

LOUGHBOROUGH
UNIVERSITY OF TECHNOLOGY
LIBRARY

AUTHOR/FILING TITLE

PRABHU, A M

ACCESSION/COPY NO.

036000895

VOL. NO.

CLASS MARK

18 JUN 1994

LOAN COPY

date due:-

16 DEC 1998

LOAN 3 WKS. + 3
UNLESS RECALLED

TN 08117

25 JUN 1999

036000895 X



BADMINTON PRESS
18 THE HALFCROFT
SYSTON
LEICESTER LE7 8LD
ENGLAND
TEL: 0533 602918

STUDY OF STRESS RELAXATION AND STRAIN RECOVERY IN ELASTOMERIC COMPOUNDS USED IN PIPE SEALS

BY

ASHOK MOODBIDRI PRABHU

B.Tech., Dip. PTE., A.M.I.E., M.Sc., Grad. PRI.

A doctoral thesis submitted in partial fulfilment of the requirements
for the award of Doctor of Philosophy of the Loughborough
University of Technology

May, 1991

Supervisor: **Professor A. W. Birley**
M.A., D.Phil., C.Engg., FPRI.

Institute of Polymer Technology and Materials Engineering,
University of Technology, Loughborough, England, U.K.

© By A. M. PRABHU, 1991

*To my wife **usha** and to the
memory of my beloved **parents'***

Loughborough University of Technology Library	
D ID	00 NW 91
C ISS	
Acc No.	036000 895

59909329

ACKNOWLEDGEMENTS

I sincerely wish to thank my supervisor, Prof. A. W. Birley for his stimulating guidance, invaluable suggestions and encouragement throughout the research period.

I gratefully acknowledge the financial and material support provided by the Department of Trade and Industry, British Standard Institute and sixteen other rubber companies.

I wish to thank my wife Usha and brother Vivek for their help and encouragement throughout my study.

I also wish to express particular thanks to:

- Dr. M. Singh
- Dr. R. H. Sigley
- Dr. H. E. Strauss
- members of the technical staff at IPTME
- Mr. C. Lines and his colleagues at the IPTME workshop
- members of the technical staff at the University Computer Centre

SYNOPSIS

Elastomer compounds have been used in pipe seals for many decades, with their main problem, the stress relaxation due to various mechanisms. In these applications, a service life of more than fifty years is expected- and obtained. The purpose of the programme was to establish mathematical models to enable longevity of seals to be predicted from laboratory measurements. It seemed that stress relaxation in compression, together with strain recovery measurements, would provide a basis for such an investigation. Accordingly, such tests were carried out with up to 23 rubber compounds, at temperatures of 5°, 23°, 40°, 70°, 100° and 125° C, with environments of air, mains water and town gas.

The work outlined above is the main thrust of the programme, the data obtained being the raw material for the development and assessment of mathematical models associated with the viscoelasticity of the various rubbers. This work has been supported by supplementary investigations, including:

- effect of loading rate
- step changes in temperature
- inclusion (or not) of mechanical working of the specimen before testing
- use of solid phase lubricant
- changing the dimensions of the specimen
- comparison of air environment with water immersion, and town gas
- comparison of air environment with vacuum and nitrogen

An important facet of the work has been the comparison of tensile behaviour with the bulk of the work carried out in uniaxial compression. A comparatively novel property has been introduced in this work: *strain recovery after compression*. This has proved to be a property related to 'permanent-set', yet more amenable to interpretation and correlation. recovery data are now available for most of the conditions in the stress relaxation programme whilst additional results have been obtained from compression set equipments.

The other objective of this programme is to investigate shortcomings of BS 2494-1986, the current rubber seal specification, and to suggest new techniques such as strain recovery.

Finally, the behaviour of seals in simulated service has been investigated to compare with the data generated in the main programme.

TABLE OF CONTENTS

DEDICATION	ii
CERTIFICATE OF ORIGINALITY	iii
ACKNOWLEDGEMENTS	iv
SYNOPSIS	v
LIST OF TABLES	xiii
LIST OF FIGURES	xvi
LIST OF SYMBOLS	xix

CHAPTER ONE *BACKGROUND*

1.1 INTRODUCTION TO THE PROBLEM	1
1.2 ELASTOMERIC MATERIALS	2
1.2.1 Thermoplastic elastomers	4
1.2.2 Theory of vulcanisation	6
1.2.3 Effect of vulcanisation on properties of elastomers	7
1.2.4 Types of vulcanisation	8
1.2.5 Sulphur vulcanisation	9
1.2.6 Mechanism of stress relaxation in sulphur vulcanisates	10
1.2.7 Peroxide curing system	11
1.3 THEORY OF RUBBER ELASTICITY	12
1.4 ELASTOMERIC SEALS	16
1.4.1 Introduction and types of seals	16
1.4.2 Current rubber seal specifications	20
1.4.2.1 Selection of test temperature	20
1.4.2.2 Determination of compression set	21
1.4.2.3 Accelerated ageing test	21
1.4.2.4 Resistance to liquids	22
1.4.2.5 Rubber seal specifications	22
1.5 STRESS RELAXATION	22
1.5.1 Introduction	22
1.5.2 Determination of stress relaxation	25
1.5.3 Modes of stress relaxation	26
1.5.4 Physical stress relaxation	27
1.5.5 Chemical stress relaxation	29

CHAPTER TWO *STRESS RELAXATION*

2.1	COMPRESSION STRESS RELAXATION	36
2.1.1	Introduction	36
2.1.2	Consideration of measuring equipment	36
2.1.3	Materials and test compounds	39
2.1.4	Preparation of test buttons	39
2.1.5	Details of the equipment	42
2.1.6	Experimental procedure	46
2.1.7	Experimental variables	47
2.1.7.1	Test medium	47
2.1.7.2	Test temperature	49
2.1.7.3	Shape and size factors	50
2.1.7.4	State and type of cure	50
2.1.7.5	Study of the effects of filler	50
2.1.7.6	Study of strain rate	50
2.1.8	Limitations and conclusions	51
2.2	TENSILE STRESS RELAXATION	51
2.2.1	Introduction	51
2.2.2	Test equipment and procedure	51
2.2.3	Test variables and limitations	54

CHAPTER THREE *RELATED PROPERTIES*

3.1	MATERIAL CHARACTERISTICS	55
3.1.1	Introduction	55
3.1.2	Assessment of cure state	56
3.1.3	Effect of state of cure on stress relaxation	58
3.1.4	Effect of processing conditions on thermoplastic elastomers	59
3.2	HARDNESS	60
3.3	SWELLING MEASUREMENTS	60

CHAPTER FOUR

RESULTS AND DISCUSSION OF STRESS RELAXATION

4.1	COMPRESSION STRESS RELAXATION	62
4.1.1	Time dependence	66
4.1.2	Temperature dependence	70
4.1.2.1	Initial force	70
4.1.2.2	Residual force	70
4.1.2.3	Physical relaxation	70
4.1.2.4	Chemical relaxation	74
4.1.3	Water immersion	78
4.1.4	Natural gas environment	79
4.1.5	Filler	80
4.1.6	Specimen lubrication	81
4.1.7	Specimen dimensions	82
4.1.8	Nitrogen environment	82
4.1.9	Temperature jumps	83
4.1.10	Strain rate	85
4.1.11	Mechanical conditioning	90
4.2	TENSILE STRESS RELAXATION	91
4.3	MODULUS ENHANCEMENT FACTOR	92
4.4	LEVEL OF CURE	95
4.5	THE IDENTIFICATION OF CHEMICAL - RELAXATION MECHANISMS	97
4.6	HARDNESS	97
4.7	SWELLING	99

CHAPTER FIVE *STRAIN RECOVERY*

5.1	INTRODUCTION	101
5.2	EXPERIMENTAL	102
5.2.1	Test procedure	105
5.2.2	Test samples and variables	105

5.3	RESULTS AND DISCUSSION	106
5.3.1	Compression time	106
5.3.2	Test temperature	108
5.3.3	Comparison of stress relaxation and strain recovery rates	114
5.3.4	State of cure	115
5.3.5	Recovery in nitrogen	116
5.3.6	The effect of filler on recovery	117
5.3.7	Influence of specimen dimensions on recovery	118
5.3.8	Effect of temperature jumps on recovery	119
5.4	CONCLUSIONS	120

CHAPTER SIX

EXPERIMENTAL SIMULATION OF SEAL BEHAVIOUR

6.1	INTRODUCTION	122
6.2	SEALS	122
6.3	HEPWORTH SEALING FORCE APPARATUS	123
6.4	WAVIN EQUIPMENT	126
6.5	CONCLUSIONS	132

CHAPTER SEVEN *MATHEMATICAL MODELLING*

7.1	INTRODUCTION	133
7.2	THE MAXWELL MODEL	133
7.3	EMPIRICAL MODELS OF PHYSICAL RELAXATION	135
7.4	TIME-TEMPERATURE SUPERPOSITION	137
7.5	CHEMICAL RELAXATION	138
7.5.1	Extrapolation of chemical relaxation	139
7.6	MATHEMATICAL MODELS OF STRESS RELAXATION	139
7.6.1	The Aben Technique	140
7.6.2	The MRPRA method	141
7.6.3	Other predictive techniques	141
7.7	SEAL LONGEVITY	143

7.8	RESULTS AND DISCUSSION	147
7.8.1	Aben extrapolation technique	147
7.8.1.1	Determination of the physical relaxation	147
7.8.1.2	Prediction of the chemical relaxation induction time	148
7.8.1.3	Separation of the chemical relaxation mechanisms	148
7.8.1.4	Extrapolation of chemical relaxation	149
7.8.1.5	Prediction of stress relaxation	150
7.8.1.6	Discussion of the Aben technique	150
7.8.2	MRPRA method	150
7.8.3	The new empirical model	155
7.8.4	Extrapolation of the physical relaxation	156
7.9	TIME-TEMPERATURE SUPERPOSITION	158
7.9.1	Discussion of superposition principle	163
7.10	ARRHENIUS EXTRAPOLATION OF DATA	163
7.11	DISCUSSION OF MATHEMATICAL MODELS	165
7.12	APPLICATION TO LONGEVITY OF SEALS	169

CHAPTER EIGHT

CONCLUSIONS AND RECOMMENDATIONS

8.1	TIME DEPENDENCE	173
8.1.1	The effect on stress relaxation	173
8.1.2	The effect on recovery	173
8.2	TEMPERATURE EFFECTS	173
8.2.1	Initial force	173
8.2.2	Physical relaxation	174
8.2.3	Chemical relaxation	174
8.2.4	The effect on recovery	174
8.3	CURE STATE	174
8.4	ENVIRONMENT	175
8.4.1	Water	175
8.4.2	Natural gas	175
8.4.3	Nitrogen	175

8.5	FILLER	175
8.6	SPECIMEN DIMENSIONS	175
8.7	COMPARISON OF STRESS RELAXATION AND RECOVERY	176
8.8	MODULUS ENHANCEMENT FACTOR	176
8.9	LOADING RATE	176
8.10	MECHANICAL CONDITIONING	177
8.11	SPECIMEN LUBRICATION	177
8.12	HARDNESS	177
8.13	TEMPERATURE JUMPS	178
8.14	SIMULATED TESTS	178
8.15	MATHEMATICAL MODELS FOR SEAL LONGEVITY	178
8.16	BS: 2494-1986: RUBBER SEAL SPECIFICATION	178
8.16.1	Quality control tests	178
8.16.2	Stress relaxation and recovery tests	179
8.17	Recommendations for further research	181
REFERENCES		183
APPENDIX		189

LIST OF TABLES

1.1	Bond dissociation energies in a typical rubber network	10
1.2	Physical properties for Rings of Type W (water)	23
1.3	Thermal and oxidative mechanisms in NR network	33
1.4	Thermal and oxidative mechanisms in EPDM network	33
1.5	Types, sites and results of the reactions which occur in rubber vulcanisates	34
2.1	List of compounds initially proposed for this programme and the corresponding nominal hardnesses.	40
2.2	List of compounds used in this programme along with the corresponding nominal and measured hardnesses	41
2.3a	Chart recorder signals, mm, at various amplification factors for different acting loads during a calibration test.	44
2.3b	Calibration results	44
4.1	Ranking of material as a function of initial load and % RSF at 100 h. normalised to initial load(zero time) and load at 0.5 h. in Compression stress relaxation	69
4.2	Initial force normalised to 25% strain at various temperatures	71
4.3	Physical relaxation data as a function of temperature	73
4.4	Chemical relaxation induction times as a function of test temperatures	75
4.5	Chemical relaxation rates as a function of temperature (assuming all relaxation after the induction time is Chemical)	77
4.6	Chemical relaxation rates as a function of temperature (assuming all relaxation after the induction time is the sum of Physical and Chemical relaxations)	77
4.7	Comparison of stress relaxation in Water and Air	78
4.8	Residual stress factors(%) after 7000 h. at 23° C in air and gas atmosphere	79
4.9	Comparison of residual stress factors at 23° C and 70° C for filled and gum rubber compounds	80

4.10	Comparison of stress relaxation data for lubricated and unlubricated Santoprene specimens	81
4.11	Comparison of stress relaxation data in Standard and Large button specimens at 70° C and 100° C at 670 h.	82
4.12	Comparison of residual stress factors(% RSF) in Nitrogen and Air at 70° C after 1000 hours	83
4.13	The effect of temperature jumps on Residual stress	84
4.14	The effect of temperature jumps on Residual stress	85
4.15	The effect of loading rate on the Stress relaxation	87
4.16	Comparison of Residual stress factors (%) at 1000 h. normalised to the initial stress at zero time and stress at 0.5h	88
4.17	Effect of mechanical conditioning on RSF	90
4.18	Comparison of Residual stress factors(%) in Tension (100% strain) and Compression (25% strain) at 23° C	91
4.19	RSF(%) as a function of tensile strain for Santoprene 101-55	92
4.20	Influence of temperature on the Modulus Enhancement Factor (MEF) for various materials	93
4.21	The effect of strain level and strain rate on the Modulus Enhancement Factor (MEF)	94
4.22	Comparison of stress relaxation data in two different directions of an isometric cube specimens	95
4.23	The effect of cure state on the Residual stress at 5000 h.	96
4.24	Effect of Water immersion on various elastomers after 1000 h. at 23°, 40° C and 240 h. at 70° C	99
5.1	The effect of Compression time on Rate of recovery and Fractional recovery at Reduced time =1, at 70° C	106
5.2	The effect of Compression time on the Rate of recovery and Fractional recovery at 100° C, at Reduced time =1	107
5.3a	The effect of Temperature on Rate and Level of Recovery	109
5.3b	Separation of chemical relaxation at various temperatures	112
5.4	Comparison of Stress relaxation and Recovery rates	114
5.5	Comparison of % Fractional recovery at different levels of Cure at Reduced time =1, after 1000 h. in compression	116
5.6	The effect of Nitrogen environment on the Fractional recovery at Reduced time = 1	117

5.7	The effect of Filler on the Fractional recovery at Reduced time =1 after 336 h. compression time at 23° C	117
5.8	Comparison of Fractional Recovery (%) in Standard and Large buttons at 70° and 100° C after 670 h. and $T_R = 1$	118
5.9	The effect of temperature jumps on Recovery	119
5.10	The effect of temperature jumps on Recovery in Filled and Gum compounds	120
6.1	Comparison of Hepworth test results with the Compression stress relaxation data	125
6.2	Comparison of Wavin test results with the Compression stress relaxation data at ambient temperature	132
7.1	Physical relaxation rates as a function of temperature	147
7.2	Comparison of predicted and measured Chemical relaxation induction times	148
7.3	Application of Aben technique for the separation of the Chemical relaxation mechanisms	149
7.4	Predicted time for the Residual stress factor to fall to 30% at 5° C and 23° C	151
7.5	Predicted time for the Residual stress factor to fall to 10% at 5° C and 23° C	152
7.6	Comparison of predicted and measured RSF(%) at 20000 h using MRPRA method and Equation 7.23 at 5° C and 23°C	153
7.7	Comparison of predicted and measured RSF(%) at 20000 h. using MRPRA method and Equation 7.24 at 5° and 23° C	154
7.8	Predicted and measured RSF after 24000 h and the predicted RSF at 50 years at 23° C using the new empirical model	155
7.9	Extrapolation of the Physical relaxation data - the Residual stress factor (% RSF) at 5°C	156
7.10	Extrapolation of the Physical relaxation data - the Residual stress factors (% RSF) at 23° C	157
7.11	Comparison of predicted Residual stress factor (% RSF) after 50 years [6.6 decades] at 23°C using various techniques	163
7.12	Comparison of predicted and measured times for the RSF to reach to relevant values at 23°C	165

LIST OF FIGURES

1.1	Schematic diagram of a three dimensional elastomeric network	3
1.2	Schematic diagram of a thermoplastic elastomer showing hard and soft blocks	4
1.3	The schematic diagram of types of block copolymers	6
1.4	Effects of vulcanisation on elastomer properties	7
1.5	Simplified vulcanisate structure	9
1.6	Force-extension curve for uniaxial extension	14
1.7	Uniaxial extension and compression	14
1.8	Schematic representation of a conformation and the associated entropy of a molecular chain during a deformation process	16
1.9	Seal design for low pressure vessels	17
1.10	Schematic diagram of a Bridgeman seal	19
1.11	Classification of O-ring seals depending on its function	20
2.1	Wykeham-Ferrance force measuring equipment	37
2.2	Typical stress relaxation plots from the Wykeham-Ferrance force measuring equipment	38
2.3	Illustration of the 'Modulus Enhancement Factor'	38
2.4	The equipment layout for the Compression stress relaxation measurements with the heating device for the jig	42
2.5	A schematic diagram of the device used for the calibration of the force measuring equipment	43
2.6	Schematic diagram of a compression stress relaxation jig	45
2.7	Experimental set-up for CSR test in natural gas	48
2.8	Experimental set-up for CSR test under nitrogen	49
2.9	Schematic diagram of tensile stress relaxation jigs	52
2.10	Tensile stress relaxometer developed at IPTME for continuous measurement of residual stress	53
3.1	Classification of Polymers	56
3.2	Typical rheometer trace for a sulphur vulcanisate	58

4.1	Force-deformation relationship for a rubber in compression	63
4.2	Bulging effect in bonded and lubricated specimens	63
4.3	Loading curve and residual force measurement for rubbers in compression stress relaxation test	64
4.4	Isochronous curve for sulphur cured EPDM, C(O)	65
4.5	Isochronous curve for a thermoplastic elastomer, I(O)	66
4.6	Residual stress factor (%) as a function of strain	67
4.7	Stress relaxation in thermoplastic elastomers - Santoprene 101-55 and 101-64	68
4.8	CSR plots for the crosslinked rubbers for 1000 h at 23°C	72
4.9	CSR curves for the TPEs for 1000 h. at 23° C	72
4.10	Long-term stress relaxation data at 23°C	76
4.11	Estimation of chemical relaxation rate by using the Arrhenius treatment for NR and SBR compounds	76
4.12	Effect of loading rate on Initial load for Santoprene	86
4.13	Effect of loading rate on Relaxation rate for Santoprene	86
4.14	Effect of loading rate on RSF(%) at 0.5 h for Santoprene	87
4.15	The effect of loading rate on the RSF in EPDM(P)	89
4.16	The effect of loading rate on the RSF in Alcryn	89
4.17	Effective hardness as a function of time	98
5.1	A cross-sectional view of a compression-set jig	103
5.2	Recovery curves for two different elastomers showing a) Good recovery b) Poor recovery	105
5.3	Schematic diagram of a typical recovery plot	111
6.1	Cross-sectional view of triangular compression type and the model lip seals used in the simulated experiments	122
6.2	Schematic diagram of Hepworth sealing force apparatus	123
6.3	Variation of sealing force on the Hepworth apparatus	125
6.4	Comparison of decay in sealing force on the Hepworth equipment with the compression stress relaxation data for the sulphur-cured EPDM	126
6.5	Schematic diagram of the Wavin equipment (original design)	127

6.6	Cross-sectional view of the seal and coupler assembly used in the Wavin equipment (view X-X) of Figure 6.5	129
6.7	Reproducibility tests for the Wavin equipment	130
6.8	Variation in residual stress with the Wavin equipment	131
7.1	Schematic diagram of the Maxwell model	133
7.2	Schematic diagram of a generalised Maxwell model	134
7.3	Preparation of master curve from experimentally measured modulus-time curves at various temperatures	137
7.4	A cross-sectional view of a deformed O-ring	144
7.5	Time-temperature superposition, sulphur-cured SBR	158
7.6	Time-temperature superposition, sulphur-cured EPDM	159
7.7	Time-temperature superposition, peroxide-cured EPDM	159
7.8	Time-temperature superposition, NBR(50 IRHD)	160
7.9	Time-temperature superposition, Epichlorohydrin rubber	160
7.10	Time-temperature superposition, Nitrile rubber(70 IRHD)	161
7.11	Time-temperature superposition, Evoprene 992	161
7.12	Time-temperature superposition, Santoprene 101-55	162
7.13	Time-temperature superposition, Alcryn 6385	162
7.14	Stress relaxation plots for the natural rubber, log RSF vs lin(time)	164
7.15	Errors in extrapolation due to diffusion shifts	168
7.16	Arrhenius analyses for the chemical relaxation rates	169

LIST OF SYMBOLS

$A, A', B, C, C_1, C_2, D, n, \beta, \psi$	Constants
$F, F_o, F_{0.1}, F_t, f_{0.1}, f_0, \sigma, \sigma_o, \sigma_t, X_c$	Stress
x	Deformation
$\epsilon, \epsilon_o, \epsilon_t$	Strain
$E, E_o, E_1, E_2, E_t, E_n$	Time dependent modulus
E', E''	Loss and gain modulus
a_T, b_T	WLF -shift factor
ω	Frequency
ν	Poisson's ratio
λ	Extension ratio
$t, t_o, t_{0.1}, t_{1000}, t_c, t_n$ (Use of these symbols are clear with the context)	time
τ, τ_o, τ_n	Relaxation time
T, T_o	Temperature (0K)
ρ, ρ_o	Density
R	Gas constant
k	Boltzman's constant
D, D_o (Use of these symbols are clear with the context)	Diameter
a, A, A_o	Area
α_o	Contact angle
w	Contact width

v, v_r, v_s	Volume fraction
χ	Interaction parameter
M_c	Average molecular weight
N	Number of stress supporting links
r_1, r_2	distance vectors between chain ends
t_s	Sample thickness
t_g	Thickness of the glass plates
t_c	Cavity depth of the jig
P, P_c, P_i, P_s	Pressure

Chapter One

BACKGROUND

1.1 INTRODUCTION TO THE PROBLEM

Elastomers are widely used in engineering applications such as seals, gaskets, bearings and hoses. It is known that during their service, these components are subjected to deformation of various types and levels. Several methods are currently available to evaluate the ageing of rubbers independent of the purposes for which they are to be used. Standard measurements of tensile strength, hardness and elongation at break may not, however, give a solution to the evaluation of ageing. This is because the ageing of undeformed rubber is different from that of one under stress. Considerable interest is therefore shown in the measurement of properties like stress relaxation of rubbers either in tension or in compression; statically or dynamically deformed.

The long term properties of elastomers can result from two fundamentally different processes. First, there can be physical relaxation processes such as the rearrangement of chains and the movement of crosslinks and entanglements. Second, there can be chemical processes such as scission of covalent bonds at crosslinks or along the main chain. Tobolsky¹ was probably the first to recognise that stress relaxation could be caused by a chemical process; he identified this by performing experiments at elevated temperature. Murakami and coworkers² used experiments in a nitrogen atmosphere to separate the different processes; they assumed that chemical processes are due to presence of oxygen and that no chemical change occurs at low temperatures.

It can be further argued that by having a suitable technique to separate the physical and chemical responses one from another, it is possible to predict the total relaxation in the rubber component for the specified conditions at any given time or temperature, with reasonable accuracy, by adding the physical and chemical contributions.

Stress relaxation measurements can be reliable and useful³⁻⁵. However, they

have many inherent drawbacks too, as discussed later in this work. The purpose of the present research is to find a reliable technique which can be used universally and easily and at the same time serves the sealing industry in predicting the required longevity in service. A way out for this is to find a new type of test or to postulate a new mathematical model to fit the complicated behaviour. Recovery is a new methodology proposed for this purpose and discussed later in Chapter 5.

Combining the stress relaxation and recovery measurements, it may be easier to deduce a suitable mathematical model. This will not only reduce the problem of running expensive stress relaxation tests over very long periods of time but also prevent the danger of erroneous extrapolations. Using the data from stress relaxation and recovery tests coupled to a suitable extrapolation theory could provide a potentially powerful tool for long term prediction of rubber properties. The subsequent chapters in this thesis are devoted to exploring the above hypothesis.

1.2 ELASTOMERIC MATERIALS

The unique property of elastomers- that from which their name derives- is their ability to undergo large elastic deformations, that is to stretch and return to their original dimensions. The term 'rubber' and 'elastomer' embrace those polymers which have useful rubberlike, highly elastic properties at ambient temperatures. However, many polymers which are non-rubbers by themselves can be modified physically or chemically to give useful products with desirable properties. Generally this requires long chain molecules consisting of many repeat units which can rotate fairly freely about their backbone bonds. The molecules when deformed attain a new conformational entropy which can drive the polymer network back to its original shape and size when the deforming force is removed. This requires the molecules to experience little or no restriction to movement. This is true when the polymer is amorphous and some 50°C above its glass transition temperature [T_g]. In order to prevent permanent movement (or flow), crosslinks are introduced which give a three dimensional polymer network structure as shown in Figure 1.1.

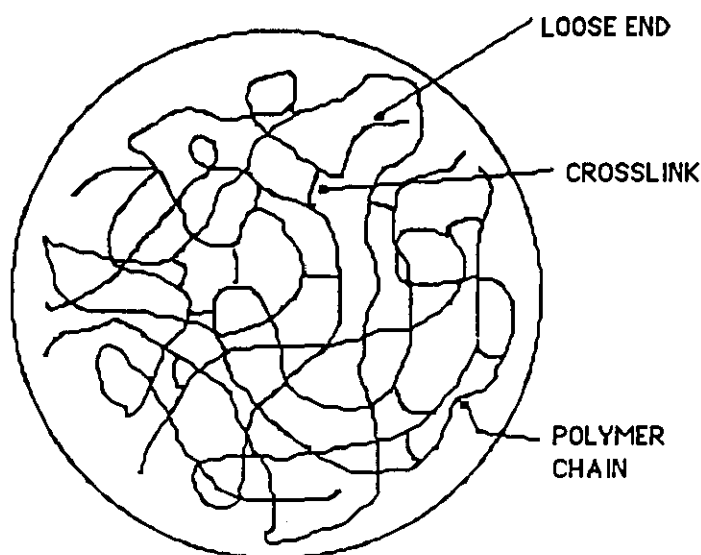


Figure 1.1: Schematic diagram of a three-dimensional crosslinked elastomeric network.

In conventional rubbers the introduction of these crosslinks is carried out through a process known as '**vulcanisation**'. Several different processes are presently available; the selection of the technique depends upon the nature of the base polymer, the final properties desired and the economics of manufacture. The majority of these are either sulphur vulcanisation or peroxide curing systems. The complexity of the particular process and its implication to product design are reported in the literature.⁶⁻⁸

Unfortunately, chemical crosslinks render the material insoluble and incapable of being further shaped by the application of heat and pressure. At the same time, crosslinks are necessary to provide enhanced physical properties (tensile strength, permanent set and lower stress relaxation and hysteresis). Thus, it can be argued that combining the thermoplasticity of a hard plastic component with the elastic properties of a soft rubbery block [Figure 1.2] can provide a new generation of elastomer.^{9, 10} These new materials are known as 'Thermoplastic Elastomers' [TPE, TPR, TPV]* or polymer blends of various types.

* TPE stands for Thermoplastic Elastomer, TPR for Thermoplastic Rubber and TPV for Thermoplastic Vulcanisate

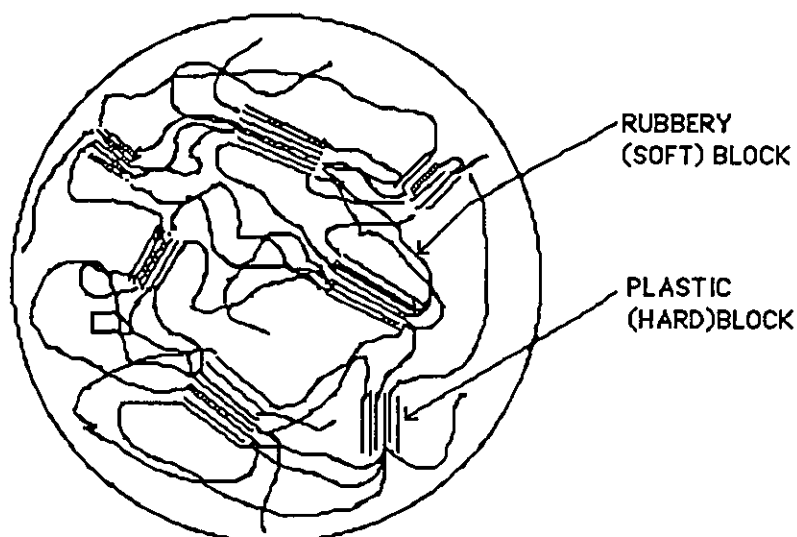


Figure 1.2: Schematic diagram of a thermoplastic elastomer system showing hard and soft blocks.

1.2.1 Thermoplastic elastomers (TPE's, TPR's and TPV's) *

These are new generation of elastomeric materials with the major advantage of reprocessability. They also possess other advantages over traditional rubbers; their greater speed and ease of processing and possibility of a wide range of colouring with elimination of the compounding stage prior to manufacture. They do not generally have resistance to high temperature, oil and solvent attack but this is now overcome by either proper selection of high resistant plastic and rubbery components or introducing crosslinks during mixing. Hence it is possible to have a wide variety of thermoplastic elastomers ranging from phase separable to single phase systems or even thermoplastic vulcanisate (TPV's) using dynamic vulcanisation.

In order to exhibit rubbery behaviour, a material must have a low glass transition temperature [T_g], the structural features must cause the material to retract after stretching (possible in a vulcanisate due to the presence of crosslinks). For thermoplasticity, these crosslinks must be heat fugitive

* TPE stands for Thermoplastic Elastomer, TPR for Thermoplastic Rubber and TPV for Thermoplastic Vulcanisate

(thermally labile). In a thermoplastic elastomer (TPE) network this is generally achieved by one of the following processes.

- ionic crosslinking
- crosslinking by hydrogen bonding
- thermally unstable covalent bonding
- linking of molecules by crystalline domains
- use of block copolymers

TPE's can also be manufactured either by modifying a thermoplastic material such as PVC, PP and PS to exhibit increased elasticity or by inducing inbuilt elasticity during polymerisation as in PU, copolyesters or copolyamides. Block copolymers attracted major attention when Shell Chemicals [U.S.A.] followed by Phillips Petroleum in U.S.A. developed the first thermoplastic rubber with styrene and butadiene monomers giving S-B-S block copolymers. Depending upon the structure and number of blocks used, these can be classified as follows.

- S-B diblock (Styrene - butadiene)
- S-B-S triblock (Styrene - butadiene - styrene)
- S-I-S triblock (Styrene - isoprene - styrene)
- S-E-B-S saturated triblock (Styrene -[ethylene - butadiene] - styrene)
- Radial mono-, di-, or multi-chain (styrene - butadiene)

More recently blending of different miscible polymers has provided an interesting solution to combine the thermoplasticity and elasticity of the two components. Fig. 1.3 describes the various types of copolymers. Segregation of molecular chain with dissimilar repeat units give rise to hard and soft phases. The hard domains serve as crosslink points for the flexible rubbery blocks and also provide reinforcement to the matrix. These rigid blocks, because they are below their glass transition temperature [T_g] or melting point [T_m] during service, can be thermally reversible. Hence thermoplastic elastomers have the advantage of thermo-processing and scrap recycling over conventional thermoset elastomeric compounds. However, such an alloy or polyblend may undergo phase separation. This is avoided by having inter- penetrating networks [IPN's] or by mechano-chemical polyblends with psuedo- crosslinks. In practice, dynamic

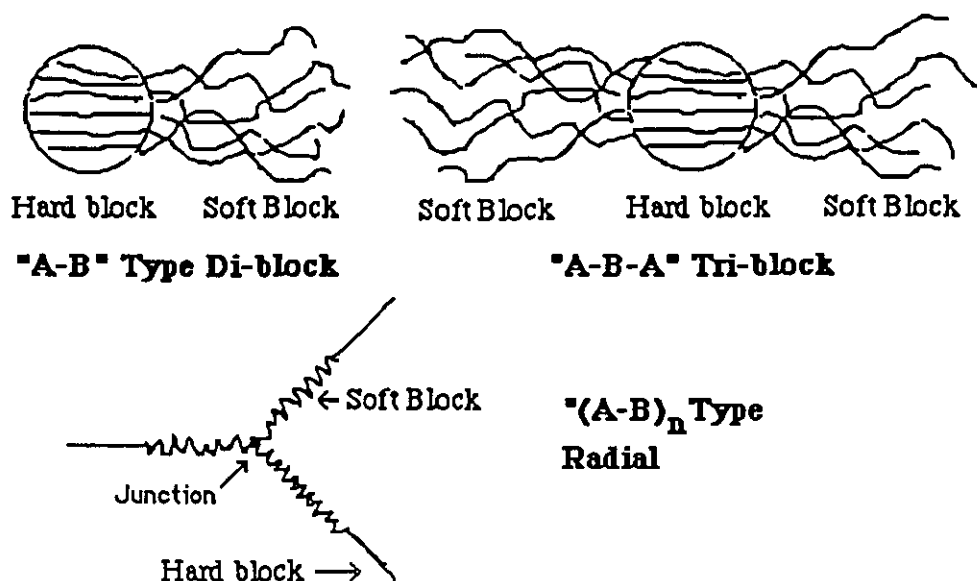


Figure 1.3: Schematic diagram of types of block copolymers

vulcanisation [DV] is used to achieve this, where a small amount of crosslinking agent is added to the blend during the compounding operation.

1.2.2 Theory of Vulcanisation:

Vulcanisation [*- after the Roman God of fire -Vulcan*] is a process in which intermolecular, chemical crosslinks are introduced between large polymer molecules by the application of heat and/or pressure with the addition of appropriate elements, to reduce plasticity and increase elastic properties of the compound. Vulcanisation thus increases the retractive force and reduces the permanent deformation(set) remaining after the removal of force.

According to the theory of rubber elasticity and the entropy effect ¹¹, the retractive force depends upon the length of molecular segments between two support points. In an unvulcanised rubber [raw gum compound], above its melting point T_m , only chain entanglements provide junction points and their number depends upon the length of molecule i.e: the molecular weight. Vulcanisation, on the other hand, generates these junction points by introducing chemical bonds. The type and nature of these bonds are functions of the vulcanisation system used and the processing conditions imposed.

There are various types of crosslinks, of which the following four are important.

- chain of sulphur atoms or a sulphur bond
- Carbon-Carbon link
- poly-valent organic radicals
- poly-valent metal ions

1.2.3 Effect of vulcanisation on properties of elastomers:

During vulcanisation, long chains become crosslinked with the vulcanisation agent, to form a three dimensional structure. This reaction transforms the soft, weak, plastic-like material into a strong, elastic, engineering material. It has been said earlier that the main reason for vulcanisation is to introduce chemical links between polymer molecules; this means a measure of crosslink-density should provide the solution to the amount of vulcanisation occurring in a particular process.⁷ The change in properties of the vulcanisate for increasing crosslink density are depicted in Figure 1.4.

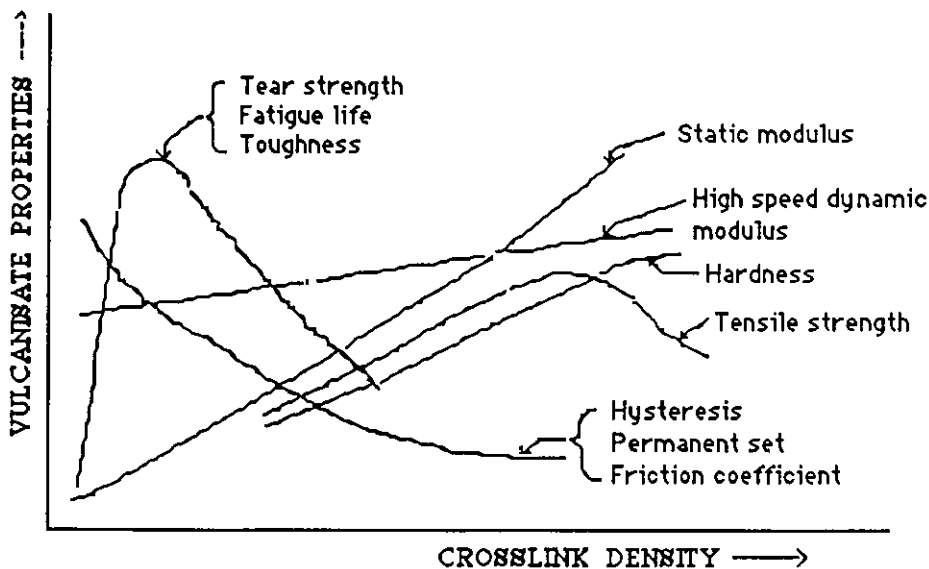


Figure 1.4: Effects of vulcanisation on elastomer properties.⁷

Comparing the changes in static modulus, a measure of the elastic component, to the dynamic modulus [a composite of viscous and elastic components], it is

clear that there is a change of the plastic or viscous property into the elastic or viscoelastic property during the vulcanisation process. Other properties such as tear strength, toughness, hardness and tensile strength either increase with the formation of crosslinks or pass through a maximum. Hysteresis, permanent set and stress relaxation reduce. It should be noted that all these properties are functions not only of crosslink density but also of type and nature of the crosslink, the base polymer, type and amount of the filler used. Further details can be found in the literature.^{6-8,12}

Reversion is a term applied to the deterioration of network structure or in other words chain scission. It is usually associated with diene rubbers such as natural rubber (NR, IR), which are sulphur vulcanised. These rubbers have a large number of unsaturated double bonds in the polymer molecule; coupled with this, a high amount of poly-sulphidic bonds due to poor or non-efficient vulcanisation process are also present. These weak bonds are believed to be the principal reasons for instability.^{2, 4, 8, 13}

1.2.4 Types of Vulcanisation:

For a general purpose rubber with carbon-carbon double bonds, sulphur is commonly used as a vulcanising agent. However, there are various curing systems, some highly specific to individual elastomers; these include:

- accelerated sulphur,
- sulphur donor,
- peroxide,
- phenolic resin,
- nitroso and urethane and
- radiation curing system

Of the above, the first three are considered important as far as the materials used in this work are considered. The discovery of sulphur vulcanisation is credited to Charles Goodyear in 1839 but was not harnessed commercially until 1843 by Thomas Hancock.

1.2.5 Sulphur Vulcanisation

The chemistry of sulphur vulcanisation is so complex that even today, a coherent understanding of only the main stages is possible. The unravelling of this complex reaction has involved efforts of many scientists such as Moore (1964), Dibbo (1966), Juve (1956) etc.

A simplified picture of a gum (sulphur) vulcanisate is shown in Figure 1.5. It comprises the network and extra-network material, the latter consisting of unreacted vulcanising ingredients and products of the vulcanisation reaction which are not combined with the network. The network consists of the main chain of original rubber molecules and the crosslinks along with modifications to the main chains. A crosslink may be present as mono-sulphide, di-sulphide, poly-sulphide [Figure 1.5a]; it may even be present as cyclic-sulphide [Figure 1.5 b] or pendant groups [Figure 1.5 c]. The unreacted material forms an extra-network structure [Figure 1.5 d]. A conventional sulphur vulcanisate may give an average of 40-45 sulphur atoms per crosslink whereas an accelerated vulcanisate may have 10-15 sulphur atoms. If an efficient vulcanisation system is adopted this figure may drop further to 4-5 atoms and even lower if a non-sulphur curing system is used.^{6,8} The relative amount of mono-, di- and poly-sulphide crosslinks can be assessed with chemical probes and if the crosslink density is known, one can estimate the amount of pendant and intramolecular sulphur which is present in the given network.

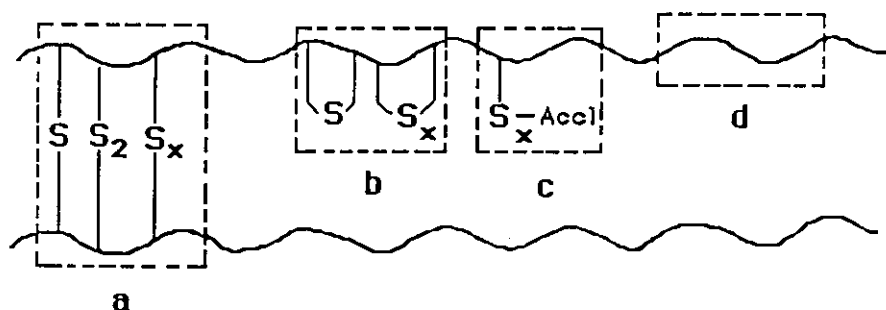


Figure 1.5: Simplified vulcanisate structure

- | | |
|-----------------------|---------------------------|
| a. Sulphur crosslinks | b. Cyclic sulphides |
| c. Pendant group | d. Extra network material |

1.2.6 Mechanism of stress relaxation in sulphur vulcanisates:

All the vulcanisates undergo thermal scission and depending upon the stability of the network and severity of the environment they degrade to different degrees. Mono- and di-sulphides are more stable links thermally, when compared to cyclic and polysulphidic bonds which can undergo exchange reactions without any alteration to the amount of crosslink density in the network. According to Tamura and Murakami,¹³ the bond dissociation energies of these links are given in the following Table 1.1.

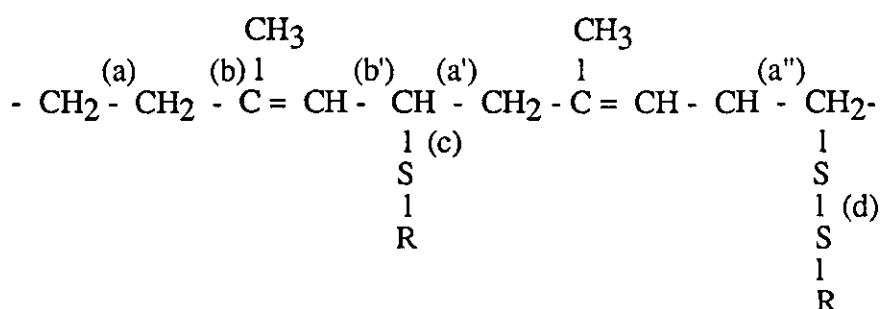


Table 1.1: Bond dissociation energies in a typical rubber network

Type of bond	Dissociation energy	Type of bond	Dissociation energy
a	93 kcal / mol	a'	unknown
a''	unknown	b,b'	90- 93 kcal / mol
c	50-60 kcal / mol	d	25-40 kcal / mol

The high accelerator / low sulphur system (the efficient vulcanisation) can be of great interest as far as ageing properties are considered. But reducing the sulphur content below 0.5 phr may not be feasible. This can be overcome by use of sulphur donors in the recipe. They are of two types; the former act as sulphur donor and accelerator eg: TMTD (tetra-methyl thiuram di-sulphide), the latter act only as a sulphur donor as in DTDM (4,4'-di-thio di-morpholine).

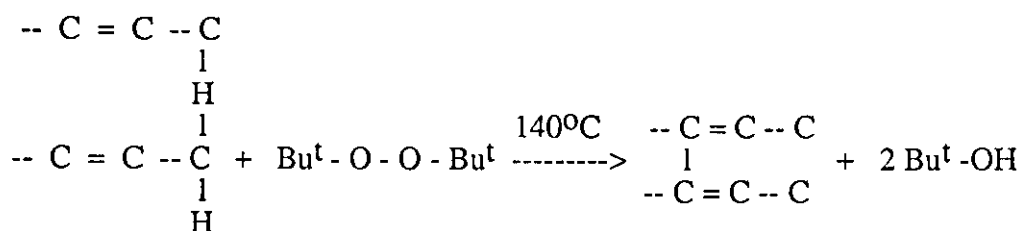
According to Cunneen¹² the effect of accelerators, zinc oxide, zinc soaps or

TMTD 'sulphurless' recipes is to simplify the network structure by reducing the cyclic sulphide formation. This will result in a reduction in main chain scission. Thus it is possible to achieve as high as 90 per cent of the crosslinks as mono-sulphidic using sulphurless vulcanisation (sulphurless vulcanisation is an vulcanisation process with no elemental sulphur in the recipe, but the sulphur is, however, available in the accelerator used). Cunneen¹² also believed that introduction of carbon black into EV system has little effect on the structure of the vulcanisate, but with accelerated sulphur recipes it increases the density of crosslinks and reduces the polysulphidic nature of crosslinks.

1.2.7 Peroxide curing system

The peroxide system, structurally the simplest type of thermoset, was first introduced by Ostrosmislenskii ¹⁴ in 1915 using benzoyl peroxide with natural rubber but remained a laboratory curiosity until 1954 when Braden et.al.¹⁴ used di-cumyl peroxide to achieve low creep and compression set properties.

As in sulphur vulcanisation, peroxide cross-linking also involves a very complex series of reactions. During mixing, the peroxide decomposes to give free radicals on the main chain polymer which combine together to form a C-C link. For example, using a simple olefin with di-t-butyl peroxide, the chemical reaction can be written as follows:



However, in rubber mixing, there are several other ingredients and the chemistry involved is far more complicated. The details of these chemical reactions are not given here but can be found in the literature.⁶⁻⁸ Because peroxide curing systems produce C-C bonds between polymer molecules, thermally stable networks result. This is because the dissociation energy of the C-C bonds is higher than those of S-X links, as can be seen from Table 1.1. Hence, these compounds are superior in ageing and stress relaxation properties.

However, stress relaxation due to breakdown of the C-C links in the main chain is still a problem and is unavoidable.

The formulation of a commercial rubber compound for any particular product such as seals and tyres contains many different chemicals. The amount of each ingredient and the order of addition during compounding is highly critical as far as the final properties of the vulcanisate are concerned. A typical formulation generally includes a base polymer, filler, curing agent, accelerator, stabiliser, anti-oxidant, anti-ozonant, lubricant, processing-aid and pigment. A large amount of filler is generally added not only to reduce the cost of the material but also to provide reinforcing effects with improvement in abrasion resistance, wet-grip and protection against photo-degradation.⁸

1.3 THEORY OF RUBBER ELASTICITY

The high elasticity and extensibility of rubber like polymers are their most striking characteristics. An amorphous crosslinked specimen of rubber may suffer a very high strain and still return to its original dimensions, with no, or very little 'set' [unrecovered deformation], while it shows negligible dilation (change in volume). The equilibrium stress of a rubber network, which is a result of the strain energy stored by the reduction of entropy^{15,16} of molecular segments, can be predicted with a reasonable accuracy using the *statistical theory of rubber elasticity*.¹⁶

According to this theory, the stress σ in the rubber chain with extension ratio λ can be written as:

$$\sigma = NkT (\lambda - \lambda^{-2}) \quad 1.1$$

where N is the number of stress supporting links in the network, k is the Boltzman's constant, T is the absolute temperature and the extension ratio λ is the ratio of the final extension and the original length. This derivation has been subjected to constant investigation to account for its accuracy and correction factors due to the effects of chain-ends,¹⁷ effects of filler¹⁸ were included to

yield the modified expression:

$$\sigma = N'kT (\lambda - \lambda^{-2})[1 + 2.5 v + 14.1 v^2] \quad 1.2$$

where N' is the value of N after correction and v is the volume fraction of filler in the rubber compound. If λ and T are constants, then the stress σ is proportional to N . During a degradation process the change in crosslink density thus reflects in the corresponding change in the force, from σ_0 to σ . Thus the above equation can be reduced to:

$$\frac{\sigma}{\sigma_0} = \frac{N}{N_0} \quad 1.3$$

Thus, the decay in stress is a direct measure of the degradation of the elastomeric network.

The stress-strain relationships of the statistical theory of rubber elasticity are considered to define the properties of an ideal rubber, in a similar way as the kinetic theory of gases is used to postulate the properties of an ideal gas. Thus the theory predicts the equilibrium gum vulcanisate stress-strain relationship for any given strain using a single elastic constant (ie: NkT , or G , the shear modulus), and predicts that the rubbery modulus will be a function of the degree of cross-linking (ie: $G = NkT = \rho RT/M_c$)

The experimental verification of the theory is credited to Treolar¹⁹, who worked on natural rubber gum vulcanisate in uniaxial compression, extension and shear. The results agreed well to a first approximation up to several hundred percent of strain where strain induced crystallisation or non-linear viscoelasticity, or both, are believed to become important (refer to Figures 1.6 and 1.7). However, the data are usually better represented by the two-constant empirical Mooney equation:

$$\sigma = 2 (\lambda - 1/\lambda^2) (C_1 + C_2/\lambda) \quad 1.4$$

where C_1 and C_2 are Mooney constants. By comparing Equations 1.1 and 1.4, if

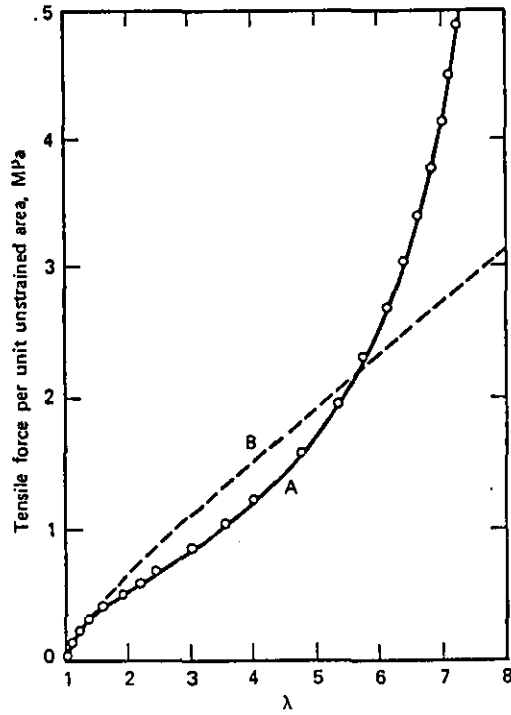


Figure 1.6: Force-extension curve for uniaxial extension 19
A- experimental; B- theoretical

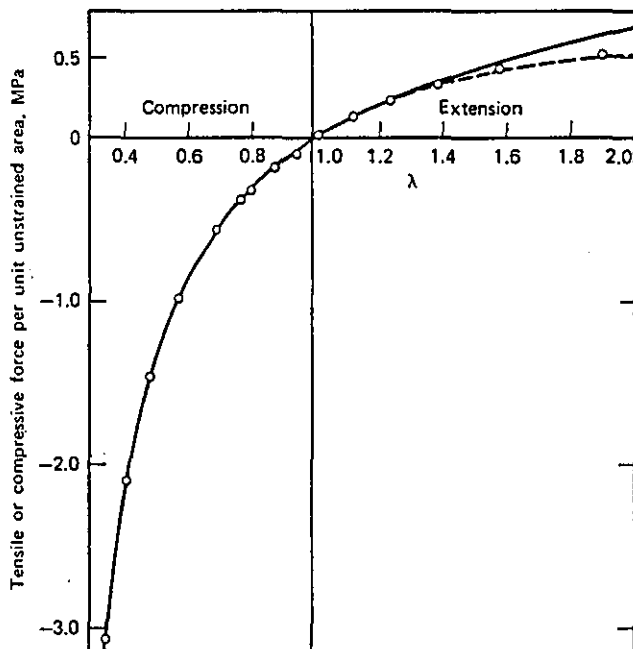


Figure 1.7: Uniaxial extension and compression 19
Broken curve- experimental; Full curve- theoretical

$2C_1 = NkT$, then the value of C_2 should give a measure of non-linearity of the system. The detailed theory is not appropriate in this review, however, more information can be found in the literature^{16,19,20}. The applicability of this to the compression stress relaxation measurements is discussed later in Chapter 4.

On the other hand, *the theory of viscoelasticity*²¹ leads to the prediction of the change of molecular conformations towards their equilibrium states. The mathematical models of linear viscoelasticity, frequently illustrated by using the responses of spring and dash pots, and the modified versions to account the nonlinearity of polymers are discussed later in Chapter 7. To appreciate the relevance of these two theories to stress relaxation phenomena, the molecular behaviour under deformation must be considered.

When a rubber network is subjected to a deformation, backbone chains have to undergo the necessary conformational changes,¹⁵ to accommodate the imposed deformation. For example, assuming that the chain changes its conformation from its original position OA to a new position OB as shown in Figure 1.8; the rate of change of conformation depends on two factors, namely:

- a) distance between the old and new conformations
- b) the time element of the chain in changing its conformation,
ie: the sluggishness

The above two parameters are generally dependent on factors such as the level and rate of strain, addition of filler, amount of crosslinks.

Thus, according to the kinetic theory²¹, this can be written as:

$$\frac{d\Delta}{dt} = -\frac{\Delta}{\tau} \quad 1.5$$

where Δ denotes the conformational deviation,
 $\tau\Delta$ denotes the retardation time, which is a measure of sluggishness of the molecule.

Figure 1.8 shows the behaviour of the chain after the chain length vector is changed from its most probable to another arbitrary value. The conformational change occurring after the deformation has ceased is termed '*physical*'

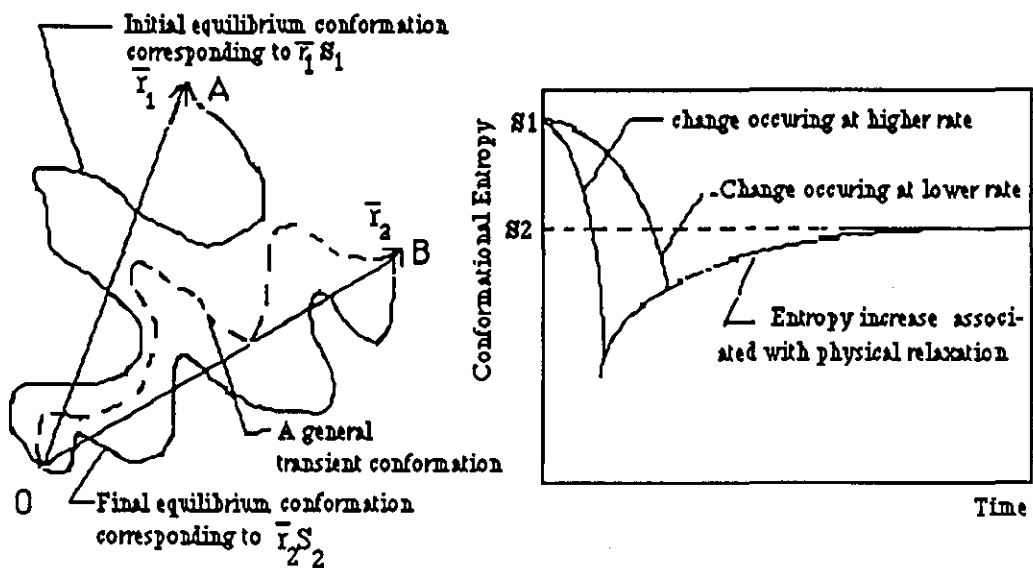


Figure 1.8: Schematic representation of a conformation and the associated entropy of a molecular chain during a deformation process.

relaxation' and is the heart of the viscoelastic theory. However, this assumes that no breakage of the molecule occurs. Nevertheless, depending upon the material properties and environmental conditions, additional relaxation occurs due to main chain and crosslink scissions and such relaxation is known as '*chemical relaxation*'. Further, it can be concluded that the more sluggish the chains, the more significant is the physical relaxation. Also, greater the damage to the network, higher is the chemical relaxation.

1.4 ELASTOMERIC SEALS

1.4.1 Introduction and types of seals

A large variety of seals is available for closures, for pressure vessels, for flexible joints and for valves. These can be analysed under the following headings.

CONFINED GASKET

The O-ring is a typical example. (Figure 1.9 a) Initial sealing is afforded by the

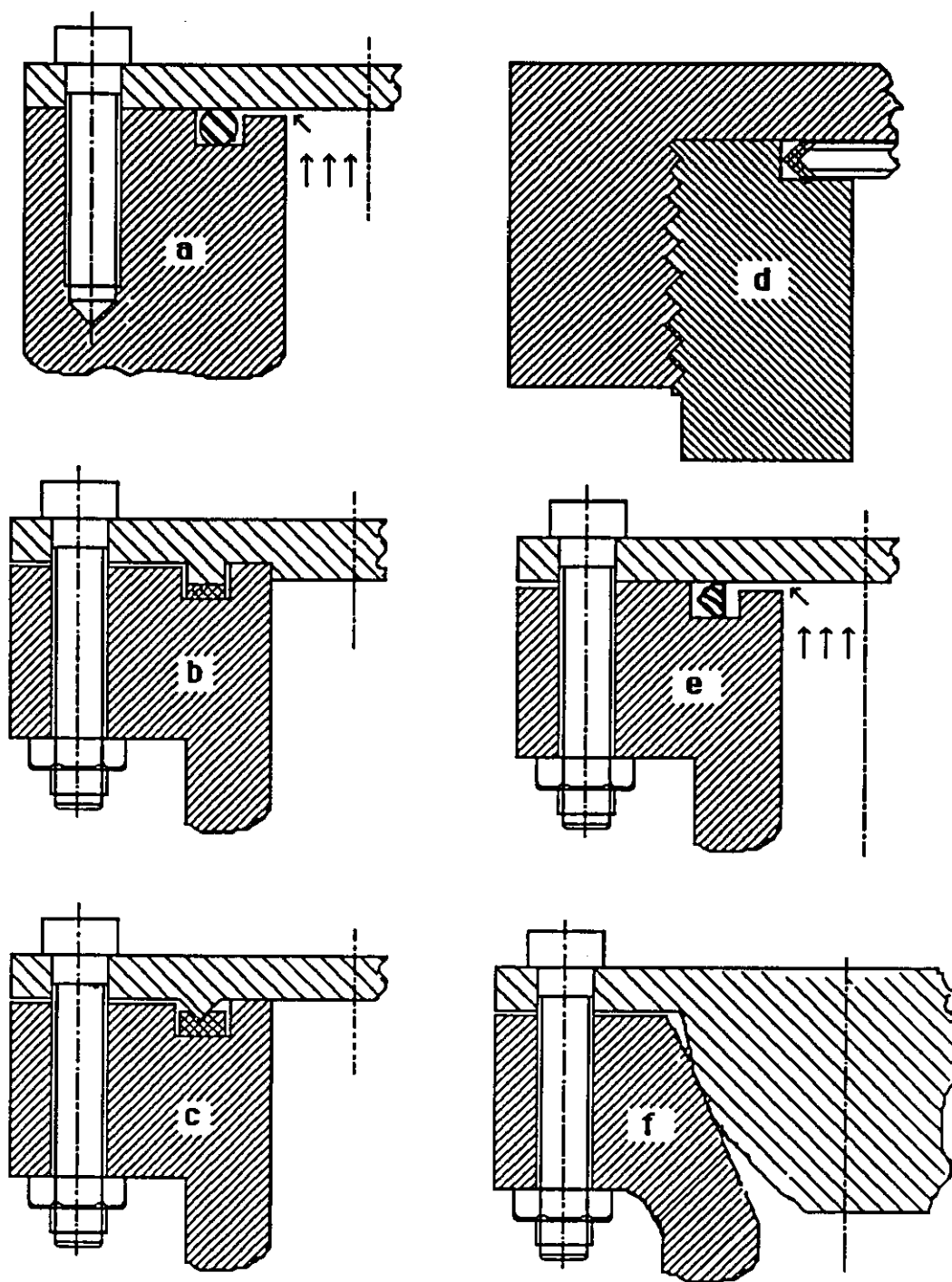


Figure 1.9 SEAL DESIGN FOR LOW PRESSURE VESSEL

- | | | |
|-------------|--------------------|-----------------------------|
| a. O-ring | b. Confined gasket | c. Confined indented gasket |
| d. Vee-ring | e. Delta-ring | f. Metal-to-metal seal |

diametral compression of the O-ring. When internal pressure is applied, the O-ring is forced against the side of the groove. Extrusion, which limits the use of this design above moderate pressures can be reduced by back-up rings, extending the use of these types even for high pressure applications.

COMPRESSED GASKET SEALS (POULTER SEALS):

This is illustrated in Figure 1.9(b) and (c). The pressure developed in the gasket P_g by closing and tightening the end closures prevents leakage until the internal pressure P_i becomes higher than P_g . It should be borne in mind that the sealing force, hence P_g , reduces with time due to inherent stress relaxation.

SELF ENERGIZING RING SEALS: [Figure 1.9 (d), (e)]

These are similar in concept to the above, but the sealing stress between the ring and pressure -vessel body and closure is provided by the elastic distortion of the ring. A variant [Figure 1.9 (f)] uses the elastic distortion of the vessel body to provide a sealing surface between body and closure. Some of these seals also utilise the pressure energizing principle.

PRESSURE ENERGIZED SEALS [BRIDGEMAN SEALS]:

These use the principles of unsupported area to provide the condition $P_s > P_i$. With reference to Figure 1.10, if the internal pressure P_i acts over the total area A , and the pressure of the packing P_s is constrained over the area $[A-a]$ where 'a' is the unsupported area, then

$$P_s = P_i \frac{A}{[A-a]} > P_i \quad 1.6$$

The seals shown in Figure 1.11 (b) use anti-extrusion rings to prevent gasket extrusion, and can effectively seal even leak-prone gases. In the ring seals shown in Figure 1.9 (d) and (e), initial sealing is provided by the elastic distortion of the ring, but at higher pressure they effectively act as unsupported area seals. Similarly, a back O-ring seal [Figure 1.11 (b) and (d)] can function

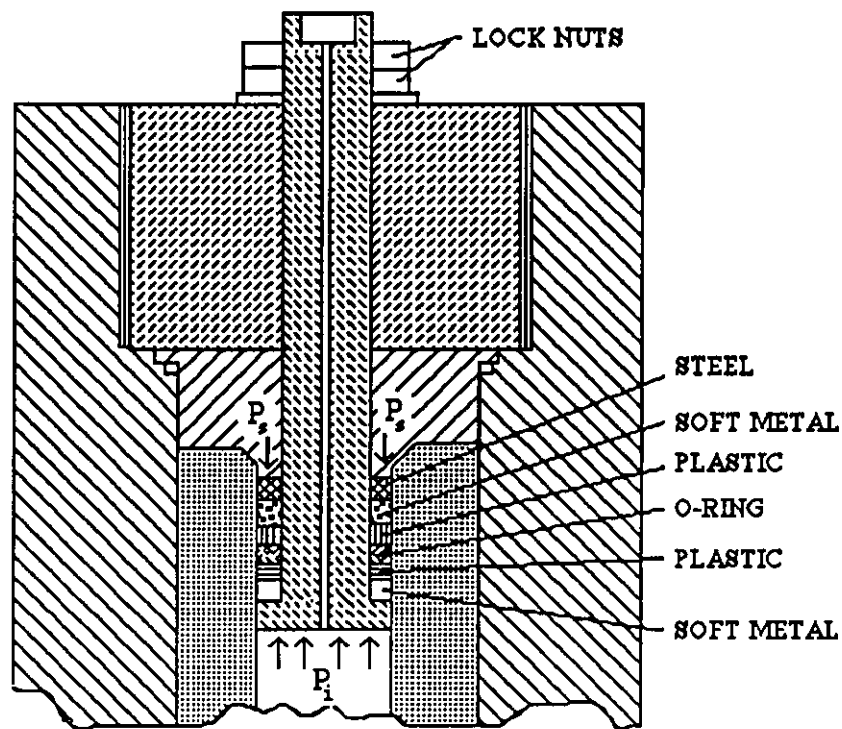


Figure 1.10: Schematic diagram of a Bridgeman seal

in this way over a limited pressure range until the backing is forced completely against the groove wall. The design shown in Figure 1.11 (d) uses an O-ring to give an initial seal pressure and the metallic sealing element acts as an unsupported area element until plastic flow reduces the unsupported area. With a tough steel back-up ring, this type of seal may withstand very high pressures.

Seals should be selected with great care to serve the particular process for which they are intended. From a safety standpoint, it is very important to provide adequate vent holes should a leak occur. In addition, retaining bolts should be torqued to the correct value and not over tightened, nor should these bolts be tightened when a leak occurs in the pressurised vessel.

The following points are to be considered during a selection process.

- The rated internal pressure and the design stress in the joint and seal.
- Effects of temperature on the assembly and in particular on the seal.
- Effects of environment in which the seal is intended to function.

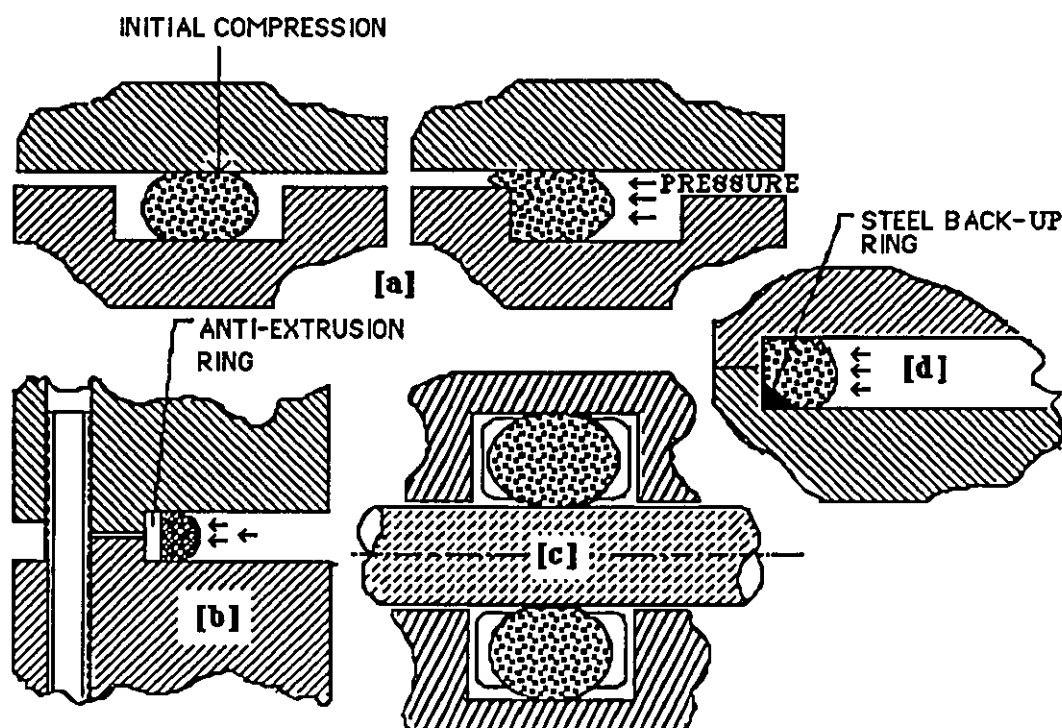


Figure 1.11: Classification of O-ring seals depending on function

- d) Effects of corrosion, bearing in mind that it increases with increasing pressure and temperatures.
- e) Effects of biological degradants eg: Fungi and bacterial attack.
- f) Effects of voids, cracks and areas of stress concentration.

1.4.2 Current rubber seal specifications:

The current generation of rubber seal specifications were written primarily for the rubber manufacturer and not for the consumer. This is because the tests covered in these specifications are based on short term qualitative test methods on individual polymers. Hence, these are inadequate for the prediction of long term performance.²² These specifications cover a group of properties which include stress relaxation, compression set, heat ageing, oil swell, tensile strength and elongation at break.

1.4.2.1 Selection of test temperature

BS 903 Part A 35-1985 defines the test temperatures and humidity conditions

for the testing of vulcanised rubbers. The standard temperatures are 23, 40, 55, 70, 100 and 125° C with a tolerance of ± 1 or $\pm 2^\circ$ C and a standard humidity of 50% RH at 23° C or 65% RH at 27° C. The conditioning periods are > 16 h for the test temperature and humidity or >3 h. for the temperature condition only.

1.4.2.2 Determination of Compression set

In this test, as described in BS 903 Part A 6 or ASTM D-395-85, the recovery of rubber test buttons after being compressed to a standard strain (or stress) is measured. The compression period is normally 24 h. at 70°C, alternatively 72 h. at 23° C. Recovery takes place at room temperature and the 'set' measurement is taken after 30 min. The compression set is expressed as:

$$\% \text{ Set} = \frac{t_o - t_r}{t_o - t_c} \times 100 \quad 1.7$$

where t_o is the original thickness of the specimen before compression, t_c is the height of the specimen during the compressive strain and t_r is the height at any given time after the strain is released.

1.4.2.3 Accelerated ageing test:

Rubber compounds suffer from network degradation as a function of temperature, time and environment. Qualitatively, a heat ageing test can be used to assess the damage to the network.

In BS 903 Part A 19, heat ageing and pressured oxygen tests are detailed. In the oxygen ageing test, specimens are exposed to pure oxygen at elevated temperature and pressure and the consequent changes in physical properties are measured. This may over-emphasize the actual situation. In the heat ageing test, the test pieces are exposed to elevated temperatures for a specified length of time (eg: at 70°C for 168 h) and the changes in tensile strength are measured. However, this again cannot simulate actual service conditions due to differences in size, chemical kinetics, stresses etc. That is why the specification warns the user of the danger of predicting service life

using the above technique by raising temperatures and also recommends the test temperature to be as close as possible to the service temperature.

1.4.2.4 Resistance to liquids

In this test, BS 903 Part A 16, the resistance of rubber vulcanizate to standard test solutions, such as 70% 2,2,4-trimethyl pentane/30% toluene, at the standard temperature is measured. The changes in swelling and other physical properties are also recorded.

