Summer 7-29-2018

Understanding Asphalt Concrete Aging Using Nanoindentation

Hasan M. Faisal

University of New Mexico

Follow this and additional works at: https://digitalrepository.unm.edu/ce_etds

Part of the Civil Engineering Commons, Geotechnical Engineering Commons, and the Transportation Engineering Commons

Recommended Citation


This Dissertation is brought to you for free and open access by the Engineering ETDs at UNM Digital Repository. It has been accepted for inclusion in Civil Engineering ETDs by an authorized administrator of UNM Digital Repository. For more information, please contact disc@unm.edu.
Student Name: Hasan Mohammad Faisal

Candidate

Graduate Unit (Department): Civil Engineering

Department

This dissertation is approved, and it is acceptable in quality and form for publication:

Approved by the Dissertation Committee:

Rafiqul A. Tarefder, Chairperson

John Stormont, Member

Tang-Tat Ng, Member

Yu-Lin Shen, Member
UNDERSTANDING ASPHALT CONCRETE AGING USING NANOINDENTATION

BY

HASAN MOHAMMAD FAISAL

B.Sc. in Civil Engineering
Bangladesh University of Engineering & Technology (BUET), Dhaka, Bangladesh

M.S. in Civil Engineering
University of New Mexico (UNM), Albuquerque, New Mexico, USA

DISSERTATION
Submitted in Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy
Engineering

The University of New Mexico
Albuquerque, New Mexico, USA

July 2018
DEDICATION

This dissertation is dedicated to my faithful, loving and ever-supportive wife, Laila Nanzin Shima, who never left my side and always encouraged and supported me patiently.
ACKNOWLEDGMENTS

I would like to express my sincere gratitude to my advisor Dr. Rafiquel A. Tarefder for his support, outstanding mentorship, and advice. Dr. Tarefder taught me how to think critically and express ideas. Special thanks to him for giving me the freedom to explore my research, and the guidance to follow through my research. Without his guidance and persistent help, this dissertation would not have been possible.

I would like to sincerely thank my dissertation committee members: Dr. John C. Stormont, Dr. Tang-Tat Ng, and, Dr. Yu-Lin Shen not only for their insightful comments and encouragement but also for the fundamental questions which helped me to widen my research perspective.

I would like to express my gratitude to the funding agencies: the Safety and Operations of Large-Area Rural/Urban Intermodal Systems (SOLARIS), and the New Mexico Department of Transportation (NMDOT) for providing the funding for this research.

Last but not the least, I thank my colleagues and friends, specifically Zafrul H Khan, Biswajit Bairgi, Mohiuddin Ahmad, Shahidul Faisal and Shaikh Ahmed, who assisted me for testing. Dr. Md Rashadul Islam and Dr. Mesbah U. Ahmed also provided me many suggestions for my Ph.D. work.
UNDERSTANDING ASPHALT CONCRETE AGING USING NANOINDENTATION

By

Hasan Mohammad Faisal
B.Sc. in Civil Engineering, Bangladesh University of Engineering & Technology, 2007
M.S. in Civil Engineering, University of New Mexico, 2012
Ph.D., Engineering, University of New Mexico, 2018

ABSTRACT

Asphalt concrete (AC) is created by mixing liquid asphalt binder with solid aggregates. When asphalt binder is mixed with aggregates, it creates a thin film (about 7-16 microns thick) around the aggregate surface. Fine aggregate (smaller than 0.075 mm size) get entrapped within the binder film or mixed with the binder, and create a phase called mastic. Both asphalt film and mastic play significant roles in aging of asphalt pavement. To this day, tests were performed mainly on the bulk liquid asphalt, but not on the film or mastic. In this study, for the first time, nanoindentation tests were done on asphalt film and mastic to identify the aging behavior of asphalt.

This study identifies aggregate, binder film and mastic phases using indentation depth resolution and creep response techniques. Creep compliance response is used to identify an individual phase. The results show that out of 100 indentations, only 30% of the indentations could be made on the mastic phase of the AC and about 5% to 9% could be made on the binder phase of the AC. The identification study confirmed that the binder phase also exists in an AC sample.
In this study, AC samples were aged using a draft oven for 2 days, 5 days, 10 days, 15 days and 20 days at 85 °C temperature. Load-displacement data was analyzed using a spring-dashpot-rigid body model to determine stiffness and hardness. Stiffness and hardness data were further analyzed as a function of time and modeled using a kinetic energy model. One of the key parameters of the kinetic energy model is the activation energy of aging. Results show asphalt binder’s activation energy is much lower (about 50%) than that of asphalt mastic. This indicates that mastic reacts with oxygen at a much slower rate than asphalt binder.

This study attempts to correlate the available voids in an AC sample using nanoindentation hardness and viscoelastic relaxation parameter. AC samples were prepared with an increasing order of air voids from 7% to 20% and aged for four years at room temperature and atmospheric conditions. Binder of the aged AC samples was extracted and recovered using the centrifuge and distillation process. The oxidative aging of asphalt binder samples was quantified using a Fourier Transformed Infrared Spectroscopy (FTIR) analysis of carboxyl and sulfoxide functional groups. Oxidation measured for ketones increases linearly with the increase of pore content in AC. Nanoindentation creep behavior was evaluated from the load-displacement behavior and then fitted in the viscoelastic model to quantify the viscoelastic relaxation time parameters. Results show the porous AC undergoes more aging compared to a dense AC sample. Oxidation measured for ketones increases linearly with the increase of pore content in AC. Nanoindentation relaxation and retardation time increase with the increase in effective voids in the AC samples. This means
higher air voids in AC causes damage to the binder which is reflected by reduction in the stress-relaxing capacity. The viscoelastic relaxation time of the AC sample with 20% air voids is 7.5 times more than that AC sample with 7% air voids. The viscoelastic relaxation behavior is compared for the mastic phase of asphalt concrete as well. The results show that the relaxation time increases only 3.9 times for 13% change in air voids.

Nanoindentation test results can be significantly affected by film thickness. Therefore, this study investigates how asphalt film thickness changes by an increase in aging time. Results show that film thickness reduces exponentially as a function of aging. After 10 days thickness reduces to 50% of its original thickness. To investigate the reason behind this reduction, aged films were tested in FTIR for chemical changes. Results show C=O and S=O increase with aging. The coagulation of the polar fractions in asphalt binder creates a thinner asphaltic film due to aging. The coagulation of the polar fraction creates a larger stiffer form of asphalt molecule, which is also known as asphaltene fraction of asphalt binder. Chromatographic analysis on aged asphalt binder shows stiffer asphaltene fraction increases with aging of asphalt.
# TABLE OF CONTENTS

ABSTRACT .................................................................................................................. vi

CHAPTER 1 ................................................................................................................ 1

INTRODUCTION ........................................................................................................ 1
  1.1 Problem Statement ......................................................................................... 1
  1.2 Hypothesis ...................................................................................................... 4
  1.3 Organization of the Dissertation ................................................................... 5

CHAPTER 2 ................................................................................................................ 6

LITERATURE REVIEW ............................................................................................. 6
  2.1 Asphalt Aging ............................................................................................... 6
  2.2 Nanoindentation ............................................................................................ 11
  2.3 Oliver-Pharr Method ...................................................................................... 13
  2.4 Indenter Tip Section .................................................................................... 17
  2.5 Applicability of Oliver-Pharr Method for Asphalt ....................................... 18
  2.6 Data Interpretation ....................................................................................... 20
    Loading Curve ....................................................................................................... 29
    Creep Curve ......................................................................................................... 29
    Unloading Curve .................................................................................................... 30
  2.7 Past Studies of Nanoindentation on Asphalt ........................................... 30
    2.7.2 Modeling of Indentation Data ............................................................... 36
  2.8 Asphalt Film Thickness .................................................................................. 38
  2.9 Pavement Aging Model ................................................................................ 40

CHAPTER 3 ................................................................................................................ 47

METHODOLOGY ....................................................................................................... 47
  3.1 General ........................................................................................................... 47
  3.2 Nanoindentation Testing on Asphalt ............................................................ 47
    3.2.1 Asphalt Binder Sample ........................................................................... 48
    3.2.2 Asphalt Concrete Sample Preparation for Nanoindentation ................... 49
    3.2.2 Nanoindentation Testing on Asphalt .................................................... 52
  3.3 Aging of Asphalt ........................................................................................... 55
  3.4 Laboratory determination of Asphalt Film Thickness .................................. 55

Chapter 4 .................................................................................................................. 58

PHASE IDENTIFICATION ......................................................................................... 58
  4.1 Introduction ..................................................................................................... 58
  4.2 Aggregate and Asphalt Binder Collection .................................................... 61
4.2.2 Asphalt Concrete Sample Preparation .......................................................... 62
4.2.3 Asphalt Binder Sample Preparation ............................................................ 65
4.3 Nanoindentation Creep Test .............................................................................. 66
4.4 Asphalt Concrete Phase Identification ............................................................. 69
4.5 Extraction of Creep Response .......................................................................... 72
4.6 Nanoindentation Load-Displacement Data Analysis ........................................... 74
  4.6.1 Nanoindentation on Binder at on Glass Slide .............................................. 75
  4.6.2 Nanoindentation on Mastic on Glass Slide ................................................. 76
  4.6.3 Nanoindentation on AC Sample ................................................................. 77
4.7 Asphaltic Phase Identification .......................................................................... 79
  4.7.1 Binder Phase of Asphalt Concrete .............................................................. 81
  4.7.2 Mastic Phase of Asphalt Concrete ............................................................. 83
  4.7.3 Aggregate Phase ....................................................................................... 85
4.8 Conclusions ...................................................................................................... 85
Chapter 5 .................................................................................................................. 87
EXTRACTION OF MATERIAL PARAMETERS FROM NANOINDENTATION
TESTING ..................................................................................................................... 87
  5.1 General ............................................................................................................ 87
  5.2 Aging of Asphalt Sample ................................................................................ 88
  5.3 Extraction of Unaged and Aged Bilk and Phase Material Property .................... 89
  5.4 Comparing Bulk vs. Phase Properties ............................................................. 90
  5.5 Conclusions ..................................................................................................... 96
Chapter 6 .................................................................................................................. 98
EFFECTS OF PORE STRUCTURE ON THE AGING OF ASPHALT CONCRETE ... 98
  6.1 General ............................................................................................................ 98
  6.1 Objectives ....................................................................................................... 99
  6.2 Outline ............................................................................................................. 100
  6.3 Materials & Sample Preparation .................................................................... 101
    6.3.1 Materials .................................................................................................. 101
    6.3.2 Asphalt Concrete Sample Preparation .................................................... 101
    6.3.3 Asphalt Binder ....................................................................................... 102
  6.4 Results and Discussions ................................................................................. 103
    6.4.1 FTIR analysis ........................................................................................... 104
    6.4.2 Chromatographic Analysis .................................................................... 107
    6.4.3 Load-Displacement Behavior .................................................................. 109
    6.4.2 Creep Behavior ....................................................................................... 111
LIST OF TABLES

Table 2.1 Recommended Hardening Code Values .............................................. 42
Table 3.1 Test Binder Details. ........................................................................... 49
Table 4.1 Elastic Modulus and Hardness of Asphalt Binder for Three Different Aging Conditions ....................................................................................... 76
Table 4.2 Creep Model Parameters of Bulk State of Binder and Phase State of Binder .......................................................... 82
Table 4.3 GPL Creep Analysis Parameters of Mastic ........................................... 85
Table 5.1 Bulk State vs Phase State for Different Aging Conditions ......................... 96
Table 6.1 Sample Air Voids ............................................................................... 102
Table 6.2 Asphalt Functional Groups and Corresponding Wavenumbers ................. 104
Table 6.3 Fitting Parameters from Burger’s Model ................................................. 117
Table 7.1 Nanoindentation Test Parameters Used to Identify the Asphalt Film Thickness ..................................................................................................... 124
LIST OF FIGURES

Figure 1.1 Different phase of Asphalt Concrete (AC) .......................................................... 3
Figure 2.1 Asphalt Chemistry ............................................................................................... 7
Figure 2.2 Asphalt oxidation ............................................................................................... 8
Figure 2.3 Relationship of Carbonyl Group and Asphalt Viscosity (Petersen 1993) ............ 9
Figure 2.4 Colloidal Structure of Asphalt before and after Oxidative Aging .................... 10
Figure 2.5 Schematic of Indentation Test ........................................................................... 12
Figure 2.6 Indentation ......................................................................................................... 14
Figure 2.7 Negative Slope during Nanoindentation and Asphalt ....................................... 19
Figure 2.8 Voigt Model ...................................................................................................... 23
Figure 2.9 Burger Model .................................................................................................. 25
Figure 2.10 SDR Model ................................................................................................... 26
Figure 2.11 Nanoindentation Loading with Creep Load ..................................................... 28
Figure 3.1 Flow chart of Nanoindentation Testing on Asphalt .......................................... 48
Figure 3.2 Gradation Curve of the Asphalt Concrete Mix ................................................ 50
Figure 3.3 AC Sample Preparation ................................................................................... 51
Figure 3.4 Asphalt Concrete Sample for Nanoindentation ............................................... 52
Figure 3.5 Nanoindentation Test on AC Sample .............................................................. 53
Figure 3.6 Loading Pattern Used During Nanoindentation Testing .................................. 54
Figure 3.7 Nanoindentation Test Setup on Asphalt Binder ............................................... 54
Figure 3.8 Nanoindentation on the Asphalt Binder Thin Film and Aggregate Substrate ... 56
Figure 4.1 Different phase of Asphalt Concrete (AC) ........................................................ 59
Figure 4.2 Gradation Curve of the Asphalt Concrete Mix ................................................ 63
Figure 4.3 AC Sample Preparation ................................................................................... 64
Figure 4.4 Asphalt Concrete Sample for Nanoindentation .............................................. 65
Figure 4.5 Asphalt Binder Sample for Nanoindentation ................................................... 66
Figure 4.6 Nanoindentation Test on AC Sample .............................................................. 67
Figure 4.7 Loading Pattern Used During Nanoindentation Testing .................................. 69
Figure 4.8 Load-displacement Curves of Nanoindentation Tests on Binder1 and Binder2 Samples ................................................................. 74
Figure 4.9 Load-Displacement Curves of Nanoindentation Tests on PG 64-22 and PG 70-22 Mastic ................................................................. 77

xiii
Figure 4.10 Load-Displacement Curves of Nanoindentations on PG 64-22 and PG 70-22 AC Sample ..................................................................................................................78
Figure 4.11 Load-displacement, Creep Response and GPL Model Fitting of Binder Sample ..................................................................................................................81
Figure 4.12 Comparison of Creep Response of Mastic Phase of Binder1 AC Samples ...84

Figure 5.1 Load-displacement Response: (a) Load-Displacement Curves of Nanoindentations on binder1 Sample; (b) Load-Displacement Curves of Nanoindentations on Mastic Sample; (c) Load-Displacement Curves of Nanoindentations on binder 1 AC Sample at Phase .................................................................91

Fig. 5.2 Load-displacement, Creep Response and GPL Model Fitting of Binder Sample: (a) Binder Phase State if Binder1 AC Sample; (b) Creep Responses of the Binder Phase; (c) Average Creep Response; (d) Model Fit of Creep Response; (e) Creep Response of Bulk Binder; (f) Model Fitting of Creep Response ..............................................94

Figure 6.1 Research Plan ..................................................................................................................100
Figure 6.2 Binder Sample Extraction and Recovery ..........................................................................103
Figure 6.3 Full Spectrum of FTIR spectroscopy output of 8% Airvoids Containing Aged Asphalt Binder Sample ..................................................................................................................105
Figure 6.4 Normalized C=O and S=O Functional Groups as a Function of Air Voids...106
Figure 6.5 Extraction Asphalten Fraction ..........................................................................................107
Figure 6.6 Asphalten Fraction in Asphalt as Function of Air Voids .................................................108
Figure 6.7 Load-displacement Curves for Increasing Amounts of Air Voids in AC ......110
Figure 6.8 Creep Behavior of Asphalt Binder for Different Levels of Air Voids in the AC Samples ....................................................................................................................................112
Figure 6.9 Hardness for different levels of air voids ........................................................................113
Figure 6.10 Burgers Model ..............................................................................................................115
Figure 6.11 Creep Data Fitting ........................................................................................................116
Figure 6.12 Relaxation Times with Increasing Amounts of Air Voids ............................................118
Figure 7.1 Outline of Thickness Change Analysis .............................................................................121
Figure 7.2 Load-Displacement Behavior of Random Nanoindentation Tests on HMA Sample ..........................................................125
Figure 7.3 Nanoindentation on Asphalt-Aggregate System ............................................................126
Figure 7.4 Nanoindentation Load-displacement Response of Unaged Asphalt aggregate System ..........................................................................................................................128
Figure 7.5 Nanoindentation Load-displacement Response of 2 days aged Asphalt aggregate System ..........................................................................................................................129
Figure 7.6 Nanoindentation Load-displacement Response of 5 days aged Asphalt aggregate System ..........................................................................................................................130
Figure 7.7 Nanoindentation Load-displacement Response of 10 days aged Asphalt aggregate System ........................................................................................................ 131
Figure 7.8 Comparative Study of the Change of Film Thickness with Oxidative Aging 132
Figure 7.9 Full FTIR Spectrum on Unaged Asphalt Binder.................................................. 134
Figure 7.10 Functional Group variation as a function of Days of Aging .............................. 135
Figure 7.11. Asphaltene Content as Function of Days of Aging of Asphalt .................... 136
Figure 8.1 Steps of Asphalt Aging Model Development.................................................. 141
Figure 8.2 Aging Trend Mastic Phase of PG 70-22 Binder Containing Asphalt Concrete Sample................................................................................................................. 143
Figure 8.3 Aging Trend Mastic Phase of AM2 Sample....................................................... 144
Figure 8.4 Aging Trend Mastic Phase of AM3 Sample....................................................... 145
Figure 8.5 Load-Displacement graph of (a) unaged and (b) 4-year field aged binder Phase in AC................................................................................................................. 148
Figure 8.6 Comparisons of Average Binder (a) Modulus and (b) Hardness in AC Sample. .................................................................................................................. 149
Figure 8.7 Load-Displacement graph of (a) unaged and (b) 4-year field aged Mastic Phase in AC................................................................................................................. 150
Figure 8.8 Comparisons of Average Mastic (a) Modulus and (b) Hardness in AC Sample .................................................................................................................. 150
Figure 8.9 Load-Displacement Plots of (a) Unaged and (b) 4-year Field Aged Aggregate Phase in AC................................................................................................................. 151
Figure 8.10 Comparisons of Average Aggregate (a) Modulus and (b) Hardness in AC Sample.................................................................................................................. 152
CHAPTER 1

INTRODUCTION

1.1 Problem Statement

Aging is a complex phenomenon, which involves physical and chemical modifications to asphalt molecules. These modifications, or changes, have dramatic effects on asphalt binder and asphalt concrete (AC) properties such as stiffness, hardness and brittleness. As asphalt binder ages the nonpolar molecule part decreases and the polar part increases (Petersen 2009). The increased polar molecules change the nature of the asphalt and lead to increased stiffness and/or decreased stress relaxation rates. Currently, aging in asphalt is one of the major concerns in the asphalt research field, as aging can lead to the development of distresses such as fatigue cracking, and thermal cracking (Raquel et al. 2011; Jielin and Tarefder 2016). Because how aging affects stiffness and hardness are unknown, several models such as the top-down cracking and fatigue models that use stiffness as a model parameter, are incomplete.

In the last decade, pavement researchers used different aging simulation tools and material characterization techniques to quantify the effects of aging on asphalt binder and AC. Examples are rheological characterization of asphalt binder and asphalt mastic samples. Researchers have used rolling thin film oven (RTFO) test to simulate the short term aging of asphalt, and pressure aging vessel (PAV) is used to simulate the long term aging of asphalt. However, mainly rheological, viscosity and consistency have been used to quantify and characterize the aged and unaged binder. To this day, test methods developed are
mostly rheological shear and bending beam tests performed on the bulk volume of aged and unaged binder. Because the existing tests used in the asphalt area cannot be performed on binder and mastic while they are an integral part of AC. Recently, nanoindentation has brought an opportunity to conduct tests on the binder, mastic, and aggregate while they are integral parts of AC (Jager 2005; Ossa 2010; Tarefder and Faisal 2013). Because, in nanoindentation test, a nanometer size tip, which is smaller than binder film thickness as well as mastic phase, can be positioned in these phases to indent them.

AC consists of asphalt binder and aggregate (Figure 1.1). Aggregate consists of: coarse aggregate and fines. Coarse aggregate is the aggregate materials that are retained on a #200 sieve (75 microns). In this study, fine aggregate is defined as the aggregate materials that pass through a #200 sieve, known as “fines”. Asphalt binder creates a coating or film around the coarse aggregate, which is defined as the binder phase. Fines are also coated by asphalt or mixed with asphalt binder, creating a composite phase called mastic. Thus, AC has three phases: mastic, asphalt film binder, and coarse aggregate. What role the phases play in governing the aging performance of AC are not yet known. Nanoindentation test can be used to measure mechanical properties such as stiffness and hardness of asphalt binder, mastic, and aggregate while they are a part of an AC sample. The stiffness and hardness can be related to aging.
Nanoindentation test on a composite material like asphalt is a very complex and difficult task, because it is very difficult to identify and understand whether the nanoindenter tip is indenting a specific phase of a composite. Researchers have used different visual, microscopic and statistical analysis to identify different phases in AC (Khorasani et al. 2013; Mohajari et al. 2014; Tarefder and Faisal 2013; Zhang et al. 2015; Barbhuiya and Benjamin 2017). Instead of validating the specific phase identification, previous research was limited to visual inspections and interpretation of the stiffness data. Further, nanoindentation test can be a trivial test to run on a homogeneous sample, however the main challenge comes with understanding the results exactly and the interpretation of the data. Researchers have employed implementation of ramp loading with extended creep hold time during nanoindentation to characterize viscoelastic asphalt material (Tarefder and Faisal 2013a; Tarefder and Faisal 2013b; Faisal et al. 2015; Faisal 2013). Employing extended creep hold during nanoindentation testing can be helpful in two interesting ways. One, the extended creep hold time helps the asphalt characterization technique to take care of the viscous flow of the material. Allowing the material to stand for a specific period of
time at a specific time allows the material enough time to take care of the delayed viscous flow. Two, the extended dwell time data can be extracted from the whole test data to interpret the viscoelastic creep response of the material.

Oxidative aging of AC is a function of the types of asphalt, asphalt aggregate interaction, availability of oxygen, time and temperature. Here availability of oxygen refers to the available oxygen in the pore structures/air voids of the AC system, and asphalt aggregate interaction refers to whether the effect of aging is the same for the binder and mastic phases of AC, when they are in the phase state with AC. In other words, how aging is affecting the mastic phase of AC compared to the binder phase of AC. This study investigates the behavior of asphalt binder and mastic as a function of time and attempts to develop a model using the kinetics of aging in asphalt. It should be mentioned that while the nanoindentation test results can be significantly affected by the sample thickness, this study investigates how and to what extent the asphalt binder thickness changes as a function of time on aging of asphalt.

1.2 Hypothesis

The aging of AC has been investigated using macroscale testing on AC or liquid binder. The aging behaviors of different phases of an AC (binder, mastic, and aggregate) has not been studied. It is hypothesized that nanoindentation on different phases of AC such as the binder, mastic, and aggregate can lead to a better understanding of aging in AC.
Specifically, this hypothesis leads to finding whether mastic is more/or less affected by aging compared to AC or binder.

