# A Novel Approach to Predicting the Lifetime of Elastomers Undergoing Stress Relaxation

## Stephen Ronan

## PhD

**Dublin Institute of Technology** 

Supervisors: Dr. Steve Jerrams

Dr. Thomas Alshuth

School of Manufacturing

and Design Engineering

September 2009

**Abstract** 

This work opens with a broad overview of several factors influencing the

behaviour of elastomeric materials under constant deformation. Following this,

an evaluation of the common difficulties surrounding industry-standard lifetime

prediction methods is presented. Subsequently, a novel method for the lifetime

prediction of stress relaxation in elastomeric materials under constant

deformation is introduced.

Experimental testing to determine the influence of filler type and content

was conducted on several natural rubber materials. The effect of altering the

vulcanising agent, crosslink density and mixing time was also examined.

Chemiluminescence was used to determine the influence that oxidation has on

the overall life of elastomers.

A critical assessment of current industry-standard lifetime estimation

methods are presented through practical examples. This work evaluates some of

the common problems surrounding these lifetime prediction methods and

discusses their limitations.

Comprehensive investigations were initiated to develop the time and

temperature dependent fitting of relaxation data using spectral analysis. A novel

concept is introduced to accurately predict the long-term behaviour of elastomers

under constant deformation. The concept of analysing relaxation spectra and

Arrhenius extrapolation offers a promising route to more accurate lifetime

predictions.

**Keywords:** stress relaxation, elastomer, lifetime prediction, spectral analysis

ii

I certify that this thesis which I now submit for examination for the award

of PhD, is entirely my own work and has not been taken from the work of others

save and to the extent that such work has been cited and acknowledged within

the text of my work.

This thesis was prepared according to the regulations for postgraduate

study by research of the Dublin Institute of Technology and has not been

submitted in whole or in part for an award in any other Institute or University.

The Institute has permission to keep, to lend or to copy this thesis in

whole or in part, on condition that any such use of the material of the thesis be

duly acknowledged.

Signature\_\_\_\_\_Date\_\_\_\_

Candidate

iii

#### Acknowledgements

First and foremost, I would like to express my sincere gratitude to Dr.

Thomas Alshuth whose extensive knowledge and experience has been immensely important to me and this work. Your understanding, encouragement and guidance have provided the backbone of this thesis.

I owe my deepest gratitude to Dr. Steve Jerrams. Thank you for your persistent confidence, your detailed and constructive comments and your invaluable support.

The following research would not have been possible without the support of the School of Manufacturing and Design Engineering and the Directorate of Research and Enterprise. Thank you for making this work a reality.

I would like to thank the entire CER team, in particular Niall Murphy who introduced me to the field of material science.

I wish to extend my warmest thanks to Prof. Robert Schuster for providing me with the opportunity to carry out my research at the Deutsches Institut für Kautschuktechnologie (DIK). Thank you for the many travel opportunities from France to Brazil to our weekend ski trips in the Harz.

During this work I collaborated with many colleagues for whom I hold the highest regard. I wish to extend my gratitude to all those who assisted in the successful realisation of this work. In particular, I would like to thank Dr. Eva Peregi for her network structure analysis and Markus Santoso for the Chemiluminescence investigations.

I am grateful to the DIK laboratory technicians, in particular Peter for his generosity and professional assistance. You continue to make DIK a fun and memorable experience for all students.

My special thanks go to my many colleagues and friends. We will always remember our city-centre office, McGowans Irish Pub, where stress relaxation increased exponentially with black filler. A special mention goes to my good friends Cristian, my IT guru, and Stefan for those in-depth Friday morning discussions.

I am indebted to John McNamara, your friendship and support throughout my time in Germany will never be forgotten.

To Izabel, thank you for your support and constant encouragement.

Finally, I remain forever indebted to my parents and family for all the support and encouragement they have given me throughout my studies. I could not have done this without you. R.R. you're a star!

