour to the same sample in air where a rapid increase in MEF occurred after 350 hours.

The significance of this observation will be more fully discussed in relation to experimental results involving antioxidants (Chap.7) and, swelling tests and MEF (Chap.8).
The stress relaxation behaviour on nitrogen exposure as compared to that in air was similarly observed by Stenberg and Dickman\textsuperscript{37}, though it contradicts an earlier work in 1947 by Carter\textsuperscript{73} who found the relaxation rate of rubber under tension measured in oxygen-free nitrogen atmosphere to have decreased considerably.

\textbf{In water}

Fig 6.5 compares the stress relaxations of protected (sample BF) and unprotected (sample B) natural rubber specimens in air and water at room temperature, and shows the relaxation of the EP specimen in water.

The Figure shows that for the time period of 7500 hours, for both natural rubber specimens, the stress relaxation is little affected by immersion in water except that the unprotected specimen in water suffers an earlier deterioration in its residual stress. In contrast, the MEF does seem to be affected by water immersion for all the specimens though to different degrees; the value decreasing progressively with time over 7500 hours whilst in air the MEF is constant over this timescale as shown in the Table 6.3.

Water may not be having an effect due to its low rate of diffusion in rubber.
TABLE 6.3

Comparison of MEF in Air and Water Over 7500 Hours

<table>
<thead>
<tr>
<th>Specimen</th>
<th>In air (constant)</th>
<th>In water (decreasing)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>2.60</td>
<td>2.77 to 2.30</td>
</tr>
<tr>
<td>BF</td>
<td>2.56</td>
<td>2.77 to 2.47</td>
</tr>
<tr>
<td>EP</td>
<td>-</td>
<td>2.47 to 2.30</td>
</tr>
</tbody>
</table>

Unfortunately, a similar comparison for the EP sample is not possible due to the absence of the corresponding data in air. However, it is worth noting that the EP specimen, probably due to its low hardness as manifested by its initial force of 170N compared to 290N for the natural rubber specimen, manages to maintain a very low relaxation rate in water, whilst its MEF shows a similar decrease with time.

From this section it can be concluded that, even though antioxidant might have been lost through its volatility, oxygen is not seen as the factor that governs stress relaxation since its replacement by nitrogen would have protected the specimen. Thus, the relaxation at high temperature, if it is oxidative in nature, could have been due to the presence of oxygen in the specimen and not from the atmosphere; a similar suggestion has been put forward by Stenberg\textsuperscript{37}.

The implications of the changes in MEF for specimens in water have not yet been resolved; swelling measurements could be
informative, but it is regarded as more important to obtain the long-term stress relaxation data in water, so precluding the swelling experiments.

However, Derham\textsuperscript{74} who made a similar observation for specimens under tension at various relative humidity from 20 to 80%, suggested that the reduction in modulus is probably due to the presence of hydrophilic material in the specimen; the amount of softening depends on the nature and extent of this material. He also observed the effect of moisture in increasing the rate of relaxation; the effect being greater for rubber with higher tendency to absorb water.

6.5 TEST SPECIMEN: LUBRICATED AND BONDED

A bonded specimen is expected, due to its restriction to slippage perpendicular to the applied force, to maintain its restoring force better than the one which is lubricated and strained to the same level. An experiment was thus designed to determine how the surface condition of a specimen affects its stress relaxation behaviour.

6.5.1 Experimental

The tests were carried out at room temperature and 100°C using compound B. Bonded specimens were prepared by conventional means. For convenience of bonding, two metal plates were employed instead of glass, each half the thickness of the glass plate used in a normal test. The surfaces of the metal plates were sand
blasted and then treated with a bonding agent and left to dry. The bonded specimens were then prepared by transfer moulding.

For the 100°C tests, the specimen and the jig were first heated for one hour prior to loading. All measurements were then made at the test temperature. The compression jig was assembled by using only one glass plate since the other was virtually replaced by the bonded metal plates of the specimen.

6.5.2 Effect of Slippage on Stress Relaxation

Even though it had been carefully calculated to produce bonded specimens of the same thickness as the normal specimen, slightly thinner specimens were unfortunately produced. Nevertheless, Fig 6.6 shows that stress relaxation is not very much affected by the surface condition of the specimen, neither is the MEF as given in the Table below: The negligible effect may be due to the low shape factor.

<p>| TABLE 6.4 |
| Modulus Enhancement Factor |</p>
<table>
<thead>
<tr>
<th>Temp °C</th>
<th>Bonded</th>
<th>Lubricated</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>2.32</td>
<td>2.56</td>
</tr>
<tr>
<td>100</td>
<td>1.80</td>
<td>1.90</td>
</tr>
</tbody>
</table>

This conclusion was also reached in an earlier work by Beatty in 1950, in which he determined the stress relaxation of the following specimens:
1. bonded to steel plates
2. unbonded to polished steel plates
3. lubricated against polished steel plates using oil.

The stress relaxation of the above specimens under 40% compression at 70°C all lie practically on the same line.

Kimmich\textsuperscript{3}, however, observed a large difference in the stress-strain behaviour between lubricated and bonded specimens under compression. Whilst Foster\textsuperscript{13}, having considered that he had found a reliable method of lubricating specimen surface under compression, up to 32%, attributed the deviation of experimental curves to the theoretical curve as a result of poor lubrication.
CHAPTER 7

EFFECT OF FORMULATION VARIABLES ON STRESS RELAXATION

7.1 INTRODUCTION

A sound approach towards obtaining a product that will satisfy a particular service condition is to decide on the compound formulation before embarking on design criteria, cost factors, market etc. For rubber under compression the ability to maintain its residual stress, such as in seals, should be one of its most important product characteristics. A knowledge of how this could be achieved would be very valuable through understanding the mechanism involved. On this basis several type of compounds were formulated, their stress relaxations and MEF determined, compared and analysed in an attempt to have a better understanding on the mechanism of stress relaxation.

Ellul and Southern have recently reported a comparison of stress relaxation behaviour with compression set data for a range of rubber compounds for sealing applications. Their work seems to support the two network theory of Tobolsky, in the sense that their measurements of set and relaxation can be reconciled by that theory. It is not possible to compare their results in detail with those in the present work, since the measuring techniques are not described adequately. However, it is clear that significant changes in relaxation behaviour result from changes in the rubber compound formulation.
7.2 ANTIOXIDANTS

Antioxidant is incorporated into rubber for protection from the degradative effect of oxygen. As mentioned earlier, stress relaxation is considered a degradation, classically believed to involve physical and chemical processes; the latter being predominant at later stages of relaxation and at high temperature when the involvement of oxygen is expected to become significant.

7.2.1 Experimental

3 types of antioxidants were used, namely:

a. Flectol H in samples BF, GF
b. Permanax B in samples BP, GP
c. Nonox WSP in sample BN.

Note: Formulations of the samples are given in Appendix 1.

1.5 parts per hundred rubber (phr) of antioxidant was incorporated into the formulation of a particular rubber compound. The stress relaxations for samples BF and BP at 25% compression were determined at 25, 38, 50, 70 and 100°C against the stress relaxation of sample B (containing no antioxidant). Sample BN was tested at 100°C only on the supposition that it would be less volatile than the other antioxidants. A similar test at 100°C was also carried out for gumstock samples GF, GP against sample G (without antioxidant).

Loading and all subsequent measurements were made at the test temperature. Swelling measurements were made on selected
samples after compression. Toluene was used as the swelling agent at 23°C and measurements were taken at 24 and 168 hours after immersion.

7.2.2 Effect of Antioxidants on Stress Relaxation

The stress relaxation of samples BP, BF and BN at a particular temperature practically coincide with one another. As such the relaxation of sample BP is taken to represent the relaxation of a black specimen containing antioxidant as shown in Fig 7.1. The closeness of the relaxation values can be appreciated by inspecting the data in Table 7.1.

The relaxation of protected specimens does not seem to be affected by temperature between 23 and 38°C for up to around 7000 hours. At 50°C and with further increase in temperature, the relaxation deteriorates at shorter time as can be seen from Fig 7.1.