1.3 Organization of the Dissertation

The dissertation consists of nine chapters. Chapter 1 defines the problem statement and hypothesis associated with nanoindentation of AC aging. Review of the current pool of literature on asphalt, modeling methods, and the studies related to asphalt using nanomechanics are presented in Chapter 2. In Chapter 3, the methodology of nanomechanical characterization of asphalt aging is explicated. In Chapter 4, phase identification technique in AC using creep response of the material is studied. Extraction of mechanical properties and comparison of mastic and binder phases responses with progressive aging are presented in Chapter 5. In Chapter 6, the mechanical properties of asphalt under different air voids content for asphalt aging are studied. Technique and effects related to change in asphalt film thickness with progressive aging are studied in Chapter 7. In Chapter 8, the aging model development and validation of nanomechanical stiffness characterization are discussed. Finally, the conclusions of this study are summarized and recommendations for further study are provided in Chapter 9.
2.1 Asphalt Aging

Asphalt concrete (AC) is the most common and popular choice of pavement construction material in all over the world. During pavement construction hot asphalt binder is mixed with aggregate of specific gradation to produce hot mix asphalt. In hot mix asphalt (HMA), asphalt binder creates a thin film of coating around the aggregate surface and sometime the fine particles entrap in the binder (Tarefder and Faisal 2014). Approximately, 95% aggregate material is mixed with 5% asphalt binder to produces 100% HMA. Asphalt binder is the main key binding ingredient that controls the property of the AC. During the service life of an asphalt pavement, asphalt binder goes through two distinct pavement issue, one is asphalt aging and another is moisture damage of asphalt. The current study focuses on aging, namely oxidative aging.

Aging of asphalt is one of the major concerns, as aging can lead to the development of distresses like fatigue or thermal cracking in asphalt pavement (Raquel et al. 2011, Huet 1965). Aging in asphalt leads to stiffening of the material as well changes in chemical composition. Fig 2.1 show that, asphalt is a mixture aliphatic, aromatic and naphthenic hydrocarbon, with a combination of Sulphur, oxygen, nitrogen and trace metals such as vanadium, nickel and iron (Martinho and Farinha 2017, Jeilin pan 2015). The separation to different molecules is very difficult due to its chemical complexity. However, with the
advancement of chromatographic analysis, it is possible to separate asphalt into four different fractions: saturates, aromatics, resins and asphaltenes (SARA) (Jielin 2016).

![Asphalt Chemistry](image)

It is well known as asphalt ages, the nonpolar molecule part decreases and polar part increases (Petersen, 2009). The increased amounts of polar molecules change the nature of the asphalt and lead to increased stiffness and hydrocarbon molecular size (Aruja et al. 2015). The increase in hydrocarbon molecular size increases the asphaltene fraction of asphalt binder (Lu and Isacsson 2002, Zhang et al. 2012, Moraes and Bahia 2015, Gamarra and Ossa 2016). In addition, the oxidation of the asphalt binder increases the polar fraction component, like ketones and sulfoxides in asphalt, as shown in Figure 2.2 (Ahmad et al. 2017, Qin et al 2014). Figure 2.2 shows that non polar hydrocarbon reacts with oxygen and creates oxidized polar parts in the molecules, like oxygen and hydroxyl parts in the molecules. In other cases, the oxygen reacts with trace element like sulfur to create sulfoxide elements. Similarly ketone, anhydride and carboxylic polar fractions evolves
during oxidation of asphalt binder. The polar elements in asphalt binders coagulates to form stiffer asphaltene fractions of asphalt.

**Figure 2.2** Asphalt oxidation.

The chemical and physicochemical mechanisms of asphalt oxidative age hardening, and changes in the performance-related properties of asphalt resulting from oxidation, have been the subject of several research investigations and speculations for last decades. Reviews of the fundamental work on aging have been published (Petersen et al., 1986; Robertson, 2001; Petersen, 2009). The carbonyl chemical functional group, as characterized by infrared (IR) spectroscopy, has long been used to indicate the level of asphalt oxidation.
Figure 2.3 Relationship of Carbonyl Group and Asphalt Viscosity (Petersen 1993).

The linear relationship between the viscosity increase and carbonyl formation during asphalt oxidation has been well established (Lau et al., 1992; Petersen et al., 1993). The ketone functional group, the major component of the carbonyl IR absorption region, is formed primarily from the oxidation of benzyl carbons in side chains attached to highly condense aromatic ring systems (Dorrence et al., 1974; Petersen, 1998). These components exist largely in the so-called asphalt polar aromatics fraction (Corbett-type separation). Ketone formation has been identified as a major factor leading to asphaltene formation on oxidation, and asphaltenes have been shown to be primarily responsible for viscosity increase on aging (Petersen, 1984; Lin et al., 1995). The ketones formed on oxidation have been shown to concentrate in the asphaltene fraction (Petersen, 2009). The increase in
The asphaltene fraction of asphalt binder is related to the increase in viscosity of the material, as shown in Figure 2.3.

![Diagram showing colloidal structure of asphalt before and after oxidative aging.](image)

**Figure 2.4** Colloidal Structure of Asphalt before and after Oxidative Aging.

Figure 2.4 shows oxidative aging of asphalt transforms resin and maltene fractions of asphalt to create oxidized asphaltene fraction. Asphaltene is the strongest fraction in asphalt binder, therefore increase in asphaltene create stiffer oxidized asphalt binder. Asphalt aging is subdivided into two parts: short term aging, which is mainly occurs during heating process and due to loss of volatile materials from asphalt binder and another part is the long term aging which is mainly occurs due to the oxidation of asphalt binder. The current study focuses on the oxidative aging or long term aging part of asphalt. Oxidative aging of asphalt causes the hardening of the material. Oxidative aging of asphalt is defined as the change of chemical composition that affects the physical properties of AC.
2.2 Nanoindentation

In a nanoindentation test, an indenter tip of a known modulus of elasticity and geometry is loaded to penetrate a sample surface and then unloaded. Modulus of elasticity of the sample is determined from the load-displacement data. The area of contact at full load is determined from the measured depth of penetration and the known geometry of the indenter tip. Sample hardness is calculated by dividing the maximum load by the contact area.

A typical load-displacement curve is shown in Figure 2.5(a). A sitting load of 0.005 mN is typically applied initially to facilitate a contact between the tip and sample surface. Next, the load is increased gradually from point $a$ to $b$. The tip is unloaded at the maximum load point $b$. The unloading path is assumed to be elastic for most of the elastoplastic material. The unloading curve does not come back to point $a$ due to plastic deformation in elastoplastic materials. The slope of the unloading curve at point $b$ is usually equal to the slope of loading curve at point $a$.

Figure 2.4(b) shows the surface profile as a function of penetration depth during loading and unloading. Here, $h_{max}$ is the total depth of indentation at a maximum load, $h_p$ is the total depth of indentation that is unrecovered, $h_s$ is the depth of the surface at the perimeter of the indenter contact and $h_c$ is the vertical depth along which contact is made between the indenter and the sample. Therefore,

$$h_c = h_{max} - h_s$$

(2.1)
Figure 2.5 Schematic of Indentation Test.

- \( h_c \): vertical depth along which contact is made;
- \( h_e \): elastic depth recovery during unloading;
- \( h_p \): Final depth after unloading;
- \( h_{\text{max}} \): Depth at maximum load;
- \( h_s \): displacement of the surface at the perimeter of the contact.

(a) Load-Displacement Curve

(b) Indentation Depth
The depth of impression that is recovered is,

\[ h_e = h_{\text{max}} - h_p \]  

(2.2)

Several researchers have developed analytical methods to analyze load-displacement data to find elastic modulus and hardness. Doerner and Nix (1986) presented a method to calculate hardness from the loading curve and Young’s modulus from the unloading curve. They assumed that the contact area remains constant as the indenter tip is retracted from the sample and the unloading curve is linear. Oliver-Pharr (1992) refined the Doerner and Nix method to account for the non-linear unloading curve, especially at the onset of unloading. According to the Oliver-Pharr method (1992), the vertical displacement of the contact periphery during the indentation test is modeled by the displacement of a “flat elastic” surface by a hard tip. The Oliver-Pharr method (1992) is the most widely used method to date for its simplicity.

### 2.3 Oliver-Pharr Method

The Oliver and Pharr (1992) method is based on the elastic contact between a rigid sphere (tip) and a flat surface (sample). Hertz (1986) found the contact radius \( a \) is related to the indenter radius \( R \), applied load \( P \) and the reduced elastic modulus \( E^* \) of a sample by (see Figure 2.6):

\[ a^3 = \frac{3PR}{4E^*} \]  

(2.3)
Contact radius $a$ is also related to the indenter radius $R$ and penetration depth by:

$$a = \sqrt{Rh}$$

(2.4)

From Eq. (2.2) and (2.3) the applied load can be written as:

$$P = \frac{4}{3} E^* R^{1/2} h^{3/2}$$

(2.5)

**Determining $E^*$**

If the indentation load $P$ penetration depth $h$ is recorded as the load-displacement curve, the reduced elastic modulus $E^*$ can be found from the load-displacement curve as shown in Eq. (2.5). However, the equation also relates to the indentation radius. The equation can be simplified by differentiating Eq. (2.5) with respect to penetration depth $h$ and using Eq. (2.4).

By differentiating Eq. (2.5) with respect to penetration depth $h$

$$\frac{dP}{dh} = \frac{4}{3} E^* R^{1/2} \left( \frac{3h^{1/2}}{2} \right)$$

(2.6)

Using the relation in Eq. (2.4):
\[ \frac{dP}{dh} = 2E \sqrt{Rh} = 2E \cdot a \]  \hspace{1cm} (2.7)

The projected area at the maximum load can be defined as: \( A = \pi a^2 \)

Therefore,

\[ S = \frac{dP}{dh} = \frac{2}{\sqrt{\pi}} E \sqrt{A} \]  \hspace{1cm} (2.8)

where \( S \) is the unloading stiffness or slope of the unloading curve;

\[ E^* = \frac{\sqrt{\pi}}{2\sqrt{A}} (S) \]  \hspace{1cm} (2.9)

**Determining \( S \)**

Oliver and Pharr (1992) used a power law function to fit the unloading path of the load-displacement curve. The power law function used by Oliver-Pharr is shown in Eq. (2.9):

\[ P = \alpha (h - h_f)^m \]  \hspace{1cm} (2.10)

where \( h \) is the depth of penetration,

\( h_f \) is plastic depth,

\( \alpha \) and \( m \) are curve fitting parameters related to tip geometry.

\( m = 1 \) for flat-ended cylindrical tip, \( m = 1.5 \) for spherical tip, and \( m = 2 \) for conical tip (Berkovich tip).

The slope is measured by differentiation the in above Eq. (2.10) at the onset of unloading.
Determining $A$

Oliver and Pharr (1992) defined the projected area $A$ as a function of $h_c$ defined in Eq. (2.1). Oliver and Pharr (1992) extrapolated the tangent line to the unloading curve at the maximum loading point down to zero loads. This yields an intercept value for depth which estimates the $h_s$ by:

$$h_s = \varepsilon \frac{P_{\text{max}}}{S}$$ \hspace{1cm} (2.11)

Therefore,

$$h_c = h_{\text{max}} - \varepsilon \frac{P_{\text{max}}}{S}$$ \hspace{1cm} (2.12)

where $\varepsilon$ is a geometric constant.

$\varepsilon = 0.72$ for conical tip, $\varepsilon = 0.75$ for Berkovich tip, and $\varepsilon = 0.72$ for spherical tip.

The project area is measured by:

$$A = \pi a^2 = \pi (Rh_c)$$ \hspace{1cm} (2.13)

where $R$ is known and $h_c$ is calculated using the above Eq. (2.13).

Determining $E$

Timoshenko and Goodier (1951) found the reduced elastic modulus, $E^*$ is related to the modulus of the indenter and the specimen and given by:

$$\frac{1}{E^*} = \frac{1 - \nu^2}{E} + \frac{1 - \nu_i^2}{E_i}$$ \hspace{1cm} (2.14)
where $E$ is Young’s modulus of the material,

$\vartheta$ is Poisson’s ratio of the material,

$E_i$ is Young’s modulus of the indenter and

$\vartheta_i$ is Poisson’s ratio of the indenter,

$E^*$ is the reduced modulus. One can find the elastic modulus of the sample, $E$ using Eq. (2.14).

**Determining Hardness, $H$**

Hardness, $H$, is defined by the maximum load divided by the projected area (Brinell 1901):

$$H = \frac{P_{\text{max}}}{A}$$

(2.15)

where $P_{\text{max}} =$ peak load and $A =$ projected area of contact at the peak load. The unit of hardness is given in N/m$^2$=Pa.

**2.4 Indenter Tip Section**

One of the main challenges of nanoindentation is choice of the nanoindentation tip, as proper choice of tip fully depends on application and proper interpretation of the results (Han et al. 2015). Among all the nanoindentation tip spherical and conical indenters are the most popular, for their wide variety of applications. Tarefder et al. (2010) have used both spherical and Berkovich tips to indent asphalt binder. However, their study concluded that Berkovich tips are more suitable than spherical tips for asphalt testing. A spherical indenter has a large tip radius compared to a sharp indenter such as Berkovich indenter. Therefore, the contact area between the indenter tip and sample surface will be higher in case of a spherical indenter. For adhesive material like asphalt binder, if the contact area is higher
then the material adheres to the indenter tip. If the material adheres to the indenter tip then the system loses its compliance. As such the nanoindentation test produce erroneous results (Faisal 2013). For this reason, Berkovich indenter is better for adhesive time-dependent material like AC. Only Berkovich tips were used for asphalt testing in the current study. The tests were conducted using a nanoindentation device manufactured by Micro Materials, from Wrexham UK. The Berkovich indenter tip is made of diamond and firmly connected in the device, therefore, it cannot not deform.

For the Berkovich tip, the projected area of the contact is given by:

\[ A = 3\sqrt{3}h_t^2 \tan^2 \psi \]  

(2.16)

where \( \psi \) = phase angle. The phase angle is \( \psi = 65.27^\circ \) for the Berkovich tip. Eq. (2.17) can be simplified as:

\[ A = 24.5h_t^2 \]  

(2.17)

2.5 Applicability of Oliver-Pharr Method for Asphalt

According to the Oliver-Pharr method the unloading portion of the load-displacement curve is fitted to the power law function to calculate material property. In the analysis, the slope is determined by differentiating the load-displacement equation with respect to displacement. The unloading slope is positive for elastoplastic materials. Most of the cases the slope is negative for asphalt, as after unloading material continues to displacement. If slope is negative, the \( E^* \) becomes negative from Eq. (2.9). Therefore, this method is not applicable for asphalt.
In asphalt, creep within the material can occur under indentation loading. Here “creep” means a time-dependent deformation due to an applied load. Figure 2.7 shows the load-displacement curve of asphalt with negative slope of the unloading part of the load-displacement curve. It can be seen from the unloading portion of the load-displacement curve that displacement continues instead of recovery of displacement. The response is due to the viscous flow of the material. Therefore, the unloading portion of the load-displacement curve becomes negative from Oliver-Pharr analysis method. Therefore, Oliver-Pharr method is not applicable.

The viscous effect, of asphalt binder can be reduced during nanoindentation by using a fast unloading rate with an extended dwell time. Previous study has proven that, this approach can minimize the viscous flow effect on data (Tarefder and Faisal 2013a, 2013b, 2014). Though the overall response of the asphaltic material is important. However, as it is a time-dependent material, the viscoelastic creep response is a very attractive parameter to model.
Previous study by the author showed if the dwell time is long enough say 100-200 sec the viscous effect of the material is minimum on data (Tarefder and Faisal 2013a). However, to quantify whether the viscous effect decreases with increase in creep hold time, we have used three different constitutive models. The results show in each case the viscosity parameter reduces as dwell time increases, The main idea behind the long dwell or creep hold time on the viscoelastic material during nanoindentation test is to allow the material enough time for the viscous flow for a specific load and when the viscous flow is minimum the material shows positive load-displacement behavior during unloading phase of the indentation test.

2.6 Data Interpretation

Nanoindentation test is a trivial test, however, the nanoindentation data interpretation is non-trivial. In this section data interpretation techniques for nanoindentation creep response of asphalt are discussed. Nanoindentation creep data, instead of loading or unloading data, is used to analyze the creep response. In the study, fast loading and unloading rate is applied, so that the loading and unloading portion of the load-displacement can be ignored.

The creep response of the material is modeled using linear viscoelastic (LVE) analysis of the material. The size and shape of indenter tip is greatly affect the indentation depth and for a three-sided pyramid, like Berkovich indenter, the load-displacement response of a Berkovich indenter is expressed by a quadratic elastic load-displacement relationship, shown in Eq. (2.16) (Faisal and Tarefder 2013b, Oliver and Pharr 1992, Oyen and Cook 2002, Oyen and Co 2007).
\[ P_0 = \frac{\pi \tan \psi}{2\gamma^2} \frac{E'}{(1-\nu^2)} h^2 \]  

\[ (2.16) \]

where \( P_0 \) = indentation load

\( h \) = displacement due to applied load in a material

\( E \) = elastic modulus of the indented material

\( \nu \) = Poisson’s ratio of the material

\( \psi \) = include a half angle of Berkovich indenter (i.e. 70.3°) and

\( \gamma \) = constant relates contact depth to total depth and is taken as unity for polymeric materials. For asphalt materials, \( \gamma = 1.0 \) was assumed.

The Eq. (2.16) can be rearranged as:

\[ h^2 = 2 \frac{P_0 \cot \psi}{E} \]  

\[ (2.17) \]

where \( E \) is the plain strain modulus.

\[ E = \frac{E'}{1-\nu^2} \]  

\[ (2.18) \]

The elastic expression in Eq. (2.17) can be modified to develop a viscoelastic expression, by replacing \( P_0/E \), with an integral over a creep function \( J(t) \), known as creep compliance, as shown below:

\[ h^2 = \frac{2 \cot \psi}{\pi} \int_{0}^{t} J(t-u) \frac{dP_0(u)}{du} du \]  

\[ (2.19) \]

where \( J(t) = 1/E \), is creep compliance and \( u \), is a dummy variable for integration and delayed response is presented by \((t-u)\) variable instead of time variable \( t \). It is a common
practice to represent the creep compliance \( J(t) \) with different combination of spring and dashpot element. Following sections discusses different model combination of spring and dashpot, which are used to represent the creep response of asphalt material.

### 2.6.1 Voigt Model

Figure 2.8 shows the Voigt model, which consists of a linear spring and a dashpot element in parallel with a linear spring series. The linear spring follows Hooke’s law, which states that stress is proportional to the strain.

\[
\sigma = E \varepsilon \tag{2.20}
\]

where \( \sigma \) is stress, \( \varepsilon \) is strain and \( E \) is the elastic modulus of the spring.

The dashpot represents the behavior of a viscous material. It states that stress is proportional to the time rate of strain.

\[
\sigma = \eta \frac{\partial \varepsilon}{\partial t} \tag{2.21}
\]

where \( \eta \) is viscosity and \( t \) is time.

Under constant stress Eq. (2.21) can be integrated to become:

\[
\varepsilon = \frac{\sigma t}{\eta} \tag{2.22}
\]
Figure 2.8 Voigt Model.

The dashpot and the spring parallel to it will have the equal displacement response. Both the spring and the dashpot have the same strain, but the total stress is the sum of two stresses, using the subscript from Figure 2.8,

\[ \sigma = E_2 \varepsilon_2 + \eta_2 \frac{\partial \varepsilon_2}{\partial t} \]  (2.23)

where \( E_2 \) is the elastic modulus of parallel spring and \( \eta_2 \) is the viscosity of parallel dashpot.

If a constant strain is applied:

\[ \int_{0}^{t} \frac{d \varepsilon_2}{\sigma - E_2 \varepsilon_2} = \int_{0}^{t} \frac{dt}{\eta_2} \]  (2.24)

or
\[ \varepsilon = \frac{\sigma}{E_2} [1 - e^{-t/\tau_2}] \]

where \( \tau_2 \) is retardation time.

\[ \tau_2 = \frac{\eta}{E_2} \quad (2.25) \]

The additional series spring element of Voigt model has an instantaneous elastic strain. Therefore, the total strain,

\[ \varepsilon = \frac{\sigma}{E_1} + \frac{\sigma}{E_2} [1 - e^{-t/\tau_2}] \quad (2.26) \]

where \( E_1 \) is the elastic modulus of the series spring.

It can be seen from Eq. (2.26) that

when \( t = 0 \) and if \( E_1 = E_2 = E \), then the instantaneous strain \( \varepsilon_1 = \sigma/E \);

when \( t = \infty \) and if \( E_1 = E_2, \varepsilon_2 = 2\sigma/E \), or the spring is fully stretched to its total retarded strain;

when \( t = \tau_2 \) and if \( E_1 = E_2, \varepsilon_3 = (2 - 1/e)\sigma/E \). Now, \( \varepsilon_3/\varepsilon_2 = (2 - 1/e)/2 = 70.5\% \) or \( \varepsilon_3 = 70.5\% \) of \( \varepsilon_2 \).

Thus, the retardation time \( \tau_2 \) of Voigt model is the time to reach 70.5\% of the total retardation strain.

Eq. (2.26) can be rearranged as:

\[ \frac{\varepsilon}{\sigma} = \frac{1}{E_1} + \frac{1}{E_2} [1 - e^{-t/\tau_2}] \quad (2.27) \]
Therefore, the basic creep compliance equation for Voigt model is,

\[
J(t) = \frac{1}{E_1} + \frac{1}{E_2} [1 - e^{t/\tau_2}]
\]  

(2.28)

2.6.2 Burger Model

Among several viscoelastic models consists of spring and dashpot, Burger’s model is the most popular one. Figure 2.9 shows a Burger model which has a dashpot in series with Voigt elements.

\[
\begin{align*}
\epsilon_1 &= \frac{\sigma}{E_1} \\
\epsilon_2 &= \frac{\sigma t}{\tau_1} \\
\epsilon_3 &= \frac{\sigma}{E_2} \left[1 - \exp\left(-\frac{t}{\tau_2}\right)\right]
\end{align*}
\]

= Burger Viscoelastic Response

**Figure 2.9** Burger Model.

The strain of the dashpot from Eq. (2.29) can be expressed as:

\[
\epsilon_{\text{Dashpot}} = \frac{\sigma t}{\eta}
\]  

(2.29)
Adding Eq. (2.29) with Eq. (2.26) gives the viscoelastic solution for Burger model:

\[ \varepsilon = \varepsilon_{Dashpot} + \varepsilon_{Voigt} \]  
(2.30)

\[ \varepsilon = \frac{\sigma}{\eta_1} + \frac{\sigma}{E_1} + \frac{\sigma}{E_2} \left[ 1 - e^{-t/\tau_1} \right] \]  
(2.31)

The equation can be rearranged as:

\[ \frac{\varepsilon}{\sigma} = \frac{t}{\eta_1} + \frac{1}{E_1} + \frac{1}{E_2} \left[ 1 - e^{-t/\tau_2} \right] \]  
(2.32)

Therefore, the basic creep compliance equation for Burger model is,

\[ J(t) = \frac{1}{E_1} + \frac{1}{E_2} \left[ 1 - e^{-\frac{t}{\tau_2}} \right] + \frac{t}{\eta_1} \]  
(2.33)

2.6.3 Spring-Dashpot-Rigid (SDR) Model with Nonlinear Spring

With the SDR model, the behavior of viscoelastic material under nanoindentation creep is modeled by three quadratic elements as shown in Figure 2.10 (Oyen and Cook 2003; Olesiak et al. 2010, Faisal et al. 2015).

