A MODEL OF THERMAL AGING OF HYPER-ELASTIC MATERIALS WITH AN
APPLICATION TO NATURAL RUBBER

by

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ABSTRACT

Understanding the degradation of material properties and stress-strain behavior of rubber-like materials that have been exposed to elevated temperature is essential for the design of rubber components and the prediction of their lifetime. The complexity of the relationship between hyper-elastic materials, crosslinking density (CLD), and chemical composition presents a difficult problem for the accurate prediction of mechanical properties under thermal aging. In the first part of this dissertation, a new and relatively simple mathematical formulation is presented to express the change in material properties of natural rubber subjected to various elevated temperatures and aging times. Tensile tests were performed in which aging temperatures ranged from 76.7 °C to 115.0 °C, and the aging times from 0 to 600 hours. Based on the experimental data, the natural rubber mechanical properties under thermal aging show a similar behavior to the rate of change of the CLD with aging time and temperature. Three mechanical properties were chosen for investigation: the ultimate tensile strength, the fracture stretch value, and the secant modulus at 11.0% strain. The proposed phenomenological model relates the mechanical properties to the rate of change of the CLD based on a form of the Arrhenius equation. The proposed equations show promising results compared to the experimental data, with an acceptable error margin of less than 10% in most of the cases studied. The second part of this dissertation proposes a closed-form set of equations based on basic continuum mechanics assumptions to define the material stress-strain behavior of natural rubber as an application of hyper-elastic materials. The proposed formulas include the influence of aging time and temperature. The newly proposed “weight function based” (WFB) method was verified against the historic Treloar’s test data for uni-axial, bi-axial and pure
shear loadings of Treloar’s vulcanized rubber material, showing a promising level of confidence compared to the Ogden and Yeoh methods. Experimental testing was performed on natural rubber strip specimens that were thermally aged and then subjected to uni-axial tension and hardness tests. A non-linear least square optimization tool in Matlab (Lscurvefitt) was used for all fitting purposes.
## LIST OF ABBREVIATIONS AND SYMBOLS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A, B, C$ and $D$</td>
<td>WFB model parameters</td>
</tr>
<tr>
<td>$CLD$</td>
<td>Cross linking density</td>
</tr>
<tr>
<td>$COR$</td>
<td>Correction Factor</td>
</tr>
<tr>
<td>$Diff$</td>
<td>Difference</td>
</tr>
<tr>
<td>$Eng.$</td>
<td>Engineering</td>
</tr>
<tr>
<td>$FSR$</td>
<td>Fracture stretch ratio</td>
</tr>
<tr>
<td>$FSR_{Cal}$</td>
<td>Calculated fracture stretch ratio</td>
</tr>
<tr>
<td>$FSR_{Test}$</td>
<td>Experimental fracture stretch ratio</td>
</tr>
<tr>
<td>$H$</td>
<td>Transition point factor</td>
</tr>
<tr>
<td>$K$</td>
<td>The slope of the change in cross linking density with time</td>
</tr>
<tr>
<td>$LSE$</td>
<td>Least Square Error</td>
</tr>
<tr>
<td>$N$</td>
<td>Number of terms used in Ogden model</td>
</tr>
<tr>
<td>$R$</td>
<td>Universal gas constant</td>
</tr>
<tr>
<td>$P$</td>
<td>Time exponent</td>
</tr>
<tr>
<td>$SMR$</td>
<td>Secant modulus ratio</td>
</tr>
<tr>
<td>$SMR_{Cal}$</td>
<td>Calculated secant modulus ratio</td>
</tr>
<tr>
<td>$SMR_{Test}$</td>
<td>Experimental secant modulus ratio</td>
</tr>
<tr>
<td>$T$</td>
<td>The ratio between temperature and $T_g$ in °K</td>
</tr>
<tr>
<td>$TP$</td>
<td>Transition point</td>
</tr>
<tr>
<td>$TPR$</td>
<td>Transition point ratio ($TP/TP_o$)</td>
</tr>
</tbody>
</table>
**USR**  Ultimate tensile strength ratio

**USRCal**  Calculated ultimate tensile strength ratio

**USRTest**  Experimental ultimate tensile strength ratio

**W**  Strain energy density

**I**  Counting index ($i = 1, 2 \text{ or } 3$)

**$E_a$**  Activation energy parameter

**$E_p$**  Preferred least square error value for numerical analysis

**$H_f$**  Highest anticipated value for the transition point factor variation. For example, the current study ($H_f$) was 2; see Fig. 3.5.

**$I_i$**  Principal strain invariant ($i = 1, 2 \text{ or } 3$)

**$L_f$**  Fracture stretch value

**$M_i$**  Transition point and fracture stretch equation parameters.

**$S_M$**  Secant modulus

**$T_g$**  Glass transition temperature for natural rubber ($T_g = 203.16 \degree K$)

**$T_k$**  Temperature in Kelvin scale

**$F_{ik}$**  Material deformation gradient

**$L_{fo}$**  Fracture stretch value for unaged natural rubber specimen (12.7)

**$S_{Mo}$**  Secant modulus for unaged natural rubber specimen (1.0 MPa)

**$A^*$**  Arrhenius equation pre-exponential factor

**hrs**  Hours

**t**  Ratio between time in hours and $t_r$

**$a_i$, $b_i$, $c_i$ and $d_i$**  WFB model temperature variables ($i = 1 \text{ or } 2$)

**$t_r$**  Reference time
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \sigma )</td>
<td>Engineering stress</td>
</tr>
<tr>
<td>( \varepsilon )</td>
<td>Engineering strain</td>
</tr>
<tr>
<td>( \sigma_K )</td>
<td>WFB engineering stress</td>
</tr>
<tr>
<td>( \sigma_i )</td>
<td>Principal stresses</td>
</tr>
<tr>
<td>( \sigma_o )</td>
<td>Fracture strength for unaged natural rubber specimen (21.62 MPa)</td>
</tr>
<tr>
<td>( \sigma_u )</td>
<td>Ultimate tensile strength</td>
</tr>
<tr>
<td>( \varepsilon_f )</td>
<td>Fracture strain</td>
</tr>
<tr>
<td>( \sigma_{Kn} )</td>
<td>WFB nominal/engineering stress</td>
</tr>
</tbody>
</table>
ACKNOWLEDGMENTS

I would like to show my gratitude to the Fiat Chrysler Challenge Fund for funding this work and to Paulstra Corporation for supplying the material. In addition, my thanks go to Dr. Alaa El-Sharkawy, Dr. Richard Sun, and Dr. Yung-Li Lee for their insight and discussions during the course of this research.

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CONTENTS

ABSTRACT ................................................................................................................................. ii

LIST OF ABBREVIATIONS AND SYMBOLS ........................................................................ iv

ACKNOWLEDGMENTS .............................................................................................................. vii

LIST OF TABLES .......................................................................................................................... x

LIST OF FIGURES ....................................................................................................................... xi

CHAPTER 1 INTRODUCTION AND LITERATURE REVIEW ..................................................... 1

1.1. Introduction ......................................................................................................................... 1

1.1.1. Hyper-elastic Materials ............................................................................................... 1

1.1.2. Hyper-elastic Material Aging ...................................................................................... 2

1.2. Literature Review ............................................................................................................... 3

1.1.3. Hyper-elastic Mechanical Properties Review ............................................................. 3

1.1.4. Hyper-elastic Stress-Strain Behavior Review ............................................................... 6

1.2. Scope of Work .................................................................................................................. 10

1.3. Thesis Organization ......................................................................................................... 10

CHAPTER 2 THE BEHAVIOR OF NATURAL RUBBER MECHANICAL PROPERTIES UNDER THERMAL AGING ......................................................................................... 12

2.1. Introduction ...................................................................................................................... 12

2.2. Experimental Testing Preparation and Procedure ........................................................ 13

2.3. Test Results ..................................................................................................................... 15

2.3.1. Tensile Test Results .................................................................................................. 15
LIST OF TABLES

Table 1.1 Aging types for rubber-like materials ................................................................. 3

Table 2.1 Specimens heat aging matrix (Temperature and Hours) ........................................ 13

Table 2.2 Ultimate tensile strength reduction percentage ..................................................... 16

Table 2.3 Specimens’ USR ratio with aging time and temperature (σ₀=21.6 MPa) .............. 24

Table 2.4 Average error of the proposed USR, FSR, and SMR formulation compared to measured test data ............................................................................................................. 25

Table 2.5 Verification of the proposed equations .................................................................. 31

Table 3.1 Hyper-elastic models’ LSE for uni-axial loading ................................................... 55

Table 3.2 Hyper-elastic models’ parameters for fitting Treloar’s uni-axial test data using Lsqcurvfitt optimization tool in Matlab ................................................................. 56

Table 3.3 Hyper-elastic models’ parameters for fitting Treloar’s bi-axial data using Lsqcurvfitt optimization tool in Matlab .................................................................................. 58

Table 3.4 Hyper-elastic models’ LSE for Treloar’s bi-axial data .............................................. 59

Table 3.5 Hyper-elastic models’ parameters for fitting Treloar’s pure shear data using Lsqcurvfitt optimization tool in Matlab ................................................................. 60

Table 3.6 Hyper-elastic models’ LSE for Treloar’s pure shear data ........................................ 61

Table 4.1 TPR and FSR equation constants ........................................................................... 69

Table 4.2 The WFB parameters’ equation constants (from Eqs. 4.5 to 4.14). ....................... 75

Table 4.3 Correction factor parameters’ values for natural rubber .......................................... 76
LIST OF FIGURES

Fig. 1.1 Mild steel engineering stress-stretch behavior versus hyper-elastic materials ........... 2

Fig. 2.1 Tensile test specimen ........................................................................................................ 14

Fig. 2.2 Unaged engineering stress strain behavior with average line (Average ± 10%). ........ 16

Fig. 2.3 Stress strain behavior for different aging times and temperatures ranging from 76.7 °C to 115.5 °C. ........................................................................................................... 18

Fig. 2.4 Hardness test data variation with time ........................................................................... 19

Fig. 2.5 CLD behavior with aging time and temperature for natural rubber based on Choi’s [14] results ........................................................................................................................................... 20

Fig. 2.6 Graphical representation of Eqs. (2.2), (2.10), and (2.13) ........................................... 21

Fig. 2.7 USR variation with aging time and temperature; see Table 3 ......................................... 24

Fig. 2.8 Hyper-elastic materials’ typical stress-strain behavior .................................................. 25

Fig. 2.9 FSR variation with aging time and temperature ............................................................... 26

Fig. 2.10 SMR variation with aging time and temperature ............................................................. 28

Fig. 2.11 Stress-strain behavior of the three random samples for verification ............................ 29

Fig. 2.12 SMR error % of Eq. (2.14) results compared to the measured test data ..................... 30

Fig. 2.13 Optical image of the fracture surface at 76.7 °C .......................................................... 33

Fig. 2.14 Optical image of the fracture surface at 82.2 °C .......................................................... 35

Fig. 2.15 Optical image of the fracture surface at 87.8 °C .......................................................... 36

Fig. 2.16 Optical image of the fracture surface at 93.3 °C .......................................................... 38

Fig. 2.17 Optical image of the fracture surface at 98.9 °C .......................................................... 40

Fig. 2.18 Optical image of the fracture surface at 104.4 °C .......................................................... 42
Fig. 2.19 Optical image of the fracture surface at 110.0 °C. ........................................44

Fig. 3.1 Loading conditions and principal stresses direction........................................47

Fig. 3.2 Strain energy function (W) relation to the second principal stretch invariant ($I_2$) of the tested natural rubber specimen........................................48

Fig. 3.3 General hyper-elastic materials’ engineering/nominal behavior and weight function representation.................................................................50

Fig. 3.4 (H) variation with the least square error of the fitted WFB engineering stresses and the experimental engineering stresses for the tensioned natural rubber specimen........51

Fig. 3.5 Weight function fitting for the tested natural rubber specimen..........................52

Fig. 3.6 The WFB model results for Treloar’s uni-axial loading test data.........................55

Fig. 3.7 The Ogden and Yeoh models results and comparison to the proposed WFB model for Treloar’s uni-axial loading test data........................................56

Fig. 3.8 The WFB model results for Treloar’s bi-axial loading test data..........................57

Fig. 3.9 The Ogden and Yeoh models results and comparison to the proposed WFB model for Treloar’s bi-axial loading test data........................................58

Fig. 3.10 The WFB model results for Treloar’s pure shear loading test data......................60

Fig. 3.11 The Ogden and Yeoh models’ results and comparison to the proposed WFB model for Treloar’s pure shear loading test data........................................61

Fig. 3.12 The natural rubber tensile test results compared to the newly proposed WFB model. 62

Fig. 3.13 Bulge test ............................................................................................................63

Fig. 3.14 Finite element analysis for bulge test .................................................................65

Fig. 3.15 WFB fitting compared to the FEA and bulge test results....................................66

Fig. 4.1 TPR and FSR variation with time and temperature for the test data and the proposed Eq.s (4.2) and (4.3). .................................................................70

Fig. 4.2 Weight function fitting at 76.7°C and 600 hrs aging conditions (TP of 2.4 and Lf of 11.5). ...........................................................71

Fig. 4.3 Parameter A properties. .....................................................................................72

Fig. 4.4 Parameter B properties. .....................................................................................73
Fig. 4.5 Parameter C properties. .............................................................................................................. 74

Fig. 4.6 Parameter D properties. .............................................................................................................. 74

Fig. 4.7 Correction function behavior by varying \((g_1, g_2)\). ................................................................. 76

Fig. 4.8 Correction factor effect on the tested natural rubber material for an aged specimen at 110.0 °C and 255 hrs. ....................................................................................................................... 77

Fig. 4.9 The WFB model parameters extraction flowchart. ................................................................. 79

Fig. 4.10 Unaged data results compared to the WFB model. .............................................................. 80

Fig. 4.11 The WFB model behavior against experimental test data for \(T = 98.89\) to 115.53 °C and various aging times. ........................................................................................................... 82
CHAPTER 1
INTRODUCTION AND LITERATURE REVIEW

1.1. Introduction

1.1.1. Hyper-Elastic Materials

Incompressible hyper-elastic (rubber-like) isotropic materials have a wide range of industrial applications, such as in rubber belts, seals, engine mounts, tires, etc. A hyper-elastic material is any material that has the ability to recover its initial dimensions after being exposed to large deformation. Rubber-like materials can be produced by the vulcanization process. In 1844, Charles Goodyear was the first chemist and manufacturing engineer to develop this process.

