

ADDIS ABABA UNIVERSITY
ADDIS ABABA INSTITUTE OF TECHNOLOGY
SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING
GRADUATE STUDIES



Assessment of Leather Solid Waste as Partial Replacement of Asphalt
Binder

By Alemayehu Bekele Wakene

Thesis submitted to School of Civil and Environmental Engineering of Addis Ababa Institute of
Technology in Partial Fulfillment of the Requirements for the Degree of

Master of Sciences

In

Civil Engineering

(Road and Transport Engineering)

Adviser: Dr.Habtamu Melese

October, 2018

Addis Ababa, Ethiopia

Addis Ababa University
Addis Ababa Institute of Technology
School of Civil and Environmental Engineering
Graduate Studies

Assessment of Leather Solid Waste as Partial Replacement of Asphalt Binder

By Alemayehu Bekele Wakene

Thesis submitted to School of Civil and Environmental Engineering of Addis Ababa Institute of
Technology in Partial Fulfillment of the Requirements for the Degree of Master of
Sciences
In
Civil Engineering
(Road and Transport Engineering)

Approved by Board of Examiners:

<u>Dr.Habtamu Melese</u> Advisor	_____ Signature	_____ Date
_____ Internal Examiner	_____ Signature	_____ Date
_____ External Examiner	_____ Signature	_____ Date
_____ Chairman	_____ Signature	_____ Date

DECLARATION

I hereby declare that research work titled “*Assessment of Leather Solid Waste as Partial Replacement of Asphalt Binder*” is my original work. The work has not been presented elsewhere for assessment and award of any degree or diploma. Where material has been used from other sources it has been properly acknowledged / referred.

Name: Alemayehu Bekele

Signature: _____

Place: Addis Ababa University

Addis Ababa Institute of Technology

School of Civil and Environmental Engineering

Graduate Studies

Road and Transport Engineering

Date: October, 2018

ABSTRACT

Asphalt binder is considered as the most expensive part of hot mix asphalt pavement material. Leather industry has been categorized as one of highly polluting industries and it has adverse impact on environment because of its generation of liquid, solid and gaseous wastes. Solid wastes generated from tanning industries contain different chemicals which are used during leather manufacturing process. Chrome Buffing Dust (CBD) is a solid waste generated during leather making process at the finishing operation.

This research study evaluated partial replacement of asphalt binder with CBD. It compares neat asphalt binder and asphalt binder mixed with CBD using laboratory tests including conventional (penetration, softening point and ductility) and rheological tests (Amplitude Sweep Test, Frequency Sweep Test, Performance Grading and Multiple Stress Creep and Recovery Tests). Six asphalt binders were obtained by mixing the asphalt binder (penetration grade 60/70) with five different percentages of CBD by weight of asphalt binder (2%, 4%, 6%, 8% and 10%).

The conventional test results of asphalt binder mixed with CBD revealed better performance improvement. In general, as percentage of CBD increases penetration decreases and softening point increases, while ductility property showed dramatic decrease as CBD percentage increases. Rheological asphalt binder tests were conducted using a Dynamic Shear Rheometer (DSR). Four rheological tests were conducted namely Amplitude Sweep Test (AST), Frequency Sweep Test (FST), Performance Grade (PG) test and Multiple Stress Creep and Recovery (MSCR) Test. The AST was conducted to determine the Linear Viscoelastic (LVE) Range, FST was conducted to construct the master curve and the MSCR test was conducted to determine the rut parameter called non-recoverable creep compliance (J_{nr}). The AST and FST were conducted at three temperatures (21.1°C, 37.8°C, and 54.4°C) while the MSCR tests were conducted at three temperatures (52°C, 58°C and 64°C). Performance Grade (PG) tests were also conducted at higher temperatures. From FST tests, CBD affected the property of asphalt binder at higher temperature ranges in improving its potential for resistance of permanent deformation. From MSCR test result analysis, addition of CBD has resulted in better improvement on the rut resistance (decrease in J_{nr} value up to 30%) of asphalt binders. In conclusion, partial replacement of asphalt binder with CBD improves the stiffness and rut resisting performance of asphalt binders at high temperature ranges. Overall, the research shows promising results that it is feasible to partially replace asphalt binder with CBD up to 6%.

Key words: Asphalt Binder, Rheology, CBD, Stiffness and Rutting

ACKNOWLEDGMENTS

First and foremost, I give all thanks and praise to the Almighty God for providing me the strength to complete this postgraduate program. I am deeply indebted to my advisor, Dr. Habtamu Melese for his invariable guidance, support and encouragement throughout the course of this study. It has been a pleasure working with him. I would like to thank Ethiopian Roads Authority and Addis Ababa Institute of Technology for giving me a chance to be part of this postgraduate scholarship program. I am also grateful to Ethiopian Leather Industry Development Institute and its staffs for their unwavering support from the inception of this study to its completion. I also appreciate and thank AAiT Civil and Environmental Department and Highway Laboratory staff members for their invaluable assistance and supports. I also appreciate CORE Consulting Engineers Plc for their support.

Once again my deepest appreciation goes to my colleagues who supported me during the course of this paper and to all whose name(s) may not appear here, I appreciate you all!

TABLE OF CONTENTS

ABSTRACT iii

ACKNOWLEDGMENTS iv

LIST OF TABLES vii

LIST OF FIGURES viii

ACRONYMY ix

CHAPTER 1: INTRODUCTION 1

 1.1 Background 1

 1.1.1 Problem Statement 1

 1.2 Objectives of Study 2

 1.2.1 General Objective 2

 1.2.2 Specific Objectives 2

 1.3 Study Scope and Limitations 3

 1.4 Organization of the Study 3

CHAPTER 2: LITERATURE REVIEW 4

 2.1 Introduction 4

 2.2 Components of Hot Mix Asphalt 4

 2.2.1 Aggregates 4

 2.2.2 Asphalt Binder 5

 2.3 Asphalt Binder Rheology 5

 2.4 Asphalt Binder Characterization and It’s Constitute 7

 2.5 The Modification of Asphalt Binder 8

 2.6 Effect of Modifiers on Asphalt Binder 9

 2.7 Leather Production 10

 2.7.1 Leather Solid Wastes 15

 2.7.2 Chrome Buffing Dust use as Construction Material 17

 2.7.3 Chemical Composition of Chrome Buffing Dust 17

 2.7.4 Environmental Impacts of Chrome Buffing Dust 18

 2.8 Summary 19

CHAPTER 3: RESEARCH METHODOLOGY 20

 3.1 Introduction 20

 3.2 Materials 20

 3.2.1 Asphalt Binder 20

 3.2.2 Chrome Buffing Dust 20

 3.3 Asphalt Binder Tests 20

 3.3.1 Experimental Design 20

 3.3.2 Conventional Tests 21

 a) Penetration 21

 b) Softening Point 21

 c) Ductility 21

d) Rolling Film Oven Test	22
3.3.3 Dynamic Shear Rheometer (DSR)	22
3.3.4 DSR Equipment.....	23
3.3.5 Asphalt Binder Specimen Preparation for Rheological Tests	25
3.3.6 Dynamic Shear Rheometer (DSR) Tests.....	26
a) Amplitude Sweep Test (AST).....	26
b) Frequency Sweep Test (FST).....	27
c) Performance Grading (PG) Determination Test.....	27
d) Multiple Stress Creep Loading and Recovery (MSCR) Test.....	28
CHAPTER 4: RESULTS AND DISCUSSIONS	30
4.1 Effect of chrome buffing dust on conventional properties of Asphalt binder	30
4.1.1 The Effect of CBD on Penetration	30
4.1.2 The Effect of CBD on Softening Point	31
4.1.3 The Effect of CBD on Ductility	31
4.1.4 Rolling Thin Film Oven Test	32
4.2 The effect of CBD on the Rheological Property of Asphalt Binder.....	32
4.2.1 Amplitude Sweep Test (AST)	32
4.2.2 Frequency Sweep Test Results (FST)	34
4.2.2 Performance Grade Determination.....	42
4.2.3 Multiple Stress Creep Loading and Recovery (MSCR) Test	45
4.2.4 Summary of Test Results Analysis	49
4.2.5 Economic Benefits	50
4.2.6 Safety Cautious while using CBD.....	50
CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS	51
5.1 Conclusions	51
5.2 Recommendations	52
5.3 Future Studies.....	52
Appendix A: AST Test Results in Graph.....	55
Appendix B: FST Test Results in Graph.....	57
Appendix C: MSCR Test Results in Graph	61
Appendix D: Black Space Diagram	64
Appendix E: Statistical Analysis of Variance (ANOVA) for FST Results.....	65
Appendix F: Leather Factories in Ethiopia	66

LIST OF TABLES

- Table 1: Generic Types of Asphalt Binder Modifiers (Bahia et al., 2001)
- Table 2: Nature and Quantity of Leather Solid Waste per 1ton of hides/skins
- Table 3: Chrome Buffing Dust
- Table 4: Neat Asphalt Binder Quality Test Results
- Table 5: Chemical Properties of chrome shavings & buffing dust (Rajaram. J.et. al (2009))
- Table 6: Penetration Value for Unaged and RTFO Aged Binders
- Table 7: Softening Point for Unaged and RTFO Aged Binders
- Table 8: Ductility for Unaged and RTFO Aged Binders
- Table 9: Mass Loss on RTFO Ageing
- Table 10: Viscoelastic Region for RTFO Aged and Unaged Binders
- Table 11: Shift factors for Complex Modulus Master Curves for RTFO Aged and Unaged Binders
- Table 12: Summary of ANOVA hypothesis testing at specified frequencies
- Table 13: Summary of Tukey Test
- Table 14: PG Determination for Unaged Binders
- Table 15: PG Determination for RTFO Aged Binders
- Table 16: Traffic Designation AASHTO M-332
- Table 17: Rutting Parameter (Jnr) and Percentage Recovery (PR) RTFO Aged Binders

LIST OF FIGURES

- Figure 1: Mechanical responses of elastic, viscous, and viscoelastic materials
- Figure 2: Leather Manufacturing Process Flow (Abajihad, 2012)
- Figure 3: Chrome Buffing Dust
- Figure 4: Configuration & loading mode of DSR (Zaniewski and Pumphrey, 2004)
- Figure 5: Dynamic Shear Rheometer
- Figure 6: Preparing Asphalt Specimens for the DSR testing
- Figure 7: Asphalt binder sample placed on the fixed platen of the DSR
- Figure 8: Linear viscoelastic region of asphalt binder (Petersen et al., 1994)
- Figure 9: Complex Modulus vs Frequency
- Figure 10: Strain vs time for MSCR Test
- Figure 11: LVER for Unaged Binders
- Figure 12 LVER for RTFO Aged Binders
- Figure 13: Complex Shear Modulus Master Curve for RTFO Aged Binders
- Figure 14: Complex Shear Modulus Master Curve for Unaged Binders
- Figure 15: Log-Log Phase Angle Master Curve for Unaged Binders
- Figure 16: Semi-Log Phase Angle Master Curve for Unaged Binders
- Figure 17: Log-Log Phase Angle Master Curve for RTFO Aged Binders
- Figure 18: Black Space Diagram for Unaged 6% CBD
- Figure 19: Black Space Diagram for RTFO Aged 4% CBD
- Figure 20: $G^*/\sin\delta$ for Unaged Binders
- Figure 21: $G^*/\sin\delta$ for RTFO Aged Binders
- Figure 22: J_{nr} for RTFO Aged Binders
- Figure 23: Strain for RTFO Aged Binders @64°C
- Figure 24: Strain for RTFO Aged Binders @64°C
- Figure 25: Strain for RTFO Aged 2% CBD

ACRONYMY

AAiT	Addis Ababa Institute of Technology
AASHTO	American Association of State Highway and Transportation Officials
AC	Asphalt Concrete
ANOVA	Analysis of Variance
AST	Amplitude Sweep Test
ASTM	American Society for Testing and Materials
BDE	Building Design Enterprise
CBD	Chrome Buffing Dust
CSA	Central Statistics Agency
DSR	Dynamic Shear Rheometer
ELICO	Ethio- Leather Industries Corporation
ELIDI	Ethiopian Leather Industries Development Institute
ERA	Ethiopian Roads Authority
FST	Frequency Sweep Test
HMA	Hot Mix Asphalt
LVER	Linear Viscoelastic Region
MSCR	Multiple Stress Creep and Recovery
NCHRP	National Cooperative Highway Research Program
SHRP	Strategic Highway Research Program
Super Pave	Superior Performing Asphalt Pavements
PG	Performance Grade
RTFO	Rolling Thin Film Oven
UNIDO	United Nations Industrial Development Organization

CHAPTER 1: INTRODUCTION

1.1 Background

Asphalt pavements are granular composites that contain mineral aggregates, asphalt binder and air voids. The two load-carrying components of the asphalt mixtures are the mineral aggregates which comprises about 90-95% and the asphalt binder which shares 5-10% of total mix by weight (Lesueur and España, 2009). Asphalt binders are obtained from the refining of crude oils. They are produced from the heavy residue after the refining of fuels and lubricants. Asphalt binders are thermoplastic materials that demonstrate viscoelastic properties under most pavement operating conditions (Anderson et al., 1994, Petersen et al., 1994). This is the fundamental property that makes them versatile for asphalt mixtures with the viscoelastic characteristics of the bituminous asphalt binders directly and significantly influencing the performance of the mixtures. HMA wearing courses are the most critical layer in a pavement structure and must be of high quality and have predictable performance. It is stated in (ERA, 2013) that, HMA wearing courses need to possess the following characteristics:-

- (i) High resistance to deformation
- (ii) High resistance to fatigue and the ability to withstand high strains i.e. they need to be flexible
- (iii) Sufficient stiffness to reduce stresses in the underlying layers to acceptable levels
- (iv) High resistance to environmental degradation
- (v) Low permeability to prevent the ingress of water
- (vi) Good workability to allow adequate compaction to be obtained during construction
- (vii) Sufficient surface texture to provide good skid resistance in wet weather and
- (viii) Predictable performance.

1.1.1 Problem Statement

In Ethiopia, road infrastructure is the dominant means of transport. According to the report of ERA, road sector development program of 19 years assessment (1997-2016), the Federal Democratic Republic of Ethiopia has invested 266.2 Billion Birr for road projects. 75% of this budget was allocated for Federal roads which consume vast amount of asphalt binder. During the same period, the expansion of road network has increased from 26,550 km to 113,066 km. Even though, the expansion of the road network is progressing in good manner, the road authorities face impending challenges due to pavement failures caused by traffic load, poor construction practice, under quality construction materials and/or lack of updated design method (Alebachew, 2005).

These have been manifested in the form of failures like rutting and fatigue cracks. The roads built by the Federal Government of Ethiopia are mostly hot mix asphalt or surface dressing which

demand high quality and quantities of asphalt binder materials. Conversely, asphalt binder is the most expensive part of the mix and requires efficient utilization. Moreover, the demand of asphalt binder increases as the built roads deteriorate frequently and requires maintenance and/or rehabilitations needs.

On the other side, Ethiopia is well known for its large livestock population. The production of leather from skins and hides is one of the leading industrial sectors in the country and the industry is relatively older with more than 80 years of involvement in processing leather (UNIDO, 2012). The tanning industry is one of the most polluting industries generating large quantities of solid wastes and creating negative impacts on environment. Chrome buffing dust is one of the solid waste generated at the finishing operation of leather manufacturing. It has negative effect on human health if it enters into human body through food chain system. The problem is pronounced as the current practice of solid management system is disposal of the solid wastes in open land fill (Abajihad, 2012).

Therefore, this research tries to address the economy and quality aspect of asphalt pavement and environmental concerns caused by leather solid waste (CBD) and tries to assess how this solid waste product can be used for road construction.

1.2 Objectives of Study

1.2.1 General Objective

The general objective of this study is to assess the suitability of chrome buffing dust (CBD) as partial replacement of asphalt binder.

1.2.2 Specific Objectives

The specific objectives of this study are:

- To analyze the conventional properties (penetration, softening point and ductility) of asphalt binder mixed with CBD
- To investigate the rheological properties (AST, FST, PG and MSCR) of the asphalt binder mixed with CBD
- To recommend the optimum CBD content for replacement of asphalt binder

1.3 Study Scope and Limitations

In this study neat asphalt binder 60/70 penetration grade and asphalt binder mixed with chrome buffing dust, rheological and physical properties were evaluated. The tests of neat and modified asphalt binders were conducted using AASHTO and ASTM testing procedures. Rheological studies (Stiffness modulus, Phase Angle) and AST, FST, PG and MSCR tests were conducted using Bohlin DSR equipment. Conventional tests (Penetration, Softening point, Ductility and Mass Loss) were done following ASTM procedures.

The experimental design used for this study provides comparison between the neat and modified asphalt binders; the effect of temperature, and percentage of CBD in asphalt binders, loading time and ageing effects. The research was conducted using 8mm, and 25mm diameter plate size for rheological tests. Chrome buffing dust was mixed in 2%, 4%, 6%, 8% and 10% by weight of asphalt binder. The asphalt binder was obtained from the laboratory of Building Design Enterprise (BDE). CBD was collected from Awash Tannery (which is a company under Ethio Leather Industry Corporation (ELICO)). Moreover, the DSR equipment of AAiT highway laboratory was used for this research purposes. This research was done only on neat and modified binders, no mix design was conducted. Due to lack of testing procedure and laboratory technician on chrome buffing dust and equipment, CBD physical and chemical tests were not conducted, instead its property was analyzed after mixing with binder in different proportions. The properties of CBD were taken from past researches. The economic savings indicated is rough indication and detailed data are required to conduct Life Cycle Cost. So, impact of CBD on Life Cycle cost of HMA is not conducted.

1.4 Organization of the Study

The research study is organized into five chapters. Following this introductory chapter is a background literature review. The literature review in chapter two provides background information for asphalt binder modifications, its purposes and the effects of different modifiers on asphalt binder rheology and its physical properties as well. The research materials and methods are presented in chapter three. The chapter includes details of the experimental program and methods utilized during testing. The analysis of the test results and the evaluation of the modifier are provided in chapter four. Concluding remarks and recommendations of the research are provided in chapter five.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

Asphalt binders play a critical role in the quality and performance of HMA pavements. Therefore, pavement engineers must have an in-depth understanding of asphalt binder behaviors. Proven testing equipment and test specifications are also necessary to accurately evaluate and select the appropriate asphalt binder for a pavement structure. Usually, pavements are classified as flexible and rigid pavements. Flexible pavements support loads through bearing rather than flexural action, as rigid pavements do (Druta, 2006). They comprise several layers of carefully selected materials designed to gradually distribute loads from the pavement surface to the layers underneath. The design ensures the load transmitted to each successive layer does not exceed the layer's load bearing capacity. HMA pavement usually comprises surfacing, base course, sub base and subgrade layers. This study will only concentrate on the top layer component, i.e., the asphalt binder.

2.2 Components of Hot Mix Asphalt

HMA is a mixture that contains aggregate and binder fastened into a strong mixture. Aggregates play an important role in determining the nature and characteristics of pavement in preparing the structure of mutual-lock while the binder acts as glue between aggregate particles with layer below the surface of the road.

The performance and property of HMA is mainly a function of the characteristics of its constituents: asphalt binder and aggregate along with the quality of the construction process.

2.2.1 Aggregates

Aggregates (or mineral aggregates) are hard, inert materials such as sand, gravel, crushed rock, slag, or rock dust. Properly selected and graded aggregates are mixed with the asphalt binder to form HMA pavements. Aggregates are the principal load-supporting components of HMA pavement.

Aggregates can be classified into three types according to their size distribution: coarse aggregates, fine aggregates, and mineral filler. Coarse aggregates are generally defined as those retained on the 4.75mm sieve i.e. it comprise the portion of the aggregates that has large particle sizes. Fine aggregates are those that pass through the 4.75mm sieve and are retained on the 0.075mm sieve (ERA, 2013). It is the aggregate particles that can fill the voids created by the coarse aggregates in the mixture. Mineral filler is defined as that portion of the aggregate passing the 0.075mm sieve. It consists of very fine, inert mineral with the consistency of flour, which is added to the hot mix asphalt to improve the density and strength of the mixture.

2.2.2 Asphalt Binder

Asphalt binder is a category of organic liquids which are highly viscous, black, sticky and wholly soluble in carbon disulfide. Asphalt binder molecules can contain thousands of carbon atoms. This makes it one of the most complex molecules found in nature. Most asphalt binders contain, Carbon (82-88%), Hydrogen (8-11%), Sulfur (0-6%), Oxygen (0-1.5%) and Nitrogen (0-1%) (Shell, 1990). It is the residual product obtained by fractional distillation of crude oil at the bottom fraction. At ambient temperature in-situ binder is solid and virtually non-volatile and the vapor pressure of in-situ binder is below the limit of detection for normal instrumentation. Normally binder is heated to $>140^{\circ}\text{C}$ to become liquid to facilitate transportation and handling (AsphaltInstitute, 2007). The physical properties of asphalt binder vary considerably with temperature. At high temperatures, asphalt binder is a fluid with low consistency similar to that of oil. At room temperature most asphalt binders will have the consistency of soft rubber. At subzero temperatures, asphalt binder can become very brittle.

Generally there are two sources of asphalt. These are:-

- A. Natural asphalt which is obtained from nature and found in so called “asphalt lakes” around the world (Shell, 1990).
- B. Petroleum asphalt is obtained during the refinery process of heavy crude oils. Asphalt used for road construction is mainly produced from the refinery process. Different types and grades of asphalt can be produced by using various operations. Vacuum and atmospheric distillations are the basic processes used in oil refineries to produce asphalt and other useful products (Shell, 1990).

2.3 Asphalt Binder Rheology

The word rheology is derived from the Greek word rheo, which translates literally as "to flow." The stiffness of asphalt binders is time dependent; they flow with time and consequently asphalt binders are classified as rheological materials. The properties of rheological materials are also temperature dependent; as a result, both the time of loading and the temperature of loading must be considered when characterizing the flow properties of rheological materials such as asphalt cement and asphalt binders.

Asphalt binders deform when subjected to loads. The properties of asphalt also change with varying temperatures. The deformation is a combination of elastic response and viscous flow. The extent of deformation, or mechanical response is dependent on load magnitude, duration, and rate of application and the temperature state of the material. Since asphalt binders display both elastic and viscous response properties, they are classified as viscoelastic materials (Anderson et al., 1994, Petersen et al., 1994, Zaniwski and Pumphrey, 2004).

The typical elastic, viscous, and viscoelastic responses to an applied stress is shown in Figure 1. An elastic material experiences recoverable deformation when subjected to a constant load, as in figure 1a, and will immediately deform and maintain a constant strain when loaded, as in figure 1b. Also, the material will immediately return to its initial shape when the creep load is removed. A viscous Newtonian material, when subjected to a constant load, will deform at a constant rate until the load is removed, like in figure 1c. The deformation of the viscous material, however, will remain after the load is removed; hence, a viscous material experiences non-recoverable deformation.

A viscoelastic material, when subjected to a creep load, experiences an immediate deformation followed by a continued time-dependent deformation (Petersen et al., 1994), as shown in figure 1d. The immediate deformation corresponds to the material's elastic response and the time-dependent deformation corresponds to the material's viscous response. Once the load is removed, the viscous deformation component immediately ceases, but this deformation is not recovered. The delayed elastic deformation component is slowly recovered at a decreasing rate. Thus, a viscoelastic material experiences only a partial recovery of the deformation resulting from creep loading. The viscoelastic behavior of asphalt can be characterized by its deformation resistance and the relative distribution of that resistance between the elastic component and the viscous component within the linear range. The relative distribution of the resistance between the elastic component and the viscous component is dependent on the asphalt cement characteristics and temperature and loading rate (Zaniewski and Nallamothu, 2003).

The previous loading-response descriptions are for responses within the linear range, which is characterized by the deformation being directly proportional to the applied load at any time and temperature. Nonlinear loading responses are difficult to model for viscoelastic materials such as asphalt binder. Linear response models, however, are sufficient for the engineering analysis of asphalt binder response to the loading conditions and environmental stresses encountered in the field (Zaniewski and Nallamothu, 2003).