![Figure 2.10 SDR Model.](image)

The model is called Spring-Dashpot-Rigid (SDR) element model. Load-displacement relations of spring, dashpot, and rigid elements are nonlinear, more specifically quadratic. Load-displacement relation of spring is defined as:
\[ P_e = k_Q h_e^2 \quad (2.34) \]

where \( k_Q \) is the quadratic stiffness. The quadratic stiffness is identified with the plain strain modulus of the material, \( E' \), via geometric considerations: \( k_Q = \alpha_1 E' \) and \( \alpha_1 = \pi/(2 \cot \psi) \). The second element is defined by a dashpot as follows:

\[
P_v = \mu_Q (\frac{dh_v}{dt})^2 \quad (2.35)
\]

where \( \mu_Q \) is a quadratic viscous coefficient. The quadratic viscosity is the product of geometric term \( \alpha_2 \) and a material property: \( \mu_Q = \alpha_2 \eta \). Here \( \eta \) is the indentation viscosity and geometric term \( \alpha_1 = \alpha_2 \). Under indentation conditions, substantial plastic deformation can occur beneath the indenter. The third element is defined by a rigid body as follows:

\[ P_p = \alpha_3 H h_p^2 \quad (2.36) \]

where \( P_p \) and \( h_p \) are the load and displacement of the rigid body element. \( H \) is the plastic deformation resistance or hardness of the material, and \( \alpha_3 = \pi \tan^2 \psi \) is a dimensionless geometry parameter for sharp indentation with effective included angle \( 2\psi \). The dimensionless constants are for Berkovich tip as: \( \alpha_3 = \pi \tan^2 \psi = 24.5 \) and \( \alpha_1 = \alpha_2 = 4.4 \) (Oyen and Cook 2003).

The total displacement is the result of the sum of displacements in three elements, can be written as:

\[ h = h_v + h_e + h_p \quad (2.37) \]

where \( h \) is the total displacement, \( h_e \) is the elastic displacement in spring, \( h_v \) is the viscous displacement in the dashpot and \( h_p \) is the plastic displacement in the rigid element.
Load in the elements can be written as:

\[ P = P_e = P_v = P_p \]  \hspace{1cm} (2.38)

As the displacement is the sum of displacement for three individual elements, the displacement rate is also the sum of the displacement rates of the individual element, which gives the following equation:

\[ \frac{dh}{dt} = \frac{dh_v}{dt} + \frac{dh_e}{dt} + \frac{dh_p}{dt} \]  \hspace{1cm} (2.39)

Substituting the values of Eq. (2.36), Eq. (2.37) and Eq. (2.38) in Eq. (2.39):

\[ \frac{dh}{dt} = \frac{P^{1/2}}{(\alpha_2 \eta)^{1/2}} + \frac{1}{P^{1/2}} \frac{dP}{dt} \frac{1}{2(\alpha_1 E')^{1/2}} + \frac{1}{P^{1/2}} \frac{dP}{dt} \frac{1}{2(\alpha_3 H)^{1/2}} \]  \hspace{1cm} (2.40)

A trapezoidal indentation load, as shown in Figure 2.11 was considered. The loading and unloading rates were kept constant. The creep hold or dwell time was applied at the maximum load.

\[ \text{(a) Load-Displacement Curve} \hspace{1cm} \text{(b) Loading Protocol} \]

**Figure 2.11** Nanoindentation Loading with Creep Load.
Here, $k$ represents the loading and unloading rate, $t_R$ represents loading and unloading time, and $t_c$ represents the dwell time.

**Loading Curve**

The slope of the loading curve can be expressed as:

$$P(t) = kt$$  \hspace{1cm} (2.41)

$$\frac{dP}{dt} = \frac{dP_R}{dt} = \frac{dP_P}{dt} = k; \hspace{0.5cm} 0 \leq t \leq t_R$$  \hspace{1cm} (2.42)

Substituting the slope value in Eq. (2.42):

$$\frac{dh}{dt} = \left(\frac{kt}{\alpha_2 \eta}\right)^{1/2} + \frac{1}{2} \frac{k}{(kt)^{1/2}} + \frac{1}{2} \frac{k}{(\alpha_1 E)^{1/2}}$$  \hspace{1cm} (2.43)

By integrating Eq. (2.43):

$$h^{LOAD}(t) = \left(kt\right)^{1/2} \left[\frac{2t}{3(\alpha_2 \eta)^{1/2}} + \frac{1}{(\alpha_1 E)^{1/2}} + \frac{1}{(\alpha_3 H)^{1/2}}\right]$$  \hspace{1cm} (2.44)

**Creep Curve**

Slope during holding time can be expressed as:

$$\frac{dP}{dt} = 0; \hspace{0.5cm} t_R \leq t \leq t_c + t_R$$  \hspace{1cm} (2.45)

Substituting this in Eq. (2.45) and integrating the resulting equation gives:

$$h^{CREEP}(t) = \int_{t_R}^{t_c + t_R} \frac{\left(P_{max}\right)^{1/2}}{(\alpha_2 \eta)^{1/2}} dt$$  \hspace{1cm} (2.46)
\[ h^{\text{CREEP}}(t) = \left( \frac{P_{\text{max}}}{\alpha_2 \eta} \right)^{1/2} (t - t_R) + h^{\text{LOAD}}(t_R) \]  

(2.47)

**Unloading Curve**

The slope of unloading curve can be expressed as:

\[ \frac{dP}{dt} = -k; \quad t_R + t_c \leq t \leq 2t_R + t_c \]  

(2.48)

Thus the unloading rate can be defined as:

\[ \frac{dh}{dt} = \left[ k(2t_R + t_c - t) \right]^{1/2} \frac{1}{\left( \alpha_2 \eta \right)^{1/2}} \left( \frac{k}{2(\alpha_1 E')^{1/2}} \right) \]  

(2.49)

The solution for unloading portion is given by (Olesiak et al. 2010):

\[ h^{\text{UNLOAD}}(t) = \left( k \right)^{1/2} \left( t_R^{1/2} - (2t_R + t_c - t)^{1/2} \right) \frac{3}{2(\alpha_2 \eta)^{1/2}} + \left( \frac{2t_R + t_c - t}{(\alpha_1 E')^{1/2}} \right)^{1/2} \]  

(2.50)

Eqs. (2.44), (2.47) and (2.50) defines the entire displacement-time history of a nanoindentation test of asphalt using trapezoidal loading.

**2.7 Past Studies of Nanoindentation on Asphalt**

Nanoindentation study on asphalt are discussed in the following sections.
2.7.1 Nanoindentation Testing of Asphalt

Pavement researchers started to use nanoindentation to characterize asphalt in last decade. Only a few studies are available and which are discussed below:

*Jager et al. (2010)*

Jager et al. (2010) employed the nanoindentation technique to study the viscoelastic properties of asphalt. They conducted nanoindentation tests on two bitumen samples to understand the effect of loading rate, maximum load and temperature. Four different loading rates on 20 µN/sec, 40 µN/sec, 80 µN/sec, and 160 µN/sec were applied. In addition, six different maximum loads were employed.

*Findings:* Maximum loads significantly affect the viscoelasticity, whereas loading rate slightly affects the viscoelastic parameters of the study.

*Limitations:* The research examined only the effects of loading rate and maximum load, but it did not consider the effects of dwell time on asphalt.

*Tarefder et al. 2010*

Tarefder et al. (2010) used nanoindentation to determine elastic modulus and hardness for a wide range of asphalt materials, i.e. binder and concrete. In that study, three different asphalt binders and two different asphalt concrete samples were used. They developed a successful nanoindentation testing protocol, based on only two loading rates and maximum loads for different phases of AC. The individual phase identification was done by using indentation tests on visual investigation of the exposed 2D surface. That study employed
two different nanoindentation indenter tips, i.e. Berkovich and Spherical indenter tips, to characterize the AC phases.

*Findings:* The study delivered a wide range of elastic modulus and hardness for different asphalt materials.

*Limitations:* The study utilized two indentations on each phase of the AC. Considering the heterogeneous nature of the asphalt aggregate system the choice of only two indentations for each phase characterization is not enough for calculating the variability in data and have confidence in data. That study could not analyze the data when the load-displacement curve produces negative slope.

*Tarefder and Faisal (2013a)*

The studies determined the effects of different loading rates and dwell times to produce successful nanoindentation test protocol, the result/load-displacement curves found using the test protocol used afterwards for traditional Oliver-Pharr method for analysis. The study identified a high enough dwell time (say 100-200 sec) during nanoindentation could allow the material long enough time for the continuous viscous flow of the material at a specific load. It should be noted, during nanoindentation asphalt produces negative slope of unloading part of the load-displacement curve due to the continuation of the viscous flow of the asphaltic material.

*Findings:* That study confirmed a dwell time 200 sec and a loading/unloading rate of 0.007 mN/sec can minimize the viscous flow of the material to produce positive slope on the unloading part of the nanoindentation load-displacement curves. The study also concluded
Berkovich indenter can successfully indent on as asphalt surface to produce successful load-displacement curves.

*Limitations:* Tarefder and Faisal (2013a) study was restricted to traditional elastoplastic Oliver-Pharr analysis. However, asphalt is a viscoelastic material. The study did not employ any viscoelastic analysis technique to quantify the viscoelastic parameters of asphalt.

*Khorasani et al. (2013)*

The study determined the elastic modulus and hardness for a fine aggregate (passing # 30 sieve) mixed with asphalt also known as fine aggregate mixture (FAM) sample. The study divided the FAM composite region into three different regions, aggregate, interface and mastic. Superpave gyratory compactor (SGC) was used to compact the sample, while pavement researchers uses SGC traditionally to produce hot mix asphalt with a combination of coarse and fine aggregates. The researchers employed Berkovich indenter to indent on the sample surface and optical technique/visual interpretation was used to identify each phase.

*Findings:* The study observed aggregate, interface, mastic elastic modulus of 84 GPa, 47 GPa and 32 GPa respectively. Two different maximum loads of 300 µN for the interface and 10,000 µN for aggregate surface were employed.

*Limitations:* The study observed mastic modulus was very high compared to the other nanoindentation test studies on asphalt. May be it was due to fact that the FAM samples were prepared by using high compaction force in the gyratory compactor, while for representative FAM preparation people used high shear mixture and standard fine
compaction techniques. In addition the study did not apply any creep load during nanoindentation, which is a common practice for nanoindentation on asphaltic material to reduce the viscous effect of the material.

_Tarefder et al. 2014_

The study observed the effects of different levels of doping of mica on asphalt binder using nanoindentation technique. Different doping levels in asphalt mastic mixture were subjected to short term and long term aging of asphalt. Therefore, the study quantified the effects of aging and mica mixed on the elastic modulus and hardness of the material.

**Findings:** The study observed modulus of the mastic increases with increase in aging of the material.

**Limitations:** The study restricted to investigate the effects of aging on different mica content with asphalt binder. The study did not investigate the effects on fines (passing #200 sieve) mixed asphalt mastic other than mica. The study only employed traditional elastoplastic analysis for material characterization.

_Faisal et al. (2014)_

The study employed nanoindentation technique to identify different AC phases using degree of softness and visual surface investigation. The study further analyzed the mastic phase data using viscoelastic Burger’s model. The main task of the study was to identify the effects of moisture damage on different pages of asphalt concrete.
Findings: The study observed 60-70% moduli reduction in different phases of AC for moisture-induced damage in asphalt.

Limitations: The study is limited to identification of each AC phases with respect to degree of softness index assumptions. However, validation was needed for the identification technique.

Mohajeri et al. (2014)

The study uses nanoindentation technique to identify whether Reclaimed Asphalt Pavement (RAP) was homogeneously blended with asphalt binder. In pavement construction it is a common practice to use recycled aged (stiffer) material at different percentages of total hot mix asphalt. However, whenever RAP is used it is assumed that the aged RAP binder is homogeneously mixed. The study used nanoindentation in the interfacial binder zone to identify whether RAP is homogeneously mixed the interfacial zone between two aggregates.

Findings: The study observed two different stiffness region in the interfacial zone of two aggregates. However, the study could not detect a successful blending zone, they recommended further study on the zone using microscopy and nanoindentation.

Limitations: The study did not consider the possibility of the presence of fines or mastic material, as it can change the whole blending zone stiffness in different zones of stiffness range. In addition, tradition elastoplastic Oliver-Pharr method was used for data analysis.
2.7.2 Modeling of Indentation Data

*Tarefder and Faisal (2013b) and Faisal (2012)*

Their studies employed different viscoelastic models, consists of spring and dashpot to produce viscoelastic parameters and to identify whether the viscous flow parameter minimizes with increase in dwell during nanoindentation testing on asphalt. Three different viscoelastic model and one visco-elasto-plastic models were used to extract the viscoelastic material. In addition, the visco-elasto-plastic model consists of spring, dashpot and rigid body (SDR) was calibrated for asphalt material analysis.

*Findings:* The studies observed reduction of viscosity parameter with increase in dwell time during nanoindentation on asphalt. The study also concluded, SDR model with nonlinear spring can successfully fit the whole load-displacement curve of nanoindentation on asphalt.

*Limitations:* The studies were restricted on the characterization of the asphalt binder samples only, and the researchers did not explore the physical significance on the viscoelastic model parameters.

*Veytskin et al. 2015*

That study proposed a model to determine the cohesion value of three different binder and 30 different asphalt mastics using nanoindentation load-displacement data. The researchers correlated the negative displacement and load during unloading part of the nanoindentation test with the cohesion of asphalt.
**Findings:** The study observed measured range of effective cohesion values, is 0.20–0.30 for different types of mastic fillers and percentages.

**Limitations:** The study observation is limited to wide range of overlapping values cohesion. Instead of repetition of specific value for a specific material, the study concluded by giving a wide range of effective cohesive value.

*Veytskin et al. 2016*

Their study determined the effects of three different loading rates, three maximum loads and three different dwell times on the nanoindentation test of asphalt binder and asphalt mastic samples. Then, the study used the creep/dwell time response of the material to obtain the creep compliance of the material, which is interconverted to the dynamic modulus of the material for validation purpose. The interconverted dynamic modulus of the material was compared with the dynamic shear modulus of asphalt binder.

**Findings:** The study proposed the use of interconversion technique for nanoindentation creep data. The study also observed good correlation of the mastic dynamic modulus with macro scale mastic dynamic shear modulus from 0.01 to 1 rad/sec frequency region at room temperature.

**Limitations:** The study could not produce the full range of complex modulus master curve, only a specific portion master curve was matched in the study for validation purpose.
2.8 Asphalt Film Thickness

Nanoindentation test largely depends on the thin film thickness of the material, because substrate has a great influence on the material properties of any indentation study. In this section, review of asphalt film thickness and aging are performed. No previous study is available regarding the change in thickness with progressive aging of asphalt.

It is well established that asphalt concrete aging is primarily related to the permeability, air voids and asphalt coating thickness (Kandhal and Chakraborty 1996, Ahmad et al. 2017). However, asphalt film thickness concept is an “average asphalt thickness”, it depends on the aggregate size and shape.

Elseifi et al. (2008) measured the asphalt film thickness experimentally using microscopic analysis technique. They reported asphalt binder film does not exist as a separate entity at the macroscopic scale, however, the large aggregates are surrounded by asphalt mastic, which is defined by the mixer of asphalt binder and fine aggregate fillers. The study found an asphalt mastic thickness more than 100 µm in the mixture they used for the research experiment. However, an asphalt binder thickness of 2 µm was found in between 2 fine fillers. Air voids are found beside the large aggregate surfaces, no air voids were found in the mastic. However, in the study, the samples were only washed with water after cutting with a diamond saw but no polishing scheme was employed to attain a smooth surface. Without employing any polishing technique, it is impossible to achieve a sample surface with minimum air voids, which is one of the biggest limitations of the study. In addition,
other than image analysis, no direct experimental technique was employed to measure the asphalt film thickness.

Except for the experimental study of Elseifi et al. (2008), no direct experimental study was performed to determine the asphalt binder thickness. All other studies have employed research studies based on average asphalt film thickness. In those studies, the average asphalt film thickness was estimated using Asphalt Institute (AI) Manual, Series No. 2 (MS-2) (2012), and the surface area of the aggregate analysis.

Kandhal and Chakraborty (1996) investigated the effects of short term and long-term aging of asphalt on asphalt film thickness. The main objective of the study was to determine the optimum asphalt film thickness and with respect to the durability of the mixtures. The researchers concluded, there is a strong correlation of asphalt binder film thickness with tensile strength and resilient modulus of the Hot Mix Asphalt (HMA). An average asphalt film thickness of 9-10 µm is recommended for an HMA with 8% air voids.

Li et al. (2009) investigated the relationship of in-place average asphalt film thickness and performance of HMA. The researchers proposed a new technique to calculate the average asphalt film thickness. The technique was originally pioneered by Heitzman (2006), which can take aggregate shape factors to calculate the aggregate volume factor and surface area factors. To calculate the average film thickness aggregate shape and size was considered in the model and the researchers showed a significant improvement to predict the durability
of the field performance data from MnROAD and rutting data of laboratory-fabricated mixtures. However, the study did not study other durability performance parameters in the study.

To find a correlation between average asphalt film thickness and moisture sensitivity of HMA samples, Sengoz and Agar (2006) concluded that an average asphalt binder film thickness of 9.5 to 10.5 μm is optimum. Nukunya et al. (2001) evaluated Voids in Mineral Aggregate (VMA), film thickness, asphalt content, and aggregate surface area on the durability age hardening rate, fracture resistance, and rutting resistance of Superpave mixtures. The research results concluded neither VMA nor film thickness provide a parameter that adequately reflects the age hardening rate of binders in asphalt mixtures.

Pavement researchers found that there is a strong correlation between asphalt film thick and age hardening behavior of asphalt, however till date researchers have attempted to correlate asphalt aging with different volumetric properties. Among all the research works following aging model has been adopted by pavement mechanical empirical (ME) design as a successful pavement design tool. Pavement aging model adopted in pavement ME is discussed in the following section.

2.9 Pavement Aging Model

Among all the asphalt aging models Global Aging System (GAS) to predict the change in dynamic modulus of Asphalt Concrete is the most popular one. Therefore, Pavement ME
has adopted the Global Aging System (GAS) model in its pavement design scheme. Pavement ME uses the $E^*$ and aged $E^*$ of asphalt concrete to find the stress and strain levels in the pavement. However, to modify the $E^*$ of the material to aged $E^*$ for parameters and models are used, these are: original to mix/lay-down model, surface aging model, air void adjustment and viscosity-depth model.

**Original to mix/lay-down model:**

During pavement construction, asphalt and aggregate is heated to properly mix with each other. The heating and mixing process requires a large amount of heat, which creates aging of the material. The aging of the material changes the viscosity of asphalt binder and the complex modulus of AC is a function of viscosity. Therefore, current model uses the change in the viscosity to change the $E^*$ of AC. In the original to mix/lay-down model accounts of short-term aging occurred due to mixing and compaction of asphalt concrete.

Equation (2.51) represents the model that accounts short-term aging in the GAS model.

$$\log \log(\eta_{t=0}) = a_0 + a_1 \log \log(\eta_{\text{orig}})$$  \hspace{1cm} (2.51)

where

$$\eta_{t=0} = \text{mix/lay-down viscosity, cP}$$

$$\eta_{\text{orig}} = \text{original viscosity, cP}$$

$$a_0 = 0.054405 + 0.004082 \times \text{code}$$

$$a_1 = 0.972035 + 0.010886 \times \text{code}$$
Here, code refers to the hardening code of asphalt which is shown in Table 2.1. Hardening code value is obtained empirically from the hardening ratio of asphalt. The hardening ratio, defined as the ratio of the log-log mix/laydown viscosity to the log-log original viscosity, Equation (2.52), provides guidance on which code to use. Following Table 2.1 shows the hardening code values for different hardening ratios:

\[
    Hardening\ Ratio = \frac{\log\ log(\text{mix or laydown\ viscosity})}{\log\ log(\text{original\ viscosity})}
\]  

(2.52)

Here it is assumed that the RTFOT viscosity is same as mix/laydown viscosity.

The purpose of the hardening code is to increase the accuracy of the short-term aging model by adjusting a specific asphalt binder’s tendency to age during mixing, transportation, and compaction.

**Table. 2.1 Recommended Hardening Code Values**

<table>
<thead>
<tr>
<th>Mix/Lay-Down Hardening Resistance</th>
<th>Expected <em>Hardening Ratio</em> (HR) Values</th>
<th>Code Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excellent to Good</td>
<td>HR $\leq 1.030$</td>
<td>-1</td>
</tr>
<tr>
<td>Average</td>
<td>$1.030 \leq \text{HR} \leq 1.075$</td>
<td>0</td>
</tr>
<tr>
<td>Fair</td>
<td>$1.075 \leq \text{HR} \leq 1.100$</td>
<td>1</td>
</tr>
<tr>
<td>Poor</td>
<td>HR $\geq 1.100$</td>
<td>2</td>
</tr>
</tbody>
</table>

Suggested code values were recommended by Mirza and Witczak (2006) and vary from -1, representing a good to excellent resistance to hardening, to +2, representing a poor hardening resistance. A code of 0 represents an average condition.
The GAS model predicts the change in viscosity of the binder to age and then shifts the unaged dynamic modulus curve according to change in viscosity. The model uses the ASTM viscosity-temperature relationship as follows:

$$\log\log(\eta_t) = A_t + VTS_t \log(T_R)$$

(2.54)

where

$$\eta_t = \text{viscosity (cP) maximum value of } 2.7 \times 10^{10} \text{ Poise}$$

$$T_R = \text{Temperature on Rankine}$$

$$A_t$$ is the regression intercept, and the variable viscosity-temperature susceptibility ($VTS$) the regression slope.

**Surface Aging Model**

The Surface Aging model predicts the aged viscosity of asphalt using mix/laydown viscosity of asphalt. The model predicts aged viscosity with time is hyperbolic in the form,

$$\eta_{aged} = \eta_{t=0} + \frac{A_t + Bt}{1 + Bt}$$

(2.55)

where

$$\eta_{aged} = \text{aged viscosity in cP and represents at an assumed depth of 0.25 in.}$$

$$\eta_{t=0} = \text{viscosity at mix/laydown in cP}$$

$$t = \text{time in months}$$
\[ A = -0.004166 + 1.41213(C) + (C) \log(MAAT) + (D) \log(\eta_{r=0}) \] (2.56)

\[ B = 0.197725 + 0.068384 \log(C) \] (2.57)

Here, A and B are used to define the shape of the curve. In equation (2.56) and (2.57),

\[ C = 10^{(274.4946 - 193.831 \log(T_R) + 33.9366 \log(T_R)^2)} \]
\[ D = -14.5521 + 10.47662 \log(T_R) - 1.88161 \log(T_R)^2 \]

\[ MAAT = \text{Mean annual air temperature, °F} \]

Therefore, the viscosity of asphalt changes with availability of air for oxidation and temperature from the surface downward. \( MAAT \) in the above mentioned equation considers the effect of temperature on the aging process of asphalt.

**Air void Adjustment**

Oxidative aging of asphalt is a function of temperature and available oxygen in the pore structures of AC. However, Pavement ME design does not include the model yet the program yet due to shortage of data. However the model is discussed below,

In GAS model uses the following equation (2.58) to adjust the aged viscosity for air void,

\[ \log \log(\eta_{\text{aged}})' = F_v \log \log(\eta_{\text{aged}}) \] (2.58)

Here, \( F_v \) correlates air voids with time. According to Eq. 2.59 with increase in air void \( F_v \) increases with increase in air void, however \( F_v \) decreases with time.

\[ F_v = \frac{1 + 1.0367 \times 10^{-4} \times VA(t)}{1 + 6.1796 \times 10^{-4} \times t} \] (2.59)
\[ VA = \frac{VA_{orig} + .011(t) - 2}{1 + 4.24 \times 10^{-4}(t)(MAAT) + 1.169 \times 10^{-3} \left( \frac{t}{\eta_{orig,77}} \right)} + 2 \]  

where

\( VA_{orig} = \) initial air voids,

\( t = \) time in months

\( MAAT = \) mean annual air temperature, °F

\( \eta_{orig,77} = \) original binder viscosity at 77 °F, MPoise

**Viscosity-depth model**

The viscosity-depth model used depth factor to predict aged viscosity. Here it should be mentioned, AC consists of permeable and impermeable pores and with increase in depth the amount of available oxygen in the pores as well as surface temperature decreases. Therefore, aging effect decreases with depth. Pavement ME considers the change of aging with depth using following Eq. (2.61) of the viscosity depth relationship,

\[ \eta_{t,z} = \frac{\eta_t(4 + E) - E(\eta_{t,0})(1 - 4z)}{4(1 + Ez)} \]

where

\( \eta_{t,z} = \) Aged viscosity at time t, and depth z, MPoise

\( \eta_t = \) Aged surface viscosity, MPoise

\( z = \) Depth, inch

\( E = 23.83e^{-0.0308MAAT} \)
Finally, the unaged dynamic modulus master curve is shifted using the following equation to calculate the reduced time of loading according to the aged viscosity:

\[
\log(t_r) = \log t - c(\log \eta - \log \eta_{tr})
\]  

(2.62)

where

- \( t \) = time of loading at the given temperature of interest
- \( t_r \) = time of loading at the reference temperature,
- \( c \) = determined previously from the unaged master curve,
- \( \eta \) = aged viscosity at a temperature of interest, and
- \( \eta_{tr} \) = the unaged viscosity at a reference temperature.