Vulcanization is a chemical reaction that promotes a process known as crosslinking, which turns liquid latex into thermosetting polymer. The crosslinked microstructure of rubber allows for considerable stretching with low damping and subsequent rapid rebounding. For most industrial applications of rubber-like materials, especially those that involve variable aging time and temperature conditions, the fatigue and lifetime predictions for these materials have been highly challenging because of their complex chemical and microstructure nature or the entangled crosslinks [1].

Unlike metals, hyper-elastic materials’ stress-strain behavior is always non-linear and more complicated than that of steel and most metals. Figure 1.1-a represents the stress-stretch behavior of mild steel, showing that the maximum extension for steel is about 1.006%. In contrast, for hyper-elastic martials (Fig. 1.1-b), the stretch value can reach from 300% to 500%. 

For most homogeneous isotropic metals, the stress-strain behaviors can be described by defining two material constants: the modulus of elasticity \((E)\) and Poisson’s ratio \((\nu)\). However, more constants are usually needed to define the behavior of hyper-elastic materials; there can be one, two, three, or more of these constants, and they can differ from hyper-elastic material to another and from loading condition to another.

![Diagram](image)

**Fig. 1.1** Mild steel engineering stress-stretch behavior versus hyper-elastic materials.

1.1.2. **Hyper-Elastic Material Aging**

The aging of rubber-like materials is a phase of polymer degradation. It can be described as the change in mechanical, physical, or chemical properties, such as the ultimate tensile strength, fracture stretch, elasticity, color, shape, oxygen content, etc., of polymer-based products, such as rubber, under the influence of one or more environmental factors, such as elevated temperature, humidity, chemical reactions, etc.

Table 1.1 presents methods of aging that may be observed in rubber-like materials for several industrial applications. The present study mainly focuses on thermal aging, which is the
exposure of the rubber-like materials to elevated temperature for a long period of time and its effect on the mechanical properties and the stress-strain behavior.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>Thermo-oxidation, additive migration aging</td>
</tr>
<tr>
<td>Ultraviolet light</td>
<td>Photo-oxidation aging</td>
</tr>
<tr>
<td>Ionizing radiation</td>
<td>Radio oxidation, crosslinking aging</td>
</tr>
<tr>
<td>Humidity</td>
<td>Hydrolysis aging</td>
</tr>
<tr>
<td>Fluids (gas, organic, vapors)</td>
<td>Chemical degradation, swelling</td>
</tr>
<tr>
<td>Mechanical loading (stress, pressure)</td>
<td>Fatigue, creep, stress relaxation, compression set</td>
</tr>
</tbody>
</table>

1.2. Literature Review

1.1.3. Hyper-Elastic Mechanical Properties Review

The aging of rubber-like materials is the degradation of their physical properties, such as elasticity and strength, due to the effect of humidity and oxygen content, often in combination with some period of exposure to elevated temperature or chemical reaction conditions. It is necessary to study the effect of aging on the strength and material behavior of rubber-like materials for the accurate prediction of rubber mechanical component lifetimes and load deformation response. As noted by Woo and Park [2], “The design of rubber components against aging is very critical as aging affects not only the strength and stress strain behavior but it also affects the rubber material composition.”
Hamza [3] investigated the aging of ethylene propylene diene (EPDM) rubber under the effect of elevated temperatures and different carbon concentrations, and found that the tensile strength increased with an increase in carbon content and decreased at high temperature values. Hu et al. [4] studied the effect of thermal aging on tensile and tearing fracture behavior of carbon black filled rubber with different filler loadings. Thermal aging experiments were performed in a convection oven at 70°C to 120°C for various aging times, up to 140 hours. The group’s research results revealed that the rubber materials become stiffer as the aging time and temperature increased, and that the tensile strength decreased with increasing aging time up to 100 hours, then subsequently increased when the material was aged over 144 hours.

Furthermore, reinforced rubber materials have been used in composites for a wide range of applications. For instance, Lion [5] experimentally investigated the material behavior of reinforced rubber under temperature, considering its behavior to follow a non-linear continuum constitutive behavior.

Similarly, Mott and Ronald [6] studied the aging of natural rubber under the effect of hot air and hot seawater. They found that the strength of the natural rubber decreased and its elasticity dropped when it was exposed to high temperature, hot air, and a seawater environment. Aging of rubber-like materials also affects other mechanical properties, such as dynamic behavior. In this vein, Wei et al. [7] investigated the change of dynamic modulus in aged rubber: they examined rubber specimens relevant to those used for heavy-duty radial tires under various temperatures and aging times.

It is commonly understood that mechanisms for the strength and degradation of rubber typically involve oxygen diffusion and increases in crosslinking density (CLD) [8]. These mechanisms are often modeled using an Arrhenius type power law. Rubber-like materials exhibit
a visco-hyper-elastic nature, making their mechanical properties time and temperature dependent as these factors affect the materials’ CLD. Elevated temperature promotes oxidative aging of rubber-like materials because of their carbon-carbon double bond [9].

Ronan et al. [10] applied the Arrhenius equation to lifetime prediction of rubber materials under relaxation effect. According to these authors, the lifetime of rubber is the time required to reduce a specific pre-chosen property of the material by 50% of its original value. In their study, they examined two kinds of tests: dynamic mechanical testing and stress relaxation testing.

In another vein, Mlyniec et al. [11] extracted the mechanical properties of Liquid Silicon Rubber (LSR) using a new proposed chemomechanical model. They suggest that this model provides a useful tool for LSR stability prediction and lifetime determination of vibration isolators. They used the Arrhenius equation as a tool for computing the change in the viscoelastic material properties.

Woo et al. [12] studied the heat aging of two kinds of rubber extensively used in the refrigeration compression motors industry: acrylonitrile-butadiene (NBR) and EPDM. The group measured the change in the CLD and activation energy along with aging time and temperature by applying the Arrhenius equation. The results revealed that the activation energy variation with time was not similar for all hyper-elastic materials, as it behaved differently for the two tested materials (NBR and EPDM). In addition, the authors also showed that the change in the CLD increased by increasing the aging time and temperature.

Choi [13], [14] tested the thermal aging effect on the variation in the CLD of natural rubber (NR) vulcanizate at three different temperatures – 40°C, 60°C, and 80°C – for aging time of up to 20 days using a 5-day interval. The study also included styrene-butadiene rubber (SBR) and
butadiene rubber (BR) vulcanizates. Based on the results, Choi proved that CLD increases with thermal aging.

South et al. [15] examined the effect of thermal degradation on natural rubber mechanical properties between 80°C and 120°C aging temperature and 3 to 24 days’ aging time. They measured the CLD change and found that the mechanical properties, such as ultimate strength, were directly proportional to the percentage of poly- and mono-sulfidic crosslinks in the natural rubber compound.

All in all, their complicated chemical structure and crosslinking nature make it challenging to predict the mechanical properties of hyper-elastic materials, especially after a time period of exposure to variable thermal or environmental conditions. Given the past and current interest in the material response of heat-aged rubber-like materials, there is a need to incorporate the aging parameters, CLD variation, and degradation of mechanical properties in a simple and time-efficient closed formulation.

1.1.4. Hyper-Elastic Stress-Strain Behavior Review

The thermo-oxidation or thermal aging of hyper-elastic materials has a large influence on these materials’ lifetime and stress-strain behavior. Incompressible rubber-like isotropic materials have a wide range of industrial applications, such as in rubber belts, seals, engine mounts, tires, etc.

In general, several continuum mechanics and microstructure based models have been introduced to define hyper-elastic materials’ stress-strain behavior over the past 60 years. However, there are very few models in which the thermal aging influence explicitly depends on model parameters. The following paragraphs briefly discuss the differences between some of these models.
Ogden [16] proposed a mathematical model describing the stress-strain curve for rubber-like materials based on the principal stretch values. Despite the flexibility of this model, however, the determination of Ogden material parameters can be challenging due to the non-linear stress-strain behavior of hyper-elastic materials. In 1983, Twizell and Ogden [17] proposed a Levenberg-Marquardt non-linear least square optimization algorithm to determine the Ogden model parameters, and suggested that their proposed algorithm improves the accuracy of the determined material parameters.

Unlike the Ogden model, which is based on principal stretch values, other models have been proposed that are based on material strain invariants: for instance, the Mooney-Rivlin model [18] and the Gaussian chain statistics, which are widely used in the field of hyper-elastic materials. However, choosing a sufficient number of intervals to best fit the hyper-elastic behavior from the Mooney-Rivlin equation is a tedious process. The Neo-Hookean model is the simplest formulation of the Mooney-Rivlin model, as it requires only one material constant to be determined: the material shear modulus.

Some other simplifications of the Mooney-Rivlin model have been proposed, such as the Isihara [19], Gent-Thomas [20], and Yeoh models. Yeoh [21] [22] studied the effect of the second principal strain invariant on the strain energy function, and his results showed that this effect was minimum compared to that of the first strain invariant.

Swanson [23] [24], Arruda and Boyce [25], Gent [26] [27], Yeoh and Felming [28], and Carroll [29] have also proposed empirical functions that can represent rubber-like materials’ stress-strain curve. Swanson [23] [24] developed an empirical formula for a new model that includes the first and second material invariants accompanied by a weighting function; this is similar in
structure to the Ogden model series. The Swanson model has the same complications as the latter, including the difficulty in predicting model parameters for hyper-elastic materials.

On the other hand, Arruda and Boyce [25] presented a new constitutive model based on expressing the molecular network of polymers by eight chains oriented from the center diagonal of the microstructure material defined cube. Furthermore, Horgan and Saccomandi [26] proposed a hyper-elastic material model, the Gent model, which can elegantly and accurately describe the stress-strain behavior by defining only two parameters in reference to a logarithmic strain energy function. Paul et al. [30] compared the Gent, Yeoh, and Arruda and Boyce models’ results for Treloar’s vulcanized natural rubber data [31], and found that they were close.

Yeoh and Fleming [28] built a new model that was based on statistical and phenomenological concepts. The model assumes a contribution of the second principal stretch invariant on the material behavior, and it yields better results than the Yeoh model does [21] [22]. Moreover, Carroll [29] proposed a constitutive model for solving hyper-elastic materials’ behavior based on free energy and error reduction.

Paul et al. [30] published an article including an in-depth comparison of most of the hyper-elastic models from the early 1990s until 2012, including phenomenological and micromechanical approaches.

Most of the above models describe the hyper-elasticity stress-strain behavior in general, with no concern for the thermal aging effect on the proposed constitutive model parameters. However, analyzing the effect of the service and ambient conditions, such as temperature and humidity, on the mechanical behavior of rubber-like components can be a highly complicated process and could involve complicated mathematical regression and design of experimental techniques.
Baystritskaya et al. [32] introduced a new phenomenological mathematical model to describe the polymeric materials aging; however, it was highly challenging to solve it numerically and the research did not consider any experimental or practical verification.

Rodionova and Pomerantsev’s [33] made a unique contribution to predicting the thermal aging effect on mechanical properties and stress-strain behavior of rubber-like materials, as their method depends on successive Bayesian estimation (SBE) technique to calculate the thermally aged rubber behavior. However, the researchers acknowledge that the process is complicated, that it does not cover a wide range of service time and temperature conditions, and that it does not include a closed-form equation for the proposed model parameters.

Several thermos-oxidation aging or thermal aging models have been introduced for several rubber-like materials, [34], [35], [7]. However, although these models describe the fatigue properties, mechanical and chemical [15] properties, and lifetime [10] variation of hyper-elastic materials under thermal aging based on Arrhenius equation formulation, they do not cover the prediction of rubber-like materials’ entire stress-strain curve. For example, Choi et al. [34] studied the fatigue life of natural rubber under thermal aging conditions, and proposed several fatigue life prediction equations for this material. They defined the fatigue life as the number of cycles at which a crack of a size 3 mm could be seen by the naked eye.

The present study aims to provide a new and innovative weight function based (WFB) [36] model that describes rubber-like materials’ stress-strain behavior efficiently, accurately, with the fewest parameters possible, and requiring less time. In addition, a further aim is to propose a new phenomenological Arrhenius equation based approach for computing the variation of hyper-elastic materials’ mechanical properties with aging time and temperature. Both the WFB model and the proposed Arrhenius formula for calculating the mechanical properties were applied to natural
rubber and are concerned with monitoring the ultimate tensile strength, fracture stretch value, and secant modulus at 11.0% strain variation, under thermal aging. Although the newly proposed model was applied to the natural rubber material, a flow chart is also provided to demonstrate the prediction of the same model parameters for other hyper-elastic materials.

1.2. Scope of Work

The present study includes an in-depth analysis of the thermal aging of hyper-elastic materials as it applies to natural rubber material. The thermal aging analysis of rubber-like materials is divided into two main parts: the thermal aging effect on a) the mechanical properties and b) the stress-strain behavior of the material. An Arrhenius equation based formulation is proposed for the determination of the mechanical properties under any thermal aging time and temperature conditions. Moreover, this study introduces a new constitutive model for predicting hyper-elastic materials’ thermal aging under various loading conditions, including uni-axial, bi-axial, and pure shear loading. Several tensile and hardness tests were performed on the natural rubber material to verify the proposed equations and constitutive model formulation.