1.4.2.5 Rubber Seal Specifications

The present seal specification is BS 2494 -1986²³ which controls the physical properties. It covers a range of rubbers depending upon the purpose of seal and broadly divides into five different classes. They are W, D, G, H and S; where W for water, D for drainage, G for town gas and other hydrocarbon gases, H for hot potable water and low pressure steam and S for hot non-potable water.

The standard specifies performance requirements and gives test methods for the above types of elastomeric seals. Table 1.2 shows the requirements set by this standard for Type W seals used for potable water. The implications of this standard to the science of rubber seal and to the consumer are discussed later in this thesis.

1.5 STRESS RELAXATION

1.5.1 Introduction

When an elastomer is deformed and held at a constant strain, the induced stress will decay with time. This process is referred to as stress relaxation. On the other hand, when a constant stress is imposed, the resulting deformation increases continuously with time; this is known as creep. When the stress or strain is removed, much of the strain is eventually recovered; the deformation that remains is known as 'set'.

Table 1.2: Physical properties for Rings of Type W (water)

Property	Unit	Test method	Test piece (see 3.7)	Hardness range					
				35 to 45	46 to 55	56 to 65	66 to 75	76 to 84	85 to 91
Tensile strength, min.	MPa	BS 903 : A2	BS 903 : A2 : 1971, type 2 or as in appendix C*	9	9	9	9	9	9
Elongation at break, min.	%	BS 903 : A2	As above	400	375	300	200	125	100
Hardness (microtest)	IRHD	BS 903 : A26	2 mm minimum thickness*	Within 3° of specified hardness					
Compression set, max., 23 °C, 70 h	%	BS 903 : A6	BS 903 : A6 : 1969, type 1 or 5 mm dia. X 3.5 mm or 7 mm dia. X 3.5 mm*	12	12	12	15	15	15
Compression set, max., 70 °C, 22 h	%	BS 903 : A6	As above	20	20	20	20	20	20
Stress relaxation, max.	%	BS 903 : A42 23 °C	BS 903 : A42 : 1983, type 1	13	13	15	15	18	18
Water absorption, swell, max.	%	BS 903 : A16 volumetric method, 70 °C, 168 h	As specified	8	8	8	8	8	8
Low temperature hardness change, max. from 23 °C value (normal test)	IRHD	Appendix D 0 °C, 70 h	As specified*	5	5	5	5	5	5
Ozone test	—	BS 903 : A43 : 1982 procedure A, 5 % strain, 30 °C, 24 h, 10 p.p.h.m. ozone, 55 ± 5 r.h.	As specified	No cracking visible under X7 magnification					
Accelerated ageing, 70 °C, 168 h		BS 903 : A19 : 1975 Method A or B†							
Tensile strength, max. change of original	%	BS 903 : A2	Same type of dumb-bell as used for 23 °C test	20	20	20	20	20	20
Elongation at break, max. change of original	%	BS 903 : A2	As above	30	30	30	30	30	30
Hardness (microtest) max. change	IRHD	BS 903 : A26	2 mm minimum thickness*	5	5	5	5	5	5

* The same size of test piece is required to be used for each batch and for any comparative purposes (see 3.7.1).

† Attention is drawn to the restrictions on method B given in 6.2 of BS 903 : A19 : 1975.

According to Gent ²⁴, these viscoelastic phenomena such as stress relaxation, creep, hysteresis and recovery are all different manifestations of what is presumably a single relaxation process. He suggested the following relations between the various entities and these were successfully applied to the experimental results on the gum vulcanisates of natural rubber and SBR compounds subjected to tension and shear. Accordingly, if the rates of creep C, stress relaxation S and recovery R are defined as:

$$C = (1/e)(\partial e/\partial t)_\sigma, \text{ OR } S = - (1/\sigma)(\partial \sigma/\partial t)_e \quad 1.8$$

$$\text{and } R = - (1/e_o)(\partial e/\partial t)_{\sigma=o} \quad 1.9$$

where e is the deformation at time t and σ is the applied stress, e_o is the original deformation and σ_o is the stress at e_o , then:

$$C = AS \quad \text{where } A = (\sigma/e)(\partial e/\partial \sigma)_t \quad 1.10$$

$$\text{and } R = BS' \quad \text{where } B = (\sigma_o/e_o)(\partial e/\partial \sigma)_{t, \sigma=o} \quad 1.11$$

where rate S' need not be equal to stress relaxation rate S. When the stress-strain curve is linear then $A=B=1$ (and is discussed in Chapter 4). Also, if no permanent structural changes occur during the relaxation process (ie: no chemical relaxation), then $S=S'$, a symmetrical relaxation process is possible. This may be the case when the temperature is low and the relaxation time is small. Gent,²⁴ in his work, employed gum vulcanisate at normal temperature in the tension and shear modes for up to 10^4 minutes. Under such conditions, chemical processes can be neglected; however, differences in rates of recovery and stress relaxation were found and attributed to the nonlinear viscoelasticity and is related to the stress-strain curve. Even though, approximately linear relations were expected in the shear mode, a similar discrepancy between recovery and relaxation rates was observed but the exact reasons were not made clear. In the present work, chemical relaxation processes at elevated temperatures and extended times are almost inevitable. Much effort has been expended in separating the physical and the chemical processes using various techniques; these are discussed in Chapter 7. However, difficulties were encountered in separation, particularly at lower temperatures and may be associated with carbon black. The exact nature of the filler relaxation due to the breakdown of filler-filler or filler-polymer bonds is still not clear and needs further work for a proper interpretation on the relaxation and recovery behaviour. As no work is done on the creep measurements in this programme, it is not possible to test the validity of equation 1.10. The application of the above principles is limited in the present programme and

is further discussed in Chapter 5.

Stress relaxation is a cumulative effect of a number of separate physical and chemical processes. Physical processes are due to viscoelastic nature of the elastomer and involve reorientation of the molecular network, the movement of entanglements and breaking of secondary valence bonds on the application of stress. Chemical relaxation mechanisms include chain scission of the rubber network through thermal and oxidative effects. Both types of process occur simultaneously but because of their different natures the times and temperatures at which one or the other dominates may be different. At high temperatures and at long times after the strain was imposed chemical relaxation dominates. It usually occurs as a linear function of time, and is sensitive to changes in temperature. Physical relaxation has been found to be an approximately linear function of log(time) for a wide variety of materials and is dependent on temperature. Other factors that may influence the stress relaxation behaviour of an elastomer include the nature of the crosslink,^{12,13,25,26} the presence of fillers²⁷ and the crosslink density.^{2, 13, 28}

1.5.2 Determination of Stress relaxation

British Standard specification BS: 903 Part A42 covers the stress relaxation property of vulcanised rubbers in compression. In this test, two methods are followed. In method A, the test piece is compressed at test temperature and is maintained at this temperature throughout the test period, where as in method B, the initial and all subsequent measurements are taken at $23 \pm 2^\circ\text{C}$ but the test piece is maintained at any desired standard temperature. In both the cases, standard, cylindrical disc shaped specimens are used, sandwiched between polished metal plates and compressed to 25 ± 2 or 15 ± 2 % strain within a period of 30 s. The initial reading (F_0) is taken after 30 minutes and the test normally runs for a period of not less than 168 hours. The stress relaxation is expressed as % reduction in counter force

$$\% R_t = \frac{[F_0 - F_t]}{F_0} \times 100 \quad 1.12$$

where F_t is the force at any given time t . The above test conditions only measure the physical component as the physical relaxation is dominant under

these conditions ($< 50^{\circ}\text{C}$), and do not provide any method of extrapolation or comparison of these data for different temperature or time scales.

In ASTM D 1390-76 ^e, a similar procedure is adopted with the test carried out at temperature of 100°C for 46 h, with a difference that the initial reading is taken 3 min. after the compression. This seems even less useful than the B.S. counterpart.

1.5.3 Modes of stress relaxation

Various types of rubber engineering components operate at temperatures substantially above normal ambient. For such components it is necessary to have some method of assessing the probable life span at these temperatures.

Stress relaxation (SR) is regarded as the most convenient method of evaluating rubber materials for sealing applications.^{22,29} In rubber components used as seals, gaskets for the transport of fluids like gas, water and sewage, compressive, tensile or shear strain occurs either continuously or intermittently. It is believed that continuous compression dominates the process. For components used in engines and hydrodynamic applications, dynamic loading may be involved. In order to study the sealing ability under dynamic conditions, stress relaxation should be measured with a dynamic compressive strain. This is referred to as dynamic mechanical stress relaxation or 'vibro-relaxation'. Bjork et.al.³⁰, Stenberg et.al.³¹ have studied long-term properties of natural rubber using dynamic relaxation. Hence stress relaxation tests vary over a wide range depending upon the particular application. In the past, the measurement of stress relaxation was usually carried out in tension and the majority of the references available to date follow this pattern. However, it was suggested that compression stress relaxation tests are more relevant for the analysis of sealing performance;^{4, 22} this is because not only do compression components dominate over the other two states but the product thickness differs widely from the sample thicknesses used in tension relaxation tests. The reason that the chemical relaxation is diffusion controlled,⁴ the tests conducted on thin samples as used in tensile relaxation measurements will not provide similar information to the behaviour of thicker samples. Hence, compression stress relaxation is studied extensively in this programme.

1.5.4 Physical stress relaxation [PR]

Visco-elasticity [time-dependent elasticity] arises from physical relaxation and is a vital factor in seal longevity. Physical relaxation can occur for a number of reasons, including physical movements of chains, aggregates or entanglements. This type of relaxation is dominant in the early stages of stress relaxation, particularly at low temperatures, and in turn consists of an early rapid relaxation with relaxation time of 10^{-6} - 10^{-2} s followed by slow decay over a period of 10^2 - 10^4 s. A third type of pseudo-physical process takes place through the breaking or forming of bonds between segments of rubber chain and carbon black particles;^{32,33} however, this is less well understood. MacKenzie and Scanlan³⁴ used double power law model to represent this additional strain dependent relaxation process attributed to the breakdown of rubber- filler bonds, with relaxation time between 10^5 and 10^6 s.

The time periods over which these processes occur is dependent upon the temperature of the rubber. As the temperature is increased, mobility of molecular chains is increased and the relaxation times will become shorter. At the temperature normally experienced by elastomer seals in Europe [$\approx 10^\circ\text{C}$] mobility is decreased and the physical relaxation process may dominate over many years. This is a major assumption of stress relaxation specification of BS 2494:1986,²³ which uses a physical relaxation rate measured over 168 h as a basis for determining long term stress relaxation properties. This assumption is only valid above the glass transition temperature of the rubber. Below this temperature the behaviour of the elastomer changes significantly.

Murakami³⁵ has pointed out that physical relaxation can occur due to breakdown of 'physical crosslinks'. These are fugitive crosslinks generally present in polymers containing a few functional groups to give rise to crosslinks between neighbouring chains; eg: hydrogen bonds, salt-linkages etc. Further work on the separation of physical relaxation from the chemical components proved that physical relaxation is independent of type of crosslink in the vulcanisates and is influenced only by the crosslink density. Bartnev and Lyalina³³ and Blokland and Prins³⁶ have suggested that physical relaxation occurs due to the presence of microzones. Thirion and Chasset³⁷ succeeded in studying physical relaxation due to movements of entanglements from their experiments on pure gum compounds. They also concluded that physical relaxation originating from

viscoelasticity is probably in pseudo-equilibrium ³⁸ zone, and forwarded an empirical relationship to represent this phenomenon, is given by:

$$f = f_e + C \cdot t^{-n} \quad 1.13$$

where f is the tensile force at time t , C , and n are constants and f_e is the limiting force and the value of f_e can be obtained from the plots f vs $\log(\text{time})$. Several mathematical expressions for the physical relaxation have been proposed based on simple models of viscoelastic behaviour, such as Maxwellian decay and its variants. These are discussed in detail in Chapter 7.

Derham ³⁹ pointed out that physical relaxation is linear with $\log(\text{time})$; physical relaxation is therefore most important in the beginning of an experiment. He reported that increase in carbon black loading increased the physical relaxation, in line with the finding of Cotten and Boonstra,³² and concluded that mechanical history such as pre-stressing (scragging) reduced relaxation, whereas, temperature jumps to higher values result in increased relaxation. Thus, the increase in physical relaxation rate due to the presence of filler was attributed due to the deformation of 'softened' regions (Mullin's-Tobin model⁴⁰); the amount of material in the softened state was found to increase with the increase in filler-rubber breakdown as a result of increase in extension or the amount of carbon black.^{39,40} According to Gregory ²⁷, if the amount of stress softening due to the presence of filler is same irrespective of the type of deformation, then pre-stressing should be effective in compression relaxation, but there seems to be not enough evidence to support this.³ Another reason for the resulting increase in stress relaxation with the increasing amount of filler loading can be best explained by the '**strain amplification theory**'. According to this theory, the strain in the elastomeric matrix between filler particles is larger than the total average strain, due to the inextensibility of particulate fillers; thus, in filled rubber, the measured macroscopic strain is not equal to the microscopic strain which is higher, and the difference becomes larger as the carbon black concentration increases.⁴ Gent ^{24,41} also reported that physical relaxation is independent of the imposed extension for unfilled vulcanisates up to levels at which stress induced crystallisation occurs.⁴¹

According to Ore ⁴², rupture of secondary bonds is the main reason for physical relaxation. Steiner and Tobolsky ⁴³ concluded that oxidative reaction

cannot be avoided even at very low temperatures where visco-elasticity is believed to be sole mechanism of stress relaxation.

In conclusion, physical relaxation becomes less important at longer times because of its linearity with logarithmic time and so even very high rates are acceptable. Secondly, if there is no structural damage to the polymer network due to reasons such as high strain rates, and the physical relaxation is not due to viscous components, then physical relaxation does not affect recovery to the same extent as chemical relaxation processes.

1.5.5 Chemical stress relaxation (CR)

Chemical relaxation is the dominant component of relaxation over long time scales. It involves the breaking and rearrangement of crosslinks and backbone chains.⁴⁴ Several mechanisms may be involved, chain scission, crosslink scission and formation. Stress relaxation in tension has been widely used to study the ageing of elastomers and to test the effectiveness of antioxidants.^{45,46}

It has been found that in the temperature range of 70-125°C, the sulphur vulcanized rubbers such as NR, SBR, EPDM, NBR etc. showed rapid decay of stress at constant extension; albeit, peroxide-cured elastomers surmounted this problem because of more stable network. Since, in principle, a thermoset elastomer network in the rubbery range of behaviour should show little relaxation [3-6% per decade time] and certainly no decay to zero stress, the phenomenon was attributed to chemical processes.

Any type of physical or chemical change in the polymer network should be reflected in stress decay. Extensive study has been carried out by several workers ^{47,48} to study the chemorheological property of vulcanizates. This involved experiments in air, various concentrations of oxygen, in nitrogen and under vacuum. It is believed ⁴⁸ that oxygen content in the environment affects the degradation mechanisms of polymers. Gent ⁴⁹ observed temperature dependent secondary creep processes, which became dominant at long periods of time even at normal temperature in the presence of oxygen and were attributed to oxidative relaxation processes. Mechanisms of chemical relaxation have been related to chain scission of the network through thermal and oxidative

mechanisms.⁵⁰ The basis for much of the discussion of chemical relaxation in the literature is the Two-Network theory of Tobolsky.¹⁶ The validity of the hypothesis has been the subject of several investigations^{51,52} and its general applicability remains open to question. However, because of its simplicity and success in interpreting data in many systems it is widely used.

The basis of Two-Network concept is the statistical theory of rubber elasticity, in which the equilibrium stress experienced by a crosslinked rubber is proportional to the number of stress supporting network chains per unit volume, with the consideration of the new network formation. If a strained rubber is undergoing a chemical reaction resulting in chain scission, the number of stress-supporting chains will reduce with time, leading to a reduction in stress. During ageing, chains can be broken and reformed simultaneously. However, only those chains originally present support the stress, new crosslinks formed are in equilibrium in the stressed state and are non load-bearing. If the stress is then removed, they will not contribute to the return of the specimen to its original strain-free condition, and thus the original specimen dimensions will not be regained. This is postulated as the reason for permanent set in elastomers.

Although all polymers degrade at high temperature in the absence of air, degradation is almost always faster in the presence of oxygen.⁵³ Hence, oxidative degradation is considered to be the most serious problem in the use of rubber components at elevated temperatures, and consequently the oxidation of rubber has been investigated extensively.^{12,54} A small amount of oxygen [$\approx 1\%$] absorbed by rubber network is found to have deleterious effect on its physical properties⁴³ and much of the research is concerned with the oxidative mechanisms. However, these results, derived from experiments carried either on thin samples or on model compounds, may not provide ideal solution for the problems encountered by bulky components formulated with numerous additives in normal engineering applications.

Oxidation of hydrocarbons is normally auto-accelerating (autoxidative); ie: the rate is slow or even negligible at first but gradually accelerates, often to a constant value. Autoxidation is defined as the free-radical chain mechanism of the oxidation process by hydro-peroxides formed in the reaction.⁵³ The addition of an initiator normally removes the slow auto-accelerating induction time and anti-oxidants and stabilisers extend it. The nature of autoxidative reaction in elastomers is often

complex as it is influenced not only by the nature of polymer but also from the type of vulcanising process and the vulcanisation products.

Cunneen¹² and Bell et. al.⁵⁵ believed that autoxidation reaction is dependent on the type and nature of the crosslinks in the vulcanizate. They suggested that in sulphurated network systems with no antioxidants, the poly-sulphides and elemental sulphur inhibit oxidation as they behave as hydro-peroxide scavengers. Whereas, the oxidative degradation of unprotected peroxide-cured or TMTD-'sulphurless' vulcanisates is auto-catalytic as the chain reaction of conjugated dienes and triens proceed without any resistance (no inhibitors). However, in vacuo these compounds (peroxide-cured or EV- vulcanisates) show very little relaxation or crosslinking during ageing as the activation energy of C-C bond is far greater than C-S_x-C crosslink (refer to Table 1.1). In protected systems (ie: systems with antioxidants), the presence of polysulphides were found to even accelerate the degradation process¹² (ie: reduce the efficiency of antioxidants). They also observed similar effects on the oxidation of peroxide and EV-systems due to the presence of carbon black.^{12,55} As these effects are much smaller when compared with those of antioxidants, the autoxidative relaxation is generally masked in conventional compounds. Effects of antioxidant on stress relaxation can be found elsewhere.^{45,46} It is, however, not appropriate to go into the depth of the above discussion as the main objective of this programme is to study the stress relaxation behaviour of commercial elastomer compounds which are generally manufactured using efficient vulcanisation or peroxide curing systems and often protected with anti-oxidants.

From the above discussion, it is clear that even very small amounts of the antioxidant are sufficient to prolong the autoxidative decay significantly. On these grounds, it has been reported that for elastomer compounds which show steady maxwellian relaxation in the earlier course of experiment may change to accelerated relaxation at very long times at which all the antioxidants or inhibitory action is expended.³¹

According to Stenberg and Jansson ⁵⁶ thermo-oxidative relaxation is diffusion controlled and can be affected due to formation of hard skin at the surface, as observed by Lindley and Teo.⁵⁷ Tamura et. al.¹³ studied the scission mechanisms of various natural rubber vulcanisates in tension at differing oxygen concentrations. When the vulcanisate network is subjected to strain and temperature, the network

scission can occur either along the main chain or near the crosslinks. According to Tamura and Murakami⁵⁸ faster decay during the initial period is due to exchange reaction of polysulphides. The occurrence of these exchange reactions does not affect the crosslink density, evident from the sol-fractions in his experiments. They also showed, in the absence of polysulphidic bonds, that the stress relaxation in a nitrogen atmosphere containing various amounts of oxygen, is mainly due to scission of main chain near crosslinks or breakdown of mono-, di-sulphidic bonds.

According to Lyubchanskaya et. al.⁵⁹ the effect of oxygen is negligible if the stress decay is due to breakdown of polysulphidic links. They reported a five fold decrease in stress relaxation when the primary scission is due to mono-, di-sulphide links. They also showed that the stability of main chains is the factor of interest as the stress relaxation increases with the amount of double bonds in main chain. They also found high rates of relaxation in rubbers having abundant unsaturation compared with more saturated polymer networks. One interesting observation in this work is that similar chemical relaxation rates were found at differing degrees of compressive strains (10-50%).

Besides the oxidative chain scission, oxidative crosslinking and thermal degradation were also observed in the relaxation process.⁴ According to Tamura and Murakami,⁵⁸ oxidative crosslinking is supposed to take place in the unsaturated network (eg: cyclopentadiene containing in EPDM network). When oxygen is excluded at high temperatures, only thermal degradation can occur. Thermal degradation has a higher activation energy and also found to be independent of the presence of carbon black;⁴ they occur mainly due to the following reasons:

- a. Thermal rupture of bonds in main chain
- b. Exchange reactions in crosslinkages, usually polysulphidic links are exchanged to mono- or di-sulphides.

Many papers have been published concerning main chain and crosslink scission in different rubbers; here only a few results of NR and EPDM are considered. Murakami³⁵ has tabulated the degradation mechanisms found in natural rubber at differing initial crosslink densities [viz: $n_1(o)$, $n_2(o)$, $n_3(o)$], given in Table 1.3. The scission rate along main chains, ie: value of k , for natural rubber cured by sulphur is found to be larger than that for rubber cured by peroxide under similar conditions.³⁵ In the present work, however, the only NR used is sulphur cured.

Table 1.3: Thermal and oxidative mechanisms in NR network ³⁵

Kind of Polymer	Structure	Thermal Degradation	Oxidative Degradation
Peroxide or Irradiation cured Natural Rubber	$\begin{array}{c} \text{CH}_3 \qquad \text{CH}_3 \\ \qquad \quad \\ -\text{C}-\text{CH}_2-\text{CH}_2-\text{C}-\text{CH}=\text{CH}_2- \\ \qquad \quad \\ \text{CH}_3 \qquad \text{CH}_3 \end{array}$	Random Scission along Main Chains. $\frac{f(t)}{f(0)} = e^{-\frac{q(t)}{n(0)} - (q(t) \langle q'(t) \rangle)}$	Random Scission along Main Chains $\frac{f(t)}{f(0)} = e^{-\frac{q'(t)}{n(0)} t} \approx e^{-k_1 t}$ $k_1 = f \{ n(0) \} \{ q(t) \langle q'(t) \rangle \}$
TMTD cured Natural Rubber	$\begin{array}{c} \text{CH}_3 \qquad \text{CH}_3 \\ \qquad \quad \\ -\text{C}-\text{CH}_2-\text{CH}_2-\text{C}-\text{CH}=\text{CH}_2- \\ \qquad \quad \quad \\ \text{S} \\ \\ -\text{C}-\text{CH}_2-\text{CH}_2-\text{C}-\text{CH}=\text{CH}_2- \\ \qquad \quad \\ \text{CH}_3 \qquad \text{CH}_3 \end{array}$	Scission at Crosslinks. $\frac{f(t)}{f(0)} = e^{-k_2 t} \quad k_2 = \text{const.}$	Random Scission along Main Chains. $\frac{f(t)}{f(0)} = e^{-k'_1 t} \quad k'_1 > k_1$ $k'_1 = g \{ n(0) \}$
Sulfur cured Natural Rubber	$\begin{array}{c} \text{CH}_3 \qquad \text{CH}_3 \\ \qquad \quad \\ -\text{C}-\text{CH}_2-\text{CH}_2-\text{C}-\text{CH}=\text{CH}_2- \\ \qquad \quad \quad \\ \text{S}_x \\ \\ -\text{C}-\text{CH}_2-\text{CH}_2-\text{C}-\text{CH}=\text{CH}_2- \\ \qquad \quad \\ \text{CH}_3 \qquad \text{CH}_3 \end{array}$	Scission at Crosslinks and Exchange Reaction. $\frac{f(t)}{f(0)} = A e^{-k_2 t} + B e^{-k_3 t} \quad k_2 = \text{const.}$	Random Scission along Main Chains and Exchange Reaction. $\frac{f(t)}{f(0)} = A e^{-k_2 t} + B e^{-k'_2 t}$

In EPDM compounds involving different curing processes, the following relaxation mechanisms were suggested by Murakami.³⁵ (Table 1.4)

Table 1.4: Thermal and oxidative mechanisms in EPDM network

	Thermal degradation	Oxidative degradation
Peroxide cured EPDM	Not observed below 160°C At higher temperatures presumably random scission along main chains occurs.	Random scission along main chains
TMTD cured EPDM	Scission at crosslinks	Random scission along main chains
Sulphur cured EPDM	Scission at crosslinks (interchange reactions)	Oxygen induced cleavage of mono- and di-sulphide linkages

Lee and Morrell⁶⁰ have studied ageing of nitrile rubber. According to their work, during service at elevated temperatures, elastomers age by two major pathways- either by thermal process or by a thermoxidative process. Both routes can lead to either scission of crosslinks and/or main chain or crosslinking with the accompanying hardening. They suggested two types of thermal reactions involving polysulphides; first, there can be lowering of sulphur rank resulting from scission and subsequent crosslinking (ie: increase in modulus); second, there can be cleavage of crosslinks with the formation of cyclic sulphide (ie: fall in modulus or reversion). These are summarised in Table 1.5.

Table 1.5: Types, sites and results of the reactions which occur in rubber vulcanisates⁶⁰

Thermal reactions		Oxidative reactions	
Scission of hydrocarbon	Crosslinking of hydrocarbon	Scission of hydrocarbon	Crosslinking of hydrocarbon
Scission of crosslink	Changes in crosslink structure	Scission of crosslink	Changes in crosslink structure

Thus, two types of reactions are in operation in an elastomer First, oxidative degradation of molecular chains. second, the thermal breakdown of the network. The ratio of these two reactions may vary widely depending on the nature of the main chain and the crosslink structure. With a stable crosslink, obtained in variety of compounds; eg: TMTD-sulphurless vulcanisation, radiation cured or peroxide cured rubbers, relaxation is determined by the degradation of the polymer chain. To summarise the above discussion:

1. Chemical relaxation (CR) is independent of the amount of compression⁵⁹ varying from 10- 50 % [against 0-250 % in tension by other workers^{61,62}], as at low strains damage to the polymer network is minimal, however, physical relaxation is found to be dependent on both the amount of strain and rate of strain particularly in filled vulcanisates due to the increase in 'softened region' and is explained earlier.^{34,39}

2. During the chemical relaxation process, Stenberg and Jansson⁵⁶ observed little change in equilibrium modulus; this indicates that the amount of crosslink ruptures are equal to the formation of new crosslinks in the unstressed state.
3. The effect of oxygen on chemical relaxation depends on
 - the type of sulphur crosslinks^{12, 13, 59}
 - the susceptibility of the polymer chain to oxidation^{55,57}
4. The presence of filler is significant on the chemical relaxation as the addition of filler reduces the activation energy of polymer for oxidation;^{18,59} and also found to increase the resistance to photo-degradation⁸.

Thus the method of vulcanisation, correct choice of vulcanising agent, careful selection of polymer and of filler are the key factors in designing a stable network for longevity.

Chapter Two

STRESS RELAXATION

2.1 COMPRESSION STRESS RELAXATION (C.S.R)

2.1.1 Introduction

Stress Relaxation is defined as the decrease in the back stress exerted by a specimen which has been compressed to a constant deformation, under specified conditions of time and temperature. For this purpose, an instrument is needed together with a technique to maintain the constant deformation and to generate reproducible results over long timescales.

2.1.2 Consideration of the equipment

The main objective of any standard test is the attainment of unique but reproducible test results when the procedural details are strictly followed, irrespective of the skill of the operator.

The Wykeham-Farrance force measuring equipment, Figure 2.1, was developed at the Institute of Polymer Technology and has been in use for ten years and has performed satisfactorily. For this reason, the author has used this apparatus for all the compression stress relaxation measurements. The equipment is described in detail by K.P. Fernando⁶³ and is available at the University. The principal features of this equipment for stress relaxation measurements have also been considered by J.C.Armah⁶⁴ and M.Tahir.⁶⁵ The force-displacement curve and the effects of slippage on the stress relaxation results are considered later in Chapter 4.

Further work carried out by M. Tahir⁶⁵ and A.W. Birley et. al.⁶⁶ have revealed the following aspects about the current standards already discussed in Chapter 1.

1. The test procedure which involves 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;

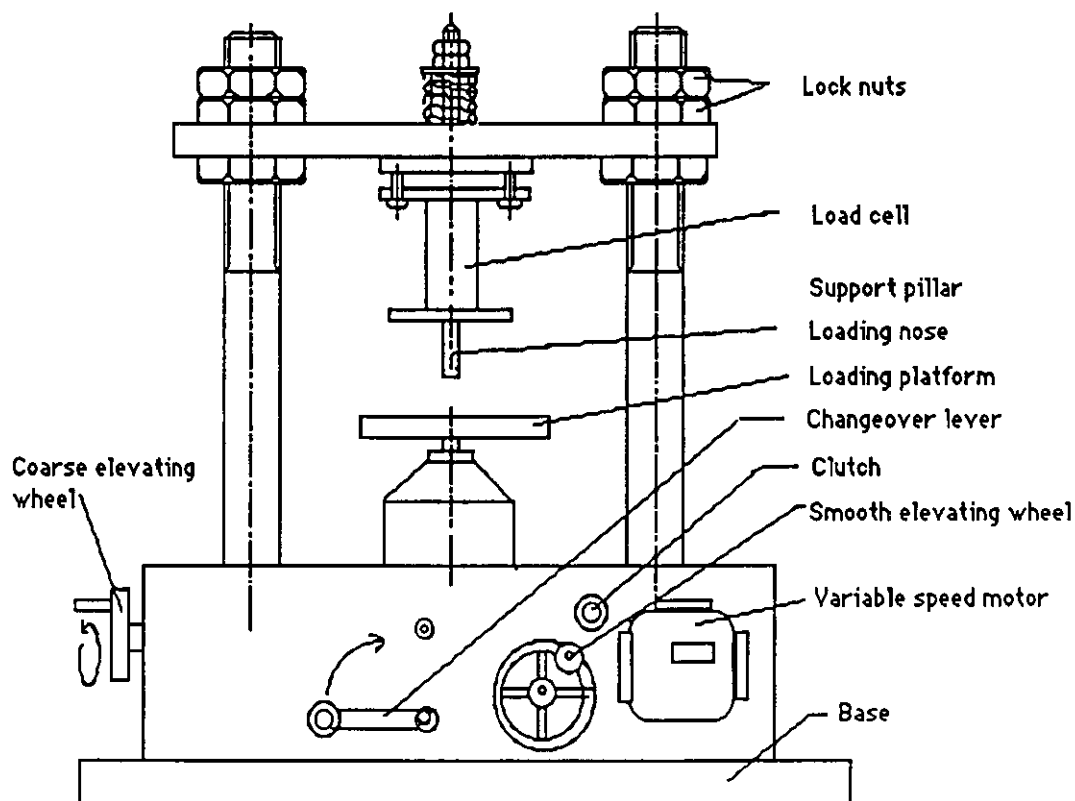


Figure 2.1: Wykeham - Ferrance force measuring equipment

2. The requirement in the British Standard²³ specifies that loading of the test piece to a specified compression should be completed in 30 s; this is possible only with a very much higher loading rate than that employed in this programme; the specification not only leads to irreproducible results due to lack of any particular loading rate, but in an equipment such as one used in this work, there is serious danger of overloading the loadcell (It is desirable, if not essential that the loading rate be reproducible).
3. Adoption of a requirement for an 'ideal curve,' would reduce the need for multiple measurements⁶³ (Figure 2.2). The ideal curve is the the force vs displacement curve obtained on a specimen held at constant strain in a jig, and is characterised by two linear loading curves at constant strain rates; the first part being the measure of relaxed force while the latter is the force-displacement plot due to an incremental strain. The ideal curve concept and its practical considerations, the various defects found in the much of the equipment currently available have been discussed elsewhere.^{63,65,66}
4. Mechanical conditioning of the sample has only a marginal effect, if any.^{65,66}
5. Extrapolation of high temperature data is dangerous.⁶⁶

6. Higher modulus, by a factor known as modulus enhancement factor ⁶³⁻⁶⁶ (M.E.F); this is the ratio of modulus of the specimen held under constant strain to the modulus during the loading process (Figure 2.3), and is obtained from the ideal curve concept. The abrupt change in slope occurs at the force still exerted by the specimen, the relaxed force, 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 compared with the modulus during the loading period.

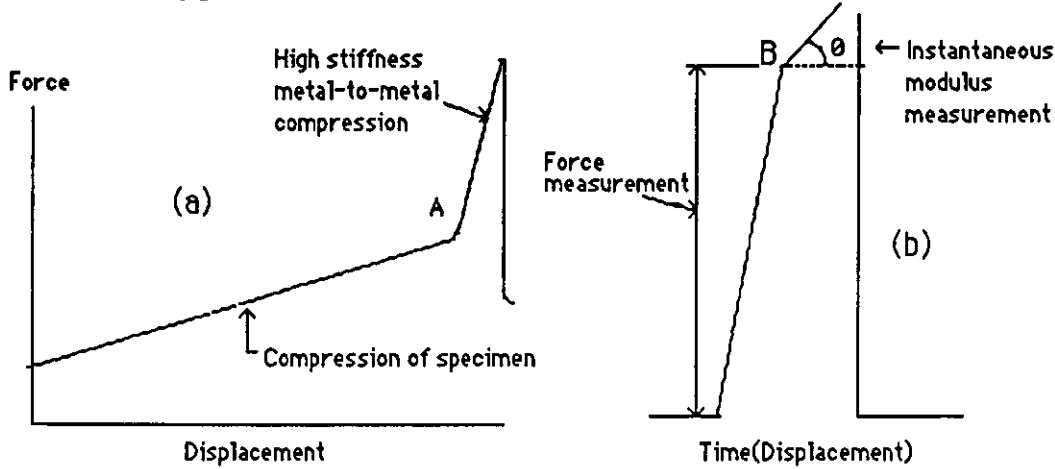


Figure 2.2: Typical force measurement plots from Wykeham-Ferrance force measuring equipment
a) Loading curve during closing of a jig
b) Ideal curve during further measurement

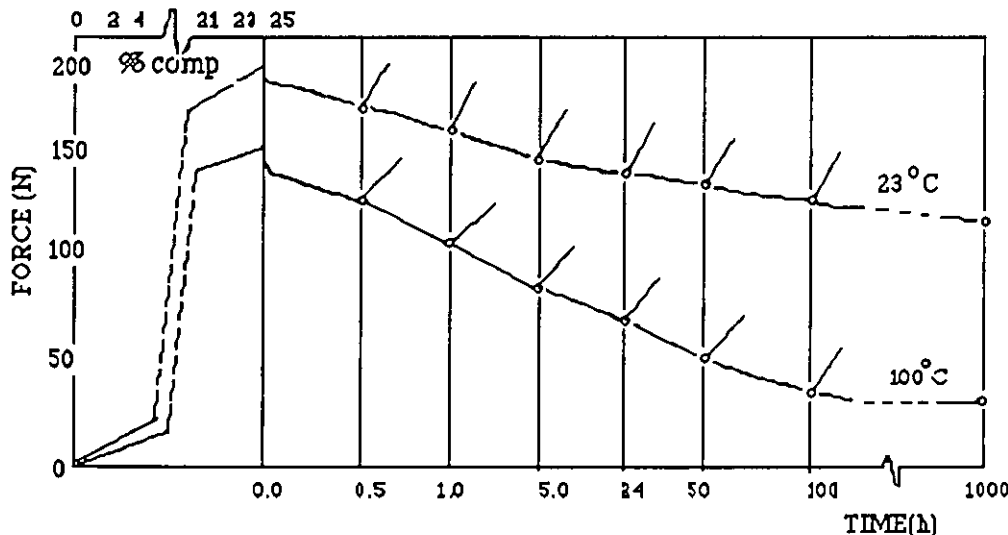


Figure 2.3: Illustration of 'Modulus enhancement factor' (M.E.F)
MEF = Stiffness of rubber under test divided by stiffness of rubber during loading (where the stiffness is the slope of the second part of the ideal curve)

2.1.3 Materials and test compounds

A vast number of elastomeric materials are used in the manufacture of rubber seals due to the individual needs and specific preferences for a particular application. However, in order to generalise the property, a broad spectrum of materials was selected in this work. These included twelve different compounds based on sulphur cured NR, SBR, EPDM, EPCL, peroxide cured EPDM, NBR rubbers and thermoplastic elastomers which included Santoprene*, Evoprene** and Alcryn***. Materials of both 50 and 70 IRHD were used; besides, with few other specific grades of TPE's were also considered. This may envisage in understanding the effects of hardness, chemistry and other related parameters on sealing behaviour.

The major part of this work is to study the compression stress relaxation performance of these compounds; they are coded as shown in Table 2.1. However, the exact formulations are not available for commercial reasons. Many of the above compounds did not meet the hardness requirement at the beginning of this work and were reformulated. Thus the compounds are further classified into original/old (O) and new (N); and in a few cases modified (Mod.) or grades -1 and -2 were also used where more than one attempt at reformulation was necessary. This increased the total number of compounds tested to 23; details are given in Table 2.2.

2.1.4 Preparation of test buttons

The normal test specimens used in the compression stress relaxation test are cylindrical with approximately 1:1 thickness to radius ratio. In this experiment the button size used is about 6.3 mm thick, except in the case of experiments

* **Santoprene** is a Monsanto trade mark for an TPV based on PP-EPDM dynamically vulcanised rubber.⁶⁷

** **Evoprene** is an Evode trade mark for an TPE based on S-E-B-S structure.

*** **Alcryn** is a Dupont Trade mark for a TPE based on a mix of highly plasticised chlorinated polyolefine, an ethylene vinyl acetate copolymer and an acrylic ester rubber. ie: a thermoplastic chloro-olefine elastomer.⁶⁷

Table 2.1: List of Compounds initially proposed for this programme and the corresponding nominal hardnesses.

Type	Description	Nominal Hardness [IRHD]
A	Natural Rubber	50
B	SBR	50
C	EPDM(S)*	50
D	EPDM(P)*	50
E	NBR	50
F	EPDM	70
G	NBR	70
H	EPCL	70
I	Santoprene 101-55	55
J	Santoprene 101-64	64
K	Evoprene 992	50
L	Evoprene 994	70
M	Alcryn 6368	50
N	Alcryn 6385	50
O	Alcryn 1201	60

* Note: S for sulphur and P for peroxide curing systems

carried out to study the effect of volume. A multi-cavity transfer mould is available at the department to make these buttons and all the earlier experiments were carried out using the stress relaxation buttons produced from this mould. However, because the gate size is significant, degating of the moulding is difficult, which always leaves a small but significant defect on the surface of the button. This affects the parallelism of the test assembly. The test for reproducibility has proved that parallelism and surface defects of the test sample are vital considerations. Hence, further experiments are carried out taking due care to smooth the surface using emery paper. This showed some improvement but was laborious. Hence, the test buttons were cut using a slow speed rotating knife from a moulded sheet of the required thickness [6.3 mm]. Reproducibility tests on these buttons have proved satisfactory.

Table 2.2: List of Compounds used in this programme along with the corresponding nominal and measured hardnesses.

No	Type	Description	HARDNESS (IRHD)		
			Nominal	Macro	Micro
1	A(O)	Natural Rubber	50	61.0	51.0
2	A(N)	Natural Rubber	50	54.5	52.0
3	B(O)	SBR	50	58.0	54.5
4	B(N)	SBR	50	51.5	51.5
5	C(O)	EPDM(S)*	50	49.5	48.5
6	D(O)	EPDM(P)*	50	49.0	49.0
7	D(N)	EPDM(P)*	50	53.0	53.0
8	D(Mod)	EPDM(P)*	50	47.0	42.5
9	E(O)	NBR	50	43.0	39.5
10	E(N)	NBR	50	52.0	51.0
11	F(O)	EPDM(P)*	70	65.5	67.5
12	G(O)	NBR	70	70.0	70.0
13	H(O)	EPCL	70	70.5	69.5
14	I(O)	Santoprene 101-55	55	56.0	55.5
15	J(O)	Santoprene 101-64	64	67.5	67.5
16	K(O)	Evoprene 992	50	46.0	42.5
17	K(Mix)	Evoprene 992/994	50	52.0	51.0
18	L(O)	Evoprene 994	70	61.0	69.0
19	L(2)	Evoprene 994	70	85.0	83.0
20	L(3)	Evoprene 994	70	78.0	78.5
21	M(O)	Alcryn 6068	50	54.0	53.0
22	N(O)	Alcryn 6385	50	53.5	54.0
23	O(O)	Alcryn 1201	60	63.0	61.5

* Note: S for sulphur and P for peroxide curing systems

A thermoset rubber should be cured to produce optimum results. This is possible when the given compound is tested for the cure characteristics. A Monsanto Oscillating Disc Rheometer (ODR) is used for this purpose. A small piece of raw rubber compound [approximately 7-8 g] is put inside a heated cavity maintained at a

constant temperature [150-185° C]. An oscillating disc senses the torque which is plotted against time producing a cure curve as detailed in Figure 3.2. The effects of states of cure on stress relaxation and recovery are discussed later in Sections 4.4 and 5.34. Cure can be either Type A, B or C, depending upon the nature of the compound. For optimum properties, the compound should be cured to 95% of the maximum torque. The significance of cure is explained in Section 3.1.

Because the thicknesses of the sheet in compression moulding and the test buttons in transfer moulding are greater than the thickness of the test sample in the Monsanto ODR test, a gradient of cure-characteristics occurs through the cross-sectional thickness of the moulding; corresponding to this variation in temperature, a corrective measure is necessary to achieve optimum results.

2.1.5 Details of the equipment

The compression stress relaxation test equipment consists of two components:

- Force measuring device
- The jig assembly

The Force measuring device: This consists of a load cell, a loading platform driven by a constant speed motor via a clutch and gear assembly, a regulated power supply, an amplifier to amplify the load signal and a chart recorder. The layout is depicted in Figure 2.4.

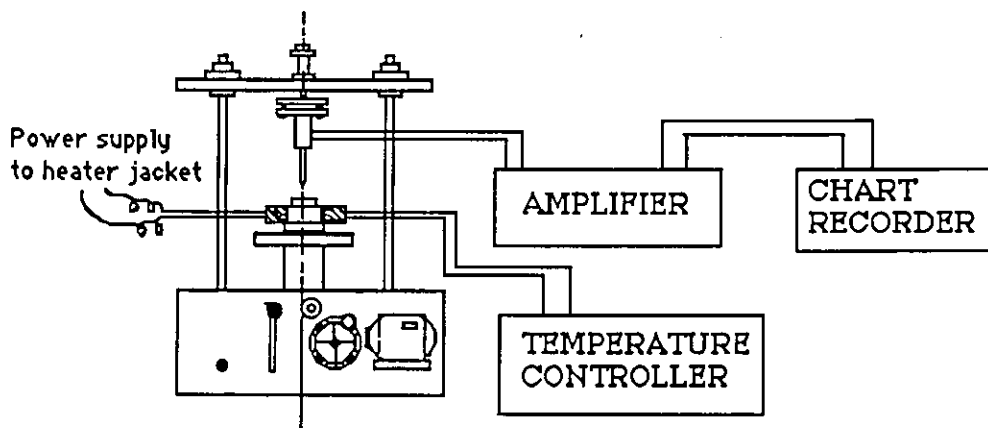


Figure 2.4: The equipment layout for the compression stress relaxation measurements with the heating device for jig.

The loading platform can be raised or lowered either manually or automatically, selecting the direction of the drive assembly. It can also be driven at any of the selected speed by proper assembly of the gear or can be disengaged via a clutch. Before starting the experiment, the load cell is calibrated, using a set of dead-weights loaded on to the calibrating arm as shown in Figure 2.5.

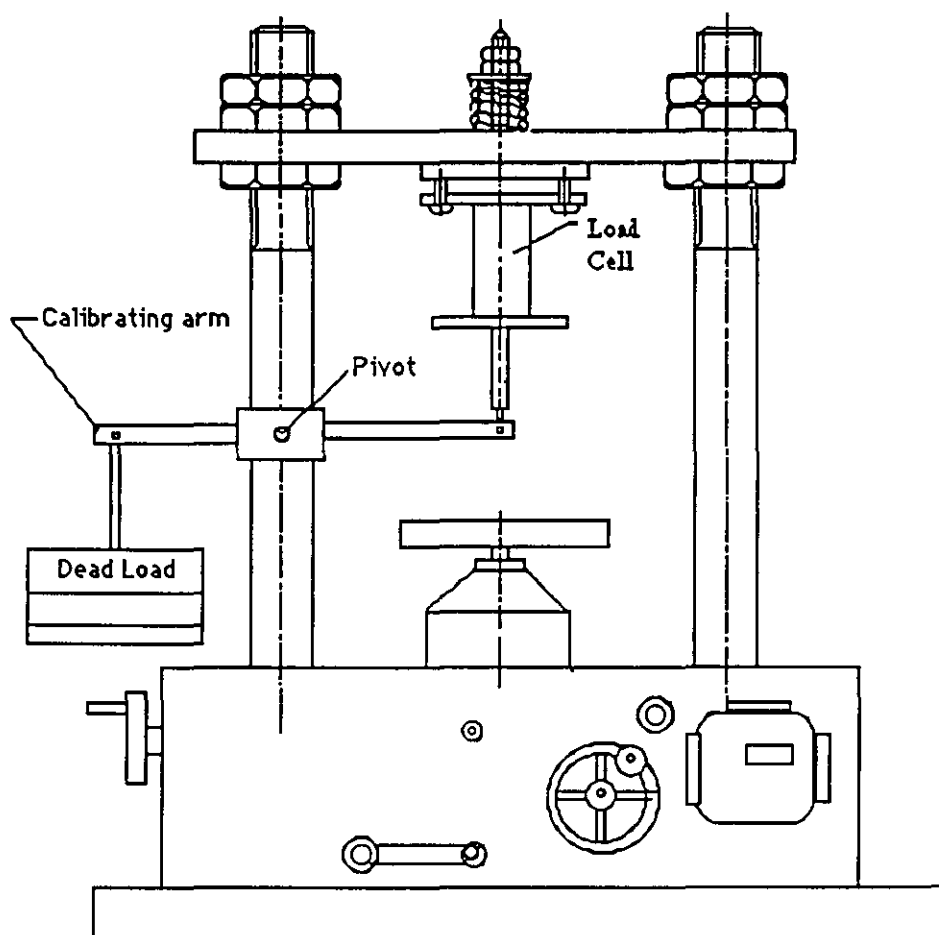


Figure 2.5: A schematic diagram of the device used for the calibration of the force measuring equipment.

The chart recorder signals at various amplification factors and for different loads are given in Table 2.3a; these values are the average values of the loading and unloading process. Because of unequal arm lengths (139:154 mm), the force acting on the load cell is different than the actual load and is also given in Table 2.3a. The values from Table 2.3a can further be used to calibrate the load cell. Typical results from the calibration test are given in Table 2.3b; the values are the mean average of the calibration test and are used to calculate the initial force or

Table 2.3a: Chart recorder signals, mm, at various amplification factors for different acting loads during a calibration test

Ampln. Factor	Dead load kg	5	10	15	20	25
	Acting load	4.51	9.02	13.54	18.05	22.56
1/5		5.3	10.5	15.8	21.3	26.5
2/5		11.7	23.3	34.7	46.5	58.0
1/2		13.7	27.5	41.0	54.8	68.5
4/5		22.2	44.3	66.3	88.5	110.5
1/1		29.0	57.8	86.7	115.5	144.4

residual stress from the chart recorder signal during a stress relaxation measurement. Once the load cell is calibrated, it remains reasonably stable for a significant length of time. However, the results are checked and updated every six to eight months.

Table 2.3b: Calibration results

Amplification Factor	N/mm	mm/kg
1/5	8.370	1.172
2/5	3.806	2.577
1/2	3.229	3.038
4/5	2.003	4.897
1/1	1.532	6.402

The jig assembly: The concept of the use of this jig is developed at IPTME^{63,65} on the following objectives:

1. To maintain a constant strain on the test button specimen throughout the test period
2. To separate the test sample from the force measuring equipment in order to enable one to conduct other measurements and to duplicate tests.
3. To store the test jig in a desired test environment during the span of a test run.

A schematic diagram of the jig assembly is shown in Figure 2.6 below; this consists of a jig cavity which houses a sandwich assembly of a test button with a pair of glass plates, a thrust plate and three socket head screws. As the depth of the jig cavity is fixed, the glass plates were so selected as to provide approximately 25 % compressive strain on the test button when the jig is fully closed. By knowing the thicknesses of the specimen, t_s , the two glass plates, t_g , and the depth of the jig cavity, t_c , the actual strain in the specimen when the jig is fully closed can be found using:

$$\% \text{ Strain} = \frac{t_c - t_g}{t_s} \times 100 \quad 2.1$$

Two other additional methods are also employed to find the compressive strain and are explained in the following section, and the mean value of the three methods is considered in the calculations of results.

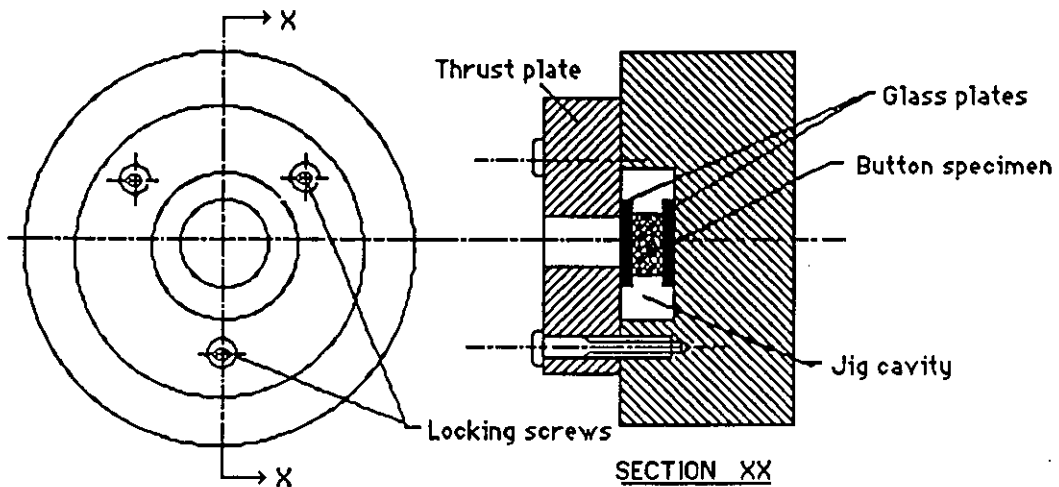


Figure 2.6: Schematic diagram of a compression stress relaxation jig

The test Jig [Figure 2.6] is assembled in the following manner. A clean sample free from surface defects and with smooth parallel surfaces is selected. Both the horizontal surfaces are lubricated using molybdenum disulphide. The thickness of the test button, the thickness of the set of glass plates and the depth of the jig cavity are noted and the jig is numbered. The test button is sandwiched between the two glass plates and then placed centrally in the jig cavity before placing the thrust plate in position. The three bolts are secured without adding any strain to the test button. The jig is now ready for the test.

2.1.6 Experimental Procedure:

Before starting the actual test, the jig assembly is conditioned for 2 to 2.5 hour at the desired test temperature by placing it in a constant temperature chamber. [5°C, 23°C, 40°C, 70°C, 100°C, 125°C]. The conditioned jig assembly is then quickly transferred to the loading platform. An insulated heater jacket is used when the test temperature is in excess of 50°C, to minimise the heat loss during the loading operation. It is assumed that below this temperature heat loss is minimal and can be neglected, as the jig housing is relatively bulky and the loading time of 5-6 minutes is small. The use of the heater band is further discussed in Section 2.1.7.2. However, it is felt that further measurements at all other test intervals greater than the loading time [$t_{o.o}$] need not use the heater band as the test duration remains small [20-30 s] and the temperature drop is insignificant. During a loading process, the loading collar is used so that the jig is closed and the specimen is strained at a constant rate simultaneously. A loading speed of 0.31 mm/min [position B on the gear assembly] and a chart speed of 1mm/s are chosen in this programme, unless otherwise specified. A typical loading curve is given in Figure 4.3. Once the loading operation is completed, the three bolts are tightened as quickly as possible before transferring the jig assembly back to the test chamber. The reading of the dial gauge fixed to the loading platform is noted at the start, d_o , and finish, d_f , of the loading process; the difference of these two readings gives the amount of compression, thus:

$$\% \text{ Strain} = \frac{d_f - d_o}{t_s} \times 100 \quad 2.2$$

The amount of compression can also be calculated from the loading curve. As the chart speed (1mm/s) is fixed, the length of the chart paper between the beginning, l_i , and ending, l_f , of the loading curve can give the time taken for the loading process; for the strain rate of 0.31mm/min, the compressive strain can be calculated using:

$$\% \text{ strain} = \frac{[(l_f - l_i) \times 0.31] / 60}{t_s} \times 100 \quad 2.3$$

where t_s is the original thickness of the test sample.

At regular intervals, the jigs are placed on the loading platform to measure the residual stress. At this stage, the loading nose is brought in direct contact with the sandwich assembly via the centre hole of the thrust plate, without exerting any incremental strain on to the specimen. The platform is then raised at the same constant speed, 0.31mm/min, until the stress is overtaken by the load cell and a small incremental strain is added to the specimen, which can be noticed from the change in force-deformation curve (refer Figure 4.3).

2.1.7 Experimental Variables

Several variables affect the test results; the following were studied at depth in this programme.

1. test medium
2. test temperature
3. shape and size factors
4. state and type of cure.
5. filled against gum compound.

2.1.7.1. Test medium:

The following media have been used to study the effects on stress relaxation.

- air
- water
- natural gas
- nitrogen

Air: Tests are conducted at six different constant temperatures using a domestic refrigerator (varying between 4°C and 9°C) and four circulating air ovens ($\pm 1^\circ\text{C}$ accuracy) in a constant temperature laboratory ($23 \pm 1^\circ\text{C}$); the results are given in Section. 4.1.

Water: Water baths maintained at three different temperature (23°, 40° and 70° C) have been used to study the effects of wet conditions. The test

samples are immersed in water for 1000 h. for 23° and 40° C and 240 h for the 70° C test prior to relaxation measurements; the changes in weight and volume (thickness) of the test sample are given in Section 4.7.

The pretreated samples from the water swell test are assembled for the compression stress relaxation test as in other tests. The jig assemblies are pre-conditioned at the test temperature by placing them in an oven, rather than in the water bath as this may dislocate the test button. The test is carried out in a normal way. The jigs are transferred to the water bath maintained at a desired test temperature after the loading process. The heater jacket is used for the 70°C test in water but only during the initial loading as in the dry-air tests. During further readings, the jig assemblies are wiped dry before the measurement. The results are detailed in Section 4.1.3

Natural Gas: Domestic gas is captured in an inverted jar over a water trough and at each time after the routine reading and at regular intervals the gas is pumped through the envelope. The test jigs are placed inside the glass chamber well above the water level as shown in Figure 2.7. Only a room temperature test has been made in this work. The test buttons, as in wet tests, are conditioned for a period of 1000 h. in the gaseous environment.

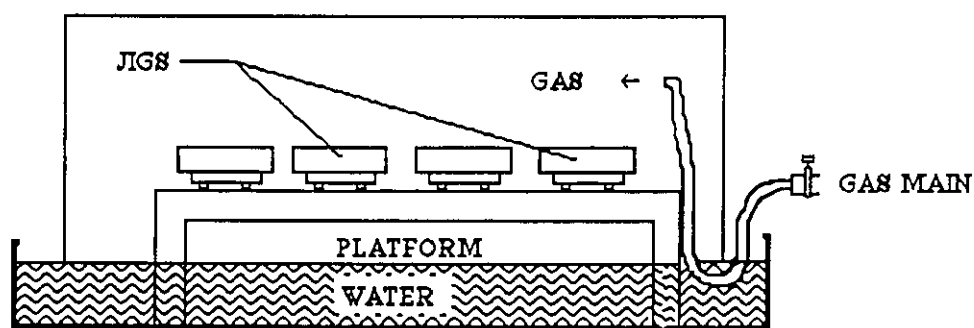


Figure 2.7: Experimental set-up for CSR test in natural gas

Nitrogen: Oxygen free nitrogen from a cylinder is fed through the test jig using special connectors as shown in Figure 2.8. The assembly can be maintained at any desired temperature using a thermostatted oven. The test is carried-out at a high temperature to accelerate chemical effects and to compare with the corresponding test in air at that temperature with respect to oxidation.

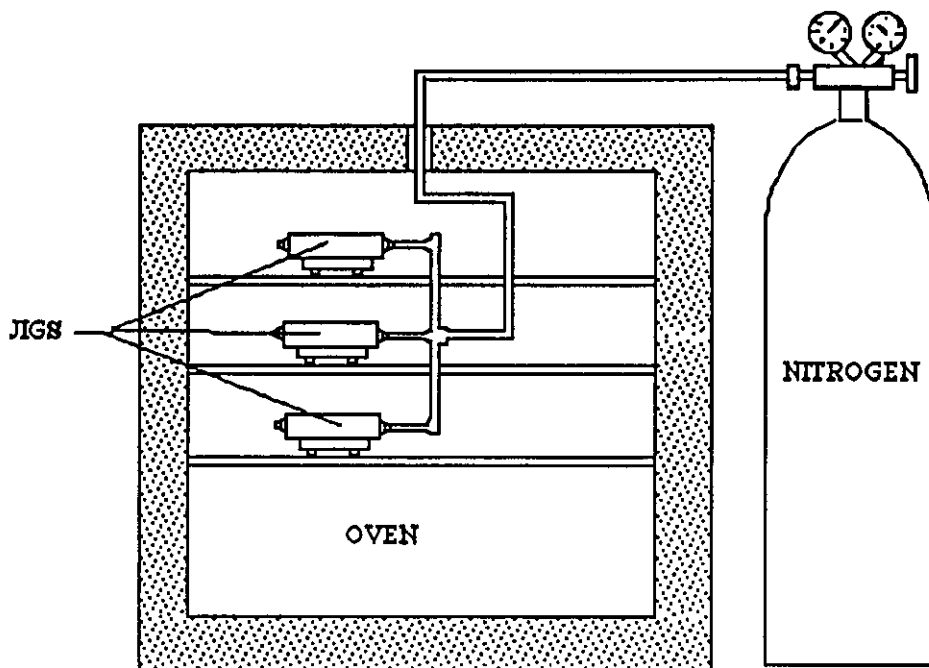


Figure 2.8: Experimental set-up for CSR tests under nitrogen

2.1.7.2. Test temperature:

Tests were carried out at various temperatures to help in the development of a suitable mathematical model using a temperature parameter. A domestic refrigerator was used for the 5°C test. The following test temperatures were selected and are identical with the testing standard temperatures in BS 2494:

5°C, 23°C, 40°C, 70°C, 100°C and 125°C

The loading procedure as described in Section 2.1.6. was followed; during loading at temperatures greater than 50°C, an insulated heater jacket is used. The temperature of the heater band is controlled using a thermostat [Figure 2.4], set at a suitable temperature obtained from a calibration test; in this test a thermocouple probe is inserted in the vicinity of the test sample inside the jig assembly and is left on the loading platform for about 5-6 minutes with the heater-band controlled at such a temperature so as to maintain the test specimen at the required temperature.

2.1.7.3. Shape and Size factors:

The effects of volume, ie: the shape and size of the specimen, on the stress relaxation of the rubber compound can be studied using different thickness/diameter ratios. For this purpose, a variable depth test jig was used. The procedure is similar to the one discussed earlier.

2.1.7.4 State and type of cure:

Experiments were carried out on all the available compounds in three different cure states, viz. under cure, over cure and optimum cure which are detailed in Chapter 3. The results are discussed in Chapter 4. For EPDM compounds, test results are also available on two types of cure systems: one on the sulphur base [Type C] and other on the peroxide crosslinking mechanism [Type D].

2.1.7.5 Study of the effects of filler

A large number of additives are used in formulating a sealing compound, to meet the test standard specifications and also to make it commercially viable. These additives generally play a major role on the service life of the products. One of the additives is a filler, generally, carbon black or silica. Numerous types are currently available to meet a particular need. They are normally graded by their particle size. However, to study the effects of these ingredients on stress relaxation, it is necessary to conduct tests on filled and gum compounds. Only a few compounds were chosen for this test as the time available was limited. The results are discussed in Section 4.1.5.

2.1.7.6 Study of strain rate

The effect of strain rate on stress relaxation was studied on all the available compounds at two different loading rates; ie: 0.31 mm/min and 1.55 mm/min. The effect of loading rate on initial force, rate of relaxation and on residual stress factor (R.S.F) are given in Tables 4.15 and 4.16 respectively. The effect is more prominent in thermoplastic elastomers, hence two additional loading rates of 0.79 mm/min and 1.19 mm/min were also used for these materials. The effect of strain rate on the above three parameters is discussed in Section 4.1.10.

Towards the end of the major programme, the importance of the rate of loading became apparent and an immediate limited programme was launched. The primary objective was to clear up differences in the response of rubbers, both cross-linked and thermoplastic, to the differences in loading rate between that specified in BS 2494 and that inherent in this programme.

2.1.8 Limitations and Conclusion:

The compression stress relaxation test has been regarded as a very good replication of seal behaviour. This is further evident from the simulated seal tests, detailed in Chapter 6. However, like other tests, CSR also suffers from following disadvantages:

- they are expensive to run.
- they are time consuming, hence there is a temptation to predict results from accelerated tests.
- they need constant attention and dedication.

However, if due care is given during a C.S.R test, the results obtained are reliable. Thus tests carried on numerous compounds at variety of test conditions can be used in the mathematical modelling of the service behaviour. This is discussed in greater detail in Chapter 7.

2.2 TENSILE STRESS RELAXATION [T.S.R.]

2.2.1 Introduction

Stress relaxation in tension has been widely used to study the ageing properties of elastomers, especially with respect to the effectiveness of antioxidants.^{45,46}

2.2.2 Test equipment and procedure:

A variety of equipments and procedures may be used to measure the stress relaxation in tension. For example, a Wallace tenso-relaxometer or a J.J.-tensile

testing machine can serve this purpose. However, there are major disadvantages. Primarily, the instruments are very expensive. Running long term stress relaxation tests means a major blockage for other tests to be conducted on that equipment. An alternative to this is by using short term tests but they can not be reliable for the prediction of long-term behaviour, until a valid mathematical model is established. This will leave one to adapt a type test using independent jigs as in the CSR-test. Some German type jigs [Figure: 2.9 a] were made available, which can be coupled with a J.J.-tensile machine to conduct stress relaxation tests in tension. After the completion of the test, the jigs can be freed from the testing instrument. However, these jigs suffered a major problem of mis-alignment, further worsening the reproducibility of test results. Hence a modified jig [Figure 2.9b] was designed and fabricated in the

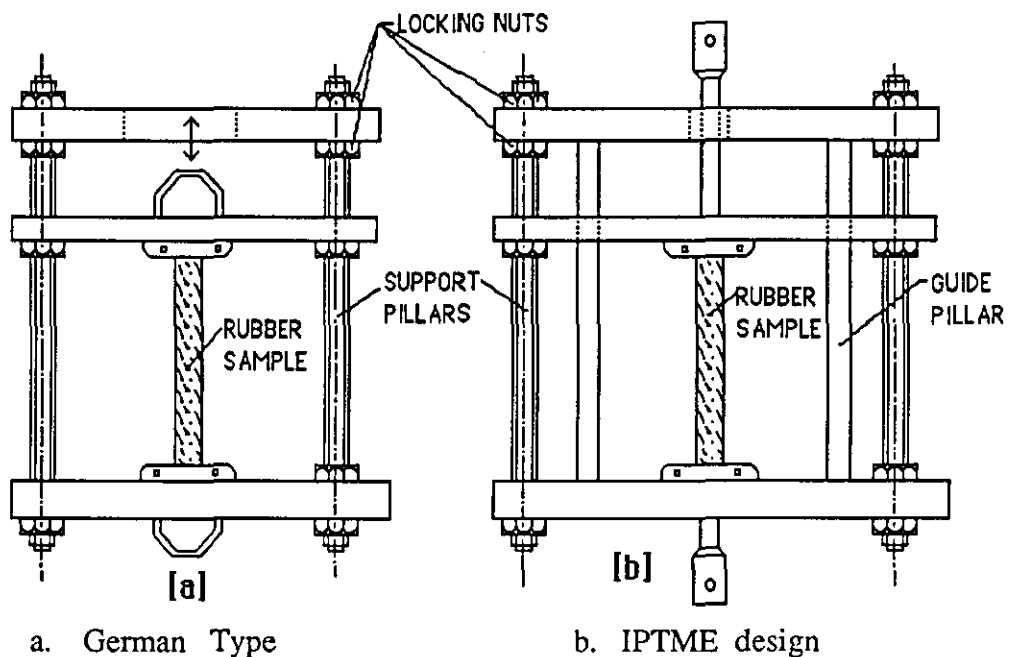


Figure 2.9: Schematic diagram of tensile stress relaxation jigs.

departmental workshop, incorporating two guide pillars. This eliminated the problem to some extent but introduced a significant amount of friction, thereby reducing the sensitivity. The amount of friction was far too high to trace any significant amount of relaxation. Efforts were made to reduce this friction, nevertheless, reproducibility of results was not achieved. A simple stress relaxometer was developed by the author based on a different

concept. A schematic diagram of this is shown in Figure 2.10. This consisted of a balanced lever arm and a slide, supported on a strong base at the centre of the platform. The wooden base was reinforced with metal to restrain distortion. This had several major advantages. Viz. cheap and simple to fabricate, very reliable and quite accurate. Six relaxometers were made in the departmental workshop.

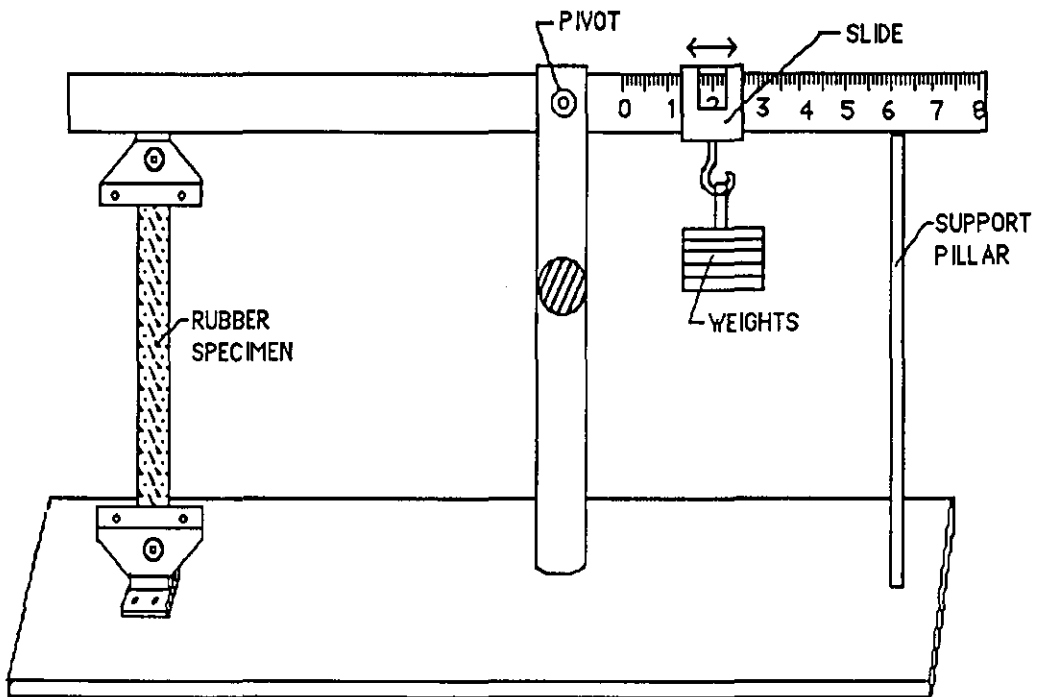


Figure 2.10: Tensile stress relaxometer developed at IPTME for continuous measurement of residual stress.

Elastomer strips, of dimension 100mm x10 mm, cut from 1 mm thick sheet are tested at strain levels of 25%, 50% and 100%. During a test, the specimen, in the form of a strip, was held between the grips, the gauge length was selected to render a predetermined strain when the arm was horizontal. Once the test sample was firmly secured in grips, dead-weights were chosen to keep the arm horizontal when the slide is at its extreme end possible. The distance of the slide from the centre of the arm was recorded against time to give a direct measure of relaxation in the specimen.

2.2.3 Test Variables and limitations:

Due to the cumbersome design of the tensile relaxometer, only the effects of strain level and the specimen surface area were studied; the strain levels and the cross-sectional area were controlled by changing the specimen geometry. The results are discussed in Section 4.2.

Like any other apparatus, the tensile relaxometer also suffers some inherent disadvantages. Although they are cheap, the instrument can run only one test at a time. Because stress relaxation tests are run for a long period of time, each test will engage a relaxometer, which remains idle between measurements but needs constant attention throughout the test period. Because of the size, these equipments are not suitable for use in an oven.