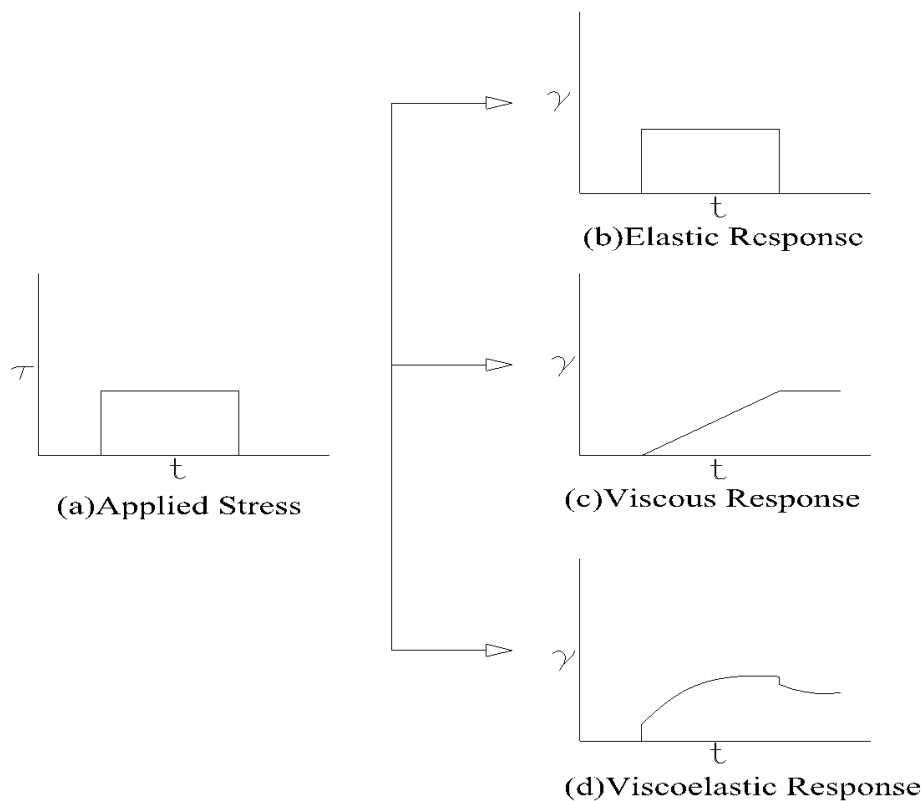


Figure 1: Mechanical response of elastic, viscous, and viscoelastic materials

2.4 Asphalt Binder Characterization and It's Constitute

According to Asphalt Institute manual series No.4 definition, asphalt binder is a dark-brown to black viscoelastic material that is produced by petroleum distillation (AsphaltInstitute, 2007). The "viscoelastic" term means that asphalt has the properties of both a viscous material, such as motor oil, or more realistically, water, and an elastic material, such as a rubber. However, the property that asphalt binder exhibits, whether viscous, elastic, or most often, a combination of both, depends on temperature and time of loading. The rheology of an asphalt binder at a given temperature is determined by both its constitute (chemical composition) and structure (physical arrangement) of predominantly hydrocarbon molecular structures in the material (Shell, 1990). Elementary analysis of asphalt binders manufactured from a variety of crude oils show that most binders contain: Carbon (82-88%), Hydrogen (8-11%), Sulfur (0-6%), Oxygen (0-1.5%) and Nitrogen (0-1%)(Shell, 1990). The precise composition varies according to the source of the crude oil from which the binder originates and the subsequent modification induced during manufacture and subsequent ageing in service (Shell, 1990). Asphalt binder modifiers can be particulate matter or additives that will disperse completely or dissolve in the asphalt binder. They range from organic to inorganic materials, some of which react with the asphalt binder, while others are added as inert fillers (Bahia et al., 2001).

2.5 The Modification of Asphalt Binder

(Park, 2012) summarized the findings of several researchers that the contribution of asphalt binder to pavement failure is among the most prominent factors. Most of the problems in asphalt concrete originate from the poor properties, including thermal sensitivity of asphalt binder. The effects of asphalt modifications were listed as improving performance regarding (1) permanent deformation, (2) fatigue cracking, (3) low temperature cracking, (4) moisture damage, and (5) oxidative aging.

Currently, the most popular choice for improving mechanical properties of asphalt concrete is to use polymer modifiers. (Bahia et al., 2001) conferred that asphalt binder modifiers can be classified in several ways: on the mechanism by which the modifier alters the asphalt binder properties; on the composition and physical nature of the modifiers; or on the target asphalt binder property that needs improvement or enhancement. Based on the literature review conducted, (Anderson et al., 1994, Bahia et al., 2001) classified modifiers into about 11 major categories depending on the nature of the modifiers and the generic types of the asphalt binder modifiers as shown in Table 1.

On the other hand, chemical modifiers such as sulfur, copper sulfate, lignin, and other metallic compounds have been used to improve workability, performances, and resistance to oxidative aging. According to physical and rheological studies conducted on AC 60/70 modified with sulfur by different researchers, it displayed that the rheological properties of the asphalt binder confirms better results with respect to penetration, stability, flow and density. The sulfur modified asphalt binder has higher complex modulus and less phase angle compared to the neat asphalt binder (Mahabir et al., 2016, Kumar and Khan, 2013). (Mahabir et al., 2016, Kumar and Khan, 2013, Prajna and Anjum, 2015). However, this research lacks rheological studies which can better describe the properties of asphalt binder like rut resistance parameters.

Table 1: Generic Types of Asphalt Binder Modifiers(Bahia et al., 2001)

Modifier Types	Class
Filler	Carbon black, Mineral (Hydrated Lime, Fly ash, Portland cement and Bag house fines)
Extenders	Sulfur, Wood lignin
Polymers-Elastomers	Styrene butadiene di-block SB, Styrene butadiene triblock/radial block (SBS), Styrene isoprene (SIS), Styrene butadiene rubber latex SBR, Ploy chloroprene latex, Natural rubber, and Acrylonite butadiene styrene (ABS)
Polymers-Plastomers	Ethylene Vinyl Acetate (EVA), Ethylene Propylene diene monomer (EDPM), Ethylene Acrylate (EA), Polyisobutylene, Polyethylene (low density and high density), Polypropylene
Crum rubber	Different sizes, treatments and processes
Oxidants	Manganese Compounds
Hydrocarbons	Aromatics, Naphthenic, Paraffinic/wax, Vacuum gas oil, Asphaltenes, shale oil, Tall oil, Natural asphalts
Anti-strips	Amines (Amido-amines and Polyamines), Hydrated Lime, Organo-Metallics
Process-based	Air blowing, steam distillation, Propane de-asphalted (PPA)
Fibers	Polypropylene, Polyester, Fiberglass, Steel, Reinforcement, Natural (Cellulose and Minerals)
Antioxidants	Carbamates (Lead and Zinc), Carbon black, calcium salts, hydrated lime, phenols, Amines

2.6 Effect of Modifiers on Asphalt Binder

As the asphalt binder is responsible for the viscoelastic behaviors of all bituminous materials, it plays a large part in determining many aspects of road performances. Resistance to permanent deformation and cracking (fatigue or thermal) are typical examples. In general the proportions of any induced strains in a bituminous material that is attributable to viscous flow (non-recoverable), increases with both loading time and temperature (Kumar and Khan, 2013, Prasad and J, 2015, Zaniwski and Pumphrey, 2004).

As stated in (Shell, 1990), one of the prime roles of asphalt binder modifier is to increase the resistance of the asphalt mixture to permanent deformation at high temperatures without adversely affecting the properties of the asphalt binder or asphalt at other temperatures. This could be achieved by either stiffening the asphalt binder so that viscoelastic response of the asphalt is

reduced with a corresponding reduction in permanent strain or by increasing the elastic component of the asphalt binder, thereby reducing the viscous component, which again results in a reduction in permanent strain. Increasing the stiffness of the asphalt binder is also likely to increase the dynamic stiffness of the asphalt mixture, thus improving the load distribution ability of the material and increases the structural strength and expected design life of the pavement. Alternatively, it may be possible to achieve the same structural strength but with a thinner layer. Increasing the elastic component of the asphalt binder will improve the flexibility of the asphalt mixture which is important where high tensile strains are expected (Shell, 1990).

2.7 Leather Production

Leather industry has been categorized as one of highly polluting industries and it has adverse impact on environment because of the generation of liquid, solid and gaseous wastes. Solid wastes generated from tanning industries contain different chemicals which are used during leather manufacturing process (Abajihad, 2012). These tannery solid wastes have different characteristics as different chemicals and mechanical processes are applied to the raw hides/skins. If these solid waste generated during various tanning operations are not properly utilized or disposed they are likely to cause a number of problems on the environment. If salt dust removed from preserved hide or skin is stored in heaps outside the tanneries or dumped in open dumping area, it is likely to be washed away during rains and cause groundwater pollution. Discharging hair waste and lime sludge wastes along with the effluents causes choking of drains. Raw and green fleshings, limed fleshings, splits (splitting waste) and trimmings decompose easily and give rise to noxious smells. In many tanneries, it is the foul odor which emanate from some of these decomposable solid wastes which accounts for much of the smell traditionally associated with tannery wastes. Some of the bio-degradable tannery solid wastes are sources of pathogenic bacteria and volatile organic compounds emission. Vegetable and chrome tanned shavings and splits do not easily decompose. If they are not utilized, problems of disposal are encountered (Abajihad, 2012).

Some of tannery solid waste contains chromium metal which is the most widely used in tanning industries as chromium salt and it causes carcinogenic effect when it enters human body through food chain (S.B.Kalaichelvi et al., 2015). Assessment of industrial solid waste management greatly varies depending on the nature of the industry, their location and mode of disposal of the waste. It is possible to divide leather industry processes of transforming raw hide to leather into four main stages (Abajihad, 2012):

i. Beam House Processes:

Generally, the conventional conversion process of hides/skins to leather involves 'do-undo' operations. The conserved skins/hides are first subjected to a trimming process for removing the unwanted parts called skin/hide trimmings, and then they are soaked to restore the lost water due to the common salt applied during curing process and to remove substances like dirt, blood and conservation salt at alkaline condition (pH ranging from 9.5 to 10.5) using wetting agents, sodium carbonate or sodium hydroxide. This is called soaking process. After soaking process the skins/hides are subjected to liming/un-hairing process which is treating the materials in alkaline (pH ranging from 12 to 13) solution of lime ($\text{Ca}(\text{OH})_2$) and sodium sulphide (Na_2S) to remove hair and swell up the skin/hide. After liming/un-hairing process the flesh and fat adhering to the hide/skin is removed by a mechanical process called fleshing process (Abajihad, 2012).

Another mechanical operation called splitting after fleshing process is applied most of the time to cattle hides to split into two or three layers or to remove some unwanted layers of the hide. De-liming is chemical process performed to decrease the pH to 8.0 to 9.0 so that to remove the lime added during liming process and to make the hide/skin more receptive to the chemicals that will be used in further stages. After de-liming process, hides/skins are exposed to an enzymatic effect for both opening up the structures of hides/skins, and the removal of unwanted proteins by a process called bating. Following the bating process, a degreasing process is applied for removing the excess natural fat using aqueous emulsification with detergents, or solvent extraction. After degreasing process the hides/skins are treated in a solution composed of salt and acids in acidic solution at an average pH of 2.5 so as to obtain a homogeneous distribution of tanning material that will be applied in the tanning process. This process is called pickling process and the product at this stage is named as pickle (Abajihad, 2012, J. Buljan, 2000).

ii. Tanning Processes:

After the hides/skins are conditioned as mention in the beam house process, the tanning process is applied with various tanning materials (materials able to form stable bonds with collagen) in order to provide the leather with a stable form and high thermal stability. Tanning materials such as vegetable tannins, mineral tanning materials and syntans (synthetic organic tanning materials) are used in tannage. Among mineral tanning materials, chrome tanning is the most widely used in leather production due to the unique features chrome that it gives to the leather; thermal stability. Chrome tanning is carried out in acidic solution at a pH ranging from 2.5 to 3.0. Aluminum and vegetable tanning materials are also widely used in leather production. The product of chrome tanning process is called as wet blue because of its color (Abajihad, 2012).

iii. Re-Tanning Processes:

At re-tanning stage the wet blue hide/skin is changed to crust leather. In this stage, structural differences within wet blue leathers are compensated to obtain uniform structure. It involves chemical and mechanical operations. The chemical process like neutralizing, re-tanning, and dyeing; and mechanical process like shaving, setting out and drying are applied subsequently.

Shaving is a mechanical process to even the hide thickness and permit greater precision than is possible by splitting while, neutralizing is removal process of the free acid present in the leather, to assure stability in heated conditions and resistant to boiling.

Re-tanning is a process done to give the material the required uniform fullness and ability to retain their consistency after the drying process that tend to flatten the hides and reduce their thicknesses. This is carried out at a pH ranging from 3.5 to 5.0. Moreover, Fat liquoring which is done to lubricate the dermic fibers to avoid gluing and to provide the finished article with fullness and softness is applied to the skins/hides.

Dyeing is a process of giving the required color characteristics. A good dyeing have good color uniformity, maximum color depth with the least amount of dye possible, good defect cover and high color and light fastness. The next mechanical process setting out which is a process of pressing the leather to reduce the residual moisture in the hide from 100% to 65-70% is conducted. It also helps the hide to be widened and the grain to be flattened. Finally, drying which is an operation to reduce the moisture content from 70% to 20-22% will be followed. It is performed in the company through vacuum drying, toggle frames, or overhead chain. After this stage, it is called as crust leather and prepared for finishing processes (Abajihad, 2012).

iv. Finishing Processes:

Finishing operation is the mechanical modifications on the appearance of the leather such as elasticity, softness and feels by applying an aesthetic covering polymeric film to the derma. Finishing operation involves surface coatings and mechanical operations. Some of the finishing processes are given as follows.

The first process is conditioning. It is a process to provide moisture in to the dried hide or skin to eliminate the occurrence of cracking for the next operation and followed by a process called staking which is mechanical operation applied to increase smoothness of the leather.

The next step is called milling which is a mechanical process to improve the softness of the leather and gives the grain a more precise design. A drum similar to the one used in the wet phases is used. Spreading on toggle frame is the subsequent process which is a useful operation of spreading out the hide under tension on the toggle frame and allow drying in a hot air tunnel for a short period of time, but long enough to reduce the humidity from 22-24% to 15-16%. The objective of this

operation is to take the advantage of the detachment of the fibers to spread and flatten the hides as much as possible.

Buffing is a mechanical operation to remove the grain completely and to obtain soft and opaque surface, to make the flesh side of the leather to be refine and smooth, or to remove a more or less significant amount of surface material from low quality hides while, impregnation is an operation aims at increasing the ability to adapt to the extension and compression caused by folding, generating a more elegant behavior.

Then, coating the application of natural or synthetic products, generally water-based, for coloring, covering, sealing effects and for giving body to the leather will be done and ironing that is pressing operation to make the leather smooth. It is performed in two different machines, flat presses that work in a discontinuous manner or cylindrical rotary presses that work in a continuous manner.

Finally, polishing which is the last finishing operation to provide a shiny appearance and pleasant feel will be applied.

The process of leather making from initial stage (Raw Hides/Skins) up to finished product (Leather) is shown on Figure 2 below.

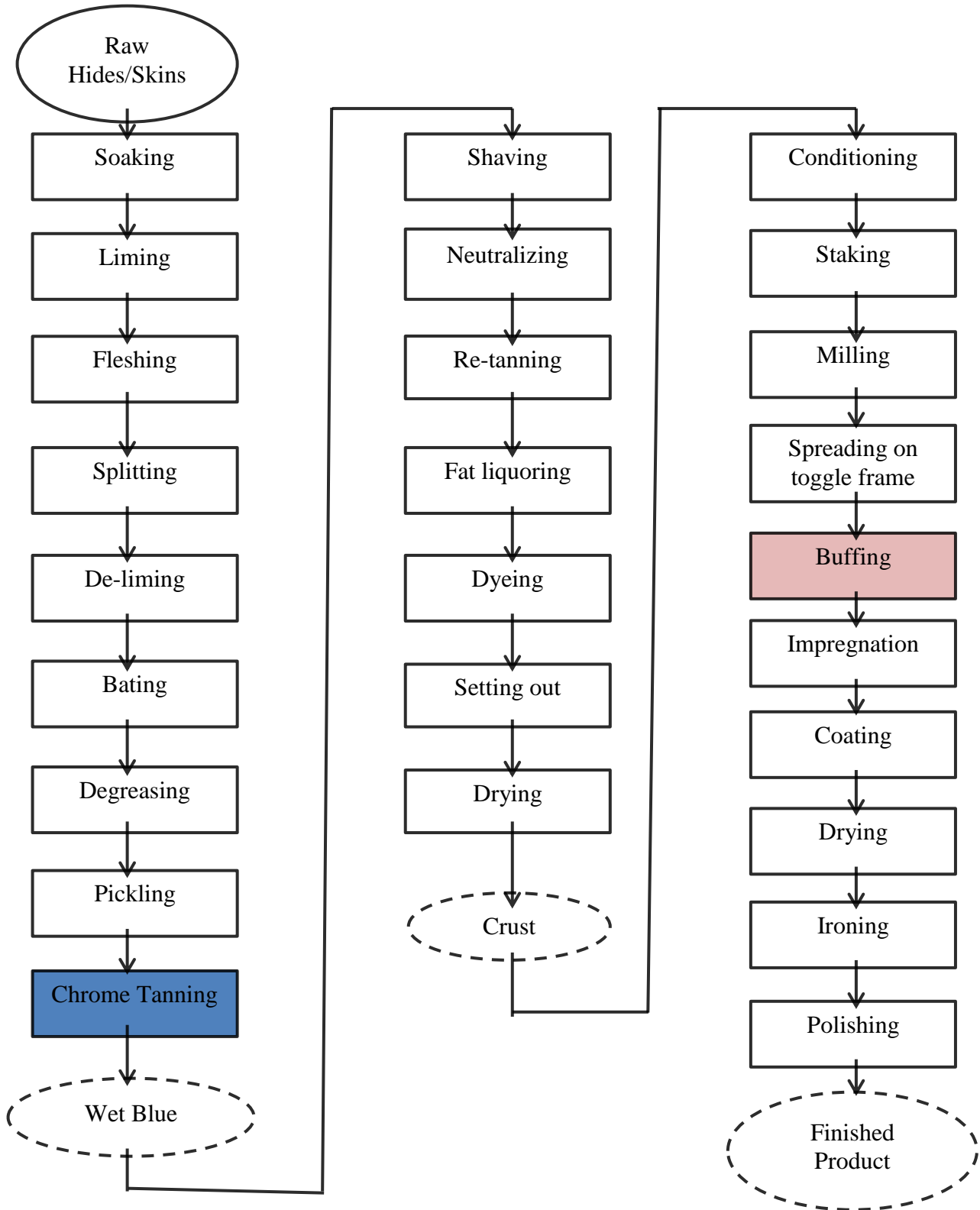


Figure 2: Leather Manufacturing Process Flow (Abajihad, 2012)

In Ethiopia, leather industry is a relatively older industry with more than 80 years of involvement in processing leather (UNIDO, 2012). Ethiopia is one of the leading countries that have the largest livestock populations in the world providing a strong raw material base for the leather industry. Its livestock population is estimated to be more than 52 million cattle, 24 million sheep and 23 million goats (CSA, 2012). About 80% of all hides and skins entering the formal market come from rural areas where they are collected by private traders. The remaining 20% are derived from slaughtering facilities found in major town and cities. About 15.5 million pieces of sheep and goat skins and 1.2 million pieces of cattle hides are supplied to the tanneries per annum according to data of 2016 which were collected from Ethiopian Leather Industry Development Institute.

The country has 29 tanneries which are currently involved in leather industry of which 27 of them are currently operating with an annual installed soaking capacity of 2.77 million hides and 45.75 million skins. According to the report obtained from ELIDI, the potential production per annum from these factories in same year was 45,746,400 skins and 2,774,800 hides while the actual production of these tanneries per annum in 2016 was 1,837,874 hides and 17,784,518 skins.

2.7.1 Leather Solid Wastes

Leather industry generates large quantities of solid wastes during leather processing and subsequently during effluent treatment. Although some of the wastes find limited applications, the safe disposal of the bulk of the solid wastes has posed serious problems. Out of which some portion of chromium containing hazardous wastes are also generated. These chrome containing wastes are categorized as hazardous wastes. The main sources of solid wastes are from trimming, fleshing, splitting and shaving processes. A further potential source of solid waste is the sludge from the effluent treatment plant (Abajihad, 2012).

Solid wastes generated from tanning industries, being highly polluting industrial wastes, should be managed in an environmentally safe way. But a report on benchmarking (Technology up-gradation) program in Ethiopian Tanning industry shows that the solid wastes generated from the tanning industries located in Addis Ababa city are collected, transported and disposed along with municipal solid wastes in open dumping area called “Koshe” or “Rapi” (Abajihad, 2012). This dumpsite is being used by the surrounding dwellers as a site for cultivation of habesha-gomen, Teff and for cattle grazing. As leather industries mostly use chrome sulphate for leather manufacturing process, some of the solid wastes generated from the industry contain chromium (Cr) which is one of the toxic heavy metals and known for contaminating ground water, soil, plants and causing carcinogenic effect on human health. This anthropogenic interference might harm the community as the chromium and other heavy metals are potentially toxic to crops, animals and humans when contaminated soils are used for crop production.

In addition to this, since the collection frequency of the municipality service is too low the solid wastes generated from the tanning industries stay in the factory compound for a long period of time that lets the wastes creates unfavorable environmental condition for the community working in the industry (Abajihad, 2012). The types of solid wastes generated in a tannery processing one ton of raw skins/hides have been quantified in Table 2.

Table 2: Nature and Quantity of Leather Solid Waste per 1ton of hides/skins

S.No	Nature of Solid Waste	Quantity (Kg)
1	Salt from handshaking	80
2	Salt from solar pans	220
3	Hair	100
4	Raw trimmings	40
5	Lime sludge	60
6	Fleshing	120
7	Wet blue trimmings	30
8	Chrome splitting	65
9	Chrome shaving	95
10	Buffing dust	65
11	Dyed trimmings	35
12	Dry sludge	125

For this research, CBD is considered for partial replacement of asphalt binder. While doing this its feasibility has to be checked. To perform this, the findings of researches done waste generation per 1ton of hide/skin were taken as a reference. In this regard, as per reports of several researchers 1ton of soaked hide/skin will generate up to 6kg (Sekaran et al., 1998, S.B.Kalaichelvi et al., 2015) of chrome buffing dust. The minimum value of CBD generated from 1ton of hide/skin (6kg/ton) from research papers is used while calculating the CBD quantity generated per 1ton of hide/skin. With this reference, the actual CBD quantity produced from Ethiopian leather factories by 2016 was estimated to be 244.8ton as shown in Table 3. This indicates that leather industry is among promising potential area to consider for utilizing the solid wastes like chrome buffing dust in hot mix asphalt mixture and its assessment to incorporate into pavement materials. The weight of skin is 1.217kg/pcs and hides 10.42kg/pcs.

Table 3: Chrome Buffing Dust

It.No	Description	Annual (Pcs)		Weight (ton)		Annual CBD (ton)
		Capacity	Actual	Capacity	Actual	
1	Skin	45,746,400	17,784,518	55,673.37	21,643.76	129.86
2	Hides	2,774,800	1,837,874	28,913.42	19,150.65	114.90
3	CBD					244.77

2.7.2 Chrome Buffing Dust use as Construction Material

(Kamaraj et al., 2016) reported that leather wastes can be used for the manufacture of bonded leather, leather boards, as a filler of carboxylate butadiene-acrylonitrile rubber. Considering the quantity of chrome shaving availability as solid waste (10-15%), and its reported to use as filler to form flexible material, the applicability of this waste was seriously considered for the preparation of micro surfacing pavement maintenance (Kamaraj et al., 2016). Micro surfacing is considered as more environment friendly alternative renewal treatment for preventive maintenance than conventional thin hot bituminous mixture. It is applied on the entire surface of the existing pavement, covering all the cracks and small defects and producing a skid resistant, durable and waterproofing surface. Micro-surfacing helps in preservation of pavement strength and therefore can be used both for preventive and periodic renewal treatment (Kamaraj et al., 2016). (S.B.Kalaichelvi et al., 2015) studied chrome buffing dust as bitumen modifier after pyrolysis of the CBD at a temperature of 400°C and suggested that utilization of chrome buffing dust with asphalt binder by 3%wt showed good physical properties of asphalt binder especially on penetration. But rheological tests which can predict better properties of an asphalt binder were not included in their study.