#### Glossary

**DMA** 

ACM Acrylic Rubber

ASTM American Standard for Testing of Materials

ATR Attenuated Total Reflection

CB Carbon Black

CBS N-cyclohexyl-2-benzothiazole sulfenamide (accelerator)

CL Chemiluminescence (emission of light from a chemical reaction)

CV Conventional Vulcanisation

DIN Deutsches Institut für Normung

EPDM Ethylene Propylene Diene Polymer

EV Efficient Vulcanisation

FEA Finite Element Analysis

IPPD N-isopropyl-N'-phenyl-paraphenylenediamine

Dynamic Mechanical Analysis

ISO International Organisation of Standardisation

NBR Acrylonitrile Butadiene Rubber

NLREG Non-linear Regularisation

NR Natural Rubber

OIT Oxidation Induction Time

PMT Photo Multiplier Tube

RSA Rheometrics Solids Analyser

SBR Styrene Butadiene Rubber

SEV Semi-efficient Vulcanisation

SLS Standard Linear Solid

TBBS N-tertbuty1-2-benzothiazole Sulfenamide

TBzTD Tetrabenzylthiuram disulfide

TMQ 1,2-dihydro-2,2,4-trimethylquinoline

TMTD Tetramethylthiuram disulfide

TTSP Time-temperature superposition principle

UV Ultraviolet

WLF Williams-Landel-Ferry

XLD Crosslink Density

#### **Nomenclature**

 $T_g$  Glass transition temperature (°C)

phr Parts per hundred resin

S<sub>1</sub> Monosulphidic crosslinks

S<sub>2</sub> Disulphidic crosslinks

S<sub>x</sub> Polysulphidic crosslinks

E' Storage modulus (Pa)

E'' Loss modulus (Pa)

E\* Complex modulus (Pa)

G' Dynamic storage modulus (Pa)

G'' Dynamic loss modulus (Pa)

Tan  $\delta$  Loss factor

ε Strain

σ Stress (Pa)

τ Relaxation time (s)

η Viscosity (Pa.s)

F Force (N)

 $F_{(1)}$  Force after 1 minute (N)

 $F_{(30)}$  Force after 30 minute (N)

 $F_{(t)}$  Force after time t(N)

E<sub>R</sub><sup>(10)</sup> Stress relaxation modulus (at 10 seconds) (Pa)

R Gas constant = 8.314 (J/Kmol)

E<sub>a</sub> Activation energy (KJ/mol)

t<sub>90</sub> 90% of time to complete curing (S)

### **Table of Contents**

Abstract		ii
Acknowledg	gements	iv
Glossary		vi
Nomenclature		
List of Figu	res	X
C	List of Tables	
Chapter 1	Introduction	13
1.1 1.2 1.3	Motivation and Industrial Imperative  Aims and Objectives  An Overview of the Research	14
Chapter 2	Stress Relaxation - A Literature Review	
2.1 2.1.1 2.1.2 2.1.3 2.1.4 2.2 2.2.1 2.2.2 2.2.3 2.3.1 2.3.2 2.3.2 2.3.3 2.3.4 2.3.5	General Properties of Elastomers Long-term Properties of Elastomers Hyperelasticity Viscoelasticity Influence of Structure on Applied Stress and Strain Theory of Stress Relaxation Physical Contributions to Stress Relaxation Chemical Contributions to Stress Relaxation Relationship between Creep and Stress Relaxation Factors Influencing Stress Relaxation of Elastomers The Influence of Fillers Influence of Crosslink Density Vulcanisation System Change in Network Structure Thermo-oxidative Degradation	1820212326262728293232
Chapter 3	Viscoelastic Modelling	38
3.1 3.2 3.3 3.4 3.5 3.6	Maxwell Model	43 45 46
Chapter 4	Standard Lifetime Prediction Methods	50
4.1 4.2 4.3 4.4	Time-Temperature Superposition Principle Williams-Landel-Ferry Concept The Arrhenius Extrapolation Limitations to ISO standard	52 54
Chapter 5	Materials and Experimental Methods	58
5.1 5.2	MaterialsContinuous Compression Stress Relaxation	

