Investigation of the Effect of Oil Modification on Critical Characteristics of Asphalt Binders

By

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To all those who believe in God, to all those who have faith.

"Great spirits have always encountered violent opposition from mediocre minds."

(Albert Einstein)
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Abstract

Thermally induced cracking of asphalt pavement continues to be a serious issue in cold climate regions as well as in areas which experience extreme daily temperature differentials. Low temperature cracking of asphalt pavements is attributed to thermal stresses and strains developed during cooling cycles. Improving asphalt binder low temperature fracture and stiffness properties continues to be a subject of particular concern. Therefore, significant amount of research has been focused on improving asphalt binder properties through modification.

In recent years, wide ranges of oil based modifications have been introduced to improve asphalt binder performance, especially at the low service temperatures. Although, significant use of these oils is seen in practice, knowledge of the fundamental mechanisms of oil modification and their properties for achieving optimum characteristics is limited. Hence, this study focuses on better understanding of the effect of oil modifiers which would help better material selection and achieve optimum performance in terms of increasing the life span of pavements.

In this study, the effect of oil modification on the rheological properties of the asphalt binder is investigated. To examine the effect of oil modification on binder characteristics, low temperature properties as well as high temperature performance of oil modified binders were evaluated. It is found that oils vary in their effects on asphalt binder performance. However, for all oils used in the study, adding an oil to binder can improve binder low temperature performance, and this result mainly attributed to the softening effect. In addition to that, a simple linear model is proposed to predict the performance grade of oil modified binder based on the properties of its constituents at high and low temperatures.

Another part of this study focuses on the oil modification effect on asphalt binder thermal strain and stresses. A viscoelastic analytical procedure is combined with experimentally derived failure stress and strain envelopes to determine the controlling failure mechanism, strain tolerance or critical stress, in
thermal cracking of oil modified binders. The low temperature failure results depict that oil modification has a good potential of improving the cracking resistance of asphalt binders during thermal cycles.
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I. Overview and Objectives

1. Introduction

In recent decades, efforts to obtain improved binder characteristics have led to the evaluation, development and use of a wide range of asphalt binder modifiers, which aim to enhance the performance of the base binder and hence, improve pavement performance (Bahia et al., 2001). In addition, due to increasing costs associated with conventional asphalt binders, a number of low-cost asphalt modification and extension techniques have been introduced to optimize cost and performance of conventional binders (Herrington, 1992; Morales et al., 2006; Rubab et al., 2011). Different blends of binders with a large variety of materials have been studied to improve the binder properties and performance, especially as determined using the Superpave performance grading specification (AASHTO M320). However, most of these approaches improve the high temperature performance grade for resistance to rutting, without addressing low temperature performance grade associated with thermal cracking.

The three distresses generally recognized as the main cause for the degradation of asphalt pavements performance are rutting, fatigue cracking and thermal cracking. Thermally induced cracking of asphalt pavement continues to be a serious issue in cold climate regions as well as in areas which experience extreme daily temperature differentials. Low temperature cracking of asphalt pavements is attributed to thermal stresses developed during cooling. Improving binder’s low temperature fracture and stiffness properties continues to be a subject of particular concern.

Recently, wide ranges of oil based modifications have been introduced as means of improving asphalt binder performance, especially at the low temperature end of the service temperatures, while maintaining the high temperature properties. Although, extensive research has focused on the effect of different polymer modifiers on the properties of asphalt binder and their mechanism of effect, knowledge on the fundamental mechanisms of oil modification and their properties for achieving optimum characteristics is
limited. Moreover, these new binders and extenders have not been tested widely and their effects on short and long term performance are not well documented. Hence, a better understanding of the effect of oil modifiers at a fundamental level will help better material selection and achieve optimum performance and increase the life span of the pavements.

2. Background

Asphalt modification plays an increasingly important role in the asphalt industry. To achieve the goal of improving binder properties, a selected additive should create a secondary network or new balance system within asphalt binders by molecular interactions or by reacting chemically with the binder. The strength, stiffness, and adhesion of asphalt to aggregate must be greatly improved in comparison with conventional asphalt binder to sustain the pavement performance. It is not surprising to witness various attempts to modify asphalt properties via chemical modification and/or physical blending (Collins et al., 1991).

An ideal binder should have enhanced cohesion and very low temperature susceptibility throughout the range of service temperatures, and also low viscosity in the range of temperatures used during production. Binder’s susceptibility to loading time should be low, whereas its permanent deformation resistance, breaking strength, and fatigue characteristics should be high. Furthermore, modified asphalts should have at least the same adhesion qualities (active and passive) as traditional binders. Lastly, its aging characteristics should be good, both for laying and in service (Brule, 1996).

