Investigation of Different Factors Affecting Asphalt Cement Ageing and Durability

by

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Author's Declaration

This thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Statement of Contributions

This thesis is partially the product of co-authored publications as follows. Chapter 4, entitled "Temperature sensitivity of rheological parameters of asphalt materials" is co-authored by myself and my supervisor. In chapter 5, "effect of aggregates containing iron sulphide on asphalt ageing, my colleague, Sarbjot Singh contributed in editing. In Chapters 6 and 7 ("Toward a better simulation of field condition in asphalt mix laboratory age testing" and "laboratory simulation of solar radiation and moisture on long-term age conditioning of asphalt mixes") my colleague, Sarbjot Singh contributed in instrumentation and calibration of the "bespoke solar radiation chamber" that has been used throughout this research as one of the conditioning procedures as well as in material collection and testing. All parts of these papers including test plan, analysis, and discussion were done solely by myself.

Chapter 4

- Azimi Alamdary Y., Baaj H., (2019). "Temperature Sensitivity of Rheological Parameters of Asphalt Materials." submitted to Road Materials and Pavement Design on 22-Feb.-2019 (under revision)

Chapter 5

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Chapter 6

- Azimi Alamdary Y., Singh S., Baaj H., (2019). "Toward a Better Simulation of Field Condition in Asphalt Mix Laboratory Age Testing" Road Materials and Pavement Design. submitted to Road Materials and Pavement Design on 30-May-2019 (under revision)

Chapter 7

- Azimi Alamdary Y., Singh S., Baaj H., (2019). "Laboratory simulation of the impact of solar radiation and moisture on long-term age conditioning of asphalt mixes.", Road Materials and Pavement Design, DOI: 10.1080/14680629.2019.1587496

ABSTRACT

Asphalt cement is an organic material and, like any other organic material tends to react with atmospheric oxygen, thus changing its physical properties (more accurately rheological properties) gradually over time. Although there is no doubt that chemical changes happen in asphalt cement due to gradual oxidation, it is not the only factor resulting in changes in asphalt cement properties over time. Other factors such as loss of volatiles, the selective absorbance of lighter oily molecules by the aggregates' surface, molecular reorientation, and so forth, could lead to changes in asphalt cement properties, most of which result in hardening. The alteration in physical properties of asphalt cement during construction and its performance period is called ageing.

The severity of the age hardening significantly depends on environmental factors such as temperature, latitude (which affects the angle of sunshine radiation), humidity, ultraviolet, etcetera, as well as mixture properties (such as aggregate gradation, aggregate type, air-void distribution, filler composition, and additive's properties). There are several conditioning procedures to simulate short- and long-term ageing for both asphalt cement and mixes. Unfortunately, most of the existing methods are using excessively high conditioning temperatures and not realistic conditioning parameters.

This project aims to identify the importance of less considered factors, such as the possible catalytic effect of minerals, solar radiation, and humidity conditioning and to define a laboratory long-term age conditioning procedure for asphalt mixes by considering different affecting factors to enable designers to include an ageing mechanism in their predictions.

To reach to the goals of this project, compacted asphalt mix samples prepared using aggregates with different petrology and conditioned using standard (AASHTO R30) procedure and bespoke methods to include as much as environmental factors as possible. Complex (Dynamic) Modulus test will be used to evaluate the changes in the rheological behaviour of mixes. The 2S2P1D model fitted on laboratory results and used to investigate the rheological behaviour. Asphalt cement of the conditioned mixes extracted for further investigation on the rheological and chemical changes in asphalt cement. Frequency sweep test performed on extracted asphalt cement and results were processed using the 2S2P1D model. FT-IR spectroscopy was also used to investigate the change in the chemistry of asphalt cement by following the changes in carbonyl and sulfoxide indices and the ratio between them. Thermal sensitivity of rheological properties of both asphalt mix and asphalt cement was also investigated using time-temperature superposition shift-factors and utilizing Arrhenius and William-Landel- Ferry (WLF) theorems to further investigate the effect of different age conditioning and aggregates.

Results of this research confirmed the effect of iron sulphide oxidation products in altering the chemistry of changes during ageing, while it didn’t capture significant acceleration in the process. Moreover, it was found that the coupling water treatment with solar radiation can effectively age asphalt mix samples and the product of ageing using these parameters are considerably different from extended heating procedures.

ACKNOWLEDGMENT

I wish to express my sincere thanks to my supervisor Professor Hassan Baaj for his support, guidance and encouragement during my Ph.D. study. I would also like to express my sincere appreciation to my Ph.D. defence committee members Prof. Susan Tighe, Prof. Hamid Jahed, Prof. Adil Al-Mayah from University of Waterloo and Dr. Jean-Pascal Planche from the Western Research Institute (WRI).

This study was funded by the Ministry of Transportation Ontario (MTO) through the Highway Infrastructure Innovation Funding Program (HIIFP-2015 and HIIFP-2016). I would like to thank Imran Bashir and Carole-Anne McDonald from MTO for their useful feedbacks during the meetings we had in the past years. Appreciation is also extended to COCO Paving Ltd., especially Ms. Selena Lavorato, Mr. Steve Manolis, Mr. Porfirio Vela, and all laboratory technicians for their guidance and continued support with Atlas Weather-O-Meter conditioning and FT-IR testing. I would also like to thank CPATT partner Steed and Evans Ltd., especially Mr. Richard Marco and Mr. Jim Karageorgos for their help with the collection of plant mixed loose asphalt and virgin binder that was utilized in this research project.

My gratitude is also extended to a number of other individuals who helped me during the course of my research studies. The outstanding technical staff members at the Department of Civil and Environmental Engineering, Mr. Terry Ridgway, Mr. Christopher Peace, Mr. Richard Morrison, Mr. Peter Volcic and Mr. Douglas Hirst, for their assistance and help with many of the laboratory tests detailed in this thesis.

I would also like to thank my other colleagues and friends at CPATT. Mr. Sarbjot Singh, Mr. Seyedata Nahidi, Mr. Taher Baghaee Moghaddam, Mr. Saeid Salehiashani, Dr. Sina Varamini, who have helped me throughout the course of my studies, be it collection of materials, getting familiar with test procedures and equipment, or emotional support and encouragement.

My gratitude goes to all my dearest friends and colleagues in Centre for Pavement and Transportation Technology (CPATT) at the University of Waterloo for their help and wonderful times and enjoyable moments we shared.

Last but not least, I am so grateful to my better half, Parinaz Ataeian and my parents for their love and support that helped me to get to where I am today.

To my parents, **Faridé** and **Godrat**, for all the love and devotion

To my better half, **Parinaz**, who's always accepted me
for me and supported me

To my daughter, **Eileen**, for all your smiles,
each of which is lovely enough to raise me from death

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List of Abbreviation

2S2P1D	Two Springs, Two Parabolic Elements, One Dashpot
AASHTO	American Association of State Highway and Transportation Officials
AC	Asphalt Concrete
AR	Ageing Residue
ASTM	American Society for Testing and Material
BBR	Bending Beam Rheometer
BRRC	Belgium Road Research Centre
CA	Christensen Anderson model
CAM	Christensen Anderson Marasteanu model
CPATT	Centre for Pavement and Transportation Technology
DIN	Deutsches Institut für Normung
DSR	Dynamic Shear Rheometer
DTT	Direct Tension Test
EN	European Norms
ERTFOT	Extended Rolling Thin-Film Oven Test
ETFOT	Extended Thin Film Oven Test
EVA	Ethylene-Vinyl Acetate
FGA	Functional Group Analysis
FT-IR	Fourier Transform Infrared
GRF	German Rotating Flask
HiPAT	High-Pressure Ageing Test
HP-GPC	High-Pressure Gel Permeation Chromatography
IDT	Iowa Durability Test
IQR	Interquartile Range
IR	Infrared
LAS	Linear Amplitude Sweep
LMS	Low Molecular Size
LPO	Low-Pressure Oxidation
LTOA	Long-Term Oven Ageing
LVE	Linear Viscoelasticity
MEPDG	Mechanistic Emperical Pavement Design Guide
MGRF	Modified German Rotating Flask
MMS	Medium Molecular Size
MSCR	Multiple Stress Creep Recovery
MSD	Molecular Size Distribution
MTFOT	Modified Thin Film Oven Test
MTO	Ministry of Transportation of Ontario
MTS	Material Testing Systems
NRTFOT	Nitrogen Rolling Thin-Film Oven Test

OPSS	Ontario Provincial Standard Specification
PAV	Pressure Ageing Vessel
PG	Performance Grading
PI	Penetration Index
PMA	Polymer Modified Asphalt
POB	Pressure Oxidation Bomb
PR	Penetration Ratio
PVN	Penetration Viscosity Number
RCAT	Rotating Cylindrical Ageing Test
REOB	Recycled Engine Oil Bottom
RMFOT	Rolling Microfilm Oven Test
RMSE	Root Mean Square Error
RTFOT	Rolling Thin Film Oven Test
SAR	Stiffness Ageing Ratio
SARA	Saturates, Aromatics, Resins, and Asphaltene
SBS	Styrene Butadiene Styrene
SEC	Size Exclusion Chromatography
SEM	Scanning Electron Microscopy
SGC	Superpave Gyratory Compactor
SHRP	Strategic Highway Research Program
SMS	Small Molecular Size
STOA	Short-Term Oven Ageing
TFAAT	Thin Film Accelerated Ageing Test
TFOT	Thin Film Oven Test
THF	Tetrahydrofuran
TODT	Tilt-Oven Durability Test
TSRP	Temperature Sensitivity of Rheological Properties
TTS	Time-Temperature Superposition
USAT	Universal Simple Ageing Test
UV	Ultraviolet
VAPro	Viennese Ageing Procedure
VECD	Viscoelastic Continuum Damage
VTB	Vacuum Tower Bottom
VTS	Viscosity Temperature Susceptibility
VUV	Vacuum Ultraviolet
WLF	William-Landel-Ferry
WMA	Warm Mix Asphalt
WRI	Western Research Institute
XRD	X-Ray Diffraction analysis

CHAPTER 1: INTRODUCTION

1.1 Preface

In addition to a general introduction, a background chapter, and a general conclusion, this thesis consists of two journal articles and two yet unpublished chapters. The first paper, which is submitted to the Journal of Road Materials and Pavement Design, presents a new temperature sensitivity parameter for rheological parameters of viscoelastic materials base on the time-temperature superposition (TTS) principle shift-factors models. This parameter can be used to follow the age-related changes and can be used to get a better understanding of rheological changes through various mechanisms. The second paper, which is published in the Journal of Road Materials and Pavement Design, investigates the effect of aggregates containing iron sulphide and their oxidation products on the age hardening procedure and durability of asphalt mixtures. It was found that the oxidation products of iron sulphide in aggregates can alter chemistry, therefore the rheology, of age-related changes. But at the same time, it was found that the main problem with such aggregates is the expansive nature of iron sulphide oxidation in the presence of moisture which can lead to crack initiation. The yet unpublished chapter describes ageing evolution by time through the solar radiation conditioning with and without water treatment. It shows when solar radiation used alone (without any water treatment) ageing process slows down considerably after a few conditioning cycles. The next chapter which is published in the Journal of Road Materials and Pavement Design, presents a comparison between four different conditioning procedures including AASHTO R30 extended heating procedure, conditioning using ultraviolet radiation in the humid environment, and dry and wet conditioning in a bespoke temperature-controlled solar radiation chamber developed in CPATT laboratory.

The work presented in this thesis was conducted under the supervision of Professor Hassan Baaj who provided tremendous help and support during my Ph.D. study. This project was funded by the Ministry of Transportation Ontario (MTO) through Highway Infrastructure Innovation Funding Program (HIIFP-2015 and HIIFP 2016). Carole-Anne McDonald and Imran Bashir from MTO also provided helpful comments in the meetings we had in the past. All the materials in the composition of the original articles provided in the thesis are the sole production of the primary investigator listed as the first author in the journal publications. The research presented in this thesis is the result of collaboration with materials and testing equipment suppliers Steed and Evans, Coco Paving, and Centre for Pavement and Transportation Technology (CPATT).

1.2 Motivation

The road network as a vital component of the larger transportation network is of crucial importance in the economic growth and social development of each society. When it comes to a country as big as Canada, the importance of the road network is more evident. Currently, Canada owns over a million kilometres road network, 40 percent of which is paved. Among all the paved roads in Canada, more than 95% are asphalt paved, which is roughly around 380 thousand kilometres. The share of paved roads of the total road network system is considerably higher for more populated areas (approximately 63% for Ontario, and 70% for Prince Edward Island). These statistical data explain why an enormous portion of tax-payers money goes for expansion and maintenance of the road network. Interestingly, a considerable amount of total budget that goes for road network was spent on maintenance rather than expansion of the road network.

The time-related changes in the mechanical properties of asphalt cement, known as ageing, have been noticed since the early 1900s, yet due to complexities and variation in the chemical structure of asphalt cement, variability in environmental and processing conditions, and large variety of additive and interacting materials and parameters (such as various types of minerals in aggregates and gradation, different modifiers, and application techniques) not thoroughly understood. The “accurate” prediction of time-related changes in mechanical and chemical properties of asphalt cement and mix in real-life condition might never be achieved in the near future and might not even be crucial for pavement engineers to make sure that the road network is durable enough to serve the purpose by preserving tax-payers money.

Pavement engineers require two essential tools to be able to put ageing-related changes in material properties into account which are appropriate mechanical testing procedures to characterize asphalt cement and mix under representative loading conditions, and proper accelerated laboratory age conditioning procedure to provide representative material, without which results of even most complicated test procedures wouldn’t assure designers of the durability of the pavement.

Although ageing happens mainly in asphalt cement and it is of vital importance to evaluate the ageing susceptibility of asphalt cement, age conditioning of asphalt mixes also must be considered seriously. At the end of the day, it is the interaction of all components of the mix, and not the binder alone, which determines the severity of ageing and the durability of the pavement. The state-of-the-practice laboratory age conditioning procedures are using many unrealistic conditioning parameters by using simplification assumptions mainly to reduce the time and cost of the process. The abundance of premature ageing associated failures mandates new efforts to understand the importance of various parameters and verification of any simplification assumption and serious reconsideration of current laboratory conditioning procedures to reduce the unpredicted failures due to ageing.

1.3 Problem Statement and Objectives

Asphalt cement properties play a decisive role in the performance and durability of the asphalt pavement. Time-related changes in the properties of asphalt cement, known as ageing, causes the gradual change in the properties of asphalt cement and consequently asphalt mixes, and need to be appropriately addressed in order to predict long-term performance.

Various mechanisms are associated in time-related changes in mechanical properties of asphalt cement, among which oxidation is known to have the dominant role in long-term ageing (after construction period). In most of state-of-the-practice laboratory age conditioning procedures, excessively high temperatures and/or higher oxygen access were used to accelerate the conditioning process and other environmental factors such as photo-oxidation, precipitation, and the effect of aggregate mineralogy was neglected mainly for simplification by assuming their influence to be negligible. This approach has faced several criticisms regarding the unrealistic conditioning parameters amongst which excessively high conditioning temperature (which can result a different final product, just as cooking bread at way higher temperature, with different chemical and rheological properties), ignoring the interaction of asphalt cement with other mix ingredients, and disregarding environmental conditions (the combined effect of solar radiation and precipitation) are the most notable ones.

The global objective of this research is to evaluate the applicability and importance of real-life long-term ageing parameters (aggregate interaction, solar radiation, and precipitation) in laboratory conditioning of compacted asphalt mix samples and to prepare representative samples for performance characterization.

The main challenge is then to select appropriate characterization parameters to assess the effect of various conditioning parameters on chemistry and rheology of corresponding asphalt cement and mix. Another challenge is to prepare a laboratory conditioning chamber capable of applying and controlling various weathering parameters including solar radiation, and precipitation at temperatures close to the highest expected performance temperature of the mix in a time-efficient way.

As an outcome of this study, the answer to the following questions would be provided

- Could the aggregate petrology affect the oxidative ageing path and lead to premature ageing?
- Does the application of real-life ageing parameters, including solar radiation and precipitation in the lab lead to any meaningful difference in the properties of the conditioned samples?

Also, a new temperature sensitivity parameter has developed based on the time-temperature superposition principle to explain how ageing would affect the thermal sensitivity of rheological parameters.

As a fruit of this research, an age conditioning procedure was developed to simulate long-term ageing on laboratory compacted asphalt mix samples to provide representative samples for asphalt mix performance testing and a bespoke temperature controlled environmental chamber were built from scratch, capable of applying high-intensity full-spectrum solar radiation and cycles of precipitation simulation.

1.4 Thesis Contribution

The main contribution of this thesis is to provide a long-term age conditioning procedure capable of applying more realistic environmental conditions including realistic conditioning temperature (close to high performance-temperature of asphalt cement), high intensity of solar radiation, and moisture and precipitation conditioning. It was found that coupling the water treatment with solar radiation significantly alters the chemical and rheological path of age-related changes. The effect of iron sulphide oxidation products on the age hardening process of asphalt cement was assessed, and results showed the chemistry and rheology of asphalt cement affected by such materials, while it doesn’t look to have a significant effect on the premature ageing of asphalt mixes.

A temperature sensitivity parameter was developed as part of this research base on the time-temperature superposition shift factors for frequency sweep testing, which used in this research to compare different age conditioning procedures. As the defined temperature sensitivity parameter is an innate property of the viscoelastic material, it can also be used as a powerful tool to evaluate the effect of various modifications on asphaltic materials.

To calibrate the 2S2P1D rheological model on the frequency sweep test results of both asphalt cement and asphalt mix, a spreadsheet has been developed capable of determining viscoelastic model parameters, time-temperature superposition shift-factors and fitting various TTS models (WLF, Arrhenius, and polynomial) and calibrate them for each sample. This spreadsheet is also capable of determining cross-over frequency and temperature using the WLF model. The author believes the prepared spreadsheet can facilitate the rheological study of pavement materials using the 2S2P1D model. Schematic representation of thesis contribution is provided in Figure 1-1.

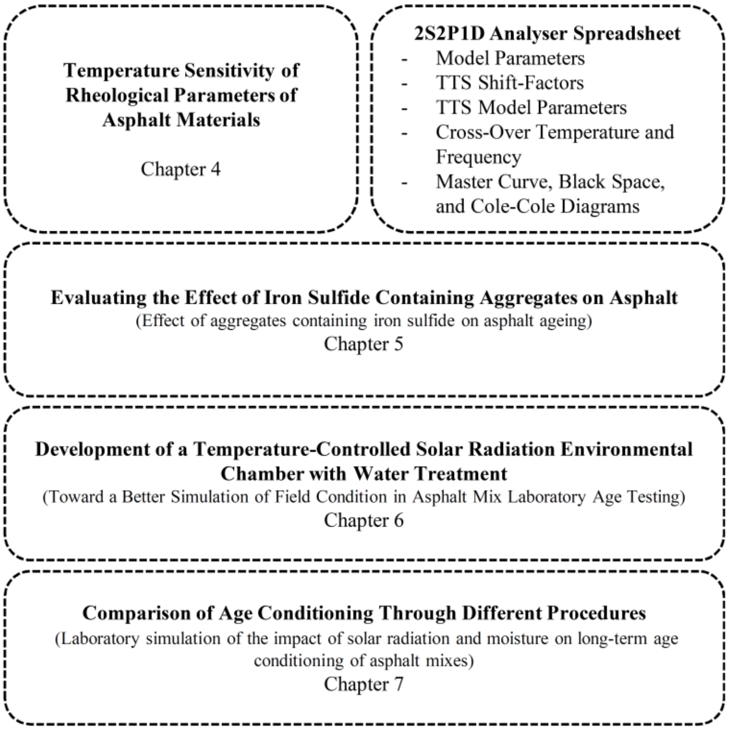

Figure 1-1 Schematic Presentation of the Thesis Contribution

1.5 Thesis Organization

This manuscript-based thesis consists of eight chapters as follows:

Chapter 1: Introduction – General scope and overall objectives of the research are explained in this chapter.

Chapter 2: Background – A comprehensive literature review is presented in this chapter covering various topics related to this research including;

Chemistry of asphalt cement

Mechanical properties of asphalt cement and asphalt mix

Asphalt cement ageing

Laboratory age conditioning procedures

Chapter 3: Methodology – The research methodology used to achieve the goals of this research described in this chapter. Description of the materials used in this research is also provided as well as laboratory tests and analysis tools.

Chapter 4: Temperature sensitivity of rheological properties – The temperature sensitivity parameter base on the time-temperature superposition principle and its capabilities to differentiate different age conditioning procedures has been described in this chapter.

Chapter 5: Effect of aggregates containing iron sulphide on asphalt ageing explained in this chapter.

> Azimi Alamdary Y., Singh S., Baaj H., (2019). "Effect of aggregates containing iron sulphide on asphalt ageing." Road Materials and Pavement Design, DOI: 10.1080/14680629.2019.1610477

Chapter 6: The evolution of ageing in the bespoke solar radiation chamber and the effect of moisture conditioning explained in this chapter.

Chapter 7: Four different age conditioning procedures are compared in this chapter using rheological and chemical analysis tools.

Azimi Alamdary Y., Singh S., Baaj H., (2019). "Laboratory simulation of the impact of solar radiation and moisture on long-term age conditioning of asphalt mixes.", Road Materials and Pavement Design, DOI: 10.1080/14680629.2019.1587496

Figure 1-2 shows the schematic representation of the thesis content.

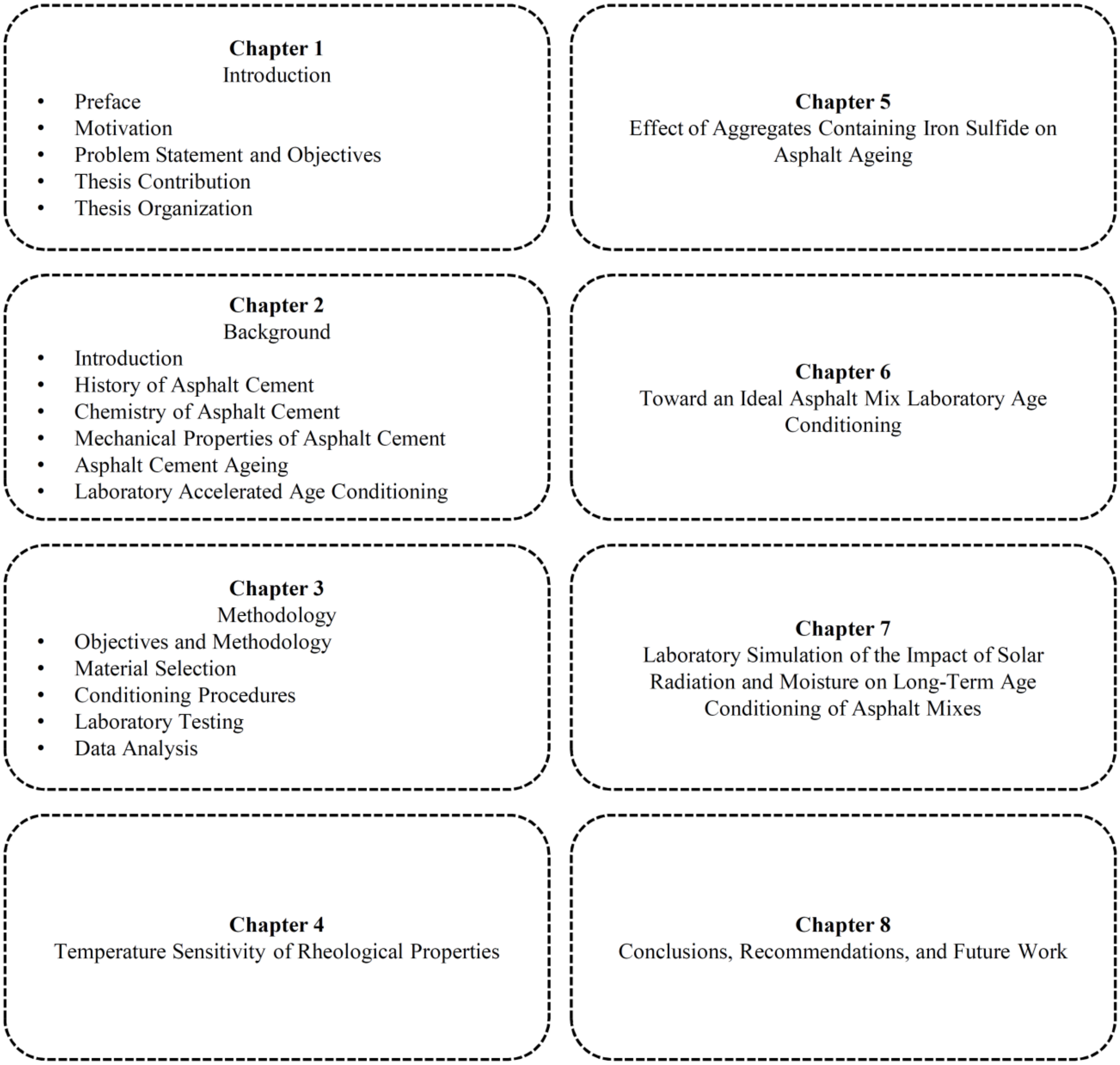

Figure 1-2 Schematic Flowchart of The Thesis Content

CHAPTER 2: BACKGROUND

2.1 Introduction

This chapter consists of nine sections. Each section provides relevant information with regards to the objectives of this research. Section 2.2 provides a brief history of the asphalt cement, its application in the pavement industry, and its manufacturing processes and origins. Section 2.3 discusses the mechanical behaviour of asphalt cement and mix as well as different classification and grading systems for paving grade asphalt cement. The time-associated changes in the properties of asphalt cement, various ageing mechanisms and the pavement durability is the topic for section 2.4. Chemistry and the chemical structure of asphalt cement as related to ageing are explained in section 2.5. Sections 2.6 and 2.7 are explaining previous efforts to simulate short- and long-term ageing on asphalt cement and mix in the laboratory.

2.2 History of asphalt cement – application and manufacturing

“asphalt,” also known as “bitumen” is a sticky, black petroleum product which can be found in natural deposits or produced by crude oil refining. In British and Australian English, the term “bitumen” is used to explain asphalt cement, while the term “asphalt” or “tarmac” refers to asphalt concrete. In Canadian and American English, the word “bitumen” refers to the extremely heavy crude oil resources, while “asphalt,” “asphalt cement,” or “asphalt binder” is used to refer to the refinery product. However, “asphalt” is also used as a shortened form of “asphalt concrete” or “asphalt mix.” To avoid the confusion from various definitions, here we use “asphalt cement” to refer to the petroleum product used as glue, and “asphalt mix” to indicate the mixture of asphalt cement and aggregates.

Interestingly, one of the earliest known uses of natural asphalt cement was by Neanderthals some 70,000 years ago, with asphalt cement adhered to ancient tools found in Neanderthal sites in Umm El Tlel and Hummal in current Syria and Gura-Cheii cave in Romania [1]. More advanced uses of natural asphalt cement were found in various civilizations for various applications including waterproofing, as an adhesive, embalming mummies, crafting arts, or as strategic weaponry. In Canada, aboriginal people used asphalt cement from Athabasca to waterproof their canoes [2].

In the modern era, a Scottish engineer named John Loudon McAdam (1816) was one of the very first engineers to use asphalt cement in road construction using a technique called “macadamization.” In North America, Edward De Smedt (1870), a Belgian-American engineer, patented the “sheet asphalt pavement,” a mixture of natural asphalt and sand. The author of the famous “the little house on the Prairie,” Laura Ingalls Wilder (1867-1957) explains her first encounter with asphalt pavement:

> *"In the very midst of the city, the ground was covered by some **dark stuff** that **silenced all the wheels** and **muffled the sound of hoofs**. It was **like tar**, but Papa was sure it was not tar, and it was **something like rubber**, but it could not be rubber because **rubber cost too much**. We saw ladies all in silks and carrying ruffled parasols, walking with their escorts across the street. Their heels dented the street, and while we watched, these **dents slowly filled up and smoothed themselves out.** It was as if that stuff were alive. **It was like magic**."*

At 1846, a Canadian physician and geologist, Abraham Gesner, devised a process to produce Kerosene and brought the idea of modern petroleum refining. In 1854, the Polish pharmacist and engineer, Ignacy Lukasiewicz built the first modern oil refinery in current Romania. Two years later at 1858 the first oil well drilled in North-America by James Miller Williams in Oil Springs, Ontario. For most of the twentieth century, Abadan refinery in Iran was considered as the largest refinery in the world, while the Jamnagar refinery in Gujarat, India is the largest refinery of the world with the capacity of up to 1,240,000 barrels per day.

Most of the modern refineries are using two-step distillation process including atmospheric and vacuum distillation, and their products can be classified into four general classes including light, middle, heavy, and residuum. The heaviest product is the residue from the vacuum distillation tower or “Vacuum Tower Bottom (VTB),” which is used directly or with some modifications (such as air rectifying process) as asphalt cement for pavement, roofing, and any other application (Figure 2-1). Amongst all the petroleum products, the quality and chemical structure of the residuum is more dependent on the crude source and details of the refining process. This is important as a wide variety of crudes do exist with significant chemical compositions. Nowadays, refinery produced asphalt cement is the dominant binder in asphalt pavements, and the application of naturally occurring asphalt cement in the pavement industry is limited.

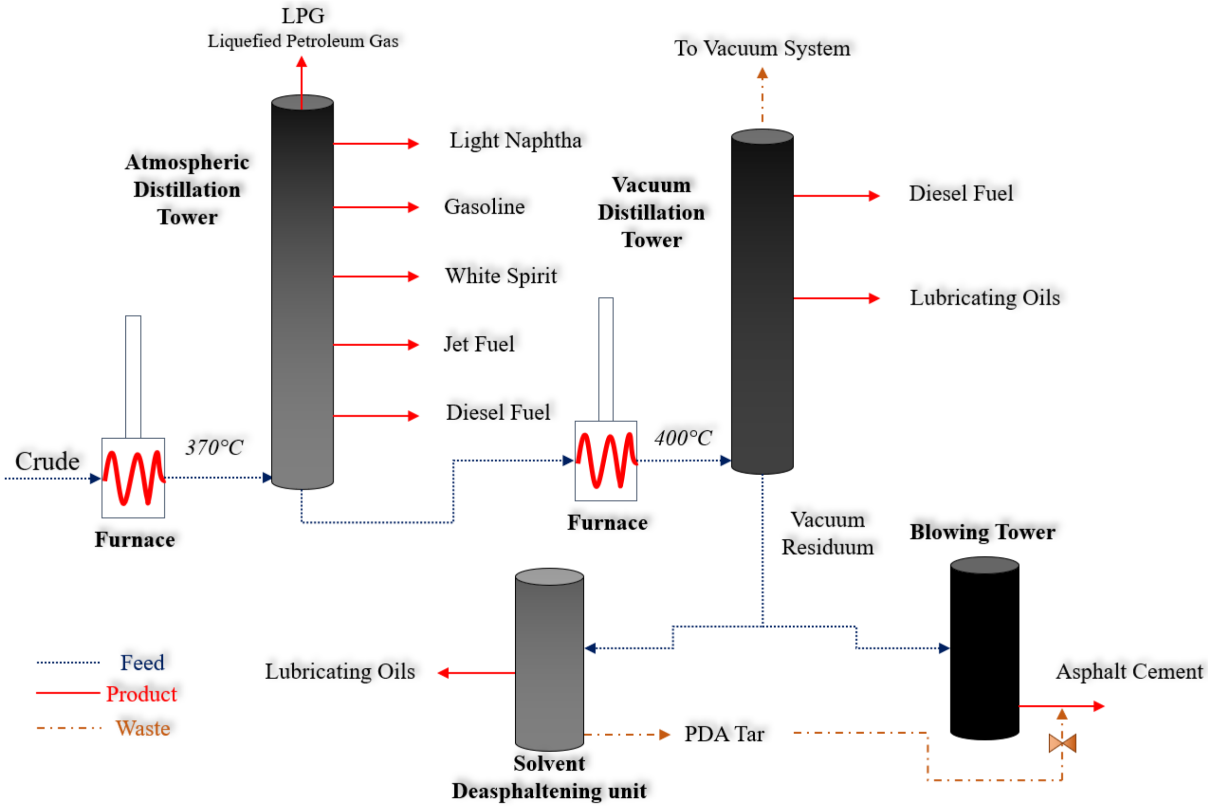

Figure 2-1 Schematic Description of Crude Oil Refining

2.3 Chemistry of Asphalt Cement

Commercial paving grade asphalt cement is a product of petroleum refining (except for a very small portion of naturally occurring asphalt, which is out of the scope of this study). Thus, the nature and chemistry of crude oil and the refining process determine the chemical composition and mechanical properties of asphalt cement [3].

In most cases, asphalt cement is the residuum of the vacuum distillation tower, which is called straight-run asphalt cement. Sometimes, the straight-run asphalt cement is soft and needs more processing to meet required specifications. Thus, some air blowing, or air rectifying processes are applied, and the distillation tower residuum is subjected to mild oxidation to increase its consistency. Other types of modification may also apply to improve the performance-related properties of asphalt cement, the most famous of which is polymer modification. All these chemical processes and modification techniques affect the chemistry of asphalt cement which subsequently results in variation in mechanical properties.

2.3.1 Asphalt Cement Fractional Composition

Asphalt cement is composed of thousands of different hydrocarbon molecules with a broad range of structure, polarity, and aromaticity. From the elemental point of view, carbon (83-87%), hydrogen (10-14%) and heteroatoms, including sulphur, oxygen, and nitrogen (1-9%) are the main constituents of asphalt cement. Asphalt cement may contain a minuscule amount of metals (mainly Vanadium, Nickel, and Iron) in their structure (1-2000 ppm) [4]. The diversity of the hydrocarbons' molecular structures not only make recognition of all of them impossible but also makes it of less interest as it varies among the various asphalt cements produced from different crude sources through various processing and modifications.

To understand the chemistry and composition of crude oil and heavy petroleum products, chemists used specific properties to categorize various hydrocarbons in asphalt cement based on different chemical properties, such as molecular weight, polarity, and aromaticity. Several researchers tried to separate hydrocarbon fractions of asphalt cement based on their tendency to dissolve in different organic solvents. This approach can make the chemistry more understandable and reduce the complexity of the situation by providing an overall understanding of the material composition. One famous example of such efforts which dates back to 1941, classifies hydrocarbons in asphalt cement into five general categories. These fractions were asphaltenes (insoluble in pentane), resins (insoluble in propane), wax (insoluble in methyl ethyl ketone-benzene solution) and paraffinic and naphthenic oils (were obtained by extraction of oil constituent with acetone in an equilibrium extraction tower) [5].

Among all separation techniques, a method developed by Corbett (1969) gained global attention due to its simplicity and accuracy [6]. In this approach, Corbett used solvent deasphaltening process to recover asphaltenes, followed by elution-adsorption chromatography to yield saturates, naphthene-aromatics, and polar-aromatics (resins) (Figure 2-2). ASTM D4124 describes this chromatography procedure, commonly known as SARA (Saturates, Aromatics, Resins, and Asphaltenes). This fractionation process identifies the four generic classes of hydrocarbons found in asphalt cement, known as SARA fractions. It must be noted that the physical properties of each fraction greatly depend on the molecular weight distribution as well as chemical structure, therefore is not constant for all asphalt cement produced from different crude sources and processes. Moreover, in just one type of asphalt cement, the physical properties of the fractions may change during the time as a result of environmental conditions and the time-associated chemical changes known as ageing [6].

- *Asphaltenes*

Asphaltenes, gigantic hydrocarbon structures, are the heaviest organic molecule that can be found in crude oil as well as distillation tower residues. They consist mainly of carbon, hydrogen, nitrogen, oxygen, and sulphur (Figure 2-3). The C:H ratio in asphaltenes depends on the crude source but is roughly close to 1:1.1. The molecular weight of asphaltenes may vary from 1,000 to 100,000, and their particle size is between 5 to 30 nm. It is impossible to define an exact chemical structure for asphaltenes, but in general, it can be said that they are mainly composed of polyaromatic carbon rings with oxygen, nitrogen, and sulphur heteroatoms in their structure, which make them massive molecular structures with highly-polarized groups [7].

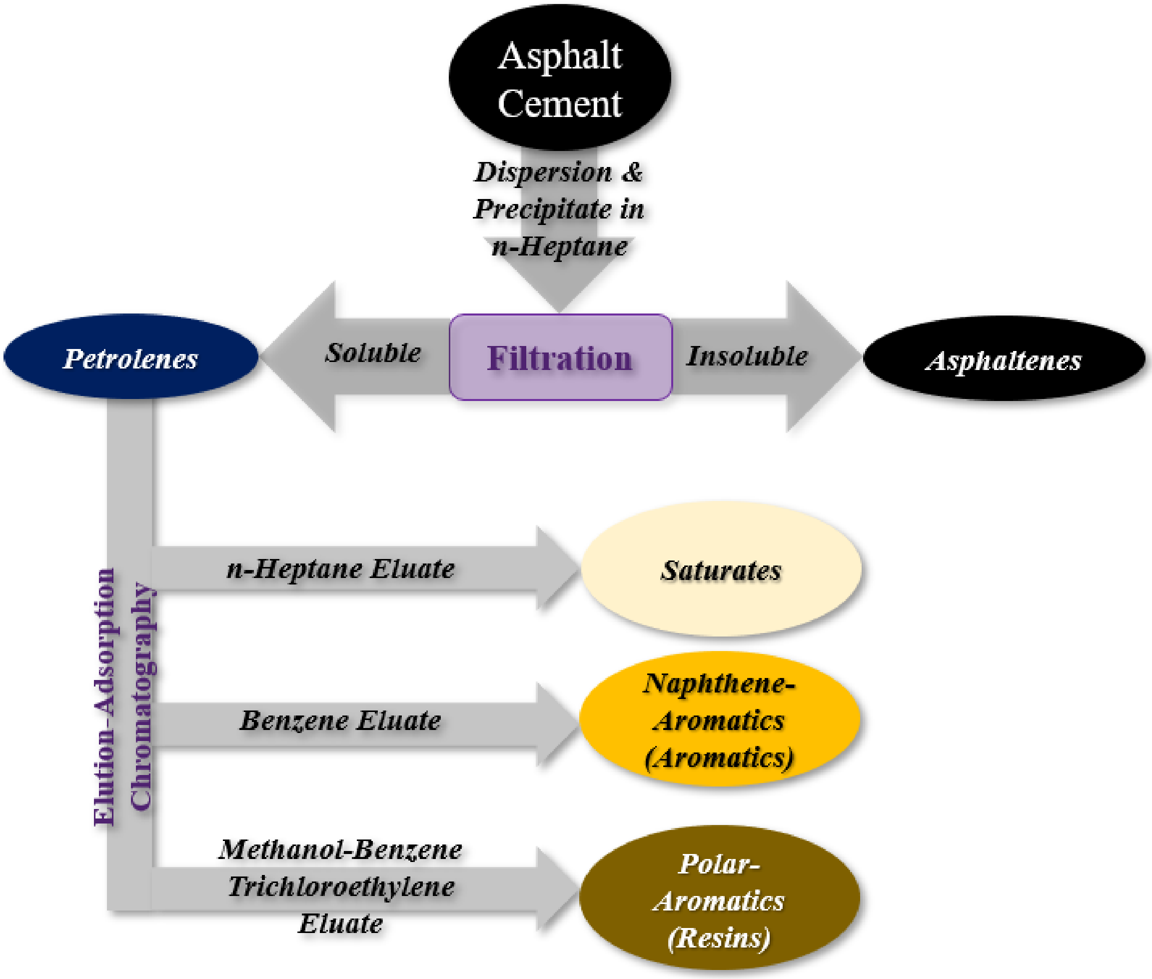

Figure 2-2 Scheme for Asphalt Cement Separation into Four Generic Constituents as Suggested by Corbett [6]

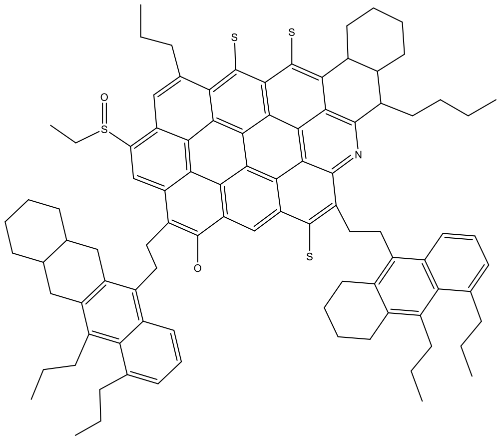

Figure 2-3 Typical Structure for Asphaltenes [8]

- *Resins (Polar Aromatics)*

Polar-aromatics or resins are a group of highly polar hydrocarbons which, like asphaltenes, are composed of hydrogen and carbon atoms and contain small amounts of heteroatoms like oxygen, nitrogen, and sulphur. In asphalt cement structure, resins coat asphaltene molecules and disperse them in the asphalt cement structure. The molecular weight of resins found in asphalt cement typically varies from 500 to 50000, and the particle size is around 1 to 5 nm. Although the C: H ratio of resins is highly source dependant, an average of 1:1.3 to 1:1.4 typically represents the resin in paving grade asphalts [3].

- *Aromatics (Naphthene-Aromatics)*

Naphthene-aromatics (which commonly called aromatics) are non-polar carbon chains with unsaturated ring systems. Aromatics form the major proportion of the dispersion medium, known as maltene, in which resin coated asphaltenes are floating. The molecular weight of naphthene-aromatics ranges from 300 to 2000. Figure 2-4 shows the typical chemical structure for naphthene-aromatics.

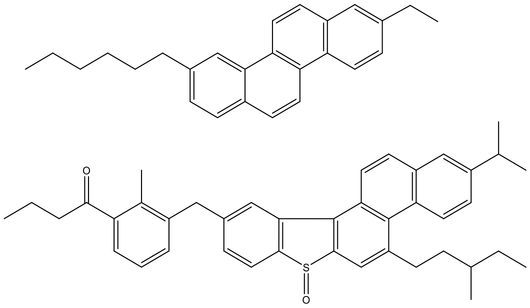

Figure 2-4 Typical Structure for Naphthene-Aromatics (Aromatics) [3]

- *Saturates*

Saturates, non-polar aliphatic[1] hydrocarbons with straight and branched chains. Saturates and naphthenic-aromatics are forming the dispersing medium known as maltene, in which, resin-coated asphaltene particles are dispersed. The molecular weight of saturates is close to aromatics and ranges from 300 to 2000. Two classes of saturates exist in the asphalt composition: waxy and non-waxy saturates. The proportion between waxy and non-waxy saturates plays an important role in the low-temperature properties of asphalt cement. Figure 2-5 shows typical structures for saturates.

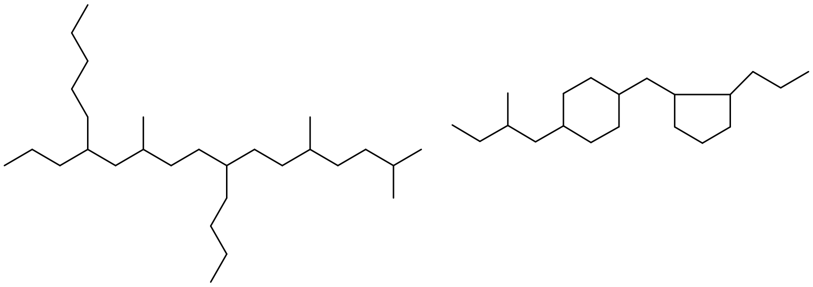

Figure 2-5 Typical Structure for Saturates

2.3.2 The Colloidal Structure of Asphalt Cement

The colloidal structure of asphalt cement was first described by Nellensteyn (1923) [10]. Asphaltenes are covered with polar-aromatics (resins) and are dispersed in a dispersing medium called maltenes. Saturates and naphthenic aromatics (aromatics) are forming the maltene phase. Colloidal systems can be divided into sol and gel structures. Colloids with sol structures exhibit Newtonian behaviour, while those with gel structures are highly non-Newtonian. Most asphalt cements behave in between of these extremes; therefore, their colloidal structure can be called "sol-gel" (a combination of sol and gel structures). Figure 2-6 presents a graphical representation of asphalt cement as well as sol and gel systems. The concentration of different SARA fractions and temperature are the dominant factors in determining the colloidal structure and the mechanical properties of asphalt cement.

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[1] An aliphatic compound or non-aromatic is a hydrocarbon containing carbon and hydrogen joined together in straight, branched chains or non-aromatic rings. The simplest aliphatic hydrocarbon is methane [9]

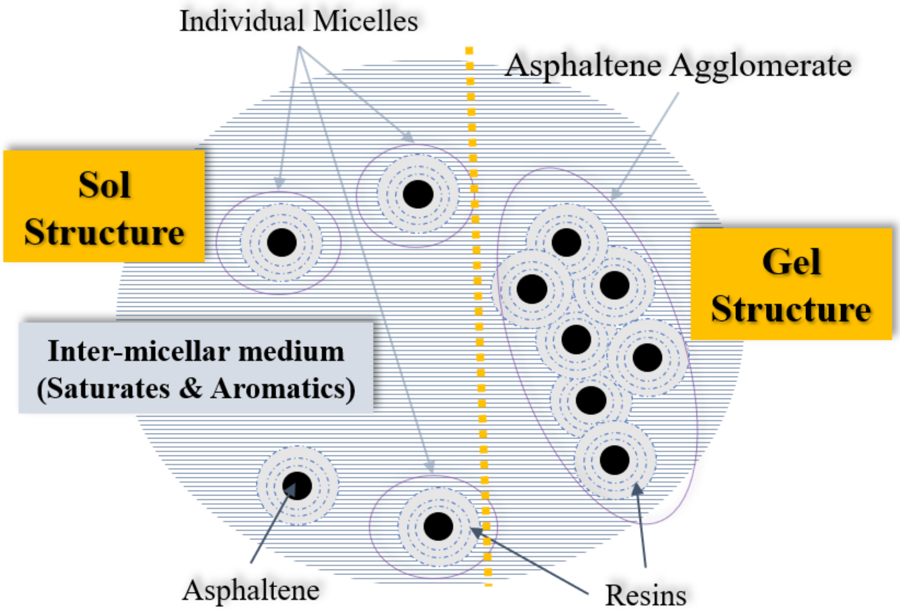


Figure 2-6 Colloidal Structure of Asphalt Cement

2.3.3 The Effect of Crude Source and Processing Fractional Composition of Asphalt Cement

The ratio between the various SARA fractions (saturates, aromatics, resins, and asphaltenes) in various types of asphalt cement is not identic [11]. The effect of crude source and process condition on the fractional composition of resulting asphalt cement have been examined by Corbett (1969) [12]. He selected four asphalt cements with the same penetration grade but from different crude sources (Venezuela, Mexico, USA, and the Middle East). Running a fractional analysis on them, he determined the proportional amount of the four fractions in each. By comparing the SARA fractions of these four asphalt cements, he found a strong dependency of chemical composition on the crude source.

Results of this research showed that the penetration and softening point values are almost equal, which shows somehow similar physical properties between 25°C to 46°C (77°F to 115°F). However, the distribution of SARA fractions was considerably different among these samples and heavily source dependent (Figure 2-7). As an example, asphalt cement from Venezuela has almost twice the amount of saturates as middle eastern asphalt cement and has approximately the same amount of asphaltene.

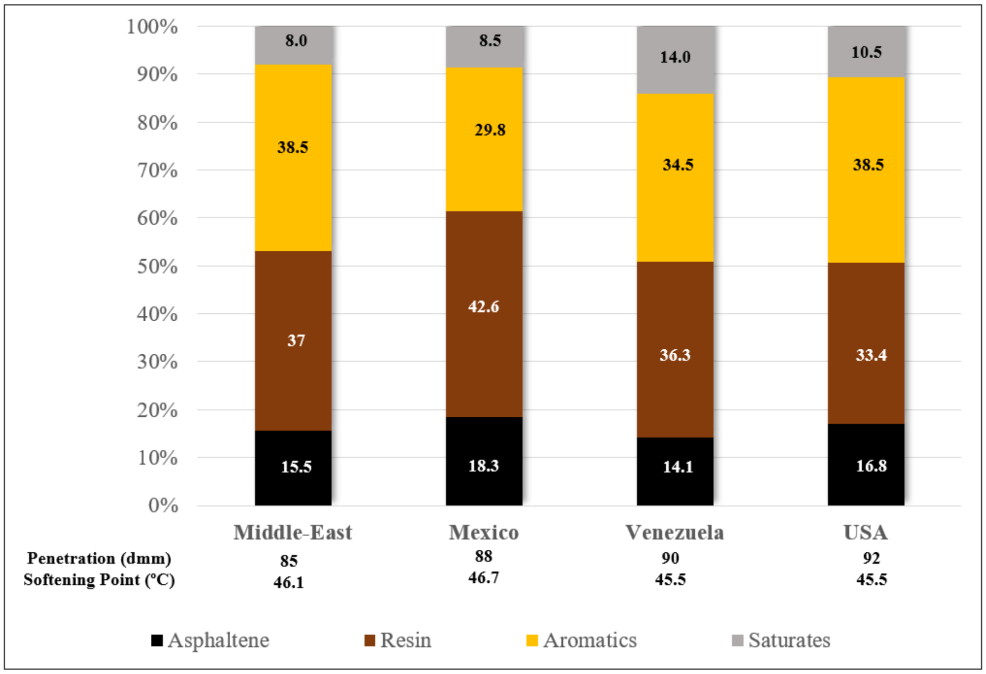


Figure 2-7 Effect of Crude Source on Composition of Residue [12]

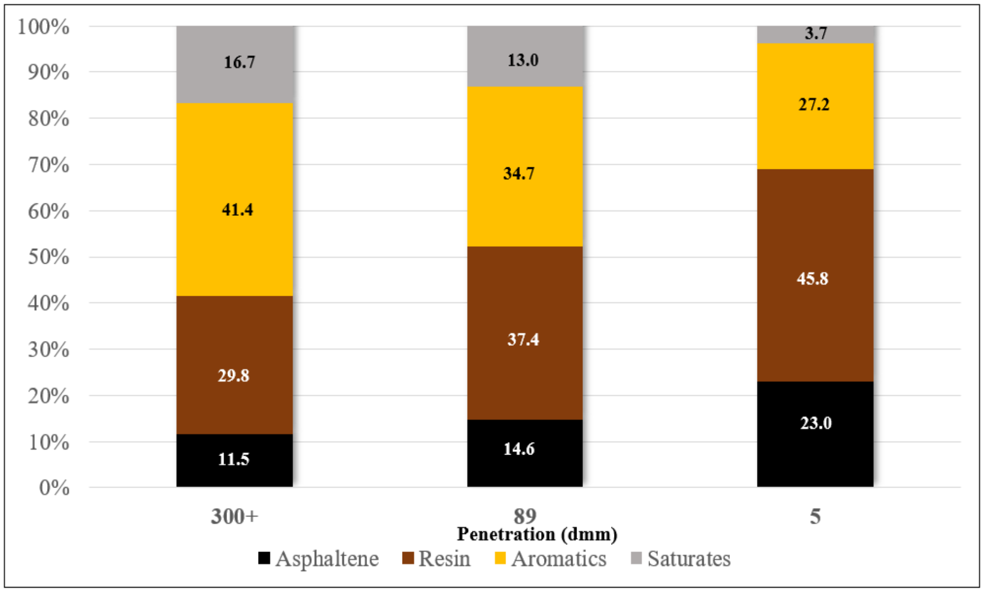


Figure 2-8 Effect of Process Condition (Vacuum Pressure) on the Residue Composition [12]

Corbett also compared the residuum of vacuum distillation tower at three different stages (Flux, Binder, and Pitch) to find the effect of process condition on the resulting asphalt cement composition. He found that as process conditions get harsher (distillation temperature and vacuum pressure increase) saturates are likely to leave the asphalt composition, followed by naphthene-aromatics. Resin content remains almost the same except in a very harsh distillation process (Pitch). Asphaltenes were considerably less likely to abandon the structure of asphalt cement due to their massive chemical structure and high molecular weight. Moreover, he found that in each fraction, molecules with fewer rings and lower molecular weight have higher tendency to leave the asphalt cement structure, causing considerable changes in each fraction's composition (Figure 2-8).

2.3.4 Molecular Size Distribution in Asphalt Cement

High-Pressure Gel Permeation Chromatography (or more simply HP-GPC) is a type of size exclusion chromatography (SEC) method which separates the components of organic material based on the apparent molecular size. This technique has found wide application in the study of polymers' molecular weight distribution. However, several researchers have tried to use this method to analyze the molecular distribution of crude oil and its products, including asphalt cement [13]–[15].

Many researchers have found this technique useful to analyze the chemistry of the asphalt cement, as this method shows the distribution of hydrocarbon chains based on their apparent molecular size. Results of HP-GPC analysis can also be used to find some correlations between mechanical and chemical properties of asphalt cement. Moreover, many studies used this robust method to quantify the chemical changes that occurred during the ageing process of asphalt cement [13].

In the HP-GPC procedure, the organic material (asphalt cement in this case) is diluted in an organic solvent (normally tetrahydrofuran or toluene) and flows through a column, packed with highly porous gel environment, at high pressure. Smaller molecules can travel with solvent throughout all the pores in the gel material while large molecules can not pass. Molecules with medium molecular size have access to a limited number of pores. The large molecular size (LMS) leave the column first, followed by medium-size (MMS). Molecules with a smaller size (SMS) are the last to exit the column because they travel through all pores and cavities (Figure 2-9). By this method, one can determine molecular size distribution (MSD), also known as molecular size profile, based on the time required to travel along the gel column.

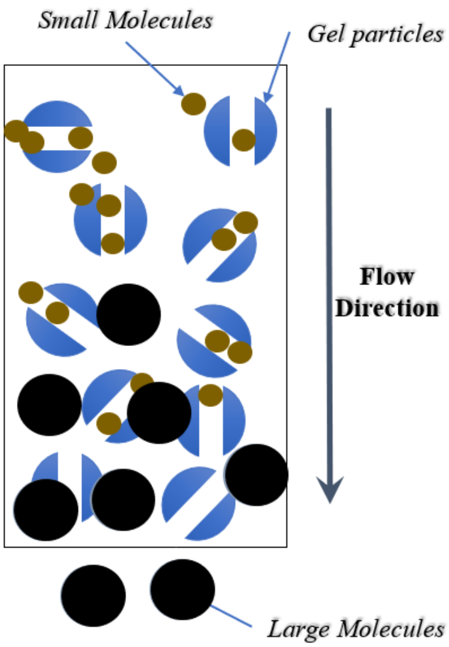


Figure 2-9 Gel Permeation Chromatography Concept, Smaller Molecules Travel Through More Pores in Gel

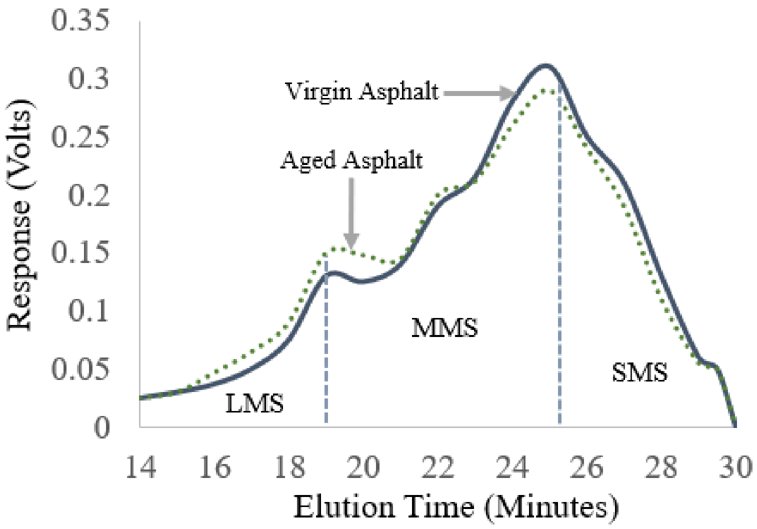


Figure 2-10 A Typical Chromatogram, Comparing Virgin and Aged Asphalt Cement

Figure 2-10 represents a typical chromatogram obtained from HP-GPC analysis. As can be seen in this chromatogram, the elution time for LMS is less than for MMS and SMS. In such diagrams, the area under the curve represents the amount of particular molecular size and is used to evaluate the size distribution of molecules among different samples. The one presented in Figure 2-10 compares molecular size distribution as a result of age conditioning.

2.3.5 Functional Groups Analysis

Although fractional and molecular size analyses are useful tools to analyze the chemistry of asphalt cement and make it easier to understand asphalt's chemistry, they do not give any detailed information related to the functionality of the asphalt molecules as related to the oxidation process. In other words, the oxidation reactivity of asphalt cement cannot be easily measured by such analytical methods. This is mainly because fractional, and molecular size analysis cannot identify the functionality and the potential reactivity of the hydrocarbon molecules, both of which play significant roles in the oxidation process.

More analytical tools have been developed to obtain detailed information on the types of chemical functionalities to be used in an organic material. These methods can provide information on the functional groups[2] (including their type and the approximate amount of them) and, therefore, can be used to analyze the chemical changes during the asphalt cement ageing process. Some functional groups (especially those containing heteroatoms such as oxygen-containing functional groups) are formed during the oxidation process and have a major impact on mechanical behaviour. The heteroatoms in asphalt cement are often associated with polar groups (strongly interacting chemical functional groups that have a disproportionately large influence on the viscoelastic properties of the asphalt cement) [17].

Infrared (IR) Spectroscopy method has proven to be able to recognize and measure the general chemical structural types and functional groups [18]. Initial efforts using IR spectroscopy have successfully identified some changes in functional groups that happen during oxidative ageing. Beitchman (1959) found that the amount of carbonyl and hydroxyl groups increases significantly as the oxidation ageing process takes place. He also concluded that the change in sulfoxide concentration could be related to the ageing process.

---

[2] Functional groups are a combination of atoms with special formation and bonds within an organic molecule that determine the reaction of that molecule. The same functional groups will experience the same chemical reactions regardless of the size of original molecule [16].

Despite the achievements in understanding the chemistry of asphalt cement and the ageing process provided by the conventional infrared spectroscopy technique, the collected data have proved to be inaccurate. This difficulty in IR spectroscopy data analysis is mainly due to overlapping absorption bands, which makes identifying the strongly polar functionalities difficult. Strong hydrogen bonding[3], which occurs among organic functional groups, causes shifting and broadening of absorption bands, therefore leading to misinterpretation of collected data and inaccuracy in functional groups identification.

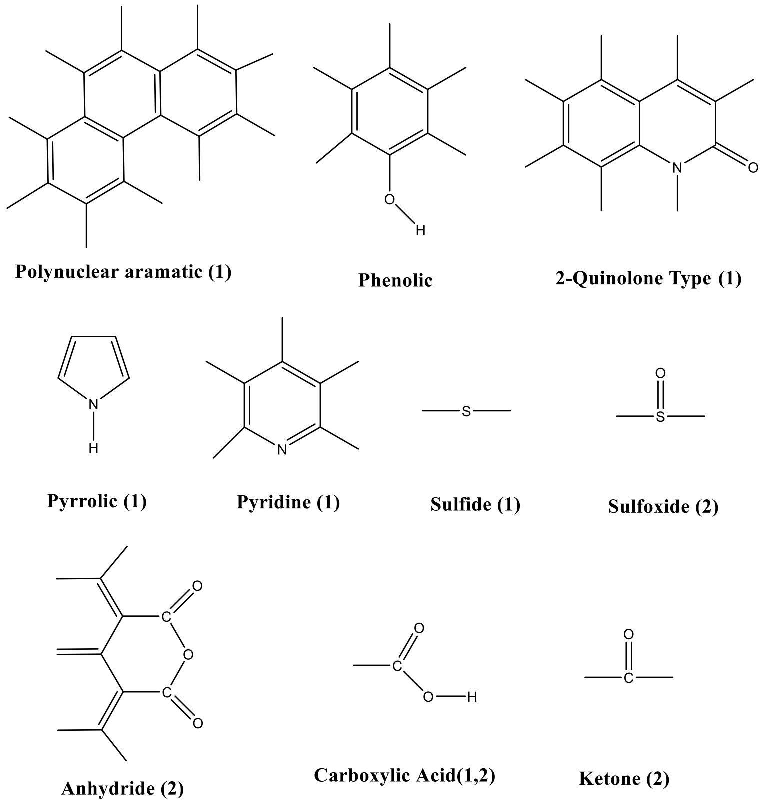
To increase the accuracy of this IR spectroscopy method, an appropriate solvent (such as Tetrahydrofuran of THF) has been used to break the hydrogen bonds between hydrocarbons. Moreover, differential infrared spectroscopy approach has been applied to differentiate narrow wavelengths better and to improve the identification procedure. Differential IR spectroscopy focuses on specific wavelengths (corresponding to certain functionalities) to avoid overlapping bands and more accurately measure the concentration of required functional group [20].

IR spectroscopy can identify and measure several functional groups in asphalt cement, including carboxylic acids and their salts, carbonyl groups (ketone), anhydrides, 2-quinolone types, sulfoxides, phenolic types, and pyrrolic types. Nitrogen compound groups that exist in the asphalt cement structure (mainly pyridine types) are not detectable by infrared spectroscopy analysis. Further developments in functional groups analysis methods (FGA) can help to determine the chemistry of the ageing process more accurately.

Figure 2-11 shows the chemical structure of the functional groups that exist in asphalt cement and those that form during oxidative ageing. Among all functionalities that the FT-IR method can detect, four groups form during oxidative ageing: dicarboxylic anhydrides, carboxylic acids, sulfoxides, and ketones (carbonyl groups). Determining the amount of these functional groups and changes in their concentration can help to measure the chemical changes during the oxidative ageing.

---

[3] Hydrogen bonding is a special case of dipole forces, where non-ionic association formed between the hydrogen of one chemical structure and an electronegative atom (commonly oxygen, nitrogen, or fluorine) from another molecule. Hydrogen bonds are much stronger than other dipole forces between different molecules, but obviously not as strong as covalent forces within a molecule [19].



(1) Naturally Occuring.

(2) Formed on Oxidative Aging

Figure 2-11 Functional Groups That Normally Present or Formed During Oxidative Ageing and Can Be Determined By FGA Using FT-IR Method [17]

Davis and Petersen (1966), used gas-liquid chromatography column oxidation procedure for simulating the asphalt cement ageing process, found that the major products of oxidation ageing are ketones and sulfoxides, while dicarboxylic anhydrides and carboxylic acids are formed in much smaller quantities [21].

Analyzing the changes in functional groups during the oxidation process and their relationship with the amount of hardening showed that age hardening is almost stopped by the cessation in ketone formation [22]. It was found that sulfoxide formation reaches a saturation level at the very early steps of the ageing process (mainly during short-term ageing) yet there is no clear correlation between sulfoxide formation and age hardening [23].

2.4 Mechanical Properties of Asphalt Cement and Mix

Like any other construction material, it is mainly the physical and mechanical properties of asphalt cement that is important for pavement engineers, though these properties are a direct result of the chemical composition and chemical structure of asphalt cement. Moreover, in case of the asphalt mix as the final product for paving purposes, the aggregates properties and their interaction with the binder (asphalt cement) plays a decisive role in the mechanical performance of the total pavement structure and its durability. For these reasons it is mandatory to understand the mechanical behaviour of asphalt cement and mix and how they are changing during the time under construction and performance conditions.

This section will look into the asphalt cement characterization different grading systems based on the mechanical properties and will present a brief description of the viscoelastic nature of asphalt cement and mix as well as analysis tools and rheological modelling techniques.

2.4.1 Viscoelastic Behaviour

Asphalt cement and asphalt mix are viscoelastic materials meaning that under applied stress they behave partially like elastic solid and partially like viscous liquid showing the time-dependent strain. While elastic materials show constant strain under the applied stress and would immediately return to their original state, viscous liquids strain is linearly increasing with a constant shear flow rate. The behaviour of the viscoelastic materials is somewhere in between of these states. Figure 2-12 shows the reaction of elastic solid, viscous liquid, and viscoelastic materials as well as their graphic representations.

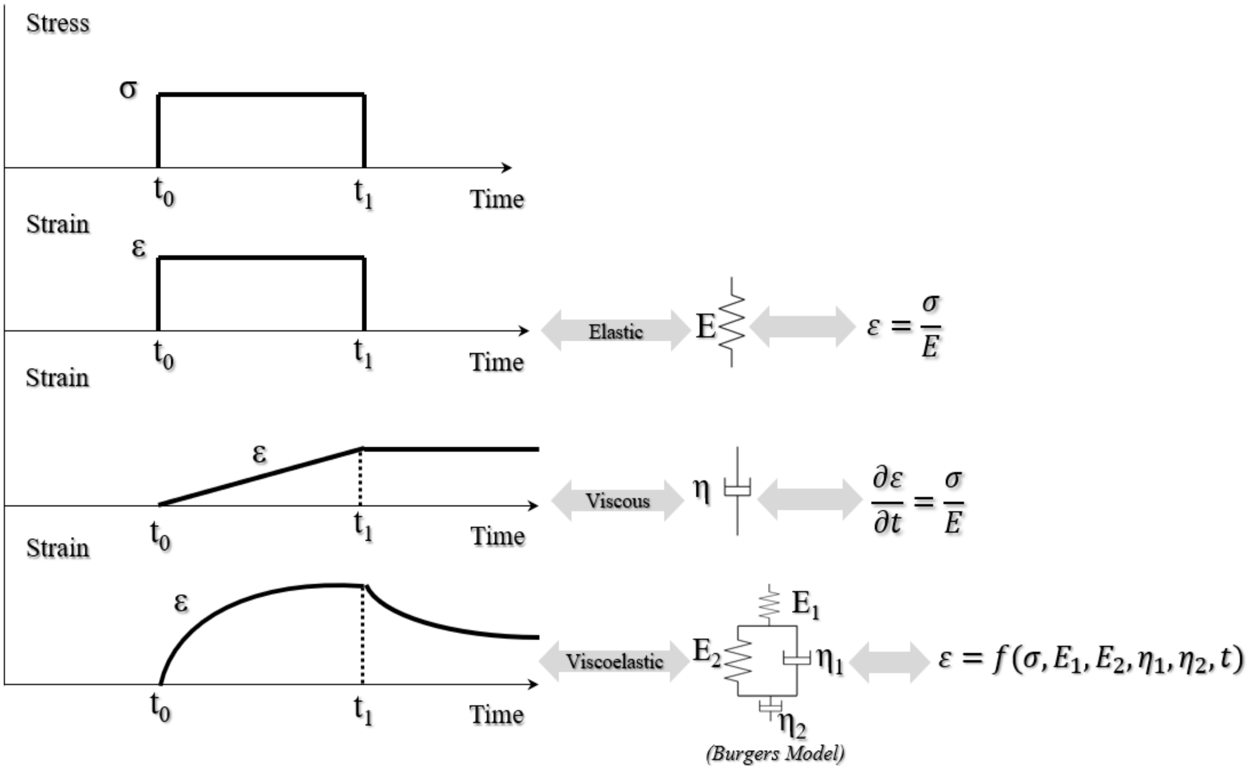


Figure 2-12 Reaction of Elastic, Viscous, and Viscoelastic Materials to Creep Test

Viscoelastic behaviour can be better understood under cyclic loading using complex modulus and phase angle concepts. These terms are graphically explained in Figure 2-13 which shows the graphs for applied stress versus replied strain for material under cyclic loading which can be performed either in tension-compression or oscillatory loading modes.

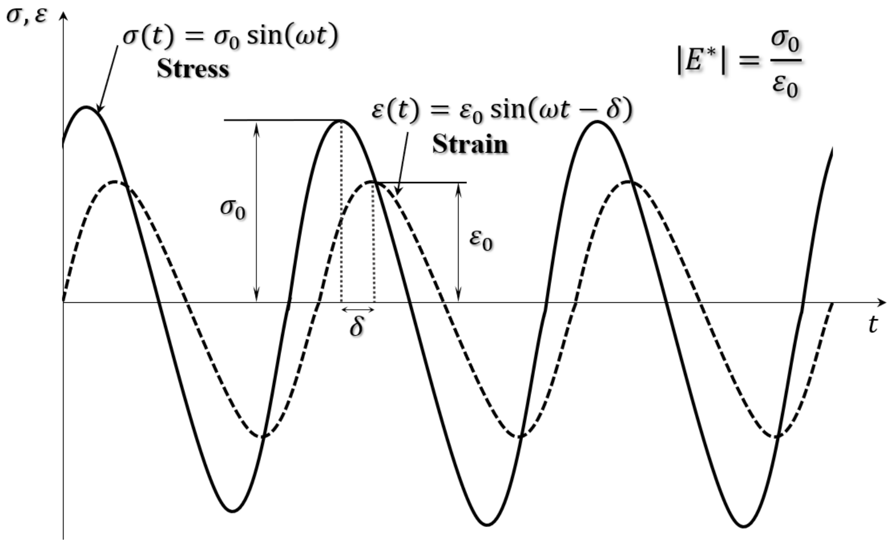


Figure 2-13 Cyclic Loading and the Response Curve for Viscoelastic Materials

For material with an ideal elastic behaviour, there would be no time lag between the applied stress and the response strain, and the two curves would be in-phase. From the other side, for an ideal viscous liquid, the phase angle will be equal to 90º. The behaviour of any other material behaving in between of these two ideal conditions can be explained as viscoelastic behaviour. Viscoelastic materials can be divided into two categories namely "viscoelastic solid" and "viscoelastic fluid" depending on the proportion of viscous and elastic components (phase angle). For viscoelastic fluids, the phase angle (δ) falls between 45º and 90º. Therefore, the material at rest is self-levelling and has no dimensional stability. In the case of viscoelastic solids, the phase angle (δ) value is between 0º and 45º.

The complex modulus can be explained by Equation 2-1, in which σ_0 is the amplitude of the applied stress and ε_0 is the amplitude of the response strain.

Equation 2-1

$$E^* = \frac{\sigma_0}{\varepsilon_0}$$

Since complex modulus explains the entire viscoelastic behaviour, it can be explained in a vector diagram by purely viscous (loss modulus) and purely elastic (storage modulus) components. The storage modulus (E') represents the quasi-elastic behaviour of the material, while the loss modulus (E") characterizes the viscous (liquid-state) portion of the viscoelastic behaviour.

In viscous deformation, the applied energy tries to overcome the internal friction between the molecules and particles and will transform into heat energy and is absorbed by the material and is dissipated. In elastic deformation, the material returns to its original shape and form after the release of the load and requires reset energy and is only possible if the energy is available the deformed material. Figure 2-14 shows the relationship between the complex modulus and the viscous and elastic components.

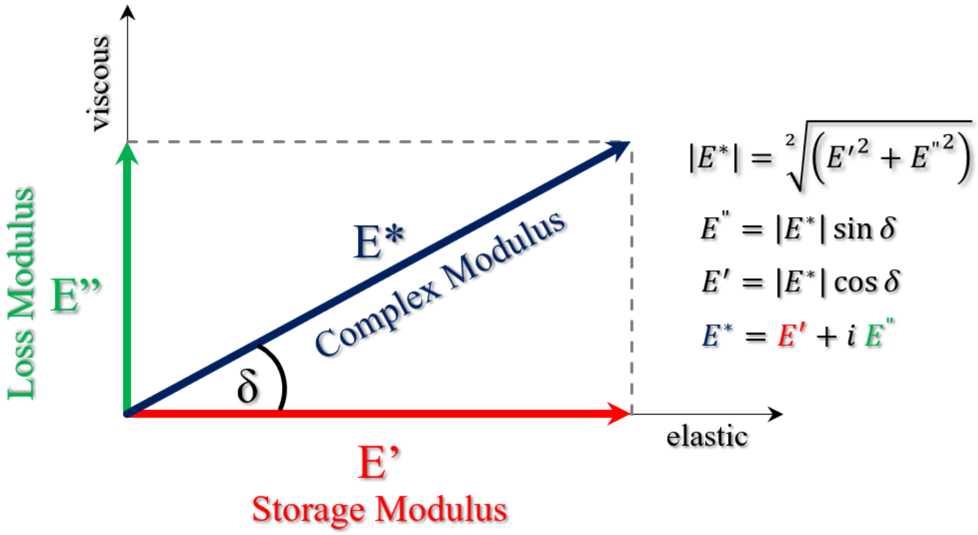


Figure 2-14 **Vector Diagram Explanation of the Relationship Between Complex, Loss, and Storage Moduli**

2.4.2 Time and Temperature Dependency of Viscoelastic Behaviour

The viscoelastic properties of the asphalt cement and asphalt mix has a strong time and temperature dependency. This twofold dependency of the viscoelastic properties is best explained by the time-temperature superposition principle (TTS). At low temperatures or high loading frequencies, asphaltic materials exhibit high modulus and more elastic values, while at high temperatures or low loading frequencies, they behave more viscous with lower modulus values. The time-temperature superpositions principle explains that for rheologic properties in one set of temperature and loading time can be translated in another set of same parameters. In other words, the change in temperature from T_1 to T_2 can be replaced by scaling the loading time t_1 by a constant factor a_T (shift factor) values of which is a function of temperatures. This principle can be expressed by the following equation;

Equation 2-2

$$E\,(T_1, t_1) = E(T_2, {}^{t_1}/_{a_T})$$

Using TTS principle allows the development of the rheological properties master curves, through which rheological behaviour of the material can be investigated in a wide range of loading frequencies and temperatures (Figure 2-15).

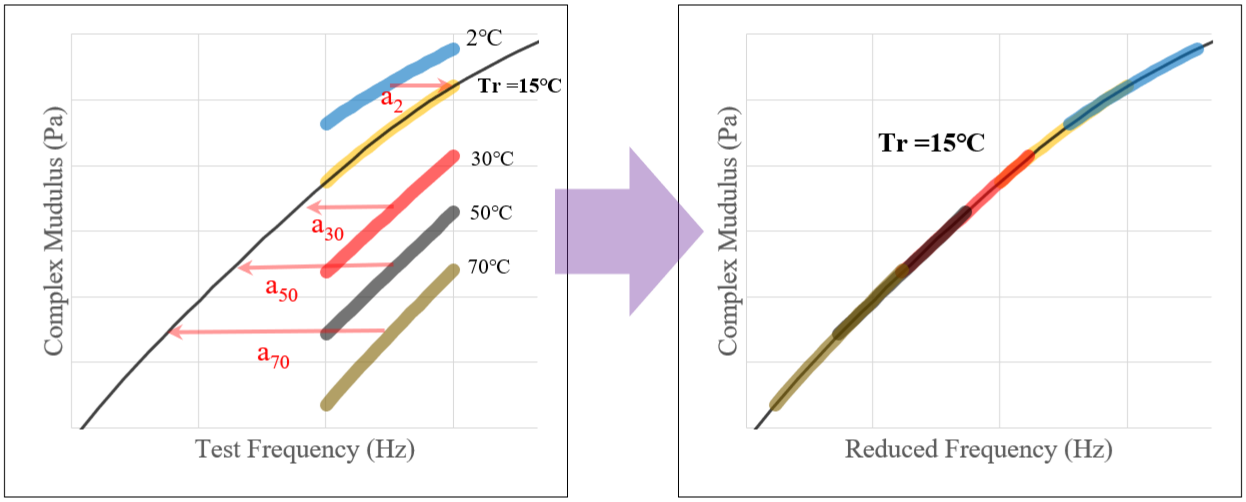


Figure 2-15 Construction of Complex Modulus Master Curve Using Time-Temperature Superposition Shift-Factors

The relationship of TTS shift factors with temperature is an intrinsic material property and has been explained by some few empirical relationships. One of the most common such equations is known as Williams-Landel-Ferry as explained in Equation 2-3.

Equation 2-3

$$\log a_T = -\frac{C_1(T - T_r)}{C_2 + (T - T_r)}$$

Where $\log a_T$ is the decadic logarithm of the TTS shift-factor, C_1 and C_2 are positive constants and are material specific, and T_r is the reference temperature [24].

Arrhenius equation is also presenting the relationship of TTS shift-factors and the temperature by the following equation;

Equation 2-4

$$\log a_T = -\frac{E_a}{2.303R}\left(\frac{1}{T} - \frac{1}{T_r}\right)$$

Where, E_a is the activation energy (J/mol), R is the universal gas constant (8.314 J/mol.K), and T and T_r are test temperature and reference temperatures in kelvins.

The MEPDG design software uses a second order polynomial equation to model TTS shift-factors using following equation;

Equation 2-5

$$\log_{10} a_T = C_1(T_r - T) + C_2(T_r - T)^2$$

Where C_1 and C_2 are material specific constants for the specific reference temperature.

Rowe and Sharrock (2011) proposed the modified Kaelble equation for the relationship between TTS shift-factor and temperature by modifying the WLF equation.

Equation 2-6

$$\log a_T = -C_1\left(\frac{T - T_d}{C_2 + |T - T_d|} - \frac{T_r - T_d}{C_2 + |T_r - T_d|}\right)$$

Where T_d is a constant and called the defining temperature. The definition of other parameters is the same as those in Equation 2-3.

2.4.3 Rheological Master Curve Models

Rheological models to explain the dependency of viscoelastic behaviour of asphalt cement and mix can be divided into rheological element models, which are using various combinations of mechanical elements, and the mathematical models, which focus only on data fitting, such as CA, CAM, GLSM, and DL models.

- *Basic Elemental Viscoelastic Models*

To express the mechanical response of viscoelastic materials, many models do exist using combinations of springs (to represent ideal elastic behaviour) and linear dashpots (to represent the ideal Newtonian viscous behaviour). The simplest of these analogical models are the Maxwell and Kelvin-Voigt models using a spring and a dashpot respectively in series and parallel configuration (Figure 2-16) [25]. These two models are not capable of explaining the rheological properties of complex viscoelastic materials such as asphalt cement and mix.

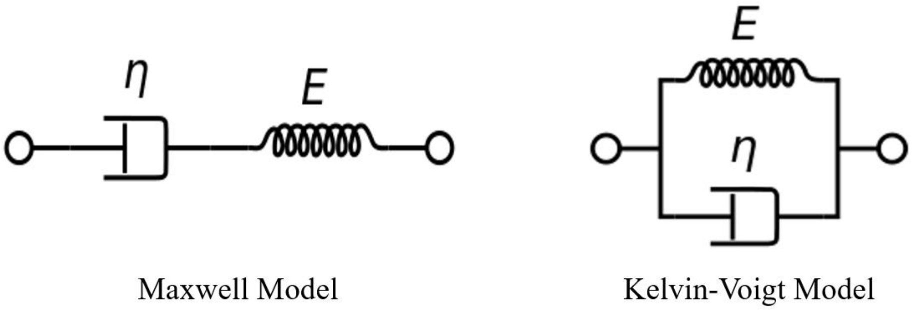


Figure 2-16 Schematic Representation of Maxwell and Kelvin-Voigt Model [26]

- *The Generalized Kelvin-Voigt Model*

The generalized Kelvin-Voigt model uses N number of unit Kelvin-Voigt elements in series (Figure 2-17). The generalized Kelvin-Voigt model with a discrete number of elements is not always successful in describing the complex viscoelastic model, while with an infinite number of elements can always characterize the viscoelastic behaviour perfectly. The creep function and the complex modulus of this model are as follows:

Equation 2-7-a

$$J(t) = \sum_{i=1}^{N} \frac{1}{E_j}\left(1 - e^{-\frac{t}{\tau_i}}\right) + \frac{1}{E_\infty} + \frac{1}{\eta_0}$$

Equation 2-7-b

$$E^*(i\omega) = \left(\sum_{i=1}^{N} \frac{1}{E_i + i\eta_i\omega} + \frac{1}{E_\infty} + \frac{1}{i\eta_0\omega}\right)^{-1}$$

Where, $\tau_i = \frac{\eta_i}{E_i}$ is the relaxation time for the *i*th Kelvin element.

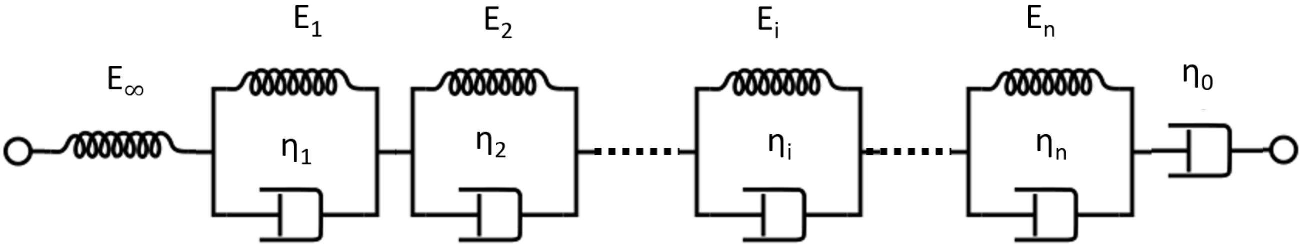


Figure 2-17 Schematic Representation of Generalized Kelvin-Voigt Model [25]

- *The Generalized Maxwell Model*

The generalized Maxwell model (also known as Wiechert model) is the most general form to describe the behaviour of linear viscoelastic materials, by putting an infinite number of Maxwell elements (spring-dashpot in series) in parallel (Figure 2-18). Just like the general Kelvin-Voigt model, a discrete number of elements would not necessarily explain the complex viscoelastic behaviour. In this model the relaxation and dynamic moduli can be calculated using the following equations:

Equation 2-8-a

$$R(t) = E_\infty + \sum_{i=1}^{N} E_i \mathrm{e}^{-\frac{t}{\tau_i}}$$

Equation 2-8-b

$$E^*(i\omega) = E_\infty + \sum_{i=1}^{N} E_i \frac{i\omega\tau_i}{1 + i\omega\tau_i}$$

E_∞ is the equilibrium modulus and is equal to zero for viscoelastic liquids.

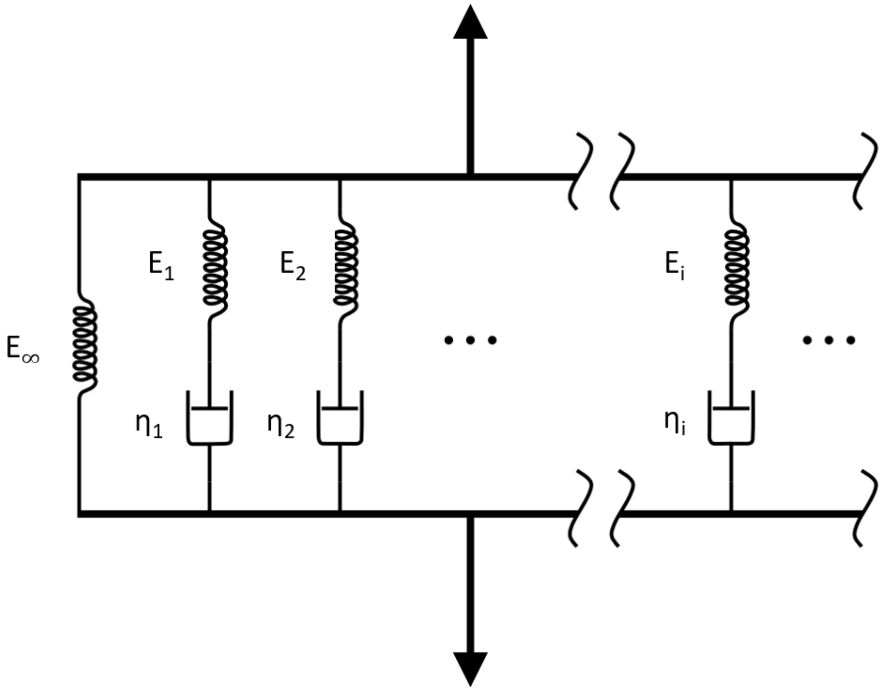


Figure 2-18 Schematic Representation of Maxwell-Wiechert Model [26]

- *Huet Model*

In 1963, Huet developed an analogical model mainly to describe the viscoelastic behaviour of asphalt cement by introducing a parabolic creep element which its complex modulus is defined by the following equation:

Equation 2-9

$$E^*(i\omega\tau) = \frac{(i\omega\tau)^h}{a\Gamma(h+1)}$$

Where h is the parabolic element characteristic (0<h<1), a is a dimensionless constant, and Γ is the gamma function ($\Gamma(n) = \int_0^\infty t^{n-1}e^{-t}dt$).

Huet model consists of two parabolic elements and an elastic spring in series (Figure 2-19). The complex modulus of this model can be calculated by the following equation:

Equation 2-10

$$E^*(\omega) = \frac{E_\infty}{1 + \delta(i\omega\tau)^{-k} + (i\omega\tau)^{-h}}$$

Where h and k are parabolic elements characteristic parameters such as $0 < k < h < 1$, E_∞ is the limit of complex modulus when $\omega\tau \rightarrow \infty$, and δ is a dimensionless constant.

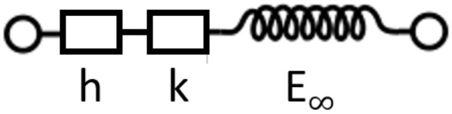


Figure 2-19 Schematic Representation of the Huet Model [27]

- *Huet-Sayegh Model*

As mentioned, the Huet model was developed mainly to explain the viscoelastic behaviour of asphalt cement. In 1965, Sayegh changed the configuration of the elements in Huet model to enable it to be used to describe the behaviour of asphalt mixes by adding an elastic element (spring) to Huet model in parallel (Figure 2-20). The following equations explain the analytical expression of the dynamic modulus for Huet-Sayegh model;

Equation 2-11

$$E^*(i\omega\tau) = E_0 + \frac{E_\infty - E_0}{1 + \delta(i\omega\tau)^{-k} + (i\omega\tau)^{-h}}$$

Where E_0 is the static modulus when $\omega\tau \rightarrow 0$.

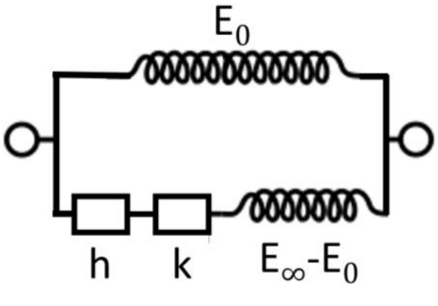


Figure 2-20 Schematic Representation of Huet-Sayegh Model [25]

- *The "2S2P1D" Model*

In 2003, Olard and Di Benedetto presented a generalized form of the Huet-Sayegh model to make it more appropriate for both asphalt cement and mix. This general model uses a simple combination of two springs, one dashpot, and two parabolic elements as depicted in Figure 2-21. The analytical form of the complex modulus for the "2S2P1D" model is explained as;

Equation 2-12

$$E^*(i\omega\tau) = E_0 + \frac{E_\infty - E_0}{1 + \delta(i\omega\tau)^{-k} + (i\omega\tau)^{-h} + (i\omega\beta\tau)^{-1}}$$

Where β is a dimensionless parameter such as $\eta = (E_\infty - E_0)\beta\tau$ represents the Newtonian viscosity.

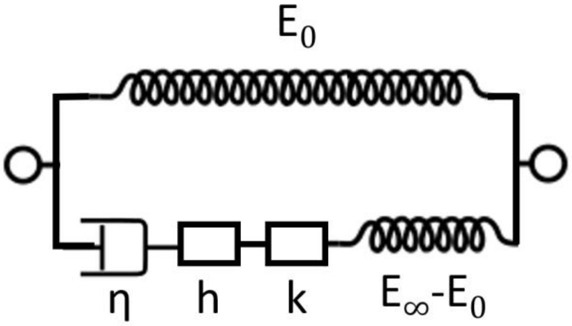


Figure 2-21 Schematic Representation of the "2S2P1D" Model

- *Christensen-Anderson and Christensen-Anderson-Marasteanu Models*

In 1992 Christensen and Anderson proposed a mathematical model for rheological behaviour of the asphalt cement as part of SHRP (Strategic Highway Research Program). Later (1999) Marasteanu and Anderson modified the original CA model which known as the CAM model. This model consists of two equations, one for the magnitude of the shear complex modulus and one for phase angle as follow;

Equation 2-13-a

$$|G^*(f,T)|(Pa) = \frac{G_g}{\left[1 + \left(f_c/_f\right)^k\right]^{m_e/k}}$$

Equation 2-13-ab

$$\delta\ (°) = \frac{90m_e}{1 + \left(f_c/_f\right)^k}$$

Where f is the loading frequency, f_c is a location parameter, G_g is the glassy modulus, and k, m_e are dimensionless shape parameters. The CA model considers $m_e = 1$ and uses crossover frequency[4] instead of f_c.

Later studies showed CAM model is more representing the unmodified asphalt cement and is not appropriate to represent the complex rheological behaviour of polymer modified asphalt cement.

- *Zeng Model*

In 2001, Zeng et al. generalized CAM model to be applicable for both asphalt cement and mixes. Moreover, this model was able to represent the complicated rheological behaviour of polymer modified asphalt better. Same as the CAM model, two different formulations were used to explain the complex shear modulus, one for the absolute value of the complex modulus and the other for the phase angle.

Equation 2-14-a

$$|G^*(f,T)|(Pa) = G_e + \frac{G_g - G_e}{\left[1 + \left({}^{f_c}/_{f'}\right)^k\right]^{m_e/k}}$$

Where G_e is the equilibrium complex modulus ($f \rightarrow 0$), G_g is the glassy modulus ($f \rightarrow \infty$), f_c is the location parameter with the same dimension as frequency, f' is the reduced frequency, and m_e and k are dimensionless shape parameters.

Equation 2-14-ab

$$\delta\ (°) = 90I - (90I - \delta_m)\left\{1 + \left[\frac{\log\left({}^{f_d}/_{f'}\right)}{R_d}\right]^2\right\}^{-m_d/2}$$

Where δ_m is the phase angle constant, f' is the reduced frequency, f_d is the location parameter with dimensions of frequency, R_d and m_d are dimensionless shape parameters, and I is the indication functions such as;

---

[4] The Crossover frequency is the loading frequency at the specific temperature where loss and storage moduli are equal (δ=45°).

$$I = \begin{cases} 0 \; if \; f > f_d \\ 1 \; if \; f < f_d \; (for \; asphalt \; cement) \\ 0 \; for \; asphalt \; mixtures \end{cases}$$

- *Sigmoidal Model*

In 2002 Pellinen, Witczak and Bonaquist developed a method to construct complex modulus master curve using a sigmoidal fitting function using experimental test data. This model adopted in MEPDG to develop complex modulus master curve [28]. The suggested sigmoidal function is;

Equation 2-15

$$\log(|E^*|) = \delta + \frac{\alpha}{1 + e^{\beta - \gamma \log(\xi)}}$$

Where ξ is reduced frequency, δ is the minimum modulus value, α is the span for the modulus values, and β and γ are dimensionless shape parameters.

- *Generalized Logistic Sigmoidal Model*

The sigmoidal model used in MEPDG was modified by Rowe et al. (2008), and named it as the generalized logistic sigmoidal model (GLSM) presented as;

Equation 2-16

$$\log(|E^*|) = \delta + \frac{\alpha}{\left[1 + \lambda e^{(\beta + \gamma A(\log \omega))}\right]^{1/\lambda}}$$

Where ω is the reduced frequency and α, δ, β, γ, and λ are model parameters.

2.4.4 Asphalt Cement Grading

As described in section 2.2, asphalt cement is a general term attributed to the heaviest refinery product, which more modification might be necessary to reach desired mechanical properties. Since the beginning of the modern application of asphalt cement in the pavement industry, engineers were looking for criteria to determine the suitability of asphalt cement for their specific application. Consistency was the very first criteria to differentiate among the various asphalt cement types and determine their suitability for different climates.

- *Chewing Test*

The very first known empirical test was the chewing test, in which an experienced person, chews a specific asphalt cement and decides whether it is suitable for the specific project. As the nature of this test implies, the temperature of this test is roughly around the temperature of the human body (close to 37ºC) [29].

- *Penetration Grading System*

The penetration grading system was developed in the early 19th century and improved gradually over time and was the dominant asphalt grading system until the invention of the "Performance Grading System." This system is still in use in many parts of the world such as Middle East, Europe, Africa, and Asia and many municipalities in north-America. This system consists of a set of empirical tests to measure mainly the consistency and purity of asphalt cement. The grade of asphalt is expressed based on the penetration (0.1 mm) of a standard no.2 sewing needle into a cup of asphalt cement at 25ºC. However, a set of tests at various temperatures are conducted mainly to examine the applicability for paving purposes such as "ring & ball softening point," "ductility," "solubility," "flash point," and "thin film oven test." Standard grades and requirements for various tests are presented in Table 2-1. The requirements and grades might be slightly different in different places, but the general concept is the same. For example, the European standard (EN) measures the low-temperature cracking resistance of asphalt by conducting the Fraass breaking point test [30].

Table 2-1 Requirements for Penetration-Graded Asphalt Cement for Use in Pavement [31]

	40-50		**60-70**		**85-100**		**120-150**		**200-300**	
	Min	*Max*	*Min*	*Max*	*Min*	*Max*	*Min*	*Max*	*Min*	*Max*
Penetration at 25ºC (dmm)	*40*	*50*	*60*	*70*	*85*	*100*	*120*	*150*	*200*	*300*
Softening Point (ºC)	*49*	--	*46*	--	*42*	--	*38*	--	*32*	--
Flash Point (ºC)	*230*	--	*230*	--	*230*	--	*220*	--	*175*	--
Ductility at 25ºC (cm)	*100*	--	*100*	--	*100*	--	*100*	--	*100*	--
Solubility (%)	*99.0*	--	*99.0*	--	*99.0*	--	*99.0*	--	*99.0*	--
Retained Penetration at 25ºC after TFOT (%)	*55*	--	*52*	--	*47*	--	*42*	--	*37*	--
Ductility at 25ºC after TFOT (cm)	--	--	*50*	--	*75*	--	*100*	--	*100*	--

- *Viscosity-Grading Asphalt Cement*

By the beginning of the 1970s, the viscosity grading system was more common than penetration grading for asphalt cement [32]. In the viscosity grading system, limiting viscosity values at two different temperature were prescribed to control the consistency of asphalt cement at around the maximum performance temperature of asphalt cement, and the other (usually measured at 135ºC) as an approximation of the construction (mixing and compaction) temperatures. The viscosity grading system is subdivided into two systems; The AC system (measuring viscosity on the fresh asphalt cement), and the AR system (measuring viscosity on aged residue). Table 2-2 and

Table 2-3 are presenting the list of required tests and grades base on each of these systems. In AC system the numerical values denote the viscosity in hundreds of poises and the allowable tolerance on each grade is ±20 percent. In the AR system, the numerical values describe the viscosity of asphalt cement at 60ºC in poises within 25 percent tolerance limit.

The main disadvantage of the viscosity grading system is that it mainly focuses on the high-performance temperature range and the construction temperature zone. Penetration and ductility measurements used in this system allows inference of the intermediate temperature zone properties of asphalt cement to some extent, while there is absolutely no indicator for low-temperature zone performance.

Table 2-2 Requirements for Asphalt Cement in Viscosity Grading Based on Original Asphalt [33]

Test	***Viscosity Grade***					
	AC-2.5	**AC-5**	**AC-10**	**AC-20**	**AC-30**	**AC-40**
Viscosity, 60ºC (Pa.s)	25±5	50±10	100±20	200±40	300±60	400±80
Viscosity, 135ºC (mm^2/s), min.	125	175	250	300	350	400
Penetration, 25ºC (dmm), min	220	140	80	60	50	40
Flash Point (ºC), min.	165	175	220	230	230	230
Solubility in TCE (%), min.	99.0	99.0	99.0	99.0	99.0	99.0
Tests on TFOT residue						
Viscosity ,60ºC (Pa.s), max.	120	250	500	1000	1500	2000
Ductility, 25ºC (cm), min.	100	100	75	50	40	25

Table 2-3 Requirements for Asphalt Cement in Viscosity Grading Based on Residue from RTFOT [33]

Tests on Residue from RTFOT	***Viscosity Grading***				
	AR-1000	**AR-2000**	**AR-4000**	**AR-8000**	**AR-16000**
Viscosity, 60ºC (Pa.s)	100±25	200±50	400±100	800±200	1600±400
Viscosity, 135ºC (mm^2/s), min.	140	200	275	400	550
Penetration, 25ºC (dmm), min	65	40	25	20	20
Percent of Original Penetration, min., (%)	--	40	45	50	52
Ductility, 25ºC (cm), min.	100	100	75	75	75
Tests on the Original Asphalt Cement					
Flash Point (ºC), min.	205	220	225	230	240
Solubility in TCE (%), min.	99.0	99.0	99.0	99.0	99.0

As mentioned above, the focus of viscosity grading is to measure the high performance temperature properties through measuring the viscous component of asphalt cement behaviour and neglects the elastic component at this temperature zone. While this approach might be suitable for conventional, non-modified asphalt cement, it is not properly addressing the properties of polymer modified cement.

- *Performance Grading System*

As part of SHRP program to develop the superior mix design, a new asphalt cement grading system was developed in order to replace empirical single point grading systems such as penetration and viscosity grading with engineering property-based system that evaluates the asphalt cement at performance temperature range. PG grading system names asphalt cement with two numbers as indicators for maximum and minimum design pavement temperature such as PG XX-XX. This system addresses three major pavement distresses including, permanent deformation (rutting), fatigue cracking, and low temperature cracking.

PG grading system measures the rheological properties of asphalt cement at three different temperature range (high-, medium-, and low-temperature zones) at three different ageing conditions (unaged and short-term aged for high temperature, long-term aged for medium- and low-temperature range). As part of this system, rotational viscosity is also measured at 135ºC to control the construction temperatures. Performance graded asphalt cement are named Figure 2-22 shows the PG grading procedure.

Selection of the appropriate asphalt cement grade for a project depends on the climate and traffic loading of the specific project. The upper limit of PG grade should be lower than the average seven-day maximum pavement temperature, and the lower limit should be higher than the minimum pavement design temperature. To reduce the potential of rutting in high volume roads and high-stress areas (such as intersections) grade bumping is suggested.

The suitability of ${G^*}/{\sin\delta}$ and $G^*.\sin\delta$ for grading highly polymer modified asphalt cements was questioned, and new approaches were considered using alternative rheological tests such as multiple-stress-creep-recovery (MSCR) and linear-amplitude-sweep test (LAS).

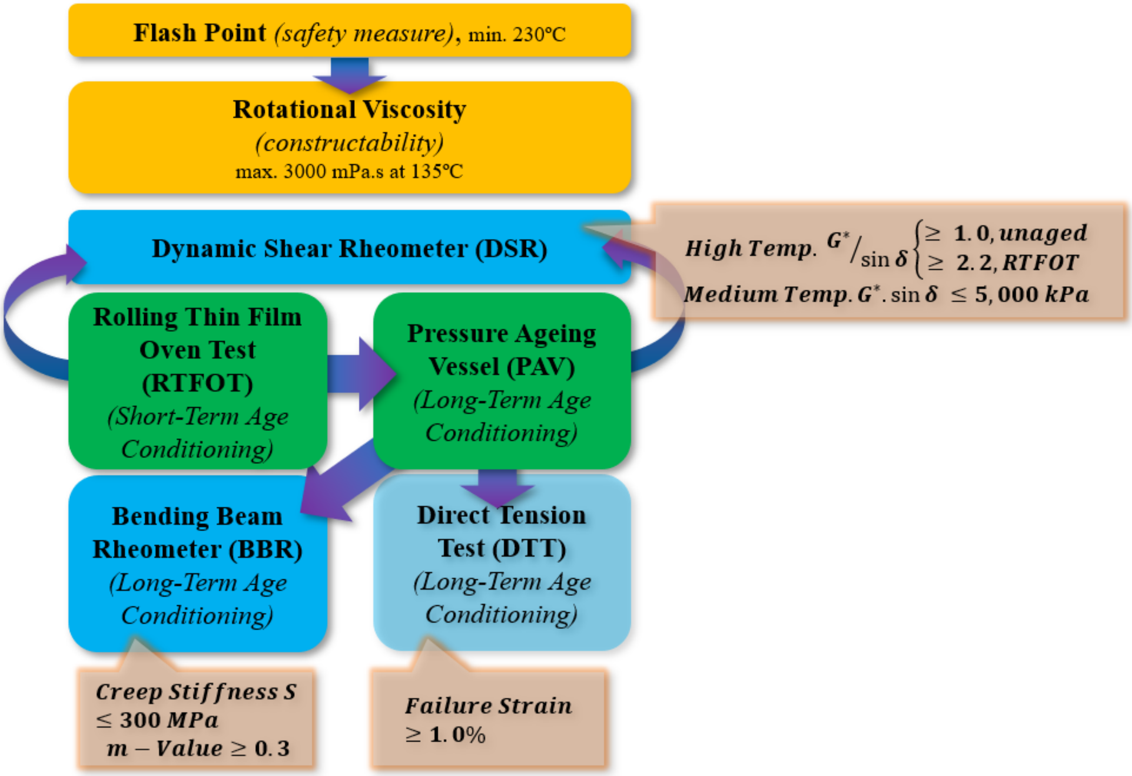


Figure 2-22 Performance Grading Procedure

2.5 Asphalt Cement Ageing – Time Associated Changes

2.5.1 The Life of Asphalt Cement

Paving grade asphalt cement is an organic material mainly produced from the refining of crude oil in refineries from various types of crude sources by using different processes. Asphalt cement may be further modified by the refinery or asphalt cement supplier via different techniques, in most cases polymers. From the production of asphalt cement, where it is first graded based on its thermo-mechanical properties, asphalt cement experiences various conditions, during each, several changes happen in the chemical composition and structure of its components. These changes consequently lead to variations in the mechanical behaviour of asphalt cement. The severity of these changes during each step is firmly related to the prevailing condition (Figure 2-23). During storage, asphalt cement is kept at high temperatures for several days or weeks. In the construction stage, the thin film of asphalt cement endures high temperatures for a relatively short time. In service, the thin film of asphalt cement experiences low or moderate temperatures for a very long time and is exposed to sunlight and moisture. Asphalt cement’s chemical composition alters during each of these steps.

Although asphalt cement experiences high temperatures (from few days to a couple of weeks) in bulk storage, slight oxidation hardening occurs. Designing a proper circulation system limits the oxygen access by limiting the surface volume ratio (surface to volume ratio is roughly something between 0.04 up to 0.1 m^2/m^3 depending on the geometry of the tank).

A considerable amount of hardening occurs during the construction period, especially mixing at the asphalt plant where hot asphalt cement and aggregate are blended, and asphalt cement coats the aggregates with a thickness of approximately 5 to 15µm [3]. This low thickness causes extremely high oxygen access, which at elevated temperatures could cause excessive oxidation and volatilization (surface area to volume ratio will be approximately 105 m2/m3). Because of such a harsh condition, considerable changes happen in the chemical structure of asphalt cement. As a very rough approximation, the penetration of asphalt cement will drop by 30% as a result of the mixing process [34]. The amount of age hardening because of mixing, transportation, and compaction operations is case specific and depends on several factors.

In a research done in North Dakota in 1974, the effect of two different mixing procedures on the short-term ageing of asphalt cement was evaluated. Using needle penetration test results, they found that using drum mixers led to less short-term age hardening compared to conventional batch mixers [35]. In another study done by Shell Bitumen, regular amount of short-term ageing in drum mixers was found to be less than half of what occurs in batch mixers, based on penetration and softening point test results [3].

As asphalt mixtures are compacted and laid, their hardening process does not stop. Although the rate of chemical changes decreases significantly at ambient temperatures, it results in severe asphalt age hardening after a few years. Several environmental factors, such as exposure to sunlight and moisture, affect the rate at which asphalt cement hardens. This hardening and embrittlement will cause asphalt concrete pavement to become more susceptible to fatigue, and thermal distress and to lose proper binding properties [36], [37].

Possibly one of the very first efforts to investigate the change in asphalt cement properties as an effect of time of exposure to weathering was that of Hubbard and Reeve (1913) [38]. They put different asphalt cement at the outdoor condition for one year and found that asphalt cement stiffness (measured with needle penetration test) and the amount of insoluble matter in CS_2 increases mainly because of oxidation. Since then several other researchers tried to find the importance of various factors. Meanwhile, some of these factors were used to simulate the ageing process in the laboratory to obtain representative samples and understand the future behaviour of asphalt cement.

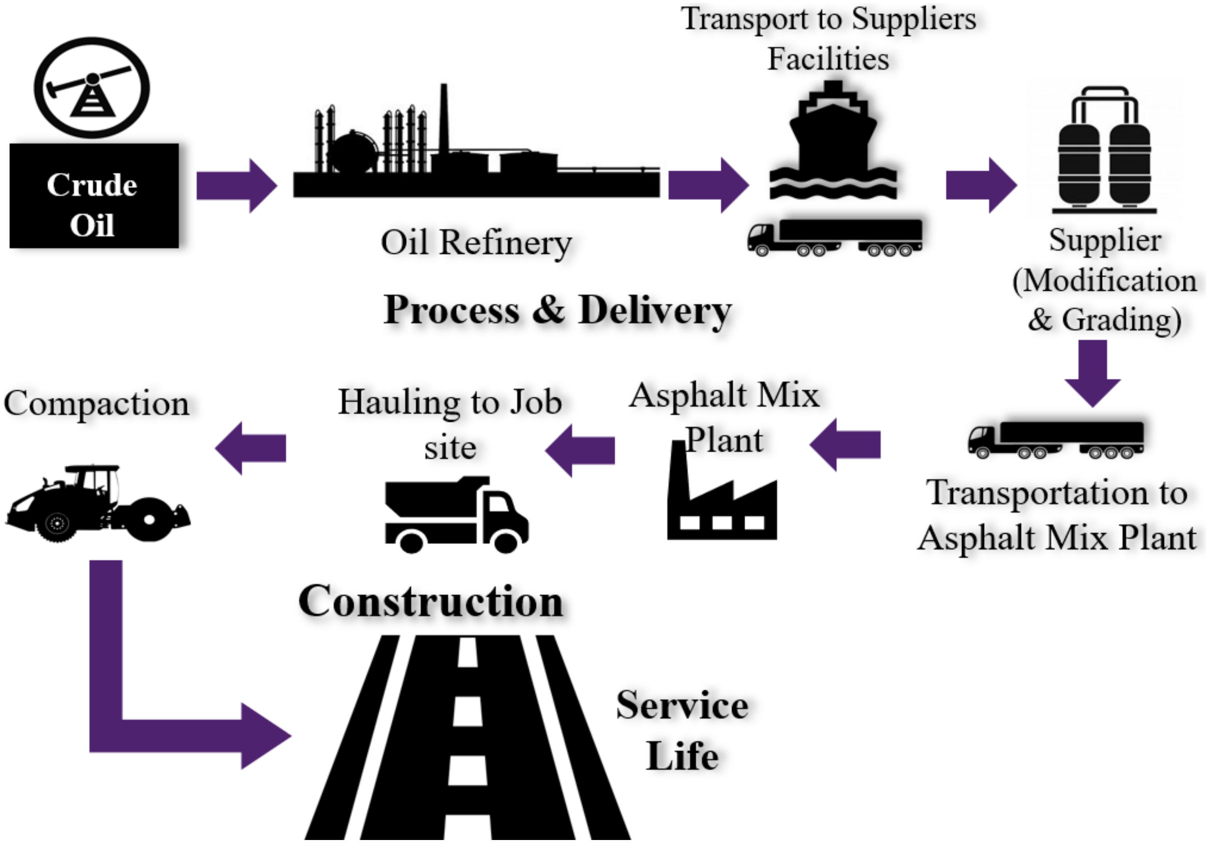


Figure 2-23 Life Cycle of Asphalt Cement from Production to Service

2.5.2 Ageing Mechanisms

As discussed in the previous sections, high-temperature oxidation and loss of volatiles are globally accepted as the main factors affecting asphalt cement hardening during the construction period, known as short-term ageing. After the construction step, asphalt age hardening will not stop, and chemical changes continually happen at a much slower pace. Several factors are attributed to this ongoing age hardening of in-place asphalt cement. Some of the most important ones are oxidation at ambient temperatures, steric hardening, photo-oxidation, polymerization, the selective absorbance of oily fractions to aggregates and so on.

Table 2-4 Factors That Can Change Physical Properties of Asphalt Cement During Time [29]

Effect	Influenced by					Occurs	
	Time	Heat	Oxygen	Sunlight	β&γ rays	At Surface	In Mass
Oxidation (in the dark)	✓	✓	✓			✓	
Photo-oxidation (direct light)	✓	✓	✓	✓		✓	
Volatilization	✓	✓				✓	✓
Photo-oxidation (reflected light)	✓	✓	✓	✓		✓	
Photochemical (direct light)	✓	✓		✓		✓	
Photochemical (reflected light)	✓	✓		✓		✓	✓
Polymerization	✓	✓				✓	✓
Development of an internal structure (Thixotropy)	✓					✓	✓
Exudation of Oil (Syneresis)	✓	✓				✓	
Changes caused by nuclear energy	✓	✓			✓	✓	✓
Action of water	✓	✓	✓	✓		✓	
Absorption by solid	✓	✓				✓	✓
Adsorption of components at the solid surface	✓	✓				✓	
Chemical reactions or catalytic effect at the interface	✓	✓				✓	✓
Microbiological deterioration	✓	✓	✓			✓	✓

Traxler (1963) [39] mentioned 15 environmental factors that can affect the chemistry of asphalt cement (Table 2-4). Lee (1969) named ten influencing factors: oxidation, volatilization, polymerization, thixotropy, syneresis (exudation of oil), separation (selective absorption of asphalt fractions by aggregates), photo-oxidation, moisture, microbiological deterioration, and photochemical action [40].

Petersen (1984) named three dominant mechanisms responsible for age hardening. In order of importance, oxidation, loss of oily components (by volatility or absorption), and thixotropic effects (caused by molecular restructuring or steric hardening) are the primary mechanisms that result in a change of mechanical properties [17]

The Shell Bitumen Handbook mentions oxidation, volatilization, steric or physical hardening, and exudation of oils as four main mechanisms that lead to age hardening and change in the mechanical properties of asphalt cement [3], [34].

Regardless of the causes, general mechanisms that cause time associated hardening (ageing) can be summarized as follows:

- Oxidation (as general, reacting oxygen with hydrocarbons)
- Volatilization (loss of lighter fraction, which occurs mainly during the construction period but can continue at a much slower pace after a few months of construction)

- Polymerization[5] (which can happen when asphalt cement heats up without access to oxygen, mainly during the hot storage and transportation of asphalt cement)
- Steric hardening[6] or hardening due to thixotropy
- Syneresis[7] and absorption[8] to aggregates (both of which result in loss of lighter fractions and asphalt cement hardening)
- Microbiological deterioration (under certain favourable environmental conditions, fungal and microbial activities can degrade the paving asphalt cement [42]. Studies have shown that, depending on the type of microorganisms, softening or hardening of asphalt cement could result [43].

As a result of gradual change in chemical composition of asphalt cement during ageing, the colloidal structure of asphalt cement changes gradually from more "Sol" like structure toward "Gel" due to the increase in the larger size particles (such as asphaltene) amount, the increase in the size of existing solid-like particle, stronger interaction between particles (due to increase in the functionality of the molecules) and loss of lighter fractions (reduction in the dispersing phase). This shift in colloidal structure results in a stiffer, more brittle mechanical behaviour of asphalt cement, which alters the mechanical properties of the asphalt cement and asphalt mix and would affect the durability of the pavement system.

The pace of oxidation reactions depends on many factors such as the chemical structure and composition of asphalt cement (which itself is a function of crude source and process condition) as well as environmental conditions under which asphalt cement ages. Following are the main environmental affecting factors that can dictate the pace of age hardening in asphalt cement.