5.3	Discontinuous Stress Relaxation Measurements	66
5.4	Relaxation Spectroscopy	
5.4.1	Dynamic Mechanical Analysis	
5.4.2	Dielectric Spectroscopy	
5.5	Change in Crosslink Density and Structure during Ageing	
5.5.1	Determination of Crosslink Type	
5.6	Chemiluminescence	74
Chapter 6	Factors which Influence Stress Relaxation Behaviour	77
6.1	Influence of Filler and Crosslink Density	77
6.2	Influence of Dispersion	
6.3	Vulcanisation System	
6.4	Network Structure Investigations	
6.5	Investigation into the Influence of Oxidation	
6.7	Compression Rate	
6.8	Oxidation Evaluation by means of Chemiluminescence	
6.9	Conclusion of Chapter 6	96
Chapter 7	Lifetime Prediction	98
7.1	Time-Temperature Superposition Principle	98
7.1.1	Application of Superposition to Dynamic Mechanical Data	
7.1.2	Application of Superposition to Dielectric Measurements	104
7.2	Williams-Landel-Ferry Principle	
7.3	Application of ISO Standard Arrhenius Extrapolation	
7.3.1	Application of the ISO/Arrhenius Concept for Predictions	111
7.4	Discussion and Conclusions concerning TTSP, WLF and	
	Arrhenius	114
Chapter 8	Spectral Analysis	
8.1	Non-linear Regularisation Validation	117
8.2	Spectral Analysis of Experimental Relaxation Data	121
8.3	Spectral Analysis and Evaluation of Activation Parameters	
8.4	Interpretation of Spectral Analysis Investigation	137
Chapter 9	Conclusion	139
9.1	Factors Influencing Stress Relaxation	139
9.2	Standard Lifetime Prediction Methods	
9.3	Spectral Analysis	142
Chapter 10	Outlook	145
Glossary of	Геrms	146
References		149
Appendices.		155
Appendix	1 – Examples of NR master-curve mismatching	156
	2 – A List of Published Papers Relevant to the Research	
Appendix 3	3 – KHK Poster Award	162

## **List of Figures**

Figure 2.1:	Temperature dependency of an amorphous polymer	.22
Figure 2.2:	2D diagram of polymer chains crosslinked into a network	.24
Figure 2.3:	(a) Undeformed elastomer and (b) in uniaxial tension	.24
Figure 2.4:	Electron microscope image of CB and surface representation	.29
Figure 2.5:	Sulphur bonds schematic	.33
Figure 3.1:	(a) Spring element and (b) Dashpot element	.38
Figure 3.2:	Maxwell model	.39
Figure 3.3:	Inflection point representing relaxation time $\tau$	.40
Figure 3.4:	Strain and stress history of stress relaxation	.42
Figure 3.5:	Voigt model	.43
Figure 3.6:	Strain and stress history of a creep experiment	.44
Figure 3.7:	A Standard linear solid model	.46
Figure 3.8:	Maxwell-Wiechert model	.46
Figure 3.9:	Two component Maxwell-Wiechert model in stress relaxation	.47
Figure 3.10:	Kelvin-Voigt model	.48
Figure 4.1:	Master-curve construction (reference temperature 25°C)	.51
Figure 4.2:	WLF plot	.53
Figure 4.3:	Material property against time	.55
Figure 4.4:	Arrhenius plot and life prediction	.55
Figure 5.1:	Elastocon relaxation apparatus	.62
Figure 5.2:	Stress relaxation test apparatus	.63
Figure 5.3:	Spring effect compensation	.64
Figure 5.4:	Discontinuous test jig cross-section and exploded view	.67
Figure 5.5:	Force-displacement curve of discontinuous measurement	.68
Figure 5.6:	Dynamic mechanical analysis (RSAII)	.69
Figure 5.7:	Experimental set-up of the broadband dielectric spectrometer	.71
Figure 5.8:	Schematic of chemiluminescence test machine	.75
Figure 5.9:	Typical CL analysis curve	.76
Figure 6.1:	Influence of filler type and content and XLD at 23°C	.79
Figure 6.2:	Influence of filler type and content and XLD at 70°C	.80
Figure 6.3:	Influence of filler dispersion at 100°C	.81
Figure 6.4:	Comparison between NR1 and NR7 at 100°C	.82
Figure 6.5:	Crosslink network change during ageing (NR1)	.83
Figure 6.6:	Crosslink structure change during ageing (NR7)	.84
Figure 6.7:	Crosslink structure change (%)	.85
Figure 6.8:	Exponential decay of polysulphidic bonds (S <sub>x</sub> )	.85
Figure 6.9:	Set-up with air inlet (a), without air inlet (b), stretched (c)	.87
Figure 6.10:	"Stretched o-ring" compression plates	
Figure 6.11:	Comparison of unstretched and stretched at O-ring at 180°C	.89
Figure 6.12:	Comparison of unstretched and stretched at O-ring at 150°C	
Figure 6.13:	Varying compression rate of NR1	
Figure 6.14:	CL analysis and OIT evaluation of NR	.92
Figure 6.15:	NR Stress relaxation data at 100°C, 120 °C and 150 °C	
Figure 6.16:	NR stress relaxation data 100°C, 120 °C and 150 °C	.94
Figure 7.1:	Stress relaxation data of NR7	
Figure 7.2:	TTSP master-curve of NR7 at $T_{ref} = 23^{\circ}C$	100
Figure 7.3.	Master-curve of NR1 at $T_{ref} = 23^{\circ}C$	