1.3. Thesis Organization

Following the introduction and literature review in chapter (1), chapter (2) introduces the experimental analysis and preparation of the natural rubber, and proposes a new phenomenological Arrhenius equation based approach for computing the variation of hyper-elastic materials’ mechanical properties with aging time and temperature. Three main material properties were chosen for investigation: a) the ultimate tensile strength, b) the fracture stretch value, and c) the secant modulus at 11.0% engineering strain.
Chapter (3) provides a new phenomenological constitutive model (the WFB model) for describing the behavior of hyper-elastic materials. The proposed WFB model is verified in this chapter against Treloar’s data for vulcanized rubber specimens for three loading conditions: uni-axial, bi-axial, and pure shear loading. The model results are also compared to those of the Yeoh and Ogden models for these conditions. In addition, chapter (3) applies the WFB model experimentally to a natural rubber material for uni-axial loading and bi-axial loading. The tensile test machine was used for uni-axial loading, and a bulge test for bi-axial loading. Furthermore, finite element (FE) analysis was generated for the bi-axial loading conditions to provide more confidence in the bulge test and the experimental results.

Chapter (4) concerns the application of the WFB model to thermally aged natural rubber specimens, and the prediction of the behavior of the model parameters with aging time and temperature. Results of the proposed model are compared to the tensile test data of the natural rubber. Finally, the chapter suggests a flowchart to describe the extraction of the WFB model parameters and constants for other hyper-elastic materials.
CHAPTER 2

THE BEHAVIOR OF NATURAL RUBBER MECHANICAL PROPERTIES UNDER THERMAL AGING

2.1. Introduction

In this chapter, a new and relatively simple mathematical formulation is presented to express the change in material properties of hyper-elastic materials under thermal aging. The proposed formulation was applied to a natural rubber. More than 130 specimens were thermally aged and then subjected to uni-axial tension and hardness tests. The aging temperatures ranged from 76.7 °C to 115.5 °C, and the aging times from 0 to 600 hours. Based on the recorded experimental data, the natural rubber mechanical properties under thermal aging showed a similar behavior to the rate of change of the CLD with aging time and temperature. Three mechanical properties were chosen for investigation in this study: the ultimate tensile strength, the fracture stretch value, and the secant modulus at 11.0% strain. The proposed mathematical formulation is a phenomenological equation that relates the material properties to the change in CLD based on a form of the Arrhenius equation. This equation showed promising results compared to the experimental data, with an acceptable error margin of less than 10% in most of the cases studied.
2.2. Experimental Testing Preparation and Procedure

Tensile test specimens (strips) were sheared from rubber pads; see Fig. 2.1-a. The nominal cross-section dimensions of each specimen were 6.35 mm × 1.29 mm; a representative specimen is shown near a grid of 2 mm x 2 mm squares in Fig. 2.1-b.

The specimens were aged in mechanical convection ovens that were instrumented with thermocouples and data logging thermocouple readers to determine their temperature variation and stability. The ovens maintained a spatial variation of temperature within +/- 0.5°C for the temperature ranges of the test matrix (Table 2.1).

Three strip specimens were aged under each condition of the test matrix. Two specimens were used for tensile testing and one was reserved for hardness testing. The specimens for the test matrix condition of “zero” aging hour were monitored with a thermocouple until the target temperature was reached. They were then removed from the oven.

| Table 2.1 Specimens heat aging matrix (Temperature and Hours). |
|-----------------------------|-----------------------------|
| T (°C) | Aging Time (hrs) |
| 76.67 | 0 100 200 300 400 600 |
| 82.22 | 0 100 200 300 400 600 |
| 87.78 | 0 100 200 403 501 601 |
| 93.33 | 0 115 215 260 311 410 |
| 98.89 | 0 115 215 260 311 410 |
| 104.44 | 0 26 51 100 255 424 |
| 110.00 | 0 26 51 100 255 424 |
| 115.53 | 0 50 100 166 |
a) Rubber pad.

b) Rubber strip (2 mm x 2 mm squares grid).

Fig. 2.1 Tensile test specimen.
To conduct the tensile testing on the specimens, pneumatic grips with a grip pressure of 2 kPa were used. The initial gage length of the specimens was 40 mm, and they were pulled in tension at a rate of 1.06 mm/s until failure. The load and displacement response for each specimen was digitally recorded throughout the tests, which were conducted at room temperature.

Engineering stress-strain data was generated from the load-displacement data by dividing the force by the original cross-sectional area, and the extension of the specimen by the initial 40 mm gage length. The ultimate tensile strength was defined to be the engineering fracture strength of the tensile specimen.

2.3. Test Results

2.3.1. Tensile Test Results

Figure 2.2 shows typical engineering stress-strain curves from two specimens. These specimens were unaged and at room temperature (25°C). In this figure, some variation in their response is seen by the differing stress levels for the same engineering strain. The two specimen curves were averaged and the maximum deviation from the average (±10%) is noted in the figure.

Next, Fig. 2.3 shows the average stress-strain response for each test condition at each aging temperature. The rubber material has an ultimate tensile strength of 21.6 MPa for the unaged specimen at room temperature.
As observed from the tensile test data, the ultimate tensile strength tends to decrease as the aging time of the specimen increases; see Table 2.2. The testing shows a trend of the ultimate strength ($\sigma_u$) decreasing in an exponential manner as the temperature increases. Table 2.2 presents the ultimate strength reduction percentage for the 87.8 °C and 155.5 °C specimens at 100 hours aging time. It can be observed that the magnitude of the reduction percentage increases dramatically from 13.8% at 87.8 °C to 76.5% at 155.6 °C.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>87.8 °C</th>
<th>115.5 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t$ (hrs)</td>
<td>Zero</td>
<td>100</td>
</tr>
<tr>
<td>$\sigma_u$(MPa)</td>
<td>20.3</td>
<td>17.5</td>
</tr>
<tr>
<td>Reduction %</td>
<td>0</td>
<td>-13.8</td>
</tr>
</tbody>
</table>
a)  $T = 76.7 \, ^\circ\text{C}$.

b)  $T = 82.2 \, ^\circ\text{C}$.

c)  $T = 87.8 \, ^\circ\text{C}$.

d)  $T = 93.3 \, ^\circ\text{C}$.
e) \( T = 98.9 \, ^\circ\text{C} \).

f) \( T = 104.4 \, ^\circ\text{C} \).

g) \( T = 110.0 \, ^\circ\text{C} \).

h) \( T = 115.5 \, ^\circ\text{C} \).

Fig. 2.3 Stress-strain behavior for different aging times and temperatures ranging from 76.7 \(^\circ\text{C}\) to 115.5 \(^\circ\text{C}\).
The stress-strain behavior of hyper-elastic materials in general is non-linear. However, to quantify the elastic modulus or stiffness behavior of the investigated natural rubber specimens at various aging time and temperature values, the slope of the secant modulus at 11.0% strain was recorded. The measured values show that the stiffness of the natural rubber increases by increasing the aging temperature and time. The secant modulus at another value of strain could have been chosen, but 11.0% strain was selected for this study. The natural rubber elasticity variation with aging time and temperature is discussed later in this chapter.

2.3.2. **Hardness Test Results**

Shore-A Durometer readings were taken on heat-aged specimens. The specimens were cut and stacked to provide the minimum required thickness for the durometer testing. Figure 2.4 shows the results of the average of three readings on each specimen. As previously stated with regard to tensile testing, the rubber material elasticity and strength are inversely proportional to aging time and temperature, and the hardness shows a generally increasing trend as the aging time and temperature increase for most of the specimens.

![Fig. 2.4 Hardness test data variation with time.](image)
2.3.3. **Material Properties Formulation**

2.3.3.1. **Ultimate Tensile Strength Analysis**

The Arrhenius equation is widely employed in applications related to the temperature effect on chemical reaction behavior. It can be used to model variations of diffusion coefficients, creep, relaxation analyses, and many other mechanical and chemical applications. It has also been employed to predict rubber-like materials’ lifetime for many industrial uses. For such materials, the Arrhenius equation can be expressed as

\[ K = A^* e^{-E_a/R T_k} \]  

(2.1)

where \( K \) is a chemical reaction property such as the change in CLD with aging conditions; \( A^* \) is the Arrhenius equation pre-exponential factor; \( E_a \) is the activation energy; \( R \) is the universal gas constant (8.31441 Joule/Kelvin); and \( T_k \) is the temperature in Kelvin.

![Graphs showing CLD behavior and ACLD slope with aging time](image)

a) CLD behavior under thermal aging.  
b) ACLD slope with aging time (K).

Fig. 2.5 CLD behavior with aging time and temperature for natural rubber based on Choi’s [14] results.

In his research, Choi [14] introduced the percentage of increase (ACLD %) of the CLD of natural rubber with aging time and temperature. Figure 2.5-a depicting Choi’s results shows that
the CLD tends to increase as the aging time does. However, as seen from the overall behavior of $\Delta CLD$ versus aging time in Fig. 2.5-a, the slope of the $\Delta CLD$ curve with aging time decreases as the aging time increases. Figure 2.5-b represents the slope of the curves in Fig. 2.5-a with time, and initially shows that the slope of the curve is higher for short aging times than longer ones. Physically, Fig. 2.5-b indicates that the rate of change of CLD decreases as aging time increases. This behavior is illustrated by the dotted line, and it is similar to the behavior of the ultimate tensile strength with aging time, as will be observed later in this section. It is noted that Choi’s thermal aging tests for natural rubber took place in close temperature and time ranges as in the present study.

Equation (2.2) below presents a proposed phenomenological relation between the slope of the $\Delta CLD$ curve with aging time ($K = d\Delta CLT/dt$), see Fig. 2.5-b, and the normalized ultimate tensile strength of the tested natural rubber ($\sigma_u/\sigma_o$), where $\sigma_o$ is the unaged ultimate tensile strength of the material (21.6 MPa).

$$\frac{\sigma_u}{\sigma_o} = e^{-1/K}$$  \hspace{1cm} (2.2)

![Graphical representation of Eqs. (2.2), (2.10), and (2.13).]
Equation (2.2) is based on the assumptions that the parameter $K$ and the ultimate tensile strength ($\sigma_u$) decrease in a similar functional form with aging time. Figure 2.6 is a graphical representation of Eq. (2.2) between the parameter $K$ and the ultimate tensile strength for natural rubber.

From Eqs. (2.1) and (2.2), the tensile strength of the proposed natural rubber material can now be represented in the form of the Arrhenius equation as

$$\ln(\sigma_{ult}/\sigma_0) = (-1/A)e^{E_a/R T_k}, \quad (2.3)$$

The pre-exponential factor can be expressed as a function in aging time and temperature as follows:

$$A = (-P_1/t)e^{(P_2-P_3 T_k)} \quad (2.4)$$

where $P_1$, $P_2$ and $P_3$ are Eq. (2.4) parameters in which $P_1$ was forced to be $1.0 \text{ hrs}$ for all analysis steps. By combining Eqs. (2.1) and (2.4), the normalized ultimate tensile strength variation with aging time and temperature can now be formulated as follows:

$$\ln(\sigma_{ult}/\sigma_0) = (t/P_1)e^{(P_2 T_k-P_3)} e^{E_a/R T_k} \quad (2.5)$$

The values of $P_2$, $P_3$, and the activation energy parameter ($E_a$) were determined by a non-linear least square (NLS) optimization tool in Matlab (*Lsqcurvefit*). By rearranging Eq. (2.5) and calling the normalized ultimate tensile strength the Ultimate Tensile Strength Ratio ($USR$), Eq. (2.6) can now be used to relate the strength variation with aging time and temperature.

$$USR = \sigma_{ult}/\sigma_0 = e^{\left(-\frac{1}{A}\right)e^{E_a/R T_k}} = F(P_2, P_3, E_a, t) \quad (2.6)$$

$$S_f(P_1) = \|F(P_2, P_3, E_a, t) - USR\|_2^2 \quad (2.7)$$

$$\|F(P_1, t) - USR\|_2^2 = \sum_{i=1}^n [F(P_2, P_3, E_a, t) - USR]^2 \quad (2.8)$$
The NLS tool calculates the parameters \((P_2, P_3\) and \(E_a\)) of a non-linear function \((F)\) by minimizing the error function \(S_f(P_i)\) compared to the test data \((USR)\); see Eqs. (2.7) and (2.8). The NLS tool was applied to evaluate \(P_2, P_3\) and \(E_a\) for all the tested data, starting from a randomly generated guess.

Table 2.3 presents the measured test data of the \(USR\) for all Table 2.1 specimens with tolerance limit. For example, point (α) in Fig. 2.7 represents the average reading of \(USR\) of two specimens after being aged for 255 hrs at 104.4 °C aging temperature. The recorded average \(USR\) for point (α) is 0.34 with an upper and lower tolerance limit of ±3.4%.

The activation energy parameter \((E_a)\) was observed to be constant with all aging temperatures and times, and its value was 9977 Joule. It is worth mentioning that the \(E_a\) value has numerical but not physical significance in finding the strength of the material: this is because it was considered as a numerical fitting output parameter and was not experimentally measured.

Figure 2.7 shows the experimental \(USR\) values, see Table 2.3, compared to the proposed phenomenological relation represented in Eq. (2.6). According to Fig. 2.7, the natural rubber material’s ability to carry more load and tolerate more stresses decreases as the aging time and temperature increase.