Chapter Three

RELATED PROPERTIES

3.1 MATERIAL CHARACTERISTICS

3.1.1 Introduction

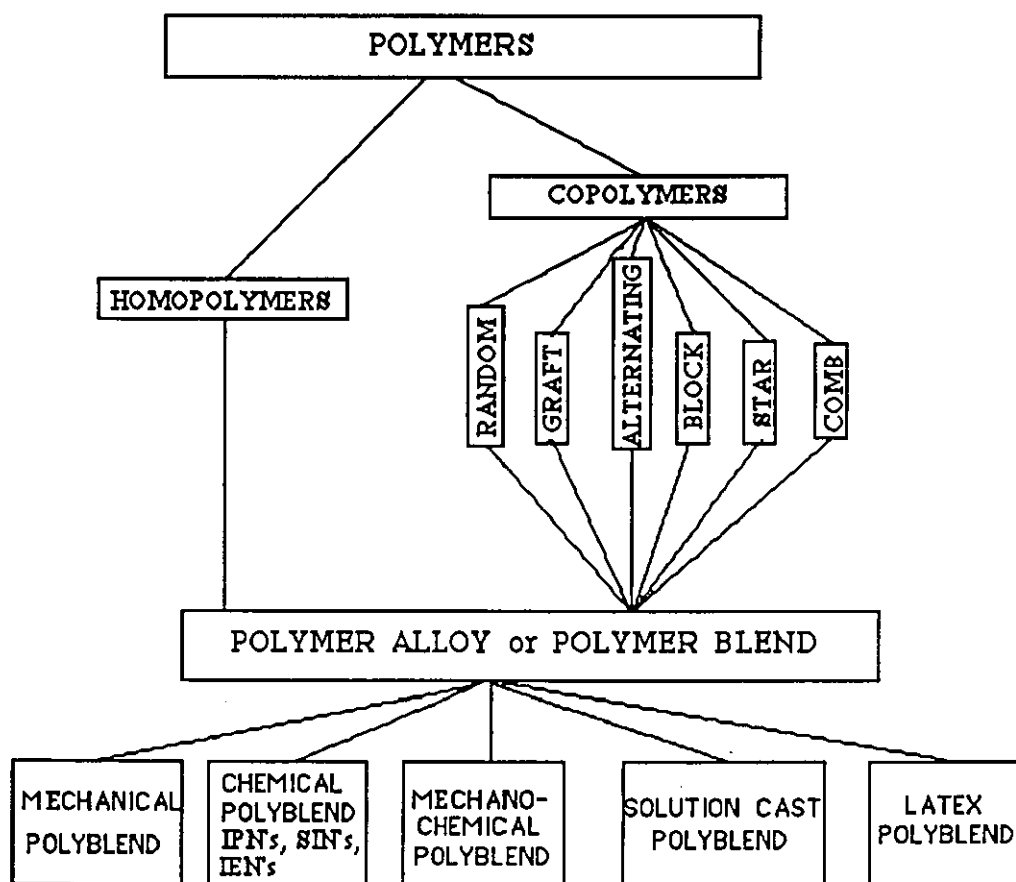
Although the use of rubber by the south American Indians from the naturally occurring trees such as *Hevea brasiliensis*, dates back to as early as the 15th century, little progress was made in its application until early in the 19th century when Charles Macintosh (1823) used natural rubber mixed with coal tar naptha to produce laminated fabric. The discovery of mastication by Thomas Hancock (1830) and vulcanisation by Charles Goodyear (1839) led to further exploitation of natural rubber. The use of rubber finally exploded during the World war periods due to the sudden surge in demand and eventually led to the production of many synthetic rubbers.

Due to the demand of high quality products by the consumers and the competition between the natural and synthetic rubber producers, a variety of elastomers were developed. Much research and manpower were devoted in understanding the science of rubbery materials. Broadly, these group of materials can be divided into two main sub-groups as shown in Figure 3.1.

The raw rubbers are generally high molecular weight, weak, tacky, plastic materials with few applications such as in adhesives and for polymer blends. In order to make an efficient use of these rubbery materials for engineering applications such as seals, gaskets, rubber mountings, tyres, hoses and bearings, they should be suitably compounded and duly vulcanised.

The purpose of vulcanisation is to introduce chemical bonds to form a three dimensionally crosslinked network to overcome the permanent set. Compounding, on the other hand couples vulcanisation with the incorporation of other additives which include filler, antioxidant, plasticiser, lubricant and processing aids; these additives normally improve the physical properties of the final

vulcanisate and also render stability to the polymer network against thermal, chemical or biological attacks during its use in service. Several types of curing systems are in use and are discussed in Section 1.2.



NOTE: IPN's : Interpenetrating Networks, SIN's: Simultaneously Interpenetrating networks
IEN's: Interpenetrating Elastomeric Networks

Figure 3.1: Classification of polymers

Thermoplastic elastomers are new materials which combine the thermo-processing of a thermoplastic material with the elastic properties of rubbers. A brief review of these materials is given in Section 1.2; more details can be found in the literature ^{9,10,67}.

3.1.2 Assessment of cure state

Introduction of crosslinks into the polymer network changes both the physical and the chemical nature of the final vulcanisate. However, the amount of crosslinking is generally a matter of compromise and

experience; this is because some of the properties deteriorate after reaching a peak value while others improve further (Figure 1.4).

The degree of crosslinking is defined as $1/2M_c$, which equals the number of gram moles of crosslinks per gram of rubber in the network, where M_c is the number average molecular weight of the rubber chain between the crosslinks, the number of network chains will be twice the number of crosslinks. The value of $1/2M_c$ can be arrived at from stress-strain measurements in simple tension using the expression:

$$f = \frac{\rho R T A_0 (\lambda - \lambda^{-2})}{M_c} \quad 3.1$$

where f is the force to extend a sample of cross-sectional area A_0 , to extension ratio λ , ρ is the density, R is the gas constant and T is the absolute temperature.

Alternatively, the Flory -Rehner⁶⁸ equation can be applied to the results of swelling the rubber in a suitable solvent:

$$- [\ln (1-v_r) + v_r + \chi v_r^2] = \frac{\rho V_s v_r^{1/2}}{M_c} \quad 3.2$$

Where v_r is the equilibrium volume fraction of rubber in swollen gel, ρ is the density of the rubber, χ is the interaction parameter of rubber and solvent and V_s the molecular volume of the swelling liquid.

In practice, the change in crosslink density during a thermal treatment is monitored using a rheometer; this measures the change in modulus or torque at a given temperature and records this against the time axis. A small amount of rubber compound (7-8 g) is loaded into a thermally controlled chamber containing a rotating/ oscillating rotor or an oscillating blade; the resistance to movement, which is a measure of modulus, is recorded as a function of time. A typical rheometer curve for a sulphur vulcanisate is shown in Figure 3.2.

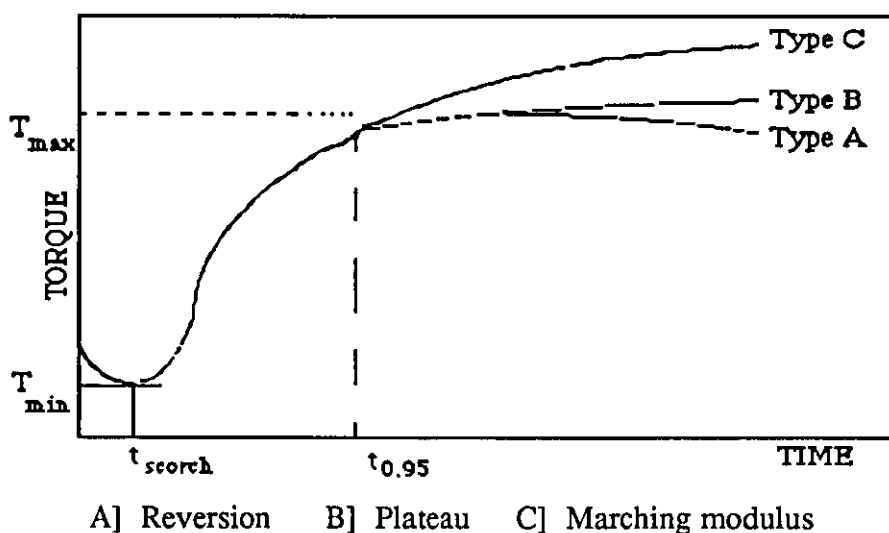


Figure 3.2: Typical rheometer trace for a sulphur vulcanisate

From the shape of the curve, it is noted that there is an induction period before a significant modulus develops; this is known as 'scorch time' and is a valuable asset to the compounder. It should be noted that vulcanisates based on peroxide and other curing systems have very little or no scorch time. The second part, following the scorch period, is the induction time where the vulcanisation begins with a rapid rise in modulus, and there after the compound ceases to be thermoplastic. Thus the cure time is sum of scorch time and vulcanisation time. The definition of optimum cure is not simple as a 'full cure' and 'technological optimum' differ due to the reasons explained earlier (Figure 1.4). After the optimum cure, the vulcanisate may undergo reversion, a plateau or marching modulus depending upon the material properties and the vulcanisation system used.

3.1.3 Effect of state of cure on stress relaxation:

According to the statistical theory of rubber elasticity,¹¹ the force in the rubber sample with an extension ratio λ can be written as:

$$f = NkTA_0 (\lambda - \lambda^{-2}) \quad 3.3$$

where N is the number of stress supporting links in the sample of cross-sectional area (unstrained) A_0 , k is the Boltzman's constant and T is the absolute

temperature. If λ and T are constants, then the force f is proportional to N . During a degradation process the change in crosslink density thus reflects in the corresponding change in the force. Thus Equation 3.3 can be rewritten as:

$$\frac{f}{f_0} = \frac{N}{N_0} \quad 3.4$$

Thus, the decay in stress is a direct measure of the degradation of an elastomeric network.

In order to study the effects of state of cure on stress relaxation, three different levels of cure were considered. The time to reach the required cure state, as defined below, is found from the Monsanto Oscillating Disc Rheometer (ODR) test.

Undercure: The compound which has attained only 50% or less of the final cure [t_{95} from the Monsanto ODR test]. For this, the cure time is selected between 0.4 -0.5 x the time required to reach 95% of maximum torque in the rheometer test.

Optimum cure: This is the state when the compound is cured to the time to reach 95 % of the maximum torque.

Over cure: This is when the compounds are cured for double the time to reach optimum cure.

From equation 3.3, undercured rubber compound should show lower initial force than the other two. Overcuring may not affect the force significantly unless reversion is a problem. Stress relaxation and recovery studies carried out on these three states of cure are discussed in Sections 4.4 and 5.3.4 respectively.

3.1.4 Effect of processing conditions on thermoplastic elastomers

The thermoplastic elastomers have a unique structure with heat-fugitive crosslinks. It is believed ⁶⁹ that the structures of these type of elastomeric compounds are dependent on thermal history, with the presence of varying amount of crystallinity. However, the study of the effects of the crystallisation in these materials on the stress relaxation is outside the aim of this project but can be found elsewhere.⁶⁹

3.2 HARDNESS

Several instruments are available to measure rubber hardness; the test procedure is described in test specifications such as BS 903 Part A6, ASTM D1415-83. Briefly, the hardness test is conducted as follows. A standard semi-spherical indenter is allowed to penetrate the surface of a standard rubber specimen under a specified load in a given time, normally 30s. The amount of penetration is then read on a dial gauge as hardness degrees. The measure of hardness is used in quality control to distinguish under-cured products. However, rubbers being visco-elastic, the time dependent component is a matter of concern, when thermoplastic elastomers are considered alongside the conventional crosslinked compounds. However, no standard specification or any theoretical explanation defines this ambiguous property of a viscoelastic material.

A major preoccupation during the programme has been defining this property. There was some uncertainty whether test data should be obtained by micro test, as would apply to seals, or whether the data should be obtained in the usual way, with a dead-load tester. The two methods were found to give different results, particularly for the thermoplastic elastomers. This time dependence of hardness is shown in Figure 4.17 over a period of one hour under a dead-load.

3.3 SWELLING MEASUREMENTS

The tendency of any material to swell when submerged in a liquid is a natural phenomenon. However, the amount of swelling depends upon the thermodynamics of the solute and the solvent and the environmental conditions, mainly, temperature and pressure. When a rubber sample is immersed in a given solvent, two things are possible. First, the solvent can enter the rubber network and make the latter swell and perhaps dissolve; the amount of swelling depends upon the interaction between the solvent and the polymer. Secondly, some of the additives, which are added during the compounding stage, may migrate to the solvent causing a loss of weight.

The swelling tests are carried out as a supplementary to stress relaxation measurements in water at three different temperatures; i.e: 23° C, 40° C and

70°C. This is to avoid the variability in stress relaxation measurements caused due to changes in dimensions. Prior to the relaxation measurements, the test samples are pretreated by water immersion for a period of 1000 h at 23° C and 40° C and for 250 h at 70° C. The height and the weight of the test sample were recorded before and after the swelling test and the percentage change is calculated. The results are discussed in Section 4.7.

Chapter Four

RESULTS AND DISCUSSION OF STRESS RELAXATION

4.1 COMPRESSION STRESS RELAXATION

Stress relaxation is an inherent property of elastomers and occurs due to physical and chemical phenomena. These mechanisms are generally superimposed and can seldom be distinguished immediately. From a practical, as well as theoretical point of view, it is desirable to find methods of distinguishing between these two types. The assumption that chemical relaxation can be neglected at normal (or sub-normal) temperatures and at very small times is a reasonable approach and has been widely accepted by previous workers.^{4,22} The experimental results of compression stress relaxation tests at various temperatures and in different environments are given in the Appendix (Figures 1-23). The experimental variables have been discussed previously in Chapter 2. Stress relaxation data are plotted as the percentage residual stress factor (R.S.F) as a function of log(time). The residual stress factor is given by:

$$\% \text{ R. S. F.} = \frac{F_t}{F_o} \times 100 \quad 4.1$$

where F_t is the retained force measured at time t , and F_o is the initial force.

As it has been suggested in the past⁴ that a linear or approximately linear viscoelastic behaviour is essential for a successful separation of the different relaxation processes, the force-deformation and isochronous stress-strain relations are considered here. The force-deformation relationship, derived from the theory of rubber elasticity,¹⁹ for a rubber specimen under compression is considered in Figure 4.1. For various reasons, a low strain rate of 0.31 mm/min. is used in this work (unless otherwise specified). It is important that the insitu relaxation in the rubber network during the loading process should be considered in understanding the force-deformation diagram (refer to Figure 4.1). Depending upon the physical relaxation behaviour of the selected material, a concave upward (ie: slow relaxing) or concave downward (ie: fast relaxing) in the force-deformation relationship can be envisaged and has been found in this research. A critical study of linear viscoelasticity is outside the objectives of this project and can be found in the literature.^{4, 20}

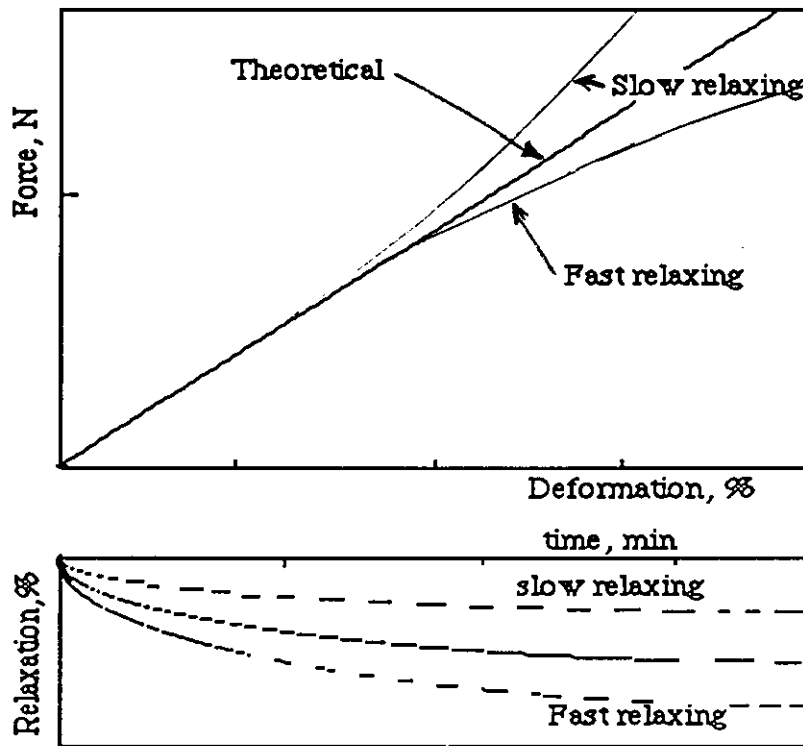


Figure 4.1: Force-deformation relationship for a rubber in compression stress relaxation test

As lubricated specimens and ground glass plates are used to assist slippage, the problem due to bulging of the specimen when strained is much reduced, however, a slight bulging can not be ruled out (refer to Figure 4.2). Because of this bulging, a well defined cross-sectional area of the specimen can not be given and hence the true stress-strain distribution is very complex, hence the force-deformation diagram is considered instead. Typical force-deformation and residual stress curves at 0.1 hour for a crosslinked rubber (sulphur cured EPDM) and a thermoplastic elastomer (Santoprene 101-55) are given in Figure 4.3.

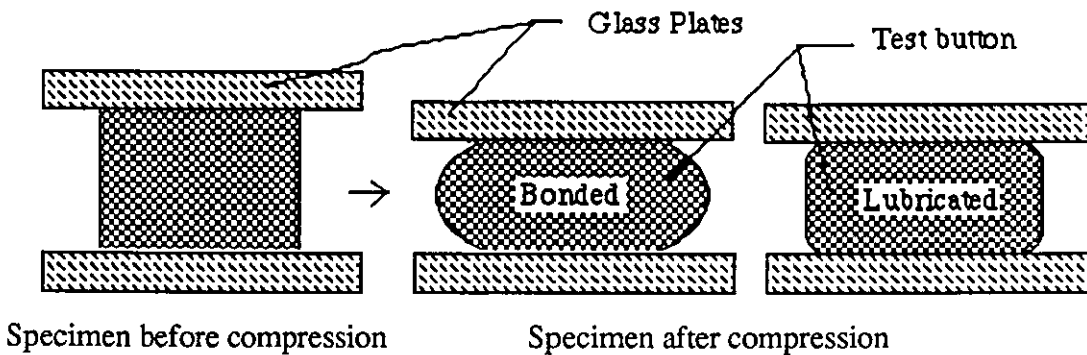


Figure 4.2: Bulging effect in bonded and lubricated specimens

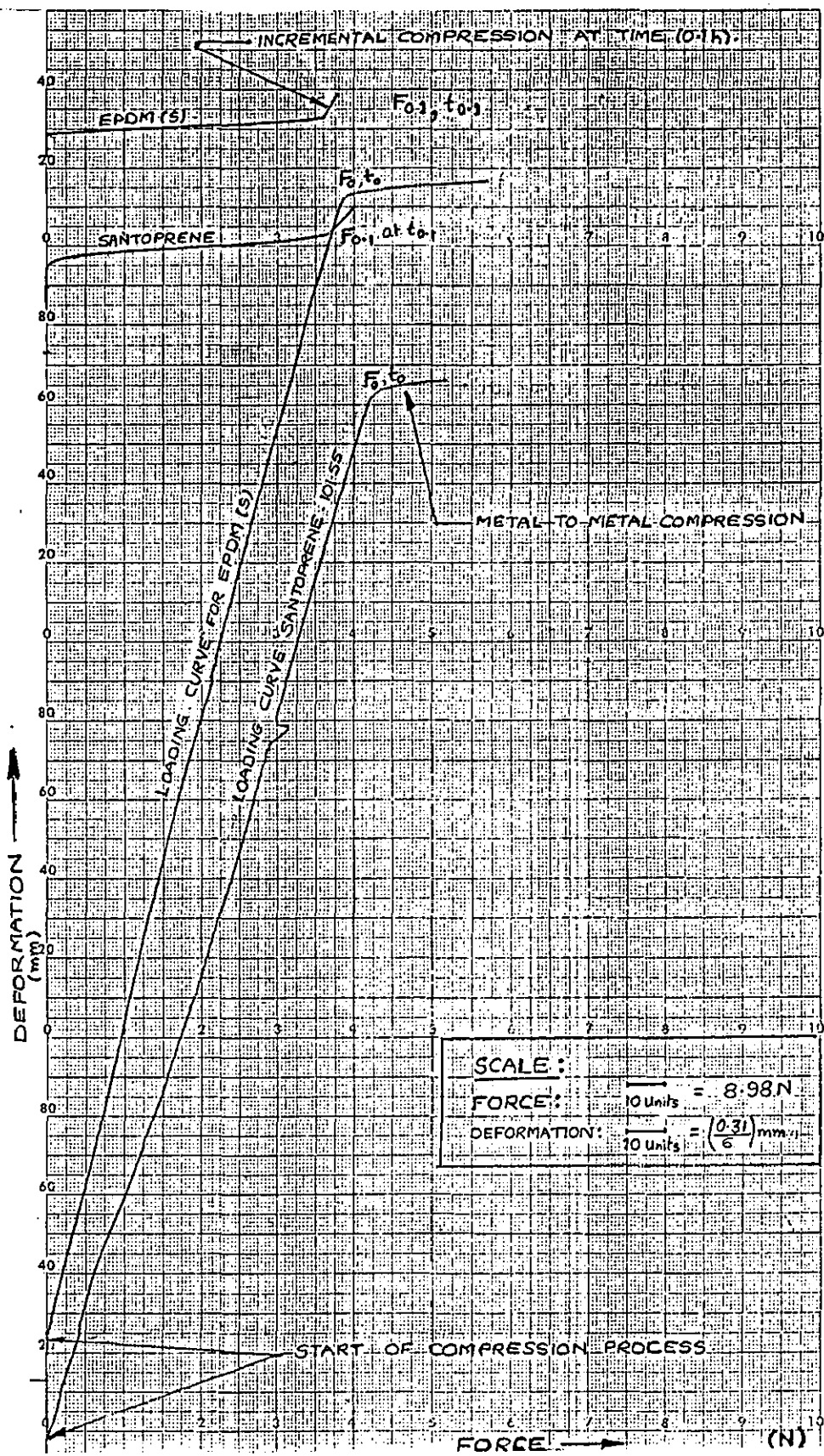


CHART No. C/P/0003/0/0

Figure 4.3. Loading curve and residual force measurements for rubbers in compression stress relaxation test

Stenberg⁴ studied the linearity of the stress-strain relationship in crosslinked rubbers by plotting the isochronous stress-strain diagrams (ie: the stress at a constant time plotted as a function of strain). He observed that most of the crosslinked rubbers behave approximately linearly viscoelastic up to 30% strain in compression when lubricated, however, for highly filled materials and for bonded samples the deviation occurred at about 20% strain. Significant deviation in stress-strain relationship has been observed in NR-vulcanisates above 150% strain in tension due to the occurrence of strain induced crystallisation.^{24,41} There is, however, no evidence of this occurring in compression at the strain levels used in this research (20-30%). Because of the difficulty in calculating the true stress, due to the reasons explained earlier, the isochronous force-deformation diagrams are considered here and were also suggested by Stenberg⁴ in his work.. The isochronous diagrams for a crosslinked rubber (sulphur cured EPDM) and a thermoplastic elastomer (Santoprene 101-55), at 1 min. and at 30 min. after the straining process and at the end of compression are given in Figures 4.4 and 4.5 respectively. The specimens are compressed, manually, within 10 s to a fixed strain and the force is recorded as a function of time. It should be noted that only in this experiment the zero time is the time at which the compression begins and not when the compression ends as used in the stress relaxation experiments. In these figures, the Force(1min) and Force(30min) are the residual forces at 1 min.

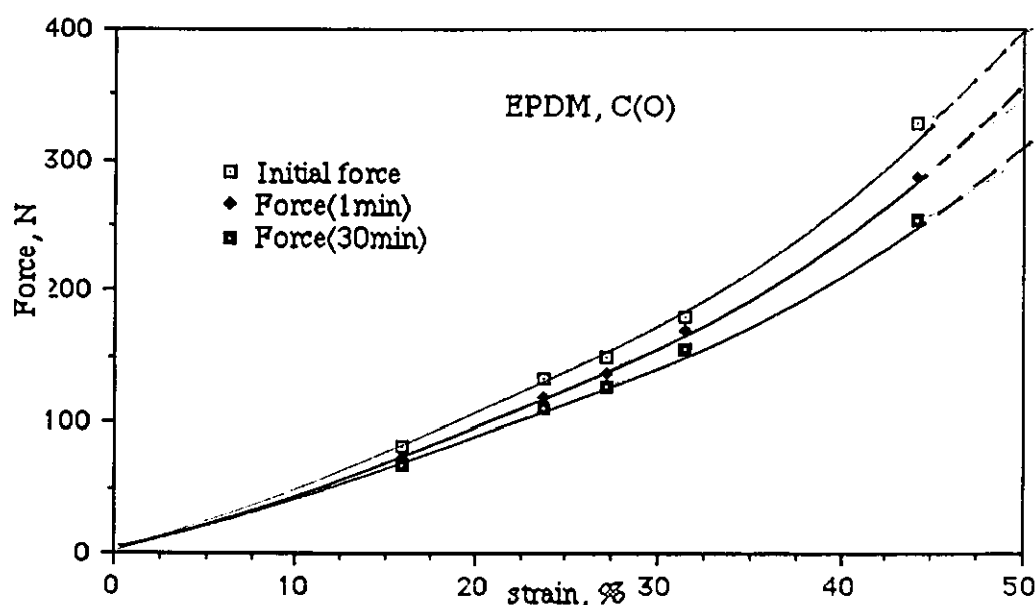


Figure 4.4: Isochronous curve for sulphur cured EPDM, C(O)

and 30 min. after the beginning of compression. From these results and similar observations on the other materials, it is clear that linear viscoelasticity is acceptable at the strain levels (@ 30%) for all the materials used in this work. Comparing the isochronous force-strain curves at 30 min. with those at 1 min. and the initial force, it is evident that the non-linearity increases at very short times, soon after the material is compressed.

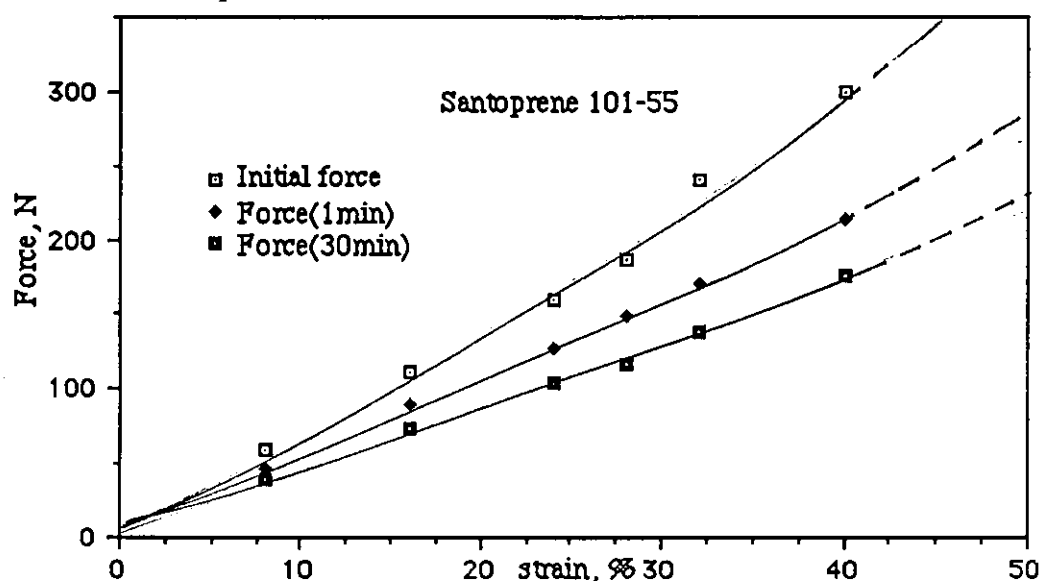


Figure 4.5: Isochronous curve for a thermoplastic elastomer, Santoprene 101-55, I(O)

In Figure 4.6, the residual stress factor (%) remaining at 30 min. after compression began is plotted as a function of strain for the sulphur cured EPDM and Santoprene 101-55. From these results, it can be inferred that the physical relaxation is largely independent of the amount of compression, at least up to 30% strain.

4.1.1 Time dependence

For all the materials at all the temperatures the initial relaxation is linear with $\log(\text{time})$, as found by other workers.^{4,22,37,39} This is assumed to correspond to physical relaxation; a relaxation rate per decade of time is calculated to give the physical rate constants [See Section 4.1.2.3]. For compounds based on NR, SBR, EPDM(S), NBR and EPCL (Figures 1, 2, 3, 4, 5, 9, 10, 12, 13 in the Appendix) the stress relaxation curve later deviated from this linearity at all the temperatures (except at 5°C in a few cases) involved in this programme, and this is assumed to indicate the onset of chemical relaxation. The elapsed time

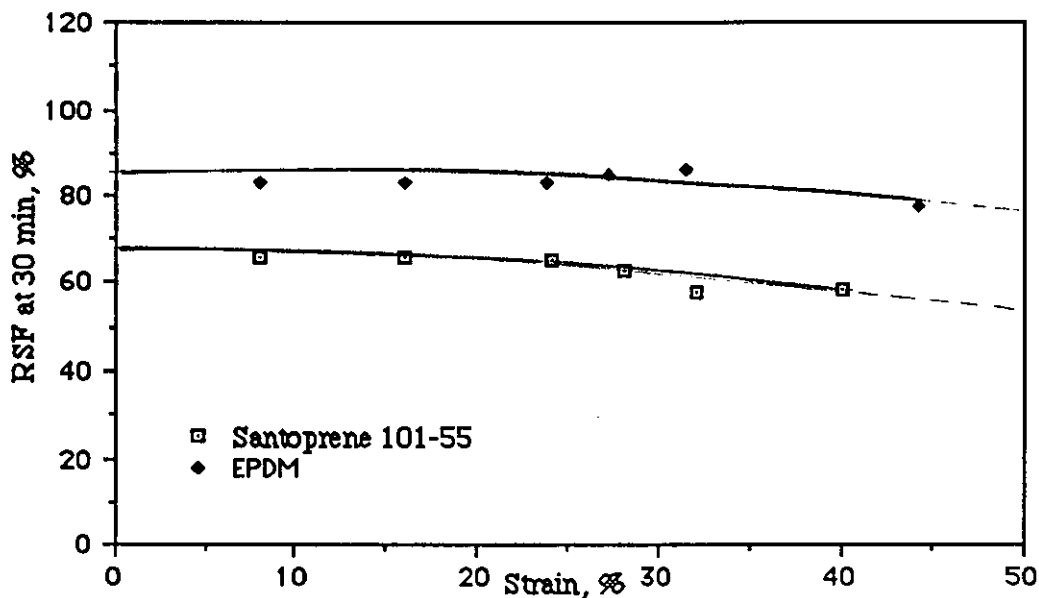
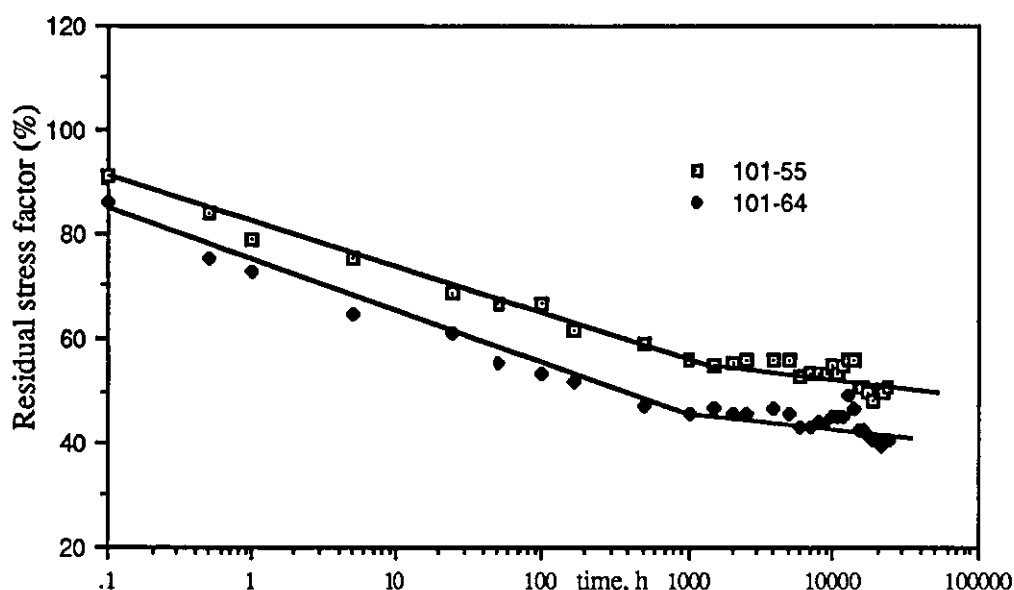


Figure 4.6: Residual stress factor (%) as a function of strain.

at this deviation is defined as the induction time. This type of behaviour has also been found in the RAPRA long-term data and in previous work at IPTME.⁶⁵

Of the other materials, some of the peroxide-cured EPDM's (Figures 7 and 8 in the Appendix) appeared in general, to display a linear relation with $\log(\text{time})$ at all the temperatures up to 24,000 h, whilst others (Figures 6 and 11 in the Appendix) showed some deviation from linearity at the later stages. The stress relaxation behaviour of the thermoplastic elastomers is approximately linear at most temperatures (Figures 14, 15, 21, 22, 23 in the Appendix) except at temperatures above 70°C. The stress relaxation curves of these TPE's (Santoprene) are found to consist of two straight lines, with a high rate of stress decay at shorter times; the intersection of these two lines is found to be affected by the strain rate, occurring at about 1000 h at 23°C for Santoprene when normal loading conditions (0.31 mm/min) are being used (See Figure 4.7).

It is well known that many TPE's such as Santoprene are capable of crystallising on cooling from the melt ⁶⁹ (eg: during processing) and this may or may not be advantageous to the overall properties of the material. Thus, it may be the crystalline phase which is responsible for the high rate of stress relaxation in these materials and which was also observed by Gent ⁴¹ in his work on NR-vulcanisates. However, it is not clear why the relaxation process of crystallised materials are slower at longer times and this needs further investigation..



**Figure 4.7 Stress relaxation in thermoplastic elastomers
- Santoprene 101-55 and 101-64.**

The later part of the relaxation curve of the Santoprene elastomer was found to be similar to that of EPDM, which in fact the rubbery phase in the TPE's such as Santoprene.⁶⁷ However, careful consideration of this type of behaviour is essential as most of the stress relaxation specifications depend on the validity of short time tests (168 h. in BS 903 Part A42). Such values should not be employed to predict the relaxation behaviour at longer intervals and may underestimate the material's performance.

It is interesting to compare the ranking of materials in terms of the R.S.F and the retained load. In Table 4.1, the materials are listed in ascending order, in terms of the retained load after 100h and the R.S.F normalised to the stress at zero time and that at 0.5h. From the results, it is clear that harder materials show higher initial force. It has been found that the hardness measurement, which is used as a quality control test in the industry, may not be reliable (later discussed in Section 4.6). Hardness test could, however, be replaced with the measurement of initial force because the increase in hardness value brought about by increase in either crosslink density or by the amount of filler loading would also bring corresponding changes in the initial force.³⁷

Table 4.1: Ranking of material as a function of Initial load and % RSF at 100h. normalised to initial load (zero time) and load at 0.5 h. in compression stress relaxation.

LOAD (N)	MATERIAL TYPE	% RSF (0.1 h)	MATERIAL TYPE	% RSF (0.5 h)	MATERIAL TYPE
78	Evoprene992,K(O)	50.0	Alcryn 1201, O(O)	63.3	Alcryn 1201, O(O)
81	Evoprene992/994,K(M)	53.4	Santoprene 101.64, J(O)	68.1	Alcryn 6385, N(O)
87	Alcryn 6368, M(O)	58.5	Alcryn 6385, N(O)	70.2	Alcryn 6368, M(O)
134	EPDM(Pero), D(N)	61.4	Evoprene994, L(O)	70.8	Santoprene101-64,J(O)
109	NBR, E(O)	66.5	Evoprene 992, K(O)	77.3	Evoprene 994, L(O)
116	Santoprene101-55,I(O)	66.9	Santoprene 101-55 I(O)	77.3	Evoprene992/994,K(M)
122	Alcryn 1201, O(O)	70.2	EPDM(Pero), D(N)	79.5	Santoprene101-55, I(O)
130	EPDM(Sul), C(O)	74.3	Evoprene992/994, K(M)	81.0	Evoprene 992, K(O)
131	SBR(sul), B(N)	74.7	EPCL, H(O)	82.9	SBR(sul), B(O)
140	Santoprene101-64, J(O)	76.7	EPDM(pero), D(N)	83.8	EPDM(pero), F(O)
142	Evoprene 994, L(O)	78.2	SBR, B(O)	84.5	EPCL, H(O)
142	SBR, B(O)	79.5	EPDM(sul), C(O)	85.2	EPDM(pero), D(N)
147	EPDM(pero),D(O)	80.1	EPDM(pero), D(O)	87.2	EPDM(pero), D(O)
173	EPDM(pero), F(O)	80.5	SBR, B(N)	87.3	EPDM(sul), C(O)
173	NR(sul), A(N)	82.3	NBR, G(O)	88.7	NBR, G(O)
226	EPCL, H(O)	85.2	NBR, E(O)	88.9	NBR, E(O)
258	NR, A(O)	87.8	NR, A(N)	92.3	NR, A(N)
329	NBR, G(O)	92.4	NR, A(O)	93.7	NR, A(O)

(Note: The hardness values are available in Tables 4.2 and 4.3)

4.1.2 Temperature dependence

4.1.2.1 Initial force

The force recorded at the end of loading process, where a sharp change in slope occurs as metal-to-metal compression begins (see Figure 4.3), is considered as the initial force. The amount of compression is calculated from the specimen and the jig geometry and also from the dial gauge and graphical analysis (see Sections 2.1.5 and 2.1.6). The force is then normalised to 25% strain for comparison purposes, assuming linear stress-strain behaviour (see Section 4.1). The effects of temperature on the initial force normalised to 25% strain are given in Table 4.2. The initial force decreased with increasing temperatures for all the TPE's as expected due to the thermoplasticity, but remained approximately constant for the crosslinked rubbers.

4.1.2.2 Residual force

The measurement of residual force is carried out at regular intervals on all the specimens maintained at constant strain and various conditions as given in Section 2.1.6. The point of the change in slope of the force-deformation curve due to an incremental compression is taken as the measure of residual force (see Figure 4.3).

The change in slope of the force-deformation curve may not be sharp - thus leading to a error in calculating the initial force or the residual force. Intersection of the tangents drawn to the corresponding parts of the curves is used to reduce the error. Use of clean, dust free glass plates and test buttons with smooth parallel surfaces was found to improve the accuracy of the measurements. Taking these into consideration, multiple trials were carried out on various compounds to test for the reproducibility. The results are given in Figures 23a to 23d in the Appendix.

4.1.2.3 Physical relaxation

The early part of relaxation is assumed to be physical, as the stress relaxation rate is linear with $\log(\text{time})$ for all the compounds (eg: Figure 4.8 for crosslinked rubbers and Figure 4.9 for thermoplastic elastomers). The effects of temperature

Table 4.2 Initial force normalised to 25% strain at various temperatures

MATERIAL	Hardness (IRHD)	INITIAL FORCE (N)				
		5° C	23° C	40° C	70° C	100° C
NR A(O)	61.0	238.9	250.3	233.0	273.2	252.0
NR A(N)	54.5	175.0	176.8	184.5	190.5	177.9
SBR B(O)	58.0	168.7	163.8	162.8	154.1	141.8
SBR B(N)	51.5	139.7	146.7	123.3	131.5	134.0
EPDM C(O)	49.5	151.2	147.1	122.2	120.3	120.1
EPDM D(O)	49.0	152.6	164.8	150.1	155.8	145.9
EPDM D(N)	53.0	168.8	157.3	161.5	147.5	162.3
EPDM D(M)	47.0	123.7	117.8	112.1	119.6	128.2
NBR E(O)	43.0	111.9	115.2	109.3	87.3	89.3
NBR E(N)	52.0	—	159.9	147.4	163.5	161.5
EPDM F(O)	65.5	269.7	221.3	232.2	275.5	268.6
NBR G(O)	70.0	308.4	359.4	359.7	327.6	257.3
EPCL H(O)	70.5	304.8	271.1	314.2	281.1	295.5
Santo.101.55 I(O)	56.0	162.8	155.3	139.4	122.3	104.3
Santo.101.64 J(O)	67.5	260.2	236.1	185.7	176.2	124.5
Evoprene 992 K(O)	46.0	91.9	104.9	83.5	55.8	46.1
Evoprene 992 K(M)	52.0	116.9	98.1	101.2	85.9	85.3
Evoprene 994 L(O)	61.0	200.7	208.3	154.2	116.0	134.7
Evoprene 994 L(2)	85.0	410.1	329.8	274.6	217.6	260.0
Evoprene 994 L(3)	78.0	339.1	263.0	260.4	180.1	197.2
Alcryn 6368 M(O)	54.0	—	145.5	139.1	48.6	24.0
Alcryn 6385 N(O)	53.5	—	165.5	139.7	49.5	27.9
Alcryn 1201 O(O)	63.0	—	244.6	166.9	87.9	58.7
NR(GUM), Type A	43.1	—	126.2	—	115.4	—
NRR (GUM), Type E	47.8	—	—	—	143.4	—
EPDM (GUM), Type D	57.3	—	189.5	—	189.3	—
EPDM (GUM), Type F	—	—	287.4	—	—	—

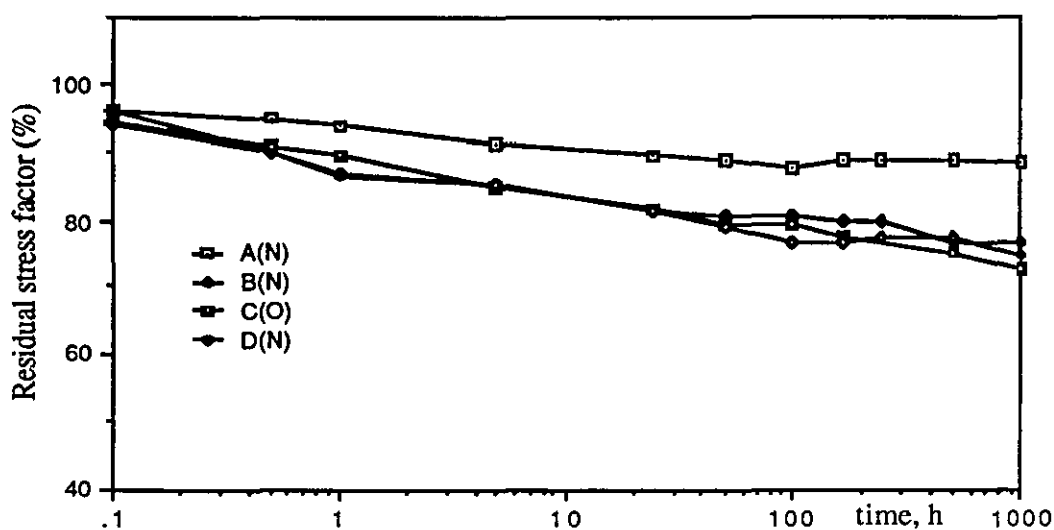


Fig: 4.8: CSR plots for the crosslinked rubbers for 1000h at 23°C

on the physical relaxation rates are shown in Table 4.3 and are in accordance with the literature.^{4,5,22,65,69} These rates are calculated using simple regression analysis from the stress relaxation data for the first 168 h. of the test.

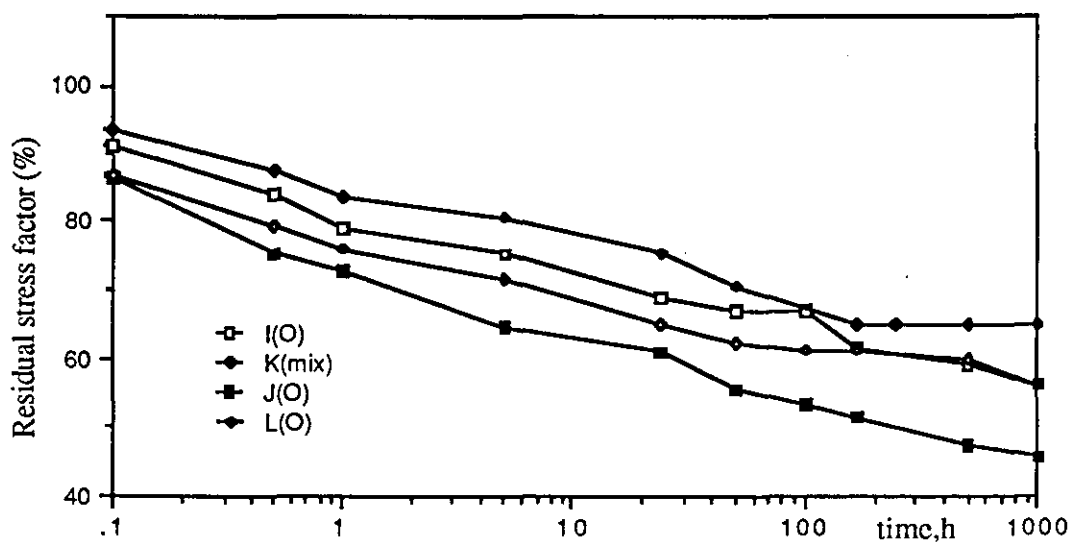


Figure 4.9: CSR curves for the TPE's for 1000h at 23°C

For some cross-linked rubbers at temperatures of 70°C and above, there is a possibility that chemical relaxation would begin within 168 h. and this would yield high rate constants. The correlation coefficients are also shown in Table 4.3 to indicate the linearity of the stress relaxation curve [A value of 1.0 corresponding to a perfectly linear relation of % R.S.F with log(time)].

Table 4.3 Physical relaxation data as a function of temperature

MATERIAL	Hardness (IRHD)	PHYSICAL RELAXATION RATE (%) PER DECADE TIME [*] AND THE CORRELATION COEFFICIENTS (1000 h data)				
		5°C	23°C	40°C	70°C	100°C
NR, A(N)	54.5	3.0±0.4 (0.92)	3.3±0.2 (0.97)	3.3±0.25 (0.98)	6.2±0.8 (0.95)	5.7±1.2 (0.88)
SBR, B(N)	51.5	3.0±0.4 (0.95)	3.9±0.3 (0.99)	3.1±0.2 (0.99)	8.7±1.6 (0.90)	16.5±2.5 (0.93)
EPDM, C(O)	49.5	5.2±0.7 (0.93)	5.4±0.2 (0.99)	4.8±0.2 (0.99)	8.6±0.7 (0.95)	10.8±1.7 (0.88)
EPDM, D(N)	53.0	3.5±0.3 (0.99)	4.7±0.2 (0.99)	4.6±0.2 (0.99)	5.6±0.5 (0.99)	5.4±0.5 (0.98)
NBR, E(N)	52.0	3.3±0.6 (0.99)	2.5±0.4 (0.99)	3.5±0.4 (0.99)	3.6±0.4 (0.98)	4.6±0.4 (0.98)
EPDM, F(O)	65.5	4.5±0.7 (0.95)	6.6±0.4 (0.98)	7.3±0.6 (0.96)	6.8±0.2 (0.97)	7.1±0.6 (0.97)
NBR, G(O)	70.0	3.3±0.3 (0.97)	4.8±0.5 (0.97)	4.8±0.5 (0.97)	4.0±0.2 (0.99)	5.0±0.6 (0.95)
EPCL, H(O)	70.5	4.9±0.5 (0.97)	5.7±0.2 (0.99)	5.4±0.2 (0.99)	9.4±1.0 (0.97)	8.4±0.4 (0.99)
Santoprene, I(O)	56.0	9.5±0.5 (0.99)	8.4±0.3 (0.99)	8.3±0.3 (0.99)	11.8±0.6 (0.98)	7.6±0.4 (0.99)
Santoprene, J(O)	67.5	6.5±0.2 (0.99)	9.8±0.4 (0.99)	9.7±0.8 (0.99)	8.1±0.6 (0.98)	10.1±0.5 (0.99)
Evoprene, K(O)	46.0	6.9±0.7 (0.97)	7.0±0.3 (0.99)	7.8±0.4 (0.99)	13.8±1.1 (0.98)	17.7±1.0 (0.99)
Evoprene, L(O)	61.0	6.4±0.8 (0.95)	7.3±0.4 (0.99)	8.2±0.4 (0.99)	10.9±0.9 (0.98)	19.2±1.4 (0.98)
Alcryn, M(O)	54.0	—	10.2±0.4 (0.99)	18.0±1.6 (0.98)	14.1±1.0 (0.98)	14.1±2.0 (0.95)
Alcryn, N(O)	53.5	—	11.0±0.1 (0.99)	14.6±1.2 (0.98)	15.5±1.0 (0.99)	19.5±1.0 (0.98)
Alcryn, O(O)	63.0	—	12.8±0.7 (0.98)	12.8±1.5 (0.99)	12.1±1.0 (0.97)	19.2±1.0 (0.99)

* (The rates are calculated using regression analysis of 1000 hour data;
the correlation coefficients are given in brackets)

The deviation from linearity, with the onset of chemical relaxation processes is noted in compounds based on NR, SBR, EPDM(S) at 100°C with the correlation coefficient of 0.95 or less (Indicated by bold figures). The correlation coefficients of less than 0.95 were also found for some specimens at 5°C. This probably represents the variability produced by the poor temperature control in the domestic refrigerator and does not imply any chemical relaxation at that temperature. The physical relaxation rate increases slightly with temperature for most materials (ignoring the effects due to chemical processes which are indicated by bold letters in Table 4.3). The effect is most marked in TPE's such as Alcryn and Evoprene, whereas for the crosslinked rubbers and Santoprene the rate remains approximately constant.

4.1.2.4 Chemical relaxation

A) INDUCTION TIME: The chemical relaxation induction time is the time after loading, determined experimentally, at which the linear relationship of residual stress factor vs log(time) no longer applies. The induction time is estimated using a graphical construction. The physical relaxation curve, obtained from the first 168 h data, is extrapolated to the end of the test period. When the measured data first deviated consistently ($> 6\%$ RSF) from the extrapolated line, chemical relaxation is assumed to be occurring, and the time at which this deviation first occurred is defined as the **induction time**. As some scatter in the measurement of residual stress is unavoidable due to reasons explained earlier, a deviation of $< 6\%$ in the RSF values is neglected in this analysis. In addition, the experimental variability in some materials such as sulphur-cured EPDM, made the estimation of induction time difficult. For lower temperature measurements (up to 40°C) the logarithmic time scale meant that it is not possible to determine the times to an accuracy of greater than ± 0.07 decade time. Also, a very low chemical relaxation rate further complicated the analysis and in many cases were outside the range of the experiment. For this reason, a second method, using an Arrhenius extrapolation from the high temperature data, is used and is discussed later in Chapter 7. For tests at 70°C and 100°C, where the onset of chemical relaxation occurred before 168 h, the small number of points for extrapolation also made the determination of induction time somewhat subjective. The experimentally determined induction times, using the graphical analysis as explained above, are given in Table 4.4.

Table 4.4: Chemical relaxation induction times as a function of the test temperature

Material	Induction time in hours				
	5°C	23°C	40°C	70°C	100°C
NR, A(O)	>24000	11000	4000	240	50
NR, A(N)	>20000	14000	2000	120	55
SBR, B(O)	>24000	15000	4500	100	50
SBR, B(N)	>20000	14200	5000	108	50
EPDM, C(O)	>24000	13600	3000	100	50
NBR, E(O)	>24000	16500	2500	180	45
NBR, G(O)	>24000	14800	4000	95	50
EPCL, H(O)	>24000	12500	1000	100	50

For materials which displayed the deviation from the linear stress relaxation with log(time) relation within the time scale of the experiment (24000 h), the effect of increasing the temperature was to reduce the elapsed time to the deviation, i.e: the induction time decreased with increasing temperatures. At 100°C, chemical effects are observed within a few tens of hours, accelerating the deterioration. There does not appear to be a threshold temperature, below which the chemical activity ceases. Data at 5°C show deviations from linearity for NR, SBR and EPCL compounds (< 6 %, hence neglected); however, longer term data than those used in this research are required to confirm this. Unfortunately, as no duplicates tests were run due to shortage of jigs, it is not possible to comment critically on any misinterpretation of the scattered results obtained at the later stage of the programme. At 23°C EPCL and all the diene rubber compounds except the soft NBR show this effect, within the time scale of this programme. Similar evidence for chemical relaxation at 23°C have been found in other investigations (refer to Figure 4.10).

B) CHEMICAL RELAXATION RATE : The effect of temperature on the stress relaxation rates for the portion of stress relaxation curves after the deviation from the linear relation with log(time) are shown in Tables 4.5 and 4.6. It is not only difficult to separate the chemical and physical relaxation mechanisms at low temperatures but also significant amount of relaxation takes place outside the range of the experiment; this is because the lower the temperature the longer is the chemical relaxation induction time. Hence, the chemical relaxation at 5°C and 23°C are estimated using the Arrhenius relation from the

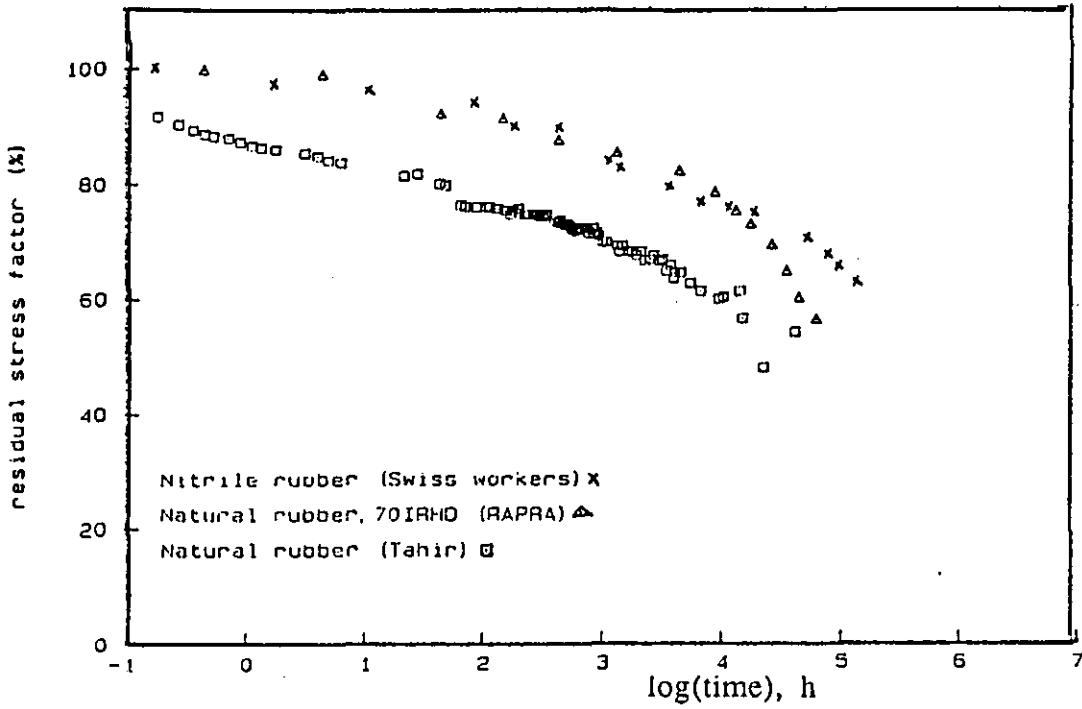


Figure 4.10: Long-term Stress relaxation data at 23°C

high temperature data, assuming a linear relation between $\ln(\text{relaxation rate})$ vs $1/T$, where T is the absolute temperature. Difficulties were encountered in obtaining a linear relation and hence regression analysis is used to minimise the error. An example of this treatment for NR and SBR compounds is given in Figure 4.11.

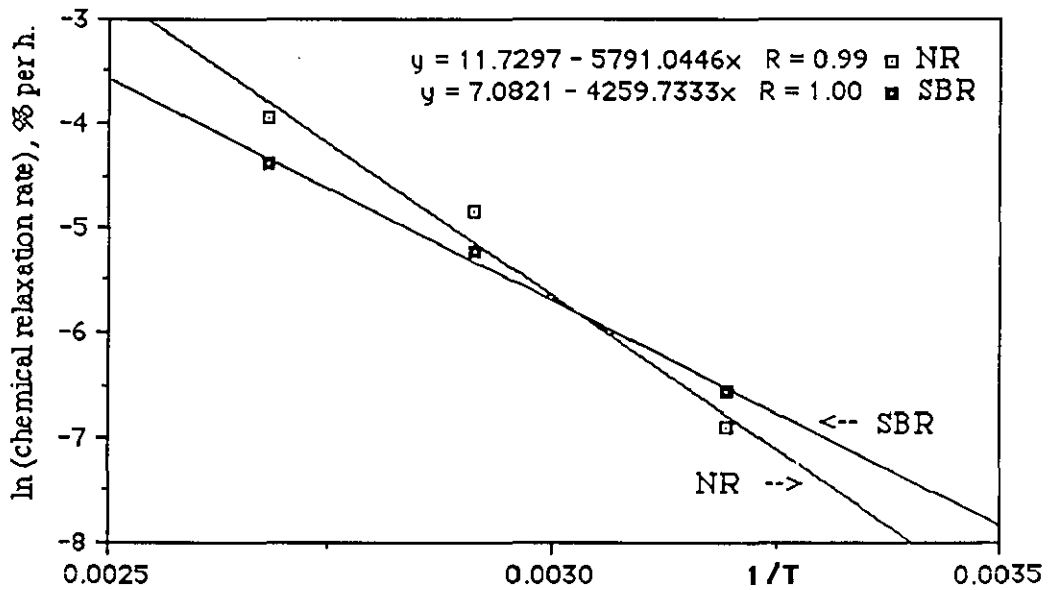


Figure 4.11 Estimation of chemical relaxation rate by using the Arrhenius treatment for NR and SBR rubber compounds.

Two methods are used in determining these relaxation rates. The first method assumed that, after the induction time, physical relaxation is negligible and all relaxation is chemical (Table 4.5). In the second method, the physical relaxation

Table 4.5: Chemical relaxation as a function of temperature
(assuming all relaxation after the induction time is chemical)

Material	Chemical relaxation rates % per hour				
	5°C *	23°C *	40°C	70°C	100°C
NR, A(N)	1.11×10^{-4}	3.93×10^{-4}	1.00×10^{-3}	0.0078	0.0191
SBR, B(N)	2.62×10^{-4}	6.66×10^{-4}	1.40×10^{-3}	0.0053	0.0124
EPDM, C(O)	3.61×10^{-5}	1.33×10^{-4}	4.29×10^{-4}	0.0017	0.0133
NBR, E(O)	4.92×10^{-5}	2.10×10^{-4}	7.69×10^{-4}	0.0038	0.0236
NBR, G(O)	7.06×10^{-5}	2.55×10^{-4}	8.31×10^{-4}	0.0031	0.0172
EPCL, H(O)	8.53×10^{-5}	3.15×10^{-4}	1.10×10^{-3}	0.0036	0.0242

[* The values at 5°C and 23°C are extrapolated data]

is extrapolated beyond the induction time and this extrapolated curve is subtracted from the total relaxation curve (The combination of physical and chemical relaxations). The relaxation rates obtained by this method are referred to as the normalised chemical relaxation data (Table 4.6); the values of relaxation rates calculated using this procedure are generally lower than the relaxation rates

Table 4.6: Chemical relaxation rates as a function of temperature
(assuming all relaxation after the induction time is the sum of the physical and chemical relaxations)

Material	Chemical relaxation rates % per hour				
	5°C *	23°C *	40°C	70°C	100°C
NR, A(N)	1.04×10^{-4}	3.71×10^{-4}	9.40×10^{-4}	0.0076	0.0182
SBR, B(N)	2.53×10^{-4}	6.33×10^{-4}	1.30×10^{-3}	0.0050	0.0111
EPDM, C(O)	1.41×10^{-5}	6.22×10^{-5}	2.20×10^{-4}	0.0012	0.0104
NBR, E(O)	3.42×10^{-5}	1.58×10^{-4}	6.01×10^{-4}	0.0035	0.0219
NBR, G(O)	6.51×10^{-5}	2.14×10^{-4}	7.13×10^{-4}	0.0027	0.0155
EPCL, H(O)	6.50×10^{-5}	2.50×10^{-4}	8.93×10^{-4}	0.0032	0.0216

[* The values at 5°C and 23°C are extrapolated data]

obtained using the earlier method (Table 4.5). These rates follow a linear relation with linear time and hence the later stages of relaxation can be assumed to be due to chemical relaxation processes.

4.1.3 Water immersion

As BS 2494 is much concerned with water and drainage pipe seals, stress relaxation measurements in water on all the available formulations were investigated at three different temperatures (23°C, 40°C and 70°C) to study the effect of water as explained in Section 2.1.7.1. The results are given in Figures 1-23 in the Appendix. The % RSF values after 7000 h in air and water are shown in Table 4.7. Immersion in water at 23°C appears to have only marginal effect on the relaxation behaviour of most of the elastomers that were shown to have some affinity for water in swelling tests (See Section 4.7), eg:Epichlorohydrin rubber, Type H(O).

Table 4.7 Comparison of Residual stress factor (%) in Air and Water after 7000 hours as a function of temperature

Material \ Temperature	23°C		40°C		70°C	
	Water	Air	Water	Air	Water	Air
Natural Rubber, A(N)	77.4	82.2	65.9	79.8	19.1	8.3
SBR, B(N)	63.9	70.1	46.2	70.3	9.6	21.6
EPDM(Sul) C(O)	69.5	67.1	60.4	71.0	47.0	56.9
EPDM(Pero) D(N)	70.6	70.0	69.0	71.9	79.6	82.6
NBR, E(N)	82.6	81.5	64.0	89.7	34.1	27.8
EPDM(pero) F(O)	69.1	57.9	72.5	64.7	71.6	77.2
NBR, G(O)	74.5	78.8	64.1	75.7	39.3	56.4
EPCL, H(O)	69.7	66.4	57.0	56.1	11.4	22.5
Santoprene 55, I(O)	49.3	53.5	40.4	53.7	30.7	51.6
Santoprene 64, J(O)	47.9	43.2	36.2	45.9	28.2	44.7
Evoprene 992, K(O)	50.0	59.5	52.3	60.0	25.7	54.1
Evoprene 994, L(O)	53.4	56.1	50.0	58.5	28.3	48.2
Alcryn 6368, M(O)	50.4	44.3	34.0	25.5	28.0	40.0
Alcryn 6385, N(O)	46.5	40.1	36.0	25.7	35.7	40.4
Alcryn 1201, O(O)	37.3	36.2	22.0	34.1	16.7	38.0

However, at elevated temperatures materials such as SBR, EPDM(S), and many TPE compounds show significant differences in stress relaxation.

Tahir,⁶⁵ who made similar observations, suggested that the increase in relaxation may be due to the presence of hydrophilic material in the specimen which is responsible for the softening of the specimen leading to greater relaxation. The amount of softening was found to depend on the nature and extent of this material. From our results, it seems that these processes may be accelerated at higher temperature.

One interesting factor noted in this experiment is the effect of water immersion on nitrile rubbers. These not only show increased absorption of water compared with the other crosslinked rubbers (such as NR, SBR, EPDM) but also show higher relaxation. This might be a reason for unexpected results in the experiments in natural gas.

4.1.4 Natural gas environment

Tests were carried out as explained in Section 2.1.7.1 on all the harder compounds due to their greater demand in the gas industry. The stress relaxation curves are shown in Figures 11,12, 13, 15, 18 and 23 in the Appendix. The %RSF after 7000 h in gas and air are given in Table 4.8. From the results, it appears that the effect of natural gas on the stress relaxation is not significant, except in the case of the peroxide-cured EPDM (Type F) and the nitrile rubber (Type G). However, in the case of the nitrile rubber, it may be due to the water absorption from the wet gas. In view of these unexpected results, further measurements are required.

Table 4.8 Residual stress factors (%) after 7000 hours at 23°C in air and gas atmosphere.

Environment Material		AIR	GAS
EPDM, F(O)		57.9	70.2
NBR, G(O)		78.8	63.1
EPCL, H(O)		66.4	70.2
Santoprene64, J(O)		43.2	47.5
Evoprene994, L(O)		56.1	56.4
Alcryn1201, O(O)		36.2	37.0

4.1.5 Filler

A series of tests has been made to investigate the influence of filler on the stress relaxation behaviour at 23°C and 70°C, and also to supplement the investigation of filler on the recovery behaviour. As a preliminary to the recovery measurements, stress relaxation data were obtained and are given in Table 4.9.

Table 4.9 Comparison of Residual stress factor (%) at 23°C and 70°C for filled and gum compounds.

Test Conditions Material	23°C after 336 h		70°C after 288 h	
	GUM [@]	FILLED*	GUM [@]	FILLED*
Natural Rubber, A(N)	97.9	94.1	104.1	100.7
EPDM, D(N)	99.7	82.6	----	----
NBR, E(N)	----	-----	92.3	96.0

@ Hardness and Initial Force values for the gum Compounds are given in Table 4.2

* The filled materials are those supplied for the programme.

Filled compounds, generally, showed higher rate of relaxation even at normal temperatures. From the relaxation in gum and filled compounds at high temperature, 70°C, it is evident that the filler does not contribute to chemical stress relaxation. The difference in the stress relaxation is due to the physical processes, as the physical relaxation rates for filled compounds are found to be greater than those of gum compounds.

Carbon black is known to have a property called 'structure' and 'surface activity', which is capable of forming the filler-filler or filler-polymer linkages in the complex network when they are incorporated. This contributes towards the reinforcing nature of the carbon black. However, during a deformation, because of inextensibility or non-compressibility of the filler, black filled specimens suffer more bond rupture than gum vulcanisates.^{39,40,44,65} This phenomena is explained by the 'strain amplification theory' discussed earlier in Section 1.5.4. According to Tobolsky's Two-Network theory,¹⁶ any damage in the network should reflect in corresponding decay of the original stress, and fully supports the observation.

4.1.6 Specimen lubrication

The original reason for employing molybdenum disulphide to lubricate the interfaces between the specimen and the glass plates was that more reproducible results were obtained thereby.^{5,65,69} The solid phase lubricant is chosen because of its greater convenience; with hindsight, it appears that this decision was a fortunate one, in respect that many of the compounds under test contain oil or similar liquid. Several cases of oil being forced out of the specimen during the test have occurred and were also reported previously.⁶⁹ This would probably affect the results significantly, were it not for the presence of the lubricant. The oil-free Santoprene samples were also considered; these were made available from the previous programme ⁶⁹ at IPTME and were prepared by soaking the test buttons in excess of petroleum ether and diethyl ether for 336h. followed by drying at room temperature for 168 h.

Table 4.10: Compression stress relaxation data for lubricated and unlubricated Santoprene specimens

Material	Temp. (°C)	Initial Force (N)		RSF at 170 h	
		Lub	Unlub	Lub	Unlub
Santoprene 101.64	23	267	253	57.4	56.6
	70	190	195	55.8	52.0
Santoprene 201.73	23	318	335	50.0	52.0
	70	240	230	43.8	46.2
Santoprene* 101.64 (oil - free)	23	1069	1066	53.0	52.3
	70	738	741	45.2	48.6

(* The sample had been extracted to remove the oil)

The behaviour of the molybdenum disulphide has been examined closely. Stress relaxation measurements carried out over a period of 170 h at 23° C and 70°C with and without lubricant have not revealed any systematic effect either on initial force or on residual stress factor (refer to Table 4.10). As the use of glass plates in both the cases might provide enough slippage during compression, the effectiveness of the lubricant may be limited. However, the conclusion that the surface effects do not affect the subsequent stress relaxation was also reached by Stenberg⁴, Beatty and Juve ⁶¹ and Gordons ⁶⁹. According to

Tahir ⁶⁵, the negligible effect may be due to the low shape factor; however, Stenberg ⁴ and Beatty and Juve ⁶¹ have reported that the shape factor does not affect relaxation.

4.1.7 Specimen dimensions

The effect of specimen dimension is investigated by conducting stress relaxation experiments at 70° C and 100° C as described in Section 2.1.7.3.

The results are given in Table 4.11. From these results, it is apparent that there is very little effect of size on the stress relaxation behaviour. This may be because small changes in the dimensions do not appear to affect the relaxation (possibly chemical) significantly as it would in tension; this is evident when stress relaxation in button specimens are compared with those in strips (see Section 4.2).

Table 4.11: Comparison of RSF(%) for standard and large button specimens at 70° C and 100°C at 670 h.

Material \ Temperature	70° C		100° C	
	Standard	Large	Standard	Large
NR, A(N)	78.0	75.4	39.0	38.8
NBR, E(N)	74.0	77.9	40.0	60.3
EPDM, D(N)	80.0	81.8	75.0	85.3

4.1.8 Nitrogen environment

The results of stress relaxation tests under a nitrogen atmosphere are given in Table 4.12. From the data, the presence of nitrogen does not appear to affect the stress relaxation behaviour significantly. The purpose of the nitrogen environment test is to exclude oxygen and thereby to find out whether it plays an important role in the relaxation process.

It has been said that oxidative degradation of vulcanisates proceed autocatalytically in the presence of polysulphides with no antioxidants ^{4,12,55}, and the presence of polysulphides were found to reduce the effectiveness of the antioxidants.⁵⁵ However, as the compounds used in this research are based on commercial formulations, antioxidants are generally incorporated in the recipes. Also, the

vulcanisation process is so selected as to minimise the occurrence of polysulphidic crosslinks; in fact their presence reduce thermal and reversion resistance. It thus appears that much of the relaxation may be attributed to thermal degradation of main chains and crosslinks and not due to autoxidation process.