**Remarks**

Pavement ME model uses above mentioned four important parameters to identify and predict aged stiffness of AC. However, it can be noticed that the full model enveloped around asphalt binder viscosity, it is not known that whether the binder and mix or mastic phase going to behave in similar manner. The current study attempts to explore whether binder aging trend is similar as mastic aging trend. In addition, the air voids in AC has a great impact on asphalt aging, which is not fully developed yet, which is also explored in the current study.
CHAPTER 3
METHODOLOGY

3.1 General

In this study, nanoindentation technique is used to characterize asphalt concrete aging. Development of nanoindentation technique to quantify asphalt concrete aging consists of different steps, like, nanoindentation testing of asphalt, aging of asphalt samples, nanoindentation load-displacement data analysis, kinetic aging model, are discussed in detail in this chapter.

3.2 Nanoindentation Testing on Asphalt

The research plan of nanoindentation testing on asphalt concrete (AC) is subdivided into four different major steps, as shown in Figure 3.1. The procedure begins with the nanoindentation test on bulk asphalt, mastic and aggregate on glass slide and nanoindentation tests on AC samples. The AC phases are identified using depth resolution and creep response of the material. Afterward, the materials parameters are extracted using spring, dashpot and rigid body (SDR) model. AC samples were progressively aged for different durations to simulate oxidative aging in the material. Finally, the SDR model parameters are compared for the mastic and binder phase state of asphalt concrete.
3.2.1 Asphalt Binder Sample

Performance Grade (PG) asphalt binder samples (PG 70-22, PG 64-22) were collected from the local contractor associated with the New Mexico Department of Transportation (NMDOT). In the paper, PG 70-22 samples are defined as binder1, and PG 64-22 samples are defined as binder2. The binder’s material properties are detailed in Table 3.1. Three replicated samples were used for each set sample. Three replicated samples are used to capture the variability within one each set.
### Table 3.1 Test Binder Details.

<table>
<thead>
<tr>
<th>Binder1 Performance Grade (PG) 70-22</th>
<th>Origin</th>
<th>HollyFrontier Refining &amp; Marketing LLC, Albuquerque, New Mexico, USA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Gravity</td>
<td></td>
<td>1.014</td>
</tr>
<tr>
<td>Constituent Analysis</td>
<td>Saturates</td>
<td>6.31%</td>
</tr>
<tr>
<td></td>
<td>Aromatics</td>
<td>53.62%</td>
</tr>
<tr>
<td></td>
<td>Resins</td>
<td>26.28%</td>
</tr>
<tr>
<td></td>
<td>Asphaltene</td>
<td>13.79%</td>
</tr>
<tr>
<td>Rheology</td>
<td>$G^* @ 64 ^\circ C = 3.32$ kPa</td>
<td>$\delta @ 64 ^\circ C = 72.68^\circ$</td>
</tr>
<tr>
<td></td>
<td>$G^* @ 70 ^\circ C = 1.29$ kPa</td>
<td>$\delta @ 70 ^\circ C = 82.2^\circ$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Binder2 Performance Grade (PG) 64-22</th>
<th>Origin</th>
<th>Western Refining, El Paso, Texas, USA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Gravity</td>
<td></td>
<td>0.998</td>
</tr>
<tr>
<td>Constituent Analysis</td>
<td>Saturates</td>
<td>5.53%</td>
</tr>
<tr>
<td></td>
<td>Aromatics</td>
<td>64.17%</td>
</tr>
<tr>
<td></td>
<td>Resins</td>
<td>17.91%</td>
</tr>
<tr>
<td></td>
<td>Asphaltene</td>
<td>12.4%</td>
</tr>
<tr>
<td>Rheology</td>
<td>$G^* @ 64 ^\circ C = 1.45$ kPa</td>
<td>$\delta @ 64 ^\circ C = 86.9^\circ$</td>
</tr>
<tr>
<td></td>
<td>$G^* @ 70 ^\circ C = 0.72$ kPa</td>
<td>$\delta @ 70 ^\circ C = 88.1^\circ$</td>
</tr>
</tbody>
</table>

Note: $G^*$ is the complex modulus and $\delta$ is the phase angle at 10 rad/sec

### 3.2.1 Asphalt Concrete Sample Preparation for Nanoindentation

A superpave gyratory compactor was used to compact the loose asphalt concrete mix. Figure 3.2 shows the gradation curve of aggregate used for making SP-III mix according to New Mexico Department of Transportation (NMDOT) specification. PG 64-22 and PG 70-22 were used to make asphalt concrete samples. The initial dimensions of the cylindrical specimens were 150 mm in diameter and around 170 mm in height. These specimens are then cored and sawed to have finished specimens of diameter 100 mm and of height 150 mm. To achieve consistency in the test results the target air void was set at 5.5±0.5 for the finished specimen, and therefore, several trial samples were compacted at the beginning to
reach the target air void. To determine the bulk specific gravity of the finished cylindrical specimens and thus the air void content, AASHTO T 166 standard specification was used.

Coring was performed to prepare nanoindentation sample from the middle part of the gyratory sample. The middle part of the gyratory compacted sample is used because this part has the most uniform air void distribution. The required sample size to conduct nanoindentation test can be as small as a few millimeters. In this study, a 25-mm diameter sample was prepared. Next, the 25-mm sample was polished to produce a smooth surface. Surface smoothness is crucial for nanoindentation test since the contact area of the nanoindenter is measured indirectly from the depth of penetration (Tarefder et al. 2010).

Figure 3.2 Gradation Curve of the Asphalt Concrete Mix.
Polishing of nanoindentation sample is performed using the water-cooled polishing machine. To produce a smooth surface without dislodging any small aggregate form the 25 mm diameter sample, a sequence of water-resistant silicon carbide polishing papers with decreasing abrasiveness are utilized. The set of polishing papers are 100, 200, 400, 600, 800, 1,200 and 1,500 grit sizes each for the duration of 150 seconds. Then the polished nanoindentation sample is washed to remove dust particles. Ideally, one can argue that damage has occurred on the sample surface during polishing. Therefore, such sample is not appropriate for aging study. The fact is that both the unaged and aged conditioned samples are subjected to polishing, which is required for the indentation tip to locate the surface during testing. Therefore, it can be counter-argued that both samples were subjected to the same damage during polishing. Figure 3.4 shows polished AC sample.
3.2.2 Nanoindentation Testing on Asphalt

In this study, nanoindentation test was done at 25 °C ± 0.2 °C, using load control mode. A maximum load of 0.5 mN was applied with a loading and unloading rate of 0.007 mN/sec. A creep time of 200 sec was applied after reaching the maximum load. A sitting load of 0.01 mN was used for all the samples. Indentation velocity is important for contact stiffness. To avoid the effect of sudden impact on the sample surface and the indenter, indenter velocity was kept low. The indenter indented the samples at a velocity of 0.05 μm/s. Indenter velocity during nanoindentation can be set prior to the start of the test. The sample stage automatically moves toward the indenter at the set indentation velocity to apply a sitting load of 0.01 mN. The nanoindentation tests were done on an array of selected points apart by 200 μm. The distance was selected so the indentation depth did not affect the subsequent indentations. In addition, based on the atomic force microscopy (AFM) test results, at micro-scale, asphalt binder is also not a homogeneous material. There exists the Catana phase, Para phase, Peri phase, Perpetua phase (Fischer 2014). So different indent
location might produce different material behaviors, therefore to simplify the process random indentations were done on the samples to produce representative average material behavior. Figure 3.5 shows a nanoindentation test setup using a Berkovich nanoindenter on an AC sample.

![Figure 3.5 Nanoindentation Test on AC Sample.](image)

According to the previous study of the authors, a loading rate of 0.007 mN/sec and dwell time of 200 sec was applied for nanoindentation tests of asphalt. However, for the current study pile-up, the effect of indentation has not taken into the account for stiffness and hardness calculation. It was assumed the fast unloading rate will minimize the effect of pile up around the indenter tip. The nanoindenter device at the University of New Mexico (UNM) nano test laboratory was used for indentation. Figure 3.6 shows the schematic of ramp load sequence used in the current study.
The nanoindenter device at the University of New Mexico (UNM) nano test laboratory was used for indentation. Figure 3.7 shows the nanoindentation test setup with the Berkovich indenter tip and sample indenting in asphalt binder.

In the previous study by the authors, both spherical and Berkovich tips were used on asphalt (Tarefder and Faisal 2013, Faisal et al. 2015). However, their study concluded that the
Berkovich tips are more suitable than the spherical tips for asphalt binder testing. In this study, a maximum load of 0.055 mN was applied with an unloading rate of 0.007 mN/sec. A sitting load of 0.005 mN was used for all the samples. A creep time of 200 seconds was applied after reaching the maximum load. The viscous effects of the test results are reduced by using a fast unloading rate and applying an extended dwell time. Tarefder and Faisal have shown that a dwell time of 100-200 seconds (long) can minimize the viscous effect of asphalt (Tarefder and Faisal 2013). Based on the previous study by the authors, a loading rate of 0.007 mN/sec, and a dwell time of 200 seconds were chosen for the nanoindentation test on asphalt binder. Each AC sample was indented at 20 locations to deal with the variability of nanoindentation results. Using the nanoindenter available at the University of New Mexico, force and displacement resolutions possible with the NanoTest, which are as low as 3 nN and 0.001 nm, and displacements (0-23 µm or more).

3.3 Aging of Asphalt

In this study, asphalt binder was aged using rolling thin film oven (RTFO) and pressure aged vessel (PAV) technique, whereas AC samples were aged at 85 °C in a draft oven for progressive aging of 0 days, 2 days, 5 days, 10 days, 15 days, and 20 days.

3.4 Laboratory determination of Asphalt Film Thickness

In the study, hot mix asphalt (HMA) samples coated with asphalt binder film were subjected to progressive aging and the asphalt film thickness was measured using nanoindentation test. The idea behind the asphalt film thickness measurement using
nanoindentation is to apply a very high load that the nanoindenter penetrates through the asphalt film and indents on the strong stone aggregate surface. Here, the HMA asphalt aggregate system is a medium of two materials asphalt binder film and stone aggregate, as shown in Figure 3.8(a). In which, asphalt binder is the softer material, therefore for same loading pattern, the softer material shows higher deformation rate compared to harder elastic stone aggregate.

Figure 3.8 Nanoindentation on the Asphalt Binder Thin Film and Aggregate Substrate.

Following steps are followed for the measurement of the asphalt film thickness:

1. Selection of a nanoindentation loading protocol so that the indenter penetrates through asphalt binder film and indents on the aggregate surface, as shown in Figure 3(b).
2. The loading protocol that means loading rate is so selected it provides good resolution of data to select the change in the slope of the load-displacement curve.

3. Post indentation comparison of the loading curve slope needs to identify the point of inflection. In the asphalt-aggregate system, asphalt is a softer layer compared to the aggregate substrate. For same load displacement rate in asphalt binder is much higher compared to the aggregate surface, as an aggregate is a hard elasto-plastic material.

4. The point of inflection is reported the asphalt binder film thickness. However, it is possible that at the interface of asphalt and aggregate after 80% or 90% of soft layer indentation, the loading curve produces point of inflection. A numerical modeling of two layer system of soft and hard can clarify the assumption, however, it requires time to create an appropriate numerical model with inclusion of slip or damage in the interface. Therefore, it is recommended for future study.

5. The sample then put in a draft oven to simulate long-term aging at 85 °C. In the study, samples are aged for 3 days, 5 days, and 10 days of oven aging, according to AASHTO R 30 long-term aging protocol.

6. After completion of each aging time samples were introduced for same loading protocol to identify the change in the asphalt binder film thickness.
CHAPTER 4

PHASE IDENTIFICATION

4.1 Introduction

Asphalt researchers have studied only the bulk state (liquid or semisolid) of asphalt binder using traditional rheometers. In roadway pavements, an asphalt binder never exists in a liquid or semisolid state, rather it exists as a solid, as one of the three phases/components (asphalt, aggregate, voids) of an asphalt concrete (AC). While rheometric techniques used mostly bulk asphalt material, recently nanoindentation technique has brought an opportunity to indent an asphalt binder while it resides in an AC at a solid phase. One problem with indentation is that, it is difficult to indent a specimen phase and it is always difficult to identify whether the indenter is indenting a void or binder or mastic. In this study, using a nanoindentation creep test, two Performance Grade (PG) binders: PG 70-22 and PG 64-22 were studied for their behavior at the bulk state and the phase state. To prepare the sample for the bulk state, simply liquid asphalt was placed on a glass slide as a thin film and indented. For the phase state, an asphalt concrete sample was sliced into rectangular pieces and indented at three phases. Though previous research on validation of asphalt film thickness shows whenever asphalt is mixed with specific aggregate gradation to produce hot mix asphalt, the probability of the existence of pure asphalt binder, is almost zero (Elseifi et al. 2008). The current research hypothesized that it is possible to find pure asphalt binder as well as asphalt mastic in AC samples. Thus, AC has three phases: mastic, asphalt binder film, and coarse aggregate, as shown in Fig. 4.1.
The test methods developed, to this day, are mostly rheological shear and bending beam tests performed on the bulk volume of binders and mastic samples. Very few studies have been performed to determine the stiffness and hardness of binder or mastic when they reside in AC as phase state (Khorasani et al. 2013; Mohajari et al. 2014; Tarefder and Faisal 2013; Zhang et al. 2015; Barbhuiya and Benjamin 2017). Instead of validating the specific phase identification, the above-mentioned research works were limited to visual inspections and interpretation of the stiffness data. In addition, the existing tests used in the asphalt area cannot be performed on binder and mastic while they are an integral part of AC. Recently, nanoindentation has brought an opportunity to conduct tests on the binder, mastic and aggregate while they are integral parts of AC (Faisal et al. 2014 and 2015; Tarefder and Faisal 2014; Veytskin et al. 2016). In nanoindentation test, a nanometer size tip, which is smaller than binder film thickness as well as mastic phase, can be used on these phases to indent them. There is an urgent need for fundamental research that would provide a clear understanding of the “different phases” of asphalt. However, during the nanoindentation test, it is difficult to identify whether the nanoindenter tip is indenting on
the binder or mastic or aggregate phase of AC. The current study attempts to develop a technique using the viscoelastic creep response of the AC phases.

In the study, nanoindentation test will be used to measure mechanical properties such as stiffness and hardness of asphalt binder, mastic, and aggregate while they are in phase state of AC sample. The use of the nanoindentation technique in the field of asphalt is rather new (Faisal et al. 2014, 2015, Tarefder and Faisal 2013a, 2013b, 2014, Veytskin et al. 2015, 2016, Ossa et al. 2005, Ossa and Collop 2007, Jager et al. 2010, Faisal et al. 2015, Zhu et al. 2016, 2017). Asphalt is known to be a viscoelastic material that exhibits creep behavior (Ossa and Collop 2007, Tarefder and Faisal 2013, Faisal et al. 2015). Tarefder et al. (2010) developed a range of indentation derived stiffness and hardness values of aged asphalt. In another study, Faisal et al. (2014, 2015) conducted a study of nanoindentation on moisture damaged AC mixes of New Mexico. Jager et al. (2010) studied the thermal effects on the mechanical properties of the asphalt binder.

The study proposes, during nanoindentation AC phases can be identified by using viscoelastic creep characterization technique. In addition, visco-elastoplastic analysis of the nanoindentation data extracted three different attractive material parameters, like stiffness, hardness and indentation viscosity, when they were an integral part of AC body. Again, in AC concrete asphalt binder plays one of the most important parts of material behavior. To date, most of the pavement material response models like the aging of AC and fatigue characterization of AC, are related to the asphalt binder behavior. However, it is not known whether the asphalt binder behaves same in bulk state as in phase state, when
the asphalt binder is an integral part of the AC system. However, to characterize the phase state behavior, it is important to identify the specific phases, which is done in the current study.

4.2 Aggregate and Asphalt Binder Collection

Performance Grade (PG) asphalt binder samples (PG 70-22, PG 64-22) were collected from the local contractor associated with the New Mexico Department of Transportation (NMDOT). In the paper, PG 70-22 samples are defined as binder1, and PG 64-22 samples are defined as binder2. The binder’s material properties are detailed in Table 4.1. Three replicated samples were used for each set sample. Three replicated samples are used to capture the variability within one each set.
### Table 4.1 Test Binder Details

<table>
<thead>
<tr>
<th>Binder 1 Performance Grade (PG) 70-22</th>
<th>Origin</th>
<th>HollyFrontier Refining &amp; Marketing LLC, Albuquerque, New Mexico, USA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Gravity</td>
<td>1.014</td>
<td></td>
</tr>
<tr>
<td>Constituent Analysis</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Saturates</td>
<td>6.31%</td>
<td></td>
</tr>
<tr>
<td>Aromatics</td>
<td>53.62%</td>
<td></td>
</tr>
<tr>
<td>Resins</td>
<td>26.28%</td>
<td></td>
</tr>
<tr>
<td>Asphaltene</td>
<td>13.79%</td>
<td></td>
</tr>
<tr>
<td>Rheology</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$G^*$ @ 64 °C = 3.32 kPa</td>
<td>$\delta$ @ 64 °C = 72.68°</td>
<td></td>
</tr>
<tr>
<td>$G^*$ @ 70 °C = 1.29 kPa</td>
<td>$\delta$ @ 70 °C = 82.2°</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Binder 2 Performance Grade (PG) 64-22</th>
<th>Origin</th>
<th>Western Refining, El Paso, Texas, USA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Gravity</td>
<td>0.998</td>
<td></td>
</tr>
<tr>
<td>Constituent Analysis</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Saturates</td>
<td>5.53%</td>
<td></td>
</tr>
<tr>
<td>Aromatics</td>
<td>64.17%</td>
<td></td>
</tr>
<tr>
<td>Resins</td>
<td>17.91%</td>
<td></td>
</tr>
<tr>
<td>Asphaltene</td>
<td>12.4%</td>
<td></td>
</tr>
<tr>
<td>Rheology</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$G^*$ @ 64 °C = 1.45 kPa</td>
<td>$\delta$ @ 64 °C = 86.9°</td>
<td></td>
</tr>
<tr>
<td>$G^*$ @ 70 °C = 0.72 kPa</td>
<td>$\delta$ @ 70 °C = 88.1°</td>
<td></td>
</tr>
</tbody>
</table>

Note: $G^*$ is the complex modulus and $\delta$ is the phase angle at 10 rad/sec

#### 4.2.2 Asphalt Concrete Sample Preparation

A superpave gyratory compactor was used to compact the loose asphalt concrete mix. Figure 4.2 shows the gradation curve of aggregate used for making SP-III mix according to NMDOT specification. PG 64-22 and PG 70-22 were used to make asphalt concrete samples. The initial dimensions of the cylindrical specimens were 150 mm in diameter and around 170 mm in height. These specimens are then cored and sawed to have finished specimens of diameter 100 mm and of height 150 mm. To achieve consistency in the test results the target air void was set at 5.5±0.5 for the finished specimen, and therefore, several trial samples were compacted at the beginning to reach the target air void. To determine
the bulk specific gravity of the finished cylindrical specimens and thus the air void content, AASHTO T 166 standard specification was used.

Figure 4.2 Gradation Curve of the Asphalt Concrete Mix.

Coring was performed to prepare nanoindentation sample from the middle part of the gyratory sample. The middle part of the gyratory compacted sample is used because this part has the most uniform air void distribution. The required sample size to conduct nanoindentation test can be as small as a few millimeters. In this study, a 25-mm diameter sample was prepared. Next, the 25-mm sample was polished to produce a smooth surface. Surface smoothness is crucial for nanoindentation test since the contact area of the nanoindenter is measured indirectly from the depth of penetration (Tarefder et al. 2010).
Polishing of nanoindentation sample is performed using the water-cooled polishing machine. To produce a smooth surface without dislodging any small aggregate form the 25 mm diameter sample, a sequence of water-resistant silicon carbide polishing papers with decreasing abrasiveness are utilized. The set of polishing papers are 100, 200, 400, 600, 800, 1,200 and 1,500 grit sizes each for the duration of 150 seconds. Then the polished nanoindentation sample is washed to remove dust particles. Ideally, one can argue that damage has occurred on the sample surface during polishing. Therefore, such sample is not appropriate for aging study. The fact is that both the unaged and aged conditioned samples are subjected to polishing, which is required for the indentation tip to locate the surface during testing. Therefore, it can be counter-argued that both samples were subjected to the same damage during polishing. Figure 4.4 shows polished AC sample.
4.2.3 Asphalt Binder Sample Preparation

PG 64-22 and PG 70-22 binder samples were used in this study. PG 64-22 and PG 70-22 binders are mostly used PG binder grade for pavement construction in the state of New Mexico. Figure 4.5 shows a laboratory prepared asphalt binder film on glass substrate. As the first step, a glass slide surface 12.7 mm × 12.7 mm was selected and weighed in scale up to 4 significant decimal digits of grams. Next, the glass slide was wrapped with high-temperature resistant tape. The tape was placed so that it formed the 6.35 mm square gap area previously outlined in the binder. Then, hot polymer modified liquid asphalt binder was poured into the gap between the tape strips. The polymer-modified binders were melted by heating them to 163 °C for an hour. The asphalt coated surface was placed in the oven at 163 °C for 10 min in order to have a smooth surface, cooled at room temperature and the tapes were removed. Finally, the glass slide with the asphalt coating was weighed again to measure the amount of asphalt binder. From the known area, the density of the asphalt binder and mass the thickness of the binder film was measured. The film thickness
varied within a range of 40 µm to 80 µm to avoid substrate effect on test results. Three replicated samples are used to capture the variability within one each set.

![Image](image.png)

(a) Asphalt Binder Sample on a Glass Slide

(b) Schematic of the Asphalt Binder Sample on a Glass Slide

**Figure 4.5** Asphalt Binder Sample for Nanoindentation.

### 4.3 Nanoindentation Creep Test

In this study, nanoindentation test was done at 25 °C ± 0.2 °C, using load control mode. A maximum load of 0.5 mN was applied with a loading and unloading rate of 0.007 mN/sec. A creep time of 200 sec was applied after reaching the maximum load. A sitting load of 0.01 mN was used for all the samples. Indentation velocity is important for contact stiffness. To avoid the effect of sudden impact on the sample surface and the indenter,
Indenter velocity was kept low. The indenter indented the samples at a velocity of 0.05 µm/s. Indenter velocity during nanoindentation can be set prior to the start of the test. The sample stage automatically moves toward the indenter at the set indentation velocity to apply a sitting load of 0.01 mN. The nanoindentation tests were done on an array of selected points apart by 200 µm. The distance was selected so the indentation depth did not affect the subsequent indentations. In addition, based on the atomic force microscopy (AFM) test results, at micro-scale, asphalt binder is also not a homogeneous material. There exists the Catana phase, Para phase, Peri phase, Perpetua phase (Fischer 2014). So different indent location might produce different material behaviors, therefore to simplify the process random indentations were done on the samples to produce representative average material behavior. Fig. 4.6 shows a nanoindentation test setup using a Berkovich nanoindenter on an AC sample.