Equation (2.9) represents the average error percent of the \(USR\) \((Error_{USR})\) of the proposed equation (Eq. (2.6)) compared to the test data in Table 2.3, where \(USR_{test}\) is the experimental tensile test data, \(USR_{Cal}\) is the data calculated using Eq. (2.6), and \(N\) is the number of tested aging times at every temperature. According to Table 2.4, the average error for all the cases is less than or close to 10%, except for the 115.53 °C specimen, where the error seems to progress rapidly for aging times above 50 hrs.
\[ \text{Error}_{USR} = \left( \frac{1}{N} \right) \sum_{i=1}^{N} \left[ \frac{\text{USR}_{\text{Test}_i} - \text{USR}_{\text{Call}}}{\text{USR}_{\text{Test}_i}} \times 100 \right] \% \]  

(2.9)

<table>
<thead>
<tr>
<th>( T (\degree C) )</th>
<th>((\text{Time (hrs)}, \text{USR}\pm\text{tolerance} %))</th>
</tr>
</thead>
<tbody>
<tr>
<td>76.7</td>
<td>(0.0.89( \pm )9.2) (100.0.96( \pm )17.8) (200.0.84( \pm )4.4) (300.1.00( \pm )10.8) (400.0.90( \pm )1.6) (600.0.80( \pm )3.5)</td>
</tr>
<tr>
<td>82.2</td>
<td>(0.0.88( \pm )9.0) (100.0.88( \pm )17.8) (200.0.82( \pm )0.1) (300.0.86( \pm )12.3) (400.0.92( \pm )4.6) (600.0.82( \pm )3.8)</td>
</tr>
<tr>
<td>87.8</td>
<td>(0.0.94( \pm )0.1) (100.0.84( \pm )3.4) (193.0.86( \pm )0.7) (403.0.84( \pm )5.4) (501.0.83( \pm )0.7) (601.0.76( \pm )5.2)</td>
</tr>
<tr>
<td>93.3</td>
<td>(0.0.89( \pm )12.7) (115.0.92( \pm )5.8) (215.0.86( \pm )14.8) (260.0.83( \pm )2.4) (311.0.89( \pm )0.3) (410.0.77( \pm )3.3)</td>
</tr>
<tr>
<td>98.9</td>
<td>(0.0.96( \pm )5.6) (115.0.77( \pm )7.6) (215.0.72( \pm )8.2) (260.0.59( \pm )1.4) (311.0.56( \pm )3.0) (410.0.44( \pm )4.5)</td>
</tr>
<tr>
<td>104.4</td>
<td>(0.0.95( \pm )5.1) (26.0.87( \pm )17.9) (51.0.77( \pm )10.7) (100.0.74( \pm )11.8) (255.0.34( \pm )13.3) (424.0.16( \pm )3.6)</td>
</tr>
<tr>
<td>110.0</td>
<td>(0.1.00( \pm )4.9) (26.0.94( \pm )4.9) (51.0.73( \pm )5.4) (100.0.62( \pm )7.3) (255.0.14( \pm )10.1) (424.0.11( \pm )5.0)</td>
</tr>
<tr>
<td>115.5</td>
<td>(0.1.02( \pm )11.0) (50.0.53( \pm )6.4) (100.0.25( \pm )15.9) (166.0.12( \pm )0.1)</td>
</tr>
</tbody>
</table>

Fig. 2.7 USR variation with aging time and temperature; see Table 3.
Table 2.4 Average error of the proposed USR, FSR, and SMR formulation compared to measured test data.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Error_USR (%)</th>
<th>Error_FSR (%)</th>
<th>Error_SMR %</th>
</tr>
</thead>
<tbody>
<tr>
<td>76.7</td>
<td>5.8</td>
<td>1.2</td>
<td>2.6</td>
</tr>
<tr>
<td>82.2</td>
<td>6.0</td>
<td>0.2</td>
<td>4.8</td>
</tr>
<tr>
<td>87.8</td>
<td>1.8</td>
<td>1.9</td>
<td>8.0</td>
</tr>
<tr>
<td>93.3</td>
<td>8.6</td>
<td>2.2</td>
<td>11.2</td>
</tr>
<tr>
<td>98.9</td>
<td>1.6</td>
<td>1.6</td>
<td>8.5</td>
</tr>
<tr>
<td>104.4</td>
<td>11.5</td>
<td>6.2</td>
<td>0.0</td>
</tr>
<tr>
<td>110.0</td>
<td>6.1</td>
<td>2.4</td>
<td>3.0</td>
</tr>
<tr>
<td>115.5</td>
<td>25.1</td>
<td>0.2</td>
<td>3.2</td>
</tr>
</tbody>
</table>

2.3.3.2. Fracture Stretch Value Analysis

Figure 2.8 demonstrates the typical behavior of hyper-elastic materials, showing that the fracture stretch is the maximum stretch value that the material can reach under loading before fracture.

By measuring the fracture stretch value for all cases in Table 1 and observing the normalized fracture stretch value ($L_f/L_0$) variation with aging time and temperature, this value is noted to follow the same behavior as the ultimate tensile strength; see Fig. 2.7 and Fig. 2.9. This
means that the natural rubber tendency to stretch more under high load values decreases by increasing the aging time and temperature.

By calling the normalized fracture stretch value the Fracture Stretch Ratio (FSR), Eq. (2.10) can now be introduced to relate the FSR to the CLD; see Fig. 2.6.

\[ FSR = \frac{L_f}{L_o} = e^{(-1/K)} \]  \hspace{1cm} (2.10)

By rearranging Eqs. (2.1), (2.4), and (2.10), Eq. (2.11) can be used to relate the fracture stretch variation to aging time and temperature.

\[ \ln(FSR) = (t/P_1)e^{(P_3/T_k-P_2)} e^{E_a/R T_k} \]  \hspace{1cm} (2.11)

where Eq. (2.11) parameters \((P_2 \text{ and } P_3)\) were evaluated using the same NLS Matlab tool (Lsqcurvefit) and their values were found to be 49.5 and 0.1 Kelvin\(^{-1}\), respectively, and \(P_1\) was forced to be 1 hrs. The activation energy parameter \((E_a)\) was observed to be the same as in the USR case with a value of 9977 Joule. Figure 9 shows the experimental FSR test data compared to the Eq. (2.11) results.

![Fig. 2.9 FSR variation with aging time and temperature.](image-url)
The absolute average error ($Error_{FSR}$) in the Eq. (2.11) results for the FSR compared to the test data were calculated using Eq. (2.12). Table 4 shows that the absolute average error is less than 6.5% for all the cases compared to the test data.

$$Error_{FSR} = \left| \left( \frac{1}{N} \sum_{i=1}^{N} \frac{FSR_{Test_i} - FSR_{Cal_i}}{FSR_{Test_i}} \times 100 \right) \right| \%$$  \hspace{1cm} (2.12)

### 2.3.3.3. Stiffness Analysis

Based on Fig. 2.8, and according to the measured stress-strain data of natural rubber in Fig. 2.3, the general stress-strain behavior of hyper-elastic material is non-linear. However, the stiffness of the natural rubber is quantified by the slope of the secant modulus ($S_M$) at 11.0% strain value; see Fig. 8.

According to the results in sections 3.3.1 and 3.3.2, the strength and the stretch ability of natural rubber are inversely proportional to the aging time and temperature. However, the natural rubber is noted to be stiffer with increasing aging time and temperature.

In this section, the secant modulus at 11.0% engineering strain is recorded for every case in Fig. 2.3, and the measured readings are recorded as a secant modulus ratio ($SMR = S_{Mo}/S_M$), which is a normalized stiffness value of the unaged natural rubber specimen ($S_{Mo} = 1.04 \text{ MPa}$).

The Secant Modulus Ratio ($SMR$) can now be related to the $CLD$ by Eq. (2.13); see Fig. 2.6.

$$SMR = \frac{S_{Mo}}{S_M} = e^{-1/K}$$  \hspace{1cm} (2.13)

where ($S_M$) is the secant modulus at 11% strain for every tested natural rubber specimen in Table 3. By combining Eqs. (2.1), (2.4), and (2.13), the stiffness variation with aging time and temperature can now be formulated as follows:

$$ln(SMR) = \left( \frac{t}{P_1} \right) e^{(P_2 T_k - P_2)} e^{E_a/R T_k}.$$  \hspace{1cm} (2.14)
By fitting test data with Eq. (2.14) using \textit{Lsqcurvefit} Matlab tool, \(P_2\) and \(P_3\) were found to be 38.2 and 0.07 Kelvin\(^{-1}\), respectively, and \(P_1\) was forced to be 1 hrs. The activation energy parameter (\(E_a\)) was observed to be the same as for the USR and FSR cases, with a value of 9977 Joule. Figure 2.10 shows the experimental \textit{SMR} values compared to the proposed phenomenological equation (Eq. (2.14)).

\[
Error_{SMR} = \left| \frac{1}{N} \sum_{i=1}^{N} \left( \frac{SMR_{Test_i} - SMR_{Cal_i}}{SMR_{Test_i}} \times 100 \right) \right| \% \tag{2.15}
\]

Equation (2.15) was applied to calculate the absolute average error (\(Error_{SMR}\)) for the calculated \textit{SMR} compared to the recorded data from the test. Table 4 shows that the absolute average error for all the cases is less than or close to 10\%, except for the readings at 93.3 °C, where it is 11.2\%.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig210.png}
\caption{\textit{SMR} variation with aging time and temperature.}
\end{figure}
2.4. Verification of the Proposed Equations

Three randomly generated aging times and temperatures for three different cases were chosen to verify the material properties prediction of Eqs. (2.3), (2.11), and (2.14). The average of two tested specimens for each case was generated, and the USR and stress-strain behavior were recorded. The three specimens were tensioned using the tensile testing machine after reaching the required aging time and temperature for each case. Fig. 2.11 presents the three specimens’ stress-strain behaviors in cases (1), (2), and (3).

![Graph showing stress-strain behavior](image)

**Fig. 2.11 Stress-strain behavior of the three random samples for verification.**

Table 7 presents the measured USR, FSR, and SMR values for the experimentally tested specimens in cases (1), (2), and (3) compared to the results of the proposed equations (Eq. (2.3), (2.11), and (2.14)). The error was calculated using Eqs. (2.9), (2.12), and (2.15). The USR shows good error values of 7.2%, 2.8%, and 3.7% for cases (1), (2), and (3), respectively. For the FSR, the error percentages compared to the tested data are 9.8% for both cases (1) and (2), and 10.4%
for case (3), which is significantly high. The SMR errors are 4.7% and 8.4% for cases (1) and (2), respectively, and 30.1% for case (3).

![Graph showing SMR error % of Eq. (2.14) results compared to the measured test data.](image)

Fig. 2.12 SMR error % of Eq. (2.14) results compared to the measured test data.

Examining the error behavior of the SMR compared to the tested data in Fig. 2.12, the error shows a rapid increase as the temperature exceeds 104.4 °C. This may explain the high error of 30.1% in case (3). According to Fig. 2.12 and the recorded error for the SMR in the three randomly tested cases, Eq. (2.14) can provide a trustworthy estimate of the secant modulus as long as the temperature is lower than 104.4 °C, after which a significant error should be expected.

In general, the proposed equations for calculating the ultimate tensile strength, the fracture strength, and the secant modulus show good prediction of the material properties of the tested natural rubber, with an average error of less than 10% compared to the tested data.
Table 2.5 Verification of the proposed equations.

<table>
<thead>
<tr>
<th>Case#</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (hrs)</td>
<td>212.0</td>
<td>556.0</td>
<td>10.3</td>
</tr>
<tr>
<td>Temp (°C)</td>
<td>103.3</td>
<td>112.2</td>
<td></td>
</tr>
<tr>
<td>USR&lt;sub&gt;Test&lt;/sub&gt;</td>
<td>0.49</td>
<td>0.75</td>
<td>0.86</td>
</tr>
<tr>
<td>USR&lt;sub&gt;Cal&lt;/sub&gt;</td>
<td>0.52</td>
<td>0.77</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Error&lt;sub&gt;USR&lt;/sub&gt; (%)</td>
<td>7.2</td>
<td>2.8</td>
<td>3.6</td>
</tr>
<tr>
<td>FSR&lt;sub&gt;Test&lt;/sub&gt;</td>
<td>0.53</td>
<td>0.80</td>
<td>0.86</td>
</tr>
<tr>
<td>FSR&lt;sub&gt;Cal&lt;/sub&gt;</td>
<td>0.62</td>
<td>0.88</td>
<td>0.94</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Error&lt;sub&gt;FSR&lt;/sub&gt; (%)</td>
<td>9.8</td>
<td>9.8</td>
<td>10.4</td>
</tr>
<tr>
<td>SMR&lt;sub&gt;Test&lt;/sub&gt;</td>
<td>0.79</td>
<td>0.71</td>
<td>0.54</td>
</tr>
<tr>
<td>SMR&lt;sub&gt;Cal&lt;/sub&gt;</td>
<td>0.76</td>
<td>0.87</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Error&lt;sub&gt;SMR&lt;/sub&gt; (%)</td>
<td>4.6</td>
<td>8.4</td>
<td>30.1</td>
</tr>
</tbody>
</table>

2.5. Fracture Surface Analysis

This section presents the fracture surface morphology of the tensile test specimens. Figure 2.13 a, b, and c show the fracture surfaces of the tensioned specimens at 76.7 °C after 0, 300, and 600 hours of aging using optical microscopy. As shown in Fig. 13, the fracture surface morphology becomes coarser as the aging time of the tested natural rubber materials increases. This behavior may be related to the increase in the rubber structure crosslinks, which increase the materials’ toughness and hardness; see Figs. 2.4 and 2.10. Figures 2.14-16 show the same conclusion for 82.2 °C, 87.7 °C and 93.3 °C.

By increasing aging temperature to more than 98 °C, the change in the surface morphology becomes more difficult to distinguish compared to low temperatures. Figures 2.17-19 show the fracture surfaces of the tensioned specimens at 98.8 °C, 104.4 °C, and 110.0 °C. Many factors control the behavior of the rubber-like materials under thermal aging: for example, the change in the CLD, the chemical composition change, the humidity change, the oxygen contents, and finally, the aging time and temperature. Rodionova and Pomerantsev [33] published an article showing that the prediction of the mechanical properties and stress-strain behavior change under thermal
aging can be difficult. This is due to the highly non-linear behavior of these materials considering all of these parameters’ effects on the thermal aging process. This may explain the decrease in the hardness values at high temperatures (above 100 °C) compared to lower temperatures at low aging time values (below 260 hours), see Fig. 2.4, and the similar morphology of the fractured surfaces at 104.4 °C and 110.0 °C for low aging time (below 260 hours); see Figs. 2.18 and 2.19 a and b.

![Image](image1.png)

a) 0 hrs aging.

![Image](image2.png)

b) 300 hrs aging.
c) 600 hrs aging.