**Table 4.12 Comparison of the Residual stress factors (%)
in Nitrogen and Air at 70°C after 1000 hours.**

Environment Material		NITROGEN	AIR
NR.	A(N)	70.1	67.0
EPDM(Sul).	C(O)	75.5	69.8
EPDM(Pero),	D(N)	88.5	85.5
NBR,	E(N)	74.7	71.5
EPDM(Pero),	F(O)	79.1	78.8
NBR,	G(O)	83.1	80.6
EPCL,	H(O)	71.7	58.7
Santoprene55,	I(O)	78.6	54.1
Santoprene64,	J(O)	67.7	54.1
Alcryn6368,	M(O)	54.2	50.0

Stenberg ⁴ has investigated the stress relaxation of natural rubber black specimens with and without antioxidants. He concluded that other factors, notably formation of hard oxide skin on the surface of the specimen can restrict the diffusion of oxygen to the interior, and by inference retarding the relaxation. He also supported the view that the stored oxygen may be enough to cause significant relaxation. The experiments in a nitrogen atmosphere do not contradict the conclusions reached that oxygen does not play an important role in the relaxation.

4.1.9 Temperature jumps

BS 903-A 42, the stress relaxation standard specified in BS 2494 has two methods. In the first of these, the test piece is compressed at the test temperature and is maintained at this temperature throughout the test period; all measurements are taken at this temperature. In the second method, compression and initial measurements take place at room temperature, the specimen is then stored at the test temperature, but all subsequent measurements are made at 23°C. The sample, is therefore subjected to a series of temperature changes during the stress

relaxation, and it is appropriate to study the effect of these on the stress relaxation behaviour.

A series of tests in which specimens experienced either a jump to a higher or to a lower temperature was carried out. Each specimen was loaded at 100°C and spent 24 h at this temperature. At the end of this duration, some specimens were removed from the 100°C oven, and placed in an oven at 70°C. This procedure is repeated at the end of next 24 h period, according to the test schedule given in Table 4.13. The first set of tests took place over 168 h. From the results, it may be tentatively concluded that the longer the time spent at 100° C the more rapid the relaxation. The data also show the superior stability of the peroxide-cured rubber (eg: EPDM) and Santoprene over the sulphur cured compound (eg: NR) in this time and temperature regime.

Table 4.13: The effect of temperature jumps on residual stress

Specimen	Temperature of test during the time jumps (°C)						
	0-24h	24-48h	48-72h	72-96h	96-120h	120-144h	144-168h
1	100	100	100	100	100	100	100
2	100	70	100	70	100	100	100
3	100	70	100	100	100	100	100
4	100	100	100	70	100	100	100
Material Specimen	Residual Stress Factor (%) after 168 hours						
	Santoprene 101-55		Natural Rubber		EPDM (Pero)		
1	71.3		44.9		96.0		
2	73.2		50.9		92.3		
3	76.5		50.5		90.1		
4	69.5		45.3		86.0		

A second series of experiments with the test schedule of Table 4.14 was also carried out. These tests suggest that any excursion to 100° from 70°C causes an increase in relaxation, which is expected. The data also reveal a slight reduction in relaxation if a jump to a lower temperature is made.

Derham³⁹, has suggested that the changes brought about by the effect of temperature jumps may be due to the breaking of some sort of temperature sensitive

bonds, probably due to Van Der Waals type forces; in the absence of any jump, these bonds would remain stable or have very long relaxation time.

Table 4.14: The effect of temperature jumps on residual stress

Specimen	Temperature of test during the time jumps (°C)		
	0 - 24 h	24 - 48 h	48 - 72 h
1	70	100	70
2	70	70	70
3	70	40	70
4	100	100	100
Material Specimen	Residual Stress Factor (%) after 72 hours		
	Santoprene 101-55	Natural Rubber (Gum)	NBR (Gum)
1	57.1	89.9	83.9
2	69.9	102.9	101.5
3	70.5	107.1	103.1
4	74.1	89.3	86.8

These results indicate that temperature changes influence stress relaxation, and the second method in BS 903-A42 may produce misleading information about stress relaxation behaviour.

4.1.10 Strain rate or Loading rate

The stress relaxation specification BS 903 Part A 42 requires that the specimen is loaded to 25 % strain within 30 s. Most of the testing in this programme used a loading rate to achieve 25 % strain within 5 minutes (0.31 mm/min). This is to try to avoid transient effects which might lead to variability in the stress relaxation data. A series of tests has been carried out in which the loading rate was varied from 0.31 mm/min to 1.55 mm/min (giving 25 % strain within 40s). The effect of loading rate on the subsequent stress relaxation is much greater for thermoplastic elastomers than for cross-linked rubbers. The loading rate affected the initial force, the relaxation rate and, therefore, the force at 0.5 h (which BS 903-A 42 specifies for the normalisation of data). The effect on these three parameters for Santoprene 101-55 and 101-64 are shown in Figures 4.12, 4.13 and 4.14.

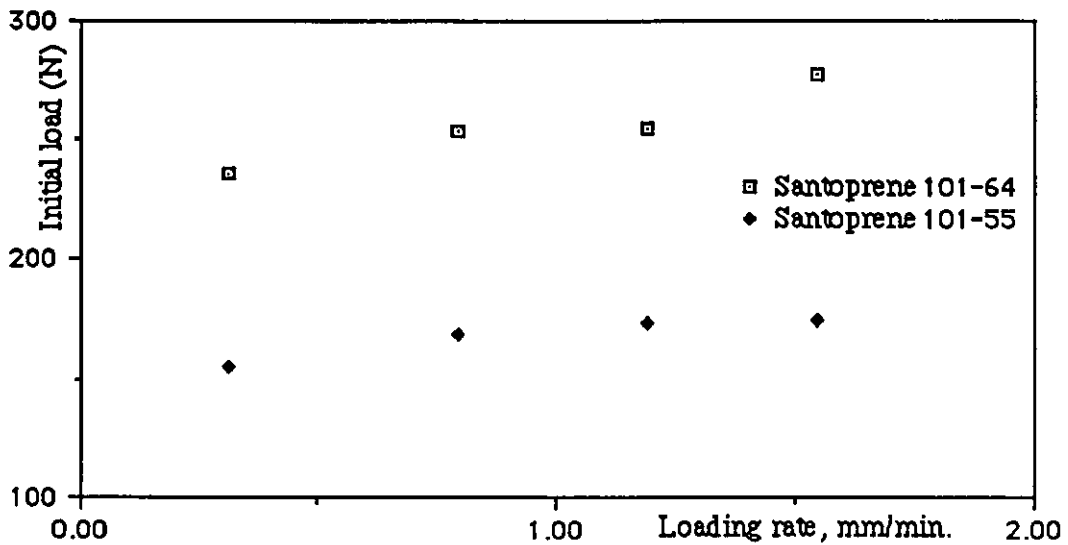


Figure 4.12 Effect of loading rate on initial load for Santoprene

These results indicate that the initial force for the slowest loading speed is considerably lower than for the others. Also, the stress relaxation rate decreases markedly with the increase in loading rate from 0.31 mm/min to 1.55 mm/min. The effects on initial load, relaxation rate and residual stress factor for a range of materials are shown in Tables 4.15 and 4.16 respectively. The initial load generated by the specimen reacting to an imposed strain of 25% is a function of the stress/strain behaviour, which is also associated with hardness. The initial load is dependent on the loading rate; the effect is more marked for the thermoplastic elastomers. The pattern of subsequent relaxation is dependent on the initial load and therefore, on the loading rate.

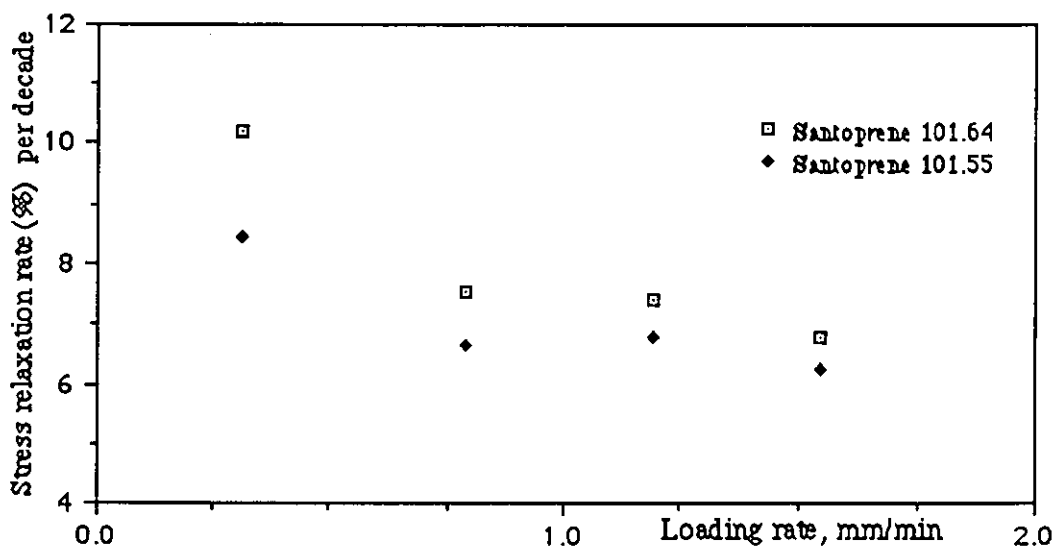


Figure 4.13: Effect of loading rate on relaxation rate for Santoprene

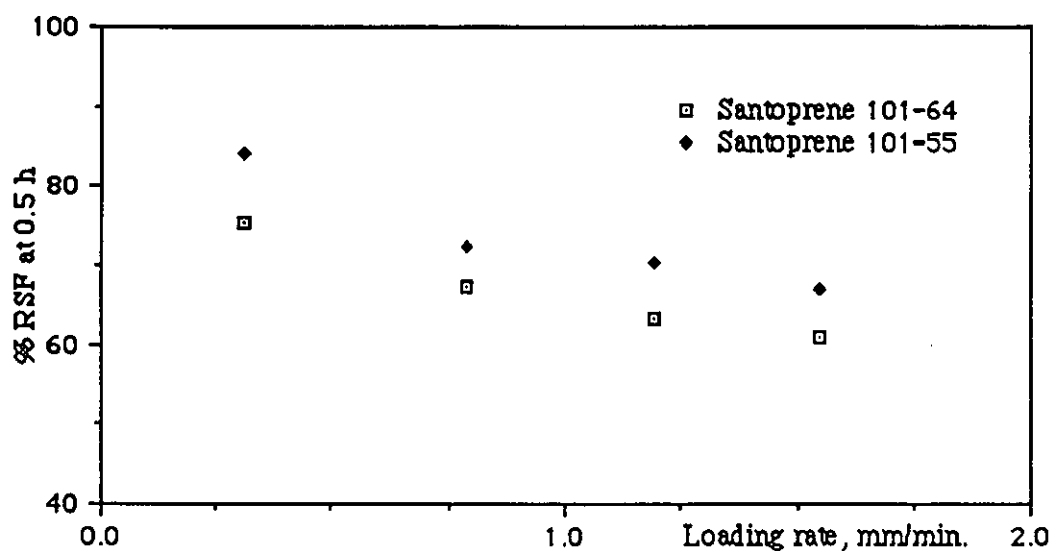


Figure 4.14 Effect of loading rate on % RSF at 0.5 h. for Santoprene

Table 4.15: The effect of loading rate on the stress relaxation

Strain Rate Material		0.31 mm/min		1.55 mm/min	
		Relaxation rate (%) *	Initial Force (N)	Relaxation rate (%) *	Initial Force (N)
NR	A(N)	3.3	177	3.6	146
SBR	B(N)	4.6	142	4.7	149
EPDM	C(O)	5.3	147	5.7	151
EPDM	D(N)	5.4	157	3.2	184
NBR	E(N)	4.5	160	2.5	170
EPDM	F(O)	6.6	221	4.6	278
NBR	G(O)	4.8	359	4.3	276
EPCL	H(O)	5.7	271	3.8	363
Santo.101.55	I(O)	8.4	155	6.4	180
Santo.101.64	J(O)	9.8	236	7.2	252
Evoprene 992	K(M)	7.0	98	7.0	126
Evoprene 994	L(O)	7.3	208	11.9	220
Alcryn 6368	M(O)	10.2	145	8.0	198
Alcryn 6385	N(O)	11.0	165	8.0	207
Alcryn 1201	O(O)	12.8	245	6.5	275

* (The rates are calculated from the 1000 h data normalised at 0.5h)

Table 4.16: Comparison of RSF (%) at 1000 h. normalised to the initial stress at zero time and the stress at 0.5h

Strain Rate Material		0.31 mm/min		1.55 mm/min	
		% Residual Stress Factor at 1000 h. normalised to			
		0.0h	0.5h	0.0h	0.5h
NR	A(N)	88.3	92.8	85.4	96.1
SBR	B(N)	81.8	90.8	69.1	83.4
EPDM	C(O)	72.6	79.7	72.8	83.3
EPDM	D(N)	74.7	83.0	72.6	85.5
NBR	E(N)	85.3	92.3	82.9	91.9
EPDM	F(O)	61.4	73.2	76.2	83.3
NBR	G(O)	78.3	84.4	70.2	85.4
EPCL	H(O)	70.5	79.7	72.9	84.5
Santo.101.55	I(O)	56.1	66.7	52.8	73.1
Santo.101.64	J(O)	45.8	60.7	45.3	70.5
Evoprene 992	K(M)	59.6	70.9	61.2	75.4
Evoprene 994	L(O)	56.1	70.6	56.3	74.3
Alcryn 6368	M(O)	52.4	61.5	50.6	66.4
Alcryn 6385	N(O)	50.0	58.2	48.9	62.8
Alcryn 1201	O(O)	43.3	54.8	44.9	64.7

The above experiments conducted at various loading rates have led to the following conclusions:

- 1) faster loading rates generate higher initial forces
- 2) decay rates are more rapid in the very early stages (before 0.1 h) for the higher stress levels
- 3) the relaxation rates appear to be independent of the loading rate for cross-linked rubbers (Figure 4.15 for peroxide-cured EPDM); but not the case for thermoplastic elastomers (Figures 4.13 and 4.16)

The effect of loading rate on the relaxation rates in the TPE's may be attributed due to their structural differences with the crosslinked rubbers, mainly the presence of crystallisation.

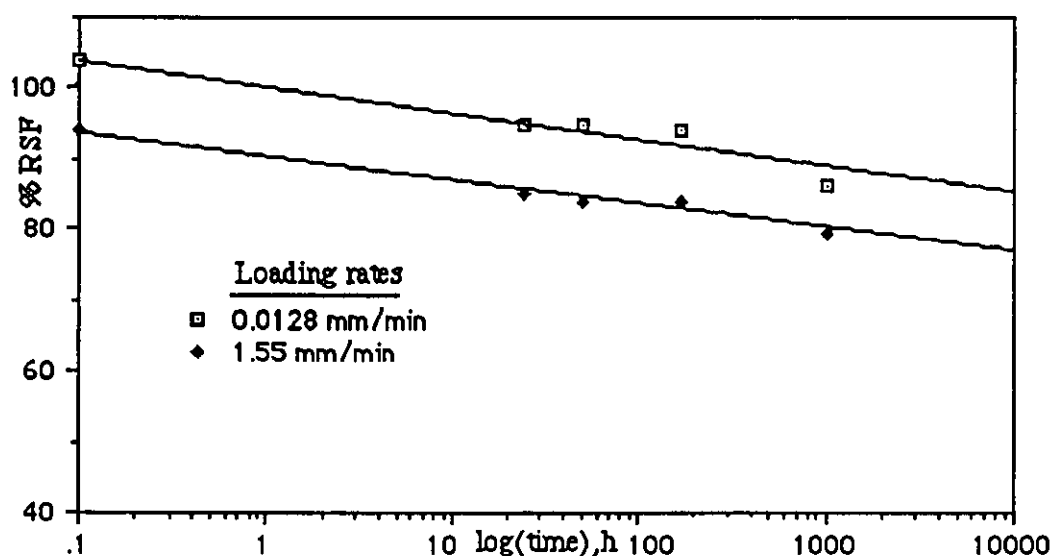


Figure 4.15 The effect of loading rate on the RSF in EPDM (P)

The argument is in favour of controlled loading; but it has been found that using the Loughborough equipment, loading requirements specified in BS 2494 can only be achieved with a serious danger of overloading the load cell, as metal to metal contact takes place at the end of compression. Whilst uncontrolled loading leads to lack of precision in the level of RSF and relaxation curve due to the effects of loading rates; this might seem to favour normalising data at 0.1h (0.5 hour as in the British Standard). Since much of physical relaxation occurs at the early stages of the relaxation process, vital information would be lost if the normalised data were to be used.

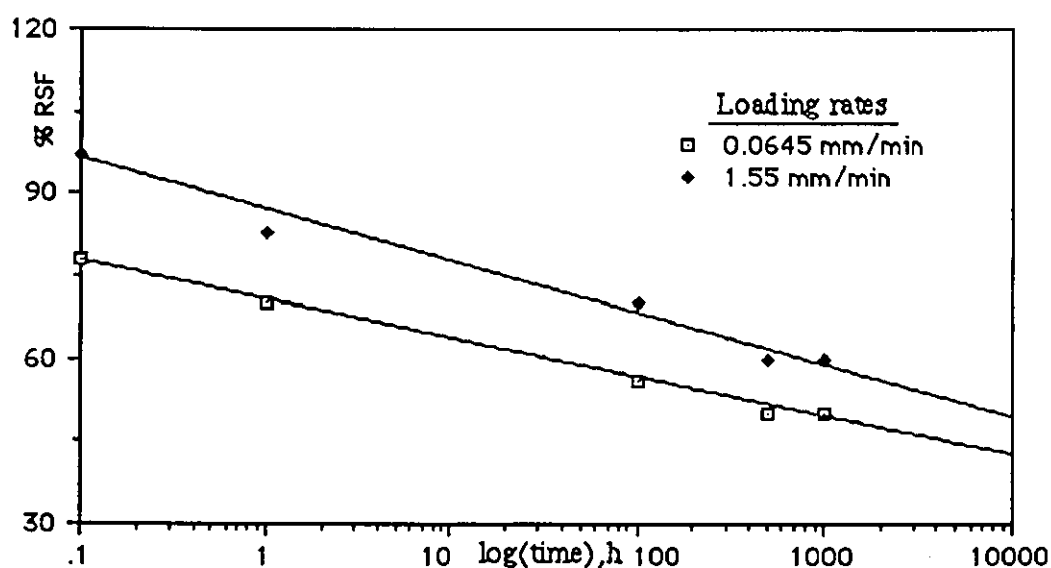


Figure 4.16 The effect of loading rate on the RSF in Alcrlyn

4.1.11 Mechanical conditioning

According to BS 903 Part A 42, the reproducibility of stress relaxation measurements may be improved by the specimen having experienced mechanical strain prior to testing. This effect has been demonstrated for filled natural rubber specimens³⁹ and was explained in terms of the pre-stressing causing changes towards an equilibrium network. However, other workers⁶⁶ have found that the effect of pre-stressing on subsequent relaxation, in compression, is minimal. BS 903 Part A42 requires that the specimens be mechanically conditioned (scragged) before the test commences. This is done by compressing the specimen by about 25% and returning it to zero deformation. The process is repeated five times. The specimen must then rest for between 16-48 hours before the stress relaxation test begins. In the majority of the tests carried out in this programme, mechanical conditioning was not carried out, in accord with previous findings in IPTME.⁶⁶ In order to consider all aspects of BS 2494, short-term tests (168 h) including scragging were carried out on the sulphur and peroxide-cured EPDMs and Santoprene 101-55 at 23°C. The residual stress factors after 168h for scragged and unscragged samples were compared. The results are the mean of three trials on each material, and are given in Table 4.17. From these results, it appears that the effect of mechanical conditioning on stress relaxation is negligible.

Table 4.17 Effect of Mechanical Conditioning on RSF (%)

MATERIAL		% Residual Stress Factor after 168 hours	
		Unscragged	Scragged
EPDM(S)	C(O)	77.9	78.1
EPDM(P)	D(N)	78.3	80.5
Santoprene 101-55,I(O)		58.3	59.3

Gent⁴¹ has reported that even a small and momentary over extension (@25%) has a marked effect on the subsequent relaxation behaviour; this is because over extension produces increased amount of material in the softened state and can be explained by the strain amplification theory.⁴⁰ He also concluded that the order of extension in the softened region (different from the actual extension due to strain amplification) to cause this transformation from the rigid to soft phase is well over 100%. However, it is not clear that how much actual extension is necessary to bring about these

transformations. The fact that a small strain is employed in this research (<30%) may be not effective to produce any significant difference in relaxation due to pre-stressing. However, whether over compression have any effects on the subsequent relaxation needs further investigation.

Derham ³⁹ suggested that mechanical conditioning offer a permanent benefit to rubber components before they are put into service. However, his conclusions were derived from the experiments on filled NR-vulcanisates in tension. Also, a much higher strain level (100%) is employed than that used in the present work (@25%). It has been observed in this work that mechanical conditioning prior to tests has only marginal effect on subsequent stress relaxation behaviour under compression and is also reported in the literature.⁶⁶ This is because the relaxation behaviour in compression can not be expected to be the same as that in tension. Thus, the necessity of mechanical conditioning prior to compression relaxation test, in order to improve the reproducibility of stress relaxation results as suggested by British Standard needs further consideration.

4.2 TENSILE STRESS RELAXATION

The experiments were carried out as detailed in Section 2.2. The stress relaxation results in tension on thin specimens and in compression on standard test buttons are compared in Table 4.18.

Table 4.18: Comparison of the RSF (%) in tension (100 % strain) and compression (25% strain) at 23°C at 100h and 3000h

Material \ Time		100 h		3000 h	
		Tension	Compression	Tension	Compression
SBR	B(N)	78.2	80.5	48.9	72.7
EPDM(S),	C(O)	66.7	79.5	57.3	70.6
EPDM(P),	D(N)	72.2	76.7	65.7	72.0
NBR,	E(N)	80.2	85.2	34.1	83.3
Santoprene 101.55,	I(O)	34.1	66.9	20.0	55.4

The pronounced difference at longer times indicates the possibility of chemical processes occurring. This view is further supported from the results obtained

on the peroxide cured EPDM rubber, which has a stable crosslinked network. The effect on Santoprene may be reasoned due to yielding at higher strains (100 %). To study the effect of strain on Santoprene, a second set of experiments has been carried out. From the results [Refer to Table 4.19], it is clear that the morphology of Santoprene makes it sensitive to the strain level.

Table 4.19: %RSF as a function of Tensile Strain for Santoprene 101-55

Strain level Time, h	25 %	100 %
100	55.7	34.1
3000	46.0	20.0

4.3 MODULUS ENHANCEMENT FACTOR (MEF)

Measurement of MEF have been made routinely throughout this programme. The MEF is the ratio of the modulus after compression and the initial tangent modulus at a fixed strain (Figure 2.3). It is approximately constant with time. The variation of MEF with temperature is given in Table 4.20. Temperature effects are variable, depending on the material. For most filled crosslinked rubber compounds the MEF is approximately independent of temperature and has a value of about 2. The MEF in gum compounds is approximately unity. For most TPEs, very high values of MEF were observed and were also reported in the past; ^{5,69} and was found to decrease with increasing temperature. Values of MEF are higher for Santoprene and Evoprene (around 3-5) than for the crosslinked rubbers and Alcryn. It is, however, not clear whether crystallisation has any effect on the MEF in TPE's and need to be considered.

The significance of MEF can be partly understood by the application of Tobolsky's 'Two Net-work theory'¹⁶. When a specimen is compressed to a specified strain (say 25%), some of the network is destroyed with time; however, at the same time new crosslinks are generated and are in their stress-free state. It can be argued that these stress-free secondary networks are responsible in increasing the modulus if the specimen is further compressed. However, because the observation that the modulus enhancement in gum compounds is negligible (MEF=1) the part played by filler in the formation of second network responsible to the modulus enhancement is not understood.

Table 4.20: Influence of Temperature on the Modulus Enhancement Factor (MEF) for various materials

MATERIAL		Hardness (IRHD)	5°C	23°C	40°C	70°C
NR	A(O)	61.0	1.9	2.0	2.2	1.7
NR	A(N)	54.5	2.2	2.1	2.0	1.6
SBR	B(O)	58.0	2.2	3.8	2.7	2.8
SBR	B(N)	51.5	3.9	3.4	3.7	1.6
EPDM	C(O)	49.5	2.3	2.5	2.2	1.7
EPDM	D(O)	49.0	1.7	2.0	2.0	1.8
EPDM	D(N)	53.0	2.1	1.9	1.9	1.8
EPDM	D(M)	47.0	2.3	1.5	1.6	1.6
NBR	E(O)	43.0	2.1	1.9	1.6	1.9
NBR	E(N)	52.0	—	2.2	1.8	2.2
EPDM	F(O)	65.5	2.3	3.1	2.6	2.2
NBR	G(O)	70.0	2.7	2.5	2.4	1.7
EPCL	H(O)	70.5	3.1	3.4	3.5	1.9
Santo.101.55	I(O)	56.0	3.3	3.9	3.4	3.1
Santo.101.64	J(O)	67.5	4.1	4.6	4.3	3.5
Evoprene 992	K(O)	46.0	3.1	3.6	2.9	2.7
Evoprene 992	K(M)	52.0	3.6	3.8	3.6	2.4
Evoprene 994	L(O)	61.0	5.0	4.4	3.3	2.7
Evoprene 994	L(2)	85.0	4.0	5.0	4.0	2.4
Evoprene 994	L(3)	78.0	5.2	5.0	4.4	3.1
Alcryn 6368	M(O)	54.0	—	1.9	1.1	1.3
Alcryn 6385	N(O)	53.5	—	1.7	1.4	1.4
Alcryn 1201	O(O)	63.0	—	1.9	1.6	2.1

Tahir ⁶⁵ has observed a sudden increase in MEF at 100°C in filled and gum NR-vulcanisates in air, but not in nitrogen atmosphere, in the region of 300-450 hours. However, he observed similar rates of stress relaxation in both atmospheres. The increase in modulus, thus, can be attributed to the formation of the new network, probably due to oxidative crosslinking mechanisms. This further implies that the stress relaxation test on its own may not provide a true measure of ageing in elastomers. However, the measurement of recovery on these strained specimens

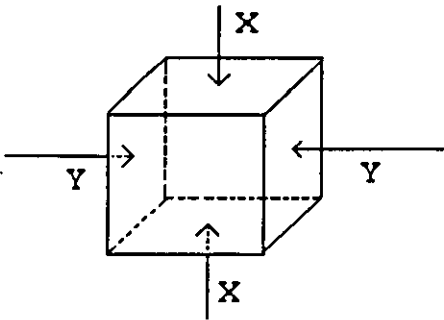
may provide a better solution to this problem and is considered later.

More recently, work carried out at IPTME on various elastomers has revealed that the MEF is dependent on the level of strain and to some extent on the rate of strain and a correlation between MEF and hysteresis is believed to exist.^{69a} Typical results on some rubbers are given in Table 4.21. From these results, it can be further argued that MEF is a material property generally dependent on the type and nature of the elastomer.

Table 4.21: The effect of Strain Level and Strain Rate on the Modulus Enhancement Factor (MEF)

Material	Strain %	M.E.F.	Loading Rate mm/min	M.E.F.
Hytel	5	1.20	1.55	2.16
	10	2.13	0.31	2.34
	15	3.19	0.065	2.28
Santoprene 101-55	15	2.64	1.55	3.31
	25	3.72	0.31	3.90
	32.8	3.79	0.065	-----
NR	21	1.25	1.55	-----
	28	1.49	0.31	-----
	36	1.52	0.065	-----

The above argument is also supported by the compression stress relaxation measurements on natural rubber specimens in two different directions at right angles to each other. In this series of experiments, isometric cube specimens were used. The specimens were compressed to 20 % strain in X-X and Y-Y directions, at right angles to each other [refer to figure below]; the initial forces



were recorded before releasing the specimen. The released specimen was then

compressed to 25% strain in Y-Y axis and let to age. The relaxation measurements were carried out at 100° C over 10 days. The % RSF at the end of the experiment confirms that the network in the Y-Y direction has undergone intense aging. For example: Specimen 2 has relaxed to 21%. (Refer to Table 4.22 below). However, the fresh measurements of initial force in X-X direction following the excursion of ageing in the Y-Y direction indicates that the network in X-X direction, which was stress free during the ageing process, has not suffered significantly. There is however a minor reduction in the final force, as indicated in the last column; this may be due to the physical processes either during the first cycle or during the ageing period.

Table 4.22: Comparison of Stress Relaxation data in two different direction of an isometric cube specimen.

Sample No.	20% Initial force, (N)		Stress Relaxation Data in YY direction at 100°C		20% Final force, (N)	$\frac{20\% \text{ Final force}}{20\% \text{ Initial force}} (\%)$
	XX	YY	25% Initial force(N)	240h.RSF (%)	XX	
1	44.5	56.7	73.5	33.3	38.3	86.1
2	52.1	62.8	87.3	21.0	44.4	85.2
3	58.2	59.7	62.8	34.0	49.0	84.1
4	49.0	68.9	79.7	42.3	39.8	81.2
5	61.3	79.6	85.8	41.1	46.0	75.0

From these results, it can be said that during a compression process, the initial force and the onset of relaxation takes place primarily in the compressed direction; the polymer network at right angles (and the new network) are assumed to be under stress-free conditions and may not take part in relaxation processes.

4.4 LEVEL OF CURE

The stress relaxation tests on the under-, optimum- and over-cured specimens were carried out as explained in Chapter 3. The tests were made over 5000h at 23°C and the results are given in Table 4.23. In general, as might be expected, the under-cured materials show very poor stress relaxation behaviour.

It is well known that for most applications of rubbery materials, it is necessary to

convert the rubbery molecules into a three dimensionally crosslinked network , via a curing process, in order that recovery after deformation and other related properties such as modulus are optimum. A number of curing systems are used and discussed earlier in Sections 1.2 Like any other chemical reaction, the curing process is a time dependent phenomenon, however, the rate of change of cross-linking and the nature and type of crosslink depends largely on the type of curing process.

The stress relaxation is a cumulative effect of a number of separate physical and chemical processes, which occur often simultaneously. Murakami,³⁵ and Lee and Morrell⁶⁰ have suggested that relaxation rates increase with the reduction in the crosslink density. The observation that the rate of stress relaxation is: undercure* (half the 95% cure) > optimum cure* (95% cure) > over cure* (1.5 times the time to 95% cure) can thus be expected. However, reversion was not observed in the materials used in this programme at the above experimental conditions.

Table 4.23: The effect of Cure State on the % RSF at 5000 h

MATERIAL	% Residual Stress Factor after 5000 h		
	Under-cured	Optimum-cured	Over-cured
SBR, B(O)	50.0	69.4	70.9
EPDM(S), C(O)	34.1	59.4	65.6
EPDM(P), D(O)	29.5	74.6	77.5
NBR, E(O)	75.5	70.8	84.5
EPDM(P), F(O)	20.6	73.9	77.8

However, the differences in stress relaxation as a function of cure between the various materials in the above table can be interpreted in terms of the curing characteristics of the elastomers. Where there are major differences in the rheometer torque either due to a steep increase or marching modulus there are large differences in relaxation rate between under-cured and optimum-cured materials, such as the peroxide-cured EPDM rubbers (Type D and F). Where the rheograph shows a plateau, SBR and NBR (Type B and E), the difference between over-cured and optimum-cured compounds is smaller. The difference

* Full definition are given in Section 3.1.3

between optimum-cured and over-cured materials is not large, but the over-cured materials will display poor mechanical properties, such as tensile strength and elongation at break.

4.5 THE IDENTIFICATION OF CHEMICAL RELAXATION MECHANISMS

To determine the chemical mechanisms involved in stress relaxation, a number of programmes were run, including a comparison of peroxide- and sulphur-cured EPDM, tests under nitrogen, tests in water and natural gas environments and on specimens of different volumes. By comparing the peroxide- and sulphur- cured EPDM rubbers, it became clear that the peroxide-cured elastomers were superior to the remainder of the crosslinked materials, in terms of thermal stability (ie: the ability of the material to withstand elevated temperatures without any degradation in the original network). The Santoprene elastomers also appeared more stable than the conventional rubbers at higher temperatures. This could be explained by the absence of conventional (sulphur) crosslinking, or to the more saturated states of polymer network.

Results of these tests indicated that the dominant factor in chemical stress relaxation is the stability of the network, which, for a conventional sulphur vulcanisate, appears to be due to efficient vulcanisation systems. Secondly, that for most rubbers included in this programme with the test pieces used, an external supply of oxygen apparently plays surprisingly little part in chemical relaxation. Whether this is due to a supply of oxygen incorporated in the specimen during fabrication is not clear. Whilst oxidation of many of the rubbers undoubtedly occurs at high temperatures, as witnessed by cracked and hardened surface of the specimen after exposure, the effect on stress relaxation is apparently only slight. This suggests that for the test conditions used in this programme, the thermal stability of a material is more important for good relaxation behaviour than its response to oxidation.

4.6 HARDNESS

A major preoccupation during the programme has been defining the rubber under test by hardness. The two test methods as described in Section 3.2 are

used to measure this property. The two methods were found to give different results, particularly for the thermoplastic elastomers. It appears that there is a possibility of disagreement between the micro test and macro hardness IRHD test results, and a correlation between these and the Shore A scale for thermoplastic elastomers seems very tenuous. It seems likely that correlation between the macro- and micro versions of IRHD is made on the basis of cross-linked rubbers; these, in contrast to the thermoplastic elastomers are not markedly time-dependent. The time dependence of hardness, over a period of one hour under a dead-load, is shown in Figure 4.17 below. These tests imply that the hardness of Santoprene (Type I and J) decreases by about 10 %, whilst nitrile rubber decreases by only 2 % and that of natural rubber compound remains approximately constant.

Thus, it is evident that the hardness test is a time dependent property and cannot be used for the quality control tests without appropriately defining its time dependence. This is because the changes in hardness value with time in thermoset elastomers (eg: NR, NBR) are different from those in thermoplastic elastomers (eg: Santoprene) over the same time period.

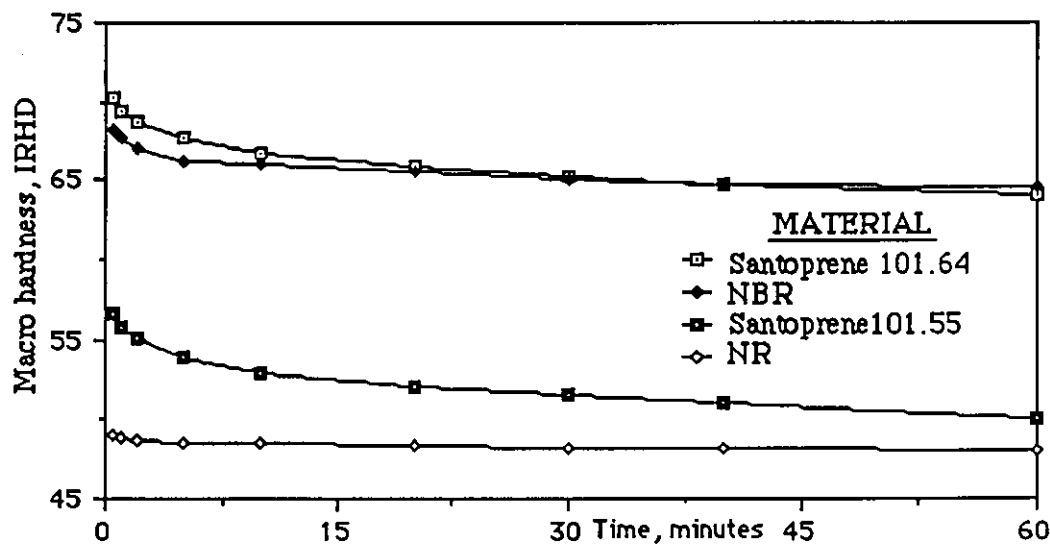


Figure 4.17 Effective hardness as a function of time

From the test, it is clear that a small change (less than 2%) in hardness value in a crosslinked rubber such as NR, NBR is insignificant when compared against a large change (10% or more) in a thermoplastic elastomer (eg:Santoprene).

4.7 SWELLING

These tests are carried out on all the available compounds as a supplementary to the relaxation tests in water at the three different constant temperatures as described in Section 3.3. Before the samples are compressed, they are immersed in tap water for 1000 h at 23°C, 40°C and 240 h at 70°C. The results are available in Table 4.24 below.

Table 4.24 Effect of water immersion on various elastomers after 1000 h at 23°, 40°C and 240 h at 70° C.

		% change in Height (ΔH) and the weight (ΔW)					
Material	Temperature	23°C		40°C		70°C	
		ΔH	ΔW	ΔH	ΔW	ΔH	ΔW
NR	A(O)	-0.16	0.91	—	—	—	—
NR	A(N)	0.15	1.03	0.30	2.19	2.03	2.75
SBR	B(O)	0.0	0.11	—	—	—	—
SBR	B(N)	0.16	0.22	0.14	0.61	0.15	0.97
EPDM	C(O)	-0.16	0.24	0.16	0.86	0.31	0.99
EPDM	D(O)	0.0	0.66	—	—	—	—
EPDM	D(N)	0.0	0.77	0.15	2.01	0.14	1.62
EPDM	D(M)	0.0	0.68	—	—	—	—
NBR	E(O)	0.16	1.00	—	—	—	—
NBR	E(N)	0.46	0.46	0.46	2.39	0.93	2.40
EPDM	F(O)	-0.31	0.11	0.0	1.49	0.29	1.44
NBR	G(O)	0.29	0.96	0.0	1.81	1.02	2.10
EPCL	H(O)	6.32	15.44	8.65	19.62	7.41	14.38
Santo.101.55	I(O)	0.32	1.54	1.62	3.28	1.76	4.33
Santo.101.64	J(O)	0.16	1.29	0.66	2.51	1.82	3.04
Evoprene 992	K(O)	0.16	0.31	0.33	0.86	2.31	0.65
Evoprene 992	K(M)	0.0	0.30	0.0	0.10	0.97	0.31
Evoprene 994	L(O)	0.0	0.20	0.0	0.32	1.12	0.51
Evoprene 994	L(2)	0.0	0.18	0.0	0.31	0.95	0.52
Evoprene 994	L(3)	-0.31	0.41	0.0	0.10	0.47	0.81
Alcryn 6368	M(O)	0.34	1.31	0.0	2.40	1.03	3.24
Alcryn 6385	N(O)	0.16	1.51	0.0	3.64	0.47	4.29
Alcryn 1201	O(O)	0.16	1.18	0.33	1.89	1.18	3.00

The absorption tests show that except Epichlorohydrin rubber, all other compounds absorb little or no water. Among the crosslinked rubbers, many compounds hardly absorb any water at ambient temperatures. However, nitrile rubbers comparatively absorbed more water than the other crosslinked rubbers, such as the NR, SBR and the EPDM's.

Tahir ⁶⁵ suggested that the presence of hydrophilic materials in the rubber compounds are responsible for the absorption of water by these materials. However, he concluded that water does not have any significant effect on the stress relaxation behaviour of crosslinked elastomers due to their low rate of diffusion and is in good agreement with our observation.

Chapter Five

STRAIN RECOVERY

5.1 INTRODUCTION

Since the measurement of standard mechanical properties, such as tensile strength, hardness, compression-set and fatigue may not provide an adequate solution to the evaluation of ageing, as the ageing of undeformed elastomer is frequently different from that of a material under stress, considerable interest is shown in assessing ageing by measurements of stress relaxation either in compression or in tension, statically or dynamically.

Recovery is defined as the ability of the test specimen to regain its original dimensions when released from strain. The deformation of the released specimen from constant strain is measured as a function of time under the same environmental conditions as applied during the relaxation stage. In the past, various workers^{24,39,70-71} have made measurements of stress relaxation, creep and recovery in tension; however, there seems to be no study of recovery in compression following stress relaxation (particularly at extended times and at elevated temperatures) in the literature and is thus considered here. The recovery test is a new method for the assessment of ageing of elastomers which has resulted from this programme.⁷²

Gent²⁴ studied the viscoelastic properties (creep, recovery and stress relaxation) of unfilled natural rubber vulcanisates in tension. He suggested that these properties are different manifestations of what is presumably a single relaxation process and can be interrelated using the following expressions: (refer to Section 1.5)

$$C = A \cdot S \quad \text{and} \quad R = B \cdot S' \quad 5.1$$

where C , R and S are the rates of creep, recovery and stress relaxation respectively, and A and B are constants of proportionality (refer to Equations 1.10 and 1.11); S' is defined as the rate of relaxation that occurs during the return of specimen to its undeformed state from prior deformation.

In the derivation of the above relationships, the following assumptions were made:

- i) The recovery and relaxation rates are comparable when the respective

deformations are equal.

- ii) 'Symmetrical relaxation' processes, ie: $S=S'$, may occur when no chemical changes take place in the network;
- iii) The vulcanisates are substantially elastic and the observed changes in deformation or stress are relatively small over the entire experimental range.
- iv) The values of A and B are considered to be time independent and when the stress-strain relationship is linear, both A and B are unity.

Stenberg⁴ studied viscoelasticity of filled rubbers using force-deformation diagrams and found that linear stress-strain relationship can be assumed up to 30% strain under compression.⁴ This finding is also confirmed in the present research (refer to Section 4.1). Therefore, the values of A and B in Equation 5.1 can be assumed to be equal to unity. However, the validity of the assumption that $S = S'$ ['symmetrical relaxation'] for the compounds used in the present study is considered later in this chapter.

Wood^{72a} and Gent⁴⁹ have reported that deviation from linearity of creep vs log(time) relationship occurs at extended time; this was suggested to be secondary creep as a result of the chemical changes in the network. However, even though the chemical processes at lower temperatures and at shorter times, can be neglected, the relaxation due to filler-filler and/or filler-polymer breakdown can not be avoided. According to Derham,³⁹ the extent of these breakdowns varies with different types of filler materials and for most purposes these changes are permanent.

In the past,⁷³ Gent's hypotheses have been applied successfully to the results of stress relaxation, creep and recovery at very small times and normal temperatures, particularly for gum compounds, where chemical processes can be neglected. In this work, an attempt is made to test the validity of Gent's relationship between stress relaxation and recovery rates, discussed later in this chapter. Measurements of creep are not made in the present programme. Therefore, it is not possible to test the relationship between creep and relaxation rates, but they are discussed in detail elsewhere.^{72a, 73, 73a}

5.2 **EXPERIMENTAL**

The recovery experiments were carried out in both the tension and compression modes; for the latter, two procedures were adopted for measuring the recovery.

A) By using compression stress relaxation test pieces after the completion of the standard stress relaxation test.^{3,5,63,65} From Figure 2.6, knowing the geometry of the jig, the glass plates and the test sample thicknesses, the recovery can be defined as the increase in thickness of the test piece after removal from compression, compared with the strain during the stress relaxation test. Thus:

$$\text{Recovery (R)} = \frac{t_T - (t_c - t_g)}{t_s - (t_c - t_g)} \quad 5.2$$

where t_T is the thickness of the test piece under recovery at any given time T

t_c is the depth of the jig cavity used in the test

t_s is the original thickness of the test piece before compression

t_g is combined thickness of two glass plates in the stress relaxation jig.

As soon as recovery measurements have been taken, the test buttons are transferred back to the appropriate test environment.

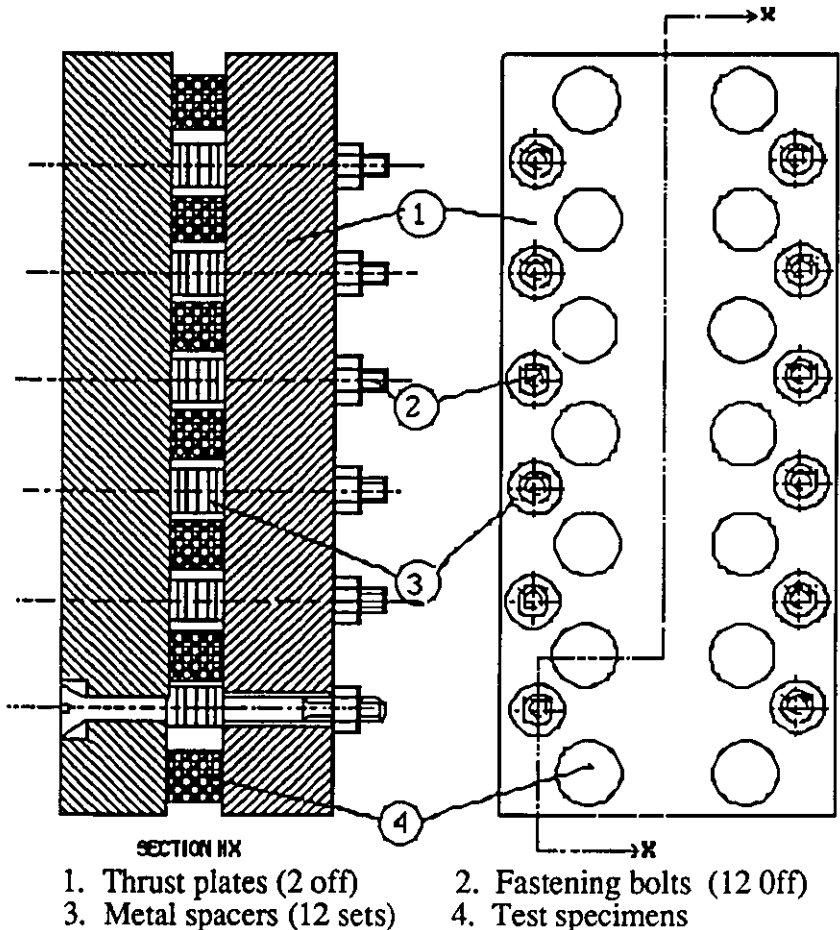


Figure 5.1: A cross-sectional view of a compression-set jig.

B) In the second method, compression set jigs, as shown in Figure 5.1, are used. Several test pieces of known thickness, lubricated with MoS₂ (molybdenum disulphide),^{63,65} are placed in position and the two parallel plates are tightened to a predetermined thickness, controlled by spacers, to impose 25% strain on the test pieces. The whole assembly is then placed in the controlled test chamber for the required length of time. Once the test pieces are released, the change in thickness, under the same environmental conditions as in the compression stress relaxation test, is recorded against time up to a reduced time T_R of unity, where:

$$\text{Reduced time } (T_R) = \frac{\text{Recovery time}}{\text{Compression time}} \quad 5.3$$

A recovery test is basically similar to a compression set test. However, the compression set measurements cannot be used to measure the sealing property under conditions of constant strain over a long period of time. Briefly, the compression set test is carried out as follows.

1. The test pieces are compressed at a specified rate, to a standard strain (BS 903 Part A6 and ASTM D- 395-84) or a standard stress (ASTM D- 395-84), using compression jigs.
2. The test pieces under constant strain or stress are then subjected for a specified time (22-24 h or 70-72 h) to a specified [elevated] temperature.
3. Removing the test pieces from the jig, the measurement of 'set' is made at 23°C after 30 minutes.

The compression set reading is too complicated for analysis, being involved with the effects of temperature jumps.⁷⁴ Clearly, such a test cannot measure a definite physical property (Refer to Section 4.1.9). This is because the compression-set test is generally carried out at one temperature whereas the 'set' measurement is done at another. Also, the time under compression and for recovery of the test piece are widely different and are difficult to compare. These variables are reduced in the recovery test, as carried out in the present work, which should give further insight into the physical aspects of relaxation. The physics of recovery can be partially understood by the application of the Two Network theory of Tobolsky¹⁶. When the compound is under stress, some of the network bonds that fail during the process may reform into new stress free links; they are no longer active

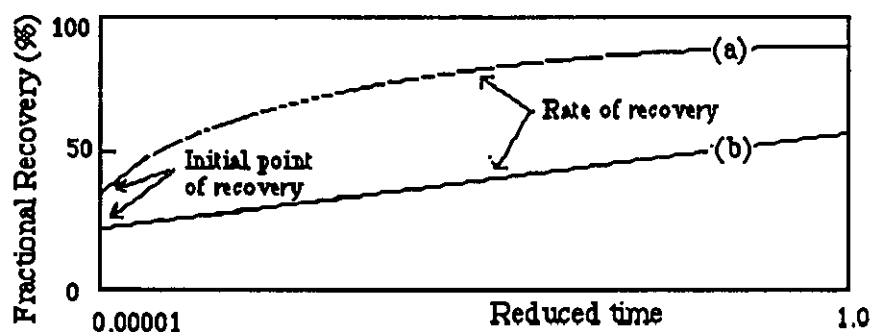


Figure 5.2: Recovery curves for two different elastomer showing
a) Good recovery and b) Poor recovery

in sustaining the stress, indeed these second network crosslinks inhibit recovery. A typical recovery plot is shown Figure 5.2 above.

5.2.1 Test procedure

Recovery is measured at various times once the specimen is freed from the imposed strain under the same environmental conditions as applied during the compression or tension phase. Specimens for the measurement of recovery are obtained in two ways. Firstly, by using the compression stress relaxation specimens after the completion of the relaxation test. However, as one of the main aims of the programme is to obtain long term stress relaxation data, this is an unsatisfactory way to acquire a large amount of recovery data; nevertheless some results are made available either because the test is terminated or when the RSF reached 30%. Secondly, compression set jigs are used to produce a large number of specimens for recovery measurement as explained above. These jigs are placed in an oven for a specified time prior to recovery measurements.

5.2.2 Test samples and variables

Recovery is studied on all the available compounds as used in the stress relaxation tests; in order to study the effect of the chemistry and structure of the polymer network, not only compounds based on different cure systems are used but thermoplastic elastomeric networks (TPE's) are also examined. Conventional rubbers consisting of compounds based on sulphur vulcanisation and peroxide curing systems with two different hardness at 50 and 70 IRHD are used. This allows analysis of the part played by the filler in the viscoelastic behaviour. The

sulphur vulcanisation process is known to produce a less stable vulcanisate for high temperature use than that based on a peroxide. The thermal stability further decreases as the number of sulphur atoms per crosslink increases. The TPE's are selected from the commercially available grades which are near to the above hardness range. In order to relate the recovery results with those of stress relaxation tests, the similar test conditions are being selected. Recovery tests are carried out at 40°, 70° and 100°C; recovery measurements under nitrogen, for different size specimens and for various states of cure are also studied.

5.3 RESULTS AND DISCUSSION

5.3.1 Compression time

The effect of time under compression upon the recovery behaviour was investigated at various temperatures; the recovery results at 70°C and 100°C are given in Tables 5.1 and 5.2 respectively.

Table 5.1: The effect of Compression Time on Rate of Recovery and Fractional Recovery at Reduced Time = 1 at 70° C

Compression Time			100 h	1000h	100h	1000h
Material		Hardness (IRHD)	Recovery Rates (% per decade)		Fractional Recovery at Reduced time = 1 (%)	
NR	A(N)	54.5	1.9 ± 0.3	1.8 ± 0.1	88.4	52.8
SBR	B(N)	51.5	3.0 ± 0.3	2.1 ± 0.1	86.1	52.5
EPDM(S)	C(O)	49.5	2.5 ± 0.3	2.0 ± 0.2	94.5	76.5
EPDM(P)	D(N)	53.0	2.4 ± 0.2	1.7 ± 0.1	100.8	100.0
NBR	E(N)	52.0	1.3 ± 0.3	0.7 ± 0.2	90.2	67.4
EPDM(P)	F(O)	67.0	1.9 ± 0.5	1.2 ± 0.1	100.5	98.3
NBR	G(O)	70.0	2.0 ± 0.2	1.6 ± 0.1	91.5	78.8
EPCL	H(O)	70.5	1.3 ± 0.2	1.1 ± 0.4	96.9	84.8
Santo.101.55	I(O)	56.0	3.7 ± 0.2	2.8 ± 0.4	92.5	87.5
Santo.101.64	J(O)	67.5	3.6 ± 0.8	3.4 ± 1.0	87.7	83.3
Evoprene 994	L(O)	61.0	11.0 ± 0.2	9.5 ± 0.5	89.0	70.2
Alcryn 6368	M(O)	53.0	10.6 ± 0.7	4.0 ± 0.3	66.2	55.2
Alcryn 6385	N(O)	54.0	3.1 ± 0.7	4.3 ± 0.3	55.0	51.8
Alcryn 1201	O(O)	61.5	7.9 ± 0.2	4.7 ± 0.3	75.7	63.2

The recovery data in Tables 5.1 and 5.2 are normalised to Reduced time of unity. The graphs of fractional recovery against the reduced time for various compounds are shown in Figures 24 - 38 in the Appendix.

Table 5.2: The effect of Compression Time on Rate of Recovery and Fractional Recovery at 100° C, at Reduced Time = 1

Compression Time			100 h	1000h	100h	1000h
Material	Hardness		Recovery Rates (% per decade)		Fractional Recovery at Reduced time = 1 (%)	
NR	A(N)	54.5	1.6 ± 0.2	2.0 ± 0.3	64.0	59.0
SBR	B(N)	51.5	1.9 ± 0.2	1.0 ± 0.1	56.6	33.7
EPDM (S)	C(O)	49.5	2.3 ± 0.3	1.7 ± 0.3	68.0	46.8
EPDM(P)	D(N)	53.0	1.1 ± 0.2	0.5 ± 0.05	71.4	51.4
NBR	E(N)	52.0	2.9 ± 0.3	1.3 ± 0.2	83.9	53.4
EPDM(P)	F(O)	67.0	1.7 ± 0.2	1.3 ± 0.2	85.9	54.9
NBR	G(O)	70.0	1.9 ± 0.2	1.7 ± 0.3	99.2	96.6
EPCL	H(O)	70.5	1.1 ± 0.2	1.3 ± 0.2	98.4	94.4
Santo.101.55	I(O)	56.0	4.1 ± 0.4	3.2 ± 0.5	82.8	72.0
Santo.101.64	J(O)	67.5	5.5 ± 0.6	3.5 ± 0.6	79.9	67.4
Evoprene 992	K(M)	52.0	7.6 ± 0.8	4.1 ± 0.4	47.6	37.8
Evoprene 994	L(O)	61.0	13.1 ± 1.4	7.3 ± 0.7	69.2	64.4
Alcryn 6368	M(O)	53.0	6.3 ± 0.6	2.2 ± 0.2	49.4	26.7
Alcryn 6385	N(O)	54.0	7.1 ± 0.6	1.8 ± 0.2	49.3	23.5
Alcryn 1201	O(O)	61.5	8.0 ± 0.7	1.2 ± 0.1	59.6	23.6

The main feature of the data is that the fractional recovery (FR) is a function of the time under compression and the temperature of the test. For stable networks, such as EPDM(P), Santoprene, the fractional recovery at 70°C are less affected by the time under compression; however, the diene rubbers and few other less stable materials such as sulphur cured-EPDM compounds showed significant differences in the recovery results. The chemical relaxation components, which are dominant over longer periods of time and at higher temperatures, seem to play a major role on the recovery behaviour of these materials. This is because greater the chemical relaxation, larger the damage done to the network. Also, like any other

reaction, the relaxation mechanism is a time dependent phenomenon; ie: the longer the time, the greater is the chemical relaxation; this eventually leads to less recovery. eg: 59% after 1000h. compared with 64% after 100 hours for the natural rubber specimen at 100°C.

According to Lee and Morrell ⁶⁰, both degradation and crosslinking processes occur during relaxation, depending upon the nature of the material and the service conditions imposed. Stable networks, such as peroxide cured compounds, undergo less chemical relaxation when compared with sulphur cured compounds; this results in greater fractional recoveries (refer to Figures 26-31 in Appendix). This is because the activation energy of C-C bond is much higher than C-S_x-C bond¹³ (refer to Table 1.1). Indirectly, it can further be argued that it is much easier for oxidative crosslinking to take place in sulfurated vulcanisates than in peroxide cured systems.⁶⁰ In fact, the formation of this new network can hinder the recovery significantly.

5.3.2 Test temperature

Typical recovery data at different temperatures are listed in the Table 5.3a. Although, recovery is a physical process, the effect of temperature on the recovery rates seems to be less significant than the effect of chemical processes.

However, as expected, a slight increase in recovery rates at higher temperatures can be noticed in some of the thermoplastic elastomers. The effect of temperature on the fractional recovery can be interpreted in terms of Tobolsky's Two-Network theory.¹⁶ During chemical stress relaxation, chain scission and reformation take place simultaneously. However, only those chains which were originally present support the stress. The new network is in stress free equilibrium, in the deformed state and does not contribute to the stress opposing the imposed compression. However, when the original stress is removed, the new network is suddenly stressed and will oppose the return to the unstrained dimensions.

Thus, the fractional recovery is a measure of the amount of chemical relaxation that has occurred. If the relaxation were purely physical, then all chains would be expected to contribute to the recovery of the specimen, and high value of fractional recovery achieved. This is the case of peroxide-cured EPDM,

D(N), which almost regains its original dimensions. In contrast, the sulphur-cured EPDM,C(O), which is less themally-stable, recovers poorly, and the fractional recovery is less at higher temperatures (ie: 46.8% at 100° C compared with 76.5% at 70° C). It is also reduced with longer residence time under compression (ie: 46.8% at 100°C for 1000h compared with 68.0% for 100 h). If the fractional

Table 5.3a: The effect of Temperature on Rate and Level of Recovery

MATERIAL		Hardnes (IRHD)	40°C		70°C		100°C	
			RR*	FR [@]	RR*	FR [@]	RR*	FR [@]
NR	A(O)	61.0	1.6 ± 0.1	94.7	2.4 ± 0.1	69.4	2.2 ± 0.4	45.5
NR	A(N)	54.5	1.5 ± 0.1	87.9	1.8 ± 0.1	52.8	2.0 ± 0.3	59.0
SBR	B(O)	58.0	1.2 ± 0.1	89.6	2.2 ± 0.1	56.2	1.1 ± 0.2	39.4
SBR	B(N)	51.5	1.8 ± 0.1	89.7	2.1 ± 0.1	52.5	1.0 ± 0.1	33.7
EPDM(sul)	C(O)	49.5	1.7 ± 0.2	94.7	2.0 ± 0.2	76.5	1.7 ± 0.3	46.8
EPDM(pero)	D(O)	49.0	2.0 ± 0.2	96.0	2.0 ± 0.2	94.9	1.5 ± 0.3	93.3
EPDM(pero)	D(N)	53.0	1.7 ± 0.2	98.3	1.7 ± 0.1	100.0	1.7 ± 0.3	96.6
EPDM(pero)	D(M)	47.0	2.2 ± 0.2	97.1	2.0 ± 0.2	95.6	1.8 ± 0.3	93.0
NBR	E(O)	43.0	1.2 ± 0.2	94.0	0.9 ± 0.1	66.2	0.7 ± 0.1	42.3
NBR	E(N)	52.0	1.0 ± 0.1	91.6	0.7 ± 0.2	67.4	0.5 ± 0.1	51.4
EPDM	F(O)	65.5	1.0 ± 0.1	97.4	1.2 ± 0.1	98.3	1.3 ± 0.2	94.4
NBR	G(O)	70.0	1.4 ± 0.1	94.5	1.6 ± 0.1	78.8	1.3 ± 0.2	53.4
EPCL	H(O)	70.5	0.7 ± 0.1	96.1	1.1 ± 0.4	84.8	1.3 ± 0.2	54.9
Santo.101.55	I(O)	56.0	3.3 ± 0.2	93.1	2.8 ± 0.4	87.5	3.2 ± 0.5	72.0
Santo.101.64	J(O)	67.5	3.3 ± 0.4	85.6	3.4 ± 1.0	83.3	3.5 ± 0.6	67.4
Evoprene 992	K(O)	46.0	4.6 ± 0.4	83.4	8.1 ± 0.6	73.2	4.1 ± 0.5	40.6
Evoprene 992	K(M)	52.0	5.3 ± 0.5	81.6	7.6 ± 0.8	73.2	4.1 ± 0.4	37.8
Evoprene 994	L(O)	61.0	4.8 ± 0.8	80.6	8.2 ± 0.7	66.9	5.5 ± 0.3	47.6
Evoprene 994	L(2)	85.0	7.8 ± 0.5	77.3	9.5 ± 0.5	70.8	7.3 ± 0.7	64.4
Evoprene 994	L(3)	78.0	5.5 ± 0.3	85.4	9.5 ± 0.3	70.2	6.8 ± 0.8	55.7
Alcryn 6368	M(O)	54.0	5.0 ± 0.4	56.4	4.0 ± 0.3	75.0	2.2 ± 0.2	26.7
Alcryn 6385	N(O)	53.5	6.0 ± 0.2	65.4	4.3 ± 0.3	55.2	1.8 ± 0.2	23.5
Alcryn 1201	O(O)	63.0	6.4 ± 0.3	72.3	4.7 ± 0.3	63.2	1.2 ± 0.1	23.6

* RR is the Rate of Recovery in percentage per decade time

@ FR is the Fractional Recovery at Reduced time = 1.

recovery can be interpreted quantitatively in terms of that part of the relaxation that is chemical in nature, then the recovery rate should give information on the physical processes involved in relaxation. The recovery rate is approximately independent of temperature and time under compression for most materials.

Table 5.3b: Comparison of the Residual Stress Factor(%) and the Fractional Recovery (%) at Reduced Time of unity as a function of Temperature at 1000 hours.

Temperature Type	Residual stress factor(%)			% Fractional recovery at reduced time =1		
	40°C	70°C	100°C	40°C	70°C	100°C
B(N)	82.9	56.5	17.2	89.7	52.5	33.7
C(O)	80.6	69.8	55.5	94.7	76.5	46.8
D(N)	78.8	85.5	82.9	98.3	100.0	96.6
F(O)	78.1	78.8	72.4	97.4	98.3	94.4
G(O)	79.5	80.6	59.3	94.5	78.8	53.4
H(O)	70.1	58.9	26.6	96.1	84.8	54.9
I(O)	55.9	54.1	63.3	93.1	87.5	72.0
J(O)	47.5	54.1	42.6	85.6	83.3	67.4
K(O)	60.0	66.7	17.8	83.4	73.2	40.6
L(O)	57.1	55.4	10.2	80.6	66.9	47.6

In Table 5.3b, the residual stress factor (RSF,%) at 1000 h. and the fractional recovery at reduced time of unity for various compounds are given. From these results it is clear that rubber compounds which show large differences in the stress relaxation at elevated temperatures recover poorly; eg: SBR compound suffered a relaxation of 82.8% at 100°C and 17.1% at 40°C recovers to only 33.7% at 100°C and 89.7% at 40°C respectively, whereas the stable network such as peroxide cured EPDM compound which shows a relaxation of less than 20% at all the temperatures under consideration recovers more than 95%.

As Gent's hypotheses²⁴ does not account for chemical relaxation processes, it is necessary to separate the chemical components from the total relaxation. The method described in Chapter 4 are used to separate the chemical relaxation at 1000 h (Table 5.3c). Because of the linearity of % RSF vs log time plot for the thermoplastic elastomers, it is not possible to separate the two processes in this way. Also, the

chemical relaxation rates calculated for 1000 h. data are found to be higher than the rates calculated using the relaxation data over a longer period. This is due to the fact that in the calculation of the chemical relaxation rates, a linear relationship of RSF vs time is assumed. However, at longer times, the experimental data tends to deviate from linearity. This deviation is believed to be due to diffusion effects.⁴

A typical recovery plot for an elastomeric compound which has suffered chemical relaxation during the deformation period is given in Figure 5.3. As the recovery is a physical phenomenon, the chemical changes are unrecoverable. This is commonly known as 'set'. If 'symmetrical relaxation' as suggested by Gent²⁴, ie $S=S'$, is to be observed and linear stress-strain relationship is assumed, ie: values of A and B in Equation 5.1 are unity, then the rates of relaxation is equal to the rate of recovery. ie: $R = B \cdot S$, where $B=1$.

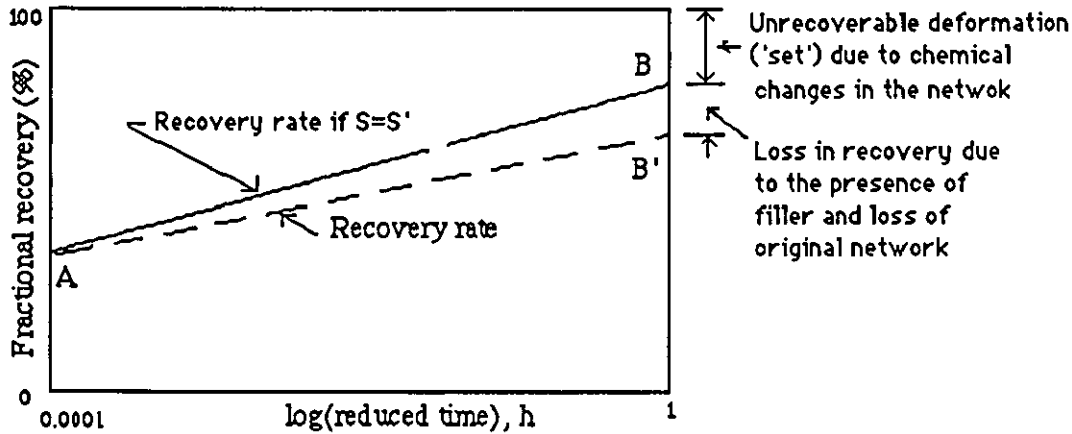


Figure 5.3. Schematic diagram of a typical recovery plot.

However, the experimental results tend to deviate from the above relationship. Both, the rate of recovery and the fractional recovery were found to be lower than those predicted using the above relation. This is because, the above relationship was derived for gum vulcanisates, whereas we are dealing with filled compounds. It is also to be noted that Gent²⁴ carried out his experiments at normal temperatures over a very small time scale (10 days), whereas, much of the present study is carried out not only at elevated temperatures (40°, 70° and 100°C) but also for a longer time period (2-3 years). Therefore, the degradation of the network due to chemical mechanisms needs consideration.

From Table 5.3c, the amount of chemical relaxation for the sulphur cured EPDM,

Type C(O), at 40°, 70°, and 100°C are 8.4, 16.7 and 33.3% respectively. If 'symmetrical relaxation' processes were to be expected as observed by Gent in his work on gum vulcanisates, then the recovery value must be equal to relaxation, except for the difference due to chemical changes. Thus, the sulphur cured EPDM compound, TypeC(O), should recover to $[100-33.3]=66.7\%$ at 100°C or $[100-16.7] = 83.3\%$ at 70°C of its original deformation. (refer to Figure 5.3); however, the fractional recoveries are only 46.8% at 100°C and 76.5% at 70°C respectively.

Table 5.3c: Separation of Chemical Relaxation at various Temperatures

Temperature Type	Total relaxation (%), 1000h			Chemical relaxation (%), 1000h		
	40°C	70°C	100°C	40°C	70°C	100°C
B(N)	17.1	43.5	82.8	2.8	31.0	55.3
C(O)	19.4	30.2	44.5	8.4	16.7	33.3
D(N)	21.2	14.5	17.1	1.5	4.5	5.0
F(O)	21.9	21.2	27.6	5.6	6.1	9.1
G(O)	20.5	19.4	40.7	2.3	12.4	29.1
H(O)	29.1	41.1	73.4	6.1	18.5	49.9

The discrepancy that the 'symmetrical relaxation' process, ie: $S = S'$, is not valid in the present programme may be due to the following reasons:

- The relaxation behaviour of filled elastomers cannot be the same as that of gum compounds because of the additional relaxation processes due to filler/filler or filler/polymer interaction.
- According to the theory of rubber elasticity, the stress in a vulcanisate at any given time is proportional to the amount of crosslinks. The changes in network structure brought about by the chemical relaxation during the deformation period prior to recovery affects the relaxation processes. Thus, the relaxation processes during the relaxation, prior to a chemical change in the network and during recovery periods can not be identical.
- The accuracy of estimating the amount of chemical relaxation (ie: the position of Point B in Figure 5.3). This again depends on the ability and accuracy of the mathematical model used to identify and separate the different processes, and is considered later in Chapter 7.

d) According to Gent,²⁴ the rates are comparable when the deformations are equal. In the present work, however, the amount of strain varied between 21 and 29%. Thus, the effects (if any) due to varied deformations must also be considered. Stenberg⁴ has reported that the effects of deformation on the compression relaxation is negligible at the strain levels used in this work and this is also confirmed here (See section 4.1); however, their effects on recovery from compressive strain and on equation 5.1 needs further investigation.

NOTE: It is to be noted that the absolute value of relaxation can not be calculated from the results obtained under the experimental conditions used in the present research. This is because, the zero time and the initial force are poorly defined. Fuller⁷⁵ suggested that a period of five times that of the time used for loading the specimen (5-6 min. in this work compared with 1-2 s in Gent's) is to be allowed before the readings are taken so as to ensure that the effects of either the loading cycle or a previous test remained negligible throughout the test period. Thus, if normalisation to 0.5h. or 1.0h is to be used, then valuable information on the physical relaxation will be lost; this is because, much of the physical relaxation takes place during the early part of the relaxation process. However, in contrast, the recovery values are well defined with the zero time and the original deformation. Thus, the application of Gent's hypotheses for a quantitative treatment of the recovery and relaxation data is limited.

According to Derham,³⁹ the relaxation due to filler-filler or filler-polymer breakdown is permanent. This is also evident from the differences in rates of physical relaxation and recovery and are considered in the following section. This difference could also be due to the loss of original network because of chemical relaxation. Thus, it is necessary to investigate the effects of carbon-black on the relaxation behaviour for a quantitative treatment. However, this is not within the objectives of the present programme. The difficulties encountered in separating the two relaxation processes, and their accuracy in estimating the relaxation rates must also be considered in future applications.

5.3.3 Comparison of stress relaxation and strain recovery rates

The relaxation rates (physical) and the recovery rates of various compounds used in the programme are listed in Table 5.4. From the results, it seems likely that there is always a substantial difference in the rates of stress relaxation and strain recovery, the former always been the greater.