![Nanoindentation Test on AC Sample](image)

**Figure 4.6** Nanoindentation Test on AC Sample.
The viscous effect of the material like viscoelastic material like asphalt binder can be reduced during nanoindentation by using a fast unloading rate and/or applying an extended dwell time. According to the researchers in the viscoelastic material area, this approach can minimize the viscous flow effect of AC (Tarefder and Faisal 2013a, 2013b, 2014, Zhang 2005). Though the overall response of the asphaltic material is important. However, as it is time-dependent material, the viscoelastic creep response is a very attractive parameter to model and identify specific phase or bulk state material characterization. It has been shown in the previous study of the authors; if the dwell time is long enough (for asphalt binder) around 100-200 sec the viscous effect of the material minimizes (Tarefder and Faisal 2013a). However, to quantify whether the viscous effect decreases with increase in creep hold time, in their research work (Tarefder and Faisal 2013c), the authors used three different constitutive models, the results show in each case the viscosity parameter or indentation viscosity parameter minimizes the increase in the amount of dwell time on the asphaltic indentation.

The main idea behind the long dwell or creep hold time on the viscoelastic material during nanoindentation test is to allow the material enough time for the viscous flow for a specific load and when the viscous flow is minimum the material shows positive load-displacement behavior during unloading phase of the indentation test. However, still, there will be a specific amount of viscous effect on the unloading part of the load-displacement curve, which makes the use of tradition Oliver-Pharr (1992) model on the unloading data of viscoelastic material debateable. According to the previous study of the authors, a loading rate of 0.007 mN/sec and dwell time of 200 sec was applied for nanoindentation tests of
asphalt. However, for the current study pile-up, the effect of indentation has not taken into the account for stiffness and hardness calculation. It was assumed the fast unloading rate will minimize the effect of pile up around the indenter tip. The nanoindenter device at the University of New Mexico (UNM) nano test laboratory was used for indentation. Figure 4.7 shows the schematic of ramp load sequence used in the current study.

![Figure 4.7 Loading Pattern Used During Nanoindentation Testing.](image)

**4.4 Asphalt Concrete Phase Identification**

As discussed in the previous sections, the current study used creep response to identify the AC phases, while in the previous study by Faisal et al. (2015a, 2015b) researchers identified the nanoscale phases of AC with respect to the degree of softness. In those studies, the following assumptions were made to the identify binder, mastic, and aggregate phases: for a maximum nanoindentation load of 0.51 mN and a dwell time of 200 s: (1) if the indentation depth remains within 1000 nm, the indented phase is defined as the aggregate phase of AC; (2) if the indentation depth remains between 1000 nm to 3000 nm for AC, the indented phase is defined as the mastic phase of AC; and (3) if the indentation
depth is higher than 3000 nm for AC, the indented phase is defined as the binder phase of AC. When nanoindentation tests are done on a composite material like AC, it is a very complex task to identify the specific phase, as one can argue the material response of a thin binder film with an aggregate right beneath it would have a different response compared to a thick binder film with an aggregate particle far beneath the surface. In other words, the substrate effect might have significant effect on the material behavior. It can be counter-argued that the presence of any fine particle or aggregate around the binder going to change the whole load-displacement response, or in the scale of degree of softness the material phase will be identified as the intermediate soft or mastic phase of AC.

The current study only identified the perfectly soft binder phase which showed very high displacement, low stiffness and matching bulk state creep response of the material. Therefore, though nanoindentation is a two-dimensional surface characterization technique, the indentation depth scale and material response during nanoindentation allows the researchers to investigate the stereological effect interpretation of AC. In the degree of softness, assumptions are used as a preliminary identification criterion of different phases of AC. However, the assumptions do not consider nanoindenter hitting a void space in AC concrete samples, which is a quite common scenario for AC. Nano/microvoids in AC show sudden high micro scale displacement of the indenter for a specific load, which invalidates the specific phase identification according to the degree of softness of the material. Therefore, the current study identifies these three distinct phases of AC according to the creep response Generalized Power Law (GPL) model parameters of the material. However, fitting all the indentation data for three replicated samples with 100 indentations on each
sample is a time-consuming process. Therefore, the current study uses the principal component analysis using statistical software R initially to identify the soft phases of AC according to maximum depth and elastic modulus analysis. Different phases of AC were identified using the above mentioned statistical approach. After analyzing each nanoindentation test result, several features can be extracted. They are maximum depth (Maxdepth), plastic depth (Plasticdepth), Hardness, Reduced modulus (Er), Elastic recovery parameter (ERP), contact compliance (ContactC), plastic work (PlasticW), and elastic work (ElasticW).

Suppose $p$ features $X = (X_1, X_2, \ldots, X_p)'$ are used to discriminate among $k$ groups. Let the mean response for the $i^{th}$ sample be $\bar{X}_i = (\bar{X}_{i1}, \bar{X}_{i2}, \ldots, \bar{X}_{ip})'$. If $S_i$ is the $p$ by $p$ covariance matrix for the $i^{th}$ sample, then the pooled covariance matrix is given by

$$S = \frac{(n_1-1)S_1 + (n_2-1)S_2 + \ldots + (n_k-1)S_k}{n-k}$$  \hspace{1cm} (4.1)

where $n_i$ is the group sample size and $n$ is the total sample size. For linear discriminant analysis (LDA), the generalized distance from an observation $X$ to the $i^{th}$ sample is

$$D_i^2(X) = (X - \bar{X}_i)'S^{-1}(X - \bar{X}_i)$$  \hspace{1cm} (4.2)

where $(X - \bar{X}_i)'$ represents the transpose of the column vector $(X - \bar{X}_i)$, and $S^{-1}$ represents the matrix inverse of $S$.

In the quadratic discriminant analysis (QDA), the generalize distance to the group $i$ is given by:

$$D_i^2(X) = (X - \bar{X}_i)'S^{-1}_i(X - \bar{X}_i) - 2\log(Pr_i) + \log|S_i|$$  \hspace{1cm} (4.3)
where $\log |S|$ is the logarithm of the determinant of the covariance matrix $S$. The posterior probability $Pr_j$ in Eq. (4.3) can be obtained as

$$Pr(j|X) = \frac{e^{-0.5D_i^2(X)}}{\sum_k e^{-0.5D_k^2(X)}}$$

(4.4)

It is required to have a training set and test set for the analysis. Forty randomly selected nanoindentation data were chosen from AC nanoindentation test for test matrix. Binder and mastic phases were equally divided among them. The analysis identifies the predominant components for each group and from the component analysis, it identifies the group. If the analysis can accurately predict the phases in the test set, then using this technique further phases in AC can be accurately identified. In the current study, the soft binder phase of AC is defined by maximum depth more than 3000 nm and elastic modulus 0.1 to 30 MPa, whereas the soft mastic phase of AC is defined by a maximum depth between 1500 nm to 3000 nm and elastic modulus 7 to 60 MPa. Afterward, the soft phases of AC are analyzed further to determine the GPL model parameters. The GPL parameters of soft phases are compared with those of bulk states of binder and mastic samples to identify specific phase.

### 4.5 Extraction of Creep Response

To extract the creep response of the material the displacement during loading and unloading are ignored. It is assumed the loading and unloading are very fast compared to creep loading time of the material. The creep response of the material is modeled using linear viscoelastic (LVE) analysis of the material. According to LVE theory, the load-

\[ h^2(t) = \frac{\pi}{2} \cot \psi \int_{0}^{t} D(t-u) \frac{dP_0(u)}{du} \, du \]  

(4.5)

where \( P_0 \) = indentation load

\( h \) = displacement due to applied load in a material

\( \psi \) = include a half angle of Berkovich indenter and

\( D(t) = 1/E \), is creep compliance and \( u \), is a dummy variable for integration and delayed response is presented by \((t-u)\) variable instead of time variable \( t \).

According to GPL, the creep compliance of thin film material can be expressed as,

\[ D(t) = D_0 + D_1 t^n \]  

(4.6)

In the study, generalized power law has been used to represent the creep compliance of the thin film material. Here, \( D_0, D_1 \), and \( n \) are regression coefficients. \( D_0 \) represents the short term behavior while \( D_1 \) represents the long-term behavior of the material. The current study used the creep compliance parameters of bulk asphalt binder and mastic material to identify the specific phases from the phase state of AC, as within LVE limit material creep compliance parameters does not depend on the state of stress. After phase identification, the load-displacement curves were introduced in Spring-Dashpot-Rigid body (SDR) model.
4.6 Nanoindentation Load-Displacement Data Analysis

As discussed in the previous sections, the current study used creep response to identify the AC phases, while in the previous study by Faisal et al. (2014, 2015) identified the nanoscale phases of AC were identified with respect to the degree of softness. In those studies following assumptions were made to identify binder, mastic and aggregate phases: for a maximum nanoindentation load of 0.51 mN and a dwell time of 200 s: (1) if the indentation depth remains within 1000 nm, the indented phase is defined as the aggregate phase of AC; (2) if the indentation depth remains between 1000 nm to 3000 nm for AC, the indented phase is defined as the mastic phase of AC; and (3) if the indentation depth is higher than 3000 nm for AC, the indented phase is defined as the binder phase of AC. In the current study, the integral AC phases are identified by adopting the two different approaches. One is related to the degree of softness as mentioned above and secondly with respect to the creep behavior of each phase.

Figure 4.8 Load-displacement Curves of Nanoindentation Tests on Binder1 and Binder2 Samples.
4.6.1 Nanoindentation on Binder at on Glass Slide

Figure 4.8(a) shows the load-displacement curves of nanoindentation tests on bulk state binder sample prepared on glass slides. 20 nanoindentation tests were done on binder sample. Binder1 samples showed a maximum displacement of 7040 nm. As discussed earlier, initially slopes of the unloading curves were used to determine the elastic modulus of the material. However, the unloading curves of the load-displacement response of Binder1 show negligible dissimilar response, it might be due to the asphaltic component distribution in asphalt binder. PG 64-22 binder showed a maximum displacement of 7040 nm, whereas PG 70-22 binder showed a maximum displacement of 4423 nm. As discussed earlier, initially slope of the unloading curves was used to determine the elastic modulus of the material. Figure 4.8(b) shows PG 70-22 has a higher amount of elastic recovery compared to PG 64-22 binder. However, the unloading curves of the load-displacement response of PG 70-22 show a negligible dissimilar response, it might be due to the heterogeneous component distribution in asphalt binder.

The load-displacement curves were further analyzed using SDR analysis method to determine the elastic modulus and the hardness of the material. Table 4.1 shows the elastic modulus and hardness of asphalt binder, it also incorporates the elastic modulus and hardness of RTFO and PAV aged asphalt binder.
Table 4.1 Elastic Modulus and Hardness of Asphalt Binder for Three Different Aging Conditions.

<table>
<thead>
<tr>
<th>Binder</th>
<th>Elastic Modulus (MPa)</th>
<th>Hardness (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unaged</td>
<td>RTFO</td>
</tr>
<tr>
<td>PG 64-22</td>
<td>3.15±0.27</td>
<td>3.97±0.48</td>
</tr>
<tr>
<td>PG 70-22</td>
<td>3.8±0.43</td>
<td>3.83±0.11</td>
</tr>
</tbody>
</table>

Aging in asphalt binder increases the variability in nanoscale elastic modulus and hardness of the asphalt binder, as it can be found in the increased standard deviation. Previous studies show the asphalt aging increases the asphaltene content in asphalt binder. During nanoindentation, the possibility of hitting the asphaltene fraction of asphalt binder increases, which also increases the stiffness as well as the stiffness variability of the thin film binder. However, due to viscoelasticity in asphalt binder, the analysis requires viscoelastic creep analysis of the material, which is done in the later part of the paper.

4.6.2 Nanoindentation on Mastic on Glass Slide

Figure 4.9(a) shows load-displacement curves on mastic samples using the binder1 sample. Maximum depth was found within 2000 to 3000 nm, which means the inclusion of fines with asphalt binder creates a stiffer sample to indent using the nanoindenter. In the current study, asphalt mastic sample was prepared using a dust to binder ratio of 1.2. Figure 4.9(b) shows the load-displacement curves of nanoindentation on asphalt mastic sample. The load-displacement curve shows the maximum displacement ranges from 1000 to 3500 nm.
Comparative analysis between Figure 4.9(a) and 4.9(b) show, the inclusion of fines with the asphalt binder sample to create asphalt mastic creates stiffer material, where indentation depths are lower compared to the maximum depth of nanoindentations on asphalt binder sample. However, comparison of PG 64-22 and PG 70-22 did not show a significant difference, except the indentation response of PG 70-22 mastic samples were followed a range of maximum depth from 1000 nm to 3500 nm.

4.6.3 Nanoindentation on AC Sample

During nanoindentation of AC sample, the indenter was set to indent a region covers the interface between two aggregates. As, AC is a heterogeneous material, a wide range of indentations on the connecting region of two stones might possibly capture all the phases of AC. In case of nanoindentation, a maximum load of 0.51 and dwell time of 200 sec always showed a maximum load within 9000 nm. Figure 4.10(a) shows the load-displacement response of PG 64-22 AC sample.
The load-displacement curve distribution shows, most of the load-displacement curves are distributed in the first 1000 nm region, which means most of the indentations were done on mastic and aggregate phase of asphalt. In the hot mix asphalt about 95% of the material is aggregate and only about five percent is binder, when binder is mixed with aggregate it makes a thin coat of binder around the aggregate and when the sample is cut from the sample it creates a surface mostly consists of aggregate phases with very few places of interface between aggregates, the interface is mostly consists of mastic material and small amount of binder phase. As nanoindentation requires a smooth perfectly level surface for indentation, the polishing process washes away some of some binder thin coats from AC sample. However, the interface remains the only source of finding binder phase in AC. In the study, all the indentation curves were further analyzed regarding their principal parameters as discussed before to preliminary identification of binder, mastic and aggregate phase of AC. Afterward, their creep responses were extracted and compared with independent material creep response. According to principal component analysis from 80
valid indentations only nine indentations were found on binder phase of AC, 10 indentations on mastic phase and 63 indentations on the aggregate phase of AC.

4.7 Asphalitic Phase Identification

As discussed in the previous sections, the current study used creep response to identify the AC phases, while in the previous study by Faisal et al. (2014, 2015) identified the nanoscale phases of AC were identified with respect to the degree of softness. In those studies following assumptions were made to identify binder, mastic and aggregate phases: for a maximum nanoindentation load of 0.51 mN and a dwell time of 200 s: (1) if the indentation depth remains within 1000 nm, the indented phase is defined as the aggregate phase of AC; (2) if the indentation depth remains between 1000 nm to 3000 nm for AC, the indented phase is defined as the mastic phase of AC; and (3) if the indentation depth is higher than 3000 nm for AC, the indented phase is defined as the binder phase of AC. However, the assumptions did not consider nanoindenter hitting a void space in AC concrete samples, which is a quite common scenario for AC. Nano/Microvoids in AC shows sudden high micro scale displacement of the indenter for a specific load, which invalidates the specific phase identification according to the degree of softness of the material. Therefore, current study identifies those three distinct phases of AC according to the creep response GPL model parameters of the material. However, fitting all the indentation data for three replicated sample with 100 indentations on each sample is a time-consuming process. Therefore, current study uses the principal component analysis using statistical software R initially to identify the soft phases of AC according to maximum depth and elastic modulus analysis. Afterward, the soft phases of AC are analyzed further to determine the GPL model
parameters of Eq. (13). The GPL parameters of soft phases are compared with those of bulk states of binder and mastic samples to identify specific phase.
4.7.1 Binder Phase of Asphalt Concrete

Fig. 4.11(a) shows the binder phase load-displacement curves of AC. As discussed before, the binder phase was preliminarily identified in the principal component analysis using statistical software R. The maximum displacements of all the indentations ranged from 2738 nm to 9607 nm. As discussed previously, the binder phase of AC is predominantly a viscoelastic material and only the creep response/dwell time of the load-displacement curve was further analyzed to validate the phase identification work. Fig. 4.11(b) shows the extracted creep responses of the load-displacement curves. Fig. 4.11(b) shows the displacement-time plot of all eight creep responses extracted from the nanoindentation data. For creep analysis, it is assumed the load and unloading time is negligible compared to creep response time. Therefore, the creep start time and load were designated as zero. Among all the creep response plots, only the first plot showed a displacement of 6.8 µm.
compared to the other curve plots average of 2.3 µm. As the first curves maximum
displacement is three times the average, it is deducted as an outlier from the analysis. Fig.
4.11(c) shows average creep response of all the binder phase data of AC. The current study
uses generalized power law to represent the creep compliance of the material. The
generalized power law parameter $D_0$ and $D_1$ can be used to describe the glassy and
transition behaviors (Veytskin et al. 2015; Park and Schapery 1999). Table 4.2 shows the
generalized power law parameter values and goodness of the fit.

<table>
<thead>
<tr>
<th>PG Grade</th>
<th>Material</th>
<th>$D_0$ (Pa)$^{-1}$</th>
<th>$D_1$ (Pa)$^{-1}$</th>
<th>$n$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binder 1</td>
<td>Binder</td>
<td>36.21±5.91</td>
<td>1.404±0.43</td>
<td>1.552±0.0015</td>
<td>0.9999</td>
</tr>
<tr>
<td></td>
<td>Phase of</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>AC</td>
<td>36.9±11.91</td>
<td>1.28±0.343</td>
<td>1.46±0.0058</td>
<td>0.9979</td>
</tr>
<tr>
<td>Binder 2</td>
<td>Binder</td>
<td>43.91±2.89</td>
<td>2.34±0.391</td>
<td>1.4982±0.05</td>
<td>0.9999</td>
</tr>
<tr>
<td></td>
<td>Phase of</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>AC</td>
<td>44.2±4.63</td>
<td>2.51±0.436</td>
<td>1.521±0.1</td>
<td>0.9979</td>
</tr>
</tbody>
</table>

Veytskin et al. (2015) found if the material loading stays within the LVE limit of the
material, the creep compliance curves follow similar trends compared to any loading
scheme. Table 2 also shows a similar pattern of creep response as both $D_0$ and $D_1$ parameter
and $n$ value shows similar value. The similar pattern and trend also infers it is possible to
identify the binder phase of AC using nanoindentation test. To validate the process whether
the analysis is analogous to other PG grade binders, binder2 samples were analyzed similarly
at bulk and phase state and results are shown in Table 4.2. It also renders similar GPL parameters.

### 4.7.2 Mastic Phase of Asphalt Concrete

A similar technique was used to identify the mastic phase of AC. Fig. 7 shows the comparison of the creep curves from phase state of mastic of the AC as well as from the bulk state of the mastic sample. Fig. 7(a) and 7(b) show the extracted creep response of the bulk state of mastic samples as well as the phase state of mastic AC. It can be noticed that bulk state of mastic samples followed the almost similar trend for all indentations. However, due to the heterogeneity of the AC sample the mastic phase creep response showed small variability among their responses. During model fitting, only nine indentation creep responses were used instead of ten. The outlier tenth creep response was not used in the model prediction. Table 4.3 shows the GPL model parameters for the bulk state of mastic samples and phase state of mastic of AC samples. To evaluate the validity similar calculations were done for binder 2 samples.
Figure 4.12 Comparison of Creep Response of Mastic Phase of Binder1 AC Samples.

Table 4.3 shows an overlap of GPL model parameters for individual PG grade sample, which also ensures it is possible to identify the mastic phase of AC. Therefore, it is found that the creep response parameters are similar and remain irrespective of the material state in the micro to nano scale, which also satisfies the LVE assumption of the study.

Table 4.3 GPL Creep Analysis Parameters of Mastic.

<table>
<thead>
<tr>
<th>PG Grade</th>
<th>Material</th>
<th>$D_0$ (Pa)$^{-1}$</th>
<th>$D_1$ (Pa)$^{-1}$</th>
<th>$n$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binder 1</td>
<td>Mastic</td>
<td>21.91±5.91</td>
<td>1.404±0.43</td>
<td>1.055±0.005</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>Mastic Phase of AC</td>
<td>18.5±6.32</td>
<td>1.2579±0.1</td>
<td>1.053±0.02</td>
<td>0.9982</td>
</tr>
<tr>
<td>Binder 2</td>
<td>Mastic</td>
<td>15.58±3.39</td>
<td>3.099±0.169</td>
<td>1.142±0.014</td>
<td>0.9999</td>
</tr>
<tr>
<td></td>
<td>Mastic Phase of AC</td>
<td>13.14±1.85</td>
<td>3.384±0.131</td>
<td>1.092±0.048</td>
<td>0.9861</td>
</tr>
</tbody>
</table>
It can be noticed that independent mastic samples followed almost similar trend for all indentations, however the due to heterogeneity of AC sample the mastic phase creep response showed small variability among their responses. However, during model fitting only nine indentation creep responses were used instead of ten. The outlier tenth creep response was not used in the model prediction. Table 4.3 shows overlapped of GPL model parameters for individual PG grade sample, which also ensures it is possible to identify the mastic phase of AC. Therefore, it is found that the creep response parameters are similar and remains irrespective of the material state in micro to nano scale, which also satisfies the LVE assumption of the study.

4.7.3 Aggregate Phase

Aggregate is strictly an elasto-plastic material and it is possible to identify and indent on the aggregate phase of AC. Elasto-plastic Oliver Pharr (OP) analysis has been used in the determination of the modulus and hardness of aggregate samples. Previous studies of Faisal et al. (2015) showed aging and moisture damage in AC do not affect the material parameters of the aggregate phase, Therefore, current study was confined to the identification of the viscoelastic property change of the binder and mastic phase of AC.

4.8 Conclusions

In the study, nanoindentation tests were conducted on bulk state of asphaltic materials and AC phases. A method is proposed in this chapter to identify specific phase of AC. The following conclusions can be made:
1. Nanoindentation test can successfully identify binder, mastic, and aggregate phases of AC. To identify the binder and mastic phases, the creep parameters of the specific phase is compared with the creep response of bulk state of the respective material. However, results of the AC indentations show that only 10%-15% of the indentations are indented on the binder and mastic phases of AC, though all the indentations were selected to indent the interface between two aggregates of AC.

2. The current research results show, whenever 100 indentations are done on AC, around 5% to 9% indentations are on the binder phase of asphalt concrete, which means it is possible to find pure binder in AC system. However, as asphalt aggregate system is mostly a homogeneous mixture, the only possible location of pure asphalt binder can be found on the surface of the aggregate surface. To identify specific phases, GPL model with LVE limit analogy is successfully used in the study.
CHAPTER 5

EXTRACTION OF MATERIAL PARAMETERS FROM NANOINDENTATION TESTING

5.1 General

Nanoindentation testing is relatively simple test, however, the main challenge comes with the challenges analysis technique of the load-displacement curves. With respect to the material and material response choosing an appropriate model to analyze the nanoindentation data is important. Nanoindentation gained large number of interest in the field of pavement researchers, as it can be used to extract different attractive material characteristics, like, elastic modulus, hardness, indentation viscosity, creep compliance (Tarefder and Faisal 2013b; Veytskin et al. 2015, 2016; Jager et al. 2010). Asphalt is a viscoelastic material, therefore in above mentioned studies researchers used the creep behavior of asphalt. To extract the material in-situ characteristic current study uses the phase identified load-displacement data from previous chapter and extracts different material parameters for aging of asphalt.