Fig 7.2 which is reproduced from Fig 6.1 shows the relaxation of unprotected specimen (containing no antioxidant) at different temperatures. Whilst the relaxation of a protected specimen at 38°C is similar to that at 23°C, for the unprotected specimen, deterioration of stress relaxation can be observed at 38°C.
TABLE 7.1

Stress Relaxation at Different Temperatures

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>Specimen</th>
<th>25hrs</th>
<th>100hrs</th>
<th>1000hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>BP</td>
<td>80.1</td>
<td>77.7</td>
<td>71.8</td>
</tr>
<tr>
<td></td>
<td>BF</td>
<td>81.1</td>
<td>75.8</td>
<td>71.4</td>
</tr>
<tr>
<td>38</td>
<td>BP</td>
<td>78.8</td>
<td>75.2</td>
<td>67.8</td>
</tr>
<tr>
<td></td>
<td>BF</td>
<td>77.9</td>
<td>75.1</td>
<td>65.3</td>
</tr>
<tr>
<td>50</td>
<td>BP</td>
<td>80.9</td>
<td>76.4</td>
<td>65.6</td>
</tr>
<tr>
<td></td>
<td>BF</td>
<td>80.7</td>
<td>75.1</td>
<td>58.7</td>
</tr>
<tr>
<td>70</td>
<td>BP</td>
<td>73.6</td>
<td>63.5</td>
<td>32.0</td>
</tr>
<tr>
<td></td>
<td>BF</td>
<td>74.5</td>
<td>64.0</td>
<td>32.5</td>
</tr>
<tr>
<td>100</td>
<td>BP</td>
<td>34.1</td>
<td>20.9</td>
<td>11.2</td>
</tr>
<tr>
<td></td>
<td>BF</td>
<td>37.4</td>
<td>20.6</td>
<td>12.3</td>
</tr>
</tbody>
</table>

Figs 7.3a - 7.3e compare the stress relaxation of protected against unprotected specimens at different temperatures. The effectiveness of antioxidant in protecting the specimen against stress relaxation can be observed up to a temperature of 70°C. However, at 100°C the effectiveness is minimal if not negligible. It was in the light of this result that the tests under nitrogen at 100°C were performed as reported in Chapter 6; its relaxation
is plotted on Fig 6.4. Again the relaxation behaviour is no different from the other specimens at 100°C, even though the results of MEF and swelling tests indicate an independent process occurring within the specimen (which will be discussed in Chapter 8).

The ineffectiveness of antioxidant at 100°C is also observed in the stress relaxation of gum specimens as shown in Fig 7.4. However, compared to that of a black specimen, the relaxation of gum specimen indicate some differences which will be discussed in the next section.

An interesting observation made in this series of experiments is the MEF. In almost all the samples tested at 70°C and below, the MEF remains nearly constant to at least 1000 hours, unaffected by the stress relaxation that is taking place. But at 100°C a rapid increase in MEF occurs in the region of 300 hours after loading when the stress relaxation has dropped to a low level; an exception is the specimen in nitrogen. The behaviour of MEF with respect to its relaxation is shown in Fig 7.5 for sample BP in air and in nitrogen at 100°C. And the negligible effect of antioxidant on MEF is given in Table 7.2.

Swelling measurements were made on the above sample BP immersed in toluene at 23°C. The measurements taken 168 hours after immersion are given in Table 7.3.
FIG 7.4

Gum at 100°C

UNPROTECTED

PROTECTED
TABLE 7.2
Effect of Antioxidant on MEF

<table>
<thead>
<tr>
<th>Temp°C</th>
<th>Specimen</th>
<th>MEF</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>B</td>
<td>2.77</td>
</tr>
<tr>
<td></td>
<td>BP</td>
<td>2.88</td>
</tr>
<tr>
<td>100</td>
<td>B</td>
<td>1.91</td>
</tr>
<tr>
<td></td>
<td>BP</td>
<td>2.02</td>
</tr>
<tr>
<td></td>
<td>G</td>
<td>1.06</td>
</tr>
<tr>
<td></td>
<td>GP</td>
<td>1.06</td>
</tr>
</tbody>
</table>

TABLE 7.3
Stress Relaxation and MEF at 100°C

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Time (hours)</th>
<th>Swelling (RSF(^a))</th>
<th>Swollen MEF (%wt inc)</th>
<th>Thickness(mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP (untested)</td>
<td>0</td>
<td>100.0</td>
<td>2.02(^b)</td>
<td>176.5</td>
</tr>
<tr>
<td>BP in N(_2)</td>
<td>1300</td>
<td>16.7</td>
<td>1.70</td>
<td>191.0</td>
</tr>
<tr>
<td>BP in air</td>
<td>1400</td>
<td>10.4</td>
<td>8.85</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>5000</td>
<td>-</td>
<td>9.68</td>
<td>129.5</td>
</tr>
</tbody>
</table>

\(^a\) RSF : Residual Stress Factor in 
\(^b\) MEF immediately after loading of a similar specimen.
So, even though the stress relaxation in air and nitrogen are similar, the specimens at the end of the test are not. In air at 100°C, the modulus of the specimen rapidly increased beginning 300 hours after loading by a factor of about 10, whilst the one in nitrogen remained unchanged up to 1300 hours. There is a decrease in the swelling, which is coincident with the sharp increase in MEF. The high development of MEF for the sample in air is followed by a 27% decrease in swelling, whilst in nitrogen there is a slight increase in swelling of 8%.

The air-exposed specimens exhibit progressive cracking on immersion in toluene, in contrast to the specimen in nitrogen which showed no sign of cracking, yet they had similar swollen thickness as given in Table 7.3.

Stenberg and Dickman studied the influence of antioxidant on stress relaxation\textsuperscript{38} and its dependence on oxygen concentration\textsuperscript{37}. At 85°C they found that antioxidant is still effective in protecting the specimens under compression against stress relaxation. However, they did not proceed to higher temperature. But in their experiment under tension at 100°C, the specimen with antioxidant still performed better than the one without\textsuperscript{38}. In the experiment to investigate the dependence of stress relaxation on oxygen concentration\textsuperscript{37}, using specimens which had been treated in different media prior to compression, the relaxation with respect to the treatment in air, vacuum and nitrogen are found to be similar even though those which had been treated with oxygen have higher rates of relaxation.
From the results of the experiment carried out in this section, the rate of stress relaxation is found to increase at higher temperature indicating that stress relaxation is temperature dependent. Incorporation of antioxidant managed to improve against this deterioration, thus stress relaxation seems to involve thermal-oxidative degradation as suggested by Tobolsky. At 100°C, however, the stress relaxations of specimens with and without antioxidant are comparable. A possible explanation for this is that the antioxidant could have been lost from the specimen due to its volatility exposing the specimen to oxidative attack. If this is true, the specimen aged in nitrogen should not suffer the oxidative attack and its relaxation should improve. However, this is not found to be the case. The stress relaxation of specimens exposed to air and nitrogen which were found to be similar, as also observed by Stenberg but contradicting earlier work by Carter, tends to support the view that atmospheric oxygen does not play an important role in the mechanism of stress relaxation although the relaxation may be due to the stored oxygen in the sample.

Similarly, Lyubchanskaya concluded that the selection of antioxidant is of secondary importance, having no appreciable effect on the rate of stress relaxation. Even the sample with no antioxidant showed only marginal increase in the stress relaxation at 90°C.
Dickman and Stenberg\textsuperscript{38} investigated the stress relaxation of natural rubber black specimens, with and without antioxidant, in tension and compression, mainly at 85°C. Their results, that the antioxidant, (N-1,3 dimethylbutyl-N’-phenyl-p-phenylenediamine), retarded the relaxation by about half decade of time, were similar to the findings of the present work, but they concluded that other features, notably the formation of hard skin on the unprotected samples, restricted the diffusion of oxygen to the interior which, by inference, retarded the relaxation. However, the course of relaxation appears not to be affected greatly by antioxidant or specimen thickness which, with our observations on nitrogen exposure, does not contradict the conclusion we have reached, that oxygen does not play an important part in the relaxation process at high temperatures.

A more unexpected result was the swollen thickness data for specimens relaxed in nitrogen, which were similar to those for the air-exposed specimens, Table 7.3. This suggests that oxygen not only plays little or no part in the relaxation process at 100°C, but neither does it participate in the formation of the secondary network which stabilises the specimen in its flattened geometry.

7.3 FILLERS

Practically all rubber products contain fillers of one kind or another either to improve their properties or to reduce the cost or both. Carbon black is among the most popular fillers
incorporated into rubber compounds resulting in improvements of many technical properties such as tensile strength, modulus, abrasion, resilience, etc.

It has been known for some time that polyethylene can also be used as a reinforcing filler for a variety of rubbers, including EPDM, imparting improvements especially in rigidity.

A number of experiments were carried out, therefore, to investigate their influence on stress relaxation.

7.3.1 Experimental

The effect of fillers on stress relaxation and MEF was studied using the samples below:

1. sample G, natural rubber gum vulcanisate
2. sample B, natural rubber containing black
3. sample EP/D, EPDM containing polyethylene (LLD type)
4. sample EP/P, EPDM containing polypropylene
5. sample EP/B, EPDM containing black.

Formulations of these compounds are given in Appendix 1.