---

[5] Polymerization is a combination of similar molecules to form larger ones, because of heating in the absence of oxygen, causing progressive hardening. The amount of polymerization depends on temperature, time, and composition of asphalt. However, there are evidences that at extremely high temperature, hydrocarbon chains can break down in a process named hydro-cracking, which will cause decrease in viscosity [40].

[6] time-associating restructuring in hydrocarbon chains resulting stronger bonds between them and increase in stiffness [41]

[7] Syneresis is an exudation reaction in which the thin oily liquids are exuded to the surface of the bitumen film. With the loss of these oily constituents, the bitumen becomes harder.

[8] Separation is the removal of the oily constituents from the bitumen caused by selective absorption of some porous aggregates.

- *Temperature*

Temperature plays a significant role in determining the speed of every chemical reaction, including oxidation. In asphalt cement oxidation, the temperature can also alter the kinetics of oxidation. Although at lower temperatures, the rate of oxidation is drastically reduced, there is still no evidence that it will stop even at very low application temperatures.

The increase in temperature affects the oxidation process in two different ways: first, by increasing the reactivity of hydrocarbons through an increase in the energy level and the entropy of the system; and second, by mobilizing more susceptible molecules to reach the other part of the reaction, which is oxygen. Temperature variation does not affect the reactivity of all asphalt cement constituents equally; some functionalities show more sensitivity to temperature change and may be degraded at very high temperatures. An example of such a functional group is sulfoxide, which is mainly produced at high performance temperature zone, while degrades at excessively high temperatures, such as construction temperatures [44]. From this point of view, it must be noted that temperature does not only affect the age hardening pace, but it dictates the final product's properties.

- *Photo-Oxidation*

The effect of sunlight radiation on the chemical structure of organic materials is well studied mainly in polymer science, where polymer decomposition is expected due to exposure to sunlight [45]. The principal mechanism of the sunlight effect is increasing the level of energy in organic material which causes instability, especially in weaker bonds. The unstable bonds show more affinity to the available oxygen, which results in decomposition of organic material and loss of desired properties. Sunlight radiation and specifically high-energy containing ultra-violet rays (with wavelengths between 3000 to 5000Å), can affect organic molecules in an asphalt cement by accelerating the oxidation process [39]. Although there is no doubt that solar radiation affects the asphalt oxidation, many questions still exist about the extent of its effect. Based on the investigations done by measuring light absorbance, it has been shown that ultraviolet waves could only penetrate up to 10μm inside the asphalt film. Thus, the photo-oxidation affected zone is limited to approximately top 50μm [46]. The UV radiation can also degrade the polymers used in asphalt cement modification, resulting in the loss of desired properties gained through the costly polymer modification process [32].

- *Water*

The oxidation products including acids and ketones are mostly soluble in water. Thus, whenever these highly oxidized materials exposed to water, they can be washed away. The removal of the highly oxidized protecting film will let oxidation and photo-oxidation to continue and affect deeper in asphalt cement [47]. Water can also act as a catalyst for many chemical oxidation and photo-oxidation reactions and can accelerate the ageing process [48]. The importance of this catalytic effect of water should be more investigated by collecting qualitative data and reliable methods. Water can also affect some moisture sensitive aggregates and minerals, and cause oxidation reaction initiation in the surface of aggregates, the product of which may also affect the ageing properties of asphalt binder.

- *Minerals*

In the study of the asphalt cement ageing, aggregates were mainly considered as neutral for filler material and not contributing in the age hardening of asphalt cement. While this assumption can be true in many cases, the possibility of interaction of some specific aggregate's ingredients in the ageing process of asphalt cement should be considered, especially when dealing with aggregates containing reactive metal compounds. Aggregates consist of several minerals where some of them can act as catalysts in the ageing process. This issue needs to be addressed properly, as it can significantly affect pavement durability. Petersen et al. (1956) studied the catalytic effect of some minerals on asphalt cement age hardening and evaluated the sensitivity of each fraction (Corbett fractions) to such catalytic effect. Results obtained from this study showed that the existence of some minerals on the surface of aggregates could speed up the oxidative ageing process [49].

Non-polar fractions of asphalt cement (saturate aromatics and naphthene aromatics) found to be more sensitive to such catalytic effect. Another study conducted by Barbour et al. (1974) to investigate the effect of aggregate type and composition on the age hardening process of asphalt cement using chemical analysis tools. Based on carbonyl (Ketone) groups formation criteria, they found that the oxidation of saturated aromatics is approximately ten times increased in the presence of quartzite aggregates [50].

Hydrated lime that is widely used to improve the water resistance of asphalt mixes was found to reduce the rate of oxidation age hardening and to have a protective effect, especially at first few years. This effect is attributed to the ability of hydrated lime to absorb more oxidation susceptible fraction and make them temporarily unavailable in the system [17].

Aggregates with sulphur-bearing compounds can become a source of deleterious sulphate attack on the surface layer of the asphalt pavements. Pyrite (FeS_2) and pyrrhotite ($Fe_{1-x}S$, x= 0 to 0.2) are the most abundant iron sulphides present in natural rocks. Iron sulphides are unstable in the presence of oxygen and moisture and are reacting with oxygen to produce ferrous-sulphate salts and iron hydroxides as shown in Table 2-5. The rates of these reactions are influenced by several factors such as surface area and morphology of the pyrite particles and oxygen concentration. The products of these reactions can, in turn, be involved in several reactions depending on the environmental conditions. The ferrous-sulphate can form a hydrated sulphate such as melanterite ($FeSO_{4.7}H_{20}$) and, after some oxidation steps, form hydronium jarosite $[Fe_3(SO_4)_2\ (OH)_{5.2}H_2O)]$.

The molar volume of such materials is much greater than that of the original pyrite and, if the latter occurs in the stone matrix, the reaction causes expansion and disintegration of the stone. Moreover, these oxidation products can react with both the mineral components of the aggregates and the asphalt cement surrounding it. Thus, the oxidation products of iron sulphide minerals may have adverse effects on the long-term performances of asphalt mixtures [51].

Table 2-5 Predominant Oxidation Reactions of Pyrite and Pyrrhotite in Aqueous Systems, and Their Associated Volume Changes [51]

Reaction	**Volume Change** (cm^3 per mole of sulphide)
$FeS_2 + \frac{9}{2}O_2 + 2H_2O \rightarrow FeSO_4.H_2O + SO_4^{2-} + 2H^+$	*209.96*
$8Fe_{1-x}S + \frac{31}{2}O_2 + 8H_2O \rightarrow 7(FeSO_4.H_2O) + SO_4^{2-} + 2H^+$	*187.08*
$FeS_2 + \frac{9}{2}O_2 + 2H_2O \rightarrow FeOOH + 2SO_4^{2-} + 2H^+$	*-3.12*
$8Fe_{1-x}S + \frac{67}{4}O_2 + \frac{25}{2}H_2O \rightarrow 7FeOOH + 8SO_4^{2-} + 16H^+$	*0.64*
$FeS_2 + \frac{17}{4}O_2 + H_2O \rightarrow \frac{1}{2}Fe_2O_3 + 2SO_4^{2-} + 2H^+$	*-8.81*
$8Fe_{1-x}S + \frac{69}{4}O_2 + 8H_2O \rightarrow \frac{7}{2}FeOOH + 8SO_4^{2-} + 16H^+$	*-4.34*
$FeS_2 + \frac{18}{4}O_2 + 2H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + H^+$	*3.05*
$8Fe_{1-x}S + 21O_2 + 11H_2O \rightarrow 7Fe(OH)_3 + 8SO_4^{2-} + H^+$	*6.04*

Metals and Metallic Compounds

The catalytic effect of metals such as Iron and their salts on oxidation process of hydrocarbons is well known in the asphalt industry, and several industrial processes have used them to increase production efficiency in the air-rectifying and oxidation units [52]. Some ferric-chlorides and iron-oxides have found their way as a catalyst for air blowing process of asphalt fluxes (some of them are not fit exactly into the scientific definition of the catalyst as they are consumed during the reaction) [53]. Unfortunately, the effect of metals on accelerating the age hardening of asphalt is not comprehensively studied, as it was believed that the only source of metals would be the remaining catalyst from the air blowing process, while there may be a considerable amount of metals on the surface of the aggregates which mentioned in the previous section.

Some researchers studied other sources of metals in the asphalt cement such as Recycled Engine Oil Bottom (REOB), which is used mainly as an extender to improve the low-temperature behaviour of asphalt cement. Some sources of REOB may contain a considerable amount of metals such as chromium, zinc, and copper [54].

2.6 Laboratory Accelerated Age Conditioning

During the mix design stage, not only the mechanical properties of freshly compacted asphalt mix are important, but the mechanical properties of the mix after long-term ageing plays a determinative role in the durability of pavement. Any change in the mechanical behaviour of the asphalt cement will affect the mechanical properties of the corresponding mix. Therefore, asphalt ageing, which is the primary source of changes in binder properties, needs to be addressed when selecting an asphalt cement for project condition.

Although hardening of asphalt cement could improve the rutting resistance properties of asphalt cement (by increasing the complex modulus and decreasing the viscous part of it), it will make the mix more susceptible to other distresses such as low-temperature cracking, fatigue cracking, and possibly moisture damages.

The need for evaluating the ageing susceptibility of asphalt cement and its behaviour after age hardening in the pavement, resulted in the invention of several approaches to prepare laboratory aged asphalt cement and asphalt mix samples for further assessment of their mechanical properties.

The primary challenge in all these methods is that how good they can simulate real-life conditions and age-hardening that occur during the life cycle of the pavement in a time-efficient way.

Laboratory ageing methods can be divided into methods simulating ageing on asphalt cement samples, and those trying to simulate ageing on asphalt mix samples. Furthermore, each category can be subdivided into those simulating short-term age hardening and long-term ageing.

This section is dedicated to review available accelerated laboratory ageing processes (for both asphalt cement and asphalt mix) and look at the advantages and disadvantages of each.

2.6.1 Accelerated Ageing Methods for Asphalt Cement

Over the last eighty years, several attempts have been made to develop laboratory age conditioning procedures for asphalt cement and correlate them with field ageing (Table 2-6). Most of these methods applied excessive heating on thin films of asphalt cement [55]. Ageing through these conditions appeared to be more representing the short-term ageing as these parameters are like what happens during the construction (mixing and compaction) period. In this section, a brief discussion of these methods is presented.

- *Thin Film Oven Test (TFOT)*

Lewis and Welborn (1940) developed one of the first ageing methods to evaluate the ageing susceptibility of asphalt cement. This scheme which is named “Thin Film Oven Test (TFOT)” was mainly designed to assess high-temperature ageing due to the volatility of asphalt cement’s lighter fractions during the mixing and compaction stages. In this technique, 50 ml of asphalt cement poured into a flat circular container to form a film thickness of 3.2 mm and placed on a rotating shelf (5 to 6 rpm) in an oven at 163°C for 5 hours. This method counted as a measure of age hardening during plant mix operation as it uses mixing temperatures on a thin film of asphalt cement, which mimics construction stages. This method is still in use in many places around the world due to its simplicity and low cost.

Although this approach gained a lot of attention and was adopted by many standardization agencies (including ASTM, AASHTO, and EN), several critics challenged its validity mainly due to relatively thick asphalt film (comparing to the asphalt thickness that coats the aggregates). From the other side, as there is no agitation in this method, skin formation on the very surface of asphalt may limit oxygen access for the rest of the sample, preventing further oxidation. Moreover, not all volatile matters leave the asphalt, as some couldn’t pass through the highly oxidized protective layer (skin).

Table 2-6 Asphalt Cement Laboratory Ageing Methods [56]

Ageing Method	Developed by	Temperature (°C)	Duration	Film thickness
Thin Film Oven Test (TFOT), ASTM D1754, EN 12607-2	Lewis & Welborn, 1940	163	5h	3.2mm
Modified Thin Film Oven Test (MTFOT)	Edler et al., 1985	163	24h	100μm
Extended Thin Film Oven Test (ETFOT)	Jemison et al., 1991	163	14.5h	3.2mm
Rolling Thin Film Oven Test (RTFOT), AASHTO T240, ASTM D2872, EN12607-1	Hveem et al., 1963	163	75m	1.25mm
Extended Rolling Thin Film Oven Test (ERTFOT)[**]	Edler et al., 1985	163	8h	1.25mm
Extended Rolling Thin Film Oven Test (ERTFOT)[**]	Kemp et al., 1981	163	5h	1.25mm
Extended Rolling Thin Film Oven Test (ERTFOT)[**]	Jemison et al., 1991	163	3.5h	1.25mm
Nitrogen Rolling Thin Film Oven Test (NRTFOT)	Parmeggiani, 2000	163	75m	1.25mm
German Rotating Flask (GRF), DIN 52016, EN12607-3	Deutsche Norm 1988	165	150m	-
Modified German Rotating Flask (MGRF)	WRI 2004	165	210m	-
Shell Microfilm Test	Griffin et al., 1955	107	2h	5μm
Modified Shell Microfilm Test (Hveem)	Hveem et al., 1963	99	24h	20μm
Modified Shell Microfilm Test (Traxler)	Traxler, Halstead & Zenewitz, 1961	107	2h	15μm
Rolling Microfilm Oven Test (RMFOT)	Schmidt & Santucci, 1969	99	24h	20μm
Modified RMFOT	Schmidt, 1973	99	48h	20μm
Tilt-Oven Durability Test (TODT)	Kemp & Prodoehl, 1981	113	168h	1.25mm
Alternative TODT	McHattie, 1983	115	100h	1.25mm
Thin Film Accelerated Ageing Test (TFAAT)	Petersen, 1989	130 or 113	24 to 72h	160μm
Modified Rolling Thin Film Oven Test (RTFOTM)	Bahia et al., 1998	163	75m	1.25mm
Iowa Durability Test (IDT)	Lee, 1973	65	1000h	3.2mm
Pressure Oxidation Bomb (POB)	Edler et al., 1985	65	96h	30μm
Rotating Cylinder Ageing Test (RCAT)	Verhasselt & Choquet, 1991	70–110	144h	2mm
Pressure ageing vessel (PAV)	Christensen & Anderson, 1992	90–110	20h	3.2 mm
High-pressure ageing test (HiPAT)	Hayton et al., 1999	85	65h	3.2mm
The Universal Simple Ageing Test (USAT)	Farrar, Planche, Grimes, Qin, 2014	130 or 150[*]	50m	300μm
The Universal Simple Ageing Test (USAT)	Farrar, Planche, Grimes, Qin, 2014	100	40h	300μm

** the temperature is set 150°C for HMA, and 130 °C for warm-mix.*

*** three methods named ERTFOT in this table, the only difference in the procedure is the exposure time.*

- *Modified Thin Film Oven Test (MTFOT) and Extended Thin Film Oven Test (ETFOT)*

Several researchers tried to modify the TFOT ageing procedure to better address real conditions

and better simulate the short-term ageing and provide more representative samples. As it was assumed that TFOT conditioned samples did not experience enough ageing and are softer than those exposed to real short-term ageing, most of the modifications were focused on making the laboratory ageing procedure harsher. These modifications mainly considered decreasing asphalt thickness, changing the temperature, and increasing the conditioning time.

One such sample is the modification done by Edler et al. (1985) named Modified Thin Film Oven Test (MTFOT). In this modified version of TFOT, asphalt film thickness reduced to 100μm and exposure time was raised to 24 hours [57]. Despite more accurate simulating of short-term ageing by applying these modifications, MTFOT didn't gain popularity and abandoned mainly due to tiny sample sizes and the difficulties to condition adequate material for comprehensive testing.

Jemison et al. (1991) suggested extending the exposure time from 5 hours to 14.5 hours using the existing TFOT equipment and sample size in a method named "Extended Thin Film Oven Test (ETFOT)" [58]. Further investigation on the conditioned samples using this technique, showed minor changes comparing to TFOT aged samples and thus didn't gain so much attention. The skin formation in the absence of proper agitation method found to be the reason behind ineffective extension time used in ETFOT approach.

- *Shell Microfilm Test*

Griffin et al. (1955) developed an accelerated ageing process named "Shell Microfilm Test" using the same approach as Edler et al. (1985) employed in developing MTFOT by using an extremely thin film thickness of asphalt cement of 5μm to increase the efficiency of the age conditioning as well as to represent the actual asphalt film thickness covering the aggregates in the in a dense-graded mix [59]. As the aim of this technique was to simulate both short- and long-term asphalt ageing conditioning temperature and exposure time were reduced to 107°C and 2 hours. This approach tried to select the laboratory conditions to be as close as possible to the field conditions in terms of asphalt film thickness, temperature, and exposure time to accurately simulate real-life ageing.

To compare the age hardening of the laboratory aged samples with those from the field, an ageing index was defined using the viscosity data before and after different age conditioning processes (Equation 2-17).

Equation 2-17

$$Ageing\ Index\ (AI) = \frac{\eta_a}{\eta_0}$$

Where η_a is the viscosity of asphalt cement after ageing, and η_0 is the viscosity of the original sample. The selection of temperature for viscosity can vary depending on the specific requirements.

In a study on asphalt cement ageing on Zaca-Wigmore test road using Microfilm laboratory ageing procedure found a strong correlation of laboratory aged samples using this technique with field data [60]. Just like MTFOT method used by Edler, using the very thin asphalt film thickness resulted in tiny sample size and unsuitable for large scale testing.

- *Rolling Thin-Film Oven Test (RTFOT)*

In 1963, the Rolling Thin Film Oven Test (RTFOT) was developed in California to improve existing laboratory short-term ageing procedures. The RTFOT is using rotating glass containers horizontally placed in a rotating rack to provide agitation during the ageing process to assure homogeneous ageing. Film thickness was also reduced from 3.2mm in TFOT to 1.25mm. A hot air injecting nozzle was embedded blowing hot oxygen-rich air into the bottles to increase the oxygen access.

Moreover, conditioning time in this RTFOT is much less than other similar procedures (75 mins), which is a practical advantage. The RTFOT ageing technique can provide adequate age conditioned material in one run required testing. Due to practical advantages such as homogeneously aged samples, comparatively short conditioning time, and adequate sample size, this method gained global attention, and many standardization agencies such as ASTM and AASHTO adopted this method for the short-term ageing of asphalt cement.

The performance grading procedure used by the Superpave® system uses the RTFOT method for short-term age conditioning of the samples for further testing and rheological analysis [61]. There are also some variations of this approach, which are using slightly different film thicknesses [56].

Huang et al. (1996) performed RTFOT and TFOT ageing procedures on various modified and unmodified asphalt samples. They applied slight changes in the conditioning temperature using both techniques and found that conditioning of samples using the RTFOT method at 185°C would represent one year of field ageing. They also compared RTFOT and TFOT methods for the kinetics of chemical reactions during age conditioning of samples using chemical analysis tools such as FTIR and discovered meaningful difference among them in terms of functional groups formation [62].

- *Extended Rolling Thin-Film Oven Tests (ERTFOTs)*

Several researchers used RTFOT ageing procedure with some minor modifications to provide samples with higher degrees of age hardening. As can be seen in Table 2-6, three extended RTFOT (ERTFOT) was developed. These methods were mainly focused on the conditioning time and changed it from 75 minutes to 3.5 (Jemison et al., 1991), 5 (Kemp et al., 1981), and 8 hours (Edler et al. 1985) respectively [57], [58], [63]. The purpose behind using these extended times was to combine short- and long-term age conditioning in a single test, the success of which faced serious criticisms due to the use of excessively high conditioning temperature.

- *Nitrogen Rolling Thin Film Oven Test (NRTFOT)*

One exciting modification to RTFOT was introduced by Parmeggiani (2000), which was developed to measure the effect of volatilization and polymerization hardening on the short-term ageing procedure.

This modified version of RTFOT, which is named “Nitrogen Rolling Thin Film Oven Test (NRTFOT),” uses pure nitrogen instead of air to prevent oxidation reactions. By preventing any oxidation reaction from happening, volatilization and any other internal chemical changes will be responsible for any changes in the properties of asphalt cement [64]. A part of the hardening occurred during this process can attribute to polymerization of hydrocarbons, but more accurate chemical analysis tools and testing is required to measure the importance of changes due to polymerization and to compare it with other short-term ageing mechanisms such as volatilization and high-temperature oxidation.

- *Rolling Micro-Film Oven Test (RMFOT)*

Schmidt and Santucci (1969) developed a method named “Rolling Microfilm Oven Test (RMFOT)” to simulate long-term age hardening procedure instead of short-term ageing in original Shell microfilm oven test. They got the agitation technique used in RTFOT, and the super thin asphalt thickness from the Shell microfilm method and mixed them together. In order to provide homogeneous microfilm, Schmidt and Santucci used benzene solvent to dilute asphalt and reduce its viscosity to provide a 20µm thick film in the same glass containers as RTFOT. This solvent will evaporate before the conditioning procedure starts. The prepared samples will then be conditioned at 99°C for 24 hours. The reduced conditioning temperature and elongated duration were to make it suitable for long-term age conditioning.

Some other variations of this method were also developed. In one such modification, Schmidt (1973) used alternative time and temperature combination using the same sample preparation technique. The temperature was lowered to 60°C, while the conditioning time increased to 48 hours. The aim of this modification was to make conditioning parameters even more realistic concerning the field conditions and make sure the conditioned sample is close in chemistry to the field aged asphalt. Asphalt samples aged by this modified version of RMFOT found to have closer mechanical properties with field aged samples from Zaca-Wigmore test project [65], [66].

- *German Rotating Flask Test (GRF)*

Another method that uses the agitation concept to mix the asphalt cement during laboratory ageing, developed by Deutsche Norm (DIN) and is named “the German Rotating Flask (GRF).” In this method, a specific amount (100 g) of asphalt cement poured into a rotary evaporator flask rotating at 20 rpm and heated for 2.5 hours at 165°C, while subjected to air flow at 500 ml/min [67]. This method aimed to prepare uniformly aged asphalt samples representing short-term field ageing. Results of ageing asphalt cement by this method showed that the loss of volatile material by this method is considerably lower than what happens in standard RTFOT procedure, while in contrast, properties of the resulting sample (ring and ball softening point and needle penetration) didn’t change significantly compared to those subjected to RTFOT procedure [68]. Some variations of this method exist most of them trying to refine age conditioning procedure by mainly changing the flask size.

- *Modified German Rotating Flask Test (MGRF)*

RTFOT method, which used in the Superpave asphalt cement classification system. However, some difficulties reported on using this RTFOT procedure for conditioning of the polymer modified asphalt cements (PMA). Non-uniform ageing and the possibility of crawling out of the bottle during the procedure were the main problems associated with specific polymer modified samples. The "Modified German Rotating Flask" method was developed in 2004 at the Western Research Institute (WRI) to address the abovementioned difficulties and find a proper replacement for RTFOT for short-term age conditioning. For this purpose, a 2-L Morton flask with four indentations was replaced the standard 500-mL in the original "German Rotating Flask" to promote faster evaporation of the volatiles. Conditioning time was also increased to 210 min (from 150 min in the original GRF technique), and the airflow rate was adjusted to 2,000mL/min to increase the severity of age conditioning [68].

By applying the abovementioned modifications, the crawling problem in RTFOT was solved. Moreover, using this new technique resulted in more uniform ageing. Evaluation of the samples aged by MGRF and RTFOT showed slightly higher degrees of age hardening using the MGRF method compared to the RTFOT technique [68].

- *Tilt-Oven Durability Test (TODT)*

An alternative version of RTFOT was developed in California by Kemp and Prodoehl (1981) using the same setup as of RTFOT to prepare age conditioned asphalt cement samples corresponding to long-term field ageing. As in this procedure, the oven tilted slightly (1.06° higher in the front) to prevent migration of the asphalt, Kemp and Prodoehl named their technique as "Tilt-Oven Durability Test (TODT)." In order to simulate long-term age hardening in asphalt samples, conditioning temperature was reduced to 113°C while conditioning time was increased t 168 hours. It was found that ageing asphalt cement using TODT will represent approximately two years of field ageing at hot desert climate [69]. This method is capable of simulating both short- and long-term ageing at one step.

- *Thin Film Accelerated Ageing Test (TFAAT)*

Petersen (1989) developed a laboratory age conditioning procedure to simulate long-term ageing on asphalt cement samples, named "Thin Film Accelerated Ageing Test (TFAAT)." This method was based on the same concept as described for "Rolling Microfilm Oven test (RMFOT)."

Comparing to RMFOT, the TFAAT method is capable of conditioning a larger sample size (4g compared to 0.5g in RMFOT), enabling more investigation and testing. Higher conditioning temperature (130°C instead of 99°C) was used to compensate for the increase in film thickness. Correlations with field data showed that samples aged using TFAAT procedure are representing 11 to 13 years old field aged asphalt cement [69].

- *Modified Rolling Thin Film Oven Test (RTFOTM)*

The modified RTFOT test or RTFOTM developed by Bahia et al. (1998) to overcome some practical issues associated with the standard RTFOT method. The overall procedure of this method is the same as in RTFOT except that a set of steel rods were placed in the glass container to prevent overflow of polymer modified asphalt. The steel rods also help the formation of more homogenized asphalt film thickness to ensure homogenized ageing throughout the sample. Like the RTFOT procedure, RTFOTM was aimed to simulate short-term asphalt ageing [70].

- *Iowa Durability Test (IDT)*

Lee et al. (1973) were developed an accelerated laboratory age conditioning procedure to simulate long-term ageing named “Iowa Durability Test (IDT).” For this purpose, they put the RTFOT short-term aged samples into a pressure vessel under 2.07 MPa pressure of pure oxygen at 65°C for 1000 hours. Studies showed that asphalt aged with IDT method have the same degree of ageing as five years in the field conditions. Chemical investigation on the functional groups formed during age conditioning showed similarity in chemical changes with field aged samples. Based on the hyperbolic relationship between ageing process and time, as found in the field, it was assumed that 48 hours ageing with IDT would provide aged samples representing 60 months of field condition ageing [71].

- *Pressure Oxidation Bomb (POB)*

Edler et al. (1985) developed a procedure to simulate long-term ageing named “Pressure Oxidation Bomb (POB)” using the same pressurized ageing concept as was used in “Iowa Durability Test (IDT).” They used IDT setup and reduced the asphalt film thickness to 30μm in order to be able to reduce conditioning time to 96 hours. Studies showed coupling POB with Extended RTFOT (ERTFOT with 8 hours conditioning) procedure the conditioned samples will represent five years of field ageing [57]. The main disadvantage of this method is due to the use of very thin film thickness, which results in low sample size and low application for comprehensive testing schemes.

- *Rotating Cylinder Ageing Test (RCAT)*

Belgium Road Research Center (BRRC) developed an ageing procedure called "Rotating Cylinder Ageing Test (RCAT)" to simulate long-term ageing of asphalt cement. This method aimed to prepare laboratory aged samples, which not only have the same mechanical properties as those aged in real field conditions but also representing the chemistry of changes as they happen in field ageing.

In this laboratory ageing scheme, 500 grams of asphalt is poured into a rotating cylinder rotating at 1 rpm and subjected to oxygen flow (75ml/min). This way, a film thickness of 2mm will form inside the bottle [72]. It was found that ageing by this technique at 85°C for 144 hours will result in the same chemical changes as in the field. In their study, asphaltene formation was selected as a measure of chemical changes of asphalt cement. Studies on the age conditioning using RCAT showed that the temperature must be kept under 100°C in any conditioning system to be able to simulate the chemical changes during long-term ageing [55].

- *Pressure Ageing Vessel (PAV)*

"Pressure Ageing Vessel (PAV)" was developed by Christensen and Anderson (1992) and proposed by the Strategic Highway Research Project (SHRP) to simulate long-term ageing (7 to 10-year period) on asphalt cement samples. This procedure was selected by the Strategic Highway Research Program (SHRP) to prepare samples for asphalt cement performance grading and got considerable attention and adopted by ASTM and AASHTO.

In this method, RTFOT aged asphalt is poured into flat pans and placed in a vessel for further ageing under 2.10 MPa (20.7 atmospheres or 305 psi) air pressure for 20 hours. The conditioning temperature could be 90, 100, or 110°C. The original PAV procedure was conducted at a lower temperature (60°C) for a longer period (6 days). Results showed insufficient age hardening. From the other side, as this procedure was supposed to be widely used in the industry, the test period deemed too long. To increase the rate of ageing and to reduce required time in a way that the total process can be done in one day, the associated temperature was raised to 100°C and conditioning time was limited to 20 hours.

During the field validation, these conditions found to be overly harsh for cold climates and too mild for hot climates. Thus, three different temperatures were selected to be used for cold, normal and hot climates. Asphalt samples with higher performance grade assumed to be subjected to warmer climatic conditions and suffer more severe ageing. Thus, PAV will be set out at a higher temperature to simulate those conditions [73].

Temperature ranges used in the standard PAV procedure are unrealistically high and were chosen to limit the test duration in a reasonable range so be applicable for industrial purposes. Studies showed that applying excessively high conditioning temperatures will cause kinetic of chemical changes to deviate from what happens in real conditions.

- *High-Pressure Ageing Test (HiPAT)*

Hayton et al. (1999) developed a pressurized age conditioning procedure, named "High-Pressure Ageing Test (HiPAT)" using the same pressurized ageing concept as was used in PAV [74]. The aim was to prepare samples that better represent the chemical changes that happen during real long-term ageing.

HiPAT uses the same equipment as PAV with different conditioning parameters. The main advantage of HiPAT over PAV is to use more realistic conditioning temperature of 85°C. Conditioning time was increased to 65 hours to compensate temperature decrease.

Chemical analysis on the field aged samples and samples aged by HiPAT method showed that asphalt samples are following the same synthetic path (base on the formation and concentration of carbonyl and sulfoxide functional groups) as they do in field ageing [56]. Despite this remarkable achievement, this method did not gain interest in the industry, especially for quality control purposes mainly due to long conditioning time.

- *Universal Simple Ageing Test (USAT)*

Farrar et al. (2014) from the Western Research Institute (WRI) developed a method to simulate short- and long-term ageing called "Universal Simple Ageing Test (USAT)." USAT was designed to replace RTFOT and PAV procedures to prepare representative samples for the performance grading system. The equipment setup is the same for short- and long-term ageing while conditioning parameters vary among them.

Current standardized age conditioning procedures are just considering short-term ageing for "hot mixing." However short-term ageing happens at a slower pace for mixes with lower construction (mixing and compaction) temperatures such as "Warm Mix Asphalt (WMA)" and needs to be addressed. With the increase in the application of various WMA techniques, the need for an ageing procedure capable of simulating age hardening under lower construction temperatures was raised. USAT was designed and calibrated to use proper short-term conditioning temperature for HMA and WMA (150 and 130°C respectively). The USAT is one of the only methods that account for lower mixing and compaction temperature for warm mixes [75].

- *Microwave Ageing Method*

Bishara et al. (2000) developed a pressurized age conditioning procedure using the microwave as the source of energy. In this technique the asphalt cement was placed in a pressurized (3.08 MPa) microwave oven (1000W output power) at 147ºC for 4.5 hours. Physical and chemical properties of conditioned samples by this technique was found to be comparable with those conditioned through both RTFOT and PAV. As this approach requires only 4.5 hours to condition the samples, it looks attractive for industrial purposes. For this reason, further correlation with asphalt source and type seems necessary [76].

2.6.2 Photo-Oxidation Treatment on Asphalt Cement

Sunlight, as reaches to the earth's surface, consists of electromagnetic waves within the 200 and 3000nm wavelength band. Around seven percent of the sunlight that reaches the earth's atmosphere can be categorized as ultraviolet light (UV) as their wavelength falls between the 10 to the 400nm band (not all reaches earth's surface). UV radiation is subdivided into the VUV band (Vacuum Ultraviolet which typically is not part of sunlight radiation with wavelengths ranging from 10 to 200nm), UVC band (with wavelengths ranging from 240 to 280nm), UVB band (with wavelengths between 280 and 315 nm), and UVA band (with wavelengths between 315 and 400nm) [77].

The degradation effect of high energy-containing electromagnetic rays, such as UV on different hydrocarbon chains (including living organisms and polymers) have been known for a long time now. In the pavement and roofing industry, many researchers noticed the effect of UV as an ageing accelerator in asphaltic materials. UV absorption causes hydrocarbon chains degradation and loss of strength at sensitive points in the chain structure. This can be followed by oxygen uptake leading to cross-linkage between large molecules [78].

Vallerga et al. (1957) applied UV treatment on TFOT aged samples and found it effective in changing physical properties of aged asphalt cement [67]. Traxler (1963) applied both UV and actinic lights[9] on the ageing procedure using asphalt samples with different film thickness and found that on ultrathin films of asphalt cement (around 3μm), photo-oxidation plays an important role, while its effect fades by increasing the film thickness [39]. Following are summarizes the phot-treatment techniques for asphalt cement application found in the literature.

- *Weather-O-Meter (WOM)*

Edler et al. (1985) developed a Weather-O-Meter conditioning chamber to simulate the same climatic condition as exists in real field condition. This Weather-O-Meter consisted of a temperature-controlled chamber equipped with an ultraviolet source (to simulate solar radiation) and a sprinkling device (to simulate rain and humidity).

In this procedure, asphalt cement was placed in a thin layer (100μm) on a plate and subjected to repeated cycles of 102 minutes of UV treatment at 60°C followed by 18 of UV plus water spray at a pressure of 300kPa (total cycle time of two hours). The sampling of the conditioned asphalt is done after 32.5 hours, 73.5 hours, seven days and 14 days [57]. Unfortunately, test results were not sufficiently strong enough to understand the chemistry of changes during this treatment and no comparison with field result was made.

- *Montepara et al. (1996)*

An ultraviolet ageing chamber was developed by Montepara et al. (1996) in which a mercury gas lamp with the ability to reproduce UV radiation between 180 and 315 nm wavelength (UVC and UVB bands) employed to simulate UV radiation and photo-oxidation on asphalt cement samples. In their method, Montepara et al. laid 1.5 mm thick asphalt cement on glass plates and placed them at a set distance from the UV lamp for 450 days. The amount of UV radiation on the samples calculated to be equal to approximately 2000 days at the real condition. They did not apply any other age conditioning parameter such as elevated temperature so they would be able to

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[9] Actinic lighting peaks in the 420-nanometer range and emits a fluorescent blue light. In chemical terms, actinism is the property of radiation that lets it be absorbed by a molecule and cause a photochemical reaction as a result [79].

measure the effect of photo-oxidation at ambient temperature alone. Chemical analysis of the conditioned samples by this method showed a combination of volatilization, oxidation, and polymerization ageing [80].

Comparison of the physical changes occurred during RTFO and PAV conditioning with this UV treatment technique showed that samples that aged by just subjecting to UV radiation get fewer changes than samples aged through either RTFOT and PAV [81].

- *Bocci and Cerni (2000)*

Bocci and Cerni (2000) developed a UV age conditioning procedure by subjecting thin layers of asphalt samples (1mm thick) to UV radiation produced by iron vapour lamp capable of producing UVA, UVB, and UVC emissions. The asphalt samples kept under this UV treatment for 12 to 35 consecutive days. They calculated the required conditioning time based on their location in the UV room to make sure all samples were exposed to a certain amount of UV radiation. Using chemical and rheological analysis tools, they found that asphalt cement evolves through different chemical paths when different conditioning parameters (such as UV radiation, high-pressure oxidation, and temperature) were applied. Therefore, the effect of each conditioning parameter cannot be reproduced by intensifying other parameters [82].

2.6.3 Accelerated Ageing Methods for Asphalt Mixtures

Comparing to numerous methods that are developed to simulate short- and long-term ageing on asphalt cement, few efforts have been made to simulate age hardening on asphalt mix samples. However, a few methods exist for conditioning and preparing representative aged asphalt mixture samples for mixture performance testing purposes. Most of these efforts are using either extended heating, pressurized oxidation, or the gas flow through the compacted asphalt samples or a combination of these techniques (Table 2-7).

The main challenge for developing a proper accelerated asphalt mix ageing procedure is to reproduce both mechanical and chemical changes in real life ageing as accurate as possible in a time-efficient way. Like in the case of asphalt cement, raising temperature can accelerate the oxidative ageing process by increasing the reactivity of hydrocarbons, while it might alter the kinetics of the chemical reactions and misrepresentation of mechanical properties of the field-aged samples.

Table 2-7 Laboratory Methods for Accelerated Asphalt Mixture Ageing

NAME	APPROACH	MIX	TEMPERATURE (°C)	OTHER CONDITIONS
Pauls & Welborn (1952)	extended heating	loose, Ottawa sand	163	
Plancher et al. (1976)	extended heating	compacted	100	
Kemp & Predoehl (1981)	extended heating	compacted	60	up to 1200h
Hugo & Kennedy (1985)	extended heating	compacted	100	80% humidity
Von Quintus et al. (1992)	extended heating	loose	135	3h
Von Quintus et al. (1992)	extended heating	compacted	60 and 107	2d at 60, 5d at 107
Kumar et al. (1976)	Low pressure oxidation	compacted	60	1, 2, 4, 6, & 10 days
Kim et al. (1986)	pressurized ageing	compacted	60	0.7MPa Oxygen
SHRP STOA (1986)	extended heating	loose	135	
SHRP LPO (1986)	Low pressure oxidation	compacted	60 or 85	oxygen flow (1.88 l/min)
SHRP LTOA (1986)	extended heating	compacted	85 or 100	5d or 2d
Khalid (2002)	Low pressure oxidation	compacted (porous mix)	60	air flow (3l/min)
Jemere (2010)	extended heating	compacted (porous mix)	135	7d
Korsgaard et al. (1996)	pressurized ageing	compacted	100	72h, 2.07MPa air
Hachiya et al. (2003)	extended heating	compacted	70	air chamber
Hachiya et al. (2003)	extended heating	compacted	60	oxygen chamber
Airey (2005), SATS	pressurized ageing	compacted		pre-saturation + humidity
Steiner et al. (2016), VAPro	Low-pressure oxidation	compacted	60	1 l/min, Highly Oxidant Gas

As discussed in previous sections, the kinetics of the chemical reactions depends on the conditioning parameters and their intensities. In case of conditioning temperature, the ageing kinetics and rate are heavily affected, especially when the conditioning temperature passes the equiviscous[10] temperature. Some researchers tried to solve this problem by replacing excessively high conditioning temperatures with the use of pure oxygen or other highly-oxidative gasses (such as nitrogen oxide and ozone) to pace up the oxidative ageing process and reduce conditioning time to more accurately simulate the long-term age hardening in asphalt mix systems.

- *Pauls and Welborn*

Pauls and Welborn (1952) exposed Ottawa sand mixtures to extended heating at 163°C for various time durations and compared the compressive strength (cylindrical samples) and the chemical composition of recovered asphalt cement. They used a compressive strength test without lateral support to evaluate the properties of the asphalt mix structure and as a measure of asphalt cement hardness. They found that the amount of ageing happened by their method is equivalent to

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[10] Equiviscous temperature (EVT) is the temperature at which the viscosity of asphalt cement is equal to 50 seconds in a standard efflux viscometer.

the ageing that occurs on asphalt cement using TFOT procedure and is just harsh enough to simulate the construction-related age hardening (short-term ageing) [83].

- *Plancher et al.*

Plancher et al. (1976) tried an extended heating procedure on compacted cylindrical samples (25mm thick, 40mm diameter) to study the effect of the hydrated lime in postponing the age hardening of asphalt mixtures. They used resilient modulus to represent the mechanical properties of the asphalt mix. Results of this study showed less age hardening (in terms of mechanical changes of the asphalt mix) occurred in the lime-treated samples [84]. Plancher et al. have also presented an explanation of the chemistry of lime action in the asphalt mix system and its retardant effect on the age-hardening procedure. They claimed that hydrated lime particles could absorb the highly-polar age-susceptible hydrocarbons and prevent them from interfering in the ongoing oxidation process in the asphalt cement.

- *Kemp and Predoehl*

Kemp and Predoehl (1981) studied the ageing process of asphalt mixtures by conditioning mix samples at 60°C for different periods up to 1200 hours. Chemical analysis was performed on the extracted asphalt cement from laboratory and field age conditioned mixtures. Their study aimed to understand the chemistry of ageing in the field and their age conditioning procedure [63]. They found that laboratory conditioning at temperatures closer to real condition (such as 60°C) can better simulate the chemistry of age-related changes but requires excessively long conditioning times to obtain desirable results.

- *Hugo and Kennedy*

In a study done on the mixture ageing in South Africa, Hugo and Kennedy (1985) used an ageing procedure to simulate ageing on gap-graded and semi gap-graded mixes. Compacted asphalt mix slabs were conditioned at 100°C for up to 7 days at dry and moist (80% humidity) conditions. After conditioning, cylindrical samples were cored and subjected to mechanical testing [85].

- *Von Quintus et al.*

Von Quintus et al. (1992), used an accelerated procedure to simulate short- and long-term ageing on loose and compacted samples. They aged loose mixtures by placing them in a forced-draft oven at 135°C for three hours before the compaction to simulate short-term ageing. This process was followed by placing compacted specimens in a forced-draft oven at 60°C for two days, then elevating the temperature to 107°C for an additional five days. They investigated the ability of different mechanical tests in capturing the effect of ageing. They found that tensile strain at the failure to be a better parameter than tensile strength for studying the age-resulted embrittlement and stiffness in asphalt mixtures [86].

- *Kumar et al.*

Kumar et al. (1976) studied the effect of mixture properties (film thickness, air void content, and permeability) on ageing susceptibility of asphalt mixtures. Their ageing procedure involved airflow (at the constant head of 0.5 mm of water) through the asphalt mix at 60°C for 1, 2, 4, 6, and ten days. Simple creep test was used to measure the changes in the mixture's mechanical properties. Asphalt mixes with various gradation and air void content were tested through this study. Results showed that for open-graded mixes, the ratio between average film thickness to permeability would be the best age hardening predictor. On the other hand, in the case of dense-graded mixes, permeability found to be a much better indicator for ageing than the air void content of the mix as it is more related to interconnected air voids and oxygen access [87].

- *Kim et al.*

Kim et al. (1986) used pressurized oxidation ageing on laboratory compacted asphalt mix samples using Pressurized Oxidation Bomb (POB) equipment. They applied 0.7Mpa of pure oxygen pressure at 60°C for 1, 2, 3, and five days. Mechanical testing performed on unaged and aged samples including resilient modulus and fatigue tests using repeated load diametral test apparatus. They defined a "Modulus Ratio" to evaluate the level of age hardening in asphalt mixes (Equation 2-18), where higher modulus ratio shows more changes in the mechanical properties of samples. Two affecting factors on the "Modulus Ratio" were found to be the exposure time to the age conditioning, and the sample's level of compaction. Base on the results of this study it was found that the increase in the air void content in a mix due to poor compaction would significantly increase the ageing susceptibility of mixtures and its rate.

The "Modulus Ratio" parameter expected to increase as a result of age conditioning, some specific samples showed values lower than one meaning decrease in the modulus of the sample as a result of age conditioning. They concluded that this loss of modulus during ageing is due to loss of adhesion between asphalt cement and aggregates.

Amazingly, fatigue life measurements, using diametral test, showed that poorly compacted samples tend to have longer fatigue life compared to well compacted, less aged, samples. These results must not be misinterpreted, as controlled tensile stress was used in this study, and more aged mixes tend to experience lower tensile strain. The different trend in fatigue life would be expected if measurements performed under control tensile strain condition [88].

Equation 2-18

$$\boldsymbol{Modulus\ Ratio} = \frac{\boldsymbol{Modulus\ of\ Age\ Conditioned\ Mix}}{\boldsymbol{Modulus\ of\ Unconditioned\ Mix}}$$

- *SHRP methods*

Under the SHRP A-003A test development program, laboratory procedures for simulating the short- and long-term ageing were developed. The short-term ageing method, which named “Short-Term Oven Ageing (STOA),” consists of curing loose mix samples in a forced-draft oven at 135°C for four hours with a constant thickness ranging between 25 to 50mm. Stirring during this period suggested in one-hour intervals to achieve a uniform and homogeneous conditioning [89].

During this program, two different procedures were also developed in parallel to simulate long-term oxidative ageing in compacted mix samples, using two different approaches namely low- A low-pressure oxidation and extended heating. In the low-pressure oxidation approach (LPO) compacted asphalt mix samples were covered with a membrane and placed into a particular cell and subjected to confining pressure. The sample then placed in a water bath set at 60°C or 85°C (depending on the target location) and oxygen flow is conducted through the specimen at a rate of 1.88 L/min for five consecutive days. The extracted specimens allowed to stand for one day before further testing [90]. Another alternative procedure to simulate long-term ageing in SHRP-A-003A program was called “Long-Term Oven Ageing (LTOA)” using extended heating approach. This procedure was conducted on compacted specimens by placing them in a forced oven at 85°C for five days (120h). Another alternative to this method was suggested to reduce the required time by increasing temperature to 100°C and reducing the exposure time to two days [89].

- *AASHTO specification for asphalt mixes conditioning*

AASHTO R 30-02 adopted and recommended the STOA and LTOA (85°C for 120h) methods developed through SHRP A-003A program for short- and long-term age conditioning of the asphalt mix samples. It was also standardized a modified STOA procedure for volumetric mix design purposes by reducing the oven ageing period to two hours instead of 4 hours suggested by Harrigan et al. (1994) [89], [91].

- *Low-Pressure Oxidation for Porous Asphalt Mix*

The Low-Pressure Oxidation method (LPO) developed through SHRP A-003A, was modified by Khalid (2002) to be applicable for porous asphalt mixes. In this method air, supplied by an external compressor, passes through a series of heat exchange coils to reach a temperature of 60°C. The warm air then is pushed through Marshall compacted samples by a constant rate of 3 l/min. Indirect tensile stiffness modulus, measured by the “Nottingham Asphalt Tester,” is used to define a stiffness ageing ratio (SAR) to compare the level of ageing by different methods (Equation 2-19) [92].

Equation 2-19

$$\boldsymbol{SAR = \frac{ITSM_{Aged}}{ITSM_{Unconditioned}}}$$

Where *SAR* is the “Stiffness Ageing Ratio,” and *ITSM* is the indirect tensile stiffness modulus.

The exposure time to reach equal field ageing by this method found to be case-specific and can vary from four days in case of unmodified asphalt to up to 21 days for mixes with EVA modified asphalt cement. They claimed to be able to reproduce the effect of steric hardening through this technique as a result of using lower conditioning temperature from what is used in extended heating procedures [92].

- *Application of LTOA for porous asphalt mixtures*

Researchers in Nederland developed a laboratory age conditioning procedure to evaluate age susceptibility of porous asphalt mixes. They used AASHTO R30 STOA procedure for short-term age conditioning (4h at 135°C for loose mix), as there is not so much difference between dense-graded mixes and porous asphalt mixes during the short-term ageing. For long-term ageing, they used a modified version of LTOA in which they used loose asphalt instead of compacted samples and increased age conditioning time and temperature (7 days at 135°C). Based on the mechanical properties of the compacted asphalt samples after conditioning, they believed that such conditioning procedure could provide samples corresponding to 10 years of field ageing [93].

- *Application of PAV for asphalt mixtures*

Korsgaard et al. (1996) used PAV setup for long-term age conditioning of gyratory compacted dense-graded asphalt mixes. Asphalt cement then extracted from conditioned samples and evaluated from both chemical and rheological points of view. The results of this study showed that 72 hours age conditioning of compacted asphalt mix samples with PAV at 100°C and under 2.07MPa air pressure would represent similar ageing as for PAV standard ageing procedure for asphalt cement. They later calibrated this method to be used for porous asphalt mixes by decreasing the conditioning time to 60h [81].

- *Application of oxygen chamber*

Hachiya et al. (2003) compared extended heating procedure, and pure oxygen age conditioning at lower temperatures approaches for long-term age conditioning with results from five-year field aged samples. For the extended heating procedure, compacted asphalt samples kept in a forced-draft oven at 70°C for an elongated time duration, while for the pure oxygen ageing, a modified version of conventional heat ageing procedure was used by keeping compacted asphalt mix samples in an oven filled with pure oxygen at 60°C.

Mechanical properties of aged mixes determined using flexural tests. Physical and rheological properties of extracted asphalt cement examined by measuring viscosity, needle penetration test, ring and ball softening point, and Fraass breaking point (for resistance to low-temperature cracking). Chemistry of changes during ageing was analyzed through the separation of the unaged and aged samples into SARA fractions (Corbett method) as well as through infrared spectroscopy analysis. Results of this study showed that the ageing mechanisms associated with these two approaches are entirely different. Oxygen oven ageing at a lower temperature was found to be better simulating the chemistry of changes in field aged samples. It was concluded that extended heating procedure for long-term age conditioning could be used to simulate the hardening occurred in real conditions in terms of measured parameters (such as stiffness, penetration, and softening point) but it is unable to reproduce the ageing chemistry [94].

- *Saturation Ageing Tensile Stiffness for high modulus base mix*

In 2005 a method developed in University of Nottingham called Saturation Ageing Tensile Stiffness (SATS) to evaluate the ageing/moisture sensitivity of high modulus base asphalt mixtures. The conditioning procedure used in this research was consists of a pre-saturation step, after which compacted samples kept at high temperatures and under wet conditions with an environmental pressure for an extended time.

The “stiffness modulus ratio” which was defined as the ratio of the retained stiffness modulus over initial stiffness modulus, and “retained saturation” were used to assess the sensitivity of compacted mixture to combined effects of ageing and moisture. The level of ageing achieved using this technique was much lower than other standardized approaches. The lower ageing level in this research was selected purposely, as the aim of the study was to analyze high-modulus base layer mixtures, where much less age-related changes expected to compare to surface pavement layers [95].

- *Viennese Ageing Procedure (VAPro)*

Steiner et al. (2016) developed a version of “low-pressure oxidation (LPO)” method, called “Viennese Ageing Procedure (VAPro)” to simulate long-term age hardening on asphalt mix samples. The main purpose of their study was to use highly oxidant gases instead of air or pure oxygen to speed up the ageing procedure at lower conditioning temperatures. The “Highly Oxidant Gas” used in this method was a combination of air, ozone, and nitrogen oxides, which have highly oxidative properties. VAPro uses a triaxial cell to force the oxidant gases to pass through the sample with a flow rate of 1 l/min at 60°C for four days. Laboratory tests showed that under these conditions, asphalt cement in the mix would reach to the same level of ageing as RTFOT and PAV together without the need to even running STOA procedure. The advantage of this method is the use of high oxidant gas that allows ageing asphalt samples at lower temperatures within a more reasonable time [96]–[98]. This low-temperature ageing procedure resulted in better resembling of the chemical changes during age conditioning.

2.6.4 Photo-oxidation treatment on asphalt cement mixture

Hveem et al. (1963) described an infrared weathering test on Ottawa sand mixtures. In their work, they applied infrared radiation on the semi-compacted mixes for different durations at 60°C. To keep the asphalt film thickness in the range of 5 to 7μm, two percent of asphalt cement content was selected to prepare samples [61]. Unfortunately, data collected in this work was not coherent enough to support or reject the role of exposure to infrared radiation as an age hardening accelerator.

Hugo and Kennedy (1985) used a Weather-O-Meter® to evaluate the effect of ultraviolet light on asphalt mixtures ageing at ambient temperatures (40 days of exposure to UV). They found the effect of this UV treatment minor, affecting only the very surface of the asphalt mixture [85].

Tia et al. (1988) used a combination of several age conditioning procedures, consisting of the forced-draft oven at 60°C, exposure to ultraviolet light, and moisture treatment for various time durations. They found conditioning by this method improved the possibility of reproducing field ageing. Moreover, they found that the effect of ultraviolet in photo-oxidation to be more important than what previous studies suggested [99].

2.7 Summary of the Literature Review

The complex viscoelastic behaviour of asphalt cement and asphalt mix is a consequence of the intricate chemical composition which varies over time in a phenomenon know as ageing. As any other construction material, understanding the mechanical properties of asphalt mix and cement and their time-associated changes are of vital importance. Various mechanisms have been known to be participating in the time-associated changes in the chemical and mechanical properties of asphalt, among which oxidation and volatilization known to be the most important ones.

Various laboratory tools do exist to evaluate the complex chemistry of asphalt cement and to follow age related changes. Among all these laboratory techniques spectroscopy and chromatography techniques, such as Fourier Transform Infrared Spectroscopy (FTIR), and High-Performance Gel Permeation Chromatography (HP-GPC) technique are among the most promising tools.

To investigate the rheology of asphalt cement and asphalt mix and the effect of age conditioning, various techniques do exist including frequency sweep testing (within the linear viscoelastic region) which allows the development of complex modulus master curve (both for its magnitude and phase angle) using available rheological models and the time-temperature superposition principle.

Various techniques and accelerated laboratory age conditioning procedures exists to simulate short- and long-term ageing in asphalt cement and asphalt mixes. Most of these techniques are using unrealistic conditioning parameters, such as excessively high conditioning temperatures and sometimes high confining pressure to reduce conditioning time for asphalt cement and mixes. Among all the laboratory procedures Thin Film Oven Test (TFOT), Rolling Thin Film Oven Test (RTFOT), and Pressurized Ageing Vessel (PAV) gained more popularity for asphalt cement conditioning, while Short-Term Oven Ageing (STOA) and Long-Term Oven Ageing (LTOA), both suggested as per AASHTO R30 meet more attention for conditioning asphalt mixes, specifically in North America.

Due to the complexity of age hardening phenomena (both in terms of chemical reactions and rheological changes) and dependency of such changes to many existing conditions (mix properties, environmental conditions, aggregates petrology, and so on) simplification in laboratory conditioning can result in unrealistic prediction of the changes in the material properties. Therefore, using more realistic conditioning parameters can be helpful in more realistic material characterization.

CHAPTER 3: METHODOLOGY

3.1 Introduction

Despite all the efforts and advancements on understanding the time-associated changes in the chemistry and rheological properties of asphalt cement, ageing is still a mystery. This is because of the complexities in asphalt cement chemical composition and mechanical behaviour described thoroughly in previous chapters. Finding each and every part of this puzzle helps to get a better understanding of the whole picture.

The main objective of this research was to develop a laboratory conditioning procedure to simulate long-term ageing on asphalt mixes which considers realistic conditioning parameters with the hope to get changes similar to real conditions in the field. Reaching this goal is impossible without a clear understanding of the affecting factors and having proper analytical tools to measure and evaluate changes in asphalt cement and mix properties.

By reviewing the literature, it was found that current state-of-practice methods are lacking an important parameter which is applying combined conditioning on asphalt mixture to make sure that real field conditions are considered for further laboratory investigation and testing. Moreover, the aggregates contribution to ageing in all available accelerated ageing procedures is assumed to be the selective absorbance of asphalt fractions only, while the importance of the catalytic effect of particular minerals in some aggregate sources has never considered properly.

Pyrite and pyrrhotite containing aggregates and the problem associating with their oxidation is a challenge especially for Portland cement industry, known as sulphate attack [100], yet its possible effect on asphalt mixtures is not thoroughly investigated. The influence of the oxidation products of iron sulphide mineral aggregates (Table 2-5) on physicochemical and rheological properties of asphalt cement and long-term performance of asphalt mixtures are not yet clearly understood. Furthermore, the chemical interaction between the oxidation products from the mineral aggregates and asphalt cement may accelerate the overall ageing of the asphalt mixture and consequently, reduce the service life of the pavement.

3.2 Objectives and Methodology

The global objective of this research is to provide an understanding of the effect of aggregate composition, solar radiation, and precipitation on the long-term ageing of asphalt mixes. To reach this goal, two subtasks were defined as follows;

- Investigating the effect of Iron Sulfide containing aggregates on the ageing pace of asphalt cement.
- Developing a laboratory procedure to investigate the coupling effect of solar radiation and precipitation on long-term age conditioning of compacted asphalt mix samples.

To achieve these goals a set of tasks were defined to analyze the chemistry, and rheology of the asphalt cement and mix.

3.2.1 Material Selection

To evaluate the effect of iron sulphide containing aggregates, three projects that used such aggregates were selected to collect material. The reason for choosing them was the fact that these projects showed visual signs of activated iron sulphides including staining, bumping aggregates, and crack initiation, thus a good candidate to evaluate any possible catalytic effect of such minerals (Figure 3-2). A source of iron sulphide free aggregates was also selected as control. Asphalt cement employed in these three projects was PG 58-34p (polymer modified). For the selected projects, field cores were available and collected mostly from the affected areas mainly to investigate the rheology and chemistry of recovered asphalt cement. In Mix A, iron sulphide only exists in the source of fine material, while in Mix C only Coarse aggregates iron sulphide in its composition. Mix B is using Iron Sulphide containing material in both coarse and fine aggregates[11].

To evaluate the effect of solar radiation and precipitation, plant-mix loose asphalt from one of the MTO projects was collected. The aggregate gradation in the collected mix was SP 12.5 (SuperPave® mix with a nominal maximum aggregate size of 12.5 mm), and the asphalt cement was PG 64-28p (polymer modified). Properties of all collected materials are presented in Table 3-1.

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[11] Mixes A, B, and C are representing MTO projects 2008-6018, 2011-5106, and 2012-4003, while the control mix is prepared from iron sulfide free portion of the three sources.

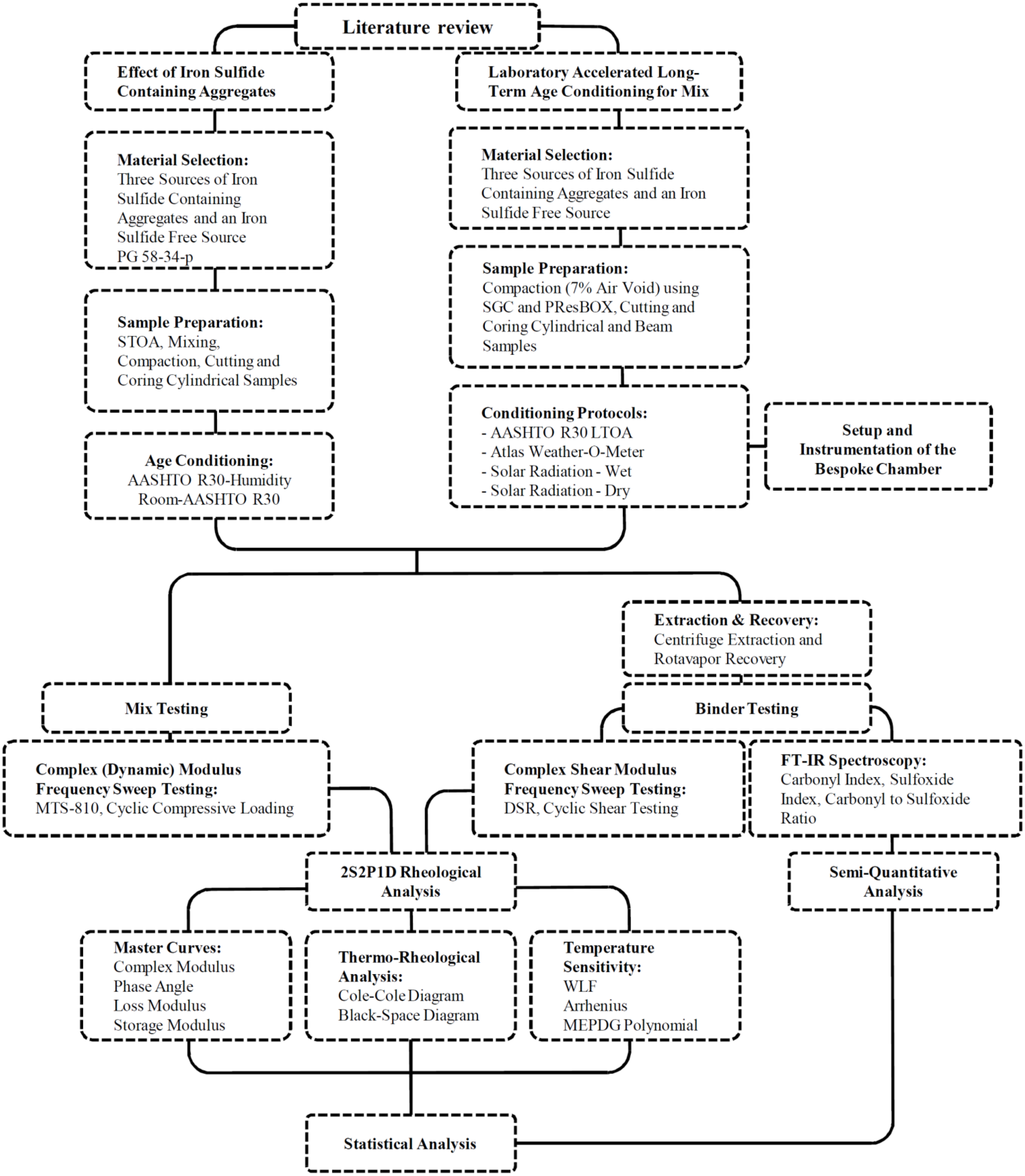


Figure 3-1 Graphical Illustration of Research Methodology

Figure 3-2 Activations of Iron Sulfide-Containing Aggregates in The Road Surface Showed Itself as Staining (Top Left), Bumping (Top Right) And Crack Initiation (Bottom)

Table 3-1 Properties of Collected Materials

	Mix Name	**Gradation**	**AC Content**	**Asphalt Cement Grade**	**Description**
The effect of Iron Sulfide containing aggregates	*Mix A*	*SP 12.5*	*4.5*	*PG 58-34p*	*Fines containing Iron Sulfide*
	Mix B	*SP 12.5*	*4.5*	*PG 58-34p*	*Iron Sulfide exists in both fines and Course*
	Mix C	*SP 12.5*	*4.9*	*PG 58-34p*	*Iron Sulfide exists in coarse material*
	Control Mix	*SP 12.5*	*4.7*	*PG 58-34p*	*No Iron Sulfide*
The effect of solar radiation and precipitation	--	*SP 12.5*	*5.0*	*PG 64-28p*	--

3.2.2 Conditioning Procedures

To evaluate the effect of iron sulphide containing aggregates on the ageing process of asphalt cement in the mix, the four aggregates were mixed with PG 58-34p at manufacturer recommended temperature of 160ºC. After mixing, loose mixtures were cooled down to ambient temperature and then conditioned for four hours at mixing temperature to simulate short-term ageing per AASHTO R30 guidelines [91]. The conditioned samples were then compacted using a Superpave Gyratory Compactor (SGC) to achieve 7.0 ± 0.5 percent air void. From each aggregate source, six compacted samples were prepared and cutting, and coring was performed on them to produce cylindrical samples appropriate for complex (dynamic) modulus measurement (10 cm in diameter and 15 cm in height).

The basic extended heating procedure for long-term age conditioning, described in AASHTO R30 [91], requires compacted samples to be placed in a forced-draft oven at 85ºC for 120 hr (5 days). As the primary purpose of this research was to investigate the effect of iron sulphide oxidation products, and the available AASHTO R30 procedure was unable to oxidize the iron sulphide minerals due to lack of humidity in the process, a new conditioning procedure was developed to include cycles of heat and humidity conditioning. This conditioning procedure comprised of 10 days humidity conditioning at 100 percent relative humidity at ambient temperature in between of two LTOA procedures (120 hr @ 85ºC). Laboratory conditioning procedures used to evaluate the effect of iron sulphide containing aggregates are listed in Table 3-2.

To evaluate the effect of solar radiation and moisture on the long-term laboratory age conditioned compacted mix samples (part two of this research) four different conditioning procedures were applied on a plant mix sample (Table 3-3). The first procedure was based on the current widely used practice (AASHTO R30), acting as a control procedure, and the other three were carefully designed, based on the guidelines extracted from the literature review to incorporate the effects of solar radiation, humidity and water.

An Atlas™ Weather-O-Meter® (Ci35A), which meant to condition 2D samples such as paints and roofing products were reconfigured to be able to hold compacted asphalt mix samples. This conditioning chamber was equipped with a high-intensity UV radiation lamp, water spraying nozzles, humidity and temperature control system, and a rotating frame to ensure uniform UV and moisture exposure (Figure 3-3).

Table 3-2 Conditioning Procedures for Investigation of the Effect of Iron Sulfide Containing Aggregates on Ageing (Mixes A, B, C, and Control Mix)

Conditioning Procedure	Duration	Temperature	Mix Cond.
Short-term (**STOA**)	4 hr.	135°C	Loose
Long-term (**LTOA**) – Extended Heating	120 hr.	85°C	Compacted
Long-term (**RHR**) – Heat & Humidity	120 hr. – 240 hr.- 120 hr.	85°C - 25°C - 85°C	Compacted

A bespoke temperature controlled solar radiation environmental chamber, capable of running wet and dry cycles on compacted asphalt samples, was fabricated in CPATT facility (Figure 3-4). This chamber was equipped with three full spectrum solar radiation lamps with a combined output power of 1800 Watts. Internally the chamber was lined with a reflective coating for more homogeneous irradiation on the samples. These lamps were also used as the heat source, and two fans were placed to control the temperature, connected to the sensors installed on the surface and inside a dummy sample.

An automated data collection unit was used to collect temperature (dummy sample and air temperatures) as well as incoming solar radiation data every five minutes. The irradiation data collected using two light sensors with different spectral range (360 to 1120 nm, and 250 to 400 nm Apogee SP-110-SS and SP-110-SS sensors). Two conditioning procedures were performed using the bespoke chamber namely dry, and wet conditioning. In dry conditioning, each cycle consisted of 24 hours of irradiation while in the wet process each cycle consisted of 24 hours of solar radiation at 64±3ºC followed by a 15 minutes water treatment. The water treatment was also performed consistently by three-time water spraying on the surface and brushing using a soft painting brush.

Table 3-3 Conditioning Procedures on the Compacted Asphalt Mix Samples to Evaluate the Effect of Solar Radiation and Moisture (Second Part)

Method	Temp. (ºC)	UV (W/m^2)	Solar Radiation (Watts)	Water Spray	Duration
AASHTO R30-LTOA	85	NO	NO	NO	120 hr.
Atlas™ Weather-O-Meter®	64	0.55	NO	5 min/hr.	1000 hr.
Bespoke Chamber (wet)	65	2.22	1800	15 min/day	480 hr.
Bespoke Chamber (dry)	65	2.22	1800	NO	408 hr.

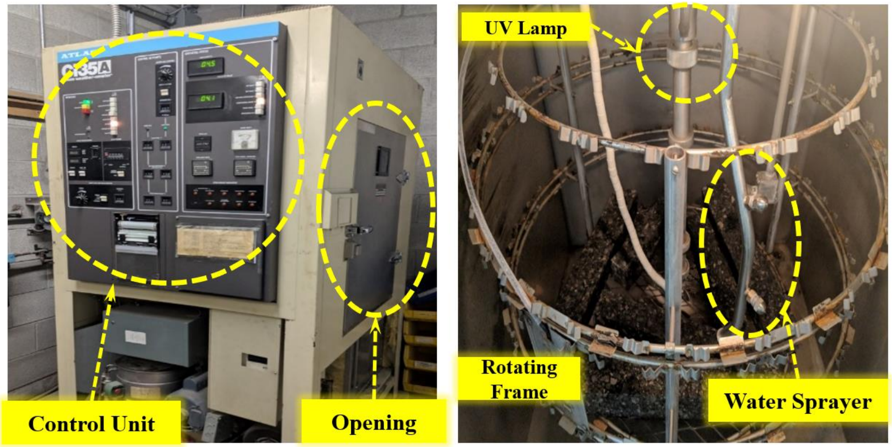


Figure 3-3 Atlas™ Weather-O-Meter® (Ci35A) UV Conditioning Chamber

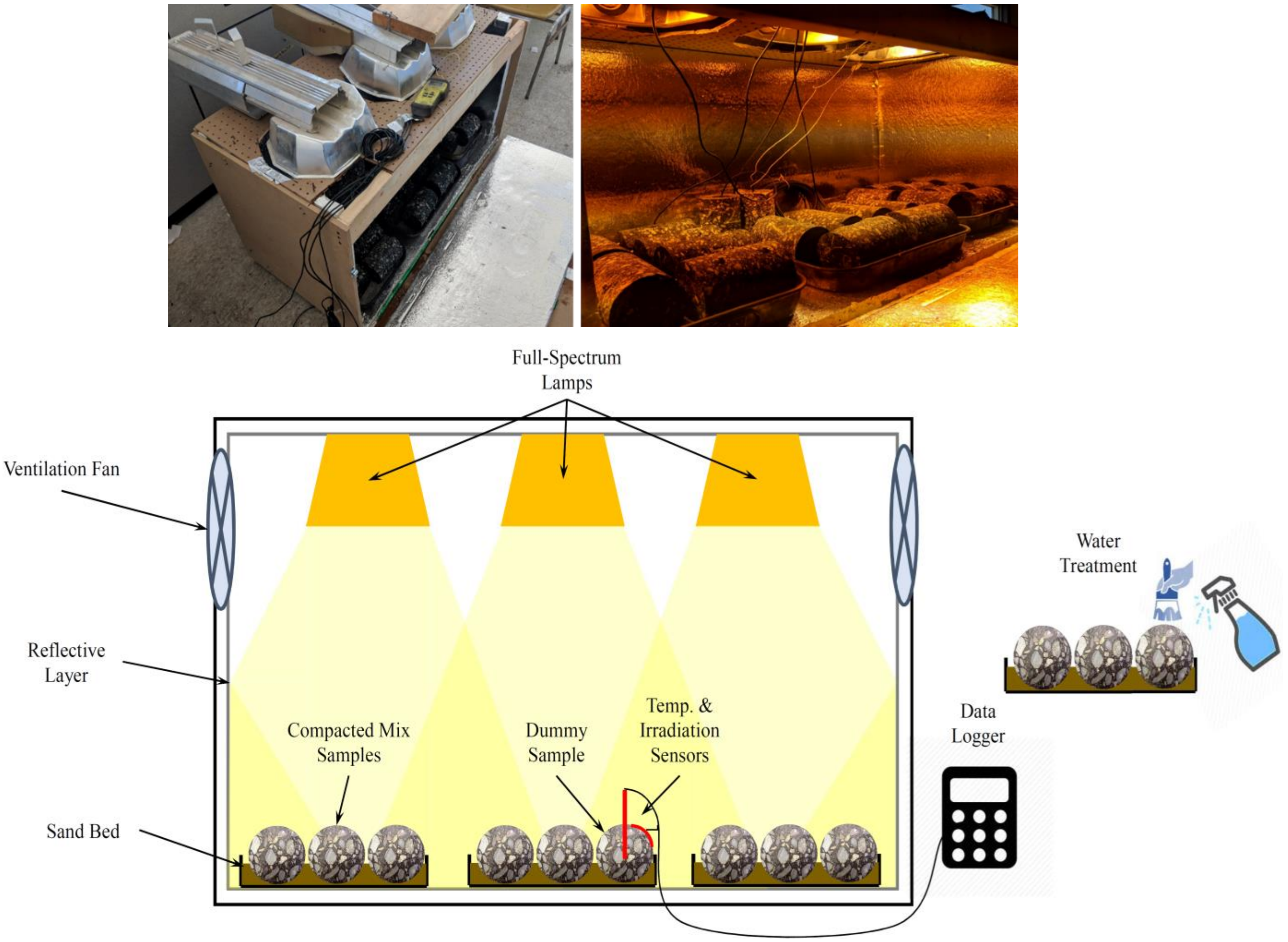


Figure 3-4 Bespoke Solar Radiation Environmental Chamber

3.2.3 Laboratory Testing

At this step, several laboratory tests were performed both for asphalt cement and asphalt mixes based on their relevance. These tests are mentioned in Table 3-4Table 3-5Table 3-6 and Table 3-7, and are briefly discussed in the following subsections.

Table 3-4 Testing Matrix for Investigation of the Effect of Iron Sulphide Containing Aggregates (Mix Side)

Effect of Iron Sulphide Containing Aggregates – Mix Preparation and Tests

Mix Name	**Number of prepared cylindrical samples[1]**	**Complex Modulus[2]**			**Extraction & Recovery[3]**			***Asphalt Cement Testing***
		Un-cond.	LTOA[4]	RHR[5]	Un-cond.	LTOA	RHR	
Mix A – *IS in fine agg.*	9	3	3	3	2	2	2	
Mix B – *IS in both fine and coarse Agg.*	9	3	3	3	2	2	2	
Mix C – *IS in Coarse Agg.*	9	3	3	3	2	2	2	
Control Mix – *No significant amount of IS*	9	3	3	3	2	2	2	

[1]- Each cylindrical sample was cored from the SGC compacted sample to reach to 10cm(diameter)×15 cm (height) using approximately 7.5 kilos of loose mix

[2]- Complex modulus testing was performed under cyclic compressive loading in the frequency sweep mode (six frequencies at five temperatures)

3- extraction and recovery was done using centrifuge extractor by a combination of 90% TCE and 10% ethanol and Rotavapor evaporator

4- Based on AASHTO R30 extended heating procedure for long-term age conditioning of compacted mixes

5- Heat and humidity conditioning, 10 days of humidity conditioning in between of two LTOA procedures

Table 3-5 Testing Matrix for Investigation of the Effect of Iron Sulphide Containing Aggregates (Asphalt Cement)

Effect of Iron Sulphide Containing Aggregates – Tests on Recovered Asphalt Cement

Recovered from		**Rheological Tests**				**Chemical Tests**
		LVE Range[6]	***Frequency Sweep***	***LAS***[7]	***MSCR***[8]	***FT-IR***
PG 58-34		✓	✓	✓	✓	✓
Mix A	*Un-Conditioned*	✓	✓	✓	✓	✓
	LTOA	✓	✓	✓	✓	✓
	RHR	✓	✓	✓	✓	✓
Mix B	*Un-Conditioned*	✓	✓	✓	✓	✓
	LTOA	✓	✓	✓	✓	✓
	RHR	✓	✓	✓	✓	✓
Mix C	*Un-Conditioned*	✓	✓	✓	✓	✓
	LTOA	✓	✓	✓	✓	✓
	RHR	✓	✓	✓	✓	✓
Control Mix	*Un-Conditioned*	✓	✓	✓	✓	✓
	LTOA	✓	✓	✓	✓	✓
	RHR	✓	✓	✓	✓	✓

[6] - *Strain Sweep Test at 10 Rad/Sec*

[7] - *Linear Amplitude Sweep test*

[8] - *Multiple Stress Creep Recovery test*

Table 3-6 Testing Matrix for Solar Radiation and Moisture Conditioning (Mix Side)

Solar and Moisture Conditioning – Mix Tests

	Conditioning Procedure	***Number of complex modulus replicates***		
SP 12.5 (No RAP)	Un-Conditioned	*36*	Extraction & Recovery (Centrifuge and Rotavapor)	***Asphalt Cement Testing***
	AASHTO R30 LTOA	*3*		
	Atlas Weather-O-Meter	*3*		
	Bespoke Chamber Dry 5 Days	*3*		
	Bespoke Chamber Wet 5 Days	*3*		
	Bespoke Chamber Dry 10 Days	*3*		
	Bespoke Chamber Wet 10 Days	*3*		
	Bespoke Chamber Dry 15 Days	*3*		
	Bespoke Chamber Wet 15 Days	*3*		
	Bespoke Chamber Dry20 Days	*3*		
	Bespoke Chamber Wet 20 Days	*3*		

Table 3-7 Testing Matrix for Solar Radiation and Moisture Conditioning (Asphalt Cement)

Solar and Moisture Conditioning – Tests on Recovered Asphalt Cement					
	Rheological Tests				**Chemical Tests**
Recovered from	***LVE Range***	***Frequency Sweep***	***LAS***	***MSCR***	***FT-IR***
PG 64-28	✓	✓	✓	✓	✓
Un-Conditioned	✓	✓	✓	✓	✓
AASHTO R30 LTOA	✓	✓	✓	✓	✓
Atlas Weather-O-Meter	✓	✓	✓	✓	✓
Bespoke Chamber Dry 5 Days	✓	✓	✓	✓	✓
Bespoke Chamber Wet 5 Days	✓	✓	✓	✓	✓
Bespoke Chamber Dry 10 Days	✓	✓	✓	✓	✓
Bespoke Chamber Wet 10 Days	✓	✓	✓	✓	✓
Bespoke Chamber Dry 15 Days	✓	✓	✓	✓	✓
Bespoke Chamber Wet 15 Days	✓	✓	✓	✓	✓
Bespoke Chamber Dry20 Days	✓	✓	✓	✓	✓
Bespoke Chamber Wet 20 Days	✓	✓	✓	✓	✓
RTFOT	✓	✓	✓	✓	✓
RTFOT+PAV	✓	✓	✓	✓	✓
RTFOT+Double PAV	✓	✓	✓	✓	✓

- *Asphalt Mix Complex (Dynamic) Modulus Testing*

Complex (Dynamic) Modulus test performed on cylindrical samples (150 mm in height and 100 mm in diameter) under frequency sweep mode at five different temperatures (six frequency for each temperature), following AASHTO T342-11. These tests were carried out using the Material Testing System (MTS) loading frame and environmental chamber under cyclic compressive mode at CPATT laboratory. Sample response, when subjected to cyclic compressive loading was measured using three extensometers attached at 120^{o} intervals at mid-height of the samples (Figure 3-5). Testing temperatures and loading frequencies are listed in Table 3-8.

Table 3-8 Temperatures and Frequencies Used for Complex (Dynamic) Modulus Test for Mixes

Temperatures (°C)	Frequencies (Hz)
-10	*25*
4	*10*
21	*5*
37	*1*
54	*0.5*
	0.1

Figure 3-5 Complex (Dynamic) Modulus Sample Preparation and Testing Equipment

- *Recovery of Asphalt Cement*

Asphalt cement from field cores and laboratory conditioned and unconditioned samples recovered through centrifuge extraction (ASTM D2172) and Rotavapor recovery procedure (ASTM D5404). A mixture of trichloroethylene (90%) and ethanol (10%) was used as the solvent in the extraction process to minimize the hardening effect of solvent during extraction and recovery process (Figure 3-6).

Figure 3-6 Centrifuge Extraction and Rotavapor Recovery Equipment

Field cores collected from all three examined projects (first part of this research related to the investigation of the effect of iron sulphide on ageing) were cut to extract top and bottom inch to represent field aged sample from top and bottom of layers.

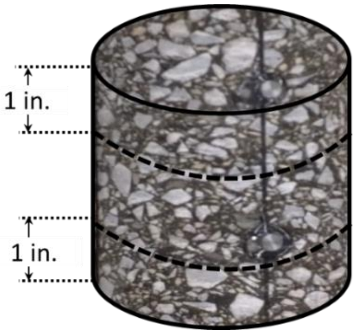


Figure 3-7 Top and Bottom 1 in. of Field Cores were Cut and Subjected to Extraction and Recovery Procedure for Chemical and Rheological Analysis of Asphalt Cement

- *Shear Strain Amplitude Sweep Test*

To run rheological analysis and develop master curves for asphalt cement samples, it is of vital importance to make sure that all measurements were performed within the linear viscoelastic region (LVE), where measured rheological parameters are independent of strain level (Figure 3-8). To determine the LVE limit for asphalt cement samples, shear strain amplitude sweep test was performed on all recovered asphalt cement at different temperatures using Anton Paar™ dynamic shear rheometer (Smart Pave 102). Consequently, the strain level in the frequency sweep test to determine complex modulus was selected within a safe distance from the LVE limit inside the linear behaviour zone (Figure 3-9). To run the shear strain sweep test frequency was selected as 10 Rad/s and the LVE limit was determined as the strain level at which G' or G" experience five percent reduction in the initial values.

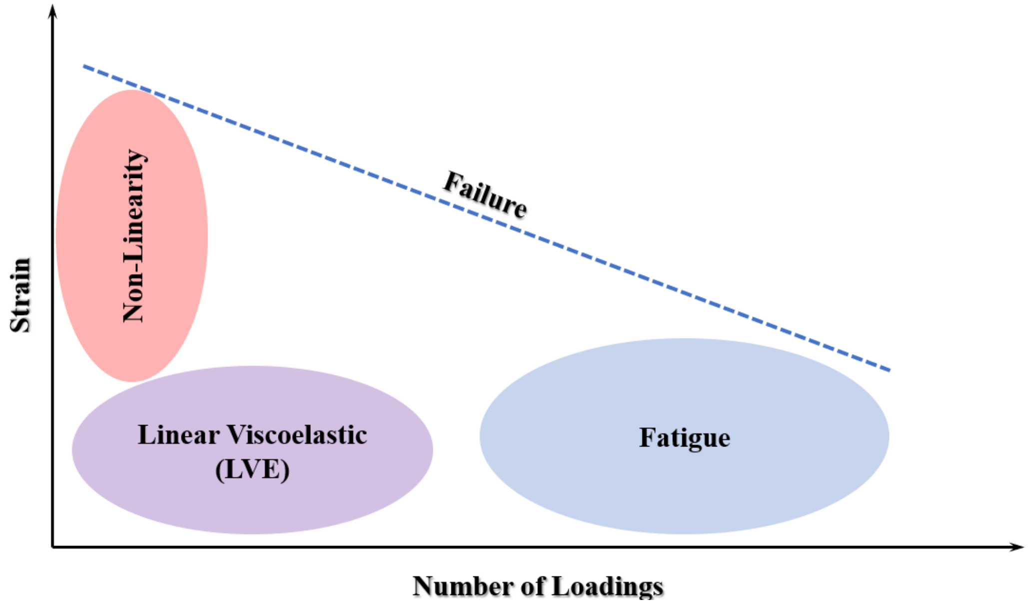


Figure 3-8 Typical Behaviour of Viscoelastic Materials According to the Strain Level, and Number of Loadings (adopted from [101])

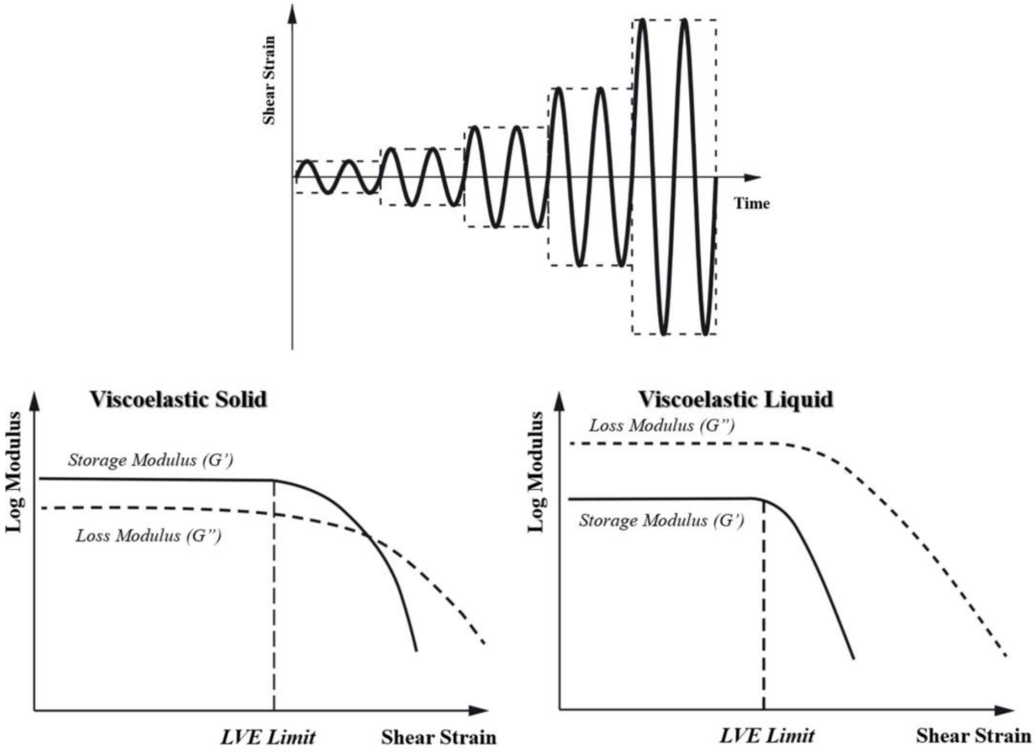


Figure 3-9 Linear Viscoelastic Behaviour Region in Shear Strain Amplitude Sweep Test

- *Complex Shear Modulus Under Frequency Sweep Test*

To develop complex shear modulus and phase angle master curves, frequency sweep test was performed on all recovered asphalt cement samples within the LVE range in a wide range of temperatures (varying from 2 to 70ºC) using 8 and 25 sample geometries in a dynamic shear rheometer (Anton Paar™ DSR smart pave 102). To make sure that all the results are within the linear region (LVE) this test was performed under strain control mode and the strain was kept within a safe distance from LVE limit. Table 3-9 shows the temperatures and frequencies used in these measurements.

Table 3-9 Temperatures and Frequencies for Frequency Sweep Test Using DSR

Temperatures (°C)	Frequencies (Rad/s)
2, 5, 15, 25, 35, 40, 50, 60, 70	*100, 63.1, 39.8, 25.1, 15.8, 10, 6.31, 3.98, 2.51, 1.58, 1, 0.631, 0.398, 0.251, 0.158, 0.1*

Collected data were then used to develop master curves and temperature sensitivity analysis. For this purpose, complex moduli values at different temperature were shifted horizontally to align with data from the reference temperature by applying time-temperature superposition shift-factors (Figure 3-10.

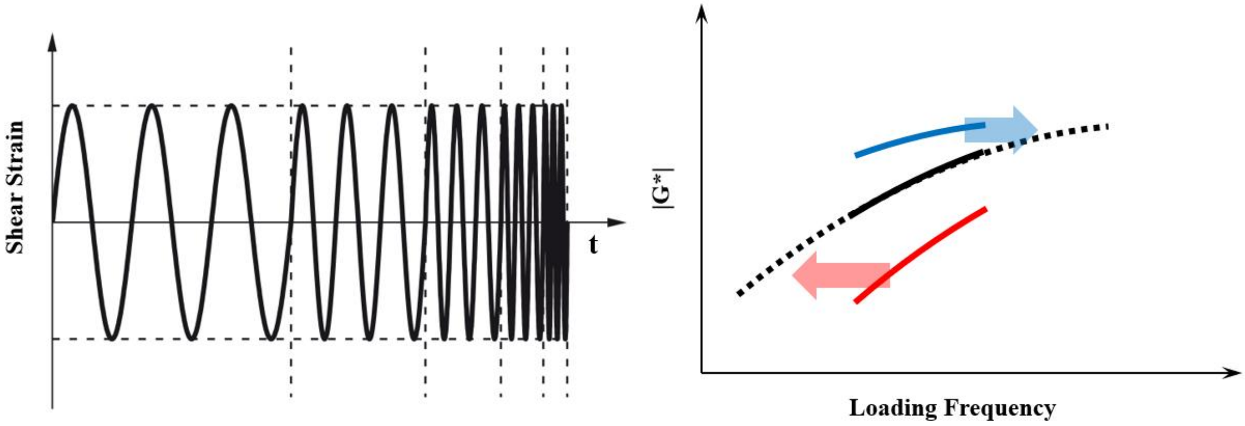


Figure 3-10 Frequency Sweep Test Loading Scheme and Application of Time-Temperature Superposition Shift-Factor in Developing Complex Modulus Master Curve

- *Linear Amplitude Sweep Test (LAS)*

Linear amplitude sweep test (LAS) is a performance testing scheme used to determine the fatigue damage resistance of asphalt cements and is standardized under AASHTO TP101. LAS is a cyclic torsion in which strain amplitude increases systematically, and failure in the material will occur. This test supposed to be run at asphalt cement's intermediate temperature. However, as the primary purpose of this research was to evaluate the effect of age conditioning on the rheological properties of asphalt cement, all recovered asphalt cements (unconditioned, long-term age conditioned, and field cores) were subjected to LAS testing at the intermediate temperature of the original binder. Two damage criteria were defined for this test. AASHTO TP-101-12 suggests calculation of N_f at 35% reduction in initial modulus while an alternative was suggested to consider failure based on peak stress [102].

- *Multiple Stress Creep Recovery Test (MSCR)*

The multiple stress creep-recovery test (MSCR) (AASHTO TP70 & MP19) is a high-temperature asphalt cement specification to evaluate the rutting performance. The MSCR is conducted by DSR (dynamic shear rheometer), by applying 1s long loading followed by a 9s rest period. This test starts with ten low-stress cycles applied (0.1 kPa) followed by ten high-stress cycles (3.2 kPa). The non-recoverable compliance (J_{nr}) is used to estimate the resistance of asphalt cement to permanent deformations (Figure 3-11).

The MSCR test performed on all conditioned and unconditioned samples as well as recovered asphalt cement from field cores at the high-performance temperature of the original binder to make comparison among the effect of different age conditioning procedures on high-temperature behaviour.

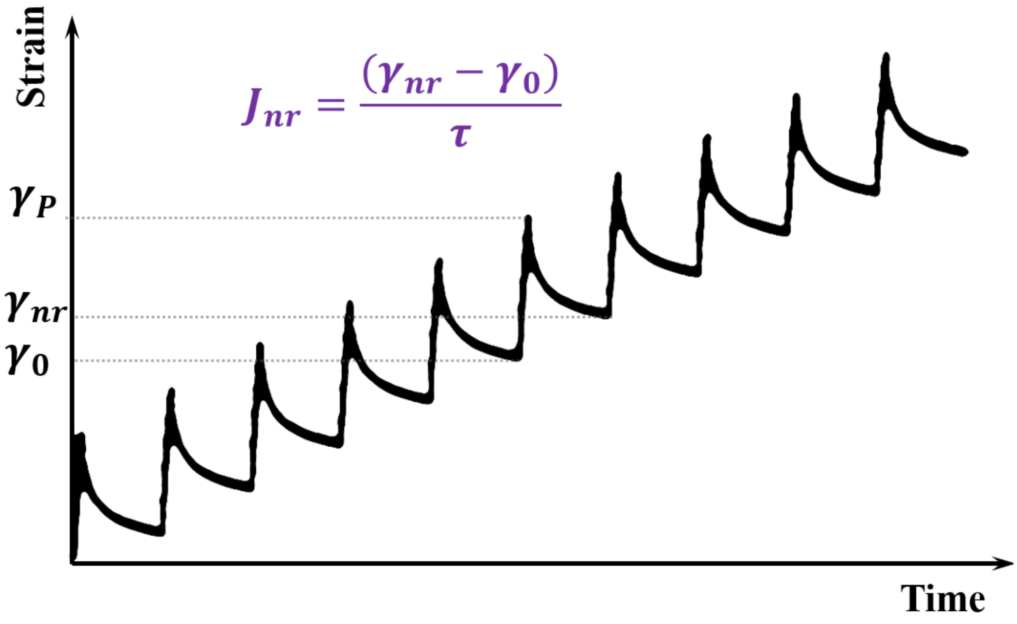


Figure 3-11 The Response of Asphalt Cement to MSCR Loading

- *Fourier-Transform Infrared Spectroscopy (FT-IR)*

Quantitative functional group analysis using FT-IR spectroscopy was also used to determine age-related changes in Carbonyl and Sulfoxide groups. Generation of Carbonyl and Sulfoxide functional groups are known to have a strong correlation with changes in mechanical properties of asphalt cement, given their contribution in increasing the polarity of hydrocarbons [53]. To follow the changes in the amount of these functional groups with ageing, functional group indices can be calculated by dividing the area under changing peaks (the ones that are of interest to follow changes) by the area of specific peak/peaks that are not generated or degenerated in the ageing process. Carbonyl and Sulfoxide indices were calculated based on CH_2 and CH_3 peaks as they are assumed to remain constant during oxidative ageing (Equation 3-1 Equation 3-2) [103], [104]. Sulfoxide functional groups are temperature sensitive and tend to decompose at excessively high temperatures, thus would be biased for laboratory age conditioning procedures that utilize excessively high temperatures [18].

Equation 3-1

$$Carbonyl\ Index\ (CI) = \frac{A_{carbonyl(1680-1750)}}{A_{CH2(1410-1495)} + A_{CH3(1360-1390)}}$$

Equation 3-2

$$Sulfoxide\ Index\ (SI) = \frac{A_{sulfoxide(980-1060)}}{A_{CH2(1410-1495)} + A_{CH3(1360-1390)}}$$

Moreover, it can be said that the ratio of carbonyl over sulfoxide indices can be used as a measure of the chemical path for oxidation (Equation 3-3). It is expected that if an asphalt cement undergoes similar age conditioning, the C/S ratio should not significantly change, although Carbonyl and Sulfoxide indices would both keep on increasing with increasing levels of ageing. This assumption can only be exempted when one of these functional groups gets close to their saturation value; however, this might not be the case for short laboratory conditioning.

Equation 3-3

$$Carbonyl\ to\ Sulfoxide\ Ratio\ ({}^{C}\!/_{A}) = \frac{A_{carbonyl(1680-1750)}}{A_{sulfoxide(980-1060)}}$$

3.2.4 Data Analysis

To analyze test data different tools were used. Regarding frequency sweep test results (for both asphalt cement and asphalt mix) the 2S2P1D analogical model used to develop complex modulus and phase angle master curves as well as loss and storage moduli. Time-temperature superposition (TTS) shift-factors and the model parameters were obtained using a spreadsheet developed during this research for calibrating the 2S2P1D model calibration using the free shifting technique (details of which is presented in detail in chapter five).

Cole-Cole and Black-Space diagrams were developed for complex modulus test data and those from the calibrated model to examine the thermo-rheological behaviour of materials. Moreover, TTS shift-factors (obtained during the model calibration process) were analyzed using WLF, Arrhenius, and polynomial model used in MEPDG and TTS model parameters were attained for all asphalt cement and mix samples. Temperature sensitivity of rheological parameters was investigated through a novel method which explained in chapter four.

To investigate LAS test results, a spreadsheet developed by the "Modified Asphalt Research Center (MARC)" was used. This spreadsheet uses viscoelastic continuum damage (VECD) analysis to calibrate fatigue life model and the number of load repetition to failure (N_f) for two different strain levels (2.5 and 5.0 percent).

To run semi-quantitative functional groups analysis using FT-IR results, a spreadsheet was developed to calculate carbonyl and sulfoxide indices using Equation 3-1 and Equation 3-2 as well as carbonyl to sulfoxide ratio (Equation 3-3) by calculating the area between each peak and the baseline drawn from valley to valley.

CHAPTER 4: TEMPERATURE SENSITIVITY OF RHEOLOGICAL PARAMETERS OF ASPHALT MATERIALS

This chapter is based on the submitted paper for the Journal of Road Materials and Pavement Design on 22-Feb.-2019.

Summary

The long-term performance and durability of asphalt pavements heavily rely on the rheological properties of asphalt mix, which is temperature dependent and varies significantly over the performance temperature range. Different temperature sensitivity parameters were introduced to address the temperature susceptibility of asphalt cement to make sure the resulted asphalt mix could withstand real-life temperature variation.

In this research, a temperature sensitivity equation was developed based on time-temperature superposition shift factors applied to develop complex modulus and phase angle master curves (named Temperature Sensitivity of Rheological Properties or TSRP). Using the TSRP parameter, temperature sensitivity of asphalt cement and mix samples were determined and compared. Results of this study showed that TSRP parameter is sensitive to age hardening in both asphalt cement and mix, therefore can also be used to evaluate the closeness of laboratory age conditioning with the real field ageing in a wide range of performance temperatures. It was also found that the temperature sensitivity of asphalt mixes is not only affected by the thermal properties of asphalt cement, but the volumetric properties of the mix are playing an important role in the temperature sensitivity of the mixture. As a result, TSRP can be used to investigate the effect of mix design properties on the temperature sensitivity of the final product. The TSRP parameter can also be used as a measure of asphalt cement performance-grading robustness by determining the level of sensitivity of rheological properties at desired temperatures such as high and low temperature limits.

4.1 Introduction

As a temperature-sensitive viscoelastic material, asphalt cement’s response to the applied stress would be a function of the load magnitude, time of loading, and the temperature [105]. Asphalt cement can transform from rock solid looking material at low temperatures to an almost

Newtonian fluid at high temperatures [106]. This characteristic makes asphalt a favourable cementitious material for pavement construction as it provides the required workability for mixing and compaction at high temperatures as well as adequate stability under applied traffic loads at ambient temperatures. The rate of change in asphalt properties by temperature is case specific and depends on the chemical composition of asphalt cement which itself is a function of crude source, production process, and other parameters like the existence of any additives [107].

From the pavement engineering point of view, at different temperatures, different and to some extent contradictory properties are demanded from the ideal asphalt cement [32]. While at low performance temperatures, lower stiffness and more viscous behaviour are favourable to reduce thermal stress build-up and accommodate induced thermal strains, at high performance temperatures less viscous behaviour and higher stiffness is demanded to control permanent deformations [108]. At intermediate temperature range, where fatigue cracking is the main distress mode, lower stiffness and more elastic behaviour is in favour to postpone crack initiation [109]. For these purposes, lower temperature sensitive material is favourable as it could be used on a broader temperature range [110].

For many years single-parameter classification systems, such as penetration grading system (Pen. Grade), viscosity grading system (AC), and aged residue grading system (AR) were dominating pavement industry. In all these systems, asphalt cement was represented by the value of a single parameter at a certain temperature. To address the temperature-related changes in the behaviour of asphalt cement, defining a measure of temperature sensitivity of material were looked inevitable [111].

Various attempts were made to define temperature susceptibility by measuring the consistency of the material at two different temperatures and use the difference to describe the temperature sensitivity of asphalt cement. Most famous and widely used ones are Penetration Ratio (PR), Penetration Index (PI), Viscosity Temperature Susceptibility (VTS), and Penetration-Viscosity Number (PVN) [112].

Penetration ratio is one of the oldest available methods to evaluate the temperature-sensitivity of paving grade asphalt cement by running traditional penetration test at two different temperatures. Two variations of penetration test have been used for 25°C (standard needle, 100 g load for 5s) and 4℃ (standard needle, 200 g load for 60s). Equation 4-1 then defines the Penetration Ratio (PR);

Equation 4-1

$$PR = \frac{Pen.@25℃(100g, 5s)}{Pen.@4℃\ (200g, 60s)}$$

Although several studies showed the existence of a correlation between penetration test results and the viscosity of asphalt cement as a measure of consistency, using two different penetration test protocols at two different temperatures makes Penetration Ratio a pure empirical parameter which is almost impossible to interpret and only useful when comparing specific samples. Another shortcoming of the PR value is the small temperature range of two measurements (from 25℃ to 4℃), which mainly represents the intermediate temperature range of asphalt cement.

Pfeiffer and VanDoormaal (1936) defined a temperature sensitivity parameter based on penetration test results (100 gr. 5s) at different temperatures known as Penetration Index (PI) [3]. They found that for unmodified asphalt cement, the logarithm of penetration value follows a linear function versus temperature such that:

Equation 4-2

$$\log Pen. = AT + K$$

Where T is the test temperature, K is the intercept constant, and A is the temperature sensitivity of logarithm of penetration.

Pfeiffer and Van Doormaal then defined Penetration Index to normalize temperature susceptibility values to reach around zero values for paving grade asphalts using Equation 4-3.

Equation 4-3

$$PI = 20\frac{1 - 25A}{1 + 50A}$$

By this definition, the value of PI ranges from -3 for highly temperature sensitive asphalt to +7 for highly-oxidized samples with low temperature-sensitivity. They also found that the needle penetration test result at asphalt's "Ring & Ball Softening Point" temperature would be approximately 800 dmm. Therefore, they defined PI base on softening point and penetration test results as Equation 4-4 [3]:

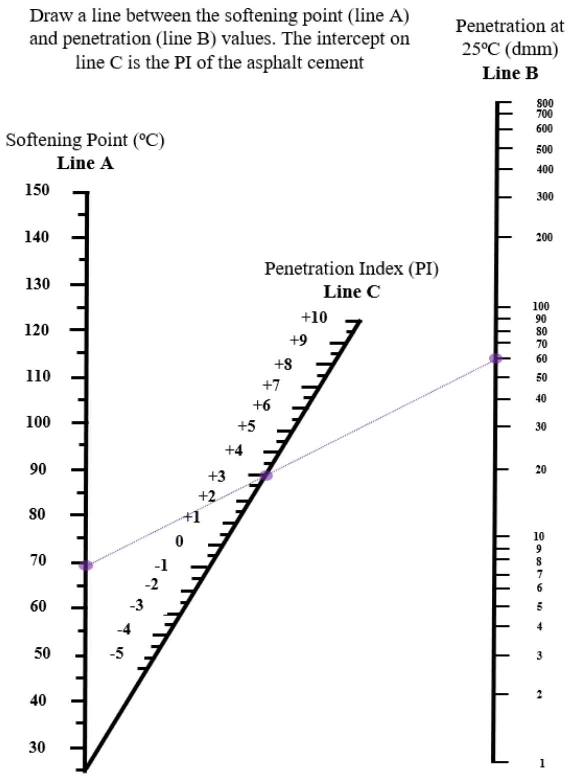
Equation 4-4

$$PI = \frac{1952 - 500\log Pen. - 20SP}{50\log Pen. - SP - 120}$$

Heukelom (1969) developed a graphical solution to find PI values base on the penetration and softening point values of asphalt cement through a nomograph (Figure 4-1).

The application of Penetration Index to determine the temperature sensitivity of asphalt cement was based on many assumptions regarding the correlation between purely empirical test results and the mechanical properties. One such critical assumption was to reach an almost complete viscous state at Ring & Ball Softening Point temperature, which is more applicable for unmodified asphalt cement types [113]. It has been shown through many studies that polymer modified asphalt still show significant elastic component at their softening point temperature, meaning softening point temperature represents different concepts for unmodified and polymer modified asphalt cements, especially if the polymer is capable of forming a network in the asphalt medium [114].

Asphalt Institute defined a temperature sensitivity criterion purely based on viscosity measurement at different temperatures, known as Viscosity Temperature Susceptibility or VTS [107]. VTS is the slope of the Log Log viscosity line over Log of temperature, as it was found that Log Log of viscosity follows a straight line when plotted against the Log of absolute temperature values, defined by Equation 4-5 [115].



Draw a line between the softening point (line A) and penetration (line B) values. The intercept on line C is the PI of the asphalt cement

Figure 4-1 Nomograph for Determining Penetration Index (PI) Using Penetration and Softening Point values [3]

Equation 4-5

$$VTS = \frac{\log\log(Vis.\,@\,60℃\ in\ poises) - \log\log(Vis.\,@135℃\ in\ poises)}{0.0888}$$

As a result of using Log Log of viscosity, the calculated values for VTS are so close to each other which makes results interpretation challenging [112]. Moreover, test temperatures were selected high enough to make viscosity measurements feasible, which makes VTS more suitable when temperature sensitivity at construction temperature range is of concern.

McLeod (1976) defined a more complex criterion to determine the temperature sensitivity of asphalt cement named Penetration Viscosity Number or PVN. He developed two equations correlating viscosity at 135℃ (centistokes) to penetration at 25℃ (dmm) for two PVN values of 0.0 and -1.5 as:

Equation 4-6

$$\log(Vis.) = 4.258 - 0.7967\log(Pen.) \qquad for\ PVN = 0.0$$

$$\log(Vis.) = 3.46289 - 0.61094\log(Pen.) \qquad for\ PVN = -1.5$$

PVN values then can be calculated using the following equation:

Equation 4-7

$$PVN = -1.5\frac{\log L - \log X}{\log L - \log M}$$

Where L is the viscosity in centistokes at 135℃ for a sample with the same penetration and PVN value of 0.0 (calculated from previous equations), X is the viscosity in centistokes at 135℃ (measured), and M is the viscosity in centistokes at 135℃ for a sample with the same penetration value and a PVN of -1.5 (calculated from previous equations) [116]. Although PVN parameter worked well for many years to classify unmodified asphalt cement based on the temperature-sensitivity mechanical properties, the validity of results lies on the two developed empirical equations to predict the viscosity of the asphalt cements with same penetration value but different temperature-sensitivity. These equations were developed for unmodified asphalt cements, and hence their validity for modified asphalt cements is questionable.

4.2 Defining the Temperature Sensitivity of Rheological Properties

Regardless of the grading system used to define the mechanical properties of asphalt cement, the final goal is to design an asphalt mix with the best field performance at all performance temperature range. To reach this goal, selecting the appropriate asphalt cement is of great importance. By the introduction of the Performance Grading (PG) system, which defines a temperature range for asphalt cement classification, an erroneous perception formed to consider temperature-sensitivity of the asphalt mix to be solely a function of the of asphalt cement grade. As temperature-related properties of asphalt cement should be endorsed as the dominant factor in temperature sensitivity of the asphalt mix, the interaction of asphalt cement and aggregates and volumetric properties of the mix should not be underestimated, as mixes prepared with the same asphalt cement could have different thermal properties regarding the interaction of asphalt cement with other mix properties.

As temperature-sensitive viscoelastic materials, the mechanical response of asphalt cement and the mix can be explained using the concept of the complex modulus (E*). Complex modulus defines the total stiffness of material as a complex number in which the real component represents the elastic response, known as storage modulus (elastic component of total stiffness or E'), and the imaginary component represents the viscous behaviour, known as loss modulus (viscous component or E") [117]. In the polar coordinate system, complex modulus can be explained by the absolute value of complex modulus ($|E^*| = \sqrt{E'^2 + E"^2}$) and the phase angle (δ), both of which are time-of-loading and temperature dependent parameters (within linear viscoelastic region, these parameters are independent from the stress level) in a way that changes in loading time can be translated to changes in temperature (increasing loading time would have the same effect as temperature increase in decreasing complex modulus absolute value |E*| and increasing phase angle δ) [24]. This relation between the mechanical properties, temperature, and time-of-loading is known as time-temperature superposition principle, which allows converting complex modulus of material at one temperature and loading frequency into another temperature with different loading frequency. In the mathematical form we have;

Equation 4-8

$$E^*(T,\omega) = E^*(T_r, a_T\omega)$$

Where T is the test temperature, ω is the loading frequency, T_r is the reference temperature, and a_T is the conversion factor to find the corresponding frequency at the reference temperature also known as TTS shift-factor. The application of time temperature superposition shift factors to develop the complex modulus master curves are described in Figure 4-2.

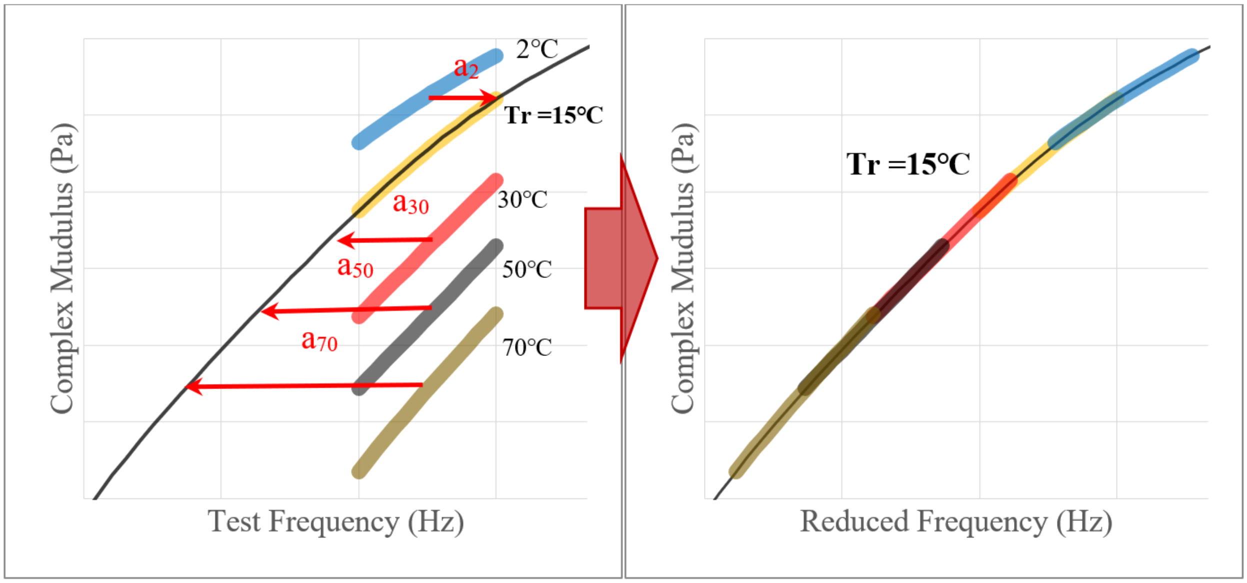


Figure 4-2 Construction of Complex Modulus Master Curve Using Time-Temperature Superposition Shift-Factors

Time-temperature superposition principle allows to determine the complex modulus of asphalt cement and mix in a wide range of loading frequencies at a reference temperature or temperatures by measuring complex modulus under frequency sweep mode at different temperatures using shift factors. Several empirical methods can explain the relationship between time-temperature superposition shift-factor and temperature. One such equation is the Williams-Landel-Ferry (WLF), which explains this relationship as:

Equation 4-9

$$\log a_T = -\frac{C_1(T - T_r)}{C_2 + (T - T_r)}$$

Where, a_T is the shift-factor used to convert results at the test temperature (T) to the reference temperature (T_r) and C_1 and C_2 are positive constants that depend on the material and reference temperature.

The Arrhenius law can also explain the relationship between shift-factor and temperature as:

Equation 4-10

$$\log a_T = \frac{-E_a}{2.303R}\left(\frac{1}{T} - \frac{1}{T_r}\right)$$

Where, E_a is activation energy, R is the universal gas constant, and T and T_r are temperatures in Kelvins.

Superpave system uses a quadratic equation to develop master curves that fit well on shift-factors obtained at test temperatures. The general form of this equation is:

Equation 4-11

$$\log_{10} a_T = C_1(T_r - T) + C_2(T_r - T)^2$$

Where, C_1 and C_2 are material specific constants for the specific reference temperature.

In order to find TTS model parameters, shift-factors at different test temperatures should be determined to make complex modulus isotherms aligned with the one at the reference temperature. This task can be accomplished by using any available rheological model that can predict the rheological properties of the material (asphalt cement or asphalt mix). The 2S2P1D (2 Springs, 2 Parabolic elements, and 1 Dashpot) rheological model was used in this research [25], as this model allows modelling with the norm (magnitude) of the complex modulus and the phase angle in one equation. By running calculations on complex numbers, model parameters and TTS shift-factors can be calibrated based on the magnitude of complex modulus and phase angle (or loss and storage moduli) simultaneously. After determining shift-factors for all test temperatures, any of three abovementioned models (WLF, Arrhenius, or quadratic) could be fitted on obtained shift-factors to find Time-Temperature Superposition model parameters. These models then would be used to find shift factors at any specific temperature, other than test temperatures, or to develop isochronal curves.

Regardless of the equation used to predict time-temperature superposition shift-factors, these numbers are representing the change in material rheological properties by temperature. Assume that two different samples are considered, namely S_1 and S_2, for which frequency sweep tests were conducted at temperatures T_1 and T_2. To convert the complex values from T_2 to T_1 shift factors of a_1 and a_2 are required for samples S_1 and S_2 respectively. Under these circumstances, if a_1 is equal to a_2 we can consider equal temperature sensitivity of the rheological parameters at the tested temperatures and if a_1 is higher than a_2 one can conclude that the selected rheological parameter of sample S_1 is more sensitive to temperature change within the tested temperature range than the one of sample S_2 (Figure 4-3).