2.7.3 Chemical Composition of Chrome Buffing Dust

Chrome buffing dust (CBD) is a micro fined solid particulate impregnated with chromium synthetic fat and oil, tanning agents and dye chemicals (S.B.Kalaichelvi et al., 2015). (S.B.Kalaichelvi et al., 2015) have studied the elemental composition of chromium buffing dust (CBD) and reported that it contains C(41.86%), H(4.95 %), N(4.40 %) and S(14.59%) and moisture content of 9.35 % by weight. The chromium buffing dust was pyrolysed in an inert atmosphere at a temperature of 400°C to arrest oxidation from Cr_3^+ to Cr_6^+ . Residual ash from pyrolysis was stabilized with asphalt binder. During pyrolysis process, carbonization occurs. Hence there was increase in carbon content in the residual ash than its precursor. But the increases in nitrogen and sulphur percentages were attributed to the fact that usually higher temperature favors decarboxylation of carboxylates which leads to evolution of gases. Since the pyrolysis was done in zero oxygen atmosphere, trivalent chromium present in the CBD was not gotten oxidized to hexavalent chromium which was hazard. (S.B.Kalaichelvi et al., 2015) stated that Selhuraman

et.al (2013) also studied the elemental composition of buffing dust by exposing the leather to a process called double pyrolysis at temperatures of 450°C and 650°C. They found that CBD consists of C (55.31%), H (7.86%), N (12.56%), S (4.68%) and O (8.54%) by weight. Since the testing procedure for elemental analysis of chrome buffing dust is not established in Ethiopia, the results from different researches are used in this research.

2.7.4 Environmental Impacts of Chrome Buffing Dust

Solid wastes generated from tanning industries contain different chemicals which are used during leather manufacturing process. Some of the solid wastes generated during leather manufacturing are shaving dusts, chrome buffing dusts and splits. These tannery solid wastes have different characteristics as different chemical and mechanical processes are applied to the raw hides/skins. If these solid waste generated during various tanning operations are not properly utilized or disposed they will cause a number of problems on the environment. Salt dust or de-dusted salt if stored in heaps outside the tanneries or dumped in open dumping area is likely to be washed away during rains and cause groundwater pollution. Hair waste and lime sludge if discharged along with the effluents are likely to choke the drains. Raw and green fleshing, limed fleshing, splits (splitting waste) and trimmings putrefy easily and give rise to noxious smells. In many tanneries, it is the foul odor which emanate from some of these putrescible solid wastes which accounts for much of the smell traditionally associated with tannery wastes. Some of the bio-degradable tannery solid wastes are sources of pathogenic bacteria and volatile organic compounds emission. Vegetable and chrome tanned shavings and splits do not easily decompose (Abajihad, 2012).

Chrome tanning is the most common type of tanning process being practiced for the leather production around the world. Chrome buffing dust is a solid leather waste generated during the finishing stage of leather manufacturing. This product contains heavy metal called chromium which is toxic to human if it enters through food chain system. Chromium is carcinogenic in nature and causes clinical problems like respiratory tract ailments, ulcers, perforated nasal septum, kidney malfunction and lung cancer in humans exposed to the environment containing buffing dust particulates (S.B.Kalaichelvi et al., 2015).

When solid leather wastes like CBD are disposed in open landfills, it can cause the following environmental problems:

- Ground water contamination by leachate
- Surface water contamination by run-off
- Bad odor
- Acidity to surrounding soil

2.8 Summary

Generally, the literature review describes basic materials for modification of asphalt binder with different polymers, chemical modifiers and their effects on the properties of asphalt binder. And how modification or replacement of asphalt binder was introduced and the main reasons behind it. Fundamentally this research mainly focuses on utilization of chrome buffing dust as partial replacement of asphalt binder. The use of CBD as asphalt modifier has been applied in limited countries worldwide and it will be beneficial to conduct researches on its suitability for our country specially as we have potential of input resources and we have waste treatment concerns as well. After reviewing the previous studies related to utilization of CBD and other modifiers, materials are prepared for conducting laboratory tests.

CHAPTER 3: RESEARCH METHODOLOGY

3.1 Introduction

For this research, the type of methodology used is experimental method. There are two main parts of this experiment. The first part includes investigation of conventional properties (Penetration, Softening point and Ductility) of asphalt binder with CBD and the second part is investigation of rheological properties (AST, FST, PG and MSCR) of asphalt binder with CBD.

3.2 Materials

3.2.1 Asphalt Binder

Asphalt binder 60/70 penetration grade was used in this research. In order to evaluate binder properties the following laboratory tests have been performed. These tests include

- Penetration AASHTO T 49
- Softening point AASHTO T 53
- Ductility AASHTO T 51
- Rolling Thin Film Oven Test

3.2.2 Chrome Buffing Dust

For this research chrome buffing dust sample was collected from Awash Tanneries and chemical composition test results which were adopted from past researches, is presented in chapter 4.



Figure 3: Chrome Buffing Dust

3.3 Asphalt Binder Tests

3.3.1 Experimental Design

The experimental tests were performed on asphalt binder mixed with different percentages of CBD varying between 2%-10% by weight of the asphalt binder. First the asphalt binder was heated to a temperature of 130°C then the required amount of CBD was added to asphalt binder. The binder was mixed with CBD manually for 3-4 minutes at 130°C and then the prepared samples were continuously stirred for 25-30 minutes at a constant temperature of 150-160°C to ensure good homogeneity, and the following different tests were performed.

3.3.2 Conventional Tests

Different tests were performed on the prepared samples according to established standards to characterize the properties of asphalt binder mixed with different percentages of chrome buffing dusts by weight of the asphalt binder. The different percentages of CBD concentration employed in this process provides a wider range of results which helps in analyzing each type of the blend at that particular concentration. These tests include penetration at 25°C, softening point and ductility tests at 27°C.

a) Penetration

According to AASHTO T 49 a sample of about 100g of asphalt binder with CBD was heated to about 130°C in a sample cup for enough time to completely soften. Then it was transferred into a 15mm penetration test cup and allowed to cool to room temperature. The sample was then placed in a temperature controller set to 25°C and allowed to condition for about 1 hour. It was then removed, dried quickly and placed under the needle of the penetrometer. Then three readings were taken for a single penetration cup after placing tip of the penetrometer needle precisely at the surface of the cup before the instrument was started. The average of three samples were taken for each sample and recorded.

b) Softening Point

According to AASHTO T 53, the same samples were poured into two small brass rings and allowed to cool. A heated knife blade was used to trim the surface of the samples to the level of the brass rings. The prepared samples were then conditioned in a temperature controller at 4°C for at least 30 minutes before the test. A steel ball bearing (weighing 3.55 g) were centered on each specimen and placed in transparent glass jar. An electric heater and thermometer was fitted into the beaker filled with clean, distilled water. The temperature at which each binder specimen touches the base plate was recorded to the nearest degree. The average of the two readings were taken and rounded to the nearest whole degree.

c) Ductility

According to AASHTO T 51, the samples were heated to 130°C and poured in the mold assembly placed on a plate. The samples were cooled in the air and then in water bath at 27°C temperature. Then the excess binder was cut until the surface was leveled using a hot knife. Then the mold with assembly containing sample was kept in water bath of the ductility machine for about 90 minutes. The sides of the molds were removed, the clips were hooked on the machine and the machine was operated. The distance up to the point of breaking of thread is the ductility value which is reported in cm.

d) Rolling Film Oven Test

This ageing procedures were developed to subject an asphalt binder sample to hardening condition that approximately simulate the condition that occur in normal, hot mix facility operation. To address the issue of volatilization, the procedure incorporate a mass change determination. The change in mass is calculated based on the weight of the sample before and after ageing.

The RTFO procedure is performed by pouring 35 g of heated asphalt binder into a glass bottle. If mass change is required measure the bottle first then measure with original asphalt binder. After ageing measure the sample for the third time and report the result as a percentage (%).

$$\text{Mass change} = [(\text{Mass before ageing}) - (\text{Mass after ageing})] * 100 / \text{Mass before ageing}$$

To start the test, the sample bottles are placed in a vertical rotating carriage in an oven operating at 163°C and air pipe is connected with a compressor. The bottle carriage rotates at 15 rpm for a total time of 85 minutes. During rotation, a jet of air flow at the rate of 4 l/min blows into each bottle as it passes the bottom position in the carriage. After 85 minutes, any sample bottles being used for determining mass change are cooled to room temperature before the final weight is determined. The remaining bottles are then poured and scraped in to a single sample container for additional testing.

3.3.3 Dynamic Shear Rheometer (DSR)

As presented in literature review, neat and modified asphalt binders are viscoelastic materials, meaning that they simultaneously show the behavior of an elastic material (e.g. rubber band) and a viscous material (e.g. oil). The relationship between these two properties is used to measure the ability of the asphalt binder to resist permanent deformation and fatigue cracking. To resist rutting, asphalt binder needs to be stiff and elastic; to resist fatigue cracking, it needs to be flexible and elastic. The equilibrium between these two requirements is a critical one.

Asphalt concrete pavements subjected to repeated traffic loads increase the consolidation of the pavement structure after construction, thus causing depressions in the traffic wheel paths. Traffic induced rutting can also result from the lateral flow of the asphalt concrete materials in the wheel paths. Although the rutting potential of asphalt concrete pavements is influenced primarily by the quality of construction (compaction), mix design, and aggregate angularity and texture, the consistency of the asphalt binder must still be considered. Rutting is more prevalent at high service temperatures due to the increased fluidity of the asphalt binder, and the rutting potential of HMA pavements decreases with time since the asphalt binder stiffens with age hardening.

For this research, the Dynamic Shear Rheometer (DSR) was used to characterize the viscous and elastic behavior of asphalt binders at intermediate and high service temperatures. This was done by measuring the viscous and elastic properties of thin neat and modified asphalt binders samples sandwiched between an oscillating and a fixed plate. Operational details of the DSR will be as per AASTHO T-315-10 “Standard Test Method for Determining the Rheological Properties of Asphalt binder using DSR.

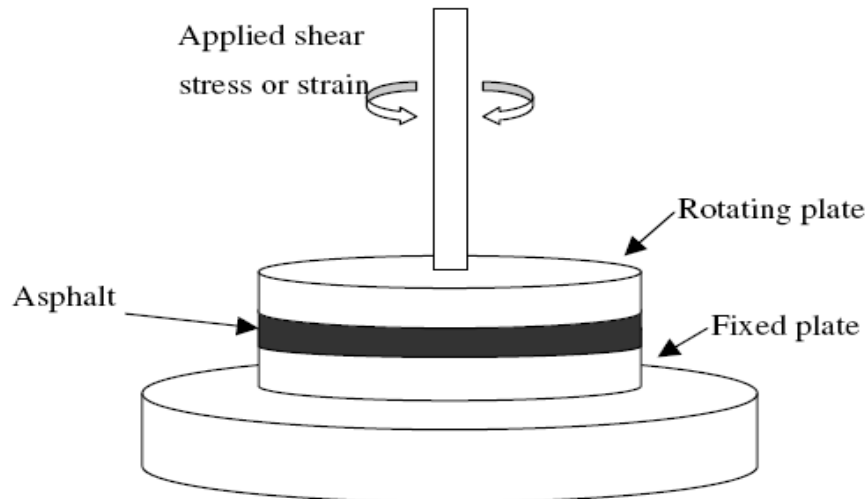


Figure 4: Configuration & loading mode of DSR(Zaniewski and Pumphrey, 2004)

The complex shear modulus, phase angle, and accumulated strain of asphalt binder, which are indicators of the asphalt’s resistance to shear deformation in the viscoelastic region, help predict the rutting potential and fatigue life of hot mix asphalt pavements (Petersen et al., 1994).

3.3.4 DSR Equipment

The apparatus used for the testing of neat and modified asphalt binders was a MARVEL BOHLIN INSTRUMENT called DSR (Figure 5). This rheometer is capable of measuring asphalt binder response over a large range of temperatures, frequencies, and strain levels. However, G^* (dynamic shear modulus, Pa) and δ (phase angle, degree), two important asphalt properties required by Super pave system, are calculated by the DSR software. Therefore, it is a simple matter of comparing results with requirements of the Super pave specification to determine compliance.



Figure 5: DSR

There are two types of dynamic shear rheometers: controlled stress and controlled strain. The controlled stress rheometers apply a sinusoidally varying stress and determine the resulting strain, while the controlled strain rheometers apply a sinusoidally varying strain and determine the resulting stress. Controlled stress rheometer is used for this research.

Various test geometries may be used, including parallel plates, cone and plate, and rectangular torsion. Parallel plate geometry is used for the specification testing because the specification measurements are in the region of linear behavior. Cone and plate geometry is required only when the test measurements are in the nonlinear region. The MARVEL BOHLIN INSTRUMENT DSR uses two different sized parallel plate sets for evaluating asphalt binder: 8mm diameter plates and 25mm diameter plates. For specification testing, parallel plates 8mm in diameter should be used at intermediate pavement design temperatures, 4 to 46°C, and 25mm diameter plate will be used for high temperatures, 46 to 82°C.

Because the properties of neat and modified asphalt binders are so temperature dependent, rheometers have a precise means of controlling the temperature of the sample. This is normally accomplished by means of a circulating fluid (water) bath, which normally surrounds the test specimen. The water is circulated through a temperature controller that precisely adjusts and maintains the sample temperature uniformly at the desired value during the entire testing period. The data acquisition unit records the test temperature, applied load, frequency and deflection angle

during the entire testing and sends the test data to the personal computer. The computer software reduces the data and calculates the shear stress, shear strain, complex modulus, phase angle, dynamic viscosity, and other parameters required by a specific project.

3.3.5 Asphalt Binder Specimen Preparation for Rheological Tests

The neat and modified asphalt binders are heated at around 130°C until fluid enough to pour. Then the heated asphalt is poured into a silicone mold 25mm in diameter as shown in Figure 6 and allowed to cool until solid enough to be removed from the mold.



Figure 6: Preparing Asphalt Specimens for the DSR testing

After removal from the mold, the asphalt disk is placed between the fixed plate and the oscillating spindle of the DSR for testing, as shown in Figure 7.

For further rheological tests, modified samples will be heated so that the hot mixture was poured into same silicone molds (25 mm in diameter) and allowed to cool until solid enough to be removed from the mold and tested with the DSR. Two specimen were used for each sample at specified testing conditions and the average values are reported.

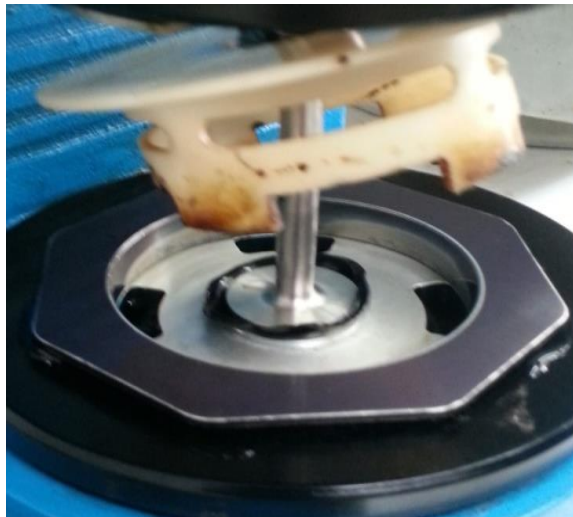


Figure 7: Asphalt binder sample placed on the fixed platen of the DSR

3.3.6 Dynamic Shear Rheometer (DSR) Tests

The rheological properties of the neat and modified asphalt binder were measured using the Dynamic Shear Rheometer (DSR), by conducting four types of tests: amplitude sweep test (AST) at single frequency of 1.596Hz, frequency sweep test (FST) from 25Hz to 0.1Hz, PG tests are conducted to determine the maximum temperature at which the asphalt binder fulfill AASHTO M-320 specification and multiple stress creep loading and recovery (MSCR) test at constant stress 0.1kPa and 3.2kPa (Petersen et al., 1994). The behavior of the materials is evaluated in terms of complex shear modulus G^* , rutting parameter $G^*/\sin\delta$, and phase angle δ for the four types of tests. Samples were tested at three temperatures (21.1°C, 37.8°C and 54.4°C) for AST and FST; higher temperature for PG and (52°C, 58°C, and 64°C) for MSCR test by MARVEL BOHLIN INSTRUMENT DSR which is found in AAiT highway laboratory. Each tests are performed using two specimens and the average values of those specimens are reported.

a) Amplitude Sweep Test (AST)

This test is performed to determine the Linear Viscoelastic Region of asphalt binders. The test is done at constant frequency of 10rad/s for varying shear stress amplitude. The tests were conducted at 21.1°C, 37.8°C, and 54.4°C and at each temperature, two samples for each percentages (2%, 4%, 6%, 8% and 10%) were used. While conducting the amplitude sweep test, 8mm parallel plates with a 2mm gap was used.

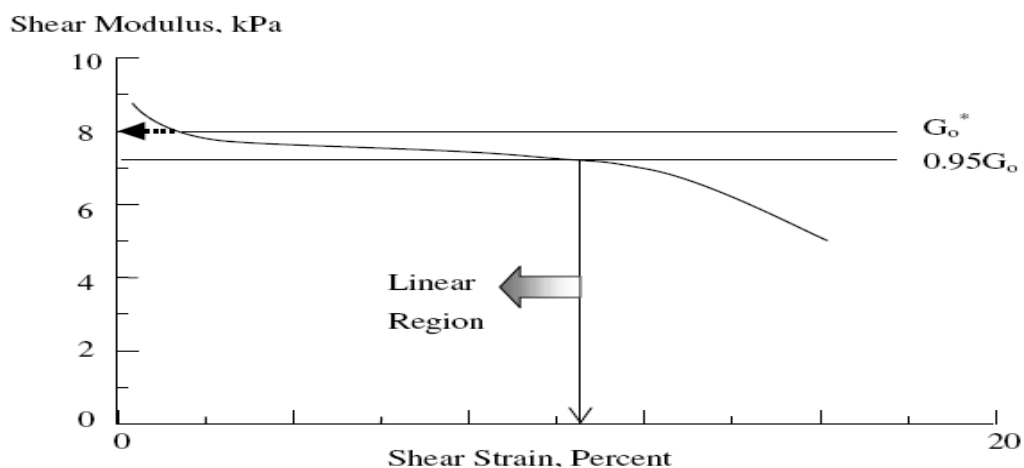


Figure 8: Linear viscoelastic region of asphalt binder ((Petersen et al., 1994)

Prior to mounting the asphalt binder specimen between the plates, the “zero gap” setting must be established at the test temperature because the frame and fixtures in the DSR change dimension with temperature. So for every 12°C temperature variation on the test, zero gap must be maintained.

The specimen preparation procedure requires the asphalt binder be heated until it is sufficiently fluid ($>130^{\circ}\text{C}$). After the asphalt sample is correctly placed in the DSR and the test temperature appears stable, ten minutes will be waited for the specimen to equilibrate to the test temperature. A controlled stress of 0.1 kPa to 9.90 kPa is applied representing traffic loading conditions. Finally, data will be generated by computer interconnected with the DSR equipment and complex shear modulus vs strain (%) will be plotted to obtain Linear Viscoelastic Region for every specimen. Amplitude sweep results are presented in Appendix A.

b) Frequency Sweep Test (FST)

During the frequency sweep test, the frequency is varied while the amplitude of the deformation or alternatively the amplitude of the shear stress is kept constant. DSR frequency sweep tests are designed to construct master curves of binder complex shear modulus (G^*) and phase angle (δ) (Petersen et al., 1994, Anderson et al., 1994). The master curves characterize binder rheological properties over a wide range of temperature or frequency.

Figure 9 shows complex modulus and phase angle versus frequency while testing with the DSR.

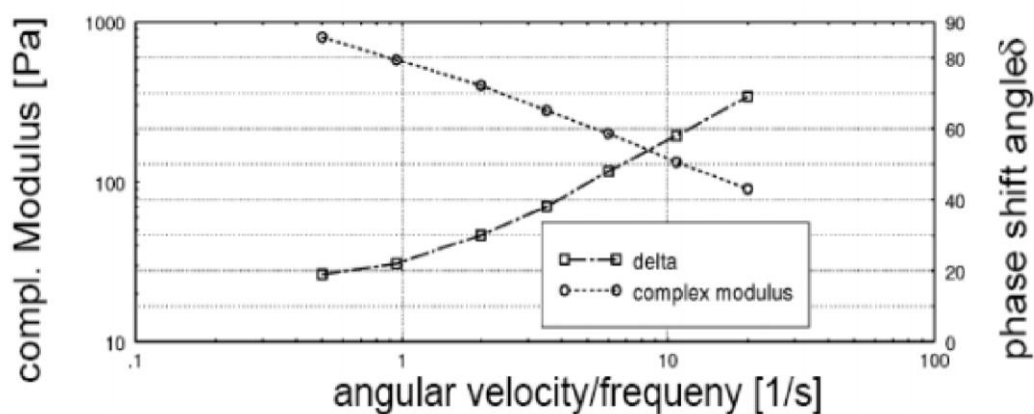


Figure 9: Complex Modulus vs Frequency

In this study, frequency sweep tests were performed on the asphalt binder (60/70) and modified asphalt binders at 21.1°C , 37.8°C , and 54.4°C . The tests were run on 8mm parallel plates with a 2mm gap after the samples were allowed to equilibrate for ten minutes at each temperature prior to testing. The frequency range applied was from 25Hz to 0.1Hz with initial stress of 0.1kPa. Two specimen were used for each sample at specified testing conditions and the average values are reported. Frequency sweep tests results are presented in Appendix B.

c) Performance Grading (PG) Determination Test

This test is conducted at high temperature to categorize the asphalt binder sample into a 6°C incremental performance grading system. A constant frequency 10 rad/sec is used; representing 80 km/hr speed on the highways. It was believed that the permanent deformation parameter $G^*/\sin\delta$ has good correlation with rut depth or rutting on the pavement. But studies show that there is poor relationship between $G^*/\sin\delta$ and rutting depth (Anderson, 2011). Therefore, in this

research $G^*/\sin\delta$ is only used for checking asphalt binder temperature resistance and to select temperature ranges where to conduct the MSCR tests.

The plate is 25mm and the gap is 1mm. After conditioning the specimen for 10 minute, the test begin with 10rad/s frequency. The temperature is adjusted manually as the asphalt binder specimen passes the first temperature. For Unaged binders, $G^*/\sin\delta$ should be greater or equal to 1.0kPa while for RTFO Aged $G^*/\sin\delta$ should be greater or equal to 2.2kPa. Two specimen were used for each sample at specified testing conditions and average values were reported.

d) Multiple Stress Creep Loading and Recovery (MSCR) Test

The MSCR test is conducted to evaluate the binder's potential for permanent deformation. It is the latest improvement on Superpave Performance Graded (PG) asphalt binder specifications. It is conducted after performing PG test and estimates the rut parameter of asphalt binders which usually happens at higher service temperatures.

A one-second creep load is applied to the asphalt binder sample. After the 1 second load is removed, the sample is allowed to recover for 9 seconds. Normally the test is started with the application of a low stress 0.1kPa for 10 creep/recovery cycles then the stress is increased to 3.2kPa and repeated for an additional 10 cycles. In the MSCR test, higher levels of stress and strain are applied to the binder, better representing what occurs in an actual pavement. This new high temperature test for asphalt binders was developed under the NCHRP, in order to address some concerns related to testing of polymer modified asphalt binders and field performance related issues (J.Zhang et al., 2015, Bahia et al., 2001).