The stress relaxation of sample B was determined at room temperature and 100°C, and compared against that of the gum specimen, sample G. The result is shown in Fig 7.6. Normal experimental procedures at room temperature and elevated temperature were followed.
The effect of polyolefines as fillers was compared to that of carbon black at 23, 70, and 100°C. The result is shown in Fig 7.7. EPDM was used as the base polymer instead of natural rubber, the reason being the high temperature requirement to blend the polyolefines at their melting points into the rubber; polyethylene at 120°C and polypropylene at 160°C, thus natural rubber will not be suitable. The preparation of these compounds was briefly described earlier in Chapter 3.

A differential scanning calorimetry (DSC) experiment was carried out on EPDM samples to investigate the reason for the sudden drop in the residual stress immediately after loading and the subsequent stress relaxation which was not observed in black specimens.

7.3.2 Effect of Fillers on Stress Relaxation

As can be seen from Fig 7.6 the specimens filled with carbon black experienced almost a similar rate of stress relaxation at both room temperature and 100°C compared to the corresponding gum specimen. Tobolsky indicated\(^7\)\(^5\) that carbon black does not affect the rate of stress relaxation, even though it is known to affect the oxidation of rubber. However, Lyubchanskaya\(^2\)\(^1\), using natural rubber containing different types of carbon black, found that all the blacks he used increase the rate of relaxation under compression compared to that of unfilled vulcanisate.
Carbon black is known to have a property called 'structure' and 'surface activity' which is capable of forming strong linkages with polymer matrices. They contribute towards the reinforcing nature of carbon black incorporated in rubber compounds. This rubber-to-filler linkage is believed to be weaker than the chemical bonds, e.g. the crosslinks formed between rubber and sulphur on vulcanisation, but is stronger than the Van der Waals attractive force.

From the two-network theory, the residual stress at any instant is a function of \( N_{0,t} \), the number of unbroken original chains at that particular time. As mentioned above, carbon black forms bondings between the polymer and the filler. \( N_{0,t} \) should include these bondings; and since they are weaker than the chemical crosslinks between polymer and sulphur, any rupture during deformation would be in their preference. Bonding of this nature is absent in a gum vulcanisate. Under this assumption, a deformed black specimen will suffer more bond rupture than that in a gum specimen, hence a lower \( N_{0,t} \) value, which means a greater stress relaxation in the former specimen.

Throughout this programme, black filled vulcanisates consistently showed a higher MEF than unfilled gum vulcanisates. The MEF of a gum is not only lower than the black but remains almost always at unity, i.e. there is no increase in modulus as shown in Table 7.4:
### TABLE 7.4

MEF of Gum and Black Specimens

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Test Condition</th>
<th>MEF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gum</td>
<td>23°C</td>
<td>1.07</td>
</tr>
<tr>
<td></td>
<td>100°C</td>
<td>1.08</td>
</tr>
<tr>
<td></td>
<td>Fast loading</td>
<td>1.06</td>
</tr>
<tr>
<td>Black</td>
<td>23°C</td>
<td>2.60</td>
</tr>
<tr>
<td></td>
<td>100°C</td>
<td>1.91</td>
</tr>
<tr>
<td></td>
<td>Fast loading</td>
<td>1.83</td>
</tr>
<tr>
<td></td>
<td>In nitrogen</td>
<td>1.94</td>
</tr>
</tbody>
</table>

If the MEF is an indication of some changes in network structure, and it is believed to be so, then the presence of black has brought about these changes. Whilst in the gum, the network more or less remains unchanged upon deformation.

From the two-network theory, the secondary crosslinks formed at the state of strain are not contributive to its residual force until the system is brought to a higher state of strain, which is what had happened when the MEF is determined. If this is true, then the MEF indirectly becomes an indicator to the formation of secondary network. Thus the data in Table 7.4 above indicate that a significant amount of secondary network had been formed in the black specimen whilst in the gum it was almost negligible.
The objective of using polyethylene as filler is to verify whether, if the breaking and reforming of crosslinks being the mechanism of stress relaxation is due to the nature of the bonding at the filler-polymer interphase, then, by substituting with fillers that can form chemical links with the matrix, the relaxation can be controlled.

The result obtained was more complicated than initially thought as shown in Fig 7.7. At room temperature the relaxation of black and polyethylene reinforced specimens were comparable. However, at 70 and 100°C, not only did the polyethylene-filled specimen relax much faster than the black specimen, but there was also a reduction in the initial stress followed by a sudden decrease in the residual stress immediately after loading, as given in Table 7.5, which did not happen to the black specimen.

Initially it was thought that this sudden decrease in the residual stress was due to insufficient curatives; however, an extra 50% of curative did not overcome this deterioration. DSC results as shown in Figs 7.8a and 7.8b identified the reason as the loss of polyethylene crystallinity at an abnormally low temperature, lower than its normal melting point at around 120-125°C. This was thought to be due to the polyethylene being joined to the rubber network by the curing system instead of remaining as discrete filler particles.
TABLE 7.5
Residual Stress of EPDM vulcanisates after loading

<table>
<thead>
<tr>
<th>Filler used</th>
<th>Temp °C</th>
<th>Initial Stress(N)</th>
<th>Stress(N) at 0.1hr</th>
<th>RSF(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene</td>
<td>23</td>
<td>516</td>
<td>504</td>
<td>97.7</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>405</td>
<td>344</td>
<td>84.9</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>304</td>
<td>232</td>
<td>76.3</td>
</tr>
<tr>
<td>Black</td>
<td>23</td>
<td>504</td>
<td>496</td>
<td>98.4</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>518</td>
<td>516</td>
<td>99.6</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>530</td>
<td>530</td>
<td>100.0</td>
</tr>
</tbody>
</table>

To prevent the polyolefine filler from melting during the vulcanisation, giving rise to the possibility of being joined to the rubber network, polypropylene of melting point around 160°C was used instead. The specimen was cured below and above this temperature at 150 and 170°C respectively. The resulting stress relaxation determined at room temperature for 100 hours is shown in Fig 7.9. Contrary to expectation, the sample cured at 150°C showed a relatively faster stress relaxation than the one cured at 170°C. However, both displayed even poorer performance than the specimen containing polyethylene.

As mentioned earlier in Chapter 6, the MEF of the polyethylene-reinforced EPDM in tests at 100°C behaved very unexpectedly in decreasing from 0.90 to 0.48, over a timespan of
2000 hours, indicating that the second network is not being established. In contrast, at 70 and 23°C, the MEF of this specimen remained constant at 1.30 to 1.40, and 1.60 to 1.90 respectively.

There are insufficient data to provide an explanation for all these observations which can only be made after further investigations. One likely reason for the sudden decay in the relaxation of polyethylene-reinforced EPDM at 70 and 100°C at about 1000 and 100 hours respectively, after a fairly stable relaxation could be due to a gradual softening, if not melting, of the polyethylene; changing its nature from a filler to a plasticiser. But the fact that this also happened to the black specimen is hard to account for at this stage.

7.4 CURING SYSTEM AND RUBBER TYPE

Different curing systems form different kind of crosslinks each with its own properties and characteristics. Two established chemical systems are sulphur-based and peroxide-based. The manner by which the rubber molecules are linked by the curatives influence many mechanical properties of rubber and this, according to a number of reports in the literature, includes the stress relaxation behaviour.

Different rubbers too have different properties depending on the molecular constituent, spatial arrangement and type of bonds present. Natural rubber, for example, is noted for its
resilience but relatively less resistance to swelling in oil or oxidative degradation, whilst EPDM has an appreciable high-temperature performance.

7.4.1 Experimental

The curing systems chosen for investigation were sulphur/CBS and 40% Dicumyl peroxide used in EPDM compounds, since the experiment was a continuation on the study of peroxide-cured EPDM of the previous section.

The stress relaxation of sulphur-cured specimens (samples EP/D/S and EP/B/S containing polyethylene and carbon black as filler respectively) were determined and compared against the corresponding peroxide-cured specimens (samples EP/D and EP/B). The test was run at room temperature for 100 hours.

Under similar test conditions, the stress relaxation of black-filled sulphur-cured EPDM (sample EP/B/S) was determined and compared to the relaxation of a similarly formulated natural rubber specimen (sample B) to study the effect of using the different type of rubbers.

To obtain a more meaningful result on the effect of compounding on stress relaxation, a peroxide-cured black-filled EPDM specimen (sample EP/B) was tested at different temperatures of 23, 70 and 100°C, for a longer period of 3000 hours. The result was then compared against that of a sulphur-cured black-filled natural rubber specimen (sample B).
7.4.2 Effect of Curing System and Choice of Rubber on Stress Relaxation

Since the tests above were run for only a short period of about 100 hours at room temperature, the results obtained were not sufficiently pronounced to deduce with certainty whether they have any effect on the relaxation behaviour. For the black-reinforced specimens the relaxation did not seem to be affected by the curing system, but for the polyethylene-filled specimens the sulphur-cured compound seemed to relax faster than the peroxide-cured material as shown in Fig 7.10. Similarly, it cannot be said with certainty whether the choice of rubber had any influence on the relaxation; even though from this short test, the EPDM specimen showed a slower relaxation than a similarly formulated natural rubber specimen, Fig 7.11.