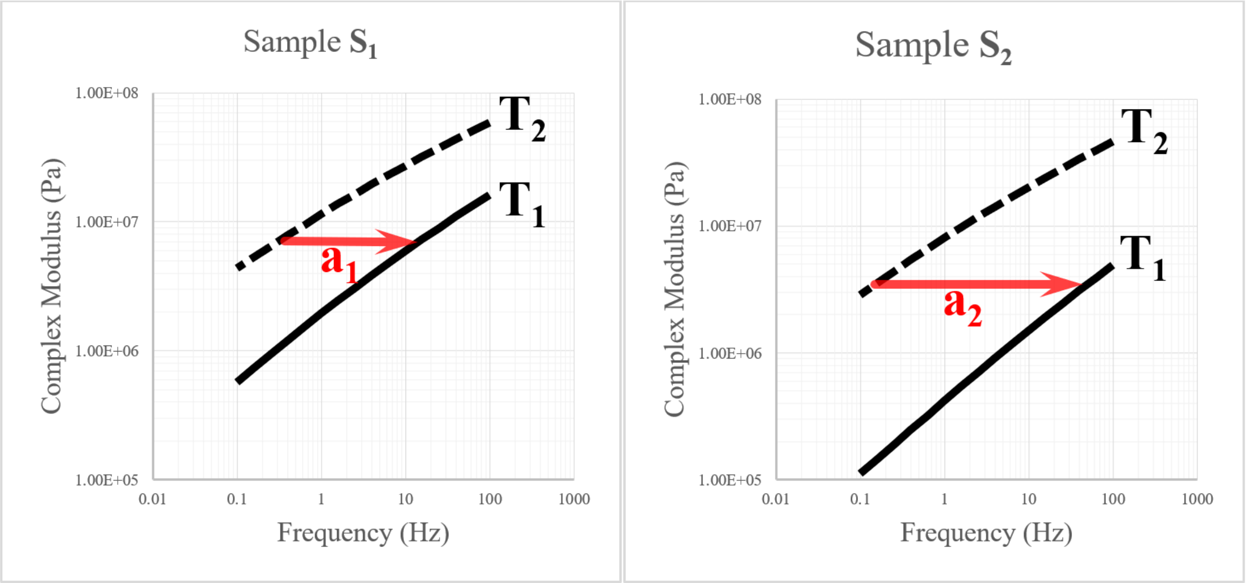


Figure 4-3 Comparison of Time-Temperature Superposition Shift-Factors for Two Different Samples to Convert Rheological Parameter Complex Modulus from T_2 to T_1

Changing the reference-temperature will move the shift-factor versus temperature curve vertically as by increasing reference temperature, will move the curve upward and vice versa. However, the change in the reference-temperature has no effect on the slope of the shift-factor curve, which means the slope of the shift-factor curve at each temperature is independent of the selected reference temperature.

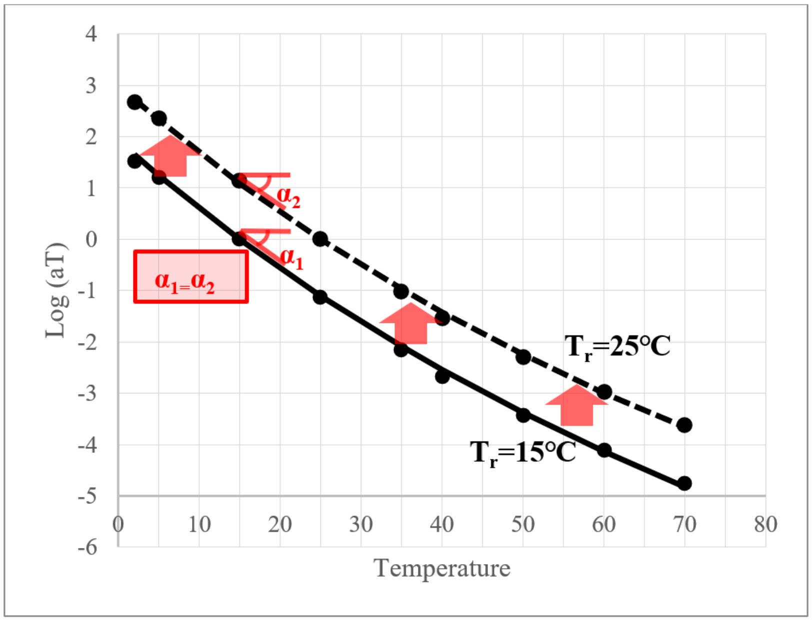


Figure 4-4 The Effect of Changing Reference-Temperature on The Shift-Factor Curve

Depending on the model that is used to predict time-temperature superposition shift-factors (WLF, Arrhenius, or Quadratic equation), the slope of the shift-factor curve, which is a measure for the temperature sensitivity of sample and an intrinsic material property can be calculated as follow:

Equation 4-12

$$TSRP = \tan\alpha = \frac{d(\log a_T)}{dT} = \begin{cases} \dfrac{-C_1 C_2}{(C_2 + T - T_r)^2} \; for\ WLF \\ \dfrac{E_a}{2.303RT^2} \; for\ Arrhenius \\ -C_1 - 2C_2(T_r - T) \; for\ quadratic \end{cases}$$

Where TSRP is the Temperature-Sensitivity of Rheological Parameters, and the rest of the parameters are the same as explained before. The appearance of the reference temperature in the above set of equations for quadratic and WLF relations should not be confused with the dependency of the slope to reference-temperature, as it should be noted that model constants in these models were developed to match with given reference-temperature in a way that the slope is independent of $\boldsymbol{T_r}$.

4.3 Comparison of Temperature-Sensitivity Calculated from Different Models

The three abovementioned models were used to calculate the temperature sensitivity of an asphalt cement sample and results are presented in Figure 4-5. As it can be seen in this figure, three completely different curves were developed for the same sample depending on the selected model for TTS shift-factors, where results of them look closer to each other in the test temperature range. Using the Quadratic equation, suggested in MEPDG to develop master curves, resulting in positive values at higher temperatures (for this specific sample higher than 95°C). The change in the sign of temperature sensitivity means that above the particular temperature (where the change in sign happens) the material gains more stiffness by the increase in temperature, which does not happen in practice. This shortcoming has resulted from the fact that in developing this equation, only mathematical fitting of the equation in the test temperature range had been considered without giving any credit to the real behaviour mechanisms, thus not favourable to be used to predict the inherent properties of material specifically out of the test temperature range.

The use of WLF model to develop Temperature-Sensitivity parameter is more favourable as in theory it was developed for materials at above their glass transition temperatures ($\boldsymbol{T_g}$) while Arrhenius model supposed to work better below the glass transition temperature [118].

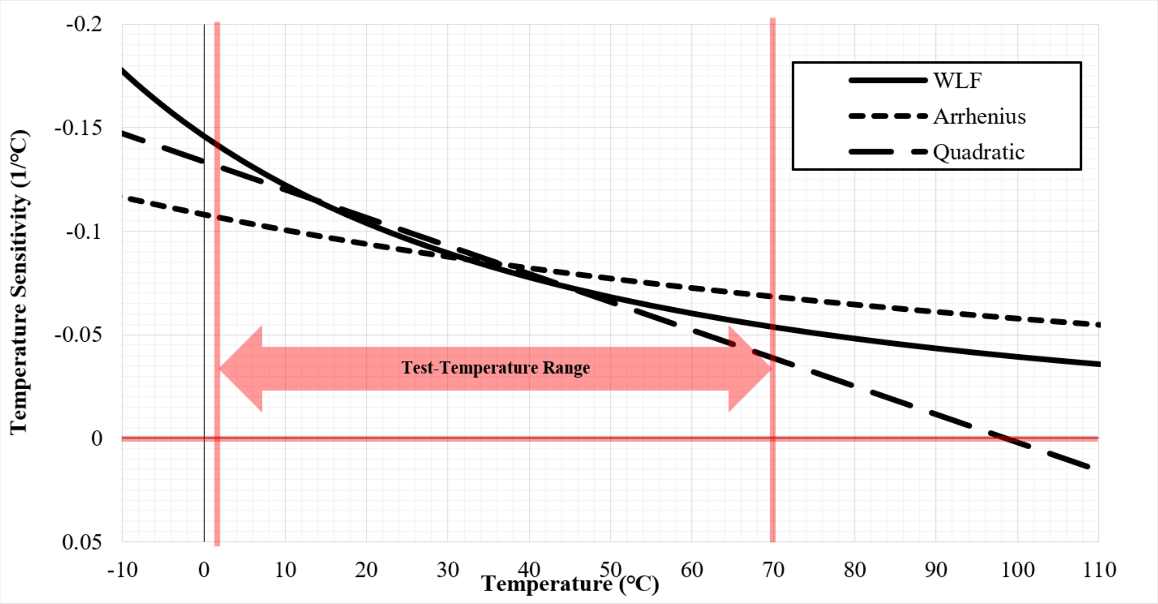


Figure 4-5 Comparison of the Three TTS Shift-Factor Models (Arrhenius, WLF, and Quadratic Equation Used in MEPDG) for Developing the Temperature Sensitivity of Rheological Properties

4.4 Application of TSRP for Age Hardening Evaluation

As an asphalt pavement ages, its mechanical properties change which result in stiffer, more elastic in almost all performance temperature range. Understanding the effect of age hardening at different temperatures is of vital importance to select the most appropriate material and design for pavements. The pace and kinetics of changes during age hardening dependent on many factors including environmental factors (temperature, solar radiation, and so on), mix design (aggregates type and gradation, air-void content), and the chemical composition of asphalt cement. Several lab conditioning procedures do exist to simulate age hardening of asphalt cement to enable better material selection, mix and structural design of the pavement, the capability of which in resembling field conditions are arguable. Temperature sensitivity curves can be used to compare different age conditioned cement and mixes and to get a better understanding of how time-related chemical changes can alter the temperature related behaviour of asphalt cement and mix.

Temperature sensitivity curves were used in another research by the authors of this paper to investigate the effect of aggregates, contaminated with iron sulphide, on the ageing process of asphalt cement. Three mixes with same gradation (SP 12.5 with no RAP), asphalt content and volumetric properties were prepared with iron sulphide containing aggregates in coarse aggregates, and fine aggregates and one with no significant amount of iron sulphide as control mix [119]. Figure 4-6Figure 4-7 are presenting the temperature sensitivity curves for asphalt mix and recovered asphalt cement from the same mixes before and after laboratory age conditioning procedure. As it can be seen in these graphs, the temperature sensitivity of both mixes and recovered asphalt are close to each other for unconditioned mixes, while a significant increase in temperature sensitivity was observed for mixes containing iron sulphide, especially when they are present in the fine aggregates, after laboratory age conditioning (consisting of heat and humidity conditioning).

The capability of Temperature Sensitivity parameter had been tested for differentiating the harshness of ageing in the samples. A compacted asphalt mix sample conditioned in the oven at 85°C for five and ten days (120 and 240 hours). Figure 4-8 shows the temperature sensitivity for these mixes and recovered asphalt samples.

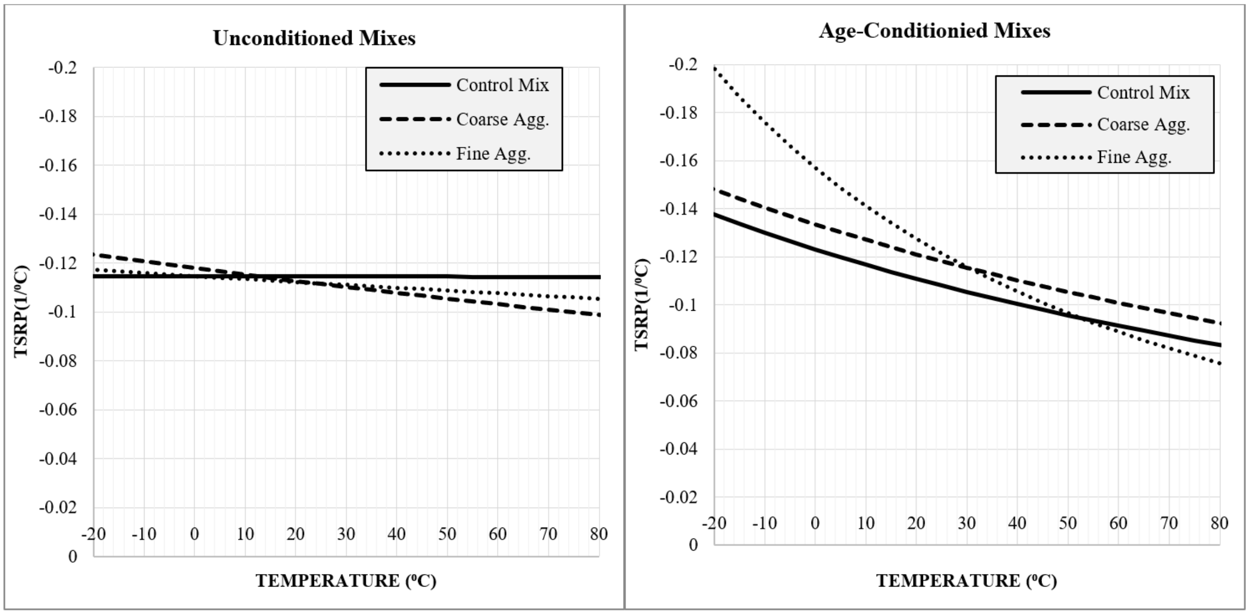


Figure 4-6 Temperature Sensitivity Curves for Prepared Compacted Mixes Before and After Laboratory Age Conditioning for Control Mix, Suspicious Material in Coarse Aggregates, and Suspicious Material in Fine Aggregates

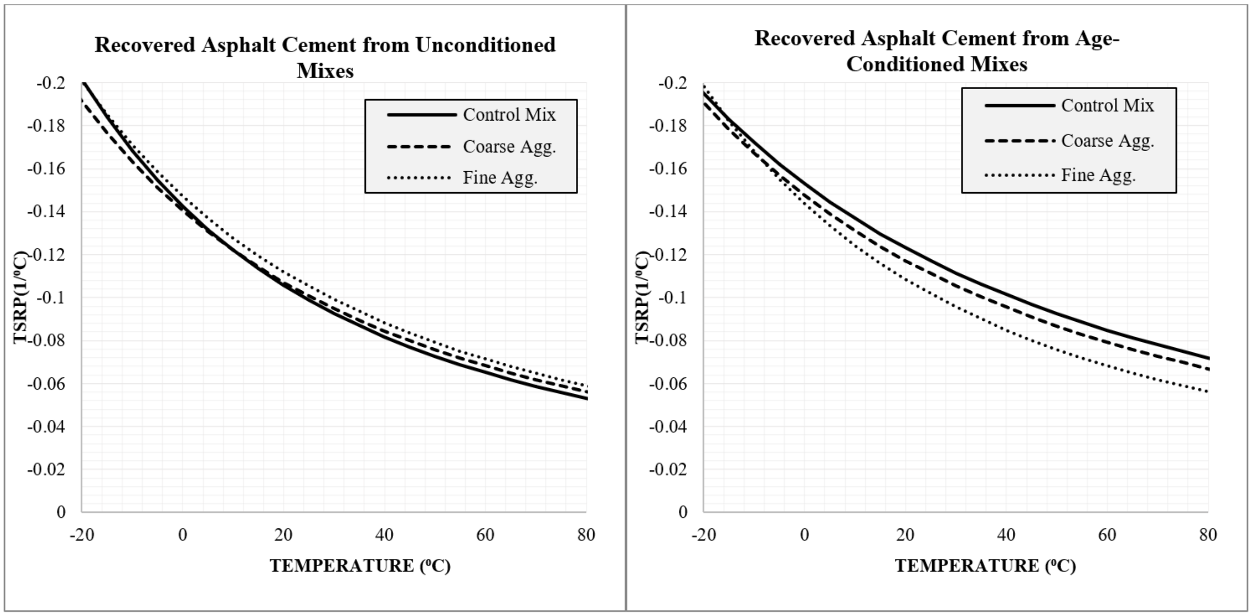


Figure 4-7 Temperature Sensitivity Curves for Recovered Asphalt Cement from Unconditioned and Laboratory Age Conditioned Mixes for Control Mix, Suspicious Material in Coarse Aggregates, and Suspicious Material in Fine Aggregates

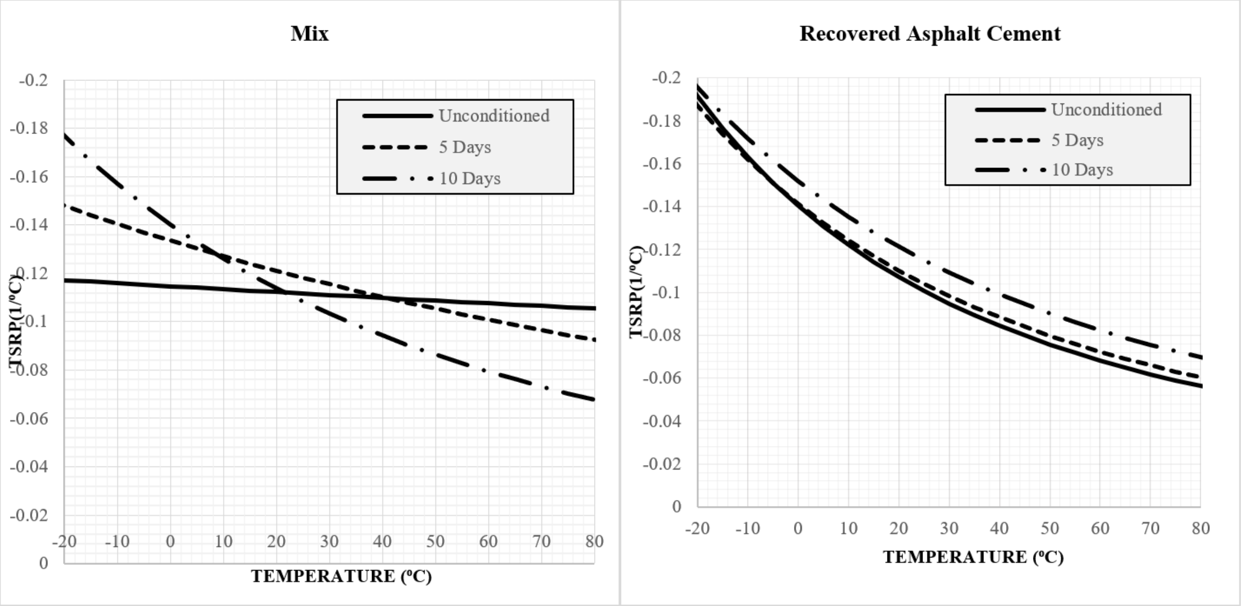


Figure 4-8 Temperature Sensitivity Curves for Asphalt mix and Recovered Asphalt Cement before age conditioning and after five and ten days of Oven conditioning at 85℃

The change in the temperature sensitivity of asphalt cement was also investigated by comparing the TSRP curves for a virgin asphalt sample (PG 64-28) by laboratory age conditioned samples including RTFOT, PAV, and Double PAV procedures. Figure 4-9 shows the TSRP, as a measure of temperature sensitivity of asphalt cement tends to get less steep as the age conditioning gets tougher by showing more sensitivity toward the change in temperature for higher values and less for low temperatures.

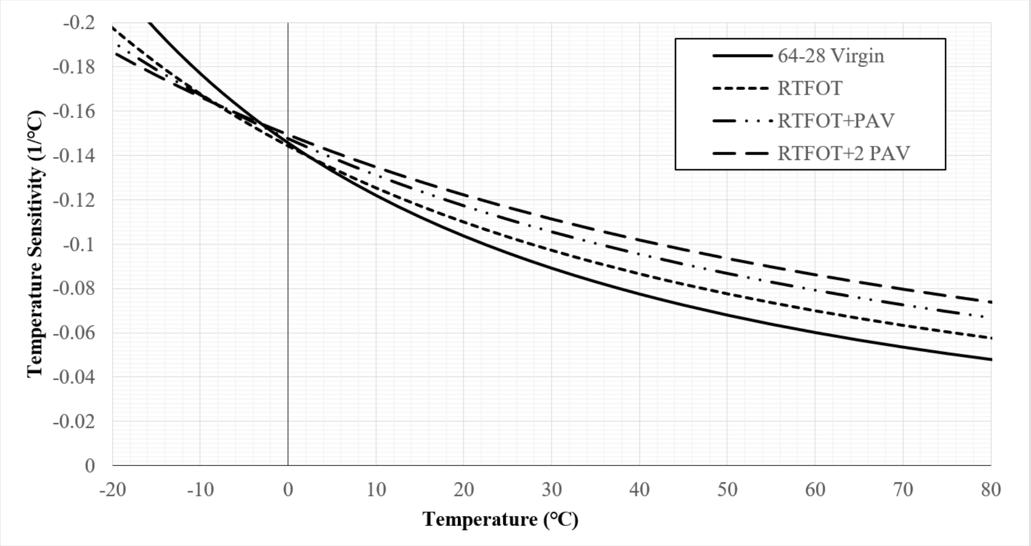


Figure 4-9 Temperature Sensitivity Curves for Asphalt Cement at Four different conditions; Virgin, RTFOT, PAV, and Double PAV

4.5 The Effect of Compaction on the Temperature Sensitivity of Mixes

The effect of volumetric properties of the mix on the temperature sensitivity of the resulting mixes was investigated by developing TSRP curves for the same mixtures with different compaction level. For this purpose, two different loose asphalt mixes were selected (Mix A, and Mix B) each having different aggregate source and gradation (both dense-graded). Each of these mixes were then divided into two sets of samples and compacted separately to reach to 7.0±0.5 and 2.0±0.2 air void using different compaction effort (number of gyrations in Superpave Gyratory Compactor). Complex (dynamic) modulus test in frequency sweep mode was performed in a wide range of temperatures (-10, 4, 21, 37, and 54°C) and frequencies (25, 10, 5, 1, 0.5, and 0.1Hz). Complex modulus and phase angle master curves were then developed for these samples using the free shifting technique to calibrate the 2S2P1D model on collected data. WLF model was then fitted on obtained shift-factors, and TSRP curves developed using WLF model parameters (**C_1** and **C_2**). Figure 4-10 represents the average temperature sensitivity for these samples. As it can be seen, the effect of compaction level on the temperature sensitivity can be captured using TSRP curves. It can be said that as compaction level increases, temperature sensitivity of the mix at high performance temperatures increases, while at lower temperatures it decreased.

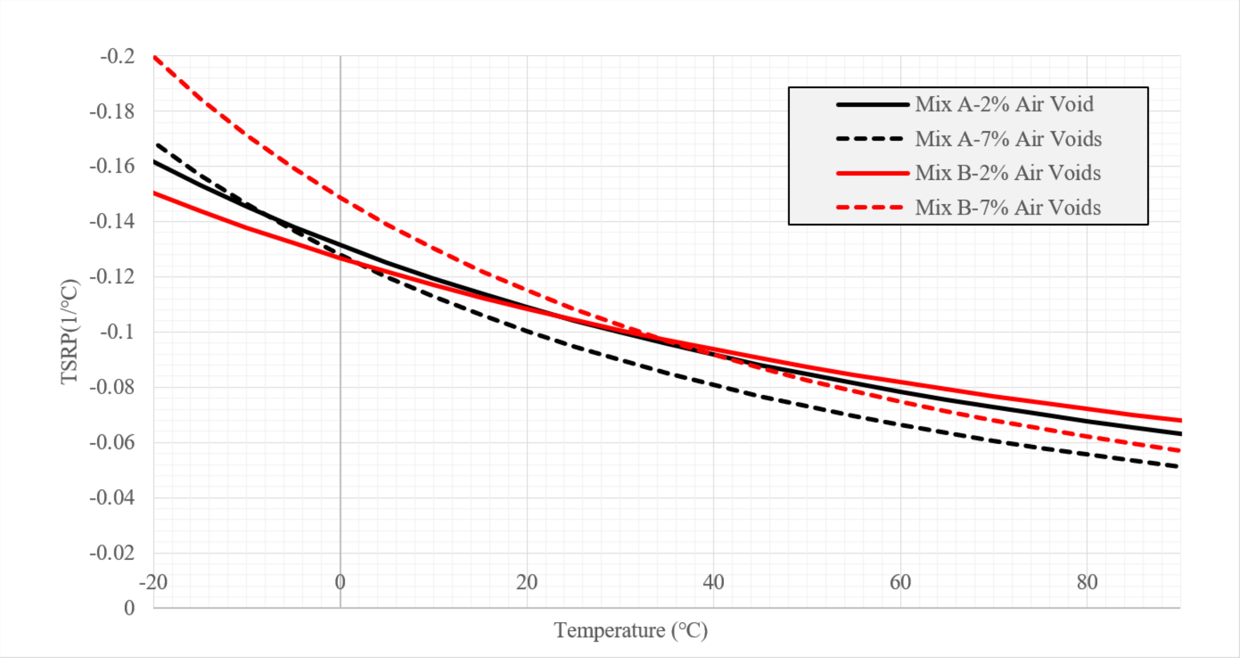


Figure 4-10 Temperature Sensitivity Curves for Asphalt Mixes with Different Air Void

4.6 Conclusions

Temperature Sensitivity of Rheological Parameters (TSRP) which is the rate of changes in TTS shift-factors by temperature, can be used as an identification of the temperature sensitivity of viscoelastic materials such as asphalt cement and mix. Although by the introduction of the Superpave PG system, the need for a temperature sensitivity parameter vanished for grading purposes, it can help understand the rheological mechanisms of changes in the material. Unlike other traditional temperature sensitivity parameters, TSRP can be used for asphalt mixes to evaluate the effect of the aggregate skeleton, compaction level, and other mix related properties on the sensitivity of asphalt mix to temperature.

TSRP itself is a temperature-related parameter, which can capture complex temperature-related behaviour of asphaltic materials in terms of temperature-related changes in rheological properties. The conclusions of this research can be summarized as follows:

- Among the three available models for the relationship of TTS shift-factors (WLF, Arrhenius, and Quadratic), William-Landel-Ferry (WLF) found to be more suitable for asphaltic materials at the performance temperature range. It works better than Arrhenius law for viscoelastic materials above the glass-transition temperature, and unlike the Quadratic equation used in MEPDG, which increases after an extremum point, it merges to an absolute value at excessively high temperatures.
- Temperature sensitivity of viscoelastic materials is temperature dependent itself and cannot be represented by a single number obtained from measuring a single property at two different temperatures. Therefore, developing a temperature sensitivity curve can accurately represent the temperature dependency of such materials.
- Unlike traditional temperature sensitivity parameters such as VTS, PVN, PI, and PR, the defined temperature sensitivity parameter, TSRP (Temperature Sensitivity of Rheological Properties) can measure the temperature sensitivity of both asphalt cement and asphalt mixes. This can help pavement engineers during the mix design step to accommodate specific environmental conditions, by evaluating the temperature

sensitivity of designed mixes, and to come up with the most appropriate design to accommodate environmental conditions.

- TSRP can be used alongside other rheological tests and analysis techniques to evaluate the ageing severity in both asphalt cement and asphalt mix. One such application can be to evaluate the intimacy of laboratory age conditioning procedures to the real-life ageing in the field.

CHAPTER 5: EFFECT OF AGGREGATES CONTAINING IRON SULPHIDE ON ASPHALT AGEING

This chapter is based on the following published article in the Journal of Road Materials and Pavement Design. Azimi Alamdary Y, Singh S, Baaj H. (2019). Effect of Aggregates Containing Iron Sulphide on Asphalt Ageing. DOI: 10.1080/14680629.2019.1610477

Summary

The impact of asphalt cement ageing on pavement durability is a well-known phenomenon for pavement engineers, yet due to complexity in the chemical structure of asphalt cement, not understood thoroughly. Accelerated laboratory ageing procedures usually consider aggregates as an inert material, which are insensitive to environmental effects. While in most cases this assumption is not far from reality, there are some cases where the aggregates could play a significant role. Iron Sulfide exists in many aggregate sources in different forms such as pyrite and pyrrhotite. Products of the reactions from such aggregates may have a catalytic effect on the ageing procedure of asphalt cement.

In this research, three different sources of Iron Sulfide-containing aggregates were selected to produce laboratory mixes, which were conditioned under moisture and heat. Complex modulus tests were performed on unconditioned and conditioned samples, and the parameters of the rheological behaviour of each mix were determined using the 2S2P1D model. After each step of conditioning, recovered asphalt was subjected to chemical and rheological analysis. The 2S2P1D model was also employed to determine the rheological parameters for recovered asphalt cement from different mixes. Shift factors determined as part of developing master curves were also used to investigate the temperature susceptibility of samples. Carbonyl and sulfoxide indices and the ratio between them were also used to study the chemical path of reactions.

The results of this study showed that for samples that were subjected to both heat and moisture, mixes containing Iron Sulfide minerals seem to follow somehow different ageing kinetics resulting in an important change in the behaviour, which is reflected through different rheological parameters and chemical indices.

5.1 Introduction

Like most other organic materials, mechanical properties of asphalt cement change gradually over time in a process known as ageing [120]. Several ageing mechanisms can affect asphalt's rheological and mechanical response over time, with oxidation and volatilization known to be the dominant causes in pavement applications [53]. Several accelerated laboratory ageing procedures have been developed over the years to simulate time associated metamorphosis, thus enabling prediction the behaviour of both asphalt cement and asphalt mixture after construction and during its service life. RTFO (Rolling Thin-Film Oven) and PAV (Pressure Ageing Vessel) are the most commonly used methods for asphalt cement conditioning, and STOA (Short-Term Oven Ageing), LTOA (Long-Term Oven Ageing, also known as Extended Heating procedure), and LPO (Low-Pressure Oxidation) are amongst the most common practices for asphalt mixture conditioning [108]. These accelerated ageing procedures usually assume the aggregates to be inert materials, which are not sensitive to environmental degradation factors, and hence do not have any effect on the oxidation process. In most cases, this assumption is not far from reality.

It is well known that specific materials and mainly metallic compounds may have a catalytic effect on the oxidation process. Some of such compounds have found their way into the refining industry, as a catalyst to accelerate the air rectifying process, while assuming that they do not have any effect at performance or service temperatures. Some metallic compounds may also exist in certain modifiers. Some sources of REOB (Recycled Engine Oil Bottom), reportedly contain a considerable amount of metals. Iron sulphide exists in many aggregate sources in different forms such as pyrite and pyrrhotite. All of these metals and metallic compounds can affect ageing, with oxidation products that may affect the durability of asphalt pavements [3], [24], [121].

5.2 The Motivation for this Research

Staining of the surface course on asphalt pavements has been reported on a number of roads in the province of Ontario. Rust-like stains appeared on newly paved roads raising questions about their quality and durability. Initial investigations showed that these rusty stains were oxidation products of pyrrhotite and pyrite. It was assumed that this surficial staining would not have any effects on pavement durability and that they would eventually get washed away once the surface layer oxidation reactions are completed. However, later investigations revealed that some of these rusty spots were associated with visible signs of crack initiation thus raising some concerns about the effect of such reactions on pavement durability. Many metallic compounds were shown to have an accelerating effect on the oxidation of hydrocarbons some of which used in various industries, including air rectifying process in asphalt cement production.

Moreover, most of the Iron Sulphide oxidation processes are expansive, resulting in considerable volume changes and crack initiations. Such effects need to be addressed and investigated. The motivation for this research project was to investigate any accelerating or catalytic effect of Iron Sulphide-containing compound, along with their oxidation products in the ageing process of asphalt cement that could result in early crack initiation and pavement deterioration.

5.3 Materials and Analysis Tools

Three different aggregate sources from different projects in Ontario containing Iron Sulphide compounds (Mixes A, B, and C) were selected alongside with an Iron Sulphide-free aggregate source (Control Mix) to produce Superpave mixes with Nominal Maximum Aggregate Size of 12.5 (SP 12.5) using PG 58-34 polymer modified asphalt cement and binder content was selected according to job mix formulas. These mixes are using Iron Sulphide containing material differently. In Mix A, the suspicious material only exists in the source of fine material, while in Mix C only Coarse aggregates were taken from the questionable source. Mix B is using Iron Sulphide containing material in both coarse and fine aggregates. Initial investigations on the collected Iron Sulphide containing aggregates using Scanning Electron Microscopy (SEM) showed that they contain roughly around 14.7% Iron and 8.32% Sulphur. X-Ray Diffraction analysis (XRD) showed that most of Iron and Sulphur combinations are in the form of Chalcopyrite and Pyrrhotite each of which forms roughly around 2% of tested aggregates.

After mixing, loose mixtures were cooled down to ambient temperature and then conditioned for four hours at mixing temperature to simulate short-term ageing per AASHTO R30 guidelines. These were then compacted using a Superpave Gyratory Compactor (SGC) to achieve 7□1 percent air voids. Properties of these mixes are tabulated in Table 5-1.

As the primary purpose of this research was to investigate the effect of Iron Sulphide oxidation products, a new conditioning procedure was developed to include cycles of heat and humidity conditioning, in addition to the extended heating procedure recommended by AASHTO R30 guidelines. This conditioning procedure comprised of 10 days humidity conditioning at 100 percent relative humidity and ambient temperature in between two LTOA procedures (120 hr @85°C). All laboratory conditioning procedures are listed in Table 5-2.

Table 5-1 Properties of Asphalt Mixes

Name	**Mix Type**	**Asphalt Cement Grade**	**Binder content (%)**	**Description**
Mix A	SP-12.5	PG 58-34p	4.5	Fines contain Iron Sulphide
Mix B	SP-12.5	PG 58-34p	4.5	Iron Sulphide exist in both fine and coarse aggregate sources
Mix C	SP-12.5	PG 58-34p	4.9	Coarse aggregates contain Iron Sulphide
Control Mix	SP-12.5	PG 58-34p	4.9	No traceable Iron Sulphide

Table 5-2 Conditioning procedures for laboratory conditioning of asphalt mixtures

Conditioning	**Duration and Temperature**	**Mix Cond.**
Short-term (**STOA**)	4 hrs. at Mixing Temperature	Loose
Long-term (**LTOA**) – Extended Heating	120 hrs. at 85°C	Compacted
Long-term (**RHR**) – Heat & Humidity	120 hrs. at 85°C – 240 hrs. at 25°C in Humidity Room - 120 hrs. at 85°C	Compacted

Samples prepared from all four asphalt mixtures were then subjected to frequency sweep complex modulus testing under compressive cyclic loading at different temperatures (Table 5-3). The 2S2P1D model was then used for modelling the rheological behaviour of these mixtures [25]. Root-mean-square error in the interquartile range or RMSEIQR of total deviations on loss and storage modulus was used as a measure of fitting goodness to calibrate 2S2P1D model parameters. Complex modulus and phase angle master curves were then developed for all four mixtures after each conditioning procedure. Temperature sensitivity analysis using shift factors was also done on the samples using Williams-Landel-Ferry (WLF) and Arrhenius theories for time-temperature superposition principle for viscoelastic materials. Asphalt cement from all samples was then recovered, using centrifuge extraction and rotavapor recovery technique with trichloroethylene (TCE) as solvent using consistent temperature and time to minimize the effect of extraction and recovery process on the properties of asphalt cement. Recovered asphalt cements were then subjected to rheological and chemical tests.

For rheological analysis of recovered asphalt cement, Strain Sweep Tests were conducted on samples at different temperatures to determine the linear viscoelastic region using Dynamic Shear

Rheometer (DSR) [105], [122]. Asphalt cements were then subjected to Frequency Sweep tests at a wide range of temperatures (Table 5-4), within the LVE range using DSR 25 mm plate setup for temperatures higher than 35°C, and 8-mm plate setup for lower temperatures. Complex modulus and phase angle master curves were then developed using 2S2P1D model. Temperature sensitivity analysis using shift factors was also done on the samples based on WLF and Arrhenius theories for the time-temperature superposition principle for viscoelastic materials [123].

Table 5-3 Temperatures and Frequencies Used for Measuring Asphalt Mixture Complex Modulus Under Frequency Sweep Mode

Temperatures (°C)	Frequencies (Hz)
-10 4 21 37 54	25 10 5 1 0.5 0.1

Table 5-4 Temperatures and Frequencies for Frequency Sweep Test Using DSR

Temperatures (°C)	Frequencies (Rad/s)
2, 5, 15, 25, 35, 40, 50, 60, 70	100, 63.1, 39.8, 25.1, 15.8, 10, 6.31, 3.98, 2.51, 1.58, 1, 0.631, 0.398, 0.251, 0.158, 0.1

5.3.1 The 2S2P1D Rheological Model

The 2S2P1D is an analogical model used to describe the rheological behaviour of viscoelastic materials based on a simple combination of physical elements. A combination of spring, dashpot, and parabolic elements are used to describe the general behaviour of both asphalt mixtures and asphalt cements (Figure 2-21) [25], [124]. The mathematical representation of this model can be described by the following expression:

Equation 5-1

$$E^*(i\omega\tau) = E_0 + \frac{E_\infty - E_0}{1 + \delta(i\omega\tau)^{-k} + (i\omega\tau)^{-h} + (i\omega\beta\tau)^{-1}}$$

Where ω is the loading frequency (rad/s), E_0 is equilibrium or static modulus ($f \rightarrow 0$), E_∞ is glassy modulus ($f \rightarrow \infty$), τ is characteristic time, k and h are parabolic element constants such that $0 < k < h < 1$, δ is dimensionless shape factor, β is viscosity parameter for dashpot element, and i the unit imaginary number.

Fitting this model on experimental test data requires the application of time-temperature superposition (TTS) principle. This principle states that for linear viscoelastic materials, the same rheological characteristics can be obtained at different temperatures by multiplying frequencies with a shift-factor (a_t). In other words:

Equation 5-2

$$E^*(\omega, T) = E^*(a_T\omega, T_0)$$

Where E^* is the complex modulus, ω is the loading frequency in terms of angular velocity, T and T_0 are test temperatures, and a_T is the shift-factor.

After converging experimental test results at different temperatures to a reference temperature, rheological parameters can be determined by optimization of the general 2S2P1D model. This is done by minimizing the following sum of errors:

Equation 5-3

$$\sum_{i=1}^{n}\left\{\left[\log_{10} E'_{exp}(\omega_i) - \log_{10} E'_{model}(\omega_i)\right]^2 + \left[\log_{10} E''_{exp}(\omega_i) - \log_{10} E''_{model}(\omega_i)\right]^2\right\}$$

Where E'_{exp} and E''_{exp} are storage and loss moduli obtained from the experiment, and E'_{model} and E''_{model} are storage and loss moduli predicted by the 2S2P1D model.

The goodness of fit can also be measured by Root Mean Square Error (RMSE) within the interquartile range (IQR) such that:

Equation 5-4

$$RMSEIQR = \frac{\sqrt{\dfrac{\sum_{i=1}^{n}\left\{\left[\log_{10} E'_{exp}(\omega_i) - \log_{10} E'_{model}(\omega_i)\right]^2 + \left[\log_{10} E''_{exp}(\omega_i) - \log_{10} E''_{model}(\omega_i)\right]^2\right\}}{n}}}{CDF^{-1}(0.25) - CDF^{-1}(0.75)}$$

Where, CDF^{-1} is the quantile function.

5.3.2 Functional groups analysis using FT-IR spectroscopy

Quantitative functional group analysis using FT-IR spectroscopy was also used to determine age-related changes in Carbonyl and Sulfoxide groups. Generation of Carbonyl and Sulfoxide functional groups are known to have a strong correlation with changes in mechanical properties of asphalt cement, given their contribution in increasing the polarity of hydrocarbons [53]. To follow the changes in the amount of these functional groups with ageing, functional group indices can be calculated by dividing the area under changing peaks (the ones that are of interest to follow changes) by the area of specific peak/peaks that are not generated or degenerated in the ageing process. Carbonyl and Sulfoxide indices were calculated based on CH_2 and CH_3 peaks as they are assumed to remain constant during oxidative ageing (Equation 3-1Equation 3-2) [103], [104]. Sulfoxide functional groups are temperature sensitive and tend to decompose at excessively high temperatures, thus would be biased for laboratory age conditioning procedures that utilize overly high temperatures [18].

Equation 3-1

$$Carbonyl\ Index\ (CI) = \frac{A_{carbonyl(1680-1750)}}{A_{CH2(1410-1495)} + A_{CH3(1360-1390)}}$$

Equation 3-2

$$Sulfoxide\ Index\ (SI) = \frac{A_{sulfoxide(980-1060)}}{A_{CH2(1410-1495)} + A_{CH3(1360-1390)}}$$

Moreover, it can be said that the ratio of carbonyl over sulfoxide indices can be used as a measure of the chemical path for oxidation. It is expected that if an asphalt cement undergoes similar age conditioning, the C/S ratio should not significantly change, although Carbonyl and Sulfoxide indices would both keep on increasing with increasing levels of ageing. This assumption can only be exempted when one of these functional groups gets close to their saturation value. However, this might not be the case for short laboratory conditioning.

Equation 3-3

$$Carbonyl\ to\ Sulfoxide\ Ratio\ ({}^{C}/_{S}) = \frac{A_{carbonyl(1680-1750)}}{A_{sulfoxide(980-1060)}}$$

5.4 Limitations to This Study

In the use of the time-temperature superposition principle (TTS) one of the main assumptions is the simplicity of the thermo-rheological behaviour of the material, which is not exactly the case for polymer modified asphalt cement and subsequent asphalt mixes. However, the TTS principle is applied in this research to avoid the associating complexities specifically in developing complex modulus and phase-angle master curves. Moreover, using two sample sizes (8 mm and 25mm) for running frequency sweep tests on asphalt cement samples using DSR equipment at different temperatures would result in problems in the application of TTS principle, specifically when the shift-factor analysis is of importance.

To evaluate the chemical and rheological properties of asphalt cement, it is mandatory to recover asphalt cement through the extraction and recovery process using an organic solvent. Several combinations of extraction and recovery processes have been used and standardized, yet the hardening effect of solvent on the properties of recovered asphalt cement and the possibility of remaining slight amounts of solvent in the recovered asphalt cement in accordance with the efficiency of extraction procedure to separate all ingredients including additives and preventing dust particles in the recovered asphalt cement is known to be a source of error in such analysis [125]–[127]. Such shortcomings of the extraction and recovery procedure can affect both rheological and chemical analysis. To minimize such effects, extensive care was taken to keep extraction and recovery procedure as consistent as possible for all samples. Furthermore, the base asphalt cement went through a similar extraction and recovery procedure before testing. However, different rheological and chemical parameters should be expected when applying any change in the extraction and recovery procedure as well as solvent.

5.5 Results and discussion

5.5.1 Asphalt cement rheology

Figure 5-1 shows Master Curves developed for asphalt cements recovered from all four mixtures at three different age conditioning steps. In all these graphs, the master curve developed for the base asphalt is also presented to act as a reference. As it can be observed in the graph (a), master curves for all samples including the control mix, overlap each other except for the sample recovered from Mix C, which follows a different path at all conditioning steps. Same phenomena were also observed for the same mix (Mix C) in phase angle master curves. This strange behaviour, which occurs even before considerable age conditioning (after STOA), can be attributed to phase separation in polymer modified asphalt, and also a probable increase in polymer content for this fraction of asphalt cement (which was used for the preparation of mix C).

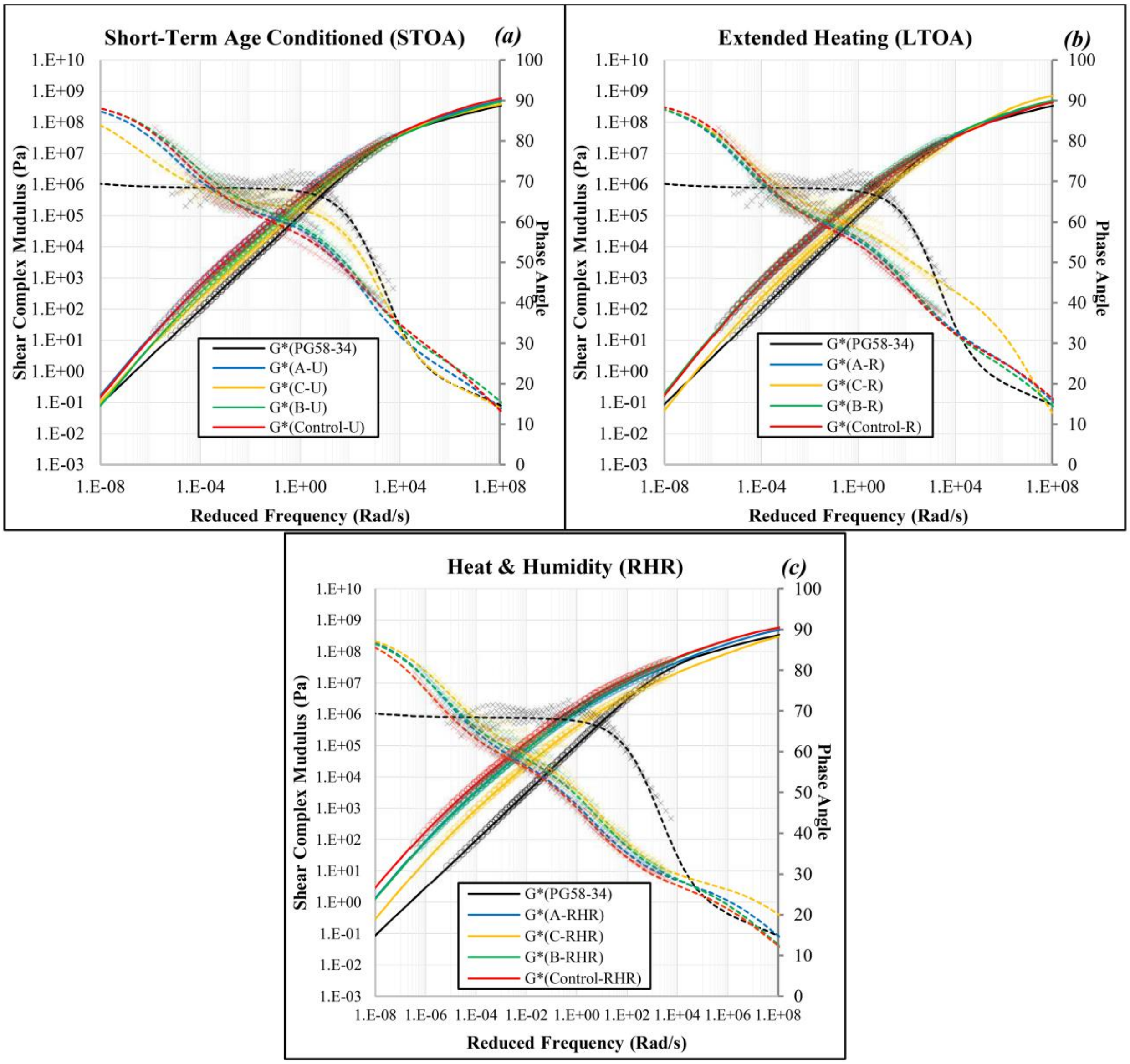


Figure 5-1 Shear Complex Modulus and Phase Angle Master Curves for Asphalt Cement Recovered from All Mixtures After (A) Compaction (STOA) (B) Heat Conditioning (LTOA) (C) Heat and Humidity Conditioning (RHR).

Figure 5-1-b presents complex modulus and phase angle master curves for all extracted samples after extended heating age-conditioning procedure (LTOA), which is meant to simulate long-term field ageing. As it can be observed, these master curves merged to similar values for almost all frequency range. This implies that the extended-heating procedure had a similar effect on all samples and the type of aggregates used in the mixtures did not have a significant impact on the ageing properties of asphalt cement. However, master curves developed after heat and humidity conditioning procedure (Figure 5-1-c) resulted in divergent master curves, both for complex modulus and phase angle, for samples containing Iron-Sulphide (Mix A and Mix B) when compared to the control mix. It seems that this effect was caused by applying humidity in the conditioning procedure, with water acting as a catalyst for the reaction between Iron-Sulphide (in the aggregates) and atmospheric oxygen. The oxidation products of such a reaction can play a catalytic role in the oxidative ageing of hydrocarbon by lowering the activation energy and altering the chemical and rheological changes during oxidative ageing.

An interesting phenomenon has been observed in phase angle master curves for all conditioning procedures. Lower phase angles were found for unconditioned asphalt at lower frequencies (higher temperatures) when compared to samples extracted from mixtures. It can be said that phase angle master curve for all samples do reach a plateau in the mid-range frequencies, but for unconditioned asphalt, this plateau seems to occur for a wider frequency range. This behaviour could be attributed to the presence of polymer in asphalt microstructure. After a certain temperature, the elastic response for unconditioned asphalt is due to the elasticity of the polymer network (in this case SBS). Extracted samples show less of such behaviour, which can be attributed to the breaking of such network due to the thermo-oxidative degradation of the polymer.

5.5.2 Temperature sensitivity analysis for asphalt cement

Temperature sensitivity analysis was performed based on the shift factors obtained for application of the TTS principle. Three different theories, WLF, Arrhenius, and Polynomial, were used to illustrate the temperature sensitivity of asphalt cement samples amongst which WLF and Arrhenius methods are more scientifically backed, while Polynomial method was developed mainly based on mathematical fitting on a performance temperature range.

Figure 4-5 shows the temperature sensitivity analysis based on these three different methods for unconditioned asphalt cement used in this research (PG 58-34). All three methods gave a similar result between 20 to 40°C. Using the Polynomial equation to correlate shift factors resulted in a strange consequence at high temperatures (above 95°C) where the sign of temperature sensitivity changes. This change would mean that the binder stiffness should increase by increasing temperature beyond the vertex of the curve, which is certainly not the case for asphalt cements. This is due to the mathematical form of this correlation which works more accurately in the test temperature range, and thus unable to predict the innate behaviour of temperature-related changes for our viscoelastic material.

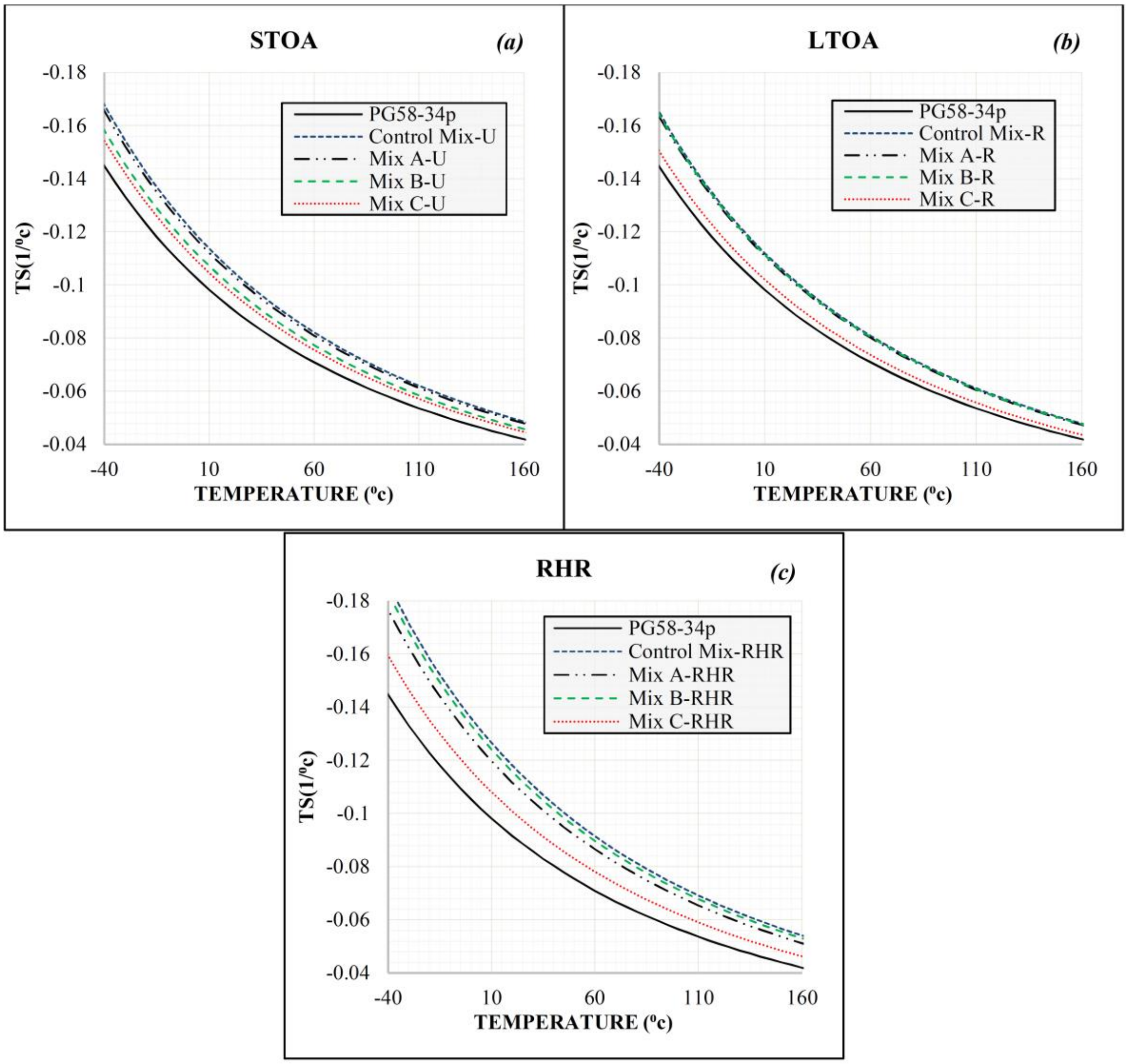


Figure 5-2 Temperature sensitivity calculated based on Arrhenius law for asphalt cements, extracted after different conditioning steps (a) short-term aged (b) extended heating (LTOA), and (c) heat and humidity conditioning

In contrast, using the WLF equation to model, the temperature sensitivity resulted in excessively high values for lower temperatures. This phenomenon was predictable as WLF law for TTS principle is more appropriate for temperatures higher than glass transition temperature (Tg) of material, and as the temperature gets closer to Tg of asphalt cement, WLF results are no more reliable (Mouton, 2006). Finally, Arrhenius law (Equation 6) provided more promising temperature sensitivity results at low-temperatures in comparison to the other two models, with a lower slope merging to nil at excessively high temperatures and its applicability even below Tg for viscoelastic materials. However, the application of Arrhenius law would not be appropriate when the temperature is considerably higher than the Tg. For the sole purpose of comparison, Arrhenius law was selected to estimate the temperature sensitivity in this research.

Figure 5-2 shows temperature sensitivity curves for asphalt cement samples extracted from all mixtures at different conditioning steps. As it can be seen in Figure 5-2-a and Figure 5-2-b (STOA and LTOA procedures), all samples show almost similar temperature sensitivity values with the exception for asphalt cement extracted from Mix C. However, after heat and humidity conditioning it was noted that the temperature sensitivity of samples recovered from mixtures containing Iron Sulphide (Mix A and Mix B) was considerably different from the control mix (Figure 5-2-c). The results from Mix C seems invalid due to possible phase separation.

5.5.3 Rheology Analysis of Asphalt Mix Samples

Complex modulus measurements were performed on compacted asphalt mixture samples (Control Mix, and Mix A, B and C) after three different conditioning procedures (STOA, LTOA, and RHR). The results were then analyzed using the 2S2P1D model to develop complex modulus and phase angle master curves. As each of the prepared mixtures has slightly different aggregate gradations, it would be inconclusive to compare the complex modulus and phase angle master curves of various mixes to each other. In this case, rheological changes in master curves for each mix at different age conditioning steps have been considered. Figure 5-3 shows the master curves alongside with data points for samples containing Iron Sulphide (Mix A, B, and C), as well as for the control mix (Iron Sulphide free sample). As it can be seen in these graphs, for samples containing Iron Sulphide (Figure 5-3-a, b, and c) there is a significant difference in rheological behaviour (increase in stiffness with higher complex modulus along with a greater proportion of elastic behaviour with lower phase angles) for extended heating and heat and humidity conditioning as compared to the control mix. For Mix A (Figure 5-3-a), complex modulus master curve for extended heating conditioning procedure (Mix A-R) is closer to the curve for heat and humidity conditioned, while for Mix C, it is closer to the curve for the short-term aged sample. Unlike the Iron Sulphide-containing mixtures, master curves of extended heat conditioned (Control Mix-R), and heat and humidity conditioned (Control Mix-RHR) samples almost overlap for the control mix showing negligible rheological changes as a result of moisture conditioning. A similar trend was also noted in phase angle master curves while comparing the horizontal location of the peak point (Elastic Return Point). Comparing “extended heating” and “heat and humidity” conditioning curves (R 30 \and RHR), this peak occurs at significantly different load frequencies for samples containing Iron Sulphide as compared to the control mix.

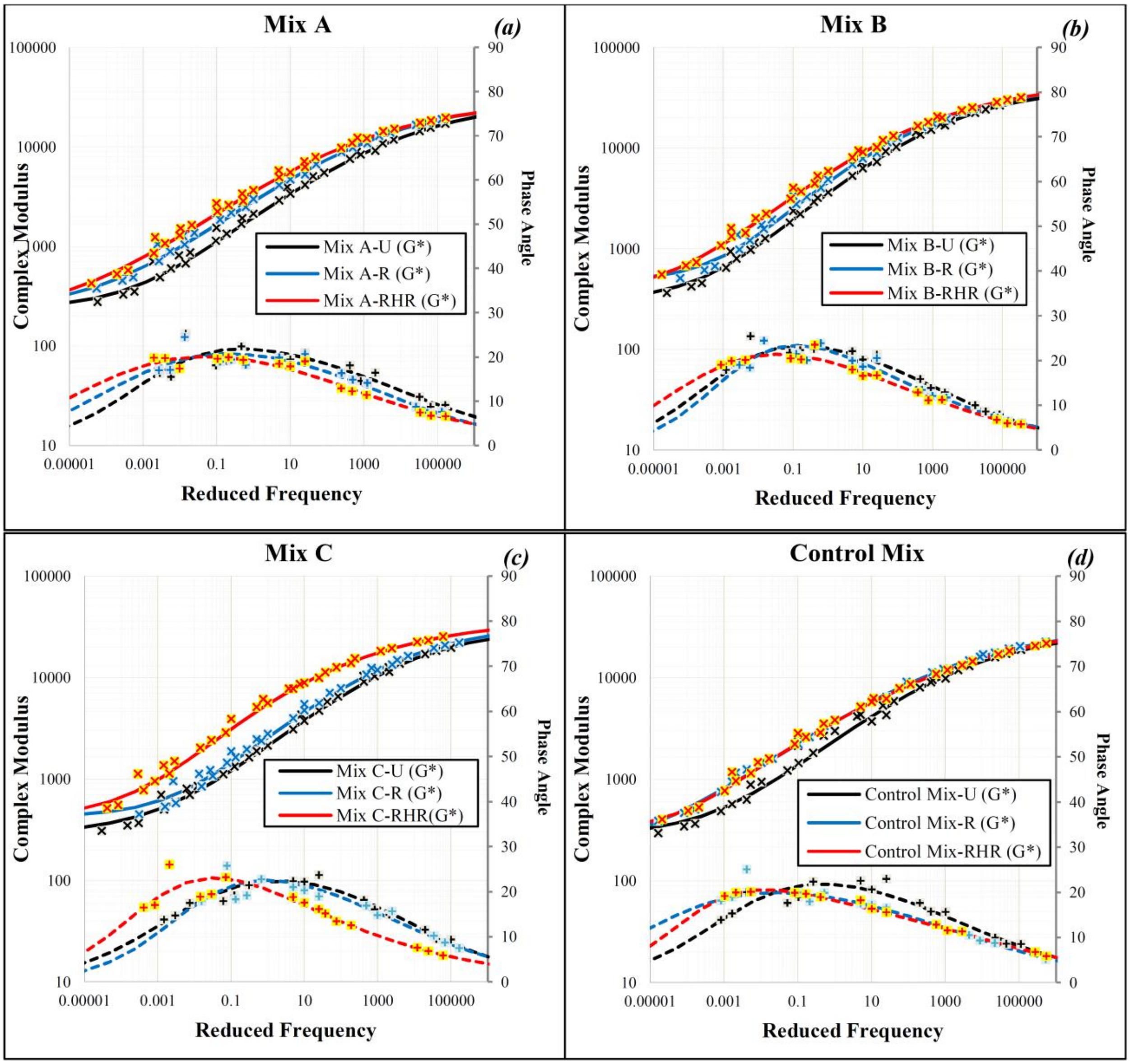


Figure 5-3 Complex Modulus and Phase Angle Master Curves at Different Conditioning

5.5.4 FT-IR Spectroscopy

Infrared spectroscopy was performed on asphalt cement samples (extracted and recovered from conditioned mixture samples) after each of the different conditioning procedures. Spectrum results for samples obtained from mixture B, along with those for virgin asphalt cement are shown in Figure 5-4. Wavenumbers related to each concerned functional group (Carbonyl, Sulfoxide, CH2, and CH3) are highlighted in this graph. From these spectra, one could notice the Carbonyl and Sulfoxide peaks are getting stronger by age conditioning. As mentioned before, quantification of Carbonyl and Sulfoxide evolution with age conditioning is carried out by calculating the ratio between the area under these peaks to the sum of the area under CH2 and CH3 peaks (assumed to be constant with varying rates of age conditioning). The ratio between these calculated indices (Carbonyl and Sulfoxide) was also used to evaluate the chemical path of oxidation for different conditioning parameters and to evaluate the effect of Iron Sulphide-containing aggregates.

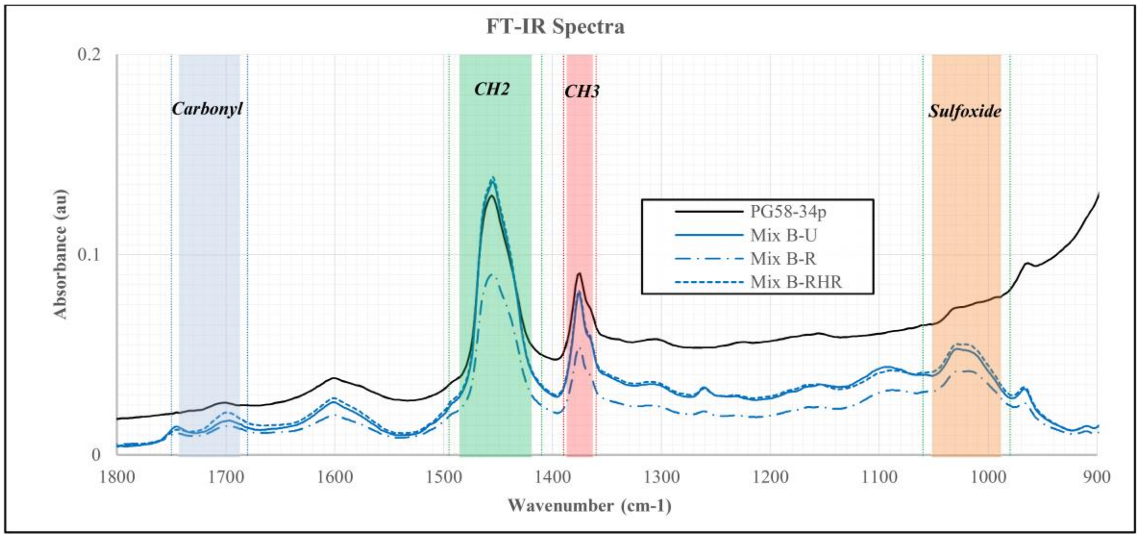


Figure 5-4 FT-IR spectra for samples extracted from Mix-B and the peaks of Carbonyl, Sulfoxide, CH2, and CH3

Figure 5-5 shows the calculated Carbonyl and Sulfoxide Indices, as well as the ratio between the two, for asphalt cement samples extracted from all types of mixtures and after each of the age conditioning procedures. It can be noted that the addition of humidity as a conditioning parameter resulted in higher amounts of Carbonyl formation in Iron Sulphide-containing samples as compared to the control mix (Figure 5-5 -a). However, a similar trend was not noted for Sulfoxide Index. For samples containing Iron Sulphide, peak Sulfoxide index values were pointed out after the extended heating procedure (LTOA) with a slight reduction noted for heat and humidity conditioning. However, this was not the case for the control mix where the Sulfoxide Index keeps on increasing with heat and humidity conditioning (Figure 5-5-b). Carbonyl over Sulfoxide ratio results (Figure 5-5-c) shows a completely different trend for samples containing Iron Sulphide as compared to the control mix. For asphalt cement samples extracted from Iron Sulphide-containing aggregates, this ratio tends to increase with increasing levels of age conditioning, which can be attributed to the cessation of sulfoxide formation after LTOA conditioning along with sulfoxide decomposition at higher levels of ageing. However, for the control mix, a contrary trend is noted with a peak value observed after short-term age conditioning (STOA), and a subsequent decrease noted with increasing levels of ageing. This changing pattern in C/S ratio for the control mix shows that the rate of Carbonyl formation is much faster at the very beginning of oxidation reactions, while Sulfoxide tends to increase subsequently as conditioning continues.

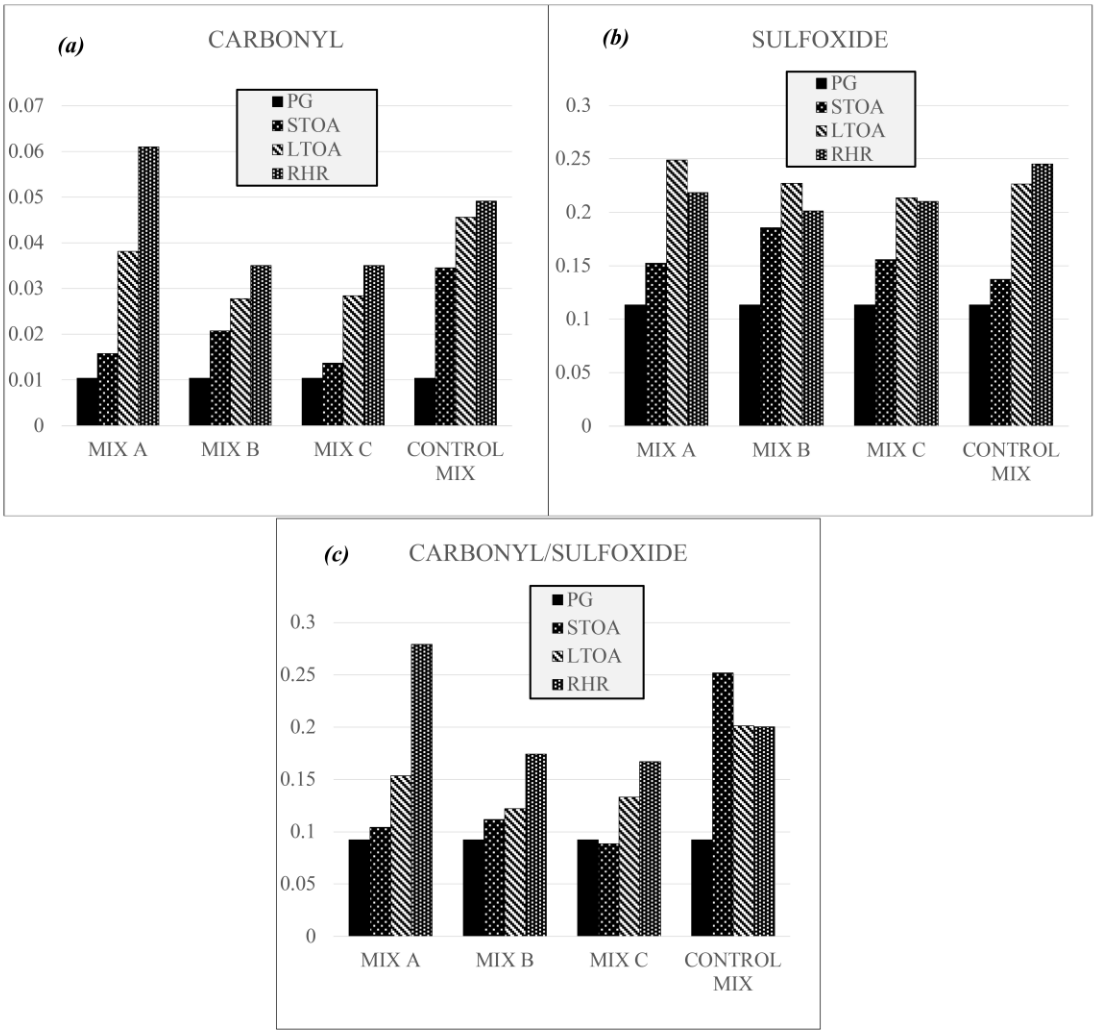


Figure 5-5 Carbonyl (a) and Sulfoxide (b) indices and Carbonyl/Sulfoxide ratio (c) for samples at different conditioning steps

5.5.5 Summary and Concluding Remarks

The main aim of this research was to evaluate the effect of Iron Sulphide-containing aggregates on oxidative ageing of asphalt cement. Three Iron Sulphide-containing aggregate sources were selected (which have been used at different locations in Ontario, Canada) alongside with a control aggregate source without a noticeable amount of Iron Sulphide. A polymer (SBS) modified asphalt cement (PG 58-34) was selected to prepare mixture samples. Three different conditioning procedures were chosen to simulate short and long-term field ageing. STOA (AASHTO R30 procedure, 4 hours conditioning of loose mixture at compaction temperature) was selected to mimic short-term field ageing. LTOA (AASHTO R30 procedure, conditioning of compacted samples for performance testing, 120 hours at 85°C) was chosen to simulate long-term ageing of asphalt mixtures. However, LTOA, an extended heating procedure considers temperature as the only affecting factor, which is why it is not regarded as a proper technique to evaluate the effect of Iron Sulphide oxidation products on asphalt cement ageing. Therefore, another age conditioning procedure was proposed in this research to assess the combined effects of humidity and temperature on Iron Sulphide-containing minerals (RHR procedure).

Rheological properties of both compacted asphalt mixture samples and asphalt cement samples (extracted from conditioned samples) were used to investigate the effects of Iron Sulphide-containing aggregates on pavement durability. Results from asphalt cement samples showed that using LTOA procedure for conditioning would not result in any meaningful difference in rheological behaviour of samples containing Iron Sulphide with respect to the control samples. This was clear from the comparison of complex modulus and phase angle master curves after LTOA conditioning (Figure 5-1-b). In contrast, applying humidity as a conditioning parameter leads to a notable difference in asphalt cement rheological properties, specifically for the complex modulus master curve (Figure 5-1-c).

Similar results were obtained for complex modulus frequency sweep tests, carried out on compacted asphalt mixture samples. These are presented in Figure 5-3 in master curve form, indicating that for the control mix, the addition of humidity does not have a considerable effect on modulus and phase angle master curve, while for samples with Iron Sulphide-containing aggregates a significant difference was observed after humidity conditioning.

Results from FT-IR spectroscopy also indicated a different chemical path in the oxidative ageing of Iron Sulphide-containing aggregates when compared to the control mix. An initial spurt in Carbonyl formation was noted during short-term ageing in the control mix, with the relatively smaller formation for long-term conditioning procedures. However, for Iron Sulphide-containing aggregates, a different trend for Carbonyl formation was noted with relatively higher formation observed with long-term conditioning procedures. With regards to Sulfoxide formation, it was pointed out that the presence of Iron Sulphide seems to stop Sulfoxide formation after the LTOA procedure, with further degradation of Sulfoxides observed during RHR conditioning. On the other hand, in the absence of Iron Sulphide, Sulfoxide index keeps on increasing as conditioning continues. The ratio between Carbonyl and Sulfoxide indices seemed to continuously increase for samples extracted from Iron Sulphide-containing aggregates, while it remained relatively constant for the control mix.

The conclusions of this research study could be summarized as follow:

- Extended heating procedures for simulating long-term ageing (e.g. LTOA procedure of AASHTO R30) are not suitable when dealing with Iron Sulphide aggregates. This is due to their inability to oxidize minerals, which would have a subsequent effect on the oxidative ageing of asphalt cement.
- A combination of extended heating and humidity conditioning (such as the RHR procedure) has the advantage of simulating more realistically the field conditions and should be employed to investigate the ageing effects of any suspected minerals in the aggregate source.
- The existence of Iron Sulphide in mineral aggregates can alter the ageing process for both asphalt cement and asphalt mixtures with regards to their chemical and rheological behaviour, and temperature sensitivity.
- Different forms of Iron Sulphide such as pyrite and pyrrhotite would have varying effects on the oxidative ageing of asphalt cement. The impact of any such materials on long-term ageing and durability of asphalt pavements should be examined by conducting accelerated laboratory long-term age conditioning procedures and subsequent chemical and performance analysis such as FT-IR spectroscopy and frequency-sweep complex modulus tests.

CHAPTER 6: TOWARD A BETTER SIMULATION OF FIELD CONDITION IN ASPHALT MIX LABORATORY AGE TESTING

This chapter is based on the submitted paper for the Journal of Road Materials and Pavement Design on 30-May-2019.

Summary

Characterization of ageing susceptibility of materials is of great importance in several industries, especially the pavement industry. The time-associated changes in the properties of asphalt cement and its impact on the performance and durability of asphalt mix has been known for decades, encouraging many researchers to develop various techniques to simulate laboratory ageing on asphalt cement and mix. A majority of these techniques use extended heating as the primary ageing mechanism to speed up the oxidation process. The effect of other environmental factors such as solar radiation, precipitation, humidity has also been considered in several researches. Most of these conclude their effect as negligible when applied in the laboratory due to the surficial impact of such parameters.

This research aims to evaluate the coupling effect of solar radiation, heat, and moisture treatment on the laboratory age conditioning of asphalt mixes. To reach this goal, a temperature controlled environmental chamber, capable of applying high-intensity solar radiation was used to apply dry and wet conditioning cycles on compacted asphalt mix samples. Frequency-sweep complex modulus measurements were then performed on samples at various stages of the conditioning process. Asphalt cement was then extracted from the conditioned mixes and examined for its rheology (using frequency sweep complex modulus testing) and chemistry (by running quantitative FT-IR spectroscopy). The 2S2P1D model was employed for rheological analysis and complex modulus, and phase angle master curves were developed. Temperature-Sensitivity of the rheological parameters were evaluated using TTS (Time-Temperature Superposition) principle shift-factors. Carbonyl and Sulfoxide Indices were calculated as well as Carbonyl to Sulfoxide ratio to assess the kinetics of the chemical ageing reactions during age conditioning of the samples. Results of this study showed that the combination of moisture and solar radiation could alter the chemistry and rheology of the resulting conditioned asphalt mixes,

and for a more accurate prediction on the age-related properties of the mixes, it is mandatory to use more realistic conditioning parameters.

6.1 Introduction

The concept of accelerating age hardening for asphaltic pavement materials was considered by many researchers to enable pavement materials designers to have a better understanding of the future behaviour of their product [108]. As an organic compound, asphalt cement tends to experience changes in its chemical composition (and as a result in its mechanical properties) gradually by the time. Several mechanisms affect the time-related changes in asphalt cement, including oxidation, volatilization, polymerization, thixotropy increase, and syneresis [39], [90]. For pavement applications, age hardening changes can be classified into those that happen during the construction period (short-term), and those that occur during the service-life of the pavement (long-term). Volatilization and high-temperature (above 130°C) oxidation are the dominant ageing mechanisms during mixing and compaction period, while low-temperature (ambient temperatures) oxidation is the most influential mechanism in the pavement service-life [53].

Asphalt cement is a combination of tens of thousand different hydrocarbons, with different tendencies toward oxidation at different temperatures. The ambient temperature has a pivotal role in determining the rate and kinetics of oxidation reactions in asphalt cement. This means that by changing the conditioning temperature, the resulting oxidized material would have different chemical structure, and therefore rheological properties [24]. To make this more imaginable, consider the final product of baking, which cannot be duplicated for temperatures of 350°F or 50°F just by changing the baking time. This shows the importance of selecting a realistic conditioning temperature in laboratory age conditioning procedure for duplicating real-life changes.

There are other environmental factors that can contribute to the oxidative ageing process, including but not limited to; the existence of catalyst (such as some metallic compounds), solar radiation (specifically high energy containing UV beams), and presence of water in the form of moisture or as precipitation (which can interfere in the ageing process by acting as a reaction catalyst or by washing the highly oxidized protective layers away) [52], [128]. The effectiveness of solar radiation, specifically those in the ultraviolet spectrum (10 to 400 nm), in accelerating the oxidation of hydrocarbon chains have been explicitly recognized in the polymer and coating industry [129], [130]. The first studies on the effectiveness of UV radiation on the asphalt cement samples showed that UV radiation affects the oxidation process, but its effect is limited to the very surface (few micrometres) of asphalt layer, and is therefore negligible [39], [131]. Howsoever, precipitation can intensify the age-accelerating effect of UV, as most of the photo-oxidation products are water-soluble and can be removed from the very surface, hence exposing further layers of the asphalt mix structure to photo-oxidation.

Over the last eighty years, several attempts have been made to develop laboratory accelerated age conditioning procedures for both asphaltic materials, most of which were focused on conditioning asphalt cement in thin films at high temperatures such as Thin Film Oven (TFOT), Rolling Thin Film Oven (RTFOT), Pressure Aging Vessel (PAV), and Universal Simple Aging Test (USAT) [56]. The use of highly oxidative gases was also considered to reduce the conditioning temperature, and hence use more realistic conditions [97], [98]. Comparing to available procedures for asphalt cement conditioning procedures, few efforts have been made for age conditioning of asphalt mixes. The available laboratory age conditioning procedures for asphalt mixes can be categorized into three general techniques; extended heating, pressurized oxidation, and gas flow through the compacted asphalt mix sample (mainly for porous asphalt mix conditioning) [96], [98], [119].

One of the most commonly used age-conditioning procedures in North-America is the AASHTO R30 procedure, which provides short- and long-term age conditioning procedures for asphalt mix performance testing sample preparation. For short-term age conditioning, loose asphalt is placed in a forced draft oven at mixing temperature for four hours. The short-term conditioned loose mix will then be compacted either by a Superpave Gyratory Compactor (SGC) or a slab compactor (such as vibratory compactor or shear box compactor) to reach to 7±0.5 percent air void. Compacted samples are then cut to the desired sample sizes. For high-temperature performance testing (resistance to rutting), prepared samples are tested immediately after compaction, while samples for performance tests regarding fatigue resistance (such as four-point bending test) and low-temperature crack resistance (such as Thermal Stress Restrained Specimen Test or TSRST) require long-term age conditioning. For long-term age conditioning, AASHTO recommends an extended heating procedure in which compacted samples are placed in a forced-draft oven at 85°C for 120 hours (5 days).

Different researchers have studied the effect of solar radiation on asphalt cement oxidation (photo-oxidation). One of the very first studies was done by Hveem et al. [61] where the effect of infrared radiation on age hardening of Ottawa sand mixtures showed a negligible effect. Hugo and Kennedy [85] examined asphalt age hardening at ambient temperatures (around 40°C) under continuous UV radiation and limited the effect of UV to the very surface of asphalt cement. Tia et al. [99] tried various age conditioning procedures including UV radiation at higher temperatures (60°C) and found that when UV radiation is coupled with water spray, the affected zone would be more significant comparing to continuous UV irradiation.

6.2 Laboratory Evaluation of the Effect of Solar Radiation and Moisture

The primary purpose of running age conditioning on both asphalt cement and asphalt mix is to simulate rheological changes at all performance temperature zones, as they happen in the field. This task cannot be accomplished without replicating the age-related chemical changes as accurately as possible. In an excessively complex hydrocarbon composite material, like asphalt cement, oxidation can happen in infinitely different ways, depending on the conditioning parameters and their intensities. Therefore, conditioning parameters and their ranges are important, especially when the performance properties of the conditioned material, such as fatigue life, and low temperature behaviour are of the question.

This research, therefore, aimed to combine the effect of solar radiation and the washing effect of precipitation as a laboratory long-term age conditioning procedure for asphalt mix samples at more realistic temperatures. For this purpose, a temperature-controlled conditioning chamber, capable of applying high-intensity solar radiation with wet and dry cycles was developed (Bespoke Chamber) and used to condition compacted asphalt mix samples using different parameter values. The bespoke chamber was equipped with three full spectrum lamps, with a combined output power of 1800 watts to simulate solar radiation and heating the samples. Internally the chamber was lined with a reflective coating, allowing for most of the radiation to bounce back and to be absorbed by the black asphalt samples. To prevent overheating, temperature sensors were installed on dummy samples, and an air ventilation system was installed for temperature control. An automated data collection unit was used to collect data every five minutes for sample temperature, box temperature, incoming solar radiation, and incoming UV radiation (Figure 3-4).

A plant mixed SP12.5 FC2 (Friction coarse Superpave mix with the NMAS of 12.5 mm, where both coarse and fine aggregates are obtained from crushed bedrock material) with no RAP material. The asphalt cement was PG 64-28p (Polymer modified asphalt). Compaction of samples was performed at 138ºC (the compaction temperature recommended by the asphalt cement supplier) to reach to 7.0±0.5 percent air void using a Superpave gyratory compactor (SGC). As plant mix used, no short-term age conditioning was performed on the samples before compaction.

Using the bespoke chamber, two types of conditioning cycles (dry and wet cycles) were applied on asphalt mixture samples. In wet cycles, samples were exposed to solar radiation for 23 hours after which water was sprayed on the surface of the samples for 15 minutes, along with slight brushing with a soft painting brush for 30 seconds. In dry cycles, samples were removed with the holding pan before water spray starts. For comparison purpose, another set of compacted asphalt mix samples were conditioned using an extended heating procedure (AASHTO R30, @85℃ for 120 hrs.). Table 6-1 shows the conditioning procedures, including parameter values. The RTFOT, PAV, and double PAV laboratory age conditioning protocols were also performed on asphalt cement.

Table 6-1 Conditioning Procedures for Laboratory Age-Conditioning of Compacted Asphalt Mixes

Asphalt Mix Conditioning Procedures				
Method	**Temp. (℃)**	**Solar Radiation (Watts)**	**Water Spray**	**Duration (hr.)**
LTOA (AASHTO R30)	85	N/A	N/A	120
BC-5 Dry	65	1800	No	120
BC-5 Wet	65	1800	15 min/day	120
BC-10 Dry	65	1800	No	240
BC-10 Wet	65	1800	15 min/day	240
BC-15 Dry	65	1800	No	360
BC-15 Wet	65	1800	15 min/day	360
BC-20 Dry	65	1800	No	480
BC-20 Wet	65	1800	15 min/day	480

Asphalt Cement Conditioning Procedures			
Method	**Temp. (℃)**	**Pressure (MPa)**	**Duration**
RTFOT	163	Atmospheric	85 (min.)
PAV	100	2.1	20 (hr.)
Double PAV	100	2.1	40 (hr.)

Frequency sweep Complex (Dynamic) modulus test (cyclic compressive loading) were performed on all unconditioned and conditioned samples at a wide range of temperature (-10, 4, 21,37, and 54℃). In this process, three replicates were tested, and results were averaged for various conditioning stages. Asphalt cement was then extracted from the unconditioned and conditioned samples (using Centrifuge extraction and Rotavapor recovery procedure) and subjected to complex shear modulus testing (frequency sweep test using Dynamic Shear Rheometer) at a wide range of temperatures (2, 5, 15, 25, 35, 40, 50, 60, and 70°C), and quantitative functional groups analysis using Fourier Transform Infrared Spectroscopy (FT-IR).

The 2S2P1D, an analogical model, used to describe the rheological behaviour of viscoelastic materials based on a simple combination of physical elements (two springs, two parabolic elements, and one dashpot) [25], was selected to run the rheological analysis on the frequency sweep test results for both asphalt cement and asphalt mix samples. The 2S2P1D model (Equation 2-12) was calibrated by minimizing the total Root Mean Square Deviation in the Interquartile Range (RMSD-IQR) of loss and storage moduli (Eq.2). Complex modulus and phase angle master curves were then developed to follow the age-related changes in rheological behaviour of the samples in a wide range of frequencies (or temperatures).

Equation 2-12

$$E^*(i\omega\tau) = E_0 + \frac{E_\infty - E_0}{1 + \delta(i\omega\tau)^{-k} + (i\omega\tau)^{-h} + (i\omega\beta\tau)^{-1}}$$

Where ω is the loading frequency (rad/s), E_0 is equilibrium or static modulus ($f \rightarrow 0$), E_∞ is glassy modulus ($f \rightarrow \infty$), τ is characteristic time which accounts for the time-temperature superposition principle, k and h are parabolic element constants such that $0<k<h<1$, δ is dimensionless shape factor, β is viscosity parameter for dashpot element, and i is imaginary unit number.

To evaluate the effect of each parameter on the fatigue behaviour of asphalt cement, Linear Amplitude Sweep test (LAS) was performed on the samples, and N_f (cycle repetition to failure) was calculated for 2.5% and 5.0% strain levels (for 35% damage level) [102].

Using the results from the FT-IR, a quantitative analysis was performed to follow the concentration of Carbonyl and Sulfoxide functional groups, the formation of which proved to be indicators of chemical changes during oxidative ageing [132], [133]. Carbonyl and Sulfoxide Indices were calculated based on CH_2 and CH_3 peaks (Equation 3-1Equation 3-2)[104], [134]. As the formation rate of these functional groups, specially Sulfoxides, are conditioning-temperature sensitive, the Carbonyl to Sulfoxide ration (Equation 3-3) was also calculated as an indicator for the kinetics of chemical changes and to compare the effect of different conditioning factors on the chemistry of the product.

Equation 3-1

$$\boldsymbol{Carbonyl\ Index\ (CI)} = \frac{\boldsymbol{A_{carbonyl(1680-1750)}}}{\boldsymbol{A_{CH2(1410-1495)} + A_{CH3(1360-1390)}}}$$

Equation 3-2

$$\boldsymbol{Sulfoxide\ Index\ (SI)} = \frac{\boldsymbol{A_{sulfoxide(980-1060)}}}{\boldsymbol{A_{CH2(1410-1495)} + A_{CH3(1360-1390)}}}$$

Equation 3-3

$$Carbonyl\ to\ Sulfoxide\ Ratio\ ({}^{C}/_{A}) = \frac{A_{carbonyl(1680-1750)}}{A_{sulfoxide(980-1060)}}$$

Where *A* represents the peak area for each wavenumber range.

6.3 Results and Discussion

6.3.1 Asphalt Cement Rheology

Shear Complex Modulus and Phase Angle master curves were developed based on the frequency sweep test results on recovered asphalt cement from the compacted and age-conditioned samples (Figure 6-1). Results showed that at the end of 5 cycles (each cycle was equal to 24 hours of conditioning) of conditioning in the bespoke chamber, asphalt cement samples from dry conditioning, gained more stiffness when compared to the wet cycles (Figure 6-1-a) showing a higher pace of ageing. The slower age hardening in the wet process at this step could be due to the temperature drop, caused by water spray on the samples. However, by continuing the conditioning procedures, the wet process showed the more aggressive ageing process (Figure 6-1-b, c, & d) by which after 15 cycles the complex modulus is higher for the wet process when compared to the dry one. This can be attributed to the fact that during dry process, the surface of the sample had reached to saturation with the much faster speed at the beginning of the conditioning process and formed a protective highly oxidized layer on the surface, thus preventing the penetration of solar radiation to the more age susceptible asphalt.

Same observations can be detected in the phase angle master curves (Figure 6-2). Applying dry conditioning procedure, an initial spurt can be observed in the phase angle master curve (Figure 6-2-a), while with the continuation of dry conditioning, the changes in phase angle master curves occur at a much slower pace. In wet conditioning procedure, age-hardening occurs with a slower pace at the first few cycles but continues more aggressively as age-conditioning continues (Figure 6-2-b).

Figure 6-3 shows the complex shear modulus and phase angle master curves of asphalt cement through different age conditioning procedures (mix and asphalt cement conditioning). Much lower changes in both parameters were observed for the RTFOT aged asphalt cement comparing to the one recovered from freshly compacted mixes. This shows the RTFOT is not severe enough on asphalt cement as it should be to represent short-term ageing. Moreover, even though the PAV age conditioning does not look to be rigorous enough comparing to mix age conditioning protocols, the double PAV procedure is excessively harsh.

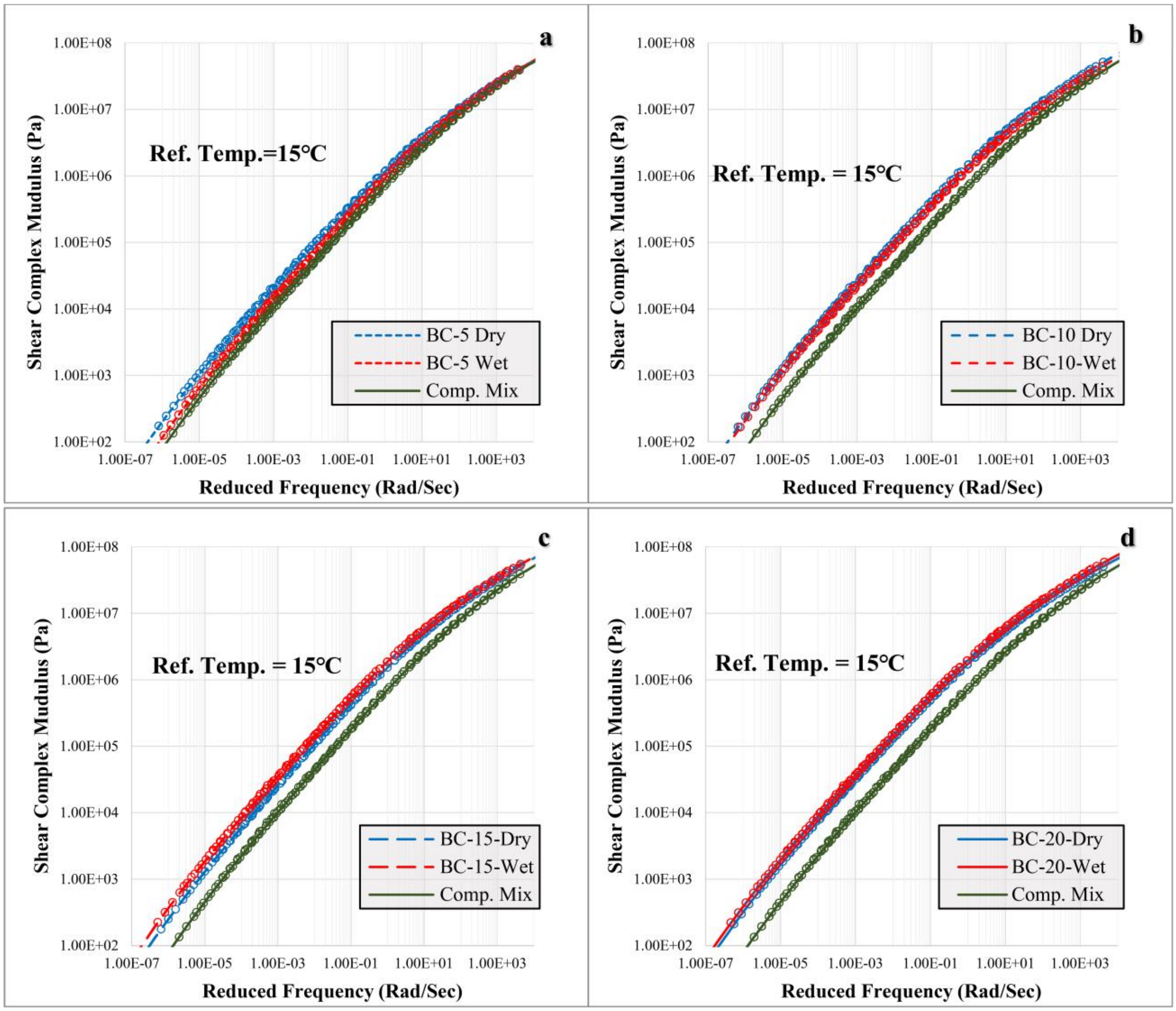


Figure 6-1 Shear Complex Modulus Master Curves For Recovered Asphalt Cement Samples After (A) 5 Cycles, (B) 10 Cycles, (C) 15 Cycles, And (D) 20 Cycles. In All These Graphs the Shear Complex Modulus Master Curve for Asphalt Cement Recovered from Unconditioned Compacted Mix Is Presented as Benchmark

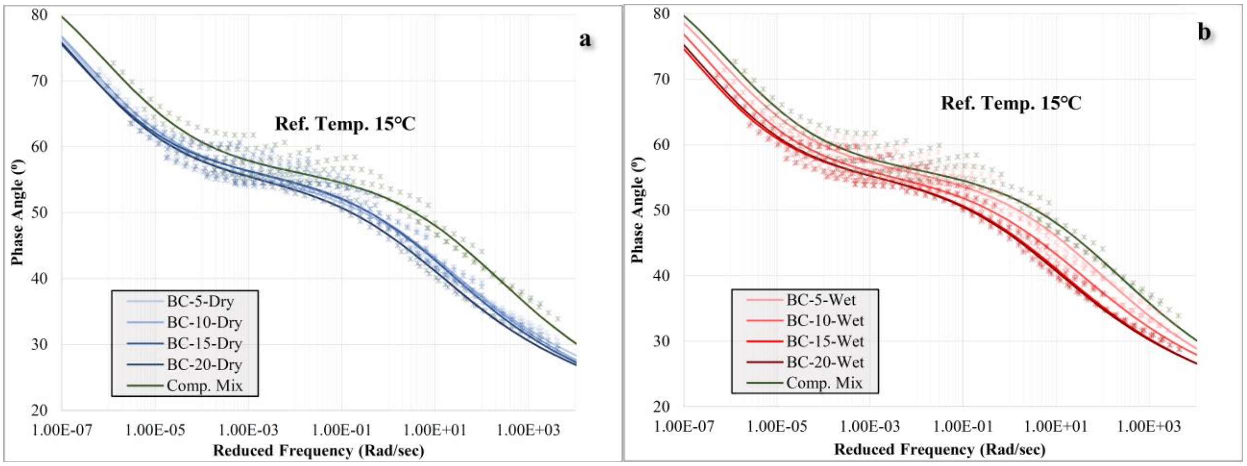


Figure 6-2 **Phase Angle Master Curves for Recovered Asphalt Cement Samples after (a) Dry Procedure, (b) Wet Procedure. Phase Angle Master Curve for the Asphalt Cement Recovered Unconditioned Compacted Mix is Presented as Benchmark**

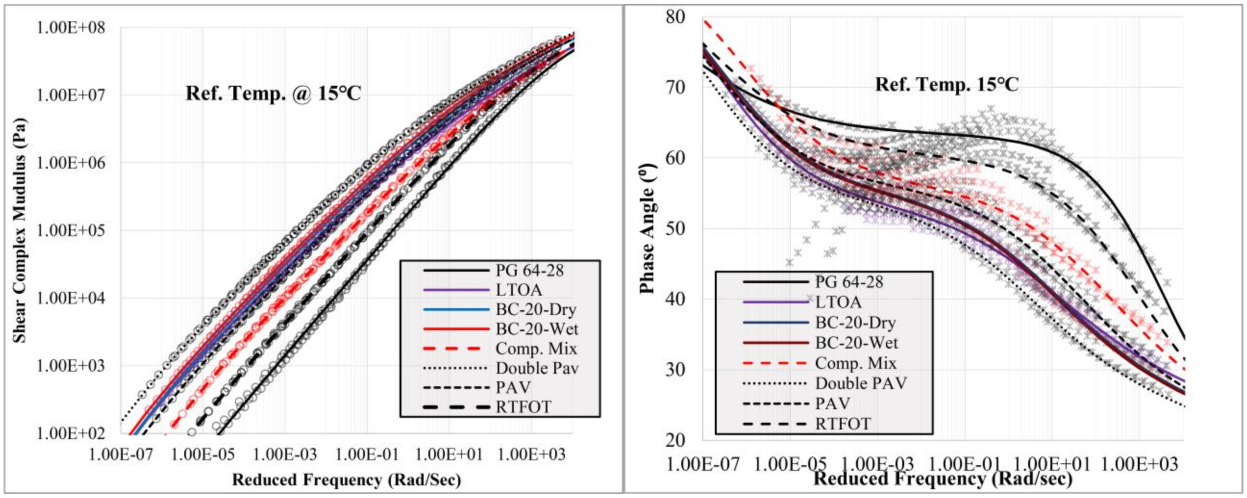


Figure 6-3 **Asphalt Cement Complex Shear Modulus and Phase Angle Master Curves of Various Laboratory Age Conditioning Procedures on Asphalt Mix and Asphalt Cement**

Temperature sensitivity analysis was performed using the slope of time-temperature superposition shift-factors versus temperature (*Log* a_T vs. Temp.). This is based on the shift-factors obtained from calibrating the 2S2P1D model on the results from frequency sweep test results using Arrhenius law for TTS shift-factors. Figure 6-4 shows the temperature sensitivity of rheological parameters (TSRP) curves for different conditioning procedures. As can be seen in these graphs, age conditioning caused an increase in temperature sensitivity of asphalt cement, meaning the faster pace of rheological changes at all measured temperature range. As the results for complex modulus and phase angle master curves, during dry conditioning, TSRP shows an initial spurt and almost stops increasing after ten cycles, while in wet process TSRP shows more increase as age conditioning continues. Regarding the age conditioning procedures on asphalt cement, results of the TSRP analysis shows a much lower increase in temperature sensitivity resulted from the short-term age conditioning on asphalt cement through the RTFOT procedure comparing to the asphalt cement recovered from the freshly compacted mix. This is in agreement with the complex modulus and phase angle master curve observations.

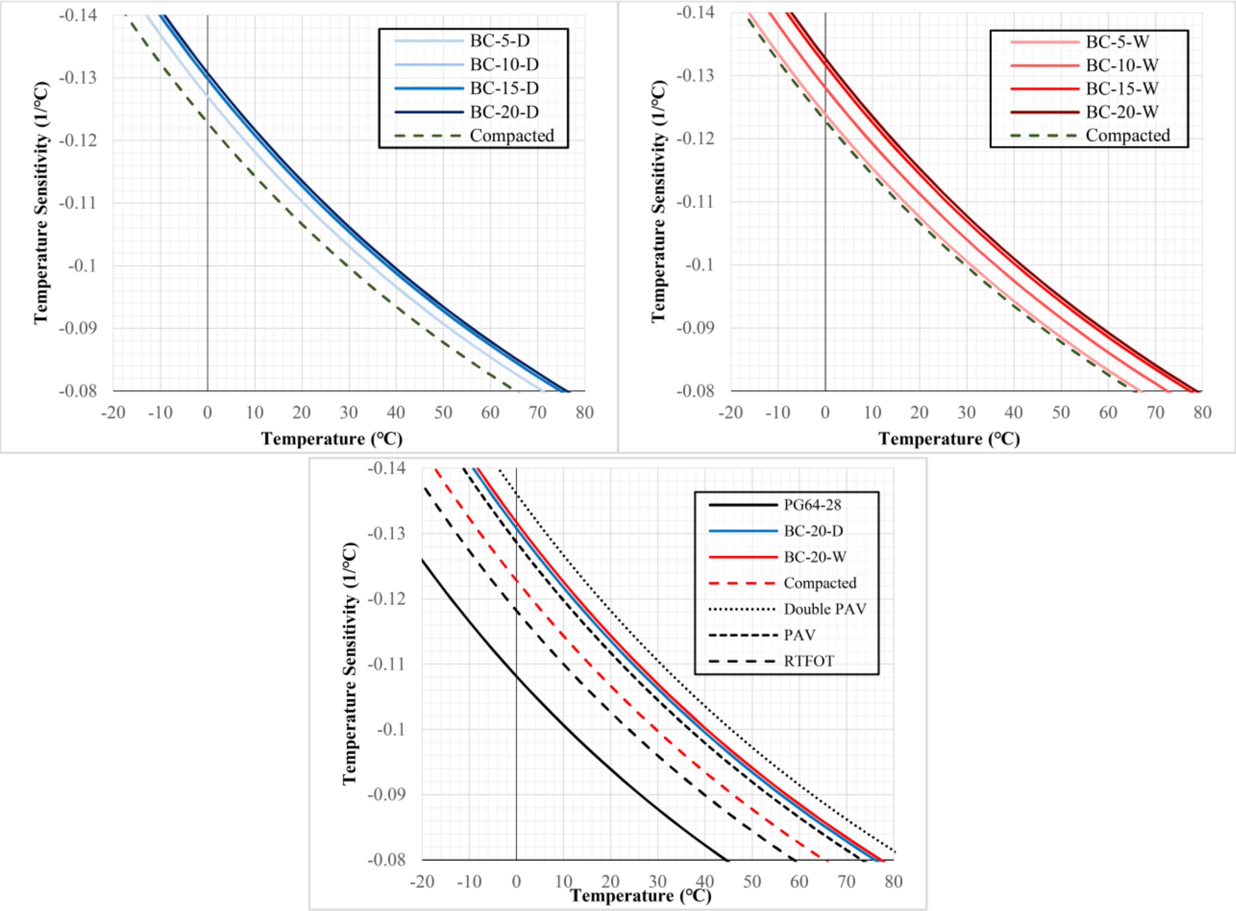


Figure 6-4 Temperature Sensitivity of Rheological Parameters (TSRP) for Asphalt Cement Samples Recovered from Unconditioned and Conditioned Samples

Cross-Over temperature, or the temperature at which the phase angle passes *45⁰* and the material changes from a viscoelastic solid to a viscoelastic liquid, was calculated for the reference frequency of 10 Rad/s for all samples. Figure 6-5 shows the evolution of Cross-Over temperature by the number of conditioning cycles for both dry and wet processes using the bespoke chamber.

This graph confirms the previous results by showing how wet procedure was able to allow age conditioning to be more effective after the first ten conditioning cycles.

Comparison of the cross-over temperature of the RTFOT age sample with the one for the sample recovered from the freshly compacted samples shows insufficient ageing level achieved by the RTFOT procedure to represent short-term ageing in real conditions. From the other hand, RTFOT plus PAV is also not harsh enough on asphalt cement comparing to asphalt mix long-term age conditioning procedures.

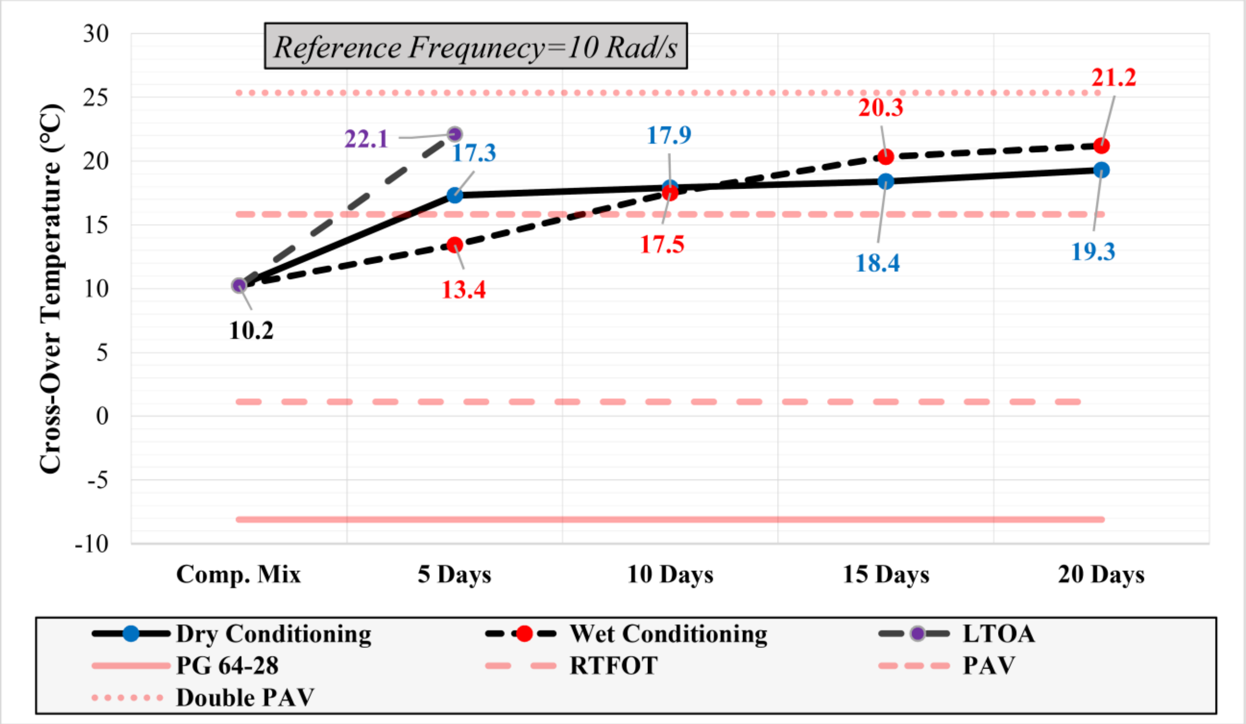


Figure 6-5 Cross-Over Temperature Graph for Asphalt Cement Recovered from Dry and Wet Conditioning Procedures

Linear Amplitude Sweep test (LAS) was also performed on all recovered asphalt cement samples at *22℃* and the results were analyzed using the Viscoelastic Continuum Damage (VECD) model to calculate the number of loading cycles at different strain levels to reach to 35% drop in Complex modulus (N_f). Figure 6-6 shows the results of this analysis for *2.5%* and *5.0%* strain levels. For both strain levels, the same trend is observable. During the first five conditioning cycles, the samples experience more severe changes by dry conditioning, while the wet conditioning allows the changes to continue with a higher pace for the rest of the cycles.

Results of the LAS test also verifies the previous observations regarding the insufficiency of the RTFOT procedure to simulate the short-term ageing as it happens in real conditions. The PAV has affected the fatigue life of asphalt cement (based on LAS test results) comparatively close to AASHTO R30 LTOA procedure while the harshest procedure was the wet solar radiation (bespoke chamber) conditioning.

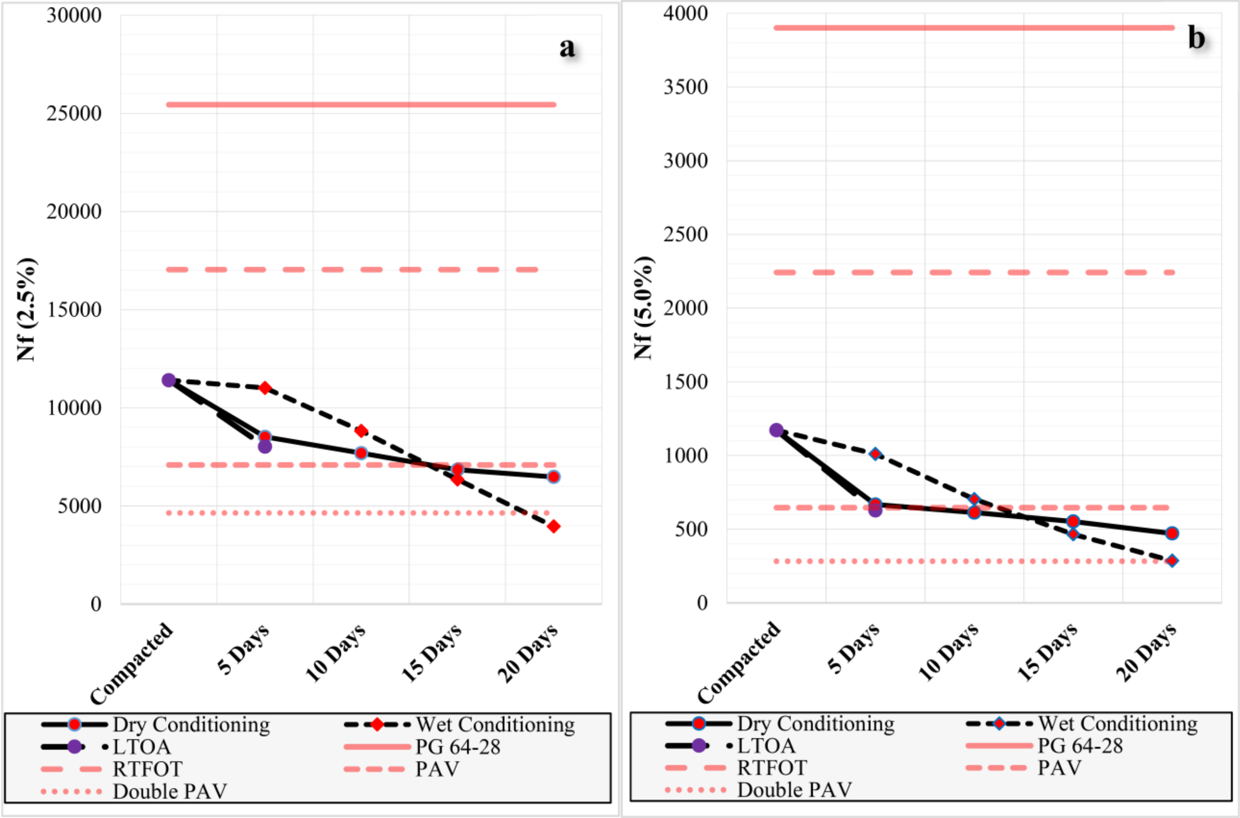


Figure 6-6 Number of Load Cycles to Failure (35% Loss of Modulus) at (a) 2.5% and (b) 5.0% Strain Levels

6.3.2 FT-IR Analysis

Using Equation 3-1Equation 3-2Equation 3-3 the Carbonyl and Sulfoxide Indices were calculated as well as the Carbonyl to Sulfoxide ratio (Figure 6-7). Following the Carbonyl index changes, all conditioning procedures increased Carbonyl functional groups concentration. The LTOA (AASHTO R30) procedure resulted in higher Carbonyl production, which is mainly a result of conditioning at a higher temperature (*85℃*). Sulfoxide groups formation followed a different trend from that of the Carbonyl groups. Wet processing caused the highest Sulfoxide formation comparing to dry conditioning and the extended heating conditioning used in the LTOA procedure.

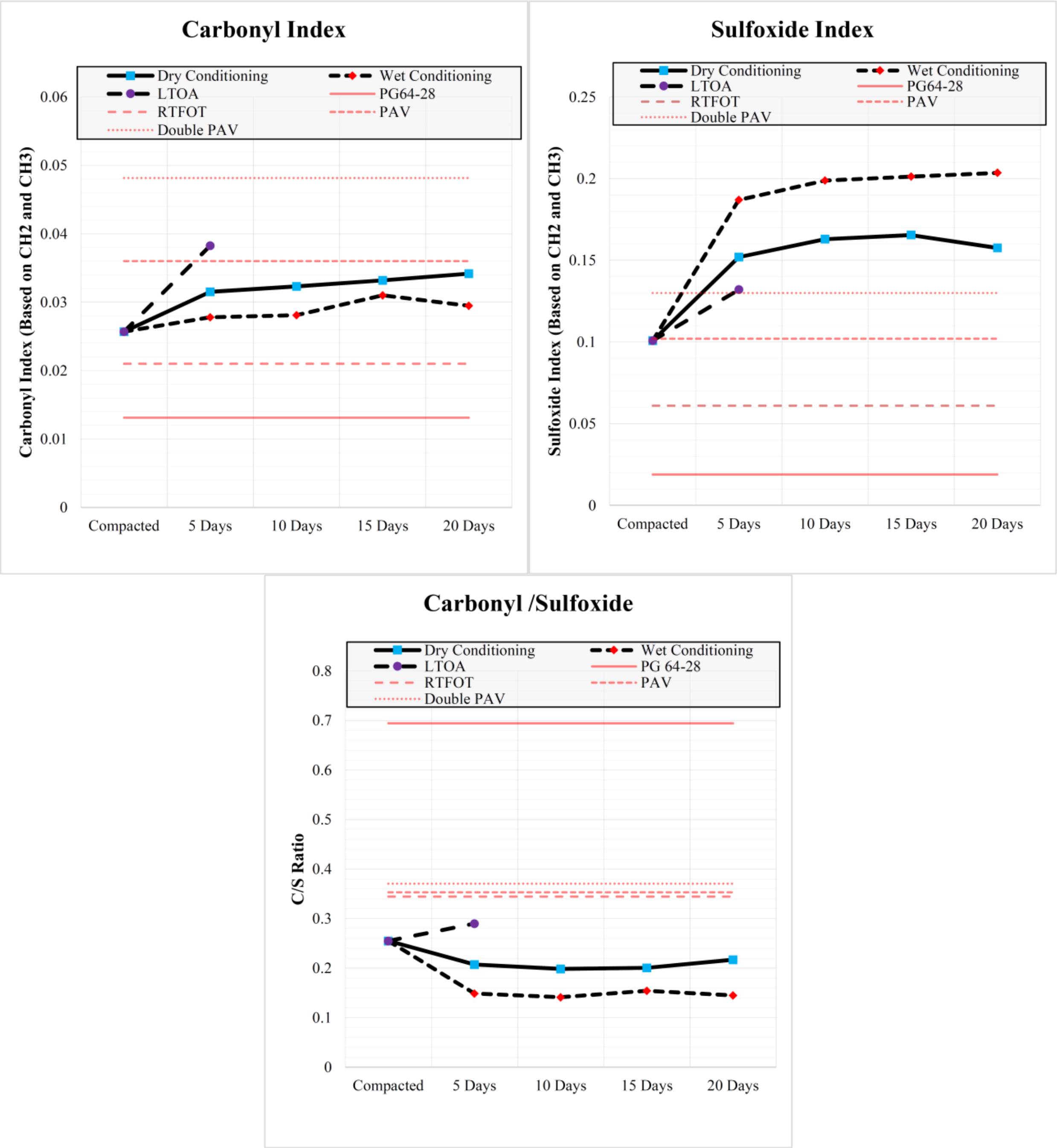


Figure 6-7 Results of Quantitative FT-IR Spectroscopy for Asphalt Cement Samples Recovered from Unconditioned and Conditioned Asphalt Mix Samples Including Dry and Wet Processes in the Bespoke Chamber and LTOA (AASHTO R30)

Comparing the Carbonyl to Sulfoxide ratio for these three procedures can shed more light into the functional groups formation during age-conditioning, as using excessively high (*85℃*) temperatures for laboratory conditioning provides a more suitable environment for Carbonyl formation, thus tends to increase the Carbonyl/Sulfoxide ratio. This can also be due to the low stability of Sulfoxide groups at high temperatures and their degradation. Based on these observations, one could conclude that Wet and Dry conditioning procedures are closer to real-life age hardening, as they have been performed at lower, and more realistic temperatures.