The repeated shear creep loading tests that were performed in this study were a controlled stress test that applied constant shear stresses of 0.1kPa and 3.2kPa to samples having 25mm in diameter and using a 1mm gap between the platens. While conducting MSCR test, a constant stress is assigned and the time-related strain is measured and it is called shear compliance $J(t)$. It defines how compliant the specimen is: the higher the compliance the easier the sample can be deformed (Druta, 2006).

$$J(t) = \gamma(t)/\tau \quad (2)$$

Where $J(t)$ = Non-recoverable creep compliance (Pa^{-1})

γ = strain

τ = Applied Stress (Pa)

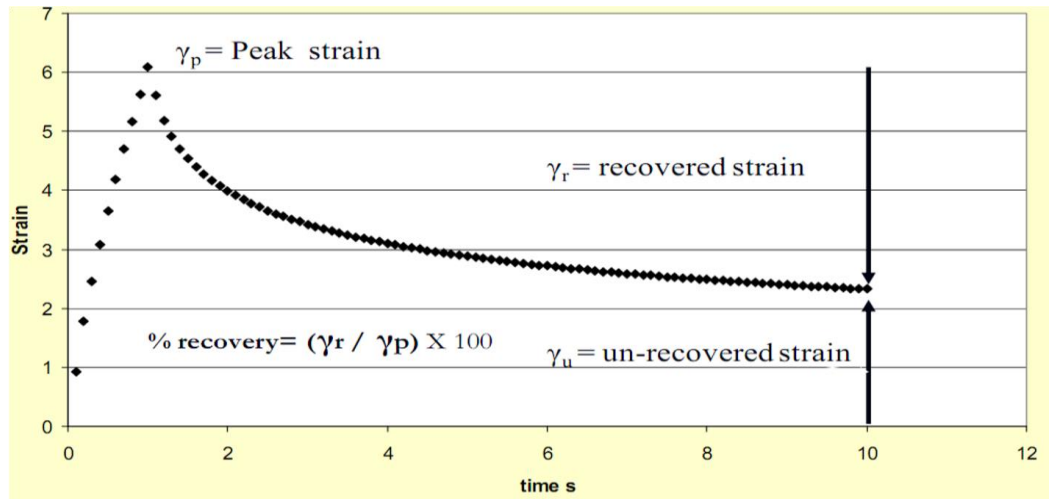


Figure 10: Strain vs time for MSCR Test

For this study, the tests were conducted on neat and CBD modified asphalt binders at five volume fractions of CBD, i.e. 2%, 4%, 6%, 8% and 10% at three temperatures 52°C, 58°C, and 64°C. Test results from the repeated shear creep loading and recovery are presented in Appendix C. Two sample specimen were tested for specified testing conditions and the average values are reported.

CHAPTER 4: RESULTS AND DISCUSSIONS

This chapter presents a discussion on the asphalt binders (neat and modified) tests results obtained in the laboratory from conventional (penetration, softening point and ductility) and rheological tests (Amplitude Sweep Test, Frequency Sweep Test, Performance Grading and Multiple Stress Creep and Recovery Test). The tests results are used to draw conclusions on the rheological and conventional properties of the neat and modified binders.

Material quality test result is show in Table 4.

Table 4: Neat Asphalt Binder Quality Test Results

Test	Result	ERA Specification
Penetration (0.1mm) at 25°C	61	60-70
Ductility (cm) at 27°C	100+	100+
Softening Point (°C)	47	46-56

Table 5: Chemical Properties of Chrome Shavings & Buffing Dust (Rajaram. J.et. al (2009))

Parameter	Value (%)
Moisture	7.92±0.22
Greases and oils	1.97±0.36
Ash	12.86±0.20
Chrome oxide	3.41±0.10
PH in water extract	4.15±0.20
Nitrogen	9.71±1.41
Protein	54.58±3.8
Decomposition temp (C)	323±10

4.1 Effect of chrome buffing dust on conventional properties of Asphalt binder

4.1.1 The Effect of CBD on Penetration

Different concentrations of chrome buffing dust have shown some improvements on the penetration properties of asphalt binder.

Table 6: Penetration Value for Unaged and RTFO Aged Binders

CBD (%)	Penetration(0.1mm)	
	Unaged	RTFO Aged
0	61	54
2	47	42
4	42	38
6	37	34
8	32	30
10	21	20

As the percentage of CBD increases, the penetration of an asphalt binder decreases up to 65% on average for both original and RTFO aged conditions. This shows that CBD has stiffened an asphalt binder. The result can be interpreted in two ways. First, the decrease in penetration value shows that the modified binder can have good load spreading capacity on high temperature ranges, and on other hand the material could lead to cracking at low and intermediate temperatures. So, the balance between the two effects should be considered while choosing specific percentage for use of CBD as asphalt modifier.

4.1.2 The Effect of CBD on Softening Point

Table 7: Softening Point for Unaged and RTFO Aged Binders

CBD (%)	Softening Point (°C)	
	Unaged	RTFO Aged
0	46	52
2	49	54
4	49	55
6	52	56
8	52	54
10	51	54

From the test results obtained, it can be perceived that addition of CBD has increased the softening point of the asphalt binder as CBD percentage increases. The increase in softening point shows that the modified asphalt binder reflect better rutting resistance at higher temperature (usually > 46°C). However, since this material can be used over a wide range of temperatures, the optimum value which can satisfy most binder properties should be checked. In regards to rutting resistance, the high temperature range is the region considered while evaluating the effect of CBD on softening point.

4.1.3 The Effect of CBD on Ductility

Table 8: Ductility for Unaged and RTFO Aged Binders

CBD (%)	Ductility (cm)	
	Unaged	RTFO Aged
0	103	103
2	55	52
4	47	45
6	39	37
8	31	30
10	23	22

The result of ductility test shows significant decrease in ductility values up on increasing percentage of CBD. The decrease in ductility value implies the breaking of the binder rapidly under a standard testing condition. The decrease in ductility value will result in poor adhesive properties of an asphalt binder. So, this material may show poor performance condition as its percentage increases.

4.1.4 Rolling Thin Film Oven Test

The result of RTFO test shows no significant difference in mass loss as show in Table 9.

Table 9: Mass Loss on RTFO Ageing

It.No	CBD (%)	Mass (gm)		Mass Loss (%)
		Before Ageing	After Ageing	
1	0	35	34.9	0.3
2	2	35	35	Nil
3	4	35	35	Nil
4	6	35	35	Nil
5	8	35	35	Nil
6	10	35	35	Nil

As observed from RTFO test results the mass loss for all binders is negligible. From the results witnessed the elements contained in CBD has some attractive bondage with volatile elements of an asphalt binder.

Overall, the modification of asphalt binder with CBD showed some improvement on the conventional properties of an asphalt binder and some caution are also drawn from the result analysis. Generally, as percentage of CBD increases, the asphalt binder stiffens which is a good characteristics of better load spreading potential, one the other hand since the ductility values decreased, it is an indication of poor adhesive properties of an asphalt binder. Therefore, the balance between stiffening and elasticity of an asphalt binder must be considered while choosing the specific percentage of CBD. To perform this, rheological test parameters are required which can better describe and evaluate viscoelastic nature of an asphalt binder.

4.2 The effect of CBD on the Rheological Property of Asphalt Binder

4.2.1 Amplitude Sweep Test (AST)

Asphalt binder is a viscoelastic material where its behavior is a continuous function of time and temperature. So performing test in a linear viscoelastic region assures that the test is repeatable

and results can be obtained using mathematical model. Amplitude sweep test is conducted to define the linear viscoelastic region (LVER) of an asphalt binder where the complex modulus is independent of stress and strain. A constant value of G^* is observed before it begins to decline and LVE strain limit can be calculated at the point beyond which the measured value of G^* decreased to 95% of its zero-strain. With this concept, the viscoelastic regions for Unaged and RTFO Aged Binders are calculated and shown in Table 10.

Table 10: Viscoelastic Region for RTFO Aged and Unaged Binders

It No	CBD	Temperature (°C)	Strain (%)	
			Unaged	RTFO Aged
1	0%	21.1	3.9	1.1
		37.8	21.4	11.3
		54.4	58.3	45.4
2	2%	21.1	2.8	1.1
		37.8	18.4	9.7
		54.4	55.8	43.5
3	4%	21.1	2.7	0.9
		37.8	14.3	5.7
		54.4	42.0	39
4	6%	21.1	2.0	0.7
		37.8	9.9	5.0
		54.4	38.9	38.3
5	8%	21.1	1.5	<0.5
		37.8	7	4.6
		54.4	39	34
6	10%	21.1	<0.5	<0.5
		37.8	7	4
		54.4	39	34

From Figure 11 and Figure 12, it is observed that Linear Viscoelastic Region of asphalt binder decreases as percentage of CBD increases. This shows that CBD has better stiffening effect on the asphalt binder which is beneficial at higher temperatures to resist permanent deformation.

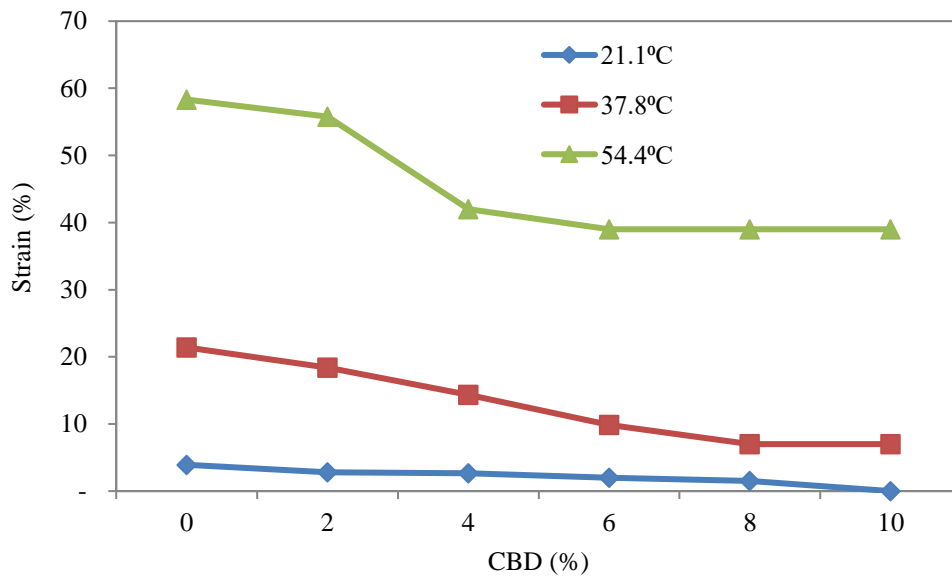


Figure 11: LVER for Unaged Binders

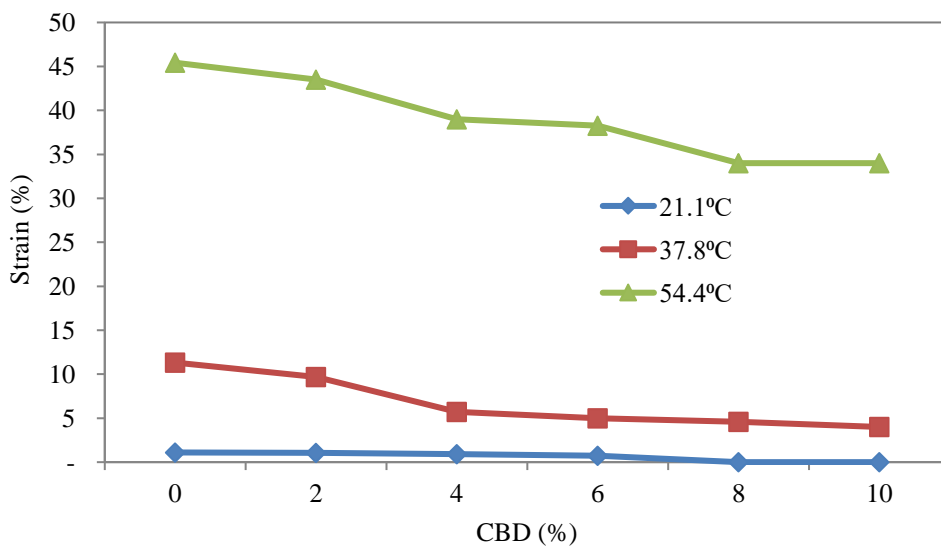


Figure 12: LVER for RTFO Aged Binders

4.2.2 Frequency Sweep Test Results (FST)

In general, multiple frequencies or frequency sweep tests are performed in order to construct the master curves that will determine the rheological properties of binders and mixes (Anderson et al., 1994, Petersen et al., 1994). Dynamic shear complex moduli at different test temperatures and frequencies could be determined by using the time-temperature superposition principle. In constructing the master curves using the time-temperature superposition principle, test data collected from the DSR at different temperatures and loading times, in terms of stiffness or shear complex modulus G^* , are compared to a reference temperature, which is 21.1°C in this case. The data at any other temperatures are then shifted with respect to time until various curves overlap almost perfectly to form a single master curve. Typically, the shear complex modulus or stiffness modulus of asphaltic mixes increases with decreasing temperature and increasing loading frequency. Thus, the technique of the determination of the master curve is based on the principle

of time-temperature correspondence, which uses the equivalence between frequency and temperature in order to determine the moduli of asphalt binders and mixes.

DSR data from the three testing temperatures (21.1°C, 37.8°C and 54.4°C) was used to construct the master curves for both neat and modified asphalt binders. The shifting was conducted using Williams-Landel-Ferry equation, which is normalized to the test temperature of 21.1 °C.

$$\text{Log}(G^*) = \delta + [\alpha / (1 + e^{(\beta + \gamma \log(fr))})] \quad (3)$$

$$\Phi = -90 * b d (\exp^{(c + d \log(fr))} / [(1 + e^{(\beta + \delta \log(fr))}]^2 \quad (4)$$

$$\text{Log}(a_T) = -C_1 (T - T_{ref}) / [C_2 + (T - T_{ref})] \quad (5)$$

Where G^* = dynamic modulus

fr = loading frequency at the reference temperature (reduced frequency)

Φ = phase angle

δ = minimum modulus value

$\delta + \alpha$ = maximum modulus value

β, γ = parameters describing the shape of the sigmoidal function

a_T = shift factor

T = temperature

T_{ref} = reference temperature

$b, c, d, C_1,$ and C_2 are model constants

In this research the master curves are constructed fitting a sigmoidal function to the measured complex modulus test data using nonlinear least squares regression, which can be done using the Solver Function in the Excel spreadsheet. The shifting could be done by solving shift factors simultaneously with the coefficients of the sigmoidal function, using any available shifting function to solve reduced frequency (fr) as a function of temperature. For complex modulus master curve, parameter γ influences the steepness of the function (rate of change between minimum and maximum) and β , the horizontal position of the turning point. Parameters β and γ , on the other hand, depend on the characteristics of the asphalt binder and the magnitude of δ and α (Anderson et al., 1994). Accordingly the DSR data from the three test temperatures (21.1°C, 37.8°C and 54.4°C) were used to construct the master curves for asphalt binder and asphalt binder containing chrome buffing dust both RTFO Aged and Unaged Binders, and the following shift factors have been developed to construct the master curves for complex modulus.

Table 11: Shift factors for Complex Modulus Master Curves for RTFO Aged and Unaged Binders

CBD (%)	Condition	α	β	γ	δ	$a_{21.1}$	$a_{37.8}$	$a_{54.4}$
0	Unaged	46.810	-1.742	-33.544	0.134	0.00	-1.404	-2.689
	RTFO Aged	42.540	-2.060	-31.770	0.181	0.00	-1.306	-2.520
2	Unaged	51.280	-2.220	-40.240	0.170	0.00	-1.300	-2.520
	RTFO Aged	41.250	-2.340	-31.220	0.200	0.00	-1.750	-3.070
4	Unaged	51.420	-2.120	-39.940	0.160	0.00	-1.240	-2.470
	RTFO Aged	42.100	-2.370	-31.900	0.180	0.00	-1.850	-3.220
6	Unaged	51.300	-2.340	-40.440	0.170	0.00	-1.680	-2.990
	RTFO Aged	42.110	-2.370	-31.890	0.190	0.00	-1.840	-3.240

Figures 13 and 14 below show the master curve for Unaged and RTFO Aged Binders.

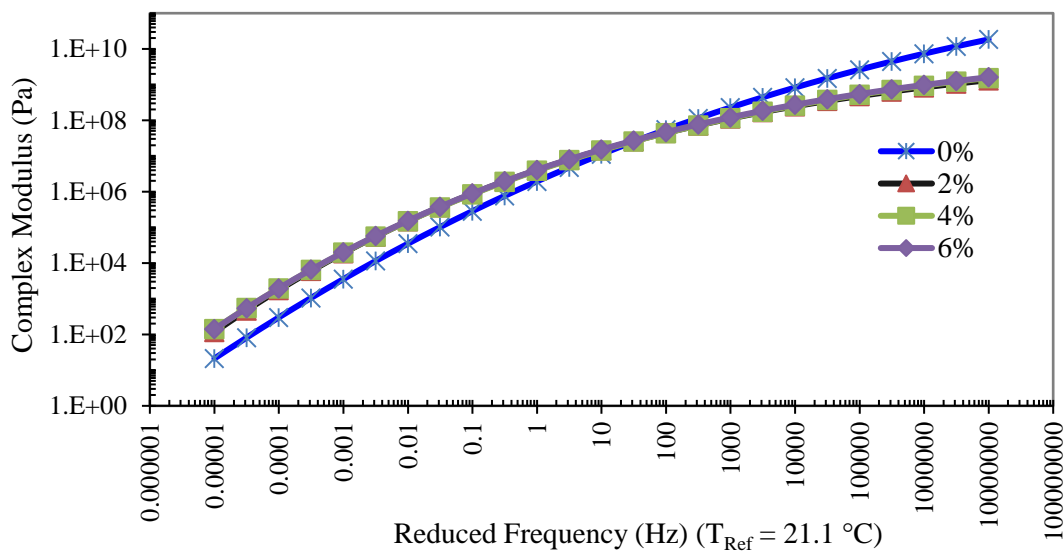


Figure 13: Complex Shear Modulus Master Curve for RTFO Aged Binders

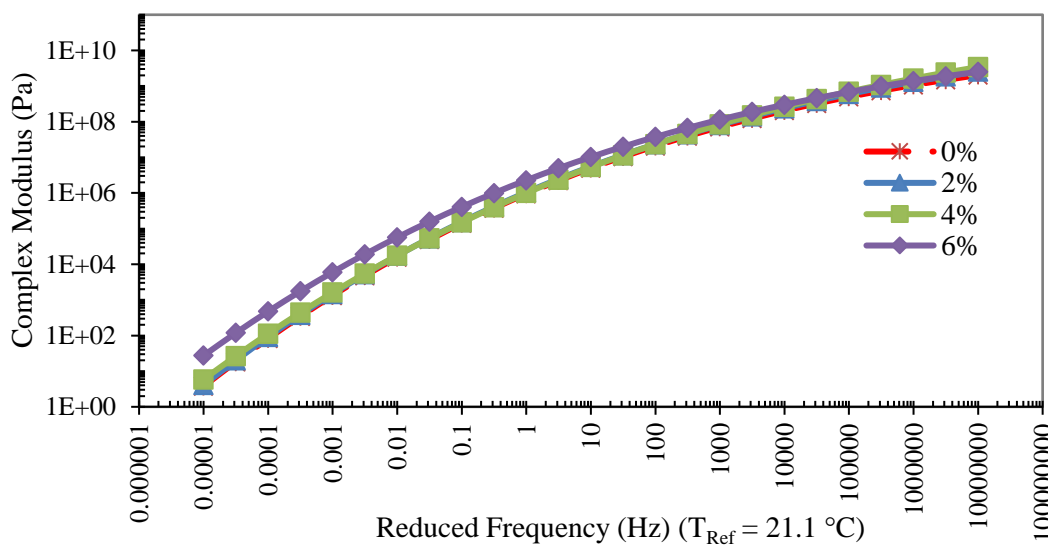


Figure 14: Complex Shear Modulus Master Curve for Unaged Binders

From the complex modulus master curve drawn, it is observed that addition of CBD to asphalt binder showed improvement for low frequencies range (higher temperature) and doesn't improve for intermediate and high frequency ranges (lower temperature). From the results observed, CBD has improved the potential of an asphalt binder to resist permanent deformation in high temperature range (>46°C)

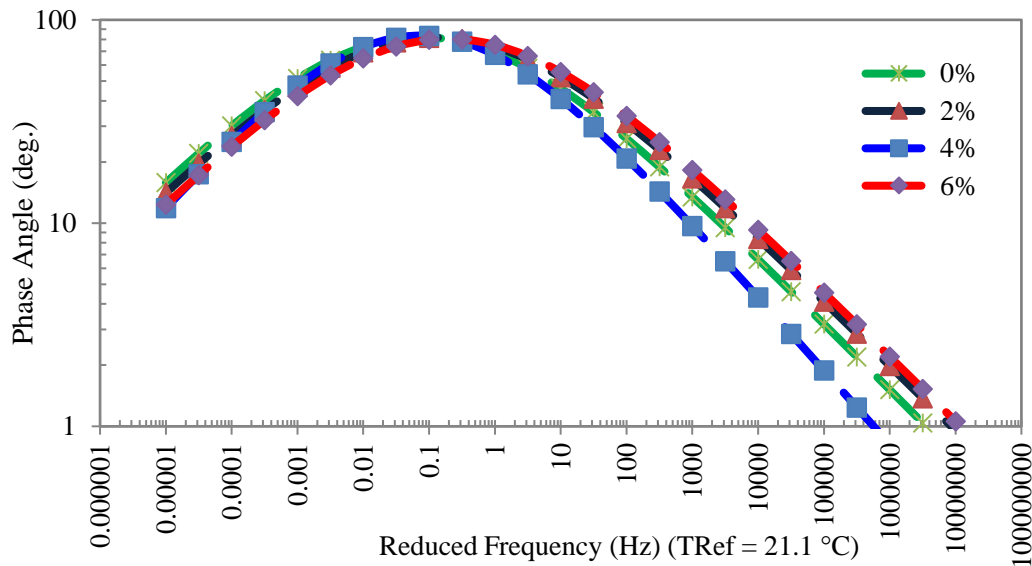


Figure 15: Log-Log Phase Angle Master Curve for Unaged Binders

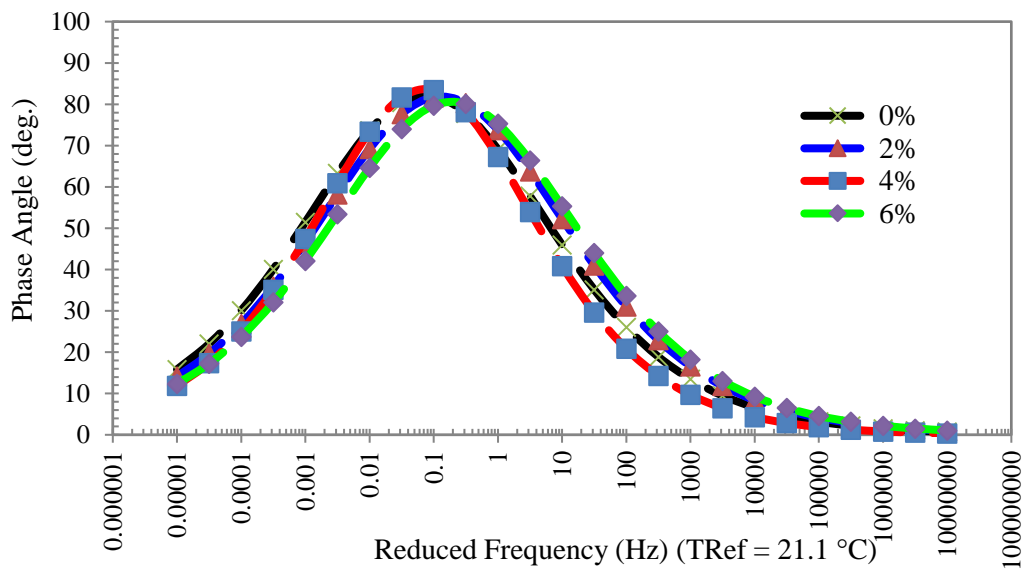


Figure 16: Semi-Log Phase Angle Master Curve for Unaged Binders

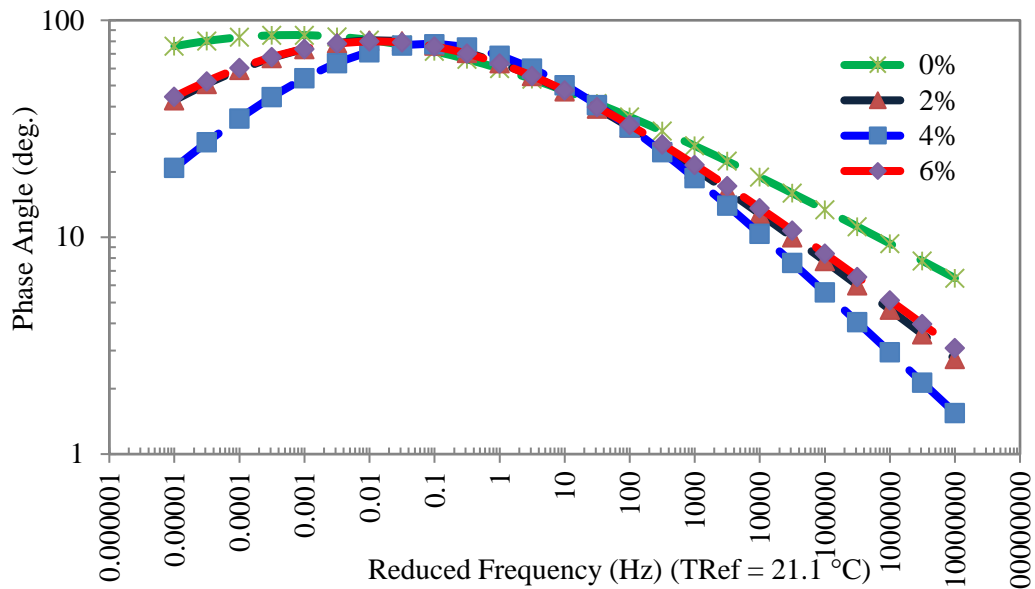


Figure 17: Log-Log Phase Angle Master Curve for RTFO Aged Binders

Moreover, black space diagram is plotted to check data consistency. Figure 18 and Figure 19 below present the black space diagram for Unaged 6% CBD and RTFO Aged 4% CBD at three temperatures 21.1°C, 37.8°C, and 54.4°C.