The change in the curing system and the rubber affected the MEF in more or less the same proportion as their corresponding stress relaxations as shown in Table 7.6:

<table>
<thead>
<tr>
<th>Rubber</th>
<th>Filler</th>
<th>Curative</th>
<th>MEF</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPDM</td>
<td>polyethylene</td>
<td>sulphur</td>
<td>2.61</td>
</tr>
<tr>
<td>EPDM</td>
<td>polyethylene</td>
<td>peroxide</td>
<td>1.58</td>
</tr>
<tr>
<td>EPDM</td>
<td>black</td>
<td>sulphur</td>
<td>1.82</td>
</tr>
<tr>
<td>EPDM</td>
<td>black</td>
<td>peroxide</td>
<td>1.83</td>
</tr>
<tr>
<td>B(NR)</td>
<td>black</td>
<td>sulphur</td>
<td>2.60</td>
</tr>
</tbody>
</table>
FIG 7.10

POLYETHYLENE

BLACK
- Peroxide cured
□ Sulphur cured

0.1  1.0  10  100  1000
HOURS

100  80  60  40  20
If there were any effect by the curative and the rubber it could possibly be enhanced by carrying out the determination at a higher temperature and for a longer period. As manifested in Fig 7.12, the influence caused by simultaneously changing the above compounding constituents can be clearly seen. At 70°C, the peroxide-cured EPDM was still gradually relaxing, exerting 78% of its initial stress after 3900 hours, when the sulphur-cured natural rubber had already reached its lowest stress, 10% of the initial stress after 1000 hours. Similarly, at 100°C the EPDM specimen had only relaxed by less than 25% of its initial stress after 500 hours compared to a loss of 90% by the natural rubber specimen, which was its lowest stress level, for the same time duration. Also the stress relaxation of the natural rubber specimen at 100°C started its downward trend almost immediately after loading, but not for the EPDM until much later at around 500 hours.

On the other hand, the MEF of the EPDM specimen had marginally decreased, if not remaining constant, from 1.30 to 1.08 at 2200 hours when its residual stress had dropped to 25% of the original value. Compared to the MEF of the natural rubber specimen which remained at a value of 1.91 for only about 300 hours, by which time it had lost more than 85% of its original stress, thereafter the MEF began to increase rapidly to a value of 9.65 at 2250 hours, a typical MEF behaviour of natural rubber specimens in air at 100°C (see Fig 7.5, sample BP at 100°C).
This considerably contrasting behaviour in stress relaxation and MEF of the two different type of specimens, suggests that the stress relaxation behaviour can be improved or influenced by the design of the compound formulation, and by identifying the factors that contribute towards the MEF value, together, they might lead to a better understanding of the mechanism of stress relaxation. There is, however, insufficient information at this stage to conclude how, and why, stress relaxation and MEF behave in such a manner.
CHAPTER 8

MODULUS ENHANCEMENT OF RUBBERS IN COMPRESSION

8.1 INTRODUCTION

Measurements of the stress relaxation of rubbers in compression have been made routinely for many years. Hitherto, however, data for the modulus at a compressive strain level of 25% for various times under load have not been reliable. The ratio of the latter to the initial tangent modulus at 25% strain defines the modulus enhancement factor, abbreviated as MEF. With the development of a new equipment in the Institute of Polymer Technology, numerous reliable data for stress relaxation and MEF have become available.

The effects of important variables on stress relaxation and MEF have been investigated; time and temperature have dominated, but antioxidant content, filler content, water immersion and mechanical conditioning have been included in the programme. A possible connection between MEF and hysteresis has also been explored. Some measurements of the swelling in toluene of rubbers and the effect of prolonged compression on the swelling have given unexpected results, especially that at 100°C, the course of relaxation and the final dimensions, after compression and swelling are the same for air and nitrogen environments.
8.2 THE MODULUS ENHANCEMENT FACTOR (MEF)

Measurements of the incremental modulus at 25% strain are made routinely in this research programme. In Fig 8.1 the loading curve has compressive strain (more accurately, time at a constant rate of loading), as abscissa up to the specimen attaining 25% compressive strain, after which the abscissa becomes time in hours (on a logarithmic scale). The stress sampling curves, termed as 'ideal curve', were taken at the appropriate times to construct the stress relaxation curve, the rate of loading being identical with that used in the initial loading; the same abscissa scale is used, making the curves directly comparable. The ratio of the slopes of the relevant parts of the ideal curves to that of the loading curve defines the modulus enhancement factor, MEF. In Fig 8.1 it is seen that, even after only very short periods of stress relaxation, the MEF has already attained a surprisingly high value for this natural rubber black specimen (sample B).

A more detailed consideration of this phenomenon is possible by examining specimens tested after stress relaxation for 1, 2, 3 and 4 hours, which were ultimately compressed to greater than 30% strain. The results in Table 8.1 indicate that MEF reverts to approximately 1.0 for an incremental strain of less than 5%; that is, for 5% incremental strain, the slope of the force versus displacement curve of a sample which has stress relaxed at 25% strain for 1 to 4 hours is similar to that for a sample subjected directly to a compressive strain of 30% at the same rate of loading.
These results are in minor disagreement with those of Fernando, who found that for short times of relaxation, the force versus displacement curve reverted to its original slope as the total force on the sample exceeded the initial value.

Fernando found, however, that for times of relaxation longer than a few hours, the modulus curve did not revert to its initial slope but remained at a high level, even at strains up to 35%. Limited work at 100°C on a natural rubber black specimen (sample B), shows that after 16 hours under load, the MEF does continue at a high level to at least 35% strain as shown in Table 8.2.

### Table 8.2

<table>
<thead>
<tr>
<th>% strain</th>
<th>MEF</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>1.63</td>
</tr>
<tr>
<td>30</td>
<td>1.50</td>
</tr>
<tr>
<td>35</td>
<td>1.45</td>
</tr>
</tbody>
</table>
8.3 MEF AND STRESS RELAXATION

That a high MEF is a common appearance is supported by the data in Fig 8.1 in which the relaxed stress and MEF are plotted as functions of the time of loading on a logarithmic scale for a carbon black filled natural rubber specimen (sample B) at 23 and 100°C.

Fig 8.2 gives limited coverage of stress relaxation and MEF data for a natural rubber specimen containing whiting (sample W). Comparison with Fig 8.1 shows that lower MEF is involved in relation to the carbon black reinforced specimen. Similarly, a few tests on a natural rubber specimen with only 25 parts per hundred rubber of black had MEF values in the range of 1.33 to 1.50.

Fig 8.3 shows the relaxation and MEF data for a natural rubber gum specimen (sample G) at 100°C. The Figure shows that the MEF is about 1.0 (up to 450 hours); that is, there is no significant modulus enhancement.

In a series of tests using commercial specimens of other type of rubbers containing high levels of black, a higher MEF up to a value of 9.0 are obtained corresponding to greater relaxation. Thus we have a range of MEF from 1.0 to almost 9.0; for all these there are the corresponding stress relaxation data. Table 8.3 below are the data at room temperature. It is natural, therefore, to seek possible relationships between MEF and stress relaxation.
TABLE 8.3

<table>
<thead>
<tr>
<th>Sample</th>
<th>MEF</th>
<th>at 24 Hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>G\textsuperscript{a}</td>
<td>1.06</td>
<td>95.6</td>
</tr>
<tr>
<td>W\textsuperscript{a}</td>
<td>1.20</td>
<td>90.7</td>
</tr>
<tr>
<td>B\textsuperscript{a}</td>
<td>2.60</td>
<td>82.6</td>
</tr>
<tr>
<td>N\textsuperscript{b}</td>
<td>4.60</td>
<td>55.5</td>
</tr>
<tr>
<td>SBS\textsuperscript{c}</td>
<td>8.80</td>
<td>52.1</td>
</tr>
</tbody>
</table>

\textsuperscript{a} see Appendix 1.

\textsuperscript{b} Commercial high acrylonitrile content nitrile rubber.

\textsuperscript{c} Commercial high hysteresis SBS thermoplastic rubber compounded for machine mounting.

Fig 8.4 replots the results in Figs 8.1 and 8.3, the stress data being normalised with respect to the respective initial stresses; it can be seen that the difference in stress relaxation is not great, bearing in mind the strain amplification factor inherent in the black compound. This, leading to a higher rate of loading of the rubber network, would be expected to facilitate relaxation, and yet the difference in stress relaxation is small, in contrast to the MEF. Direct comparison of the black and gum natural rubber specimens which have been compressed to different strains to give similar initial restoring forces has not given unequivocal results; at 100°C, the filled specimen still relaxed the faster. This leads to the view that
the filler is somehow responsible for the rapid relaxation, as well as the high MEF. This is supported by measurements of the MEF at 100°C; the highly deformed natural rubber gum specimen compressed to 35% retained the same low MEF as was observed at 25% compression, 1.10 and 1.05 were the respective values. On the other hand, the natural rubber black specimen compressed to only 15% showed lower MEF than for 25% compression, 1.6 compared to 1.9 (see Chap. 5).