The carbonyl index growth for samples conditioned by the asphalt cement conditioning procedures (RTFOT, PAV, and double PAV) are following almost the same pattern as it was observed in rheological analysis, comparing to samples recovered from aged mixes. From the other side, while the sulfoxide index is still increasing by harshening the age conditioning (from RTFOT to PAV and double PAV), it reaches lower values compared to the recovered samples. This difference is also observable in the carbonyl/sulfoxide ratio, where its values do not change considerably by harshening the conditioning procedure and is also considerably different from what observed for recovered samples. This is a sign of the difference in the chemistry of changes happened during asphalt cement age conditioning and asphalt mix ageing procedures.

6.3.3 Asphalt Mix Rheology

To evaluate the evolution of the rheological properties of asphalt mixes in "Dry" and "Wet" conditioning in the bespoke chamber, complex modulus and phase angle master curves, as well as loss and storage moduli master curves (Figure 6-8), were developed for different number of cycles (5, 10, 15, and 20 days). For "Dry" cycles, rheological changes of the mix were noticeably slowed down after 5 cycles of conditioning meaning that most of the changes happened in the mix during the first few cycles and giving more time for "Dry" conditioning couldn't effectively increase the age hardening in the mix (Figure 6-8-a and b). The increase in the magnitude of the complex modulus for samples aged for a various number of cycles in "Dry" conditioning procedure is almost equal to LTOA procedure, while phase angle master curves show more reduction in its maximum value (the elastic return point) using "Dry" conditioning procedure. The elastic return location is also changed considerably using "Dry" cycles, comparing to the LTOA procedure which did not change the horizontal location (frequency) of the elastic return point, using solar radiation conditioning at a lower temperature (Dry) caused an elastic return to happen at lower frequencies (higher temperatures).

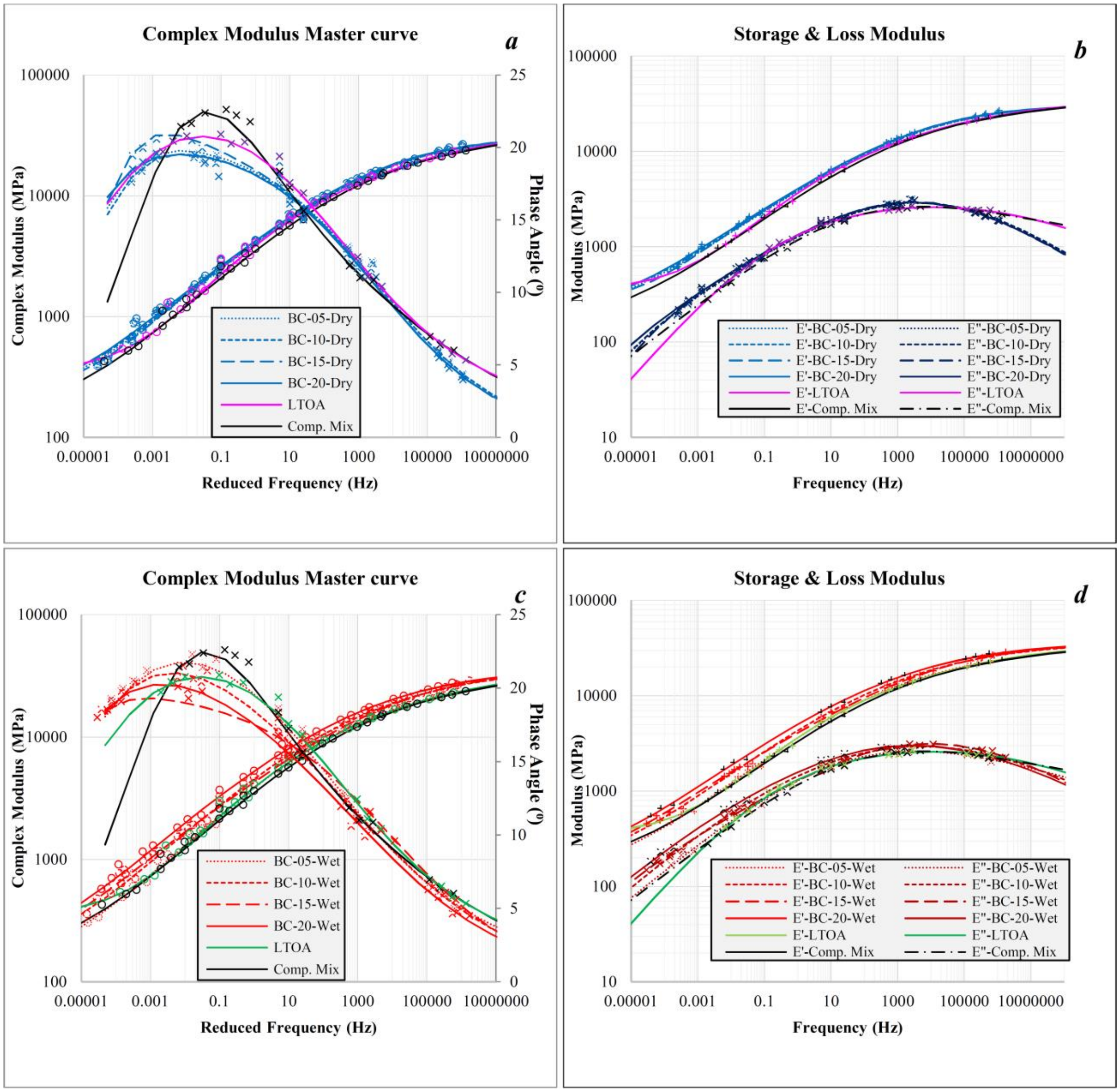


Figure 6-8 Modulus (Complex, Loss, and Storage Moduli) and Phase Angle Master Curves for Asphalt Mix Samples Before and After Various Conditioning Procedures (LTOA, BC Dry, and BC Wet)

Despite "Dry" conditioning, rheological changes continue with conditioning cycles in "Wet" solar radiation conditioning procedure, showing a considerable increase in complex modulus value and a decrease in phase angle (Figure 6-8-c). This observation shows that coupling moisture conditioning with solar radiation and heat can alter age hardening in asphalt mix samples. Due to the nature of moisture conditioning in this research, which included water spray and slight brushing of the mix samples, this difference can be attributed to the disappearance of the highly oxidized protective layer formed on the very surface of the samples as a result of water treatment. These observations for asphalt mix samples follow previous observations for the recovered asphalt cement, regarding the lower initial pace of changes for “Wet” process when compared to those of “Dry” one.

6.4 Summary and Conclusions

This research aimed to develop a conditioning procedure for laboratory simulating the long-term ageing in compacted asphalt mix samples using realistic conditioning parameters, including solar radiation, precipitation, and temperature. For this purpose and to assess the effect of each parameter, a temperature-controlled conditioning chamber was developed (bespoke chamber) and used to apply dry and wet conditioning cycles on cylindrical compacted mix samples for an extended exposure time. For “Wet” conditioning procedure, a protocol of water spray and brushing the surface of the samples was used to better simulate the washing effect during precipitation.

Rheological properties of the samples were then examined using compressive complex (dynamic) modulus testing, after which asphalt cement samples were extracted through centrifuge extraction and rotary evaporator method using Trichloroethylene solvent. The recovered asphalt cement was then subjected to the FT-IR spectroscopy to evaluate the kinetics of changes, as well as rheological analysis using frequency-sweep testing and linear amplitude sweep test (LAS). To develop complex modulus and phase angle master curves for asphalt cement and mix samples, the 2S2P1D model was used. A temperature sensitivity analysis was also used to evaluate the effect of each conditioning protocol on the properties of asphalt cement samples. The cross-over temperature was also employed to understand the optimum conditioning time.

Based on the results of this research, the following conclusions could be drawn:

- Conditioning temperature is an important factor which can alter both rheology and chemistry of age conditioning. This can be observed in the complex modulus and phase angle master curve of asphalt cement and mix as well as by following the changes in Carbonyl and Sulfoxide indices.
- Cross-Over temperature is a useful tool to examine the severity of ageing, but it must be considered that it does not give any information on the rheological changes in the full frequency (temperature) range. Thus, it should be used with care, especially when conditioning parameters are different from each other.

- Age conditioning of samples using only solar radiation can not simulate the severity of field ageing, as the process slows down significantly, mainly due to the formation of highly oxidized protective skin on the very surface.
- Coupling the water treatment with solar radiation will increase the capability of the conditioning system in order to simulate ageing in the asphalt mix samples, even though it would slow down the ageing at the first few cycles mainly due to the reduction in temperature.
- From the chemical point of view, conditioning samples using the combination of solar radiation and water treatment would result in higher sulfoxide index and relatively lower carbonyl index comparing to “Dry” cycles of solar radiation and LTOA method.
- The Carbonyl to Sulfoxide ratio can be used as a measure for kinetics of changes during oxidative ageing as it would illustrate the comparative formation of different functional groups as a result of oxidative ageing.
- The RTFOT age conditioning procedure seems to be insufficient to simulate short-term ageing in the field from both chemical and rheological points of views. The complex shear modulus and phase angle master curve of the RTFOT aged samples falls between the one from the original asphalt and the one recovered from the fresh compacted mix.
- Base on the FT-IR carbonyl and sulfoxide indices and the ration between them, the chemistry of changes during asphalt cement conditioning procedures (RTFOT, PAV, and double PAV) seems to follow a different path than what happens in mix age-conditioning procedures.

CHAPTER 7: LABORATORY SIMULATION OF THE IMPACT OF SOLAR RADIATION AND MOISTURE ON LONG-TERM AGE CONDITIONING OF ASPHALT MIXES

This chapter is based on the following published article in the Journal of Road Materials and Pavement Design. Azimi Alamdary Y, Singh S, Baaj H. (2019). Laboratory Simulation of the Impact of Solar Radiation and Moisture on Long-Term Age Conditioning of Asphalt Mixes. DOI: 10.1080/14680629.2019.1587496.

Summary

Ageing is a renowned phenomenon for pavement engineers that can substantially affect the durability and long-term performance of flexible pavements. Several factors affect the mechanism of age-related changes, including asphalt cement's chemical composition, mix properties, and environmental conditions. Most of the laboratory accelerated age hardening procedures are trying to simplify conditioning by considering heat as the main affecting factor and neglecting the others, such as humidity, precipitation, and solar radiation. This research aims to examine the validity of such an assumption and evaluate the effect of photo-oxidation, moisture and precipitation on the chemical and rheological properties of the asphalt cement and mix.

In this research, a plant produced asphalt mix was selected and subjected to four different age conditioning procedures including Long-Term Oven Ageing procedure (AASHTO R30), Atlas® Weather-O-Meter™, and using a bespoke chamber by applying dry and wet cycles of solar radiation and water conditioning. After running the Complex Modulus test on unconditioned and conditioned asphalt mix samples, asphalt cement was recovered and subjected to chemical and rheological analysis. The 2S2P1D model was employed to develop Complex Modulus and Phase Angle master curves. Results of this research showed that concerning chemical changes, extended heating at excessively high temperatures would result in different chemical products of oxidation as compared to solar radiation technique in terms of Carbonyl and Sulfoxide Indices. Moreover, it was observed that the extended heating procedure resulted in less stiffening at the low-temperature range in comparison with solar radiation. From the results of this research, it can also be concluded that water plays a vital role in the age conditioning procedure using solar radiation.

7.1 Introduction

Asphalt cement found its application in the road industry almost by chance and found its way to be one of the most crucial components of pavements all around the world [24]. Interesting mechanical properties such as liquid behaviour at high temperatures, strong adhesion to granular materials, waterproofing, and the ability to accommodate certain levels of imposed thermal strains made it an attractive construction material [11]. As an organic binder, chemical composition and mechanical properties of asphalt cement change gradually over time in a process known as ageing [135]. However, the extent and pace of changes will heavily depend on the chemical composition and weathering conditions. Several mechanisms were attributed to ageing in asphalt cement, while oxidation and volatilization of lighter oils are known to be the main ones [44].

Several laboratory age conditioning procedures were developed to simulate age conditioning on asphalt cement and mixes to enable designers to acknowledge age-related changes in mechanical properties [56]. While ageing happens mainly just in the binder, it is essential to run laboratory age conditioning on asphalt mixes [90]. Most of the efforts to simulate ageing were focused on the binder side while few techniques were developed for mixes, most of which use extended heating procedures with or without pressurized oxidation or gas flow through samples. The use of highly oxidative gases (a combination of Ozone and Nitrogen Oxides proved to be effective and helped to run conditioning at more realistic temperatures [97], [98]. Among all available techniques short-term oven ageing or STOA (four hours at compaction temperature) and long-term oven ageing or LTOA procedures (120 hours at 85ºC), both recommended by AASHTO R30 gained more popularity in North American pavement industry mainly due to the simplicity of the process [136].

The rate and kinetics of oxidative ageing are heavily dependent on the chemical composition of the asphalt cement, weathering conditions and mix volumetric properties [53]. Photo-oxidation is a known phenomenon in organic materials which had proved to have an accelerating effect on ageing by providing the required initial energy of oxidation process resulting in more cross-linked structure and polarized environment [137]. Despite the awareness of such effect, many age conditioning protocols did not consider photo-oxidation as the general assumption was to neglect photo-oxidation due to the surficial effect on the top few microns of asphalt cement. Precipitation can alter this assumption as parts of photo-oxidation products are water soluble and can be washed into the pores and expose new surfaces to high energy containing beams of solar radiation [17], [138]. Water can also participate in oxidative ageing by activating susceptible minerals (such as pyrite and pyrrhotite) which exist in some sources of aggregate or by acting as a catalyst in the oxidation process [52], [128].

Asphalt is a viscoelastic material of which the mechanical and rheological properties are heavily dependent on the chemical composition. Any changes in this chemical composition due to oxidative reactions will hence consequently lead to changes in rheological properties [139]. For an ideal laboratory age conditioning procedure, it is crucial to apply realistic conditions to mimic ageing as it happens in the field. Using excessively high temperatures to reduce conditioning time can alter chemical reactions and functional groups formation, and thus unrealistic rheological changes as well [53].

7.2 The motivation for this Research

All aforementioned complexities in age hardening of the asphalt cement process show the importance of having a reliable laboratory age conditioning procedure to provide representative asphalt mix sample for performance testing and predicting the durability of mixes. This research aimed to test the validity of the primary assumption of current state-of-practice procedure of long-term oven ageing (LTOA) for simulating long-term field ageing of asphalt mixes, which neglects moisture and solar radiation in the conditioning and uses excessively high temperatures to achieve acceleration in ageing.

7.3 Materials and Analysis Tools

The tested mix is a Superpave mix with a Nominal Maximum Aggregate Size of 12.5 mm. The mix designation is SP12.5 FC2, based on the Ontario Provincial Standard Specification (OPSS.PROV 1003), where FC stands for Friction Course and the 2 indicates that both coarse and fine aggregates are obtained from crushed bedrock materials to ensure good skid resistance. The mix does not contain RAP (Reclaimed Asphalt Pavement), and the binder is a Polymer Modified Asphalt Cement PG64-28. As the mix was plant-produced, no short-term conditioning procedures were applied to the mix. Four different long-term age conditioning procedures were selected. All compacted mix samples were tested for complex modulus before and after conditioning. Results of the complex modulus tests were then analyzed using the 2S2P1D model to develop complex modulus and phase angle master curves. Asphalt samples were recovered from the mix at different steps of ageing through centrifuge extraction and Rotavapor recovery procedure for chemical and rheological analysis. To minimize the effect of extraction and recovery procedures on the analysis, virgin asphalt cement was dissolved in the solvent (Trichloroethylene) and recovered. Strain sweep test was performed on all samples to determine the linear viscoelastic region of samples at different temperatures. Strain-controlled frequency sweep test was then performed on asphalt cement samples using Dynamic Shear Rheometer (DSR) within the linear viscoelastic range (LVE), and results were also analyzed using the 2S2P1D model. Cross-over temperature was also determined for all samples as a measure of age hardening by determining the Cross-Over frequency from the 2S2P1D model and converting it to the equivalent temperature at reference frequency (10 Rad/s) using WLF (William-Landel-Ferry) equation for Time-Temperature Superposition Principle. Carbonyl and Sulfoxide ratios from Fourier-Transform Infrared Spectroscopy (FT-IR) were used to evaluate the chemical changes for each conditioning procedure. Carbonyl to Sulfoxide ratio was also determined as a measure of the kinetics of changes. Time-temperature superposition (TTS) shift factors were also used to determine the temperature sensitivity of rheological parameters of both mix and binder samples.

7.3.1 Sample preparation

Compaction temperature was determined as 138ºC based on supplier’s recommendation. Compacted samples were then produced using Superpave Gyratory Compactor (SGC) following AASHTO PP60. A uniform level of compaction with targeted air void content of 7±1 percent was selected to prepare cylindrical samples (15 cm in diameter and 18 cm in height). The resulted compacted samples were then cored and cut into desired dimensions as required for Complex Modulus testing (10 cm in diameter and 15 cm in height).

Four different conditioning procedures were selected for long-term age conditioning of compacted samples (three replicated samples for each conditioning procedure). The first procedure was long-term oven ageing (LTOA) as recommended by AASHTO R30. This procedure was used as a control procedure as it only considers the effect of temperature. In this procedure, compacted samples were placed in an oven at 85ºC for 120 hours (5 days).

The second procedure was the use of consecutive cycles of UV radiation and water spray. For this purpose, an Atlas Weather-O-Meter Ci35A was utilized. The conditioning chamber was originally designed to condition 2D samples such as paints and coatings with a rotating frame to ensure uniform exposure. To be able to condition compacted mix samples using this machine, some modifications were done on the rack to be able to place four mix samples at a time with the same distance from the light source to ensure that all mixes experience similar conditions. Sample rotation was also performed to make sure that samples were evenly conditioned.

For running the third and fourth procedures, an environmental chamber was developed for this specific research, capable of applying intense dry and wet cycles of solar radiation while controlling the temperature. This chamber was equipped with three full spectrum lamps with a combined power output of approximately 1800 Watts. An air-cooling system was provided for the chamber to prevent excessive heat due to intense solar radiation. The chamber was equipped with temperature and radiation sensors alongside with data logger to collect information regarding the internal temperature of samples, surface temperature, incoming solar and UV radiation in five-minute intervals. Wet cycles were defined as five days of continuous radiation (1800 Watts) at 65±3 ºC and daily water spray for 5 minutes. Dry cycles were almost the same with no water spray on the samples. Specification of the applied procedure is described in Table 3-3.

7.3.2 Laboratory Testing

Samples were then subjected to Complex (Dynamic) Modulus testing (cyclic compressive), before and after each conditioning procedure, under frequency sweep (from 0.1 to 25 Hz.) mode at a wide range of temperatures ranging from -10ºC to 54ºC (Table 3-8). After collecting data from asphalt mix samples, asphalt cement was recovered from samples through Centrifuge extraction (ASTM D2172) and Rotary Evaporator (ASTM D5404) recovery procedure. For rheological analysis of recovered asphalt cement, Strain Sweep Tests were conducted on samples at different temperatures to determine the linear viscoelastic region (LVE). Frequency sweep test was then performed on all recovered samples within the LVE region at different temperatures and a wide range of frequencies using Dynamic Shear Rheometer (DSR) (8mm plates for temperatures below 35 and 25mm for higher temperatures) (Table 3-9).

The 2S2P1D model was then used to develop complex modulus and phase angle master curves for both asphalt mixes and asphalt cement samples. To calibrate 2S2P1D model parameters and

TTS Shift-Factors, root-mean-square error in the interquartile range (RMSE-IQR) of the total deviations on loss and storage modulus was minimized. The 2S2P1D is an analogical model used to describe the rheological behaviour of viscoelastic materials based on a simple combination of physical elements [25]. The 2S2P1D model is using the Complex modulus as a complex number in the calculation; thus both phase angle and the magnitude of complex modulus are considered for model calibration. A combination of spring, dashpot, and parabolic elements are used to describe the general behaviour of both asphalt mixtures and asphalt cement (Figure 2-21).

Semi-quantitative Infrared spectroscopy analysis was also performed on all recovered asphalt cement samples to follow the Carbonyl and Sulfoxide functional groups, the formation of which is strongly correlated with oxidative age hardening of asphalt cement [103]. Carbonyl and Sulfoxide indices were calculated based on CH2 and CH3 peaks (Equation 3-1Equation 3-2). Sulfoxide functional groups are temperature sensitive and tend to decompose at excessively high temperatures, which are usually used in extended heating procedures. Therefore, in this research, Sulfoxide index and the ratio between Sulfoxide and Carbonyl indices (Equation 3-3) were selected to follow the kinetics of chemical changes due to oxidative ageing.

Equation 3-1

$$\boldsymbol{Carbonyl\ Index\ (CI)} = \frac{\boldsymbol{A_{carbonyl(1680-1750)}}}{\boldsymbol{A_{CH2(1410-1495)} + A_{CH3(1360-1390)}}}$$

Equation 3-2

$$\boldsymbol{Sulfoxide\ Index\ (SI)} = \frac{\boldsymbol{A_{sulfoxide(980-1060)}}}{\boldsymbol{A_{CH2(1410-1495)} + A_{CH3(1360-1390)}}}$$

Equation 3-3

$$Carbonyl\ to\ Sulfoxide\ Ratio\ \left({}^{C}\!/_{A}\right) = \frac{A_{carbonyl(1680-1750)}}{A_{sulfoxide(980-1060)}}$$

Where A is the area of each spectral band.

7.4 Results and Discussion

7.4.1 Asphalt Cement Rheology

Figure 7-1 shows shear complex modulus master curves, developed for virgin asphalt cement and samples recovered from the loose mix (before compaction), unconditioned compacted mix

(Comp. Mix) and conditioned samples. Although the general positions of all laboratory aged samples are very close to each other (comparing the curves for virgin asphalt and samples extracted from loose and compacted mixes), it can be seen in Figure 7-1-a that at low loading frequencies (high temperatures) complex modulus values of samples extracted from extended heating procedure (LTOA) are located between the sample aged using Atlas Weather-O-Meter and those from Solar conditioning chamber (Bespoke Chamber BC-20- Dry and Wet), while at higher frequencies (lower temperatures) LTOA samples are softer compared to the other laboratory methods.

Comparing the dynamic modulus results from samples conditioned under solar radiation (Dry and Wet conditioning procedures in Solar conditioning chamber), it can be observed that at all loading frequency levels, wet conditioned samples reached slightly higher stiffness values comparing to dry conditioned samples.

This type of twofold behaviour in the sample aged through LTOA is observable in the phase angle master curves in Figure 7-2. At high loading frequencies, or at low temperatures, LTOA conditioned sample shows higher viscous behaviour (phase angle) which can be translated into better thermal cracking resistance properties on the asphalt cement side (Figure 7-2-c). On the other side of the frequency spectrum (Figure 7-2-b) which represents the high-temperature behaviour, LTOA aged sample shows slightly lower phase angle values which are more favourable regarding rutting resistance.

Cross-over temperature is a measure of age hardening that occurred in an asphalt sample. It describes the distinction between liquid and solid viscoelastic behaviours at the selected loading frequency, which is usually considered as 10 Rad/s [140]. The red line in Fig. 3-b shows the position of critical phase angle ($\delta=45^{o}$) which was used to determine the Cross-Over frequency at the reference temperature and subsequently Cross-Over Temperature using Time-Temperature Superposition Principle (WLF equation). Figure 7-3 shows the cross-over temperatures for conditioned and unconditioned samples. As it was expected, age conditioning increases the cross-over temperature. Among all conditioned samples, LTOA aged samples do have the highest value. This looks to be in contradiction with previous results as it was expected that the extent of age hardening in this method is less than UV and Solar radiation techniques. Following the phase angle master curve, it is slightly after the cross-over temperature that the phase angle in samples aged through UV and Solar radiation starts to drop faster than in the LTOA conditioned sample. On the other side for samples aged through radiation techniques, slightly higher values are observed for the wet process of the solar radiation technique.

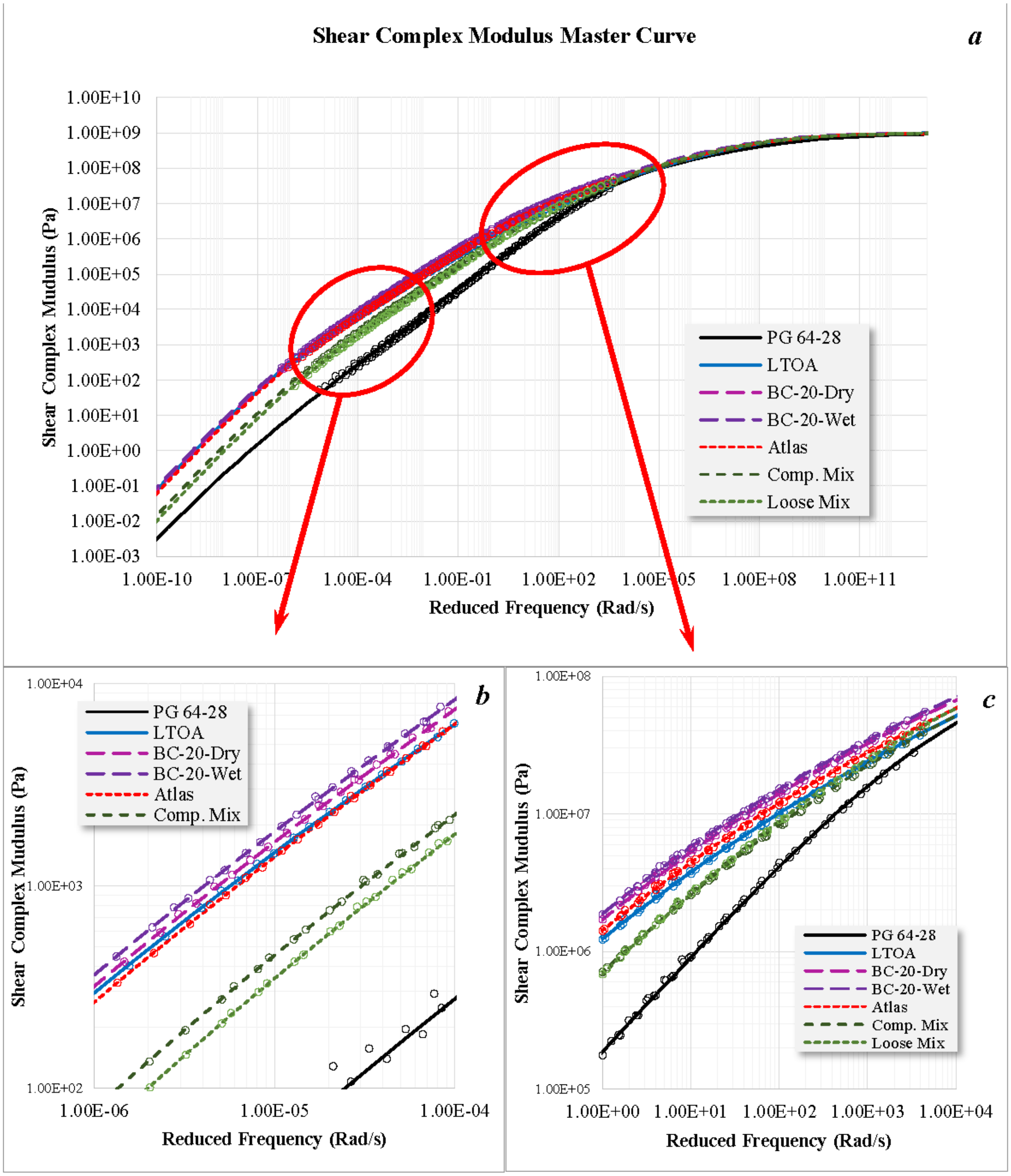


Figure 7-1 Complex Modulus of Asphalt Cement Samples Before and After Different Conditioning Procedures.

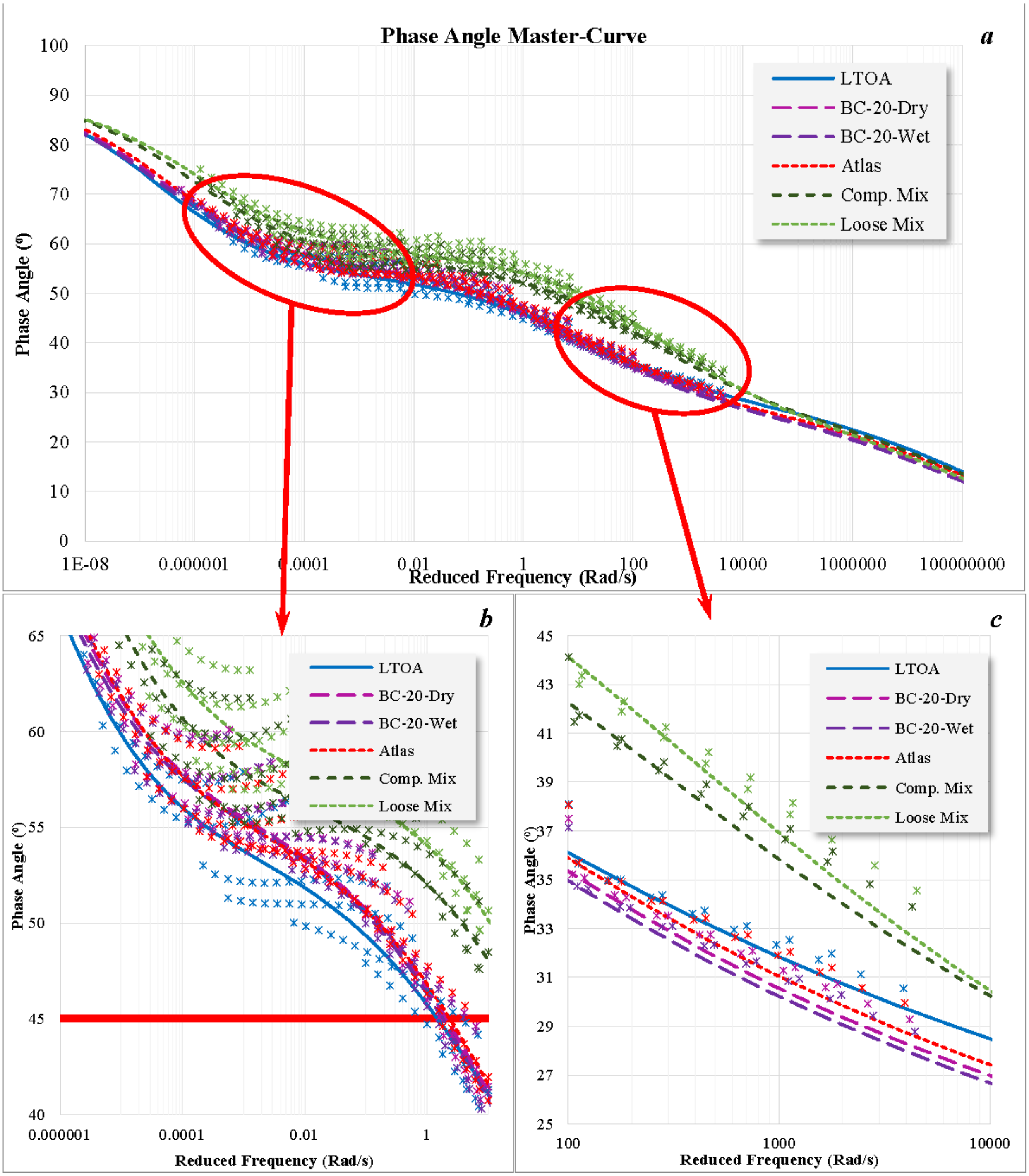


Figure 7-2 Phase Angle Master Curve of Asphalt Cement Samples Before and After Different Conditioning Procedures

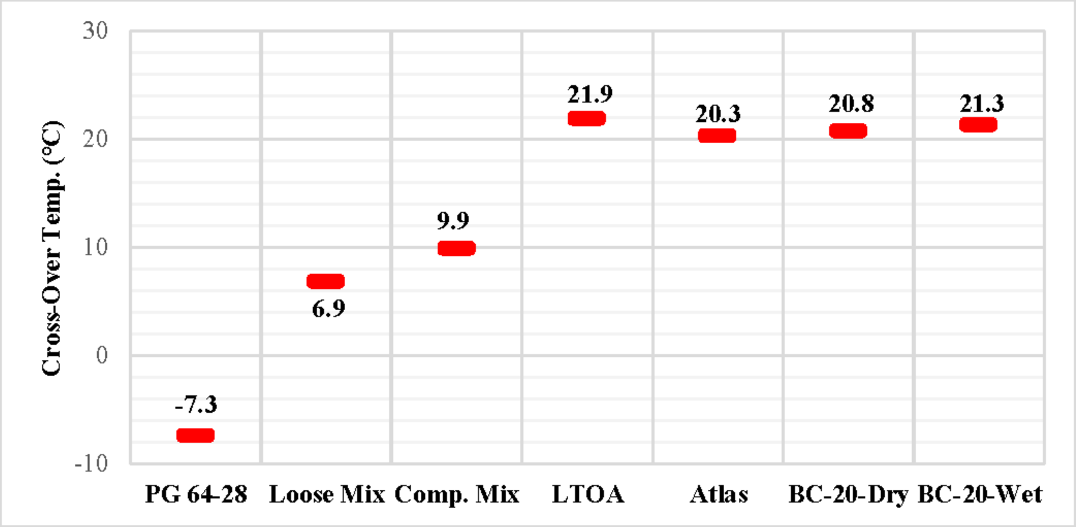


Figure 7-3 Cross-Over Temperature for Conditioned and Unconditioned Asphalt Cement Samples

7.4.2 Functional Groups Analysis

Functional groups analysis was performed on all samples (before and after conditioning) via Fourier Transform Infrared Spectroscopy. Carbonyl and Sulfoxide indices were then calculated based on CH2 and CH3 peaks. Figure 7-4 shows these indices and the ratio between them (Carbonyl over Sulfoxide). As it was expected, age-conditioning caused an increase in both Carbonyl and Sulfoxide indices comparing to unconditioned sample. However, the ratio between Carbonyl and Sulfoxide indices shows considerable reduction as age conditioning continues. The sample aged at Atlas Weather-O-Meter chamber under UV radiation reached to highest Carbonyl index when compared to the extended heating procedure while the Sulfoxide Index reached to same values in both methods. For samples aged through solar radiation (bespoke Solar radiation chamber) different trends were observed for change in both indices. While wet conditioned samples do have considerably lower Carbonyl index, the sulfoxide index in them is much higher than all other samples, resulting in much lower Carbonyl to Sulfoxide ratio.

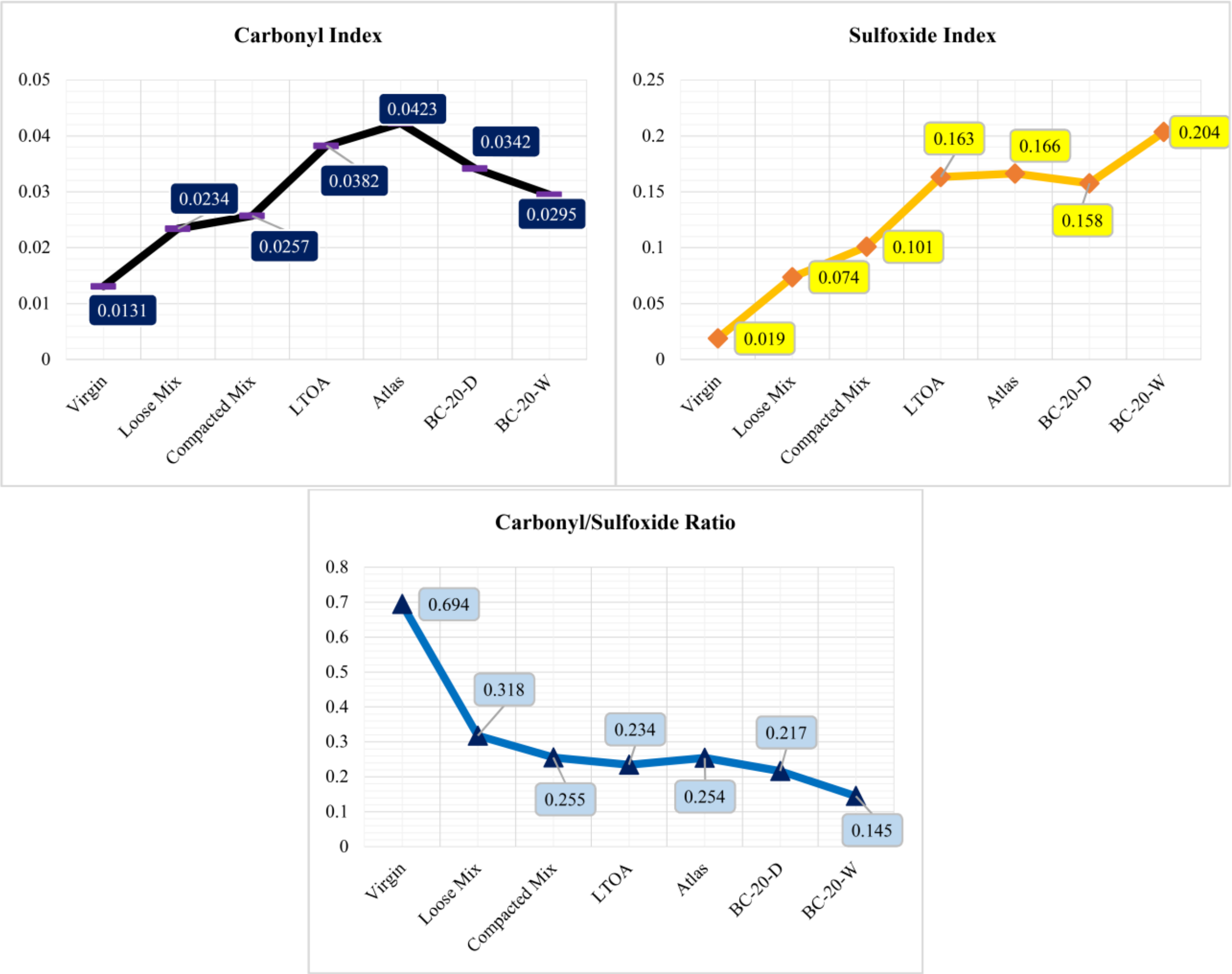


Figure 7-4 Carbonyl and Sulfoxide Indices for Conditioned and Unconditioned Samples

7.4.3 Asphalt Mix Rheology

The effect of laboratory age conditioning on the compacted mix samples can be observed through complex modulus and phase angle master curves (Figure 7-5.). All laboratory age conditioning procedures used in this research caused an increase in complex modulus at all frequencies comparing to Short-Term Aged samples (STOA), but this increase is not equal for all procedures. It was found that using the extended heating procedure (LTOA) causes fewer changes in complex modulus master curve in all loading frequencies, while conditioning using Atlas Weather-O-Meter caused more stiffness at lower frequencies (High-temperature range). For samples conditioned in the bespoke conditioning chamber, a uniform increase in the complex modulus values can be observed for all frequencies, where wet conditioning showed higher impact. By comparing the complex modulus master curves, it can be said that conditioning compacted asphalt mix samples in the bespoke chamber affected high and low-temperature properties almost equally, while Atlas Weather-O-Meter was harsher on high-temperature properties of mixes and less effective on the low-temperature properties.

For all conditioning procedures, phase angle master curves were shifted toward lower frequency levels (or higher temperature side) which is a sign of a reduction in viscous behaviour of asphalt cement in the mix. The main difference between the conditioning procedures is the phase angle value at the peak point. While samples conditioned in solar radiation chamber show a decreased peak value in phase angle master curves, LTOA conditioned samples show increased values for phase angle at the peak point. The increase in phase angle peak point value in LTOA conditioned sample looks to be due to change in mix volumetric properties as a result of excessively high temperature which causes a slight change in geometry of the sample under the sample weight.

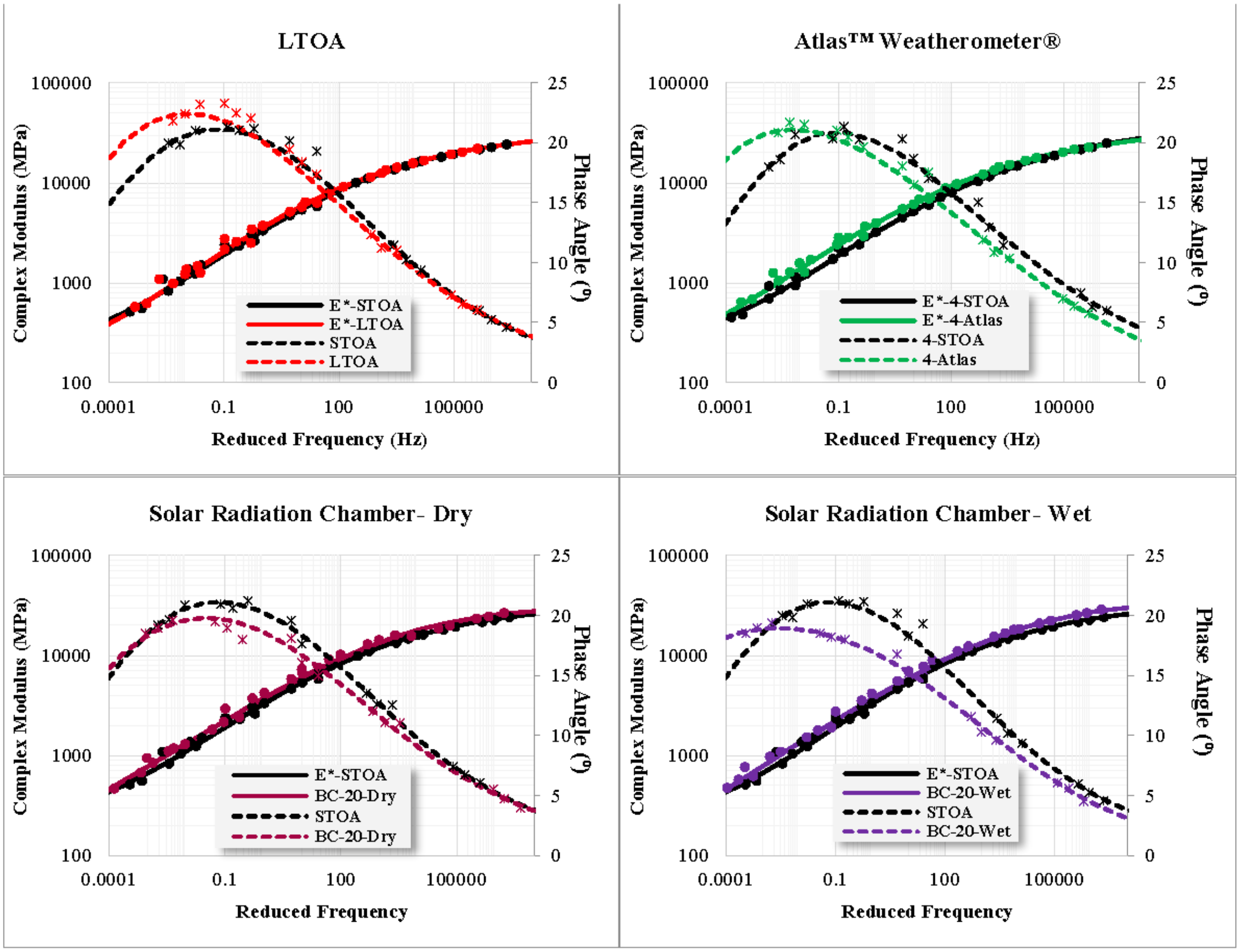


Figure 7-5 Complex Modulus and Phase Angle Master Curves for Different Conditioning Procedures

7.5 Conclusions

The main purpose of this research was to evaluate the effect of different weathering conditions on the age hardening process of compacted asphalt mix and the rheological and chemical changes on asphalt cement.

Asphalt cement rheology analysis using shear complex modulus and phase angle master curves showed that extended heating procedure results in almost equal stiffness at low-frequency levels (high temperatures) when compared to samples aged using UV and Solar radiation chambers, while lower complex modulus values were obtained at high frequencies (low temperatures). On the other side, samples aged through LTOA procedure exhibit lower phase angle values at lower frequencies (high temperatures) among all conditioning procedures, showing more elastic behaviour as a result of age conditioning, while at high frequencies (low temperatures) higher phase angles are observed in LTOA conditioned samples which is in favor for low-temperature crack resistance. From the rheological point of view, this is a sign of the difference in age-hardening mechanisms by applying different conditioning parameters. While using heat as the only conditioning parameter asphalt cement would reach to equal hardening (changes in complex modulus value) and more elastic behaviour (lower phase angle) when compared to conditioning at a lower temperature using solar radiation and moisture. At lower temperatures, they are comparatively softer (lower complex modulus) with more capability to accommodate thermal strains due to more viscous behaviour (having a higher phase angle). In more simple words, while the LTOA procedure is harsh at high temperatures, it is not rigorous enough on low-temperature properties of the samples.

Comparing wet and dry processes at solar radiation chamber showed that precipitation simulation does influence asphalt cement hardening by increasing complex modulus and decreasing phase angle at all tested frequencies. This effect can be attributed to the washout of the highly oxidized surface layer and the loss of the protective layer by water spray hence exposing further layers to solar radiation.

Chemical analysis of samples was done through semi-quantitative infrared spectroscopy to measure Carbonyl and Sulfoxide indices as well as the ratio between them (Carbonyl over Sulfoxide). All age conditioning procedures caused an increase in Carbonyl and Sulfoxide groups but not with the same proportion. The wet process of solar radiation resulted in less increase in Carbonyl group while the highest increase in Sulfoxide group was observed for this procedure. By comparing the Carbonyl to Sulfoxide ratio, it can be concluded that using wet solar radiation process resulted in lower ratios which shows considerably different chemical path comparing to another process.

Complex modulus and phase angle master curves developed for conditioned and unconditioned compacted mixes are also in agreement with asphalt cement test results showing more increase in complex modulus values for the wet solar radiation process while lowest changes were reported for the extended heating procedure.

The conclusions of this research could be summarized as follow:

- When compared to solar radiation age conditioning, extended heating procedures are lenient on low-temperature properties of asphalt cement resulting in less stiff with more viscous behaviour at high frequencies or low temperatures.
- At similar solar radiation and temperature conditioning, water spray can make age conditioning harsher possibly by dissolving the highly oxidized protective layer from the very surface of the samples and exposing more asphalt cement to age conditioning. This can be observed by comparing the functional group's indices and the shear complex modulus and phase angle master curves.
- Although cross-over temperature has been identified as a measure of age hardening in asphalt cement, it gives a biased interpretation when different age conditioning procedures are applied. A full range frequency (temperature) behaviour master curve should be used for comparing age conditioning procedures.
- Using temperature as the only age conditioning parameter may result in entirely different chemical and rheological changes in the sample. While it can be harsh on high-temperature properties, it is less rigorous on low-temperature properties as it should be. This can cause overestimation of thermal resistance.
- To better simulate the chemical and rheological changes that happen in real life ageing of asphalt cement and its subsequent impact of the properties of asphalt mixes, more realistic temperature (close to high temperatures that pavement will experience) should be selected to avoid significant alteration of chemical processes. Using solar

radiation technique in association with water spraying off the samples seems to be an effective approach for laboratory conditioning of mix samples by using more realistic conditions. However, the similarity with real-life long-term age conditioning needs to be validated.

CHAPTER 8: CONCLUSIONS, RECOMMENDATIONS, AND FUTURE WORK

8.1 Overall Summary

Along with a comprehensive literature review on available asphalt cement and mix conditioning procedures, and chemical and rheological tools to evaluate age-related hardening in asphaltic materials, the effect of iron sulphide containing aggregates and their oxidation products on age hardening process of asphalt cement was assessed. Moreover, a laboratory procedure for long-term age conditioning of asphalt mixes were developed using a temperature-controlled bespoke solar radiation chamber.

Complex (dynamic) modulus testing was used in frequency sweep mode at a wide range of temperatures for rheological analysis of asphalt mix samples (complex, loss, and storage moduli master curves, phase angle master curves, Cole-Cole diagrams, and the black space diagram). To evaluate the effect of asphalt mix conditioning on the chemical and rheological properties of asphalt cement, centrifuge extraction and Rotavapor recovery procedures were conducted using a mixture of trichloroethylene and ethanol to minimize solvent related changes in the properties of recovered asphalt cement. Rheological properties of recovered asphalt cement were measured through running complex shear modulus measurements under frequency sweep mode as well as linear amplitude sweep test (LAS). The 2S2P1D analogical model was used to analyze frequency sweep test results and to develop master curves for both asphalt mix and recovered asphalt cement samples.

A temperature sensitivity parameter for rheological properties of viscoelastic materials was developed using various models for time-temperature superposition (TTS) shift-factors. This parameter was used to investigate the effect of different age conditioning protocols and various affecting factors on the thermal sensitivity of asphaltic materials as an innate property of the material.

Fourier transform infrared spectroscopy used to investigate the chemical changes in recovered asphalt cement samples to follow the changes in carbonyl and sulfoxide functional groups. To evaluate the effect of various parameters on the kinetics of changes, carbonyl to sulfoxide ratio was employed.

The following summarize chapters of this thesis.

Chapter 1: This chapter introduces this thesis starting by describing why it is important to simulate long-term ageing on laboratory samples, the importance of evaluating the susceptibility of asphalt pavement to age hardening, and how ageing affects the durability of pavement infrastructure. Contributions of this thesis and the organization of this thesis are also explained in this chapter.

Chapter 2: This chapter summarizes the literature on asphaltic materials ageing and rheological and chemical analysis tools to evaluate ageing. In the introduction to asphalt cement production, chemistry, and rheology is also included in this chapter to provide more insight information. Various existing age conditioning protocols to simulate short- and long-term ageing for both asphalt cement and asphalt mix samples are described.

Chapter 3: Methodology of this research explained in this chapter. The description of materials that have been used in this research (including aggregates, asphalt cement, and plant-mixed loose asphalt) have been presented in detail. Laboratory age conditioning procedures that have been used throughout this research was elucidated as well as laboratory tests. Analytical tools to assess the effect of tested parameters on the age hardening of asphaltic materials were also declared.

Chapter 4: This chapter explains the concept of temperature sensitivity of rheological parameters used throughout this research to evaluate the effect of various conditioning parameters on the behaviour of asphaltic materials. This chapter has been submitted to the journal of “Road Materials and Pavement Design” and is still under review. Time-temperature superposition shift-factors obtained during the 2S2P1D model calibration were used. Three different TTS models were fitted on these results including William-Landel-Ferry (WLF), Arrhenius, and the polynomial (quadratic) model that been used in the MEPDG software. Results of this study showed that different age conditioning procedures affect this parameter differently, and this parameter can be used to investigate the effect of ageing in a wide frequency (temperature) range.

Chapter 5: The effect of iron sulphide containing aggregates on the age hardening of asphalt mix and cement evaluated in this chapter. Three iron sulphide containing mixes were used in this study alongside with a control (containing only iron sulphide free aggregates). AASHTO R30 procedure found to be insufficient for activating iron sulphide compound of aggregates. Therefore, a specific conditioning procedure used to include two cycles of LTOA in between of which humidity conditioning was performed at room temperature. Results of this study showed that the age hardening process is affected by the existence of iron sulphide, specifically when existing in fines. It was also noticed that when age conditioning is combined with humidity conditioning, aggregates expansion causes crack initiation.

Chapter 6: This chapter presents the evolution of asphalt cement ageing by the time during the accelerated age conditioning using the bespoke solar radiation chamber through dry and wet processes. Compacted cylindrical samples (15 cm in height and 10 cm in diameter) subjected to up to 20 cycles (each cycle was 24 hours of solar radiation for dry cycles while 15 minutes of water treatment added to this process for wet cycles) of dry and wet conditioning. The primary purpose of doing this procedure was to evaluate the coupling effect of water treatment and solar radiation at elevated temperature (65ºC). Results of this study showed that at first few cycles, dry conditioning reaches to higher ageing levels (in terms of general stiffness) while the rate of age-related changes decreases significantly by the continuation of dry solar radiation conditioning. For wet solar radiation process, it was observed that despite lower initial hardening, samples reached higher levels of ageing by the continuation of the process comparing to those conditioned through the dry procedure.

Chapter 7: One of the main hypotheses of this research was the change in the chemical and rheological path of age-related changes as a result of using different conditioning parameters and different levels of each conditioning parameter. This chapter tries to evaluate this hypothesis by comparing four conditioning procedures. Rheological and chemical properties of all mix and cement samples were compared. It was found that using excessively high conditioning temperature in the AASHTO R30 procedure and not considering other environmental parameters would result in underestimating the loss of desired properties at the low-temperature range.

8.2 Conclusions

This study investigated the importance of real conditioning factors in laboratory age conditioning of asphalt mixes alongside with evaluating the impact of iron sulfide containing minerals in the age hardening process of asphalt cement. Several laboratory tests and analysing tools were used during this research, which were described comprehensively in previous chapters. Following shows the general conclusions of this research.

- The rate of change in rheological parameters over temperature (temperature sensitivity of rheological parameters) is an innate property of material which like any other rheological property of the viscoelastic materials are prone to change as the material ages. Frequency sweep test can be used in accordance with the time-temperature superposition principle to evaluate this intrinsic material.
- Among the three available models for the relationship of TTS shift-factors (WLF, Arrhenius, and Quadratic), William-Landel-Ferry (WLF) is found to be more suitable for asphaltic materials at the performance temperature range. It works better than Arrhenius law for viscoelastic materials above the glass-transition temperature, and unlike the Quadratic equation used in MEPDG which increases after an extremum point, it merges to an absolute value at excessively high temperatures.
- TSRP can be used alongside other rheological tests and analysis techniques to evaluate the ageing severity in both asphalt cement and asphalt mix. One such application can be to evaluate the intimacy of laboratory age conditioning procedures to the real-life ageing in the field.
- Extended heating procedures for simulating long-term ageing (e.g. LTOA procedure of AASHTO R30) are not suitable for evaluating the effect of aggregates (such as iron sulfide containing aggregates) as it is unable to activate susceptible minerals as it happens in real conditions. Therefore, more realistic conditioning parameters are required specially if the goal is to assess the effect of minerals.
- The existence of Iron Sulphide in mineral aggregates can alter the ageing process for both asphalt cement and asphalt mixtures with regards to their chemical and rheological behaviour, and temperature sensitivity.

- Conditioning temperature is an important factor which can alter both rheology and chemistry of age conditioning. This effect can change the complex modulus and phase angle master curves of asphalt cement and mix as well as the rate of changes in the carbonyl and sulfoxide indices and the ratio between them. When compared to solar radiation age conditioning, extended heating procedures are lenient on low-temperature properties of asphalt cement resulting in less stiff with more viscous behaviour at high frequencies or low temperatures.
- Cross-Over temperature is a useful tool to examine the severity of ageing, but it must be considered that it does not give any information on the rheological changes in the full frequency (temperature) range. Thus, it should be used with care, especially when conditioning parameters are different from each other.
- Age conditioning of samples using only solar radiation can not simulate the severity of field ageing, as the process slows down significantly, mainly due to the formation of highly oxidized protective skin on the very surface. However, coupling the water treatment with solar radiation will increase the capability of the conditioning system in order to simulate ageing in the asphalt mix samples, even though it would slow down the ageing at the first few cycles mainly due to the reduction in temperature.
- The Carbonyl to Sulfoxide ratio can be used as a measure for kinetics of changes during oxidative ageing as it would illustrate the comparative formation of different functional groups as a result of oxidative ageing. From the chemical point of view, conditioning samples using the combination of solar radiation and water treatment would result in higher sulfoxide index and relatively lower carbonyl index comparing to solar radiation alone and extended heating procedures.
- The RTFOT age conditioning procedure seems to be insufficient to simulate short-term ageing in the field from both chemical and rheological points of views. The complex shear modulus and phase angle master curve of the RTOFOT aged samples falls between the one from the original asphalt and the one recovered from the fresh compacted mix. Moreover, base on the FT-IR carbonyl and sulfoxide indices and the ration between them, the chemistry of changes during asphalt cement conditioning procedures (RTFOT, PAV, and double PAV) seems to follow a different path than what happens in mix age-conditioning procedures.

- In order to better simulate the chemical and rheological changes that happen in real life ageing of asphalt cement and its subsequent impact of the properties of asphalt mixes, more realistic temperature (close to high temperatures that pavement will experience) should be selected to avoid significant alteration of chemical processes. Using solar radiation technique in association with water spraying of the samples seems to be an effective approach for laboratory conditioning of mix samples by using more realistic conditions. However, the similarity with real life long-term age conditioning needs to be validated.

8.3 Recommendations and Future Researches

- *The Use of Iron Sulphide Containing Aggregates in Asphalt Mixes*

Effect of iron sulphide containing aggregates were evaluated in this research using chemical and rheological analysis on both asphalt cement and asphalt mixes. Three iron sulphide containing aggregates were subjected to laboratory age conditioning procedures developed mainly to address this specific issue by using a combination of heat and humidity conditioning parameters. Chemical and rheological analysis show slight change in the chemistry and rheology of asphalt mix and cement aged in the presence of iron sulphides, comparing to the control mix (sample not containing any significant amount of iron sulphide) and preliminary studies showed it also has the potential to postpone age hardening in the asphalt cement due to consuming part of available oxygen.

Although the existence of iron sulphide in the aggregate sources didn’t found to be a source of premature ageing (based on the testing procedure described in the body of this thesis), it was found that it can physically affect the pavement by initiating cracks due to large volume change during the iron sulphide oxidation process. This type of crack initiation was observed both on field and in laboratory conditioned samples (when they conditioned through heat and humidity conditioning procedure) (Figure 8-1).

The major recommendation in this case is to limit the application of the iron sulphide containing aggregates to produce asphalt mixes to be used in surface layers where humidity and oxygen is abundant to activate such materials. From this perspective the use of such materials in binder course would not be suggested, though due to minimum availability of moisture and oxygen, oxidation of iron sulphide is unlikely. The use of iron sulphide containing aggregates in the unbound granular layers are would not result to any expansion related issue due to flexibility of the structure to accommodate such volume changes.

Despite these recommendations there might be always times that due to many practical and economical issues the use of iron sulphide containing aggregates is inevitable. In such cases pre-conditioning the crushed aggregates in the presence of moisture in order to allow the major part of iron sulphide oxidation reactions to be done before getting involved in asphalt mix is suggested to minimize the aggregates expansion and crack initiation on the pavement surface.

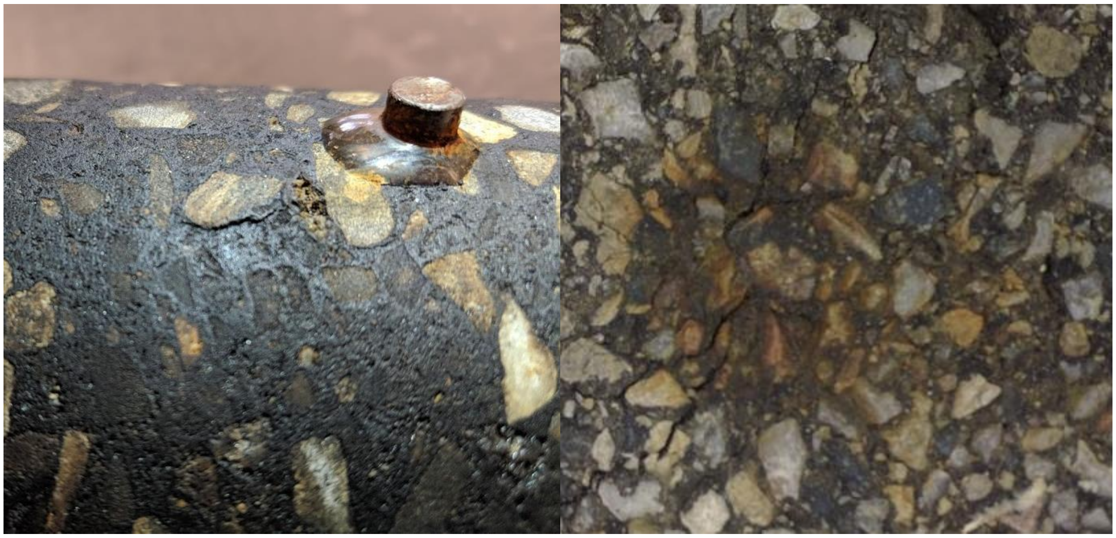


Figure 8-1 The Initiation of Cracks Around the Activated Iron Sulphide Containing Aggregates in (a) Laboratory Conditioned Sample (b) on The Surface of Pavement

- *Solar Radiation and Moisture Treatment of Asphalt Mixes for Laboratory Long-Term Conditioning*

The use of more realistic conditioning parameters (the use of lower conditioning temperatures and coupling solar radiation with water treatment) during long-term age simulation on the compacted mix samples is suggested as doing so would result in different chemical and rheological changes. Due to lack of comparison between field aged samples and samples aged through solar radiation bespoke chamber, no calibration of applied parameters (temperature, solar radiation intensity, water treatment, and the number of conditioning cycles) was performed. However, it was clearly shown how changing the conditioning parameters alters the chemistry and rheology of changes. As the state-of-the-practice procedure for long-term age conditioning, the procedure recommended as per AASHTO R30 (LTOA) results in samples with better low temperature properties (in terms of complex modulus and phase angle) comparing to those conditioned through bespoke solar radiation chamber (solar radiation and moisture conditioning). Therefore, the properties of samples conditioned through the existing AASHTO R30 procedure should be considered with care, specifically when low temperature properties are of interest.

As mentioned in the body of this thesis, plant mixed SP 12.5 was selected for the second part of this research (laboratory conditioning of asphalt mix samples using solar radiation and moisture conditioning). The main purpose of selecting this specific mix was to make sure the exact location that it has been used for future comparison and field validation of results (Hwy. 8). Unfortunately, the time restraints didn’t allow this researcher to perform field validation. Future researcher can use the results presented in this thesis to compare the chemical and rheological properties of the recovered asphalt cement (as it would be impossible to perform complex modulus on field cores and to compare them with laboratory compacted samples) with those presented in this research.

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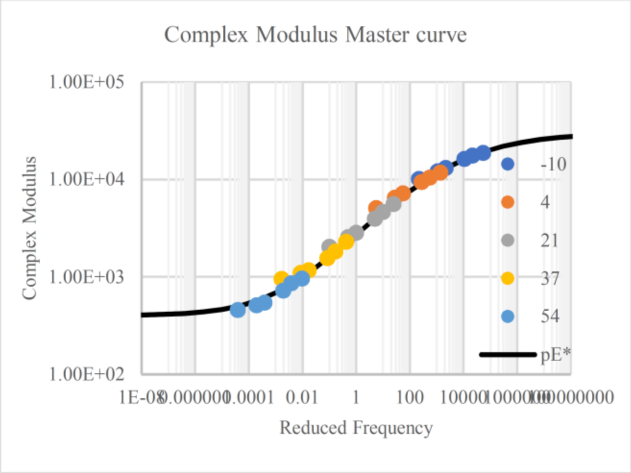
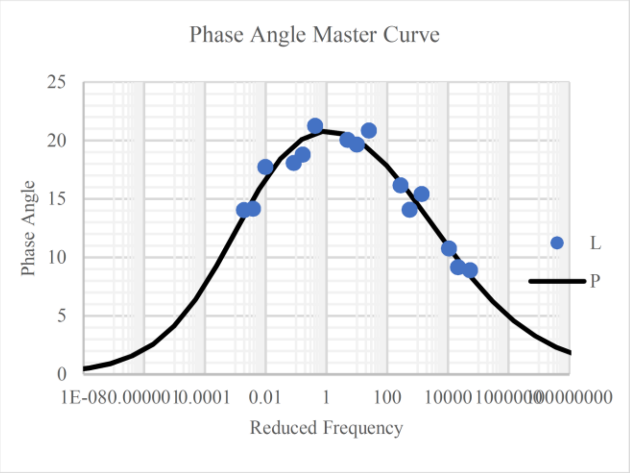
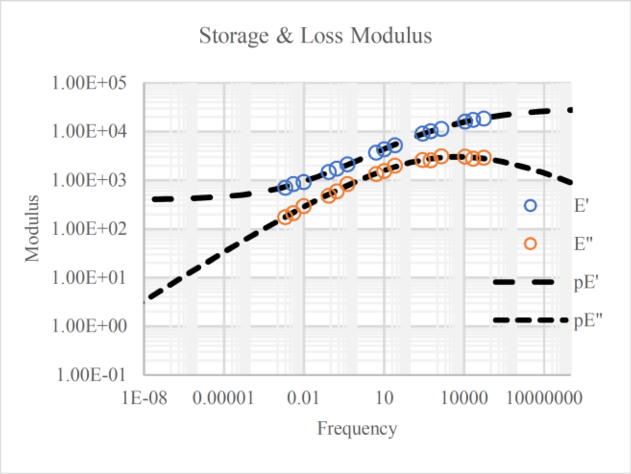
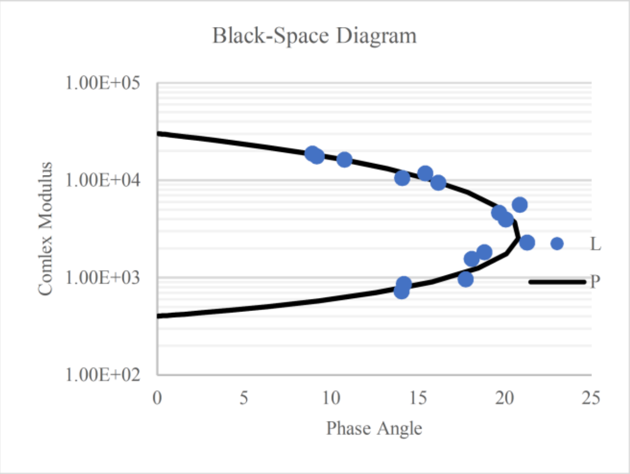
APPENDIX A: Rheology of Asphalt Mixes

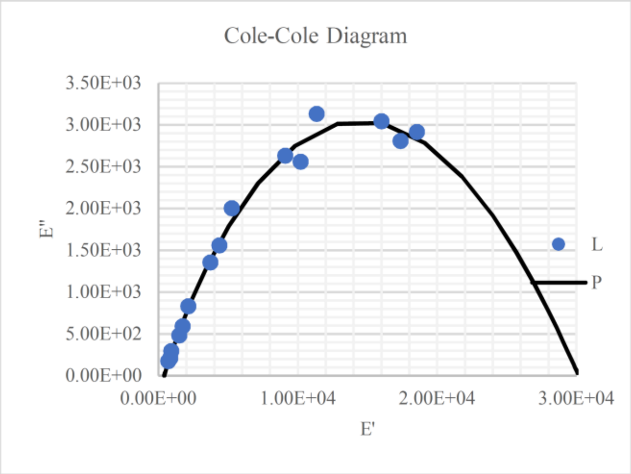
Mix A-Unconditioned

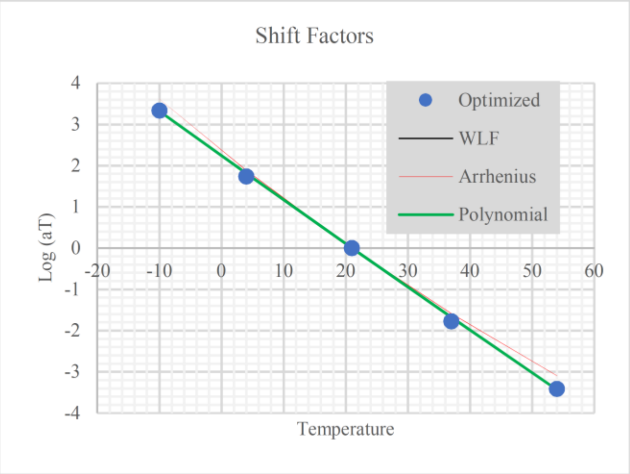




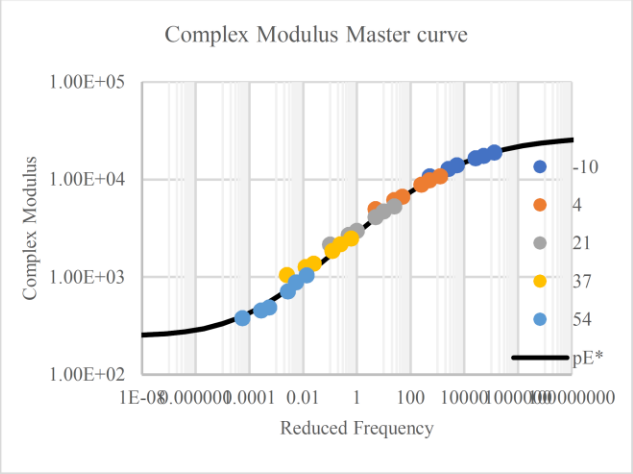








Mix A- LTOA


Complex Modulus Master curve
Complex Modulus
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1.00E+04
1.00E+03
1.00E+02
1E-08
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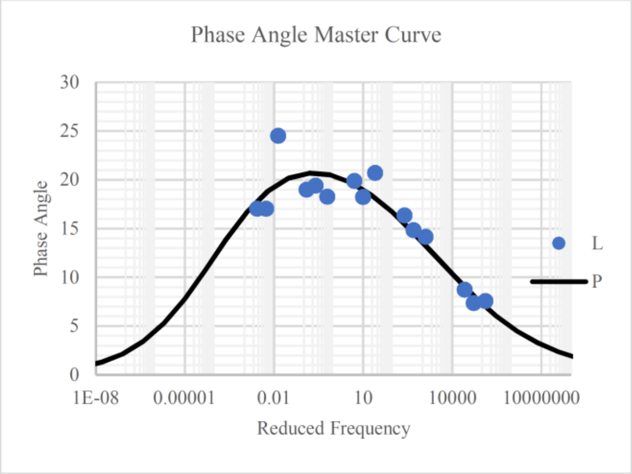
0.0001
0.01
1
100
10000
1000000
100000000
Reduced Frequency
-10
4
21
37
54
pE*


Phase Angle Master Curve
Phase Angle
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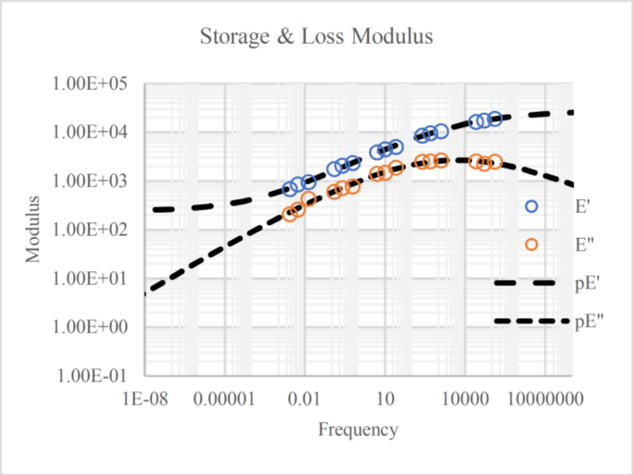
25
20
15
10
5
0
1E-08
0.00001
0.01
10
10000
10000000
Reduced Frequency
L
P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Modulus
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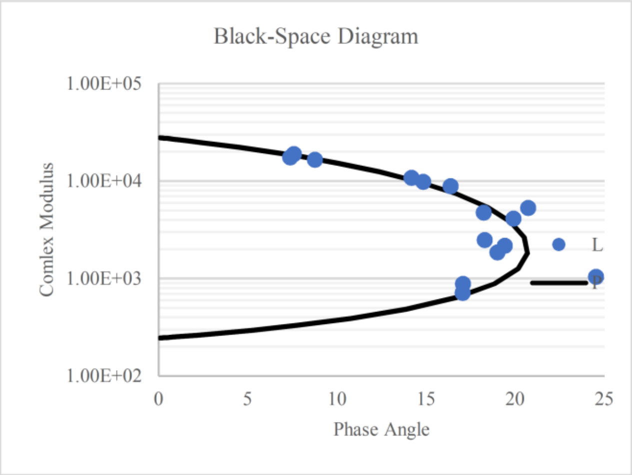
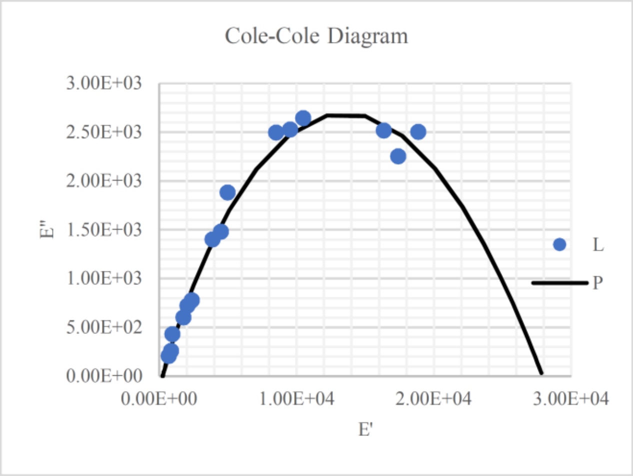
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1E-08
0.00001
0.01
10
10000
10000000
Frequency
E'
E"
pE'
pE"


Black-Space Diagram
Comlex Modulus
1.00E+05
1.00E+04
1.00E+03
1.00E+02
0
5
10
15
20
25
Phase Angle
L
P


Cole-Cole Diagram
E"
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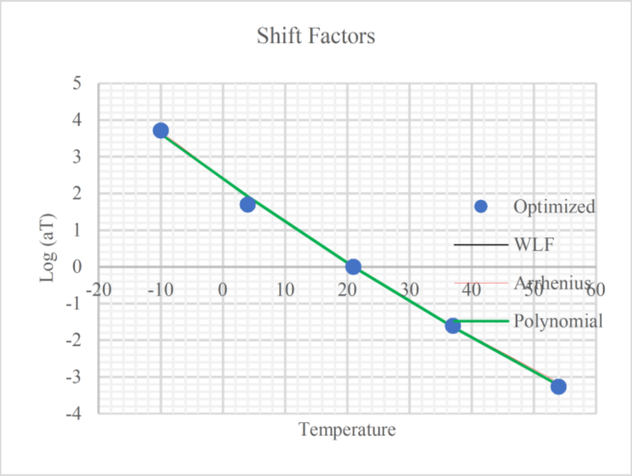
2.50E+03
2.00E+03
1.50E+03
1.00E+03
5.00E+02
0.00E+00
0.00E+00
1.00E+04
2.00E+04
3.00E+04
E'
L
P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Log (aT)
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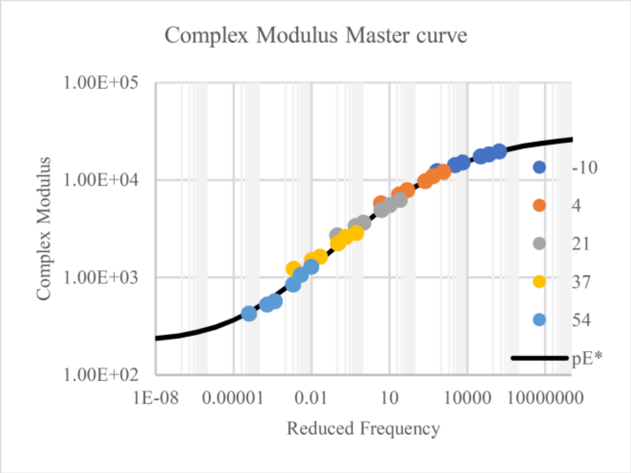
4
3
2
1
0
-1
-2
-3
-4
-20
-10
0
10
20
30
40
50
60
Temperature
Optimized
WLF
Arrhenius
Polynomial

Mix A- RHR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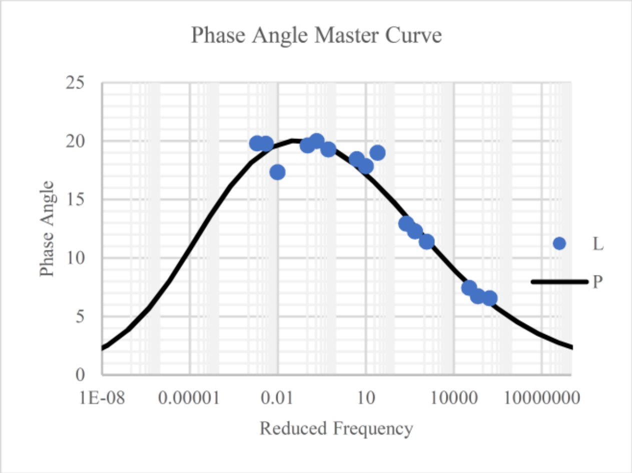
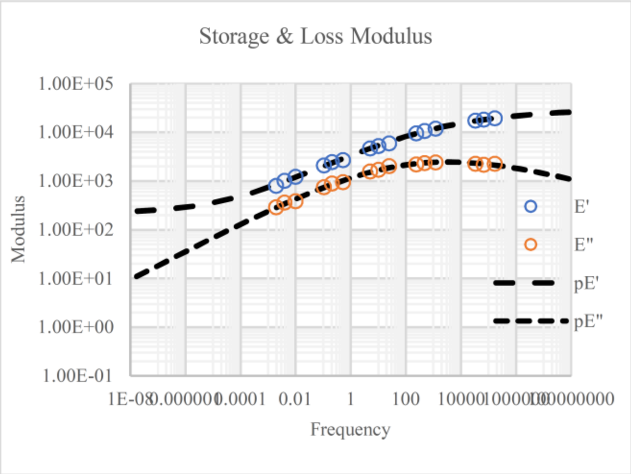
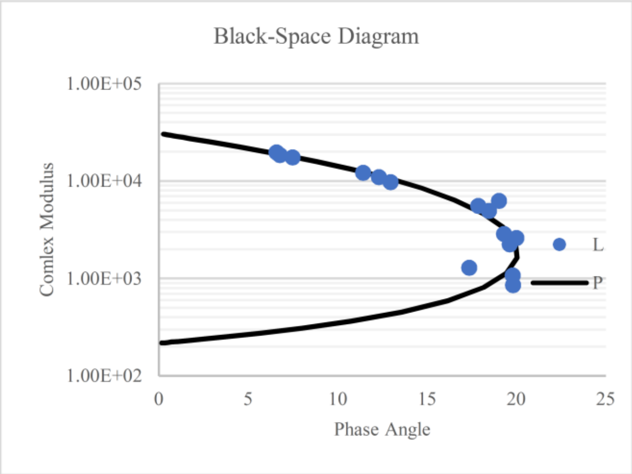
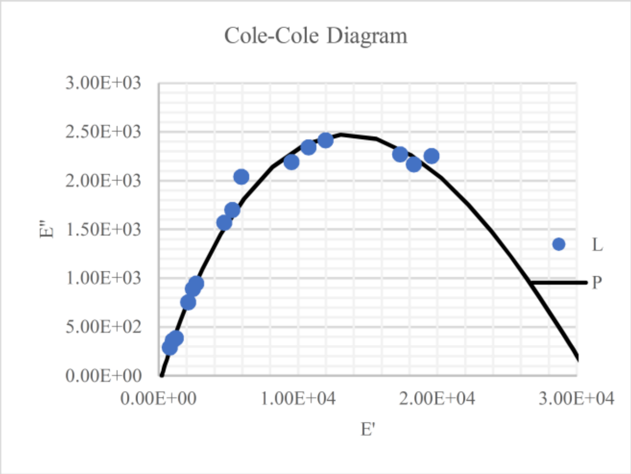
1.00E+04
1.00E+03
1.00E+02
Complex Modulus
1E-08
0.00001
0.01
10
10000
10000000
Reduced Frequency
-10
4
21
37
54
pE*


Phase Angle Master Curve
25
20
15
10
5
0
Phase Angle
1E-08
0.00001
0.01
10
10000
10000000
Reduced Frequency
L
P


Storage & Loss Modulus
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
Modulus
1E-08
0.000001
0.0001
0.01
1
100
10000
1000000
100000000
Frequency
E'
E"
pE'
pE"


Black-Space Diagram
1.00E+05
1.00E+04
1.00E+03
1.00E+02
Comlex Modulus
0
5
10
15
20
25
Phase Angle
L
P


Cole-Cole Diagram
3.00E+03
2.50E+03
2.00E+03
1.50E+03
1.00E+03
5.00E+02
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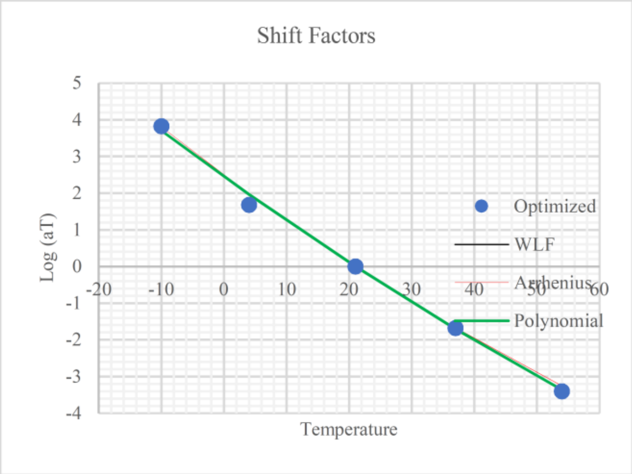
E"
0.00E+00
1.00E+04
2.00E+04
3.00E+04
E'
L
P


Shift Factors
5
4
3
2
1
0
-1
-2
-3
-4
Log (aT)
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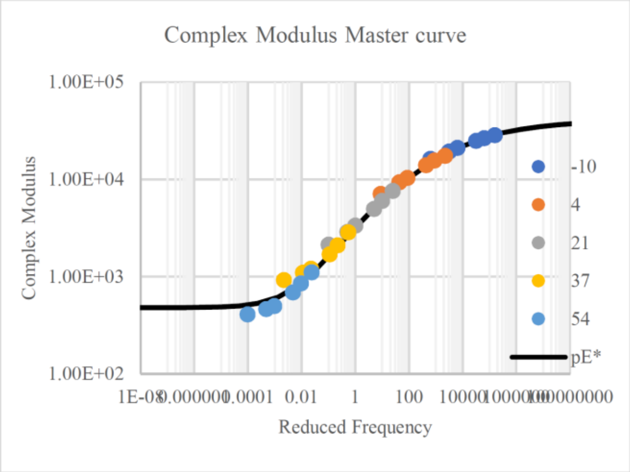
-10
0
10
20
30
40
50
60
Temperature
Optimized
WLF
Arrhenius
Polynomial

Mix B- Unconditioned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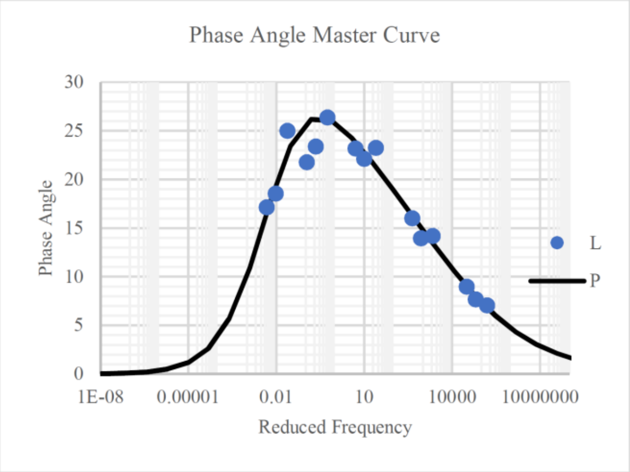
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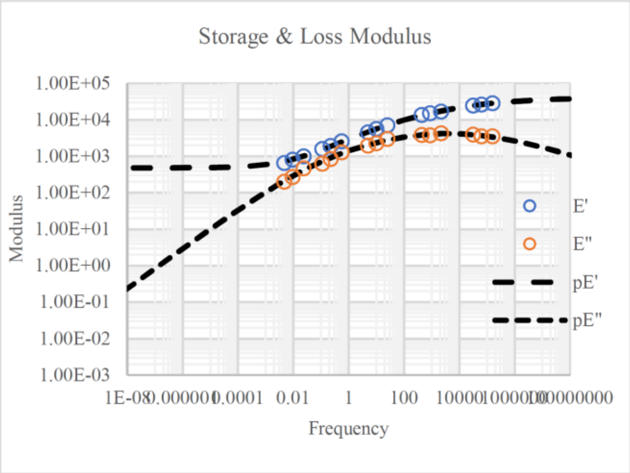
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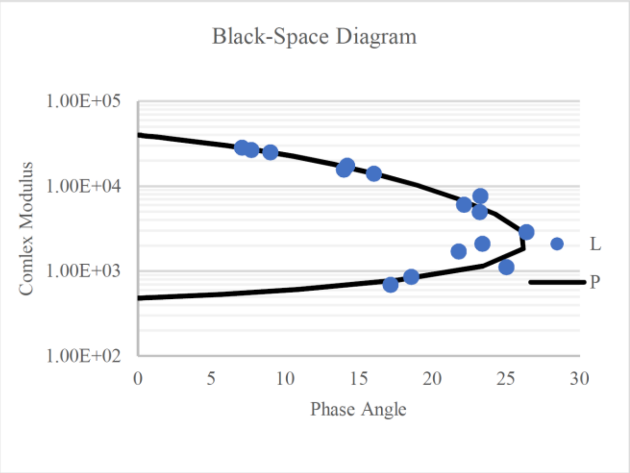
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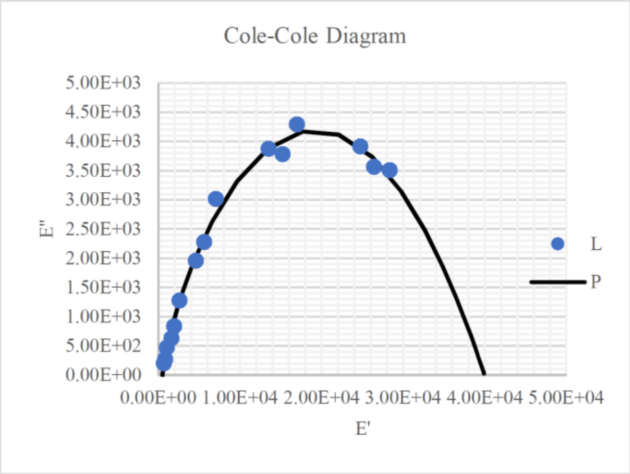
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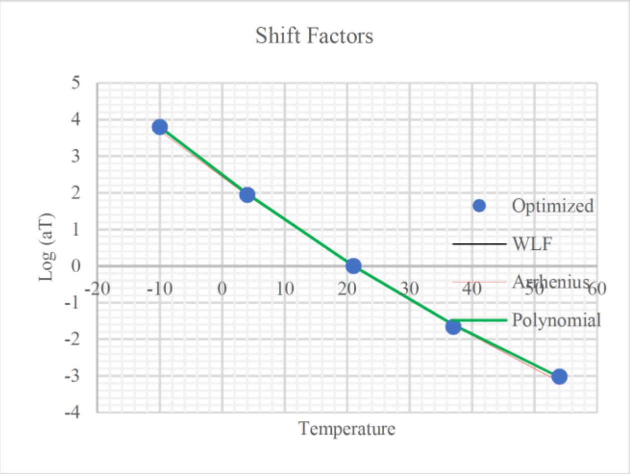
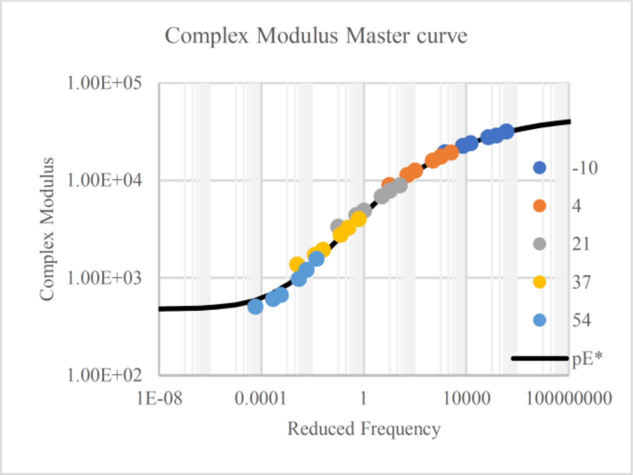

Shift Factors

Mix B- LTOA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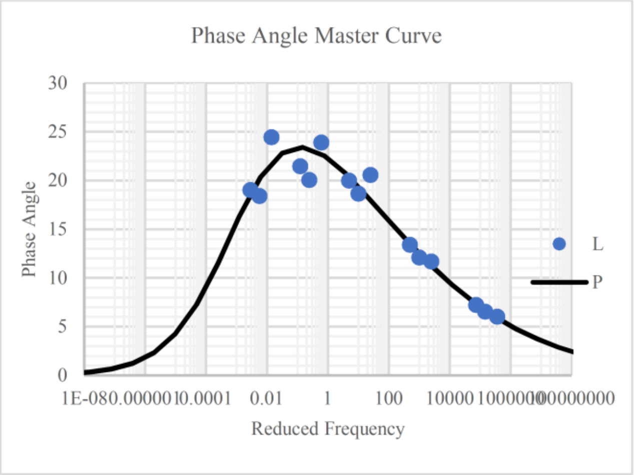
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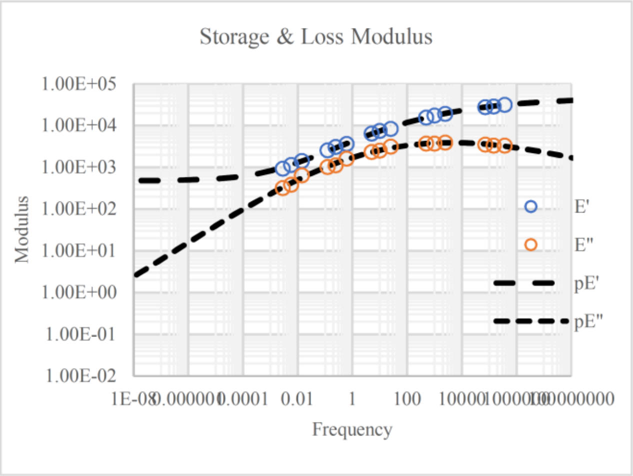
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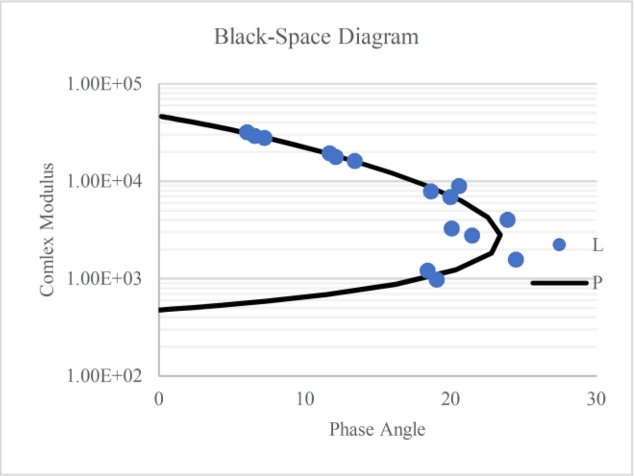
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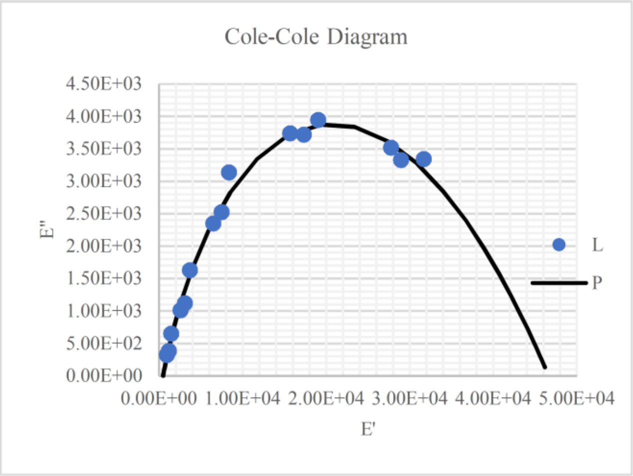
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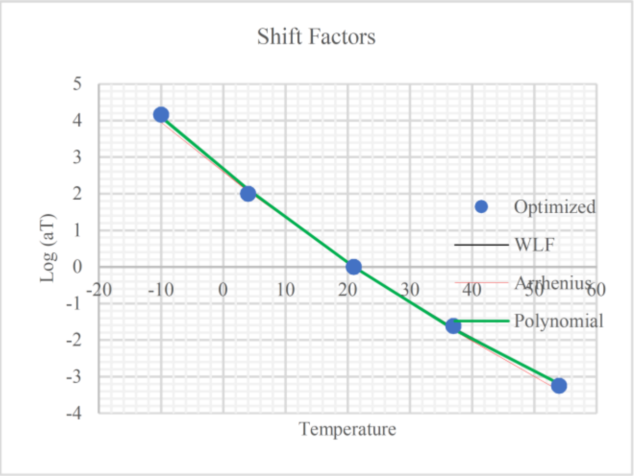
Shift Factors

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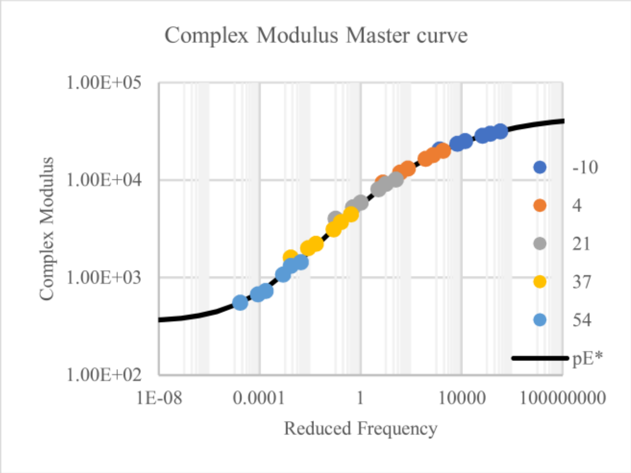
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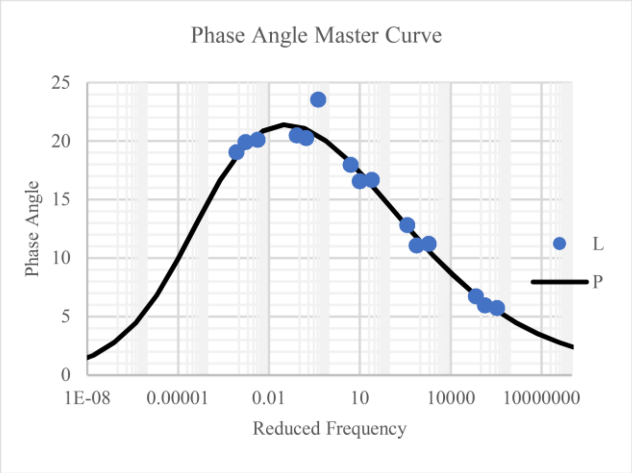
pE*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Reduced Frequency
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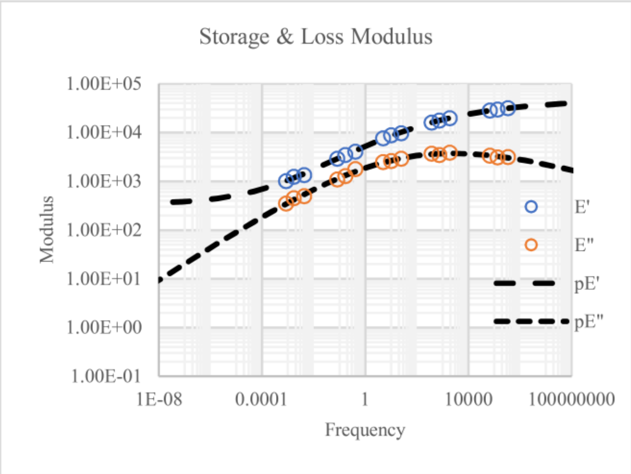
P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Modulus
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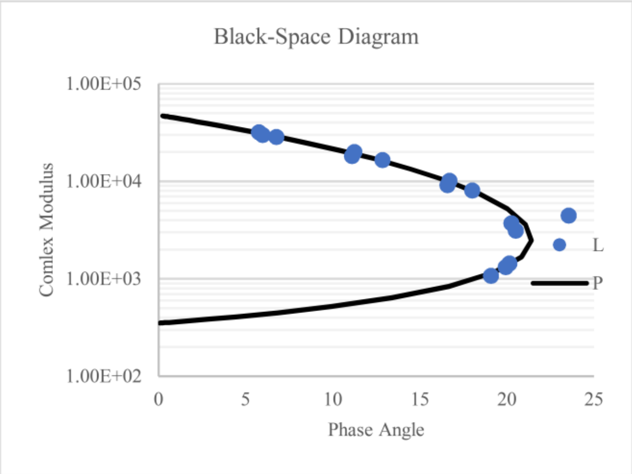
Frequency
E'
E"
pE'
pE"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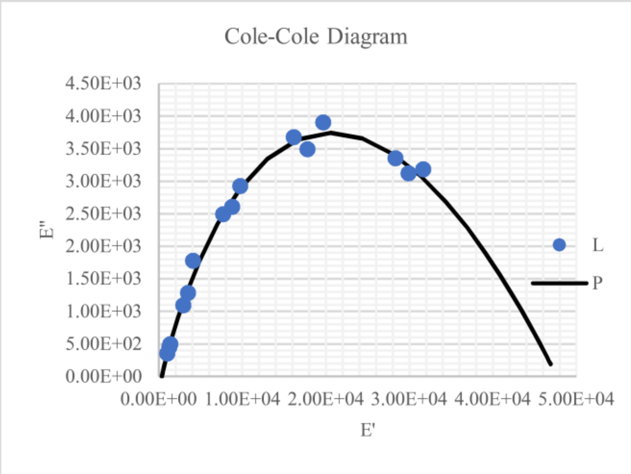
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1.00E+03
5.00E+02
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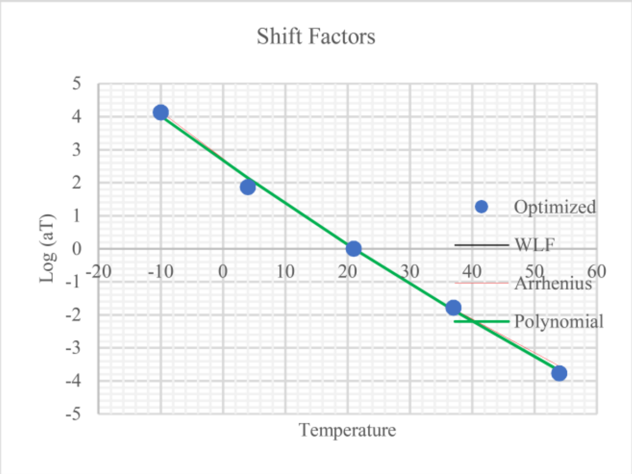
L
P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-4
-5
Log (aT)
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10
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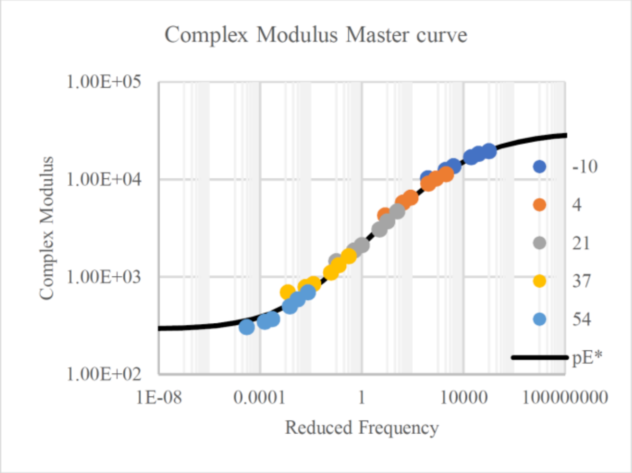
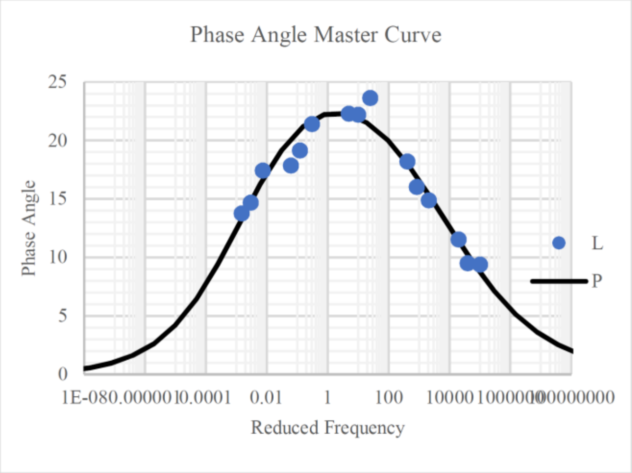
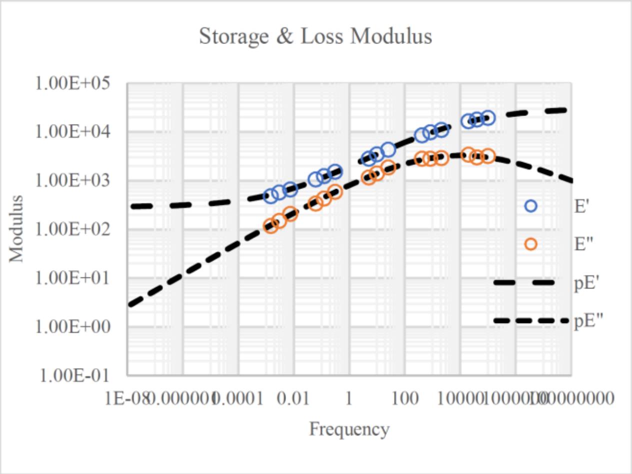
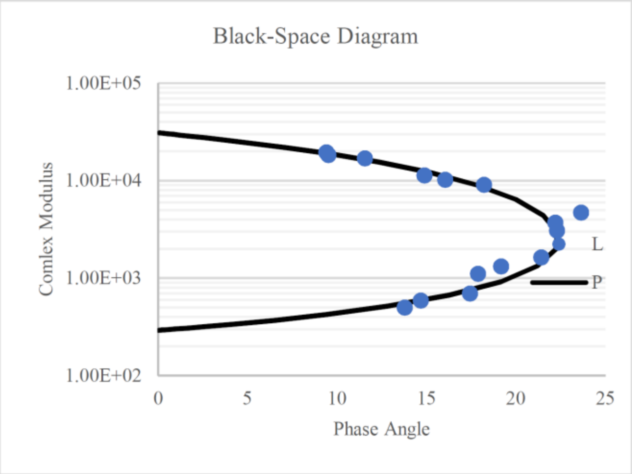
40
50
60
Temperature
Optimized
WLF
Arrhenius
Polynomial

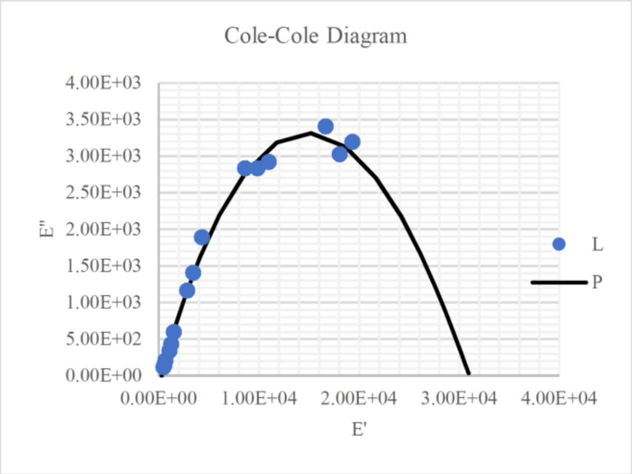
Mix C- Unconditioned

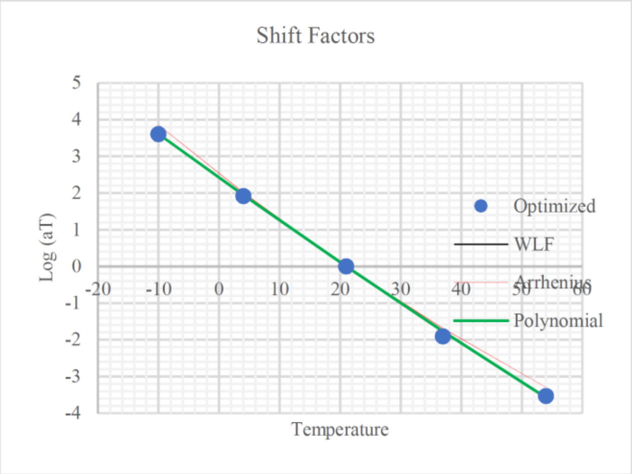




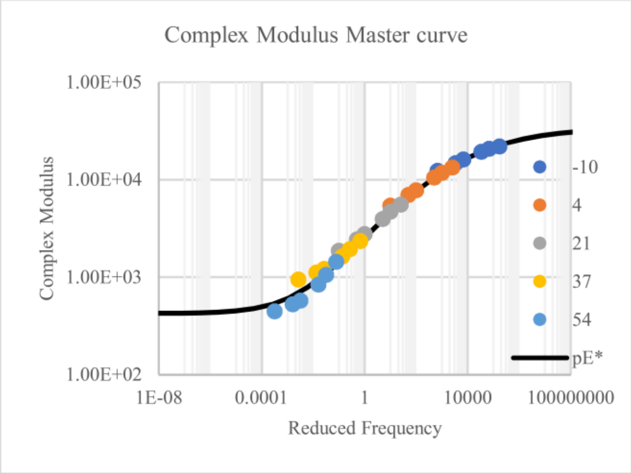


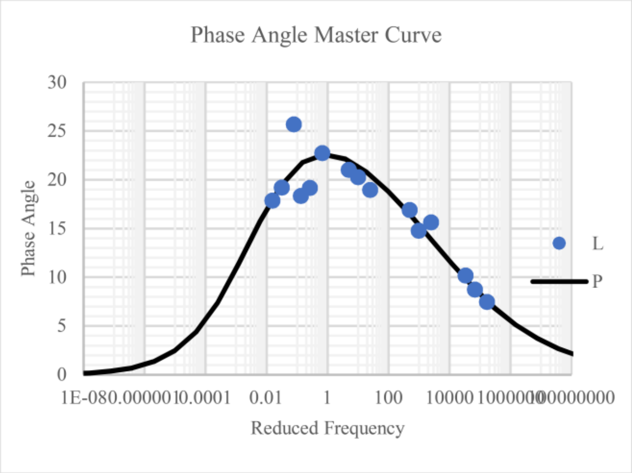


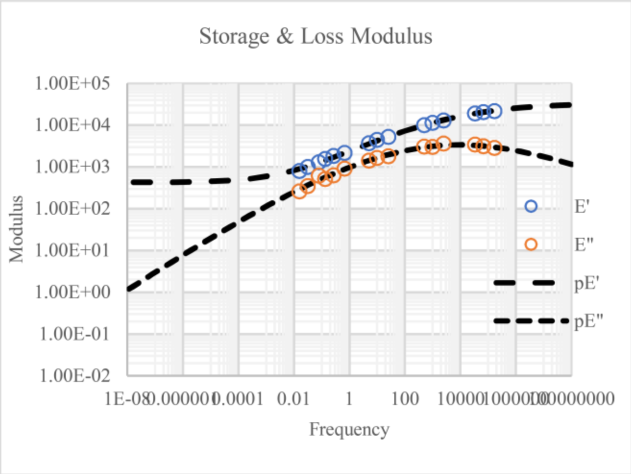


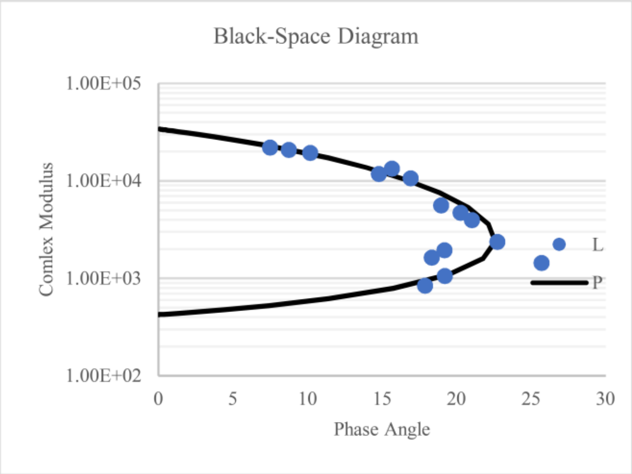


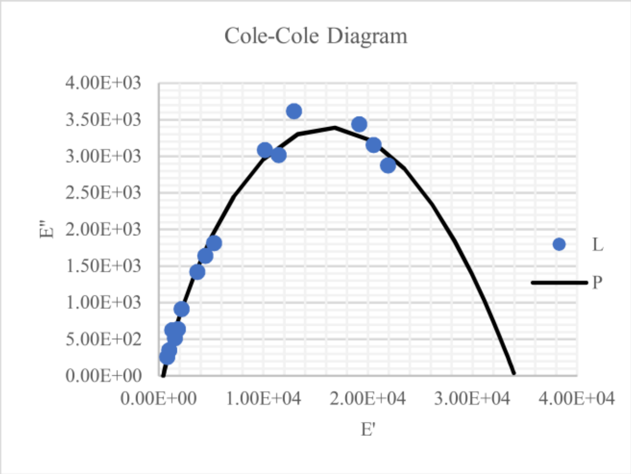
Mix C- LTOA

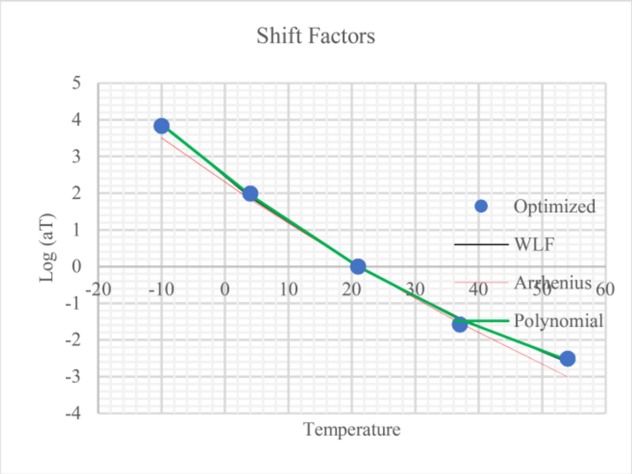

Complex Modulus Master curve
Complex Modulus
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1E-08
0.0001
1
10000
100000000
Reduced Frequency
-10
4
21
37
54
pE*