Fig. 2.13 Optical image of the fracture surface at 76.7 °C.
a) 0 hrs aging.

b) 300 hrs aging.
c) 600 hrs aging.

Fig. 2.14 Optical image of the fracture surface at 82.2 °C.
Fig. 2.15 Optical image of the fracture surface at 87.8 °C.

a) 0 hrs aging.

b) 200 hrs aging.
a) 0 hrs aging.

b) 260 hrs aging.
c) 410 hrs aging.

Fig. 2.16 Optical image of the fracture surface at 93.3 °C.
a) 0 hrs aging.

b) 260 hrs aging.
c) 410 hrs aging.

Fig. 2.17 Optical image of the fracture surface at 98.9 °C.
a) 0 hrs aging.

b) 255 hrs aging.
c) 425 hrs aging.

Fig. 2.18 Optical image of the fracture surface at 104.4 °C.
a) 0 hrs aging.

b) 255 hrs aging.
Chapter (2) introduced a new phenomenological approach to the calculation of the mechanical properties of natural rubber that is exposed to thermal aging. A series of tensile tests were performed using a tensile test machine at different aging times and temperatures. The change in stress-strain behaviors as well as the ultimate tensile strength, the fracture stretch value, and the secant modulus at 11.0% strain was recorded for the aged natural rubber test specimens. However, the model is not limited to the calculation of these three material properties: other mechanical, static, and dynamic properties such as dynamic modulus [7] and yield strength can be calculated using the same formulation.

Choi’s [14] results for natural rubber CLD change with thermal aging conditions were related to the behavior of the mechanical properties using Eqs. (2.2), (2.10), and (2.13). Equations
(2.3), (2.11), and (2.14) were based on Choi’s data, tested for various aging time and temperature values, and proved to calculate the natural rubber mechanical properties efficiently under thermal aging conditions with an error margin of less than 10%.

According to the results of this study, under aging, the strength of natural rubber decreases and loses its ability to stretch more and carry more load as the aging time and temperature values increase. In contrast to the strength and stretch behaviors, the tested natural rubber becomes stiffer as the aging time and temperature values increase. The hardness test results confirm that the elasticity of the natural rubber decreases as the aging temperature and time increase.

The proposed equation was introduced as a form of Arrhenius equation, and the activation energy parameter $E_a$ is a fitting output in the proposed formulation of the mechanical properties. The $E_a$ was found to be constant with all aging temperatures and times for all tested natural rubber specimens, with a value of 9977 Joule.

In verifying the proposed mechanical properties’ equations for three randomly generated tests of aged natural rubber specimens at different aging time and temperature values, the ultimate tensile strength and the fracture stretch equation results are close to the tested data with an error of less than 10.0%. However, the error in the secant modulus equation (Eq. (2.14)) compared to in the tested data is noted to increase rapidly as the temperature rises beyond 104.44 °C.

In general, the proposed phenomenological equations for predicting the ultimate tensile strength, the fracture strength, and the secant modulus fit the experimental data well, with an acceptable error margin of less than 10%.
CHAPTER 3
THE WEIGHT FUNCTION BASED MODEL METHODOLOGY

3.1. Introduction

This chapter defines a new model (WFB model) that describes hyper-elastic materials’ stress-strain behavior. The WFB model is verified against Treloar’s test data for uni-axial, bi-axial, and pure shear loadings of Treloar’s vulcanized rubber material, showing a promising level of confidence compared to the Ogden and Yeoh methods. An NLS optimization Matlab tool was used to determine the WFB, Yeoh, and Ogden models’ material parameters. The results of the three models are compared, showing that the newly proposed model is more accurate for uni-axial tension as it has an error value that is less than those of the Ogden and Yeoh models by 1.0 to 39%. Also, the processing time of calculating the WFB model parameters is less than that of the Ogden model by 95%.

3.2. The WFB Hyper-Elastic Model

3.2.1. The WFB Model Methodology

Mooney [18] was the first to propose the strain energy theory for non-linear elastic materials. The theory assumes that the strain energy \( W \) of rubber-like materials is a function of the material principal stretch invariants \( I_i \).
\[ W = F(I_1, I_2, I_3) \]  
\[ I_1 = F_{ik}F_{ik} = \lambda_1^2 + \lambda_2^2 + \lambda_3^2 \]  
\[ I_2 = 0.5 \left[ F_{ik}F_{ik}F_{jq}F_{jq} - F_{ik}F_{jk}F_{iq}F_{jq} \right] = \frac{1}{\lambda_1^2} + \frac{1}{\lambda_2^2} + \frac{1}{\lambda_3^2} \]  
\[ I_3 = \text{det} \{ F_{ik} \} = \lambda_1^2 \lambda_2^2 \lambda_3^2 \]  

Where \( \lambda_i \) are the principal stretch values and \( F_{ij} \) is the material deformation gradient. The constitutive response for the Cauchy stress tensor can be formulated as follows:

\[ \sigma_{ij} = -p \delta_{ij} + F_{ik} \frac{\partial W}{\partial F_{jk}} = -p \delta_{ij} + \lambda_i \frac{\partial W}{\partial \lambda_k} \frac{\partial \lambda_k}{\partial \lambda_j} \]  
\[ F_{ik} = \frac{\partial x_i}{\partial x_k} \]  
where, \( p \) is an arbitrary additive pressure.
By assuming an incompressible isotropic material, the third principal stretch invariant \( I_3 \) turns to unity \( (I_3 = 1) \), leaving the principal Cauchy stress tensor function only in the first and second principal stretch invariants,

\[
\sigma_i = -p + \lambda \left[ \frac{\partial W}{\partial \lambda_i} + \frac{\partial W}{\partial I_1} \frac{\partial I_1}{\partial \lambda_i} + \frac{\partial W}{\partial I_2} \frac{\partial I_2}{\partial \lambda_i} \right]
\]  

(3.7)

3.2.1.1. The WFB Model for Uni-axial Loading

For uni-axial tension behavior \( (\sigma_2 = \sigma_3 = 0) \), see Fig. 3.1, the principal stretches, Cauchy’s first principal stress \( (\sigma_1) \), and the arbitrary pressure \( (p) \) can be represented as follows:

\[
\lambda_2 = \lambda_3 = \lambda_1^{-0.5} = \lambda^{-0.5}
\]  

(3.8)

\[
p = \frac{2}{\lambda} \frac{\partial W}{\partial I_1} + 2 \left[ \lambda + \frac{1}{\lambda^2} \right] \frac{\partial W}{\partial I_2}
\]  

(3.9)

\[
\sigma_1 = \left[ 2 \frac{\partial W}{\partial I_1} + \frac{1}{\lambda} \frac{\partial W}{\partial I_2} \right] \left( \lambda^2 - \frac{1}{\lambda} \right)
\]  

(3.10)

Fig. 3.2 Strain energy function \( (W) \) relation to the second principal stretch invariant \( (I_2) \) of the tested natural rubber specimen.
The WFB model depends on the Yeoh [21] model assumption, where the strain energy function is independent of the second principal stretch invariant \( \frac{\partial W}{\partial I_2} \approx 0 \), and as per which Cauchy’s principal stress for uni-axial tension can be simplified to

\[
\sigma_1 = 2 \frac{\partial W}{\partial I_1} \left( \lambda^2 - \frac{1}{\lambda} \right)
\]

(3.11)

Figure 3.2-a and b demonstrate the variation of the strain energy function \( W \) with respect to the second principal stretch invariant \( I_2 \) for a uni-axial tension test on the natural rubber specimen. Figure 3.2 proves the Yeoh model assumption, as it shows that \( W \) is almost constant and very close to zero if the \( I_2 \) is higher than 0.05, after which it starts to increase rapidly. Most of the rubber-like materials’ applications have stresses that are less than 25% of the ultimate tensile strength value under normal working conditions. At this value, the stretch in the rubber component is usually less than 5.5. This gives a second principal stretch invariant of more than 0.033, which make the Yeoh model assumption safe up to \( \lambda \) of 5.5.

Equation (3.12) is the proposed equation for the strain energy function. According to this equation, the WFB model assumes that the strain energy is only a function in the first principal stretch value \( \lambda_1 \). Equation (3.12) can be calculated numerically or solved directly after choosing a proper formula of the weight function \( F(\lambda_1) \). The present author has avoided giving a closed-form solution for Eq. (3.12) as it depends on the weight function \( F(\lambda) \) which is, according to the proposed model, a user pre-defined function and can take any mathematical form as long as it satisfies the weight function constraints and conditions; see Fig. 3.3-b.

\[
W = W(\lambda_1) = \int_1^{\Lambda_f} \left\{ F(\lambda_1) A(\lambda_1 e^{-B I_1}) + C(\lambda_1 I_1^{-D}) \right\} \left( \lambda_1 - \frac{1}{\lambda_1} \right) d\lambda_1
\]

(3.12)
where \((L_f)\) is the fracture stretch value. By substituting Eq. (3.12) into Eq. (3.11), the first Cauchy principal stress equation for uni-axial tension \((\lambda_1 = \lambda)\) can now be represented by the following formula:

\[
\sigma_1 = \{F(\lambda) A(\lambda e^{-B I_1}) + C(\lambda I_1 - D)\} \left(\lambda^2 - \frac{1}{\lambda}\right) \tag{3.13}
\]

where \(A, B, C,\) and \(D\) are the proposed WFB model parameters.

Based on several experimental observations, it was found that the accuracy of the proposed model is related to the stress-stretch curve slope transition point \((TP)\). \(TP\) represents the stretch value of the minimum slope on the stress-stretch curve for hyper-elastic material; see Fig. 3.3. Physically, \(TP\) is the stretch value after which the hyper-elastic material stops resisting the applied load.

From Eq. (3.13), the exponential term \((\lambda e^{-B I_1})\) is multiplied by a weight function to restrict the effect of the exponential term after a specific stretch value. Compared to experimental data, the least square error \((LSE)\) is observed to be minimum when the weight function \(F(\lambda)\) is forced to
be zero for \( \lambda \) greater than a specific ratio from the \( TP \) value \((H^*TP)\), see Fig. 3.3-b and 3.4, where \( H \) is a transition point factor and a material constant that can vary from one material to another. \( H \) was chosen to be 1.409 for the tested natural rubber materials, as this yielded a minimum error compared to the tested data; see Eq. (3.28) for the error calculation.

![Graph showing H variation with least square error](image)

**Fig. 3.4** (H) variation with the least square error of the fitted WFB engineering stresses and the experimental engineering stresses for the tensioned natural rubber specimen.

Figure 3.5 represents a sample of a weight function for the tested natural rubber specimen. The present author used Eq. (3.14) to fit the weight function curve,

\[
F(\lambda) = FP_1(\lambda^2 + FP_2)^{-FP_3}
\]  

(3.14)

where the weight function parameters \( FP_1, FP_2 \), and \( FP_3 \) can be evaluated using the optimization tool from Matlab \((\text{Lsqcurvefit})\) or any other linear or non-linear optimization fitting tool; their values are 2.378E8, 15.5128, and 7.0574, respectively. Equation (3.14) is not necessary for \( F(\lambda) \) fitting: the user can use any smooth piecewise function as long as it fits the main weight function assumptions and shape; see Fig. 3.3-b.
3.2.1.2. The WFB Model for Bi-axial Loading

For the bi-axial stress state ($\sigma_1 = \sigma_2 = \sigma$ and $\sigma_3 = 0$), see Fig. 3.1, the principal stretches, Cauchy’s principal stress ($\sigma$), and the arbitrary pressure ($p$) can be represented as follows:

$$\lambda_1 = \lambda_2 = \lambda \text{ and } \lambda_3 = \lambda^{-2} \quad (3.15)$$

$$p = \frac{2}{\lambda^4} \frac{\partial W}{\partial I_1} + \frac{2}{\lambda^2} \frac{\partial W}{\partial I_2} \quad (3.16)$$

$$\sigma_1 = \sigma_2 = \left[ 2 \frac{\partial W}{\partial I_1} + \lambda^2 \frac{\partial W}{\partial I_2} \right] \left( \lambda^2 - \frac{1}{\lambda^4} \right) \quad (3.17)$$

By using the same equation (Eq. (3.12)) for the strain energy function, and by applying the Yeoh model assumption ($\frac{\partial W}{\partial I_2} \approx 0$), the Cauchy principal stresses $\sigma_1$ and $\sigma_2$ can now be represented as

$$\sigma_1 = \sigma_2 = \left( \frac{1}{2} \right) \left[ F(\lambda) A(\lambda e^{-B I_1}) + C(\lambda I_1^{-D}) \right] (\lambda^2 - 1) \quad (3.18)$$
3.2.1.3. The WFB Model for Pure Shear Loading

For pure shear stress state \((\sigma_1 = -\sigma_3 \text{ and } \sigma_2 \neq 0)\), see Fig. 3.1, the principal stretches, Cauchy’s principal stress \((\sigma)\), and the arbitrary pressure \((p)\) can be represented as follows:

\[
\begin{align*}
\lambda_1 &= \lambda, \quad \lambda_2 = 1 \quad &\text{&} \quad \lambda_3 = \lambda^{-1} \\
p &= \frac{2}{\lambda^2} \frac{\partial W}{\partial I_1} + \left[ 1 + \frac{2}{\lambda^2} \right] \frac{\partial W}{\partial I_2} \\
\sigma_1 &= 2 \left[ \frac{\partial W}{\partial I_1} + \frac{\partial W}{\partial I_2} \right] \left( \lambda^2 - \frac{1}{\lambda^2} \right), \quad \& \quad \sigma_2 = 2 \left[ \frac{\partial W}{\partial I_1} + \lambda^2 \frac{\partial W}{\partial I_2} \right] \left( 1 - \frac{1}{\lambda^2} \right)
\end{align*}
\] (3.19) (3.20) (3.21)