Further study of Figs 8.1 and 8.3 reveals a sharp increase in MEF after some 500 hours at 100°C; there is no equivalent discontinuity in the stress relaxation curve. This large change in MEF, occurring for both gum and black vulcanisates, must be the result of a large change in the rubber network, which should be amenable to investigation by other classical techniques, such as swelling measurements. This will be discussed after the next section.

8.4 MEF AND HYSTERESIS

The MEF behaviour of natural rubber gum and filled vulcanisates reflects their hysteresis characteristics in the respect that low MEF is associated with low hysteresis and high MEF with high hysteresis. This is illustrated in Fig 8.5; A for gumstock (sample GP) at 23°C, B and C for filled vulcanisates (samples BP) at 23 and 100°C respectively. The hysteresis loop was generated by strain cycling, as indicated, at the same rate used for loading in the relaxation tests. For gumstock at 23°C
(A), it shows the very low hysteresis, characteristic of this type of rubber vulcanisate, whilst B and C illustrates for 23 and 100°C, the much higher hysteresis of the filled vulcanisates.

Inspection of curves B and C of Fig 8.5 reveals that after strain cycling, the slope of the stress versus strain curve, i.e., the tangent modulus, at 25% strain is higher than during the initial loading. It is significant, perhaps, that the modulus at 25% strain when unloading (at the same rate as for loading in the stress relaxation measurements) is similar to the enhanced modulus for incremental strains beyond 25%. The ratio of this hysteresis modulus to the relaxation modulus is given in the following Table 8.4:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp (°C)</th>
<th>Hysteresis</th>
<th>Relaxed</th>
<th>Hyst : Relax</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gum</td>
<td>23</td>
<td>0.36</td>
<td>0.34</td>
<td>1.05</td>
</tr>
<tr>
<td>Black</td>
<td>23</td>
<td>1.87</td>
<td>1.60</td>
<td>1.13</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>1.27</td>
<td>1.07</td>
<td>1.19</td>
</tr>
</tbody>
</table>

It is possible that these effects are related to the behaviour which has been described by Mullins, having the following characteristics:
a. softening is only observed at strains lower than the previous strain, at higher values the stress versus strain curve reverts to the original relationship; and MCF are.

b. the softening is greater, the greater the stiffening effect of the filler; and

c. there is a rapid increase in stress as the strain approaches the previous maximum strain.

Kraus et al\textsuperscript{76} demonstrated that the previous stretching of carbon black filled rubbers has very little effect on the equilibrium degree of swelling in suitable solvents. They concluded that no significant network breakdown is caused by previous extension, and the softening is due to breakdown of carbon black structure, rather than involving the network.

Observations on MEF parallel those made on the Mullins effect in some ways, but are very different in others:

Whilst for short times of stress relaxation the force versus displacement curve reverts to the original curve after a small incremental strain - after 1 hour an extra 2\% strain is required; for loading times in excess of 16 hours, the enhanced modulus persists to at least 35\% strain.
8.5 MEF AND SWELLING MEASUREMENTS

Only a limited amount of work has been carried out on this topic. Nevertheless, the results are sufficiently interesting and significant to warrant reporting. Most of the work covered in this section is on natural rubber; this led to the adoption of toluene at 23°C as the swelling agent. Measurements were being made after 24 and 168 hours immersion. A further measurement made was the thickness of the specimen after 168 hours immersion, since swelling had little effect on the secondary network generated under compression.

Results are given in Table 8.5 where it can be seen that there is no relationship between stress relaxation and the equilibrium (168 hours) swelling behaviour, which remains constant whilst the stress relaxes to a small fraction of its initial value. This finding is in harmony with the conclusions reached by Kraus et al.\textsuperscript{76} that the filler and not the rubber network is responsible for the major part of the relaxation.

Perhaps of greater importance than the swelling data are the measurements of specimen thickness, following swelling, after prolonged compression. The unexpected general feature is that swelling in toluene does not restore the original geometry of the specimens, but they remain flattened, and the flattening is increased by longer times under compression. Fig 8.6 shows the progressive decrease in swollen thickness i.e. an increase in permanent set with time under load. (As guidelines 9.6 mm swollen
<table>
<thead>
<tr>
<th>Specimen</th>
<th>Environment</th>
<th>Temp °C</th>
<th>time (hrs)</th>
<th>RSF %</th>
<th>MEF</th>
<th>24hrs</th>
<th>168hrs</th>
<th>Edge</th>
<th>Centre</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF</td>
<td>air</td>
<td>23</td>
<td>0</td>
<td>100.0</td>
<td>-</td>
<td>173.0</td>
<td>183.0</td>
<td>9.45</td>
<td>9.65</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td>87.2</td>
<td>2.56</td>
<td>172.0</td>
<td>182.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5</td>
<td>84.2</td>
<td>2.61</td>
<td>169.5</td>
<td>179.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>24</td>
<td>81.1</td>
<td>2.56</td>
<td>172.0</td>
<td>182.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>96</td>
<td>75.8</td>
<td>2.29</td>
<td>171.0</td>
<td>181.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>500</td>
<td>73.4</td>
<td>2.46</td>
<td>173.5</td>
<td>183.0</td>
<td>9.37</td>
<td>9.55</td>
</tr>
<tr>
<td>BF</td>
<td>air</td>
<td>100</td>
<td>0</td>
<td>100.0</td>
<td>-</td>
<td>173.0</td>
<td>183.0</td>
<td>9.25</td>
<td>9.36</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td>74.2</td>
<td>1.67</td>
<td>172.5</td>
<td>180.5</td>
<td>8.99</td>
<td>9.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>25</td>
<td>31.4</td>
<td>2.01</td>
<td>169.0</td>
<td>176.0</td>
<td>8.02</td>
<td>8.21</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>100</td>
<td>18.4</td>
<td>2.01</td>
<td>169.5</td>
<td>178.0</td>
<td>7.89</td>
<td>8.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>340</td>
<td>11.0</td>
<td>2.18</td>
<td>153.0</td>
<td>164.5</td>
<td>7.96</td>
<td>8.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>500</td>
<td>9.8</td>
<td>2.23</td>
<td>147.5</td>
<td>154.0</td>
<td>7.83</td>
<td>8.07</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>720</td>
<td>-</td>
<td>3.69</td>
<td>142.5</td>
<td>151.5</td>
<td>7.73</td>
<td>7.92</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4000</td>
<td>-</td>
<td>10.67</td>
<td>130.0</td>
<td>136.0</td>
<td>7.53</td>
<td>7.75</td>
</tr>
</tbody>
</table>

TABLE 8.5
Swelling Measurements
### TABLE 8.5 (continuation)

Swelling Measurements

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Environment</th>
<th>Temp °C</th>
<th>Loading time(hrs)</th>
<th>RSF %</th>
<th>MEF</th>
<th>Weight increase% 24hrs 168hrs</th>
<th>Swollen thickness mm Edge Centre</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP</td>
<td>nitrogen</td>
<td>100</td>
<td>0</td>
<td>100.0</td>
<td>-</td>
<td>167.0 176.5</td>
<td>9.25 9.36</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td>90.1</td>
<td>1.88</td>
<td>- -</td>
<td>- -</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1344</td>
<td>16.7</td>
<td>1.70</td>
<td>182 191</td>
<td>7.74 7.91</td>
</tr>
<tr>
<td>BP(dupl.)</td>
<td>nitrogen</td>
<td>100</td>
<td>675</td>
<td>-</td>
<td>-</td>
<td>189.0 196.0</td>
<td>- 7.93</td>
</tr>
<tr>
<td>BP</td>
<td>air</td>
<td>100</td>
<td>5000</td>
<td>-</td>
<td>9.68</td>
<td>125.0 129.5</td>
<td>7.44 7.67</td>
</tr>
</tbody>
</table>

Commercial samples in air at 23°C:

<table>
<thead>
<tr>
<th></th>
<th>Temp °C</th>
<th>Loading time(hrs)</th>
<th>RSF %</th>
<th>MEF</th>
<th>Weight increase% 24hrs 168hrs</th>
<th>Swollen thickness mm Edge Centre</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural rubber</td>
<td></td>
<td>0</td>
<td>100.0</td>
<td>-</td>
<td>210.0 222.5</td>
<td>- -</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12800</td>
<td>83.0</td>
<td>1.85</td>
<td>203.5 213.0</td>
<td>- -</td>
</tr>
<tr>
<td></td>
<td></td>
<td>18600</td>
<td>80.0</td>
<td>1.92</td>
<td>- -</td>
<td>- -</td>
</tr>
<tr>
<td>EP rubber</td>
<td></td>
<td>0</td>
<td>100.0</td>
<td>-</td>
<td>91.5 90.5</td>
<td>- -</td>
</tr>
<tr>
<td></td>
<td></td>
<td>21900</td>
<td>70.0</td>
<td>2.68</td>
<td>82.0 80.0</td>
<td>- -</td>
</tr>
<tr>
<td></td>
<td></td>
<td>27700</td>
<td>66.0</td>
<td>2.77</td>
<td>- -</td>
<td>- -</td>
</tr>
<tr>
<td>Epichlorhydrin</td>
<td></td>
<td>0</td>
<td>100.0</td>
<td>-</td>
<td>90.5 102.5</td>
<td>- -</td>
</tr>
<tr>
<td></td>
<td></td>
<td>21900</td>
<td>35.6</td>
<td>2.13</td>
<td>111.5 127.0</td>
<td>- -</td>
</tr>
<tr>
<td></td>
<td></td>
<td>27700</td>
<td>38.0</td>
<td>2.37</td>
<td>- -</td>
<td>- -</td>
</tr>
</tbody>
</table>
thickness represents 0% permanent set, and 6.94 mm represents 100% set).