Several studies have been conducted to investigate effects of polymer modifiers on mixture performance (Read and Whiteoak 2003; Airey 2004; Lu and Isacsson 1998; Zanzotto et al. 2000). From the engineering point of view, polymer modified asphalt (PMA)s are materials with superior rheological properties with respect to the unmodified asphalt binders, and their use in the construction of modern asphalt pavements is increasing especially for high traffic volume roadways. In-service performance
surveys indicates that HMA constructed with polymer modified binder exhibits greater resistance to rutting, decreased fatigue damage, and improved resistance to moisture damage, however the most commonly used modifiers do not provide mechanisms to address low temperature issues. Therefore, a new class of modifiers have been used specifically to improve low temperature properties such as extender oils. However, there is a significant lack of literature about oil modification mechanisms and effects on performance relative to polymer modifiers. There are some limited studies that report some effects of oil modification (Herrington et al., 1992; Villanueva and Zanzotto, 2008; Hesp and Raymond, 2011) but their structure and effect on asphalt binder are not fully known (McCready and Williams, 2008; Hesp and Raymond, 2011).

3. Problem Statement

Modification of asphalt binders is becoming increasingly expensive and difficult due to increase in prices of petroleum products. However, it is possible to develop new engineering materials by blending and mixing byproducts or waste materials with asphalt binders. Extender oils are one of the new candidates to use as asphalt modifier to improve the low temperature properties and reduce the cost of the final blend. Therefore, there is need to investigate the effect of oil modifiers and extenders on asphalt binder properties to promote increased use of these byproducts as asphalt binder modifiers based on a thorough understanding of their specific effects on composition and performance.

Introduction of oils into base binder may disturb its internal structure, thereby resulting in changes of some structure-sensitive properties, such as rheological and fracture properties. Although, several studies have investigated the effect of oil modification on the properties of asphalt binder, there is no extensive research on the fundamental mechanisms driving this type of modification. The goal of this study is to determine the effect of oil on asphalt binder and to ascertain if the oil can enhance the low-temperature properties and performance of asphalt binders. To investigate the appropriateness of extender oil as a
modifier for asphalt binders, rheological and fracture properties of these oils will be evaluated at various service temperatures. Furthermore, thermal, mechanical and physical engineering properties of oil modified binders will be investigated to obtain a comprehensive understanding of the effect of oil modification.

4. Research Hypotheses

It is hypothesized that:

I. Oil modification introduces an additional phase to the asphalt medium, which has lower molecular weight and higher average free volume. Incorporating the oil fraction into an asphalt binder will lead to a decrease in creep stiffness and glass transition temperature ($T_g$) plus an increase in relaxation rate of the final blend. Such effects enhance the low temperature performance of oil modified binders.

II. Through proper analysis, individual assessment of oil and binder rheological properties can be used as a practical method for assessing the effectiveness of oil modification and an oil selection criteria can be defined based on the rheological properties of the individual constituents and oil modified binder properties.

5. Research Objectives

The purpose of this study is to investigate the effect of oil modification and explain how the asphalt binder rheological properties are influenced when oil is introduced. The general objective of the present work is to characterize different types of oil rheological properties more accurately; and to explore the contribution of oil modifier in improving low temperature performance of asphalt binder.

The specific objectives are:
• Evaluation of the effect of extender oils on the high and low temperature performance of oil modified binders in terms of rheological properties change of binder due to addition of oil by using the Bending Beam Rheometer (BBR), and the Dynamic Shear Rheometer (DSR).

• Evaluation of the effect of oil modification on low temperature fracture properties through the use of the three point bending fracture test, the Single Edged Notched Beam (SENB).

• Investigation of the oil modification effect on asphalt binder rheology through different experimental tests such as the dilatometric measurement of \( T_g \), and the DSR frequency sweep test.

• Using the characteristics of different types of oil and binders to develop a prediction method for the estimation of the modified binder high and low temperature performance grades.

• Incorporation of oxidative aging in mechanism evaluation in order to accurately predict effects of oils on asphalt binder performance.

• Developing a criterion based on the measured oil rheological properties and numerical prediction of cracking to select oil modifier to achieve desirable low temperature performance.

6. Dissertation Outline

This thesis is structured into six main sections with the following content:

Chapter 1: Introduction – This chapter includes a background on asphalt binder modification. The background is followed by the problem statement, research hypothesis and research objectives.

Chapter 2: Literature Review – This chapter is divided into three sections. The first section presents a literature review of the low temperature distress of asphalt pavements. The second discusses binder
characterization and the tests for low temperature cracking. The last section presents the effect of binder modification and introducing oil modification, its limitations and challenges.