By using the same equation (Eq. (3.12)) for the strain energy function, and by applying the Yeoh model assumption \(\frac{\partial W}{\partial I_2} \approx 0\), the Cauchy principal stresses \(\sigma_1\) and \(\sigma_2\) can now be represented as

\[
\begin{align*}
\sigma_1 &= 2 \{ F(\lambda) A(\lambda e^{-B I_1}) + C(\lambda I_1^{-D}) \} \left( \lambda^3 - \frac{1}{\lambda} \right) \\
\sigma_2 &= 2 \{ F(\lambda) A(\lambda e^{-B I_1}) + C(\lambda I_1^{-D}) \} \left( \lambda - \frac{1}{\lambda^2} \right)
\end{align*}
\] (3.22) (3.23)

3.2.2. The WFB Model Verification

3.2.2.1. Uni-axial Stress State

The WFB model parameters were determined using the NLS optimization tool from Matlab: Lsqcurvefit. The NLS tool theory depends on minimizing \(S_f(P)\), see Eqs. (3.25) and (3.26), according to a specific criterion. A random guess was used for the parameters \((P_i)\) to find the values that generate the best curve fit to the test data. The WFB model was applied to nominal instead of Cauchy stresses, where the nominal stress is the stress obtained by dividing the force by the cross-sectional area of material before deformation. The nominal stresses \((\sigma_{Kn})\) for the WFB model for uni-axial tension can be represented by the following equation:

\[
\sigma_{Kn} = \lambda_2 \lambda_3 \sigma_R = \frac{\sigma_R}{\lambda} = \{ F(\lambda) A(\lambda e^{-B I_1}) + C(\lambda I_1^{-D}) \} \left( \lambda - \frac{1}{\lambda^2} \right)
\] (3.24)
\[ S_f(P) = \| F(P_i, \lambda) - \sigma_K \|_2^2 \]  
(3.25)

\[ \| F(P_i, \lambda) - \sigma_K \|_2^2 = \sum_{i=1}^{2} [F(P_i, \lambda) - \sigma_K] \]  
(3.26)

The starting values for all parameters in every model were assumed to be as close as possible to the exact solution. The iterations stop either when the Newton’s step becomes less than 1E-12, when the infinity norm of the estimated gradient of the objective function is less than 1E-12 value, or when a maximum number of iterations of 2.0E6 iteration steps is reached. To verify the proposed WFB model, the nominal uni-axial stresses for Treloar’s historic vulcanized rubber data [31] were fitted using the WFB, Yeoh, and Ogden models with three and four series parameters (N=3 and N=4); see Fig. 3.7. Figure 3.7-a presents the nominal stress results for all the models compared to Treloar’s uni-axial tension test data, and Fig. 3.7-b shows the difference between the fitted data from every model compared to the test data. Table 3.2 includes all the models’ parameter values calculated using the Lsqcurvefit optimization tool. Figure 3.7-b and Table 3.1 indicate that the WFB model recorded the second lowest LSE, with 0.0104 compared to 0.0174, 0.0100, and 0.0105 for the Yeoh model and the Ogden model N=3 and N=4, respectively; see Eq. (3.27) and Eq. (3.28) for the error difference (Error Diff) and LSE formulas.

\[ Error \ Diff = \sigma_{test} - \sigma_{fitt} \]  
(3.27)

\[ LSE = \sqrt{\frac{\sum (Error \ Diff)^2}{Number \ of \ Data \ Points}} \]  
(3.28)
a) WFB fit for $H = 1.964$.  

b) Least square error variation with $H$.

**Fig. 3.6** The WFB model results for Treloar’s uni-axial loading test data.

<table>
<thead>
<tr>
<th>Model</th>
<th>$LSE$</th>
<th>Processing time (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yeoh</td>
<td>0.0173</td>
<td>0.0156</td>
</tr>
<tr>
<td>Ogden (N=3)</td>
<td>0.0100</td>
<td>16.9219</td>
</tr>
<tr>
<td>Ogden (N=4)</td>
<td>0.0105</td>
<td>76.3906</td>
</tr>
<tr>
<td>WFB</td>
<td>0.0104</td>
<td>0.0313</td>
</tr>
</tbody>
</table>

Table 3.1 also lists the processing times of all the models compared to the proposed WFB model. The WFB model comes in second place, with a processing time of 0.0313 sec compared to 0.0156 sec for the Yeoh model. Despite being faster in the processing, however, the Yeoh model $LSE$ is higher than the WFB: 0.0173 compared to 0.0104, respectively. Numerically, the Ogden model should be more accurate as it has a more flexible formulation compared to the Yeoh and the WFB models; however, it takes a long time to extract its parameters.

The results of the comparison show that the proposed WFB model reduces the parameters processing time compared to the Ogden models by 99.82% and 99.96% for $N=3$ and $N=4$, respectively. According to the WFB methodology, the weight function is related to the $TP$ value for reaching the minimum $LSE$ in fitting the test data the test data. Observing the $LSE$ variation
with \((H)\), see Fig. 3.3, reveals that the \(LSE\) is minimized when \(H = 1.964\), where \(TP\) is 2.4 for
Treloar’s vulcanized rubber material; see Fig. 3.6.

![Graph showing fitting results and error difference](image)

**Fig. 3.7** The Ogden and Yeoh models results and comparison to the proposed WFB model for Treloar’s uni-axial loading test data.

**Table 3.2 Hyper-elastic models’ parameters for fitting Treloar’s uni-axial test data using Lsqcurvfit optimization tool in Matlab.**

<table>
<thead>
<tr>
<th>Yeoh Model:</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(\sigma = [2C_{Y1} + 4C_{Y2}(I_1 - 3) + 6C_{Y3}(I_1 - 3)^2](\lambda - \lambda^{-2}))</td>
<td>(C_{Y1} = 0.1784) MPa</td>
<td>(C_{Y2} = -2.3285E-3) MPa</td>
</tr>
<tr>
<td>(C_{Y3} = 5.2020E-5) MPa</td>
<td>(A = 0.1661) MPa</td>
<td>(B = -0.1986)</td>
</tr>
<tr>
<td>(C = 0.6683) MPa</td>
<td>(D = -0.6831)</td>
<td></td>
</tr>
<tr>
<td>Ogden Model (N=3):</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\sigma = \sum_{N} \mu [\lambda^{\alpha_{N-1}} - \lambda^{-0.5} \alpha_{N-1}])</td>
<td>(\mu_1 = 3041831.3200) MPa</td>
<td>(\mu_2 = 20.1005E-3) MPa</td>
</tr>
<tr>
<td>(\mu_3 = -8.6585E-12) MPa</td>
<td>(\alpha_1 = 2.8910E-7)</td>
<td>(\alpha_2 = 3.5329)</td>
</tr>
<tr>
<td>(\alpha_3 = -8.5202E-12) MPa</td>
<td>(\alpha_4 = -25.6997)</td>
<td></td>
</tr>
<tr>
<td>Ogden Model (N=4):</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\sigma = \sum_{N} \mu [\lambda^{\alpha_{N-1}} - \lambda^{-0.5} \alpha_{N-1}])</td>
<td>(\mu_1 = 3124.9202) MPa</td>
<td>(\mu_2 = 20.0566E-3) MPa</td>
</tr>
<tr>
<td>(\mu_3 = -8.5202E-14) MPa</td>
<td>(\mu_4 = -1988.5227) MPa</td>
<td></td>
</tr>
<tr>
<td>(\alpha_1 = -21.2802E-5)</td>
<td>(\alpha_2 = 3.5343)</td>
<td></td>
</tr>
<tr>
<td>(\alpha_3 = -25.7149)</td>
<td>(\alpha_4 = -21.3121E-5)</td>
<td></td>
</tr>
<tr>
<td>WFB Model:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\sigma = {F(\lambda) A(\lambda e^{-B I_1}) + C(\lambda I_1^{-D})} (\lambda - \lambda^{-2}))</td>
<td>(A = 0.1661) MPa</td>
<td>(B = -0.1986)</td>
</tr>
<tr>
<td>(C = 0.6683) MPa</td>
<td>(D = -0.6831)</td>
<td></td>
</tr>
</tbody>
</table>
3.2.2.2. **Bi-axial Stress State**

The proposed WFB model equation for bi-axial loading (Eq. (3.18)) was verified against Treloar’s data for bi-axial loading. Figure 3.9-a presents the nominal stress results for all three models compared to Treloar’s bi-axial tension test data, and Fig. 3.9-b shows the difference between the fitted data for every model compared to the test data. Table 3.3 includes all the models’ parameter values, which were calculated using the Lsqcurvefit optimization tool. Figure 3.9-b shows that the WFB model reaches good fitting results compared to the Ogden model, with a good LSE of 0.066 compared to 0.0036, 0.0040, and 0.0263 for Yeoh and Ogden N=3 and N=4, respectively; see Table 3.4. However, the Yeoh model has the shortest processing time with 0.01563 sec compared to 0.03125 sec for the WFB and Ogden N=3 and N=4.

Although the WFB is not the optimum tool for fitting Treloar’s bi-axial data, it shows a better fitting that reduces the LSE by 74.9% compared to the Ogden model for N=4 for the same processing time. The LSE variation with \( H \) is minimized when \( H \) equals 2.0, where TP is 1.943 for Treloar’s vulcanized rubber material; see Fig. 3.8.

![Graphs](image)

a) The WFB fit for \( H=2.0 \).

b) Least square error variation with \( H \).

Fig. 3.8 The WFB model results for Treloar’s bi-axial loading test data.
Table 3.3 Hyper-elastic models’ parameters for fitting Treloar’s bi-axial data using Lsqcurvfitt optimization tool in Matlab.

<table>
<thead>
<tr>
<th>Yeoh Model:</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ \sigma = [2C_{Y1} + 4C_{Y2}(I_1 - 3) + 6C_{Y3}(I_1 - 3)^2] (\lambda - \lambda^{-5}) ]</td>
</tr>
<tr>
<td>[ C_{Y1} = 0.1857 \text{ MPa} ]</td>
</tr>
<tr>
<td>[ C_{Y2} = -16.0075E-3 \text{ MPa} ]</td>
</tr>
<tr>
<td>[ C_{Y3} = 3.2246E-3 \text{ MPa} ]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ogden Model (N=3):</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ \sigma = \sum \mu [\lambda^{\alpha N-1} - \lambda^{-2} \alpha N^{-1}] ]</td>
</tr>
<tr>
<td>[ \mu_1 = 387.7853 \text{ MPa} ]</td>
</tr>
<tr>
<td>[ \mu_2 = 6.2636E-2 \text{ MPa} ]</td>
</tr>
<tr>
<td>[ \mu_3 = -1.0625E-6 \text{ MPa} ]</td>
</tr>
<tr>
<td>[ \alpha_1 = 1.9945E-3 ]</td>
</tr>
<tr>
<td>[ \alpha_2 = 2.4213 ]</td>
</tr>
<tr>
<td>[ \alpha_3 = -9.4590 ]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ogden Model (N=4):</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ \sigma = \sum \mu [\lambda^{\alpha N-1} - \lambda^{-2} \alpha N^{-1}] ]</td>
</tr>
<tr>
<td>[ \mu_1 = 6236.6000 \text{ MPa} ]</td>
</tr>
<tr>
<td>[ \mu_2 = 2.5774 \text{ MPa} ]</td>
</tr>
<tr>
<td>[ \mu_3 = -8.4648E-11 \text{ MPa} ]</td>
</tr>
<tr>
<td>[ \alpha_1 = 4.7817E-2 ]</td>
</tr>
<tr>
<td>[ \alpha_2 = 1.5143 ]</td>
</tr>
<tr>
<td>[ \alpha_3 = -14.1835 ]</td>
</tr>
<tr>
<td>[ \alpha_4 = 0.1668 ]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>WFB Model:</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ \sigma = {F(\lambda) A(\lambda e^{-B^1}) + C(\lambda_1^{-D})} (\lambda - \lambda^{-1}) ]</td>
</tr>
<tr>
<td>[ A = 483.667 \text{ MPa} ]</td>
</tr>
<tr>
<td>[ B = 2.8522 ]</td>
</tr>
<tr>
<td>[ C = 0.4767 \text{ MPa} ]</td>
</tr>
<tr>
<td>[ D = 2.3057 ]</td>
</tr>
</tbody>
</table>

Fig. 3.9 The Ogden and Yeoh models results and comparison to the proposed WFB model for Treloar’s bi-axial loading test data.
Table 3.4 Hyper-elastic models’ $LSE$ for Treloar’s bi-axial data.

<table>
<thead>
<tr>
<th>Model</th>
<th>$LSE$</th>
<th>Processing time (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yeoh</td>
<td>0.0036</td>
<td>0.01563</td>
</tr>
<tr>
<td>Ogden (N=3)</td>
<td>0.0040</td>
<td>0.03125</td>
</tr>
<tr>
<td>Ogden (N=4)</td>
<td>0.0263</td>
<td>0.03125</td>
</tr>
<tr>
<td>WFB</td>
<td>0.0066</td>
<td>0.03125</td>
</tr>
</tbody>
</table>

3.2.2.3. Pure Shear Stress State

The proposed WFB model equation for bi-axial loading (Eq. (3.22)) was verified against Treloar’s data for pure shear loading test data for the first principal nominal stresses. Figure 3.11-a presents the nominal stress results for all three models compared to Treloar’s pure shear test data, and Fig. 3.11-b shows the difference between the fitted data for every model compared to the test data. Table 3.5 lists all the models’ parameters values, calculated using the Lsqcurvefit optimization tool. Figure 3.11-b shows that the WFB model’s accuracy is in third place with an $LSE$ of 0.0071 compared to 0.0027, 0.0256, and 0.0017 for Yeoh and Ogden N=3 and N=4, respectively; see Table 3.6. However, the WFB and Yeoh models are the fastest in processing time, with 0.01562 sec and 0.04688 sec compared to 429.87500 and 2.28125 sec for Ogden N=3 and N=4, respectively.

Although the WFB model is not the optimum tool for fitting Treloar’s pure shear data, it shows a better fitting that reduces $LSE$ by 99.99% and 97.9% compared to the Ogden model for $N=4$ and $N=3$, respectively.
Table 3.5 Hyper-elastic models’ parameters for fitting Treloar’s pure shear data using Lsqcurvfitt optimization tool in Matlab.