The most unexpected results, however, were the swollen thickness data for specimens relaxed in nitrogen, which were similar to those for air-exposed specimens, see Fig 8.6. This suggests that oxygen plays little or no part in the relaxation process at 100°C, nor in the formation of the secondary network, which stabilises the specimen in its flattened geometry.

There is a decrease in the swelling, which is coincident with the sharp increase in MEF after 250-500 hours loading at 100°C in air. Such air-exposed specimens also exhibit progressive cracking on immersion in toluene, as can be seen in Plate 8.1. By contrast, a specimen exposed to nitrogen at 100°C for more than 1300 hours gave no cracking on immersion in toluene, but had a similar swollen thickness, see Plate 8.2. The MEF for the nitrogen exposed specimens did not change in the duration of the experiment.

The conclusion reached from the swelling measurements, including the specimen dimensions, is that oxygen is not an important contributor to stress relaxation in natural rubber vulcanisates at 100°C. Further, the stress relaxation mechanism is associated with the establishing of a second network, which tends to stabilise the specimen in the deformed (i.e. flattened) state. Oxygen does react with the rubber, however, giving a hard
PLATE 8.1

PLATE 8.2

untested unswollen

100 hours

340 hours

untested swollen

500 hours

720 hours

4000 hours

5000 hrs. in air at 100°C

1344 hrs. in N₂ at 100°C

untested swollen
product, which is presumably highly cross-linked, since it swells to a lesser extent and gives serious cracking on immersion in toluene. The escalating MEF is a further indication that some of the rubber has reacted to give a harder product; this change in MEF does not appear to be associated with any discontinuity in the permanent set characteristics.

8.6 MEF AND AGEING

The rapid increase in MEF after a few hundred hours at 100°C for natural rubber vulcanisates, formulated to very simple compounds, (see Appendix 1), is supported by the data in Table 8.6 which reports the time for the onset of the rapid increase in MEF at 100°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time of MEF increase (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>450</td>
</tr>
<tr>
<td>GP</td>
<td>600</td>
</tr>
<tr>
<td>GF</td>
<td>450</td>
</tr>
<tr>
<td>B</td>
<td>300</td>
</tr>
<tr>
<td>BP</td>
<td>350</td>
</tr>
<tr>
<td>BF</td>
<td>300</td>
</tr>
<tr>
<td>BN</td>
<td>250</td>
</tr>
</tbody>
</table>
That this abrupt change in MEF (or incremental modulus) is associated with an increase in the level of cross linking, a natural inference, is supported by the swelling data in Table 8.5.

The unexpected feature of the ageing results, summarised in Table 8.6, is the very small influence of conventional antioxidants on the onset of this process. Further, as have been noted earlier in this chapter, there is no associated change in the stress relaxation curve. This poses the question whether oxygen plays a significant part in the network changes associated with stress relaxation; more especially, the doubt concerns the participation of oxygen in a chain reaction, since the antioxidants are notable 'chain stoppers'.

Tests under nitrogen at 100°C indicate that the MEF increase is retarded considerably, if not entirely eliminated, although the MEF for short and intermediate times is not affected and the MEF of 1.97 is comparable to that in air at 2.02. The stress relaxation is affected only slightly by testing under nitrogen; typical results are given in Fig 7.5 (of Chapter 7). This test was terminated at 1350 hours, by which time the MEF for this BP formulated specimen had, if anything, decreased marginally, showing very different behaviour to the same sample in air.
8.7 DISCUSSION AND CONCLUSIONS

For completion on the subject matter concerning MEF it is felt appropriate to briefly described all the facts and factors related to MEF which have and have not been discussed previously either in this chapter or in the earlier chapters.

The phenomenon of modulus enhancement, which is manifested when a filled rubber is subjected to compressive strain, has been investigated. The effect is not observed for gum rubbers, suggesting that the filler is an important contributor. Some change in the rubber network is indicated, but equilibrium swelling measurements have failed to distinguish between virgin specimens and those which have been subjected to compressive strain.

The rapid increase in MEF occurring after a few hundred hours after loading at 100°C seems to be universal for simple natural rubber vulcanisates. Incorporation of antioxidant brings no effect to the MEF as seen in Table 7.2, whilst changes in the curing systems could not indicate a definite effect, Table 7.6; they are discussed in Chapter 7. However, MEF is found to vary over a wide range of values, from about unity for an unfilled natural rubber specimen to about 9.0 for a commercially compounded high-hysteresis SBS thermoplastic rubber, Table 8.3.

The influence of temperature on MEF for a wide range of rubber compounds which are manufactured commercially for seals
and gaskets, has not given unequivocal results: nitrile rubber seems to be temperature independent; natural rubber MEF appears to decrease with increasing temperature, mentioned in section 6.2.2 of Chapter 6; whilst ethylene/propylene and epichlorhydrin rubbers show the opposite trend\textsuperscript{42}, as well as the polyethylene-filled EPDM described in 7.3.2 of Chapter 7.

Temperature dependence, on itself, does not seem likely to offer much hope of explaining this behaviour, although the sudden increase in MEF, manifested for all the natural rubber vulcanisates listed in Appendix 1, (G, GP, GF, B, BP, BF and BN), obviously reflects some considerable change in the material; reduced equilibrium swelling indicating that the system becomes more cross linked. It is difficult to advance a reaction scheme for this process, although a chain mechanism seems unlikely in view of the marginal retardation for compounds containing appreciable amounts of 'chain stopper' antioxidant.

Despite the adverse effect of temperature jump on stress relaxation as discussed in 6.3.2 of Chapter 6, it has negligible effect on the MEF. Similarly, MEF is not affected by the rate of loading, the extent of deformation (within limited range), and the strain amplification effect experienced by a specimen.

The small effect of mechanical conditioning ('scragging') on either the pattern of stress relaxation or the MEF behaviour is surprising and in disagreement with classical findings. The
consequences of scragging, which is completed in a timescale of 10-20 minutes, might be expected, by analogy with other polymer behaviour, to influence the response in the 10-100 minutes timescale, thereafter having decreasing effect. The results in Fig 5.2 of Chapter 5 are generally in accord with this experience, and they do not support the thesis advanced in Reference 45 that scragging leads to more reproducible results.

Perhaps the most fruitful correlation is that observed between hysteresis and MEF; the similar magnitude of the tangent modulus in the 'unload' stage in hysteresis and the incremental modulus obtained in the stress relaxation experiments suggests that a single explanation might cover both phenomena. However, the inescapable difference appears to be that, whereas the hysteresis effects are observed within the previous mechanical strain limits of the rubber's history, the MEF occurs at strain levels to which the rubber has not been subjected hitherto. There is little doubt that the nature of the network is changed by the imposition of compressive strain: the effect of such change is to cause a more rapid decay in stress as the strain is reduced; apparently the stress at 25% strain is carried by a 'high modulus network'. Such an interpretation satisfies the MEF and hysteresis result, but leaves unexplained the reversion of the loading curve in the hysteresis experiment to something like its original slope, whereas the MEF remains high up to 35%. This whole area calls for more experimental investigation of a standard comparable with that obtained in the stress relaxation programme.
Classical swelling measurements and novel measurements of the thickness of specimens after immersion in toluene, following compressive strain, have contributed to the conclusion that oxygen is not an important factor in the stress relaxation of natural rubber at 100°C. However, reaction of the rubber with oxygen has been observed, leading to a rapidly increasing MEF and decreased absorption of toluene by the rubber. This reaction does not occur homogeneously throughout the rubber, the inference being that some form of diffusion control is exercised.
CHAPTER 9

GENERAL DISCUSSION AND CONCLUSIONS

9.1 GENERAL DISCUSSION

It has been a major objective of this work to provide industry with a method of determining stress relaxation in compression and in particular to explore the value of accelerated tests in predicting service performance. It has been a further objective to provide a Standard in this field, based on an understanding of all contributing factors.