Table 5.4: Comparison of Stress Relaxation and Recovery Rates

Stress relaxation and Recovery Rates (% per decade)						
Material \ Temperature	40°C		70°C		100°C	
	SR	RR	SR*	RR	SR*	RR
Natural Rubber, A(N)	3.3	1.5	6.2	1.8	5.7	2.0
SBR, B(N)	3.1	1.8	8.7	2.1	16.5	1.0
EPDM(Sul) C(O)	4.6	1.7	7.8	2.0	6.2	1.7
EPDM(Pero) D(N)	4.6	2.2	7.7	2.0	6.2	1.8
NBR, E(N)	3.5	1.0	3.6	0.7	6.2	0.5
EPDM(pero) F(O)	7.3	1.0	6.8	1.2	7.1	1.3
NBR, G(O)	4.8	1.4	4.0	1.6	4.6	1.3
EPCL, H(O)	5.4	0.7	9.4	1.1	5.0	1.3
Santoprene 55, I(O)	8.3	3.3	11.8	2.8	7.6	3.2
Santoprene 64, J(O)	9.7	3.3	8.1	3.4	10.1	3.5
Evoprene K(mix)	7.8	5.3	13.8	7.6	17.7	4.1
Evoprene994, L(O)	8.2	4.8	10.9	8.2	19.2	5.5
Alcryn6368, M(O)	18.0	4.0	14.7	2.2	14.1	2.2
Alcryn 6385, N(O)	14.6	4.3	15.5	1.8	19.5	1.8
Alcryn 1201, O(O)	12.8	4.7	12.1	1.2	17.6	1.2

* (Stress relaxation rates are based on 1000 h relaxation data)

According to Gent,²⁴ recovery and stress relaxation rates in gum compounds are comparable as only physical processes are involved. However, as filled compounds are used in this research, the filler relaxation is also to be considered. This implies that harder materials relax to a greater amount and thus can indeed be observed (ie: Relaxation rates of 50 IRHD compounds, ie: Type A,B,C,D and E,

are much lower than 70 IRHD compounds, ie: Type F, G and H) The physical relaxation rates at higher temperatures may not be comparable in this way as chemical processes may be involved. However, in the case of recovery rates at high temperatures, this may not be a problem as the rate of recovery is purely physical. Also, the effect of filler on rates of recovery seems to be negligible; this is because the breakdown of filler-filler or filler-polymer bonds is often permanent.³⁹ Very high relaxation rates were also observed in the TPE's; however, the above discussion may not be applicable as other processes such as crystallisation may be involved.⁶⁹ Even though higher crystallinities are associated with higher relaxation rates, their effect on recovery needs further investigation.

Both stress relaxation (at low temperatures and short times) and recovery are linear with respect to $\log(\text{time})$ (Figures 1- 38 in the Appendix), indicating that both are dominated by physical processes. It thus seems likely that if recovery is involved with one physical process, such as movement of chains and entanglements, then stress relaxation must have at least one other process; this second process could be related to mobility of the chains coming into play as filler matrix bonds are broken.^{32,33,39}

5.3.4 State of cure

Recovery tests were carried out after the completion of the investigation of the influence of cure state on stress relaxation at 23°C. Recovery data are shown in the Table 5.5. The tests were over 1000 h. The different terminologies involved with the state of cure and their effects on other properties of the vulcanisates are given in Chapter 3.

Under-cured materials recover poorly in comparison with the optimum and over-cured formulations. According to the theory of rubber elasticity,¹⁶ the force in the rubber network during a deformation is dependent on the number of support links. Because under-cured materials have fewer stress support links in their network, there aren't enough links to oppose the imposed strain; this reflects in high stress relaxation and permanent set even at room temperature. The same can be argued about their inability to recover fully.

Table 5.5: Comparison of % Fractional Recovery at different levels of Cure at Reduced Time=1, after 1000 h. in compression.

Material \ Cure state	Under-cure*	Optimum-cure*	Over-cure*
	% Fractional recovery at Reduced Time = 1		
SBR, B(N)	33.5	87.8	91.2
EPDM(Sul), C(O)	66.7	91.8	91.2
EPDM(Pero), D(N)	84.9	92.4	92.6
NBR, E(N)	77.0	92.4	98.6
EPDM(Pero), F(O)	75.7	93.4	94.7

* Note that complete definition of these are available in Section 3.1.3

5.3.5 Recovery in nitrogen

Recovery measurements were made on specimens which had been compressed under nitrogen for 1000 hours at 70° C or 500 h. at 100° C. The results are given in Table 5.6. The fractional recovery at a reduced time of one are compared with specimens compressed in air at the same time/ temperature conditions. In general, the recovery under nitrogen atmosphere seems to be better for both the thermoplastics and the crosslinked materials, when compared with that in air.

According to Lee and Morrell⁶⁰, the ageing mechanisms may involve either scission reactions of crosslinks and breakdown of main chains or crosslinking reactions with the accompanying hardening or embrittlement. These reactions are dependent on the service temperatures and the surrounding atmosphere,¹³ particularly the oxygen content. Both these processes, the breakdown of the network and the reformation due to crosslinking, affects recovery. The results from the stress relaxation experiments under nitrogen atmosphere show that oxygen has negligible effect on the rate of relaxation. This, further infer that effect of nitrogen on the recovery behaviour may be to retard the formation of second network, which possibly could have occurred due to oxidative crosslinking. This is because, according to the Two-Network theory, the formation of new network does not affect the relaxation data (unless the test is carried out in intermittent mode).

Table 5.6: The effect of nitrogen environment on the Fractional Recovery at Reduced Time = 1.

Temperature Material		Fractional Recovery (%)			
		70°C		100°C	
		Nitrogen	Air	Nitrogen	Air
NR.	A(N)	48.7	50.0	69.6	59.0
SBR,	B(N)	82.7	79.8	56.5	33.7
EPDM(Sul),	C(O)	88.9	87.0	55.8	46.8
EPDM(Pero),	D(N)	93.5	97.4	98.7	96.6
NBR,	E(N)	66.2	66.1	69.0	51.4
EPDM(Pero),	F(O)	93.2	98.3	98.6	94.4
NBR,	G(O)	85.0	76.6	68.2	53.4
EPCL,	H(O)	83.6	82.3	74.1	54.9
Santoprene55,	I(O)	88.9	87.0	87.0	72.0
Santoprene64,	J(O)	82.7	79.8	64.6	67.4
Evoprene992,	K(O)	----	----	57.0	37.8
Evoprene994,	L(O)	----	----	58.8	47.6
Alcryn6368,	M(O)	39.5	45.5	40.5	26.7
Alcryn6385,	N(O)	----	----	41.8	23.5
Alcryn1201,	O(O)	----	-----	56.8	23.6

(Note: The specimens were compressed for 1000 hours at 70°C and 500 hours at 100°C under Nitrogen)

5.3.6 The effect of filler on recovery

Recovery data for gum compounds for specimens recovering at 23°C are compared with those of filled materials originally supplied for the programme, and are listed in Table 5.7.

Table 5.7: The effect of Filler on the Fractional Recovery at Reduced Time=1 after 336 h. compression time at 23°C

Material	Fractional Recovery (%)	
	GUM	FILLED
Natural Rubber, A(N)	98.0	97.3
EPDM(Pero), D(N)	96.6	99.0

In this experiment, as the temperature is low and time is small, chemical relaxation can be neglected in both the cases. Thus, almost complete recovery, with a very small 'set' (< 4%) is achieved. It seems that the effect of filler may be significant at longer timescales and higher strains and needs further consideration. However, if symmetrical relaxation as suggested by Gent,²⁴ is to be expected, then the following points needs consideration:

- The accuracy of the fractional recovery data, as the measurement of specimen thickness is carried out using a dial gauge (0.01mm least count). Even a small error of $\pm 0.01\text{mm}$ can cause an error of @ 1.5 % in the recovery value; however, this may not be the case in tension because of the possibility of more accurate measurements of tensile recovery, the errors can be reduced significantly.
- The amount of filler relaxation in compression at low strains (@ 25%), as the effect of scragging was found to be negligible at these conditions compared with those in tension, where mechanical conditioning has been found to have significant effect on physical relaxation.³⁹
- The amount of chemical relaxation, as it is often said that there does not seem to be a temperature below which the chemical relaxation ceases.⁴³

5.3.7 Influence of specimen dimensions on recovery

The recovery of specimens with a volume four times that of the standard specimen was measured at 70°C and 100°C, and are compared with those of standard specimens in Table 5.8. In general, the fractional recovery is better for large specimens.

Table 5.8: Comparison of Fractional Recovery (%) in standard and large buttons at 70°C and 100°C, after 670h and $T_R=1$

<div>Temperature</div> <div>Material</div>	70°C		100°C	
	Large	Standard	Large	Standard
NR, A(N)	75.7	52.8	61.1	59.0
NBR, G(O)	88.2	78.8	71.8	53.4
EPDM, F(O)	97.6	98.3	96.3	94.4

Tamura and Murakami¹³ have reported that oxygen plays an important part in the chemical relaxation of vulcanisates. Thus, if the penetration of oxygen is to play its part, depending up on the affinity of the material to oxygen, then the specimen dimension has to provide a clue for that part of recovery resulting from oxidation.

5.3.8 Effect of temperature jumps on recovery

Following the investigation into the effects of temperature jumps on stress relaxation, the strain recovery measurements were made. The first set of tests took place over 168 h; the test schedule and the corresponding fractional recovery of natural rubber, peroxide-cured EPDM and Santoprene 101-55 are given in Table 5.9.

Table 5.9: The effect of Temperature Jumps on Recovery

Specimen	Temperature of test during the time jumps (°C)						
	0-24h	24-48h	48-72h	72-96h	96-120h	120-144h	144-168h
1	100	100	100	100	100	100	100
2	100	70	100	70	100	100	100
3	100	70	100	100	100	100	100
4	100	100	100	70	100	100	100
Material Specimen	Fractional Recovery (%) at 168 h, reduced time = 1						
	Santoprene 101-55		Natural Rubber		EPDM (Pero)		
1	88.9		66.1		100.6		
2	90.8		66.1		100.6		
3	89.4		68.8		101.2		
4	89.4		65.9		100.0		

The second series of tests, involving temperature jumps one to a higher temperature (100° C) and the other to a lower temperature (40° C) and both back to the original temperature (70° C), has also been carried out; the results are given in Table 5.10. Differences in recovery behaviour were apparent shortly after measurements commenced.

The specimens at 100°C recover poorly in comparison with the specimens at the other two temperatures. It may be tentatively concluded that longer the time spent at lower temperature (ie: 70° or 40°C), better the recovery. Thus, the effect of

Table 5.10: The effect of Temperature Jumps on Recovery in Filled and Gum compounds

Specimen	Temperature of test during the time jumps (°C)		
	0 - 24 h	24 - 48 h	48 - 72 h
1	70	100	70
2	70	70	70
3	70	40	70
Material Specimen	Fractional Recovery (%) *		
	Santoprene 101-55	Natural Rubber (Gum)	NBR (Gum)
1	76.8	73.0	85.5
2	88.0	88.0	96.2
3	89.5	93.0	97.9

*(Note: The fractional recovery values in the above table are after 72 h for Santoprene and 24 h for Nitrile and Natural rubber compounds.)

temperature jumps on recovery behaviour has an implication for the compression set test, where the specimen is compressed at 23°C, placed in an air oven at a specified temperature for 22 h, then allowed to cool before measurement. This will produce a different result to a specimen compressed, stored and measured at the same fixed temperature.

5.4 CONCLUSIONS

The recovery test can be very useful because of the following reasons. First, the recovery test is simple and economical to run and can be easily duplicated. Second, the results give very useful information about both the chemical and the physical changes the test specimen has undergone during the imposed strain. This is measured by the rate of recovery (physical) and the fractional recovery (chemical changes). The recovery test is superior when compared to compression-set test used in quality control ^{75a} as the recovery measurements

provide more vital information on both the physical and the chemical changes. The major finding is that the physical stress relaxation rate of filled rubber compounds is always greater than the recovery rate; indicating that if recovery were associated with one process (movement of chains), then stress relaxation has at least one or more additional mechanism, such as filler/filler or filler/polymer breakdown, which require further investigation.

Chapter Six

EXPERIMENTAL SIMULATION OF SEAL BEHAVIOUR

6.1 INTRODUCTION

One of the objectives of the programme was to compare the decay in sealing force of commercial seals with the relaxation in standard test buttons from the compression stress relaxation experiments. Two sets of equipments were used for this measurement; one working on spring force while the other based on a pneumatic pressure and were provided by Hepworth Building Products and Wavin Limited respectively. The main requirement for such apparatus was to allow long-term testing on several seals. To do this economically one measuring device and several jigs were needed. Both the equipments used uPVC coupler and mandrel arrangement produced by Wavin with the same size of seal. The Hepworth equipment is used by the company for short-term tests on sealing compounds, and certain modifications to the technique had been suggested to allow longer timescale tests to be carried out. The Wavin equipment was developed especially for the programme, and unfortunately, the prototype had not been tested before its delivery to IPTME; this meant that considerable development and modification were necessary to obtain data. The details of each set of equipment, necessary modifications and the results are discussed in Sections 6.3 to 6.5.

6.2 SEALS

Two types of seals were used and are given in Figure 6.1 below. Both Wavin

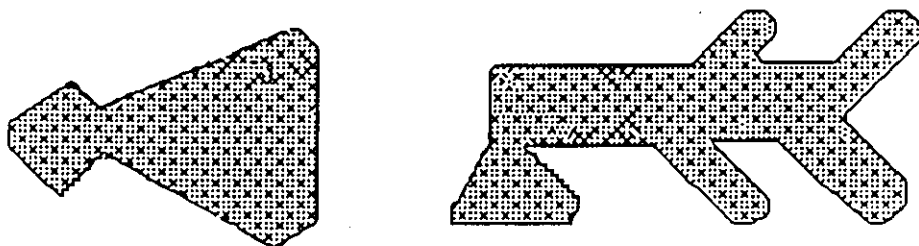


Figure 6.1: Cross-sectional view of triangular compression type and model lip seals used in the simulated experiments.

and Hepworth apparatus, discussed later in this Chapter, were designed to use a 110 mm diameter model lip seal. Compression seals with a triangular cross-section, and of same diameter were also supplied for use with the Hepworth equipment. Both these types of seals were supplied by Ketch Couplings Ltd. and were moulded in Santoprene, Evoprene, sulphur-cured SBR and EPDM compounds and were of same formulations as used earlier in the programme.

6.3 HEPWORTH SEALING FORCE APPARATUS

A schematic diagram of the equipment is given below in Figure 6.2. The equipment uses a calibrated compression spring to measure the force required to push the seal a given distance from the mandrel. Both, the amount of compression of the spring, and hence the force, and the movement of the test seal are monitored using separate dial gauges as shown in the Figure.

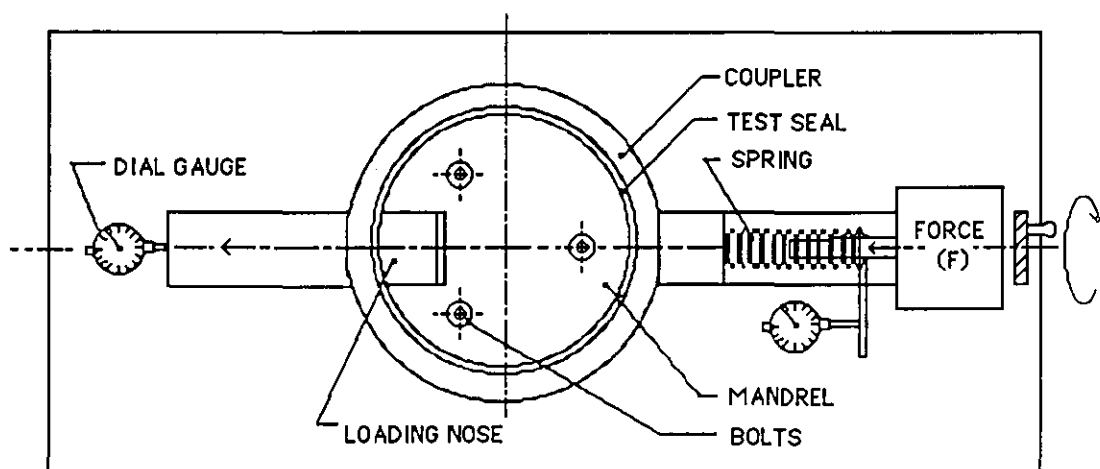


Figure 6.2: Schematic diagram of Hepworth sealing force apparatus

The seal, mounted in the PVC coupler, is placed on the steel mandrel of diameter 110mm. A 25 mm wide segment of the mandrel is mounted on a long cranked shaft, which is supported on linear bearings. By compressing the force measuring spring, the loading nose moves radially and pushes the seal from the mandrel. This is true when the compression force in the spring is greater than the sealing force on the mandrel. The amount of spring compression, hence the sealing force, necessary to move the loading nose 0.0005 inch is read from the corresponding dial gauge.

The force is measured as soon as the coupler and seal are mounted and then at various intervals to determine the variation of the sealing force with time.

In order to allow several seals to be tested, after measurement of the sealing force, coupler assembly was removed from the measuring mandrel to a steel storage mandrel (of the same dimensions) until the next measurement was due. The first data obtained following this procedure were not very satisfactory, as considerable variability in results was apparent. The initial force was found to be different for the same seal measured at different points around the circumference, with variation of up to 50%. The values of residual stress were also found to be affected with the position of measurement; the range for any one material at a given time varied from 90% to 65%. The performance of the model lip seal appeared to be particularly sensitive to the system geometry. The couplers were not quite circular, with a variation in diameter of about 0.5mm. This was reflected in the values of initial sealing force obtained from a single seal and coupler in different positions on the measuring mandrel. However, even when the same point on the coupler was aligned with the measuring nose, there was little pattern to the results apart from a general decrease in sealing force with time

Another problem was that the coupler was difficult to remove from the storage mandrel, because of the similar dimensions of coupler and mandrel. This was overcome by using larger size couplers provided by Hepworth Ltd, with the triangular compression seals. These couplers were more flexible than the Wavin type. The variation in initial force was much less than for Wavin coupler (about 10%), but it was not clear if this was solely due to the coupler geometry or whether the flexibility of the sleeve contributed to this. The possibility that the process of removing and replacing the coupler on the mandrel affected reproducibility, and was investigated. A series of 168 h tests was carried out, in which the seal and coupler remained on the measuring mandrel. The data for this test and one in which the coupler was removed to the storage mandrel between tests was shown in Figure 6.3. It was apparent that reproducibility was considerably improved if the coupler was not removed between measurements. This caused a problem, as this difficulty could not be overcome without having several sets of apparatus, each dedicated to a single seal and coupler, which would have meant considerable financial investment.

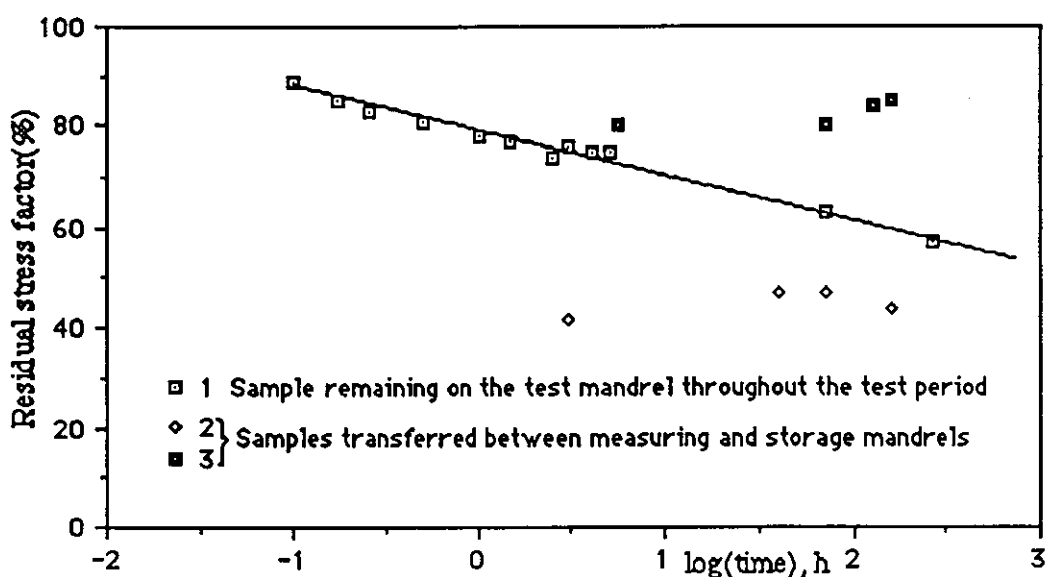


Figure 6.3: Variation of sealing force on the Hepworth equipment

It was therefore decided to use the Hepworth equipment for a series of short-term tests of up to 360 hours, leaving the coupler system on the measuring mandrel for the duration of the test. In all cases, stress relaxation was approximately linear with $\log(\text{time})$, and the results were expressed as percentage relaxation per decade of time. In the following Table results for both lip seals (used with the Wavin coupler) and the compression seals (Hepworth sleeve) are compared with stress relaxation data from button specimens.

Table 6.1: Comparison of Hepworth test results with the compression stress relaxation data

Material	Reduction in sealing force (% per decade)		
	Compression seal	lip seal	button specimen
SBR	5.3	5.8	4.5
EPDM(S)	6.3	3.7	5.5
Santoprene 101-55	8.6	6.5	6.9
Santoprene 101-64	7.6	4.0	7.2
Evoprene 992	8.5	3.7	5.0
Evoprene 994	7.7	6.0	4.8

One unusual observation was that the increase in residual force a short time after loading for Santoprene 101-55 and Evoprene 994 lip seals. This was not observed in the other materials. Tests on these two materials were repeated, and residual stress factors greater than 100% were again obtained. A variation of about 5% was found in residual stress, at a given time, between seals of the same material. However, a considerable difference in initial force (~40%) was noted. This was probably due to a combination of seal variability and coupler geometry.

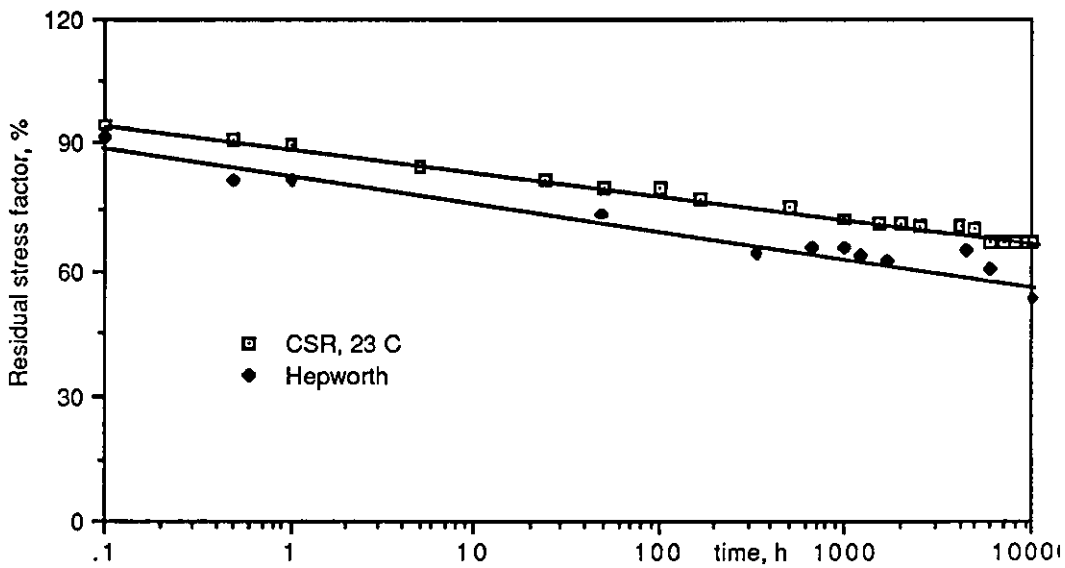


Figure 6.4: Comparison of decay in sealing force on Hepworth equipment with the compression stress relaxation data for sulphur-cured EPDM

Leaving the seal on the measuring mandrel, during a test, has proved to be successful even for long term tests. Figure 6.4 shows the result for the sulphur-cured EPDM wedge shaped seal, left on the mandrel for 10000 h. The residual stress factor at the end of this test was found to be 53.6%, compared with 67.1% for the corresponding button specimen in the compression stress relaxation test.

6.4 WAVIN EQUIPMENT

This apparatus (Figure 6.5) is based on pneumatic pressure. Compressed air or gas is fed to the aluminium cylinder which encloses the seal/coupler assembly to

be tested. The pressure at which the seal is pushed from the mandrel, allowing the gas to leak from the lid, through the upper mandrel, is measured. This does not test a lip seal as it would be used in service conditions, as in that case the pressure inside the pipe system would be greater than outside, further compressing

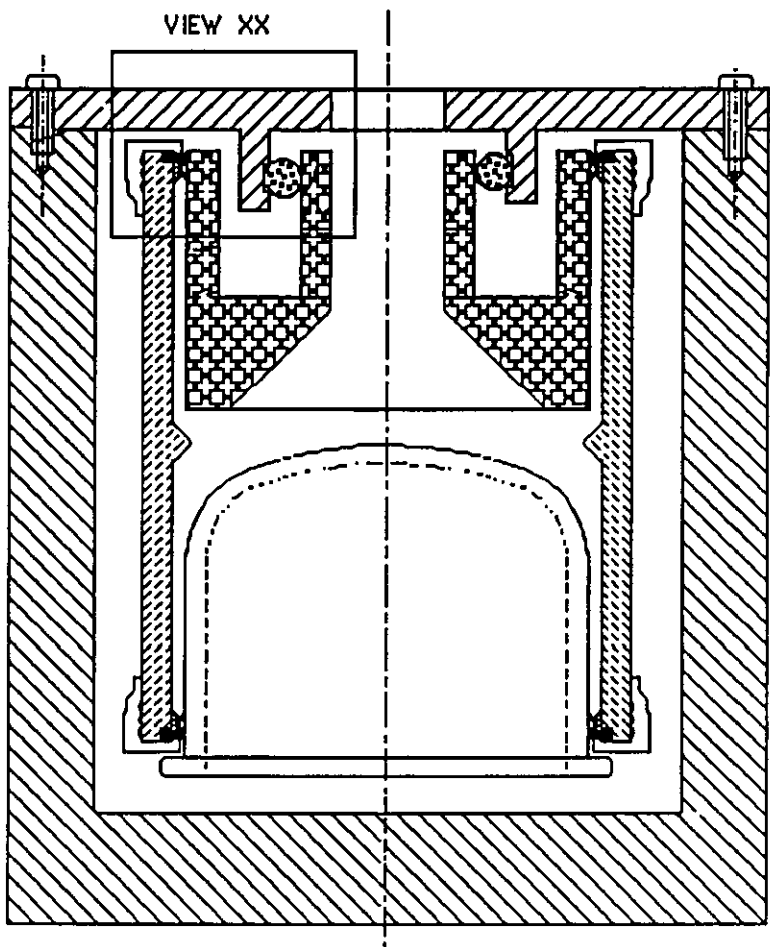


Figure 6.5: Schematic diagram of Wavin equipment (original design)

the seal. In this equipment, the opposite is true; the external pressure is greater than the interior, and in effect, the seal is tested 'in reverse', only its compression properties being measured. In actual service conditions tensile and flexural components would also be involved in determining seal performance.

The original apparatus consisted of an aluminium cylinder with a lid, a PVC coupler of internal diameter 116mm, with seals at either end and two PVC mandrels, of 110mm external diameter. The lower mandrel and seal were intended to close off that end of the coupler. In addition, there was an O-ring seal between

the lid and the inner surface of the upper mandrel, and one between the cylinder and the lid. Of these four seals, the seal between the upper mandrel and coupler was to be tested. The aim of the apparatus was that a series of coupler/mandrel systems could be used, each with a different seal. When the sealing force was not being measured, the whole coupler system could be removed from the aluminium cylinder arrangement, and another seal tested. This would also permit tests to be made on seals at other temperatures or in different environments, as the coupler/mandrel system would easily fit in an oven or into a water bath, if necessary.

Several problems were experienced with the apparatus.

- a) movement of the bottom mandrel, which lead to further compression of the seal due to extra thickness of the rim.
- b) during a test, on application of pressure, the two mandrels moved towards each other forming a seal at the interface
- c) there was an internal ridge, halfway down the coupler, which acted both as a stopper (to further movement) and as a seal
- d) dismantling of the coupler/mandrel assembly from the lid was difficult, and frequently the upper mandrel remained attached to the lid; this resulted in unloading the seal and the test was terminated.

Remedial measures were made to the equipment to try to overcome these problems. Large sections of the ridge in the coupler were cut away to try to prevent sealing at the ridge. Some of the upper mandrels were turned down to 109 mm diameter, to make the assembly and dismantling easier. The diameter of the part of the lid sealing with the upper mandrel was slightly reduced, and the O-ring replaced with one of thicker cross-section seal. This was to allow proper sealing when the mandrel was mounted on the lid and to make removal of the assembly easier. These modifications had limited success. Removal of sections of the inner ridge in the coupler did not stop the upper mandrel from sealing on the rim. The alteration of the lid was successful for some mandrels and not for others, probably because of the lack of concentricity of the mandrels. Reduction of the upper mandrel diameter to 109 mm was successful. The coupler/mandrel system was still difficult to dismantle, and so the upper mandrel diameter was further reduced to 107.5 mm. This caused the mandrel to move towards the bottom mandrel and seal at the

interface. This was overcome by incorporating a spacer between the mandrels. Even with all these efforts, it was impossible to determine whether the lower or upper seal was leaking, because of the large amount of scatter in results. The equipment was therefore modified to eliminate the lower seal.

An aluminium coupler was made to replace the original PVC design, and was one-half the length of the PVC piece, with a closed bottom. This eliminated the need for the lower seal. Some aluminium mandrels of external diameter 110 mm were also made. This all aluminium system appeared initially to be successful, but problems were revealed when it was compared with an aluminium coupler/PVC mandrel combination, both with a sulphur-cured EPDM lip seal. The two all-aluminium systems leaked at a pressure of about 50 psi; however the aluminium/PVC set did not leak even at a maximum pressure of 62 psi. The aluminium mandrels were found to be much more easily removed from the lid than the PVC mandrels, which suggested that the mandrel/lid seal rather than the lip seal was leaking. This is illustrated in the following diagram.

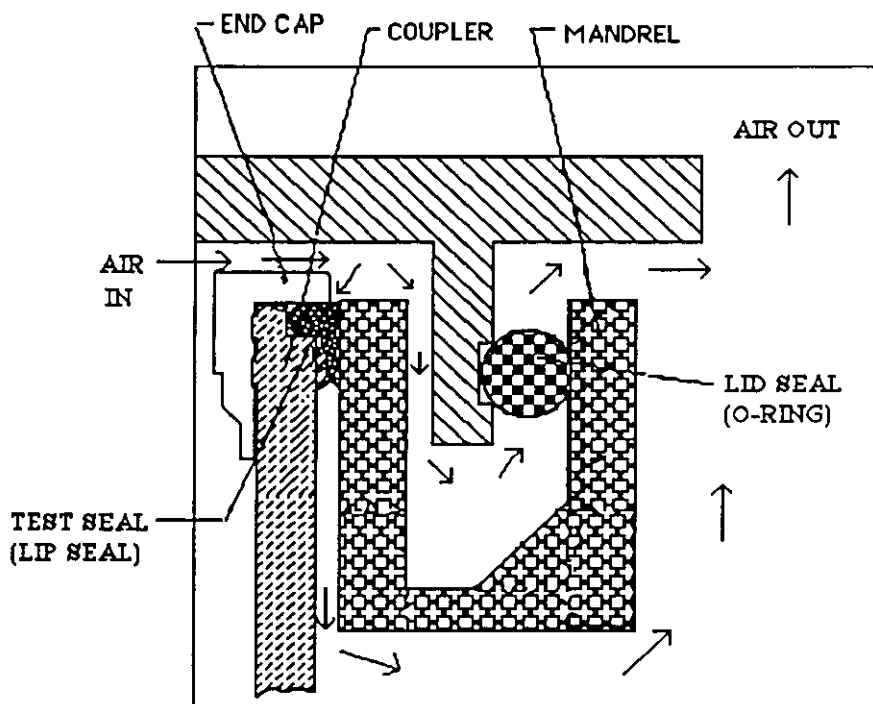


Figure 6.6: Cross-sectional view of the seal and coupler assembly used in Wavin equipment (View X-X of Figure 6.5)

This shows that gas may leak from the outer cylinder either by pushing past the lip seal or by the lid seal. To overcome this, it was necessary to either eliminate the lid seal completely, by combining the lid and mandrel into a single piece or to make it easier for the lip seal to leak, since presumably, the lid seal was leaking at a lower pressure than the lip seal. The latter was chosen, because of economics.

The aluminium mandrel diameter was reduced to 109 mm. Using this system, a sulphur-cured EPDM seal leaked at a pressure of 12 psi, an Evoprene 994 at 48psi. A series of reproducibility tests was carried out with the modified aluminium system, using Evoprene 994 seals. Results are shown in Figure 6.7. The data obtained for coupler 2 do not seem to indicate that stress relaxation was taking place. Further tests were carried out to determine the range of initial leakage and resealing pressures for the same type of seal with the same coupler/mandrel system. Seven Evoprene 994 seals were tested. The initial leakage pressures ranged from 32 psi to no leakage up to the maximum pressures of 62 psi. For these tests the coupler system was aligned to a mark on the outer cylinder. If the lid (and the coupler and seal) were rotated through 90° the two seals which had not leaked at all, leaked at pressures of 38 and 32 psi respectively. This suggested that either the lid seal was leaking or the position of the seal with respect to the outer cylinder affected leakage. Hence, a combined mandrel and lid was made, to eliminate the lid seal. This left only two seals in the apparatus; the seal between outer cylinder and lid and the lip seal to be tested.

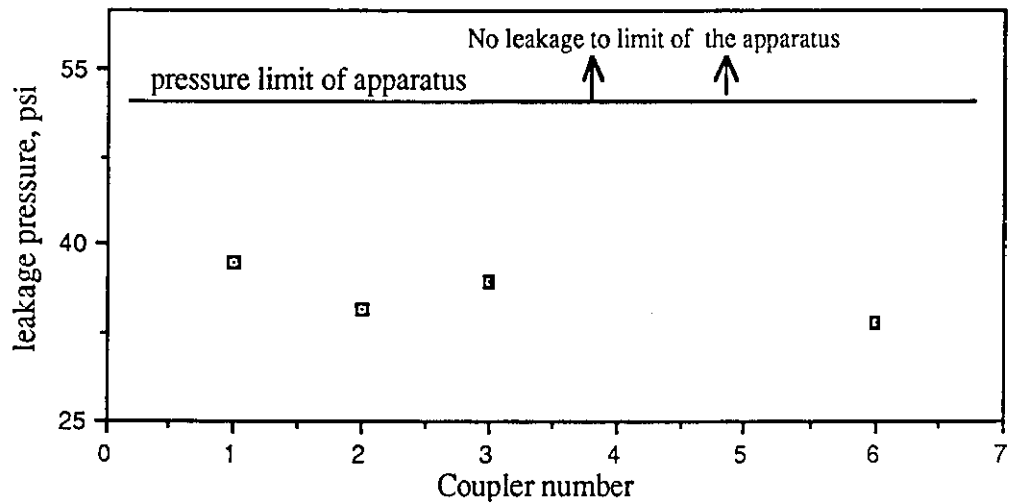


Figure 6.7: Reproducibility tests for the Wavin equipment

Using the combined lid/mandrel, two 168 h tests were carried out on Santoprene 101-64 and sulphur-cured EPDM seals. Both tests showed a decrease in leakage pressures that was approximately linear with $\log(\text{time})$, with sealing force decay of 7.25 % and 5.25 % per decade of time respectively. These data apparently showed the apparatus was working successfully, a series of long-term tests was started, using Evoprene 992, Santoprene 101-64 and two sulphur-cured EPDMs seals.

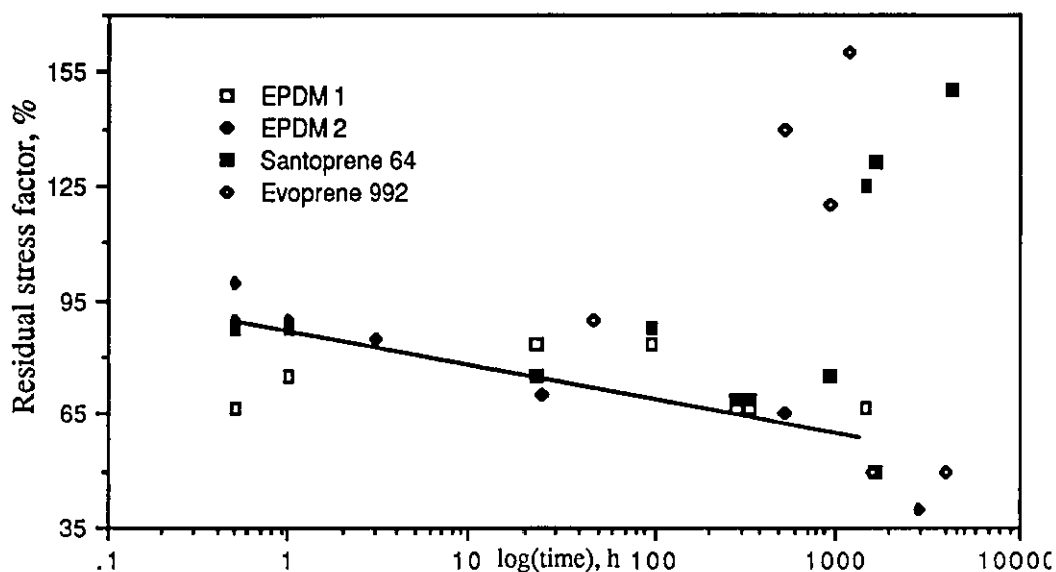


Figure 6.8: Variation in residual stress with the Wavin equipment

These tests were continued for between 3000 to 4000 h. Only one of the sulphur-cured EPDMs showed a steady decrease in leakage pressure with time (Figure 6.8), with a rate of 12 % per decade. The other three seals failed to show any regularity for a meaningful interpretation.

The residual stress factors at the end of this experiment (3000-4000 h) together with that of the corresponding button specimens are given in Table 6.2. The results on Santoprene seal suggest that other factors apart from stress relaxation are involved in sealing. When this coupler system and an EPDM seal were tested after being replaced for 100 h at 100° C, the leakage pressure was less than 2psi, suggesting that relaxation had occurred in the lip seal.

Table 6.2: Comparison of Wavin test result with the Compression stress relaxation data at ambient temperature.

Run	Material	Residual stress factor (%)	
		SEAL	BUTTON
1	EPDM(S)	33	71
2	EPDM(S)	40	71
3	Santoprene 101-64	150	47
4	Evoprene 992	50	60

6.5 CONCLUSIONS

The Hepworth apparatus appears to provide reproducible results, but is limited to short term tests. These tests imply that short-term relaxation rates are similar for the compression seal and the button specimen. The lip seal also showed similar rates of relaxation as it was acting as a compression seal in the Hepworth equipment. Thus, the equipment measures the force to push the seal away from the mandrel rather than the force to push it away from the pipe face. It is thus relevant for compression seals, but not for lip seals.

The wavin equipment tests only the compression part of the seal; in fact the test is done '*in reverse*', ie: the external pressure is greater than the internal. In a lip seal, increasing the pressure inside the pipe would increase the seal compression, and hence the sealing force. The results from this apparatus are difficult to interpret. Considerable effort has been expended in modifying the equipment, and despite the elimination of all but the test seal, the results still appear to be without any pattern. A reason for this irregularity may be due to the movement of the coupler assembly due to the reasons such as the tilting of the coupler axis or the vertical shift in position with respect to the stationary mandrel. This may result in change in deformation of the seal and needs further investigation.

Chapter Seven

MATHEMATICAL MODELLING

7.1 INTRODUCTION

Various models to represent the stress relaxation behaviour of elastomers are cited in the literature;^{76,77} a few of the more applicable are considered here.

7.2 THE MAXWELL MODEL

The Maxwell model of an viscoelastic solid consists of a Hookean spring and a Newtonian dashpot in series as shown below in Figure 7.1. One element represents a linear elastic solid, and the other a linear viscous fluid, thus the model combines

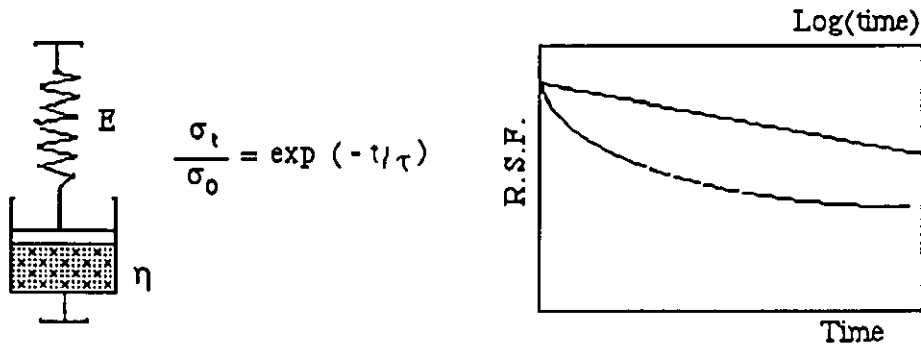


Figure 7.1: Schematic diagram of the Maxwell model

the characteristics of the two linear components. Under constant deformation the stress relaxation in the model can be given by:⁷⁸

$$\sigma_t = \sigma_0 \exp(-E.t/\eta) \quad 7.1$$

where σ_t is the stress at time t , σ_0 is the original stress, E and η are the modulus and the damping constant of the spring and dashpot. Equation 7.1 may be rearranged to give:

$$\sigma_t = \sigma_0 \exp(t/\tau) \quad \text{or} \quad \ln(\sigma_t) = -t/\tau = -k.t \quad 7.2$$

where τ is the relaxation time (the time for the stress to decay to $1/e$) and σ_t is the

stress relaxation at time t with rate constant k .

This is not an accurate model of polymer viscoelasticity, as real polymers have a large number of relaxation times distributed over many decades of time. Also, the Maxwell model, a combination of two linear components, predicts a linear relation between logarithm of the stress relaxation and time, not the logarithm of time as found in practice. To overcome these deficiencies, a more complex model consisting of a large number of Maxwell elements in parallel, the generalised Maxwell model, was proposed (Figure 7.2).

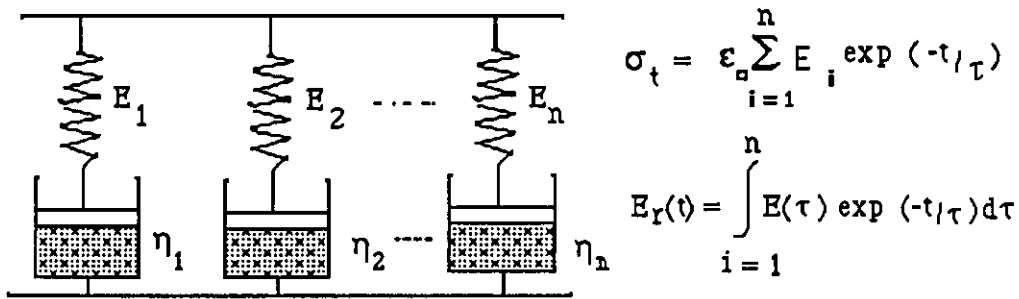


Figure 7.2: Schematic diagram of the generalised Maxwell model

Each element has its own relaxation time and elastic modulus. The resultant stress relaxation equation is:

$$\sigma_t = \epsilon_0 \sum_{i=1}^n E_i \exp(t/\tau_i) \quad 7.3$$

where n is the number of elements and ϵ_0 is the initial strain. A more generalised equation for the above with a continuous distribution of relaxation times $E(\tau)$ can be written as:

$$E_r(t) = \int_0^\infty E(\tau) \exp(-t/\tau) d\tau \quad 7.4$$

The distribution of relaxation times can be estimated from a relaxation modulus, E_r , vs log(time) curve⁷⁹ using the following Equation:

$$H(\tau) \approx \frac{-d[E_r(t)]}{d \ln t} \approx \frac{-1}{2.303} \frac{d[E_r(t)]}{d \log_{10} t} \quad 7.5$$

where the relaxation spectrum $H(\tau) = \tau \cdot E(\tau)$ 7.6

In order to obtain an accurate distribution of relaxation times, the experimental data should cover many decades of time.⁷⁸ It is difficult to get data covering such a range of time in a single experiment at one temperature, so *master curves*, which uses the principle of *time-temperature superposition* are developed and is described in Section 7.4.

The distribution of relaxation times is generally used to calculate viscoelastic properties such as creep or dynamic mechanical data, however, relaxation spectra have been successfully used to extrapolate physical relaxation data.⁸⁰ It has been said⁸¹ that the relaxation spectrum approach is no more than a convenient way of representing experimental data. The analysis may be helpful in relating different types of experiment within a limited range of timescales, but it cannot be legitimately used to extrapolate beyond the range of time covered by the experimental data. Nor does it, by itself, provide any information as to molecular or other structural processes responsible for stress relaxation.⁸²

7.3 EMPIRICAL MODELS OF PHYSICAL RELAXATION

Physical relaxation can occur for a number of reasons, including physical movements of chains, aggregates or entanglements. This type of relaxation is dominant in the early stages of relaxation (10^{-6} - 10^{-2} s) and at lower temperatures.³² The rapid relaxation is then followed by a slowly decaying process (10^2 - 10^4 s). Several empirical models of physical relaxation are available in the literature.^{32,34,37} An empirical relation frequently cited is that of Cotten and Boonstra³²

$$f_t = f_{1.0} t^{-n} \quad 7.7$$

where $f_{1.0}$ is the stress at one hour, and measurements are done at room temperature. They found a good correlation with the measured data over a period of 6 months on raw and vulcanised compounds in accordance with other

workers.^{39,83,84} From these experiments, it can be written that:

$$n = (df / f) / \log t \quad 7.8$$

ie: a percentage decrease in stress per unit log cycle of time. This corresponds to the definition of stress relaxation given by Gent,²⁴ and the expression is fitted by data on many materials.

According to Thirion and Chasset³⁷ the stress f_t in a natural rubber compound under tension at any given time t could be represented by:

$$f_t = f_e + c \cdot t^{-n} \quad 7.9$$

where f_e is a constant; the equilibrium force at infinite time. It cannot be determined empirically; its value is determined from $\log(f - f_e)$ vs $\log(t)$ plot. From this straight line plot, values of c and n are also calculated. The expression 7.9 implies the existence of an equilibrium value of the relaxed stress. An equilibrium value was obtained for a nitrile rubber in vacuum at 25° C after 50 hours. This suggests that chemical relaxation in air is appreciable at this temperature after this time where viscoelasticity might be presumed to be the sole mechanism of relaxation.⁴³

Another model of physical relaxation applied for a variety of polymer systems including SBR is the Nutting's equation^{85,86} which can be written as:

$$\sigma = e \beta \psi t^{-n} \quad 7.10$$

where e is the imposed strain, ψ , β and n are material constants. The constant n is closely related to δ , obtained from dynamic mechanical experiments and found to vary with the gel content and the gel structure of polymer.⁸⁶ The parameter ψ is also related to the dynamic modulus.

All the empirical models discussed above show a linear relation between stress relaxation and $\log(\text{time})$. This relation has been the basis for extrapolation techniques, as it may be assumed that long-term physical relaxation at a given temperature may be determined from short-term data.

7.4 TIME-TEMPERATURE SUPERPOSITION

The technique of time-temperature superposition uses short-term data obtained over a range of temperatures to predict the long-term viscoelastic behaviour of polymers.^{87,88,89} This method is based on the principle that the modulus of a viscoelastic material is a function of both temperature and time; thus, two methods can be used to determine a polymer's behaviour at longer times. First, by directly measuring the response at longer times, or secondly, by conducting a series of short time measurements at various temperatures and then using these short time test data from high temperature shifted accordingly to a longer time at lower temperature (refer to Figure 7.3). For the construction of the superposed curve, a horizontal shift to compensate for the change in time scale brought about by changing temperature, and an vertical shift to account for the change in modulus and density, are used.

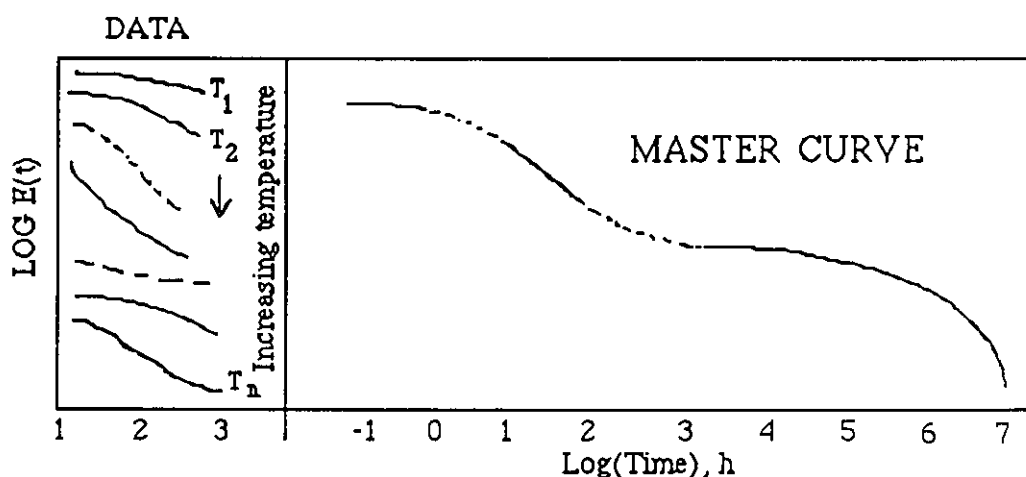


Figure 7.3: Preparation of master curve from experimentally measured modulus-time curves at various temperatures.

Each curve at temperature T can be shifted to a reference temperature T_0 along the horizontal time axis by a factor known as shift factor a_T . The temperature dependence of the shift factor is given by the WLF-equation⁸⁹

$$\log a_T = \frac{-C_1 (T - T_0)}{C_2 + T - T_0} \quad 7.11$$

where C_1 and C_2 are constants and depend on the material.

The vertical shift, b_T , to account for the inherent change in modulus brought about by a change in temperature can be applied by multiplying the corresponding values of the force or modulus by the correction factor, k , is given by:

$$k = T_0 \rho_0 / T \rho \quad 7.12$$

where T and ρ are the test temperature ($^{\circ}\text{K}$) and density, and T_0 is the reference temperature and ρ_0 is the density at the reference temperature.

The WLF- equation was originally developed for amorphous materials. Also the shift factor only allows for viscoelastic changes, and chemical relaxation effects cannot be taken into account. Many modifications have been applied to extend its applicability to lightly cross-linked systems and crystalline materials with varying degrees of success. The accuracy of the WLF-shift equation diminishes above $T_g + 120^{\circ}\text{C}$, and for rubbers this could be in the region of 50°C .

The use of time-temperature superposition to construct a master curve for cross-linked elastomers has been criticised for several reasons.^{22,90} Despite this, time-temperature superposition has been successfully carried out on nitrile and natural rubbers⁹¹ and poly-isobutylene compounds.⁸⁸ The work on natural and nitrile rubbers compared the superposed master curve with the data obtained after 16 years at 23°C . The measured values started deviating from the predicted values after 12 years for natural rubber and 6 years for nitrile rubber. The deviation is due to the dominance of chemical relaxation at longer times. This suggests that this method of extrapolation is not satisfactory for elastomers where chemical relaxation might be expected to play an important role, but time-temperature superposition is a possible method of extrapolation for other materials such as peroxide-cured EPDM and the thermoplastic elastomers discussed in Section 7.9.

7.5 CHEMICAL RELAXATION

Chemical relaxation is the dominant component of relaxation at elevated temperatures and over extended timescales. It involves the breaking and rearrangement of crosslinks and backbone chains, both from chemical reactions and as the results of stress; the relaxation times were found to be of the order of 10^7 to 10^9 s at 20°C ⁴⁴. The mechanisms responsible for this behaviour have been

discussed earlier in Chapter 1. Stress relaxation in tension has been widely used to study the ageing properties of elastomers and to test the effectiveness of antioxidants.^{45,46} Mechanisms of chemical relaxation have been widely investigated using Tobolsky's two-network theory by several workers^{51,52} (see Sec. 1.5.4)

Reactions of mono- and poly-sulphidic crosslinked vulcanisates of natural rubber⁵⁶ and polybutadiene, isoprene and SBR compounds⁹² have been shown to undergo first order reactions. Peroxide-cured natural rubber has also been shown to follow a similar process.⁴⁸

7.5.1 Extrapolation of relaxation mechanisms

The chemical reaction rates generally increase with the temperature. The temperature dependence of the rate coefficient of many reactions has been found to fit an expression first proposed by Arrhenius:

$$k = A \exp (-E/RT) \text{ or } \ln k = \ln A - E/RT \quad 7.13$$

where k is the rate constant, A is a constant, E is the activation energy of the process, R is the gas constant and T the absolute temperature. The above equation gives a straight line when $\ln k$ is plotted against the reciprocal of absolute temperature; from the slope of the line, the reaction rate at any desired temperature can be easily predicted.

The Arrhenius expression is empirical, but it is obeyed experimentally in many situations and is often a fair first approximation to the actual situation. Once a reaction is found to obey the Arrhenius relation, it can be conveniently used for the prediction of reaction rates at the temperatures of interest. This method of extrapolation has been used in several ways to model both the chemical^{93,94,95} and physical⁹⁶ relaxation behaviour.

7.6 MATHEMATICAL MODELS OF STRESS RELAXATION

Techniques for the extrapolation of the physical and chemical components have been described previously. In this section, various models for the separation of

these two entities, their separate extrapolation and recombination are considered.

7.6.1 The Aben technique

This method ^{22,93} is based upon the separation and then extrapolation of individual components contributing to the overall relaxation curve. The following assumptions are made:

1. physical relaxation is linear with $\log(\text{time})$ and chemical relaxation is linear with time.
2. the rate of physical relaxation is independent of temperature over long times.
3. the point at which the residual stress curve rapidly falls away from a linear relation with $\log(\text{time})$ is taken as the induction time for the chemical relaxation;
4. the induction time is a material property and is a function of temperature only
5. Several chemical relaxation mechanisms occur simultaneously at one temperature after the induction time; prior to this all relaxation is physical.
6. both, the induction time and the chemical relaxation follow a first order Arrhenius type relation.

Using stress relaxation data obtained at various temperatures, the induction times for chemical relaxation are determined. Arrhenius extrapolation is then applied to estimate the induction time at the required temperature. The physical relaxation, measured at this temperature, is then extrapolated to the induction time. Then the chemical relaxation is extrapolated. In order to do this, the extrapolated physical relaxation is subtracted from the total measured relaxation at each temperature, to give a series of chemical relaxation curves. The different degradation mechanisms are separated from the total chemical relaxation using 'Procedure X', suggested by Tobolsky ⁹⁷. Arrhenius extrapolation treatment is then applied to each mechanism to give the reaction rate at the required temperature. These extrapolated curves are added together to give the total chemical relaxation at the lower temperatures and longer time periods. The total extrapolated physical and the chemical relaxation are then recombined at the extrapolated induction time to give the predicted overall stress relaxation behaviour.

Wright ²² using this technique obtained a life time of 65 years for the nitrile rubber

compounds. The difficulty of the separation of chemical relaxation mechanisms was blamed for as the result did not correlate with the values obtained using other methods. However, Wright²² suggested that the accuracy of the technique can be greatly improved if relaxation data over one or two years are obtained. As data for this time period were produced during this programme, the Aben extrapolation technique has been used to predict the long-term behaviour of the elastomers. This is discussed in Section 7.8.1

7.6.2 The MRPRA method

This method was developed at the MRPRA laboratory to predict the creep behaviour of natural rubber mounts used as building supports.⁹⁸ It was found to give reasonable agreement between predicted and measured creep after 16 years. As in the Aben technique, this method also assumes that :

1. physical relaxation is logarithmic with time, and the chemical relaxation linear with time.
2. the total predicted relaxation is the combination of the extrapolated physical and the chemical relaxation mechanisms and is given by:

$$SR = A \log (t / t_0) + B (t - t_0) \quad 7.14$$

where A is the physical relaxation rate in % per decade of time
 B is the chemical relaxation rate in % per unit time, and
 t_0 is the time of the initial stress reading

The technique is much simpler to operate as it considers a single chemical process and not the splitting and recombination of the degradation mechanisms used in the earlier method. Physical relaxation data can be obtained from measurements over a few days. Chemical relaxation is measured at, for example, 50°, 60° and 70°C, and then extrapolated to the service temperature.

7.6.3 Other predictive techniques:

Most extrapolation techniques are based on the principle that the physical and chemical relaxation mechanisms can be separated, extrapolated to the required

temperature and then superimposed to give the predicted overall relaxation. For the separation of the two relaxation processes it is assumed that there exist a time or temperature range over which the chemical process can be neglected.

Russian workers^{94,96} have applied the Arrhenius treatment of extrapolation to stress relaxation data obtained at several temperatures using $\log(\text{stress relaxation})$ against linear time plots. The technique appears to have been successfully applied to nitrile rubber O-ring seals aged in oil in compression at 50°, 70°, 90° and 110°C.⁹⁴ Values of activation energy were calculated for the relaxation processes involved. The tests in tension were carried out over 1 hour, and under these conditions, it appears that physical relaxation would predominate. The tests in oil were longer term, from a period of several hours to over 400 days. However, no comparison of measured and predicted lifetimes was quoted, so it is not possible to comment critically on the technique.

An alternative procedure to measure the physical relaxation behaviour was suggested by Stenberg and Jansson.⁹⁹ They used the real and imaginary parts of the complex modulus, $E'(\omega)$ and $E''(\omega)$ respectively, at different frequencies and temperatures from dynamic measurements to find the total modulus¹⁰⁰ using:

$$E(t) = E'(\omega) - 0.4 E''(0.4\omega) + 0.014 E''(10\omega) \quad 7.15$$

where ω is the frequency. $E(t)$ was determined from measurements at frequencies between 50 μHz and 50 mHz . The relaxation modulus data were shifted to the same temperature at which compression stress relaxation data were measured. These measured curves were a combination of physical and chemical relaxation. The measured curves were compared with the predicted stress relaxation to determine the chemical components.

The method has some limitations. Firstly, it is based on the assumptions that there exist a time temperature range over which chemical relaxation can be neglected. Secondly, there may be a loss of accuracy in measurement at very low frequencies. Thirdly, the method requires an additional type of test, measurement of the complex modulus, to be added to relaxation measurements in order to predict life times.

Another separation and extrapolation technique is that of Curro and Salazar.^{101,102} This method uses the principle of time-temperature superposition principle to extrapolate the physical stress relaxation behaviour from the service temperature to a higher temperature; the extrapolated value is then subtracted from the total relaxation measured at the higher temperature to isolate the chemical component of the relaxation. From this, the kinetics of the chemical processes can be analysed. The chemical relaxation is then extrapolated to a lower temperature and recombined with the measured physical data to give the overall, long term relaxation.

This method also relies heavily on the assumption that the chemical relaxation may be neglected over a certain time scale at the temperatures of interest. The tests were carried out at temperatures between 25° and 110°C over 100h. For the data obtained in this programme this assumption is not justified, and cannot be applied universally over a wide range of elastomeric materials. The extrapolation of the chemical relaxation data assumes that the network reactions can be covered by a single first order reaction, which is also not applicable to all elastomers. Published data using this treatment have covered ethylene-propylene rubber and a fluoroelastomer, where the assumptions may be valid. However, as the method is so complex, and may be not applicable to all elastomers it will not be considered further.

7.7 SEAL LONGEVITY

It has been stressed^{103,104,105} that the success of predicting seal longevity in underground pipelines is important and this depends on the accuracy of the technique used. However, there is very little quantitative work reported. It is generally agreed that stress relaxation is mainly responsible for the loss of seal life when other factors such as failure due to microbiological degradation or fatigue are neglected. However, there are a few reported cases where natural rubber seals and bearings have lasted many tens of years in service^{106,107} where laboratory tests have suggested that the stress in these components should have decayed to zero. Sewer rings in London¹⁰⁶ that were installed over a century ago were retrieved, and the rubber found to have retained reasonable physical properties, with the potential for many more years of useful life. This suggests that other aspects, such as formation of a thick oxidised skin⁴ or surface adhesion effects may be involved in determining sealing performance.

A mathematical analysis of the mechanical behaviour of a compressed O-ring was made by Curro and Salazar.¹⁰⁸ They derived expressions by modelling the seal as an infinite cylinder compressed between parallel plates, on the following assumptions:

- the major diameter (D_o) of the O-ring is much larger than the cross-sectional diameter (D),
- there is no interference of the deflected ring with the sides of the groove, ie: the O-ring is unrestrained and bulge freely during deformation..

Using the time-dependence transforms, the viscoelastic effects were determined assuming the material to follow linear viscoelasticity.

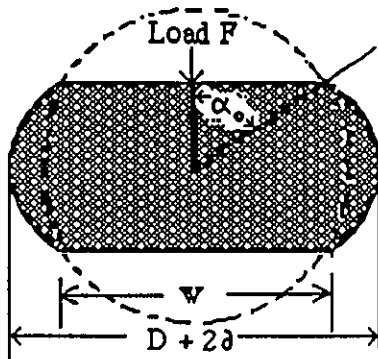


Figure 7.4:

**A cross-sectional view
of a deformed O-ring**

The sealing force, the average load per unit length was given by:

$$Q(t) = \frac{F}{\pi D_o} = \frac{\alpha_o^2 \pi D E(t)}{8 [1 - \nu^2]} \quad 7.16$$

Where α_o is the contact angle, ν is the Poisson's ratio, F is the total load, $E(t)$ is the modulus, D_o and D are the major and the cross-sectional diameters of the O-ring respectively. The above equation predicts that the reduction in sealing force with time is proportional to the change in sealing modulus, $E(t)$, with time. The expression could be rewritten in terms of the seal dimensions (Figure 7.4), as the contact angle can be estimated by:

$$\alpha_o \approx w/D \quad 7.17$$

where w is contact width of the seal against the pipe wall. Substituting this in

Equation 7.17 and rearranging:

$$Q(t) = \frac{\pi w^2 E(t)}{8 D [1 - \nu^2]} \quad 7.18$$

Their analysis on silicone rubber cylinders and O-rings gave reasonable agreement between theory and experiment for up to 15% strain. Beyond this level the theory was not expected to fit the data because of the non-linearity in the stress-strain curves of the rubber, but no measurements were made. However, stress relaxation rates in compression have been found to be fairly independent of the strain,^{4,61} so the expression may apply at higher strains.

Another analysis giving the compressive load per unit length was derived by Lindley;¹⁰⁹ his expression was:

$$Q(t) = \frac{w^2 \pi E(t)}{6 D} \quad 7.19$$

Lindley extended the analysis to consider the effect of a pressure difference across the seal, and the conditions necessary for leakage. Two cases were considered; firstly, when the frictional resistance of the rubber against the pipe surfaces is sufficient to preclude slip and secondly, when it is not. In the absence of slip, leakage will occur when the peak contact pressure is just exceeded by the pressure difference across the seal. This peak contact stress is given by:

$$f_{\max} = \frac{4 Q(t)}{2.4 \pi x} \quad 7.20$$

If P is the pressure difference across the seal, and e is the compressive strain ($= x/D$, where x is deformation) the condition for the sealing is given by:

$$\frac{3 \pi P^2}{16 E^2} < 1.25 e^{1.5} + 50 e^6 \quad 7.21$$

If E decreases with time, and the strain and pressure difference across the seal remain constant, then the quantity (P/E) will increase and approach the critical value of the maximum contact stress, leading to leakage.

A similar analysis was produced for the conditions under which the seal would slip ('blow-out' of the seal), leading to leakage. At a given radial strain,

failure would occur, theoretically, at the lower of the two pressures. In practice, the radial compression is not uniform around the seal, and a small amount of slip over a limited section of the ring could be restrained by the remainder of the ring which had not slipped. Besides, variation in annular gap due to the ovality of pipe and other dimensional variations needs consideration.

A comparison of stress relaxation rates with sealing ability¹¹⁰ concluded that the reduction in sealing force is about 4% per decade less than the stress relaxation measured in the laboratory samples of the same material. Russian work¹¹¹ has suggested that a seal must retain at least 10% of its initial stress to maintain adequate sealing. This work also proposed a simple Arrhenius extrapolation technique for the estimation of seal service life. Using stress relaxation tests at elevated temperatures, relaxation rates were determined, and extrapolated to the service temperature. The service lifetime was calculated using the expression:

$$\ln(X_1) - \ln(F.X_C) = k_T \cdot \tau \quad 7.22$$

where X_1 is the residual stress factor at 0.1 h, X_C is the critical residual stress factor (in this case 0.1), F is a safety factor, k_T is the extrapolated relaxation rate at the service temperature T , and τ is the service temperature.

According to Lyubchanaskaya et. al.¹¹² reliable sealing is only achieved by a certain contact pressure, occurring as a result of compression of the rubber on the sealing surfaces. The contact stress is a function of several factors such as the stiffness of the rubber (the modulus), the condition of the surface, the presence of lubricant and the type of the filler used.

There is some disagreement over whether compression set or stress relaxation is the better technique for the prediction of longevity and as a quality control test for seals. Several reports^{103,104,113} have stated that compression set is not directly related to stress relaxation or seal performance. Ellul and Southern¹¹⁴ compared stress relaxation and compression-set to investigate whether the simple compression- set test could be used instead of stress relaxation. They concluded that there was insufficient agreement between the two types of measurements to permit this. A similar conclusion was also reached by Dunn¹¹⁵ working with nitrile rubber seals.

7.8 RESULTS AND DISCUSSION

This section considers extrapolation of the data obtained at various conditions as described in Chapter Two. The extrapolated data are then applied to stress relaxation models; the predicted values are then compared with the observations. The procedure uses the techniques described earlier in this Chapter and the new empirical model given in Section 7.8.3

7.8.1 The Aben extrapolation technique

As described earlier in Section 7.6, first the physical relaxation is determined and separated from the total relaxation obtained over various temperatures. Then the chemical mechanisms are analysed and extrapolated to lower temperatures.

7.8.1.1 Determination of the physical relaxation:

The Aben technique assumes the physical relaxation to follow a linear relation with $\log(\text{time})$, and the chemical relaxation to be linear with linear time. Thus the slope of the residual stress factor (%RSF) vs $\log(\text{time})$ curve in the early part of relaxation process is considered to be the rate of physical relaxation occurring at that temperature. The values calculated using this procedure, over a period of first 1000 h. for different compounds, are listed in Table 7.1.

Table 7.1: Physical relaxation rates as a function of temperature

MATERIAL		Relaxation rate (%) per decade		
		5°C	23°C	40°C
NR,	A(N)	3.06	3.31	3.32
SBR,	B(N)	2.93	3.94	3.08
EPDM(S),	C(O)	5.33	5.37	4.81
EPDM(P),	D(N)	3.48	4.72	4.60
NBR,	E(O)	3.24	4.47	3.52
EPCL,	H(O)	4.94	5.68	5.43
Santoprene101.55,	I(O)	9.39	8.33	8.33
Evoprene992,	K(O)	6.88	6.95	7.83
Alcryn 6368,	M(O)	-----	10.21	14.94

7.8.1.2 Prediction of the chemical relaxation induction time

The deviation from a linear relation of stress relaxation with $\log(\text{time})$ is taken to indicate that the chemical relaxation is beginning to play a significant role in the overall relaxation. This type of behaviour is apparent in all the diene rubbers used in the present programme and in the sulphur-cured EPDM and the epichlorohydrin rubber.

Table 7.2: Comparison of predicted and measured chemical relaxation induction times.

Material	Induction time in hours			
	5°C		23°C	
	Predicted	Measured	Predicted	Measured
NR, A(N)	25900	>20000	5520	14000
SBR, B(N)	125427	>20000	17218	14200
EPDM(S), C(O)	223421	>24000	21830	13600
NBR, E(O)	444444	>24000	7818	16500
NBR, G(O)	42443	>24000	6174	14800
EPCL, H(O)	88229	>24000	13195	12500

Using the data obtained at elevated temperatures (40°, 70° and 100°C), the time at which the stress relaxation curve deviates from linearity was determined. Because of the logarithmic scale it is not possible to determine these times very accurately; besides, longer the induction time, greater is the error. Graphs of $1/T$, where T is the absolute temperature, versus $\ln(\text{induction time})$ are plotted; the gradient calculated and used to predict the induction times at 5° and 23°C. Where the data are available (those materials which showed early chemical relaxation), the predicted induction times are compared with the measured values to check the validity of the Arrhenius treatment. These data are shown in Table 7.2. Where a direct comparison of predicted and observed induction times is not possible; this is also indicated in the above Table.

7.8.1.3 Separation of the chemical relaxation mechanisms

Graphs of the total relaxation are plotted and the physical relaxation is

extrapolated beyond the induction time. The extrapolated physical relaxation is then subtracted from the total relaxation to give the residual chemical relaxation. The chemical relaxation is replotted with a linear time scale. Procedure X⁹⁷ is then applied - a tangent is drawn to the chemical relaxation curve to give the rate constant for the first mechanism. The intercept of the residual stress axis gives the percentage contribution of this mechanism to the overall chemical relaxation. This extrapolated tangent is subtracted from the chemical relaxation and another tangent drawn to the remaining curve. The procedure is repeated until all the mechanisms are accounted for, and for all the test temperatures where it is possible to determine the induction time. The method then assumes that each reaction obeys a simple Arrhenius process, and the rate and contribution of each mechanism can be calculated at lower temperatures. The procedure is used for two materials, natural rubber and nitrile rubber; the results are available in Table 7.3 below.