Yeoh Model:
\[
\sigma = \left[ 2C_{Y1} + 4C_{Y2}(I_1 - 3) + 6C_{Y3}(I_1 - 3)^2 \right] (\lambda - \lambda^{-3})
\]
\[
C_{Y1} = 0.1776 \text{ MPa} \quad C_{Y2} = -16.5325 \times 10^{-4} \text{ MPa}
\]
\[
C_{Y3} = 5.3164 \times 10^{-5} \text{ MPa}
\]

Ogden Model (N=3):
\[
\sigma = \sum \mu \left[ \lambda^{\alpha N-1} - \lambda^{-\alpha N-1} \right]
\]
\[
\mu_1 = 387.7853 \text{ MPa} \quad \mu_2 = 0.06264 \text{ MPa}
\]
\[
\mu_3 = -1.0625 \times 10^{-13} \text{ MPa} \quad \alpha_1 = 19.9449 \times 10^{-4}
\]
\[
\alpha_2 = 2.4213 \quad \alpha_3 = -9.4590
\]

Ogden Model (N=4):
\[
\sigma = \sum \mu \left[ \lambda^{\alpha N-1} - \lambda^{-\alpha N-1} \right]
\]
\[
\mu_1 = 6236.6000 \text{ MPa} \quad \mu_2 = 2.5774 \text{ MPa}
\]
\[
\mu_3 = -8.4648 \times 10^{-11} \text{ MPa} \quad \mu_4 = -1086.4000 \text{ MPa}
\]
\[
\alpha_1 = 47.8172 \times 10^{-3} \quad \alpha_2 = 1.5143
\]
\[
\alpha_3 = -14.1835 \quad \alpha_4 = 0.1668
\]

WFB Model:
\[
\sigma = \{ F(\lambda)A(\lambda e^{-B_1}) + C(\lambda_1^{-D}) \} (\lambda - \lambda^{-1})
\]
\[
A = 0.8642 \text{ MPa} \quad B = 0.3018
\]
\[
C = 0.2409 \text{ MPa} \quad D = -0.1331
\]

Although the accuracy of the Ogden model should improve by increasing the number of intervals, this is not the case in the pure shear results, as the model reaches the maximum number of iterations of 2.0E6 for N=4 without reaching the optimum solution. Observing the LSE variation...
with \((H)\) reveals that the \(LSE\) is minimized when \(H = 2.0\), where \(TP\) is 2.402 for Treloar’s vulcanized rubber material; see Fig. 3.11.

![Graph](image1)

a) Hyper-elastic models’ fitting results.  

![Graph](image2)

b) Error difference.

**Fig. 3.11** The Ogden and Yeoh models’ results and comparison to the proposed WFB model for Treloar’s pure shear loading test data.

**Table 3.6 Hyper-elastic models’ LSE for Treloar’s pure shear data.**

<table>
<thead>
<tr>
<th>Model</th>
<th>LSE</th>
<th>Processing time (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yeoh</td>
<td>0.0027</td>
<td>0.01562</td>
</tr>
<tr>
<td>Ogden (N=3)</td>
<td>0.0256</td>
<td>429.87500</td>
</tr>
<tr>
<td>Ogden (N=4)</td>
<td>0.0017</td>
<td>2.28125</td>
</tr>
<tr>
<td>WFB</td>
<td>0.0071</td>
<td>0.04688</td>
</tr>
</tbody>
</table>

### 3.2.3. The WFB Model Results for Natural Rubber

#### 3.2.3.1. Uni-axial Loading

The WFB model was applied to the tested natural rubber specimen. Equation (3.24) was used to fit the tensile test data in Fig. 2.2 for engineering stress and strain of the natural rubber specimen. The \(H\) value and the \(TP\) values were found to be 1.409 and 2.5, respectively; see Figs. 3.4 and 3.5.
Figure 3.12 presents Eq. (3.24) fitting for uni-axial tension compared to the tested natural rubber specimen. The WFB model parameters were determined using the *Lsqcurvefit* optimization tool: their values are 0.1178 MPa, -0.0790, 0.1638 MPa, and 0.0432 for A, B, C, and D, respectively. The model shows a very good match compared to the test data, with an average error percentage of 0.44%.

![WFB model fit](image1)

![WFB model fit Error % compared to experimental data](image2)

**Fig. 3.12** The natural rubber tensile test results compared to the newly proposed WFB model.

3.2.3.2. **Bi-axial Loading (Bulge Test)**

**Experimental testing**: The WFB model was applied to the bi-axial loading with the same natural rubber material that was tested for the uni-axial tension loading, discussed in the previous section. Figure 2.1-a presents the specimen for the bi-axial loading. A bulge test arrangement was manufactured to generate the bi-axial loading condition; Fig. 3.13 demonstrates the whole test arrangement. The test consisted of applying pressure to a flat rubber pad and measuring the bulge height as well as the change in the bulge diameter, and converting these parameters to stress and strain measurements.
The bulge test is a simple pressure vessel problem where the stresses in the bulge surface can be calculated using the following formula:

$$\sigma_1 = \sigma_2 = \frac{P \cdot \rho}{r \cdot t_0 \cdot \lambda_3}$$  \hspace{1cm} (3.29)
where \( P \) is the applied pressure value, \( t_o \) is the initial pad thickness (1.29 mm), \( \lambda_3 \) is the third principle stretch value, and \( \rho \) is the bulge radius. \((t_o \cdot \lambda_3)\) is the instantaneous bulge thickness at every pressure value; \((\lambda_3 = \lambda_1^{-2} = \lambda_1^{-2} = (\frac{D_s}{D_o})^{-2})\). The bulge radius is related to the change in an initial circular reference diameter \((D_o)\) and the height of the bulge by the following relation:

\[
\rho = \frac{(\frac{D_s}{2})+h^2}{2h} \tag{3.30}
\]

where \( D_s \) is the final diameter of \( D_o \) after applying pressure, and \( h \) is the bulge height, which can be identified by a dial gage during the test after applying pressure.

**Finite element model testing:** To increase confidence regarding the tested natural rubber materials in the bulge test, a finite element model (FEM) was generated using a 2D axisymmetric model on Abaqus. The model had two main materials: the natural rubber material for the test pad, and a steel A36 for the top holder. The Yeoh model was chosen to describe the rubber material behavior, including the uni-axial tension stress-strain experimental results from section 3.2.3.1. Figure 3.14-a presents the FEM boundary conditions and loading, while Fig. 3.14-b shows the stresses generated after applying a pressure of 0.031 MPa. The type of element used for the rubber material was a CAX4RH, which is a 4-node bilinear axisymmetric quadrilateral hybrid element; and the top holder was meshed using a CAX4R, which is 4-node bilinear axisymmetric quadrilateral element.
a) FEM boundary conditions and loading.

b) FEM true stresses results at \( P = 0.031 \text{ MPa} \).

\[ S, \text{ Mises} \]
\[ \text{(Avg: 75\%)} \]

\begin{tabular}{c}
+1.183e+00 \\
+1.084e+00 \\
+9.859e-01 \\
+8.873e-01 \\
+7.887e-01 \\
+6.901e-01 \\
+5.915e-01 \\
+4.930e-01 \\
+3.944e-01 \\
+2.958e-01 \\
+1.972e-01 \\
+1.859e-02 \\
+0.000e+00
\end{tabular}

**Fig. 3.14** Finite element analysis (FEA) for bulge test.

**WFB results compared to the FEM and the experimental data:** Figure 3.15 compares the engineering stress-strain results of the bulge test, the FEA, and the WFB model. The WFB model was applied using Eq. (3.18) for bi-axial stresses, and the experimental data was fitted using the \textit{Lscurvefitt} Matlab tool; the parameters’ values are -331574.6487, 8.0405, 0.0635, and -0.7233.
for A, B, C, and D, respectively. The WFB model shows an average error of 15% compared to the experimental test data, and the FEA results have an average error of 5% compared to the bulge test data.

![Graph showing WFB fitting compared to the FEA and bulge test results.](image)

**Fig. 3.15** WFB fitting compared to the FEA and bulge test results.

### 3.3. Conclusion

The WFB model is a new hyper-elasticity model that describes rubber-like materials’ stress-strain behavior. The WFB model assumes the strain energy ($W$) to be a function only in the first principal stretch value ($\lambda_1$), and predicts the principal stresses based on the strain energy theory assumptions and the applied loading condition.

The model was applied to Treloar’s data for uni-axial, bi-axial, and pure shear loading conditions. The WFB model shows a very good degree of confidence compared to the Ogden and Yeoh models. An NLS optimization tool (*Lsqcurvefit*) was used for all fitting purposes, including the determination of the material parameters of the WFB, Yeoh, and Ogden models for Treloar’s data and the tested natural rubber material data. For Treloar’s uni-axial loading data, the WFB
model shows an $LSE$ of 0.0104, which is the second-best result after that of the Ogden model for $N=3$. However, the proposed model also reduces the processing time by 99.82% for approximately the same accuracy, which makes it a better choice than the other models.

For the bi-axial loading test data, the WFB model shows the same processing time of 0.03125 sec as the Ogden models, with a better accuracy than the Ogden model for $N=4$. However, the Yeoh model shows the best processing time and accuracy of all.

For the pure shear loading, the WFB model accuracy is in third place with an $LSE$ of 0.0071, and in second place with a processing time of 0.04688 sec, which reduces the processing times of the Ogden model for $N=4$ and $N=3$ by 99.99% and 97.9%, respectively.

In general, the WFB model is highly time-efficient compared to the Ogden model, especially for the uni-axial and pure shear loading, and it is more accurate than the Yeoh model for the uni-axial tension.

The WFB model was applied to a natural rubber material under uni-axial tension and matched the tensile test data with an average error percentage of 0.44%.
CHAPTER 4
APPLYING THE WEIGHT FUNCTION BASED MODEL TO NATURAL RUBBER

4.1. Introduction

After defining the material properties’ variation with aging time and temperature in Chapter (2) and verifying the accuracy of the WFB against Treloar’s data, the present chapter concerns the application of the WFB model to the aged natural rubber specimens. More than 130 natural rubber specimens were heated in an oven and exposed to a uni-axial tension test to extract the stress-strain interaction under variable temperatures and times. The temperature ranged from 76.7 °C to 115.5 °C, and the aging time from zero to 600 hours. The proposed WFB model is based on the Yeoh model and basic continuum mechanics assumptions, and it was applied to the tested natural rubber materials. The same NLS optimization tool in Matlab was used to determine all hyper-elastic models’ material parameters and all other fitting purposes.

4.2. The WFB Parameters’ Variations with Aging Time and Temperature

\[
\frac{\sigma_{KB}}{\sigma_0} = \text{COR} \cdot \left\{ F(\lambda) \left( A e^{-B I_1} + C \left( \lambda I_1^D \right) \right) \right\} \left( \lambda - \frac{1}{\lambda^2} \right) 
\]  

Equation (4.1) represents the final normalized formulation of the WFB model nominal stresses of natural rubber, where \(\sigma_0 = 21.6 \text{ MPa}\) is the tested fracture strength for an unaged natural rubber specimen. \(A, B, C,\) and \(D\) represent the main model parameters; \(F(\lambda)\) is a piecewise smooth weight function; and \(\text{COR}\) is a correction factor that is related to aging time and temperature for error reduction purposes.
The WFB model depends heavily on the formulation of \( F(\lambda) \), as it represents the core of the model. \( F(\lambda) \) can be fitted using any adequate smooth piecewise function, but the values of \( TP \) and \( L_f \) should be identified first.

By following the same base as in Chapter (2) for the variation of the natural rubber mechanical properties with time and temperature, and by recording the change of \( L_f \) and \( TP \) with aging time and temperature from the tensile test experimental data, Eqs. (4.2) and (4.3) were chosen to fit the values for both \( TP \) and \( L_f \):

\[
TPR = \frac{TP}{TP_0} = e^{-100(e^{M_1 T - M_2})} t^\frac{M_3}{T} \tag{4.1}
\]

\[
FSR = \frac{L_f}{L_{f0}} = e^{-100(e^{M_1 T - M_2})} t^\frac{M_3}{T} \tag{4.3}
\]

where \( TPR \) is the transition point ratio, \( FSR \) is the fracture stretch ratio, and \( M_i \) are equation constants that can be determined using the same NLS optimization tool from Matlab (Lsqcurvefit). \( TP_0 \) and \( L_{f0} \) in Eqs. (3.2) and (3.3) represent the transition point and fracture stretch values for the unaged natural rubber specimen, which are 2.5 and 12.7, respectively.

| Table 4.1 TPR and FSR equation constants. |
|-----------------|-------|-------|
| Constant        | TPR   | FSR   |
| \( M_1 \)       | 17.609| 21.697|
| \( M_2 \)       | 42.761| 49.470|
| \( M_3 \)       | 5.9067| 5.9067|

Table 4.1 presents the results of Eqs. (4.2) and (4.3) constants \( (M_i) \) after fitting using the (Lsqcurvefit) tool. The aging time and temperature in these equations are dimensionless, as the normalized temperature \( T \) represents the ratio between the temperature in °K and the natural rubber glass transition temperature of 203.2 °K, and the normalized time \( t \) represents the ratio between the aging time in hours and the reference time \( (t_r) \) of 100 hrs. The reference time is the time after
which the WFB parameters \((A, B, C, \text{ and } D)\) stop behaving linearly with time, as will be shown later in this section.

**Fig. 4.1** TPR and FSR variation with time and temperature for the test data and the proposed Eqs. (4.2) and (4.3).
Once the transition point and the fracture length have been identified according to the aging time and temperature values, any function can be used to fit the weight function presented in Fig. 3.3-b. Fig. 4.2 shows a sample of a weight function fitted curve for 76.7°C and 600 hrs aging time.