Phase Angle Master Curve
Phase Angle
30
25
20
15
10
5
0
1E-08
0.000001
0.0001
0.01
1
100
10000
1000000
100000000
Reduced Frequency
L
P

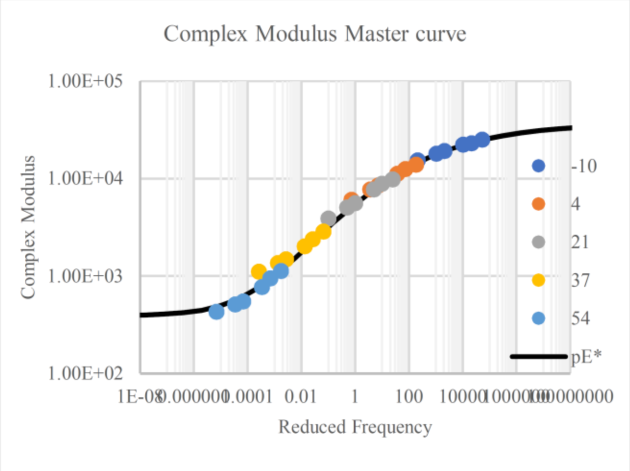

Storage & Loss Modulus
Modulus
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
1E-08
0.000001
0.0001
0.01
1
100
10000
1000000
100000000
Frequency
E'
E"
pE'
pE"

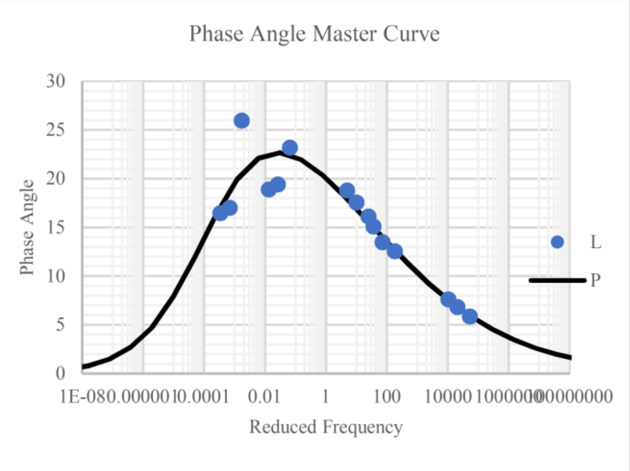

Black-Space Diagram
Comlex Modulus
1.00E+05
1.00E+04
1.00E+03
1.00E+02
0
5
10
15
20
25
30
Phase Angle
L
P

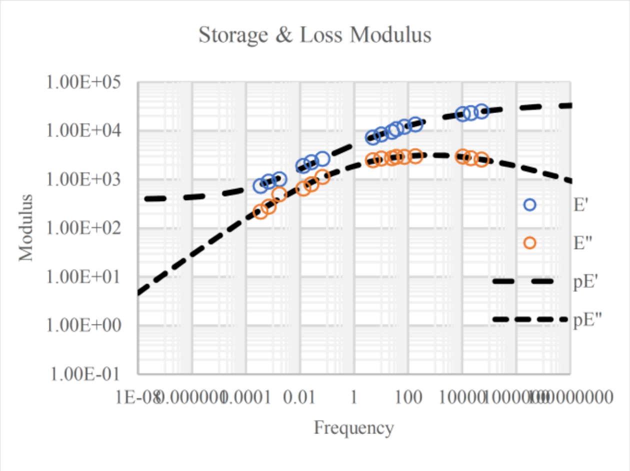

Cole-Cole Diagram
E"
4.00E+03
3.50E+03
3.00E+03
2.50E+03
2.00E+03
1.50E+03
1.00E+03
5.00E+02
0.00E+00
0.00E+00
1.00E+04
2.00E+04
3.00E+04
4.00E+04
E'
L
P

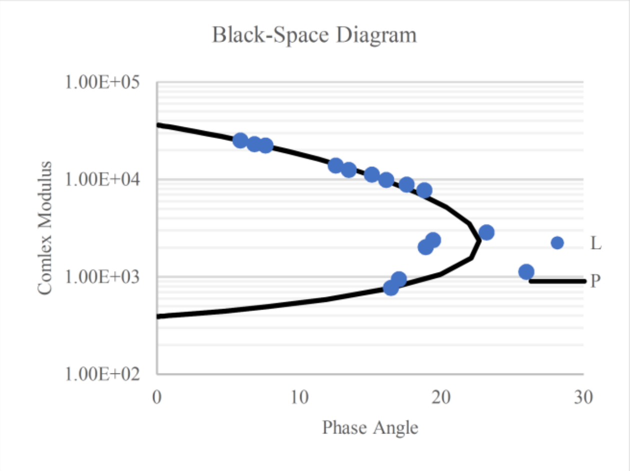

Shift Factors
Log (aT)
5
4
3
2
1
0
-1
-2
-3
-4
-20
-10
0
10
20
30
40
50
60
Temperature
Optimized
WLF
Arrhenius
Polynomial

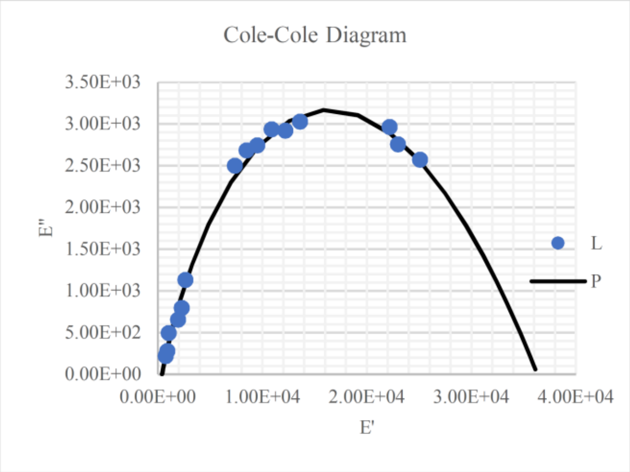
Mix C-RHR

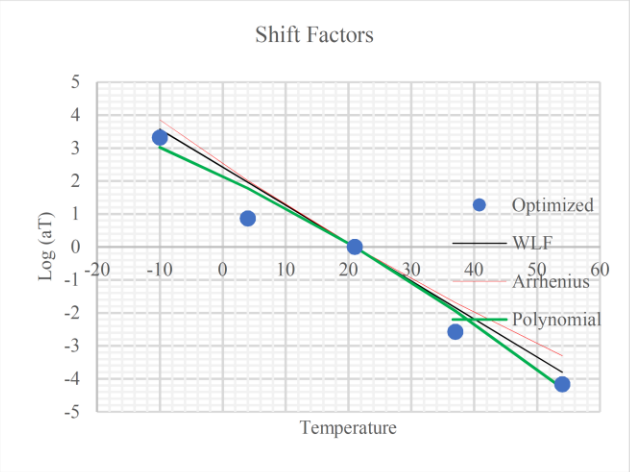

Complex Modulus Master curve


Phase Angle Master Curve

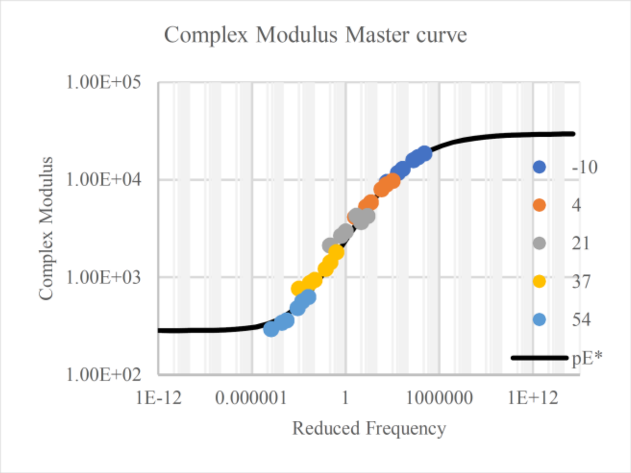

Storage & Loss Modulus

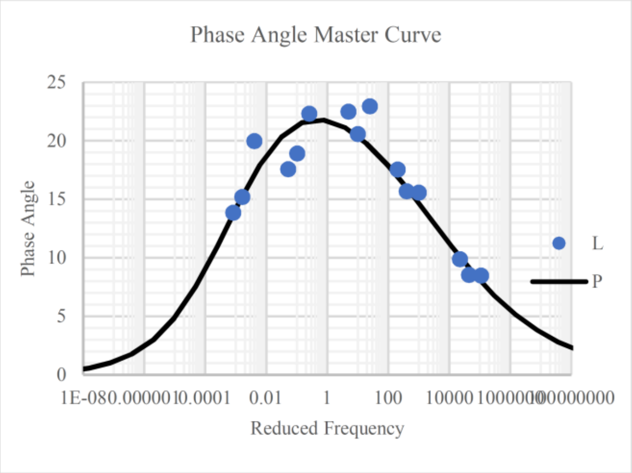

Black-Space Diagram

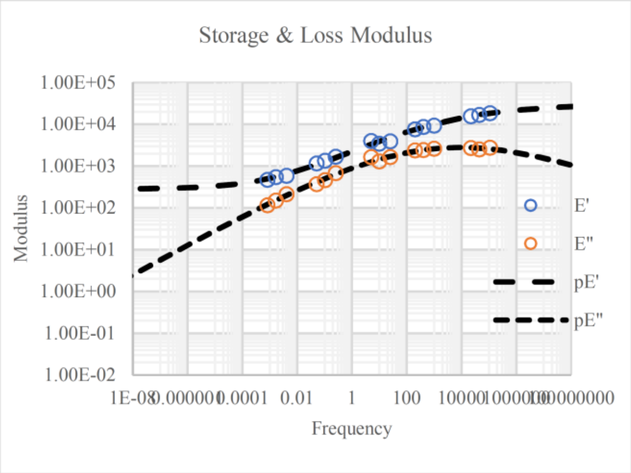

Cole-Cole Diagram

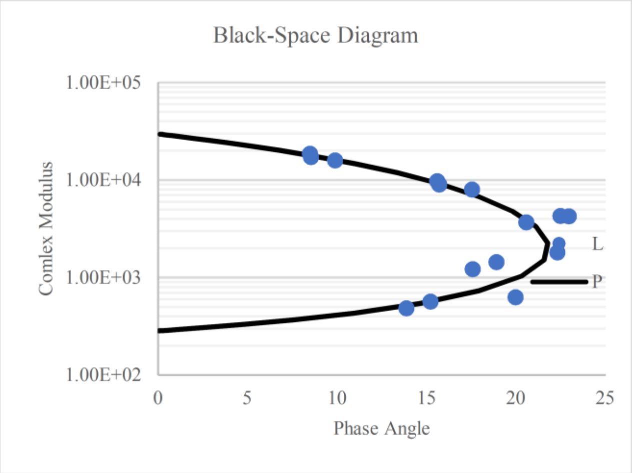

Shift Factors

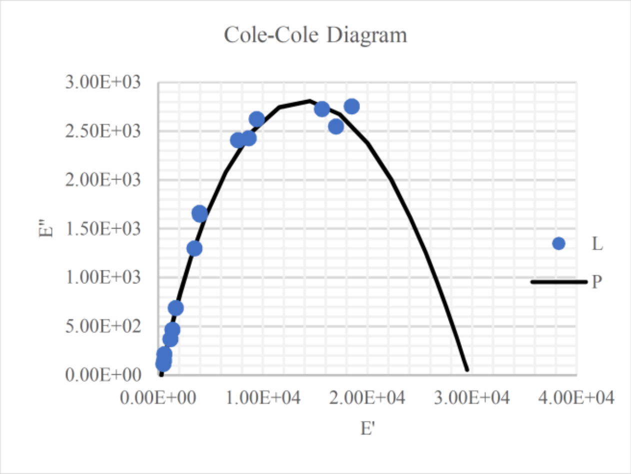
Control Mix – Unconditioned

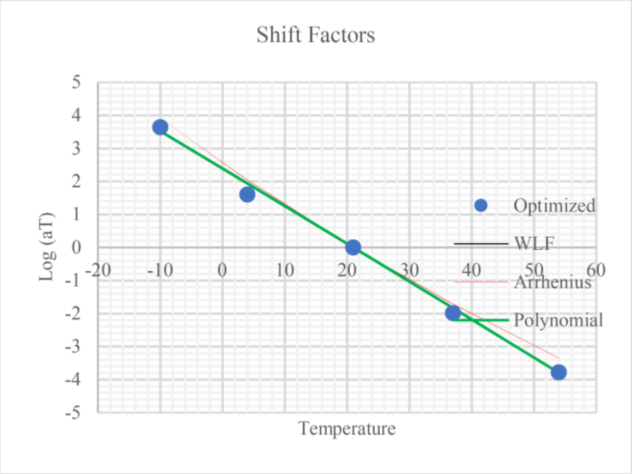

Complex Modulus Master curve


Phase Angle Master Curve

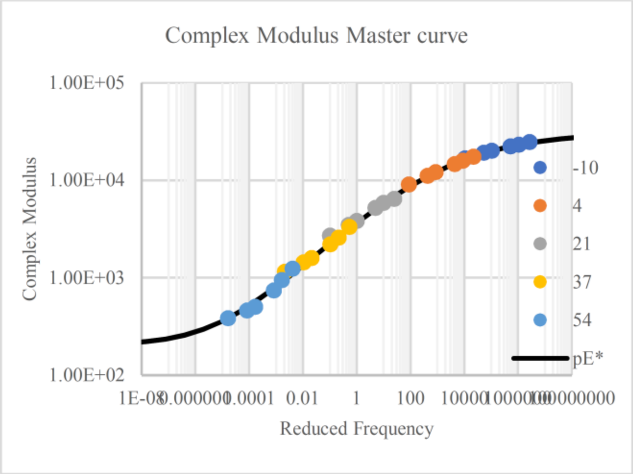

Storage & Loss Modulus

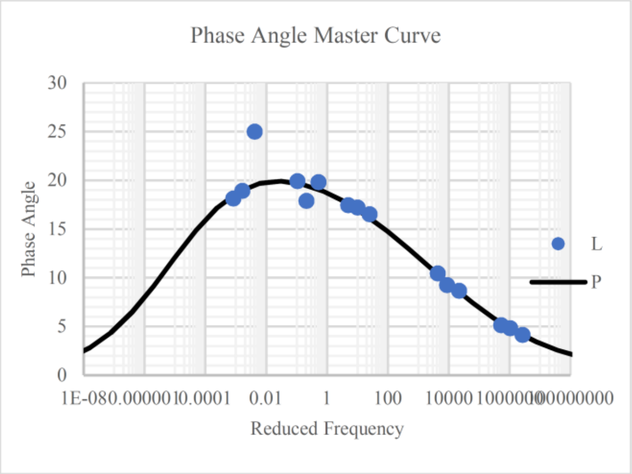

Black-Space Diagram

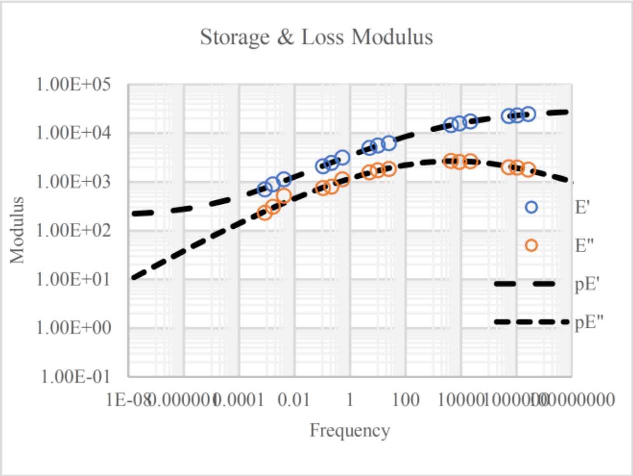

Cole-Cole Diagram

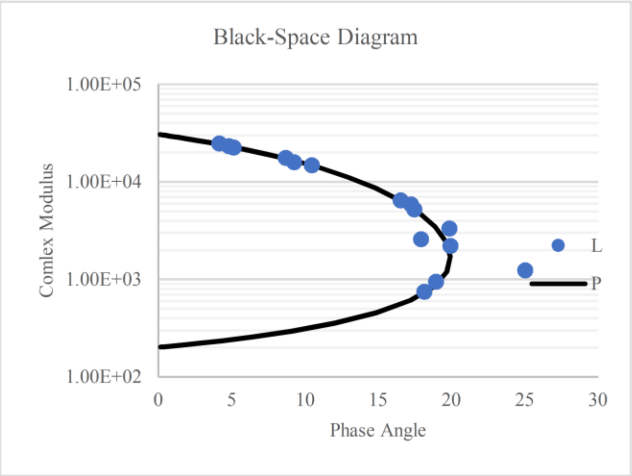

Shift Factors

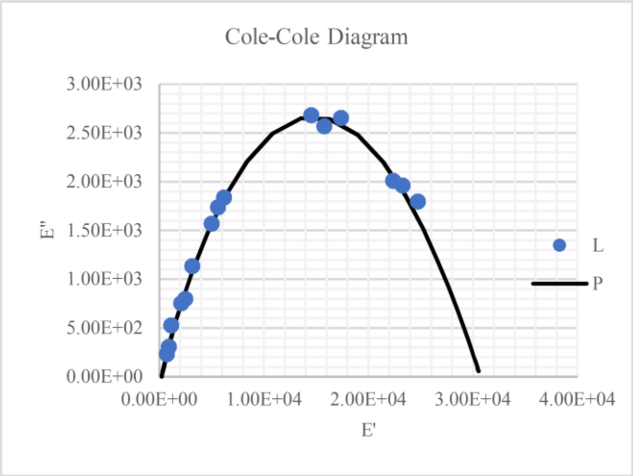
Control Mix – LTOA

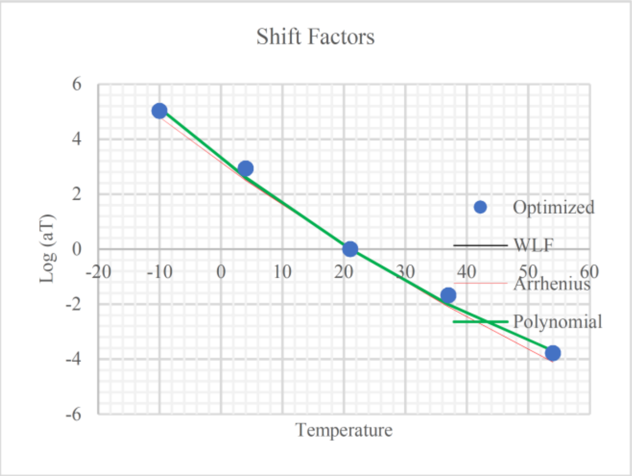




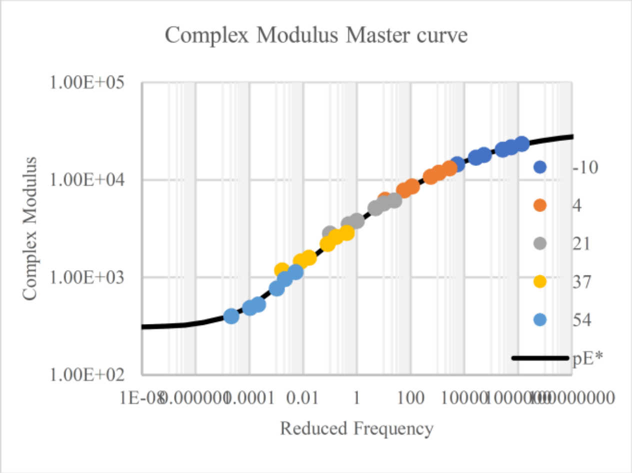


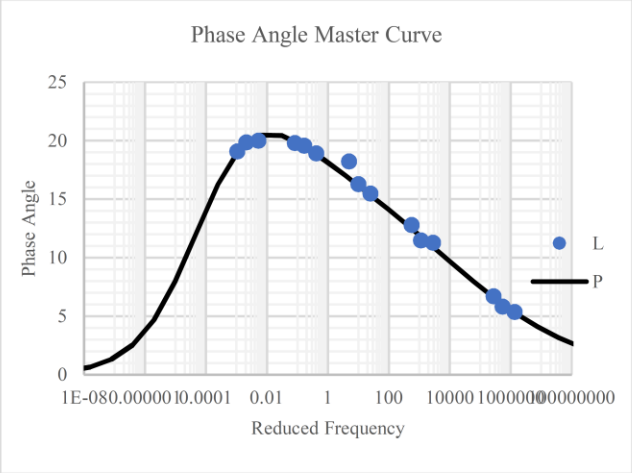


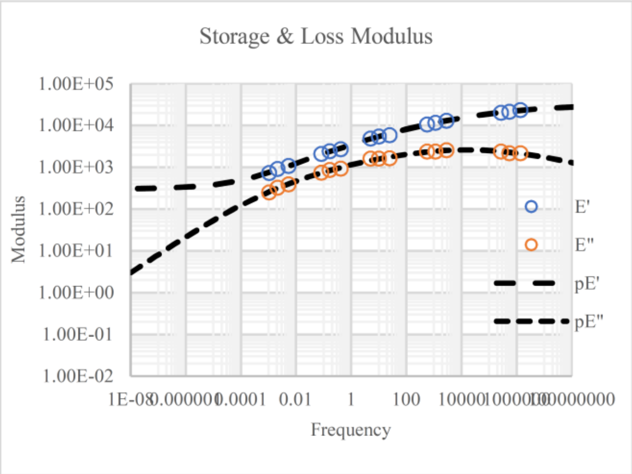


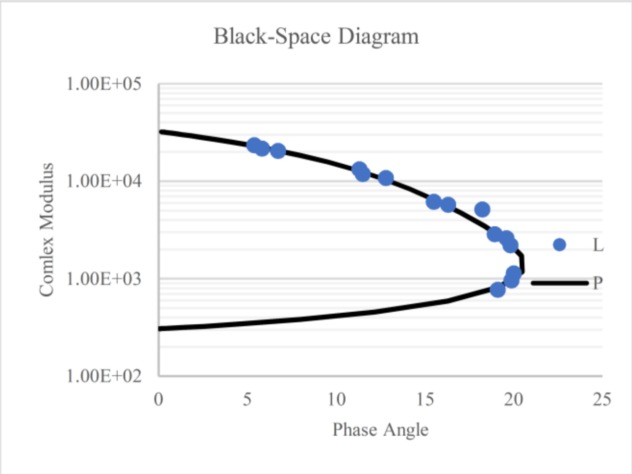


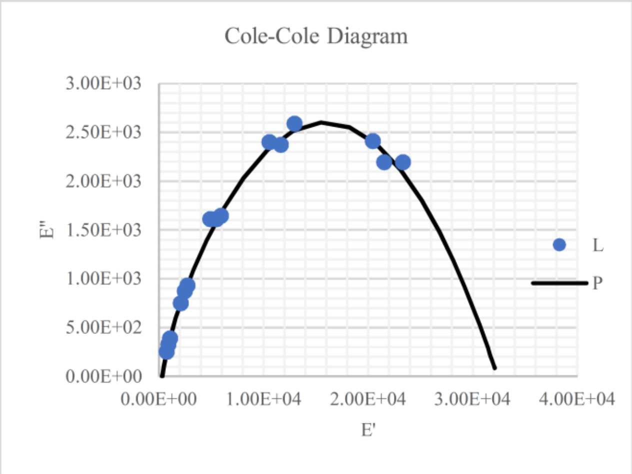
Control Mix- RHR

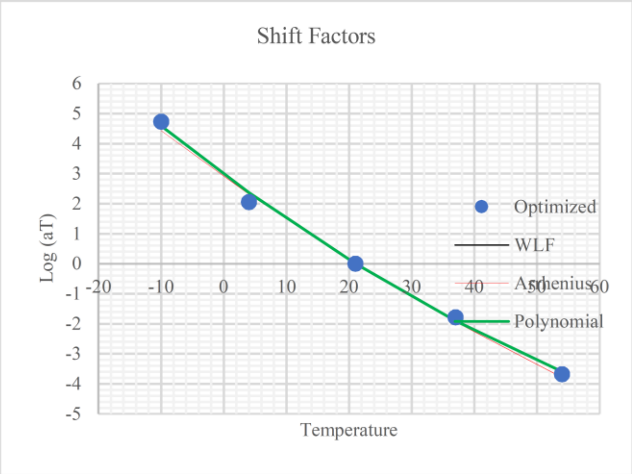

Complex Modulus Master curve


Phase Angle Master Curve


Storage & Loss Modulus


Black-Space Diagram

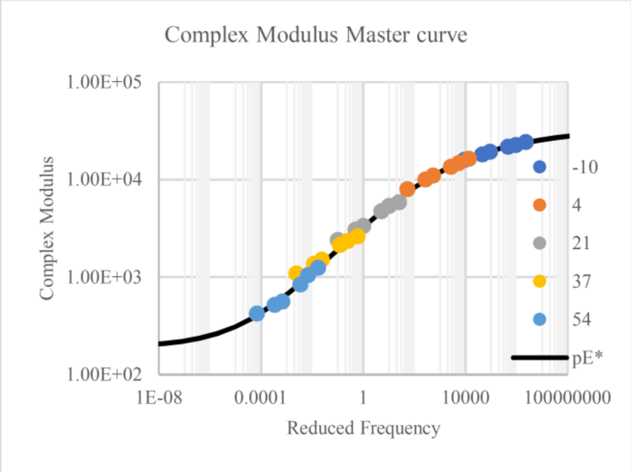

Cole-Cole Diagram

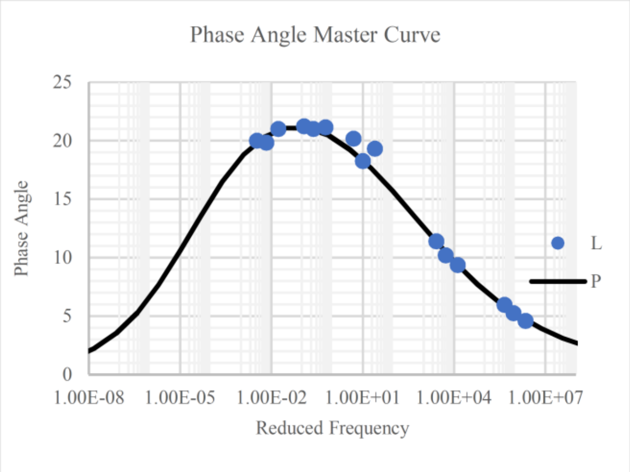

Shift Factors

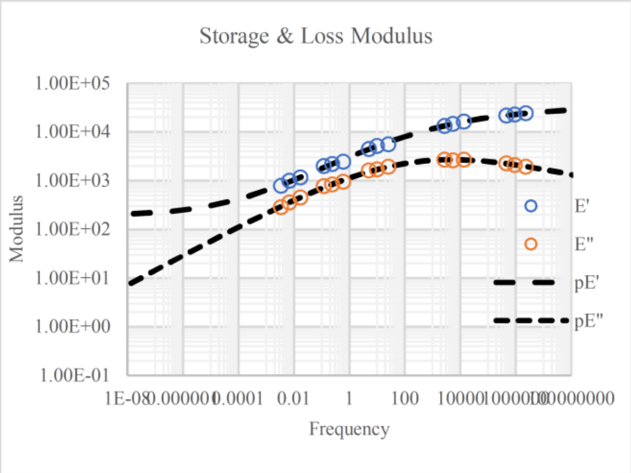
Model Parameters

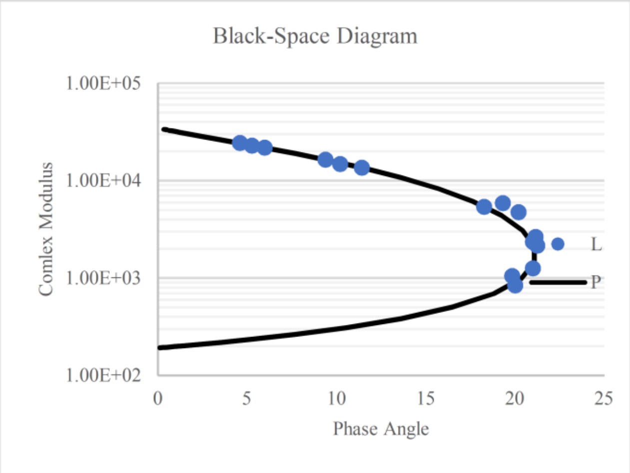
PROJECT	CONDITION	SAMPLE NUMBER	CODE	SHIFTFACTORS					MODEL PARAMETERS							RMSEIQR					WLF		Arrhenius	Polynomial	
				a1	a2	a3	a4	a5	E0	E∞	δ	τ0	k	h	β	E*	δ	E'	E"	E',E"	C1	C2	Ea/R	C1	C2
				-10	4	21	37	54																	
2008	U	1	08-U-1	3.81	1.92	0.00	-1.72	-3.24	240	28485	3.542	1.83E-03	0.224	0.401	9.02E+09	1.56%	47.13%	2.08%	5.15%	2.68%	32	293	9453.9	1.104E-01	3.730E-04
		2	08-U-2	3.69	1.80	0.00	-1.64	-3.11	376	31060	2.121	1.02E-03	0.214	0.397	9.02E+09	2.06%	24.51%	2.37%	4.05%	2.26%	30	286	9114.0	1.064E-01	3.664E-04
		3	08-U-3	3.34	1.74	0.00	-1.77	-3.41	402	30162	1.881	1.06E-03	0.226	0.357	9.02E+09	1.10%	18.48%	1.25%	2.84%	1.46%	245	2319	9029.9	1.057E-01	4.567E-05
		4	08-U-4	3.56	1.99	0.00	-1.70	-3.39	300	26936	2.314	1.18E-03	0.276	0.276	9.02E+09	1.27%	25.99%	1.29%	3.27%	1.68%	60	552	9372.5	1.096E-01	1.992E-04
	R30	1	08-R-1	3.72	1.70	0.00	-1.61	-3.27	245	27917	2.464	3.15E-03	0.222	0.348	9.02E+09	2.17%	37.76%	2.50%	6.07%	3.00%	38	352	9210.7	1.076E-01	2.962E-04
		2	08-R-2	3.98	1.91	0.00	-1.74	-3.65	225	32773	2.454	5.11E-03	0.201	0.326	9.02E+09	1.74%	13.33%	1.79%	5.33%	2.33%	68	577	10144.9	1.186E-01	1.999E-04
	RHR	1	08-RHR-1	3.83	1.68	0.00	-1.68	-3.41	218	30897	1.100	4.65E-04	0.147	0.300	9.02E+09	2.15%	13.91%	2.32%	5.21%	2.39%	43	391	9497.4	1.109E-01	2.735E-04
2011	U	1	11-U-1	3.52	1.95	0.00	-1.80	-3.62	308	40429	2.521	2.44E-03	0.221	0.394	9.02E+09	1.18%	16.69%	1.27%	2.00%	1.12%	210	1870	9581.1	1.121E-01	6.003E-05
		2	11-U-2	3.31	1.85	0.00	-1.86	-3.55	313	40368	2.730	3.60E-03	0.228	0.401	9.02E+09	1.02%	9.72%	1.15%	2.34%	1.17%	19145	176791	9242.3	1.082E-01	-2.305E-05
		3	11-U-3	3.64	1.82	0.00	-1.66	-3.10	371	40639	3.124	3.58E-03	0.238	0.452	9.02E+09	1.07%	20.72%	1.33%	3.54%	1.68%	32	301	9060.0	1.058E-01	3.481E-04
		4	11-U-4	3.80	1.94	0.00	-1.66	-3.02	480	39957	4.285	9.28E-03	0.254	0.552	9.02E+09	1.43%	17.59%	1.58%	4.21%	1.95%	24	226	9236.8	1.077E-01	4.746E-04
		5	11-U-5	3.76	1.95	0.00	-1.81	-3.36	393	42759	3.654	5.36E-03	0.222	0.467	9.02E+09	1.20%	12.47%	1.41%	2.99%	1.52%	44	394	9603.6	1.122E-01	2.850E-04
		6	11-U-6	3.57	1.83	0.00	-1.94	-3.66	296	43167	3.621	7.62E-03	0.219	0.416	9.02E+09	2.39%	19.86%	1.17%	2.87%	1.36%	403	3547	9706.7	1.136E-01	3.177E-05
	R30	1	11-R-1	4.16	2.00	0.00	-1.61	-3.24	477	46612	2.581	3.29E-03	0.188	0.420	9.02E+09	1.60%	17.75%	1.85%	5.23%	2.23%	23	203	9875.9	1.151E-01	5.518E-04
		2	11-R-2	4.13	2.00	0.00	-1.69	-3.20	487	45484	2.892	4.93E-03	0.187	0.448	9.02E+09	1.58%	14.75%	1.79%	4.85%	2.10%	23	206	9839.4	1.147E-01	5.487E-04
	RHR	1	11-RHR-1	4.13	1.87	0.00	-1.78	-3.77	351	47649	1.730	1.78E-03	0.161	0.341	9.02E+09	1.64%	10.42%	1.71%	4.90%	2.00%	50	419	10362.7	1.211E-01	2.787E-04
2012	U		12-U-1	3.60	1.92	0.00	-1.91	-3.53	292	31031	0.957	1.23E-04	0.217	0.338	9.02E+09	1.32%	17.57%	1.45%	2.56%	1.44%	100	891	9618.4	1.125E-01	1.274E-04
		2	12-U-2	3.79	1.98	0.00	-1.85	-3.44	310	34360	2.584	8.73E-04	0.230	0.407	9.02E+09	1.43%	22.57%	1.64%	3.60%	1.91%	48	426	9749.0	1.139E-01	2.677E-04
		3	12-U-3	3.79	2.13	0.00	-1.74	-3.21	348	33201	2.107	2.66E-04	0.243	0.390	9.02E+09	1.61%	17.81%	1.81%	2.85%	1.68%	31	280	9567.6	1.117E-01	4.040E-04
		4	12-U-4	3.86	2.10	0.00	-1.88	-3.52	388	29220	3.527	1.50E-03	0.307	0.307	9.02E+09	1.55%	15.59%	1.73%	2.95%	1.69%	49	422	9994.3	1.168E-01	2.789E-04
	R30	1	12-R-1	3.83	2.00	0.00	-1.57	-2.50	425	34056	3.034	2.09E-03	0.232	0.430	9.02E+09	2.24%	40.75%	2.36%	5.67%	2.71%	14	140	8759.7	1.019E-01	7.405E-04
		2	12-R-2	3.86	1.83	0.00	-1.79	-2.92	252	34801	0.229	3.87E-05	0.117	0.286	9.02E+09	1.57%	20.78%	1.84%	2.83%	1.59%	22	208	9203.0	1.073E-01	5.162E-04
	RHR	1	12-RHR-1	3.32	0.86	0.00	-2.58	-4.16	392	36310	2.500	1.91E-02	0.196	0.408	9.02E+09	1.71%	34.29%	2.19%	5.50%	2.63%	9.E+08	8.E+09	9624.8	1.131E-01	-5.071E-04
NEUTRAL	U	1	N-U-1	3.65	1.61	0.00	-1.98	-3.78	284	29677	2.089	9.09E-04	0.209	0.369	9.02E+09	4.19%	28.95%	4.24%	5.15%	3.29%	3.E+04	2.E+05	9769.4	1.144E-01	-2.088E-05
		2	N-U-2	3.51	1.85	0.00	-1.79	-3.75	263	26597	2.776	1.84E-03	0.275	0.275	9.02E+09	1.76%	21.60%	1.99%	2.34%	1.53%	4.E+04	4.E+05	9626.1	1.127E-01	-1.101E-05
		3	N-U-3	3.23	1.52	0.00	-2.32	-4.16	258	26034	2.176	1.99E-03	0.275	0.275	9.02E+09	1.31%	36.28%	1.47%	2.85%	1.59%	4.E+09	3.E+10	9780.8	1.149E-01	-4.287E-04
		4	N-U-4	2.96	1.10	0.00	-2.75	-4.54	235	27022	1.542	3.30E-03	0.278	0.277	9.02E+09	1.40%	26.10%	1.47%	2.72%	1.51%	1.E+13	1.E+14	9798.7	1.155E-01	-8.302E-04
	R30	1	N-R-1	5.03	2.94	0.00	-1.68	-3.78	201	30715	3.069	1.02E-02	0.203	0.340	9.02E+09	2.23%	15.67%	1.49%	4.79%	1.77%	23	168	11970.5	1.394E-01	8.302E-04
		2	N-R-2	5.30	2.67	0.00	-1.88	-3.72	273	33246	1.648	1.84E-03	0.157	0.330	9.02E+09	2.61%	10.01%	2.16%	8.82%	2.90%	21	151	12163.7	1.416E-01	9.264E-04
	RHR	1	N-RHR-1	4.74	2.05	0.00	-1.78	-3.68	307	32368	5.933	6.33E-02	0.200	0.455	9.02E+09	1.99%	5.44%	2.00%	4.44%	2.09%	26	203	11064.3	1.290E-01	6.087E-04

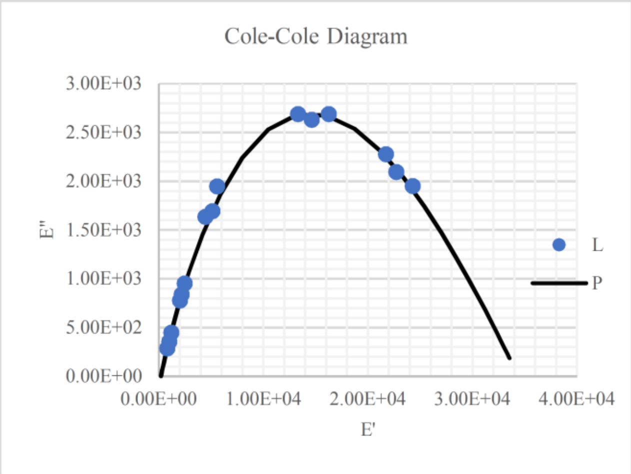
Unconditioned Mix (Plant mixed)

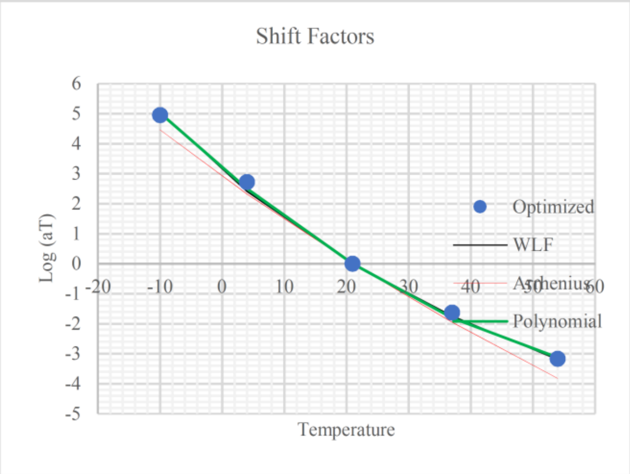




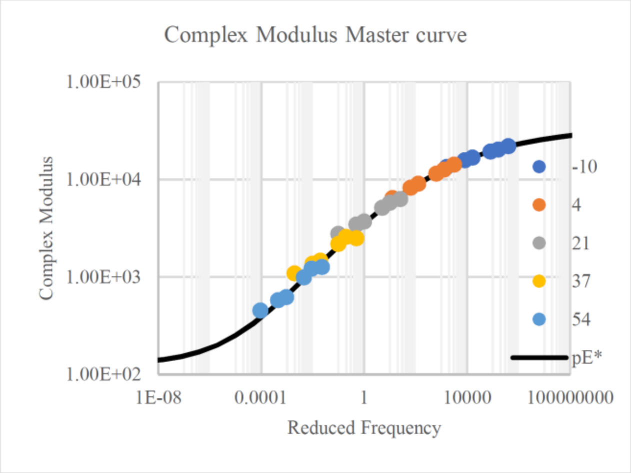


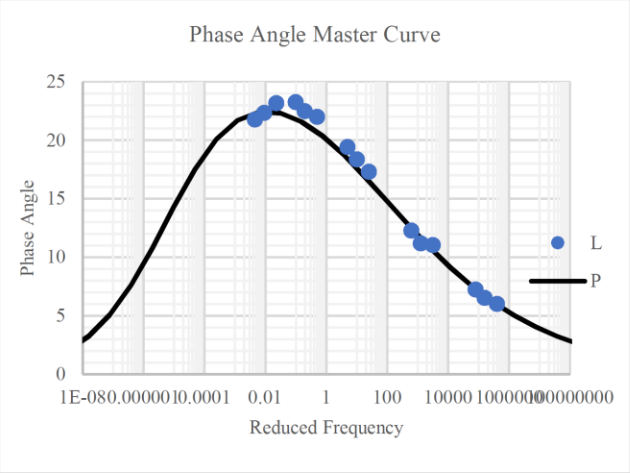


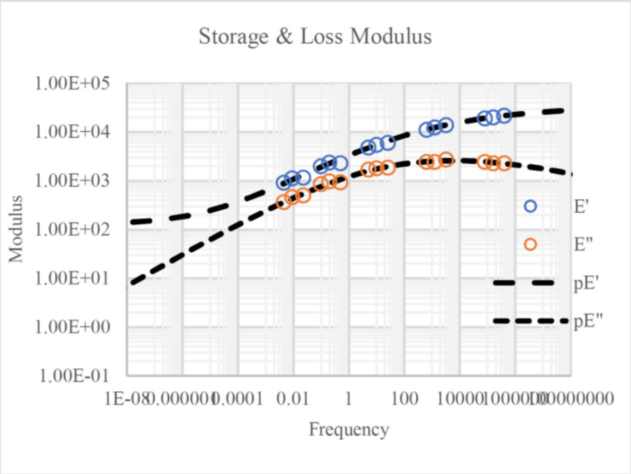


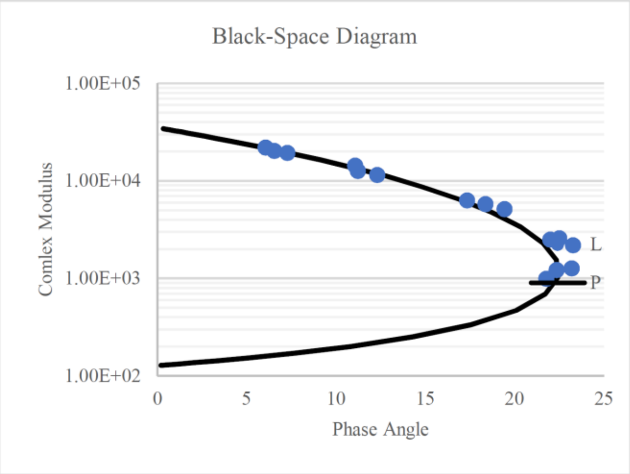


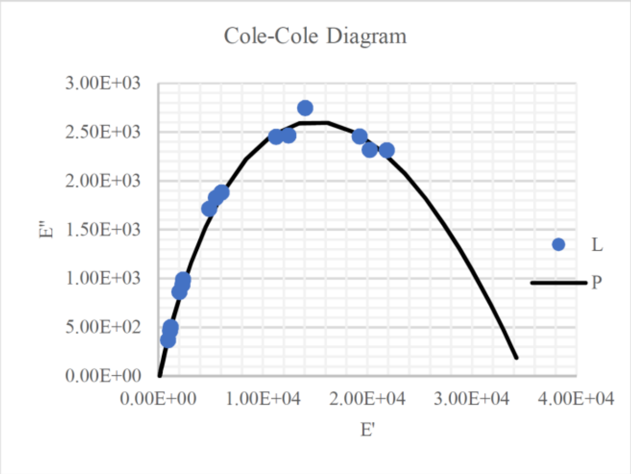
AASHTO R30-LTOA

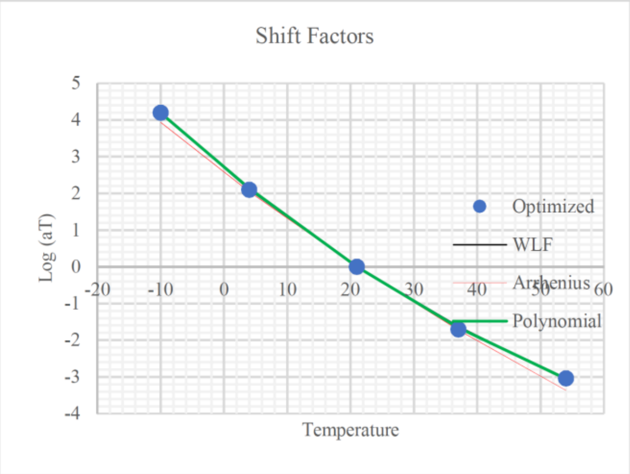




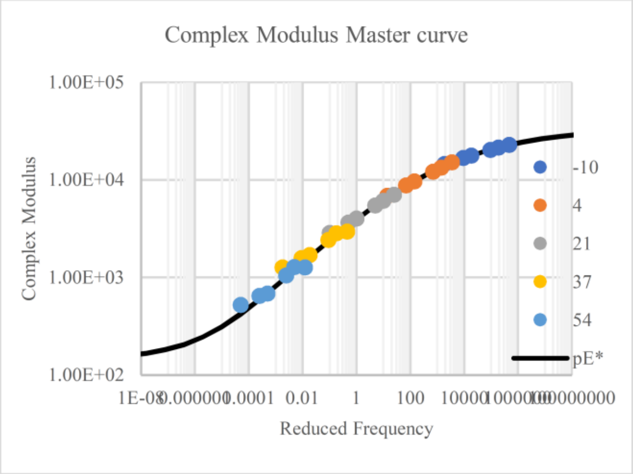


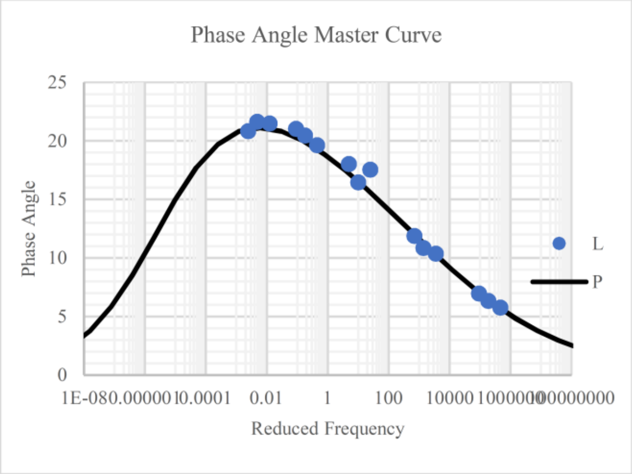


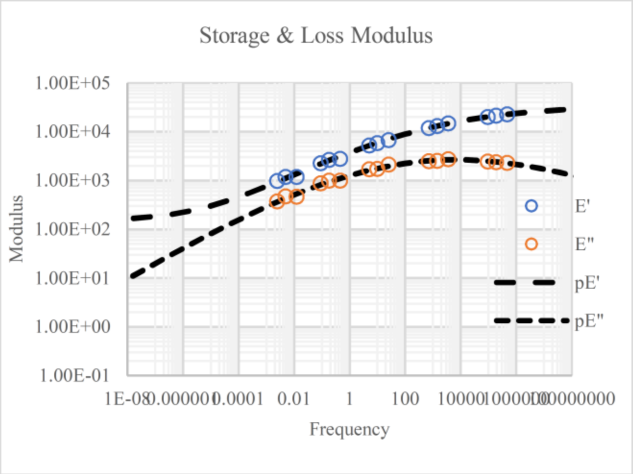


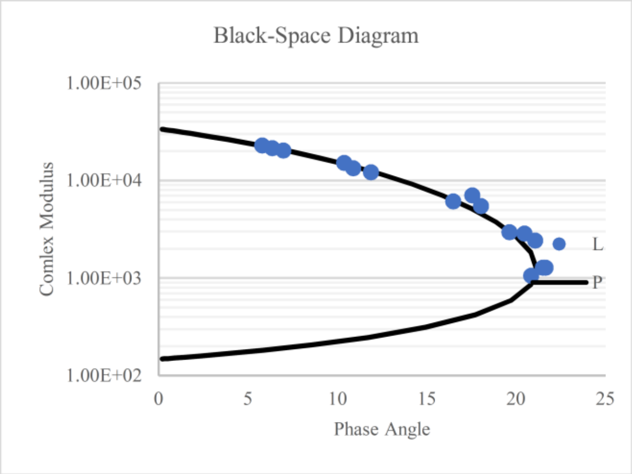


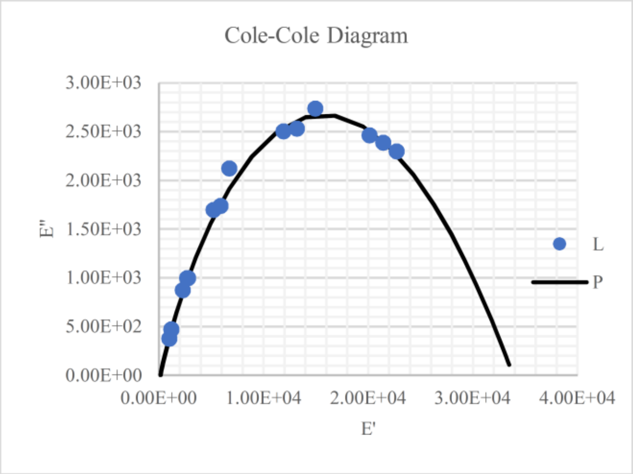
Atlas Weather-O-Meter

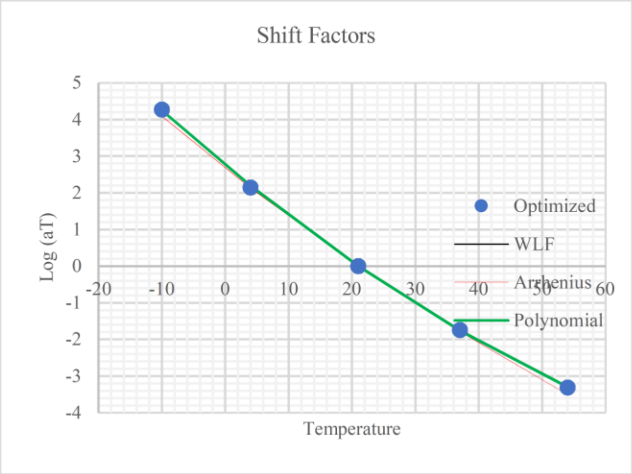




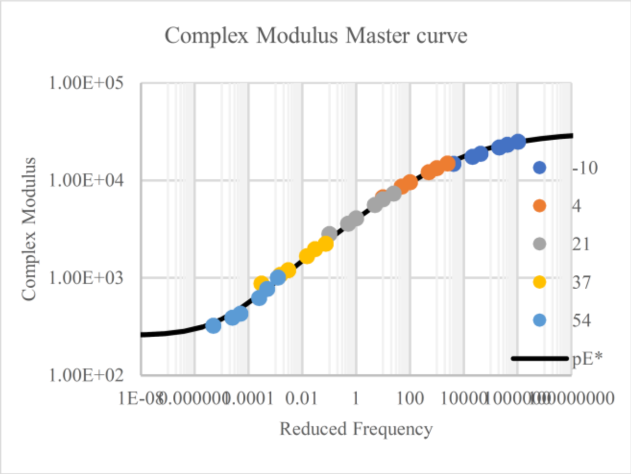


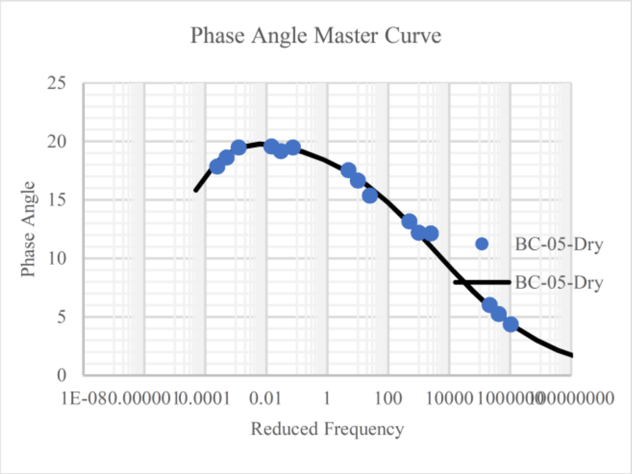


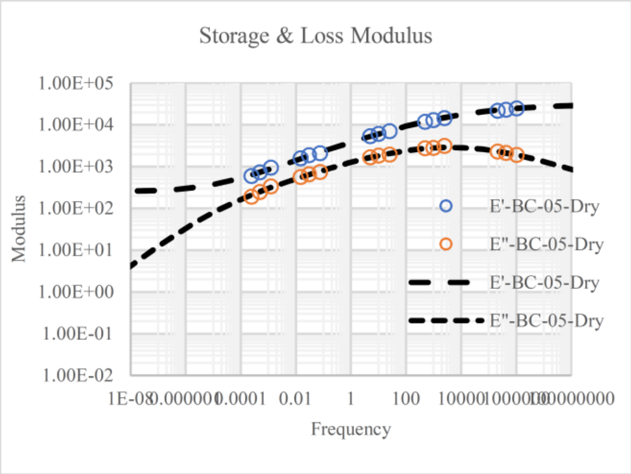


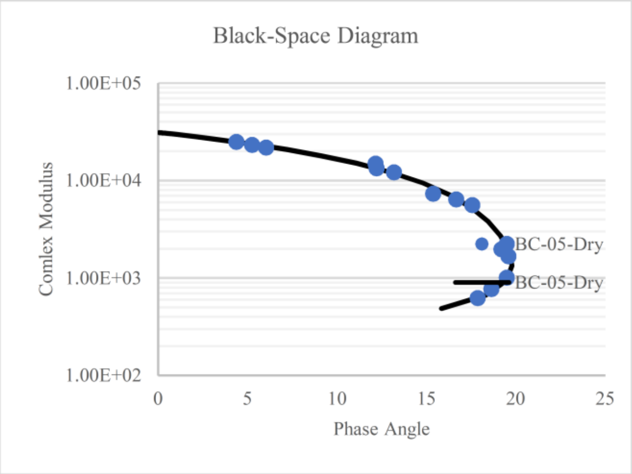


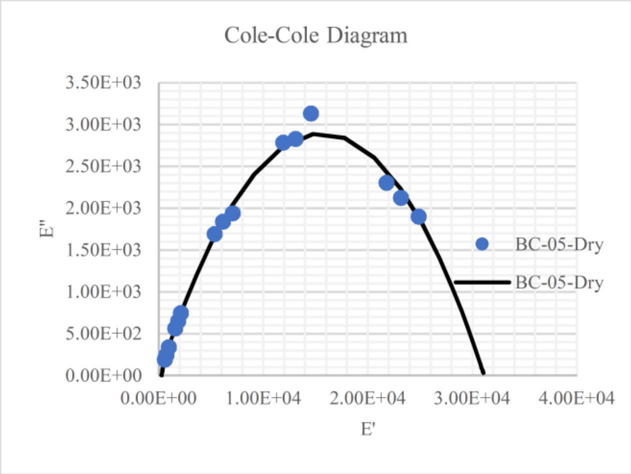
BC-05-Dry

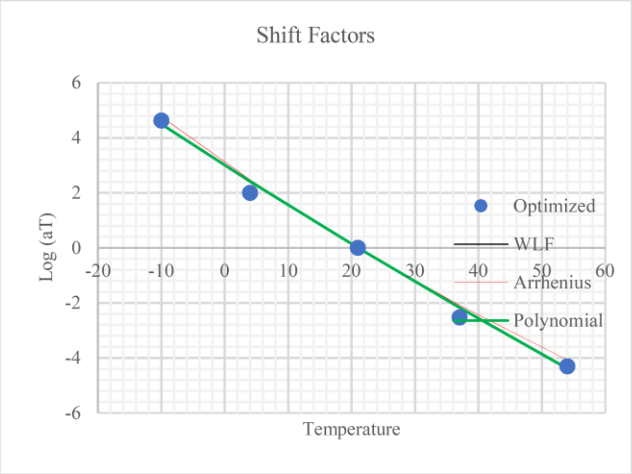

Complex Modulus Master curve
Complex Modulus
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1E-08
0.000001
0.0001
0.01
1
100
10000
1000000
100000000
Reduced Frequency
-10
4
21
37
54
pE*


Phase Angle Master Curve
Phase Angle
25
20
15
10
5
0
1E-08
0.000001
0.0001
0.01
1
100
10000
1000000
100000000
Reduced Frequency
BC-05-Dry
BC-05-Dry

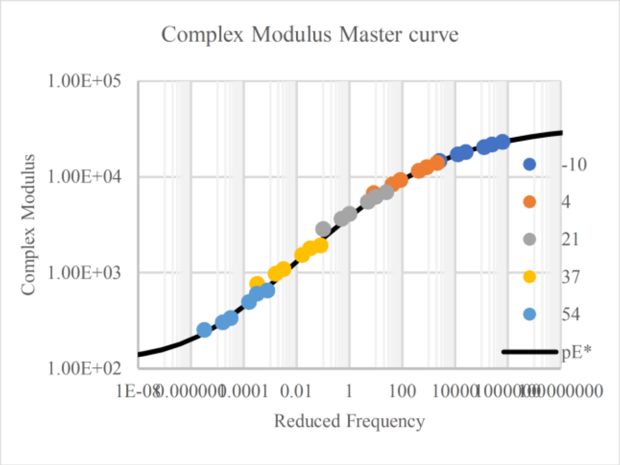

Storage & Loss Modulus
Modulus
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
1E-08
0.000001
0.0001
0.01
1
100
10000
1000000
100000000
Frequency
E'-BC-05-Dry
E"-BC-05-Dry
E'-BC-05-Dry
E"-BC-05-Dry

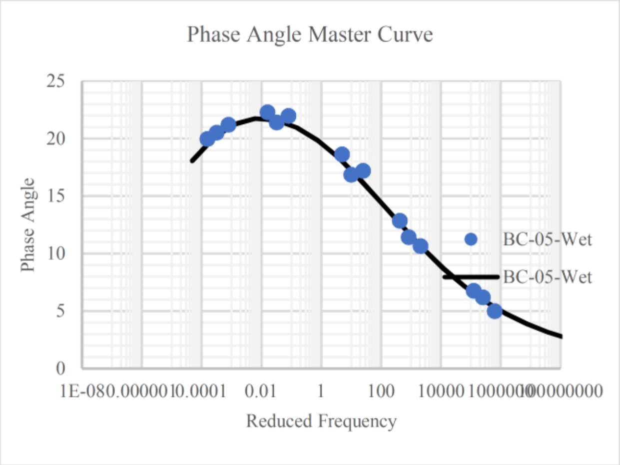

Black-Space Diagram
Comlex Modulus
1.00E+05
1.00E+04
1.00E+03
1.00E+02
0
5
10
15
20
25
Phase Angle
BC-05-Dry
BC-05-Dry

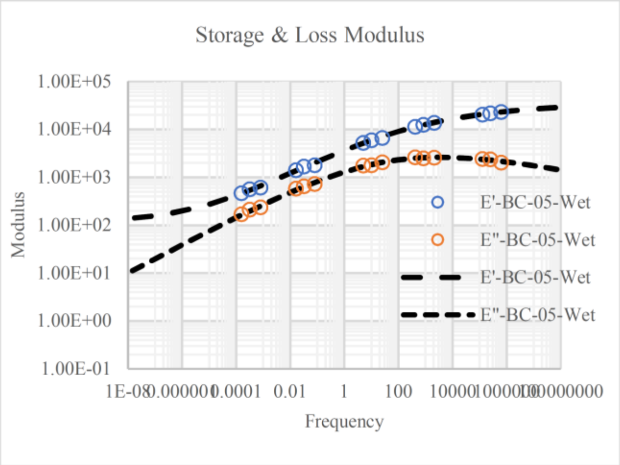

Cole-Cole Diagram
E"
3.50E+03
3.00E+03
2.50E+03
2.00E+03
1.50E+03
1.00E+03
5.00E+02
0.00E+00
0.00E+00
1.00E+04
2.00E+04
3.00E+04
4.00E+04
E'
BC-05-Dry
BC-05-Dry

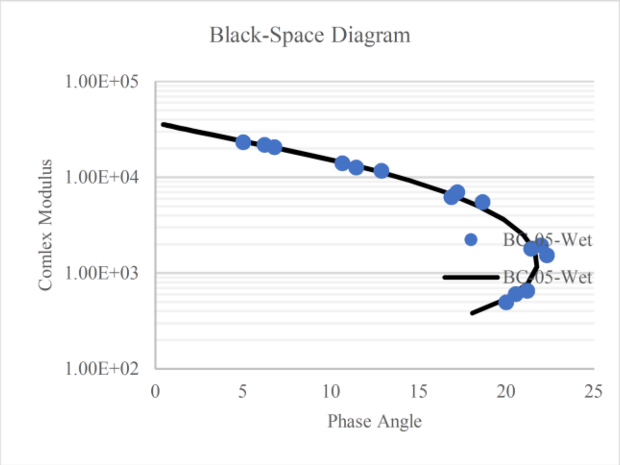

Shift Factors
Log (aT)
6
4
2
0
-2
-4
-6
-20
-10
0
10
20
30
40
50
60
Temperature
Optimized
WLF
Arrhenius
Polynomial

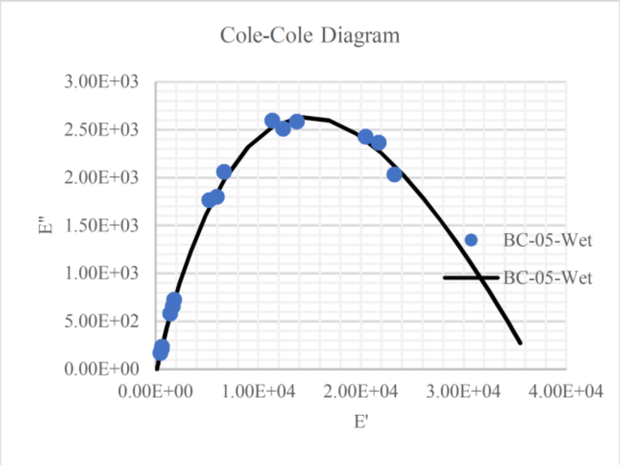
BC-05-Wet

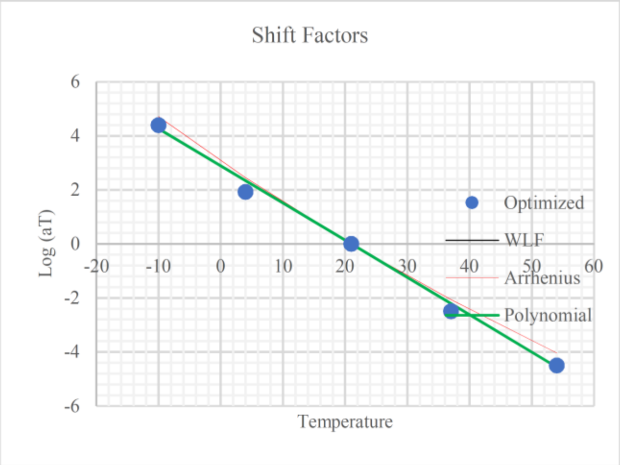

Complex Modulus Master curve
1.00E+05
1.00E+04
1.00E+03
1.00E+02
Complex Modulus
1E-08
0.000001
0.0001
0.01
1
100
10000
1000000
100000000
Reduced Frequency
-10
4
21
37
54
pE*


Phase Angle Master Curve
25
20
15
10
5
0
Phase Angle
1E-08
0.000001
0.0001
0.01
1
100
10000
1000000
100000000
Reduced Frequency
BC-05-Wet
BC-05-Wet

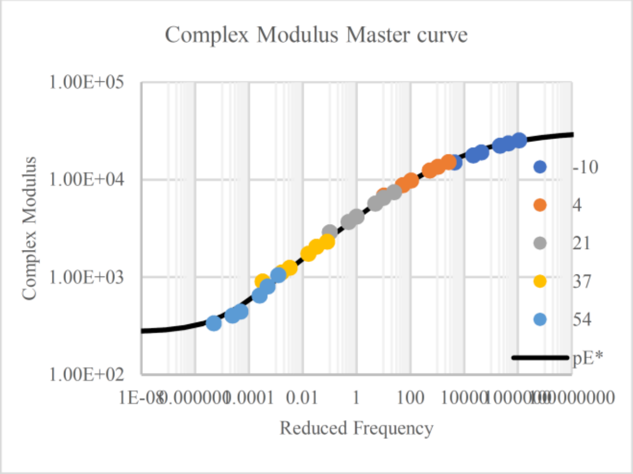

Storage & Loss Modulus
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
Modulus
1E-08
0.000001
0.0001
0.01
1
100
10000
1000000
100000000
Frequency
E'-BC-05-Wet
E"-BC-05-Wet
E'-BC-05-Wet
E"-BC-05-Wet

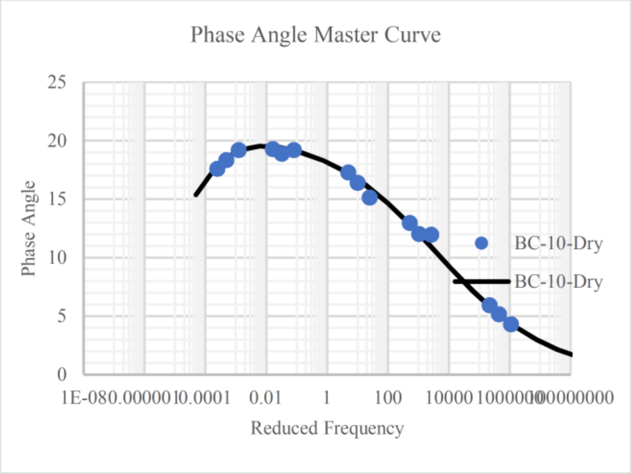

Black-Space Diagram
1.00E+05
1.00E+04
1.00E+03
1.00E+02
Comlex Modulus
0
5
10
15
20
25
Phase Angle
BC-05-Wet
BC-05-Wet

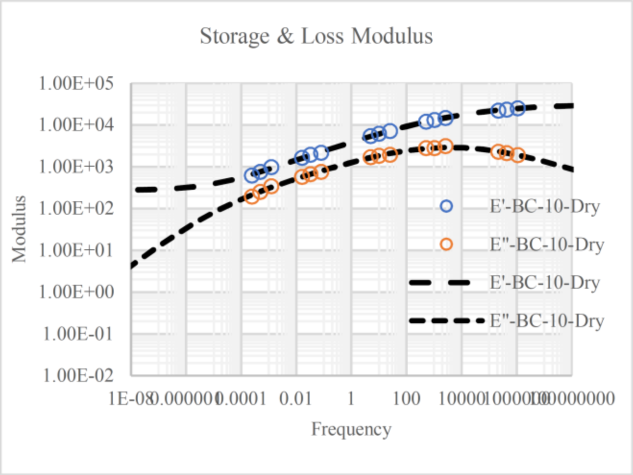

Cole-Cole Diagram
3.00E+03
2.50E+03
2.00E+03
1.50E+03
1.00E+03
5.00E+02
0.00E+00
E"
0.00E+00
1.00E+04
2.00E+04
3.00E+04
4.00E+04
E'
BC-05-Wet
BC-05-Wet

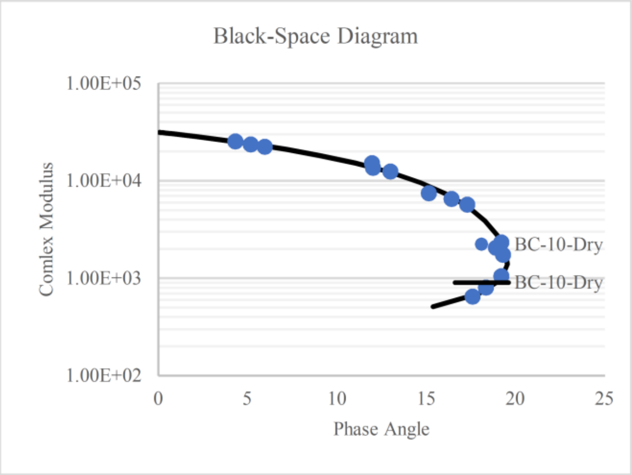

Shift Factors
6
4
2
0
-2
-4
-6
Log (aT)
-20
-10
0
10
20
30
40
50
60
Temperature
Optimized
WLF
Arrhenius
Polynomial

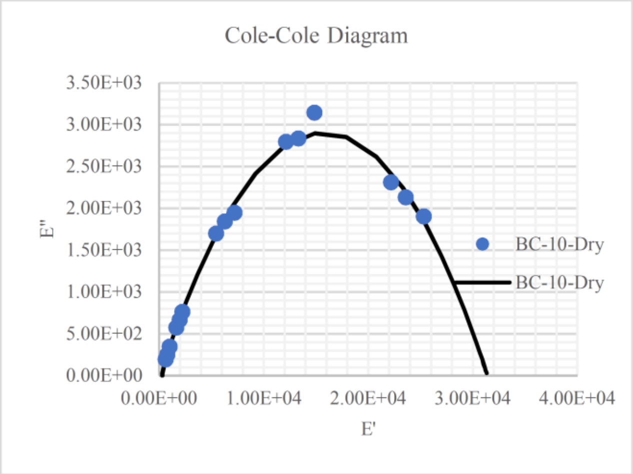
BC-10-Dry

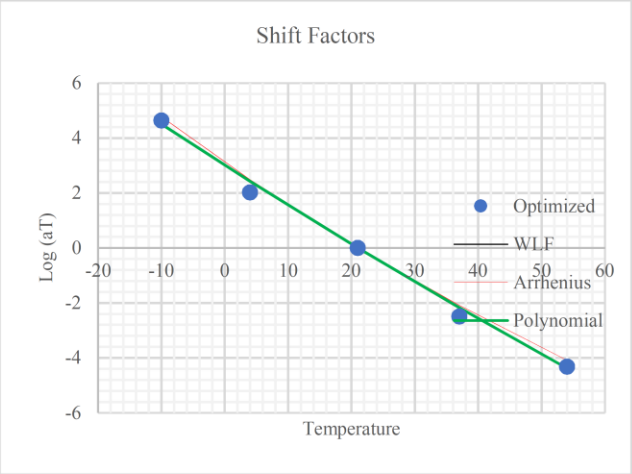

Complex Modulus Master curve
1.00E+05
1.00E+04
1.00E+03
1.00E+02
Complex Modulus
1E-08
0.000001
0.0001
0.01
1
100
10000
1000000
100000000
Reduced Frequency
-10
4
21
37
54
pE*


Phase Angle Master Curve
25
20
15
10
5
0
Phase Angle
1E-08
0.000001
0.0001
0.01
1
100
10000
1000000
100000000
Reduced Frequency
BC-10-Dry
BC-10-Dry

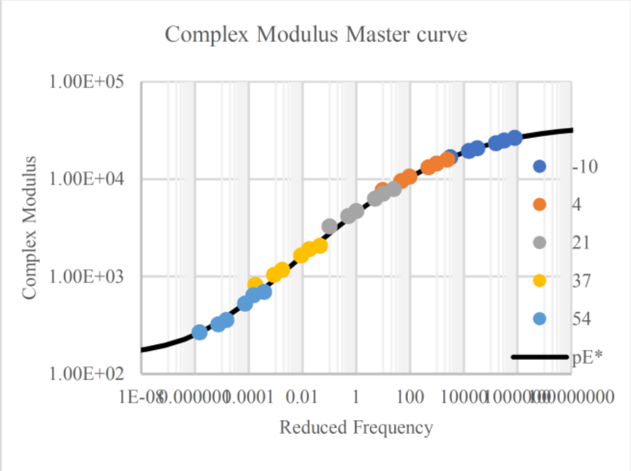

Storage & Loss Modulus
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
Modulus
1E-08
0.000001
0.0001
0.01
1
100
10000
1000000
100000000
Frequency
E'-BC-10-Dry
E"-BC-10-Dry
E'-BC-10-Dry
E"-BC-10-Dry

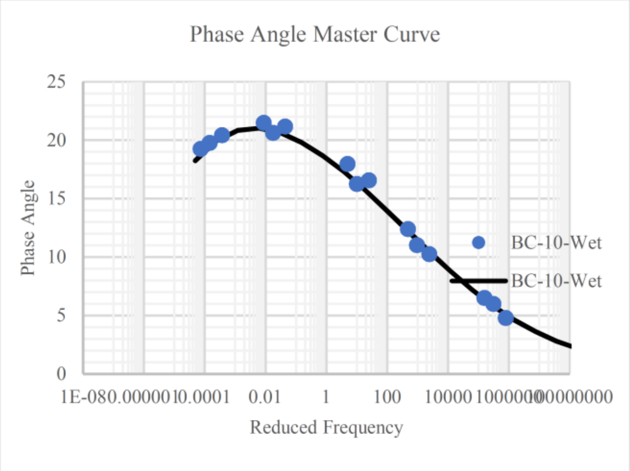

Black-Space Diagram
1.00E+05
1.00E+04
1.00E+03
1.00E+02
Comlex Modulus
0
5
10
15
20
25
Phase Angle
BC-10-Dry
BC-10-Dry

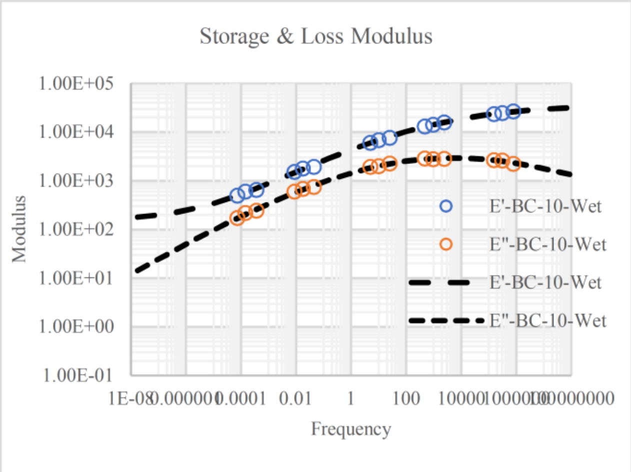

Cole-Cole Diagram
3.50E+03
3.00E+03
2.50E+03
2.00E+03
1.50E+03
1.00E+03
5.00E+02
0.00E+00
E"
0.00E+00
1.00E+04
2.00E+04
3.00E+04
4.00E+04
E'
BC-10-Dry
BC-10-Dry

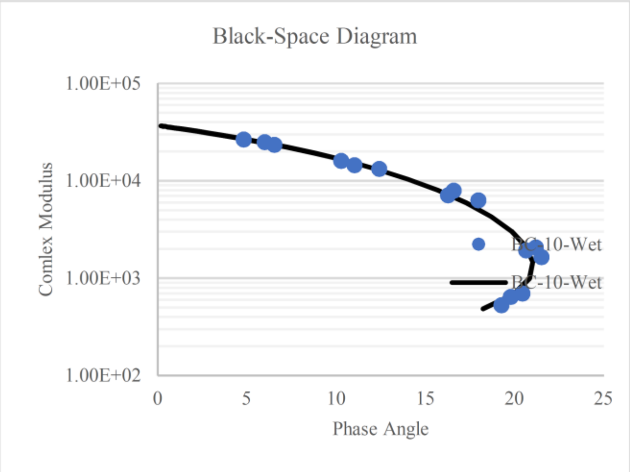

Shift Factors
6
4
2
0
-2
-4
-6
Log (aT)
-20
-10
0
10
20
30
40
50
60
Temperature
Optimized
WLF
Arrhenius
Polynomial

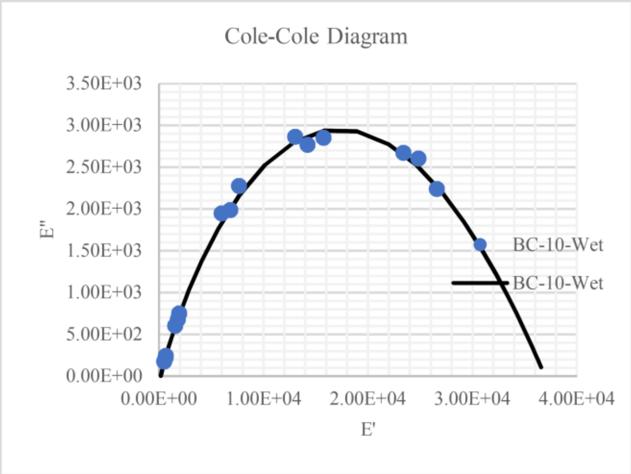
BC-10-Wet

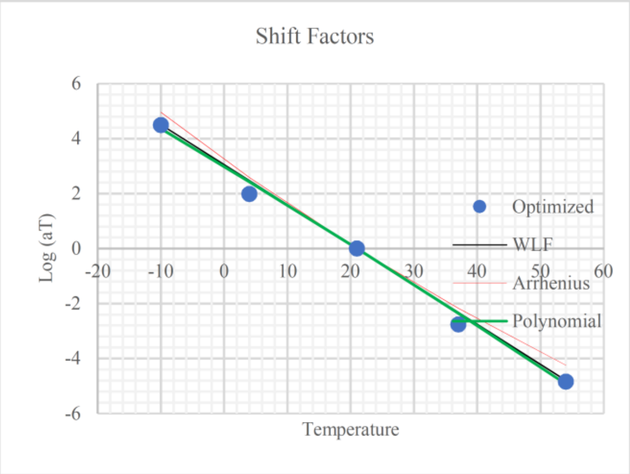

Complex Modulus Master curve


Phase Angle Master Curve

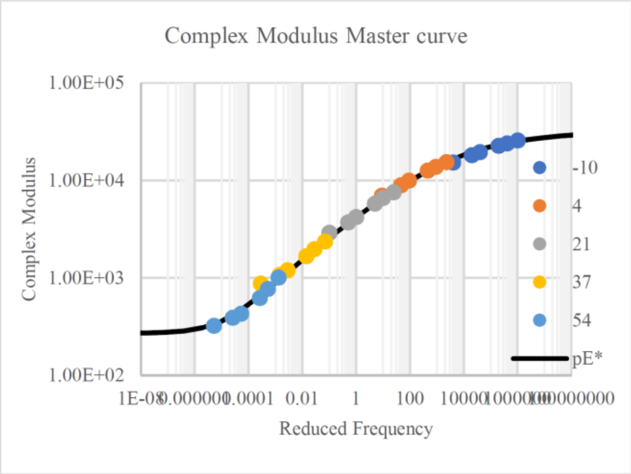

Storage & Loss Modulus

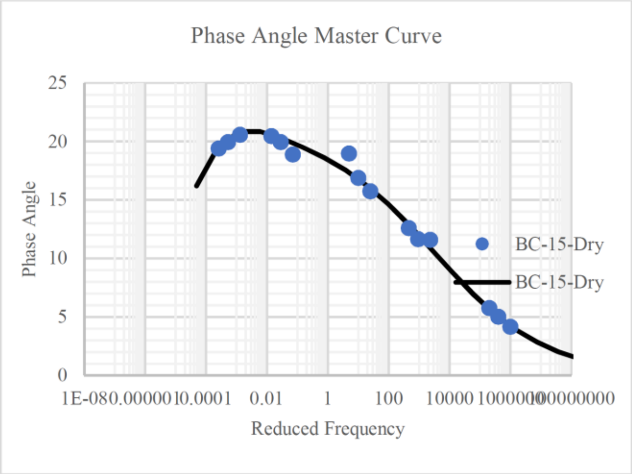

Black-Space Diagram

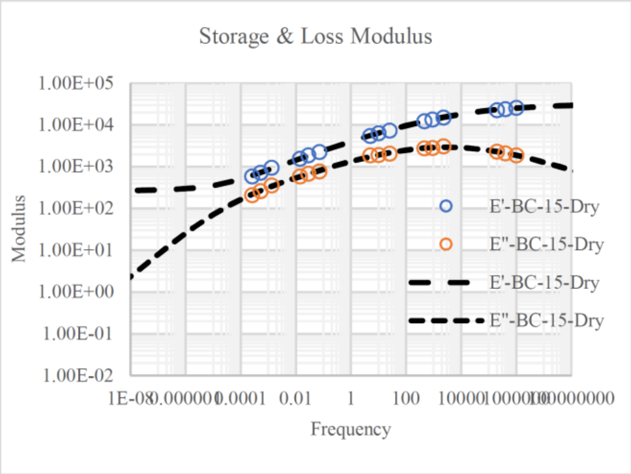

Cole-Cole Diagram

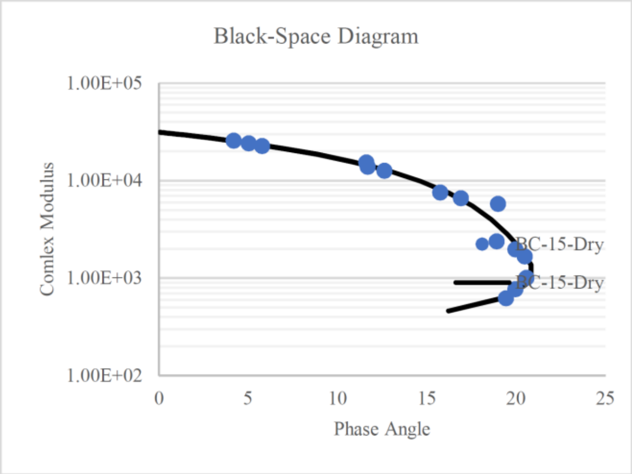

Shift Factors

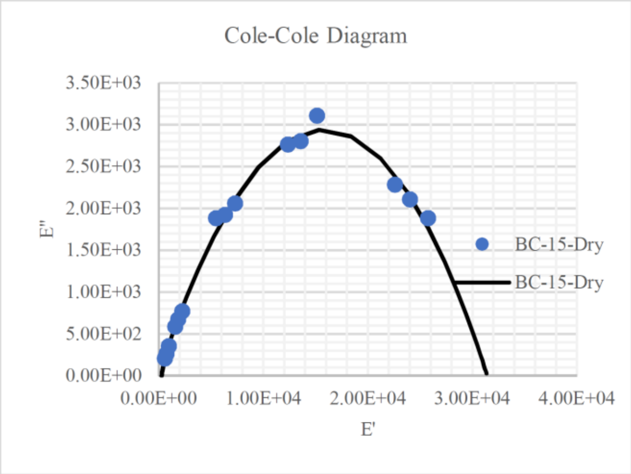
BC-15-Dry

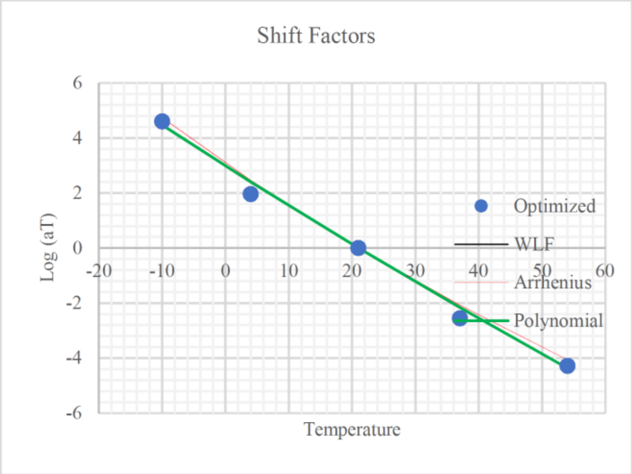

Complex Modulus Master curve
Complex Modulus
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1E-08
0.000001
0.0001
0.01
1
100
10000
1000000
100000000
Reduced Frequency
-10
4
21
37
54
pE*


Phase Angle Master Curve
Phase Angle
25
20
15
10
5
0
1E-08
0.000001
0.0001
0.01
1
100
10000
1000000
100000000
Reduced Frequency
BC-15-Dry
BC-15-Dry

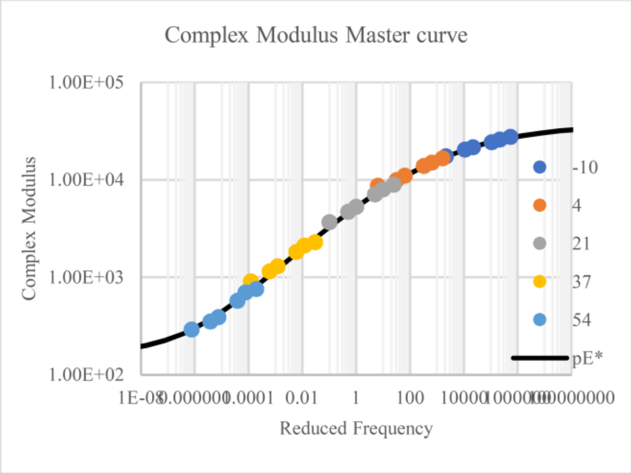

Storage & Loss Modulus
Modulus
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
1E-08
0.000001
0.0001
0.01
1
100
10000
1000000
100000000
Frequency
E'-BC-15-Dry
E"-BC-15-Dry
E'-BC-15-Dry
E"-BC-15-Dry

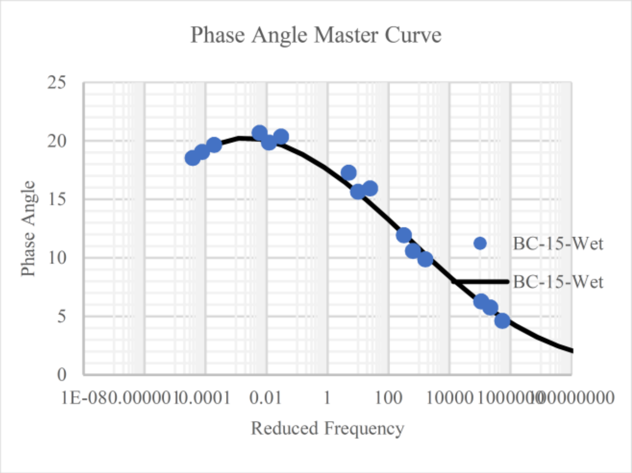

Black-Space Diagram
Comlex Modulus
1.00E+05
1.00E+04
1.00E+03
1.00E+02
0
5
10
15
20
25
Phase Angle
BC-15-Dry
BC-15-Dry

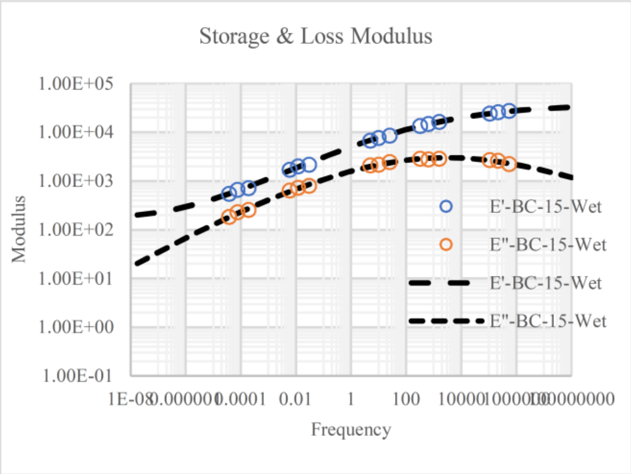

Cole-Cole Diagram
E"
3.50E+03
3.00E+03
2.50E+03
2.00E+03
1.50E+03
1.00E+03
5.00E+02
0.00E+00
0.00E+00
1.00E+04
2.00E+04
3.00E+04
4.00E+04
E'
BC-15-Dry
BC-15-Dry

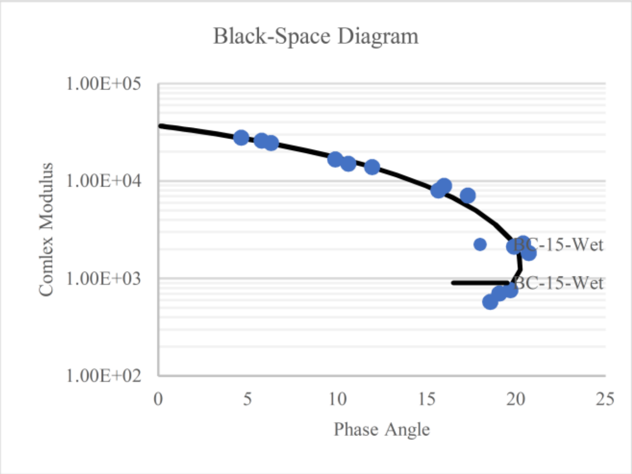

Shift Factors
Log (aT)
6
4
2
0
-2
-4
-6
-20
-10
0
10
20
30
40
50
60
Temperature
Optimized
WLF
Arrhenius
Polynomial

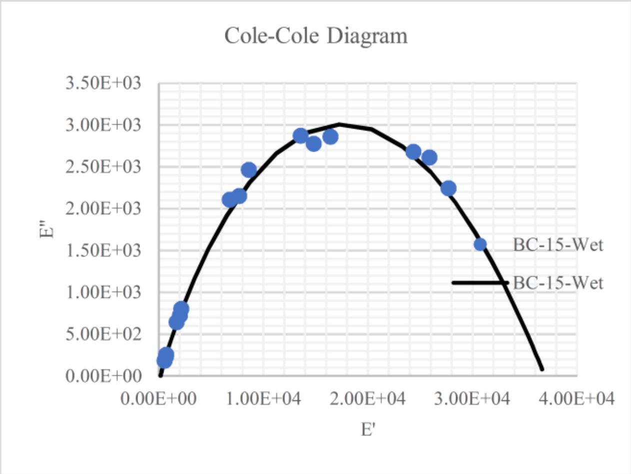
BC-15-Wet

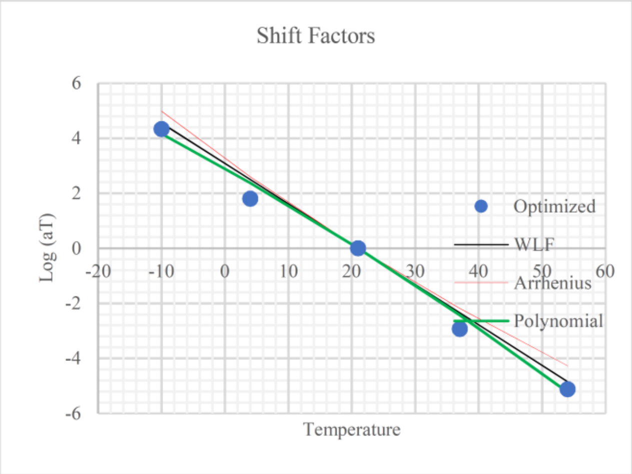

Complex Modulus Master curve
1.00E+05
1.00E+04
1.00E+03
1.00E+02
Complex Modulus
1E-08
0.000001
0.0001
0.01
1
100
10000
1000000
100000000
Reduced Frequency
-10
4
21
37
54
pE*


Phase Angle Master Curve
25
20
15
10
5
0
Phase Angle
1E-08
0.000001
0.0001
0.01
1
100
10000
1000000
100000000
Reduced Frequency
BC-15-Wet
BC-15-Wet

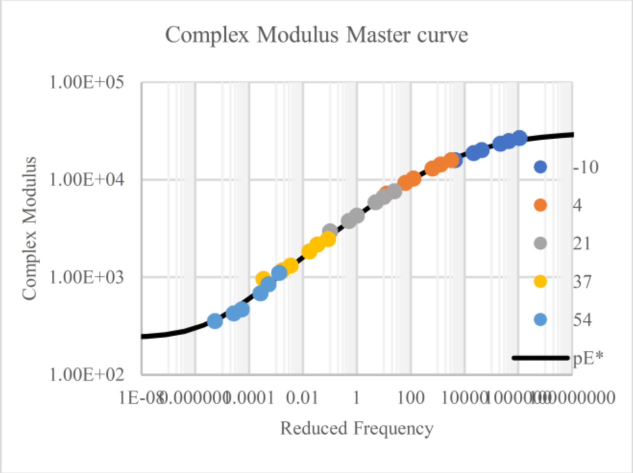

Storage & Loss Modulus
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
Modulus
1E-08
0.000001
0.0001
0.01
1
100
10000
1000000
100000000
Frequency
E'-BC-15-Wet
E"-BC-15-Wet
E'-BC-15-Wet
E"-BC-15-Wet

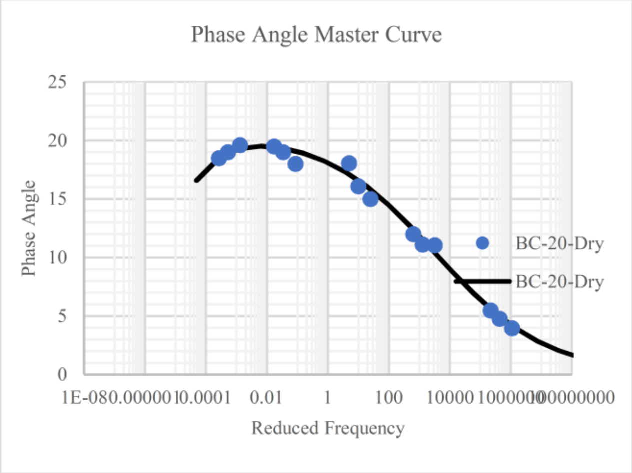

Black-Space Diagram
1.00E+05
1.00E+04
1.00E+03
1.00E+02
Comlex Modulus
0
5
10
15
20
25
Phase Angle
BC-15-Wet
BC-15-Wet

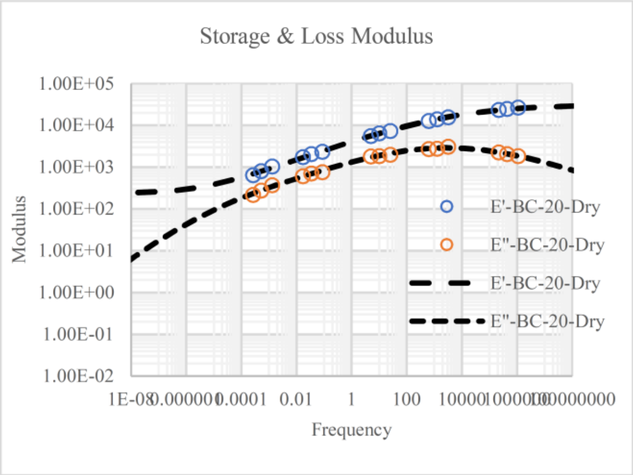

Cole-Cole Diagram
3.50E+03
3.00E+03
2.50E+03
2.00E+03
1.50E+03
1.00E+03
5.00E+02
0.00E+00
E"
0.00E+00
1.00E+04
2.00E+04
3.00E+04
4.00E+04
E'
BC-15-Wet
BC-15-Wet

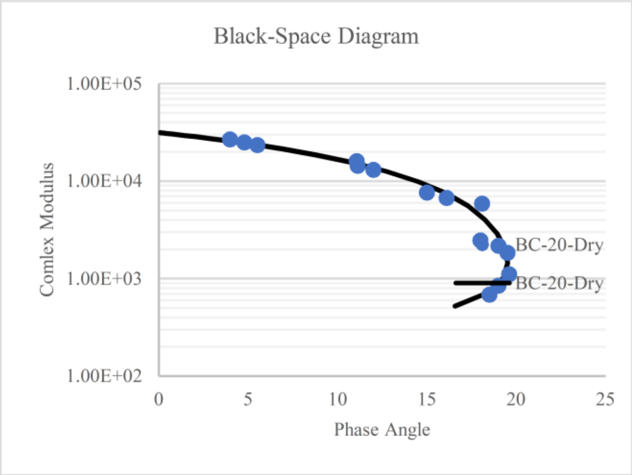

Shift Factors
6
4
2
0
-2
-4
-6
Log (aT)
-20
-10
0
10
20
30
40
50
60
Temperature
Optimized
WLF
Arrhenius
Polynomial

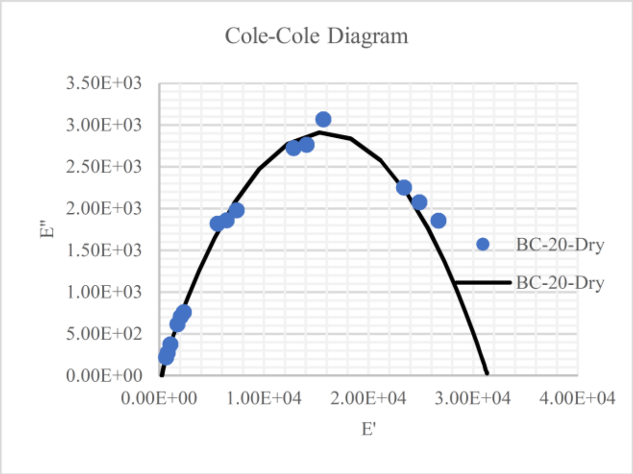
BC-20-Dry

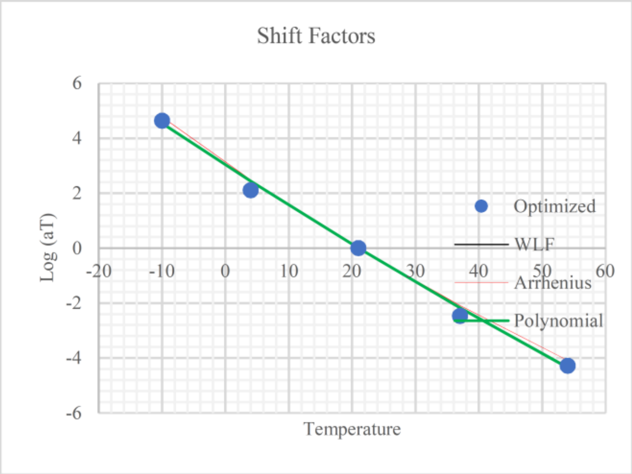

Complex Modulus Master curve


Phase Angle Master Curve

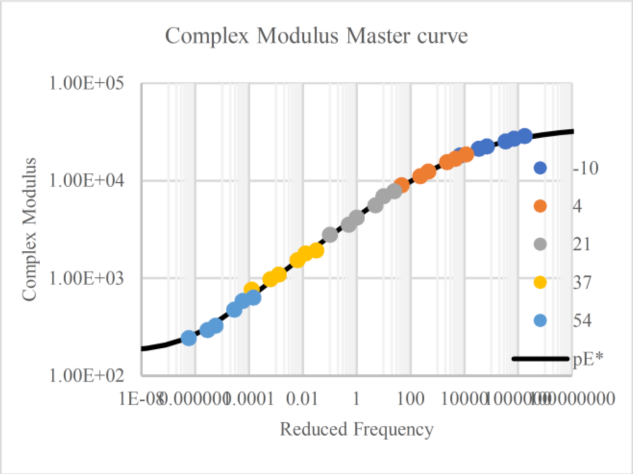

Storage & Loss Modulus

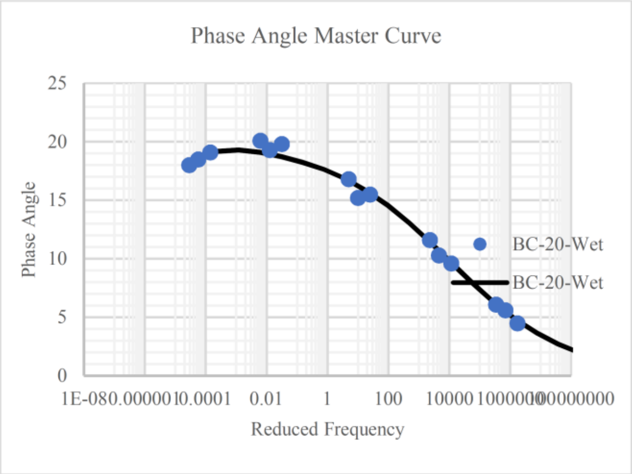

Black-Space Diagram

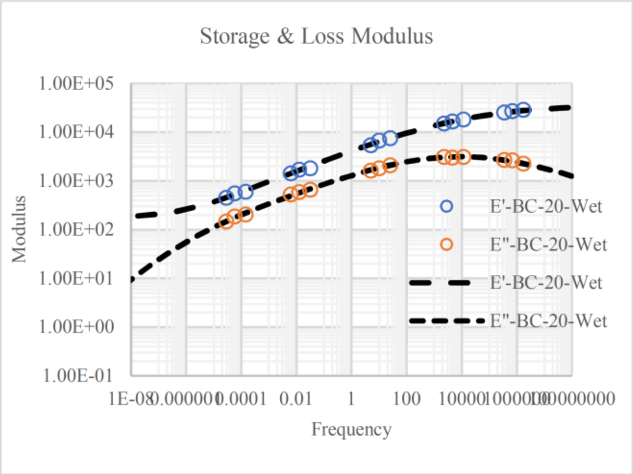

Cole-Cole Diagram

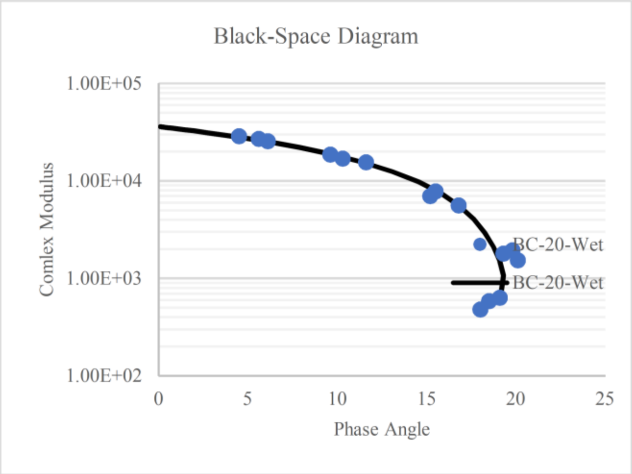

Shift Factors

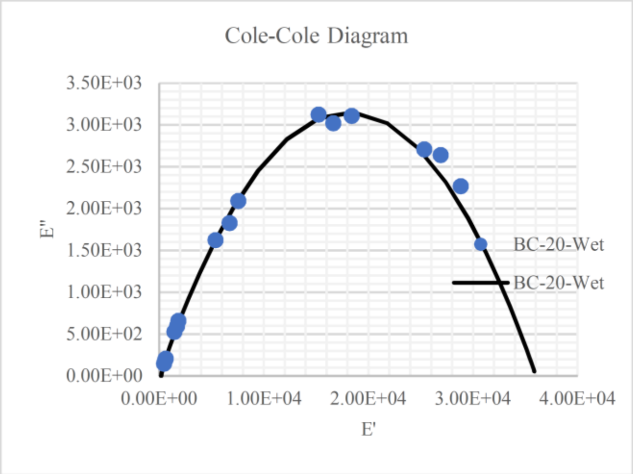
BC-20-Wet

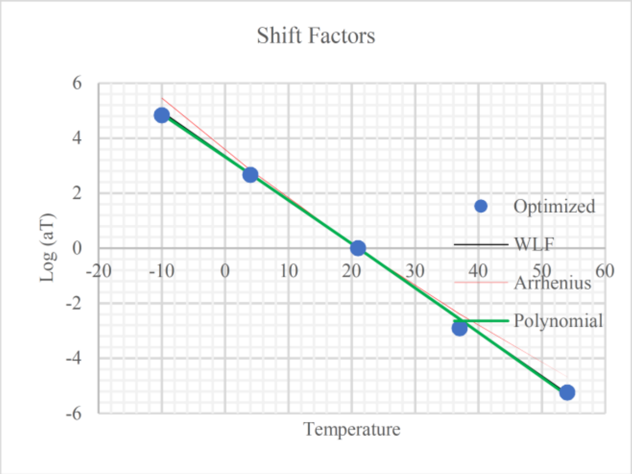

Complex Modulus Master curve
1.00E+05
1.00E+04
1.00E+03
1.00E+02
Complex Modulus
1E-08
0.000001
0.0001
0.01
1
100
10000
1000000
100000000
Reduced Frequency
● -10
● 4
● 21
● 37
● 54
pE*


Phase Angle Master Curve
25
20
15
10
5
0
Phase Angle
1E-08
0.000001
0.0001
0.01
1
100
10000
1000000
100000000
Reduced Frequency
● BC-20-Wet
BC-20-Wet


Storage & Loss Modulus
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
Modulus
1E-08
0.000001
0.0001
0.01
1
100
10000
1000000
100000000
Frequency
○ E'-BC-20-Wet
○ E"-BC-20-Wet
E'-BC-20-Wet
E"-BC-20-Wet


Black-Space Diagram
1.00E+05
1.00E+04
1.00E+03
1.00E+02
Comlex Modulus
0
5
10
15
20
25
Phase Angle
● BC-20-Wet
BC-20-Wet


Cole-Cole Diagram
3.50E+03
3.00E+03
2.50E+03
2.00E+03
1.50E+03
1.00E+03
5.00E+02
0.00E+00
E"
0.00E+00
1.00E+04
2.00E+04
3.00E+04
4.00E+04
E'
● BC-20-Wet
BC-20-Wet

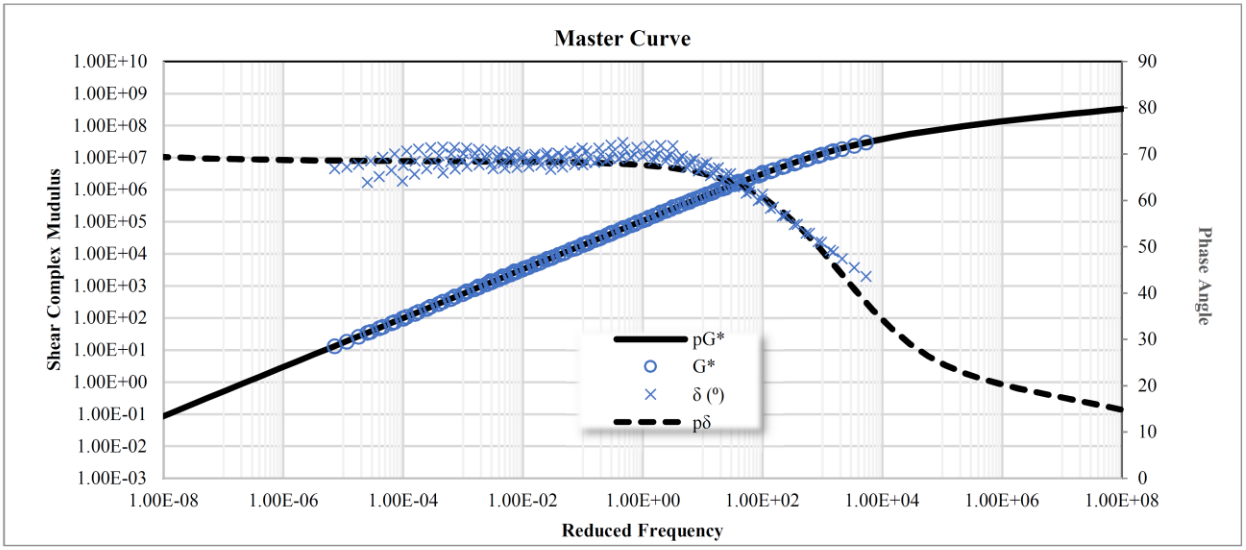

Shift Factors
6
4
2
0
-2
-4
-6
Log (aT)
-20
-10
0
10
20
30
40
50
60
Temperature
● Optimized
WLF
Arrhenius
Polynomial