Experiments at elevated temperature have shown that simple interpretation of stress relaxation on a classical Arrhenius basis is not satisfactory. In this investigation, however, many interesting facts emerged which are relevant to an understanding of stress relaxation and to establishing an acceptable 'Standards' test procedure.

The method developed, of loading a test jig under prescribed conditions, followed by a sensing of RSF (Residual Stress Factor) at various times in a force-monitoring rig, is well proven. Following the 'ideal curve' concept, highly reproducible relaxation curves are obtained, normalised either to the initial force at the end of loading, or to the RSF at 0.1 hour. The latter has been found to give very reproducible relaxation curves, although inevitably the early relaxation information is lost.
The test equipment has continued to perform very satisfactorily although two shortcomings have been observed. The first of these, reduction of the force measured by the load cell when the compression drive is discontinued with further discrete reductions as the three bolts are tightened seems to be related to the ability of the gear train to remain stationary although a restoring force of 100-200N is striving to move the gear train. The act of tightening the individual bolts will inevitably allow further mechanical movement and a further reduction in the force registered by the load cell.

The second shortcoming in the equipment has been observed when specimens with very little relaxation are tested. For such systems it is sometimes observed that the RSF at 0.1 hours exceeds the initial force by up to 5%. Close inspection of the thrust plates of the jigs revealed that many were no longer flat with bottom and top faces parallel to ± 0.01 mm. Many were bowed, a form of distortion which may have developed in the 4½ years use since manufacture. All the thrust plates are now being reground to accurate flatness and parallelism, which has decreased but not entirely removed the discrepancy between initial load and residual force at 6 minutes.

Working with one of the refurbished jigs, experiments with a metal spring illustrate these minor deficiencies in the equipment. The results are introduced at this stage as they demonstrate clearly the behaviour of the system. The loading
stage provides a linear relationship defined by the characteristic spring constant (refer Fig 3.6). When the thrust plate is firmly in contact with the base of the jig, the slope increases abruptly, point A. On switching off the drive the stress relaxes slowly, but much more precipitously if the system is disturbed mechanically (refer Fig 3.7: regions a and b). The load of the load cell is also reduced as the bolts are tightened and may decrease to very low values; in the extreme, the force of the load cell may decrease to zero. The residual force has been measured in the usual way, and the reading of force found to be around 1-2% higher than the initial force from the loading curve, indicating that tightening the bolts increase the effective strain by this same margin, equivalent to a movement of the thrust plate of a few hundredths of a mm. With the standard of finish of the mating metal surfaces, this is entirely feasible. The reproducibility of the RSF measurement is excellent.

Accepting, therefore, that the results are accurate and meaningful the pattern of stress relaxation, principally of natural rubber vulcanisates has been monitored for compounds, unfilled and with carbon black or whiting. Whilst monitoring stress relaxation by the IPT method, further information is available in the tangent modulus at 25% compressive strain. This is obtained as part of the 'ideal curve' and must provide information about the network complementary to the stress relaxation data.
The ratio of the modulus at a compressive strain level of 25% for various times under load to the initial tangent modulus at the end of loading is defined as the modulus enhancement factor, abbreviated as MEF. MEF ranges from about 1.0 for gum vulcanisates to about 2-2.5 for sealing type carbon black filled vulcanisates, to about 4 for a high acrylonitrile NBR carbon black filled and to about 8.0 for an SBS compounded for vibration damping. High MEF appears to be related with high stress relaxation - particularly for the SBS compound (MEF about 9, stress relaxation after 24 hours at 23°C is around 50%). However, gumstocks and carbon black loaded compounds have similar stress relaxation when normalised to the initial load and very different MEF's.

MEF seems, however, to be closely related to hysteresis, a relationship which might be helpful in interpreting MEF. In dynamic mechanical work, peak losses are related to 'modulus' change with temperature; and peak losses mean high hysteresis which, in the filler polymer systems investigated in this programme, is related to high MEF. On the other hand, modulus change means time dependent modulus and is equivalent to stress relaxation. Hence, MEF is related to stress relaxation. Schematically, the relationship can be represented as follows:
Peak losses are related to 'modulus' change with temperature, means
High hysteresis time dependent modulus seems to be related to is equivalent to
High MEF stress relaxation

The fact that filler introduces mechanical losses (an interfacial problem) without a time-dependent modulus points to at least 2 contributors to MEF, only one of which is related to the stress relaxation via the nature of the polymer and the other depends on the filler-polymer interface. For both contributors, MEF and hysteresis behave similarly. There is a third factor which contributes to MEF - chemical reactions which lead to hardening of the rubber, as example in the behaviour of natural rubber after a few hundred hours at 100°C; distinguished by MEF changing during the course of the experiment.

The conclusions about the multiple origin of MEF indicate that the difference in MEF between gum and carbon black filled rubber is dependent on the carbon black-rubber interface whilst the considerable differences between rubbers is a function of the rubber and is related to its stress relaxation behaviour. The behaviour of MEF as a function of temperature might help in interpreting the MEF results: rubbers whose modulus is temperature independent might be expected to show MEF which is either independent of temperature or slightly decreases (non polar polymers).
The stress relaxation behaviour in compression is unexpected in many ways being apparently not strongly dependent on the presence of oxygen, even at temperatures as high as 100°C. Stress relaxation in nitrogen proved to be virtually identical with that in air at 100°C and, perhaps even more surprising, the compression set, even after swelling in toluene for a week was similar for an air and nitrogen exposed samples. The swelling index of the air-exposed samples decreased, however, undoubtedly as a consequence of the hard region which forms after some 300-500 hours at 100°C.

By contrast the effect of temperature on stress relaxation is qualitatively as expected, with the rate of relaxation increasing with increasing temperature. Quantitatively there does not appear to be a satisfactory model to reconcile the stress relaxation behaviour over a range of temperatures, so that the use of temperature to accelerate stress relaxation is not tenable as a means of assessing service behaviour. The viable technique for possible standardisation appears to be to take advantage of the accuracy inherent in the IPT equipment and method to establish a short term (336 hours) test for quality control with a 10,000 hours type test.

A different effect of temperature is associated with step changes in temperature which have been found to have deleterious effects on stress relaxation. The effect seems to be confined to step changes in temperature where the stress relaxation might be
expected to be largely chemical in nature. Thus low temperature step changes, such as 23-5-23°C reported here and 23-(-27)-23°C investigated by Armah do not appear to affect stress relaxation adversely, whereas high temperature step changes are deleterious agreeing with the findings of other workers .

Further light on the nature of stress relaxation is shed by the stress relaxation of a variety of antioxidant-containing vulcanisates at temperature from 23 to 100°C. Permanax B and Flectol H, added at the level of 1.5 phr appear to have minimal effect on stress relaxation at 23°C (up to 2 years under compression, although the unprotected specimen is beginning to show slight deterioration) and at 100°C, at which temperature stress relaxation was very rapid for a simple natural rubber black vulcanisate, with or without antioxidant. However, at intermediate temperatures, 38, 50 and 70°C there is some retardation in stress relaxation (about half decade of time). This suggests that oxygen might participate in the processes causing stress relaxation. The cause of the change at 100°C might be volatilisation of the antioxidant or the overtaking of the oxidation route for stress relaxation by a more temperature-dependent relaxation route not involving oxygen. However, from the MEF observations it appears that the filler-rubber interface is implicated at all temperatures from 23 to 100°C. The MEF does not show any variation to correlate with the behaviour towards oxygen.
Attempts to clear up the influence of the polymer-filler interface involved the incorporation of crystalline polyethylene as reinforcing agent in EPDM rubber. The use of peroxide for curing would be expected to link the filler and rubber matrix with primary bonds and thus circumvent the filler-polymer interfaces which was suspected of major complicity in the stress relaxation process. However, this approach proved abortive in that at 23°C behaviour of carbon black filled EPDM was at least comparable with the EPDM reinforced by linear low density polyethylene. Results at 100°C which might have been expected to favour the PE-reinforced systems showed the failure of these materials. This was traced by differential scanning calorimetry to the bonding of the rubber and polyethylene restricting the crystallisability, reducing the melting point and, therefore, the reinforcing power at 100°C. Thus rapid stress relaxation was observed, but inexplicably, the MEF decreased significantly with time, reaching the previously unattained level of 0.48. This means that the tangent modulus at 25% strain decreased with time under compression at 100°C. The loss of polyethylene crystallinity was partly a consequence of the cross-linking reaction being carried out at a temperature above 123-124°C, the melting region for this particular species of LLDPE (Dowlex 2045, an ethylene-octene copolymer). To investigate this, polypropylene was used as the crystalline reinforcement (melting point 163°C) and curing was effected both above (170°C) and below (150°C) the melting temperature. The simple concept of this programme was, however, difficult to achieve practically and few unambiguous results were obtained.
Finally, it has been observed that the rate of stress relaxation can be influenced mechanically, e.g. by the rate of loading, and chemically by the compound formulations. Further investigation in this area may perhaps reveal other factors that enable adjustment of the stress relaxation of a rubber product to the advantage of its service requirements.