In previous research of nanoindentation on asphalt concrete (AC) by the authors, aging characterization on mastic and aggregate phases were conducted by visual observation and using elastoplastic model (Tarefder and Faisal 2013b). In contrast current study uses visco-elastoplastic analysis of the nanoindentation data extracted three different attractive material parameters, like stiffness, hardness and indentation viscosity, when they were an integral part of the AC body. Again, in AC asphalt binder plays one of the most important
roles of the material behavior. To date, most of the pavement material response models like the aging of AC and fatigue characterization of AC are related to the asphalt binder behavior. It is not known whether the asphalt binder behaves same in bulk state as in phase state, when the asphalt binder is an integral part of the AC system. To characterize the phase state behavior, it is important to identify the specific phases. In addition, the study attempts to answer whether the binder phase behavior is same as mastic phase of AC.

In order to understand, how and to what extent the AC phases play a role in-situ state compared to the bulk, on glass slide state, the current study uses the aging phenomena to compare the different conditions. Aging is a complex phenomenon and involves physical and chemical modifications to asphalt molecules. These modifications, or changes, have dramatic effects on asphalt binder and AC properties such as viscoelasticity (stiffness, hardness), and adhesion/cohesion (Newcomb et al. 2015; Veytskin et al. 2015). An understanding of the phenomena of aging can be benefited or enhanced by measuring the stiffness and hardness of asphalt using the nanoindentation technique, which is done here.

5.2 Aging of Asphalt Sample

The current study uses aging of the asphalt samples as a tool to quantify the difference between bulk state and phase state samples. Afterwards, in-situ binder phase is compared with the mastic phase of AC. Therefore, the 150 mm gyratory compactor prepared samples were conditioned according to the AASHTO R 30 (2002) draft oven aging standard practice. Samples were kept in a forced draft oven at a temperature of 185 °F (85 °C) for 5
days. This is to simulate long-term aging of a mix in the field over a period of 5 to 7 years (Tarbox and Daniel 2012). Samples are subjected to zero days/control sample, 2 days and 5 days of oxidative aging. In the paper, unaged represents rolling thin film oven (RTFO)/short term aged binder and mastic samples. As the AC sample preparation involves short-term aging of the sample. Therefore, short-term aged bulk state samples were used in the study to represent the unconditioned/unaged state of the samples. It can be noted, one can argue regarding the use of AASHTO R 30 (2002) protocol for simulating oxidative aging in the study as the standard is not validated yet. However, AC is a combination of permeable and non-permeable pores, therefore aging in the compacted sample as well as in real pavement is not uniform. Nanoindentation can capture non-uniform aging distribution as well as the variability of the asphalt aging process. Therefore, the current study adopts forced draft oven aging to simulate oxidative aging of the asphaltic sample.

5.3 Extraction of Unaged and Aged Bulk and Phase Material Property

In this chapter, bulk and phase state material property of AC phases are done using SDR model described in section 2.6.3. In the section, Eqs. (2.44), (2.47) and (2.50) define the entire displacement-time history of a nanoindentation test of asphalt using trapezoidal loading. Nanoindentation data is used to fit the above Eqs. (2.44), (2.47) and (2.50). Displacement data is fitted first to Eq. (2.47) to estimate indentation viscosity $\eta$. Next, the unloading data is fitted to Eq. (2.50), to estimate all the model parameters. The curve fitting of the displacement time curve was done in MATLAB using nonlinear least square fitting, with the trust region algorithm. Model parameters were obtained from the whole load-
displacement response of nanoindentation. Eq. (2.47) estimates indentation viscosity \( \eta \), Eq. (2.50) is used to determine stiffness, \( E \), and hardness, \( H \) of the material.

5.4 Comparing Bulk vs. Phase Properties

As discussed and shown in previous sections, the creep response of the bulk and phase state of asphalt can be used to identify the specific AC phases. However, it will be interesting to find out whether the bulk state shows or extracts similar/different results compared to the phase state of AC. Viscoelastic SDR model has been used to extract the modulus, hardness and indentation viscosity of the material. To compare bulk state vs. phase state of AC, samples were aged using a draft oven for two days and five days. As discussed previously, the behavior of the binder and mastic phase of AC is strictly viscoelastic; however, the behavior of aggregate phase is purely elastic (Faisal et al. 2015a, 2015b; Tarefder and Faisal 2013c). SDR model has been adopted to extract the modulus, hardness and indentation modulus of the material.
Figure 5.1 Load-displacement Response: (a) Load-Displacement Curves of Nanoindentations on binder1 Sample; (b) Load-Displacement Curves of Nanoindentations on Mastic Sample; (c) Load-Displacement Curves of Nanoindentations on binder 1 AC Sample at Phase.

Fig. 5.1(a) shows bulk binder stiffness of the binder1 sample. All three replicated samples were prepared on a glass slide and then twenty nanoindentation tests were done on the sample. Each point in Fig. 5.1(a) represents the average of 20 valid nanoindentations. In the plots, the standard error for each point of 20 indentations is shown. It can be noticed that as the aging time increases the variability among the sample increases as well as the standard error. It might be due to the increase in asphaltene content of asphalt binder, which creates a heterogeneity among the same sample to create the higher amount of variability.

Fig. 5.1(b) and 5.1(c) compare the stiffness of the bulk state and phase state of AC. Both plots show aggregate samples have the highest stiffness of around 82 MPa, and with aging, they do not show any change in the stiffness, which is also expected. The oxidative aging of only five days does not affect the stiffness of bulk as well as the phase state of the
aggregate samples. However, in both cases stiffness of the material increases, compared to the unaged stiffness of the binder, the bulk state binder samples showed 3.81 and 8.27 times higher stiffness for two and five days oxidative aging respectively. The phase state of binder showed 2.38 and 5.71 times increase in stiffness for two and five days draft oven aging. Therefore, the phase state of asphalt binder showed less stiffening due to the oxidative aging of the sample. The reason might be related to void spaces present in AC, the aging process of the bulk, and the phase state of the material. In the study, cylindrical AC samples were prepared using gyratory compactor and they were aged using the draft oven technique, AASHTO R30 (2002). The rectangular samples were collected from middle part of the cylinder, where aging of the sample fully depends on the available oxygen through the pores of AC.

It is well known that AC is a combination of impermeable and permeable pores. Test on impermeable pore trapped asphalt binder shows lower stiffness than the fully aged binder. In the case of bulk material, it was subjected to oxidation directly on the draft oven, where the surface was fully exposed to the oven oxygen for the oxidation process. Therefore, less available oxygen in the AC pores might be related to less aging of the phase state of AC. One can argue, the characterization of the aged material can always be done using extraction, recovery, and characterization of the aged material. Whenever binder is extracted and recovered from the AC mixes it creates a homogenous mixer, which might not offer the intrinsic property of the binder and mastic phase of AC when they are an integral part of the compacted sample. In addition, the phase state characterization value of the binder and mastic phase can be used further to relate whether the phase state of
binder property is co-related with phase state of mastic material. Due to time constraint, this has been recommended for the future study of AC. Similarly, aged mastic stiffness is compared with unaged mastic stiffness. Results show the bulk state stiffness increased by 3.22 and 8.68 times for 2 days and 5 days draft oven respectively. The phase state mastic stiffness showed 2.31 and 6.15 times increase for the same amount of aging. In this case, the phase state of the material also showed lower stiffening in the material due to oxidative aging.
Fig. 5.2 Load-displacement, Creep Response and GPL Model Fitting of Binder Sample:
(a) Binder Phase State if Binder1 AC Sample; (b) Creep Responses of the Binder Phase;
(c) Average Creep Response; (d) Model Fit of Creep Response; (e) Creep Response of
Bulk Binder; (f) Model Fitting of Creep Response.

Fig. 5.2 compares the hardness and indentation viscosity of the binder and mastic sample. Fig. 5.2(a) and 5.2(b) show hardness comparison of the bulk state and phase state of binder1 binder and the mastic sample. The hardness of the material increases with the increase of aging of the material. Comparing with the unaged bulk binder hardness of 60 kPa, the aged binder hardness shows 2.71 and 4.3 times higher value for 2 days and 5 days of oxidative aging respectively. Similarly, the mastic hardness increased by 1.71 and 4.15 times compared to the bulk state mastic hardness. It should be noted; the aged hardening rate of the mastic samples was higher than compared to binder sample and it might be related to the binder absorption of aggregate present in the mastic samples. A similar comparison of the hardness of the phase state of binder shows an increase of 2.53 and 3.6 times compared
to unaged condition for 2 days and 5 days draft oven aging. However, age hardening of the phase state of the mastic samples are 2.75 and 5.1 times compared to the unaged state.

Fig. 5.2(c) and 5.2(d) show the comparison of indentation viscosity. Indentation viscosity is an attractive parameter, as asphalt researchers show there is a strong correlation between asphalt aging and viscosity. However, nanoindentation gives indentation viscosity, which also showed an increase with the increased aging of the material, as shown in Fig. 5.2(c). Indentation viscosity ranged from 30 Pa-s² to 800 Pa-s² for asphalt binder. Here, indentation viscosity also is higher in bulk binder compared to binder phase material. In addition, the rate of viscosity change in mastic samples is higher than that of binder samples. Table 5.1 summarizes the stiffness, hardness, and indentation viscosity comparison between the bulk state and phase state of asphalt. Comparing the stiffness and hardness ratio, it can be observed that both the aged bulk state stiffness and hardness show an average of 1.3 times higher than that of the phase state stiffness of the material, whereas indentation viscosity ranges from 1.0 times to 1.25 times higher. To validate whether bulk state material parameters are always higher than that of the phase state of AC, binder2 samples were tested. Comparison of material parameters show they are analogous to the findings of binder1 samples.
### Table 5.1 Bulk State vs Phase State for Different Aging Conditions.

<table>
<thead>
<tr>
<th>Material</th>
<th>State</th>
<th>Stiffness Ratio = $(E_{\text{Bulk}}/E_{\text{Phase}})$</th>
<th>Hardness Ratio = $(H_{\text{Bulk}}/H_{\text{Phase}})$</th>
<th>Indentation Viscosity Ratio = $(\eta_{\text{Bulk}}/\eta_{\text{Phase}})$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unaged</td>
<td>2 Days</td>
<td>5 Days</td>
<td>Unaged</td>
</tr>
<tr>
<td>Binder1</td>
<td>1.02</td>
<td>1.45</td>
<td>1.32</td>
<td>1.07</td>
</tr>
<tr>
<td>Mastic</td>
<td>0.94</td>
<td>1.28</td>
<td>1.29</td>
<td>1.05</td>
</tr>
<tr>
<td>Binder2</td>
<td>1.12</td>
<td>1.67</td>
<td>1.54</td>
<td>1.01</td>
</tr>
<tr>
<td>Mastic</td>
<td>1.03</td>
<td>1.57</td>
<td>1.64</td>
<td>1.12</td>
</tr>
</tbody>
</table>

### 5.5 Conclusions

In this chapter, nanoindentation tests were conducted on the bulk state of asphaltic materials and AC phases. A mathematic modeling technique has been proposed and implemented to identify specific AC phases. Afterward, $E$, $H$, and viscosity from SDR model have been extracted to make a comparative analysis. In a nanoindentation test with a conical or pyramidal indenter, it is always subjected to visco-plastic damage. Although a very small amount of load is applied during nanoindentation test, an impression is created on the sample surface from the indenter tip during the test. Furthermore, a high amount of stress generates on the material under the indenter tip during the nanoindentation test, and in most cases, the material exceeds elastic limit and reaches plastic phase. The plastic response is attributed to a rigid body in the SDR model and the viscous flow by a dashpot.
element. This exceeding of the elastic limit under nanoindentation can be termed as damage. Therefore, nanoindentation creates damage at the nano level in the material, which is accounted for in the analysis of the material response. The stiffness, hardness, and viscosity data comes from the regression of the proposed constitutive model. The proposed constitutive model was used to obtain the material property parameters. Additional modification and verification of the model parameters can lead to a novel research. Therefore, further modifications and verification of the proposed constitutive model have been recommended for future study. The following conclusions can be made:

1. Currently, there is no widely accepted nanoindentation model for visco-elastoplastic materials such as AC. This study shows that the SDR model gives satisfactory results on nanoindentation of asphalt concrete. However, more studies are required under different environmental conditions to validate the model for AC.

2. Comparison between different aging conditions shows aging increases the nanoscale modulus, hardness, and indentation viscosity of the bulk binder and mastic material. A similar trend is found for the binder and mastic phase when they are in AC phase state. However, results show bulk material aging creates a higher amount of stiffening and hardness. In the AC phases, the effect of aging is comparatively lower. Nanoindentation was able to capture the high variability of stiffening in the binder and mastic phases of aged AC.
CHAPTER 6

EFFECTS OF PORE STRUCTURE ON THE AGING OF ASPHALT CONCRETE

6.1 General

Aging of asphalt concrete (AC) is one of the major concerns to asphalt researchers, as aging in asphalt shows an increase in stiffness and leads to the brittleness of the material. Asphalt oxidation occurs in AC through the permeable pores of the concrete material as well as oxygen present in the impermeable pores of AC. The current study attempts to investigate the effects of oxidative aging on the extracted asphalt binder of AC as a function of available pores in the concrete sample. The thin film asphalt binder’s property was examined using nanoindentation test.

Aging is a complex phenomenon and involves both physical and chemical modifications to asphalt molecules. These modifications, or changes, have dramatic effects on asphalt binder and AC properties such as viscoelasticity (stiffness, hardness), and adhesion/cohesion. As asphalt binder ages, the nonpolar molecule part decreases and the polar part increases (Petersen 2009). The increased amounts of polar molecules change the nature of the asphalt and lead to increased stiffness and slower stress-relaxation rates. However, in practice to integrate the aging response of AC, the relaxation time parameter of the material is usually assumed constant; by which an aged dynamic modulus master curve is constructed by only shifting the unaged dynamic modulus master curve in the vertical axis. In Pavement ME design change in air void of AC is considered for aging by changing the dynamic modulus or stiffness only. However, viscoelastic analysis of the aged material infers the aging mechanism of asphalt is a complex phenomena (Rahmani et al.
Aging in asphalt can lead to the development of distresses like fatigue or thermal cracking in asphalt pavement (Glover et al. 2009, Petersen et al. 1996, Qin et al. 2014, Tarefder and Faisal et al. 2013, Tarbox and Daniel 2012). Because aging phenomena is not yet well understood, several models such as top-down cracking model, fatigue model, used in the pavement ME design software, are incomplete or underdeveloped. There is a need for a mechanical understanding of aging in asphalt.

A number of methods have been developed and used to predict the behavior of asphalt binders (Tarefder et al. 2010; Huang and Turner 2014). In the last decade alone, there have been significant improvements in aging simulation equipment such as rolling thin film oven and pressure aging vessel. Our understanding of the bulk thermal and rheological properties such as viscosity and consistency of aged and unaged asphalt binders has also improved. However, the test methods developed, are mostly rheological shear and bending beam tests performed on the bulk volume of aged and unaged binders. No studies have been conducted using nanoscale compression stiffness and viscoelastic creep characterization of asphalt for the varying amount of air voids. The current study attempts to correlate pores/air voids with the nanoindentation hardness and relaxation behavior of asphalt. Nanoindentation investigation on AC’s air voids and aging behavior can lead more understanding how stiffness and relaxation behavior of both binder and mastic materials.

6.1 Objectives

The objective of the objective of this study is to evaluate the effect of air void on aging process using nanomechanical behavior of AC.
6.2 Outline

The detailed research methodology is presented by the flow chart in Figure 6.1.

Figure 6.1 Research Plan.
The major time for prolonged work lies with the first 2 steps, where compacted HMA samples were prepared and left in room temperature for four years to simulate aging in the samples. However, as AC samples have a wide variety of connected pours, samples can have different amounts of aging in specific micrometer scale areas. Therefore, to capture the whole scenario, asphalt binder samples were extracted and recovered using trichloroethylene extraction and rotavapor recovery technique, which is the 3rd step of Figure 6.1. One can argue, whether any aging really occurred or happened during four years of time or whether different aging is different from each other at different air void content. The study attempts to capture whether different amount of aging occurred in asphalt binder with varying air voids content by investigating the aged asphaltene and oxidized functional group content. The chemical analysis was further investigated using the nanomechanical characterization technique, which is step five and six of the flow chart.

6.3 Materials & Sample Preparation

6.3.1 Materials

Hot Mix Asphalt samples were collected during construction of a new overlay on I-40, mile marker 142. The mix was a dense graded Superpave, type SP-III with the nominal maximum aggregate size of 19.00 mm. The asphalt content was 4.4% by the weight of the mixture.

6.3.2 Asphalt Concrete Sample Preparation

Three slab samples of 12 inch by 18 inches were prepared using a linear kneading compactor. The target air voids of was remained within 7 to 20 percent. It is assumed that
each slab is homogeneous and material properties determined for any part of a slab represents the whole slab. The slabs were kept under open air inside the laboratory for four years. It was expected the samples would undergo a significant amount of aging during that four years of time. The aged samples were crushed, and binder samples were extracted and recovered for laboratory testing. One four-inch diameter core was collected from the center of each of the slabs. The bulk specific gravity and five percent absorption of the cores were determined as per ASTM standards. The sample air voids are reported in Table 5.1. Afterwards, the binder samples were extracted from collected using ASTM D2172 (Standard Test Methods for Quantitative Extraction of Bitumen from Bituminous Paving Mixtures) and recovered using ASTM D5404 (Standard Practice for Recovery of Asphalt from Solution Using the Rotary Evaporator). Instead of using different air voids notations, Table 6.1 was used in rest of the paper discussion. It should be noted that samples air voids ranged from 6.9% to 20.4%. This range of air voids was chosen to represent air voids in previous studies (Ahmad and Tarefder 2017, Ahmad et al. 2017).

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Air voids(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAV1</td>
<td>7</td>
</tr>
<tr>
<td>SAV2</td>
<td>8</td>
</tr>
<tr>
<td>SAV3</td>
<td>9</td>
</tr>
<tr>
<td>SAV4</td>
<td>14</td>
</tr>
<tr>
<td>SAV5</td>
<td>15</td>
</tr>
<tr>
<td>SAV6</td>
<td>20.5</td>
</tr>
</tbody>
</table>

**Table 6.1 Sample Air Voids.**

### 6.3.3 Asphalt Binder

Extracted and recovered binder samples as shown in Figure 6.2, are used to prepare nanoindentation samples on a glass substrate. As the first step, a glass slide surface 12.7 mm × 12.7 mm was selected and weighed in scale up to 4 significant decimal digits of
grams. Next, the glass slide was wrapped with high-temperature resistant tape. The tape was placed so that it formed the 6.35 mm square gap area previously outlined for the binder. Then, hot polymer modified liquid asphalt binder was poured into the gap between the tape strips. The polymer-modified binders were melted by heating them to 163 °C for an hour. The asphalt coated surface was placed in the oven at 163 °C for 10 min to have a smooth surface, cooled at room temperature and the tapes were removed. Finally, the glass slide with the asphalt coating was weighed again to measure the amount of asphalt binder. From the known area, the density of the asphalt binder and mass the thickness of the binder film was measured. The film thickness varied within a range of 40 µm to 80 µm to avoid substrate effect on test results.

![Extraction of Asphalt Binder Using Trichloroethylene Solvent Extractor](image1.jpg) ![Recover of Asphalt Binder Using Rotavapor Distillation Process](image2.jpg)

**Figure 6.2** Binder Sample Extraction and Recovery.

### 6.4 Results and Discussions

In this paper, attempts are made to correlate the void structures of AC with the aging of the thin film asphaltic material. Here, void structures of AC are referred to the air voids in AC. Air voids can be connected or isolated in AC. Higher air voids in AC is related to more oxygen availability in the asphalt mixes. In the current study, air voids are ranged from
seven to twenty percent in the material. Previous studies show more air voids means more susceptibility to the oxidative aging of AC. Therefore, the current study is divided in two segments. First stage, samples were checked for oxidative aging using Fourier Transform Infrared Spectroscopy (FTIR) and filtration Chromatography. In second stage, the nanomechanical viscoelastic property has been explored for different air voids containing aged HMA samples.

6.4.1 FTIR analysis

In FTIR test, a beam of light passes through the sample and part of the infrared ray is absorbed according to the functional groups present and its frequency of vibrations. In the study, for each sample, six times scans were done to achieve a smooth plot with a resolution of 4 cm$^{-1}$. Different functional groups present in the asphalt binder showed different functional groups, however, the study interest is limited to the area under sulfoxide (S=O) and/or ketones (C=O). It should be mentioned, the sulfoxide peak is observed approximately at the wave number 1030 cm$^{-1}$ and for ketones, and it was approximately at the wave number 1695 cm$^{-1}$. In the study, the influence area for each peak was calculated and they are normalized with respect to the full wavenumber range of 600 cm$^{-1}$ to 2000 cm$^{-1}$. The full wavenumber range is known as signature bandwidth for asphalt oxidation, as most of the changes happen within this region during asphalt oxidation. Table 6.2 shows the common functional groups and their corresponding wavenumbers.
Table 6.2 Asphalt Functional Groups and Corresponding Wavenumbers.

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Functional Group Name</th>
<th>Approximate Wave Number (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=O</td>
<td>Carbonyls, Stretch</td>
<td>1695</td>
</tr>
<tr>
<td>C=O</td>
<td>Unsaturated carbonyls, stretch</td>
<td>1600</td>
</tr>
<tr>
<td>C-C</td>
<td>Saturate, Bending</td>
<td>1455</td>
</tr>
<tr>
<td>-C-H</td>
<td>Methylene, Bending</td>
<td>1376</td>
</tr>
<tr>
<td>C-O, S=O</td>
<td>Secondary, Tertiary</td>
<td>1100</td>
</tr>
<tr>
<td>S=O</td>
<td>Primary, Sulfonate</td>
<td>1030</td>
</tr>
</tbody>
</table>

Figure 6.3 shows the full FTIR spectrum on three replicated samples of 8% air voids containing aged asphalt binder samples. Full FTIR spectrum were obtained for all six different binders and each with three replicated samples. In all cases, no variations is observed for wave number more than 1800 cm$^{-1}$.

![FTIR Spectrum](image)

**Figure 6.3** Full Spectrum of FTIR spectroscopy output of 8% Air voids Containing Aged Asphalt Binder Sample.
Spectrum of each binder sample did not show any significant difference with each other. Two strong peaks are observed at wave number 1455 and 1030 cm\(^{-1}\), which is mainly saturate and sulfoxide functional groups, respectively.

Figure 6.4 shows the normalized functional group as a function of air voids. Only two functional groups of aging study interest are plotted here as a function of increasing amount of air voids in different samples. Here it should be mentioned that sulfur is an active substance and it reacts rapidly compared to ketones, which can be found from the figure also. Though it should be mentioned the S=O functional group ranges from 0.02 to 0.05 region, however the stretch of C=O functional group is higher, as carbon is main hydrocarbon element in asphalt.

![Normalized C=O and S=O Functional Groups as a Function of Air Voids](image)

**Figure 6.4** Normalized C=O and S=O Functional Groups as a Function of Air Voids.

The plot includes both the change of normalized C=O and S=O functional groups as a function of air voids. As the amounts of air voids in the sample increases both C=O and S=O functional groups show increases, which means rate of oxidation is higher as oxygen
availability increases in the samples. Again, rate of oxidation in S=O is higher than compared to rate of oxidation of C=O. To capture the trend both oxidation of S=O and C=O functional group was calculated using exponential function. The fitting shows the R squared value of S=O follows closer trend compared to C=O functional group. As both S=O and C=O functional groups increasing with increase in air voids in AC samples. It can be concluded that higher amount of aging occurs as air voids/pores increases in the compacted hot mix asphalt and the aging occurred in an exponential rate with increase in air voids in AC. Analysis of Variance (ANOVA) is used to identify, whether the functional groups normalized functional values are changing with change in the airvoids. An ANOVA analysis for 95% confidence shows p-value of 0.000293. Therefore, it can be concluded that normalized functional group values are different from each other.