Table 7.3: Application of the Aben technique for the separation of the chemical relaxation mechanisms.

Temperature	Reaction	Natural Rubber, A(N)		Nitrile Rubber, E(O)	
		Rate constant (%per hour)	Contribution (%)	Rate constant (%per hour)	Contribution (%)
40°C	1	9.41×10^{-4}	90	4.7×10^{-4}	93
	2	None		1.2×10^{-3}	5
70°C	1	1.8×10^{-3}	28	5.3×10^{-4}	46
	2	8.6×10^{-3}	39	5.2×10^{-3}	42
	3	2.1×10^{-2}	28	1.8×10^{-2}	20
100°C	1	7.1×10^{-3}	48	8.4×10^{-3}	63
	2	4.5×10^{-2}	42	2.8×10^{-2}	36
	3	None		None	

7.8.1.4 Extrapolation of the chemical relaxation

For the nitrile rubber, the Arrhenius extrapolation predicted a rate of 1.13×10^{-4} % per hour for reaction 1 at 23°C, and this reaction contributes 96% to the overall chemical relaxation. The contribution of the second reaction is only 2% at 23°C,

and at a rate of 3.6×10^{-4} % per hour. These two reactions occur only after an induction time of 0.89 years. It is not possible to extrapolate the natural rubber data by a simple Arrhenius treatment.

7.8.1.5 Prediction of stress relaxation

If the physical relaxation rate of the nitrile rubber is assumed to be constant at 4.47% per decade, its contribution to the total relaxation may be calculated. From the start of the test until $t = 7818$ h (0.89 years) only physical relaxation is involved. After this time, in addition to the physical relaxation there is chemical relaxation. As there are two degradation mechanisms, it is necessary to calculate the relative contributions separately. Thus the total relaxation after a period of, say 25 years, is predicted to be 53.7%; 28.4 % due to physical and 25.3% due to chemical relaxation (i.e: reaction 1= 23.7%, reaction 2 = 1.6%). The relaxation of the nitrile rubber after 24000 h is predicted to be 26.7% at 23°C. The measured relaxation is 20.4 % (ie: RSF=79.6%).

7.8.1.6 Discussion of the Aben technique

There is considerable difference between the measured and predicted stress relaxation values using this technique. The major contribution to the error is the estimate of the chemical relaxation induction time. The extrapolation predicts it should be 7818h at 23°C for the nitrile rubber, E(O), but the measured induction time is found to be 16500 h. In general, the predicted induction times show little relation to the measured data, particularly for the 5° C data. The technique also requires data to be collected over a considerable timescale, at least 10000h depending upon the material. The procedure for separating the chemical relaxation mechanisms by drawing tangents to curves is subjective, and introduces errors into the extrapolation. These problems are probably encountered because the technique was developed for tensile stress relaxation, where chemical relaxation may occur sooner, due to thinner specimens used.

7.8.2 The MRPRA method

This technique is described in Section 7.6.2. In this method, the residual stress factor (RSF) at any given time t can be written as:

$$\text{RSF (\%)} = 100 - \{ A \log (t/t_0) + B (t - t_0) \} \quad 7.23$$

where A is the physical relaxation rate in % per decade of time

B is the chemical relaxation rate in % per unit time, and

t_0 is the initial time

Physical relaxation rates are obtained from the first 1000 h of each stress relaxation test at 5° and 23° C (refer to Table 7.1). For all the materials where chemical relaxation is involved as in the sulphur-cured natural rubber, SBR, EPDM(S), nitrile rubber and epichlorohydrin rubber, the induction times at 5° and 23°C are obtained by extrapolation. The chemical relaxation rates at 40°, 70° and 100°C are calculated; using an Arrhenius treatment, rates at lower temperatures are determined. Where chemical relaxation is apparently negligible at all temperatures within the timescales of the experiments (eg: peroxide-cured EPDM and TPE's), the chemical relaxation rate, B, is set to zero. The times at which the residual stress factor (RSF) would have fallen to 30 % (the nominal failure criterion used in the present programme) and to 10% (the requirement for sealability¹¹) are determined; in fact, the stress in the rubber does not reach zero value prior to the seal failure. The values are listed in Tables 7.4 and 7.5.

Table 7.4: Predicted time (years) for the residual stress factor to fall to 30% at 5° C and 23°C

Material	5° C	Predicted Time in Years	
		Predicted (Method 1)	Predicted (Normalised)
NR,	A(N)	59.7	63.6
SBR,	B(N)	22.5	23.3
EPDM(S),	C(O)	104.4	243.1
NBR,	E(O)	110.0	156.6
NBR,	G(O)	77.2	83.6
EPCL,	H(O)	49.8	64.5

Material	23° C	Predicted Time in Years	
		Predicted (Method 1)	Predicted (Normalised)
NR,	A(N)	16.5	17.5
SBR,	B(N)	8.1	8.5
EPDM(S),	C(O)	28.6	57.6
NBR,	E(O)	22.7	29.9
NBR,	G(O)	18.0	21.2
EPCL,	H(O)	14.5	18.0

Two procedures for determining the chemical relaxation rates are used. The first method assumes that, after the induction time, physical relaxation is negligible and all relaxation is chemical. In the second method, the physical relaxation is extrapolated beyond the induction time and this extrapolated curve subtracted from the total relaxation curve (the combination of physical and chemical relaxations). The chemical relaxation rates obtained by this method are referred to as the normalised chemical relaxation data.

Table 7.5: Predicted time (years) for the residual stress factor to fall to 10% at 5°C and 23°C

Material	5 °C	Predicted Time in Years	
		Predicted (Method 1)	Predicted (Normalised)
NR,	A(N)	80.1	85.5
SBR,	B(N)	31.0	32.1
EPDM(S),	C(O)	164.5	387.1
NBR,	E(O)	155.3	221.0
NBR,	G(O)	108.8	117.8
EPCL,	H(O)	75.4	97.9

Material	23 °C	Predicted Time in Years	
		Predicted (Method 1)	Predicted (Normalised)
NR,	A(N)	22.8	23.6
SBR,	B(N)	11.4	12.0
EPDM(S),	C(O)	44.8	92.2
NBR,	E(O)	33.2	43.9
NBR,	G(O)	26.6	31.5
EPCL,	H(O)	21.4	26.7

In Table 7.6, the predicted and measured residual stress factors after 20,000 h at 5° C and 23° C are calculated using Equation 7.23. The predicted values are in agreement with the experimental values for the natural rubber, the sulphur-cured EPDM, softer NBR at 5° C and SBR at 23° C. For other materials there is a significant difference between the predicted and the measured stress relaxation.

As the major contribution to the total stress relaxation under these conditions is physical relaxation, the accuracy of extrapolation must be considered. Physical relaxation rates are calculated from the first 1000 h data, plotted on a logarithmic scale, with the first measured RSF taken at 0.1 h after loading is completed.

Table 7.6: Comparison of predicted and measured RSF(%) at 20000h using MRPRA method and Equation 7.23 at 5° and 23°C

Material 5° C		Residual Stress Factor (%) after 20000 hours		
		Predicted (Method 1)	Predicted (Normalised)	Measured
NR,	A(N)	88.1	88.2	87.2
SBR,	B(N)	79.2	79.4	74.7
EPDM(S),	C(O)	71.3	71.5	70.3
NBR,	E(O)	81.8	82.1	80.2
NBR,	G(O)	81.3	81.6	73.1
EPCL,	H(O)	72.1	72.5	62.6

Material 23° C		Residual Stress Factor (%) after 20000 hours		
		Predicted (Method 1)	Predicted (Normalised)	Measured
NR,	A(N)	80.8	81.2	76.7
SBR,	B(N)	65.8	66.5	64.9
EPDM(S),	C(O)	69.0	70.4	63.0
NBR,	E(O)	71.5	73.2	79.6
NBR,	G(O)	69.3	70.2	73.2
EPCL,	H(O)	63.6	64.9	60.9

Thus the initial time t_0 in Equation 7.23 is 0.1 h. From the Figures 1-23 in the Appendix, it can be seen that, in general, the residual stress factor at 0.1 h is not 100 %. Equation 7.23 may be modified to take this into account:

$$RSF (\%) = F_{0.1} - \{ A \log (t/t_{0.1}) + B (t - t_{0.1}) \} \quad 7.24$$

where $F_{0.1}$ is the measured RSF at 0.1 h.

RSF values predicted using Equation 7.24 are listed in Table 7. 7. Values predicted using this expression are much closer to the measured values than those predicted using Equation 7.23, except in the case of nitrile rubbers at 23°C and the SBR at 5°C. Thus, it implies that the rapid physical relaxation in the early part of the relaxation process, although vital in understanding the viscoelasticity of the material such as hysteresis and MEF, should be neglected in the prediction of longevity.

Errors may be introduced during the extrapolation of the chemical relaxation from higher temperature data. Besides, the model assumes that there is a single relaxation process at all temperatures (unlike the Aben model, which allows for several relaxation mechanisms).

Table 7.7: Comparison of predicted and measured RSF(%) at 20000h using MRPRA method and Equation 7.24 at 5° and 23°C

Material	5 °C	Residual Stress Factor (%) after 20000 hours		
		Predicted (Method 1)	Predicted (Normalised)	Measured
NR,	A(N)	90.8	91.0	87.2
SBR,	B(N)	69.9	70.1	74.7
EPDM(S),	C(O)	71.9	72.2	70.3
NBR,	E(O)	79.9	80.2	80.2
NBR,	G(O)	70.6	70.8	73.1
EPCL,	H(O)	64.4	64.8	62.6

Material	23 °C	Residual Stress Factor (%) after 20000 hours		
		Predicted (Method 1)	Predicted (Normalised)	Measured
NR,	A(N)	76.8	77.3	76.7
SBR,	B(N)	61.9	62.5	64.9
EPDM(S),	C(O)	63.5	64.9	63.0
NBR,	E(O)	69.7	71.4	79.6
NBR,	G(O)	66.5	67.3	73.2
EPCL,	H(O)	57.4	58.7	60.9

Other sources of error may be in the calculation of the chemical relaxation rate, due to difficulties in the determination of the induction time for lower temperatures or at longer times, and in the extrapolation of physical relaxation at higher temperatures (where chemical relaxation started relatively quickly and only a few points are available for extrapolation of the linear portion of the curve). Such errors in the predicted chemical relaxation rate will have little effect on the total predicted relaxation at 5° and 23° C for short time scales, but will be more significant for predictions over a period of 50-100 years.

For physical relaxation, however, using Equation 7.24 instead of 7.23 would only lead to a difference of 1.3 year in the time predicted for natural rubber to relax to 30 % of the original stress at 23° C (Table 7.4). In order to reduce uncertainties in the predicted chemical relaxation, either more data over a longer period at 40° C, in excess of the length of tests in this programme, would be required, or an extrapolation from higher temperatures, such as 50° or 60° C, to provide more information on the chemical relaxation within a shorter timescale is necessary. Because the Method 1 of the MRPRA technique assumes that all the relaxation after the induction time is chemical, this leads to an overestimation of the chemical mechanisms and results in smaller values of the

predicted residual stress and hence the longevity of sealing behaviour. This is clear when the results from the two methods are compared(Tables 7.4 - 7.7 above).

7.8.3 The new empirical model

This is a new technique which arose in the programme. In this method, the stress relaxation is plotted as log(RSF) vs log(time) and lin(time). Physical relaxation rates may be determined in the usual way, whereas chemical relaxation rates at higher temperatures are calculated from log(RSF) vs lin(time) plots, and used to determine the rates at lower temperature (23°C) using Arrhenius extrapolation technique. It has been found empirically that reasonable agreement between predicted and measured relaxation data are obtained (Table 7.8) using the following expression:

$$\log(\text{RSF}) = \log(\text{RSF})_{1.0} - (C \log t + D \cdot t) \quad 7.25$$

where $(\text{RSF})_{1.0}$ is the RSF after 1.0 h,

C is the physical relaxation rate from the log/log plot and

D is the chemical relaxation rate from log/lin plot.

Table 7.8: Predicted and measured RSF at 24000 h, and the predicted RSF at 50 years at 23°C using the new empirical model.

Material 23 °C	% RESIDUAL STRESS FACTOR		
	Predicted 24000 h	Measured 24000 h	Predicted 50 years
NR, A(O)	63.0	78.9	0.05
EPDM(S),C(O)	64.1	63.0	56.5
EPDM(P),D(O)	65.4	67.0	23.3
NBR, E(N)	68.2	78.3	1.0

Note that Equation 7.25 is derived on practical terms. The values of predicted and measured RSF using this new method are compared in Table 7.8.

Both these extrapolations, using Log(RSF) or Lin(RSF), demonstrate the importance of using values of the chemical relaxation rate that are as accurate

and long term as possible. For compressive stress relaxation, this requires data to be obtained at elevated temperatures over at least 10,000 h and preferably 20,000 h.

7.8.4 Extrapolation of the physical relaxation

For materials where there is no apparent chemical relaxation within the timescale of the test (24,000 h so far), both the Aben and MRPRA methods predict the same amount of relaxation, as they both assume the physical relaxation rate is constant with the logarithm of the elapsed time. Data is extrapolated using Equation 7.24, with the constant B (Chemical relaxation rate) set to zero. The predicted residual stress factors after 20,000 h and after 50 years are given in Tables 7.9 and 7.10 and also the measured RSF after 20,000 h.

Table 7.9: Extrapolation of the physical relaxation data
- the residual stress factors (%RSF) at 5° C

Material	5° C	RESIDUAL STRESS FACTOR (%)			
		Predicted 20,000 h	Measured 20,000 h	Predicted 50 years (Egen.7.24)	Predicted 50 years (Egen. 7.26)
EPDM (P),	D(N)	72.4	70.5	67.7	-----
EPDM (P),	F(O)	68.0	72.2	61.9	-----
Santoprene 101.55,	I(O)	41.7	49.4	29.1	49.2
Santoprene 101.64	J(O)	39.7	42.5	31.0	36.9
Evoprene 992,	K(O)	61.3	60.2	52.1	53.3
Evoprene 994,	L(O)	53.3	53.4	44.7	44.3

For the peroxide-cured EPDMs the predicted residual stress factors (RSF) at 20,000 h at both 5° C and 23° C are similar to measured values, as are those for Santoprene 101-64 and both Evoprene compounds at 5° C.

The predictions for the Santoprene and Evoprene compounds are, in general, pessimistic compared with the measured values. This is due the shape of the stress relaxation curves for these materials (refer to Figure 4.7),

**Table 7.10: Extrapolation of the physical relaxation data
- Residual stress factors (%RSF) at 23°C**

MATERIAL (23°C)	RESIDUAL STRESS FACTOR (%)			
	Predicted 20,000 h	Measured 20,000 h	Predicted 50 years (Egen. 7.24)	Predicted 50 years (Egen. 7.26)
EPDM (P), D(N)	68.7	66.6	60.0	----
EPDM (P), F(O)	56.1	53.9	45.5	----
Santoprene 101.55, I(O)	46.9	50.3	34.0	47.2
Santoprene 101.64 J(O)	39.5	39.8	18.1	37.8
Evoprene 992, K(O)	50.3	55.3	40.9	55.6
Evoprene 994, L(O)	47.9	50.8	35.7	49.5
Alcryn 6368, M(O)	41.2*	43.4*	23.5	----
Alcryn 6385, N(O)	38.8*	39.4*	19.7	----
Alcryn 1201, O(O)	35.6*	34.8*	6.5	----

* 11000h data are used here.

where a reduction in the rate of relaxation apparently occurs after certain time, t_c , where t_c is a function of loading rate and is approximately about 1000h when normal loading conditions are used as stated earlier in the programme. The predicted RSF's at 11000 h for the Alcryn are reasonably near to the measured values.

Using the data obtained over 24,000 h the predicted RSF after 50 years may be determined for the Santoprene and Evoprene compounds using:

$$\text{RSF (\%)} = F_{1000} - A' \log(t/t_{1000}) \quad 7.26$$

where F_{1000} is the RSF at 1000 h, where the change in relaxation rate occurs, and A' is the relaxation rate after the change. These calculated values are given in the final column in Tables 7.9 and 7.10.

7.9 TIME-TEMPERATURE SUPERPOSITION

Time-temperature superposition, described in Section 7.4, is carried out on data for several materials. Stress relaxation curves at 5°, 23°, 40°, 70°, 100°C, and 125° C where available, are plotted as the variation of corrected force with $\log(\text{time})$; the vertical shift factor is applied to the data to obtain the corrected force, taking account of the change in material properties with temperature. 23° C is chosen as the reference temperature. All curves are plotted on the same axes. A horizontal line is drawn from the 0.1 h corrected value of the 40° C curve and the intersection of this line with the 23°C curve is determined. The elapsed time at which the intersection occurred gives the shift factor, a_T , for the 40°C data. This procedure is repeated for other temperature data, and the superposed curve is constructed. The results are given in Figures 7.5 to 7.13. Values of a_T are used to calculate the constants in the WLF equation, for comparison with values in the literature.⁹¹

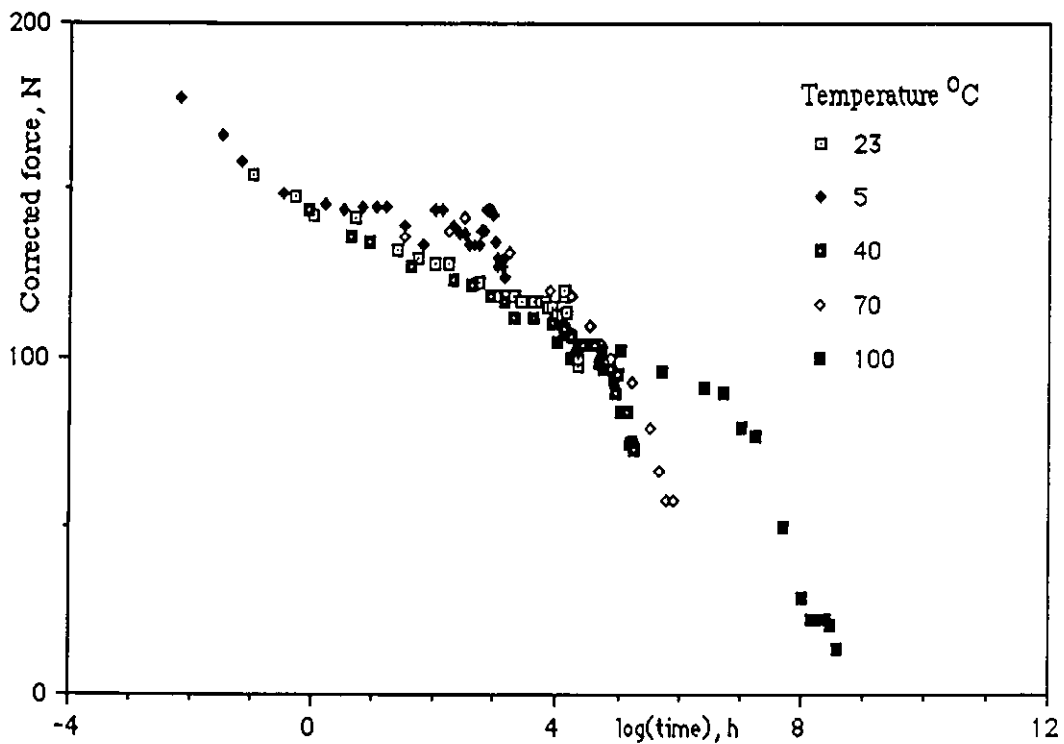


Figure 7.5: Time-temperature superposition, sulphur-cured SBR

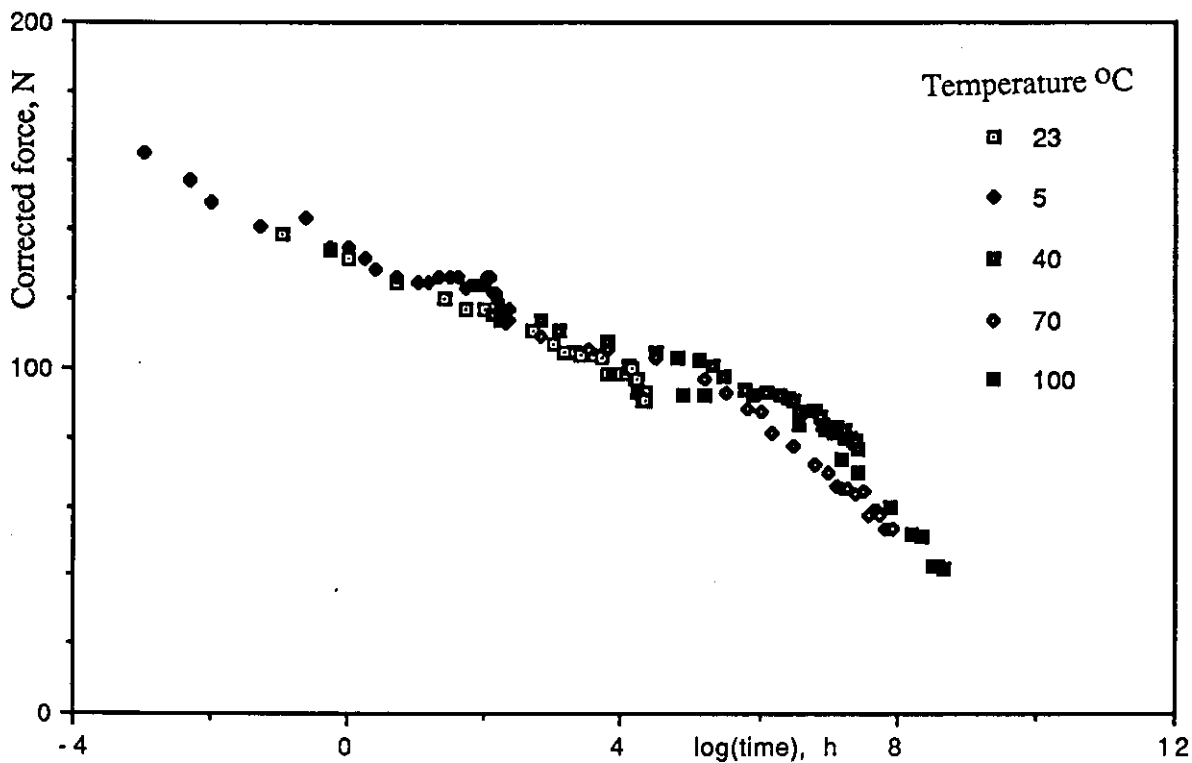


Figure 7.6: Time temperature superposition, sulphur-cured EPDM

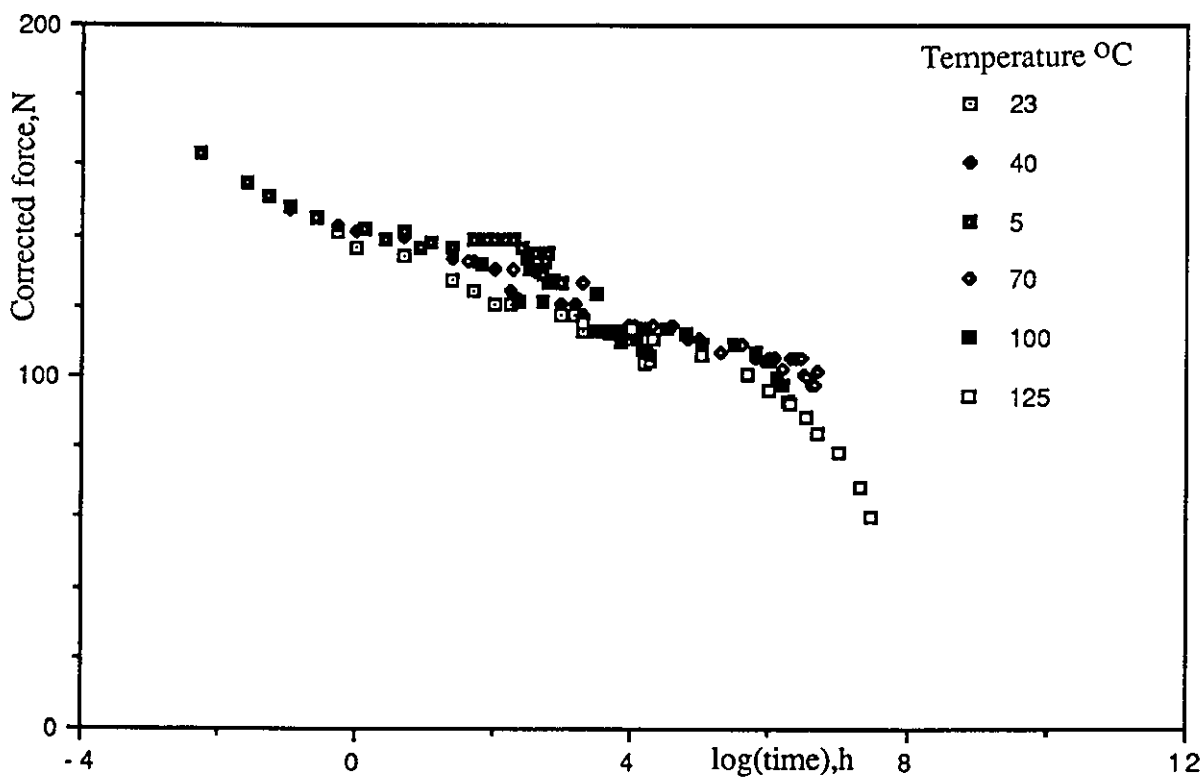


Figure 7.7: Time-temperature superposition, peroxide-cured EPDM

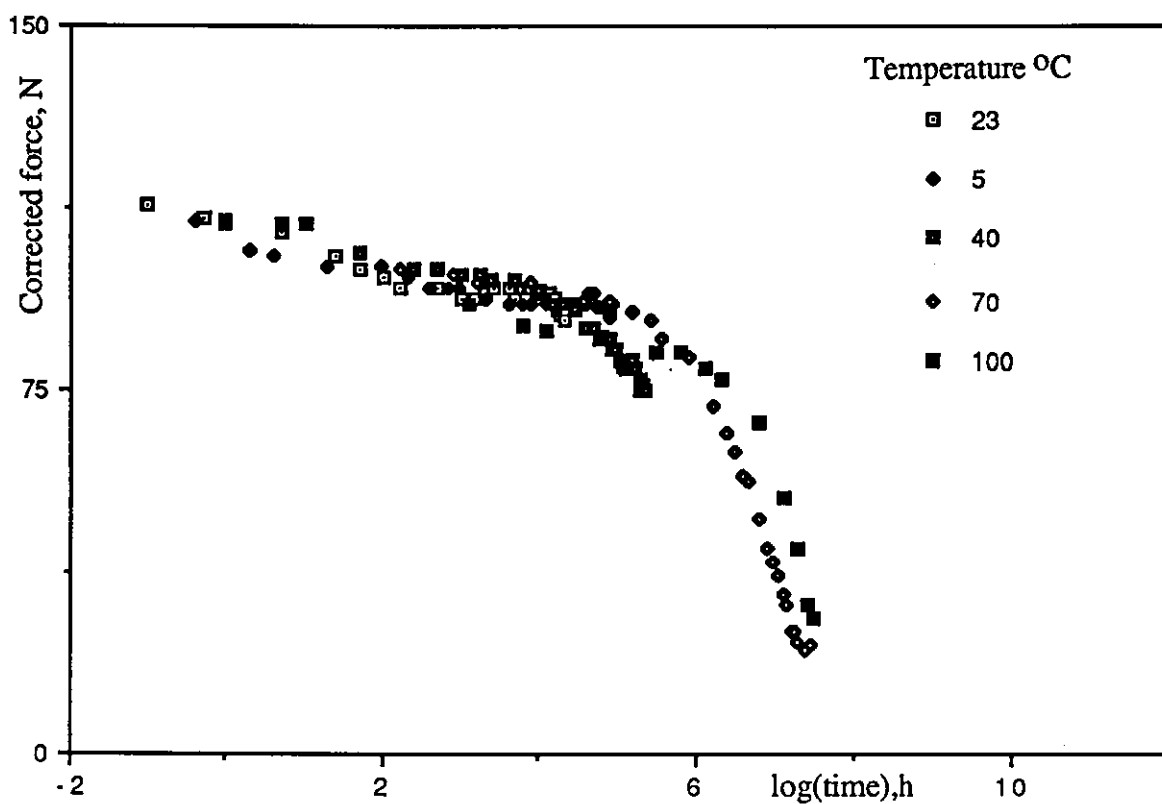


Figure 7.8: Time-temperature superposition, NBR(50 IRHD)

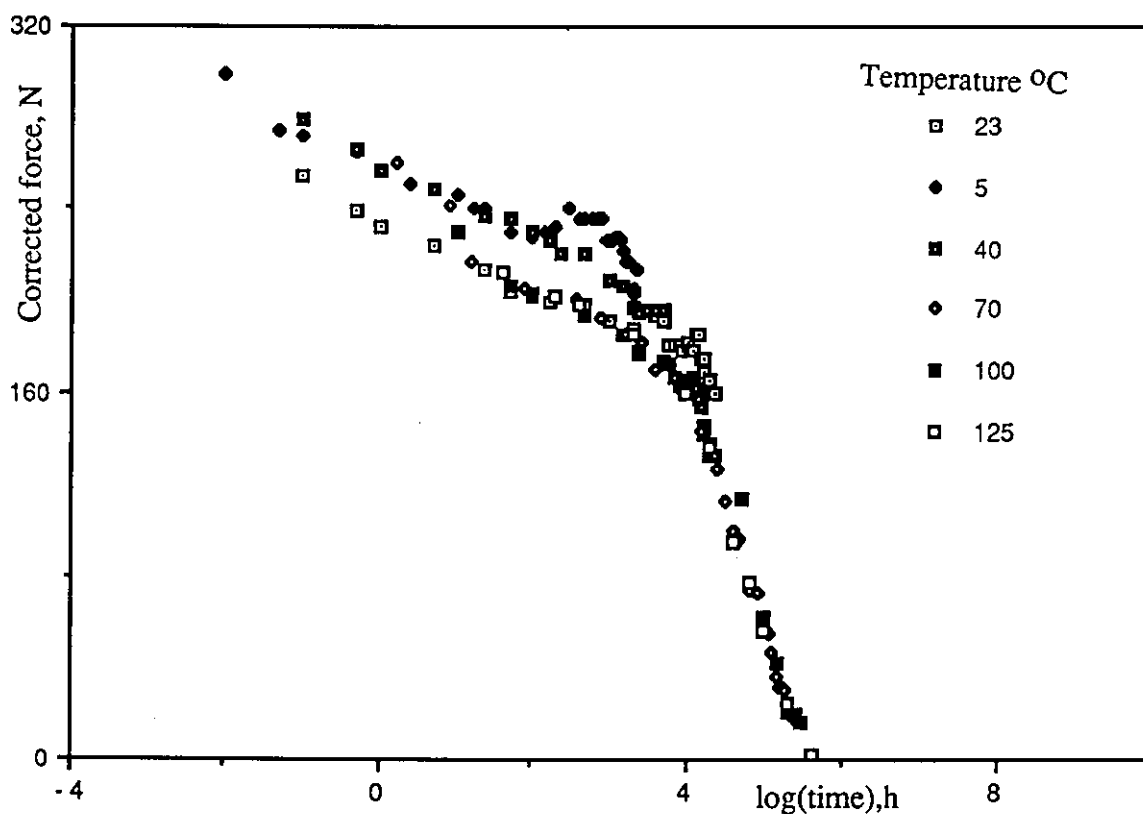


Figure 7.9: Time-temperature superposition, Epichlorohydrin rubber

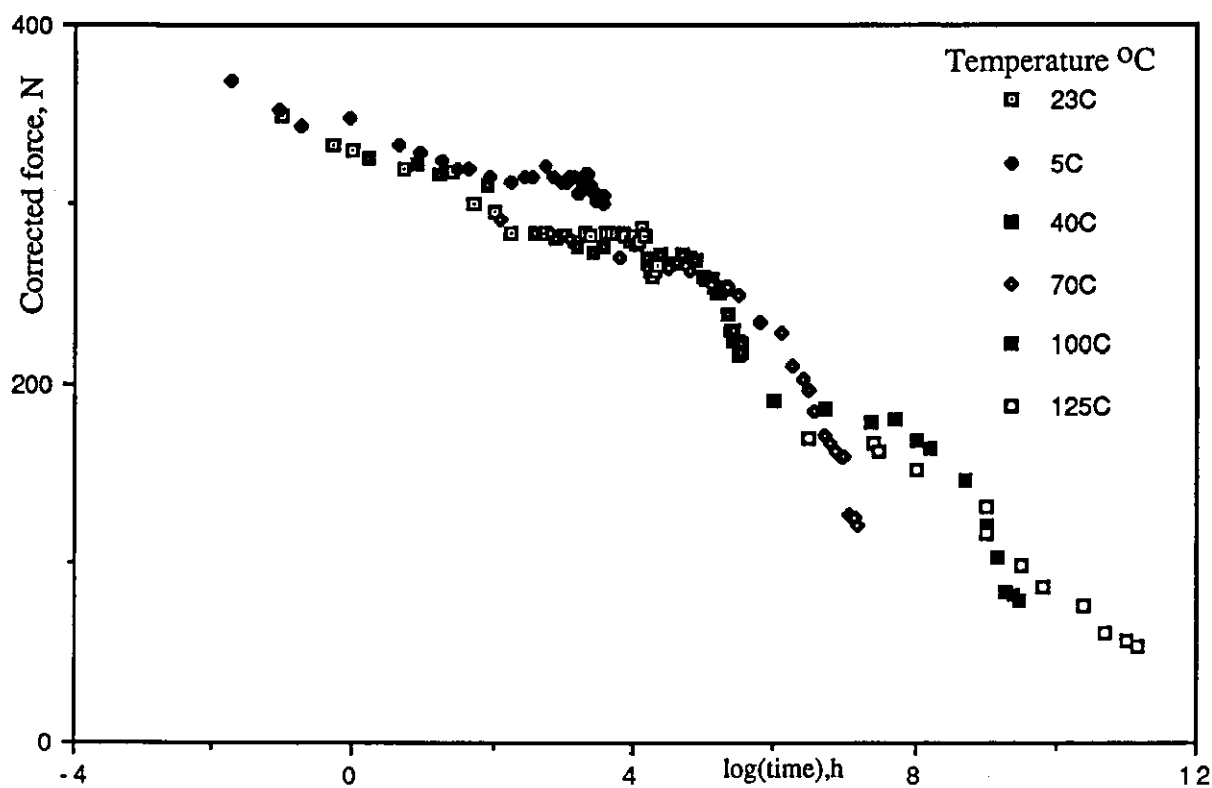


Figure 7.10: Time-temperature superposition, Nitrile rubber (70 IRHD)

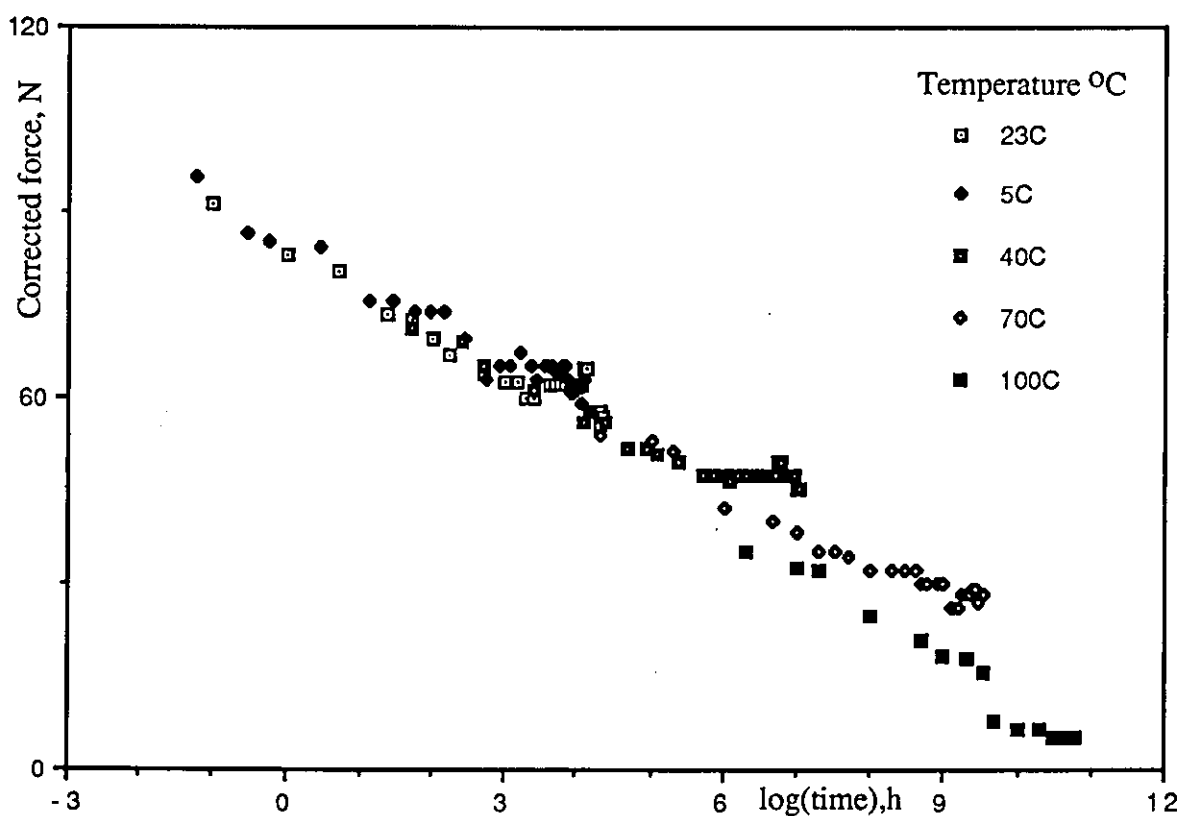


Figure 7.11: Time-temperature superposition, Evoprene 992

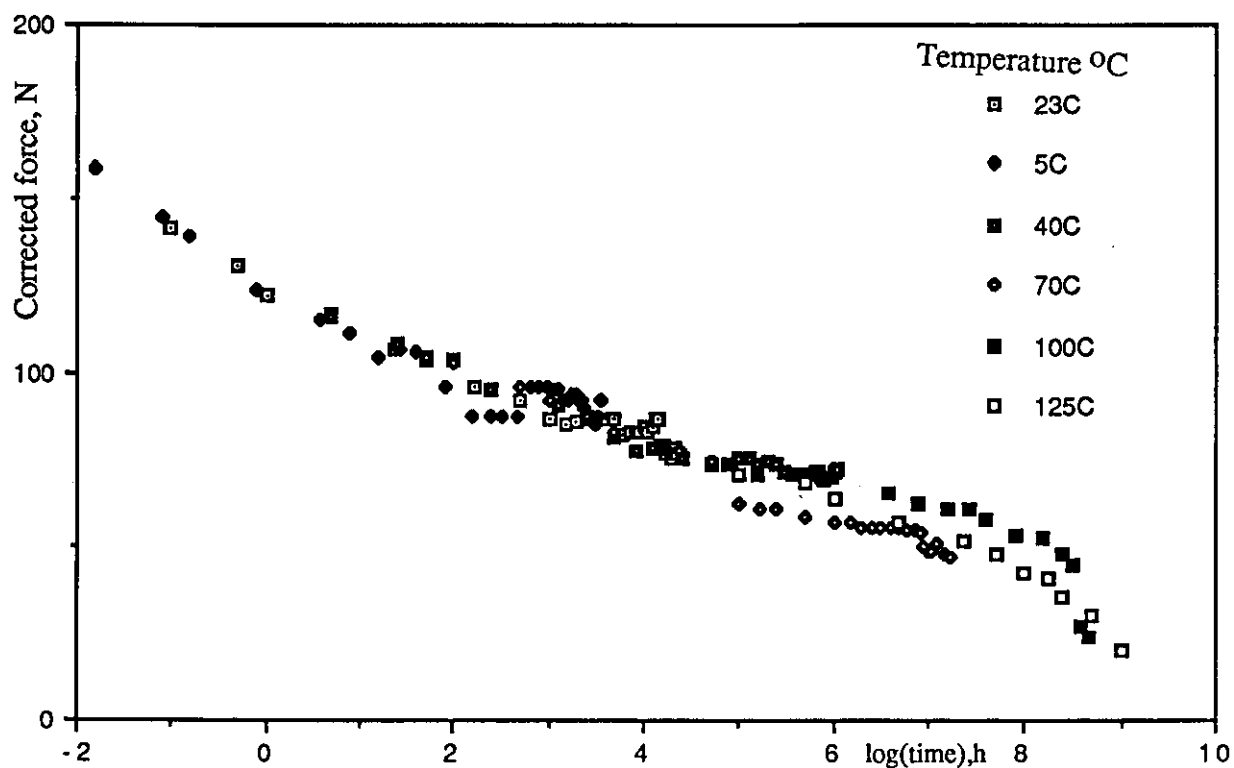


Figure 7.12: Time-temperature superposition, Santoprene 101-55

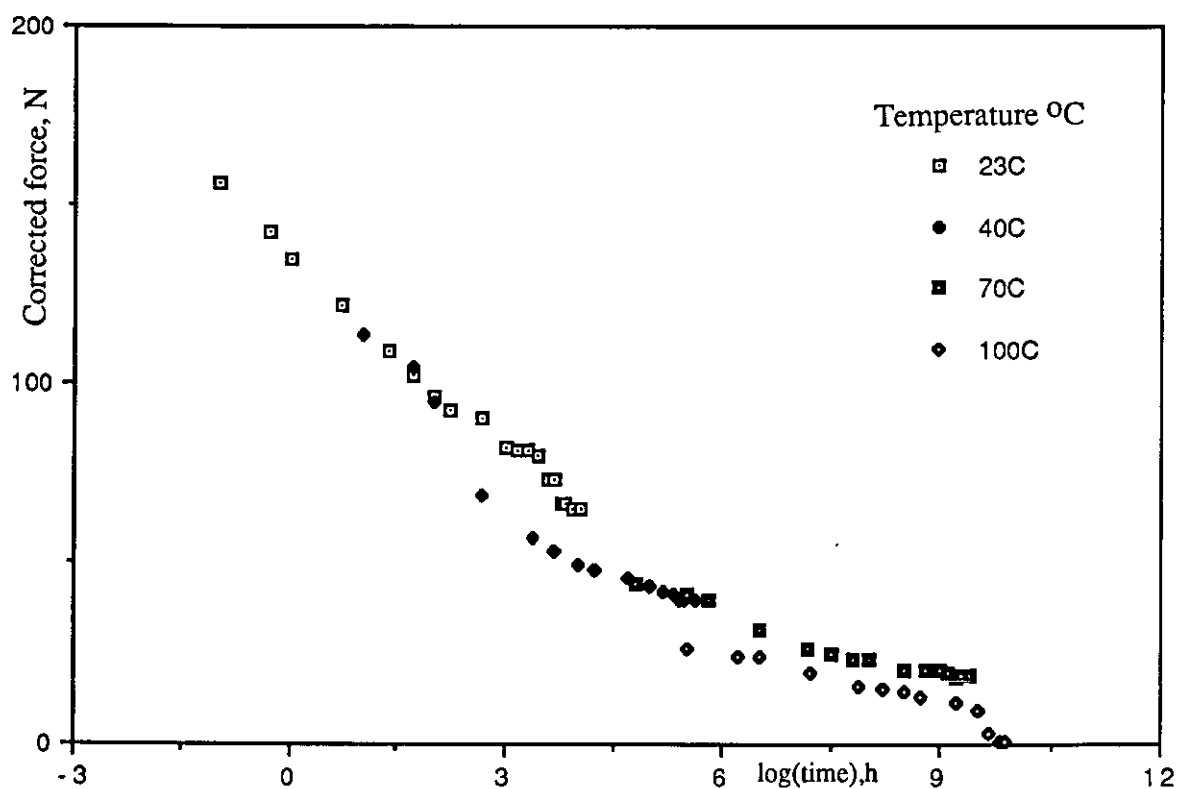


Figure 7.13: Time-temperature superposition, Alcryn 6385

7.9.1 Discussion of the superposition principle

Where the material does not show a large deterioration in properties as the temperature is increased as in peroxide-cured EPDM and TPE's such as Santoprene 101-55 and Evoprene 992, there is reasonably good agreement between time-temperature superposition and the MRPRA predictions (refer to Table 7.11). Where there is considerable chemical relaxation, however, time-temperature superposition does not take this into account, and deviations from the master curve are apparent.

Table 7.11: Comparison of predicted residual stress factor(% RSF) after 50 years [6.6 decades] at 23°C using various techniques.

MATERIAL		Residual Stress Factor at 50 years (%), 23°C	
		Time-temperature	MRPRA
SBR,	B(N)	54.8	0
EPDM(S),	C(O)	68.0	43.0
EPDM(P),	D(N)	69.0	60.1
NBR,	E(N)	63.0	2.1
EPCL,	H(O)	10.0	0
Santoprene 101.55,	I(O)	46.4	47.2
Evoprene 992,	K(O)	44.2	55.6
Alcryn 6368,	M(O)	20.0	19.7

As the stress relaxation curves have relatively small slopes, errors in the horizontal shift factors are possible. Typical errors in $\log a_T$ of ± 0.3 are quoted by Meier.⁹¹ A criterion for satisfactory superposition is that the coefficients C_1 and C_2 of the WLF equation (Equation 7.12) should have magnitudes comparable to those previously found for similar materials. Values for natural rubber and nitrile rubber are slightly lower than those found by Meier.⁹¹

7.10 ARRHENIUS EXTRAPOLATION OF DATA

Russian methods of extrapolation^{94,95} use the relaxation rate calculated from $\log(\text{stress relaxation})$ as a function of linear time, treated as simple Arrhenius process. The technique assumes that only chemical relaxation process occur at

high temperature and long timescales. Stress relaxation data obtained for natural rubber are plotted in this way (Figure 7.14), and relaxation rates calculated for the 40°, 70° and 100° C data, for the straight line portion of the curves, and the data extrapolated using an Arrhenius treatment. However, the data do not follow the Arrhenius relation sufficiently well to permit accurate prediction of stress relaxation rates at 5° and 23° C. The extrapolation actually predicts a slight increase with increasing time, with a rate of $7.58 \times 10^{-6} \%$ per hour. The measured rate of stress decay is $8.43 \times 10^{-6} \%$ per hour. Because the lower temperature data have such shallow slopes, considerable errors may be introduced into the extrapolation and this probably accounts for the prediction of an increase in stress with time. The method is based on the assumption that all physical relaxation is completed after about 2 days at 50°C, but this assumption is not supported by the experimental results.

A similar technique, but using a log(time) stress relaxation plot, has been proposed in a draft Swedish standard. This uses an Arrhenius treatment of data obtained at 70°, 85° and 100°C, extrapolated to 10° C. The stress relaxation test is carried out until a residual stress of 25% is reached. The times at each temperature for the stress to relax to 25% are then used in the extrapolation. If a relaxation of 75% is not achieved after 9 months at 70° C, the extrapolation is carried out with the actual result after 9 months.

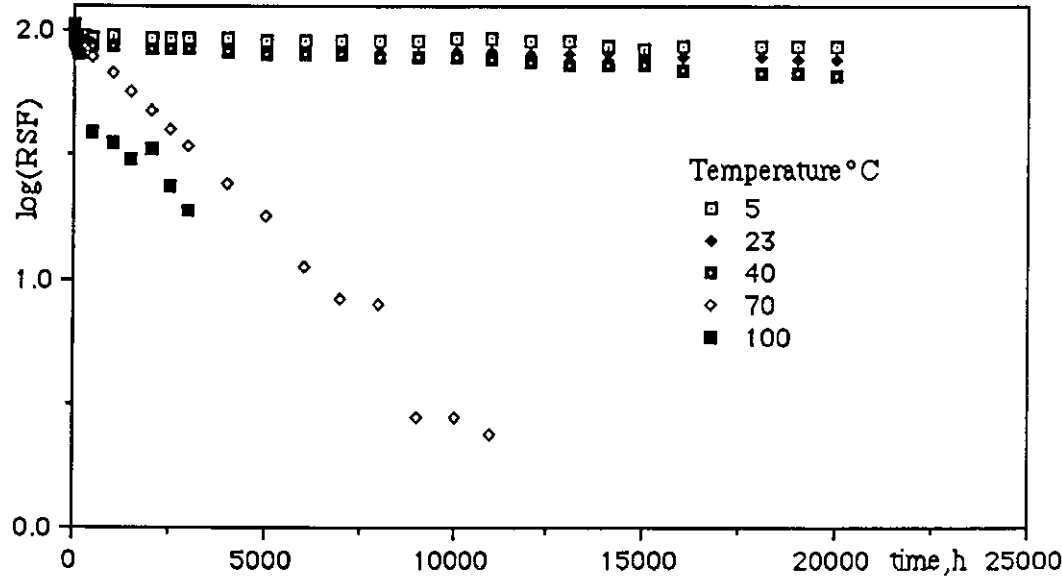


Figure 7.14 Stress relaxation plots for the natural rubber, log (%RSF) vs lin (time)

The standard also specifies that tests at 125° C may be used, if a quick preliminary result is needed. The method is tried using the data obtained in the programme at 70°, 100° and 125° C, as the nearest temperatures available, and extrapolating data to 5° and 23° C. For all the materials considered, the residual stress factor did not reach 25% within 9 months at 70°C, and so extrapolations are carried out using the residual stress actually obtained. The comparison of predicted and measured times for the stress to relax to the relevant values is given in Table 7.12. The predictions for the two peroxide-cured EPDMs are considerably greater than the measured values, but it is not possible to comment on the predictions for the other EPDM and Santoprene 101-64.

Table 7.12: Comparison of predicted and measured times (h) for the RSF to reach relevant values at 23°C.

Material		RSF(%)	Predicted (hours)	Measured (hours)
EPDM(S),	C(O)	55.5	2.2×10^6	>24000
EPDM(P),	D(N)	82.6	6.9×10^5	23
EPDM(P),	F(O)	77.5	3.3×10^5	5
EPCL,	H(O)	25.0	1.9×10^5	>24000
Santoprene101-55,	I(O)	51.6	5.1×10^5	14500
Santoprene101-64,	J(O)	45.5	5.6×10^5	14800

It has also been suggested⁹⁶ that physical relaxation data obtained from the linear part of the residual stress/log(time) curve might be extrapolated to lower temperatures using the Arrhenius relation. This will permit the rate at the seal working temperature to be calculated. This was carried out on the physical relaxation data obtained during the programme, but the method is unsatisfactory, as the data do not fit an Arrhenius relation. It appears unlikely that physical processes can be represented in this way.

7.11 DISCUSSION OF MATHEMATICAL MODELS

The Aben technique for separation of the relaxation processes can not be applied with any real success to the long term data obtained during the

programme. Predicted relaxation at 5° and 23° C is, in general, much higher than the observation, implying a greater rate of chemical relaxation than actually occurs. This may be due to those mechanisms which occur only at higher temperatures and longer times and not at lower temperatures or at shorter timescales. Another possible reason can be the justification of the assumption that the induction times to follow Arrhenius type relation.

The separation of the physical and chemical relaxation is a much simpler procedure, which is used in the calculation of normalised chemical relaxation rates in the MRPRA method, when compared with the splitting of the total chemical relaxation into its components adopted in the Aben technique. Although drawing a tangent to the non-linear part of the stress relaxation curve, due to the onset of chemical processes is subjective, this introduces uncertainty into the extrapolation of data to lower temperatures; this is the main reason for the differences in predicted and measured values using the MRPRA technique. This is a consequence of using a method developed for thin tensile stress relaxation specimens, where chemical relaxation can be rapid, but its application to compression relaxation data has proved limited.

Time-temperature superposition analyses are successful for only two materials, the peroxide-cured EPDM and the softer NBR compounds. In the case of NBR compound, there is some uncertainty as to the exact form of the composite curve between 10^4 and 10^6 h (which is the region of interest for the prediction of lifetimes in the range 50 to 100 years). For the SBR and sulphur-cured EPDM the measured 23°C data deviated from the composite curve at about 10,000 h, a similar value to the chemical relaxation induction time. For these two materials, time-temperature superposition gives optimistic predictions of the stress relaxation behaviour. In contrast, for epichlorohydrin, Santoprene 101-55, Evoprene 992 and Alcryn 6386 the 23° C data decreased more slowly with time than the composite curve, and the superposition predicts pessimistic results. Both these predictions are probably due to the use of the adjusted 100°C data to give the long-term relaxation behaviour.

As the time-temperature superposition method was developed for viscoelastic materials with little chemical relaxation, this technique may be ineffective for the materials used in this programme. This is supported particularly by SBR and sulphur-cured EPDM, and the superposition will predict a much lower level of stress relaxation than would be observed. Evoprene 992 and Alcryn 6386

are considerably softened at 100° C, and relax more rapidly than at 23° C, leading to erroneous predictions. The discrepancy for TPE's may be due to the shape of the stress relaxation curve (Figure 4.7) and this may also contribute to error in the prediction. Although it is possible to resolve these errors qualitatively, a more quantitative treatment to take into account the effects of chemical relaxation and softening is necessary before the superposition technique can be used to give an accurate prediction of long-term stress relaxation in these materials.

The extrapolation of physical relaxation data for materials which displayed no chemical relaxation up to 3000 h at 100° C assumes that if there is no chemical relaxation by this time, then none will occur at longer times. This is a possible source of error in peroxide-cured EPDM, as some 100° C data showed a slight deviation from linearity at 3000 h (Figure 11 in the Appendix), but the data are insufficient for any firm conclusion to be reached. The residual stress factor at 20000h is accurately predicted from 1000 h stress relaxation data at 23° C for the softer peroxide-cured EPDM,D(N), at both the temperatures, the harder EPDM, F(O), all the three Alcryn at 23°C and both the Evoprene at 5° C. However, the predictions are pessimistic in all other cases. Due to the change in slope of the stress relaxation curves of the thermoplastic elastomers at about 1000 h, and hence predictions for Santoprene and Evoprene are too low. The extrapolation method never predicts less relaxation at 24000 h than is actually measured; for the peroxide-cured EPDMs this may be due to some chemical component of relaxation. For the thermoplastic elastomers this is due to the change in slope of the relaxation curve. The change in slope may be taken into account by using Equation 7.26 to determine the relaxation for periods longer than 1000 h.

In order to use the superposition principle effectively, at 23°C or at any other temperature, tests at higher temperatures should be conducted to detect the presence of chemical processes. From the data obtained in the programme, a test of at least 3000h at 100°C may be necessary to eliminate most materials showing signs of chemical relaxation, and the test may have to be continued up to about 10000h for the peroxide-cured EPDMs in the programme. For the TPEs, tests of at least 10000h may be required to gain data on the change in relaxation rate after about 1000h, to be used in Equation 7.26. Thus, in order to predict long-term data, tests at either 23°C(TPE's) or 100°C (crosslinked materials) for 10000h would be necessary.

If tests at 100° C on crosslinked elastomers showed chemical relaxation, then the

MRPRA extrapolation method can be used. This has previously proved to give reasonable agreement between theory and observation for a period of 16 years for the creep of natural rubber bearings. For the data obtained in this programme, the MRPRA method is successful in predicting the residual stress at 20000 h for most materials, when allowance is made for the magnitude of the RSF at t_0 (Equation 7.24). The only discrepancies are for the nitrile rubbers at 23°C and SBR at 5°C. However, this may not be true at very long times (refer to Table 7.11).

In general, the simple extrapolation techniques, by extending the curves, appear to give the best predictions of stress relaxation over 20,000 h, and presumably over a much longer timescale. However, the MRPRA method has demonstrated the dominance of chemical relaxation in determining the long-term stress relaxation behaviour at all temperatures. Thus, in order to extrapolate accurately the chemical relaxation behaviour, long-term tests (in excess of 10,000 h) are necessary, particularly for tests at 40° C, to obtain adequate data. The other alternative is to carry out tests at higher temperatures, such as 80°, 100° and 120° C to obtain chemical relaxation data in a shorter period of time. This can, however, introduce more uncertainties into the extrapolation. The attempts to separate the various chemical reactions at different temperatures (Section 7.8.1.3) has suggested that more than one degradation process may occur simultaneously at 100°C, whilst only one is present at 40°C for a similar timescale. Extrapolation from higher temperatures may, therefore overestimate chemical relaxation at lower temperatures.

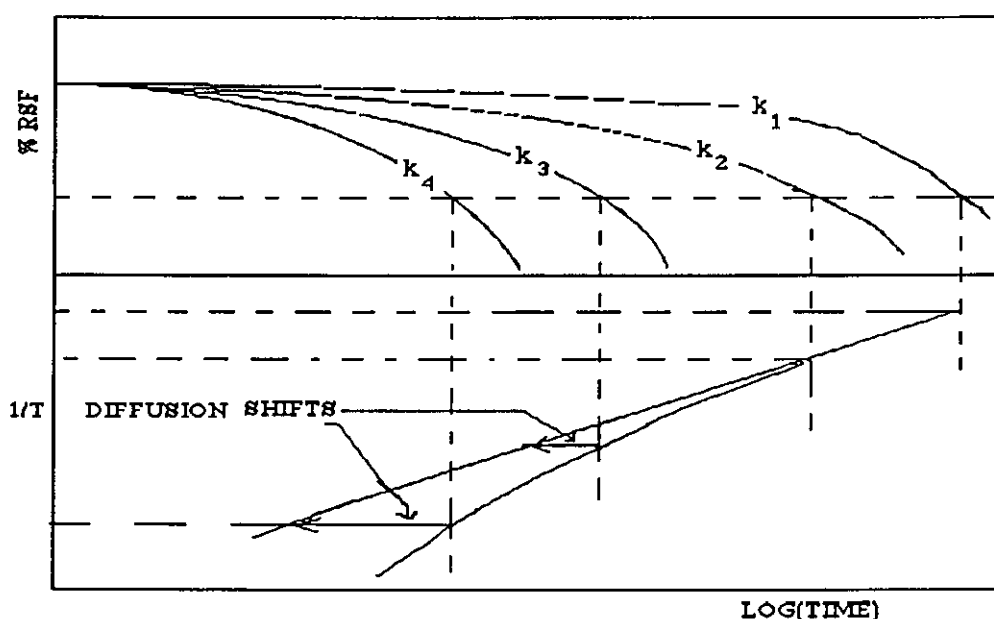


Figure 7.15: Errors in extrapolation due to diffusion shifts

One possible explanation for the failure of the Arrhenius principle in the extrapolation technique for the estimation of chemical relaxation may be due to diffusion shifts; this is shown in Figure 7.15. There can possibly be several reasons for the diffusion shifts to occur. Thus, the formation of oxide skin, and the presence of secondary or tertiary relaxation process at elevated temperatures may be the prime reasons. However, a proper understanding needs further investigation. An example of the Arrhenius analyses for the extrapolation of chemical relaxation rates of crosslinked materials (ie: NR, EPDM) is shown in Figure 7.16

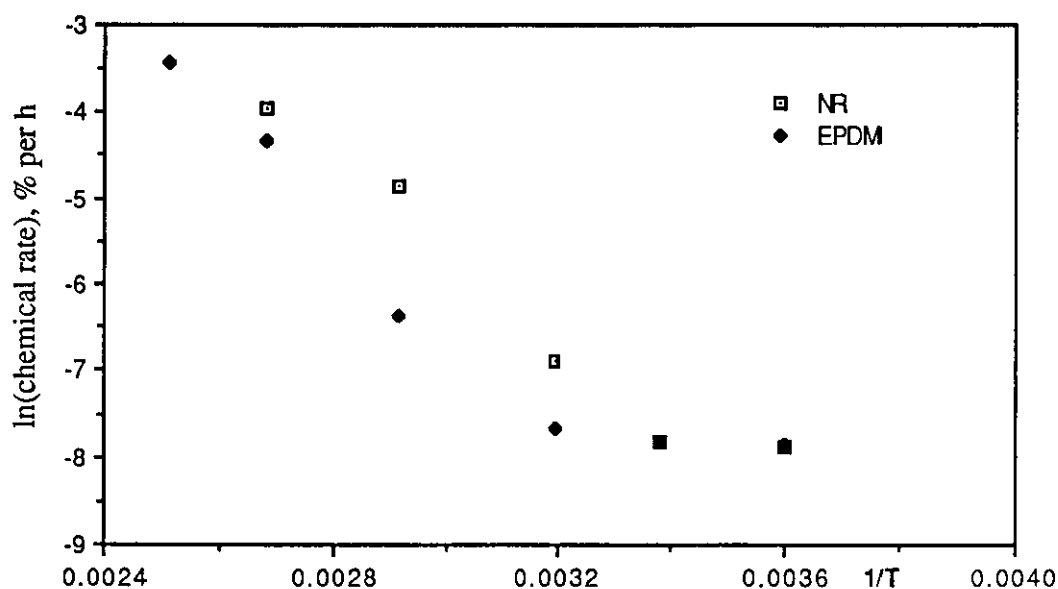


Figure 7.16: Arrhenius analyses for the chemical relaxation rate

7.12 APPLICATION TO LONGEVITY OF SEALS

The various models for the stress relaxation behaviour of cross-linked elastomers all predict that the stress in natural rubber and SBR will relax completely within 50 years. If sealing ability were determined solely by the stress relaxation, typical seal lifetimes would be of the order of 25-50 years, with the major factor limiting longevity being the rate of chemical relaxation. However, relatively primitive formulations (without antioxidants) have successfully functioned for almost 100 years,^{106,107} whereas, failure of seals due to microbiological deterioration rather than loss of sealing force resulting from stress relaxation were also reported in the literature.^{116,117} This implies that other factors are involved in seal longevity.

One possibility is surface adhesion.¹¹⁸ Even if all the original network has reformed in the compressed state, adhesion between seal and pipe surface may be sufficient to maintain sealing ability so long as the pipeline remains undisturbed. If the pipe moves laterally causing separation between spigot and pipe, the seal would be unable to respond elastically, leading to leakage.

Another relevant factor may be the formation of an oxide skin on the seal surface. The effect of specimen thickness on the stress relaxation behaviour in tension has been demonstrated;¹¹⁶ samples of a natural rubber O-ring have been found to have a hard oxide skin on the surface with the rubber inside of similar modulus to when originally installed. Stenberg has also commented on the formation of oxide skins on compressive stress relaxation specimens at high temperatures.⁴ He suggested, implying that chemical relaxation is oxygen dependent, the formation of oxide skin in effect limits the oxygen diffusion, thus limiting the amount of chemical relaxation. The oxide skin may be fractured if the seal has to move to accommodate movement, but presumably forms another skin soon after. If this interpretation is correct, then a large difference in stress relaxation rates would be expected for different specimen sizes (as in small specimens, oxygen might be able to permeate throughout the specimen before the skin was formed). Russian workers⁹⁵ proposed a quantitative expression for the effect of specimen volume, from their experiments on specimens up to eight times the original volume. Work in this programme on the effect of specimen volume and shape factor is not in agreement with this (4 x original volume). Also work in a nitrogen environment have suggested that oxygen is not necessary for the chemical degradation observed in these materials (Section 4.5).

In order to assess the contribution of surface adhesion and oxide skins to seal longevity, it is necessary to examine failed seals or functioning seals that have been removed from service. However, despite several attempts, this has not been possible and hence no conclusions may be drawn.

Most analyses for the sealing behaviour consider the relatively simple case of a laterally unstrained, circular cross-section O-ring,¹⁰⁸ but practical pipe seals are of more complex design.¹⁰⁵ Joints incorporate features to aid the location of the seals during the joint assembly, and the combination of joint geometry and

seal geometry could lead to seal experiencing almost a state of hydrostatic compression. Hydrostatic compression has the effect of increasing the glass-transition temperature of the elastomer.¹¹⁹ This would lead to an increase in the rubber modulus at a given temperature, due to the increase in glass transition temperature, T_g , resulting in an increase in sealing force exerted by the seal on the pipe. If Lindley's¹⁰⁹ analysis of the seal failure criterion (Equation 7.23) is considered, any increase in modulus will reduce the possibility of leakage. The effect of compression modulus on the stress relaxation rate does not seem to have been investigated directly, but the effect of hardness has been considered. If a compound has its hardness (and hence its modulus) increased by adding more filler, the stress relaxation rate will increase.³⁹ If, however, hardness is increased by increasing the number of cross-links the rate will decrease.⁸ At high hydrostatic pressures, stress has been found to relax for a much longer time than at atmospheric pressure. It was suggested that the effect of the pressure was to shift some of the relaxation times to longer times; that is, the relaxation rate is decreased in the presence of hydrostatic compression. This may be due to the decrease in free volume in the elastomer, making chain rearrangements more difficult. Hydrostatic compression may have a significant effect in high pressure pipelines.

It is generally assumed that stress relaxation is one of most important properties determining seal longevity,^{103,104} and indeed, this assumption is implicit in this programme. The experimental data obtained, and the mathematical modelling have indicated the importance of chemical relaxation in determining long-term properties. This is based on the assumption that as the original rubber network is degraded, a second network is formed that is in equilibrium in the compressed state, thus making no contribution to the sealing force, and therefore, give an indication of the proportion of original network remaining. However, in a pipeline there is a pressure difference across the seal, usually transverse to the original compressed state. It has been suggested by Flory¹⁵ that both networks will contribute to the elastomer's response to the attempted change in deformation. He proposed a model of elasticity for a composite network formed by introducing a certain number of cross-links in a state of isotropy (ie in an undeformed state) and others in a state of deformation (ie: new chains formed in equilibrium in the compressed state), which was then generalised to a subsequent deformation (relative to the

compressed state). This subsequent deformation could be, for example, due to the pressure gradient across the seal. He proposed that, irrespective of the distribution of the cross-links, both the original and newly-formed networks contribute to the elastic free energy of the system. The contribution of second network to elastomeric properties along the compression axis may be one interpretation of the Modulus Enhancement Factor (M.E.F.) and is previously discussed in Section 4.3.

Chapter Eight

CONCLUSIONS AND RECOMMENDATIONS

This chapter summarises the findings concerning stress relaxation and recovery behaviour of the elastomeric materials examined in the present programme.

8.1 TIME DEPENDENCE

8.1.1 The effect on Stress Relaxation

The initial relaxation was linear with $\log(\text{time})$ and was assumed to correspond to the physical relaxation process. The deviation from this linearity at a later stage in the relaxation curve is assumed to be due to the onset of chemical processes. The rates of these two relaxation processes and the time before the onset of chemical relaxation mechanisms were found to be dependent on the type of polymer structure.

8.1.2 The effect on Recovery

The fractional recovery of stable network rubbers such as peroxide-cured rubber compounds (eg: Type D and F) and other thermoplastic elastomers such as Santoprene are relatively independent of the time under compression. However, recovery in other crosslinked rubbers such as NR, SBR, EPCL, Sulphur-cured EPDM, NBR are found to be highly affected by the time under compression, due to the onset of chemical processes.

8.2 TEMPERATURE EFFECTS

8.2.1 Initial Force

The initial force remains fairly constant for the crosslinked rubbers but decreases for all the thermoplastic elastomers with the increase in temperature.

8.2.2 Physical Relaxation

An increase in the rate of physical relaxation with increasing temperature is expected. However, the effect is more pronounced for thermoplastic elastomers such as Alcryn, Evoprene than for crosslinked or more stable networks such as EPDM, NBR rubbers and Santoprene.

8.2.3 Chemical Relaxation

For materials which displayed a departure from linearity of residual stress vs log(time) relationship within the timescale of the present experiment (24000 h), the effect of increasing the temperature was to reduce the time to the deviation. i.e: the induction time decreased with increasing temperature. However, there does not appear to be a threshold temperature, below which the chemical activity ceases. On the other hand, the effect of temperature on the rate of chemical relaxation is found to be more drastic than that on the physical relaxation rate. This is found to increase severely at higher temperature for less stable networks such as NR, SBR, EPDM(S) rubbers.

8.2.4 The effect on Recovery

If the fractional recovery can be interpreted quantitatively in terms of that part of the relaxation that was chemical in nature, then the recovery rate should give information on the physical processes involved in relaxation. The recovery rate is found to be independent of temperature and time under compression for most materials.

8.3 CURE STATE

Under-cured materials show poor stress relaxation and recovery behaviour. The differences in relaxation and recovery values of optimum and over-cured materials are not great, but over-cured materials will display poor mechanical properties.

8.4 ENVIRONMENT

8.4.1 Water

Immersion in water appears to have little effect on the stress relaxation behaviour of most of the elastomers that were shown to have some affinity for water in the swelling measurements, such as epichlorohydrin and natural rubber. However, this is not the same in case of the nitrile rubbers which exhibited greater relaxation in water.

8.4.2 Natural gas

Of the six compounds tested in a moist gas environment, Alcryn and nitrile rubber showed higher relaxation in gas than in air, whereas peroxide-cured EPDM showed better performance. The other materials Santoprene 101-64, Evoprene- 994, Epichlorohydrin show little effect of a natural gas environment. These findings might have been affected due to the absorption of water from the moist gas and should be interpreted accordingly.

8.4.3 Nitrogen

In general most materials including thermoplastic elastomers, showed lower stress relaxation and higher recovery performance under nitrogen, indicating that oxygen is a probable contributor to the relaxation process.

8.5 FILLER

Stress relaxation of gum vulcanisates is found to be lower than that of their filled counterparts. This is because of their lower physical relaxation rates. The effects of fillers on chemical relaxation are uncertain and a region requiring further research.

8.6 SPECIMEN DIMENSIONS

From the experiments carried out on specimens of different dimensions, it is found that the effect of specimen dimension on the stress relaxation at 70° C is marginal. However, some differences in relaxation at 100°C were observed.

This effect could have been greater if the polysulphidic crosslinks had dominated the network. The influence of specimen size on the chemical (oxidative) degradation can be noticed in the recovery measurements of the natural and the nitrile rubbers. Recovery is better for large specimens.