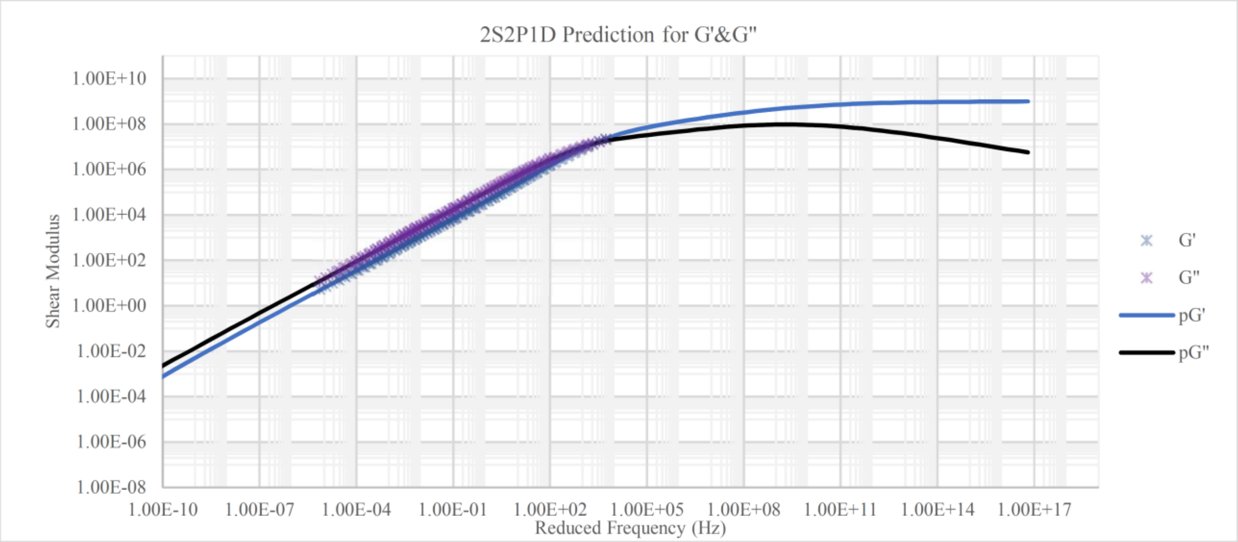
Model Parameters

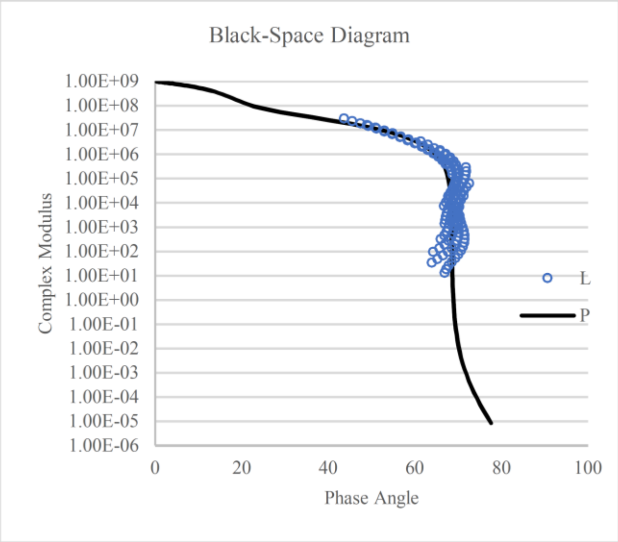
sample number	Condition	a1	a2	a3	a4	a5	2S2P1D Model Parameters						RMSEIQR					WLF		Arrhenius	Polynomial		Elastic Return Temperature		
		-10	4	21	37	54	E0	E∞	δ	τ0	k	h	E*	δ	E'	E"	E',E"	C1	C2	Ea/R	C1	C2	WLF	Arrhenius	Polynomial
1	STOA	4.96	2.73	0.00	-1.62	-3.17	193	34395	1.14	2.43E-04	0.14	0.31	2.17%	5.95%	2.23%	3.59%	1.79%	15.3	124.6	11143.2	0.130	1.05E-03	44	41	43
2	STOA	5.10	2.83	0.00	-1.69	-3.36	158	35581	2.18	1.95E-03	0.16	0.34	2.26%	5.25%	2.17%	6.54%	2.34%	16.7	130.8	11586.6	0.135	1.04E-03	52	47	52
3	STOA	4.85	2.12	0.00	-1.76	-3.46	127	35666	2.15	1.72E-03	0.15	0.32	2.41%	6.42%	2.35%	6.27%	2.59%	19.8	160.0	11014.5	0.128	7.71E-04	56	52	57
4	STOA	4.75	2.01	0.00	-1.86	-3.56	239	38960	2.00	4.26E-04	0.16	0.33	1.40%	7.54%	1.42%	3.10%	1.52%	23.5	188.3	10978.7	0.128	6.53E-04	41	40	41
5	STOA	4.24	1.94	0.00	-1.66	-3.22	362	32235	2.33	2.29E-03	0.18	0.37	2.39%	8.51%	2.41%	4.12%	2.12%	21.8	193.1	9926.9	0.116	5.82E-04	41	40	41
6	STOA	4.50	2.16	0.00	-1.77	-3.63	144	33245	2.43	3.35E-03	0.17	0.33	1.65%	7.53%	1.61%	4.87%	1.99%	28.3	228.7	10804.1	0.126	5.37E-04	51	50	51
7	STOA	4.22	1.87	0.00	-1.78	-3.67	127	35065	0.95	1.96E-04	0.12	0.28	2.45%	9.51%	2.43%	5.96%	2.57%	39.9	332.3	10358.1	0.121	3.50E-04	48	49	48
8	STOA	4.20	1.94	0.00	-1.81	-3.45	363	32228	5.52	4.64E-02	0.22	0.49	1.71%	8.90%	1.75%	3.94%	1.81%	30.3	258.4	10181.7	0.119	4.49E-04	46	46	46
9	STOA	3.86	1.61	0.00	-1.83	-3.56	209	31771	1.48	1.60E-03	0.18	0.33	2.07%	10.38%	2.18%	4.12%	1.99%	64.3	566.7	9725.6	0.114	1.94E-04	45	46	45
10	STOA	4.09	2.03	0.00	-1.75	-3.57	118	34024	1.97	2.00E-03	0.19	0.32	2.12%	3.97%	2.07%	3.76%	1.86%	38.1	322.9	10195.5	0.119	3.62E-04	50	51	50
11	STOA	3.95	1.97	0.00	-1.90	-3.27	376	30685	5.23	3.91E-02	0.23	0.46	0.75%	6.52%	0.70%	2.87%	1.17%	31.8	281.4	9786.3	0.114	4.07E-04	41	41	41
12	STOA	4.62	2.04	0.00	-1.77	-3.63	154	43987	1.66	2.58E-04	0.13	0.30	1.25%	6.99%	1.14%	4.03%	1.69%	26.2	210.9	10876.9	0.127	5.77E-04	49	48	49
13	STOA	4.26	3.29	0.00	-1.78	-3.54	112	33680	2.15	2.76E-03	0.18	0.33	1.80%	4.35%	1.79%	4.17%	1.79%	21.7	178.1	10729.4	0.125	7.53E-04	55	52	56
14	STOA	4.09	3.18	0.00	-1.67	-3.46	226	37575	1.17	3.12E-04	0.12	0.31	0.87%	6.14%	0.98%	3.63%	1.32%	31.2	268.0	10104.5	0.118	4.36E-04	44	44	44
15	STOA	4.14	3.18	0.00	-1.65	-3.44	193	37204	1.18	1.84E-04	0.12	0.30	1.90%	3.41%	1.87%	3.75%	1.74%	29.2	250.3	10131.0	0.118	4.68E-04	44	44	44
16	STOA	4.35	3.36	0.00	-1.82	-3.69	136	34038	1.65	1.66E-03	0.17	0.32	2.27%	3.87%	2.26%	4.96%	2.14%	34.2	275.1	10776.7	0.126	4.54E-04	54	48	56
17	STOA	4.34	3.27	0.00	-1.81	-3.68	239	30929	1.97	2.40E-03	0.19	0.32	1.32%	3.82%	1.32%	3.38%	1.39%	33.9	273.5	10743.5	0.126	4.56E-04	43	43	43
18	STOA	4.20	3.89	0.00	-1.76	-3.05	311	37971	1.50	1.54E-04	0.15	0.29	1.65%	5.04%	1.60%	3.62%	1.70%	19.6	175.6	9832.0	0.115	6.61E-04	40	39	39
19	STOA	4.39	4.07	0.00	-1.81	-3.10	220	33611	2.38	8.72E-04	0.17	0.31	1.84%	4.94%	1.77%	4.47%	2.00%	18.9	164.1	10165.7	0.119	7.33E-04	45	43	44
20	STOA	4.42	3.95	0.00	-1.94	-2.72	94	38537	4.61	1.57E-03	0.18	0.36	1.44%	4.74%	1.46%	2.41%	1.31%	14.4	131.2	9854.4	0.116	9.08E-04	62	54	67
21	STOA	4.43	3.93	0.00	-1.67	-2.59	179	39462	3.29	8.56E-04	0.15	0.38	2.50%	2.41%	2.43%	4.63%	2.29%	12.0	114.9	9566.2	0.113	9.93E-04	54	47	54
22	STOA	4.38	4.09	0.00	-1.64	-2.46	253	39493	3.26	9.44E-04	0.16	0.37	1.16%	3.98%	1.23%	2.35%	1.17%	11.0	108.6	9342.9	0.110	1.03E-03	51	45	51
23	STOA	4.02	3.99	0.00	-1.59	-2.64	106	36323	1.92	2.32E-04	0.16	0.31	2.09%	3.63%	2.07%	3.67%	1.89%	14.1	139.5	9046.3	0.106	7.68E-04	56	51	57
24	STOA	5.62	3.25	0.00	-1.66	-3.37	187	32980	3.30	2.09E-03	0.19	0.36	1.58%	3.94%	1.58%	3.16%	1.44%	14.9	111.0	12417.7	0.144	1.33E-03	43	40	43
25	STOA	5.67	3.36	0.00	-1.82	-3.65	147	30175	5.63	1.14E-02	0.21	0.37	1.63%	5.29%	1.66%	2.95%	1.42%	17.7	124.7	12899.4	0.150	1.23E-03	42	39	42
26	STOA	5.34	3.14	0.00	-1.77	-3.54	190	35706	1.30	1.82E-04	0.16	0.30	1.44%	3.92%	1.46%	2.77%	1.27%	17.9	131.9	12260.1	0.143	1.11E-03	40	38	40
27	STOA	5.70	3.32	0.00	-1.76	-3.44	244	35974	1.06	8.68E-05	0.14	0.30	1.44%	6.51%	1.51%	2.70%	1.26%	15.6	113.2	12680.1	0.147	1.34E-03	37	34	36
28	STOA	5.52	3.24	0.00	-1.66	-3.44	261	32477	2.09	4.85E-04	0.18	0.35	1.71%	5.95%	1.81%	1.55%	1.21%	15.8	117.4	12374.9	0.144	1.25E-03	35	34	35
29	STOA	5.28	3.23	0.00	-1.68	-3.46	181	29929	2.79	2.08E-03	0.21	0.35	2.36%	3.99%	2.30%	4.94%	2.13%	17.1	128.1	12125.0	0.141	1.13E-03	39	37	38
30	STOA	5.67	3.44	0.00	-1.60	-3.15	294	33115	3.82	3.29E-03	0.20	0.42	1.67%	3.79%	1.67%	3.35%	1.49%	13.3	100.9	12348.4	0.143	1.49E-03	39	36	38
1	LTOA	4.20	2.10	0.00	-1.71	-3.04	128	35037	1.79	9.65E-04	0.15	0.33	3.95%	6.87%	3.92%	7.02%	3.43%	19.0	170.9	9827.6	0.114	6.67E-04	55	52	55
2	LTOA	4.45	2.00	0.00	-1.41	-2.89	322	43280	3.06	2.39E-03	0.14	0.39	3.16%	8.14%	3.17%	7.62%	3.22%	13.6	126.8	9763.3	0.114	8.64E-04	52	47	52
3	LTOA	4.54	2.01	0.00	-1.55	-2.75	371	42637	2.67	1.37E-03	0.13	0.37	3.45%	3.87%	3.37%	6.93%	3.15%	12.5	116.7	9803.8	0.114	9.54E-04	50	44	49
4	Atlas	4.27	2.15	0.00	-1.74	-3.31	148	33853	2.66	5.62E-03	0.18	0.34	3.37%	6.35%	3.32%	6.51%	3.06%	23.7	203.3	10213.4	0.119	5.80E-04	56	53	56
5	Atlas	4.02	1.74	0.00	-1.68	-3.58	232	31030	2.85	8.95E-03	0.18	0.34	4.35%	8.67%	4.31%	7.44%	3.82%	43.8	379.9	9923.6	0.116	2.92E-04	49	50	49
6	Atlas	4.31	2.20	0.00	-1.55	-3.23	116	32538	2.92	1.27E-02	0.18	0.35	4.58%	5.71%	4.47%	10.64%	4.25%	20.2	176.3	10116.9	0.118	6.57E-04	64	59	66

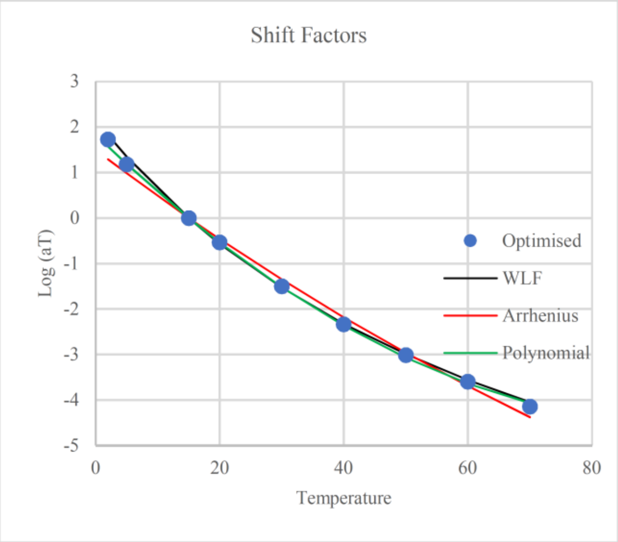
APPENDIX B: Rheology of Recovered Asphalt Cement

PG 58-34p

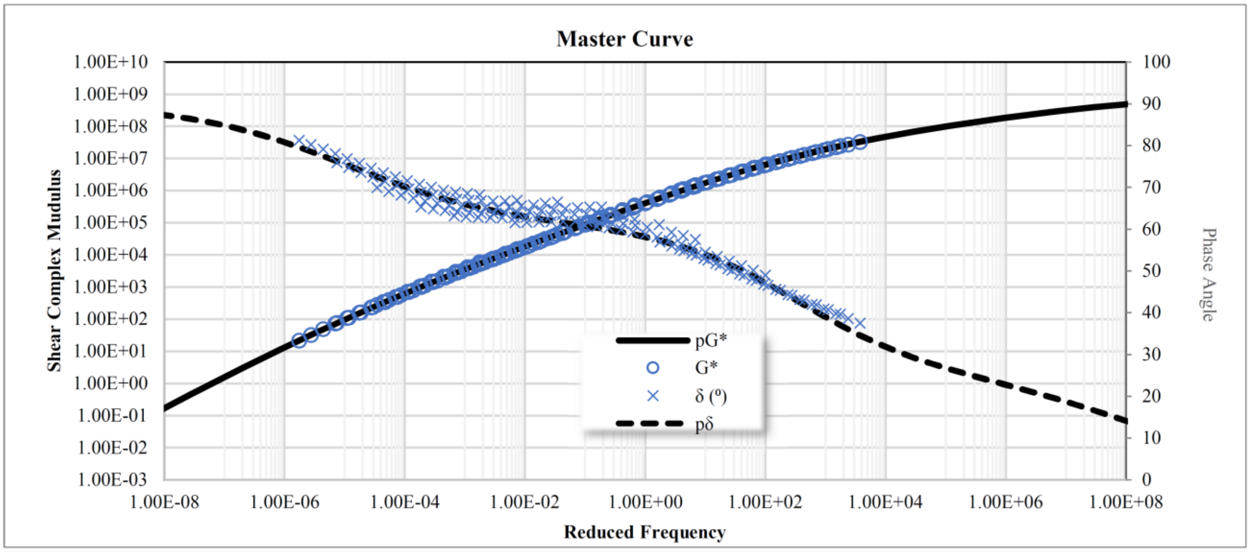

Master Curve
Shear Complex Mudulus
1.00E+10
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
1.00E-03
Phase Angle
90
80
70
60
50
40
30
20
10
0
1.00E-08
1.00E-06
1.00E-04
1.00E-02
1.00E+00
1.00E+02
1.00E+04
1.00E+06
1.00E+08
Reduced Frequency
pG*
G*
δ (º)
pδ

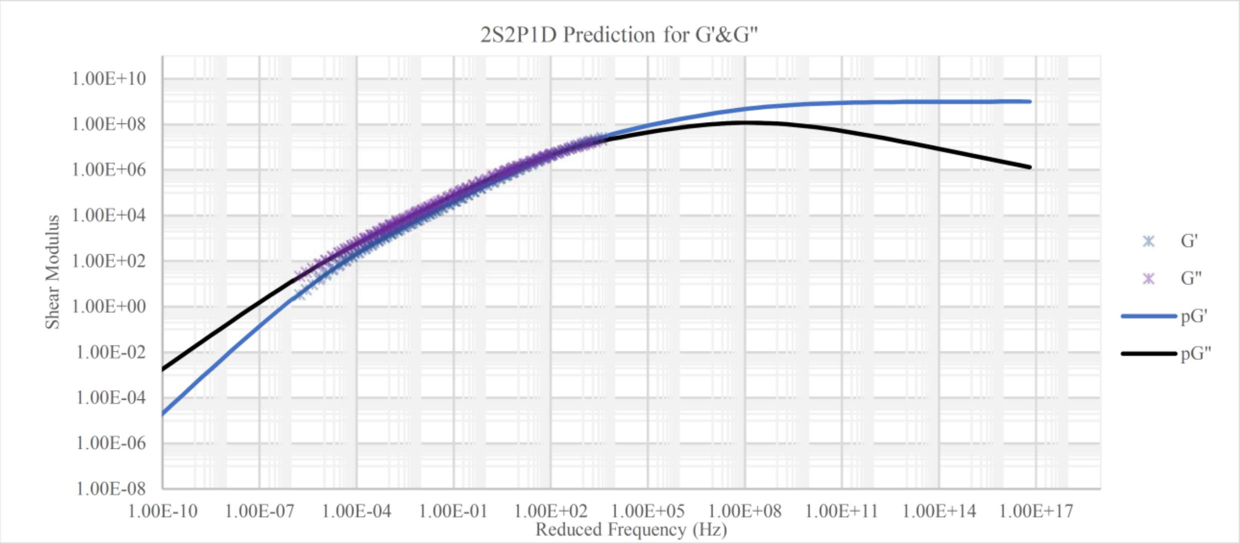

2S2P1D Prediction for G'&G"
Shear Modulus
1.00E+10
1.00E+08
1.00E+06
1.00E+04
1.00E+02
1.00E+00
1.00E-02
1.00E-04
1.00E-06
1.00E-08
1.00E-10
1.00E-07
1.00E-04
1.00E-01
1.00E+02
1.00E+05
1.00E+08
1.00E+11
1.00E+14
1.00E+17
Reduced Frequency (Hz)
G'
G"
pG'
pG"

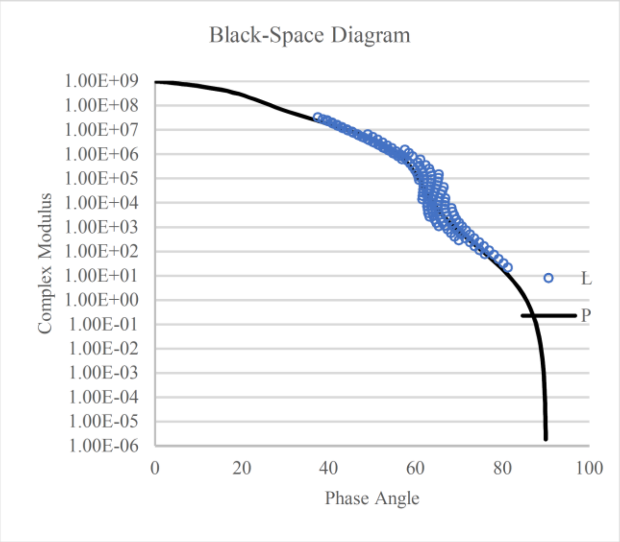

Black-Space Diagram
Complex Modulus
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
1.00E-03
1.00E-04
1.00E-05
1.00E-06
0
20
40
60
80
100
Phase Angle
L
P

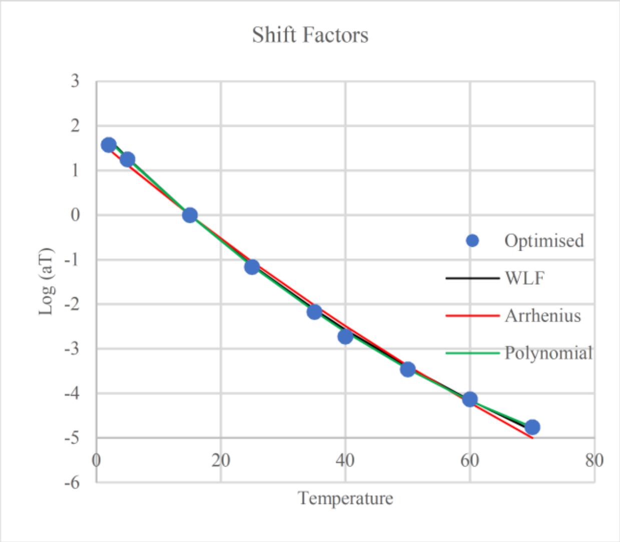

Shift Factors
Log (aT)
3
2
1
0
-1
-2
-3
-4
-5
0
20
40
60
80
Temperature
Optimised
WLF
Arrhenius
Polynomial

Mix A- Unconditioned

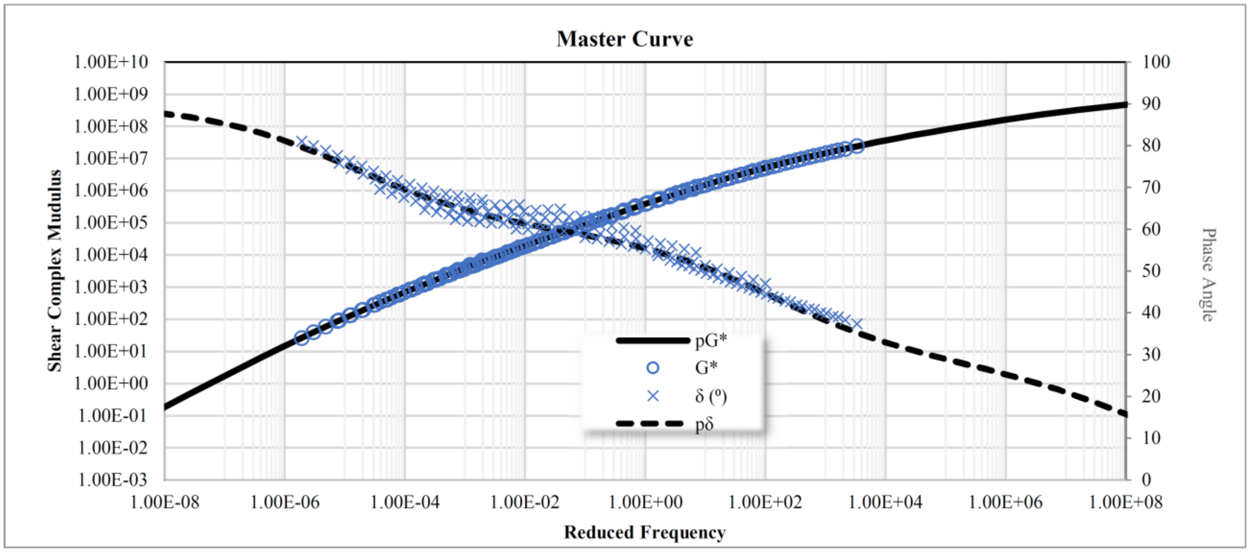


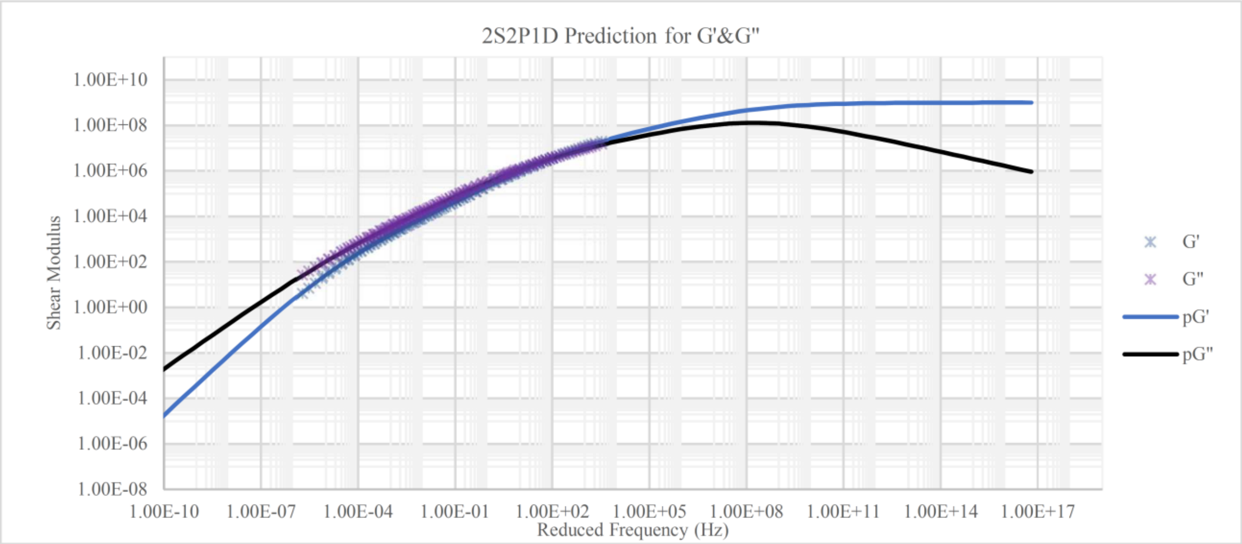


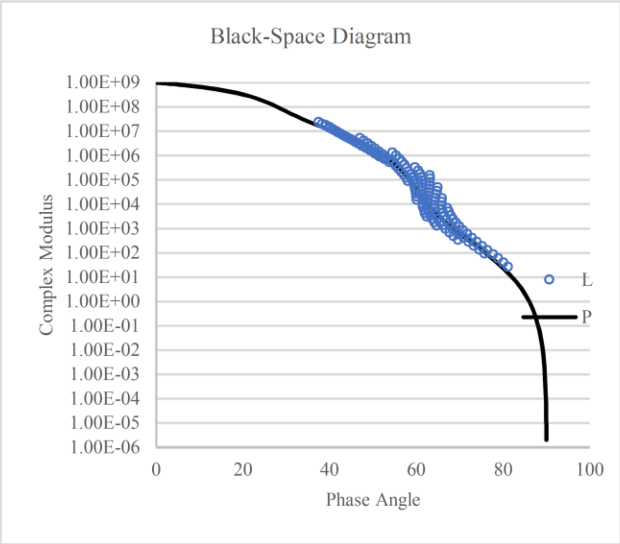


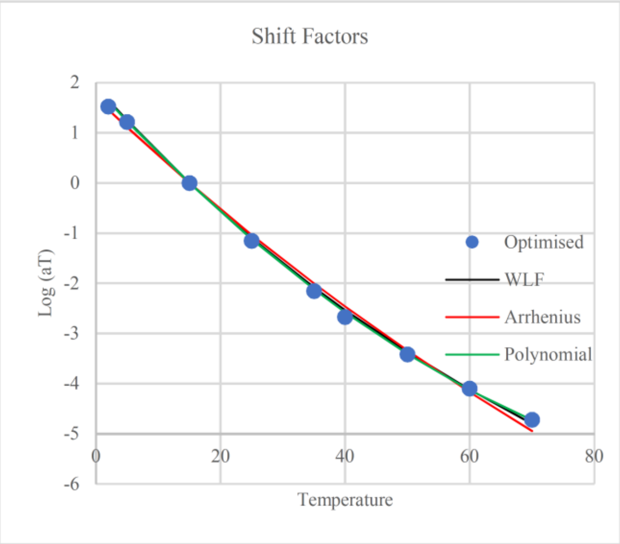


Mix A – LTOA

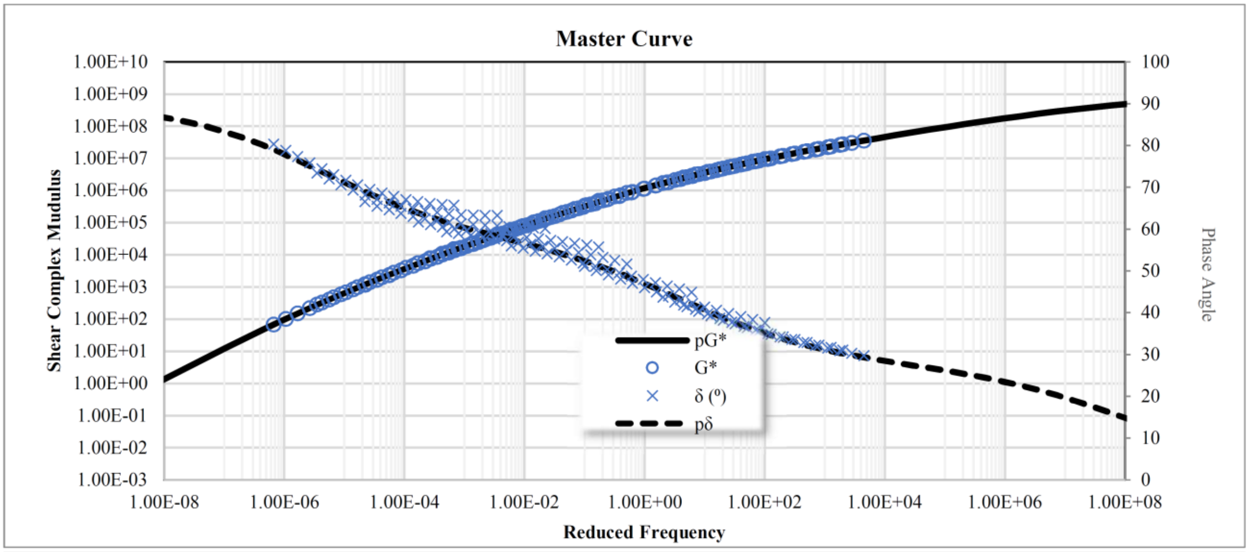

Master Curve
Shear Complex Modulus
1.00E+10
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
1.00E-03
1.00E-08
1.00E-06
1.00E-04
1.00E-02
1.00E+00
1.00E+02
1.00E+04
1.00E+06
1.00E+08
Reduced Frequency
Phase Angle
100
90
80
70
60
50
40
30
20
10
0
pG*
G*
δ (º)
pδ

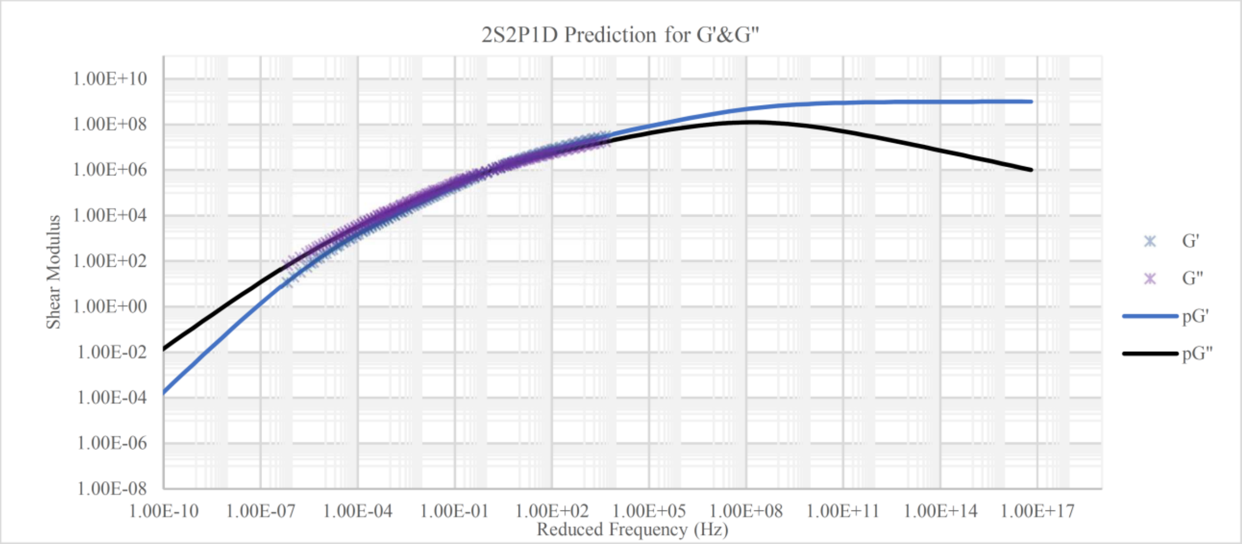

2S2P1D Prediction for G'&G"
Shear Modulus
1.00E+10
1.00E+08
1.00E+06
1.00E+04
1.00E+02
1.00E+00
1.00E-02
1.00E-04
1.00E-06
1.00E-08
1.00E-10
1.00E-07
1.00E-04
1.00E-01
1.00E+02
1.00E+05
1.00E+08
1.00E+11
1.00E+14
1.00E+17
Reduced Frequency (Hz)
G'
G"
pG'
pG"

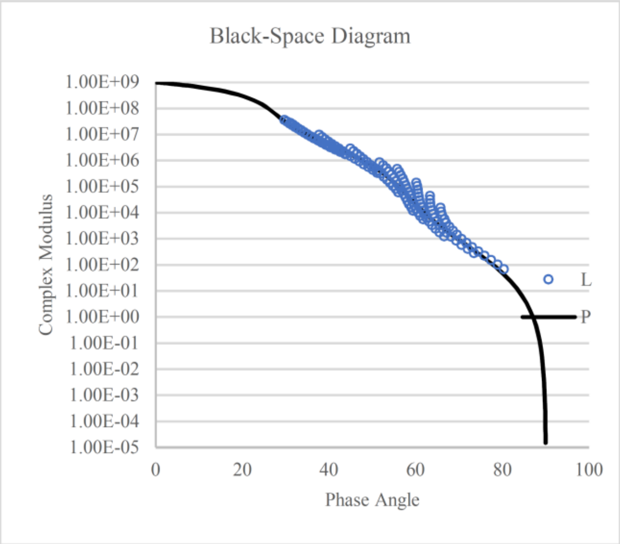

Black-Space Diagram
Complex Modulus
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
1.00E-03
1.00E-04
1.00E-05
1.00E-06
0
20
40
60
80
100
Phase Angle
L
P


Shift Factors
Log (aT)
2
1
0
-1
-2
-3
-4
-5
-6
0
20
40
60
80
Temperature
Optimised
WLF
Arrhenius
Polynomial

Mix A – RHR


Master Curve
Shear Complex Mudulus
1.00E+10
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
1.00E-03
1.00E-08
1.00E-06
1.00E-04
1.00E-02
1.00E+00
1.00E+02
1.00E+04
1.00E+06
1.00E+08
Reduced Frequency
Phase Angle
100
90
80
70
60
50
40
30
20
10
0
pG*
G*
δ (º)
pδ


2S2P1D Prediction for G'&G"
Shear Modulus
1.00E+10
1.00E+08
1.00E+06
1.00E+04
1.00E+02
1.00E+00
1.00E-02
1.00E-04
1.00E-06
1.00E-08
1.00E-10
1.00E-07
1.00E-04
1.00E-01
1.00E+02
1.00E+05
1.00E+08
1.00E+11
1.00E+14
1.00E+17
Reduced Frequency (Hz)
G'
G"
pG'
pG"


Black-Space Diagram
Complex Modulus
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
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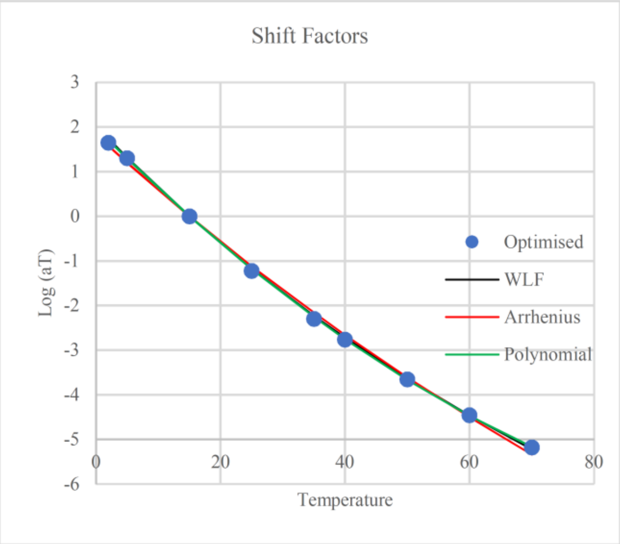
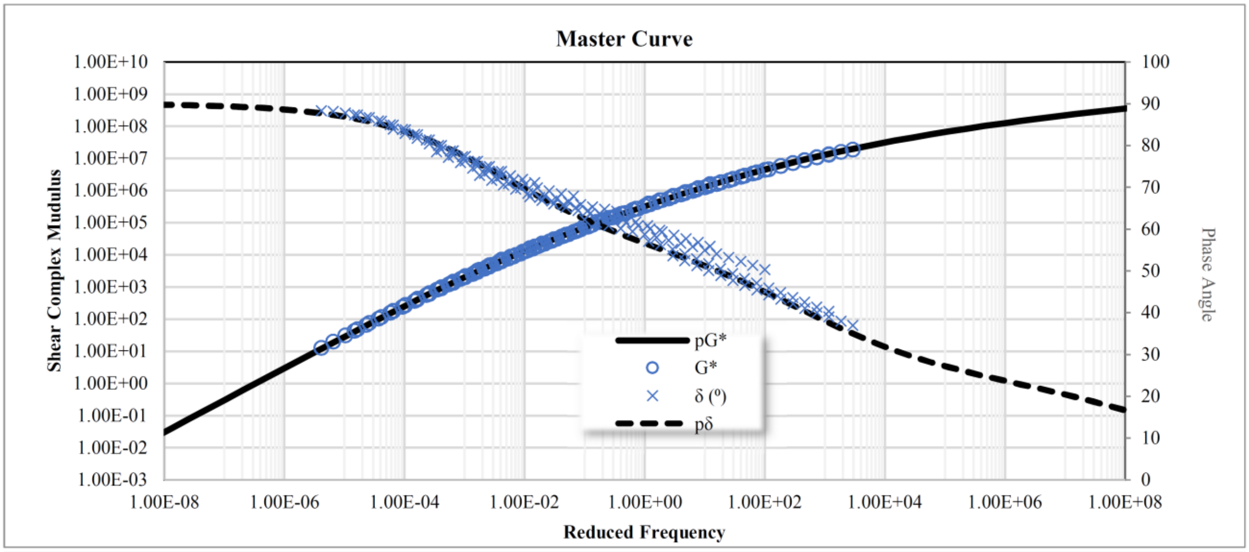
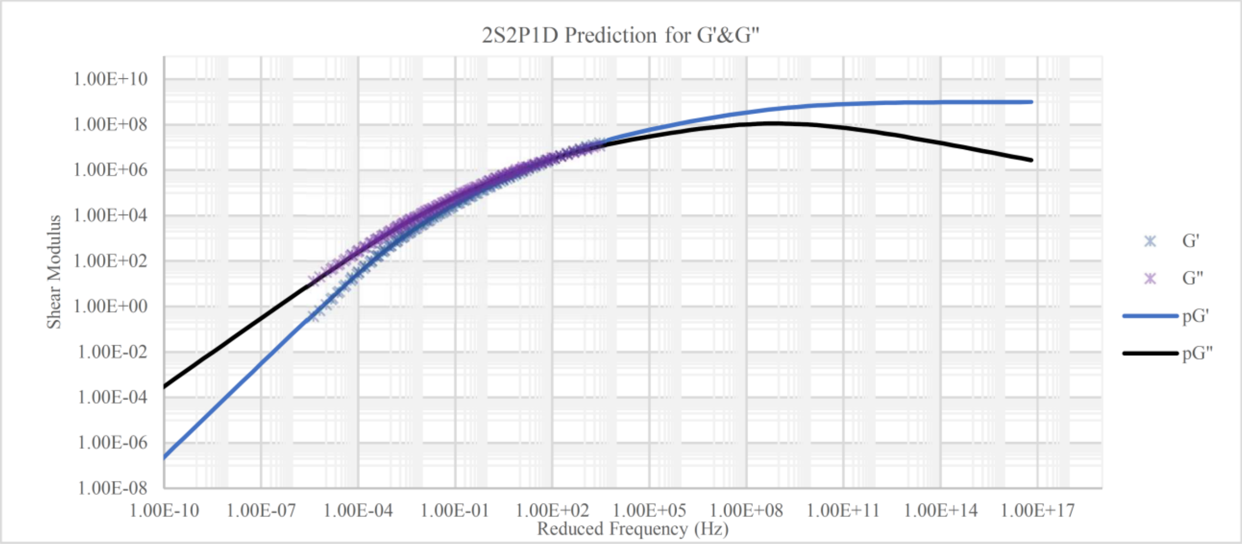
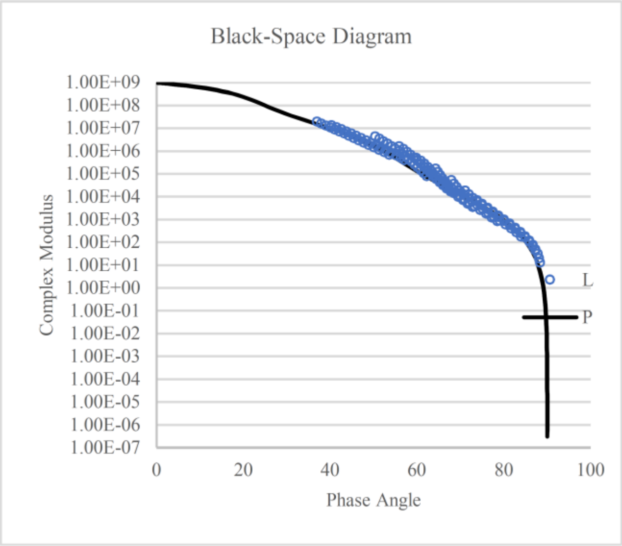
1.00E-04
1.00E-05
0
20
40
60
80
100
Phase Angle
L
P

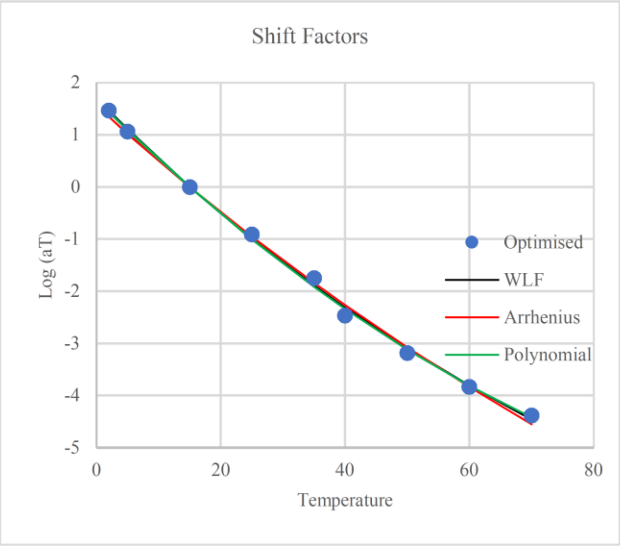

Shift Factors
Log (aT)
3
2
1
0
-1
-2
-3
-4
-5
-6
0
20
40
60
80
Temperature
Optimised
WLF
Arrhenius
Polynomial

Mix A – Field Aged – Top

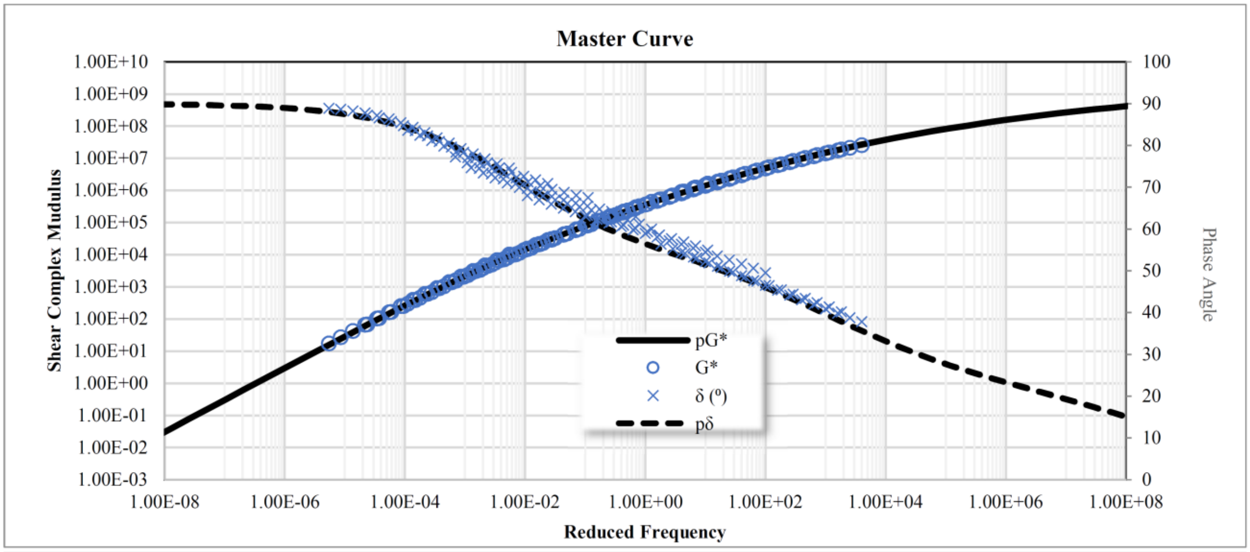


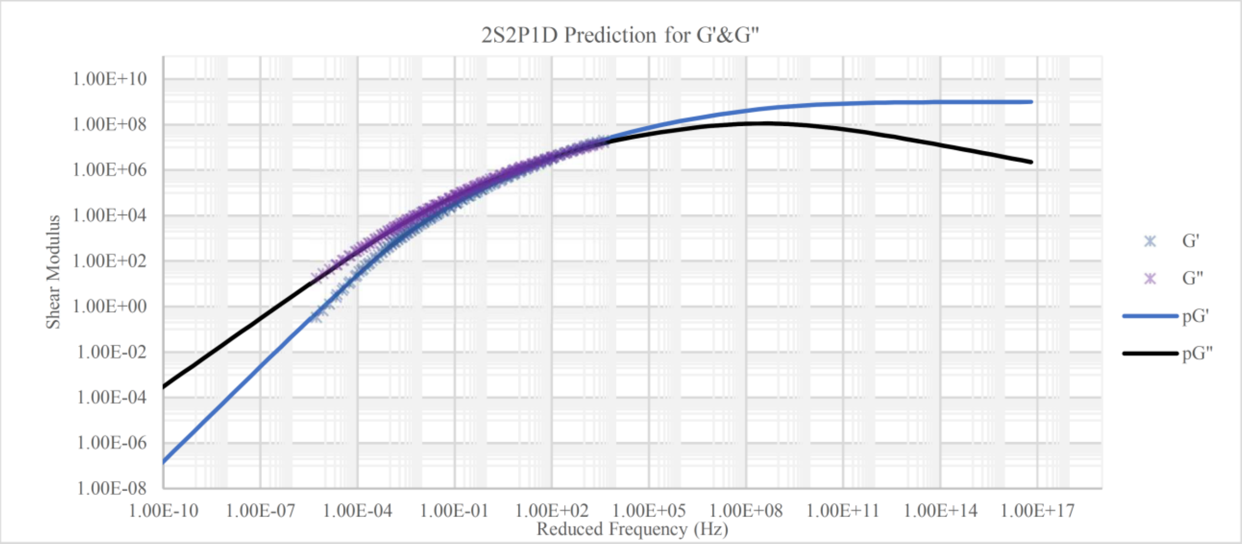


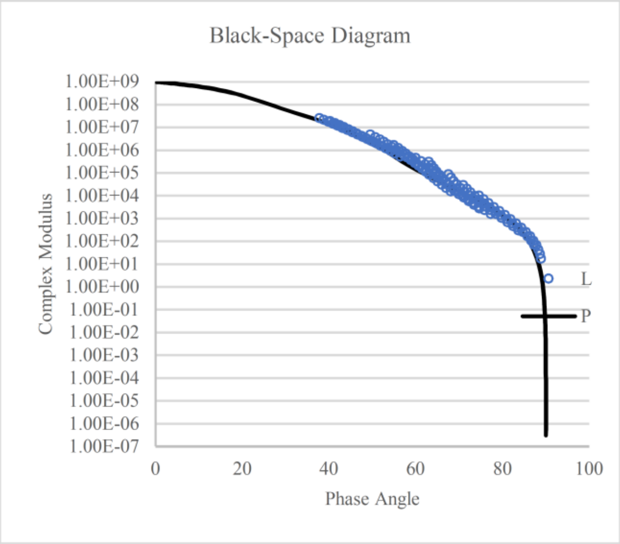


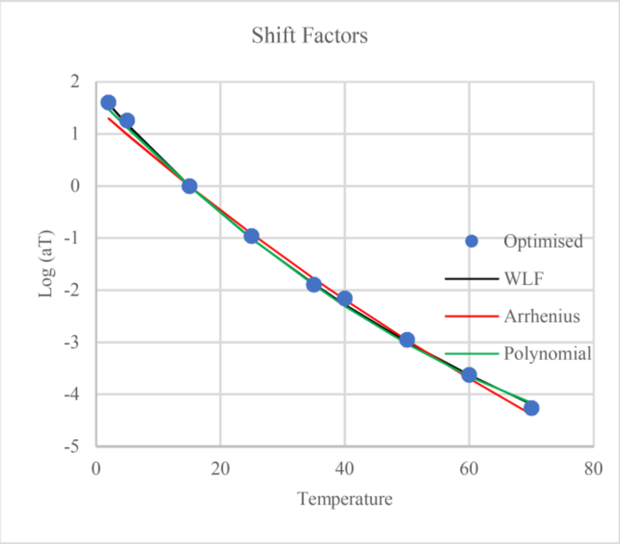


Mix A – Field Aged – Bottom

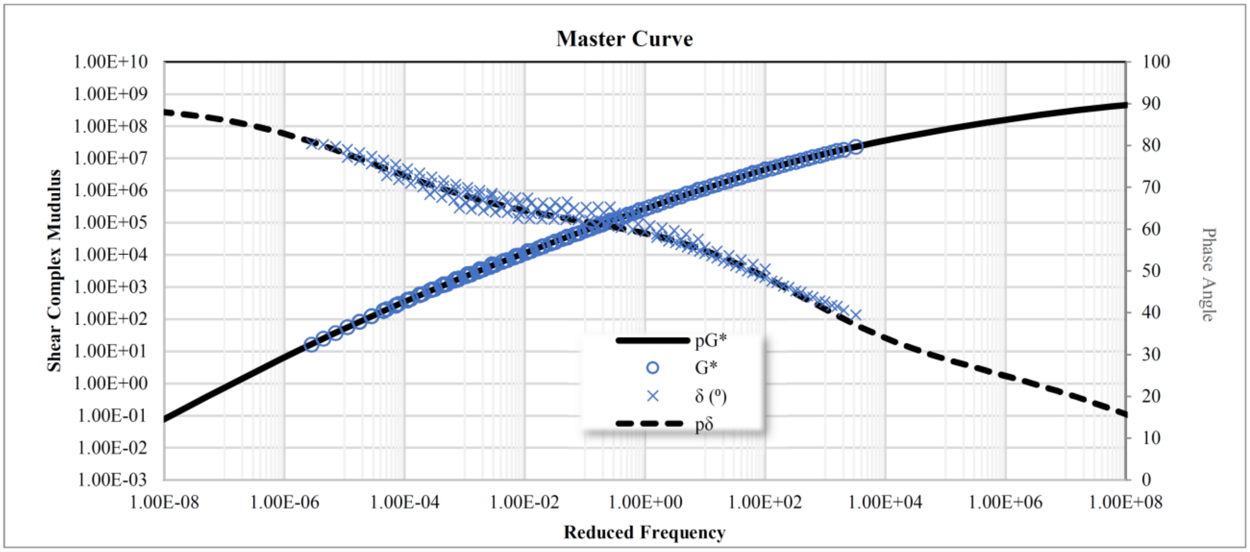


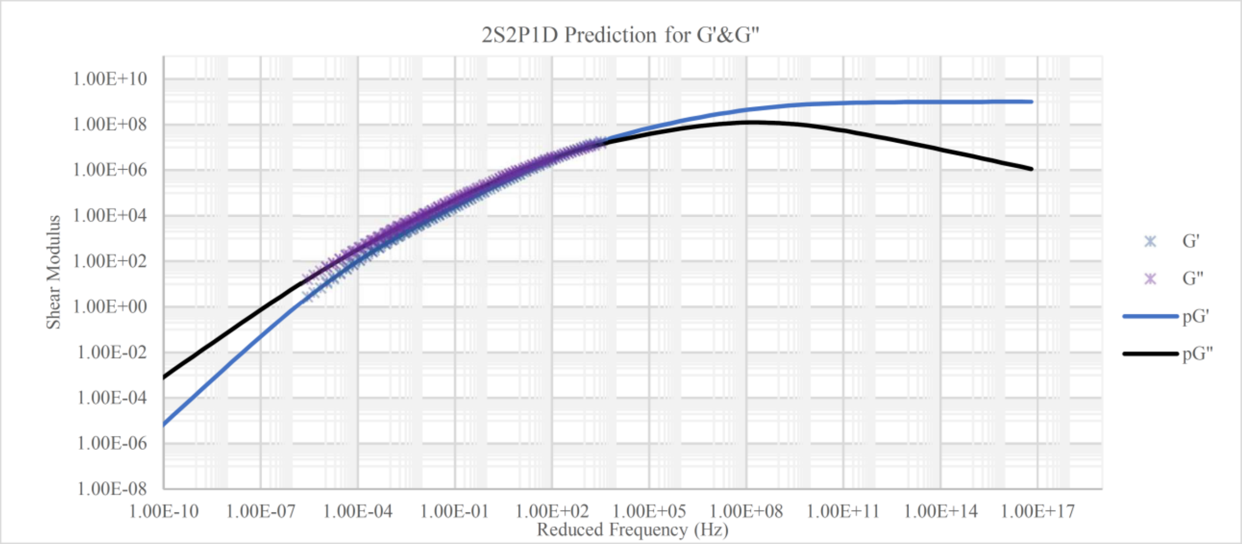


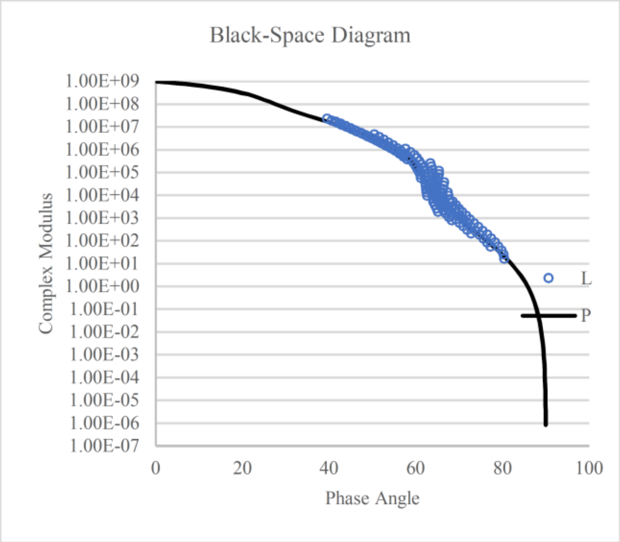


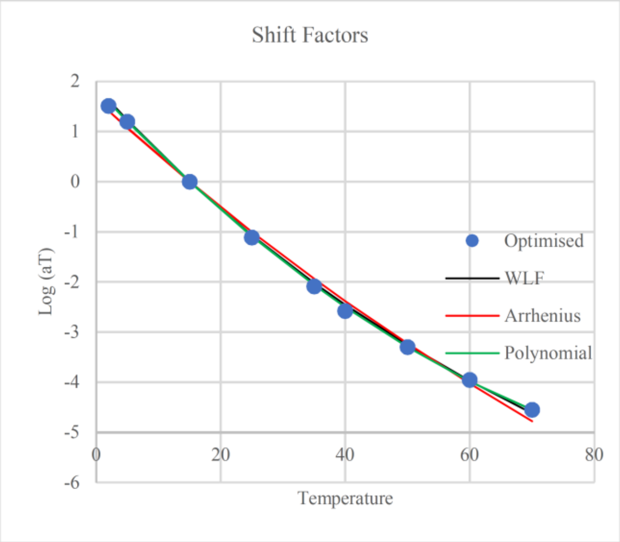


Mix B – Unconditioned

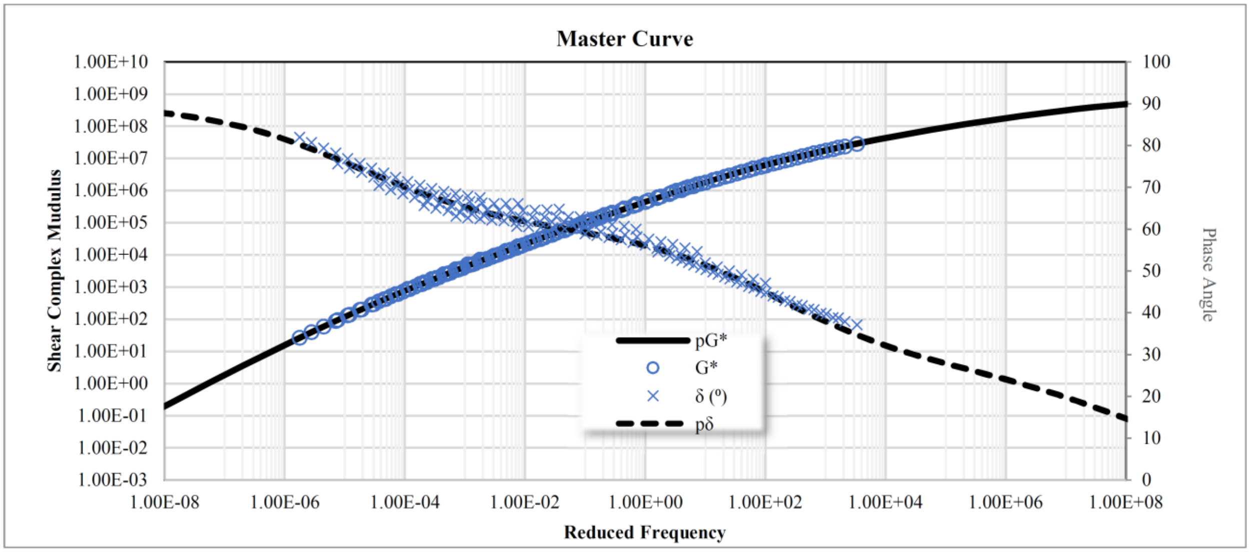


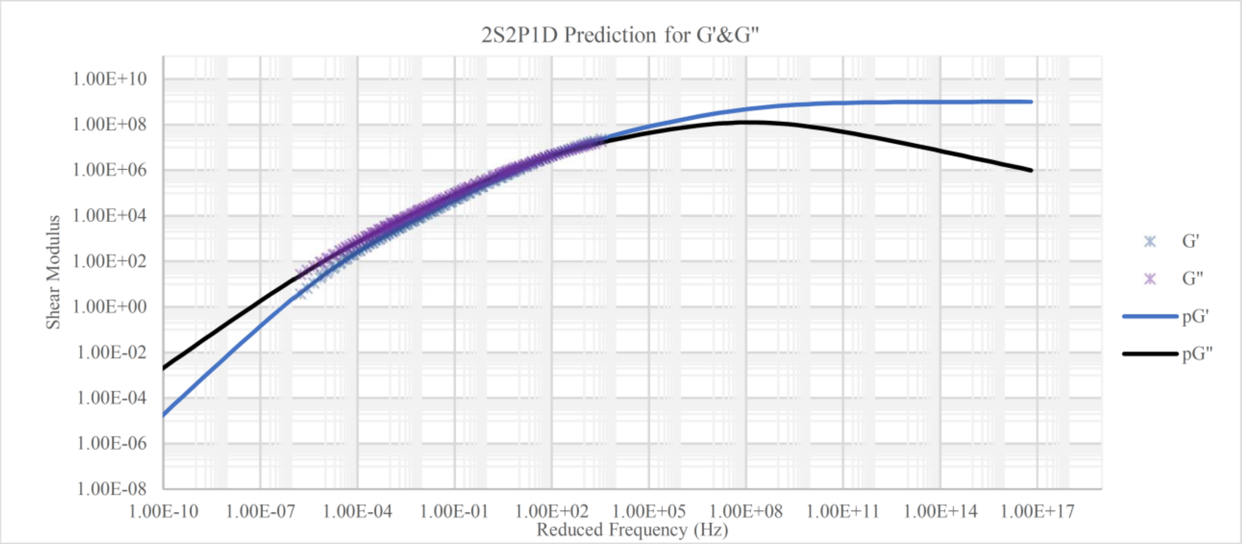


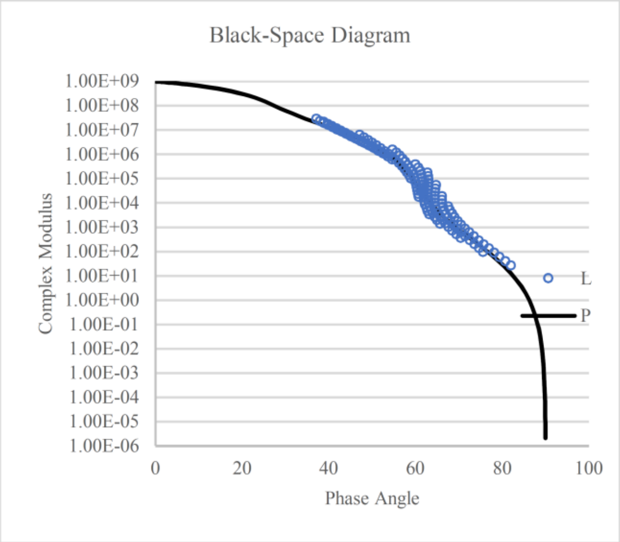


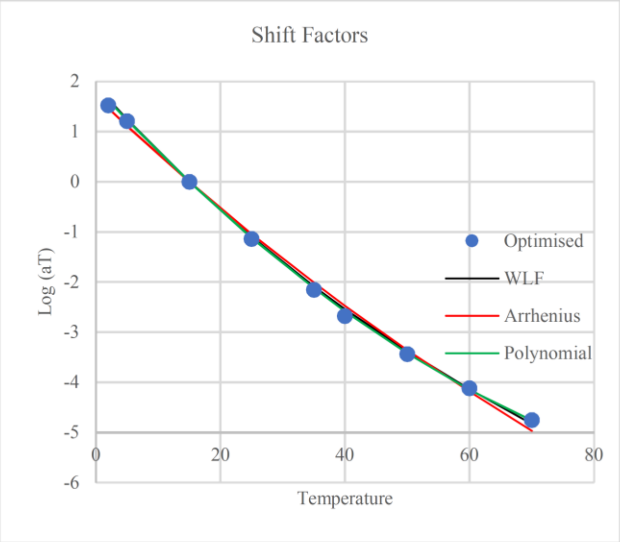


Mix B – LTOA

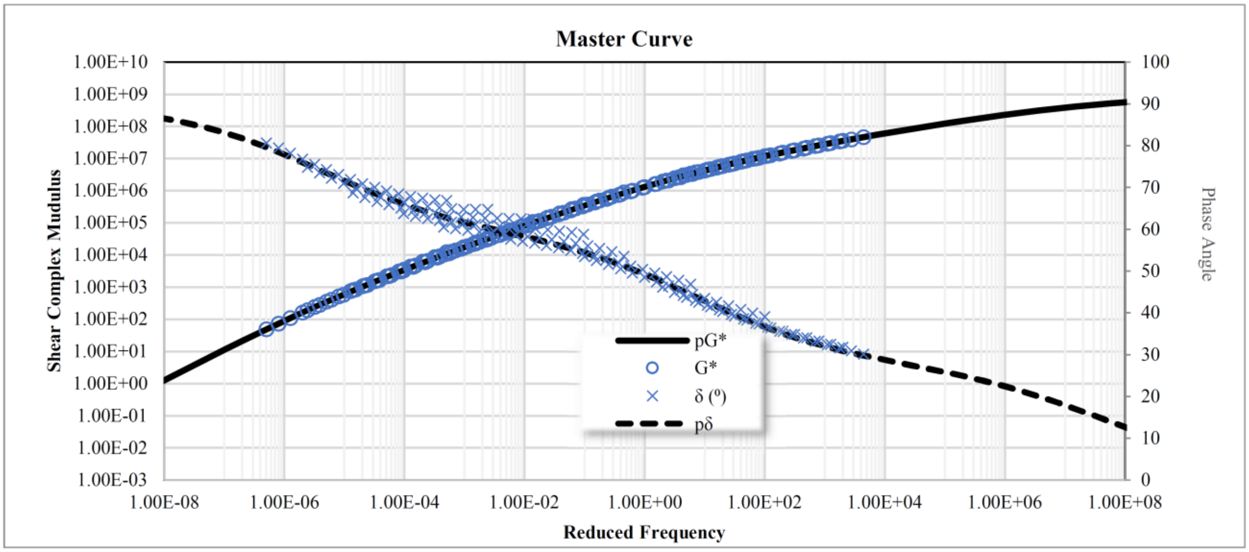

Master Curve
Shear Complex Mudulus
1.00E+10
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
1.00E-03
Phase Angle
100
90
80
70
60
50
40
30
20
10
0
1.00E-08
1.00E-06
1.00E-04
1.00E-02
1.00E+00
1.00E+02
1.00E+04
1.00E+06
1.00E+08
Reduced Frequency
pG*
G*
δ (º)
pδ

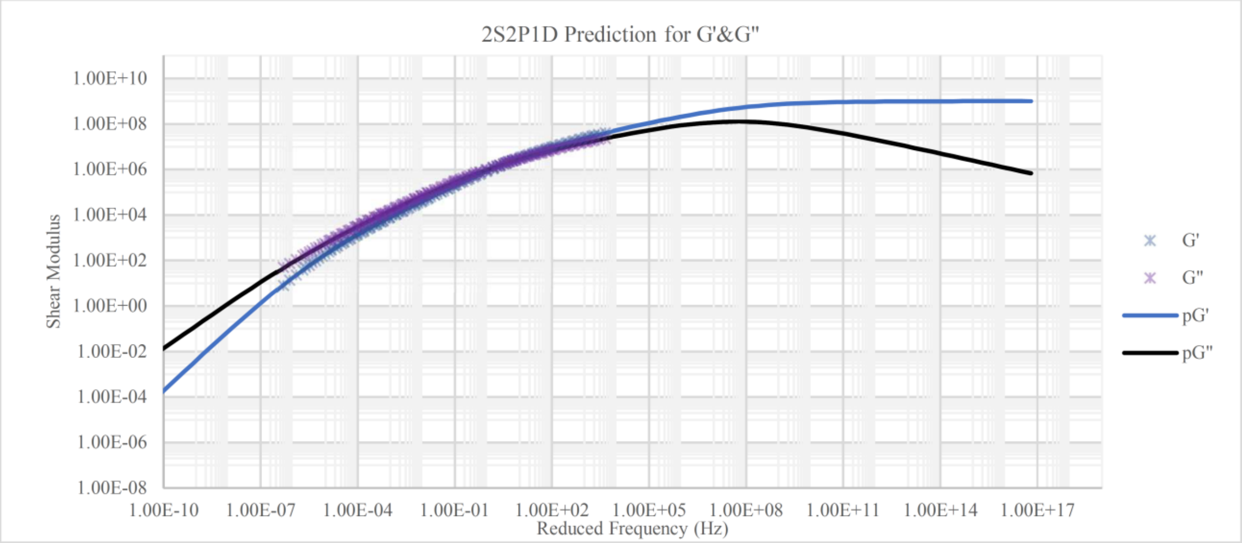

2S2P1D Prediction for G'&G"
Shear Modulus
1.00E+10
1.00E+08
1.00E+06
1.00E+04
1.00E+02
1.00E+00
1.00E-02
1.00E-04
1.00E-06
1.00E-08
1.00E-10
1.00E-07
1.00E-04
1.00E-01
1.00E+02
1.00E+05
1.00E+08
1.00E+11
1.00E+14
1.00E+17
Reduced Frequency (Hz)
G'
G"
pG'
pG"

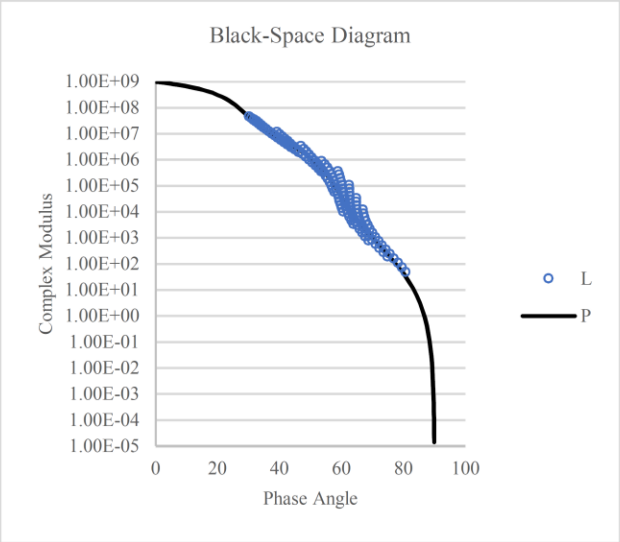

Black-Space Diagram
Complex Modulus
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
1.00E-03
1.00E-04
1.00E-05
1.00E-06
0
20
40
60
80
100
Phase Angle
L
P


Shift Factors
Log (aT)
2
1
0
-1
-2
-3
-4
-5
-6
0
20
40
60
80
Temperature
Optimised
WLF
Arrhenius
Polynomial

Mix B – RHR


Master Curve
Shear Complex Mudulus
1.00E+10
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
1.00E-03
Phase Angle
100
90
80
70
60
50
40
30
20
10
0
1.00E-08
1.00E-06
1.00E-04
1.00E-02
1.00E+00
1.00E+02
1.00E+04
1.00E+06
1.00E+08
Reduced Frequency
pG*
G*
δ (º)
pδ


2S2P1D Prediction for G'&G"
Shear Modulus
1.00E+10
1.00E+08
1.00E+06
1.00E+04
1.00E+02
1.00E+00
1.00E-02
1.00E-04
1.00E-06
1.00E-08
1.00E-10
1.00E-07
1.00E-04
1.00E-01
1.00E+02
1.00E+05
1.00E+08
1.00E+11
1.00E+14
1.00E+17
Reduced Frequency (Hz)
G'
G"
pG'
pG"


Black-Space Diagram
Complex Modulus
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
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1.00E-04
1.00E-05
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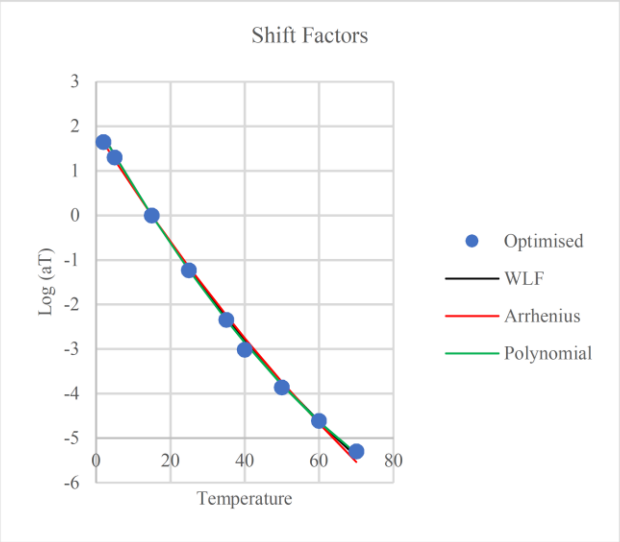
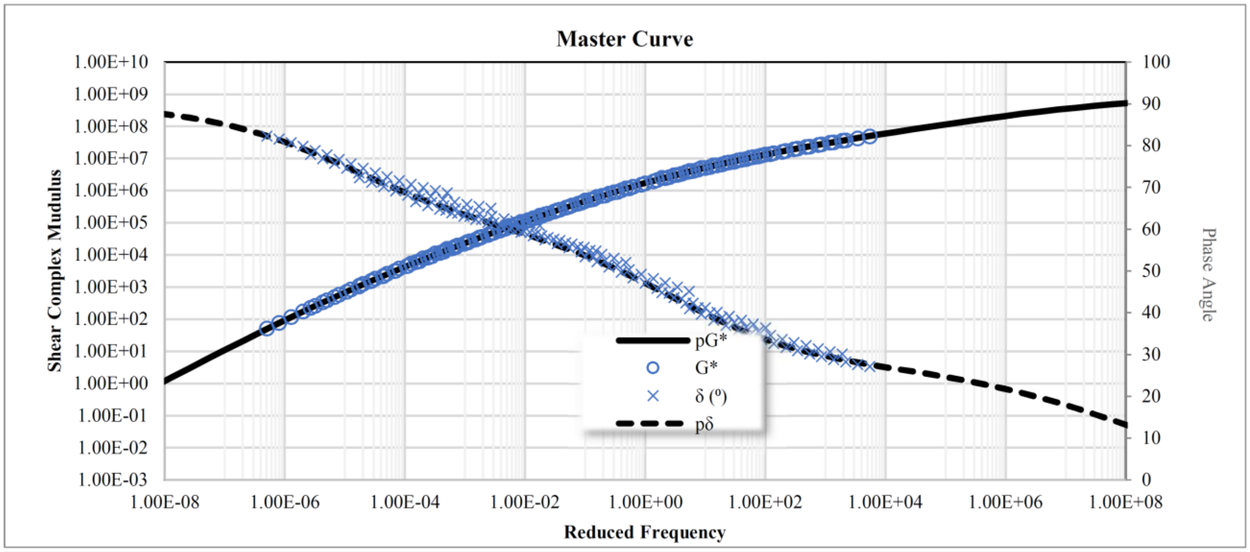
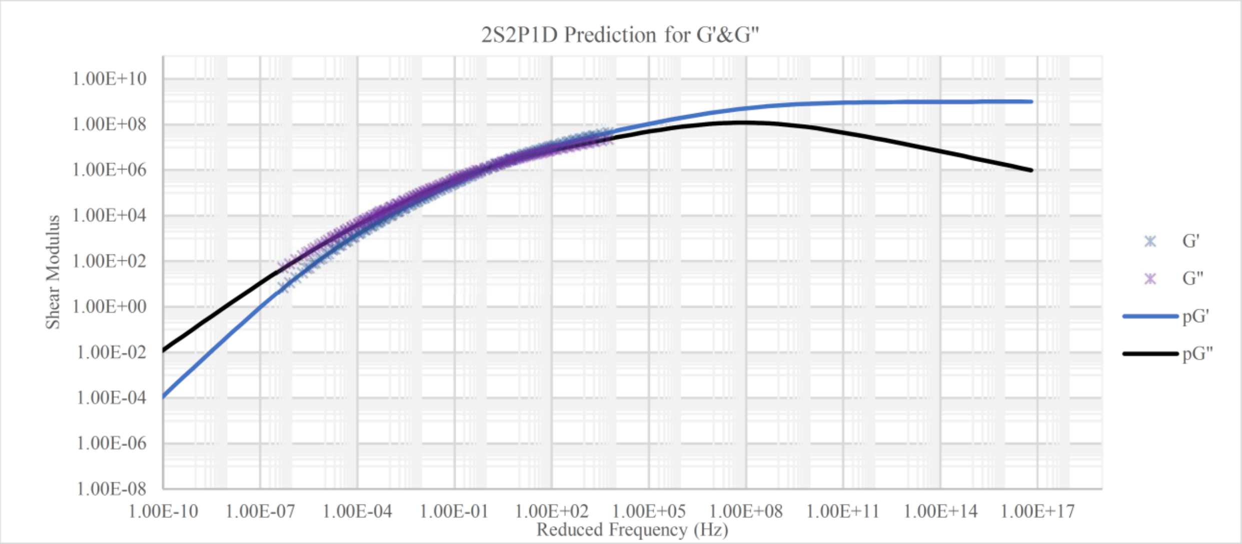
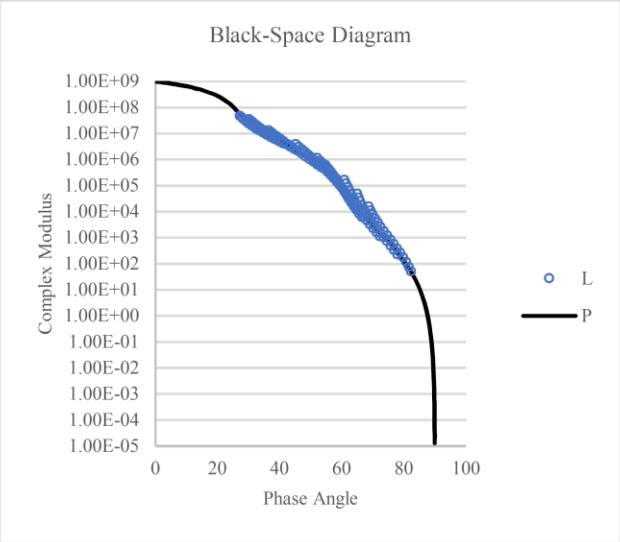
20
40
60
80
100
Phase Angle
L
P

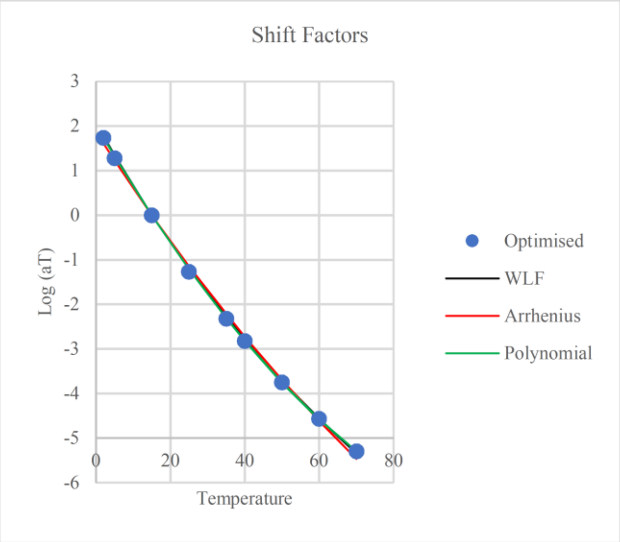

Shift Factors
Log (aT)
3
2
1
0
-1
-2
-3
-4
-5
-6
0
20
40
60
80
Temperature
Optimised
WLF
Arrhenius
Polynomial

Mix B – Field Aged – Top

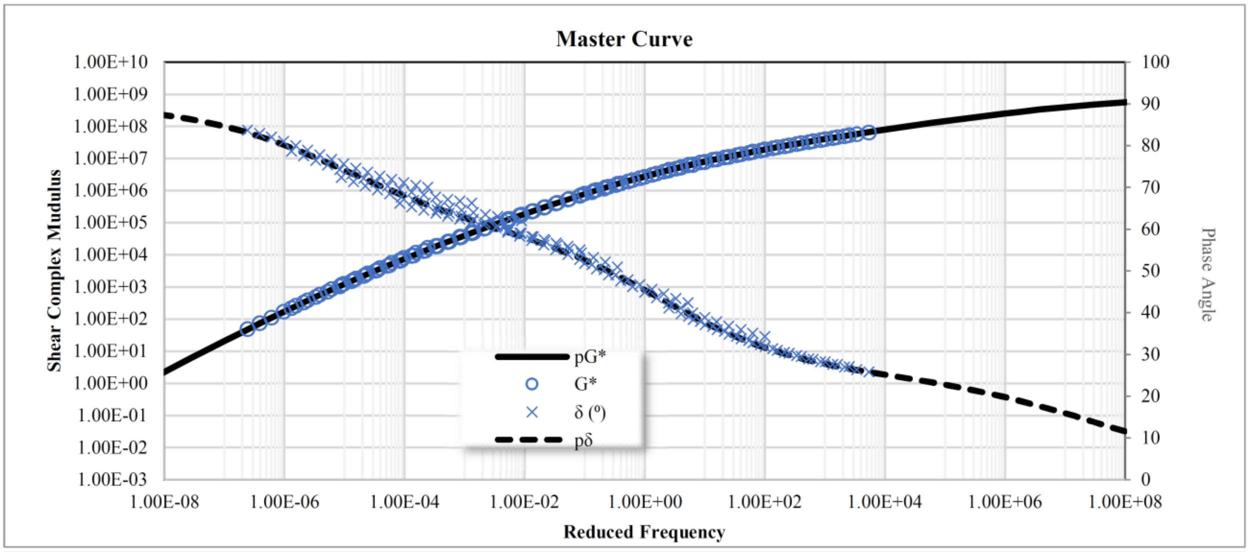


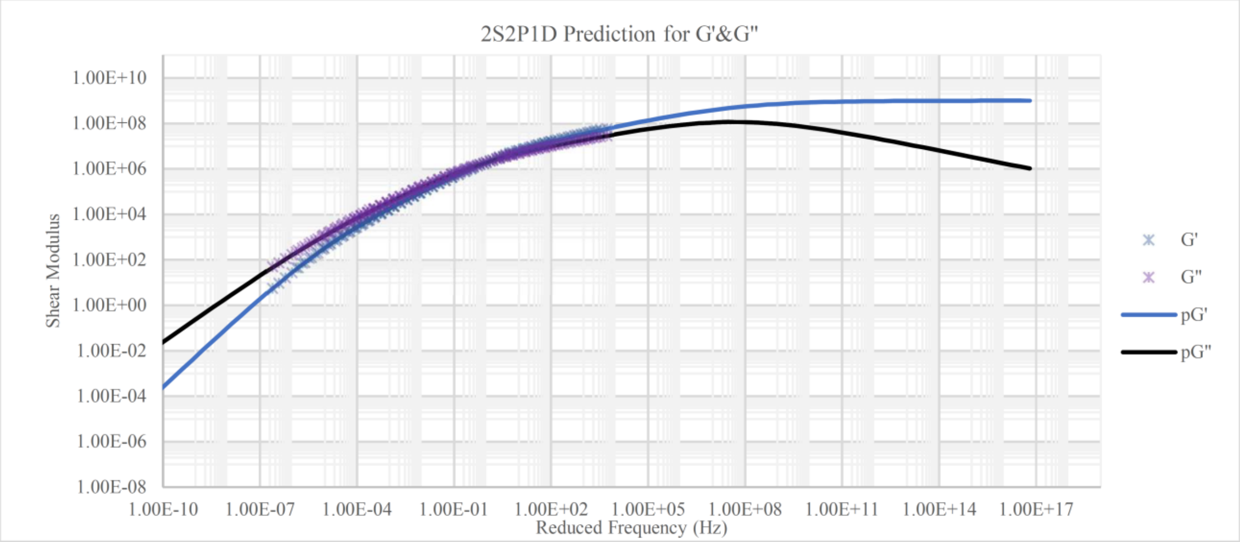


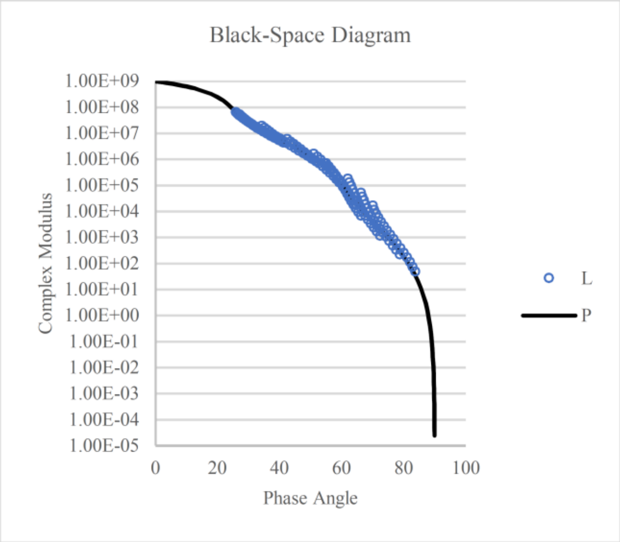


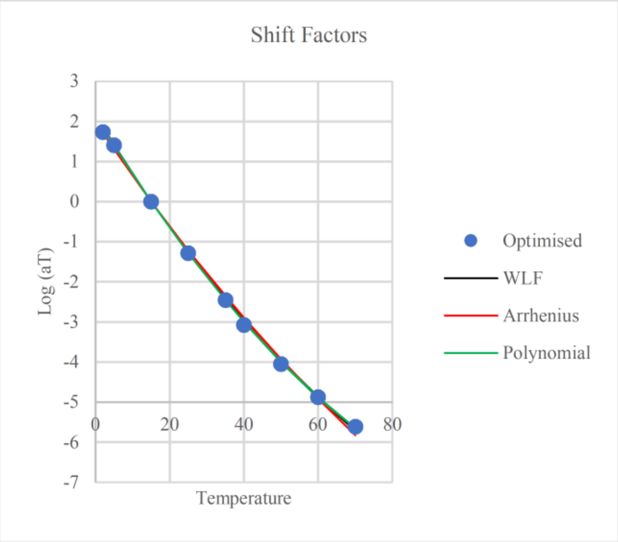


Mix B – Field Aged – Bottom

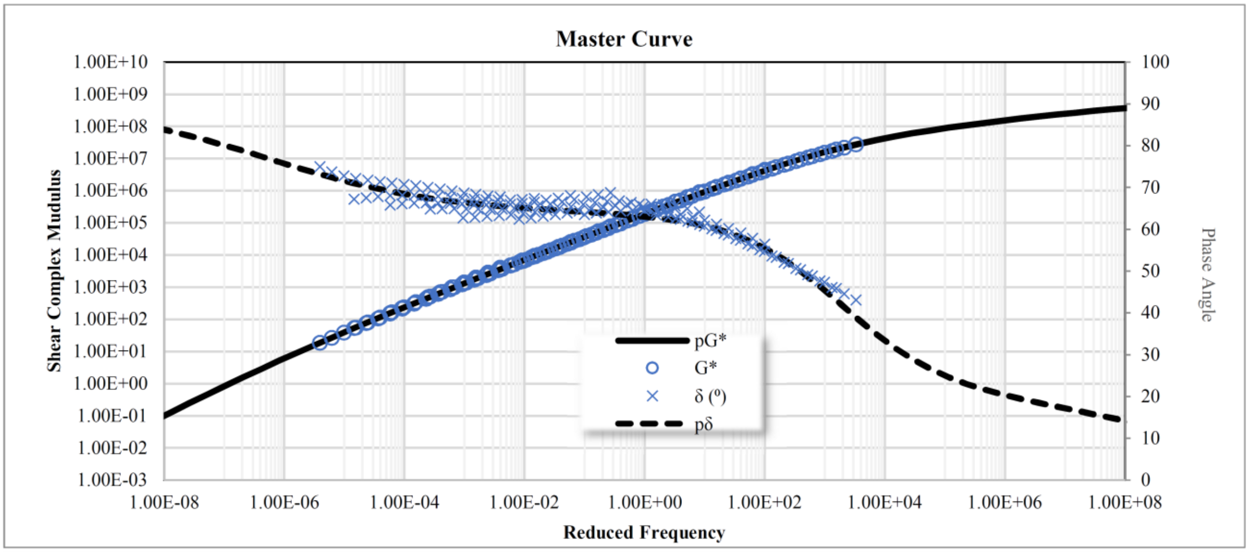


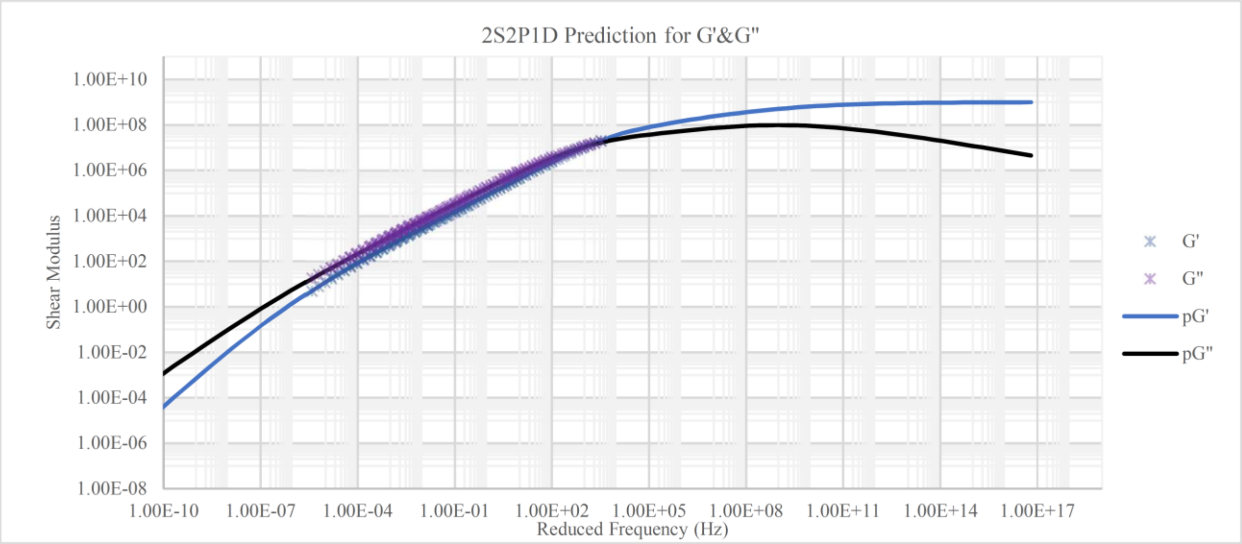


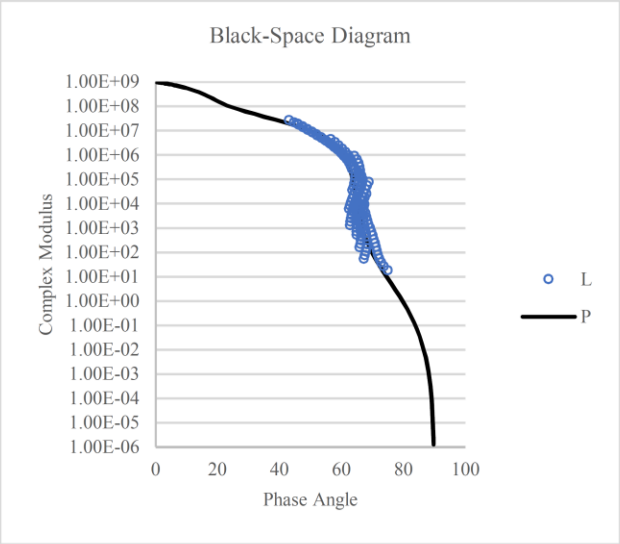


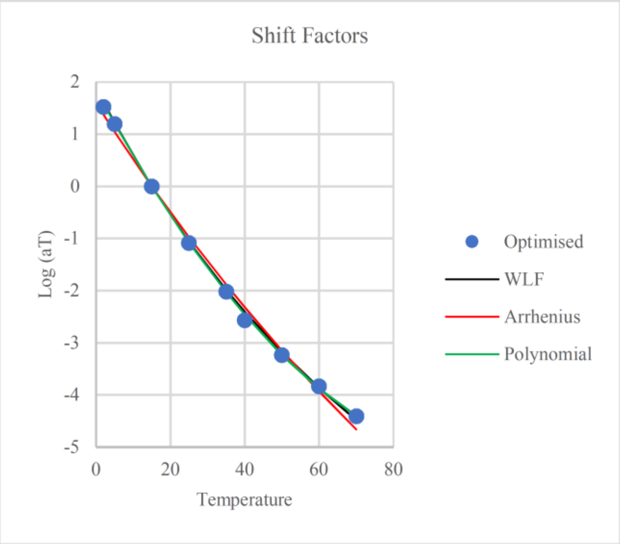


Mix C – Unconditioned

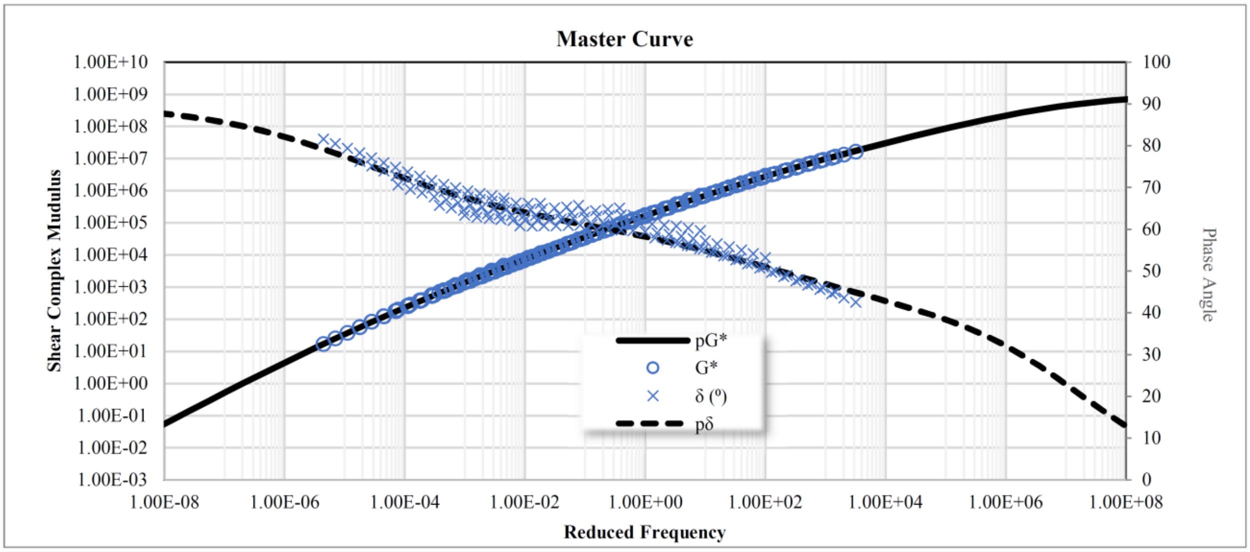


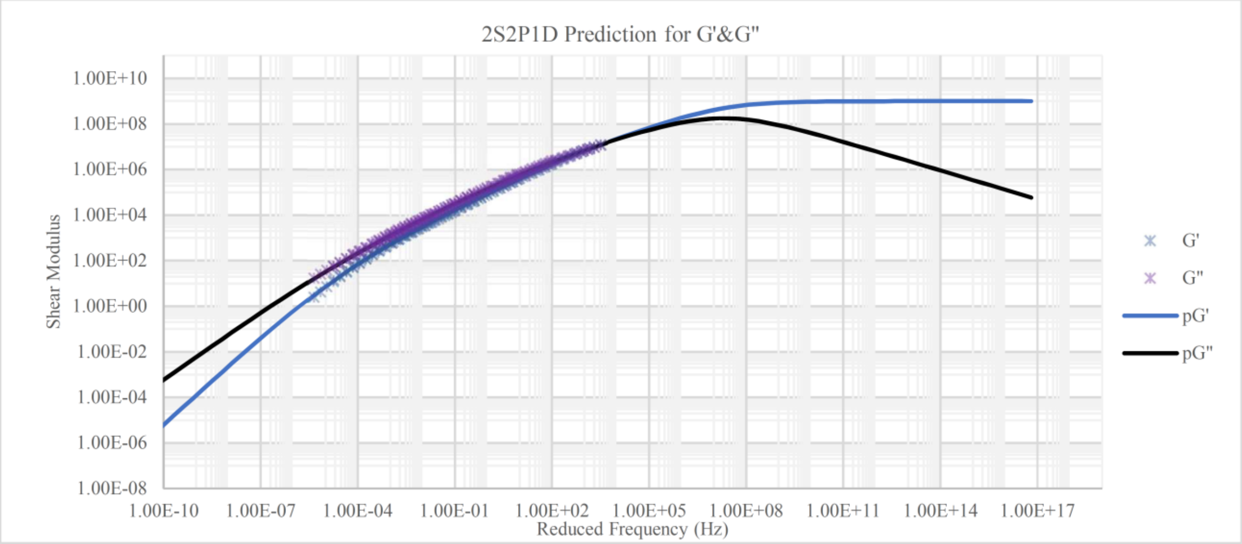


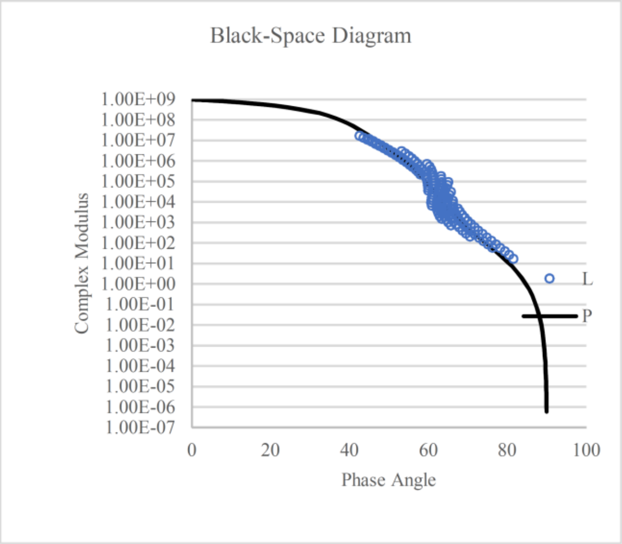


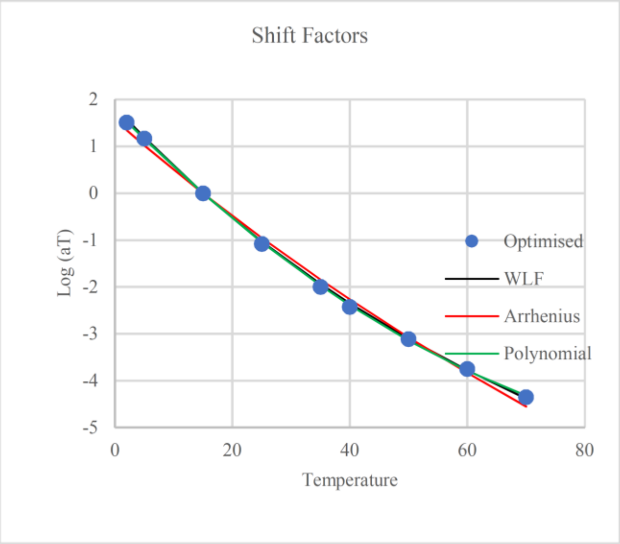


Mix C – LTOA

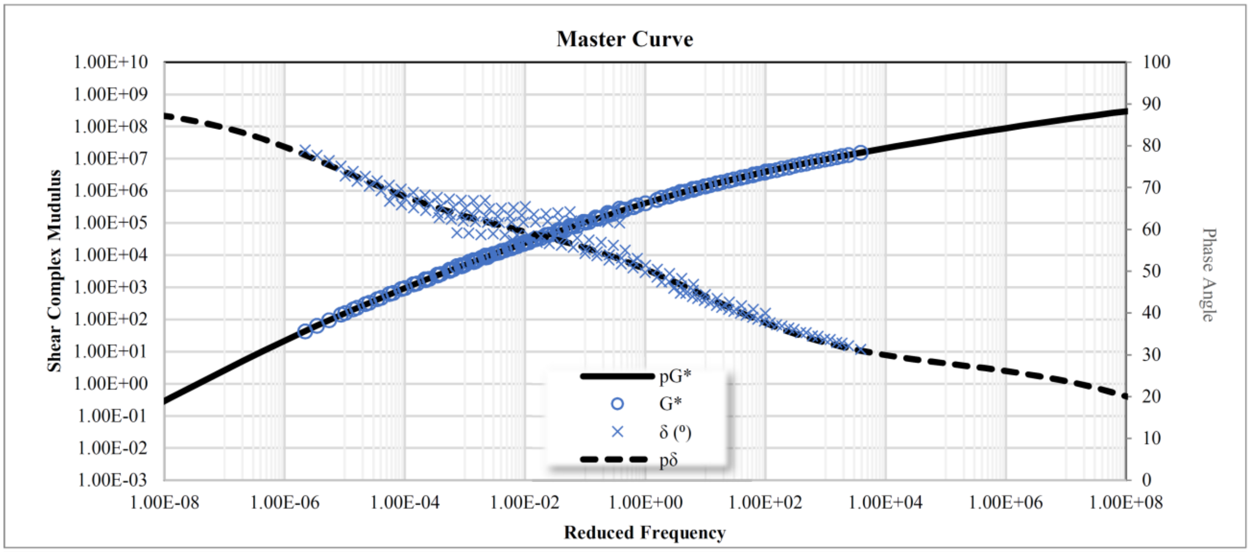

Master Curve
Shear Complex Mudulus
1.00E+10
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
1.00E-03
1.00E-08
1.00E-06
1.00E-04
1.00E-02
1.00E+00
1.00E+02
1.00E+04
1.00E+06
1.00E+08
Reduced Frequency
Phase Angle
100
90
80
70
60
50
40
30
20
10
0
pG*
G*
δ (º)
pδ

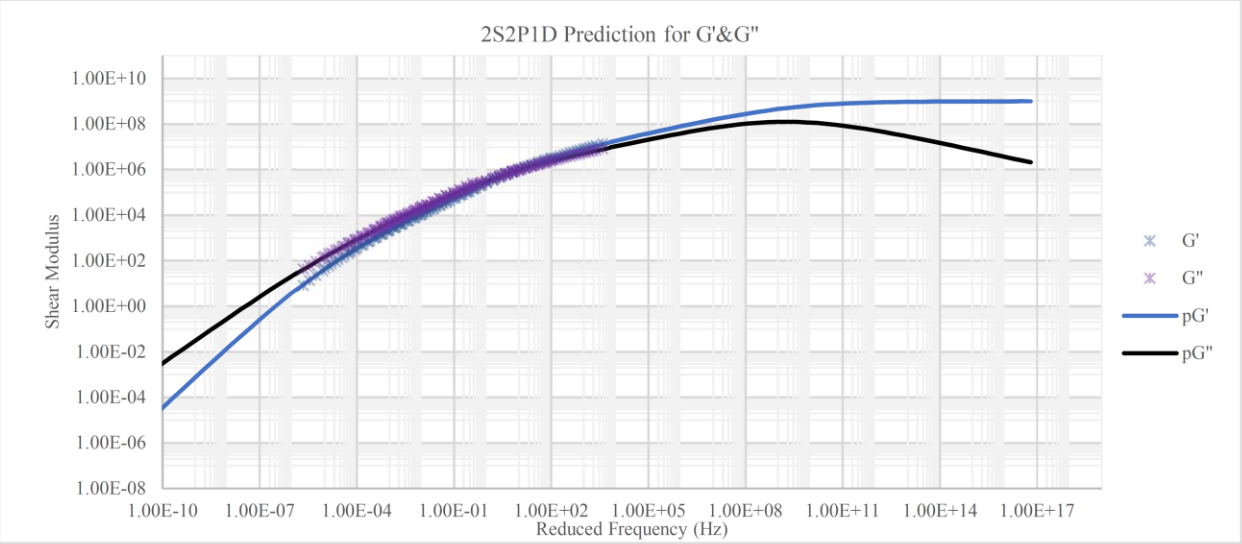

2S2P1D Prediction for G'&G"
Shear Modulus
1.00E+10
1.00E+08
1.00E+06
1.00E+04
1.00E+02
1.00E+00
1.00E-02
1.00E-04
1.00E-06
1.00E-08
1.00E-10
1.00E-07
1.00E-04
1.00E-01
1.00E+02
1.00E+05
1.00E+08
1.00E+11
1.00E+14
1.00E+17
Reduced Frequency (Hz)
G'
G"
pG'
pG"

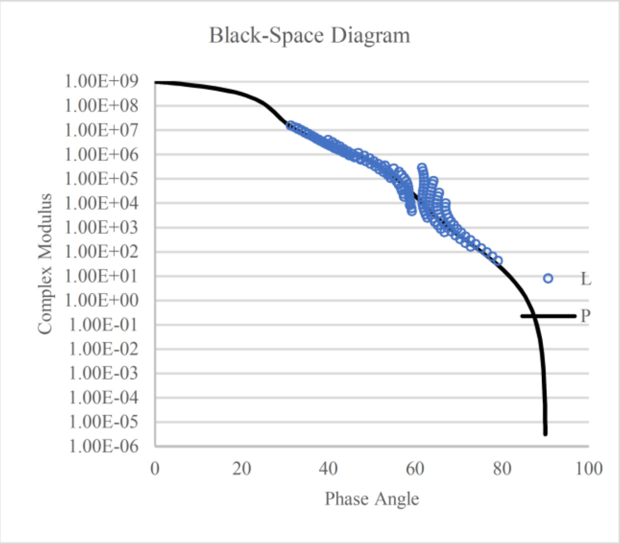

Black-Space Diagram
Complex Modulus
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
1.00E-03
1.00E-04
1.00E-05
1.00E-06
1.00E-07
0
20
40
60
80
100
Phase Angle
L
P

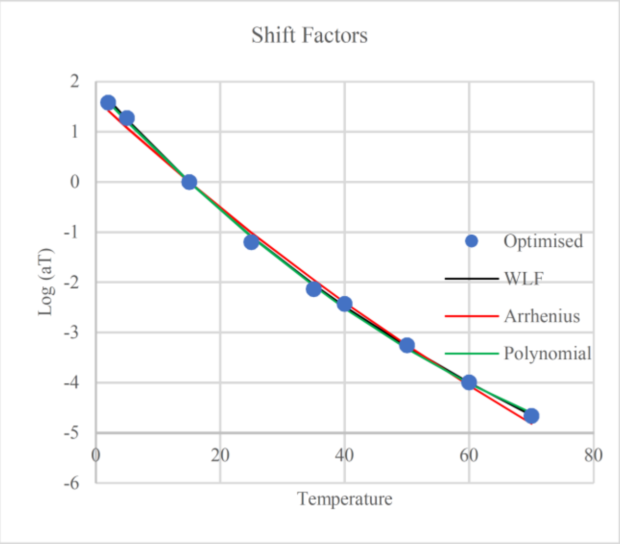

Shift Factors
Log (aT)
2
1
0
-1
-2
-3
-4
-5
0
20
40
60
80
Temperature
Optimised
WLF
Arrhenius
Polynomial

Mix – RHR

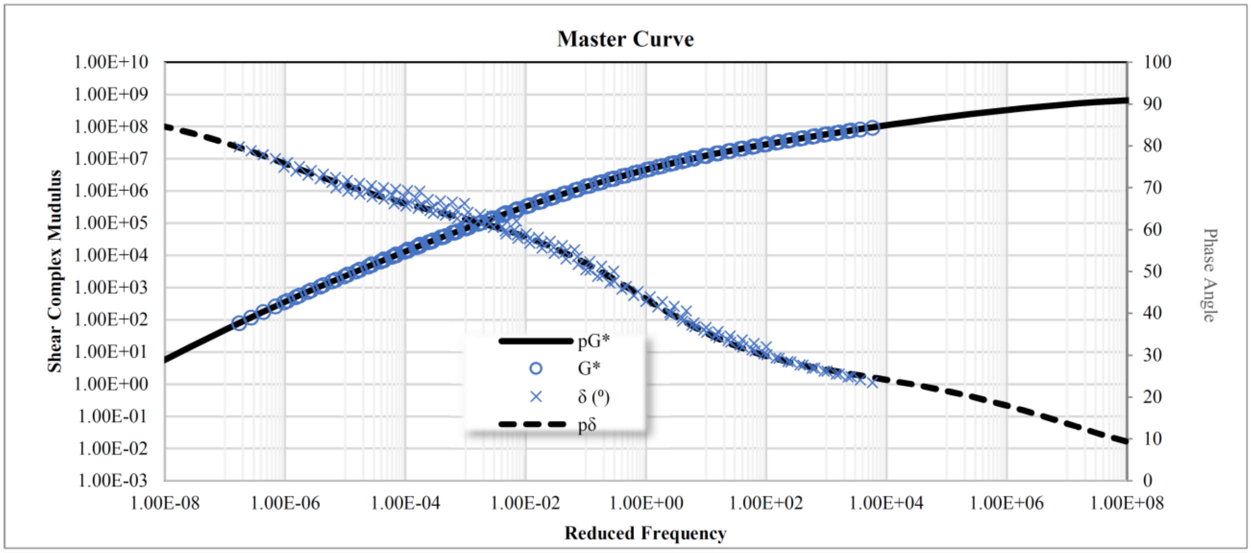

Master Curve
Shear Complex Mudulus
1.00E+10
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
1.00E-03
100
90
80
70
60
50
40
30
20
10
0
Phase Angle
1.00E-08
1.00E-06
1.00E-04
1.00E-02
1.00E+00
1.00E+02
1.00E+04
1.00E+06
1.00E+08
Reduced Frequency
pG*
G*
δ (º)
pδ

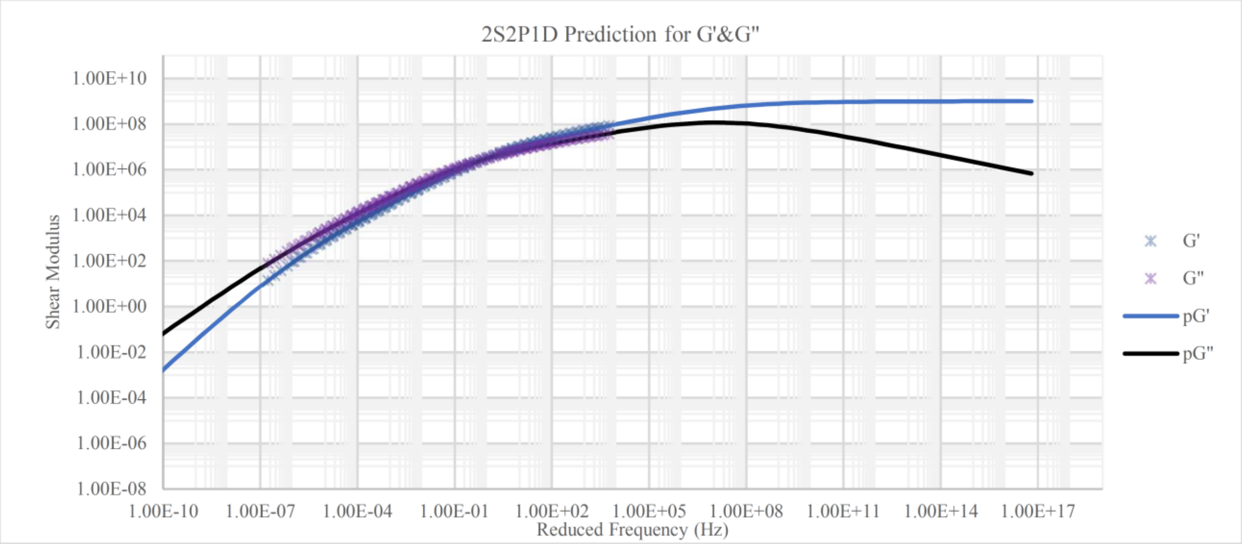

2S2P1D Prediction for G'&G"
Shear Modulus
1.00E+10
1.00E+08
1.00E+06
1.00E+04
1.00E+02
1.00E+00
1.00E-02
1.00E-04
1.00E-06
1.00E-08
1.00E-10
1.00E-07
1.00E-04
1.00E-01
1.00E+02
1.00E+05
1.00E+08
1.00E+11
1.00E+14
1.00E+17
Reduced Frequency (Hz)
G'
G"
pG'
pG"

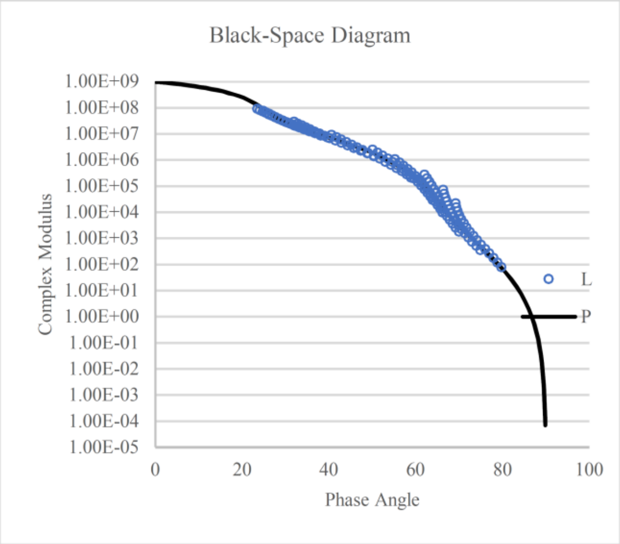

Black-Space Diagram
Complex Modulus
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
1.00E-03
1.00E-04
1.00E-05
1.00E-06
0
20
40
60
80
100
Phase Angle
L
P

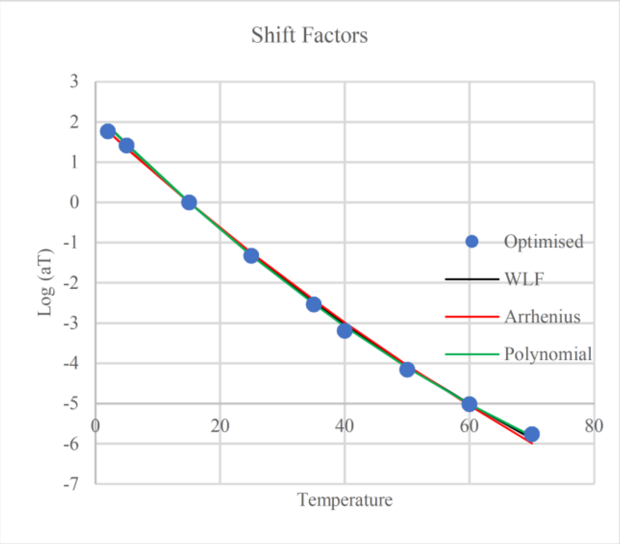

Shift Factors
Log (aT)
2
1
0
-1
-2
-3
-4
-5
-6
0
20
40
60
80
Temperature
Optimised
WLF
Arrhenius
Polynomial