6.4.2 Chromatographic Analysis

Chromatographic Analysis was performed on the same samples with varying amount of air voids to identify amount of aging in asphalt. Here it should be mentioned that the chromatographic analysis was done using the n-heptane solvent only. As mentioned in the literature, asphaltene is the main ingredient that occurs with oxidation of asphalt compounds. The stiffer asphaltene fraction is the key compound to identify the amount of aging in asphaltic material. Figure 6.5 shows the extraction and filtration unit used along with the vacuum suction to separate the asphaltene fraction of the asphalt binder.
Three replicated binder samples were taken to quantify the amount of asphaltene compound content in the binder. Afterward they are averaged to identify whether aging is happening with higher amount of asphalt availability in the compacted AC sample. Results are presented in Figure 6.6.

**Figure 6.5** Extraction Asphaltene Fraction.

**Figure 6.6** Asphaltene Fraction in Asphalt as Function of Air Voids.
Figure 6.6 shows the increase in asphaltene content with increasing amount of air voids in compacted HMA samples. It can be observed that 2 times higher air voids increase the asphaltene content in asphalt binder by 13.5% and 3 times higher air voids increases the asphaltene content in the samples by 50.4% compared initial aged asphaltene content of 7% air voids containing samples. From the results it can be concluded that higher air voids in compacted asphalt concrete increases the amount of aging in the asphaltic material. Therefore, in the following section, thin film mechanical characterization of the aged asphalt binder has been investigated. In addition, statistical ANOVA analysis for a 95% confidence interval a p-value of 0.000447 is obtained. Therefore, it can be concluded that the asphaltene fraction content changes with change in air voids of the compacted HMA samples.

6.4.3 Load-Displacement Behavior

Figure 6.7 shows load-displacement curves of the nanoindentation tests on different samples with varying amount of air voids. Each curve shows the loading, creep and unloading part. As expected none samples showed any noise in load-displacement curves and the loading and unloading curves almost overlapped on each other except for one indentation on SAV6 sample. The coefficient of variations of each samples maximum displacements were 2.59%, 2.49%, 2.54%, 2.79%, 3.15%, 3.18% respectively for SAV1 to SAV6. Therefore, the data show the very low dispersion of data. One thing can be noted that the coefficient of variations was high for high air voids containing samples. It might be related to the higher amount of asphaltene molecular substances in asphalt binder. All
the samples except SAV6 show a maximum displacement of around 6000 nm. Only SAV6 showed a maximum displacement within 4000 nm.

![Load-displacement Curves](image)

**Figure 6.7** Load-displacement Curves for Increasing Amounts of Air Voids in AC.
It can be noted, all the samples showed positive unloading trend, which means 200 sec of creep time is appropriate for producing positive unloading slope. Therefore, the load-displacement curves were further analyzed using the Oliver-Pharr method.

6.4.2 Creep Behavior

Asphalt binder is predominantly a viscoelastic material. Past references show usual elastic analysis of the nanoindentation load-displacement of asphalt binder to obtain the nanoindentation modulus and hardness can lead to wrong interpretation (Tarefder and Faisal 2013, Faisal et al. 2015). Therefore, in the current study, the nanoindentation creep data was used to further analyze for creep parameters of asphalt binder. The nanoindentation creeps data was extracted from the dwell time data of the material. In doing so, it was assumed the loading and unloading time is very negligible compared to the creep time of the nanoindentation test. Figure 6.8 shows the creep response the extracted creep data for SAV1 to SAV6 samples. For 12 indentation creep data, the coefficient of variations are 2.64%, 2.49%, 2.53%, 2.08%, 3.12% and 10.12% for SAV1, SAV2, SAV3, SAV4, SAV5 and SAV6 samples respectively. Therefore, there is a negligible dispersion of the data among different indentations. Depths of indentation during creep phase of nanoindentation found decreasing with increasing amount of air voids in AC samples.
Figure 6.8 Creep Behavior of Asphalt Binder for Different Levels of Air Voids in the AC Samples.
6.5 Nanoindentation Hardness

The load-displacement curves of the previous section were further analyzed using the hardness of the material. Figure 6.9 shows the hardness comparison at room temperature with increasing amount of air voids in AC samples. Results from the nanoindentation hardness show samples with around 8% air voids show 17.2% higher hardness compared to 7% air voids containing samples and the extracted asphalt binder of 9% air voids containing samples show 39.5% higher hardness compared to that of 7% air voids. Furthermore, samples with 13.7% show 43.3% higher hardness compared to 7% air voids and 52.6% higher compared to 7% air voids. Samples with 20.4% air voids show highest amount of hardness increases around 137.7% higher than that of 7% air voids containing the sample.

![Hardness for different levels of air voids.](image)

Figure 6.9 Hardness for different levels of air voids.

In addition, the coefficient of variations was calculated for all the air voids containing samples and found to be 4.8%, 5.1%, 3.7%, 9.4%, 12.1% and 7.5% for six different samples. Therefore, the data shows the low dispersion of data among same sample
indentations, however, the dispersion increased at for the samples extracted from AC samples with higher air voids. Again the cause might be related to the increase in high molecular weight containing substance (i.e. asphaltene) in asphalt binder with an increase in air voids in AC samples. It should be noted, the nanoindentation hardness is extracted from the plastic response of the material, in other words, which is related to the brittleness of the material. Therefore, it can be concluded, higher amounts of pores in AC form more brittle material during the aging process of asphalt.

6.6 Viscoelastic Analysis

Asphalt is predominantly a viscoelastic material. Use of elastic Oliver-Pharr analysis to analyze nanoindentation load-displacement data usually results in wrong nanoindentation modulus of the material. Therefore, the creep responses were further analyzed using Burger’s Model. Previous studies of the author it is found that creep response of the asphaltic material shows a very good correlation with the Burger’s viscoelastic model. In addition, the previous section shows the creep responses overlap with each other, with a negligible dispersion of data among themselves. Figure 6.10 shows a four element Burger model, which was found to be the most suitable model for asphalt in a previous study by the authors (Tarefder and Faisal 2013).
The final form of the Burger model can be found in Tarefder and Faisal (2013) and is given below:

\[
h^2 = \frac{\pi}{2} P_0 \cot \psi \left[ \frac{1}{E_1} + \frac{1}{E_2} \left[ 1 - e^{-t/\tau_2} + \frac{t}{\eta_1} \right] \right]
\]

(6.1)

where \( P_0 = \) indentation load

\( h = \) displacement due to applied load in a material

\( E' = \) elastic modulus of indented material

\( \nu = \) Poisson’s ratio of the material

\( \psi = \) include a half angle of Berkovich indenter.

As shown in Eq. (6.1) it can be noted that compliance under Berkovich indenter is proportional to the quadratic displacement/depth under indentation. From Eq. (6.1) for the
known values of \((h, P_0 \text{ and } t)\) from an indentation test, the values of \(E_1, E_2, \tau_1\) and \(\tau_2\) can be obtained from the simplified Eq (5.2).

\[
h^2(t) = A_1 + A_2 (1 - e^{-t/\tau_2}) + A_3 t
\]  

(6.2)

where \(A_1 = \frac{\pi}{2} P_0 \cot \psi \frac{1}{E_1}\) and \(A_2 = \frac{\pi}{2} P_0 \cot \psi \frac{1}{E_2}\) and \(A_3 = \frac{\pi}{2} P_0 \cot \psi \frac{E_1 t}{\tau_2}\).

In this study, Eq (6.2) is fitted to laboratory data to find \(A_1, A_2\) and \(A_3\). A nonlinear curve fitting algorithm is used in MATLAB to optimize those parameters.

**Figure 6.11 Creep Data Fitting.**

Fig. 6.11 shows the MATLAB fitting of raw creep load-displacement data using Burger’s Model. The R square of the fitting was 0.9998. The average fitting parameters are shown in Table 6.3.
Table 6.3 Fitting Parameters from Burger’s Model.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Air Void</th>
<th>$E_1$ (MPa)</th>
<th>$E_2$ (MPa)</th>
<th>$\tau_1$ (sec)</th>
<th>$\tau_2$ (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAV1</td>
<td>6.9</td>
<td>0.016</td>
<td>0.05155</td>
<td>0.032175</td>
<td>0.1198</td>
</tr>
<tr>
<td>SAV2</td>
<td>7.7</td>
<td>0.020097</td>
<td>0.056236</td>
<td>0.08759249</td>
<td>0.1209</td>
</tr>
<tr>
<td>SAV3</td>
<td>8.9</td>
<td>0.044664</td>
<td>0.1369</td>
<td>0.13213</td>
<td>0.1316</td>
</tr>
<tr>
<td>SAV4</td>
<td>13.7</td>
<td>0.7928</td>
<td>0.2266</td>
<td>0.2155</td>
<td>0.1816</td>
</tr>
<tr>
<td>SAV5</td>
<td>14.3</td>
<td>0.9226</td>
<td>0.24</td>
<td>0.1924</td>
<td>0.1923</td>
</tr>
<tr>
<td>SAV6</td>
<td>20.4</td>
<td>1.89</td>
<td>0.68226</td>
<td>1.217</td>
<td>0.45</td>
</tr>
</tbody>
</table>

Two things can be noticed from the creep model fitting data. One the spring modulus shows an increasing trend with an increasing amount of air voids in AC, which can be related to the increase in stiffness of the material with an increase in aging of the samples. Secondly, the relaxation behavior of the material. To understand the relaxation behavior the relaxation times are plotted w.r.t. a varying amount of air voids, as shown in Figure 6.12. From the figure 6.12(a) and figure 6.12(b), the relaxation time $\tau_1$ and the retardation time $\tau_2$ increases with an increase in air voids/aging in asphalt concrete. High time is required to release stresses and the binder becomes more viscous while the retardation terms increases (Khattak and Kyatham 2008, Imran et al. 2015, Rahmani et al. 2017)). Therefore, higher air voids caused damage to the binder by reducing its stress-relaxing capacity.
On the same note, creep behavior of mastic phase of AC has been explored in the study. It should be noted, mastic phase of asphalt concrete is explored only for three different air voids: 7%, 13% and 20% of air voids. Figure 6.13 shows the load displacement plots of 100 indentations on 7% air voids containing AC sample.
In the figure, maximum displacements are ranged from 300 nm to 10 µm. Mastic phase states are identified according to creep response of the material. Again, it was assumed the loading and unloading time is negligible compared to the creep time of the nanoindentation test. The extracted creep response of each nanoindentation is modeled using Burger Model. The viscoelastic parameters of stiffness and relaxation are shown in Table 6.4.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Air Void</th>
<th>$E_1$ (MPa)</th>
<th>$E_2$ (MPa)</th>
<th>$\tau_1$ (sec)</th>
<th>$\tau_2$ (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAV1</td>
<td>6.9</td>
<td>13.5</td>
<td>26.22</td>
<td>13.6</td>
<td>0.0011</td>
</tr>
<tr>
<td>SAV4</td>
<td>13.7</td>
<td>31.6</td>
<td>285</td>
<td>28.1</td>
<td>0.024</td>
</tr>
<tr>
<td>SAV6</td>
<td>20.4</td>
<td>61.98</td>
<td>502</td>
<td>53.1</td>
<td>0.09</td>
</tr>
</tbody>
</table>

Again, two observations can be made from the creep model fitting data. One, the spring modulus shows an increasing trend with the increase of aging, which can be related to increase in stiffness of the mastic. The other one is the relaxation behavior of the material. It is observed that both the relaxation time $\tau_1$ and the retardation time $\tau_2$ increase with an increase in aging. Additional time is required to release stresses and the mastic becomes more viscous as retardation increases. As such, it can be concluded that aging causes damage to the mastic phase by reducing its stress-relaxing capacity. Results show relaxation time is increased by 3.9 times for a change of 13% air voids in AC.
6.10 Summary

In the current study, asphalt concrete samples were prepared with varying amounts of air voids. Afterwards, the samples were aged for four years and binder samples were extracted and recovered to characterize whether the varying amount of air voids caused any differentiation in asphalt aging. Nanoindentation and asphalt creep behavior was quantified to draw following conclusions:

i. The nanoindentation hardness of the material increases with increasing amount of voids in AC, which means the higher pores in AC is going to form more brittle material.

ii. Aging in AC concrete decreases the stress relaxation capacity of asphalt binder and mastic. As both the modulus or compliance and retardation terms are changed with the change in the number of available pores in AC. That means, it can be argued, the current practice of shifting dynamic modulus with respect to compliance or relaxation parameter can lead to wrong interpretation of aging of asphalt, instead both compliance and relaxation parameters should be used in aging characterization.
CHAPTER 7
LABORATORY DETERMINATION OF ASPHALT FILM THICKNESS

7.1 Introduction

In asphalt concrete (AC), the asphalt binder film around the stone aggregate is the most important constituent that controls the main properties of the AC. Researchers believe an asphalt composite should have adequate asphalt film thickness to perform well in its whole service life. However, recently, numerous studies have been conducted to identify what would be the appropriate asphalt binder film thickness for better performance of a pavement structure. All the studies are limited to surface area and volume calculations of asphaltic material. Other that one microscopic study from Elseifi et al. (2008), no studies attempted to determine the asphalt film thickness in the laboratory. No study has ever attempted to quantify the change in the asphalt binder film thickness with progressive aging of asphalt. In this chapter, a nanomechanical technique is proposed and adapted to measure and compare the thin film asphalt binder thickness around an aggregate surface with progressive oxidative aging.

7.2 Outline

This study focuses on the laboratory asphalt film thickness determination in the context of the fact that film thickness can greatly affect the results of nanoindentation modulus and hardness. Figure 7.1 shows the outline of the study. In the beginning, random indentations were done to determine the load resolution needed to measure asphalt film thickness in the asphalt-aggregate system. The determined optimum load resolution is used afterward to determine the change in asphalt film thickness as a function of progressive asphalt aging.
7.2 Average Asphalt Film Thickness Calculation

As discussed in Chapter 2, the asphalt film thickness estimation uses the AI MS-2 technique of surface area calculation of aggregates. An average asphalt film thickness of 7 μm to 16 μm is generally found in the optimum range of asphalt film thickness from the literature of the last half of the century, as it provides acceptable pavement performance. The film thickness calculation procedure follows the following equation (7.1),

\[ T_F = \frac{P_{be}}{SA \times P_s \times G_b} \]  

(7.1)

where

\[ T_F = \text{average asphalt film thickness in mixture (mm)}; \]
\(P_{be}\) = percent (by weight) of effective asphalt binder in the mix;

\(SA\) = aggregate surface area (m\(^2\)/kg);

\(P_s\) = percent (by weight) of aggregate;

\(G_b\) = specific gravity of the asphalt binder.

Now we know,

\[P_s = \frac{1-P_{be}}{1+P_{ba}}\]  \hspace{1cm} (7.2)

where

\(P_{be}\) = effective binder content by weight of the mixture (%);

\(P_{ba}\) = absorbed asphalt binder by weight of the aggregate (%).

Therefore the Eq. (7.1) becomes,

\[T_F = \frac{P_{be} \times (1+P_{ba})}{SA \times (1-P_{be}) \times G_b}\]  \hspace{1cm} (7.3)

However, the surface area factor of Eq. (7.3) can be defined as,

\[SA = \frac{1}{100} \times \sum_{i=0}^{N} (PP_i \times CP_i)\]  \hspace{1cm} (7.4)

where

\(PP_i\) = percent of aggregate by weight passing the \(i\)th sieve;

\(CP_i\) = surface area factor as outlined in asphalt institute MS-2.
7.3 Results and Discussion

At the initial stage of the study, trials were made to identify the specific set of loading pattern necessary to penetrate through the asphalt binder film layer and reach the stone aggregate surface. After several trials, following set of loading setup, Table 7.1, was found to be appropriate to penetrate the asphalt binder film surface.

**Table 7.1** Nanoindentation Test Parameters Used to Identify Asphalt Film Thickness.

<table>
<thead>
<tr>
<th>Test Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test Mode</td>
<td>Load Control</td>
</tr>
<tr>
<td>Maximum Load</td>
<td>8 mN</td>
</tr>
<tr>
<td>Initial Load</td>
<td>0.05 mN</td>
</tr>
<tr>
<td>Loading Rate</td>
<td>0.1 mN/sec</td>
</tr>
<tr>
<td>Unloading Rate</td>
<td>0.1 mN/sec</td>
</tr>
<tr>
<td>Dwell at Maximum Load</td>
<td>50 sec</td>
</tr>
</tbody>
</table>

It was found that by using the above mentioned loading protocol it is possible to identify the asphalt film layer thickness. However, the nanoindenter can only identify a maximum thickness of 23000 nm in the study. Therefore, the loading protocol was controlled so it can identify the binder layer thickness.
As mentioned before, in the study, nanoindentation tests were conducted on one of the asphalt-aggregate systems of HMA. However, before nanoindentation, it was necessary to identify the region where the presence of asphalt binder with filler material is minimum. Without selecting a specific region, it is difficult to find a range of data to identify the asphalt film thickness. Figure 7.2 shows the load-displacement behavior of random indentations on the asphalt-aggregate system. However, without a preliminary selection of a specific region, most of the indentations did not show any change of slope in the loading curve. Therefore, in the study, preliminary inspection was done of the HMA sample to identify a region with minimum asphalt film thickness. Figure 7.3(a) shows the selection
of a uniform thickness region for nanoindentation testing. The region was selected by visual observation and random indentations of the HMA sample, as shown in Figure 7.3(b). The results and comparative analysis for thickness change are reported in the following sections. One can argue, the study should have done by indented the whole surface of the asphalt-aggregate sample, which was the initial idea of the study. However, as mentioned before, the maximum displacement resolution of the nanoindentation system used was only 23 µm. After that range, it is out of the nanoindentation system compliance. Secondly, the main goal of the study is to identify and quantify the change in asphalt binder film layer thickness with progressive aging. Without selecting a specific small uniform thickness region, the comparative analysis between different aging states makes it invalid. Therefore, in synthetic asphalt aggregate system samples were prepared in a smooth flat aggregate and tested.

![Selected Region for Nanoindentation Testing](image1)

![Nanoindentation Test on the Selected Region](image2)

**Figure 7.3** Nanoindentation on Asphalt-Aggregate System.
Afterward, the sample was introduced for draft oven aging and after each stage of aging samples were tested in the same region to quantify and compare the change in average asphalt film thickness in the asphalt-aggregate system. Figure 7.4 shows a synthetic asphalt aggregate system used for nanoindentation testing. Since the main objective of the study is to identify the change of asphalt film as a function of progressive aging, the study used only used a synthetic asphalt thin film over a smooth aggregate substrate.

Figure 7.4 Synthetic Asphalt-Aggregate System Sample.

Unaged HMA Sample

Figure 7.5 shows the load-displacement response of the asphalt-aggregate system of unaged material. Nanoindentation load-displacement data show that each of the twenty nanoindentation tests data has changed in the loading curve slope. Twenty indentation tests
were done on 5 row × 4 column matrix of indentation. Each indentation was at a distance of 400 µm. The large nanoscale distance was considered to accurately quantify the apparent asphalt binder film thickness. Analysis of the loading curve reveals that displacement rate of the initial loading curve is much higher than that of the second loading curve, which means the indenter indented on a softer material first; afterward the indenter indented on a hard surface.

**Figure 7.5** Nanoindentation Load-displacement Response of Unaged Asphalt Aggregate System.

The indentation on the hard aggregate surface resulted in a sharp change in the loading curve of the nanoindentation test. In addition, the second distinct feature is the low creep displacement on the hard surface. Therefore, each loading curve is further analyzed to determine the point of inflection, which indicates the asphalt film thickness of asphalt. An average asphalt film thickness of 6.4 microns was found for unaged asphalt binder.
However, from the figure, it can be noticed a range of 4 microns to 9.5 microns was found in the study for the unaged asphalt binder. The coefficient of variation of unaged asphalt binder film thickness was found to be 19.8%, which is within considerable range considering variation in nanoindentation test data.

3 Days Aged HMA Sample

![Graph showing load-displacement response of 2 days aged asphalt aggregate system.](image)

**Figure 7.6** Nanoindentation Load-displacement Response of 2 Days Aged Asphalt Aggregate System.

Figure 7.6 shows the load-displacement response of the asphalt-aggregate system of 3 days aged material. Nanoindentation load-displacement data show each of the twenty nanoindentation tests data has shown a sharp change in the loading curve slopes. The Point of inflections were determined for each load-displacement curve. Analysis of twenty load-displacement curves shows an average asphalt film thickness of 4.02 microns, which ranges from 2.06 microns to 4.39 microns.
5 Days Aged HMA Sample

Figure 7.7 shows the load-displacement response of the asphalt-aggregate system of 5 days aged material. Nanoindentation load-displacement plots show each of the five nanoindentation tests data has been changed in their loading curve slopes.

![Nanoindentation Load-displacement Response of 5 days aged Asphalt-Aggregate System](image)

Further analysis of the loading curve reveals displacement rate of the initial loading curve much higher than that of the second loading curve, which means the indenter indented on a softer material first; afterward the indenter indented on a hard surface. The indentation on the hard aggregate surface resulted in a sharp change in the loading curve of the nanoindentation test. Each loading curve is further analyzed to determine the point of inflection, which indicates the asphalt film thickness of asphalt. Average asphalt film thickness for 5 days aged asphalt concrete is 3.2 \( \mu \text{m} \), with a standard deviation of 0.48 \( \mu \text{m} \).
Figure 7.8 Nanoindentation Load-displacement Response of 10 days Aged Asphalt-Aggregate System.

Figure 7.8 shows the load-displacement response of the asphalt-aggregate system of 10 days aged asphaltic material. Nanoindentation load-displacement plots show each of the twenty nanoindentation test data has changed in the loading curve slopes. Further analysis of the loading curve reveals displacement rate of the initial loading curve much higher than that of the second loading curve, which means the indenter indented on a softer material first afterward the indenter indented on a hard surface. The indentation on the hard aggregate surface resulted in a sharp change in the loading curve of the nanoindentation test. Each loading curve is further analyzed to determine the point of inflection, which indicates the asphalt film thickness of asphalt. The analysis result shows an average asphalt film thickness of 2.47 microns, which has a range from 1.2 microns to 2.95 microns. The coefficient of variation (COV) is 18.18%.
7.4 Comparison

Figure 7.9 Comparative Study of the Change of Film Thickness with Oxidative Aging.

Figure 7.9 shows the change of asphalt film thickness with increasing amount of oxidative aging. It can be noticed that the unaged samples show the highest amount of variations. The variation in asphalt film thickness decreases with an increase in draft oven aging of asphalt. Aging of asphalt film decreases the variability of asphalt film thickness. As the asphalt ages, it becomes stiffer and the asphalt film coating thickness decreases. It might be related to the fact that as the thickness of the asphalt binder decreases the variability of asphalt thickness decreases and with the heat and oxidation of the thin film layer, it shows a uniform thickness of asphalt over the aggregate sample.

In addition, it can be noticed that the change in asphalt film thickness shows an exponential curve plot. The equation of the exponential curve is shown in the following equation,

$$ y = 6318e^{-0.1356x} $$

(7.5)
Here, \( y \) = asphalt film thickness in nanometer, \\
\( x \) = Draft oven aging time in days.

Here the R-square of the fitting is 0.7222. Therefore, it is reasonable to identify that the asphalt thin film layer of an asphalt-aggregate system was subjected to the highest amount of thickness reduction in the first five days of aging of asphaltic material. The thickness reduction rate decreases with increase in aging of the asphalt-aggregate system and it becomes asymptotic after 4-5 days, which means 5 years of asphalt aging. To ensure the repeatability, three synthetic asphalt–aggregate samples were tested. Sample 2 had an initial thickness of 8.24 microns and sample 3 showed an asphalt film thickness of 5.7 microns.

\[
y = 8754 \times e^{-0.0921x} \tag{7.6}
\]

\[
y = 5921 \times e^{-0.117x} \tag{7.7}
\]

Eq. (7.6) and (7.7) show the exponential change of trend with aging in asphalt. If the equation is normalized with respect to the initial unaged asphalt film thickness, the equation can be written as,

\[
y = A_{unaged} \times e^{-px} \tag{7.8}
\]

where, \( A_{unaged} \) = Initial Unaged Thickness of Asphalt,

\( p \) = decay constant (ranges from 0.0921 to .157).