Figure 7.4:	Unshifted DMA data (a) and master-curve at $T_{ref} = 23$ °C (b) (N	
Figure 75.	NR1 master-curve at T <sub>ref</sub> = 23°C	102
Figure 7.5:		
Figure 7.6:	Frequency and temperature dependent dielectric loss $\varepsilon''$	
Figure 7.7:	NR1 dielectric master-curve	
Figure 7.8:	Shift factor comparison of SR, DMA and dielectric data (NR1)	
Figure 7.9:	EPDM stress relaxation data	
Figure 7.10:	EPDM master-curve at $T_{ref} = 23^{\circ}C$	
Figure 7.11:	EPDM master-curve of DMA data $T_{ref} = 23^{\circ}C$	
Figure 7.12:	Shift factor comparison of SR, DMA and dielectric data (EPD)	
Figure 7.13:	NR1 Arrhenius lifetime prediction	
Figure 7.14:	NR7 Arrhenius lifetime prediction	
Figure 7.15:	EPDM Arrhenius lifetime prediction	
Figure 7.15:	EPDM Arrhenius plot ( $F_t/F_{30}$ )	
Figure 8.1:	<b>1</b>	
C	Two process relaxation curve and relaxation spectrum	
Figure 8.2:	Reduced data curve with resulting spectrum.	
Figure 8.3:	Scattered relaxation curve investigation	
Figure 8.4:	Example of relaxation curve and spectrum - NR7 120°C	
Figure 8.5:	Relaxation data showing oscillating spectral curve	
Figure 8.6:	Example of linear subtraction procedure – NR7 120°C	
Figure 8.7:	NR1 (CV) spectral analysis at 70°C	124
Figure 8.8:	NR1 (CV) spectral analysis at 100°C	
Figure 8.9:	NR1 (CV) spectral analysis at 120°C	
Figure 8.10:	NR1 (CV) Arrhenius plot	
Figure 8.11:	Fitting of NR1 data at predictions at lower temperatures	
Figure 8.12:	NR7 (SEV) spectral analysis at 70°C	
Figure 8.13:	NR7 (SEV) spectral analysis at 100°C	
Figure 8.14:	NR7 (SEV) spectral analysis at 120°C	
Figure 8.15:	NR7 (SEV) Arrhenius plot	
Figure 8.16:	Fitting of NR7 and predictions at lower temperatures	
Figure 8.17:	Improved 120°C fitting of NR7 using a two process spectrum	132
Figure 8.18:	CV / SEV comparison at 23°C	133
Figure 8.19:	EPDM spectral analysis at 100°C	
Figure 8.20:	EPDM spectral analysis at 120°C	
Figure 8.21:	EPDM spectral analysis at 150°C	134
Figure 8.22:	EPDM spectral analysis at 180°C	135
Figure 8.23:	EPDM Arrhenius plot	
Figure 8.24:	Fitting of EPDM data and prediction at lower temperatures	136
Figure A1.1:	NR master-curve mismatching – NR 2	
Figure A1.2:	NR master-curve mismatching – NR 3	
Figure A1.3:	NR master-curve mismatching – NR 4	
Figure A1.4:	NR master-curve mismatching – NR 5	
Figure A1.5:	NR master-curve mismatching – NR 6	

## **List of Tables**

Table 2.1:	First digit assignment to carbon black by ASTM	31
Table 5.1:	Natural rubber compounds (phr: parts per hundred rubber)	
Table 5.2:	Sulphur cured EPDM compound	
Table 5.3:	Dynamic mechanical test parameters	
Table 6.1:	Dispersion times (mins) of NR8 natural rubber compound	
Table 8.1:	List of NR1 τ values determined by spectral analysis	126
Table 8.2:	Activation energy values of NR1	
Table 8.3:	List of NR 7 τ values determined by spectral analysis	130
Table 8.4:	Activation energy values of EPDM	136