Mix C – Field Aged – Top

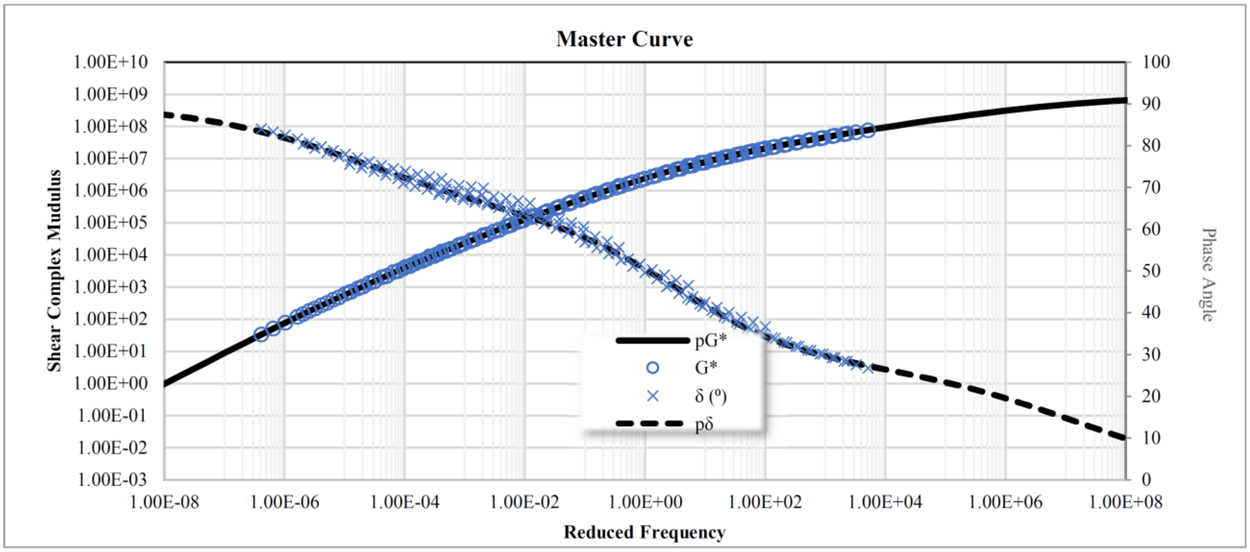


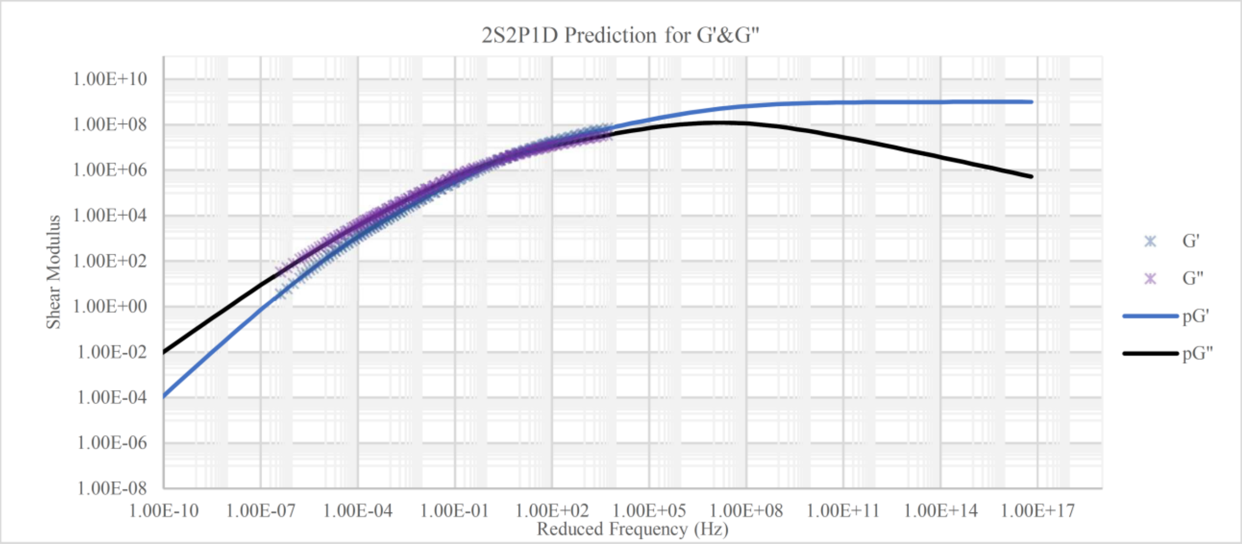


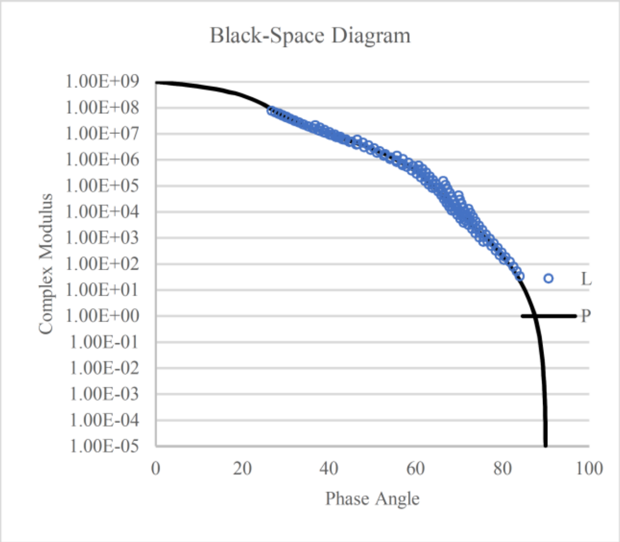


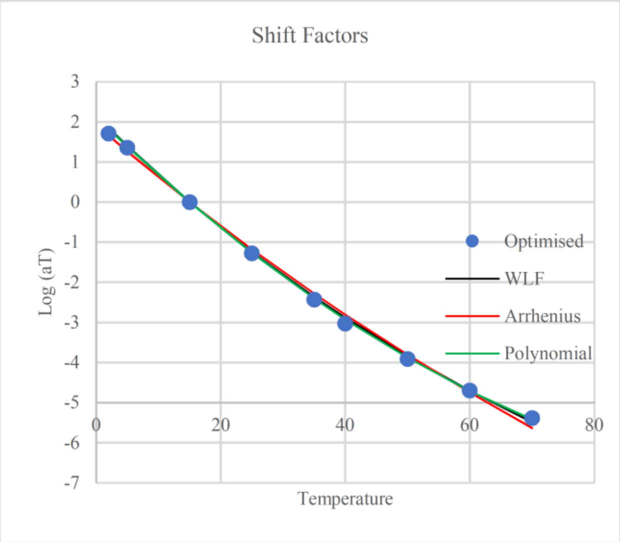


Mix C – Field Aged – Bottom

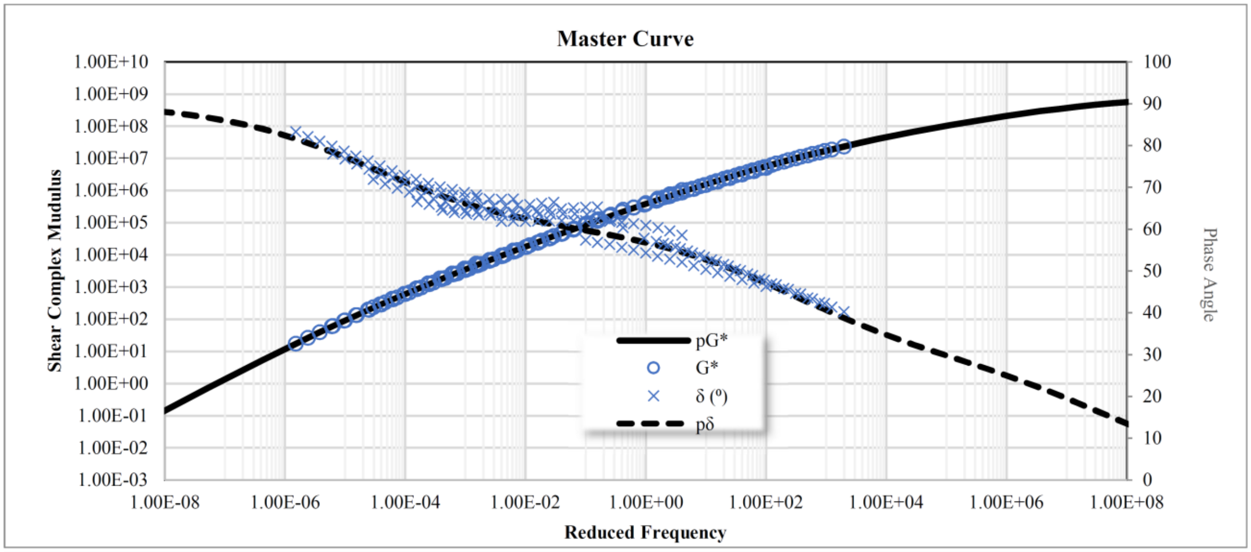


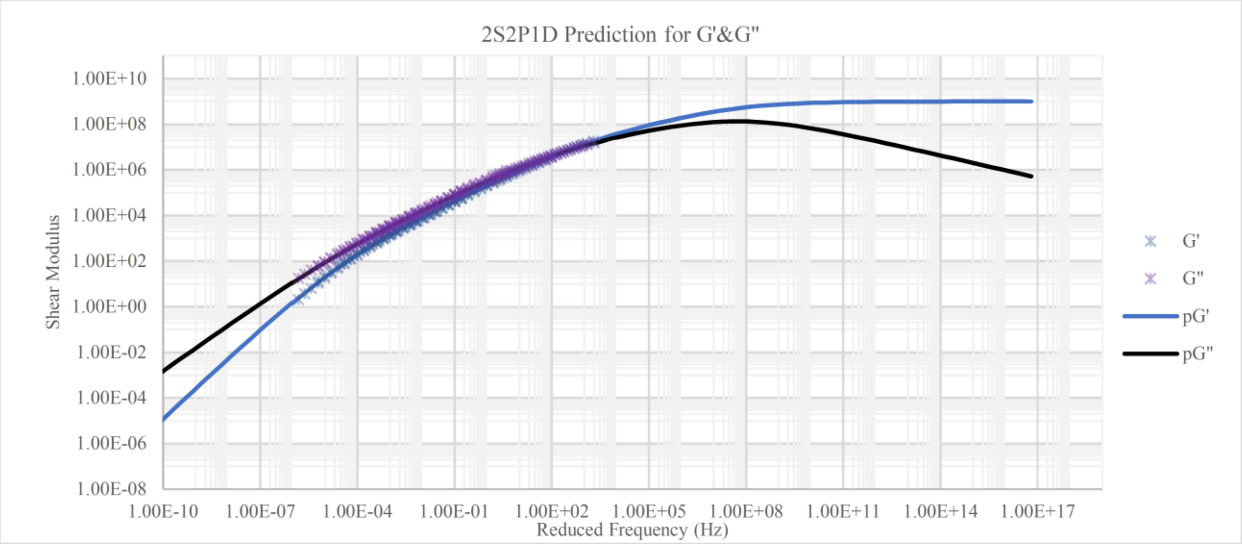


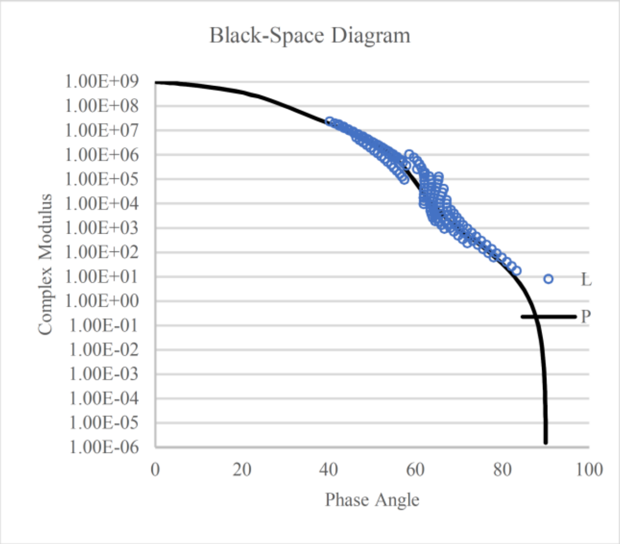


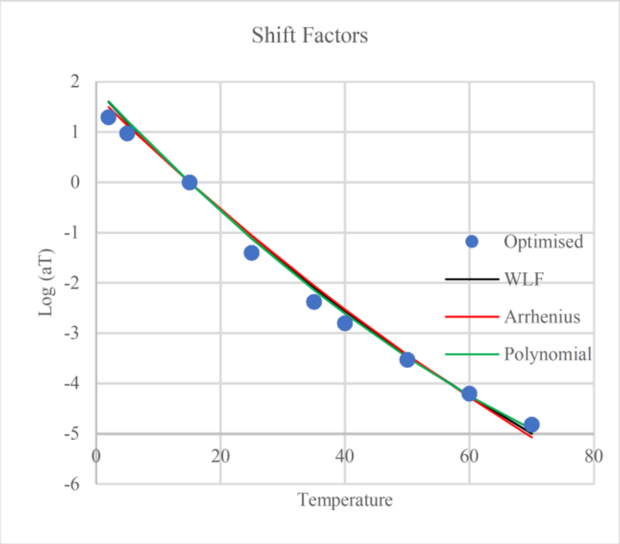


Control Mix – Unconditioned

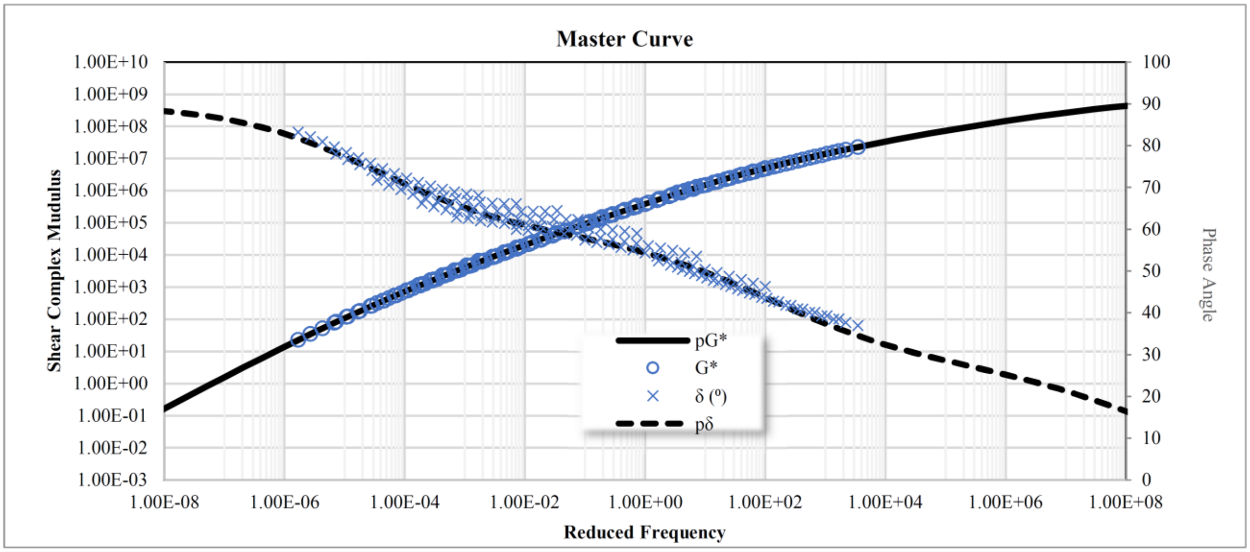


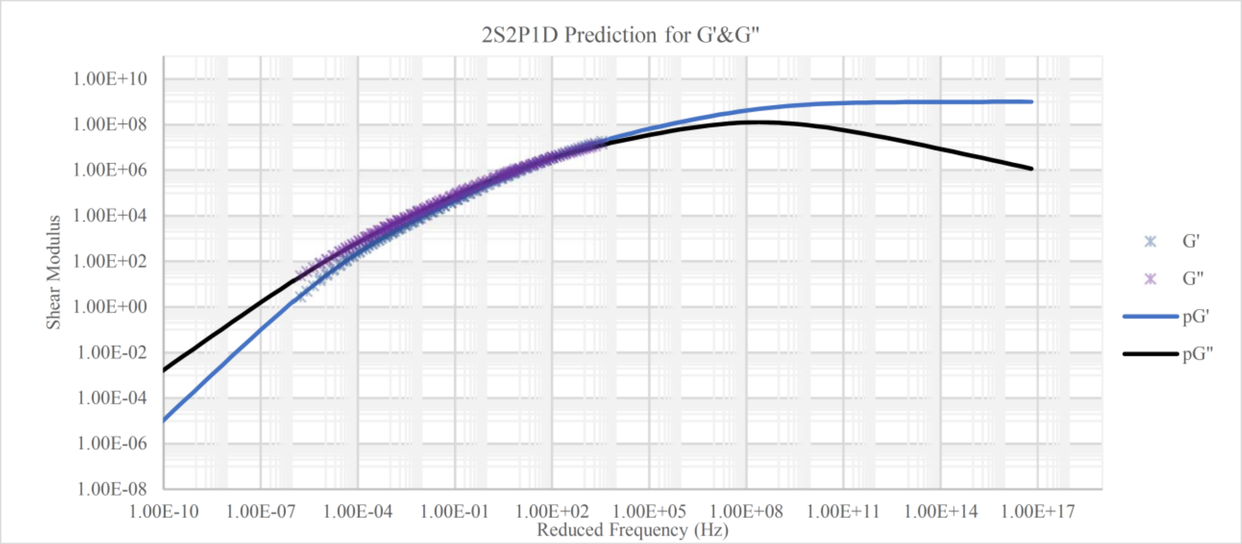


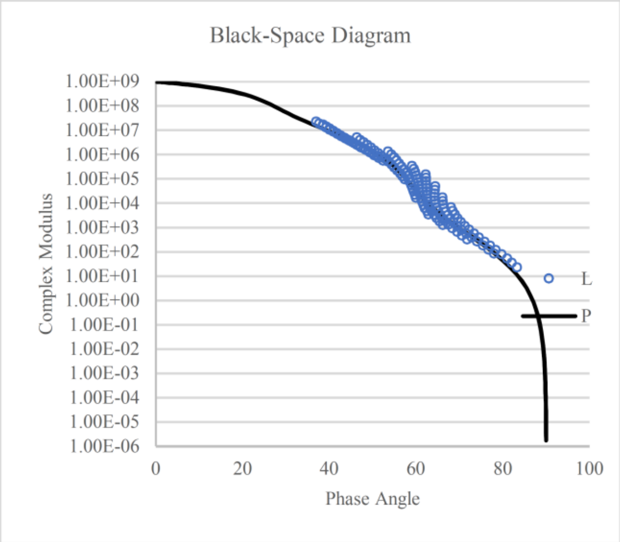


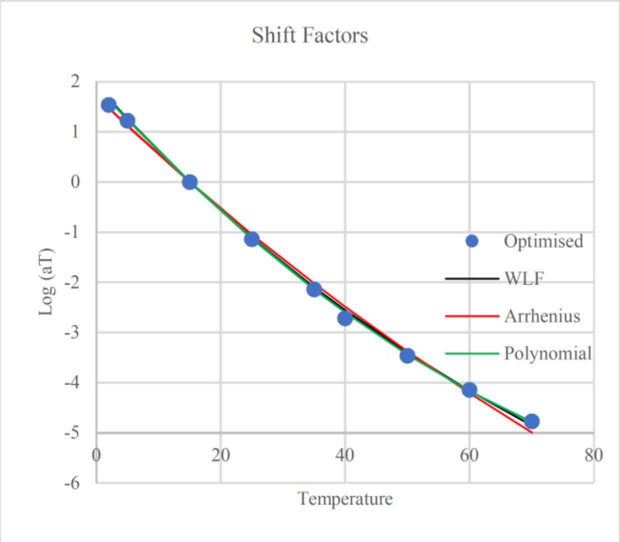


Control Mix – LTOA

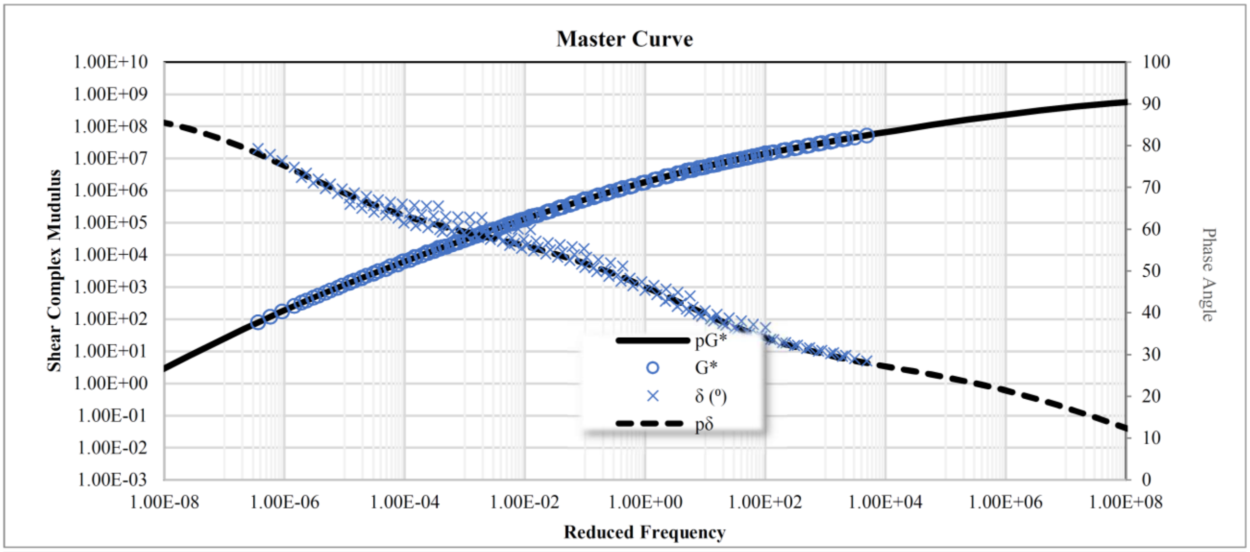


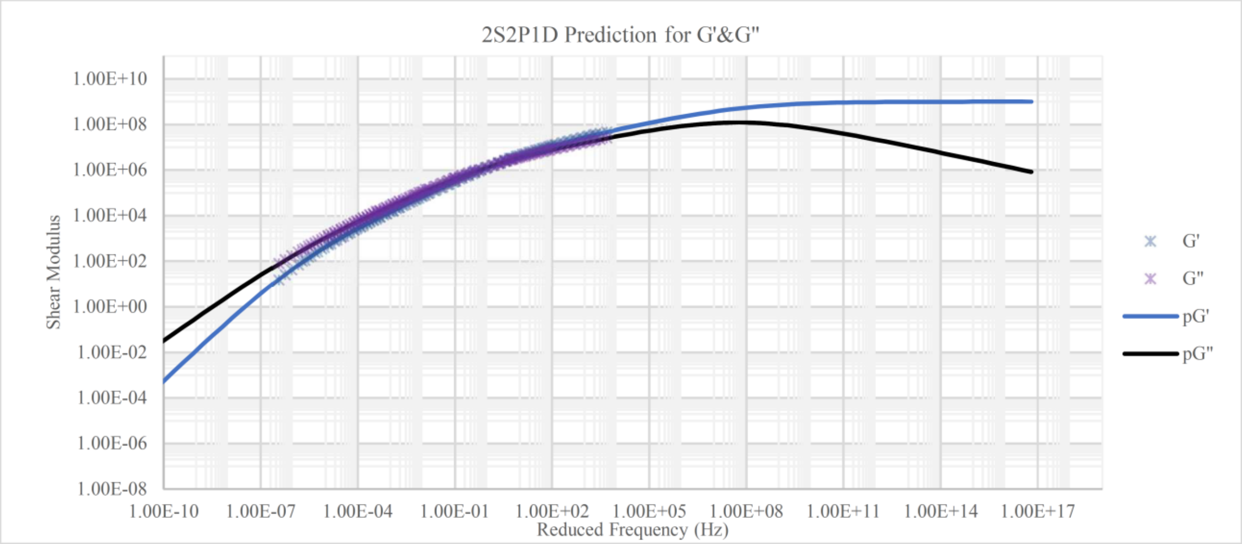


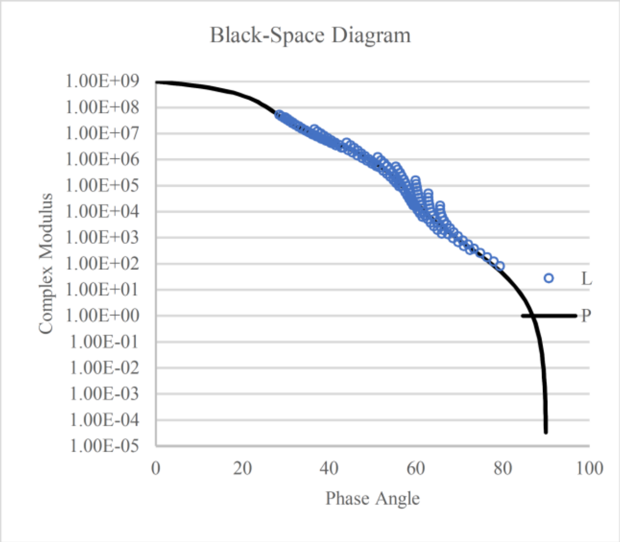


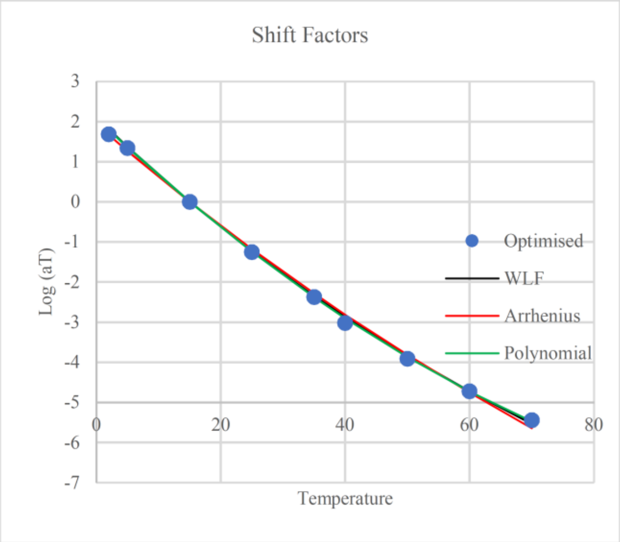


Control Mix – RHR





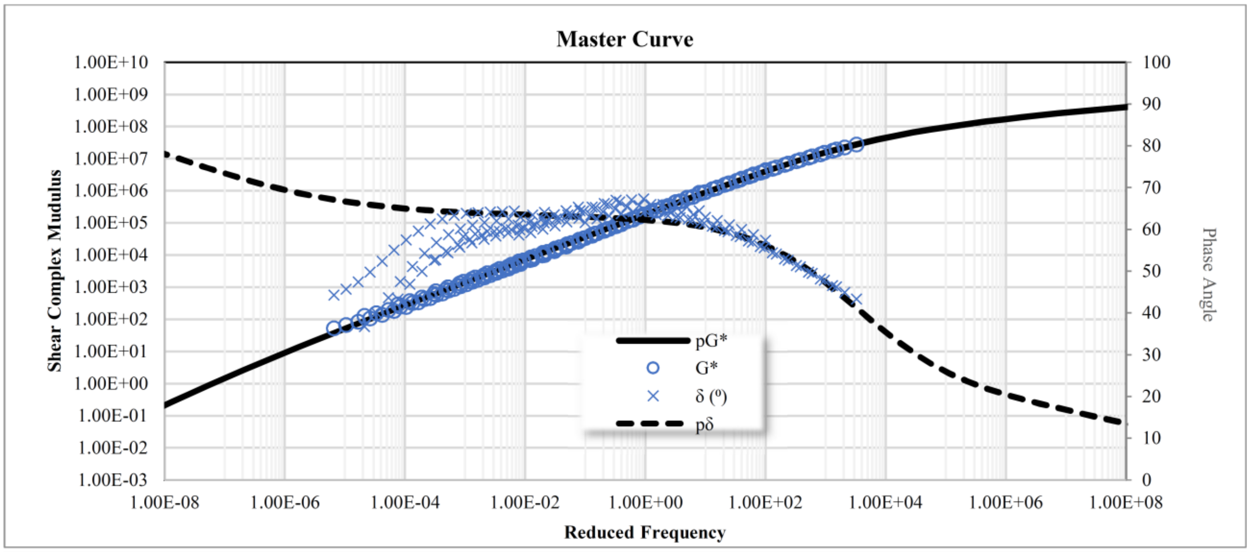


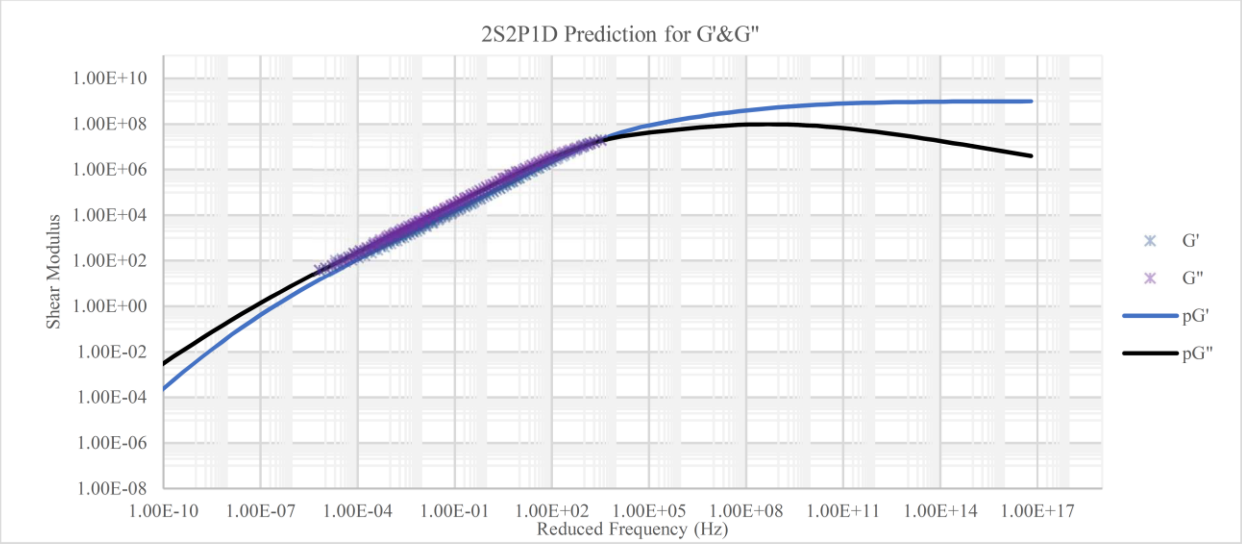


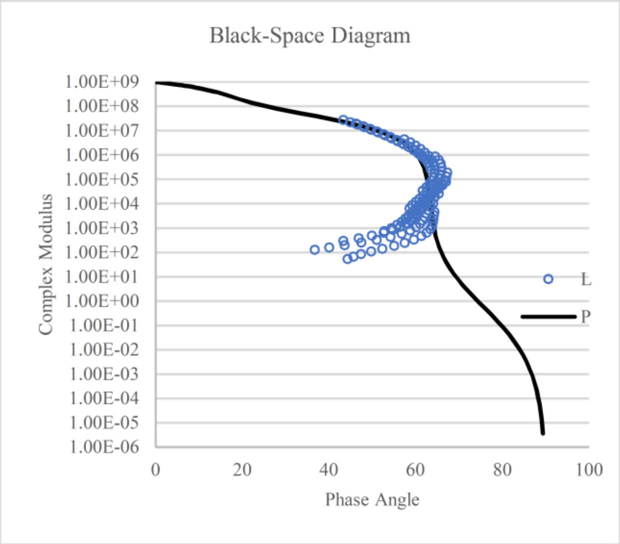
Model Parameters

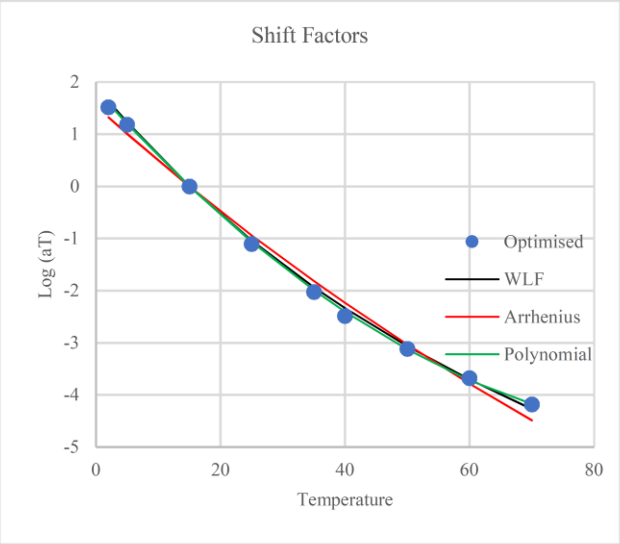
CONDITION	SAMPLE NUMBER	CODE	SHIFT FACTORS									MODEL PARAMETERS							RMSEIQR					WLF		Arrhenius	Polynomial		Cross-Over Frequency @ 15	Cross-Over Temperature @ 10 Rad/s
			a1	a2	a3	a4	a5	a6	a7	a8	a9	E0	E∞	δ	τ0	k	h	β	E*	δ	E'	E''	E',E''	C1	C2	Ea/R	C1	C2		
			2	5	15	20	30	40	50	60	70																			
VIRGIN	**PG58-34-p**	**58-34**	1.73	1.18	0	-0.54	-1.50	-2.33	-3.01	-3.60	-4.14	0	1.00E+09	9.72	6.13E-06	0.241	0.760	3.16E+04	0.71%	57.66%	1.11%	0.87%	0.71%	10.5	88.1	7871	0.112	6.89E-04	1697.8	-9.1
STOA	**4**	**08-U-4**	1.58	1.25	0	-1.16	-2.18	-2.73	-3.46	-4.13	-4.76	0	1.00E+09	8.79	1.13E-05	0.292	0.676	1.64E+03	0.62%	17.20%	1.07%	0.80%	0.67%	18.3	152.9	8990	0.120	6.09E-04	186.2	3.6
LTOA	**2**	**08-R-2**	1.53	1.21	0	-1.15	-2.16	-2.67	-3.42	-4.10	-4.72	0	1.00E+09	10.30	8.94E-06	0.318	0.662	2.24E+03	0.60%	14.15%	1.01%	0.81%	0.65%	18.9	161.6	8889	0.118	5.73E-04	88.9	6.5
RHR	**1**	**08-RHR-1**	1.65	1.30	0	-1.22	-2.30	-2.76	-3.65	-4.45	-5.18	0	1.00E+09	16.54	5.90E-05	0.309	0.647	2.52E+03	0.49%	8.35%	0.77%	0.77%	0.55%	22.3	180.1	9601	0.124	5.40E-04	2.1	20.4
Bottom	**B**	**08-B-TCE**	1.60	1.26	0	-0.96	-1.90	-2.16	-2.95	-3.62	-4.26	0	1.00E+09	6.86	3.03E-06	0.275	0.610	1.00E+03	0.97%	10.66%	1.77%	1.12%	1.09%	14.0	128.9	7890	0.106	5.52E-04	100.5	4.9
Top	**T**	**08-T-TCE**	1.47	1.06	0	-0.91	-1.75	-2.47	-3.19	-3.83	-4.38	0	1.00E+09	9.48	3.59E-06	0.279	0.625	8.54E+02	0.84%	11.23%	1.52%	1.01%	0.94%	19.7	188.3	8186	0.105	4.41E-04	150.5	3.2
STOA	**4**	**11-U-4**	1.51	1.20	0	-1.11	-2.09	-2.58	-3.30	-3.95	-4.55	0	1.00E+09	9.40	6.81E-06	0.309	0.681	1.23E+03	0.57%	14.75%	0.92%	0.72%	0.59%	17.5	153.3	8589	0.115	5.78E-04	291.4	1.0
LTOA	**2**	**11-R-2**	1.53	1.21	0	-1.14	-2.15	-2.68	-3.43	-4.12	-4.75	0	1.00E+09	9.58	1.14E-05	0.308	0.665	1.86E+03	0.55%	13.17%	0.94%	0.74%	0.60%	19.4	166.4	8928	0.117	5.58E-04	97.6	6.1
RHR	**1**	**11-RHR-1**	1.65	1.30	0	-1.23	-2.35	-3.01	-3.86	-4.61	-5.29	0	1.00E+09	13.21	7.35E-05	0.313	0.657	1.91E+03	0.45%	8.02%	0.70%	0.68%	0.49%	23.4	182.8	9950	0.129	5.77E-04	4.8	17.5
Bottom	**B**	**11-B**	1.73	1.41	0	-1.28	-2.46	-3.08	-4.05	-4.88	-5.61	0	1.00E+09	15.56	2.98E-04	0.288	0.660	8.24E+02	0.46%	5.08%	0.66%	0.63%	0.46%	25.6	191.1	10476	0.134	5.71E-04	1.9	20.5
Top	**T**	**11-T**	1.74	1.28	0	-1.27	-2.32	-2.82	-3.75	-4.57	-5.29	0	1.00E+09	16.66	1.38E-04	0.300	0.662	9.29E+02	0.49%	5.78%	0.67%	0.66%	0.47%	22.8	179.8	9829	0.127	5.52E-04	1.1	21.8
STOA	**4**	**12-U-4**	1.52	1.19	0	-1.09	-2.02	-2.57	-3.24	-3.84	-4.41	0	1.00E+09	8.23	5.87E-06	0.244	0.709	2.21E+03	0.63%	42.49%	1.07%	0.79%	0.67%	15.9	140.2	8384	0.114	6.15E-04	1072.3	-5.5
LTOA	**2**	**12-R-2**	1.51	1.17	0	-1.08	-2.00	-2.42	-3.11	-3.75	-4.35	0	1.00E+09	6.74	4.75E-06	0.422	0.690	1.26E+03	0.77%	23.96%	1.40%	0.97%	0.86%	15.8	142.9	8179	0.110	5.73E-04	2903.0	-11.5
RHR	**1**	**12-RHR-1**	1.59	1.28	0	-1.20	-2.13	-2.43	-3.25	-3.99	-4.66	0	1.00E+09	22.82	1.29E-05	0.312	0.662	2.45E+03	0.90%	13.06%	1.27%	1.25%	0.89%	17.2	148.3	8662	0.115	5.67E-04	7.2	16.2
Bottom	**B**	**12-B**	1.71	1.36	0	-1.28	-2.43	-3.02	-3.91	-4.69	-5.38	0	1.00E+09	13.73	3.39E-04	0.306	0.698	3.08E+02	0.36%	4.38%	0.56%	0.49%	0.38%	22.7	171.9	10129	0.132	6.17E-04	0.7	23.2
Top	**T**	**12-T**	1.76	1.41	0	-1.33	-2.54	-3.19	-4.16	-5.02	-5.76	0	1.00E+09	16.14	1.10E-03	0.291	0.688	6.38E+02	0.35%	4.30%	0.49%	0.57%	0.37%	26.6	194.0	10765	0.138	5.84E-04	4.2	17.7
STOA	**4**	**N-U-4**	1.29	0.97	0	-1.40	-2.38	-2.80	-3.53	-4.20	-4.82	0	1.00E+09	7.68	9.25E-06	0.328	0.666	1.66E+03	0.82%	17.69%	1.24%	1.07%	0.82%	24.0	209.2	9118	0.117	5.09E-04	213.9	2.7
LTOA	**2**	**N-R-2**	1.54	1.23	0	-1.14	-2.14	-2.71	-3.46	-4.14	-4.77	0	1.00E+09	10.80	7.64E-06	0.311	0.651	2.28E+03	0.62%	12.96%	1.03%	0.84%	0.67%	19.4	164.7	8980	0.118	5.68E-04	62.1	8.0
RHR	**1**	**N-RHR-1**	1.69	1.34	0	-1.25	-2.37	-3.01	-3.91	-4.72	-5.44	0	1.00E+09	14.44	1.24E-04	0.302	0.647	2.70E+03	0.41%	7.11%	0.65%	0.64%	0.46%	24.6	189.8	10147	0.130	5.58E-04	1.6	21.8

PG 64-28 p – Original

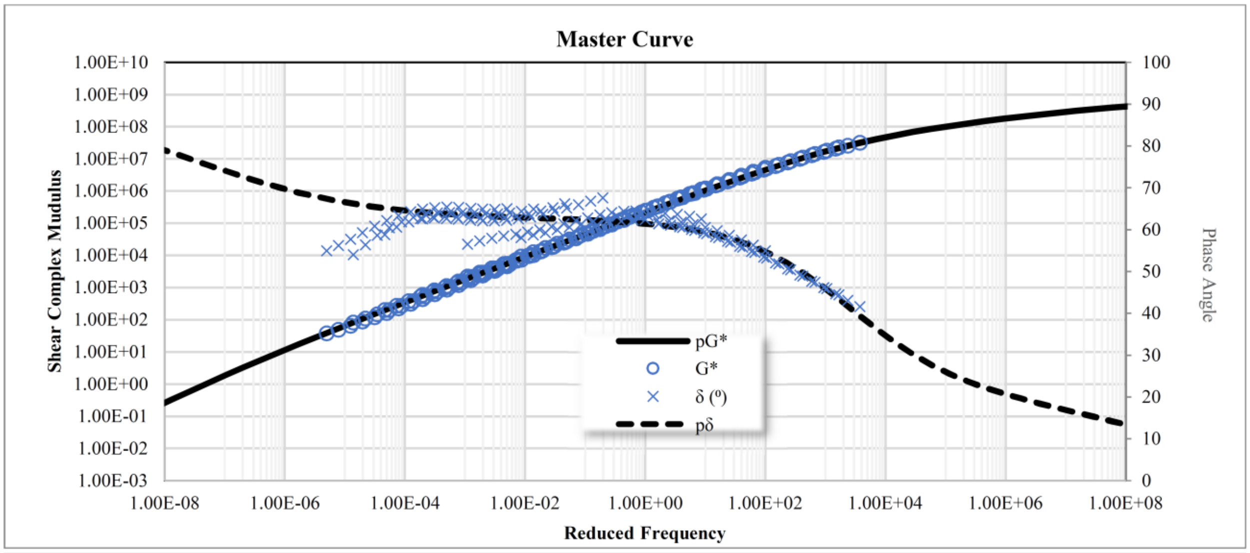


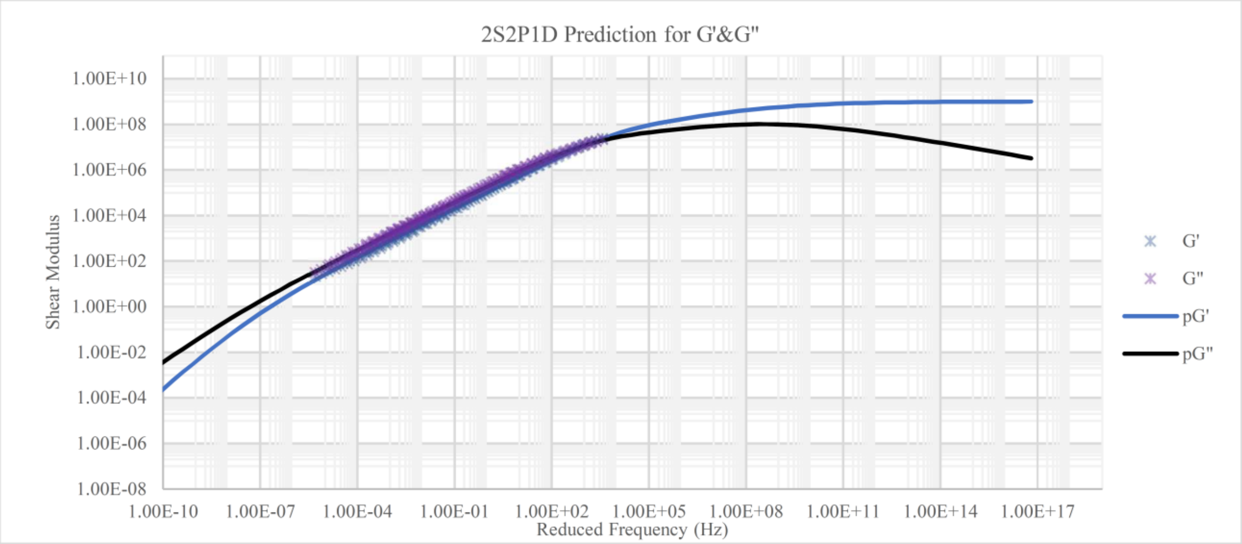


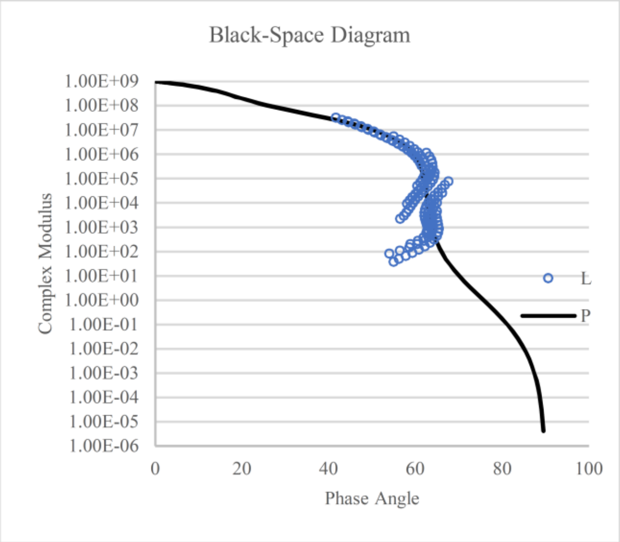


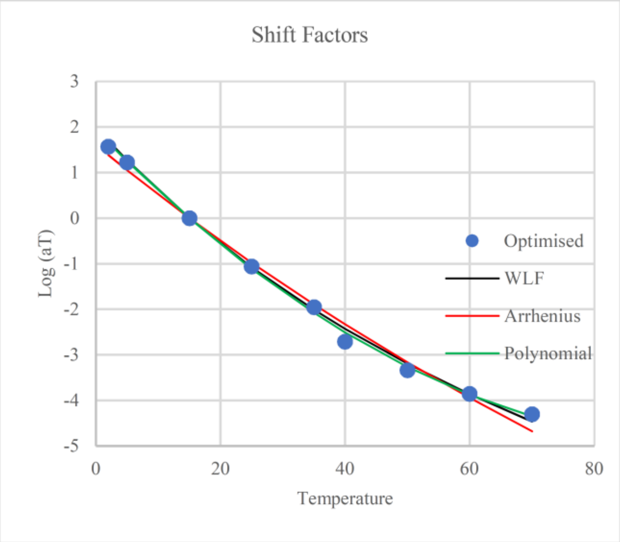


PG 64-28 p – Ex & Re

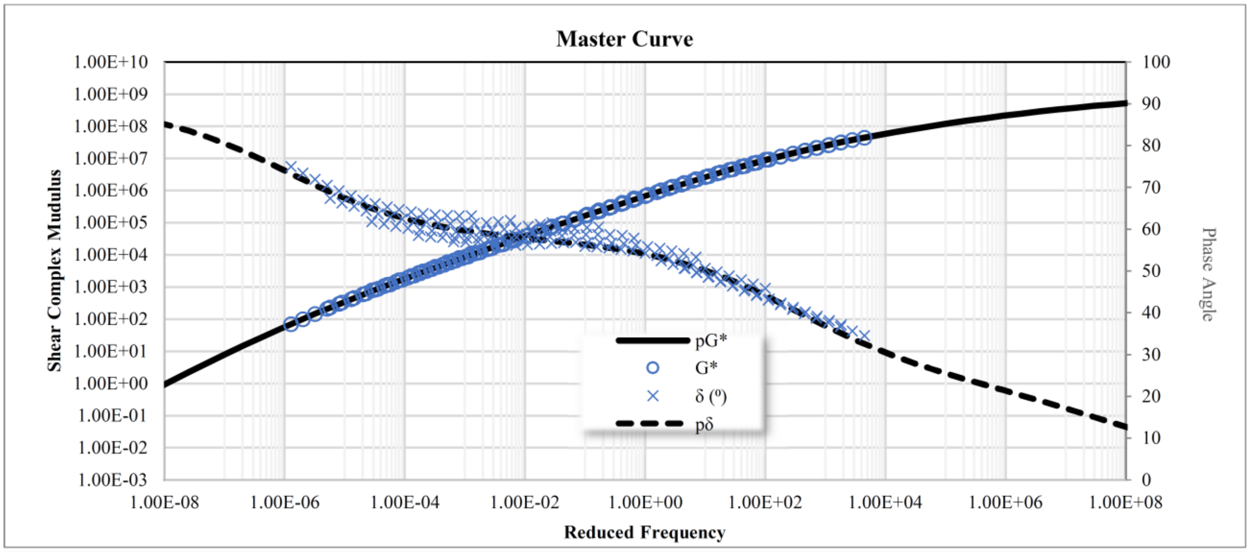


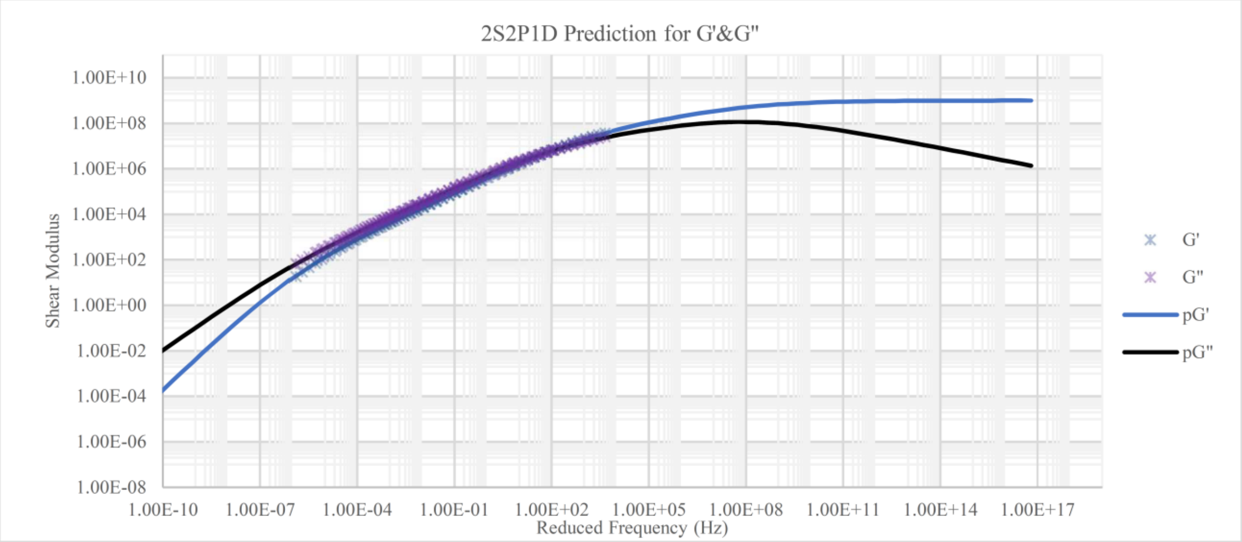


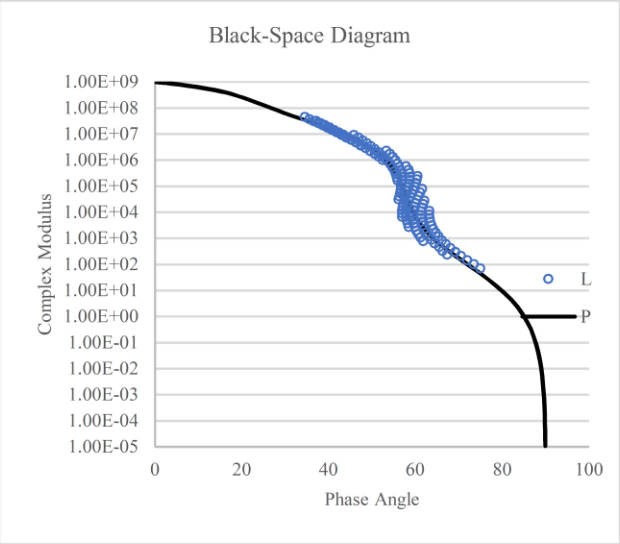


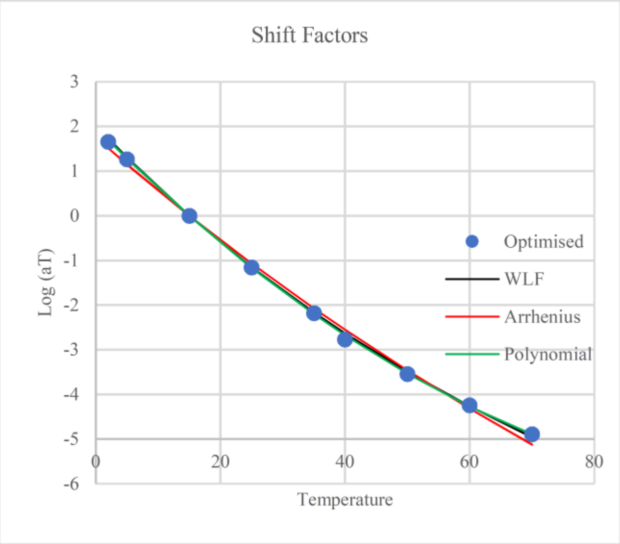


Fresh Loose Mix

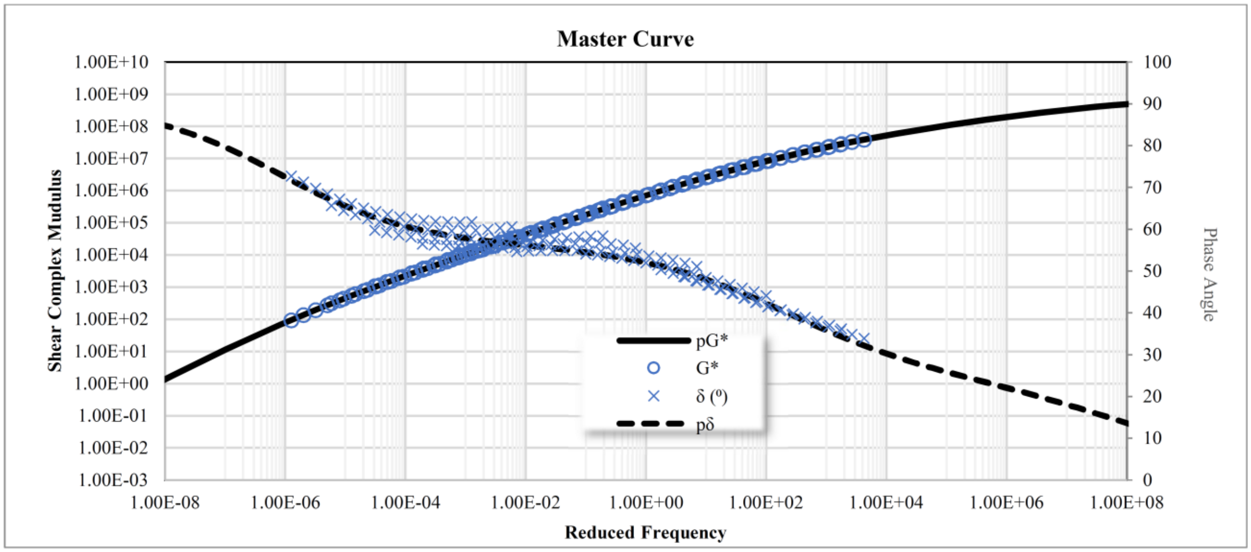


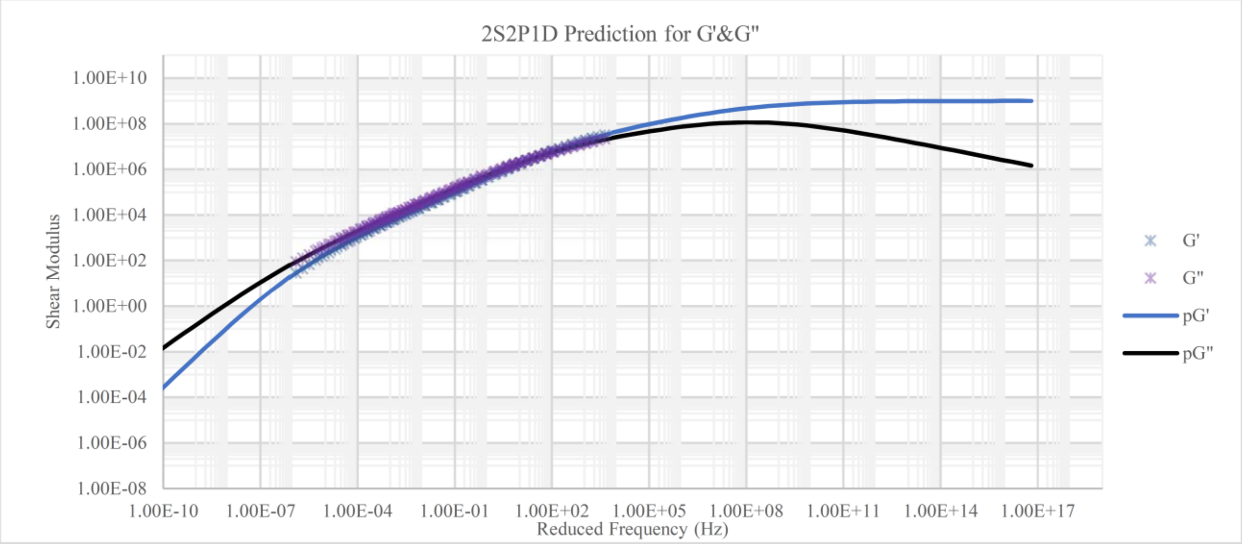


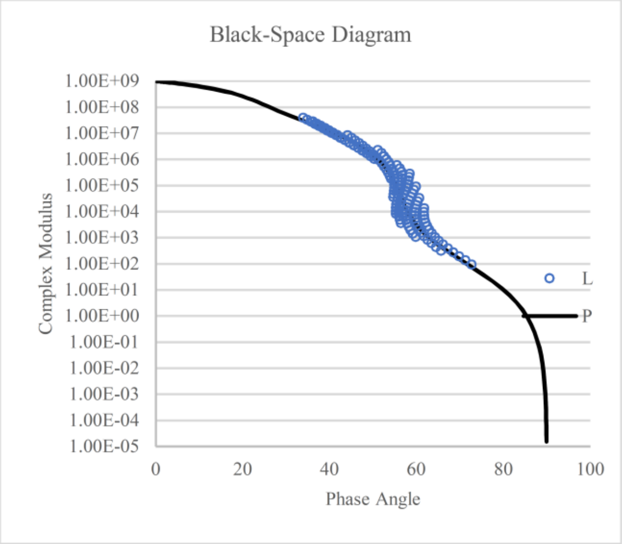


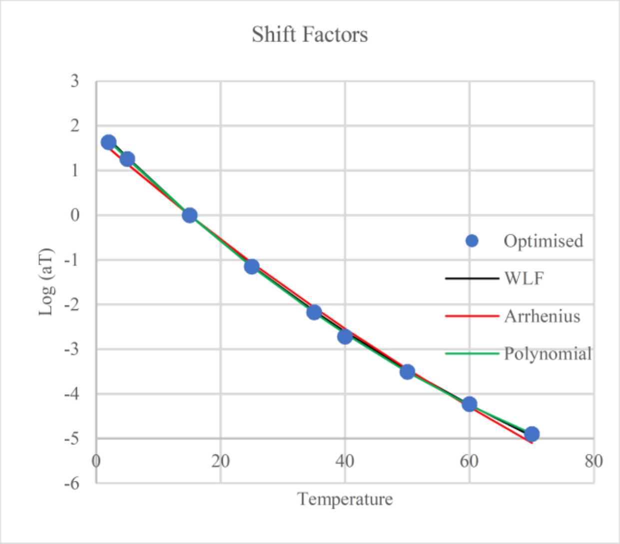


Compacted Mix

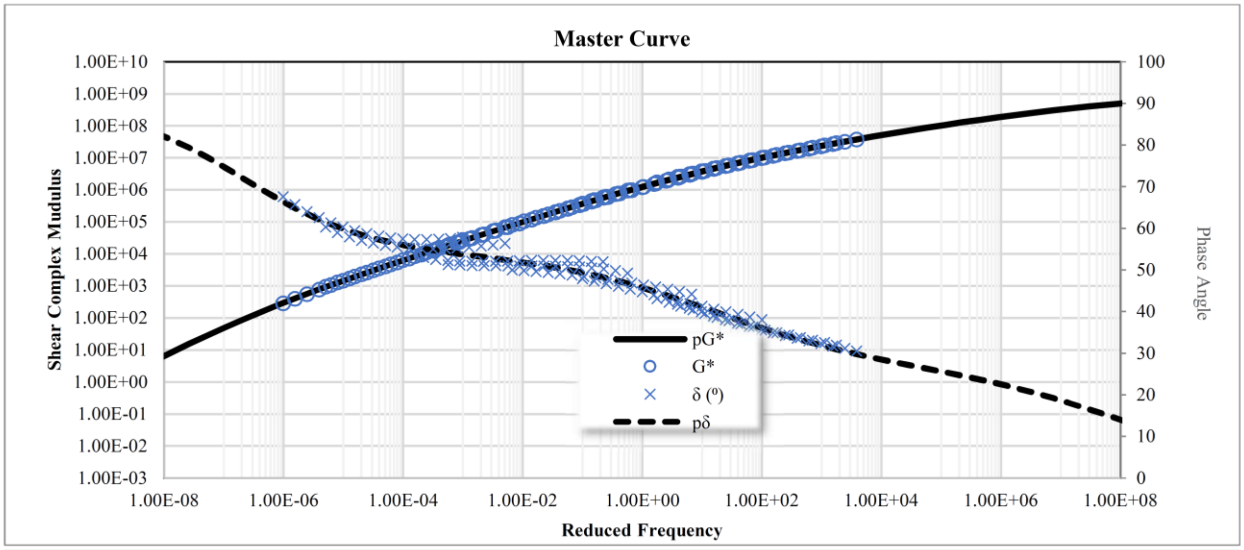


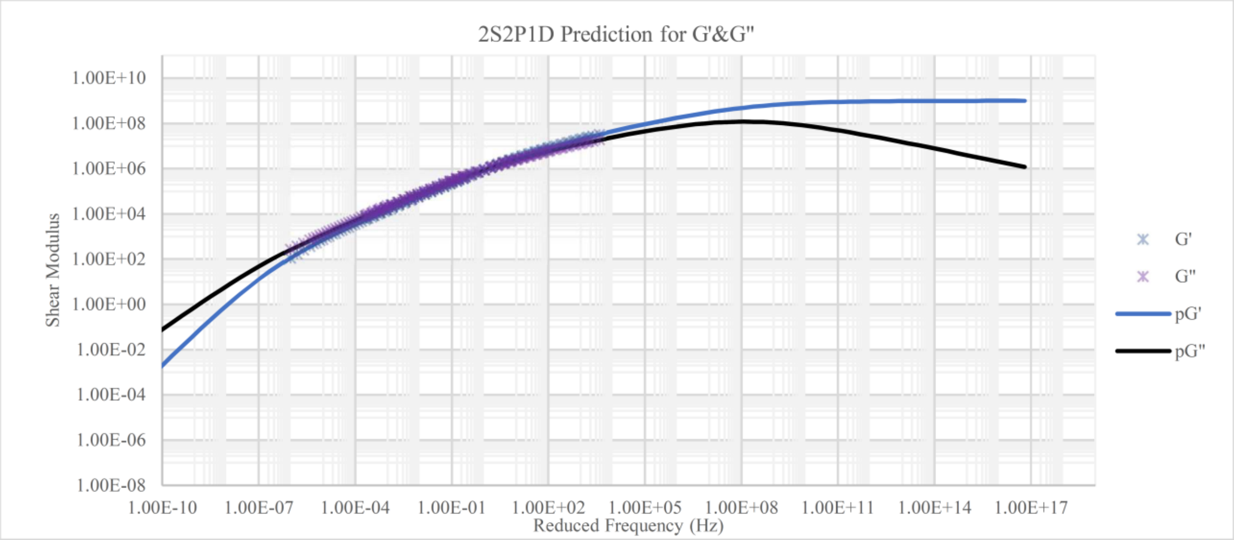


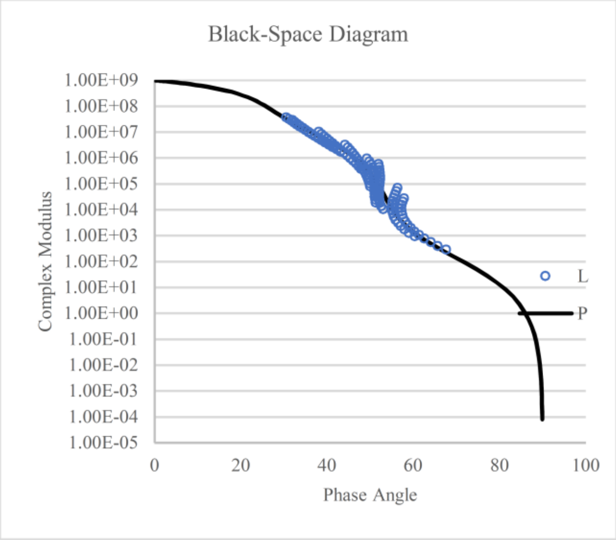


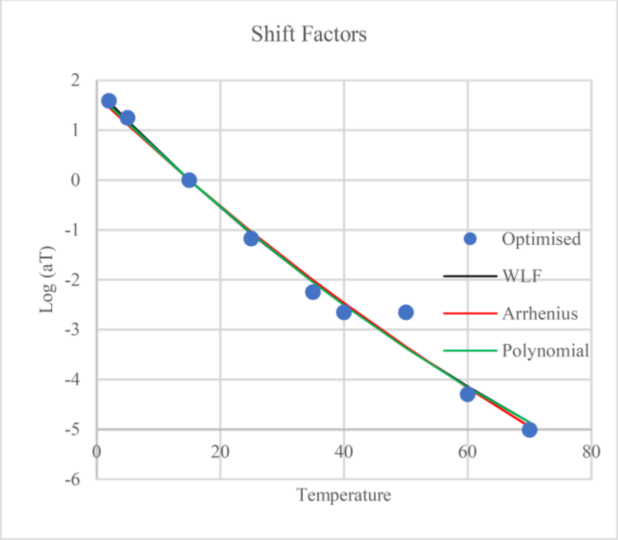


LTOA

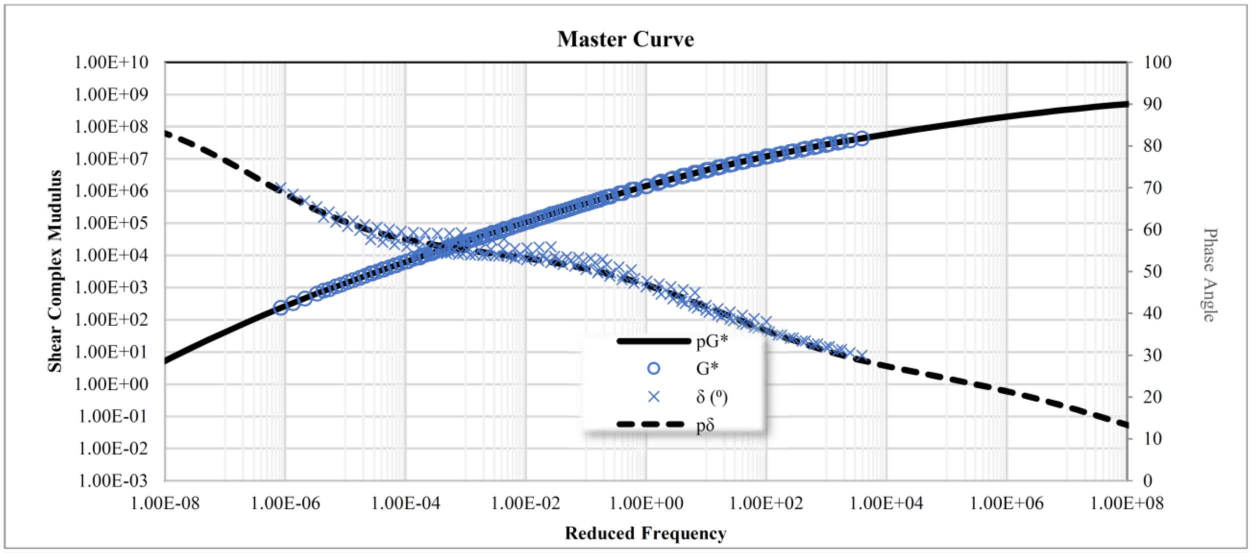

Master Curve
Shear Complex Modulus
1.00E+10
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
1.00E-03
Phase Angle
100
90
80
70
60
50
40
30
20
10
0
1.00E-08
1.00E-06
1.00E-04
1.00E-02
1.00E+00
1.00E+02
1.00E+04
1.00E+06
1.00E+08
Reduced Frequency
pG*
G*
δ (º)
pδ

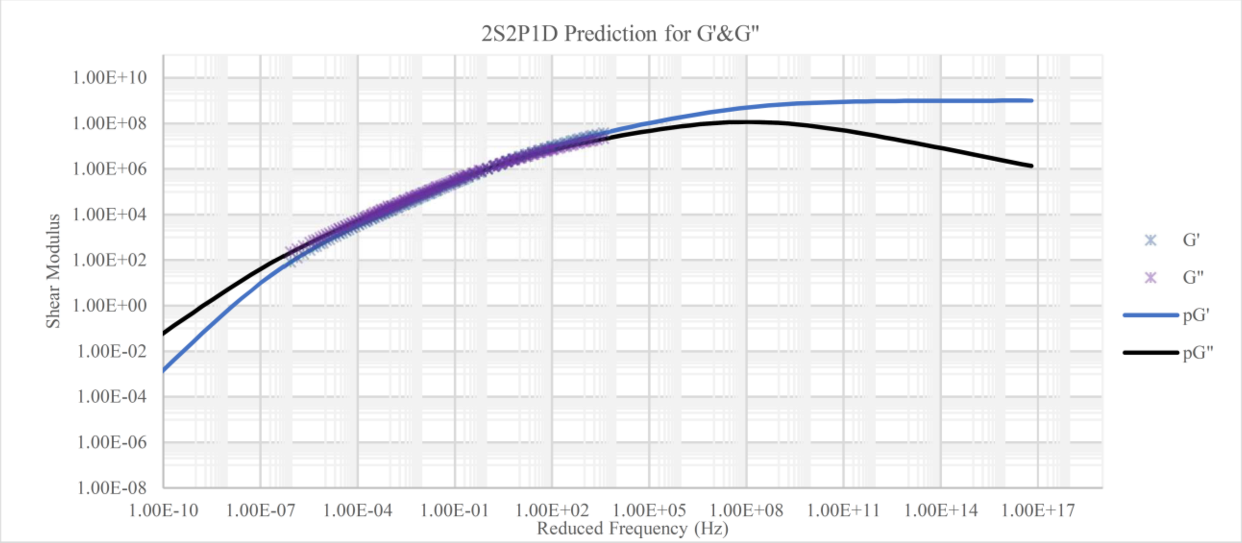

2S2P1D Prediction for G'&G"
Shear Modulus
1.00E+10
1.00E+08
1.00E+06
1.00E+04
1.00E+02
1.00E+00
1.00E-02
1.00E-04
1.00E-06
1.00E-08
1.00E-10
1.00E-07
1.00E-04
1.00E-01
1.00E+02
1.00E+05
1.00E+08
1.00E+11
1.00E+14
1.00E+17
Reduced Frequency (Hz)
G'
G"
pG'
pG"

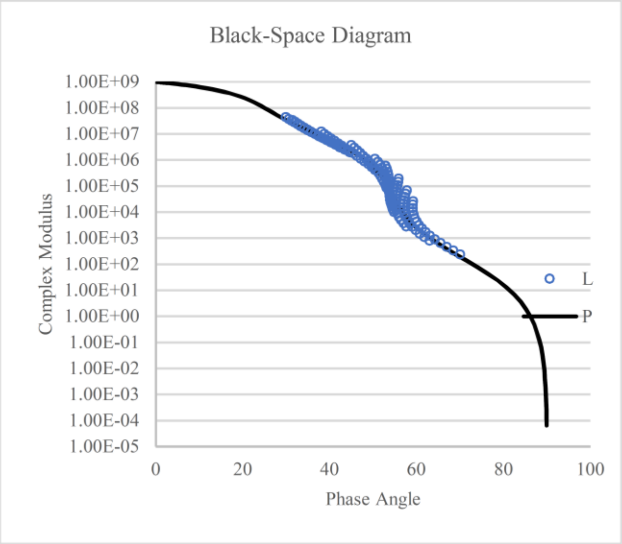

Black-Space Diagram
Complex Modulus
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
1.00E-03
1.00E-04
1.00E-05
0
20
40
60
80
100
Phase Angle
L
P

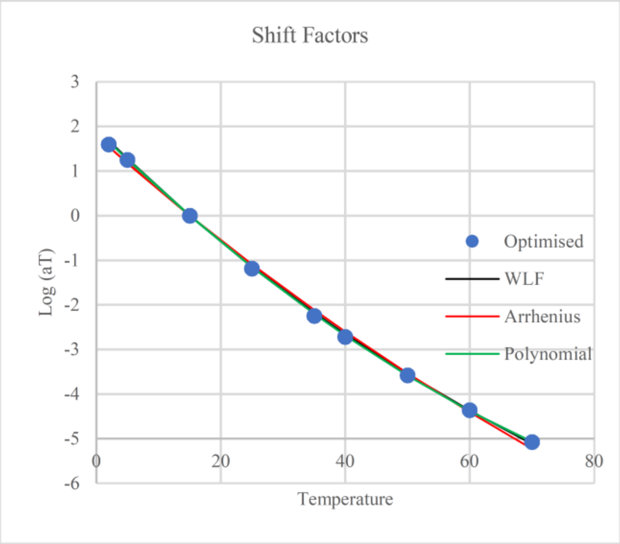

Shift Factors
Log (aT)
2
1
0
-1
-2
-3
-4
-5
-6
0
20
40
60
80
Temperature
Optimised
WLF
Arrhenius
Polynomial

Atlas Weather-O-Meter

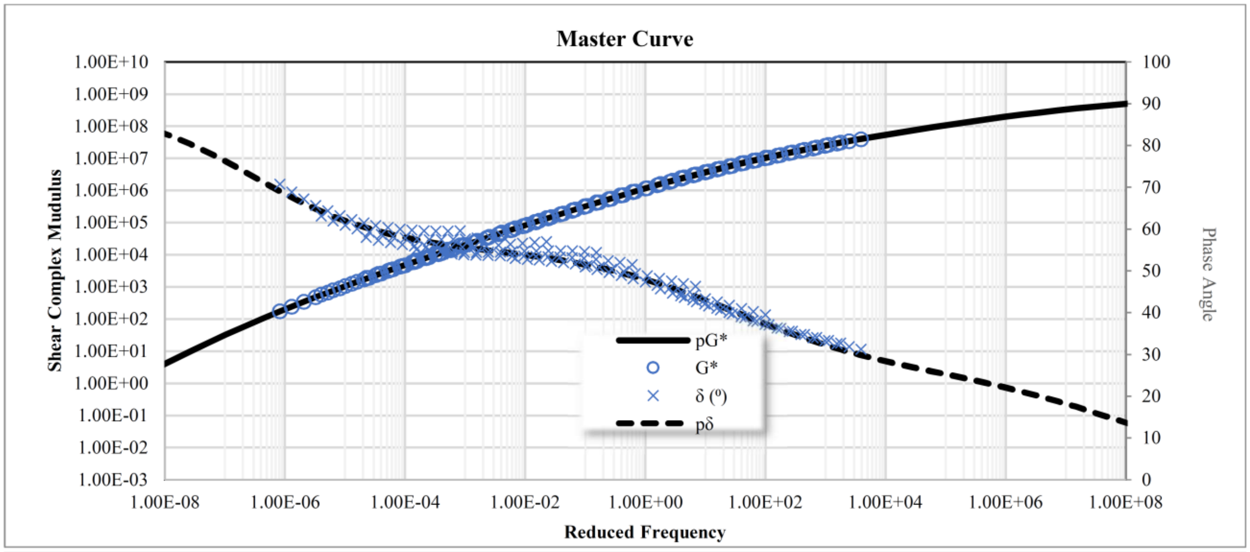


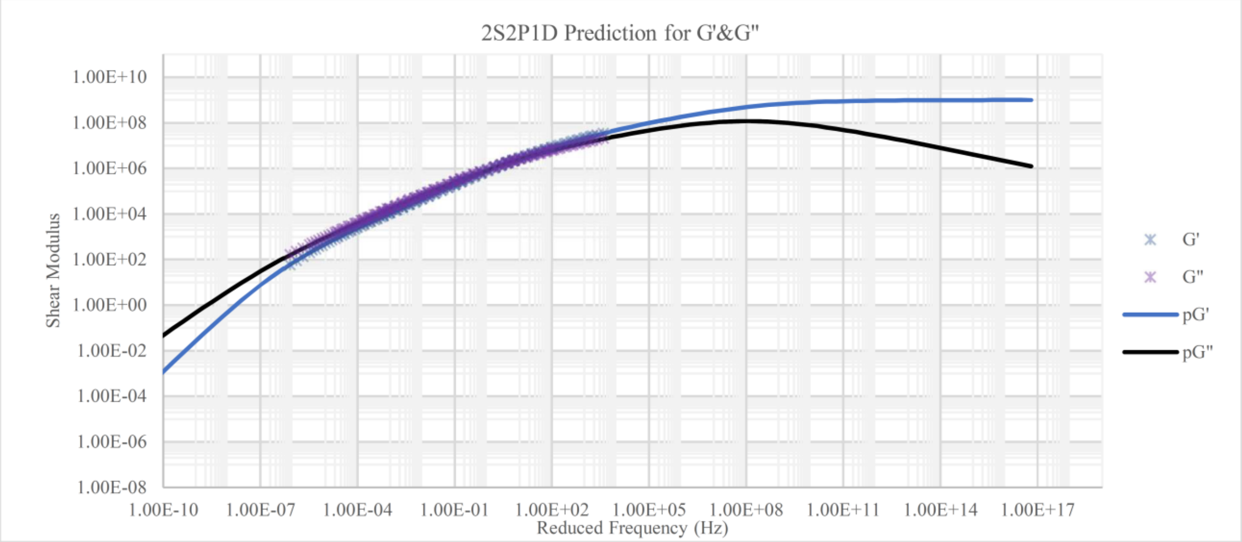


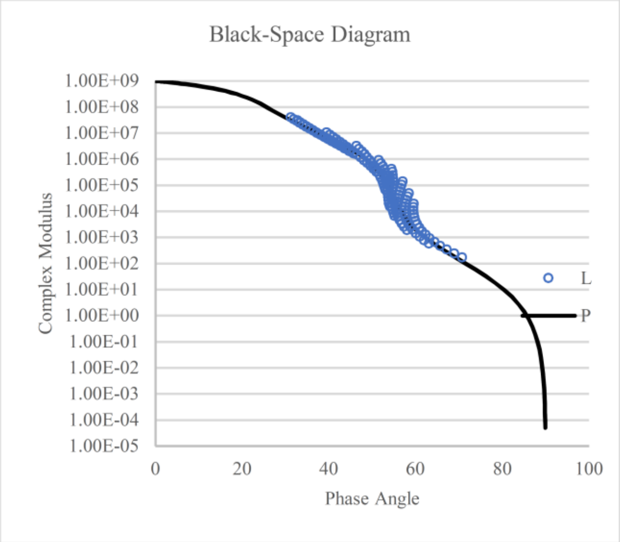


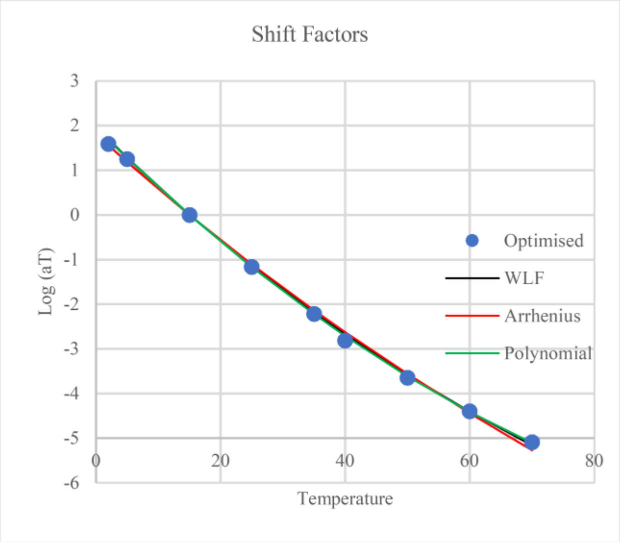


BC-05-Dry

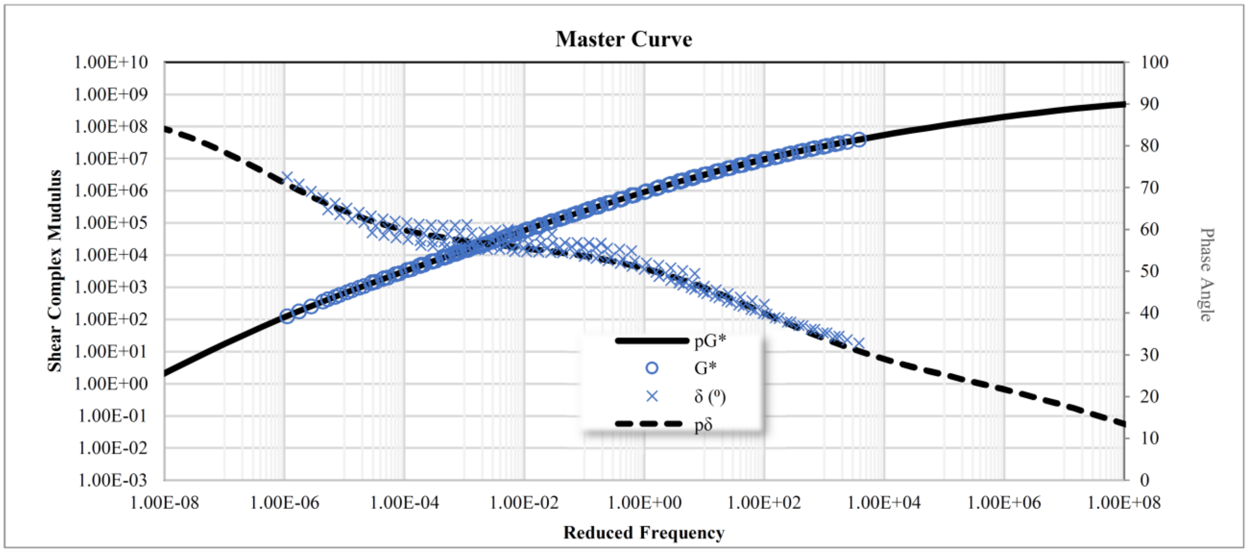

Master Curve
Shear Complex Mudulus
1.00E+10
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
1.00E-03
1.00E-08
1.00E-06
1.00E-04
1.00E-02
1.00E+00
1.00E+02
1.00E+04
1.00E+06
1.00E+08
Reduced Frequency
Phase Angle
100
90
80
70
60
50
40
30
20
10
0
pG*
G*
δ (º)
pδ

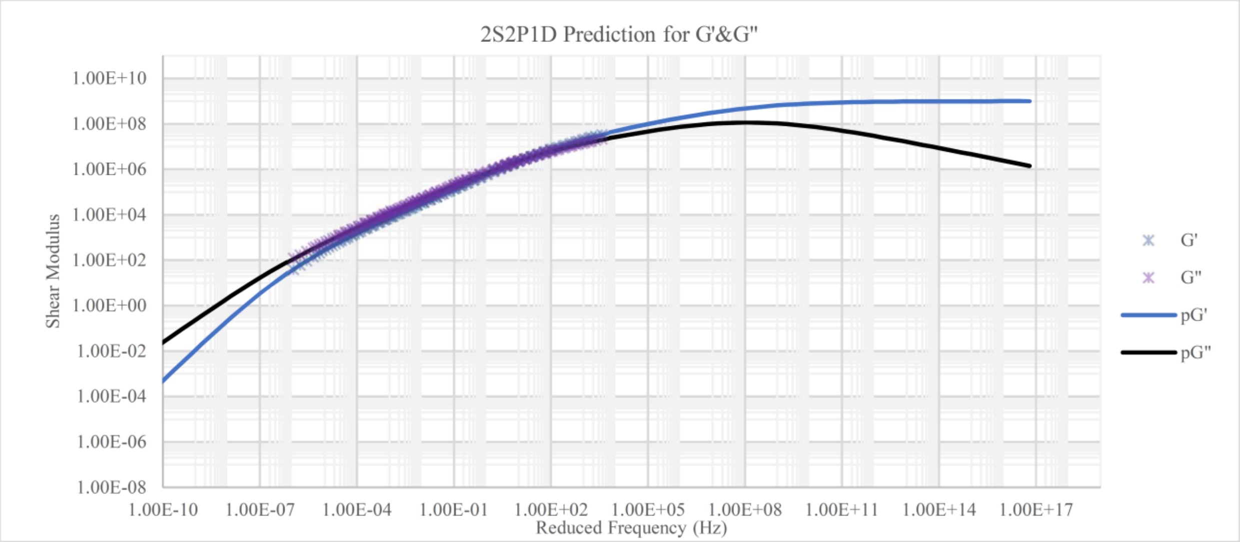

2S2P1D Prediction for G'&G"
Shear Modulus
1.00E+10
1.00E+08
1.00E+06
1.00E+04
1.00E+02
1.00E+00
1.00E-02
1.00E-04
1.00E-06
1.00E-08
1.00E-10
1.00E-07
1.00E-04
1.00E-01
1.00E+02
1.00E+05
1.00E+08
1.00E+11
1.00E+14
1.00E+17
Reduced Frequency (Hz)
G'
G"
pG'
pG"

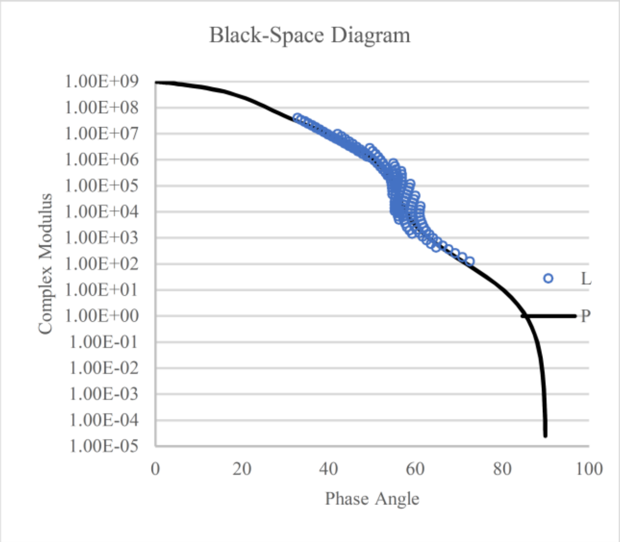

Black-Space Diagram
Complex Modulus
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
1.00E-03
1.00E-04
1.00E-05
0
20
40
60
80
100
Phase Angle
L
P

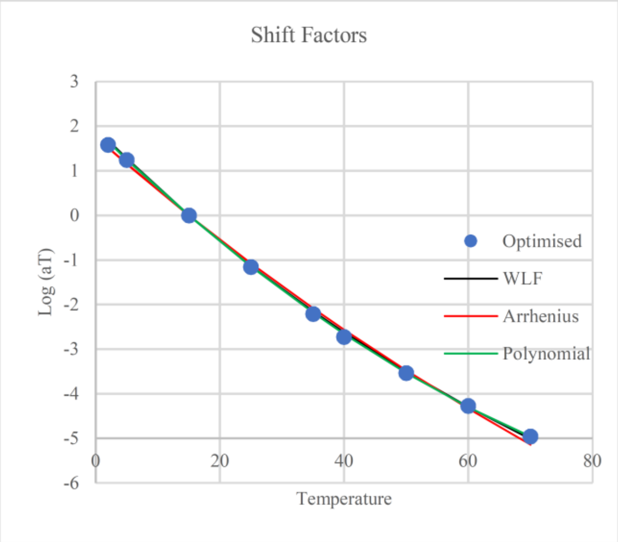

Shift Factors
Log (aT)
3
2
1
0
-1
-2
-3
-4
-5
-6
0
20
40
60
80
Temperature
Optimised
WLF
Arrhenius
Polynomial

BC-05-Wet

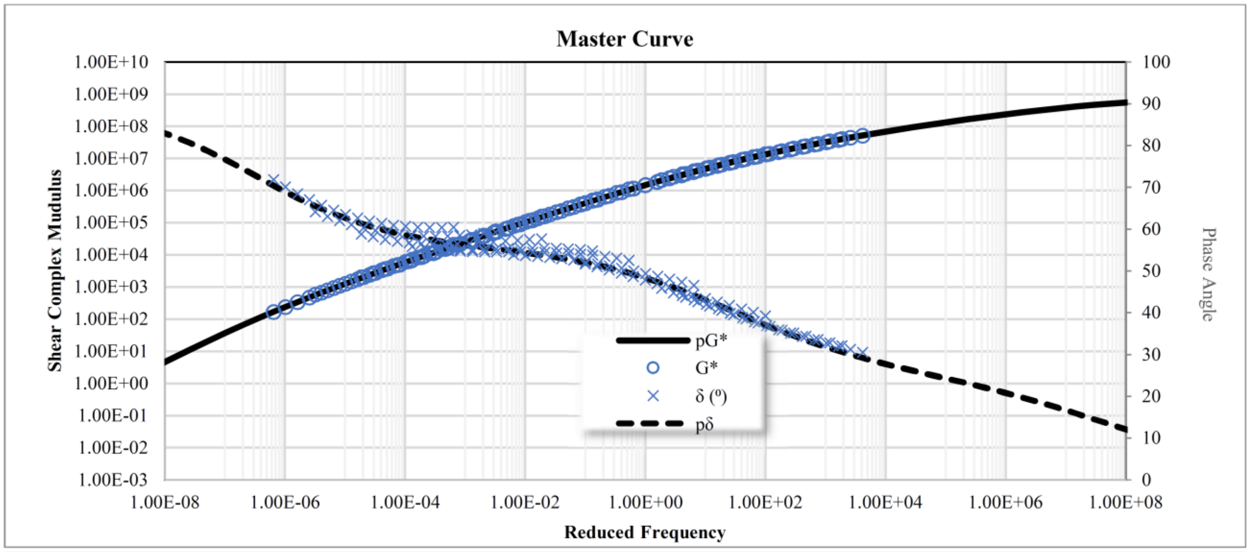

Master Curve
Shear Complex Mudulus
1.00E+10
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
1.00E-03
1.00E-08
1.00E-06
1.00E-04
1.00E-02
1.00E+00
1.00E+02
1.00E+04
1.00E+06
1.00E+08
Reduced Frequency
100
90
80
70
60
50
40
30
20
10
0
Phase Angle
pG*
G*
δ (º)
pδ

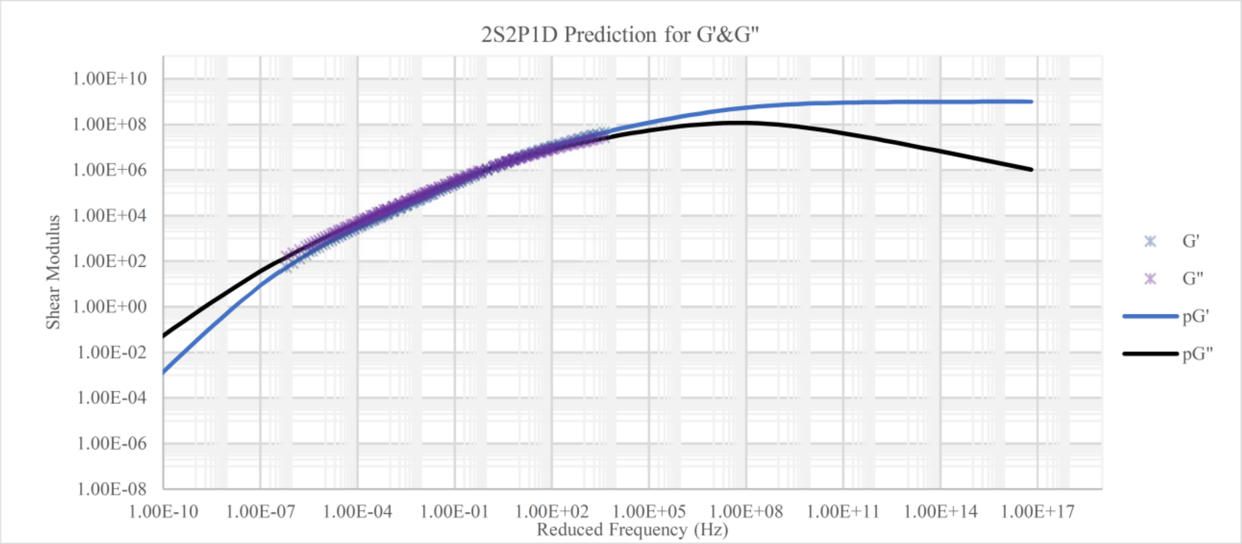

2S2P1D Prediction for G'&G"
Shear Modulus
1.00E+10
1.00E+08
1.00E+06
1.00E+04
1.00E+02
1.00E+00
1.00E-02
1.00E-04
1.00E-06
1.00E-08
1.00E-10
1.00E-07
1.00E-04
1.00E-01
1.00E+02
1.00E+05
1.00E+08
1.00E+11
1.00E+14
1.00E+17
Reduced Frequency (Hz)
G'
G"
pG'
pG"

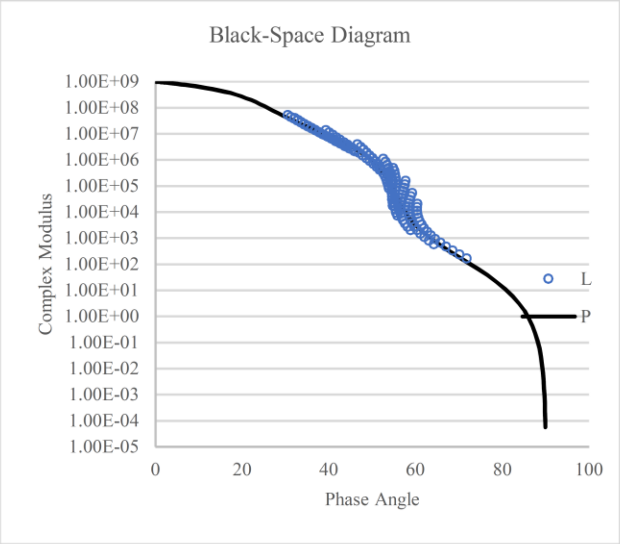

Black-Space Diagram
Complex Modulus
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
1.00E-03
1.00E-04
1.00E-05
0
20
40
60
80
100
Phase Angle
L
P

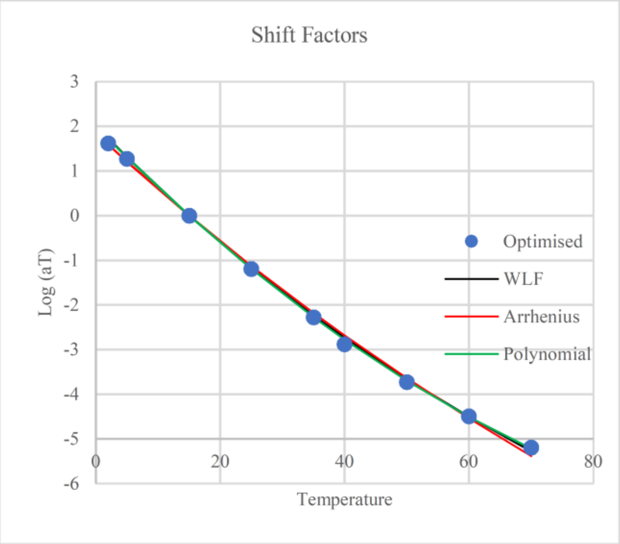

Shift Factors
Log (aT)
3
2
1
0
-1
-2
-3
-4
-5
-6
0
20
40
60
80
Temperature
Optimised
WLF
Arrhenius
Polynomial

BC-10-Dry

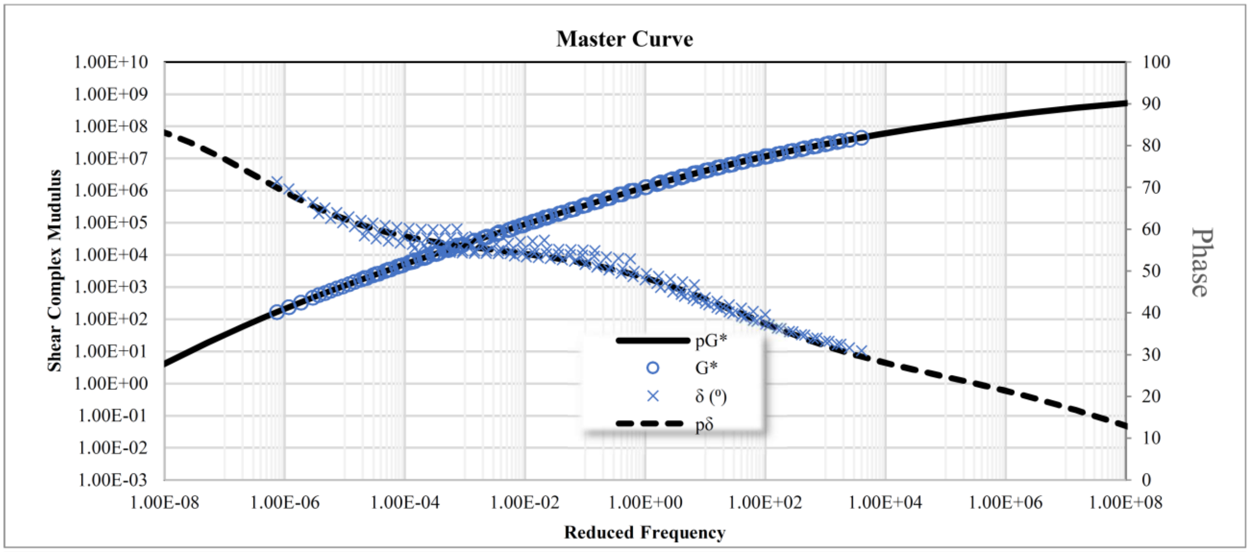

Master Curve
Shear Complex Mudulus
Phase Angle
Reduced Frequency
1.00E+10
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
1.00E-03
100
90
80
70
60
50
40
30
20
10
0
1.00E-08
1.00E-06
1.00E-04
1.00E-02
1.00E+00
1.00E+02
1.00E+04
1.00E+06
1.00E+08
pG*
G*
δ (º)
pδ

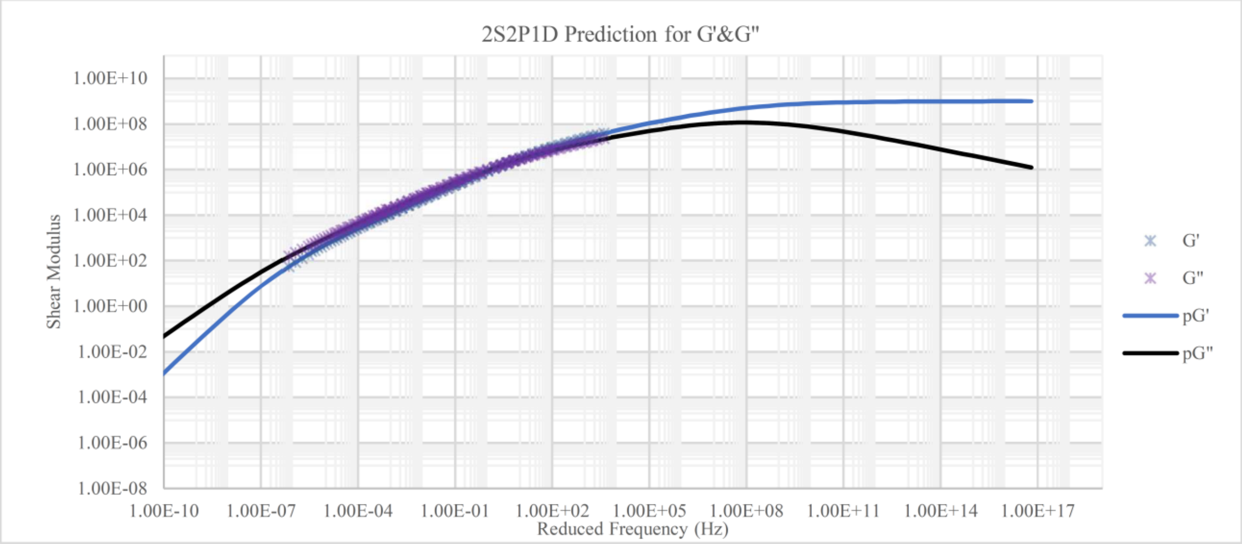

2S2P1D Prediction for G'&G"
Shear Modulus
Reduced Frequency (Hz)
1.00E+10
1.00E+08
1.00E+06
1.00E+04
1.00E+02
1.00E+00
1.00E-02
1.00E-04
1.00E-06
1.00E-08
1.00E-10
1.00E-07
1.00E-04
1.00E-01
1.00E+02
1.00E+05
1.00E+08
1.00E+11
1.00E+14
1.00E+17
G'
G"
pG'
pG"

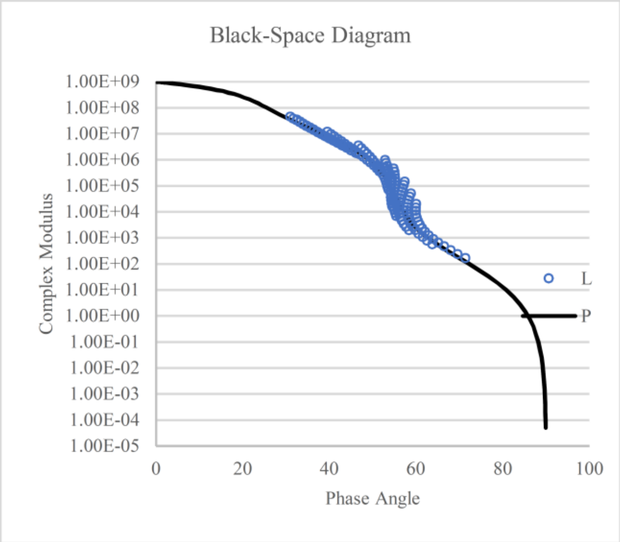

Black-Space Diagram
Complex Modulus
Phase Angle
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
1.00E-03
1.00E-04
1.00E-05
0
20
40
60
80
100
L
P

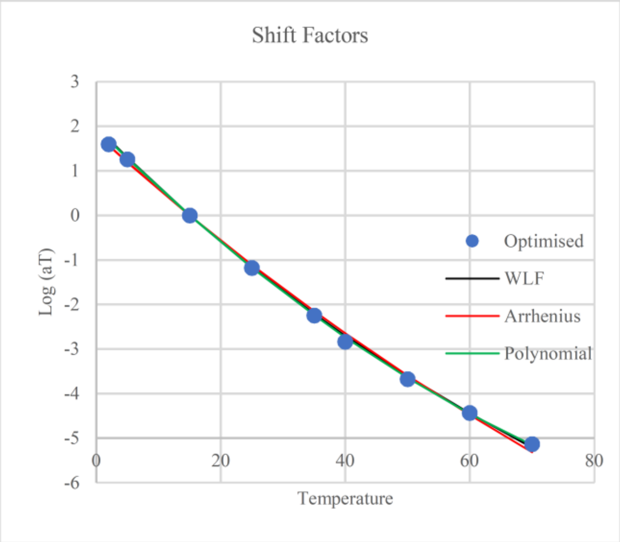

Shift Factors
Log (aT)
Temperature
3
2
1
0
-1
-2
-3
-4
-5
-6
0
20
40
60
80
Optimised
WLF
Arrhenius
Polynomial

BC-10-Wet

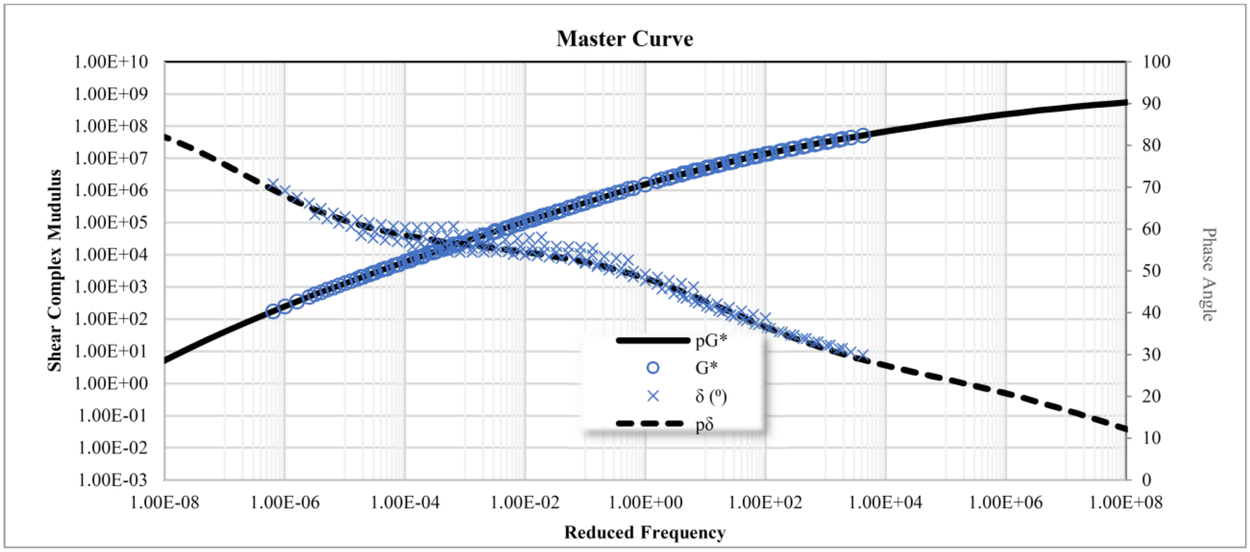

Master Curve
Shear Complex Mudulus
1.00E+10
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
1.00E-03
1.00E-08
1.00E-06
1.00E-04
1.00E-02
1.00E+00
1.00E+02
1.00E+04
1.00E+06
1.00E+08
Reduced Frequency
Phase
100
90
80
70
60
50
40
30
20
10
0
pG*
G*
δ (º)
pδ

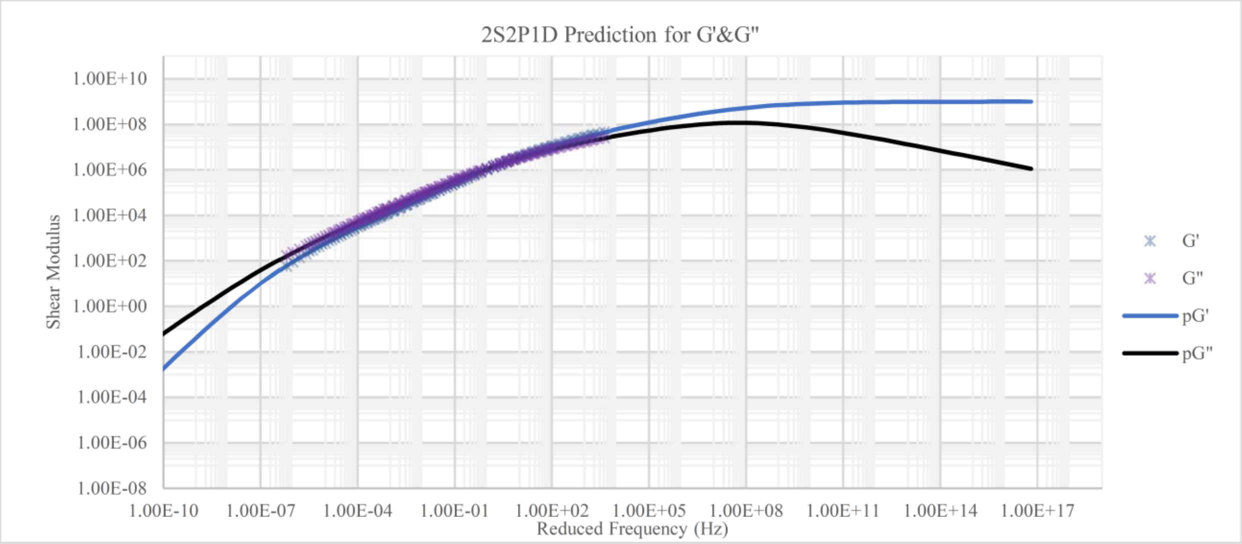

2S2P1D Prediction for G'&G"
Shear Modulus
1.00E+10
1.00E+08
1.00E+06
1.00E+04
1.00E+02
1.00E+00
1.00E-02
1.00E-04
1.00E-06
1.00E-08
1.00E-10
1.00E-07
1.00E-04
1.00E-01
1.00E+02
1.00E+05
1.00E+08
1.00E+11
1.00E+14
1.00E+17
Reduced Frequency (Hz)
G'
G"
pG'
pG"

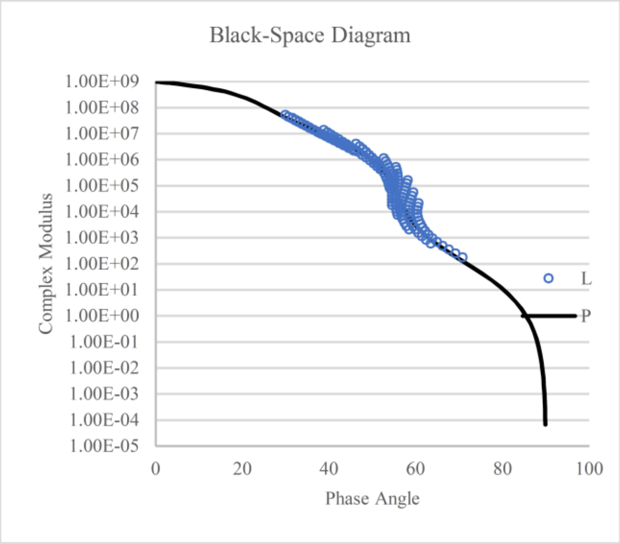

Black-Space Diagram
Complex Modulus
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
1.00E-03
1.00E-04
1.00E-05
0
20
40
60
80
100
Phase Angle
L
P

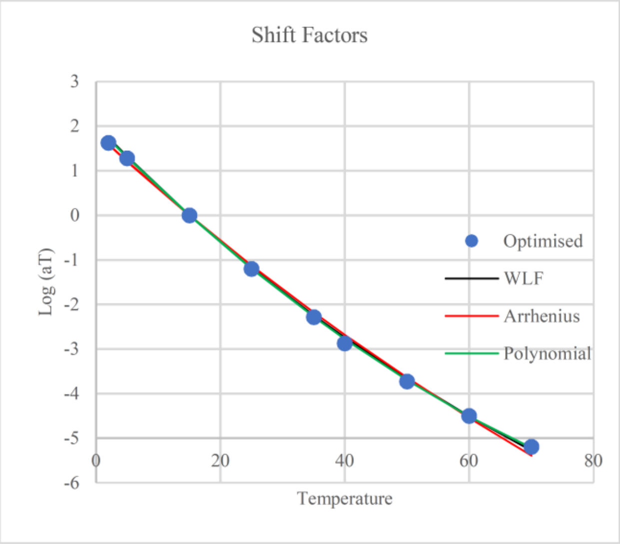

Shift Factors
Log (aT)
3
2
1
0
-1
-2
-3
-4
-5
-6
0
20
40
60
80
Temperature
Optimised
WLF
Arrhenius
Polynomial