8.7 COMPARISON OF STRESS RELAXATION AND RECOVERY

Substantial differences in the rates of stress relaxation (physical) and recovery were observed. Gent's hypothesis ²⁴ was not valid in this work and the 'symmetrical relaxation process' ^{24,41} was found to be unsuitable in filled elastomers. Both stress relaxation (at low temperatures and short times) and recovery are linear with respect to log(time), indicating that both are dominated by the physical processes. It thus seems likely that if recovery is involved with 'n' number of processes, then relaxation should have at least 'n+1' number of processes. This could be due to the mobility of chains coming into play as filler-filler or filler/polymer bonds are broken.

8.8 MODULUS ENHANCEMENT FACTOR

From the present work, it can be concluded that for most filled crosslinked rubbers the modulus enhancement factor (MEF) is approximately independent of temperature, and has a value of 2. The MEF in gum vulcanisates is approximately unity. For most thermoplastic elastomers, MEF was found to decrease with increasing temperature. Values of MEF are higher for the Santoprene and Evoprene (around 3-5) than for the crosslinked rubbers and the Alcryn. Recent investigation at IPTME has indicated that the MEF is dependent on the rate of strain and a reasonable correlation between the MEF and Hysteresis is found to exist. Even though, the science of MEF is partly clear with the application of Tobolsky's Two-Network theory, the part played by the filler is not understood and needs further investigation.

8.9 LOADING RATE

The study on loading rate has shown that:

- a) Faster loading rate generates higher initial stress

- b) Decay rates are more rapid in the very early stages (before 0.1 h) for the higher stress levels
- c) The rate of stress relaxation appears to be independent of the loading rate for crosslinked rubbers but not for the thermoplastic elastomers.

The above conclusions appear to be a strong argument in favour of the controlled loading method followed at IPTME instead of a poorly defined loading rate as specified in the rubber seal specification BS:2494-86. It should also be noted that very high loading rates not only lead to poor reproducibility but also there is a serious danger of overloading the load cell.

8.10 MECHANICAL CONDITIONING

Even though the test specification BS 2494-1986 strongly insists on the mechanical conditioning prior to the stress relaxation measurements, there appears to be negligible effect of this on the test results, especially after a rest period.

8.11 SPECIMEN LUBRICATION

It was found that the use of solid-phase lubricant did not have any systematic effect on stress relaxation behaviour.

8.12 HARDNESS

Irrespective of successive efforts to find a correlation between either hardness and other properties, such as initial stress, compression modulus, residual stress factor and hysteresis, or between the macro and micro hardness measurements, not only poor results were obtained but also irregular variations were noted. Further investigations have revealed that hardness is time dependent (thixotropic) property. This dependence was found to vary widely with the type of material under test. Hence, proper definition of hardness test needs further consideration and specification.

8.13 TEMPERATURE JUMPS

The results obtained on test buttons undergoing a series of temperature cycles imply that temperature jumps influence relaxation. Thus, the second method given in BS 903 Part A 42 may produce misleading information about stress relaxation behaviour.

8.14 SIMULATED TESTS

From the work carried out on Hepworth apparatus, it is found that the stress relaxation rates of the compression seals are always greater than those of the compression buttons. However, the consistency of experiments on the Wavin equipment using the lip seals was found to be very poor. This might be due to the other factors involved such as design of seals and surface adhesion but more work is required to confirm this.

8.15 MATHEMATICAL MODELS FOR SEAL LONGEVITY

The mathematical analysis of the stress relaxation data and the application of various models for the prediction of seal longevity have shown that the accuracy in predicting the long term stress relaxation property mainly depends upon the analysis of chemical components. For this, the new technique of recovery measurements can be useful. However, the application of these stress relaxation models in the prediction of longevity of pipe seals is still doubtful, pending proper understanding of seal design.

8.16 BS 2494:1986: RUBBER SEAL SPECIFICATION

This section discusses one of the objectives of the programme, which was to consider BS 2494 in the light of the data obtained during the programme.

8.16.1 Quality Control Tests

Several tests in BS 2494:1986 are apparently to provide quality control measurements on the materials used for pipe seals. They are:

- a) Elongation at break

- b) Tensile strength
- c) Hardness
- d) Compression set

The quality control aspect of the standard could be achieved by replacing tests 2, 3 and 4 with the determination of the compression modulus during the stress relaxation experiment, followed by recovery measurements. The inferiority of hardness and compression set tests are already investigated in this programme. Under-cured materials will be apparent from their lower modulus and subsequent poor stress relaxation and recovery. Elongation at break gives an ultimate measure of a material's property. Over-cured materials could also be detected by their inferior elongation at break or recovery.

8.16.2 Stress Relaxation and Recovery Tests

The chemical relaxation processes are dominant in determining long-term stress relaxation. This is clear from the discussion on mathematical modelling. It is necessary to consider how much chemical relaxation can be permitted, and how rubbers can be assessed for this property. The current standard specifies a maximum stress relaxation of 18 % in 168 h at 23° C for Types W and D, and 10 % for Type G, normalised to 0.5 h. These correspond to relaxation rates of 7.12 % and 4.4 % per decade respectively.

If the only relaxation mechanism in an elastomer is physical, then much higher amount of relaxation can be permitted. The stress in Types W and D joint rings would relax to 30 % of their initial value in about 10 decades (ie: 571,160 years) of time [with data normalised to 0.5 h]. In order for the stress to relax to the same value in 100 years, the physical relaxation rate would need to be 11% per decade (equivalent to the relaxation of 28 % in 168h).

It has been found that the stress relaxation in some of the TPE's such as Santoprene and Evoprene, at low temperatures consist of two straight lines, with a higher rate of stress decay at shorter times. The intersection occurring at about 1000 h. at 23°C (Figure 4.7). This type of behaviour was not found in the Alcryn or in any of the crosslinked rubbers used in the present programme

The above finding has many implications of importance in design and with respect to BS 2494-86. Much of the stress relaxation phenomena can be summarised by extrapolating the data obtained at 23° C over 168 h., thus providing a measure of the physical relaxation. However, with a change in slope at about 1000 h, the present method gives too pessimistic result. The slope after the transition is much less, implying greater longevity. The observation has been repeated in further programmes, the results of which fully support the findings reported here. All the Santoprene and Evoprene compounds show the transition, but it is not observed in crosslinked systems. This finding is also found by Monsanto in their company research laboratory.

The standard must include some test to determine if an elastomer shows appreciable chemical relaxation. It is suggested that a recovery test at 70° C over 168 h would provide this information. Materials which show considerable chemical relaxation, in general, recover poorly at 70° C, whilst those which are relatively stable recover to almost 100% at a reduced time of unity. The recovery test at 70° C for 168 h would replace the compression set at 70° C for Types W, D and G. This test would also replace the accelerated ageing test for these materials. In determining an allowable fractional recovery, it should be remembered that other factors may affect sealing behaviour, and materials such as natural rubber apparently display long seal lifetimes whilst experiencing considerable relaxation. A fractional recovery of 85 % after 168 h at 70°C and 90% at 23°C at a reduced time of unity should eliminate those materials whose properties are severely affected by chemical degradation. This criterion should pass natural rubber and other crosslinked rubbers in this programme. The results obtained in this work indicate that stress relaxation and recovery measurements give adequate information on ageing properties.

8.17 RECOMMENDATIONS FOR FURTHER RESEARCH

From the conclusions reached in this programme, the following areas are suggested for future work:

1. Thermoplastic elastomers are being used increasingly in applications previously dominated by the conventional rubbers. Hence, a better understanding of their relaxation behaviour is necessary for their proper use. The stress relaxation of these materials is different to that of conventional elastomers, showing a improvement in properties at longer timescales. In order to gain a full understanding of their relaxation behaviour, a proper study of their morphology may be necessary.
2. The role of fillers in determining the stress relaxation, modulus enhancement factor (MEF), hysteresis and recovery is still not understood. Further work is desirable in this area
3. The effects of mechanical conditioning on subsequent stress relaxation behaviour needs further consideration, presumably with higher strain levels than those used in this programme.
4. It appears that a relationship exists between MEF, stress relaxation and hysteresis. Although it has not been fully established in this programme, further investigation, possibly relating recovery to MEF will help to establish it fully.
5. It is recognised that diffusion control eg: oxygen, water and gas may play a significant role on relaxation behaviour described in these experiments, because of relatively thick specimens. Some of the conflicts between tensile and compression tests may be clarified further by more investigation of the effects of size on stress relaxation and recovery with a larger range than used in this programme.

6. The consideration of the hardness test as a quality control test in the rubber industry with respect to its reliability and reproducibility must be questioned, with a possible replacement by the initial force measurement.
7. This research has shown that mathematical models for the prediction of the service life depends mainly on the ability to identify, separate and estimate the different relaxation processes. However, application of these models for the prediction of longevity of rubber seals must be considered in conjunction with other aspects such as seal design.

* * * * *

REFERENCES

- 1 Tobolsky A. Y, 'Properties and Structure of Polymers', John Wiley and Sons, New York, 1960
- 2 Murakami K and Ono K, 'Chemorheology of Polymers', Elsevier Scientific Publishing Company, Amsterdam, 1979
- 3 Tahir M. and Birley A.W, J. Polymer Testing, 7, 1987, 3
- 4 Stenberg B, Ph.D. Thesis, 'Compression relaxation of rubbers' Department of Polymer Technology, Royal Institute of Technology, Stockholm, 1977
- 5 Prabhu A. M, 'Stress relaxation of thermoplastic elastomer compounds in compression', M.Sc thesis, Loughborough University, 1986
- 6 Hepburn C. and Blow C.M, 'Rubber Technology and Manufacture' Butterworth, 1982
- 7 Eirich F. R, 'Science and Technology of Rubbers', Academic Press, New York, 1978, Chapter 7.
- 8 Roberts A. D., 'Natural Rubber Science and Technology', Oxford University Press, New York, 1987.
- 9 Holden G., Bishop E.T. and Legge N.R., 'Thermoplastic Elastomers' Proceedings of International Rubber Conference, Brighton 1967, 287
- 10 Dunn J. R., Rubb. Chem. Technol., 49, 1976, 978
- 11 Treolar L.R.G, 'The Physics of rubber elasticity', Clarendon Press, England, 1975
- 12 Cunneen J.I, Rubb. Chem. Technol., 41, 1968, 182
- 13 Tamura S. and Murakami K., J. Polymer, 21, 1980, 1398
- 14 Brydson J. A., 'Rubbery materials and their compounds', Elsevier Science Publishers Limited, England, 1988, p 367
- 15 Flory P. J., Trans. Faraday Soc., 56, 1960, 722
- 16 Tobolsky A. V. and Andrews W., Chem. Phys., 13 (1), 1945, 3
- 17 Mullins L. and Thomas A.G., J. Poly. Sci; 43, 1960, 13
- 18 Oono R, J. Poly. Sci.; Poly. Phys.; 12, 1974, 1383
- 19 Treolar L.R.G., Rubb. Chem. and Technol., 47, 1974, 626

- 20 Yannas I. V., J. Poly. Sci., Macromol. Review, 9, 1974, 163
- 21 Christensen R.M., 'Theory of Viscoelasticity-An Introduction'; 2nd Edn., Academic Press, New York, 1982
- 22 Wright N, 'Stress relaxation ageing techniques to predict the service life of elastomeric seals', M.Sc dissertation, Newcastle upon Tyne Polytechnic, England, 1981
- 23 BS 2494: 1986 'Elastomeric joint rings for pipeworks and pipeline'
- 24 Gent A. N., J. Appl. Poly. Sci., VI 22, 1962, 433
- 25 Dunn J. R., Moore C G. and Trego B.R., J. Appl. Poly. Sci, Vol. 8, 1964, 723
- 26 Berry J.P. and Watson W. F., Rubb.chem.Technol, 29, 1956, 398
- 27 Gregory M.J., Metherell C. and Smith J. F., Plastics and Rubber; Materials and Applications, Feb. 1978 (3), 37
- 28 Scholtens B. J. R., J. Poly. Sci.; Poly. Phys., 22, 1984, 317
- 29 Burton T, Delanaye J, European Rubber J, Jan 1989, 30
- 30 Bjork F., Dickman O. and Stenberg B., Rubb.chem.Technol, 62, 1989, 387
- 31 Stenberg B. et. al., Rubb. Chem. Technol, 59, 1986, 70
- 32 Cotten C.R. and Boonstra B.B, Rubb. Chem. and Technol, 40, 1967, 829
- 33 Bartenev G. M. and Lyalina N. M., Vysokomol. Soyed. A 12 (2), 1970, 368
- 34 MacKenzie C. I. and Scanlan J., J. Polymer, 25, April 1984, 559
- 35 Murakami K., Rubb. Chem. Technol., Vol. 48, 1975, 913
- 36 Blokland R. and Prins W., J. Poly. Sci., 7 Part A2, 1969, 1595
- 37 Thirion P. and Chasset R., Rubb. Chem. Technol., 36, 1963, 50
- 38 Ferry J. D.; 'Viscoelastic properties of polymers', Wiley, New York, 1960, p 294
- 39 Derham J., J. Materials Science, 8, 1973, 1023
- 40 Mullins L., and Tobin N.R., J. Appl. Poly. Sci., 9, 1965, 2993
- 41 Gent A.N., Fourt Rubb. Technol. Conf., London, 1962
- 42 Ore. S. , Rubb. Chem. Technol., 29, 1956, 1043

- 43 Steiner G. and Tobolsky A.V.,
Rubb. Chem. Technol., 43, 1970, 1036
- 44 Bartenev G. M. and Lyalina N. M.,
Rubb. Chem. Technol., 45, 1972, 82
- 45 Dunn J. R., Rubb. Chem. Technol., 41, 1968, 304
- 46 Dunn J. R., Scanlan j., Rubb. Chem. Technol., 32, 1959, 739
- 47 Murakami K. and Tamura S., J. Poly. Sci., A1, Vol. 9, 1971, 423
- 48 Berry J. F. and Watson W. F., J. Poly. Sci., 18, 1955, 201
- 49 Gent A. N., J. Appl. Poly. Sci., Vol. 6, 22, 1962, 442
- 50 Tobolsky A. V., Prettyman I. B. and Dillon J. H.,
J. Applied Physics, 15, 1944, 309
- 51 Scanlan J., Trans. Faraday Soc., Vol. 57, 1961, 839
- 52 Thomas D. K., J. Polymer, 7, 1966, 125
- 53 Grassie N. and Scott G., 'Polymer Degradation and Stabilisation'
Cambridge Uni. Press, England, 1985, Chapter 4
- 54 Barnard D. et.al., Rubb. Chem. Technol., 45, 1972, 381
- 55 Bell C.C.M. and Cunneen J., J. Appl. Poly. Sci., 11, 1967, 2201
- 56 Stenberg B. and Jansson S. F.,
Rubb. Chem. and Technol., 46, 1973, 1316
- 57 Lindley P.B. and Teo S. C.,
J. Plastics and Rubber; Mats. and Appln., May 1977, 82
- 58 Tamura S. and Murakami K., J. Appl. Poly. Sci., 16, 1972, 2803
- 59 Lyubchanaskaya L. I. et al, Soviet Rubb. Technol., 21, 1962, 20
- 60 Lee T. C. P. and Morrell S. H., Rubb. Chem. Tecnol., Vol. 50, 1977, 483
- 61 Beatty J. R. and Juve A. E., India Rubber World, 121, 1950, 537
- 62 Tobolsky A.V. et. al., J. App. Phys., 15 (4), 1944, 380
- 63 Fernando K. P. 'Stress relaxation in compression; Instruments,
measurements and their interpretation for rubbers'
Ph.D thesis, Loughborough University, 1984
- 64 Armah J. C., M.Sc. thesis, Loughborough University, 1985
- 65 Tahir M, 'Further studies of the relaxation behaviour of rubber in
compression', Ph.D. thesis, Loughborough University, 1985

- 66 Birley A.W, Fernando K.P.and Tahir M, J. Poly. Testing,6, (2),1986,85
- 67 Whelan T., British Plastics and Rubber, April 1990, 29
- 68 Flory P. J., Rehner J., J. Chem. Phys., 11, 1943, 512
- 69 Gordons T. G., Ph. D. thesis, "Stress relaxation behaviour in compression and some other mechanical properties of TPE's"
IPTME, Loughborough University, 1990
- 69a Zhang Y. and Birley A. W., Short Communication,
Polymer Testing (accepted for publication)
- 70 Gent A.N., J. Poly. Sci, Poly. Sympto., 48, 1975, 1
- 71 Djiauw L. K. and Gent A.N., J. Poly. Sci., Poly. Sympto., 48, 1974, 159
- 72 Prabhu A. M., Birley A.W. and Sigley R.H,
Polymer Testing , 10, 1991, 39
- 72a Wood L. A., Rubber Chem. and Technol., 54, 1981, p 334
- 73 Fuller K. N. G., Int. Rubber Conf., Paris, 1982, p I-22
- 73a Farlie E. D., J. Appl. Poly. Sci., Vol. 14, 1970, 1127
- 74 McCrum N. G.; Read, B.E. and Williams, G., 'Anelastic and Dielectric Effects in Polymer Solids', Wiley, New York, 1967
- 75 Fuller K.N.G., Phil. Mag. A., 57, 1988, 225
- 75a C. Blow, 'Rubber Technology and Manufacture' Newness Butterworths Publishers, London, 1971, p 444
- 76 McCrum N. G., Buckley C. P., Bucknall C. B., 'Principles of Polymer Engineering', 2nd Edn., Oxford University Press, Oxford, 1988
- 77 Buche F., 'Physical properties of Polymers'
Interscience Publishers., New York, 1962
- 78 Nielsen L. E, 'Mechanical Properties of polymers',
Volume I, p 78, Reinhold Publishing Co., New york, 1962
- 79 Alfrey T, 'Mechanical behaviour of high polymers,' Appendix 2, p 553,
Interscience Publishers, New York, 1948
- 80 Curro J. G. and Salazar E. A.;
J. Applied Polymer Science, 19, 1975, 2571-2581
- 81 Treolar L. R. G., 'The physics of rubber elasticity', Second Edition,
Clarendon Press, Oxford, 1958, p 351
- 82 Slonimsky G. L., Journal of Polymer Science C, 16, 1967, 1667

- 83 Tobolsky A. V. and Takahashi M, J. Appl. Poly. Sci., 7, 1963, 1341
- 84 Dean K, and Edwards S, Philosophical Transactions of Royal Society, 280, A 1296, 1976, 27
- 85 Nutting P. , ASTM Proceedings, 21, 1921, 1162
- 86 Buchdahl R. and Neilsen L. E, J. App. Phys., 22, 1951, 1344
- 87 Landel R. F. and Stedry P. J, J. App. Phys., 31(11), 1960, 1885
- 88 Chang F.S.C.; J. Applied Polymer Science, 6 (21), 1962, 297
- 89 Williams M. L., Landel R.F. and Ferry J. D., Journal of Americam Chemical Society, 77, 1955, 3701
- 90 Nishida N, Murai M. and Sasaki N., Journal of Applied Polymer Science, 30, 1985, 1333
- 91 Meier U. and Kuster J., Rubb. Chem. Technol, 57, 1984, 254
- 92 Tarasova Z. N. and Dogadkin B. A, Rubb. Chem. and Technol., 39, 1966, 1625
- 93 Aben W. J. G.H., Plastica, 27 (3), 1974, 82
- 94 Lyubchanskaya L.I, Degteva. T. G., Angert L. G. and Kuz'minskii, Soviet Rubber Technology, 1964, No. 4, 18-20
- 95 Khaikin M. L. and Gorelik B. M., Khauchuk i Rezina, No. 9, 1982, 19 (translated in International Polymer Science and Technology 10, 1983, T/71)
- 96 Darovskikh G.T., Kusov A. B. and Pyass L. E., Soviet Rubber Technology, 25, 1966, No. 5, 13
- 97 Tobolsky A. V. and Murakami K, J. Polymer Science, 40 (15), 1959, 443
- 98 Derham C. J., Lake G. J. and Thomas A. G, Natural Rubber Conference, Kaula Lumpur, 1968
- 99 Stenberg B, and Jansson J.F, Rubb. Chem. and Technol., 50, 1977, 906
- 100 Ferry J. D., 'Viscoelastic Properties of polymers', John Wiley and Sons, Third Edition, 1980, p 90
- 101 Curro J.G. and Salazar E.A., J. Appl. Poly. Sci., 19, 1975, 2571
- 102 Salazar E. A. and Curro J. G. and Gillen K.T., J. Applied Polymer Science, 21, 1977, 1597
- 103 Morrell S. H., and Watson W. F., RAPRA Members Journal, 4, 1976, 59
- 104 Derham C. J. and Lindley P.B., Fifth International Conference on Fluid Sealing, Warwick, U.K., Paper C1, 1971

- 105 Brister D., Progress in Rubber Technology, 44, 1981, 105
- 106 Davies B., Rubber Developments, 41, 1988, 102
- 107 Stevenson A., Plastics and Rubber, Proces. and Applns., 5, 1985, 253
- 108 Curro J. G. and Salazar E. A., Rubb. Chem. and Technol., 46, 1973, 530
- 109 Lindley P. B., Journal of IRI, July/August 1967, 209
- 110 Eller S. A., Rubber Age, 79, 1956, 455
- 111 Degteva T. G. et al, 'Starenie i Zashchita Rezin'
(Translated NIIRP, Sb. 6, 69), RAPRA translation 961, 1962
- 112 Lyubchanskaya L.I., Tsapina N.A. and Kuz'minskii A.S.,
Soviet Rubber Technology, No. 9, 1965, 24
- 113 Annonymous, Natural Rubber Technology, 4, 1973, 7
- 114 Ellul M. D. and Southern F.,
Plastics and Rubber - Processing and Applications, 5, 1985, 61
- 115 Dunn J. R., 126th meeting - Fall, American Chemical Society,
Rubber Division, Houston, Texas, October 25 - 28th 1985, Paper 42
- 116 Dickmam O. and Stenberg B.,
Plastics and Rubber; Processing and Applications, 4, 1984, 337
- 117 Derham C. J., NRPR, Third Rubber in Engineering Conference,
1974, Paper F
- 118 Bartnev G.M. and Kolyadina N.G.,
J. Soviet Rubber Technology, 5, 1962, 27
- 119 Paterson M. S., J. Applied Physics, 35, 1964, 176

APPENDIX

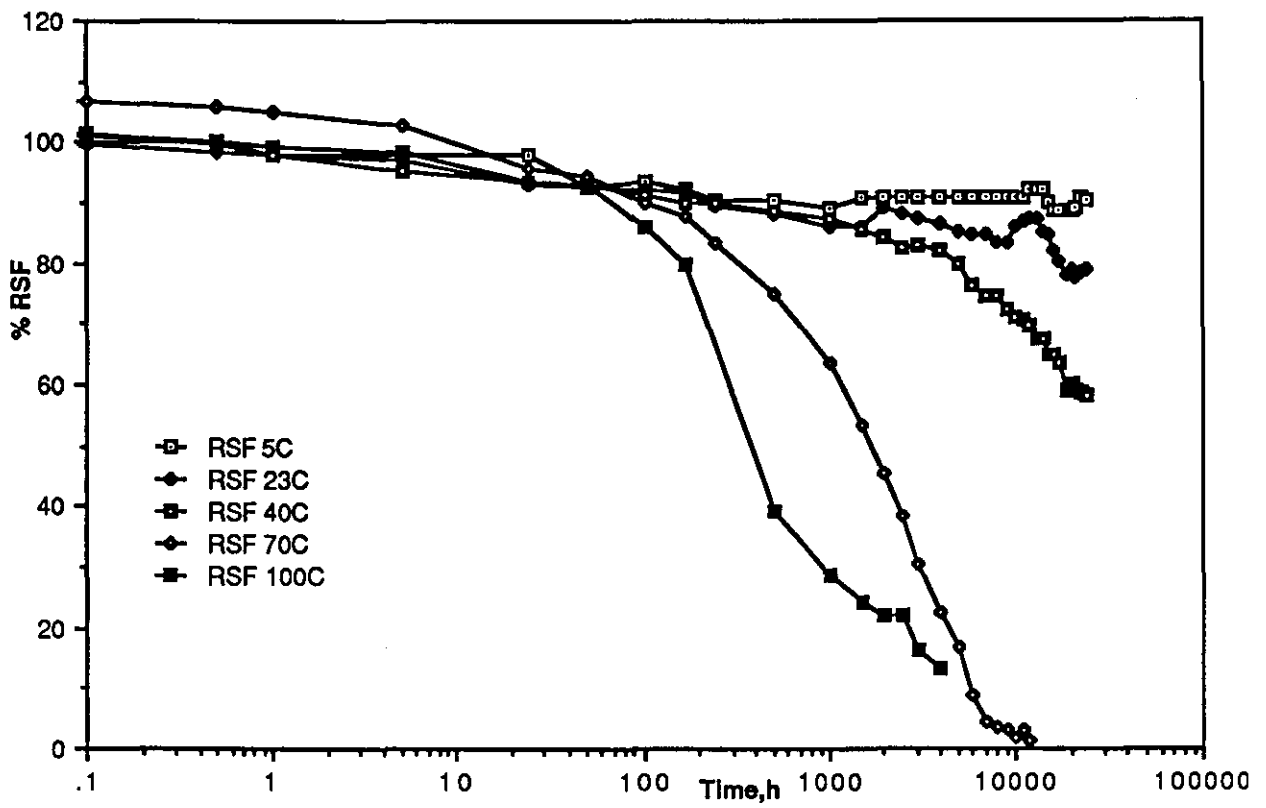


Figure 1 Compression stress relaxation curves for Natural rubber, A(O)

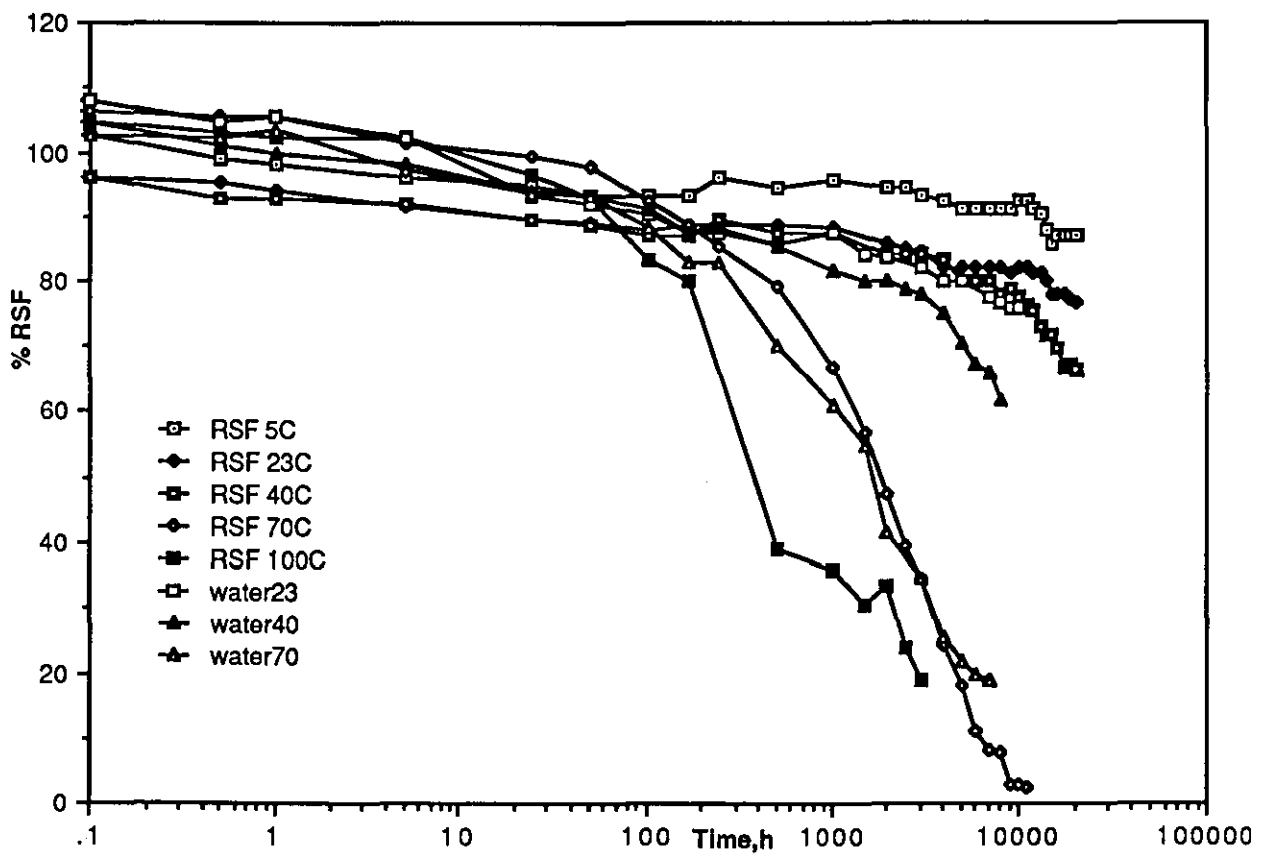


Figure 2 Compression stress relaxation curves for Natural rubber, A(N)

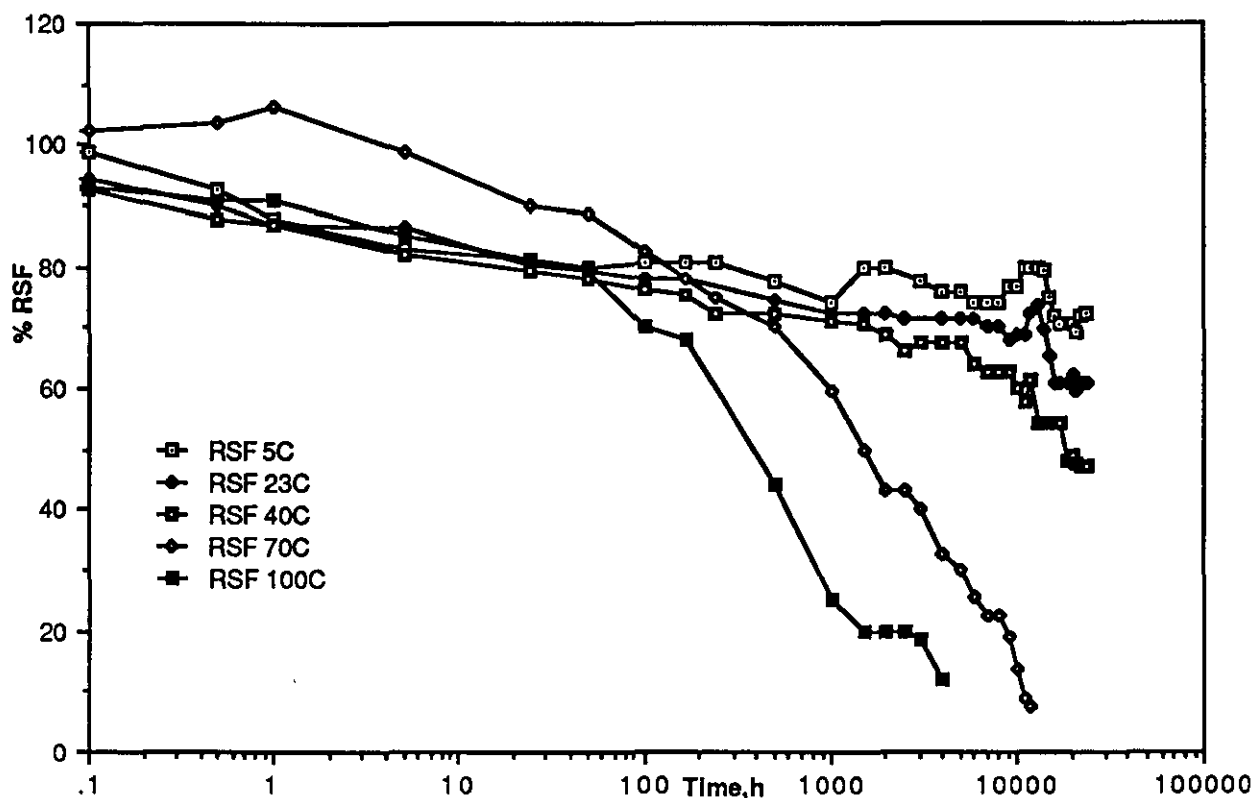


Figure 3 Compression stress relaxation curves for SBR, B(O)

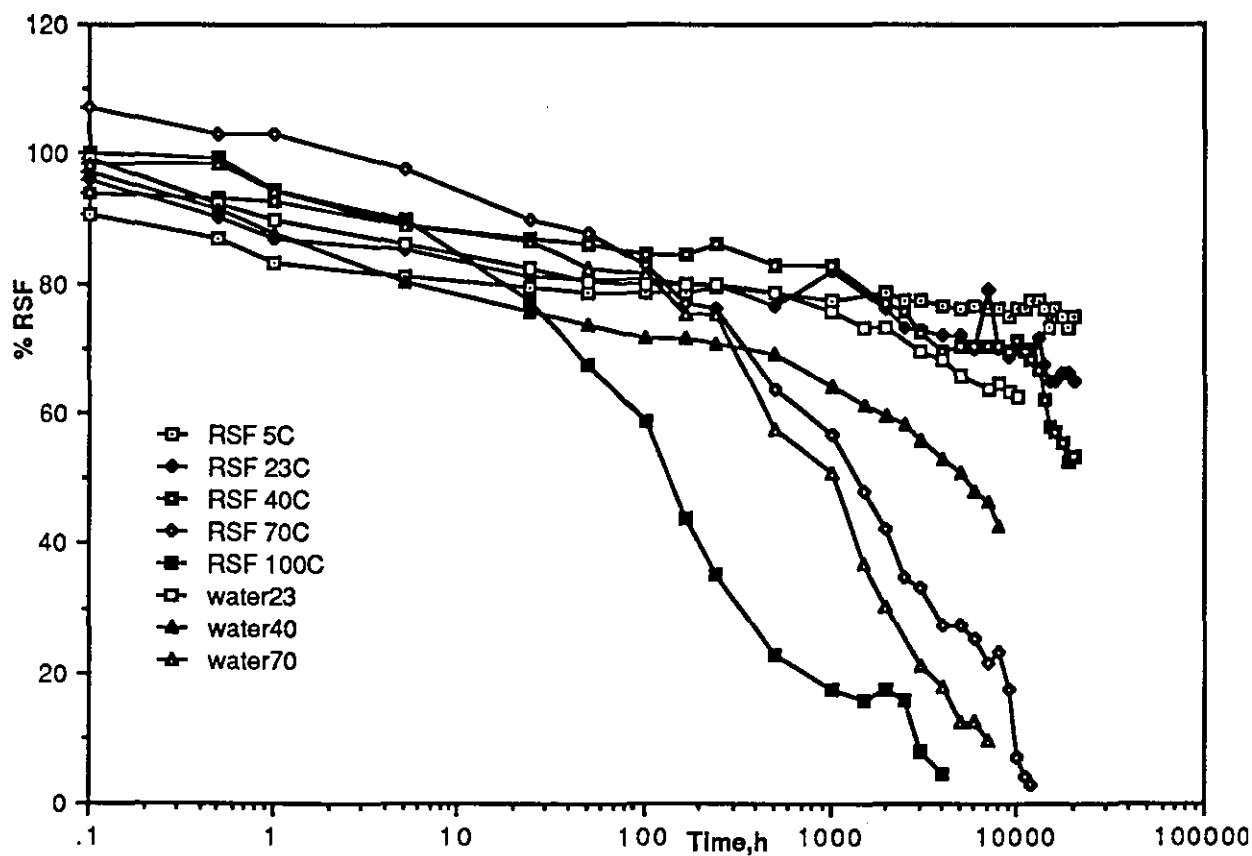


Figure 4 Compression stress relaxation curves for SBR, B(N)

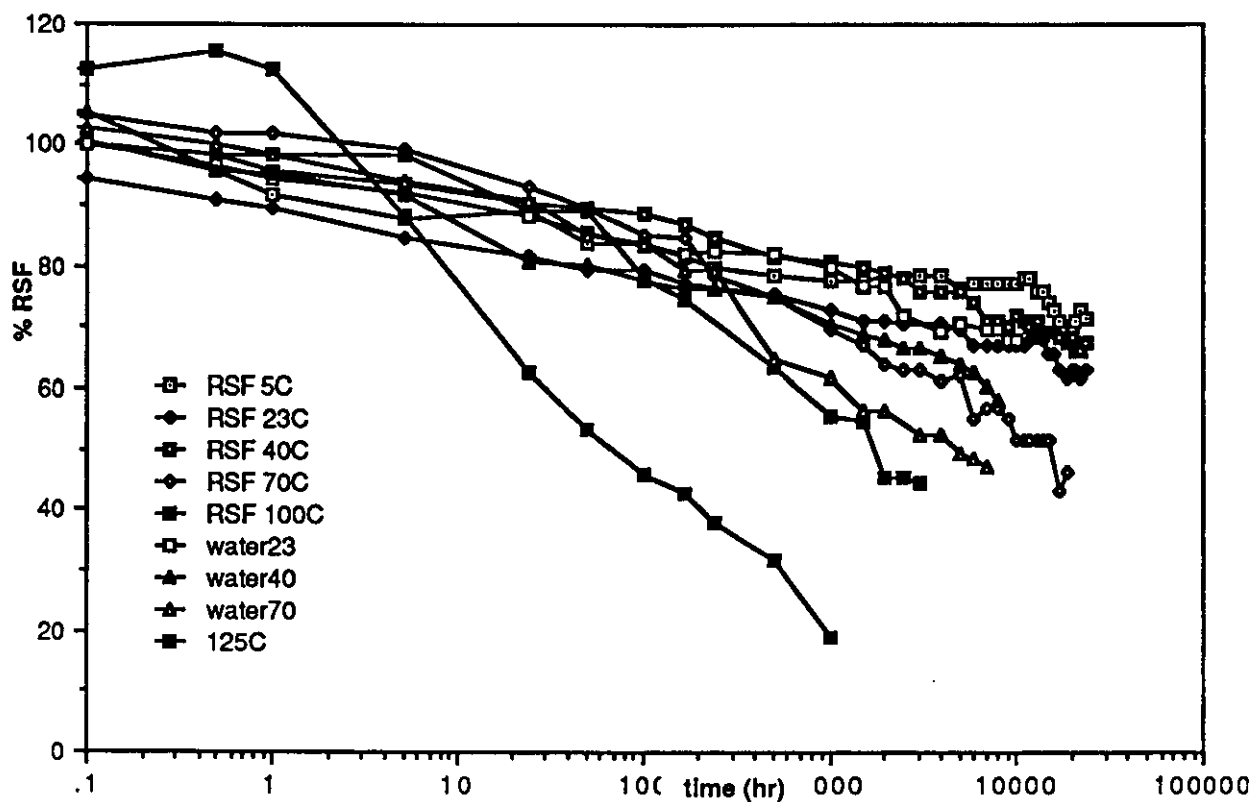


Figure 5 Compression stress relaxation curves for EPDM (Sulphur-cured), C(O)

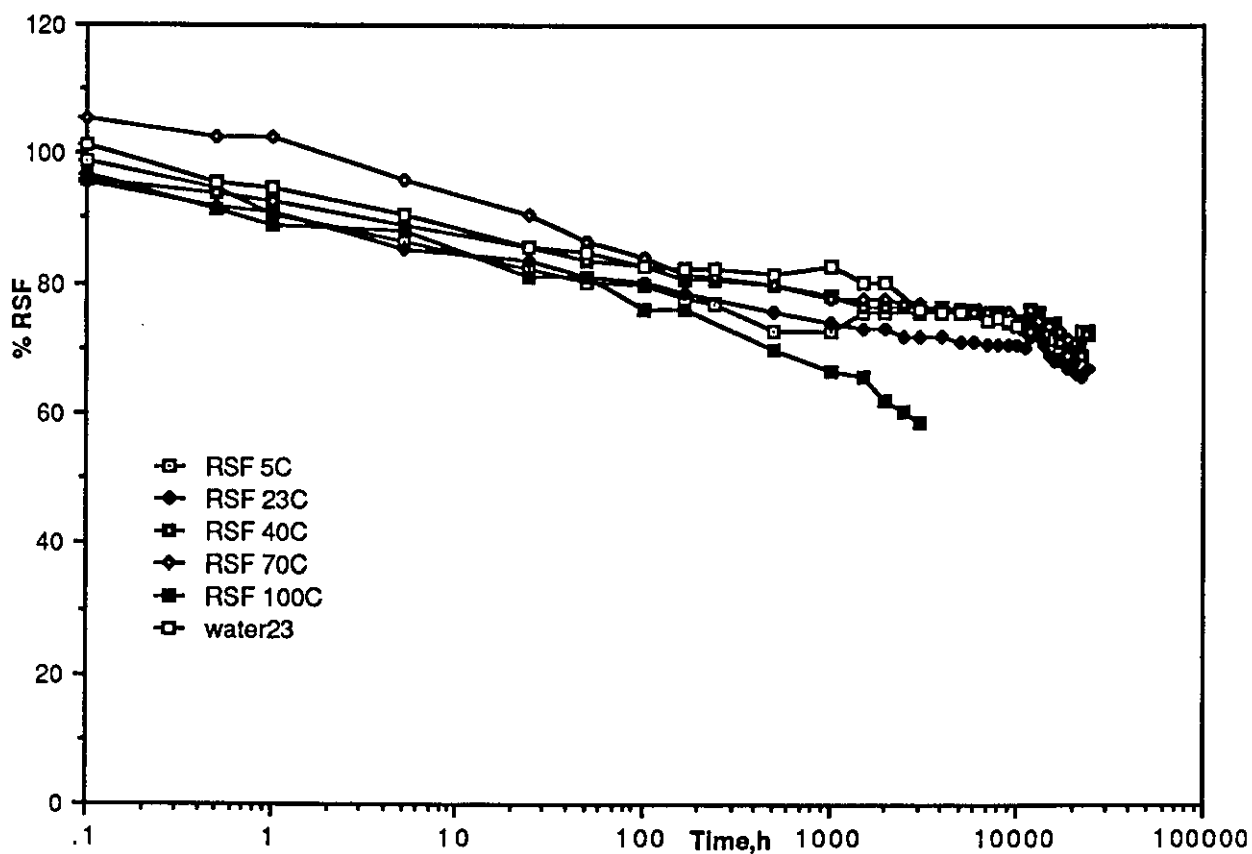


Figure 6 Compression stress relaxation curves for EPDM (Peroxide-cured), D(O)

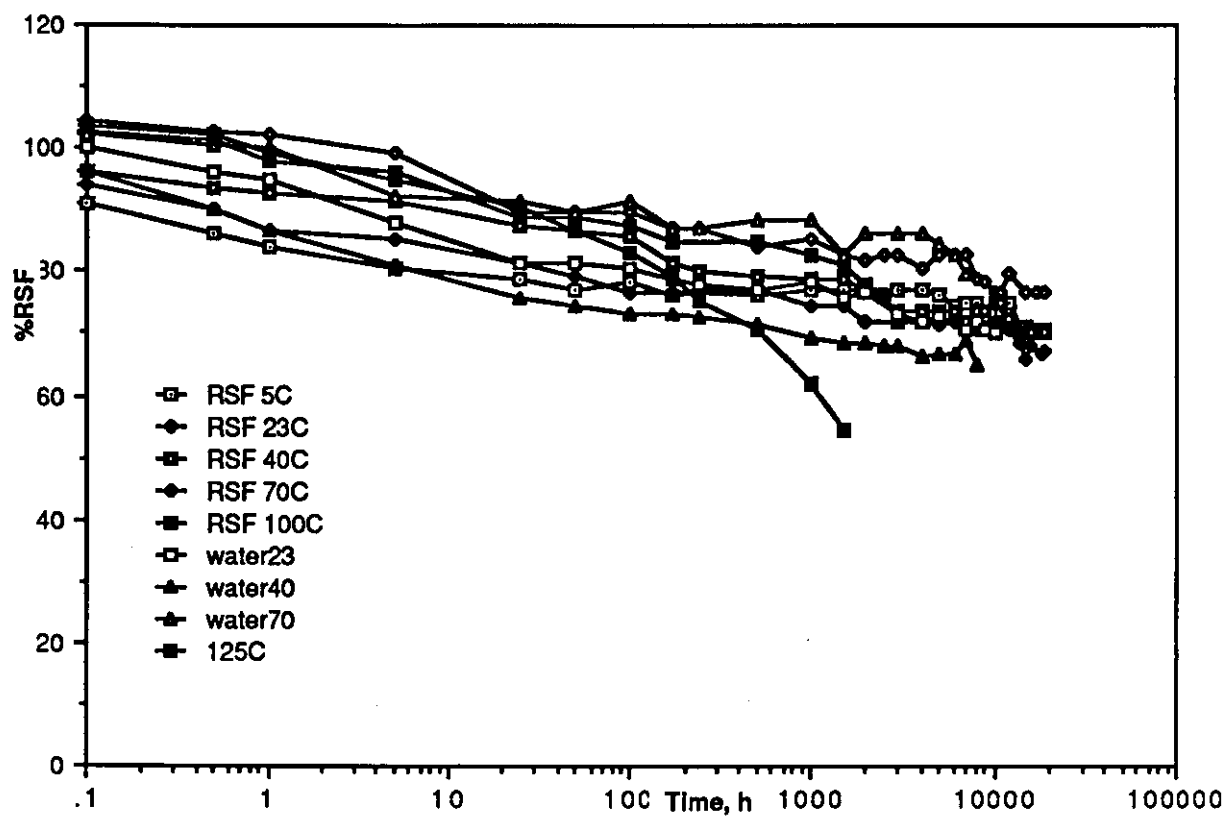


Figure 7 Compression stress relaxation curves for EPDM (peroxide-cured), D(N)

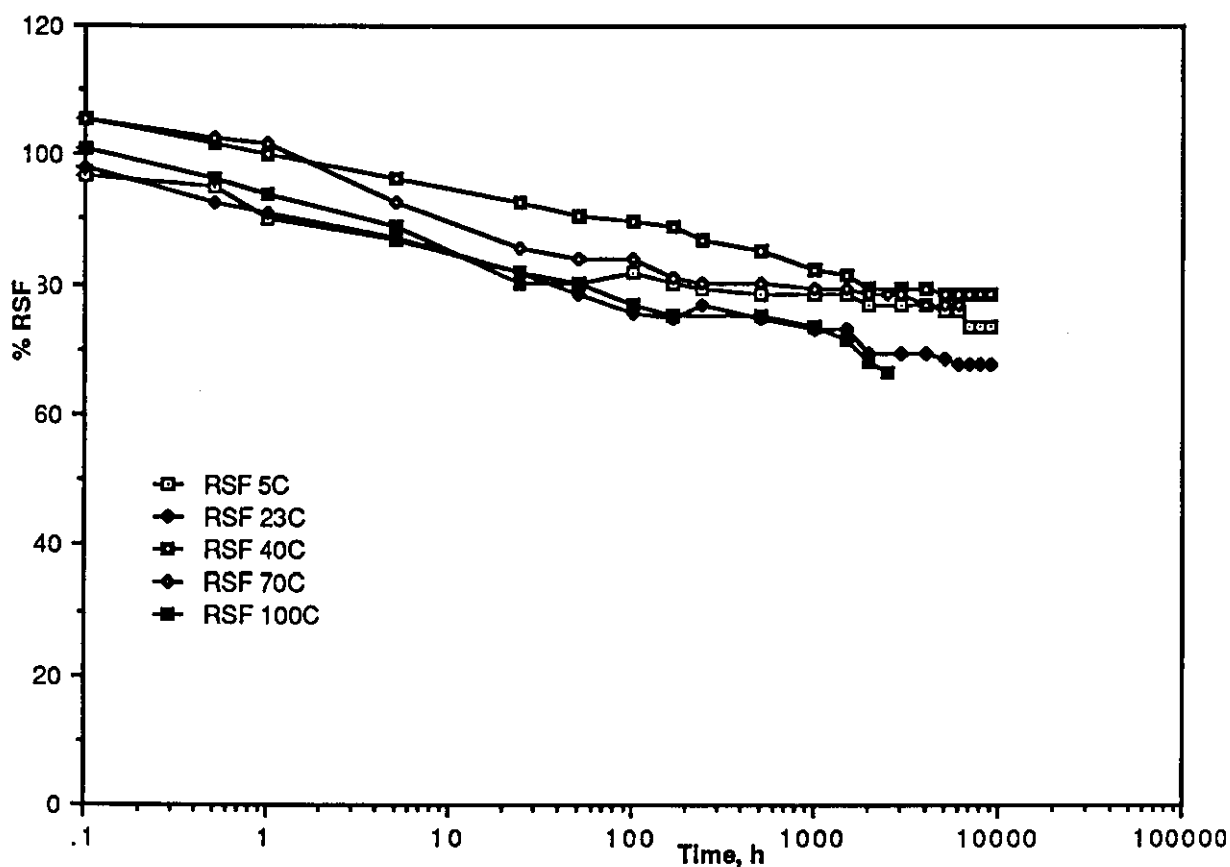


Figure 8 Compression stress relaxation curves for EPDM (Peroxide-cured), D(2)

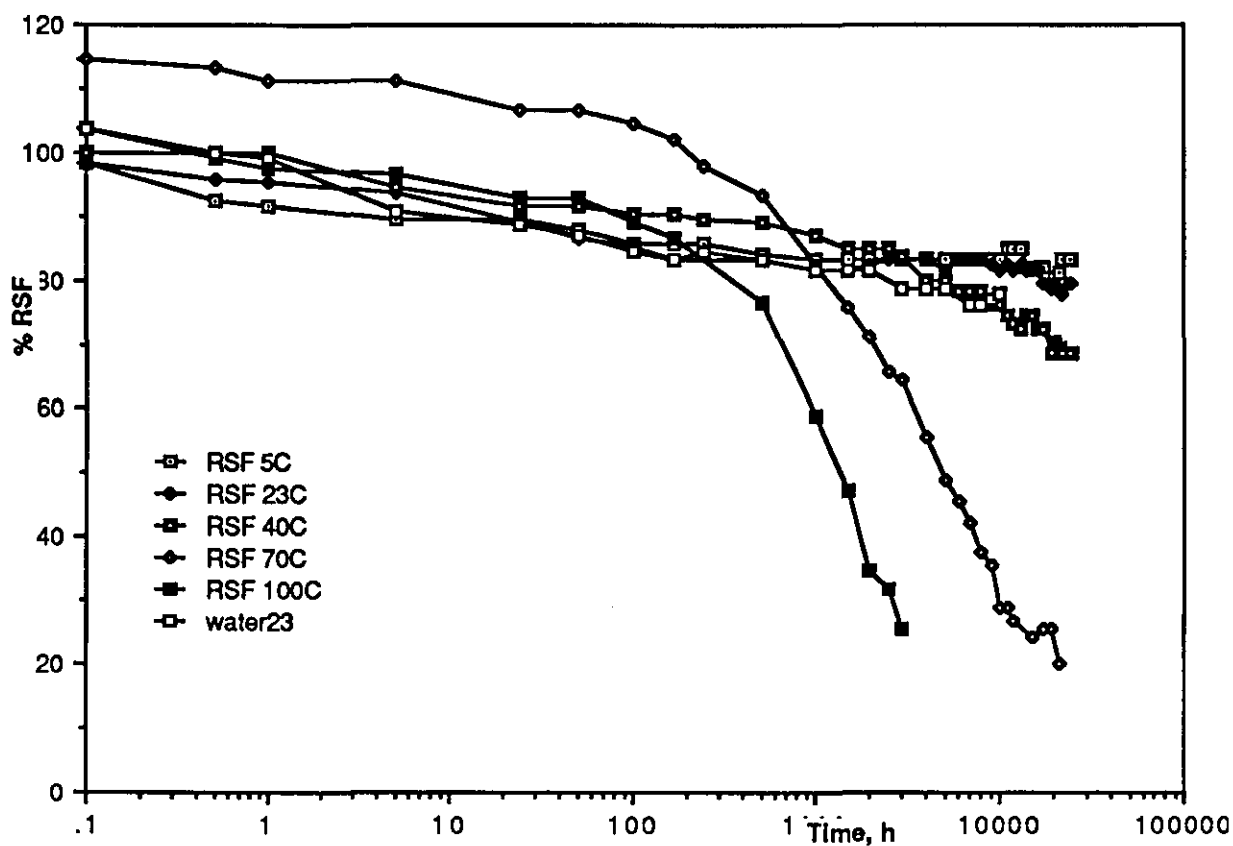


Figure 9 Compression stress relaxation curves for Nitrile rubber, E(O)

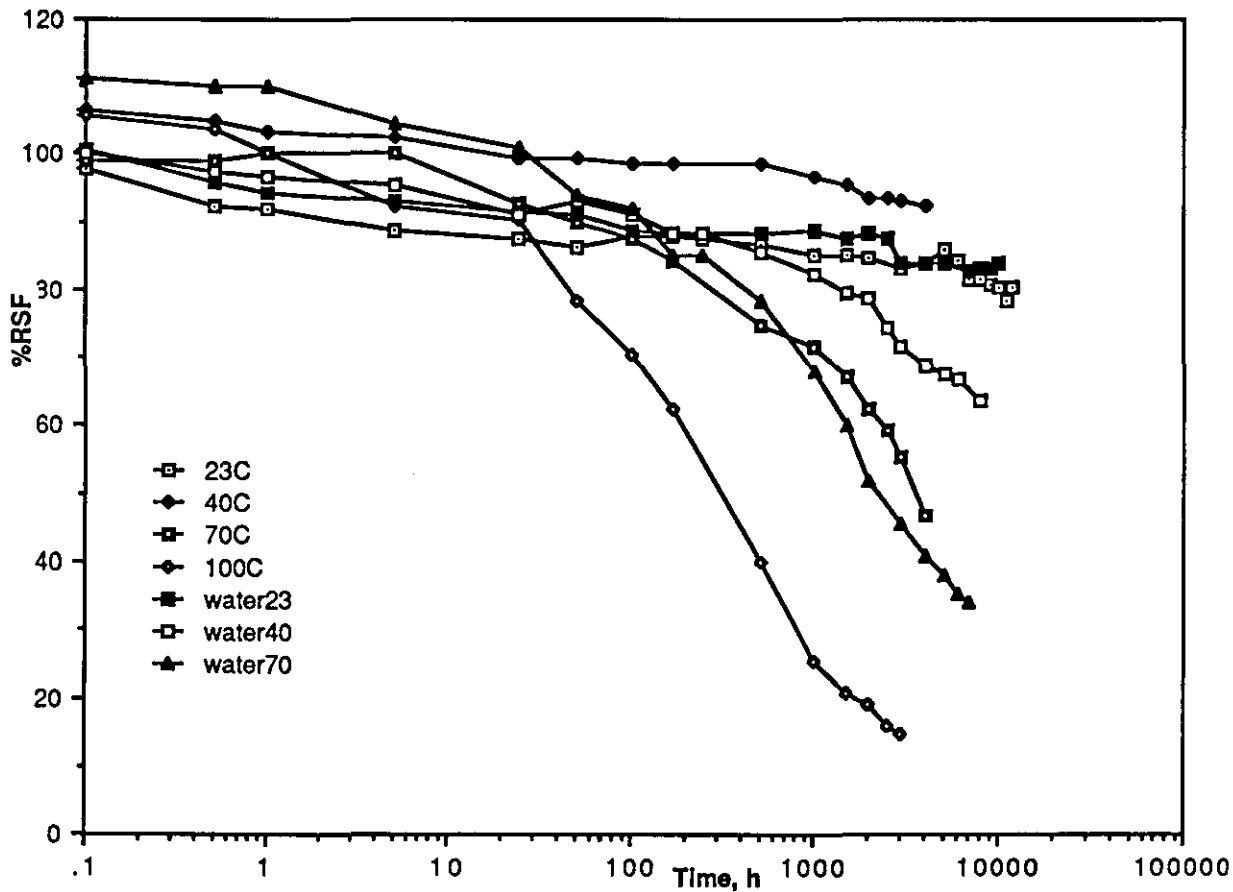


Figure 10 Compressive stress relaxation curves for Nitrile rubber, E(N)

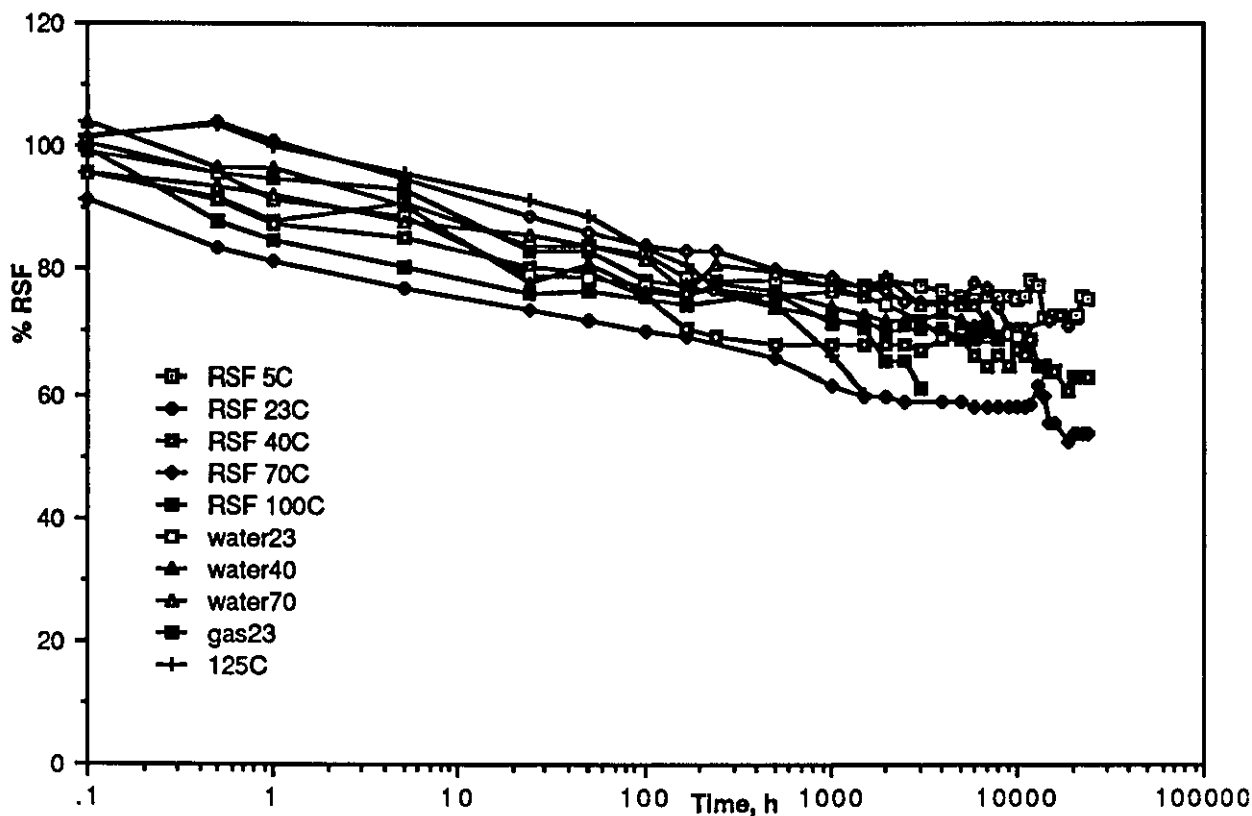


Figure 11 Compression stress relaxation curves for EPDM (Peroxide-cured), F(O)

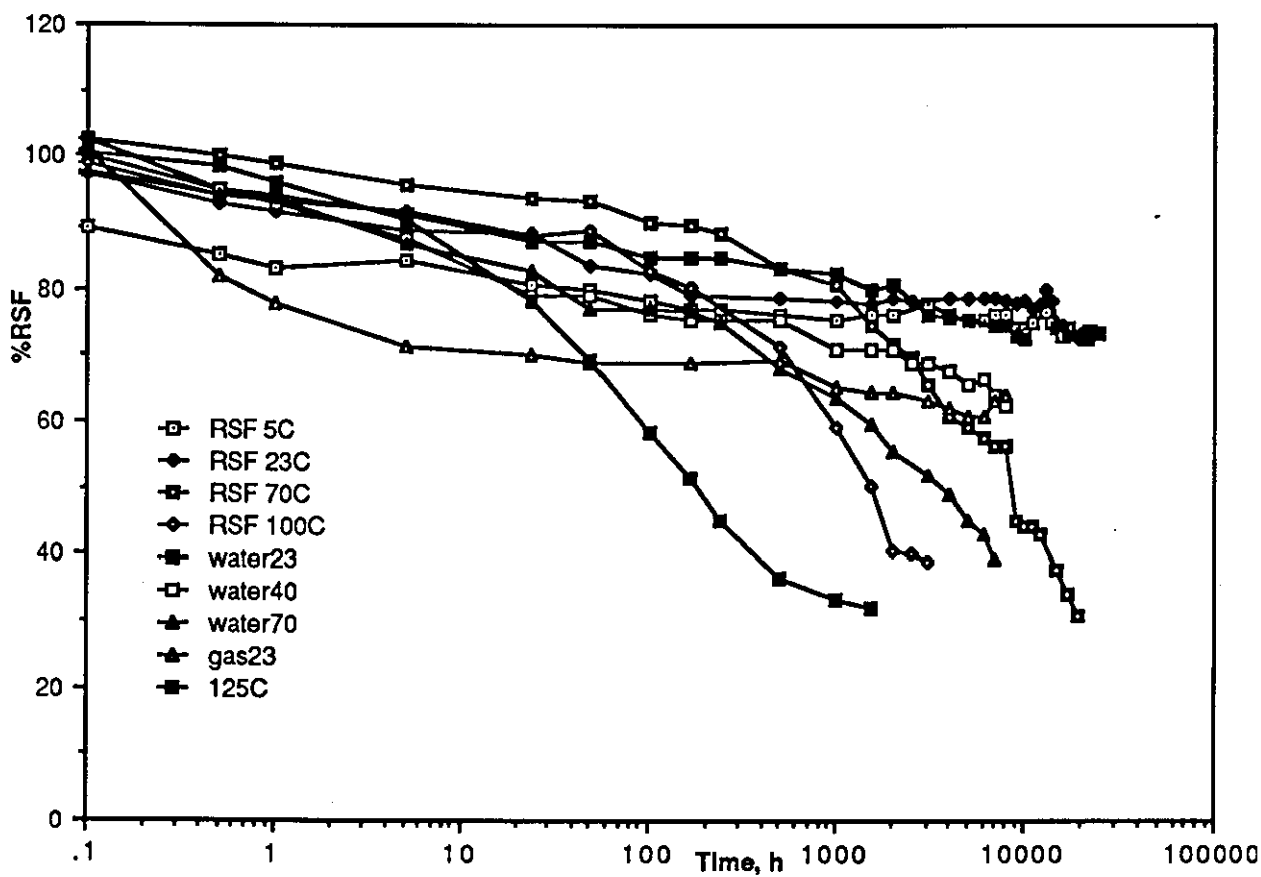


Figure 12 Compression stress relaxation curves for Nitrile rubber, G(O)

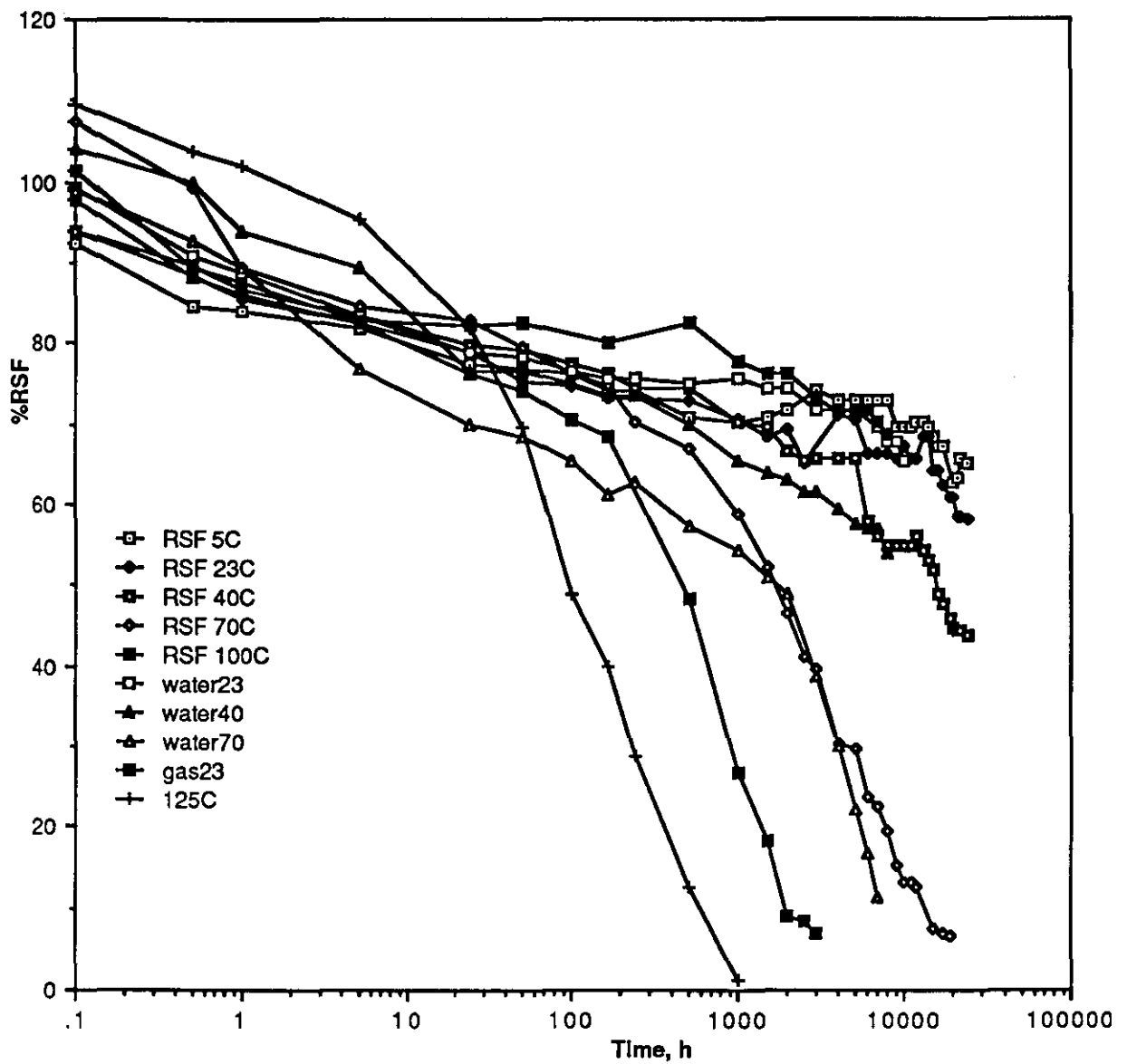


Figure 13 Compression stress relaxation curves for Epichlorohydrin, H(O)

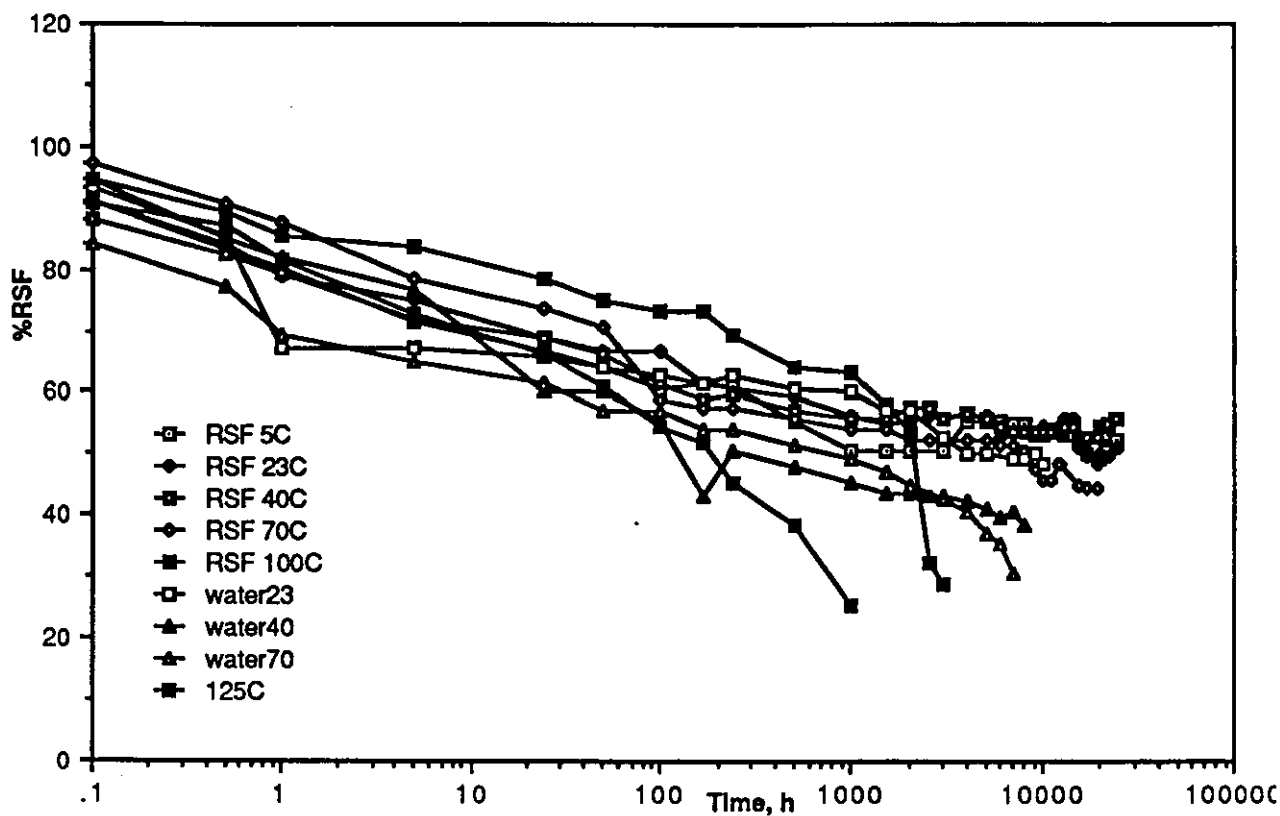


Figure 14 Compression stress relaxation curves for Santoprene 101-55, I(O)