In can be noted that, the current study did not include the effects of temperature cycle/climatic load, freeze-thaw and moisture damage of the change of asphalt film thickness. Including one or two variabilities might infer interesting insight of the asphalt-
aggregate system. However, at this point the study tries to identify, the reason behind the thickness reduction asphalt thin film layer. It is well known that aging in asphalt binder increases the polar molecular content in the material, the increase of the polarity in the system makes the polar molecules come together to form a stiffer component of the thin film material, which is also known as the asphaltene component of asphalt binder. However, at this stage of the study, whether the increase in aging in asphalt binder increases the polar functional group has been explored. The study uses Fourier-transform infrared (FTIR) spectroscopy technique on different aged asphalt binder samples to identify the change in the functional group in asphalt binder. Figure 7.10 shows the full spectrum of FTIR absorption scan on three different replicable samples.

![FTIR Spectrum](image)

**Figure 7.10** Full FTIR Spectrum on Unaged Asphalt Binder

FTIR scan on three replicated samples produced an almost similar response. However, for aging study main concentration has been given to the increase in C=O and S=O groups concentration, similar analogy as in chapter 5 has been used to analyze the data. The results
are shown in the Figure 7.1. It is found that increase of aging increases the oxidized polar functional group content of in the asphalt binder system, Figure 7.1.

![Graph showing variation of functional group as a function of days of aging.](attachment:figure7_1.png)

**Figure 7.11** Functional Group variation as a function of Days of Aging.

The rate of change C=O group is found to be much higher than that of S=O group. Therefore, as the aging progresses in asphaltic material, more trace materials in asphalt binder oxidized to form the higher amount of sulfoxide and carboxylic content as polar molecules, which makes the system come closer to each other to form a stiffer and lower volume of the material. In other words, closer molecules might be related to form bigger and stiffer form of asphalt binder fraction, which is also known as asphaltene fraction of asphalt binder.
Figure 7.1 shows asphaltene content of different asphalt binder as a function of days of aging. Asphaltene content increases with the increase of aging in asphalt, which means the most stiffer part of asphalt binder increases with increase in aging in asphalt.

7.5 Summary

In this chapter, a novel technique is proposed and implemented to quantify the asphalt film thickness. However, the main concentration is given how the asphalt film thickness changes due to the aging of asphalt. Following conclusions can be drawn from asphalt film thickness study of this chapter:

1. Using the proposed technique, it is possible to successfully determine asphalt film thickness and its change over the aging process of asphalt. However, the results show that it is difficult to accurately identify and quantify the asphalt film thickness in an asphalt-mastic-aggregate system. Therefore, the study is limited to the only quantification of change in asphalt film thickness in an asphalt-aggregate system.
2. Quantification of asphalt film thickness with increase in asphalt aging shows the change follows an exponentially decreasing trend, and the asphalt film thickness reduction rate reduces as more aging happens in an asphalt-aggregate system. Following trend line equation is found from non-linear least square fitting in MATLAB,

\[ y = A_{unaged} \times e^{-px} \]  

(20)

where, \( A_{unaged} \) = Initial Unaged Thickness of Asphalt,

\( x \) = days of draft oven aging,

\( p \) = decay constant (ranges from 0.0921 to .157).

The decay equation shows the asphalt film thickness reduces to the half of its original thickness within 5.3 years to 7 years of its service life.

3. The study attempts to quantify the reason behind why thickness is reducing with the aging of asphalt, the analysis results show an increase in asphalt binder increases the amount of polar functional group, which makes the asphalt system to coagulate to produce more complex big asphaltene fraction of asphalt binder. Therefore, the asphalt binder volume decreases with long-term aging of asphalt.
CHAPTER 8
AGING MODEL DEVELOPMENT

8.1 Introduction

Oxidative aging of asphalt is one of the major concerns in the asphalt research field, as aging can lead to the development of distresses like fatigue or thermal cracking in asphalt pavement (1-9). Aging in asphalt leads to stiffening of the material as well as it changes its chemical composition. It is a well-known fact that when asphalt ages, the nonpolar molecules decreases and polar part increases (5). The increased amounts of polar molecules change the nature of the asphalt and leads to increased stiffness and slower stress-relaxation rates.

8.2 Objectives

The specific objective is to develop a kinetic-based aging model for mastic phase nanoindentation modulus of asphalt concrete.

8.3 Kinetic Based Aging Model

Aging studies on asphalt mixtures show that the aging can be simulated using kinetics based aging model. A kinetics based aging model contains Arrhenius equations that describe both fast rate and constant rate periods. The constant rate period mainly refers to the long-term aging and oxidative aging of asphalt mixtures. The main motivation of developing the aging model is to evaluate, how the aging kinetics evolves with increasing amount of aging in HMA sample. However, the current study is limited to constant rate reaction co-efficient/long-term aging of asphalt and reaction rate constant. Equation (8.1) represents the kinetic base aging model,
\[ E = E_i + (E_0 - E_i)(1 - e^{-k_i t}) + k_c t \]  \hspace{1cm} (8.1)

where \( E \) = modulus of an asphalt mixture at a given time;

\( E_i \) = initial modulus of an asphalt mixture in the unaged condition;

\( E_0 \) = the intercept of the constant rate line of the modulus;

\( k_f \) = fast rate reaction constant;

\( k_c \) = constant rate reaction constant;

\( t \) = aging time in days.

A non-linear trust region curve fit algorithm is applied to fit the kinetic-energy based model.

Now,

\[ k_f = A_f e^{ \frac{E_f}{RT} } \] \hspace{1cm} (8.2)

\[ k_c = A_c e^{ \frac{E_c}{RT} } \] \hspace{1cm} (8.3)

here, \( A_f \) = fast rate pre-exponential component;

\( A_c \) = constant rate pre-exponential component;

\( E_f \) = fast rate aging activation energy;

\( E_c \) = constant rate aging activation energy;

\( R \) = universal gas constant;

\( T \) = aging absolute temperature.
Equation (8.2) and (8.3) show that the reaction rate constants have an exponentially disproportional relationship with an aging activation energy, which means that activation energy will have opposite trend of reaction constant.
8.4 Experimental Plan

![Experimental Plan Diagram]

**8.5 Aging Process**

To simulate long-term aging, the fabricated specimens are conditioned according to the AASHTO R30 standard practice (AASHTO R 30). The standard requires that the specimens should be kept in a forced draft oven at a temperature of 185 °F (85 °C) for 5 days. According to the AASHTO R30 standard, this procedure is expected to simulate
long-term aging of a mix in the field over a period of 5 to 7 years. However, aging of asphaltic material is a strict non-linear process and it needs field verification as well as research work to predict the long-term aging time of 10, 15 and 20 days of draft oven aging.

8.6 Nanoindentation Testing

In this chapter, nanoindentation tests are done on different phases of Asphalt Concrete (AC). However, from the study presented in chapter 4, with nanoindentation, it is possible to identify the mastic phase of AC compared to binder phase of AC. In addition, the aging trend of mastic phase follows a similar trend as of binder aging. Therefore, current study uses the mastic phase aging data for aging model characterization of AC.

8.7 Results of Aging Model Development

In this study, three different AC samples are used for nanomechanical aging characterization. Three different samples are: (a) AM1: PG 70-22 binder containing AC sample, (b) AM2: PG 70-22 binder containing AC sample with 35% RAP, (c) AM3: PG 64-22 binder containing AC sample. The samples are chosen to capture the degree of oxidative aging reactivity of asphalt. After laboratory compacted sample preparation, the samples were cut and polished for nanoindentation. 100 nanoindentations are conducted on each sample and the mastic phase is identified according to the phase identification technique described in chapter 4.
Figure 7.2 shows the increasing stiffness trend of the mastic phase of AC. Two distinct features can be noticed from the figure. Firstly the fast reaction or faster stiffness increasing trend in first 5 years of asphalt concrete life and secondly, the constant rate age hardening of asphalt concrete. Afterwards, the mastic modulus is fitted using curve fitting program of MATLAB trust region algorithm. The results show the following equation for PG 70-22 binder containing asphalt concrete sample.

\[ E = E_i + (E_0 - E_i)\left(1 - e^{-k_f t}\right) + k_c t \]

where, \(E_i = 7.6\) MPa, \(E_0 = 73.52\) MPa, \(k_f = 0.1649\) MPa/Day, \(k_c = 0.2996\) MPa/Day.

A similar procedure has been used to identify the aging trend of AM2 sample. Figure 7.2 shows the modulus increasing trend of mastic phase of AC. The results show, the rate of stiffness increase is much higher than the later part of age hardening behavior.
The age hardening trend is fitted with the kinetic aging model and following equation has been found for the AM$_2$ material.

\[ E = E_i + (E_0 - E_i)(1 - e^{-k_f t}) + k_c t \]

where, \(E_i = 12.3\) MPa, \(E_0 = 43.43\) MPa, \(k_f = 1.341\) MPa/Day, \(k_c = 0.1593\) MPa/Day.

From the equation following can be concluded:

- The initial modulus of the RAP mixed AC samples is higher compared to the no RAP mixed AC samples.
- Both fast and constant reaction constant decreases with increasing amount of RAP in HMA samples.

Equation (8.2) and (8.3) show reaction rate constants have exponentially disproportional relationship with an aging activation energy, which means activation energy has opposite trend of reaction constant. Trivially, one should determine the activation energies from nanoindentation testing at different temperatures, however in the current study, only one
temperature is used to calculate the kinetic aging model, therefore it is beyond the scope of this study to determine the activation energy values for above-mentioned HMA samples, which is recommended for future study. The constant rate aging activation energy shows an increasing trend with increasing amount of RAP in HMA sample, which means that it requires more energy to activate the oxidative aging in asphalt mixes with a higher amount of RAP. Therefore, the kinetics based aging model also shows similar results found from the laboratory data, which means higher RAP mixed HMA samples going to age slowly as the required aging activation energy is high.

![Figure 8.4 Aging Trend Mastic Phase of AM3 Sample](image)

**Figure 8.4 Aging Trend Mastic Phase of AM3 Sample**

Figure 8.4 shows the aging trend of Mastic phase of AC using nanoindentation technique. The trend follows a similar pattern as AM1 and AM2 samples. The age hardening trend is fitted with the kinetic aging model and following equation has been found for the AM3 material.

\[
E = E_0 + (E_0 - E_i)(1 - e^{-k_f t}) + k_c t
\]
where, $E_i = 6.1$ MPa, $E_0 = 231.6$ MPa, $k_f = 0.0248$ MPa/Day, $k_c = 0.0001315$ MPa/Day.

The main motivation of testing AM$_3$ samples is to quantify the aging trend of different PG grade binders and the results of the kinetic based aging model shows, the activation energy and reaction coefficient is quite different from PG 70-22 binder. Therefore, aging of asphalt concrete is completely dependent on the oxidative reactivity of each binder, which is a unique property.

### 8.8 Validation of the Kinetic Aging Model

Validation of a kinetic aging model of AC is segmented into two different parts. In the first part, the four years field aged AC’s mastic stiffness is compared with the model stiffness. Secondly, macro-scale testing on different RAP mixed HMA samples are tested to quantify similar technique to identify model parameter trend.

### 8.9 Field Aging Quantification of AC

**Sample Preparation**

AC samples with four years of field aging are collected from I-40 instrumented section. The cores are cut with a fine electric saw to prepare 50.8 mm × 50.8 mm (2 in × 2 in) cubes of AC sample for nanoindentation testing. For nanoindentation testing, it is imperative that the indentation test surface is smooth and parallel to each other. As the contact area is measured indirectly from the depth of indentation, rough surface will give an error in calculating the contact area, which will subsequently give an erroneous result. Therefore, the AC sample are polished at the University of New Mexico (UNM) geology lab by a
grinding machine rotating at an angular speed of 150 rpm with a series of SiC paper placed in a decreasing order. Afterward, the polished samples are used for nanoindentation study.

**Nanoindentation of Field Aged AC**

After conducting 100 nanoindentation tests on the field aged AC sample, phase identification technique is employed to identify each phase and quantify nanomechanical property of each phase. Following sections have present the discussion on nanomechanical properties of each field aged AC phase.

**Binder Phase**

Figure 8.5 (a) and (b) show that the load displacement curves for the binder phase of the unaged and 4-year field aged AC. During unloading, average maximum indentation depth at the maximum load is observed around 3000 nm for the unaged binder; and for the field aged binder, the value is around 2000 nm. This shows around 33% decrease in the indentation depth at maximum load during unloading phase. This decrease is primarily due to the aging effect. Moreover, comparing with results from binder only nanoindentation test in the previous section, it can be observed that percent decrease in maximum indentation depth is lower for AC binder phase due to aging. The reason of this difference lies in the mechanism of aging. For binder only test, the aging is done through PAV, which simulates aging of 7-10 years. However, the field AC sample is 4 years aged. In addition, for binder phase, noise during unloading is significantly higher in field aged sample than in unaged sample. Freeze-thaw cycle or moisture may be the reason of this noise during unloading in the field aged sample.
**Figure 8.5** Load-Displacement Plots of (a) Unaged and (b) 4-year Field Aged Binder Phase in AC

Figure 8.6(a) compares the average modulus and Figure 8.6(b) compares the average hardness of the binder phase among the unaged and 4-year field aged AC sample. Modulus is important for elastic analysis and hardness is important for plastic analysis. Binder modulus is observed 4.22 MPa for the unaged AC sample and 9.41 MPa for the 4-year filed aged AC sample. Binder hardness among the unaged and field aged AC sample is observed to be around 107 kPa and 396 kPa. This means that due to 4 years of field aging binder modulus increases about 123% and binder hardness increases about 270% in AC sample.
Figure 8.6 Comparisons of Average Binder (a) Modulus and (b) Hardness in AC Sample.

Mastic Phase

Figure 8.7(a) and 8.7(b) compares the load-displacement curves for the mastic phase of the unaged and 4-year field aged AC. Average maximum displacement at the maximum load is observed around 1200 nm for the unaged mastic; and for the field aged mastic, the value is around 850 nm. This implies that due to aging, maximum indentation depth decreases around 30% for mastic phase in AC sample. However, noise, in the mastic phase of the field aged AC sample is less than what is observed for a binder phase.
Figure 8.7 Load-Displacement Plots of (a) Unaged and (b) 4-year Field Aged Mastic Phase in AC.

From Figure 8.8(a), average mastic modulus is 12.98 MPa for the unaged AC sample and 38.1 MPa for the 4-year filed aged AC sample. Average binder hardness among the unaged and field aged AC samples is around 2510 kPa and 4410 kPa, as shown in Figure 8.8(b). This means that due to aging mastic modulus increases about 193%; and mastic hardness increases about 75% in AC sample.

Figure 7.7 Comparisons of average mastic (a) modulus and (b) hardness in AC sample
Aggregate Phase

Figure 8.9 illustrates the Load-Displacement curve of the aggregate phase of the unaged and the 4-year field aged AC sample. From Figure 8.9 (a) and (b) it can be seen that there is not much difference in the load displacement curve due to the aging of the AC sample.

![Load-Displacement curve](image)

**Figure 8.9** Load-Displacement Plots of (a) Unaged and (b) 4-year Field Aged Aggregate Phase in AC.

Figure 8.10 (a) compares the average modulus and Figure 7.9 (b) compares the average hardness between aggregate phase of the unaged and field aged AC sample. Like Figure 7.8, virtually no aging effect was observed on the aggregate phase of the AC sample. For AC aggregates, igneous rock is used. Igneous rocks are practically inert in nature. Therefore, no change in modulus and hardness is observed due to 4 years of field aging. For unaged and filed aged AC sample, aggregate modulus is observed to be around 55 GPa respectively, and hardness is observed to be around 7 GPa.
Figure 8.10 Comparisons of Average Aggregate (a) Modulus and (b) Hardness in AC Sample.

The average modulus and hardness comparison graphs for the binder, mastic and different phases of AC (shown in Fig. 7, 9, 11, and 13) have standard error bar. It can be observed that error bar increases with aging for the binder and mastic phases. However, almost no change is observed in error bar due to aging in aggregate phase. The reason for an increment of error bar in binder and mastic phase due to aging may lie within the aging mechanism of different components of the binder. The major components of binder asphaltene, maltene, and resin. It has been found that these binder components oxidized at different rates (Kai-Fu et al. 2001). Therefore, the variation in the oxidation of these components may have caused the error bars to increase in aged binder and mastic.

Comparison Between Field vs. Model Data

The field aged sample used in the current study, has a binder grade of PG 70-22, with 35% RAP samples in HMA mixes. Therefore, it is similar to AM2 samples of the study.
Nanoindentation tests on the field aged sample show a mastic modulus of 37 MPa, whereas the model produced modulus is 39 MPa. Therefore, it can be concluded the kinetic based aging model can successfully predict the field aged modulus.

**Summary**

In this study, a kinetic energy-based aging model has been developed and proposed for AC aging characterization technique. The model is validated by extracting the mastic modulus of the field aged AC sample. Macro scale dynamic modulus testing technique is used to quantify the aging trend of RAP mixed HMA samples and to validate the nanomechanical aging model of AC. However, the aging in RAP mixed HMA samples are investigated at five different percentages of RAP. Three levels of aging: 5 days, 10 days and 15 days of draft oven aging on HMA samples are examined. Following conclusions can be made from the study of this chapter:

- The kinetic energy-based asphalt aging model using mastic phase modulus of AC can successfully capture the age hardening behaviour of AC. The results from the model are compared with the mastic phase modulus of 4-years field aged samples, the results show good agreement between model and filed aged sample data.

- In addition, the kinetic based aging model can successfully capture the oxidative aging behavior of RAP mixed HMA samples. The model parameters like reaction rate constant and activation energy can successfully predict the aging behavior of RAP in asphalt mixes. The results show, the required activation energy to constant rate aging is higher in RAP mixed HMA samples, which means the RAP mixed HMA samples are going to age less compared to virgin HMA material. Similar aging trend is found from the nanomechanical study of the mastic phase of AC.
CHAPTER 9
CONCLUSIONS & RECOMMENDATIONS

9.1 Summary

This study attempts to understand the aging behavior of asphalitic materials using the nanomechanical characterization technique of nanoindentation. Nanoindentation test has been used to characterize different asphalitic phases. There are three distinct phases of asphalt concrete (AC), (i) asphalt binder, (ii) asphalt mastic and (iii) aggregate. The creep response of different AC phases is compared with bulk asphalitic materials. Generalized power-law (GPL) coefficients are used to identify different phases. After phase identification, the technique is used to quantify the effect of progressive aging on different asphalitic phases. In addition, the effects of aging are quantified for different air voids and effects on asphalt film thickness. Finally, the results are summarized to develop an asphalt aging model.

9.2 Conclusions

Based on the findings of this study, the following conclusions were found:

Phase Identification of AC

Nanoindentation test can successfully identify binder, mastic and aggregate phases of composite AC. To identify the binder and mastic phases, the creep parameters of the specific phase is compared with the creep response of bulk state of the respective material. However, results of AC indentations show only 5% to 9% indentations are indented on the binder and around 30% indentations are indented on the mastic phases of the interfacial
zone of AC. The proposed technique of comparing GPL model parameters can successfully be used to identify viscoelastic phases.

Effects of Air Voids on Asphalt Aging

- The nanoindentation hardness of the material increases with an increasing amount of voids in AC, which means the higher pores in AC are going to form more brittle material.
- Aging in AC concrete decreases the stress relaxation capacity of asphalt binder. Both the modulus or compliance and retardation terms are changed with the change in the number of available pores in AC. This means the current practice of shifting dynamic modulus with respect to compliance or relaxation parameter can lead to wrong interpretation of aging of asphalt, instead, both compliance and relaxation parameters should be used in aging characterization.

Asphalt Thickness

- Using the proposed technique, it is possible to successfully determine asphalt film thickness and its change over the aging process of asphalt. However, the results show it is difficult to accurately identify and quantify the asphalt film thickness in an asphalt-mastic-aggregate system, as mastic film thickness in AC found to be more than 23 microns, which could not be measured using the nanoindenter available at the University of New Mexico. Therefore, the study is limited to the only quantification of change in asphalt film thickness in an asphalt-aggregate system as a function of progressive aging.

- Quantification of asphalt film thickness with an increase in asphalt aging shows the change follows an exponentially decreasing trend, and the asphalt film thickness reduction
rate reduces as more aging happens in an asphalt-aggregate system. The following trend line equation is found from non-linear least square fitting in MATLAB,

$$y = A_{unaged} \times e^{-px}$$  \hspace{1cm} (9.1)

where $A_{unaged} = $ Initial Unaged Thickness of Asphalt,

$x = $ days of draft oven aging,

$p = $ decay constant (ranges from 0.0921 to .157).

The decay equation shows that asphalt film thickness reduces to half of its original thickness within 5.3 years to 7 years of its service life.

- In addition, cause of thickness reduction with the aging of asphalt is further analyzed; the analysis results show an increase in asphalt binder increasing the amount of the polar functional group, which makes the asphalt system coagulate to produce more complex big asphaltene fractions of asphalt binder. Therefore, the asphalt binder volume decreases with long-term aging of asphalt.

**Asphalt Aging Model**

- Currently, there is no widely accepted nanoindentation model for visco-elastoplastic materials such as AC. Therefore, this study shows that the Spring Dashpot Rigid Body (SDR) model gives satisfactory results on nanoindentation of AC. However, more studies are required under different environmental conditions to validate the model for AC.
• Comparison between different aging conditions shows aging increases the nanoscale modulus, hardness and indentation viscosity of bulk binder and mastic material. A similar trend is found for binder and mastic phase when they are in the phase state of AC. However, results show that on bulk material aging creates a higher amount of stiffening and hardness; in AC phases the effect of aging is comparatively lower. Nanoindentation was able to capture the high variability of stiffening in the binder and mastic phases of aged concrete.

• The kinetic energy-based asphalt aging model using mastic phase modulus of AC can successfully capture the age hardening behavior of AC. The results from the model are compared with the mastic phase modulus of 4-year old field aged samples, the results show good agreement between model and field aged sample data.

9.3 Recommendations

The following points can be recommended for future studies:

1. Development of a new model with respect to asphalt film thickness as a function of aging, as the thickness of aging, is directly related to durability and performance of AC. Further investigation of the effects of temperature, traffic and freeze-thaw cycles on the asphalt binder film thickness is needed. Incorporation of other effects on asphalt binder film thickness will provide more insight on the durability and performance issues of AC.
2. The study has successfully investigated the effects of air voids on asphalt aging. The results show both stiffness and relaxation of asphalt binder changes with increasing amount of air voids in AC. Development and improvement of Mechanical Empirical (ME) design air void models with respect not only to stiffness but also with the incorporation of both stiffness and relaxation will help to predict more accurate asphalt pavement performance.

3. The study successfully validated the asphalt aging model with respect to RAP and aging activation energy of asphalt. However, the study can be further explored for another type of asphaltic material mixes like polymer modified asphalt or warm mix asphalt, which has not been done in the current study due to time constraints. However, this is recommended for future study.

4. The study has successfully captured the change in asphalt film thickness as function of progressive aging. The identification of the proposed point of inflection point can identify the thickness. However, it is possible that at the interface of asphalt and aggregate after 80% or 90% of soft layer indentation, the loading curve produces point of inflection. A numerical modeling of two layer system of soft and hard can clarify the assumption, however, it requires time to create an appropriate numerical model with inclusion of slip or damage in the interface. Therefore, it is recommended for future study.
REFERENCES


Kim, Y., Richard (2009), “Modeling of Asphalt Concrete.” *ASCE Press*