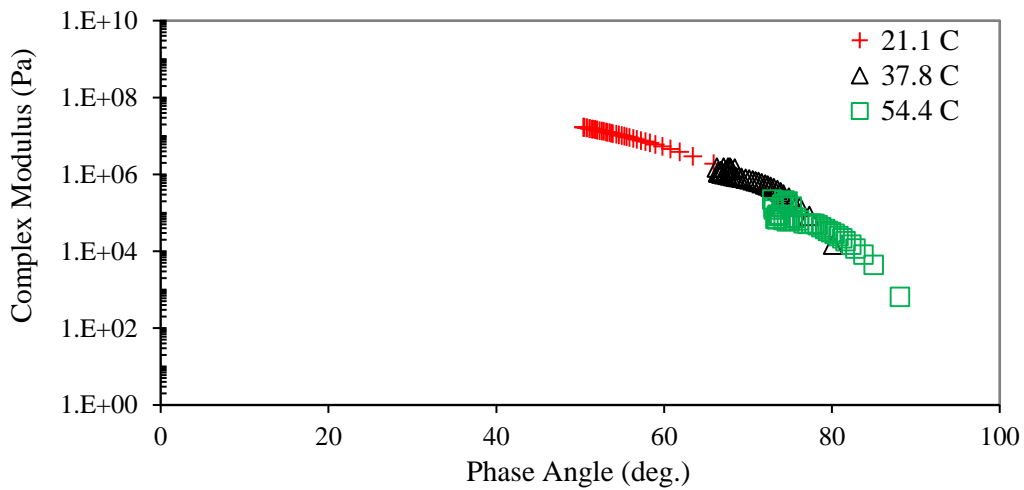


Figure 18: Black Space Diagram for Unaged 6% CBD

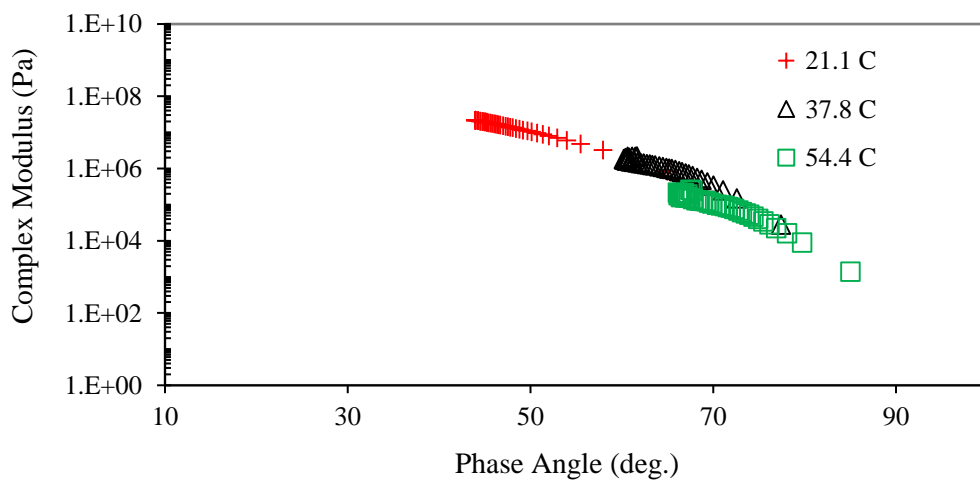


Figure 19: Black Space Diagram for RTFO Aged 4% CBD

Statistical Analysis of FST Result Using ANOVA

Statistical analysis of FST results using Analysis of Variance (ANOVA) succeeding the laboratory procedures and data analysis, was performed to evaluate the significance of addition of CBD to asphalt binder using one-way analysis of variance.

There are different types of test analysis that could be used to observe the significance of CBD addition to asphalt binder. T-test is used to compare two variables, while F-test is used to compare two or more variables at a time. When an F test is used to check a hypothesis concerning the means of three or more populations, the technique is called analysis of variance (commonly abbreviated as ANOVA). The reason why F-test is chosen over t-test is that first, when we are comparing two means at a time, the rest of the means under study are ignored. With the F test, all the means are compared simultaneously. Second, when we are comparing two means at a time and making all pairwise comparisons, the probability of rejecting the null hypothesis when it is true is increased, since the more t tests that are conducted, the greater is the likelihood of getting significant differences by chance alone. Third, the more means there are to compare, the more t tests are needed. For this paper F-test is used since we have six samples to compare (0%, 2%, 4%, 6%, 8% and 10%).

With the F test, two different estimates of the population variance are made. The first estimate is called the between-group variance, and it involves finding the variance of the means. The second estimate, the within-group variance, is made by computing the variance using all the data and is not affected by differences in the means. If there is no difference in the means, the between-group variance estimate will be approximately equal to the within-group variance estimate, and the F test value will be approximately equal to 1. The null hypothesis will not be rejected. However, when the means differ significantly, the between-group variance will be much larger than the within-group variance; the F test value will be significantly greater than 1; and the null hypothesis will be rejected.

For test of the difference among three or more means, the following hypotheses should be used:

H_0 (Null Hypothesis): $\mu_0 = \mu_2 = \mu_4 = \mu_6 = \mu_8 = \mu_{10}$

H_1 (Alternative Hypothesis): At least one mean is different from the others.

The degrees of freedom for this F test are d.f.N. = k-1, where k is the number of groups, and d.f.D. = N-k, where N is the sum of the sample sizes of the groups $N = n_1 + n_2 + \dots + n_k$. The sample sizes need not be equal. The F test to compare means is always right-tailed.

Between Group Variance

$$S^2_B = \frac{\sum n_i (X_i - X_{GM})^2}{(k-1)} \quad (6)$$

Where S^2_B = between group variance

n_i = number of sample size

X_i = Mean of individual samples

X_{GM} = Grand mean of all samples

k = number of groups

Within Group Variance

$$S^2_w = \frac{\sum (n_i - 1) S_i^2}{\sum (n_i - 1)} \quad (7)$$

Where S^2_w = within group variance

S_i^2 = variance for each samples

n_i = number of sample size

Therefore, F-test is calculated by dividing the between group variance to within group variance.

$$\mathbf{F-Value} = \frac{S^2_B}{S^2_w} \quad (8)$$

Six groups of independent variables i.e. 0%, 2%, 4%, 6%, 8% and 10%, were considered in this paper. The ANOVA consists of two random samples from each of six independent groups. And the null hypothesis (H_0) is that the neat asphalt binder and the five percentages of chrome buffing dust are equally effective. This means, there is no rheological behavior change in asphalt binder up on addition of different percentages of chrome buffing dust. Therefore the null hypothesis $H_0: \mu_0 = \mu_2 = \mu_4 = \mu_6 = \mu_8 = \mu_{10}$, whereas the alternative hypothesis H_1 : at least one percentage has a change in rheological property of asphalt binder up on addition of chrome buffing dust. This analysis testing of the hypothesis is done at ($\alpha=0.05$) level of significance at three frequencies i.e. at 10^7 , 10 and 10^{-5} Hz. This frequency range is taken to represent low, medium and high rate of loading conditions.

The degree of freedom for between group variance is $6-1=5$ and degree of freedom within group variance is $12-6=6$. From the ANOVA, the results are summarized and presented in the table below. Details of ANOVA hypothesis testing is presented in Appendix E of the research paper.

Table 12: Summary of ANOVA hypothesis testing at specified frequencies

Frequency(Hz)	k-1	N-k	F-Value	P-Value	F Critical	Decision
10^{-5}	5	6	17.75	0.0066	4.39	Reject
10			3.41	0.0883		Accept
10^7			1.78	0.1520		Accept

The decision to accept or reject the null hypothesis is made by comparing the test statistics computed F with the critical value from the table. If the computed F value exceeds the critical value, the hypothesis is rejected; if not, the hypothesis is accepted. The ANOVA result for FST result i.e. Master Curve, indicates that the F value exceeds the critical value for frequency of 10^{-5} Hz at $\alpha=0.05$ level of significance. While for 10Hz and 10^7 Hz the reverse is true, the critical value exceeds the calculated F value. Therefore the null hypothesis is rejected for frequency of 10^{-5} Hz and accepted for frequencies of 10Hz and 10^7 Hz.

When the null hypothesis is rejected using the F test, more analysis will be conducted to know where the difference among the means is. Several procedures have been developed to determine where the significant differences in the means lie after the ANOVA procedure has been performed. Among the most commonly used tests are the Scheffé test and the Tukey test.

Scheffé Test

To conduct the Scheffé test, you must compare the means two at a time, using all possible combinations of means. For example, if there are three means, the following comparisons must be done:

\bar{X}_1 versus \bar{X}_2 , \bar{X}_1 versus \bar{X}_3 and \bar{X}_2 versus \bar{X}_3

$$F_s = (\bar{X}_i - \bar{X}_j)^2 / S_w^2 [(1/n_i) + (1/n_j)] \quad (9)$$

Where, \bar{X}_i and \bar{X}_j are the means of the samples being compared, n_i and n_j are the respective sample sizes, and S_w^2 is the within-group variance. To find the critical value F' for the Scheffé test, multiply the critical value for the F test by $k - 1$:

$$F' = (K-1) (C.V.)$$

Tukey Test

The Tukey test can also be used after the analysis of variance has been completed to make pairwise comparisons between means when the groups have the same sample size.

The symbol for the test value in the Tukey test is q . For simplicity q is denoted as F -calculated in this paper.

$$F\text{-calculated} = (\bar{X}_i - \bar{X}_j)^2 / \text{sqrt}(S_w^2 / n) \quad (10)$$

Where \bar{X}_i and \bar{X}_j are the means of the samples being compared, n is the size of the samples, and S_w^2 is the within-group variance. When the absolute value of F is greater than the critical value for the Tukey test, there is a significant difference between the two means being compared.

The Scheffé test is the most general, and it can be used when the samples are of different sizes. Furthermore, the Scheffé test can be used to make comparisons such as the average of \bar{X}_1 and \bar{X}_2

compared with \bar{X}_3 . However, the Tukey test is more powerful than the Scheffé test for making pairwise comparisons is to use the Tukey test when the samples are equal in size and the Scheffé test when the samples differ in size. Since the sample sizes taken for this research are equal, Tukey test is used for comparison among the control and other samples.

Table 13: Summary of Tukey Test

Group	F-Calculated			F
	f=10 ⁷	f=10	f=10 ⁻⁵	
0 & 2	0.42	2.01	8.77	4.39
0 & 4	2.13	1.35	11.38	
0 & 6	2.83	2.42	9.74	
0 & 8	0.34	1.36	3.80	
0 & 10	0.21	1.57	3.65	

From the statistical analysis made, chrome buffing dust from 2-6% on asphalt binder affects the rheological property of asphalt binder at low frequency, i.e $f=10^{-5}$ or high temperature region in such a way that it improves the rutting resistance potential of an asphalt binder while it doesn't have an effect at high frequency (low temperature) and intermediate temperature. On the other hand, 8-10% CBD addition has no significant effect on the rheological behavior of asphalt binder based on the results of ANOVA at all frequency ranges. So, these two samples were neglected. But some results are shown for documentation purpose only.

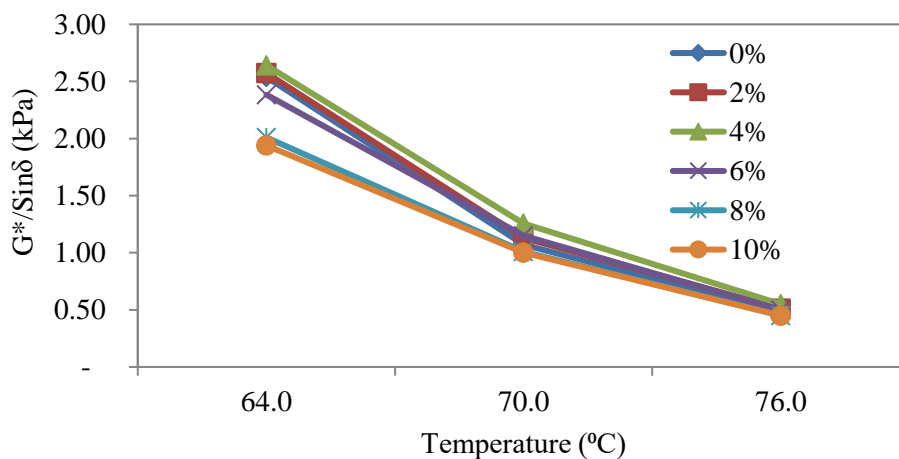
4.2.2 Performance Grade Determination

Basically, $G^*/\sin\delta$ was recommended as the Super Pave specification parameter to give a measure of the rutting resistance of asphalts. The higher the G^* value, the stiffer and thus the more resistant to rutting the asphalt binders will be. The lower the δ value, the more elastic the asphalt binder, that makes the asphalt binder more resistant to permanent deformation. The minimum specification limit for Unaged Binders is 1kPa and all binders are checked against the requirement.

Table 14: PG Determination for Unaged Binders

Temperature (°C)	CBD (%)	Phase Angle (deg)	Complex Modulus (kPa)	$G^*/\text{Sin}\delta \geq 1.0$ (kPa)	Remark
64	0	86.7	2.28	2.28	Pass
	2	86.8	2.31	2.31	Pass
	4	85.6	2.37	2.38	Pass
	6	86.3	2.30	2.30	Pass
	8	86.5	2.01	2.01	Pass
	10	86.5	1.94	1.94	Pass
70	0	87.7	1.01	1.01	Pass
	2	87.5	1.06	1.06	Pass
	4	86.5	1.18	1.18	Pass
	6	87.1	1.06	1.06	Pass
	8	87.1	1.01	1.01	Pass
	10	87.1	1.0	1.0	Pass
76	0	87.9	0.48	0.48	Fail
	2	87.7	0.51	0.51	Fail
	4	86.7	0.55	0.55	Fail
	6	87.5	0.50	0.50	Fail
	8	87.21	0.45	0.45	Fail
	10	87.65	0.45	0.45	Fail

From the test results obtained, all asphalt binders at unaged condition fall into PG70-XX category. In order to classify the asphalt binder by Performance Grading, the asphalt binder has to fulfill all criteria at Unaged, RTFO Aged and Pressure Ageing Vessel condition. Due to lack of testing equipment, Pressure Ageing Vessel test was not done for this study. So, Unaged and RTFO Aged conditions have been checked for PG classification.


 Figure 20: $G^*/\text{sin}\delta$ for Unaged Binders

In similar test procedure, the PG determination for RTFO Aged Binders for all sample were done and the results are shown below in Table 15.

Table 15: PG Determination for RTFO Aged Binders

Temperature (°C)	CBD (%)	Phase Angle (deg)	Complex Modulus (kPa)	$(G^*/\sin\delta) \geq 2.2$ (kPa)	Remark
64	0	85.6	3.06	3.07	Pass
	2	84.3	3.8	3.82	Pass
	4	84.2	3.74	3.76	Pass
	6	84.8	3.72	3.74	Pass
	8	84.8	3.29	3.31	Pass
	10	84.9	3.08	3.09	Pass
70	0	87.1	1.30	1.30	Fail
	2	85.8	1.83	1.84	Fail
	4	85.4	1.81	1.82	Fail
	6	86.3	1.77	1.77	Fail
	8	86.5	1.49	1.50	Fail
	10	86.7	1.46	1.46	Fail

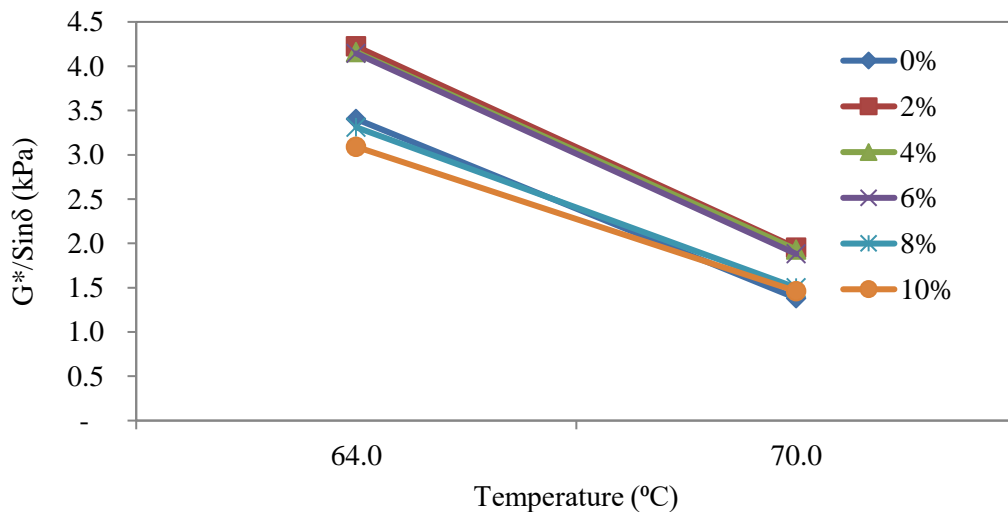


Figure 21: $G^*/\sin\delta$ for RTFO Aged Binders

The rut-parameter ($G^*/\sin\delta$) requirement according to AASHTO MP1 for asphalt binder at RTFO Aged condition must be greater or equal to 2.2kPa. In this regard, the $G^*/\sin\delta$ value of asphalt binders which fulfill the requirement is obtained at 64°C. Since the result of $G^*/\sin\delta$ is satisfied both for unaged and RTFO aged conditions at PG 64-XX, the performance grade of all samples is PG64-XX. The performance grading rutting resistance $G^*/\sin\delta$. criteria has weak correlation with field condition like rut depth (Petersen et al., 1994, Anderson et al., 1994). So, another high

temperature test which can better predict the performance of an asphalt binder for high temperature range was developed by AASHTO.

4.2.3 Multiple Stress Creep Loading and Recovery (MSCR) Test

PG asphalt binder rutting resistance parameter $G^*/\sin\delta$ is based on complex modulus and doesn't correlate well with field rutting measurements. Since G^* is measured in the linear viscoelastic range and rutting is a non-linear failure, a better test parameter was required. The NCHRP Project 9-10 was initiated in order to address some of these concerns, and lead to the development of a new high temperature test for asphalt binders called the repeated shear creep test. The MSCR test is performed using the Dynamic Shear Rheometer by applying controlled shear stresses of 0.1kPa and 3.2kPa for 1 second load followed by a 9 second rest period. During each cycle, the asphalt binder reaches a peak strain and then recovers before the shear stress is applied again. The permanent strain is then accumulated for 10 cycles (or 100 seconds).

For this study, MSCR tests were conducted on control and modified asphalt binders at three temperatures 52°C, 58°C and 64°C and six volume fractions of CBD, i.e. 0%, 2%, 4%, 6%, 8% and 10%. However, the J_{nr} value for 8% and 10% CBD is greater than 4kPa^{-1} which is the maximum limit for standard traffic class for PG64-xx; so the results are neglected. However, the MSCR test results of J_{nr} values for all proportions of CBD is presented in Table 17.

J_{nr} and PR values are calculated using the formulas listed below when every sample is subjected constant stress loads of 0.1kPa and 3.2kPa at required temperatures.

$$J_{nr(0.1)} = \sum_{N=1}^{10} [J_{nr}(0.1, N)] / (10) \quad (11)$$

$$J_{nr(3.2)} = \sum_{N=1}^{10} [J_{nr}(3.2, N)] / (10) \quad (12)$$

$$PR_{(0.1)} = \sum_{N=1}^{10} [\epsilon_r(0.1, N)] / (10) \quad (13)$$

$$PR_{(3.2)} = \sum_{N=1}^{10} [\epsilon_r(3.2, N)] / (10) \quad (14)$$

Where

$$J_{nr(0.1)} = \epsilon_{10}/0.1$$

$$J_{nr(3.2)} = \epsilon_{10}/3.2$$

ϵ_{10} = the strain value at the end of recovery portion

$J_{nr(0.1)}$ = average non-recoverable creep compliance at 0.1kPa

$J_{nr(3.2)}$ = average non-recoverable creep compliance at 3.2kPa

$J_{nr(0.1, N)}$ = non-recoverable creep compliance at 0.1kPa

$J_{nr(3.2, N)}$ = non-recoverable creep compliance at 3.2kPa

$\epsilon_{r(0.1, N)}$ = percent recovery at 0.1kPa

$\epsilon_{r(3.2,N)}$ = percent recovery at 3.2kPa

N = number of cycles

PR = Percentage Recovery

The maximum Jnr value for standard grade traffic designation for PG64-xx is 4kPa^{-1} . If heavy traffic is expected the specification requirement is changed, i.e. a lower Jnr value is required to reflect the deformation resistance potential of the pavement for the anticipated traffic load, but testing is still done at maximum temperature. This approach eliminates grade bumping which is applied to PG determination, for high traffic or slow moving vehicles road network. It can be achieved by modifying the asphalt binder without changing the PG grade. Table 16 presents AASHTO 332, which specify maximum Jnr values for the corresponding traffic load (ESALs) and speed.

Table 16: Traffic Designation AASHTO M-332

Traffic Designation	Traffic Level(ESALs)	Load Rate (Km/hr)	Jnr@3.2kPa
Standard Traffic "S"	<10Million	>70	4.0
Heavy Traffic "H"	10-30Million	20-70 (Slow)	2.0
Very Heavy Traffic "V"	>30Million	<20	1.0
Extremely Heavy Traffic "E"	>30Million	<20 and Standing	0.5

Non-recoverable creep compliance (Jnr) is calculated by dividing unrecoverable strain (γ) to the applied stress (τ). The $PR_{3.2}$ which gives information about binder elastic behavior is recoverable strain/ unrecoverable strain times 100. A summary of MSCR test results for all asphalt binders are presented in Table 17.

Table 17: Rutting Parameter (Jnr) and Percentage Recovery (PR) RTFO Aged Binders

CBD (%)	Temperature (°C)	Jnr(1/kPa)		PR (%)	
		0.1kPa	3.2kPa	0.1kPa	3.2kPa
0	52	0.39	0.39	13.96	9.16
	58	1.22	1.30	12.48	2.59
	64	3.13	3.56	8.67	0.98
2	52	0.27	0.27	17.74	13.69
	58	0.81	0.90	12.71	5.50
	64	1.89	2.28	11.06	2.16
4	52	0.26	0.28	20.76	14.32
	58	0.75	0.84	14.75	6.22
	64	1.93	2.33	11.65	2.16
6	52	0.29	0.32	16.54	10.65
	58	0.88	1.01	12.98	4.53
	64	2.08	2.35	8.84	1.59
8	52	0.80	0.91	9.90	8.57
	58	1.50	1.77	5.75	2.14
	64	3.48	4.10	5.05	0.75
10	52	0.85	1.06	8.96	7.60
	58	1.52	1.69	5.03	1.72
	64	3.74	4.20	4.08	0.69

The non-recoverable compliance increases as temperature increases. While the recoverable percentage decreases as temperature increases for all binders. Compared to the control asphalt binder, the mixing of CBD with neat binder shows good improvement in non-recoverable compliance. The addition of CBD to asphalt binder decreased the non-recoverable compliance which means CBD has improved the rutting resistance potential of an asphalt binder. The creep compliance value decreased up to 32% for 2% CBD, 33% for 4% CBD and 25% for 6% CBD, while it doesn't decrease for 8% and 10%.