BC-15-Dry

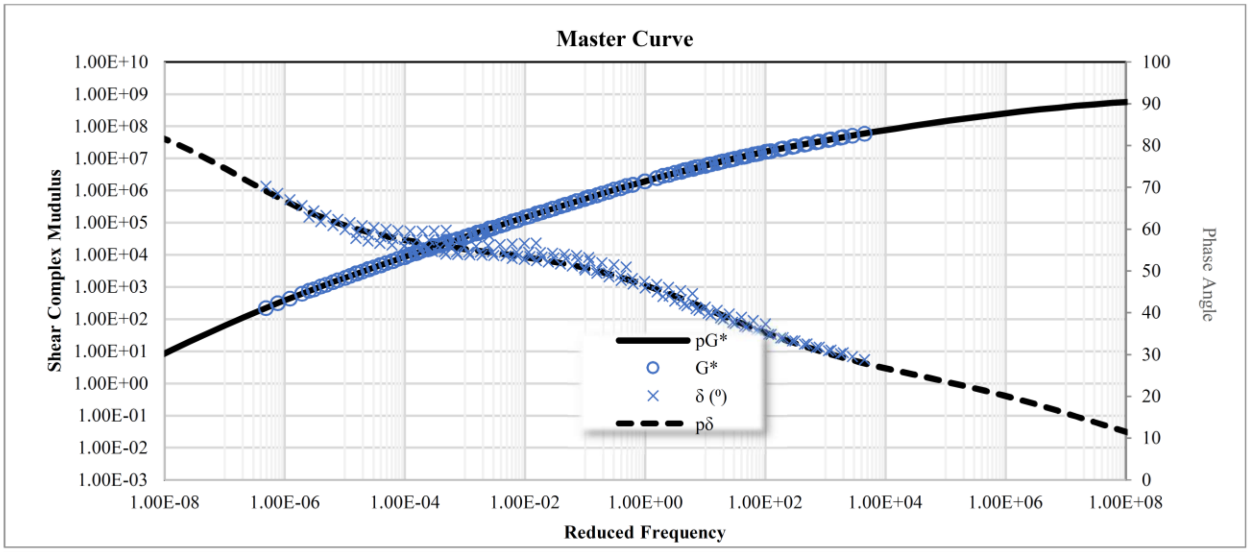

Master Curve
Shear Complex Mudulus
1.00E+10
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
1.00E-03
Phase Angle
100
90
80
70
60
50
40
30
20
10
0
pG*
G*
δ (º)
pδ
1.00E-08
1.00E-06
1.00E-04
1.00E-02
1.00E+00
1.00E+02
1.00E+04
1.00E+06
1.00E+08
Reduced Frequency

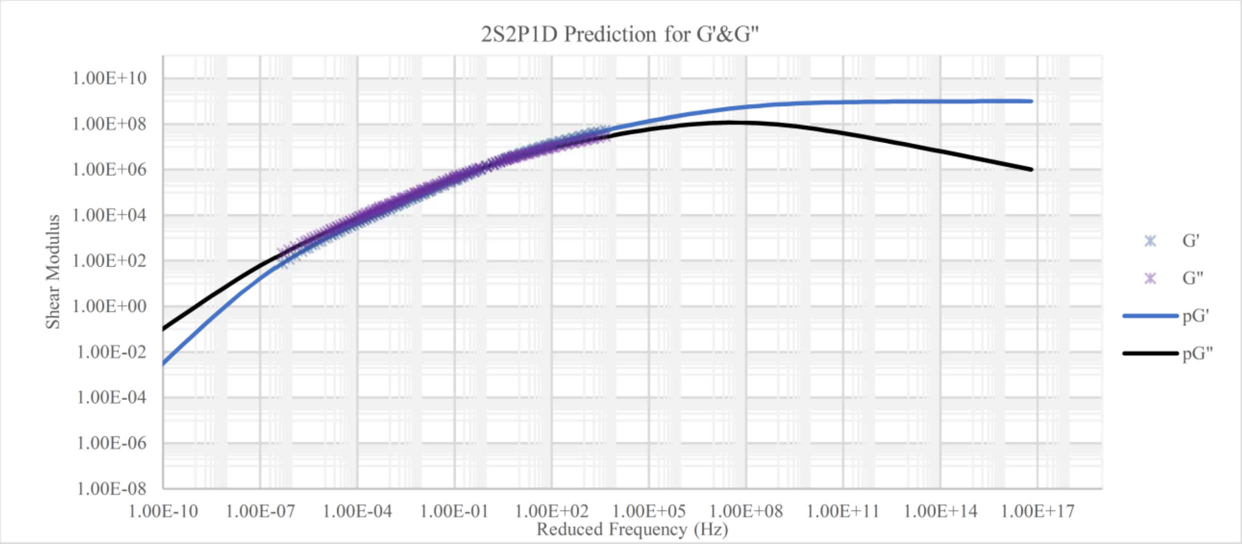

2S2P1D Prediction for G'&G"
Shear Modulus
1.00E+10
1.00E+08
1.00E+06
1.00E+04
1.00E+02
1.00E+00
1.00E-02
1.00E-04
1.00E-06
1.00E-08
G'
G"
pG'
pG"
1.00E-10
1.00E-07
1.00E-04
1.00E-01
1.00E+02
1.00E+05
1.00E+08
1.00E+11
1.00E+14
1.00E+17
Reduced Frequency (Hz)

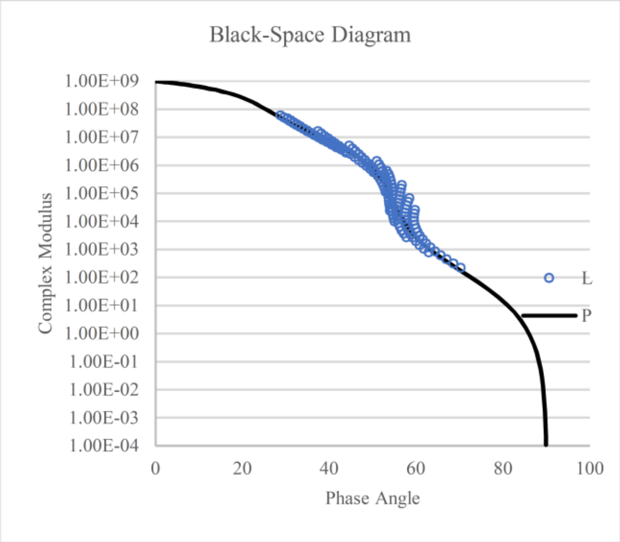

Black-Space Diagram
Complex Modulus
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
1.00E-03
1.00E-04
1.00E-05
L
P
0
20
40
60
80
100
Phase Angle

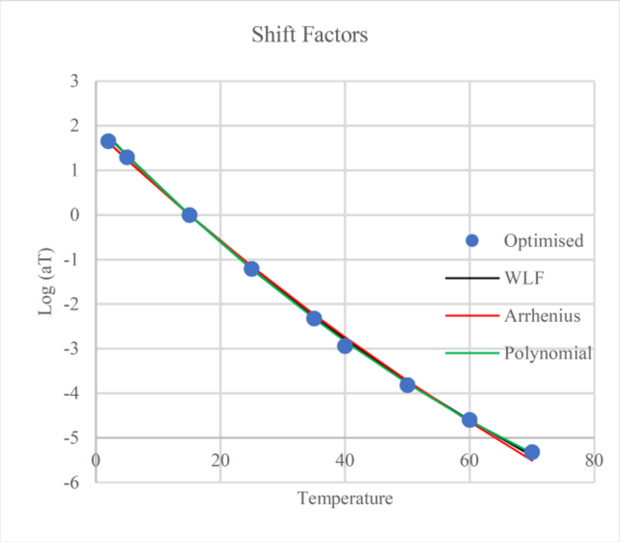

Shift Factors
Log (aT)
3
2
1
0
-1
-2
-3
-4
-5
-6
Optimised
WLF
Arrhenius
Polynomial
0
20
40
60
80
Temperature

BC-15-Wet

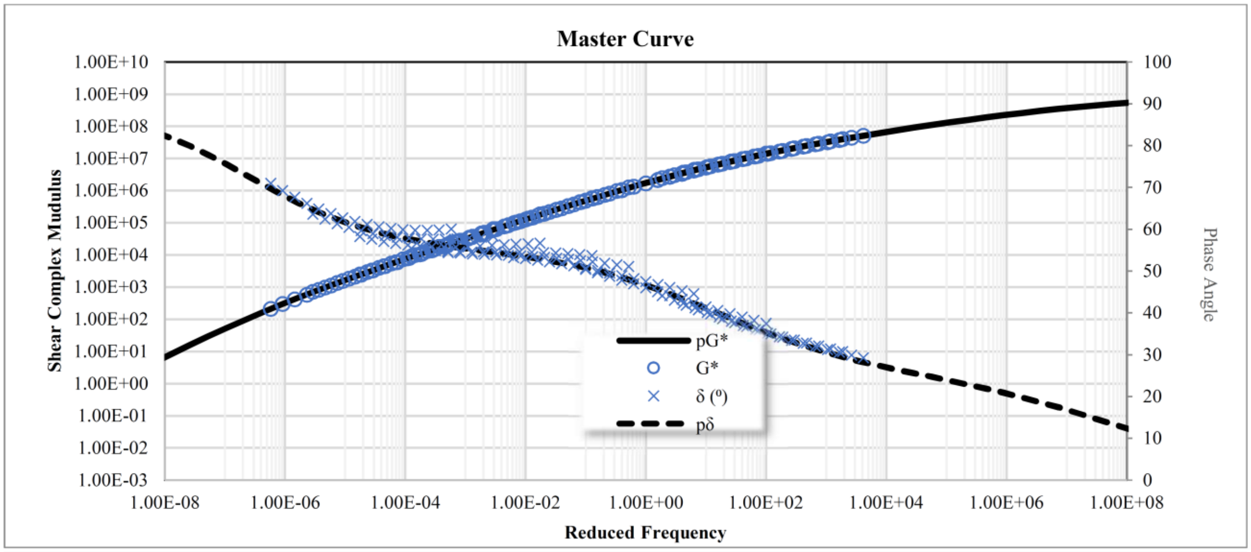

Master Curve
Shear Complex Mudulus
1.00E+10
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
1.00E-03
Phase Angle
100
90
80
70
60
50
40
30
20
10
0
1.00E-08
1.00E-06
1.00E-04
1.00E-02
1.00E+00
1.00E+02
1.00E+04
1.00E+06
1.00E+08
Reduced Frequency
pG*
G*
δ (º)
pδ

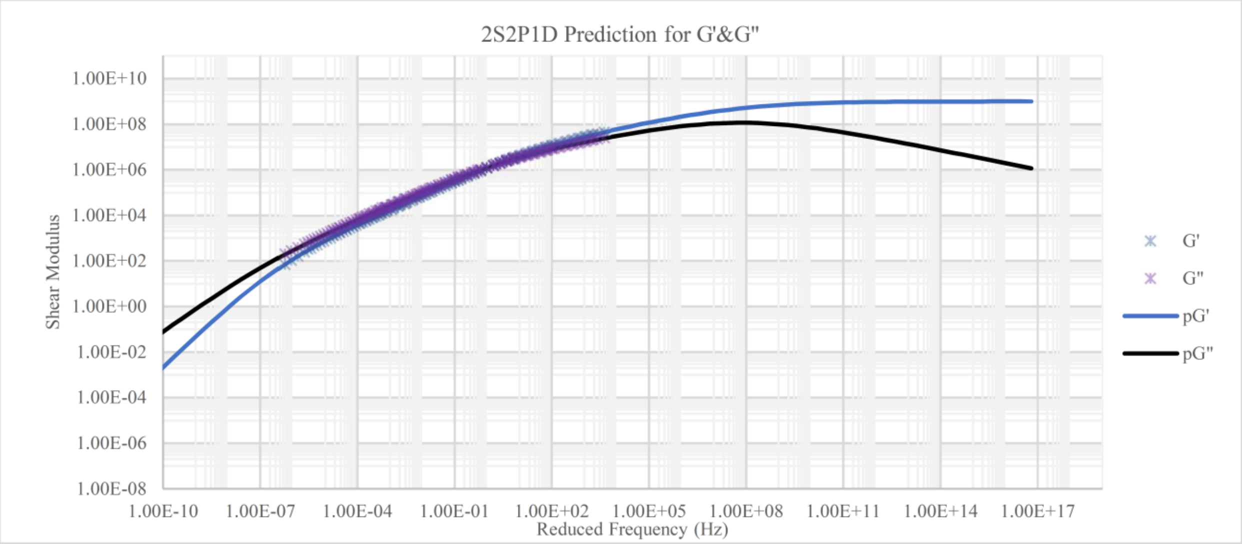

2S2P1D Prediction for G'&G"
Shear Modulus
1.00E+10
1.00E+08
1.00E+06
1.00E+04
1.00E+02
1.00E+00
1.00E-02
1.00E-04
1.00E-06
1.00E-08
1.00E-10
1.00E-07
1.00E-04
1.00E-01
1.00E+02
1.00E+05
1.00E+08
1.00E+11
1.00E+14
1.00E+17
Reduced Frequency (Hz)
G'
G"
pG'
pG"

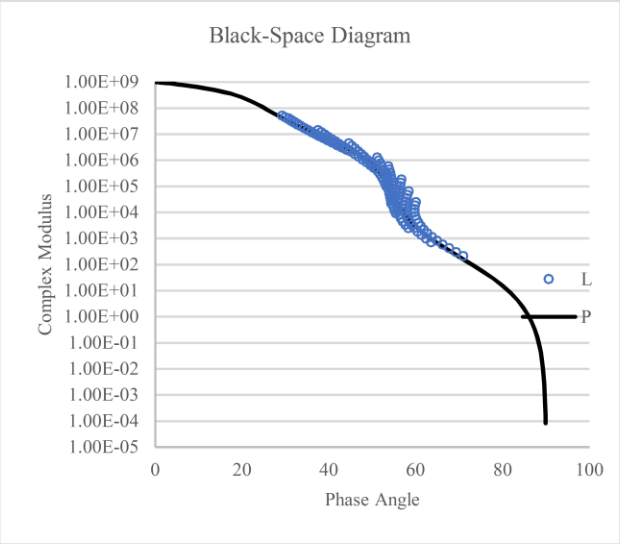

Black-Space Diagram
Complex Modulus
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
1.00E-03
1.00E-04
0
20
40
60
80
100
Phase Angle
L
P

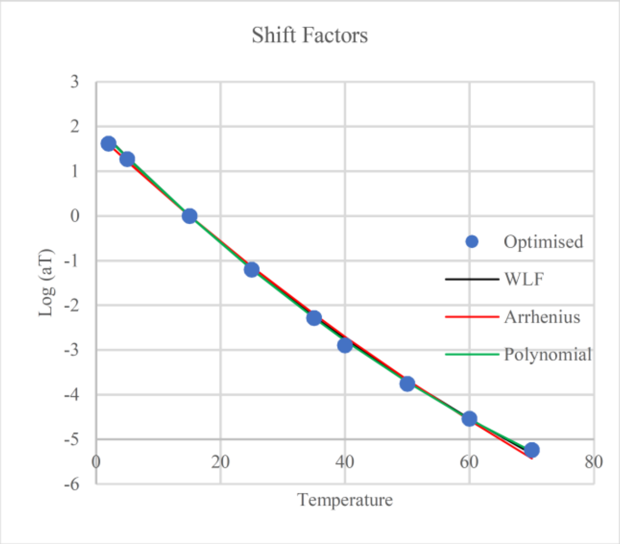

Shift Factors
Log (aT)
3
2
1
0
-1
-2
-3
-4
-5
-6
0
20
40
60
80
Temperature
Optimised
WLF
Arrhenius
Polynomial

BC-20-Dry

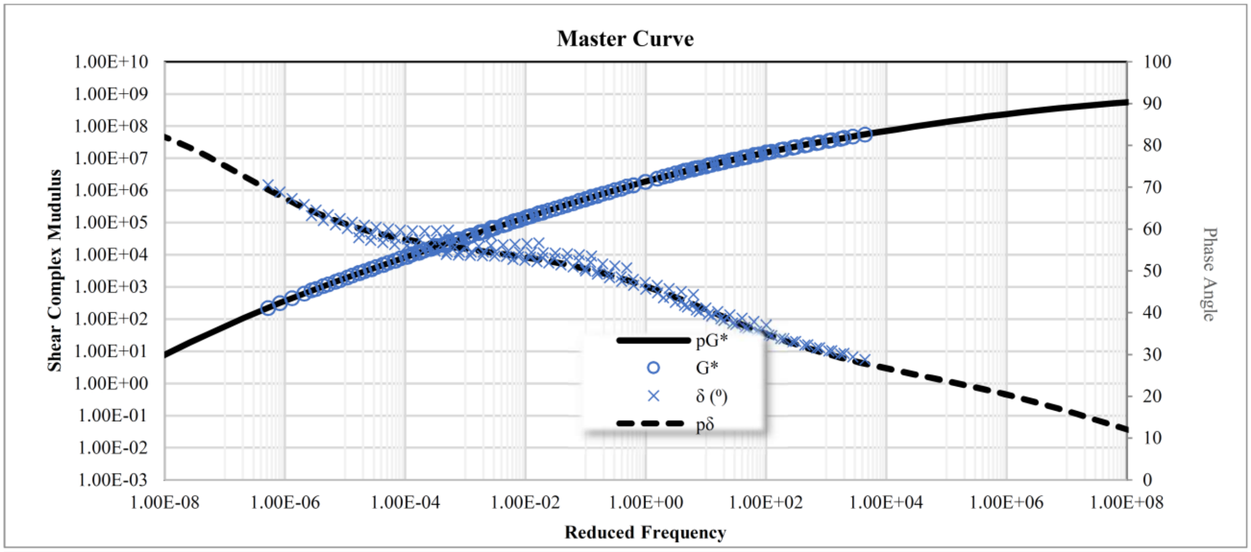

Master Curve
Shear Complex Mudulus
1.00E+10
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
1.00E-03
Phase Angle
100
90
80
70
60
50
40
30
20
10
0
1.00E-08
1.00E-06
1.00E-04
1.00E-02
1.00E+00
1.00E+02
1.00E+04
1.00E+06
1.00E+08
Reduced Frequency
pG*
G*
δ (º)
pδ

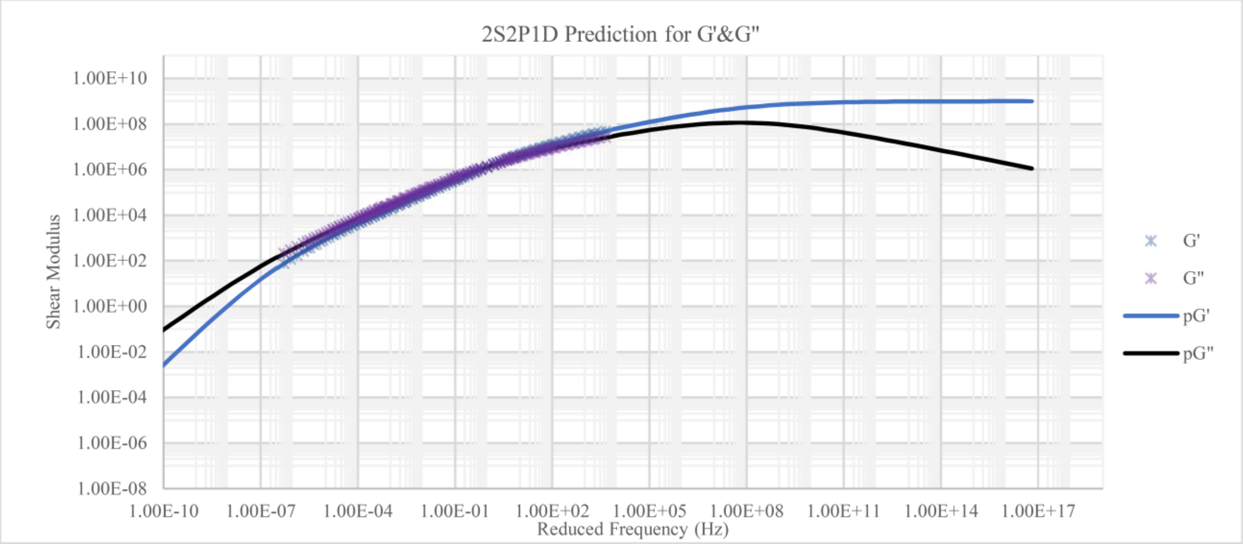

2S2P1D Prediction for G'&G"
Shear Modulus
1.00E+10
1.00E+08
1.00E+06
1.00E+04
1.00E+02
1.00E+00
1.00E-02
1.00E-04
1.00E-06
1.00E-08
1.00E-10
1.00E-07
1.00E-04
1.00E-01
1.00E+02
1.00E+05
1.00E+08
1.00E+11
1.00E+14
1.00E+17
Reduced Frequency (Hz)
G'
G"
pG'
pG"

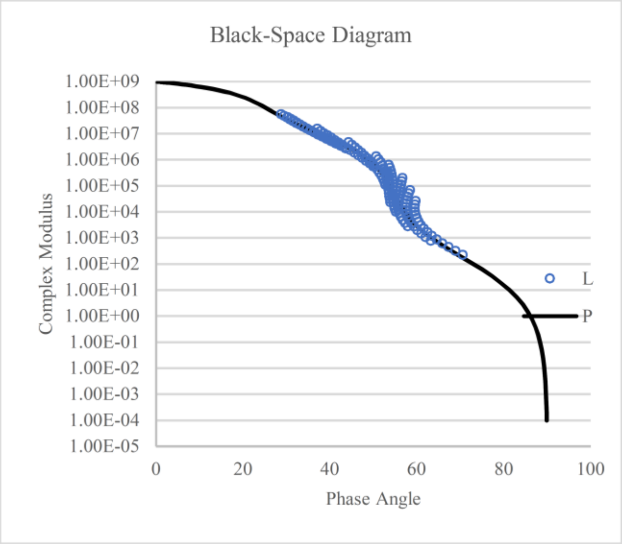

Black-Space Diagram
Complex Modulus
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
1.00E-03
1.00E-04
1.00E-05
0
20
40
60
80
100
Phase Angle
L
P

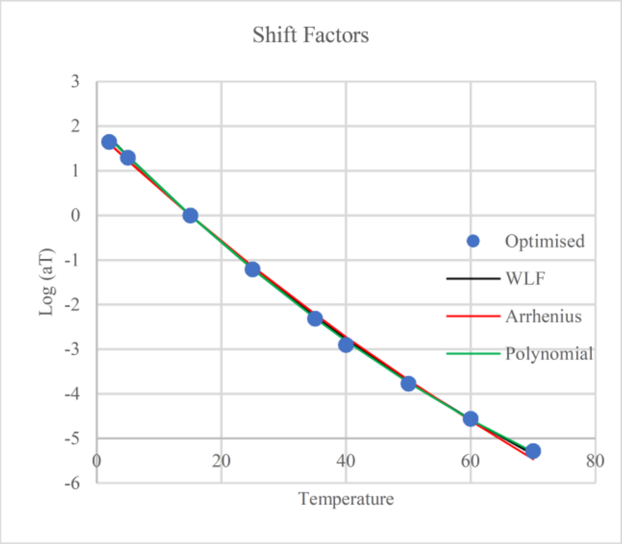

Shift Factors
Log (aT)
3
2
1
0
-1
-2
-3
-4
-5
-6
0
20
40
60
80
Temperature
Optimised
WLF
Arrhenius
Polynomial

BC-20-Wet

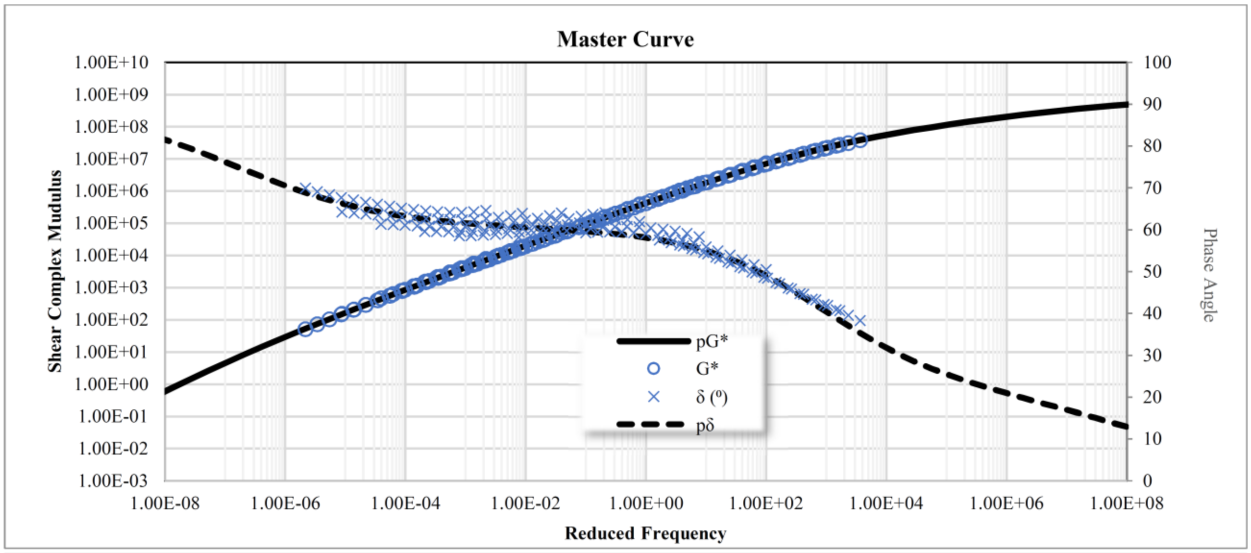

Master Curve
Shear Complex Modulus
1.00E+10
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
1.00E-03
Phase Angle
100
90
80
70
60
50
40
30
20
10
0
1.00E-08
1.00E-06
1.00E-04
1.00E-02
1.00E+00
1.00E+02
1.00E+04
1.00E+06
1.00E+08
Reduced Frequency
pG*
G*
δ (º)
pδ

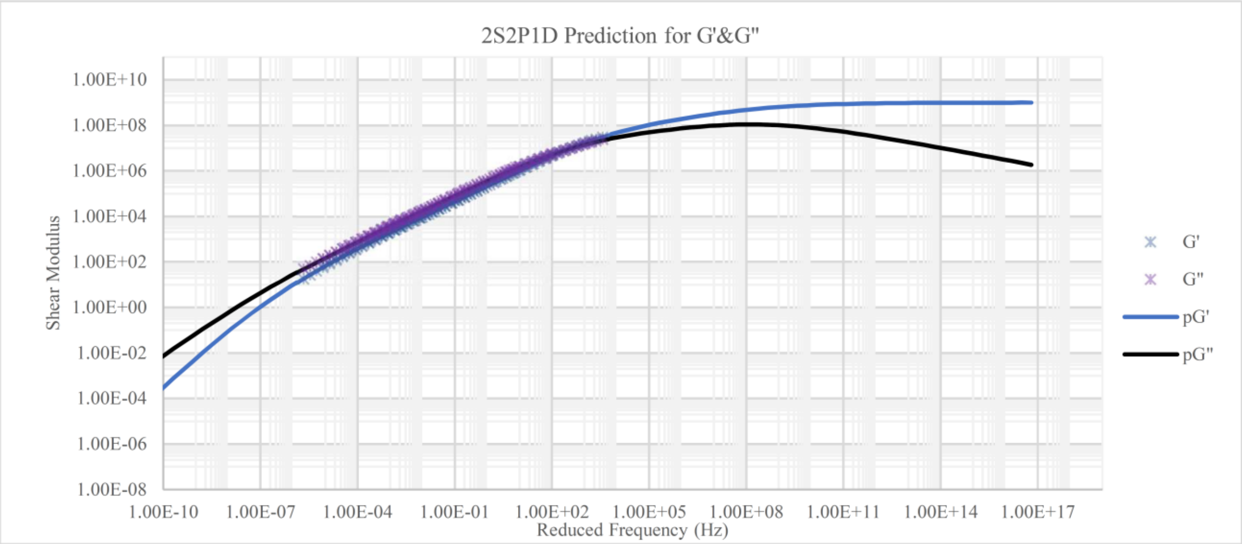

2S2P1D Prediction for G'&G"
Shear Modulus
1.00E+10
1.00E+08
1.00E+06
1.00E+04
1.00E+02
1.00E+00
1.00E-02
1.00E-04
1.00E-06
1.00E-08
1.00E-10
1.00E-07
1.00E-04
1.00E-01
1.00E+02
1.00E+05
1.00E+08
1.00E+11
1.00E+14
1.00E+17
Reduced Frequency (Hz)
G'
G"
pG'
pG"

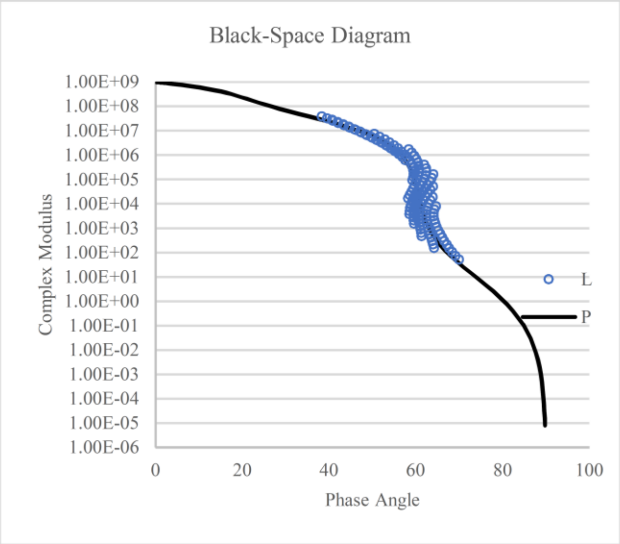

Black-Space Diagram
Complex Modulus
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
1.00E-03
1.00E-04
1.00E-05
0
20
40
60
80
100
Phase Angle
L
P

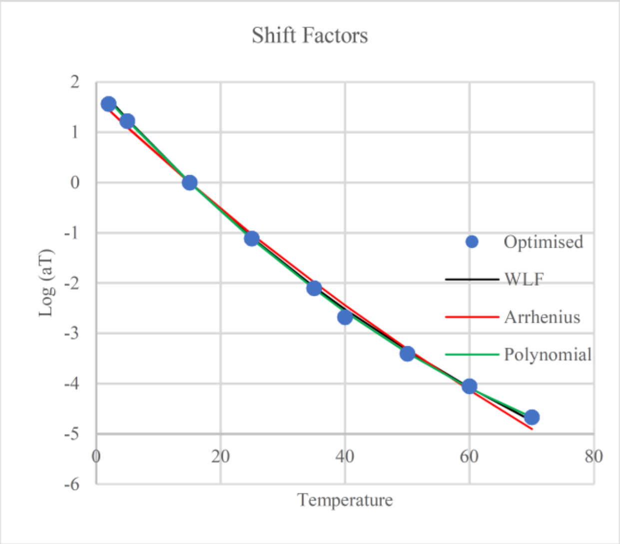

Shift Factors
Log (aT)
3
2
1
0
-1
-2
-3
-4
-5
-6
0
20
40
60
80
Temperature
Optimised
WLF
Arrhenius
Polynomial

RTFOT

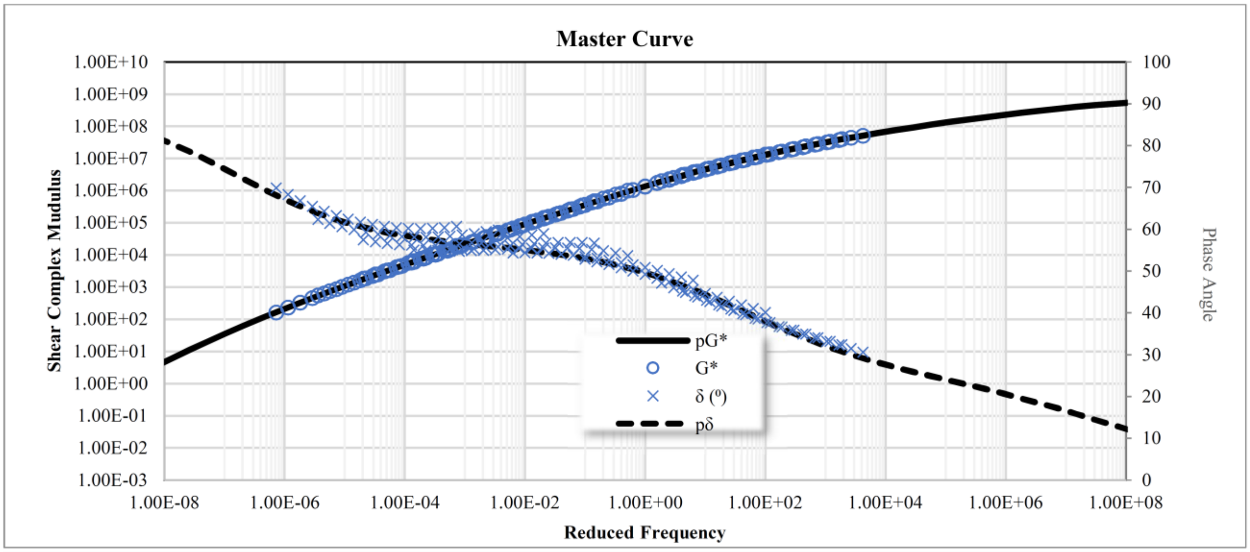

Master Curve
Shear Complex Mudulus
1.00E+10
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
1.00E-03
1.00E-08
1.00E-06
1.00E-04
1.00E-02
1.00E+00
1.00E+02
1.00E+04
1.00E+06
1.00E+08
Reduced Frequency
Phase Angle
100
90
80
70
60
50
40
30
20
10
0
pG*
G*
δ (º)
pδ

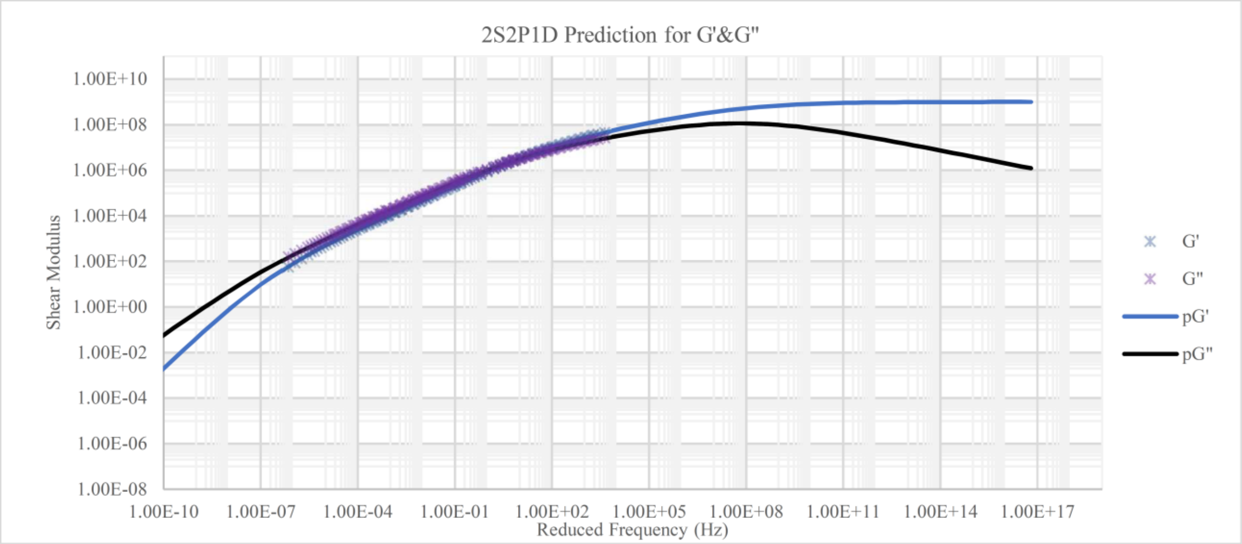

2S2P1D Prediction for G'&G"
Shear Modulus
1.00E+10
1.00E+08
1.00E+06
1.00E+04
1.00E+02
1.00E+00
1.00E-02
1.00E-04
1.00E-06
1.00E-08
1.00E-10
1.00E-07
1.00E-04
1.00E-01
1.00E+02
1.00E+05
1.00E+08
1.00E+11
1.00E+14
1.00E+17
Reduced Frequency (Hz)
G'
G"
pG'
pG"

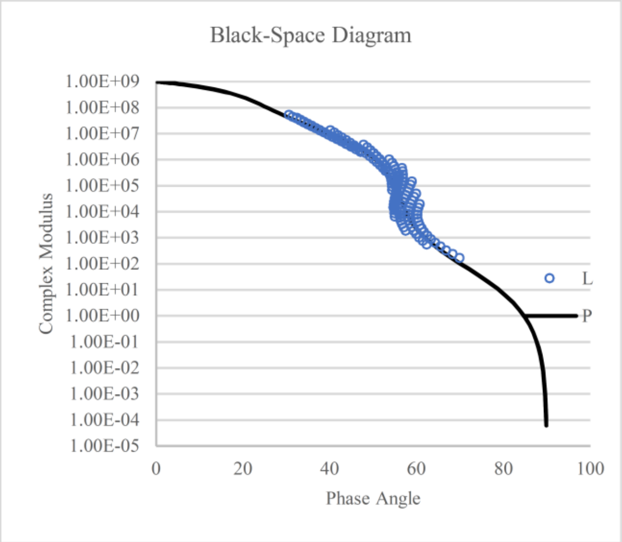

Black-Space Diagram
Complex Modulus
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
1.00E-03
1.00E-04
1.00E-05
1.00E-06
0
20
40
60
80
100
Phase Angle
L
P

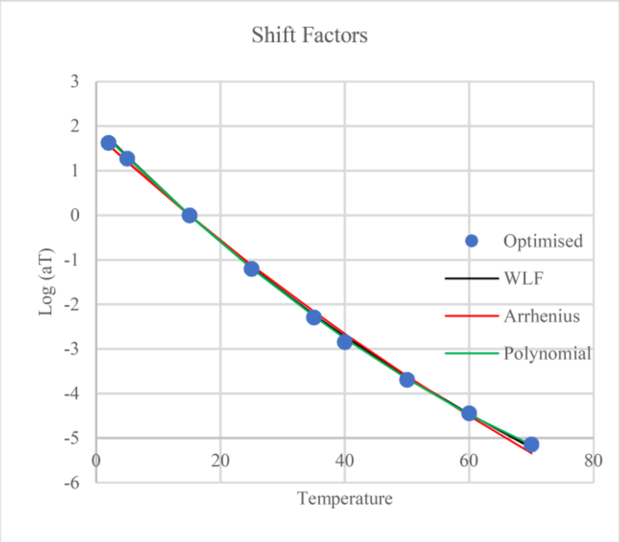

Shift Factors
Log (aT)
2
1
0
-1
-2
-3
-4
-5
-6
0
20
40
60
80
Temperature
Optimised
WLF
Arrhenius
Polynomial

RTFOT+PAV

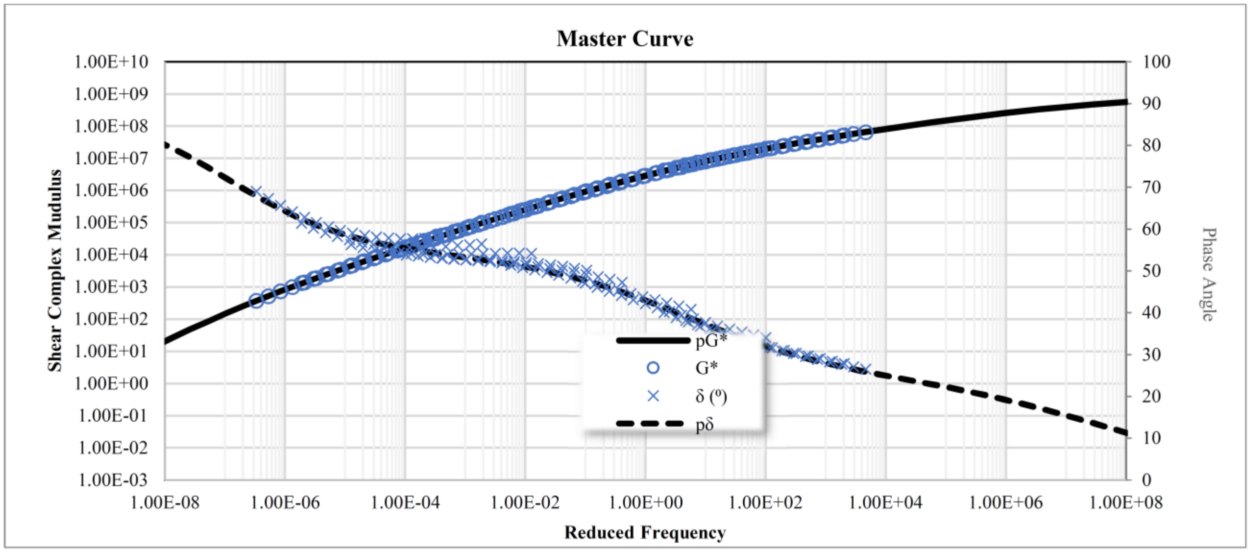

Master Curve
Shear Complex Mudulus
1.00E+10
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
1.00E-03
Phase Angle
100
90
80
70
60
50
40
30
20
10
0
pG*
G*
δ (º)
pδ
1.00E-08
1.00E-06
1.00E-04
1.00E-02
1.00E+00
1.00E+02
1.00E+04
1.00E+06
1.00E+08
Reduced Frequency

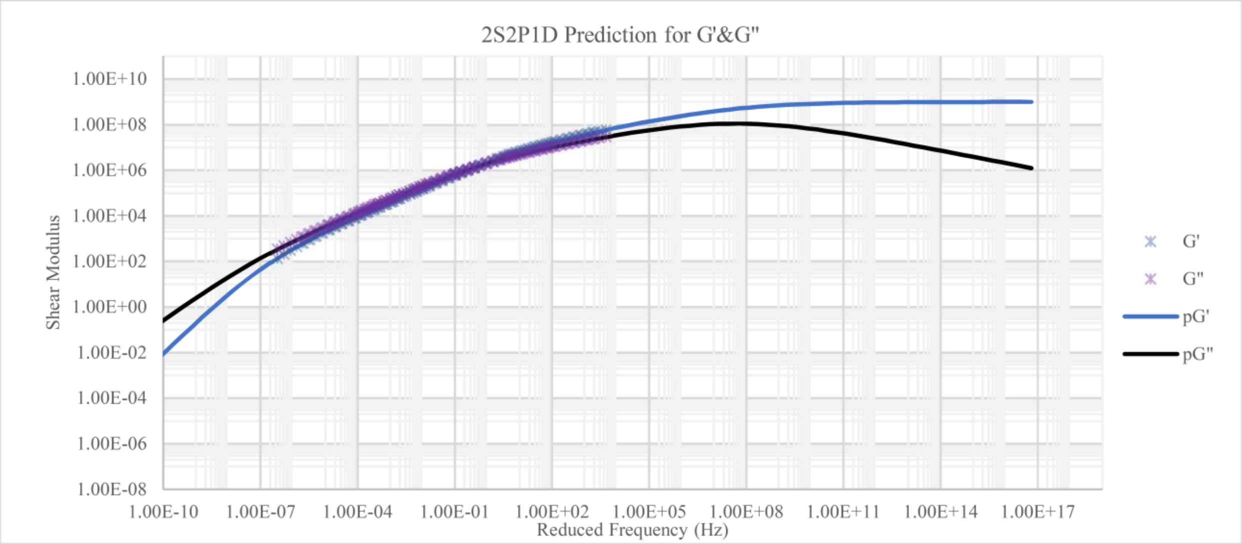

2S2P1D Prediction for G'&G"
Shear Modulus
1.00E+10
1.00E+08
1.00E+06
1.00E+04
1.00E+02
1.00E+00
1.00E-02
1.00E-04
1.00E-06
1.00E-08
G'
G"
pG'
pG"
1.00E-10
1.00E-07
1.00E-04
1.00E-01
1.00E+02
1.00E+05
1.00E+08
1.00E+11
1.00E+14
1.00E+17
Reduced Frequency (Hz)

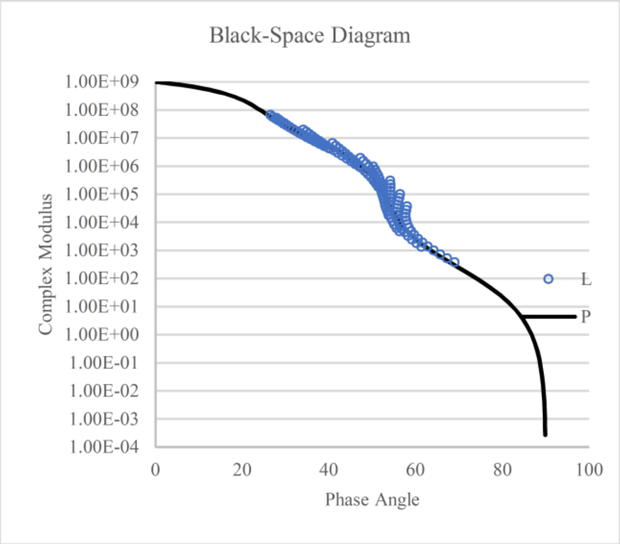

Black-Space Diagram
Complex Modulus
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
1.00E-03
1.00E-04
1.00E-05
L
P
0
20
40
60
80
100
Phase Angle

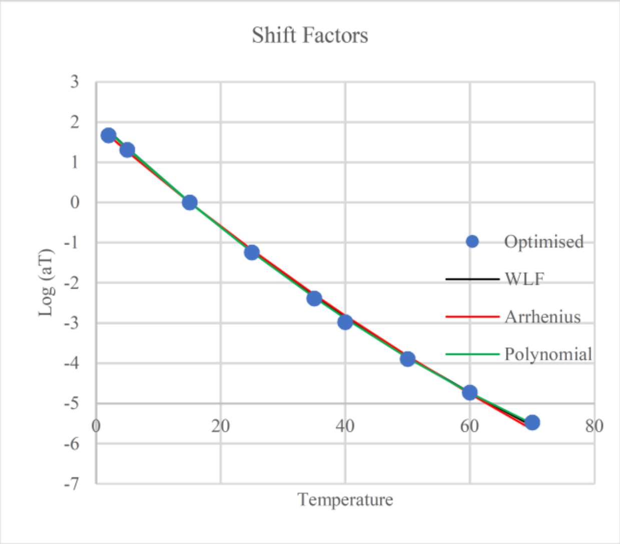

Shift Factors
Log (aT)
3
2
1
0
-1
-2
-3
-4
-5
-6
Optimised
WLF
Arrhenius
Polynomial
0
20
40
60
80
Temperature

RTFOT+ Double PAV







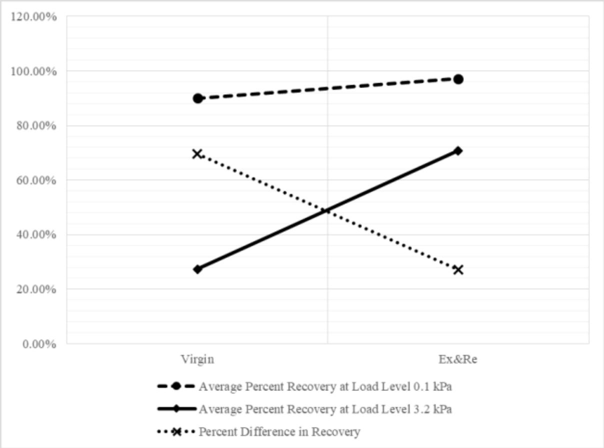


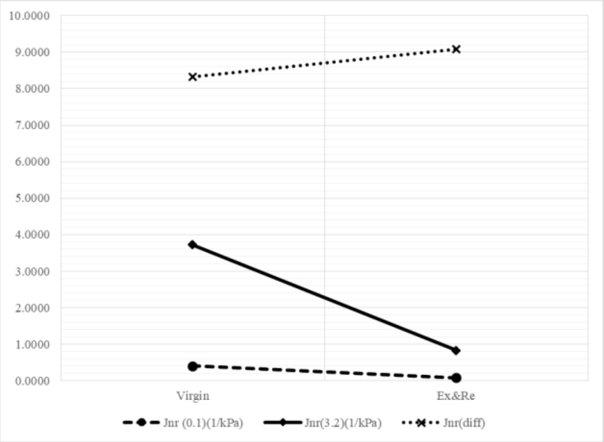
Model Parameters

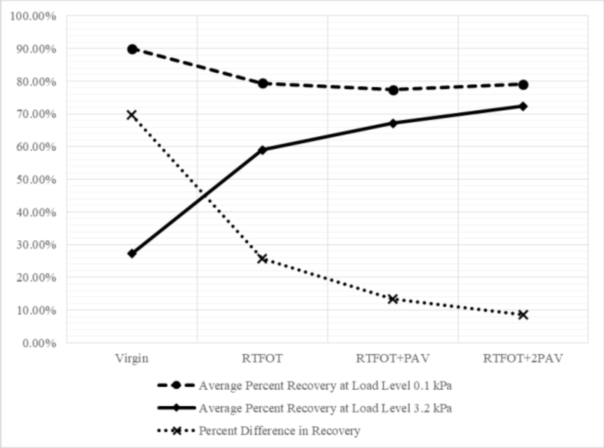
Condition	2S2P1D							a1	a2	a3	a4	a5	a6	a7	a8	a9	WLF		ARRHENIUS	POLYNOMIAL		CROSS-OVER	CROSS-OVER
	G0	G∞	δ	τ0	k	h	β	2	5	15	25	35	40	50	60	70	C1	C2	Ea/R	c1	c2	TEMPERATURE	FREQUNECY
EX&RE	0	1.0E+09	6.76	5.5E-06	0.25	0.69	7693	1.57	1.22	0	-1.06	-1.95	-2.71	-3.34	-3.86	-4.30	14.6	125.5	8410	0.118	7.06E-04	-5.8	1200.5
64-28 VIRGIN 2ND	0	1.0E+09	6.86	5.0E-06	0.23	0.70	7696	1.63	1.29	0	-1.02	-1.91	-2.40	-3.02	-3.54	-4.02	11.6	101.6	7815	0.114	7.53E-04	-8.8	1585.1
64-28 VIRGIN	0	1.0E+09	6.86	4.8E-06	0.24	0.70	7696	1.52	1.18	0	-1.10	-2.03	-2.49	-3.12	-3.68	-4.18	13.8	123.0	8067	0.113	6.78E-04	-8.1	1539.7
AASHTO R30	0	1.0E+09	10.96	2.5E-05	0.30	0.60	32035	1.59	1.25	0	-1.17	-2.25	-2.65	-2.65	-4.30	-5.01	22.5	199.5	8890	0.110	4.00E-04	22.1	1.5
BC-5-D	0	1.0E+09	10.47	2.6E-05	0.29	0.61	19214	1.59	1.25	0	-1.16	-2.22	-2.81	-3.64	-4.40	-5.09	22.8	187.9	9475	0.122	5.23E-04	18.1	4.2
BC-5-W	0	1.0E+09	9.10	1.8E-05	0.29	0.62	13881	1.58	1.24	0	-1.16	-2.21	-2.72	-3.54	-4.28	-4.95	21.1	176.1	9242	0.120	5.40E-04	13.4	15.4
BC-10-D	0	1.0E+09	9.54	4.2E-05	0.29	0.62	13673	1.62	1.27	0	-1.19	-2.27	-2.88	-3.73	-4.49	-5.19	23.3	188.0	9681	0.124	5.37E-04	17.7	4.6
BC-10-W	0	1.0E+09	9.81	3.0E-05	0.29	0.62	16743	1.60	1.26	0	-1.18	-2.24	-2.84	-3.68	-4.43	-5.13	23.1	189.0	9558	0.123	5.26E-04	17.5	4.9
BC-15-D	0	1.0E+09	10.07	4.7E-05	0.29	0.62	14062	1.62	1.28	0	-1.20	-2.28	-2.88	-3.73	-4.50	-5.19	23.2	186.7	9690	0.125	5.40E-04	18.0	4.2
BC-15-W	0	1.0E+09	9.99	6.8E-05	0.29	0.61	16139	1.65	1.29	0	-1.21	-2.32	-2.94	-3.81	-4.60	-5.31	24.2	191.7	9902	0.127	5.39E-04	20.3	2.0
BC-20-D	0	1.0E+09	10.74	5.5E-05	0.29	0.62	15099	1.62	1.27	0	-1.20	-2.28	-2.90	-3.76	-4.53	-5.24	24.0	193.2	9757	0.125	5.27E-04	20.3	2.1
BC-20-W	0	1.0E+09	10.63	6.4E-05	0.29	0.61	15449	1.64	1.29	0	-1.21	-2.32	-2.90	-3.77	-4.56	-5.28	23.9	190.3	9826	0.126	5.36E-04	20.8	1.8
COCO-4	0	1.0E+09	10.92	3.6E-05	0.29	0.61	17809	1.59	1.25	0	-1.18	-2.25	-2.72	-3.58	-4.36	-5.07	22.6	187.4	9398	0.120	5.13E-04	20.1	2.3
COMPACTED	0	1.0E+09	8.11	1.1E-05	0.29	0.62	13530	1.63	1.25	0	-1.15	-2.18	-2.72	-3.51	-4.23	-4.90	19.6	162.4	9164	0.120	5.73E-04	10.2	36.2
LOOSE MIX	0	1.0E+09	7.37	1.3E-05	0.28	0.64	8096	1.65	1.27	0	-1.16	-2.18	-2.77	-3.55	-4.24	-4.89	19.0	155.8	9211	0.122	6.04E-04	7.5	74.5
RTFOT+Double PAV	0	1.0E+09	11.38	1.3E-04	0.28	0.60	20892	1.67	1.31	0	-1.24	-2.39	-2.98	-3.90	-4.73	-5.47	26.2	204.5	10153	0.129	5.18E-04	25.4	0.4
RTFOT+PAV	0	1.0E+09	9.21	3.7E-05	0.28	0.62	16780	1.62	1.27	0	-1.20	-2.29	-2.85	-3.69	-4.44	-5.14	22.2	179.4	9600	0.124	5.56E-04	15.8	7.9
RTFOT	0	1.0E+09	7.04	1.0E-05	0.27	0.67	8083	1.56	1.22	0	-1.12	-2.10	-2.68	-3.40	-4.05	-4.66	17.9	152.6	8818	0.118	5.96E-04	1.1	310.6

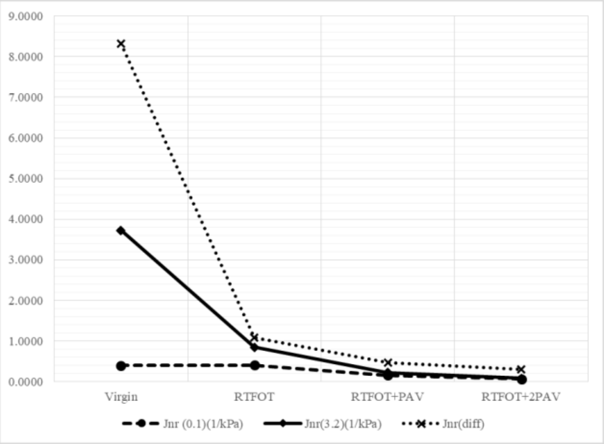
APPENDIX C: MSCR Results

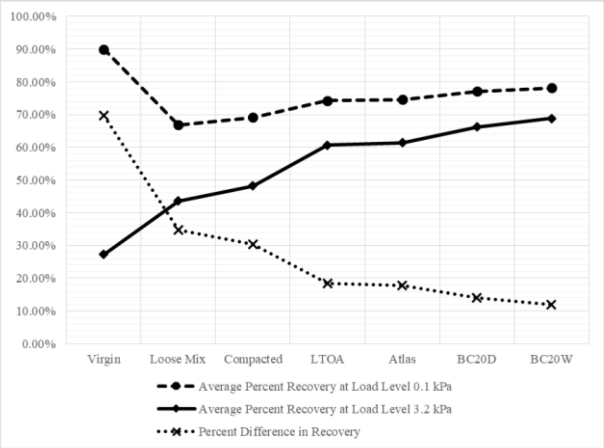
Sample	Average Percent Recovery at Load Level 0.1 kPa	Average Percent Recovery at Load Level 3.2 kPa	Percent Difference in Recovery	J_{nr} (0.1)(1/kPa)	J_{nr}(3.2)(1/kPa)	J_{nr}(diff)
Virgin	89.97%	27.27%	69.69%	0.3995	3.7250	832.49%
Ex&Re	97.22%	70.77%	27.21%	0.0826	0.8284	908.27%
Loose Mix	66.82%	43.61%	34.73%	0.4658	0.8345	79.15%
Compacted	69.17%	48.19%	30.33%	0.3382	0.5814	71.92%
RTFOT	79.45%	58.98%	25.77%	0.4059	0.8465	108.54%
RTFOT+PAV	77.45%	67.14%	13.31%	0.1539	0.2253	46.33%
RTFOT+2PAV	79.09%	72.37%	8.50%	0.0618	0.0800	29.47%
LTOA	74.25%	60.68%	18.34%	0.1446	0.2109	45.85%
Atlas	74.56%	61.36%	17.71%	0.1411	0.2053	45.49%
BC5D	78.72%	64.54%	18.04%	0.1278	0.2048	60.21%
BC10D	77.42%	65.08%	15.94%	0.1338	0.1981	48.09%
BC15D	77.08%	65.51%	15.01%	0.1370	0.2041	48.97%
BC20D	77.06%	66.24%	14.05%	0.1134	0.1603	41.39%
BC5W	74.68%	58.29%	21.94%	0.2060	0.3366	63.39%
BC10W	77.33%	64.29%	16.87%	0.1395	0.2135	53.01%
BC15W	78.33%	68.94%	11.98%	0.1024	0.1411	37.75%
BC20W	78.16%	68.83%	11.94%	0.1012	0.1383	36.74%

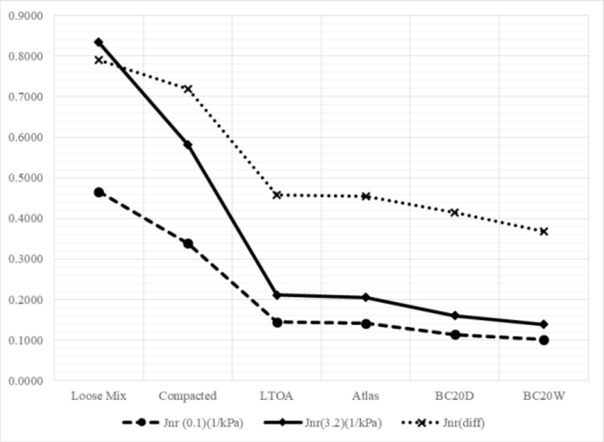


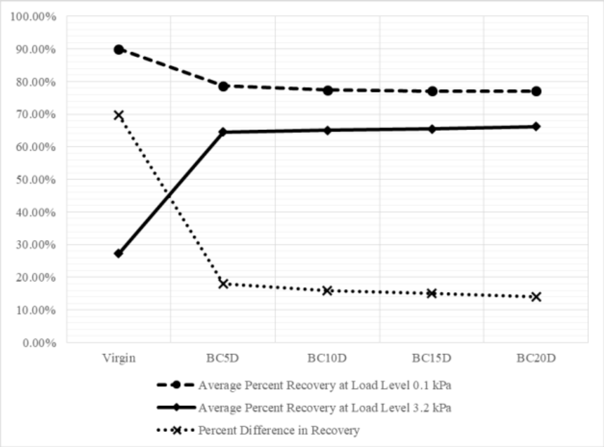


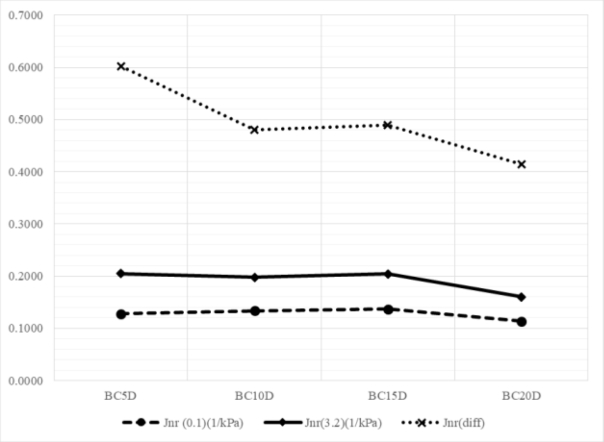


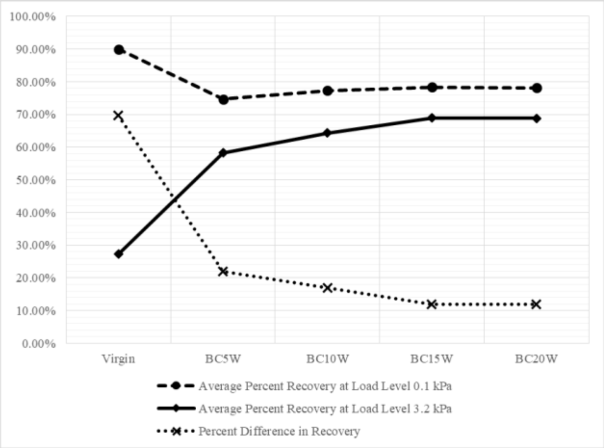


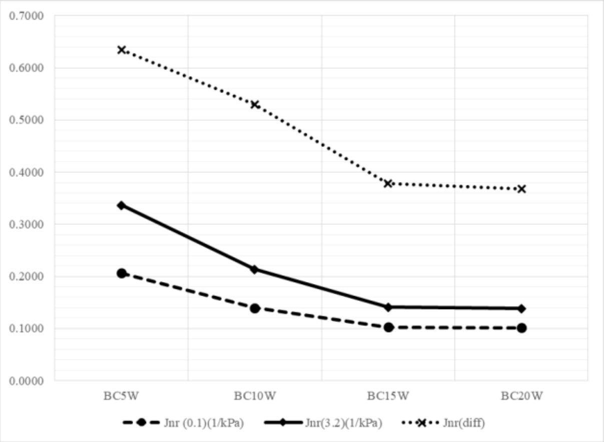

100.00%
90.00%
80.00%
70.00%
60.00%
50.00%
40.00%
30.00%
20.00%
10.00%
0.00%
Virgin
Loose Mix
Compacted
LTOA
Atlas
BC20D
BC20W
Average Percent Recovery at Load Level 0.1 kPa
Average Percent Recovery at Load Level 3.2 kPa
Percent Difference in Recovery


0.9000
0.8000
0.7000
0.6000
0.5000
0.4000
0.3000
0.2000
0.1000
0.0000
Loose Mix
Compacted
LTOA
Atlas
BC20D
BC20W
Jnr (0.1)(1/kPa)
Jnr(3.2)(1/kPa)
Jnr(diff)

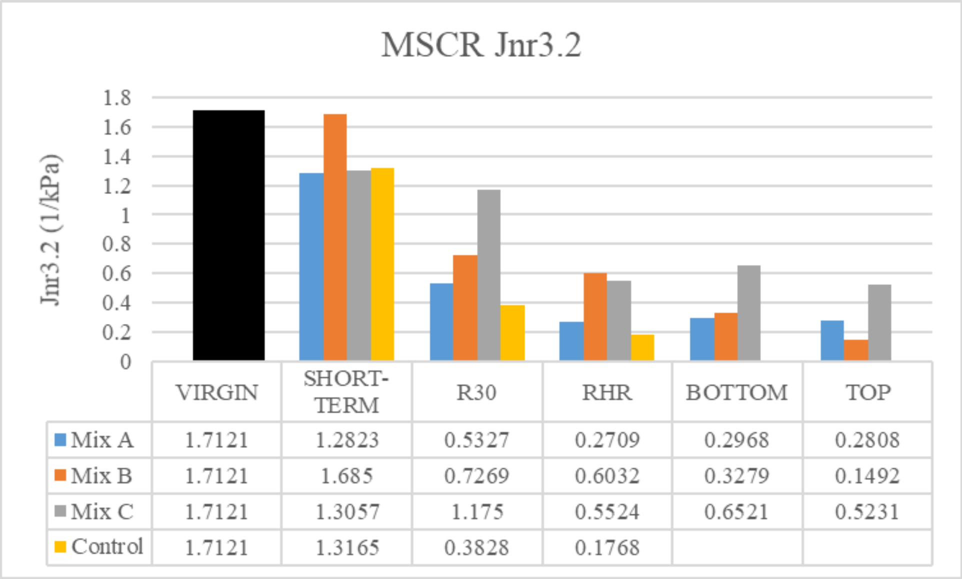

100.00%
90.00%
80.00%
70.00%
60.00%
50.00%
40.00%
30.00%
20.00%
10.00%
0.00%
Virgin
BC5D
BC10D
BC15D
BC20D
Average Percent Recovery at Load Level 0.1 kPa
Average Percent Recovery at Load Level 3.2 kPa
Percent Difference in Recovery


0.7000
0.6000
0.5000
0.4000
0.3000
0.2000
0.1000
0.0000
BC5D
BC10D
BC15D
BC20D
Jnr (0.1)(1/kPa)
Jnr(3.2)(1/kPa)
Jnr(diff)

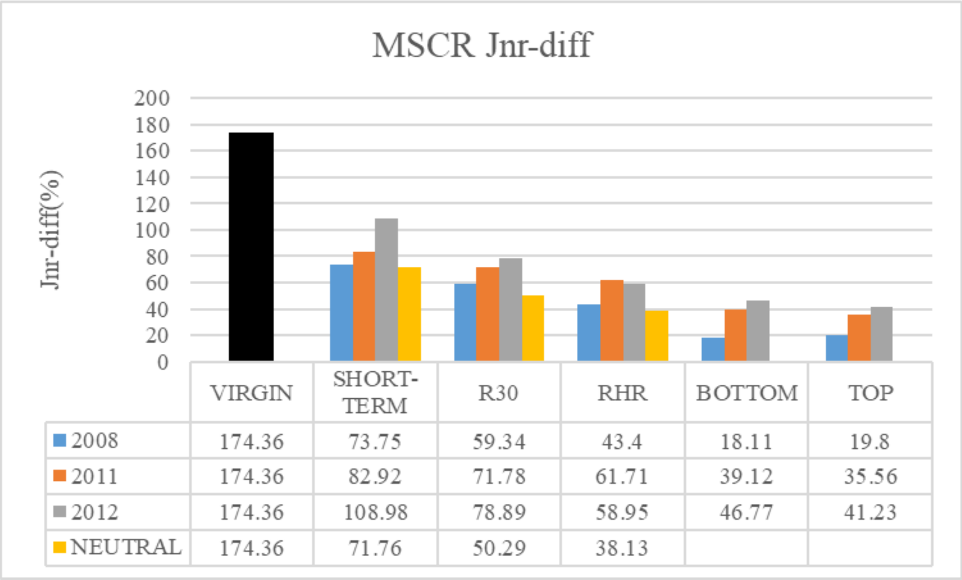

100.00%
90.00%
80.00%
70.00%
60.00%
50.00%
40.00%
30.00%
20.00%
10.00%
0.00%
Virgin
BC5W
BC10W
BC15W
BC20W
Average Percent Recovery at Load Level 0.1 kPa
Average Percent Recovery at Load Level 3.2 kPa
Percent Difference in Recovery


0.7000
0.6000
0.5000
0.4000
0.3000
0.2000
0.1000
0.0000
BC5W
BC10W
BC15W
BC20W
Jnr (0.1)(1/kPa)
Jnr(3.2)(1/kPa)
Jnr(diff)

SAMPLE	AVERAGE PERCENT RECOVERY		PERCENT DIFFERENCE OF RECOVERY	AVERAGE NON-RECOVERABLE CREEP COMPLIANCE		
	R-0.1	**R-3.2**	**R-DIFF**	**Jnr-0.1**	**Jnr-3.2**	**Jnr-DIFF**
PG58-34	80.94	47.29	41.58	0.624	1.7121	174.36
08-4-U	58.06	28.97	50.1	0.738	1.2823	73.75
08-2-R30	64.71	41.26	36.24	0.3343	0.5327	59.34
08-1-RHR	63.28	45.59	27.95	0.1889	0.2709	43.4
08-B	35.02	24.76	29.29	0.2513	0.2968	18.11
08-T	38.99	28.08	27.98	0.2338	0.2808	19.8
11-4-U	53.5	21.68	59.48	0.9212	1.685	82.92
11-2-R30	60.51	33.52	44.61	0.4232	0.7269	71.78
11-1-RHR	56.22	31.02	44.82	0.373	0.6032	61.71
11-B	51.1	32.58	36.24	0.2357	0.3279	39.12
11-T	58.76	44.14	24.89	0.1101	0.1492	35.56
12-4-U	75.28	47.18	37.32	0.6248	1.3057	108.98
12-2-R30	59.83	30.01	49.83	0.6568	1.175	78.89
12-1-RHR	64	42.05	34.3	0.3475	0.5524	58.95
12-B	44.53	22.1	50.37	0.4443	0.6521	46.77
12-T					0.5231	41.23
N-4-U	55.68	26.96	51.58	0.7665	1.3165	71.76
N-2-R30	63.54	43.83	31.02	0.2547	0.3828	50.29
N-1-RHR	67.61	53.63	20.69	0.128	0.1768	38.13



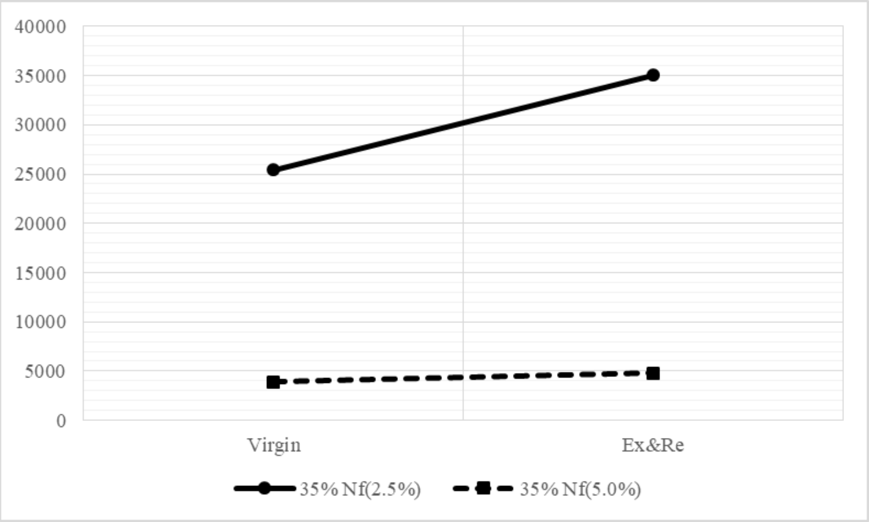
	VIRGIN	SHORT-TERM	R30	RHR	BOTTOM	TOP
🟦 Mix A	1.7121	1.2823	0.5327	0.2709	0.2968	0.2808
🟧 Mix B	1.7121	1.685	0.7269	0.6032	0.3279	0.1492
■ Mix C	1.7121	1.3057	1.175	0.5524	0.6521	0.5231
🟨 Control	1.7121	1.3165	0.3828	0.1768		

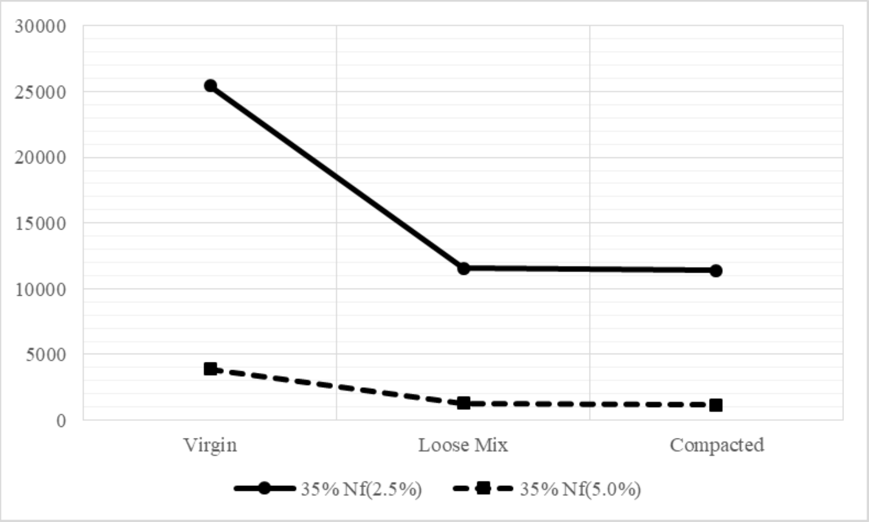


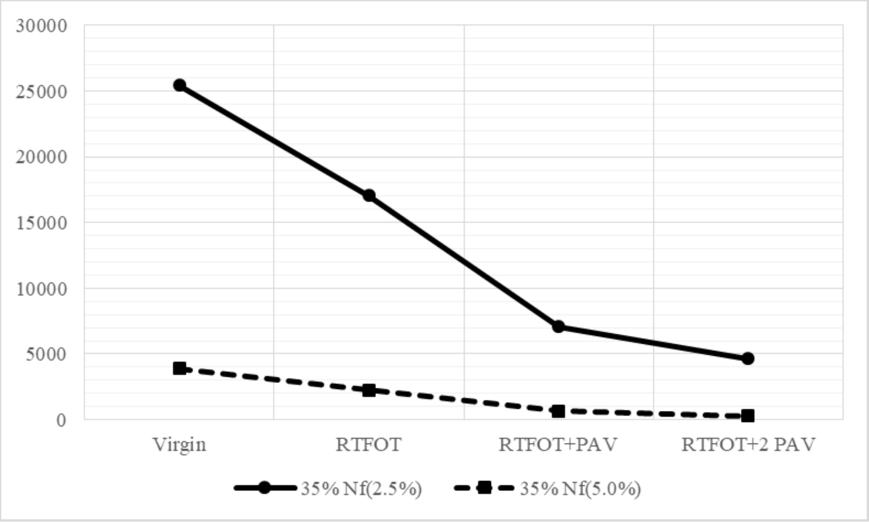
	VIRGIN	SHORT-TERM	R30	RHR	BOTTOM	TOP
🟦 2008	174.36	73.75	59.34	43.4	18.11	19.8
🟧 2011	174.36	82.92	71.78	61.71	39.12	35.56
■ 2012	174.36	108.98	78.89	58.95	46.77	41.23
🟨 NEUTRAL	174.36	71.76	50.29	38.13		

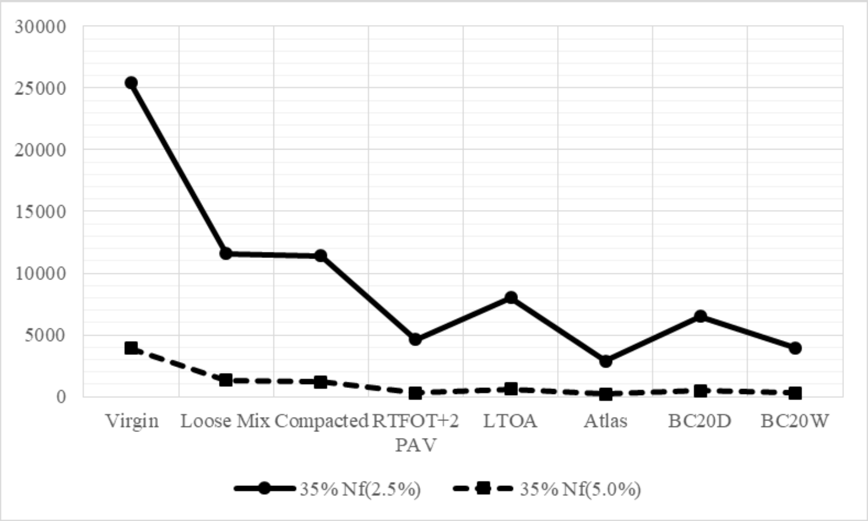
APPENDIX D: LAS Results

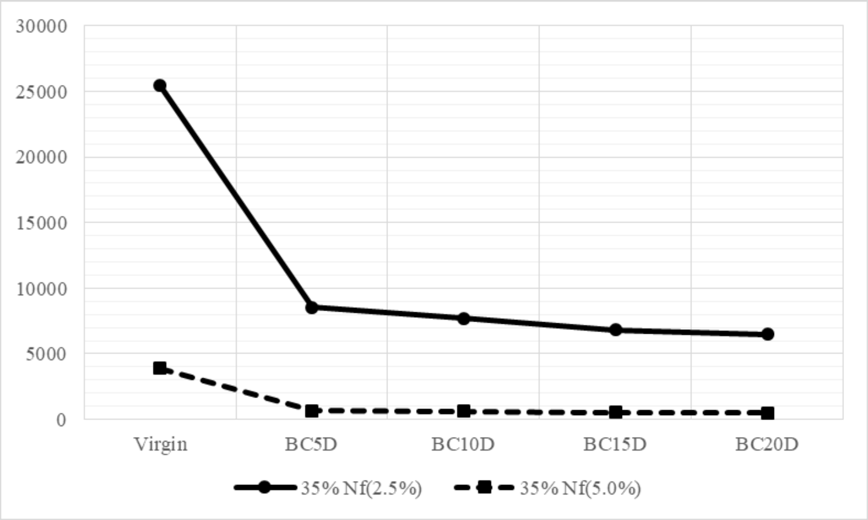
		35%	DL		
sample	Nf(2.5%)	Nf(5.0%)	Nf(2.5%)	Nf(5.0%)	Damage Level
Virgin	25436.50933	3900.852075	28031.33094	4298.784634	0.374204923
Ex&Re	35040.75992	4796.9977	56551.44314	7741.75969	0.440564111
Loose Mix	11581.15477	1300.917752	57161.49282	6420.983243	0.570366441
Compacted	11407.41463	1170.893201	121424.0404	12463.34845	0.642646333
RTFOT	17036.60334	2241.511418	66451.91053	8743.099386	0.555624008
RTFOT+PAV	7087.49083	645.9828347	145199.3553	13234.06172	0.689876143
RTFOT+2 PAV	4639.438105	282.0991894	153741.3452	9348.18137	0.687498583
LTOA	8024.711803	625.6227299	241830.534	18853.59656	0.708281287
Atlas	2885.532532	215.6157877	3896.405887	291.1513266	0.439424275
BC5D	8522.810937	666.0297624	126272.2012	9867.758983	0.654007346
BC10D	7686.9039	613.2478169	246620.3394	19674.94152	0.716993956
BC15D	6836.469495	551.8240103	193839.0365	15646.23883	0.703721665
BC20D	6474.87023	470.8295443	253611.3261	18441.71402	0.721244076
BC5W	11007.76357	1010.43421	180387.1266	16558.25206	0.674326849
BC10W	8817.591814	704.1621023	245587.2559	19612.29801	0.706948942
BC15W	6346.218014	464.6302313	287678.6268	21062.02255	0.734345176
BC20W	3954.072864	285.3123667	49911.87658	3601.470211	0.628407059

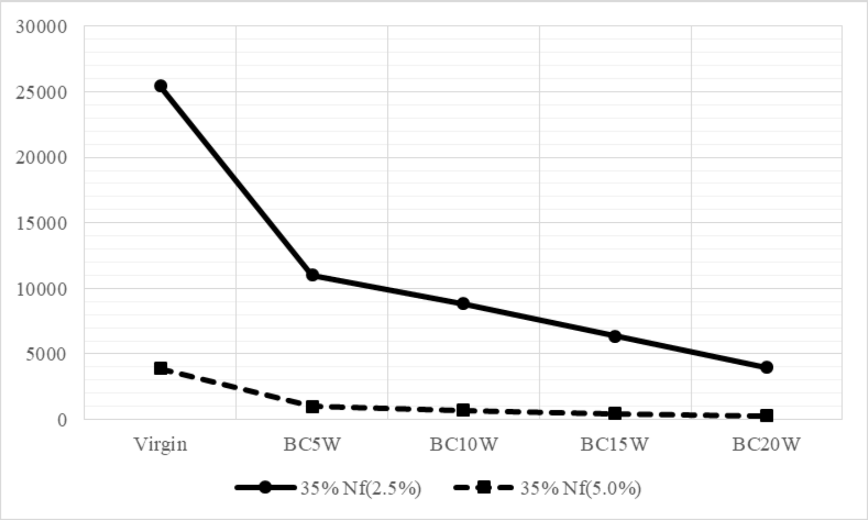

40000
35000
30000
25000
20000
15000
10000
5000
0
Virgin
Ex&Re
35% Nf(2.5%)
35% Nf(5.0%)


30000
25000
20000
15000
10000
5000
0
Virgin
Loose Mix
Compacted
35% Nf(2.5%)
35% Nf(5.0%)

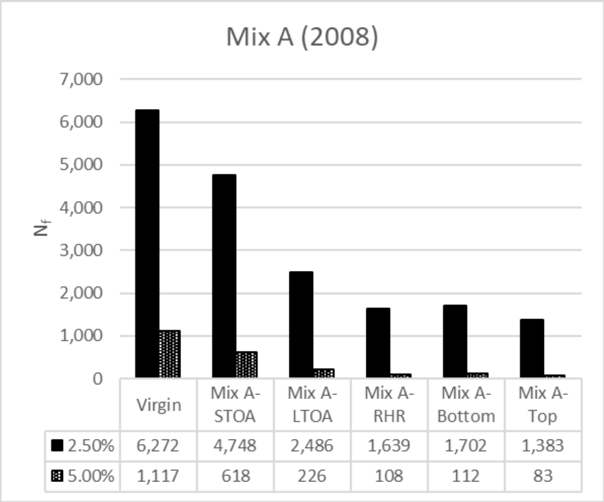

30000
25000
20000
15000
10000
5000
0
Virgin
RTFOT
RTFOT+PAV
RTFOT+2 PAV
35% Nf(2.5%)
35% Nf(5.0%)


30000
25000
20000
15000
10000
5000
0
Virgin
Loose Mix
Compacted
RTFOT+2 PAV
LTOA
Atlas
BC20D
BC20W
35% Nf(2.5%)
35% Nf(5.0%)

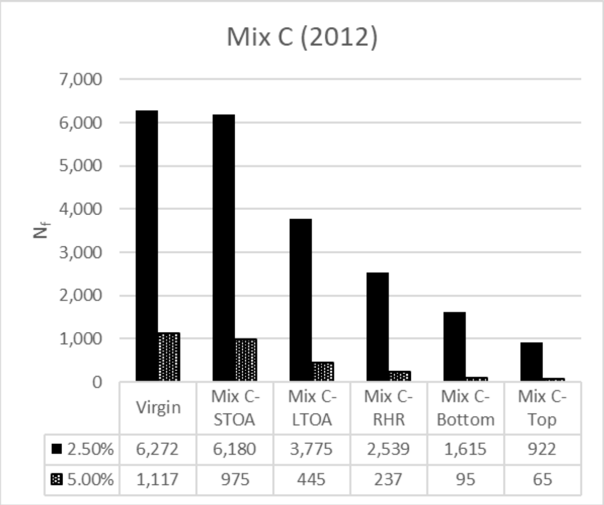

30000
25000
20000
15000
10000
5000
0
Virgin
BC5D
BC10D
BC15D
BC20D
35% Nf(2.5%)
35% Nf(5.0%)


30000
25000
20000
15000
10000
5000
0
Virgin
BC5W
BC10W
BC15W
BC20W
35% Nf(2.5%)
35% Nf(5.0%)

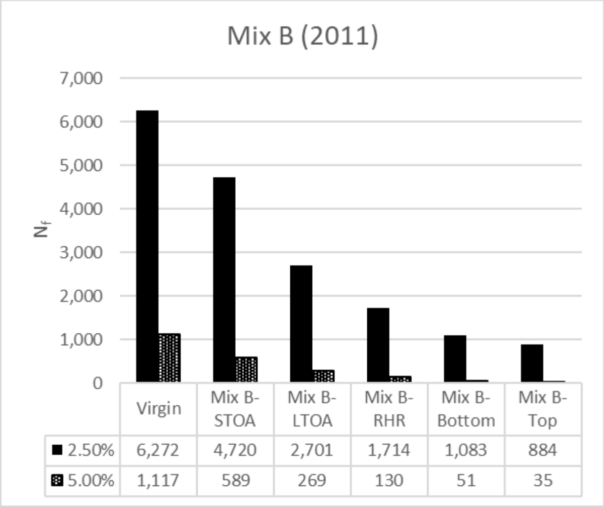
SAMPLE	35%DAMAGE										
	C_0	C_1	C_2	α	$\|G^*\|_{initial}$	D_f	k	A	B	$N_{f(2.5)}$	$N_{f(5.0)}$
PG58-34	1	0.044979	0.540116	1.244447	2.618966	44.6435	1.572301	61357.96	-2.48889	6,272	1,117
08-4-U	1	0.083387	0.424434	1.470949	3.174507	29.36095	1.846629	70347.58	-2.9419	4,748	618
08-2-R30	1	0.127217	0.353996	1.729645	4.271645	17.44228	2.117357	2900991	-3.45929	2,486	226
08-1-RHR	1	0.148013	0.336348	1.960769	5.490926	12.91975	2.301268	59598.87	-3.92154	1,639	108
08-B	1	0.142694	0.358086	2.029645	12.78128	12.25133	2.302858	57033.85	-4.05929	1,702	112
08-T	1	0.135677	0.362836	1.965221	10.37467	13.62359	2.252168	62386.25	-3.93044	1,383	83
11-4-U	1	0.083151	0.428175	1.501693	2.90274	28.69571	1.858705	73976.54	-3.00339	4,720	589
11-2-30	1	0.117017	0.370768	1.663683	4.244975	19.20153	2.046843	56966.44	-3.32737	2,701	269
11-1-RHR	1	0.140401	0.346118	1.862739	5.854641	14.00017	2.218013	52076.91	-3.72548	1,714	130
11-B	1	0.162624	0.331769	2.207776	8.242741	10.07766	2.475304	61917.23	-4.41555	1,083	51
11-T	1	0.173664	0.321013	2.333559	14847372	17.99563	2.745553	63623.39	-4.66712	884	35
12-4-U	1	0.054816	0.503468	1.332121	2.352733	39.73948	1.661441	70990.01	-2.66424	6,180	975
12-2-R30	1	0.098599	0.395879	1.542217	3.239854	24.53586	1.931685	63726.32	-3.08443	3,775	445
12-1-RHR	1	0.121392	0.365686	1.709916	4.767938	18.09586	2.084624	58273.98	-3.41983	2,539	237
12-B		0.140401	0.346118	1.862739	5.854641	14.00017	2.218013	30411.44	-3.81548	1,615	95
12-B	1	0.149648	0.352193	1.907739	8.870855	11.16136	2.235847	30411.44	-3.81548	922	65
N-4-U	1	0.106512	0.384132	1.580726	4.19648	22.13278	1.973519	58559.41	-3.16145	3,232	361
N-2-R30	1	0.141846	0.338573	1.871457	5.535922	14.40604	2.237832	60253.36	-3.74291	1,952	146
N-1-RHR	1	0.155029	0.333209	2.179451	7.787817	11.51754	2.453238	86136.03	-4.3589	1,587	77


Mix A (2008)

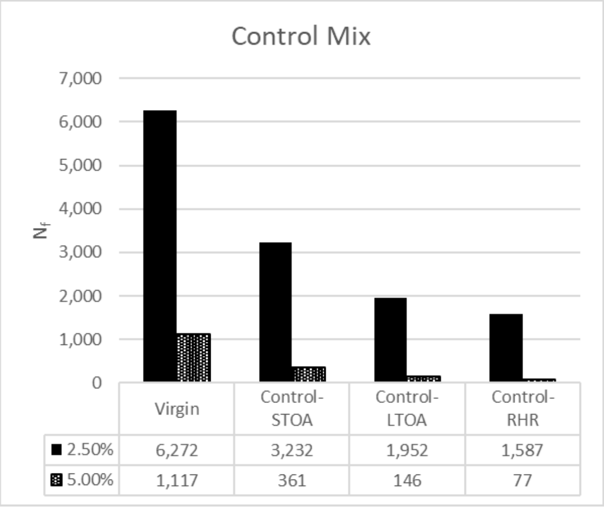
	Virgin	Mix A-STOA	Mix A-LTOA	Mix A-RHR	Mix A-Bottom	Mix A-Top
■ 2.50%	6,272	4,748	2,486	1,639	1,702	1,383
▨ 5.00%	1,117	618	226	108	112	83


Mix C (2012)

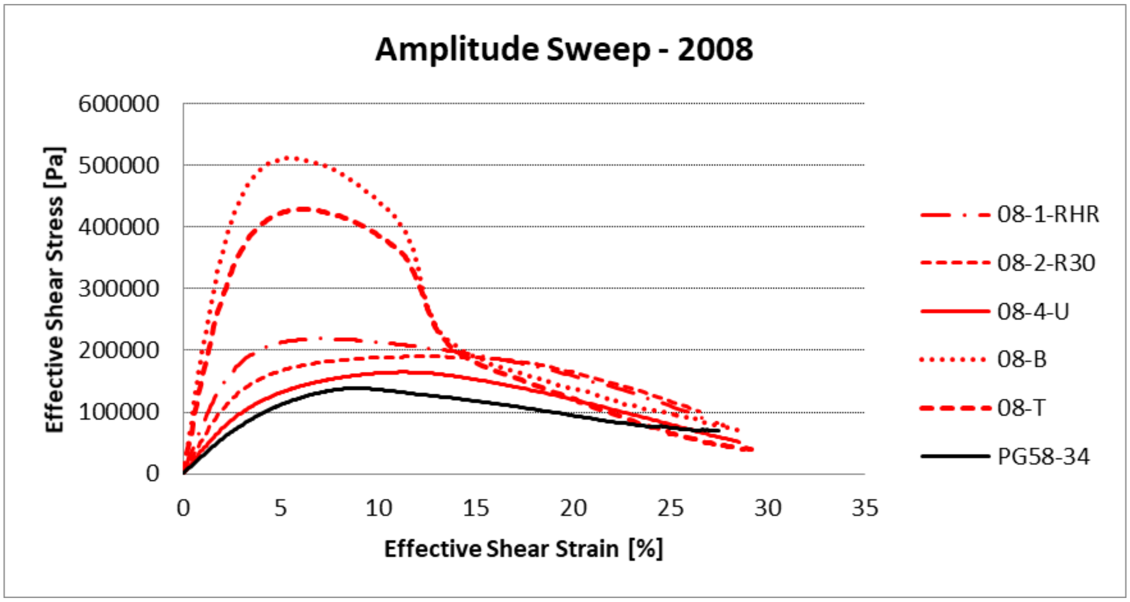
	Virgin	Mix C-STOA	Mix C-LTOA	Mix C-RHR	Mix C-Bottom	Mix C-Top
■ 2.50%	6,272	6,180	3,775	2,539	1,615	922
▨ 5.00%	1,117	975	445	237	95	65

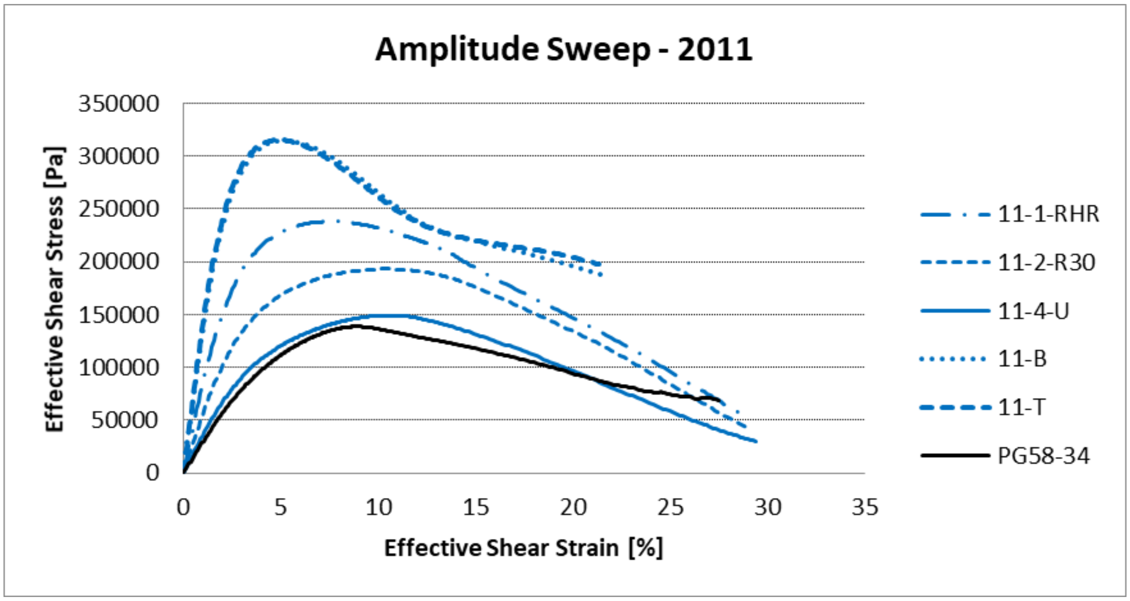

Mix B (2011)

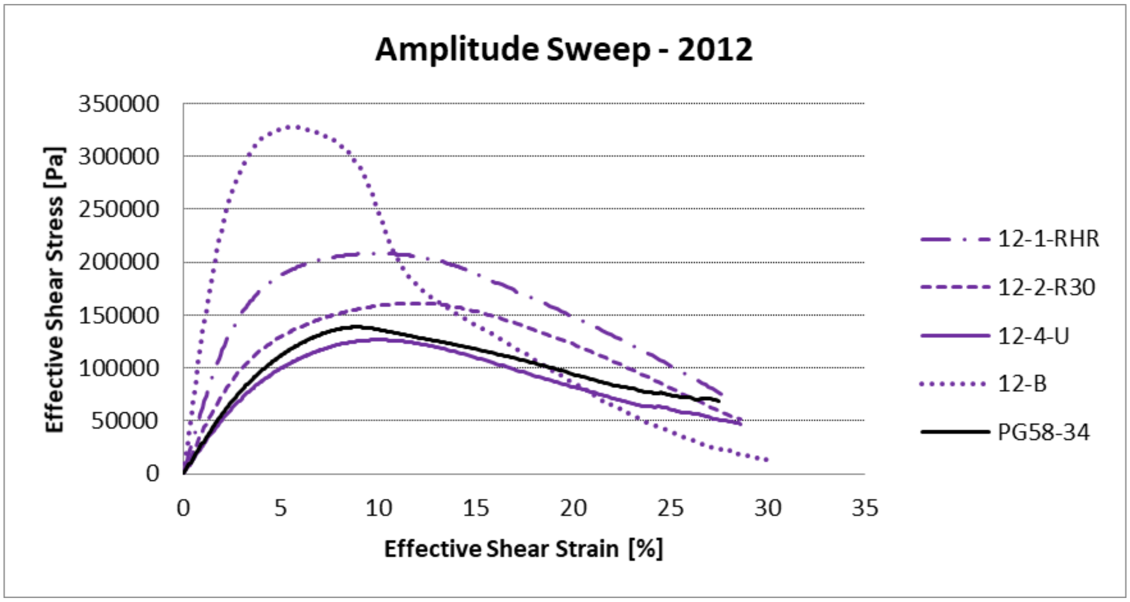
	Virgin	Mix B-STOA	Mix B-LTOA	Mix B-RHR	Mix B-Bottom	Mix B-Top
■ 2.50%	6,272	4,720	2,701	1,714	1,083	884
▨ 5.00%	1,117	589	269	130	51	35

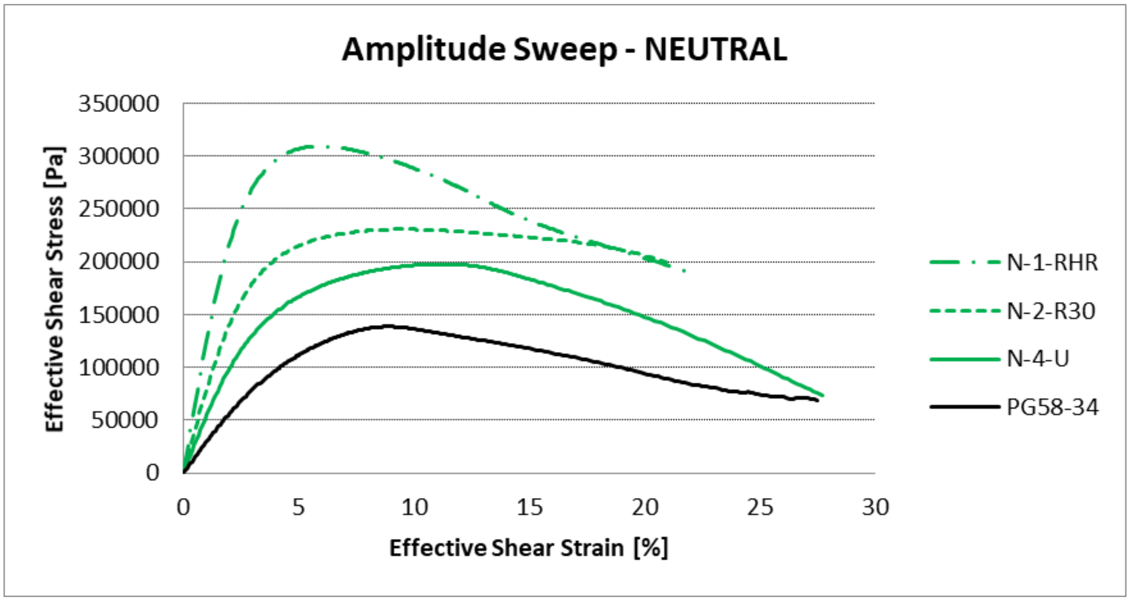

Control Mix

	Virgin	Control-STOA	Control-LTOA	Control-RHR
■ 2.50%	6,272	3,232	1,952	1,587
▨ 5.00%	1,117	361	146	77

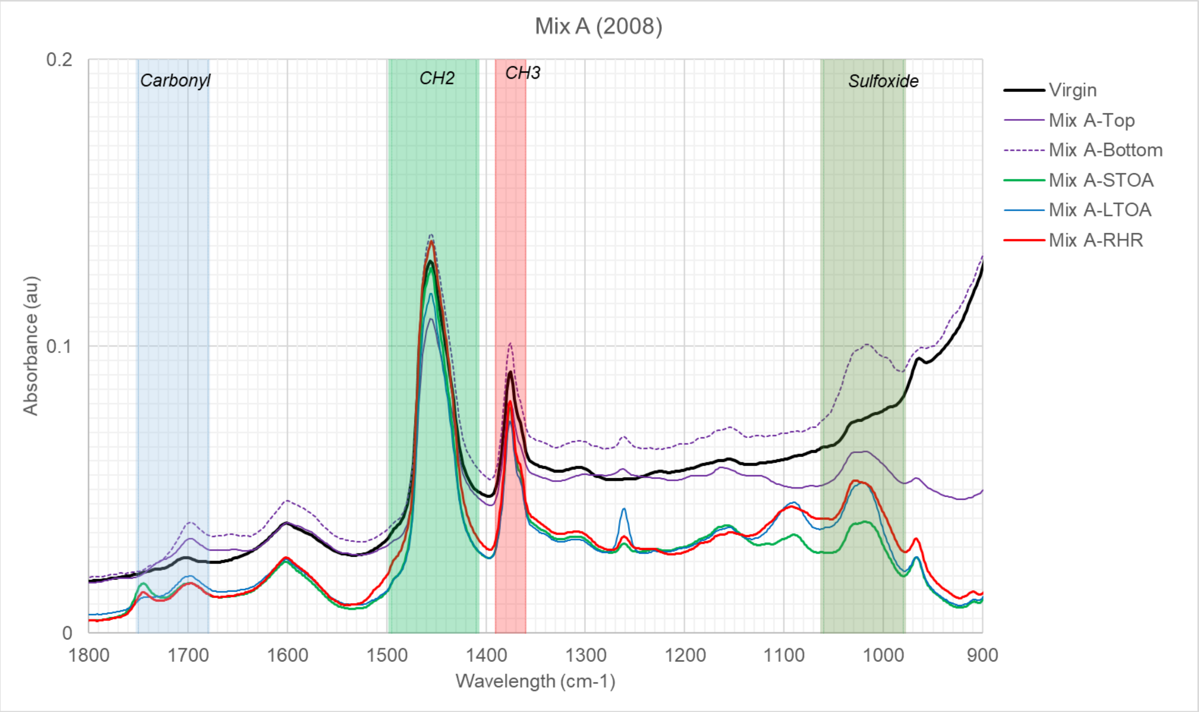

Amplitude Sweep - 2008
Effective Shear Stress [Pa]
600000
500000
400000
300000
200000
100000
0
0
5
10
15
20
25
30
35
Effective Shear Strain [%]
08-1-RHR
08-2-R30
08-4-U
08-B
08-T
PG58-34

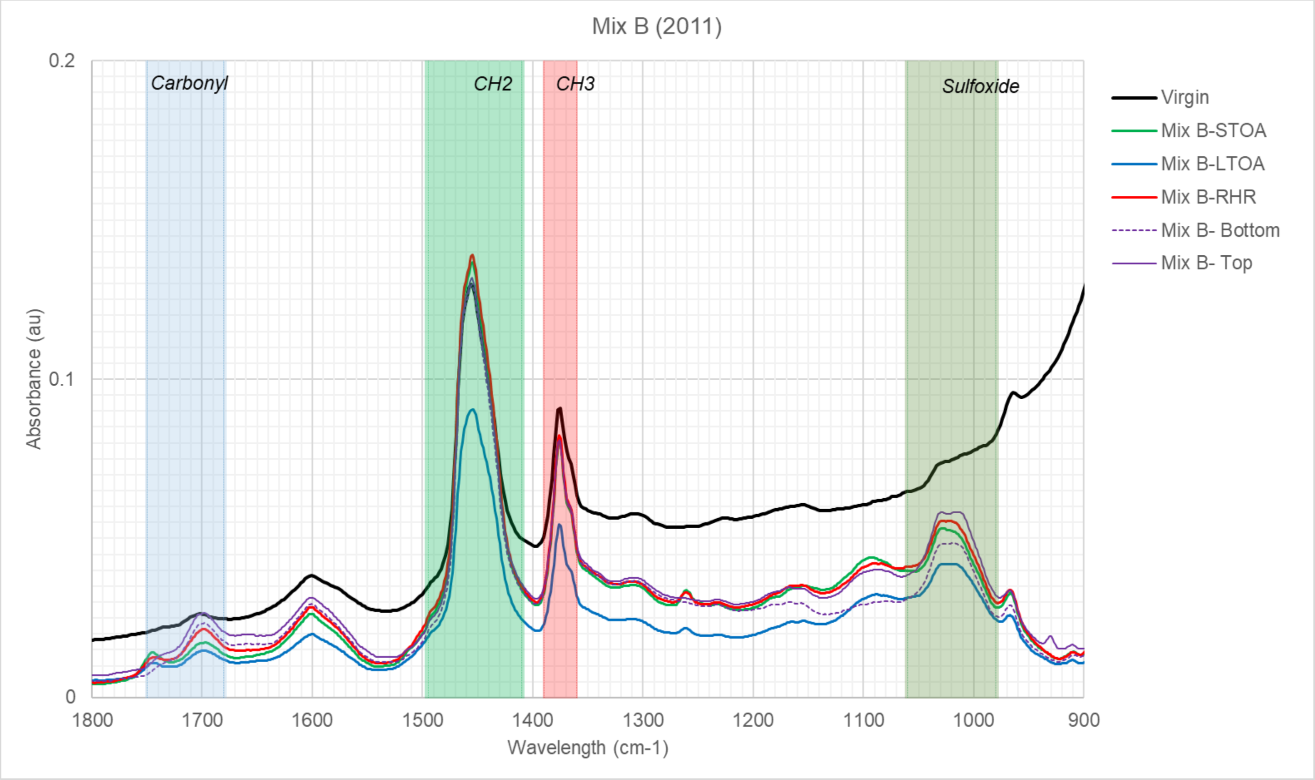

Amplitude Sweep - 2011
Effective Shear Stress [Pa]
350000
300000
250000
200000
150000
100000
50000
0
0
5
10
15
20
25
30
35
Effective Shear Strain [%]
11-1-RHR
11-2-R30
11-4-U
11-B
11-T
PG58-34

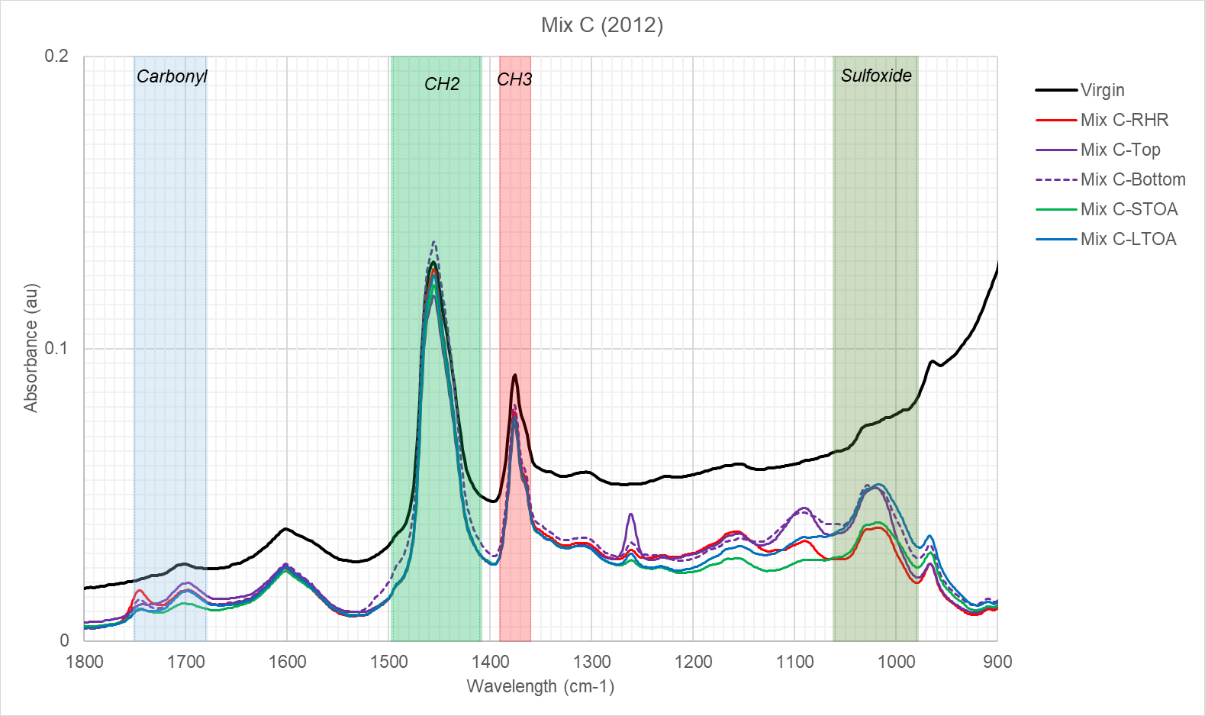

Amplitude Sweep - 2012
Effective Shear Stress [Pa]
350000
300000
250000
200000
150000
100000
50000
0
0
5
10
15
20
25
30
35
Effective Shear Strain [%]
12-1-RHR
12-2-R30
12-4-U
12-B
PG58-34

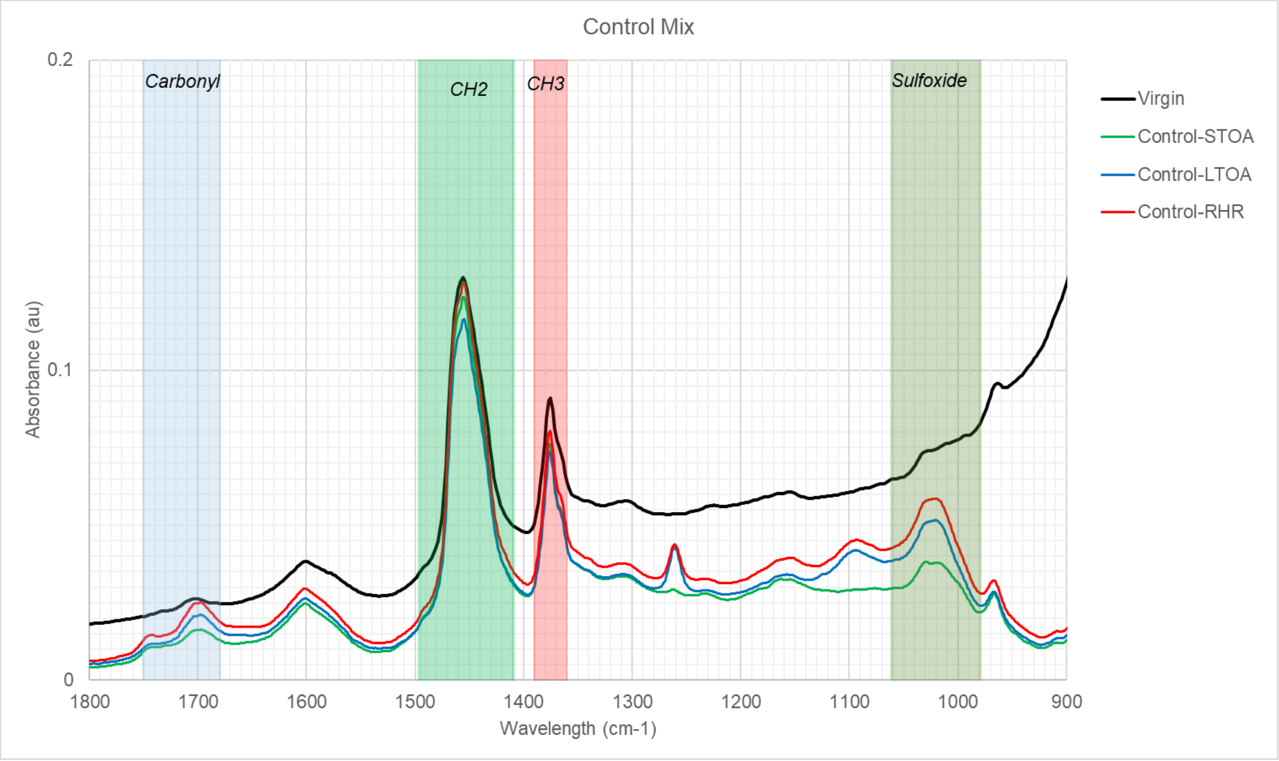

Amplitude Sweep - NEUTRAL
Effective Shear Stress [Pa]
350000
300000
250000
200000
150000
100000
50000
0
0
5
10
15
20
25
30
Effective Shear Strain [%]
N-1-RHR
N-2-R30
N-4-U
PG58-34

APPENDIX E: FT-IR


Mix A (2008)
0.2
0.1
0
Absorbance (au)
Carbonyl
CH2
CH3
Sulfoxide
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
Wavelength (cm-1)
Virgin
Mix A-Top
Mix A-Bottom
Mix A-STOA
Mix A-LTOA
Mix A-RHR


Mix B (2011)
0.2
0.1
0
Absorbance (au)
Carbonyl
CH2
CH3
Sulfoxide
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
Wavelength (cm-1)
Virgin
Mix B-STOA
Mix B-LTOA
Mix B-RHR
Mix B- Bottom
Mix B- Top


Mix C (2012)
0.2
0.1
0
Absorbance (au)
Carbonyl
CH2
CH3
Sulfoxide
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
Wavelength (cm-1)
Virgin
Mix C-RHR
Mix C-Top
Mix C-Bottom
Mix C-STOA
Mix C-LTOA


Control Mix
0.2
0.1
0
Absorbance (au)
Carbonyl
CH2
CH3
Sulfoxide
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
Wavelength (cm-1)
Virgin
Control-STOA
Control-LTOA
Control-RHR