The present author used Eq. (4.4) to fit the weight function curve,

\[ F(\lambda) = P_1(\lambda^2 + P_2)^{-P_3} \]  

where \( P_1, P_2, \) and \( P_3 \) can be evaluated using the same NLS optimization tool from Matlab (Lsqcurvefit), or any other linear or non-linear optimization fitting tool. Equation (22) is not necessary for \( F(\lambda) \) fitting: the user can use any smooth piecewise function as long as it fits the main weight function assumptions and shape.

Figure 4.2 presents parameter A variation with time and temperature. Parameter A tends to be constant with time as the temperature reaches the room temperature of 298.2 °K. Moreover, this parameter is observed to be almost linear as long as the aging time is less than the reference
time \((t_r)\) value of 100 hrs, after which it decreases rapidly until it reaches zero, and then starts to vanish. Equations (23) to (25) are the main equations of parameter \(A\). The aging temperature effect on parameter \(A\) decreases as the temperature tends to reach room temperature; see Fig. 4.3-a. Parameter \(B\)'s behavior is similar to that of \(A\); see Fig. 4.4 and Eqs. (4.8) to (4.10).

\[
A = a_1 \cdot e^{\left(-\frac{T}{a_2}\right)^2}
\]  

(4.5)

where

\[
a_1 = \begin{cases} 
k_1 - k_2 \cdot e^{-\left(\frac{T-1.7217}{k_3}\right)^2}, & T \geq 1.7217 \cdot T_g \\
  k_1 - k_2, & T < 1.7217 \cdot T_g
\end{cases}
\]

(4.6)

\[
a_2 = \begin{cases} 
k_4 \cdot e^{-\left(\frac{T-1.7217}{k_5}\right)^2}, & T \geq 1.72178 \cdot T_g \\
  k_4, & T < 1.72178 \cdot T_g
\end{cases}
\]

(4.7)
a) Parameter $B$ variation with time and temperature.

\[
B = b_1 \cdot e^{-\left(\frac{t}{b_2}\right)^2}
\]  

(4.8)

where

\[
b_1 = \begin{cases} 
  k_6 - k_7 e^{-\left(\frac{T - 1.721}{k_8}\right)^2}, & T \geq 1.72178 T_g \\
  k_6 - k_7, & T < 1.72178 T_g
\end{cases}
\]  

(4.9)

\[
b_2 = \begin{cases} 
  k_9 e^{-\left(\frac{T - 1.721}{k_10}\right)^2}, & T \geq 1.72178 T_g \\
  k_9, & T < 1.72178 T_g
\end{cases}
\]  

(4.10)

b) $b_1$ and $b_2$ in Eqs. (4.6) and (4.7) variation with temperature.

Fig. 4.4 Parameter $B$ properties.
a) Parameter $C$ variation with time and temperature.

b) Parameter $C$ rate of change with time.

Fig. 4.5 Parameter $C$ properties.

---

a) Parameter $D$ variation with time and temperature.

b) Parameter $D$ rate of change with time.

Fig. 4.6 Parameter $D$ properties.
The WFB model parameters $C$ and $D$ tend to increase rapidly until the time reaches a reference value of 100 hrs ($t_r$), after which they try to reach a constant value with a slower rate of change; see Fig. 4.5 and Fig. 4.6, and Eqs. (4.11) to (4.14).

$$C = c_1 + 0.00925 \left(1 - \frac{1}{0.0142 \ t + 1}\right) + c_2 \left(1 - \frac{1}{t+1}\right)$$  \hspace{1cm} (4.11)

$$c_1 = 0.007784, \hspace{1cm} c_2 = k_{11}e^{k_{12}(T-1.477)}$$  \hspace{1cm} (4.12)

$$D = d_1 + 0.2 \left(1 - \frac{1}{0.0142 \ t + 1}\right) + d_2 \left(1 - \frac{1}{t+1}\right)$$  \hspace{1cm} (4.13)

$$d_1 = 0.04322, \hspace{1cm} d_2 = k_{13}e^{k_{14}(T-1.477)}$$  \hspace{1cm} (4.14)

<table>
<thead>
<tr>
<th>Constant</th>
<th>Value</th>
<th>Constant</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$</td>
<td>0.0243</td>
<td>$k_8$</td>
<td>0.3110</td>
</tr>
<tr>
<td>$k_2$</td>
<td>0.0154</td>
<td>$k_9$</td>
<td>13.0271</td>
</tr>
<tr>
<td>$k_3$</td>
<td>0.9260</td>
<td>$k_{10}$</td>
<td>0.0983</td>
</tr>
<tr>
<td>$k_5$</td>
<td>17.9088</td>
<td>$k_{11}$</td>
<td>2.8920e-5</td>
</tr>
<tr>
<td>$k_4$</td>
<td>0.7882</td>
<td>$k_{12}$</td>
<td>18.9340</td>
</tr>
<tr>
<td>$k_6$</td>
<td>0.7882</td>
<td>$k_{13}$</td>
<td>63.4400e-6</td>
</tr>
<tr>
<td>$k_7$</td>
<td>0.4000</td>
<td>$k_{14}$</td>
<td>22.2860</td>
</tr>
</tbody>
</table>

The correction factor in Eq. (4.1) aims to reduce the error as much as possible for the WFB model fit. The correction factor is function in aging time and temperature. After several trials, the correction factor was chosen to follow Eq. (4.15).

$$COR = 1 - 0.2 \ G_1(t) \ast G_2(T)$$  \hspace{1cm} (4.15)

where

$$G_1(t) = 0.5 + 0.5 \ Tanh \left(\frac{t-g_1}{g_2}\right)$$  \hspace{1cm} (4.16)

$$G_2(T) = 0.5 + 0.5 \ Tanh \left(\frac{T-g_3}{g_4}\right)$$  \hspace{1cm} (4.17)
are the correction factor parameters $g_i$ depending on the desired accuracy, where ($i$) ranges from 1 to 4. $G_1$ and $G_2$ are two smooth step functions that vary from 0 to one. Figure 4.7 illustrates the behavior of the correction function $G_i$ by varying both constants $g_1$ and $g_2$.

![Graph showing correction function behavior by varying ($g_1$, $g_2$).](image)

Fig. 4.7 Correction function behavior by varying ($g_1$, $g_2$).

<table>
<thead>
<tr>
<th>Constant</th>
<th>TPR</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g_1$</td>
<td>0</td>
</tr>
<tr>
<td>$g_2$</td>
<td>1</td>
</tr>
<tr>
<td>$g_3$</td>
<td>1.7</td>
</tr>
<tr>
<td>$g_4$</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 4.3 Correction factor parameters’ values for natural rubber.

According to the behaviors of Eqs. (4.15), (4.16), and (4.17), one can notice that the correction factor for the WFB model ($COR$) ranges from 0.8 to 1. The correction factor parameters can be determined by applying any optimization tool, or essentially by observing the hyper-elastic material behavior at various times and temperatures. Table 4.3 presents the current values of the correction factor parameters ($g_i$) for the tested natural rubber materials; these values were determined using simple trial and error in accordance with the recorded stress-strain behavior of the tensile test results at various aging time and temperature values. Figure 4.8 shows an example of the results before and after applying the correction factor to the tested natural rubber material.
The figure shows that the error percent is reduced from 27.0% without correction to 1.6% after applying the correction factor. The Error was calculated using Eq. (4.17).

\[
Error = \frac{\sigma_{test} - \sigma_{fit}}{\sigma_{test}} \cdot 100\% \tag{4.17}
\]

a) The natural rubber specimen stress-strain behavior.

b) The WFB model results’ error % compared to the test data with and without applying the correction factor (COR).

Fig. 4.8 Correction factor effect on the tested natural rubber material for an aged specimen at 110.0 °C and 255 hrs.
4.3. WFB Fitting Discussion and Results

The WFB model is the first mathematical model to describe the behavior of rubber-like materials, directly as a function of aging time and temperature, making it unique compared to other hyper-elastic material models. The method is based on experimental observations and typical continuum mechanics assumptions without direct relation to the microstructure or the hyper-elastic materials’ crosslinking theories. The main drawback of the WFB model is that it requires a wide range of experiments to be able to extract the WFB parameters as accurately as possible. The author recommends the following to define the WFB parameters for any other hyper-elastic materials: a) using at least five temperature ranges in the range from $1.7 \cdot T_g$ to $1.9 \cdot T_g$; b) for every temperature range, testing at least four aging time values in the range of zero to 1000 hours; c) identifying the WFB parameters’ constants ($k_{ij}$) (see Table 4.2) that can give the best fit of the tested data using the steps in Fig. 4.9; and d) defining a function for the correction factor, if needed, to reduce the error as much as possible. Figure 4.9 shows the main steps for generating the WFB parameters’ constants for any hyper-elastic material.

Based on the WFB parameters’ ($A, B, C,$ and $D$) variation with time and temperature shown in section 3.3, the temperature effect on the stress-strain behavior of rubber materials’ aging is negligible as the temperature drops below 350 °K (77 °C or $1.7 \cdot T_g$). This means that, for low temperatures, the aging time is the dominant factor controlling the parameters and the stress-strain behavior change.
Fig. 4.9 The WFB model parameters extraction flowchart.
Figure 4.10-a presents the unaged data compared to the WFB model stresses for the same material using room temperature and aging time of zero hours. Figure 4.10-b shows the error percentage compared to the experimental results for unaged natural rubber material; see Eq. (4.17). The WFB stresses match well with the experimental data, with an average error of 3.2%.

Figure 4.11 shows the WFB model generated stresses compared to experimental tensile test data. The figure represents two cases from every tested temperature value in Table 2.1 at two different aging time values. Both the tested data and the WFB model shows that, for the tested natural rubber material, the fracture strength decreases as the aging time and temperature increase. For example, in Fig. 4.11-g, the fracture strength for the tested natural rubber material at 110 ºC decreases from 20.7 MPa to 2.9 MPa after 26 hrs and 255 hrs of aging, respectively, with 86% reduction. Moreover, by increasing the aging temperature from 76.7 ºC to 82.2 ºC, the fracture strength decreases from 19.8 MPa to 17.5 MPa, respectively, with 11.6 % reduction; see Figs.
4.11-a and b. Thus, both aging time and temperature seem to reduce the fracture strength of the tested natural rubber material.

- **a)** $T = 76.7 \, ^\circ C$ with zero and 600 hrs aging time.
- **b)** $T = 82.2 \, ^\circ C$ with zero and 600 hrs aging time.
- **c)** $T = 87.8 \, ^\circ C$ with zero and 601 hrs aging time.
- **d)** $T = 93.3 \, ^\circ C$ with zero and 311 hrs aging time.
e) \( T = 98.89^\circ C \) with zero and 410 hrs aging time.

f) \( T = 104.44^\circ C \) with zero and 424 hrs aging time.

g) \( T = 110^\circ C \) with 26 and 255 hrs aging time.

h) \( T = 115.53^\circ C \) with zero and 311 hrs aging time.

Fig. 4.11 The WFB model behavior against experimental test data for \( T = 98.89 \) to \( 115.53^\circ C \) and various aging times.

The average error magnitude of the test data in Fig. 4.11 ranges from 0.39\% to 20.0\%, which is still acceptable considering that this model can provide a clear estimate of the stress-strain
behavior of any aged natural rubber material at any aging time and temperature without the need for any further testing or CLD measurements.

Table 4.4 Three verification samples.

<table>
<thead>
<tr>
<th>Case#</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (hrs)</td>
<td>212.0</td>
<td>556.0</td>
<td>10.3</td>
</tr>
<tr>
<td>Temp (°C)</td>
<td>103.3</td>
<td>78.9</td>
<td>112.2</td>
</tr>
</tbody>
</table>

Fig. 4.12 The WFB model verification against the three tested cases.

Table 4.4 presents three randomly generated aging times and temperatures for three different cases that were chosen to verify the proposed WFB model equations. In each case, the three specimens were tensioned using the tensile testing machine after reaching the required aging time and temperature.

Fig. 4.12 shows the results of the proposed WFB model compared to the three tensioned cases. The WFB model shows good results compared to these cases, with an average error percentage of 4.2%, 6.7%, and 4.8% for case (1), (2), and (3), respectively.
Several improvements can be suggested for the WFB model error reduction. These include but are not limited to a) increasing the tensile test specimens for every case in Table 2.1, which could yield a better estimate of the stress-strain behavior at various aging time and temperature values; b) suggesting a better fitting equation for the weight function $F(\lambda)$, $TP$, and $L_f$; c) increasing the accuracy of the pre-selected non-linear optimization fitting Matlab tool ($Lsqcurvefit$); d) choosing a better and more time-efficient fitting tool than the $Lsqcurvefit$; and e) choosing a better correction factor formula.

4.4. Conclusion

The WFB model is the first model to describe the thermal aging behavior of hyper-elastic material using a set of closed-form equations. One of the drawbacks of the model is that it takes a relatively long time to define the model parameters. To generate the WFB model parameters for any other rubber-like material, a set of experimental tensile testing has to be generated, a) covering at least five temperature ranges in the range from $1.7 \cdot Tg$ to $1.9 \cdot Tg$ and b) testing at least four aging time values in the range of zero to 1000 hours for every temperature range.

Applying the WFB model to the tested specimens with aging temperature values above 115.5 ºC yields an average error of more than 10%. Several improvements can be suggested to reduce this error, such as increasing the number of tensile test specimens, which can provide a better estimate of the stress-strain behavior at various aging time and temperature values, and suggesting a better fitting equation for the weight function $F(\lambda)$. The accuracy of the model depends on both the $TP$ and $L_f$ values, as they affect the weight function $F(\lambda)$’s behavior. By increasing the number of pre-tested specimens, the accuracy in determining the $TP$ and $L_f$ values at various aging temperature and time values will increase, thereby enhancing the accuracy of the
WFB model. Furthermore, choosing a better and more time-efficient fitting tool than the \textit{Lsqcurvefit} or choosing a better correction factor formula may also enhance the WFB model accuracy in defining rubber-like materials’ behaviors. In general, the WFB model presents an easy determination of the stress-strain behavior of rubber-like materials under thermal aging with an acceptable error margin.
REFERENCES