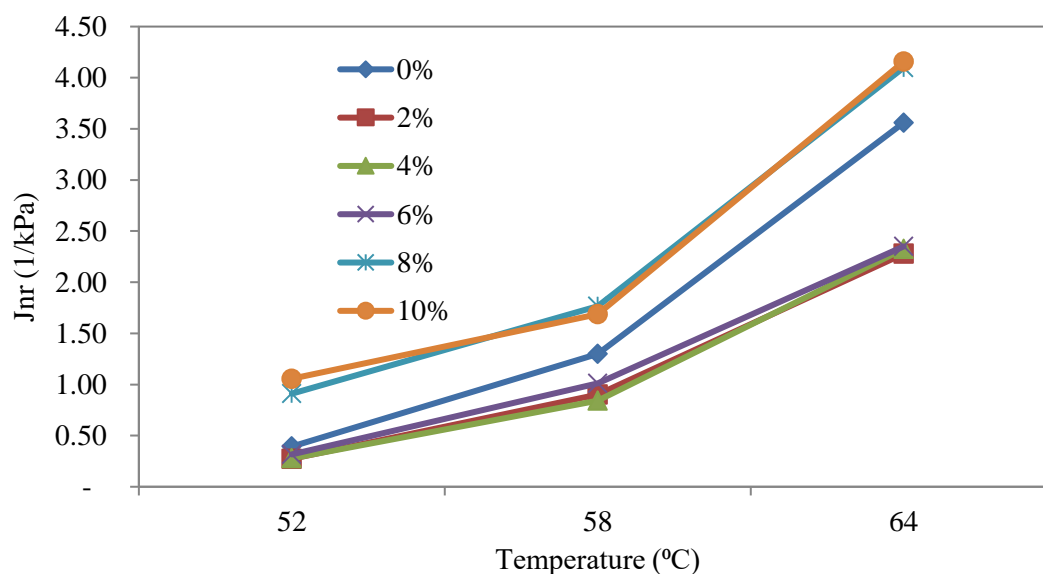


Figure 22: Jnr for RTFO Aged Binders

The non-recoverable creep compliance J_{nr} is temperature dependent. It will increase as the testing temperature increases. In this research the modified binders show good improvement on compliance measure. So, all binders show good potential for rut resistance except 8% and 10%.

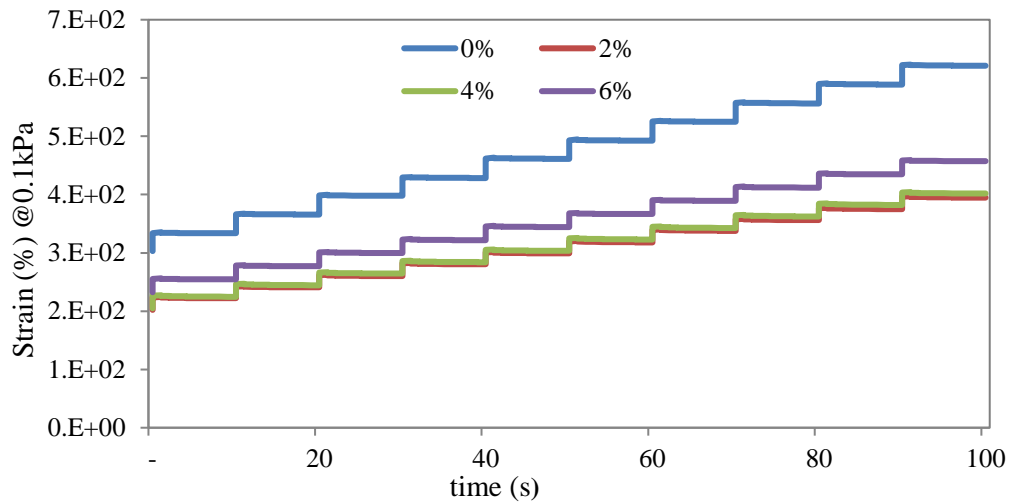


Figure 23: Strain for RTFO Aged Binders @ 64°C

From Figure 33, it can be said that addition of CBD has decreased the strain developed in asphalt binder due to multiple creep load application at higher temperature which simulates traffic loading condition. The strain developed in the asphalt binder has direct relationship with the non-recoverable compliance J_{nr} . So, decreasing the strain level will decrease the non-recoverable creep compliance which in term improves the resistant to permanent deformation of asphalt binders. 2% and 4% CBD have shown better improvements compared to the control asphalt binder.

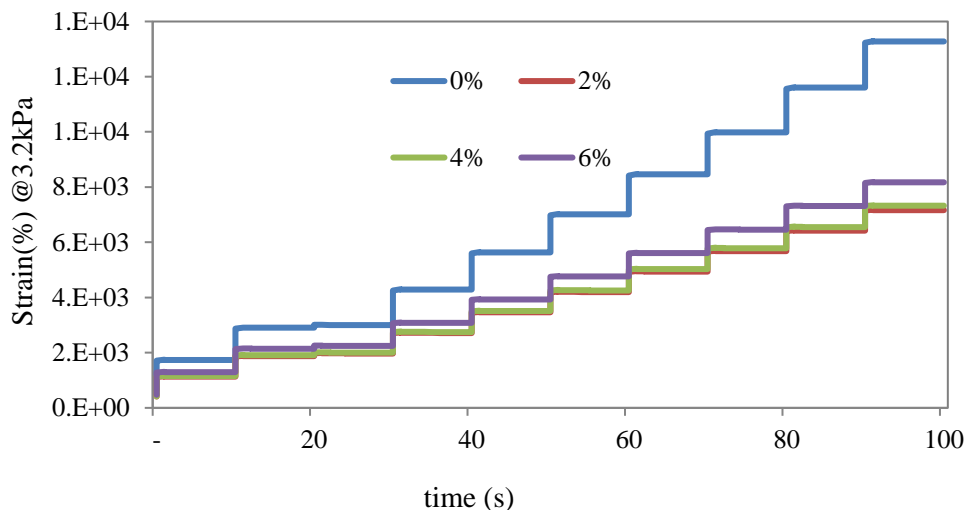


Figure 24: Strain for RTFO Aged Binders @ 64°C

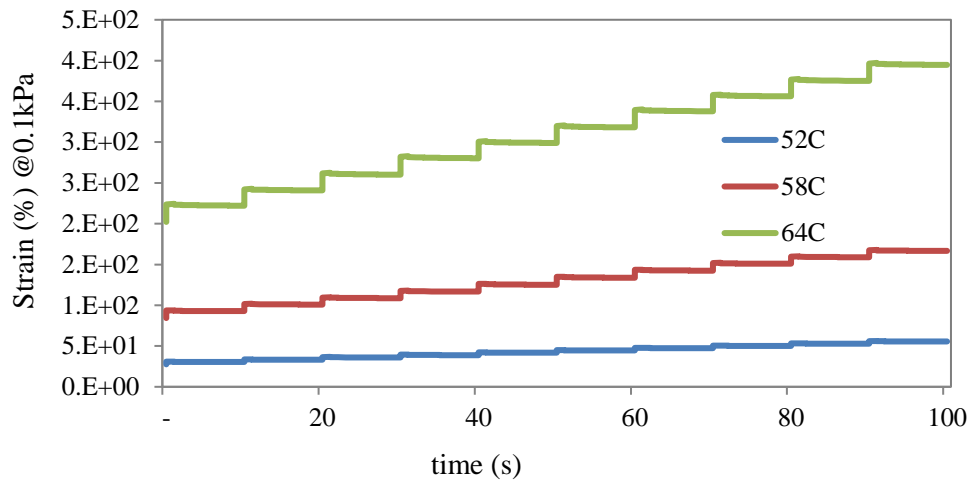


Figure 25: Strain for RTFO Aged 2% CBD

4.2.4 Summary of Test Results Analysis

From the test results of conventional and rheological test parameters, the modification of asphalt binder with CBD has stiffening effect on asphalt binder as percentage of CBD increases, but the elasticity of the asphalt binder will decrease which could lead to fatigue cracking and fretting at intermediate temperature (4-46°C) and low temperature ranges (<4°C).

Based on the laboratory study presented in this chapter, the following conclusions can be drawn. The penetration value increased, the softening point decreases, the ductility decreases as the CBD content increased. The effect of CBD on Penetration and softening point is the indication of better improvement on rut resisting and load spreading capacity of the material, while the result observed from ductility tests is precautionous that as percentage of CBD increases the adhesive property of an asphalt binder is affected in such a way that its adhesive nature decreases. This could lead to fatigue cracking of an asphalt binder at intermediate temperature.

From rheological tests (AST, FST, PG and MSCR), the test results can be summarized as follows.

- The LVER of the binder decreased as the CBD content increased. So, asphalt binder is stiffened. This indicates that asphalt binder has good potential for load distribution.
- At high temperature range and low loading frequency conditions the stiffness of the binder increased as the percentage of CBD increased which shows addition of CBD improves rutting resistance performance of an asphalt binder.
- The strain value and the rutting parameter J_{nr} decreases as the CBD content increases which implies that addition of CBD in asphalt binder reduces rutting of asphalt pavements. The J_{nr} value of PG 64-XX, decreased up to 33% up on modification of asphalt binder with CBD. The J_{nr} value is a good indicator of rut parameter. As the J_{nr} value increases, the potential of an asphalt binder to resist permanent deformation decreases and vice-versa.

4.2.5 Economic Benefits

Based on the improvements observed for rutting resistance effect of CBD on asphalt binder, a simple and rough calculations are made to indicate the economic benefits that might be obtained.

Assumptions

- The carriage way width which requires HMA is assumed to be two way single lane asphalt road with 7m width
- Optimum asphalt binder required is assumed to be 5.5%
- Density of HMA is assumed to be 2,570kg/m³
- HMA thickness is assumed to be 50mm
- CBD generated per year from Ethiopian leather factories on average is 245ton
- 4% CBD is taken for this analysis

Using the above data 1km asphalt road requires 631.93ton of asphalt mixture of which 34.76ton is asphalt binder. When we use 4% CBD for modification, 1km of asphalt road requires 1.39ton of CBD. So, the annual liberated amount of CBD i.e. 245ton will cover around 176km per year for new asphalt road construction by modification of asphalt binder. Therefore, the amount of cash that would be budgeted for 245ton asphalt binder would be substantially saved per year as Ethiopia imports asphalt binder from overseas. As the Federal Government of Ethiopia is giving attention to industrial sector, the number of leather factories in Ethiopia will increase and the solid wastes generated will definitely increase as well. Moreover, the routine and periodic maintenance of asphalt paved roads can benefit from utilizing this product. Therefore, the cost savings of this product can have its positive impact on the budget required for roads built in Ethiopia.

4.2.6 Safety Cautious while using CBD

The current practice for disposal of solid wastes generated from leather industries is open land fill. Since the CBD material has some health concerns like cancer, kidney malfunction, and respiratory problems when Cr³⁺ is converted into Cr⁶⁺, safety precautions are necessary to be developed.

The following procedures should be taken into consideration during the process of mixing and laying the HMA which composes CBD material.

- 1) Every personnel who has close proximity to CBD shall wear hand gloves in order to avoid any contact with the CBD material
- 2) Safety shoes shall be worn to avoid direct contact with CBD
- 3) Every personnel should wear Mouth and Noise protectives to avoid inhaling of gaseous material that would come out of the mix at mixing and laying temperatures.
- 4) Eye Goggle should be worn for protectives against any gaseous emissions that would come out of the mix

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

The main goal of this research study is to partially replace asphalt binder with chrome buffing dust in order to have more economical pavement structure and utilize locally available material. Accordingly, it has been found that the addition of chrome buffing dust to asphalt binder has shown promising results on most conventional and rheological properties of asphalt binder.

5.1 Conclusions

This research study tries to learn the conventional and rheological properties of neat asphalt binder and binder mixed with different proportions of chrome buffing dust. Based on the results obtained from this study, the following conclusions can be made:

- Modification asphalt binder with CBD showed that as percentage of CBD increases, the penetration values decreased up to 40% on average and the softening point increased up to 10% on average. So, its effect indicates that the modified binder is stiffened which result in better rutting resistance performance.
- From FST test results obtained, the master curve shows an improvement in the behavior of asphalt binder up on modification with CBD. It increases the stiffening property of asphalt binder at high temperatures ($>46^{\circ}\text{C}$). So, CBD improved the potential of an asphalt binder to resist permanent deformation at higher temperatures.
- From the MSCR test result acquired, the smallest total strain value is obtained at 2% and 4% CBD. The J_{nr} values decreased up to 33%. Therefore modification of asphalt binder with CBD indicates promising result in improving the rut resistance of asphalt pavements.
- Since, 2% and 4% CBD showed similar improvement on the creep compliance parameter J_{nr} value (rut resistance criteria), 4% CBD can be considered as optimum content from economic aspect.

In general the replacement of asphalt binder with CBD has shown promising results in affecting the overall properties of asphalt binder. Therefore, this material can be considered for modification/replacement of asphalt binder up to 6%.

5.2 Recommendations

Based on the study results the following recommendations are made.

- Chrome buffing dust can be considered as asphalt binder modifier since it improves the stiffness of an asphalt binder and its rut resisting performance.
- CBD material can be used for routine and periodic maintenance projects as the quantity required and its implementations are relatively easy for such projects
- Due to economic benefit and environmental concerns that will be caused by CBD, its utilization is recommended. However, further studies should be conducted for verification and to understand the wide range of CBD materials.

5.3 Future Studies

Since the researches done on CBD mixed with asphalt binder is limited, it is wide open to conduct more researches on the area of asphalt binders and mix characterization. For this reason, future research work may include:

- Further studies on the characterization of binders composed of CBD and neat asphalt binder using different grade bitumen and mix.
- Further investigations are needed to determine the Optimum CBD content.
- Further studies can be done on other leather solid waste products like shaving dust mixed with binder.
- Life cycle cost analysis can be conducted for control and CBD modified binders.

REFERENCES

- ABAJIHAD, Z. 2012. *ASSESSMENT OF TANNERY SOLID WASTE MANAGEMENT AND CHARACTERIZATION*
A Case of Ethio-Leather Industry Private Limited Company (ELICO). Master's of Science, ADDIS ABABA UNIVERSITY.
- ALEBACHEW, F. 2005. *Pavement Distresses on Addis Ababa City Arterial Roads, Causes and Maintenance Options*. Masters of Science, Addis Ababa University Faculty of Technology.
- ANDERSON, D. A., CHRISTENSEN, D. W., BAHIA, H. U., DONGRE, R., SHARMA, M. G., ANTLE, C. E. & BUTTON, J. 1994. *Binder Characterization and Evaluation*. DC Washington: SHRP National Research Council.
- ANDERSON, R. M. 2011. *Understanding the MSCR Test and its Use in the PG Asphalt Binder Specification*. Asphalt Institute
- ASPHALTINSTITUTE 2007. *Asphalt Hand Book*, USA.
- BAHIA, H. U., HANSON, D. I., ZENG, M., ZHAI, H., KHATRI, M. A. & ANDERSON, R. M. 2001. *Characterization of Modified Asphalt Binders in Superpave Mix Design*. Washington, DC.
- CSA 2012. *Ethiopia Information on The Leather Sector*.
- DRUTA, C. 2006. *A MICROMECHANICAL APPROACH FOR PREDICTING THE COMPLEX SHEAR MODULUS AND ACCUMULATED SHEAR STRAIN OF ASPHALT MIXTURES FROM BINDER AND MASTICS*. PhD, Louisiana State University and Agricultural and Mechanical College
- ERA 2013. *Pavement Design Manual*, Addis Ababa, Ethiopia: Ethiopian Roads Authority.
- J. BULJAN, G. R. A. J. L. 2000. *MASS BALANCE IN LEATHER PROCESSING*.
- J.ZHANG, WALUBITA, L. F., FARUK, A. N. M., KARKI, P. & SIMATE, G. S. 2015. Use of the MSCR test to characterize the asphalt binder properties relative to HMA rutting performance - A laboratory study. *Construction and Building Materials*, Vol.94, pp.218-227.
- KAMARAJ, C., LAKSHMI, S., ROSE, C., MANI, U., PAUL, E., MANDAL, A. B. & GANGOPADHYAY, S. 2016. Experimental Study on Micro Surfacing using Chrome Shaving Impregnated with Modified Bitumen Emulsion. *Journal of Scientific & Industrial Research*, Vol. 75, pp.378-382.
- KUMAR, P. & KHAN, M. T. 2013. Evaluation of Physical Properties of Sulphur Modified Bitumen and its Resistance to Ageing. *Elixir International Journal*, pp.13104-13107.
- LESUEUR, D. & ESPAÑA, E. 2009. *The Colloidal Structure of Bitumen: Consequences on the Rheology and on the Mechanisms of Bitumen Modification*. Madrid, Spain.

MAHABIR, P., JHUNARANI, O. & SIDDHARTH, P. 2016. Development and Evaluation of Sulfur Modified Bitumen Binder. Proc. of the Eighth Intl. Conf. on Maintenance and Rehabilitation of Pavements, 2016 Singapore. Singapore: Research Publishing, pp.774-783.

PARK, P. 2012. *Characteristics and Applications of high-performance fiber reinforced asphalt concrete*. PhD, The University of Michigan.

PETERSEN, J. C., ROBERTSON, R. E., BRANTHAVER, J. F., HARNSBERGER, P. M., J. J. DUVALL, S. S. K., ANDERSON, D. A., CHRISTIANSEN, D. W., BAHIA, H. U., DONGRE, R., ANTLE, C. E., SHARMA, M. G., BUTTON, J. W. & GLOVER, C. J. 1994. Binder Characterization and Evaluation. Washington, DC: Strategic Highway Research Program National Research Council.

PRAJNA, P. & ANJUM, M. I. 2015. Suitability of Sulfur as Modifier in Bitumen for road construction. *International Journal of Research in Engineering and Technology*, Vol. 4, pp.32-37.

PRASAD, A. R. & J, S. N. 2015. Bituminous Modification with Waste Plastic and Crumb Rubber. Vol.12, pp.108-115.

S.B.KALAICHELVI, K.MOHANDOSS & G.SEKARAN 2015. Studies on Utilization of Chromium Impregnated Buffing Dust as a Modifier in Bitumen. Vol. 02, pp.1247-1253.

SEKARAN, G., SHANMUGASUNDARAM, K. A. & MARIAPPAN, M. 1998. Characterization and utilisation of buffing dust generated by the leather industry. Vol. B 63, pp.53-68.

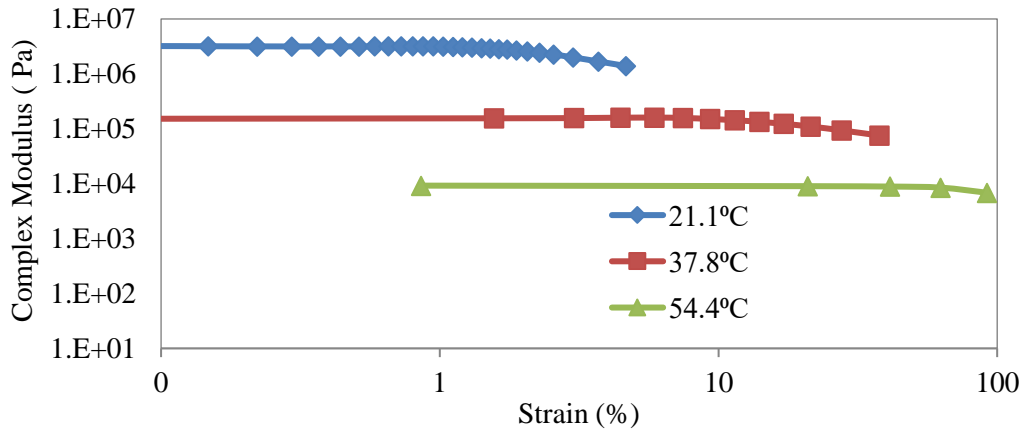
SHELL 1990. The Shell Bitumen Handbook. Shell Bitumen, UK.

UNIDO 2012. Technical assistance project for the upgrading of the Ethiopian leather and leather products industry. Vennia: UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION.

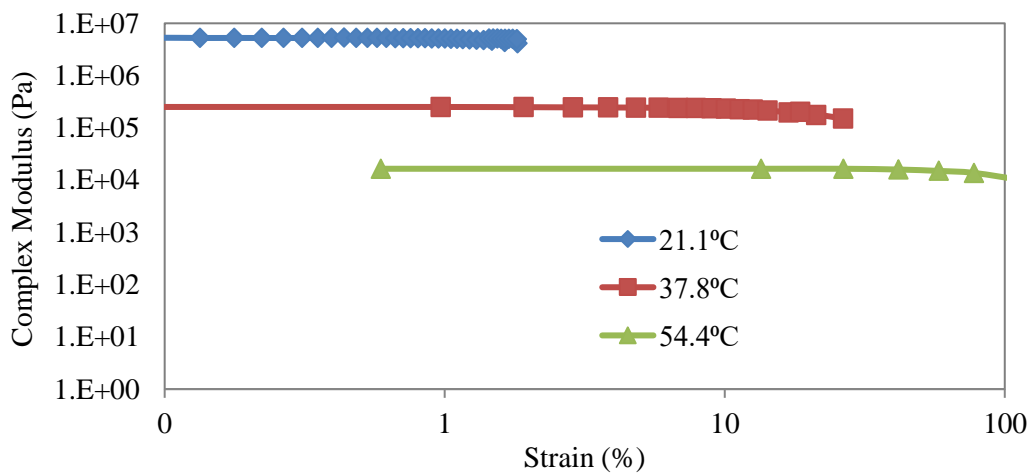
ZANIEWSKI, J. P. & NALLAMOTHU, S. H. 2003. Evaluation of Binder Grades on Rutting Performance. *In: ENGINEERING, D. O. C. A. E. (ed.)*. Morgantown, West Virginia.

ZANIEWSKI, J. P. & PUMPHREY, M. E. 2004. Evaluation of Performance Graded Asphalt Binder Equipment and Testing Protocol. *In: ENGINEERING, D. O. C. A. E. (ed.)*. Morgantown, West Virginia: Asphalt Technology Program.