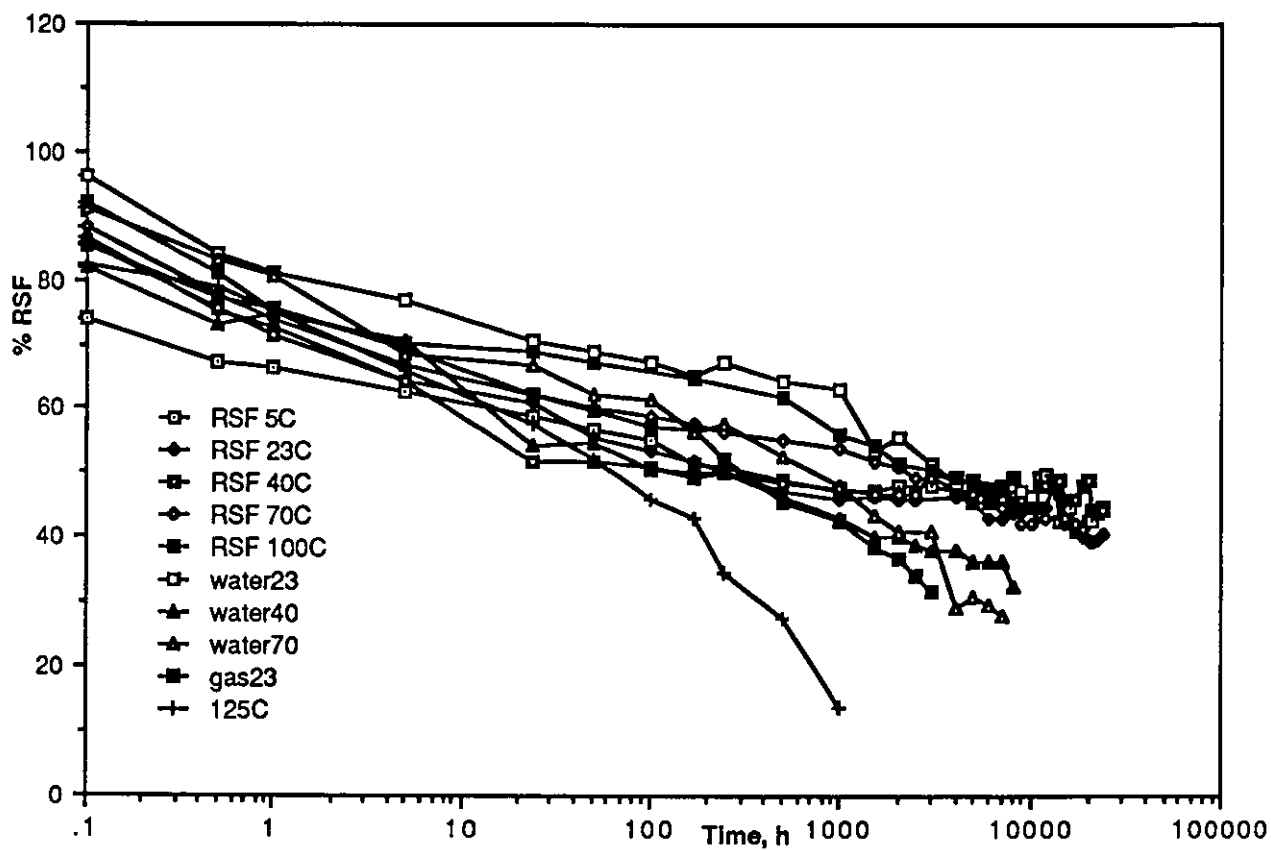


Figure 15 Compression stress relaxation curves for Santoprene 101-64, J(O)

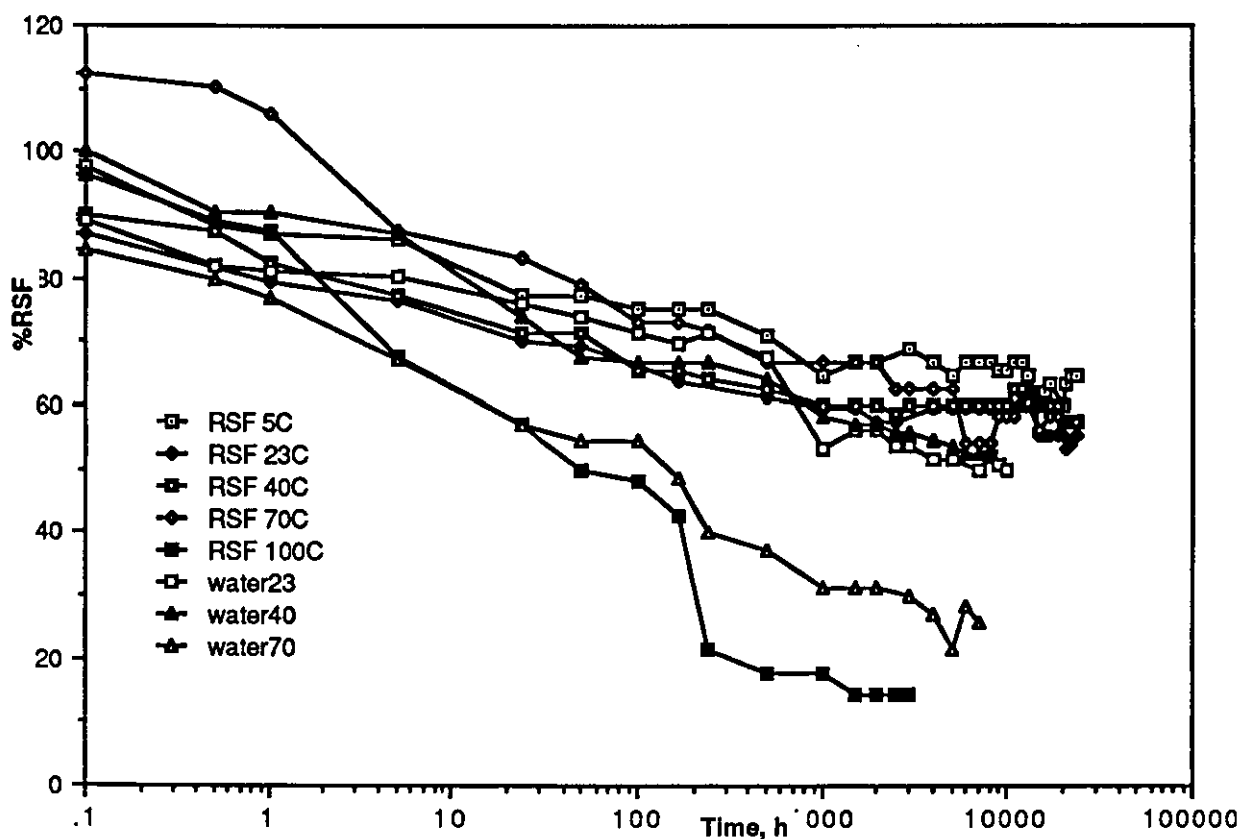


Figure 16 Compression stress relaxation curves for Evoprene 992, K(O)

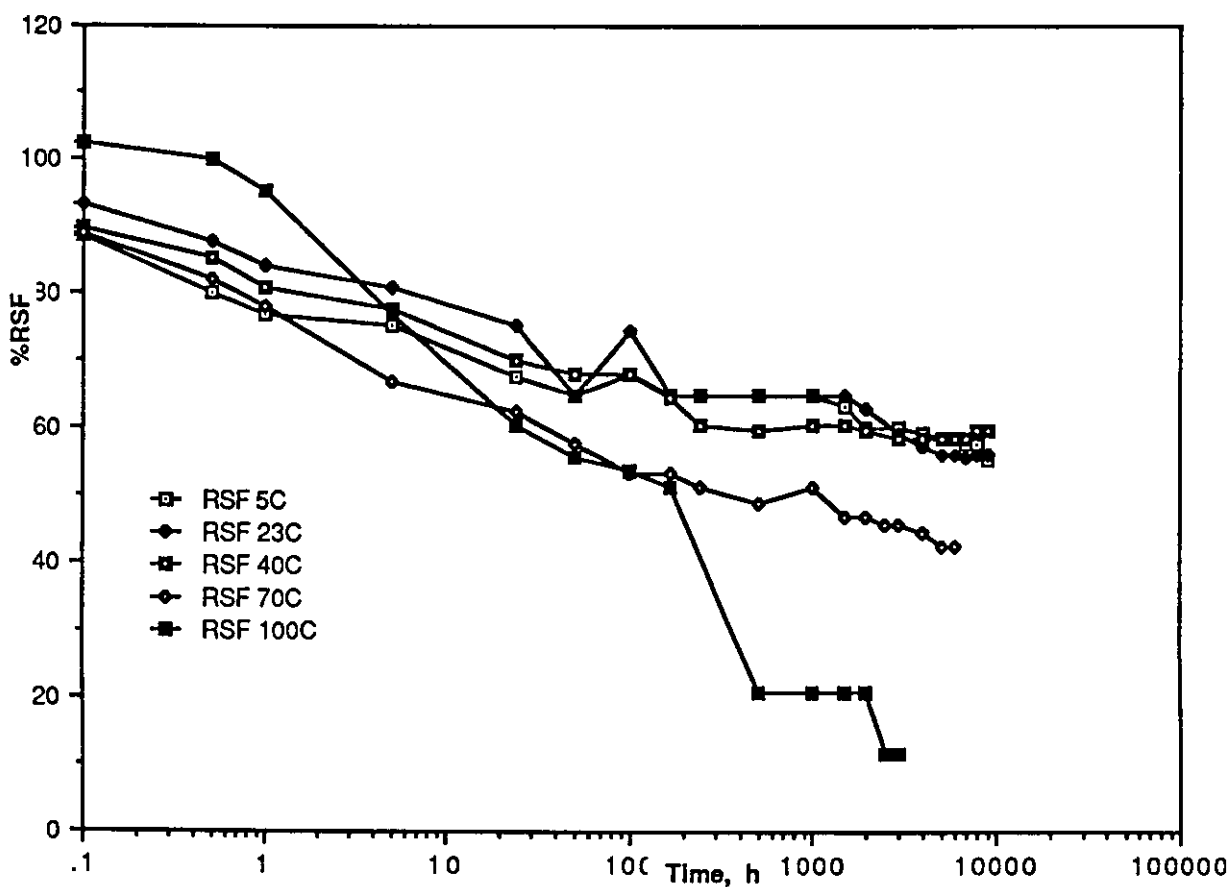


Figure 17 Compression stress relaxation curves for Evoprene 992/994, K(mix)

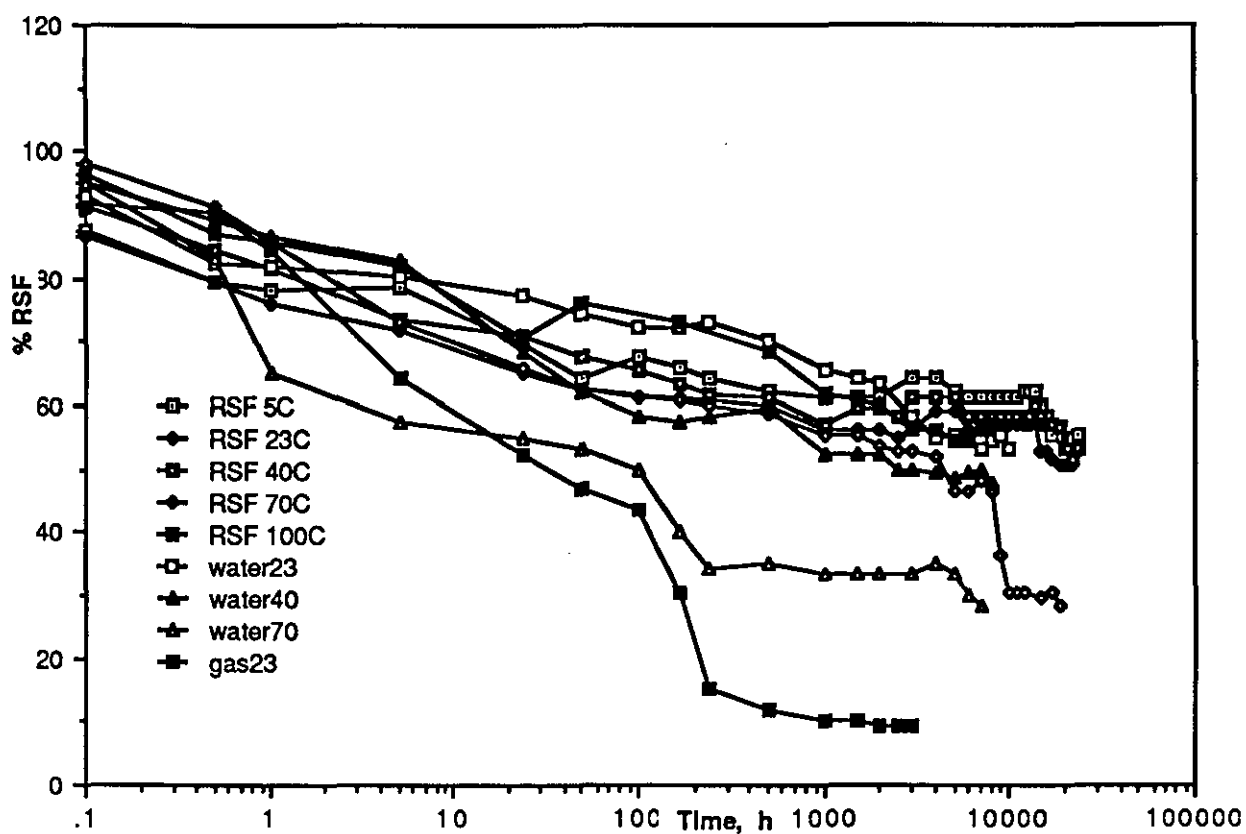


Figure 18 Compression stress relaxation curves for Evoprene 994, L(O)

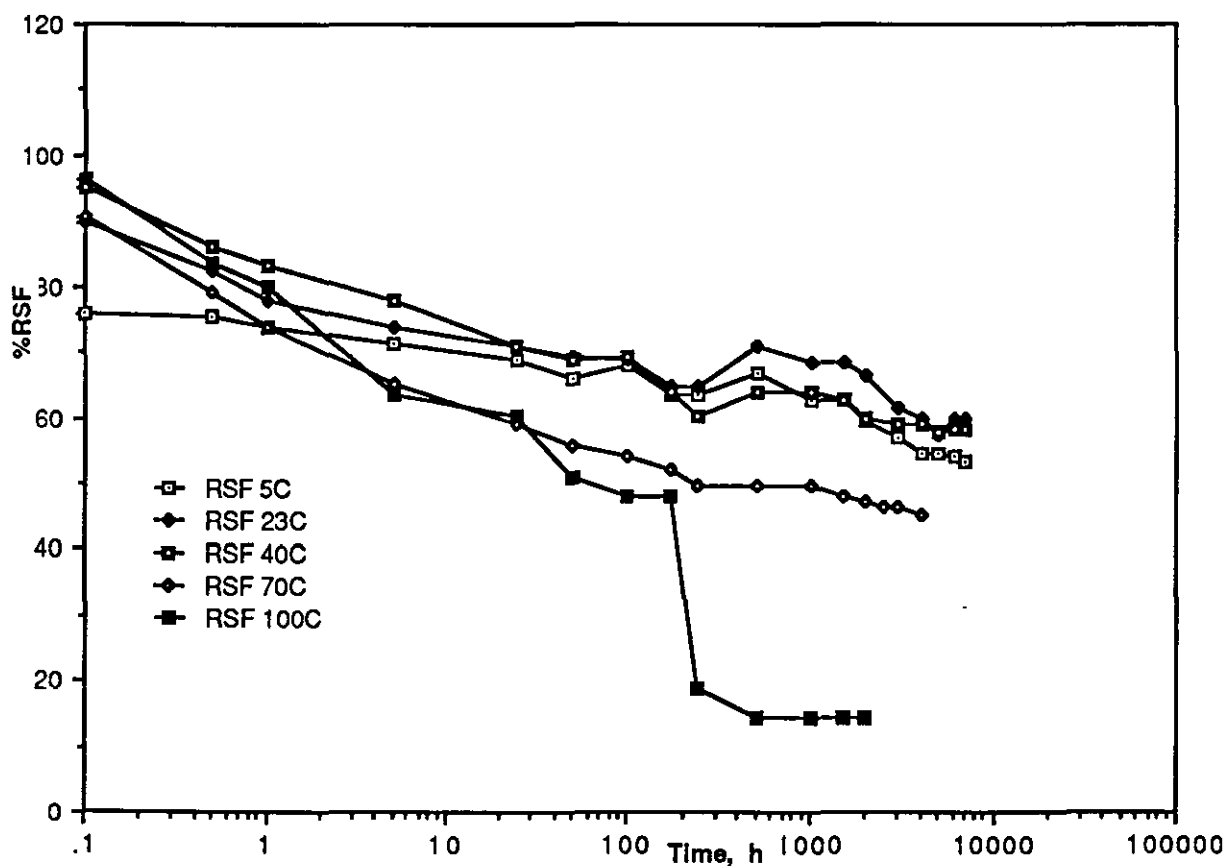


Figure 19 Compression stress relaxation curves for Evoprene 994.2, L(2)

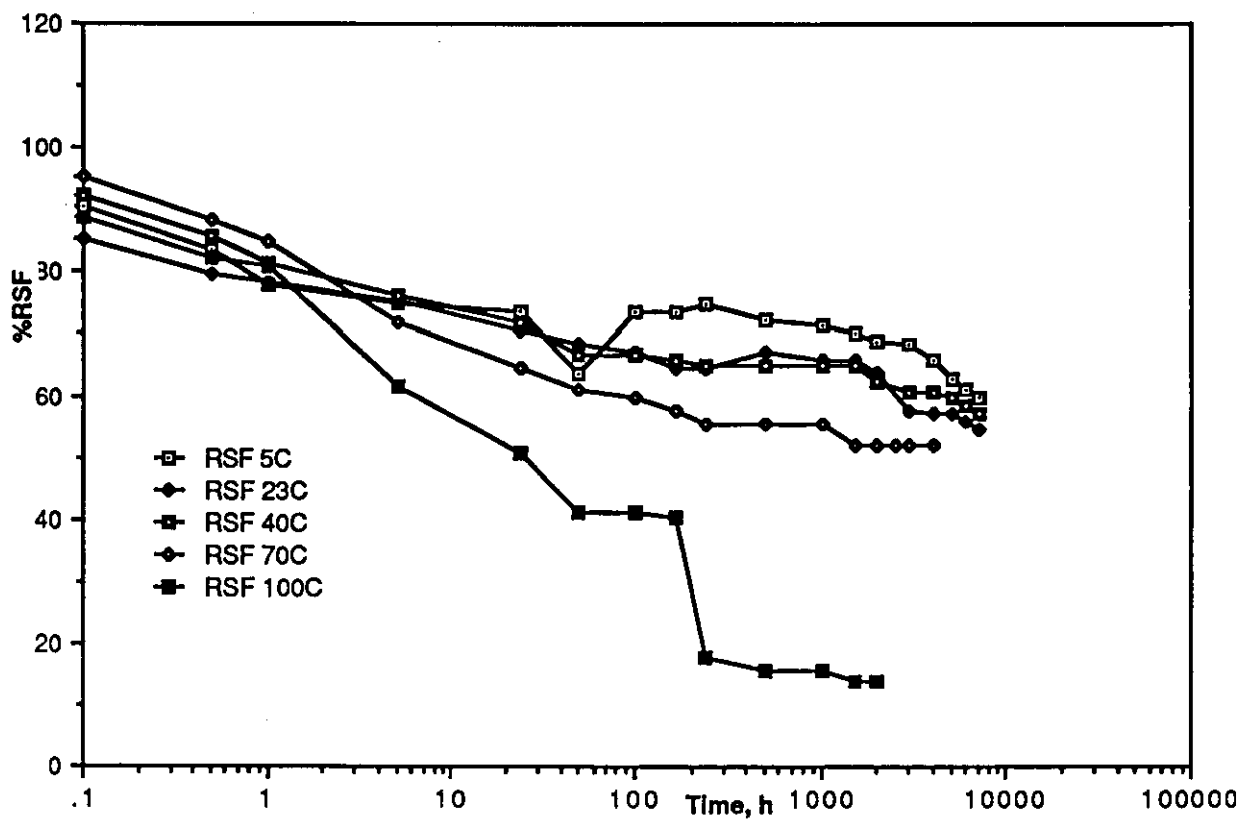


Figure 20 Compression stress relaxation curves for Evoprene 994.3, L(3)

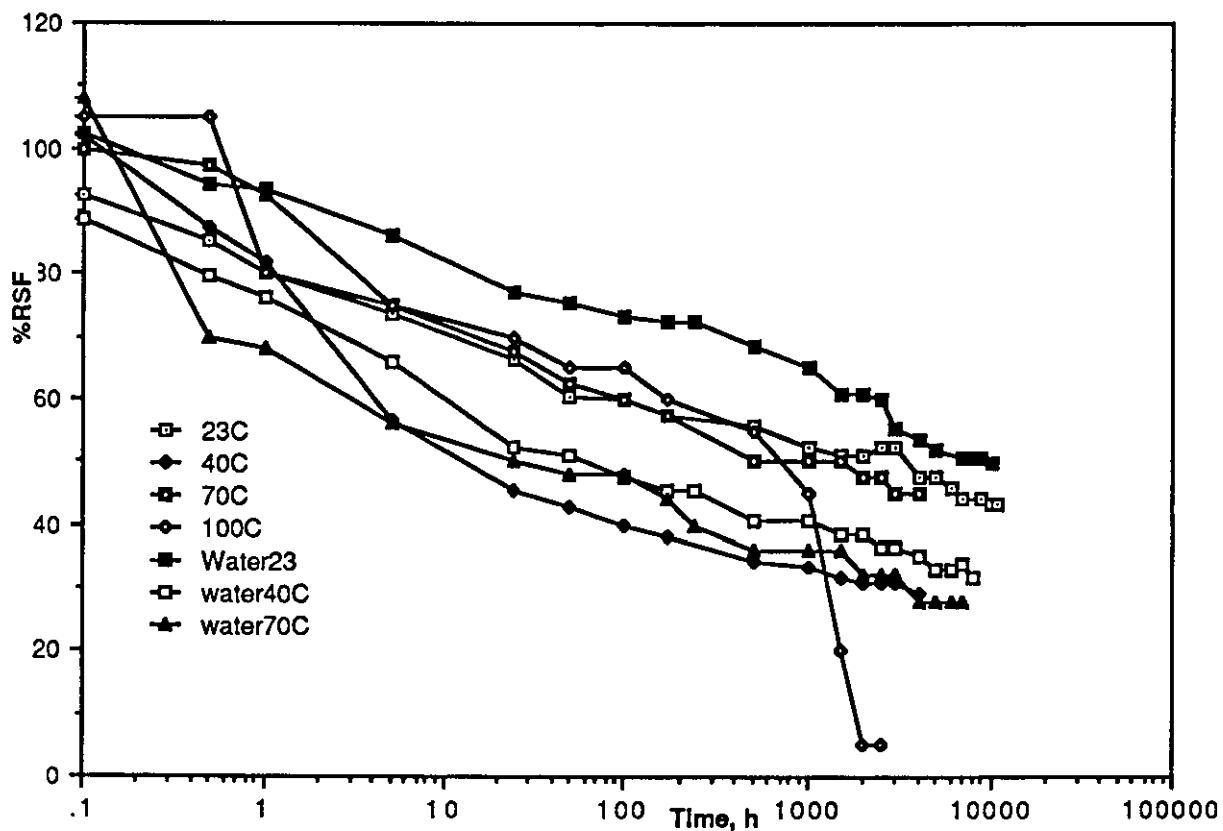


Figure 21 Compression stress relaxation curves for Alcryn 6368, M(O)

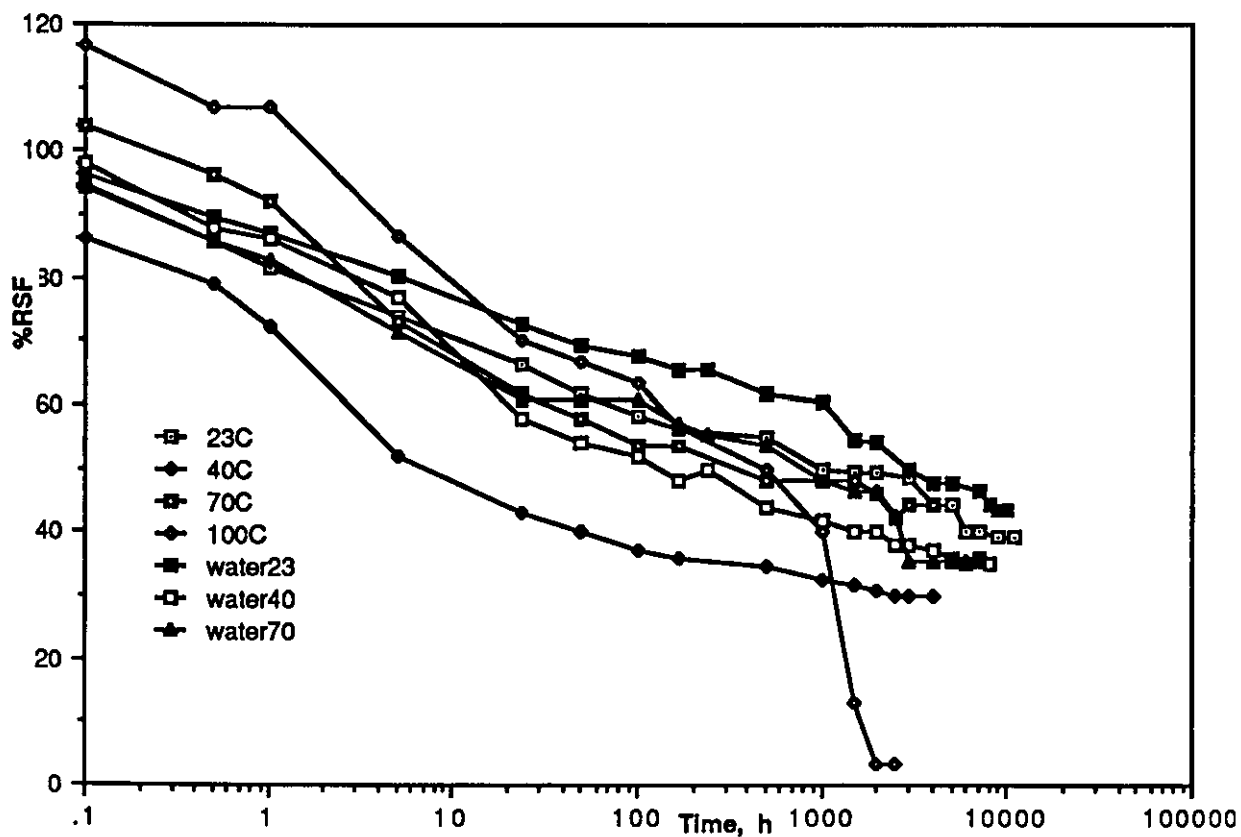


Figure 22 Compression stress relaxation curves for Alcryn 6385, N(O)

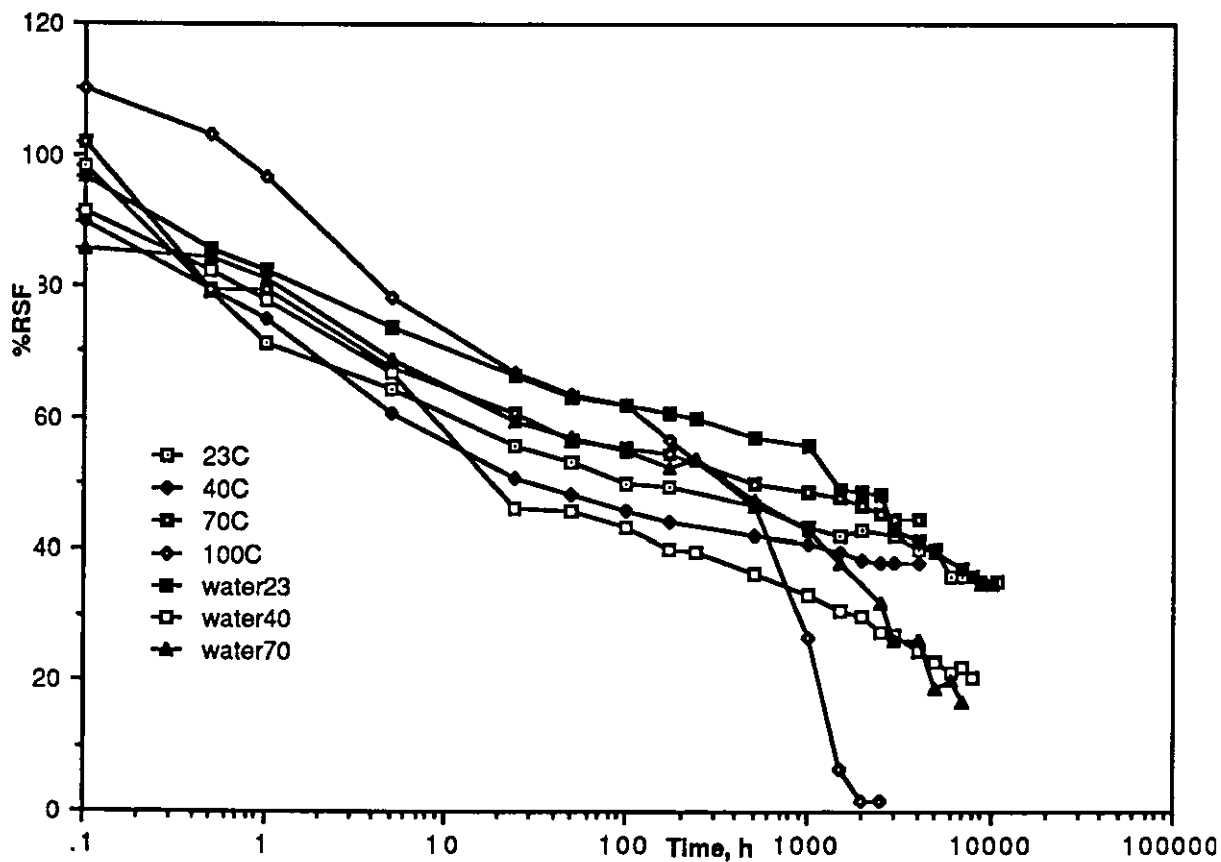
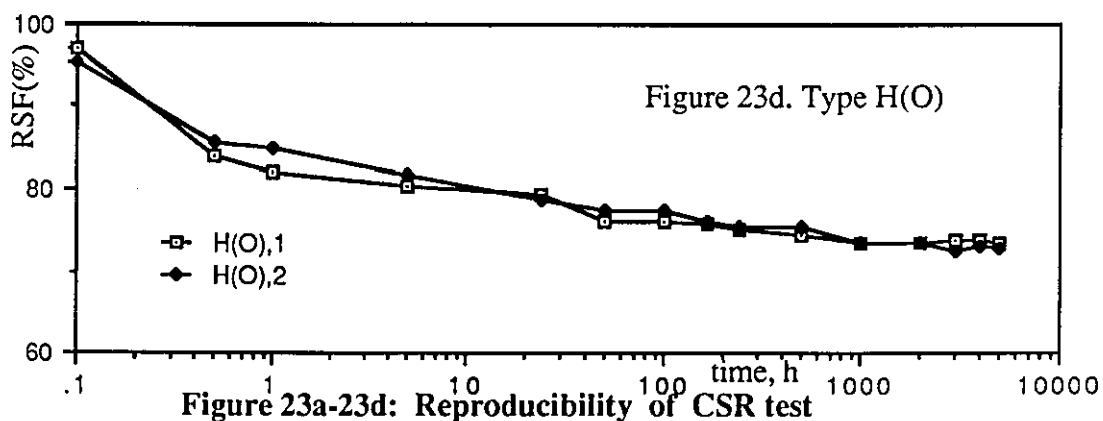
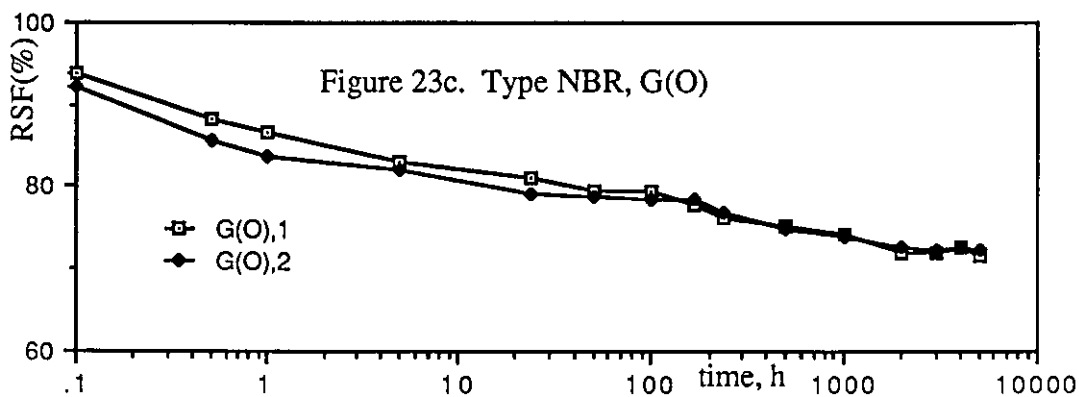
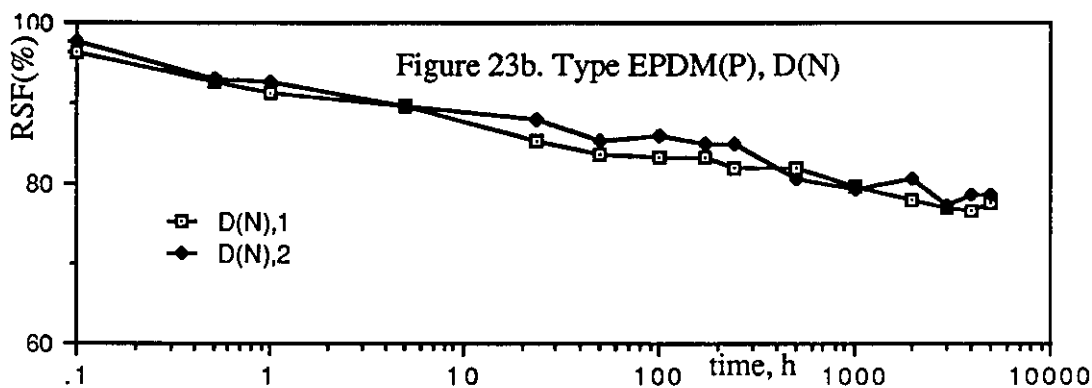
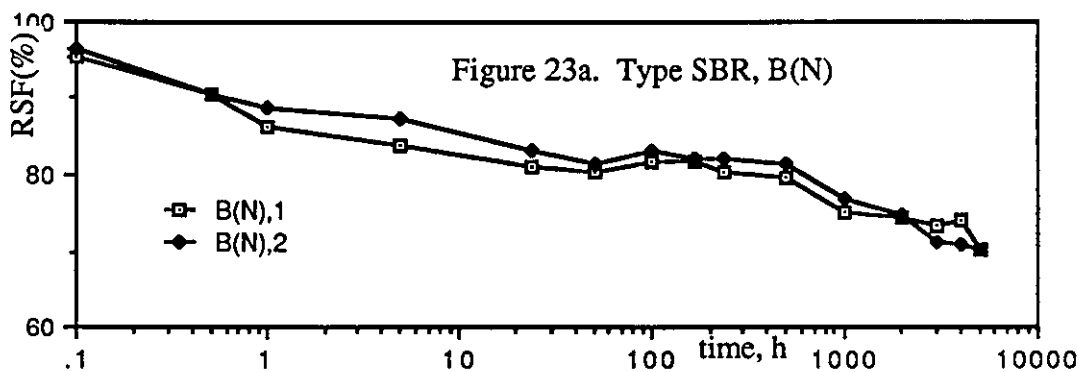


Figure 23 Compression stress relaxation curves for Alcryn 1201, O(O)



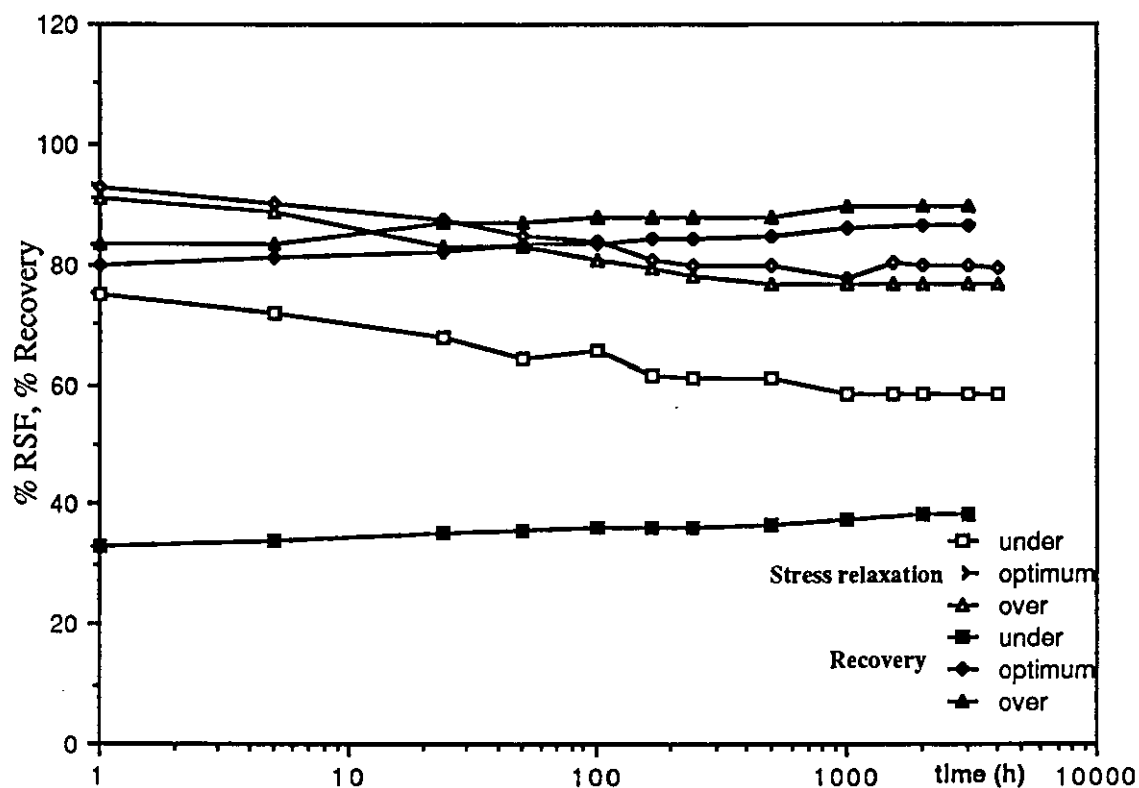


Figure 24. CSR and Recovery curves for a SBR(S), B(O), at 23C

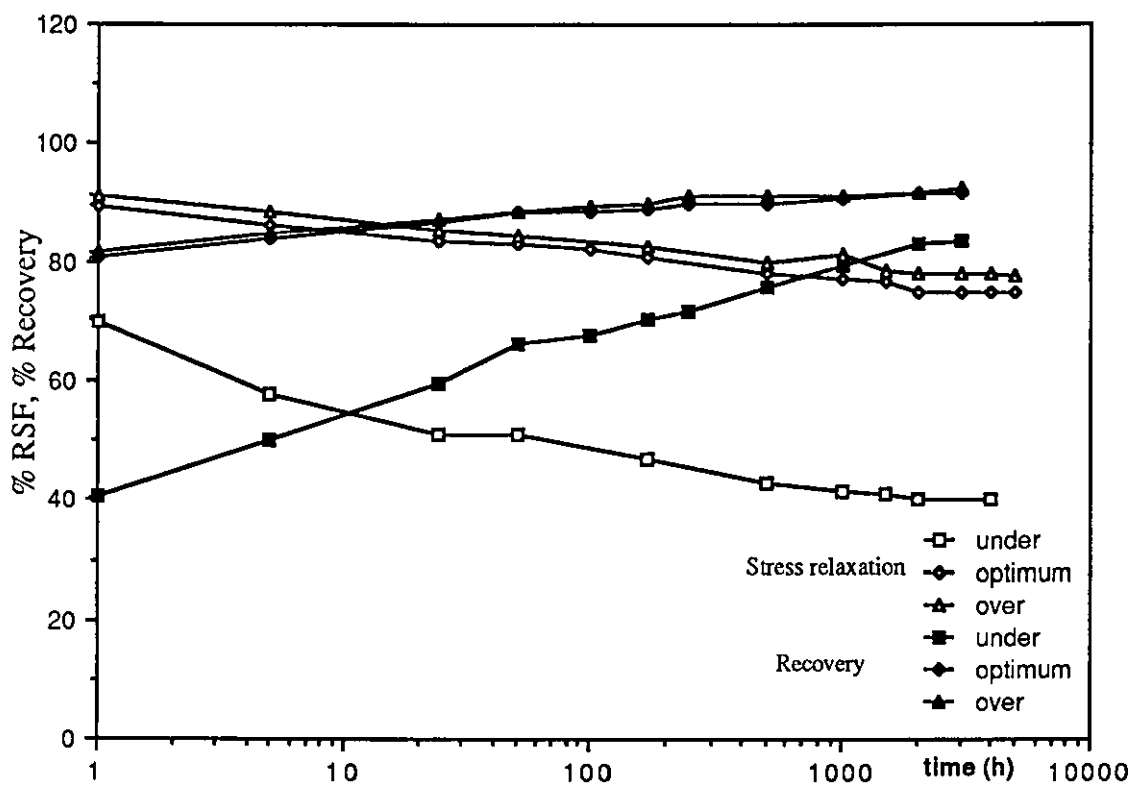


Figure 25. CSR and Recovery curves for the EPDM (P), D(O), at 23C

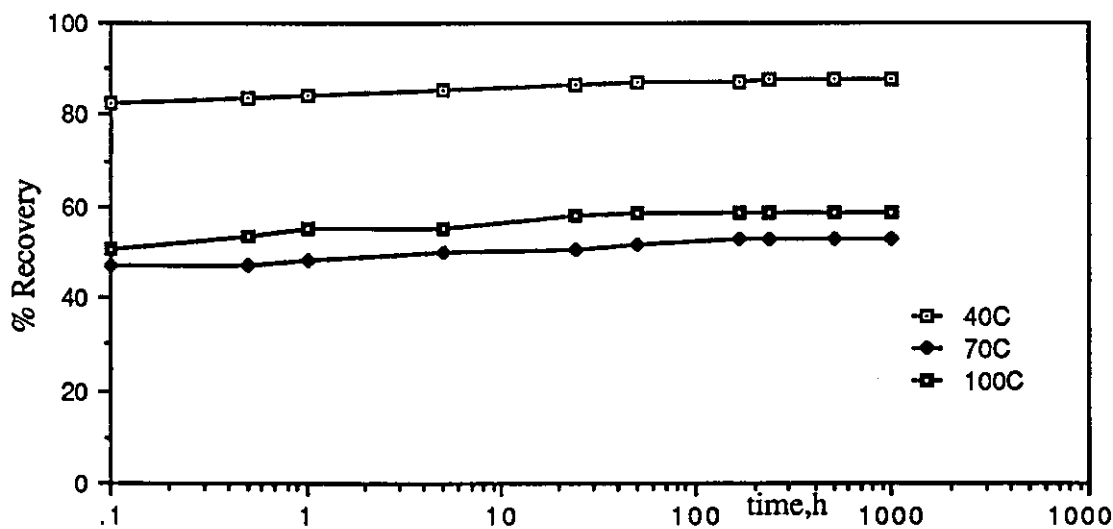


Figure 26: Recovery curves for Natural rubber, A(N), after 1000 h. in compression

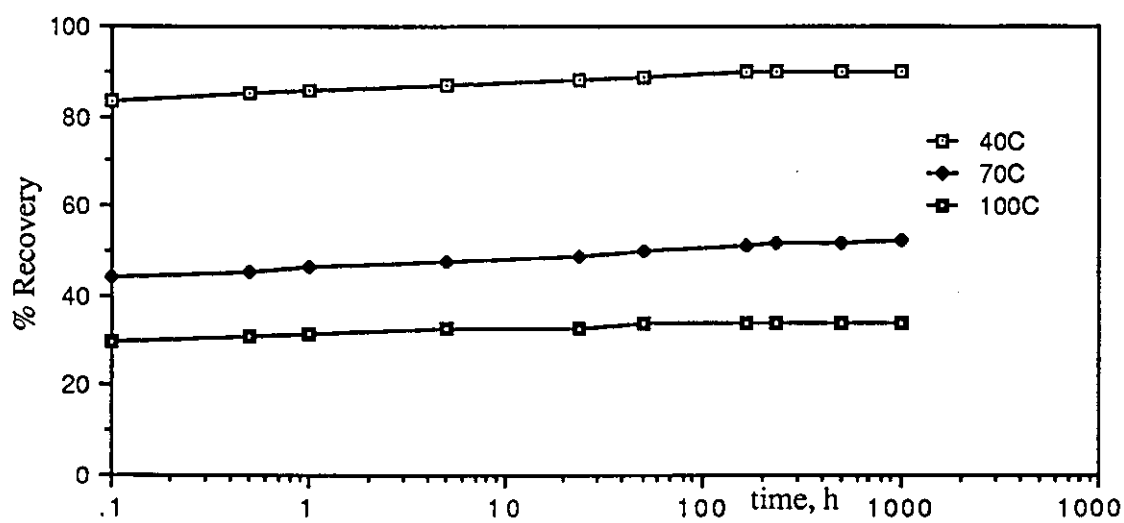


Figure 27: Recovery curves for SBR, B(N), after 1000 h. in compression

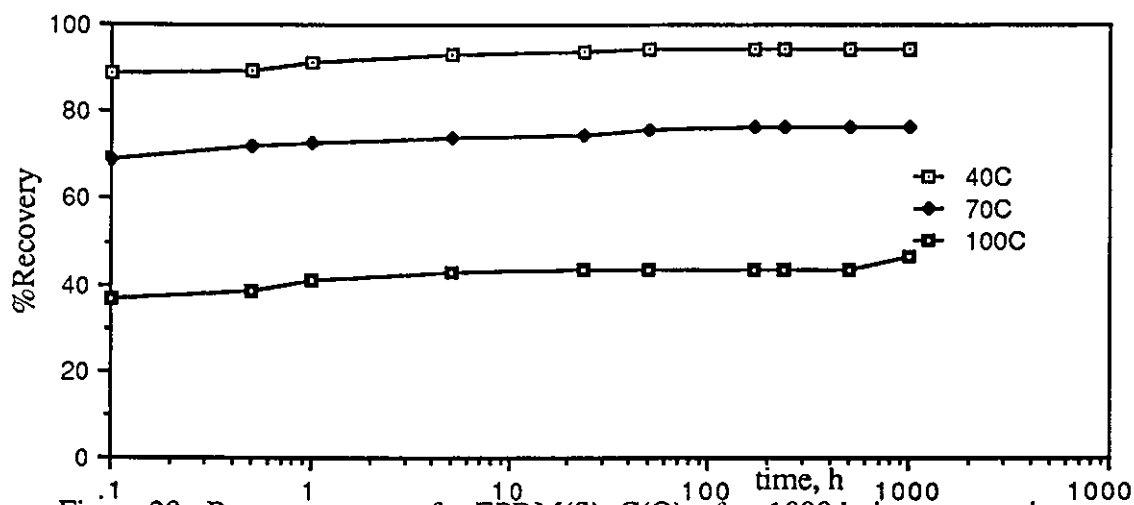


Figure 28: Recovery curves for EPDM(S), C(O), after 1000 h. in compression

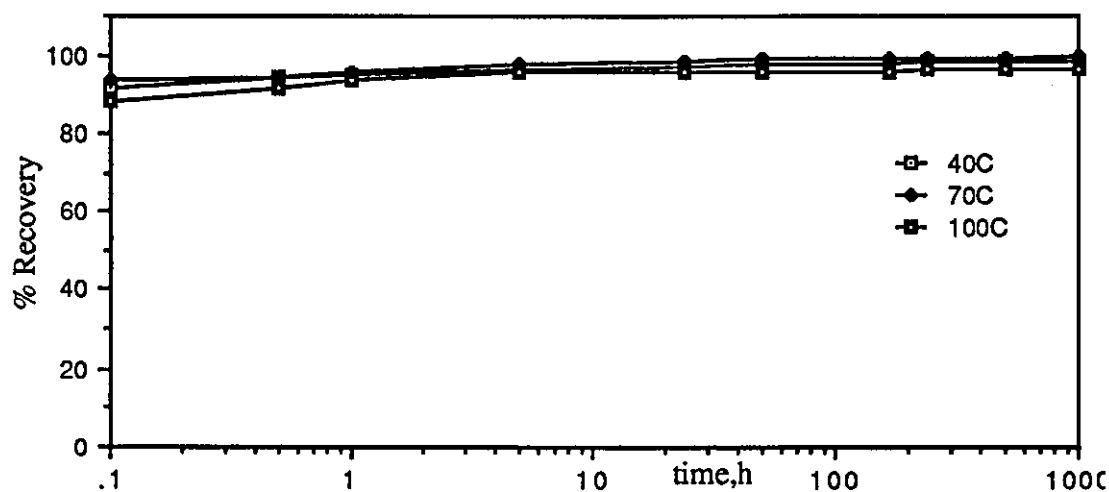


Figure 29: Recovery curves for EPDM(P), D(N), after 1000 h. in compression

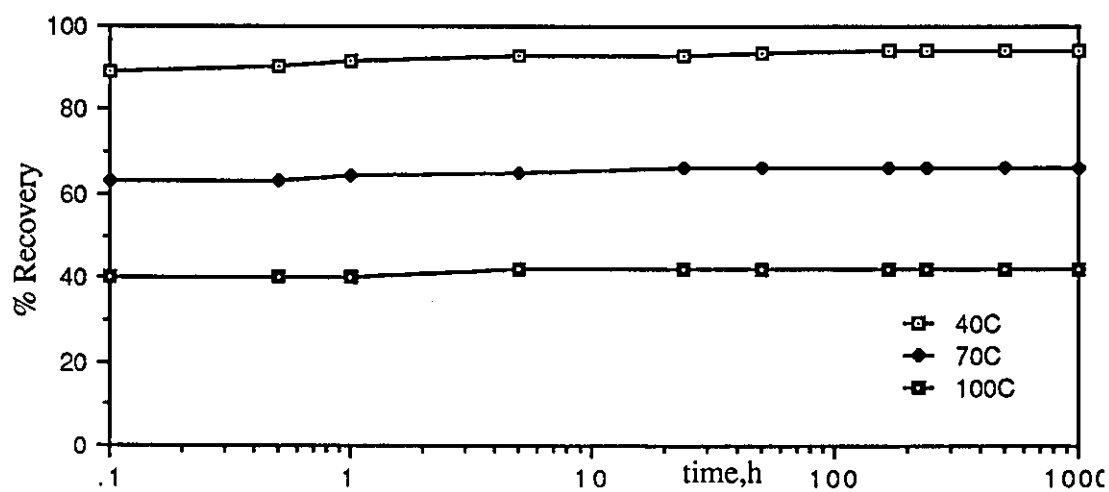


Figure 30: Recovery curves for Nitrile rubber, E(O), after 1000 h. in compression

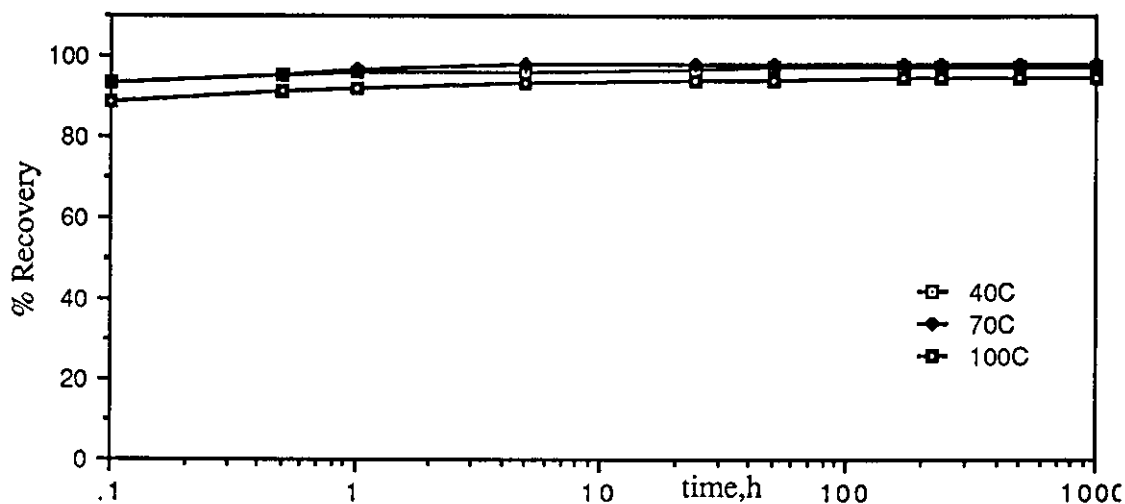


Figure 31: Recovery curves for EPDM(P), F(O), after 1000 h. in compression

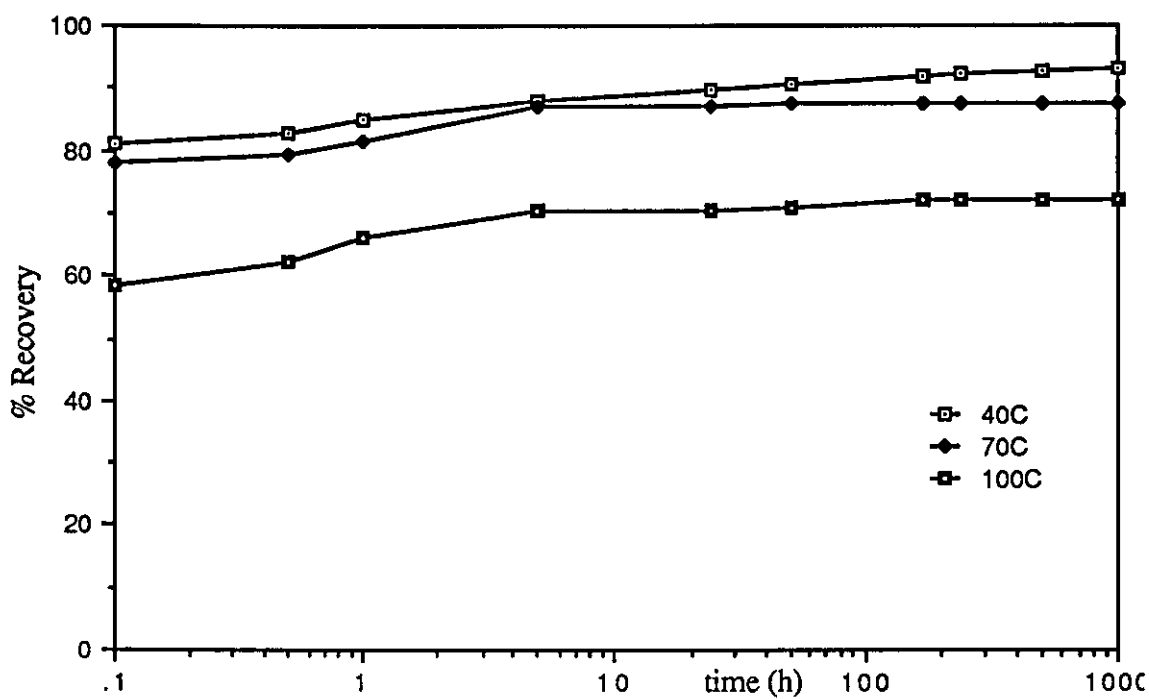


Figure 32: Recovery curves for Santoprene101.55, I(O), after 1000h. in compression

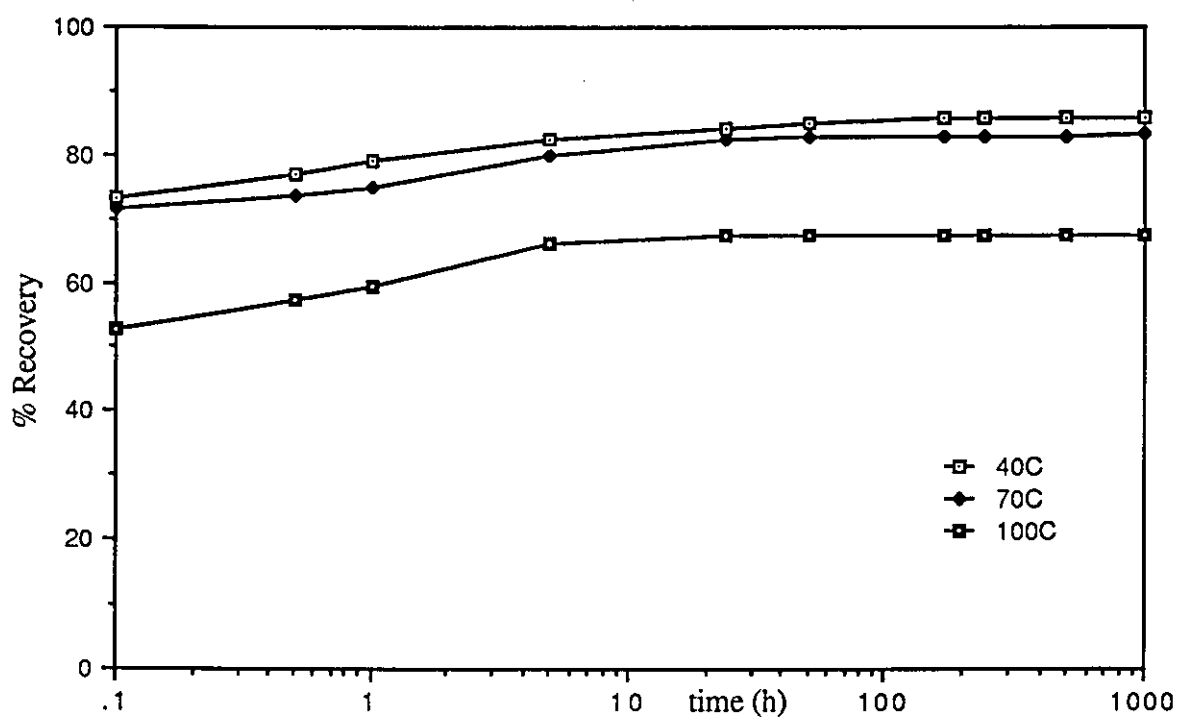


Figure 33. Recovery curves for Santoprene101.64, J(O), after 1000h in compression

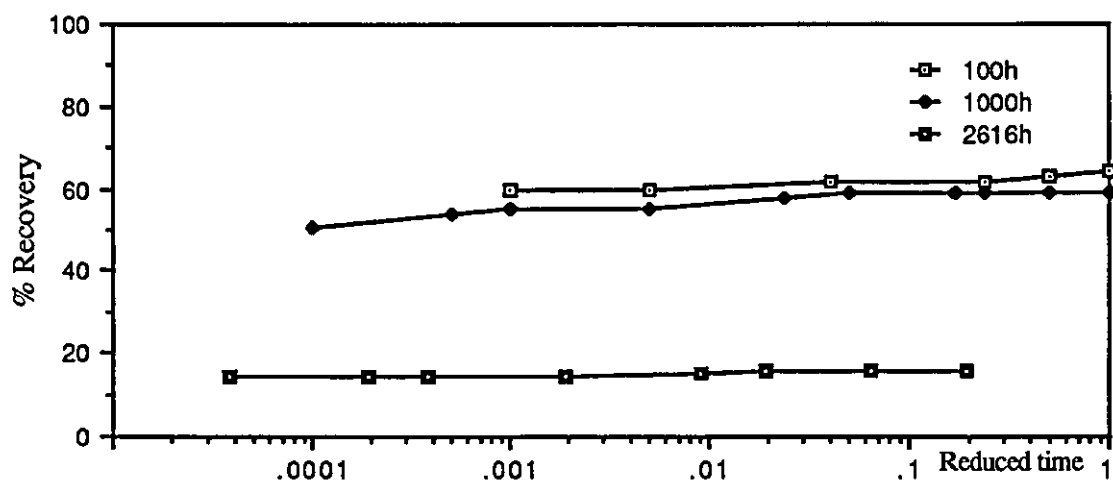


Figure 34: Recovery data for NR ,A(N), with varying time in compression

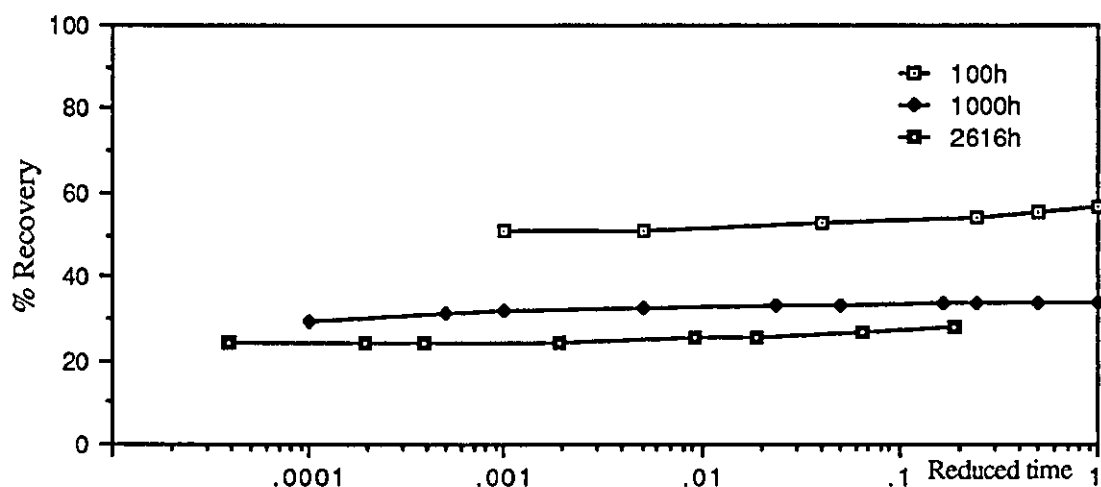


Figure 35: recovery data for SBR,B(N), with varying time in compression

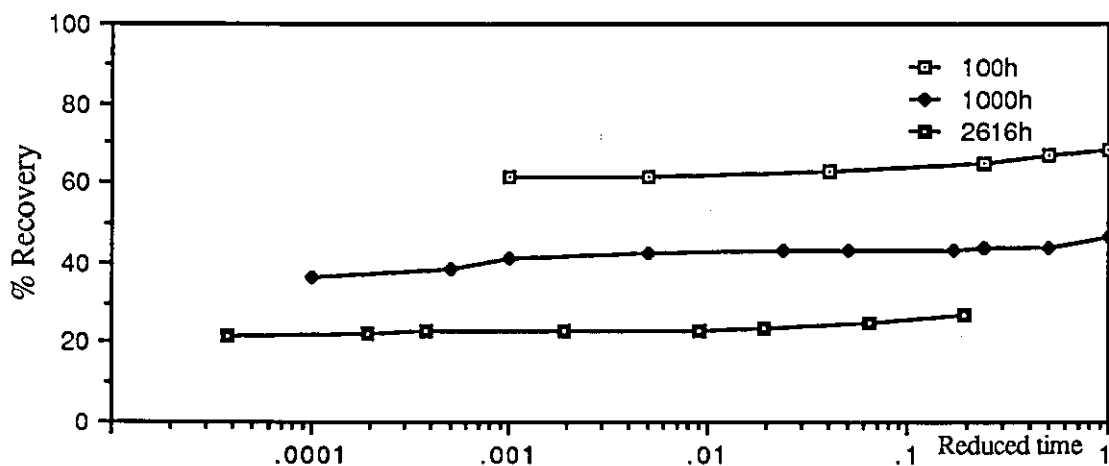


Figure 36: Recovery data for EPDM(S),C(O), with varying time in compression

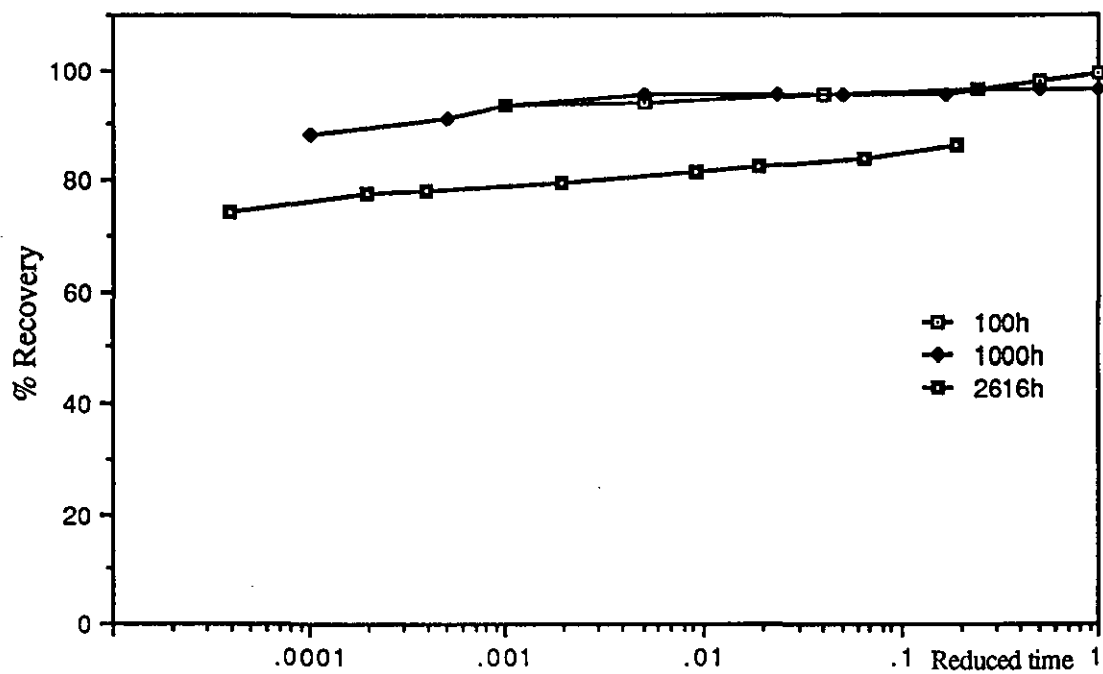


Figure 37: Recovery data for EPDM(P),D(N), with varying time in compression

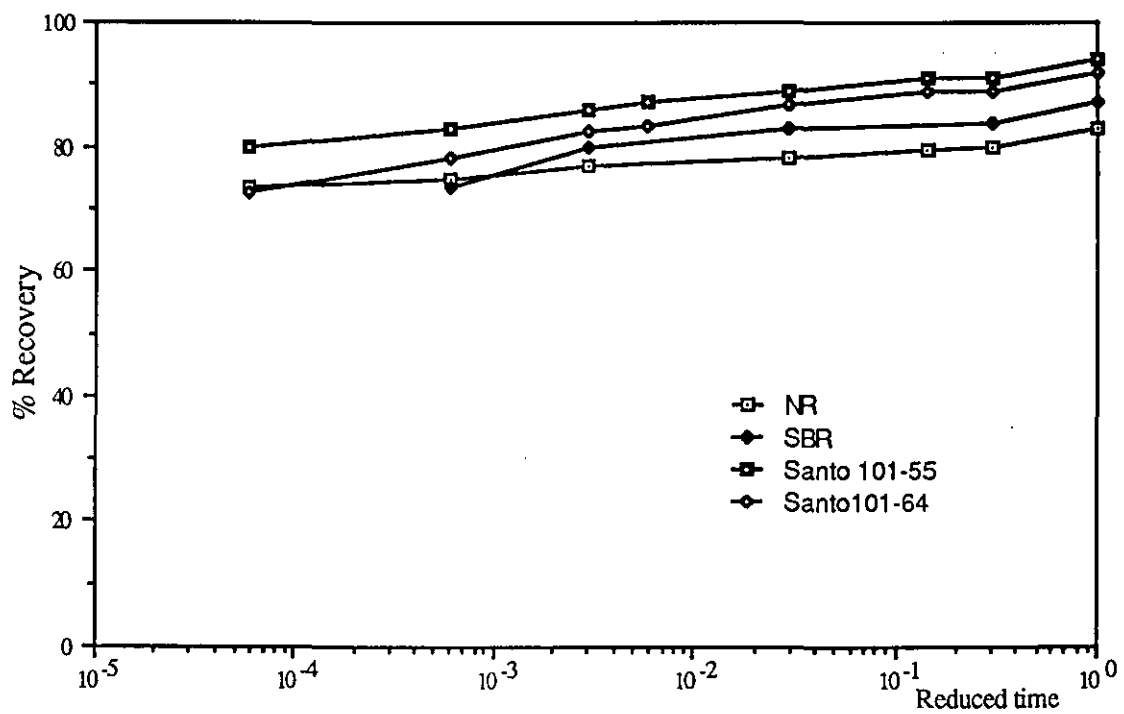


Figure 38: Tensile recovery data (50% strain) at 70C, after 168 h. in tension