9.2 RECOMMENDATIONS FOR FURTHER WORK

1. It is expected that a relationship exists between MEF and stress relaxation even though it has not been fully established within this thesis. Further investigation involving a wider range of rubber types e.g. thermoplastic rubbers, cross-linked rubbers and PVC-plasticised systems will provide more information required to establish the MEF-stress relaxation relationship.

2. The effect of $T_g$ (and its magnitude) above and below room temperature, on stress relaxation and MEF can be studied using a system of random copolymers such as butadiene-styrene.

3. The role of fillers in influencing stress relaxation and MEF should be further explored in relation to entanglements and rubber-filler interactions.

4. Low temperature T-jump should also be more thoroughly explored to further develop the concept of micro-stresses.
5. It is recognised that diffusion control e.g. of oxygen, water etc. may play a significant role in the relaxation behaviour described in these experiments because of the relatively large specimen size. This may explain some of the apparent conflicts between results in tension and compression. In order to clarify the importance of diffusion control it will be necessary to carry out experiments on different size specimens.

6. The insignificant effect of nitrogen exposure or antioxidant content on the stress relaxation at 100°C suggests that at this temperature the mechanism of relaxation may involve labile cross-links. The use of curing systems which lead to monosulphidic cross-links should be investigated.

7. Further work on the possible relationship of hysteresis and MEF particularly for strain cycling between 25 and 24% compression using a wide variety of rubbers with different hysteresis behaviour is likely to provide further knowledge of MEF.

8. Of no less importance there should be a continued development of the equipment which includes:

   a. exploring the possibility of 'locking' the strain level by means of isolating the jig from the gear train at the end of loading,

   b. eradication of the $F_{0.1} > F_0$ problem involving further 'adjustment' of the jig (material as well as design and finish) to give perfect metal-to-metal contact.
## APPENDIX 1: COMPOUND FORMULATIONS.

### 1. Natural Rubber

<table>
<thead>
<tr>
<th></th>
<th>G</th>
<th>GP</th>
<th>GP</th>
<th>B</th>
<th>BP</th>
<th>BF</th>
<th>BN</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rubber (SMR 5CV)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>CBS</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Sulphur</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td><strong>Filler:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon black (HAF)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>-</td>
</tr>
<tr>
<td>Whiting</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>50</td>
</tr>
<tr>
<td><strong>Antioxidant:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Permanax B</td>
<td>-</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Flectol H</td>
<td>-</td>
<td>-</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Nonox WSP</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.5</td>
<td>-</td>
</tr>
<tr>
<td><strong>Cure(mins @ 160°C)</strong></td>
<td>9</td>
<td>10</td>
<td>9</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>10</td>
</tr>
</tbody>
</table>

### 2. EPDM

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Rubber (Intolan 140)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>40% DCP</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CBS</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Sulphur</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td><strong>Filler:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P.E (Dowlex 2045)</td>
<td>50</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>50</td>
</tr>
<tr>
<td>P.E (XDG 33)</td>
<td>-</td>
<td>50</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P.P (Profax 7824)</td>
<td>-</td>
<td>-</td>
<td>50</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Carbon Black</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>50</td>
<td>50</td>
<td>-</td>
</tr>
<tr>
<td><strong>Cure(mins @ 160°C)</strong></td>
<td>30</td>
<td>30</td>
<td>60(^{\text{a}})</td>
<td>30</td>
<td>60</td>
<td>50</td>
</tr>
</tbody>
</table>

\(^{\text{a}}\)Cured at 150°C
\(^{\text{b}}\)Cured at 170°C
This apparatus has been jointly developed by the above organisations for the measurement of compression stress relaxation of rubber. The equipment is manufactured by Wykeham Farrance Engineering.

The basis of a stress relaxation measurement is to monitor the force exerted by a rubber specimen; which is maintained at constant strain and under defined conditions of temperature and environment, with time. The specimens, preferably prepared by transfer moulding, are compressed at the required strain (25±1%) between two glass plates (5), in individual jigs.

The force exerted by the specimen is sampled in the load measuring frame by driving the plunger into the jig. When the plunger makes contact with the top glass plate the force in the rubber is transferred progressively to the load cell, manifested by a steep straight line on the chart recorder. At the point that the load cell force exceeds that exerted by the specimen, the specimen starts to compress further, shown on the recorder by a significant change in force/time (displacement) response. The gradient of this response provides a measure of the instantaneous modulus, in addition to the time dependent force at the discontinuity. This response pattern, of two intersecting straight lines is known as the 'ideal curve' and is the justification of the reliability of the measurement.

The technique is unique in the sense that it allows the initial measurement (by which the results are usually normalised) to be obtained as the specimen attains the required strain level.
Technical Specifications

Approximate Dimensions

<table>
<thead>
<tr>
<th>LOAD FRAME</th>
<th>JIG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Height</td>
<td>700mm</td>
</tr>
<tr>
<td>Base</td>
<td>660 × 320mm</td>
</tr>
<tr>
<td>Load Capacity</td>
<td>10kN</td>
</tr>
<tr>
<td>Weight</td>
<td>42kg</td>
</tr>
<tr>
<td>Power supply</td>
<td>240v 50Hz 1ph</td>
</tr>
<tr>
<td>or 110v 60Hz 1ph</td>
<td></td>
</tr>
<tr>
<td>Speed range</td>
<td>25 speeds</td>
</tr>
<tr>
<td>Load Cell</td>
<td>0.0001 to 0.025 mm/sec</td>
</tr>
</tbody>
</table>

Load Cell

Range 0-0.5kN or 0-1.0kN

Power supply 10v dc

Amplifier permits full width operation of chart recorder, 5kN, 2.5kN or 1.5kN

Chart Recorder

Full scale 10mV-100mV (5 positions)

Chart speeds 0.1mm/min-10.0 mm/s (11 positions)

Effective chart width 210mm

ORDERING INFORMATION

<table>
<thead>
<tr>
<th>Item</th>
<th>Unit Price*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Compression load measuring frame, including load cell and load cell plunger combination and parallelism setting attachment</td>
<td>£1858.00</td>
</tr>
<tr>
<td>2. Chart recorder</td>
<td>£716.00</td>
</tr>
<tr>
<td>3. Power supply and the amplifier</td>
<td>£445.00</td>
</tr>
<tr>
<td>4. Compression stress relaxation jig</td>
<td></td>
</tr>
<tr>
<td>5. Ground glass location plates (two per jig) (a)</td>
<td>£75.50</td>
</tr>
</tbody>
</table>

OPTIONAL ACCESSORIES

<table>
<thead>
<tr>
<th>Item</th>
<th>Unit Price</th>
</tr>
</thead>
<tbody>
<tr>
<td>6. Load cell Calibrating lever</td>
<td>£75.00</td>
</tr>
<tr>
<td>7. Dial Gauge and bracket for the platform traverse</td>
<td>£94.00</td>
</tr>
<tr>
<td>8. Spanners (3) for the precision rod setting up of load cell</td>
<td></td>
</tr>
<tr>
<td>9. Heater accessories (including the temperature controller) for the in situ heating of jig and the compression sleeve</td>
<td>Price on application</td>
</tr>
<tr>
<td>10. Transfer mould for rubber specimen</td>
<td>Price on application</td>
</tr>
</tbody>
</table>

*NOTE: Prices valid until April 30th 1984

(a) Three different thicknesses of the ground glass are available to compensate the variations in thickness of specimens which may result from mould shrinkage differences. Minimum quantity supplied is 20.
LOW COST COMPRESSION STRESS RELAXATION APPARATUS FOR RUBBER

Specimen compressed between two glass plates.
WYKEHAM FARRANCE MANUFACTURE
A WIDE RANGE OF SPECIALISED EQUIPMENT FOR MATERIALS TESTING

For further information
contact:
WYKEHAM FARRANCE ENGINEERING LIMITED
WESTON ROAD
TRADING ESTATE
SLOUGH, BERKS SL1 4HW
ENGLAND
Telephone: (0753) 71241
Telex: 847301
REFERENCES


11. Schay G. and Sczor P., Engineer's Digest, 14, 6, (1953), 211.


47. Wykeham Farrance Brochure (Compression Stress Relaxation Apparatus For Rubber), Appendix 2.