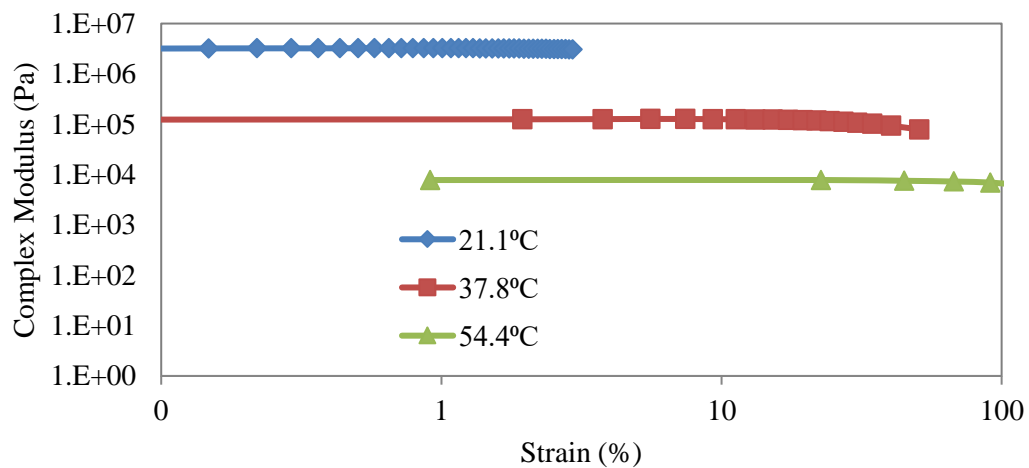
Appendix A: AST Test Results in Graph



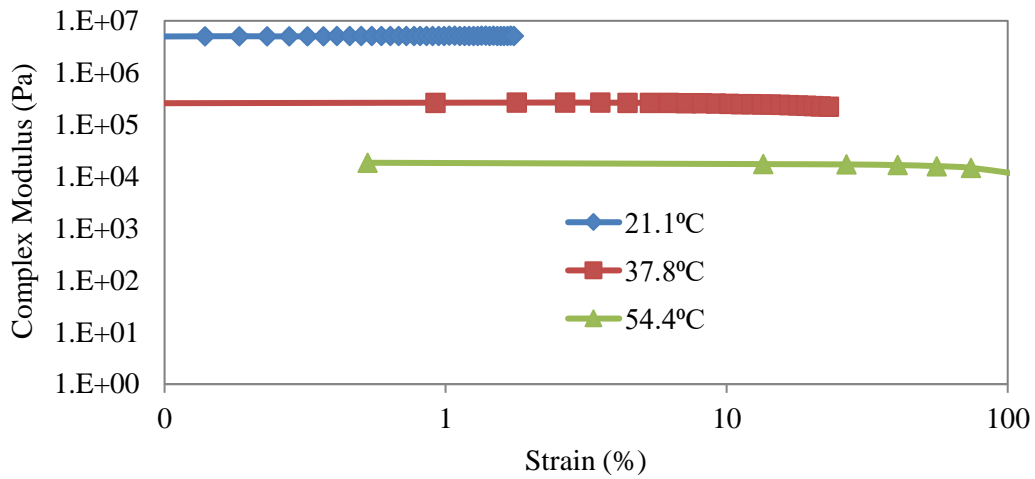
a) Unaged Neat Binder



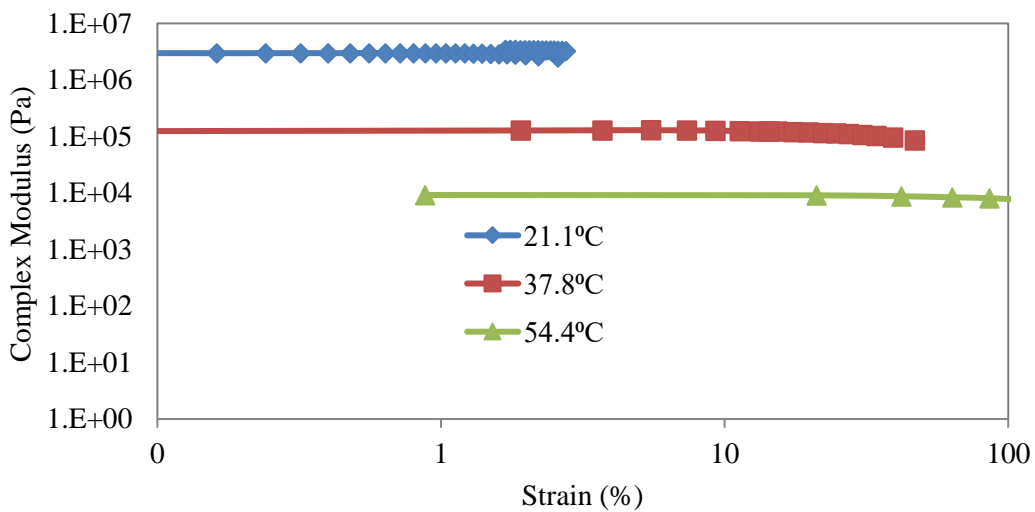
b) RTFO Aged Neat Binder



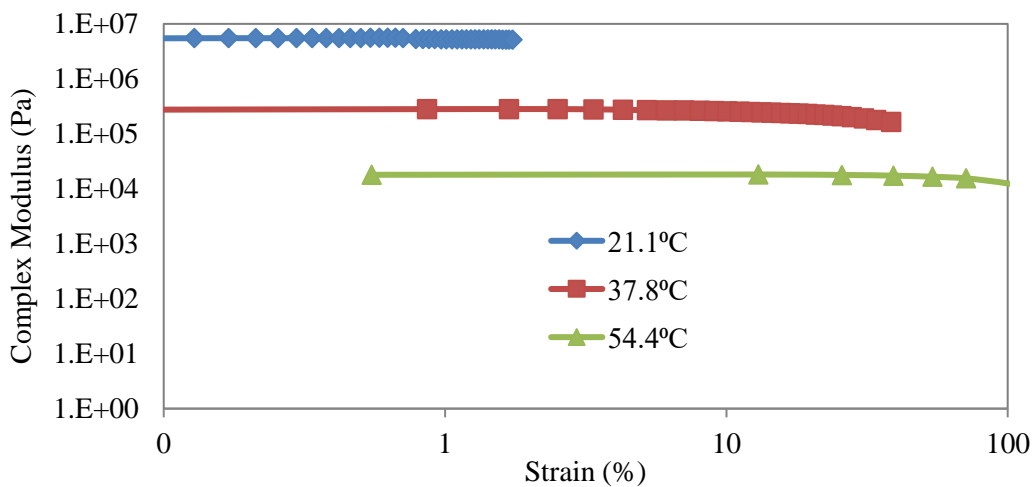
c) Unaged 2% CBD



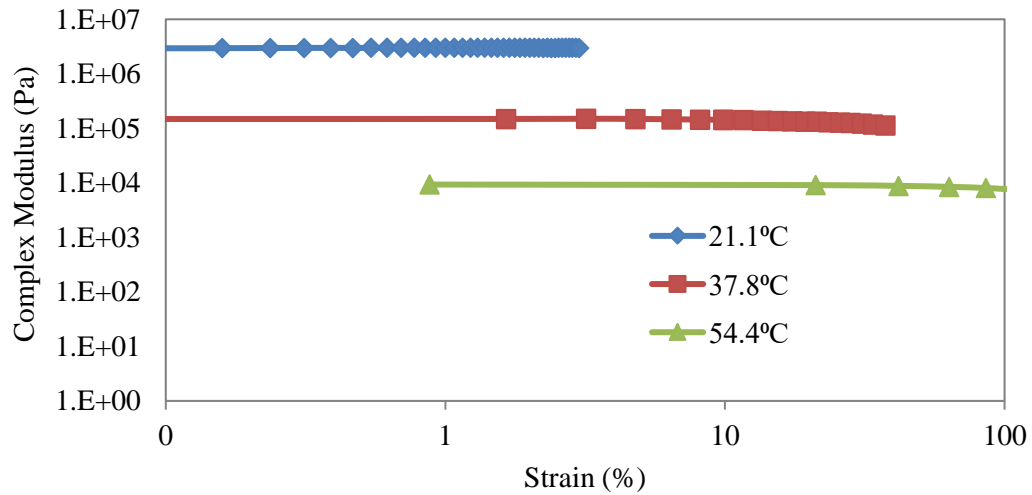
d) RTFO Aged 2% CBD



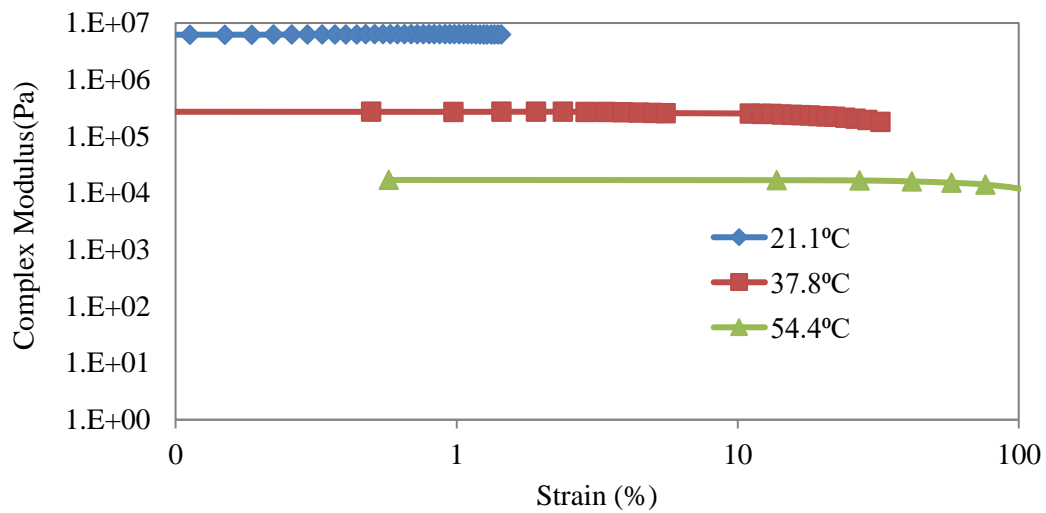
e) Unaged 4% CBD



f) RTFO Aged 4% CBD

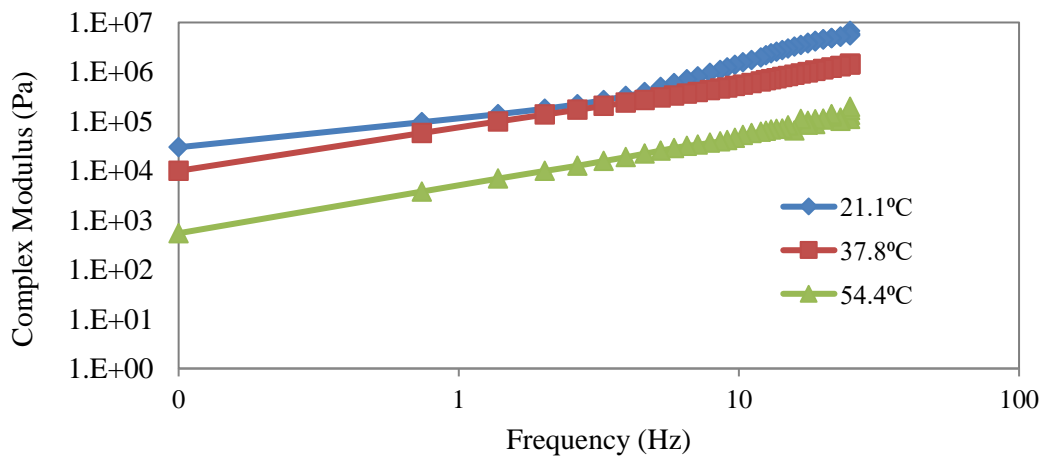


g) Unaged 6% CBD

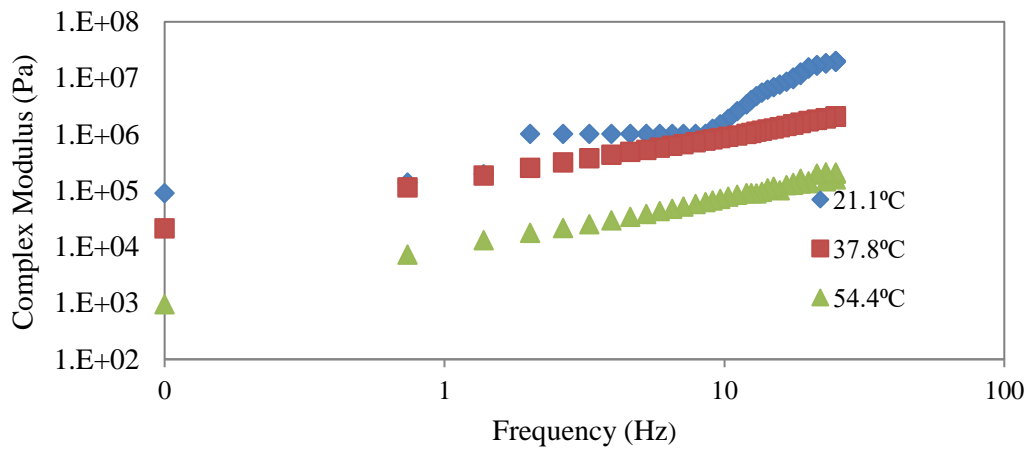


h) RTFO Aged 6% CBD

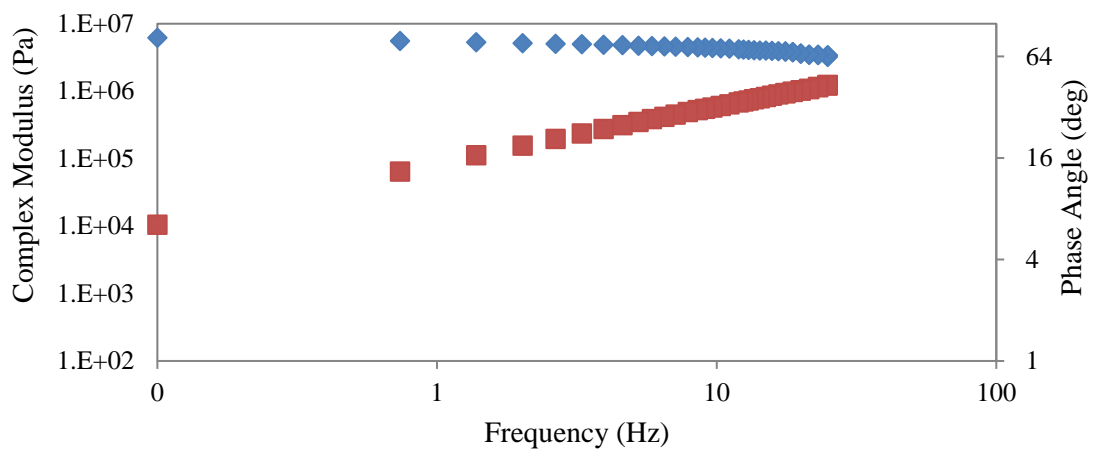
Appendix B: FST Test Results in Graph



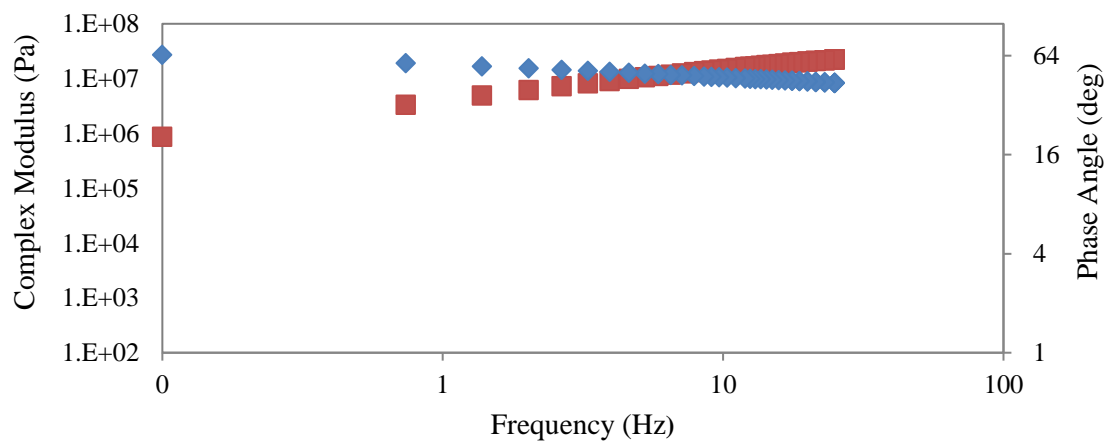
a) Unaged Neat Binder



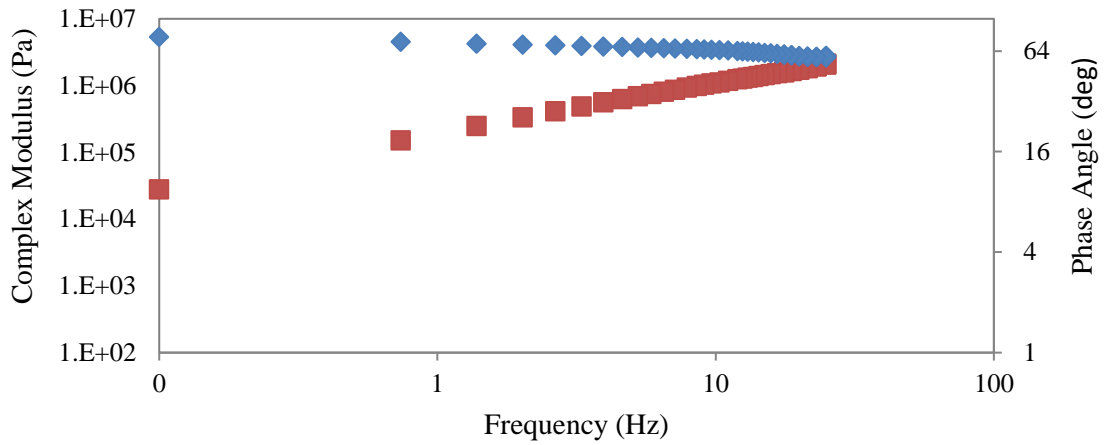
b) RTFO Aged Neat Binder



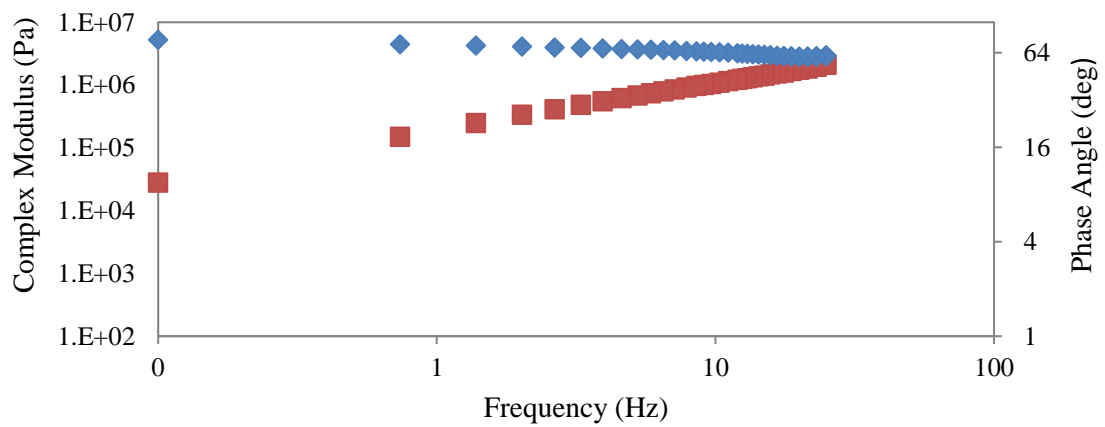
c) Unaged 2% CBD at 37.8°C



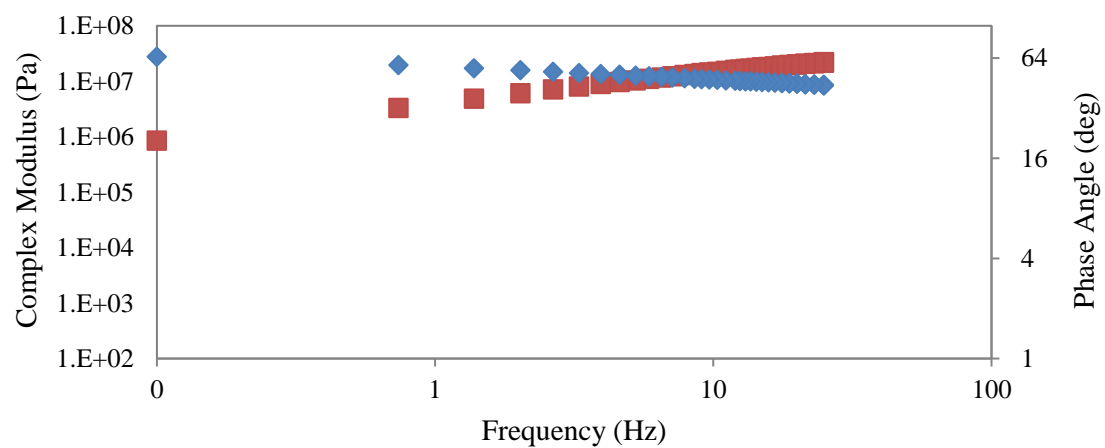
d) RTFO Aged 2% CBD at 21.1°C



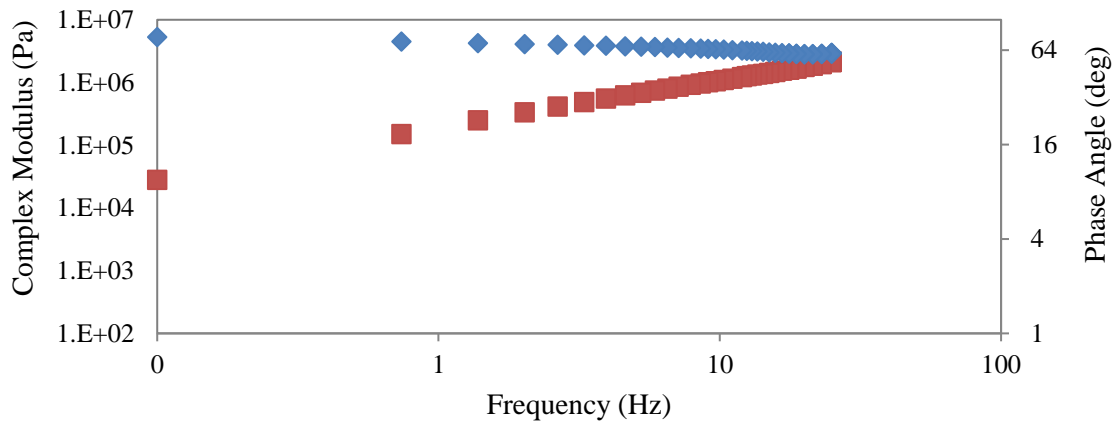
e) RTFO Aged 2% CBD at 37.8⁰C



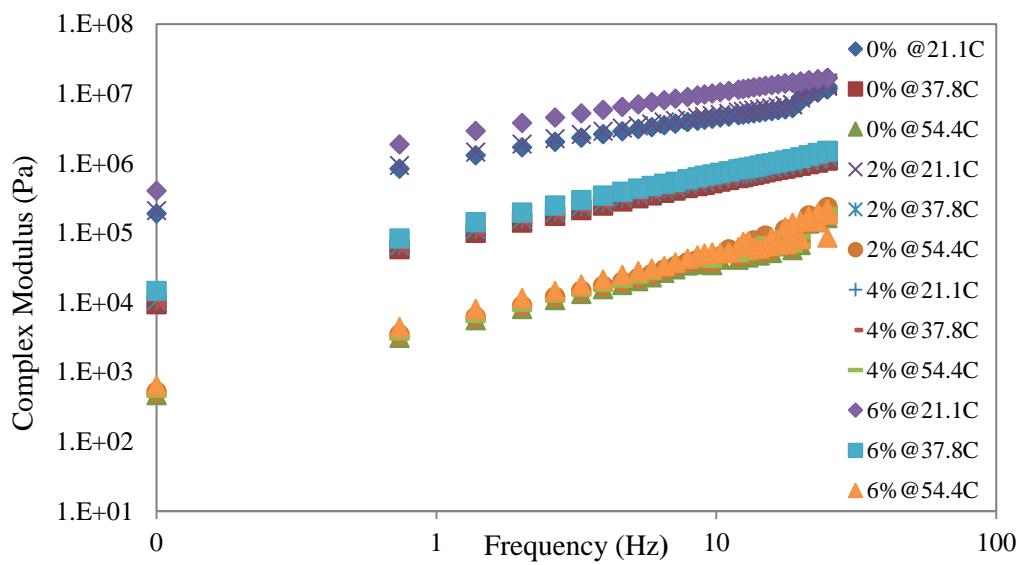
f) Unaged 4% CBD at 37.8⁰C



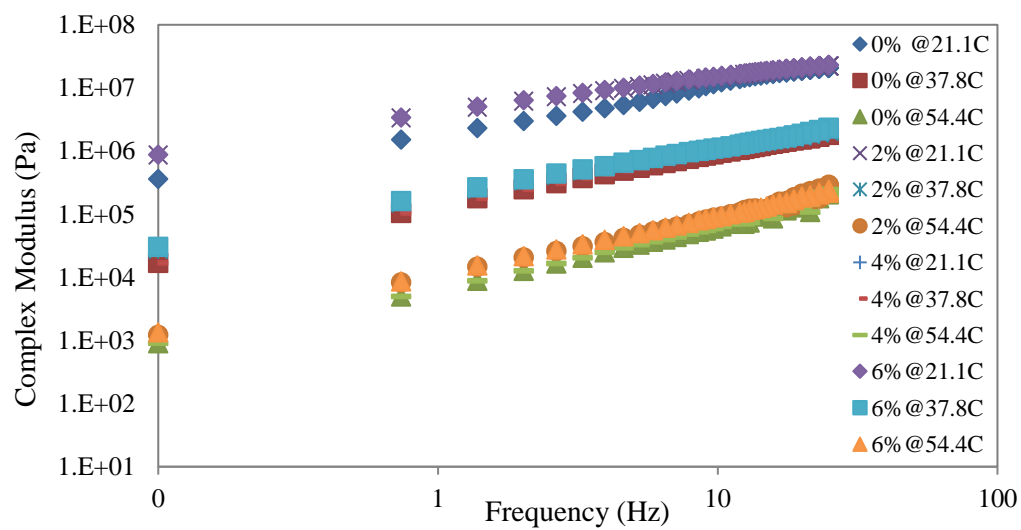
g) RTFO Aged 4% CBD at 37.8⁰C



h) RTFO Aged 4% CBD at 54.4°C



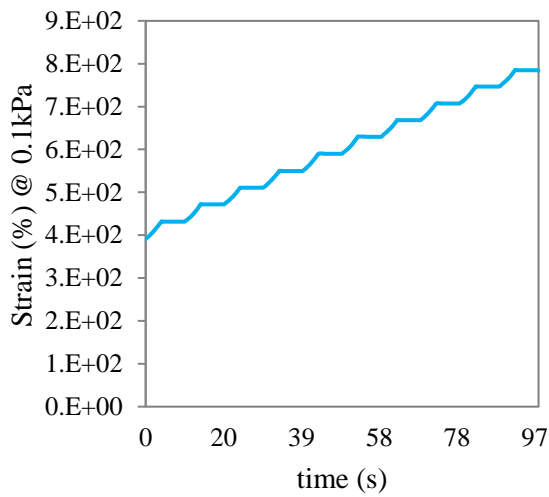
i) Unaged Binders



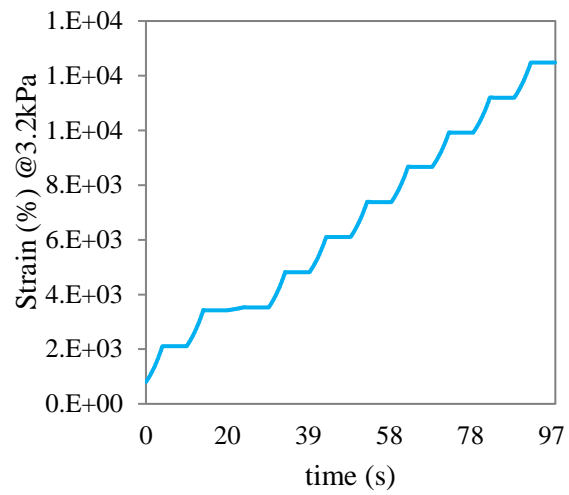
j) RTFO Aged Binders

Appendix C: MSCR Test Results in Graph

1) Unaged Neat Binder @64°C

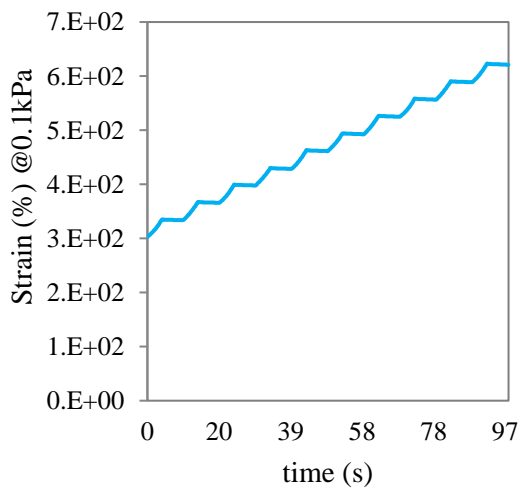


(a)

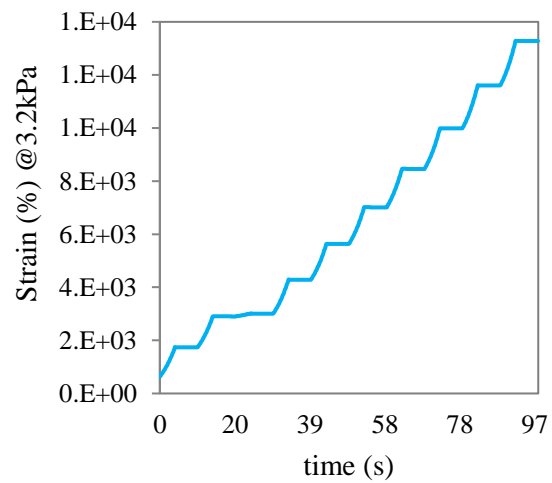


(b)

2) RTFO Aged Neat Binder @64°C

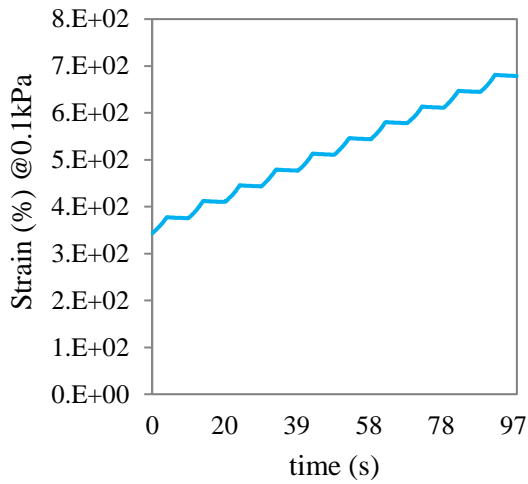


(a)

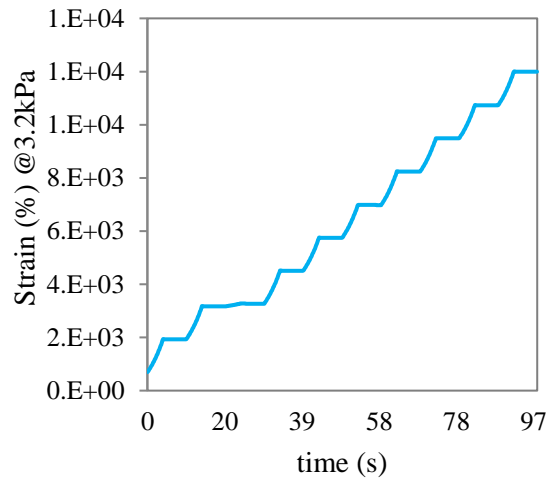


(b)

3) 2% CBD Unaged Binder @64°C

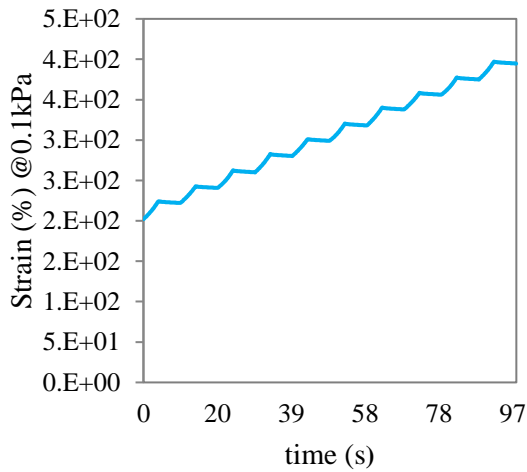


(a)

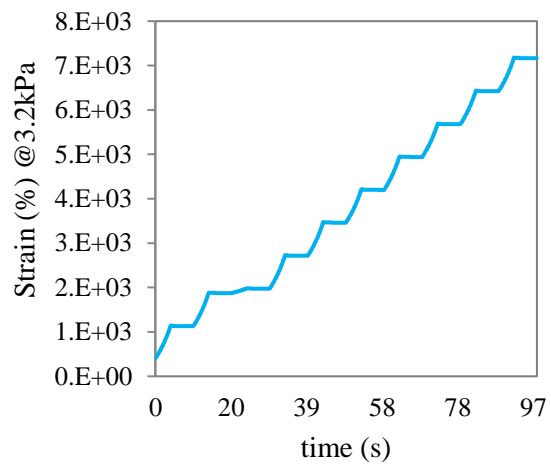


(b)

4) 2% CBD RTFO Aged Binder @64°C

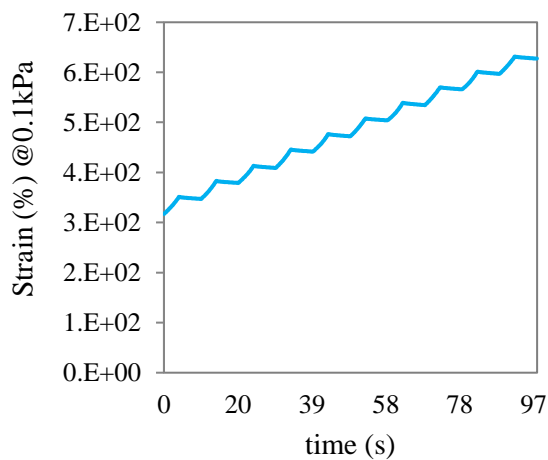


(a)

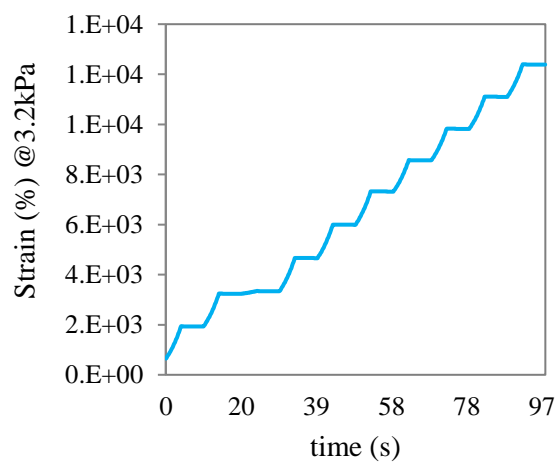


(b)

5) 4% CBD Unaged Binder @64°C

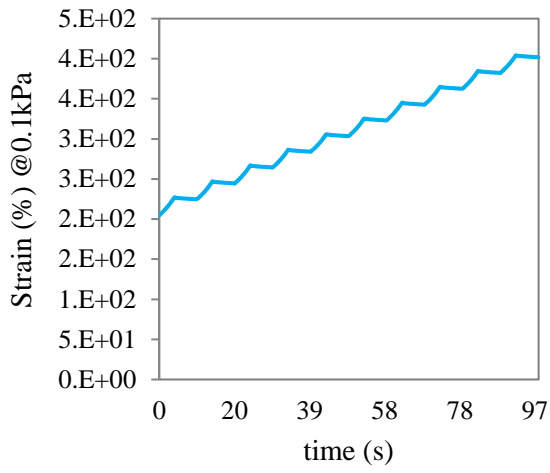


(a)

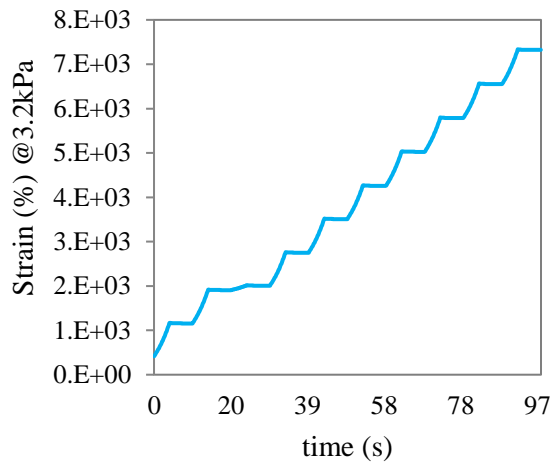


(b)

6) 4% CBD RTFO Aged Binder @64°C

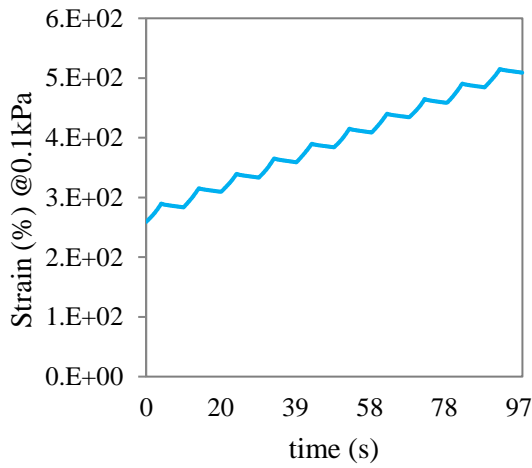


(a)

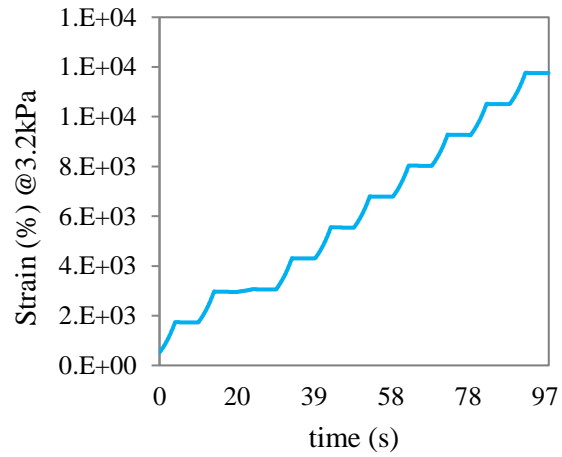


(b)

7) 6% CBD Unaged Binder @64°C

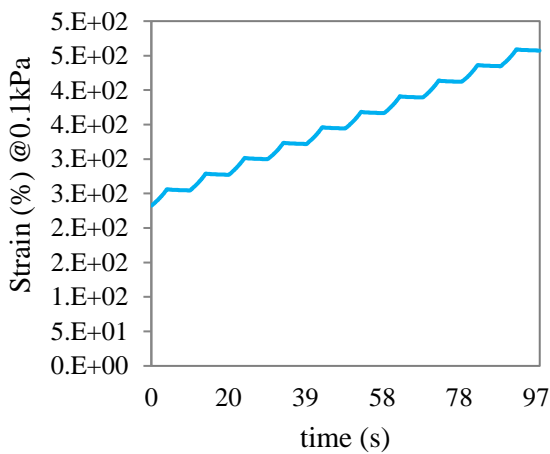


(a)

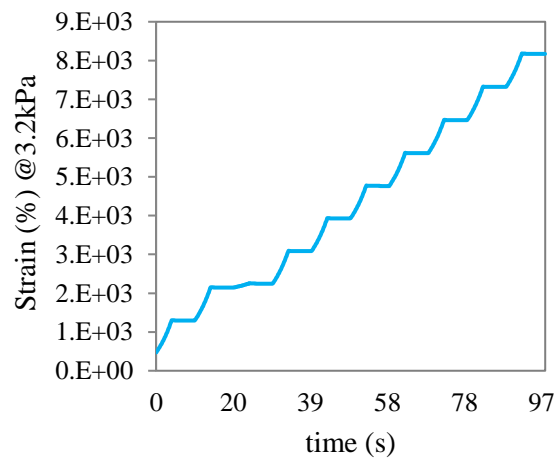


(b)

8) 6% CBD RTFO Aged Binder @64°C

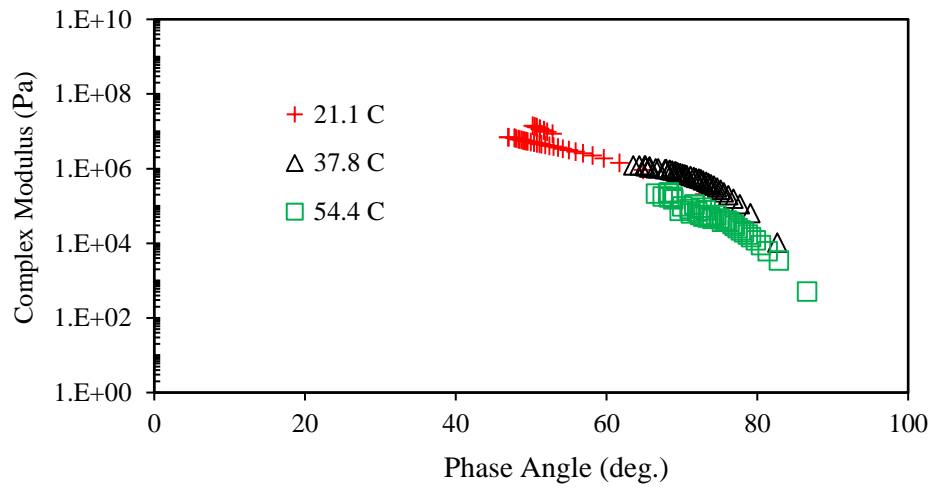


(a)

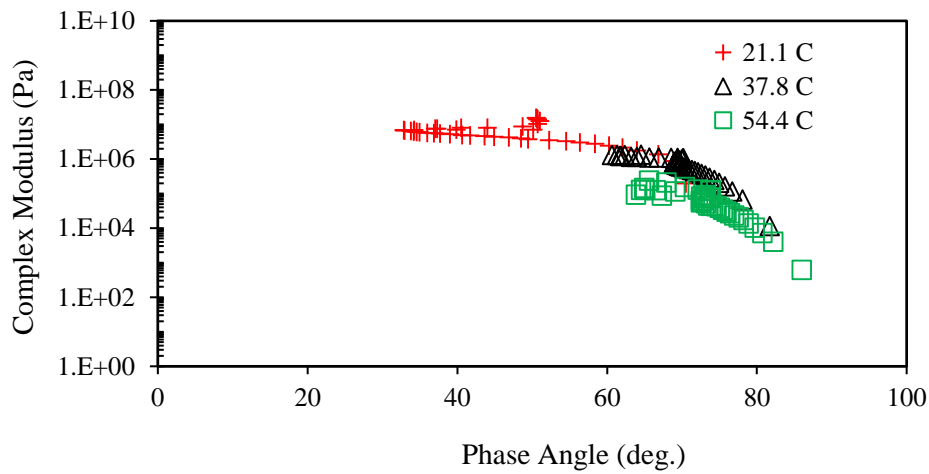


(b)

Appendix D: Black Space Diagram



a) Black Space Diagram for Unaged 2% CBD



b) Black Space Diagram for Unaged 4% CBD

Appendix E: Statistical Analysis of Variance (ANOVA) for FST Results

Statistical analysis for FST at $f = 10^7$ Hz

CBD	0%	2%	4%	6%	8%	10%
Sample1	1.18E+09	1.22E+09	1.25E+09	1.55E+09	1.07E+09	1.31E+09
Sample2	1.16E+09	1.22E+09	1.56E+09	1.41E+09	1.15E+09	9.08E+08
Mean(X)	1.17E+09	1.22E+09	1.40E+09	1.48E+09	1.11E+09	1.11E+09
Variance(S_i^2)	2.78E+14	7.97E+12	4.63E+16	1.01E+16	3.28E+15	8.04E+16
Grand Mean(X_{GM})	1.25E+09					
	N=12			K=6		
Between Group	$S_B^2 = \frac{\sum n_i (X_i - X_{GM})^2}{k-1}$					
		$\frac{2[(3.65E+09-1.84E+09)^2+(1.22E+09-1.84E+09)^2+(1.40E+09-1.84E+09)^2+(1.48E+09-1.84E+09)^2+(1.47E+09-1.84E+09)^2+(1.81E+09-1.84E+09)^2]}{6-1}$				
	S_B^2	4.15E+16				
Within Group	$S_w^2 = \frac{\sum (n_i-1)S_i^2}{\sum (n_i-1)}$	$\frac{(2-1)[(1.77E+18)+(7.97E+12)+(4.63E+16)+(1.01E+16)+(2.28E+16)+(1.53E+17)]}{12-6}$				
		12-6				
	S_w^2	2.34E+16				
F	$F = S_B^2 / S_w^2$	F	P-Value		F from table ($\alpha=0.05$)	
		1.78	0.15		4.39	

Statistical analysis for FST at $f = 10$ Hz

CBD	0%	2%	4%	6%	8%	10%
Sample1	1.23E+07	1.47E+07	1.38E+07	1.53E+07	1.06E+07	1.07E+07
Sample2	1.44E+07	1.50E+07	1.49E+07	1.49E+07	1.30E+07	9.62E+06
Mean(X)	1.34E+07	1.48E+07	1.44E+07	1.51E+07	1.18E+07	1.02E+07
Variance(S_i^2)	2.16E+12	4.36E+10	6.47E+11	7.88E+10	2.88E+12	5.71E+11
Grand Mean(X_{GM})	1.33E+07					
	N=12			K=6		
Between Group	$S_B^2 = \frac{\sum n_i (X_i - X_{GM})^2}{k-1}$					
		$\frac{2[(1.07E+07-1.45E+07)^2+(1.48E+07-1.45E+07)^2+(1.44E+07-1.45E+07)^2+(1.51E+07-1.45E+07)^2+(1.51E+07-1.45E+07)^2+(1.69E+07-1.45E+07)^2]}{6-1}$				
	S_B^2	3.63E+12				
Within Group	$S_w^2 = \frac{\sum (n_i-1)S_i^2}{\sum (n_i-1)}$	$\frac{(2-1)[(1.86E+13)+(4.36E+10)+(6.47E+11)+(7.88E+10)+(1.49E+12)+(1.58E+12)]}{12-6}$				
		12-6				
	S_w^2	1.06E+12				
F	$F = S_B^2 / S_w^2$	F	P-Value		F from table ($\alpha=0.05$)	
		3.41	0.09		4.39	

Statistical analysis for FST at f = 10-5Hz

CBD	0%	2%	4%	6%	8%	10%
Sample1	6.90E+00	1.19E+02	1.42E+02	1.71E+02	7.49E+01	9.57E+01
Sample2	7.00E+00	1.09E+02	1.50E+02	1.23E+02	1.08E+02	9.68E+01
Mean(X)	6.95E+00	1.14E+02	1.46E+02	1.47E+02	9.14E+01	9.62E+01
Variance(S _i ²)	5.86E-03	4.70E+01	3.37E+01	1.17E+03	5.45E+02	5.61E-01
Grand Mean(XGM)	1.00E+02					
	N=12			K=6		
Between Group	$S_B^2 = \frac{\sum n_i (X_i - X_{GM})^2}{k-1}$					
	k-1	$\frac{2[(6.06E+01-1.26E+02)^2+(1.14E+02-1.26E+02)^2+(1.46E+02-1.26E+02)^2+(1.47E+02-1.26E+02)^2+(1.27E+02-1.26E+02)^2+(1.61E+02-1.26E+02)^2]}{6-1}$				
	S _B ²	5.30E+03				
	Within Group	$S_w^2 = \frac{\sum (n_i - 1) S_i^2}{\sum (n_i - 1)}$	$\frac{1[(5.72E+01)+(4.70E+01)+(3.37E+01)+(1.17E+03)+(1.47E+03)+(4.53E+00)]}{12-6}$			
	S _w ²	2.99E+02				
F	F=S _B ² /S _w ²	F	P-Value		F from table (α=0.05)	
		17.75	0.01			4.39

Appendix F: Leather Factories in Ethiopia

Leather Company Profile						
Local Companies						
It.No	Name of Factories	Report of 2016				
		Installed Soaking Capacity (pcs)/Annum		Actual Soaking (pcs)/Annum		
		Hide	Skin	Hide	Sheep	Goat
1	Addis Ababa Tannery	252,000	700,000	194,204	18,106	33,184
2	Hora Tannery	-	896,000	-	223,236	38,638
3	Modjo Tannery	140,000	2,240,000	66,723	1,019,898	369,252
4	Colba Tannery	168,000	1,680,000	120,677	1,381,116	679,884
5	Batu Tannery	280,000	700,000	309,518	-	8,700
6	Bahirdar Tannery	84,000	560,000	3,804	343,982	19,245
7	Sheba Leather Industry	168,000	1,680,000	132,442	631,473	1,362,997
8	Kombolcha Tannery	-	1,680,000	-	32,048	165,708
9	Dire tannery	168,000	1,680,000	113,758	1,126,682	-

10	Gelan tannery	-	840,000	-	93,663	20,912
11	Hafede Tannery	70,000	1,680,000	7,969	2,157	69,781
12	Walia Tannery	280,000	1,400,000	35,000	356,250	52,500
13	Debrebirhan Tannery	-	1,680,000	-	212,907	66,439
14	Habesha Tannery	-	1,120,000	-	69,196	352,408
15	Sun Industry	-	840,000	-	280,000	-
	Total	1,610,000	19,376,000	984,095	5,790,714	3,239,648
Foreign Companies						
It.No	Name of Factories	Installed Soaking Capacity (pcs)/Annum		Actual Soaking (pcs)/Annum		
		Hide	Skin	Hide	Sheep	Goat
1	China Africa Overseas	112,000	3,360,000	89,000	1,095,590	225,607
2	Ethiopia Tannery	336,000	3,360,000	308,897	1,297,352	135,808
3	Friendship Tannery	280,000	2,800,000	-	467,412	2,969,633
4	Elico Tannery	294,000	3,640,000	153,433	451,815	97,669
5	East Africa Tannery	-	2,240,000	-	222,621	151,802
6	Farida Tannery	-	1,960,000	8,199	523,853	396
7	United Vasn Tannery	-	1,400,000	-	64,428	63,555
8	New wing tannery	2,800	50,400	1,250	28,419	17,426
9	Zingzian Tannery	140,000	1,400,000	293,000	30,000	90,000
10	DX Tannery	-	2,240,000	-	-	815,770
11	Blue Nile Tannery	-	1,120,000	-	-	-
12	EBA PLC Tannery	-	-			
13	George Gloria Tannery	-	-			
14	Houdaochen Tannery/Mesako Global	-	2,800,000	-	2,000	3,000
	Total	1,164,800	26,370,400	853,779	4,183,490	4,570,666