**Chapter 3: Materials and Methods** – In this part various neat and oil modified binders will be tested at different temperatures using different devices such as the Dynamic Shear Rheometer, Bending Beam Rheometer, Glass transition measurement device, etc. Test methods such as PG tests, Frequency Sweep test will be used to characterize the binder and oil rheological properties. Afterwards the mechanical and cracking performance of these modified binders will be evaluated as well using the SENB.

**Chapter 4: Evaluation of Oil Modification Effect on the Performance** – This chapter presents an through evaluation of oil modification from different performance aspects. Different properties of oils and modified binders are investigated by testing at different temperatures, identifying the critical issues to be addressed in this study. In the next stage, different results are evaluated to get more accurate and comprehensive picture of oil modification effect on binder properties and performance.

**Chapter 5: Investigation of Oil Effect on Asphalt Binder Viscoelastic and Thermal Properties**– This chapter explores The oil and modified binders time dependency and relaxation rate are evaluated and the results are discussed regards possible oil effect on binder structure and also physical hardening effect. Furthermore, the first part compares oil’s rheological and thermo-volumetric measurements obtained from the different test with fundamental parameters that quantify the characteristic of binders. In the second part, the effect of oil modification on binder’s low temperature cracking resistance is studied and the relation between these factors to binder’s cracking criteria is defined. Non-linear thermal contraction rate data from the Glass transition ($T_g$) test, and relaxation modulus data from conversion of BBR creep stiffness values were used to calculate thermal strain and stress build up in the oil modified binders in comparison with unmodified binders. Fracture properties and critical stress and strain values were measured at different temperatures using the SENB test procedure.
Chapter 6: Estimation and Prediction of Oil Modified Binder Performance – This chapter is divided into two main sections. In the first section, the analytical procedure to predict oil modified binder high and low temperature properties is introduced based on the oil and neat binder data. In the other part, the characteristics of different oil modified binders related to binder’s performance grade properties will be defined and criteria that represent the oil selection is going to be developed upon different conditions.

Chapter 7: Summary of Findings and Recommendations for Future Work – Findings gathered from the most relevant testing and modeling results and recommendations based on these findings are offered in this section. The recommendations for future work are also provided in this section.
II. Literature Review

This chapter includes three sections to cover the topic of fundamental principles of asphalt binder’s low temperature cracking resistance. These sections are as follows: definition and background of thermal cracking, binder characterization and tests for low temperature performance, effect of modifiers on binder performance, and oil modification and its limitations and challenges.

1. Low Temperature Distress of Asphalt Pavements

Asphalt pavements are granular composites that contain mineral aggregates, asphalt binder and air voids. The two load-carrying components of the asphalt mixtures are the mineral aggregates and the binder. Asphalt binders are obtained from the refining of crude oil. They are produced from the heavy residue after the refining of fuels and lubricants. Asphalt binders are thermoplastic materials that demonstrate viscoelastic properties under most pavement operating conditions (Van der Poel, 1954). This is the fundamental property that makes them versatile binders for asphalt mixtures with the viscoelastic characteristics of the bituminous binders directly and significantly influencing the performance of the mixtures.

The low-temperature cracking of asphalt concrete pavements is a major pavement distress mechanism in cold regions costing hundreds of millions of dollars in rehabilitation costs to various agencies. Thermal cracking of asphalt pavement is an environment-related distress, since it does not depend on the load applied to the pavement. As the term suggests, thermal cracking is related to thermally induced tensile stresses within the asphalt layer by temperature changes and it takes place when the pavement is subjected to low field temperatures. It usually occurs in the form of regularly spaced transverse cracks, initiating at the surface of the asphalt layer and further propagating downward. Consequences of thermal cracking are
an immediate increase of the roughness of the pavement surface (i.e. a reduction of the comfort and safety of the ride) and the loss of the sealing function of the pavement for the underlying layers. Through the crack, water can infiltrate the pavement, leading to loss of support from soil layers and increasing the risk of moisture damage for lower asphalt-bound materials. However, predictions of this distress have not been accurate enough, often resulting in premature road failures. It is believed that the excessive brittleness due to the increase in stiffness and decrease in the ability to relax stress leads to the buildup of thermally induced stress and ultimately cracking of mixtures in pavements.

1.1. Mechanism of Low-Temperature Cracking Phenomenon

One of the most detrimental phenomena of asphalt pavement is thermal cracking (low-temperature transverses cracking), which occurs mostly during the winter season in the northern states and high latitude areas throughout the world. The low-temperature transverse cracking in flexible pavements is the result of a combination of three distress mechanisms: 1) single event thermal cracking and 2) thermal fatigue. Out of these two, the single event thermal cracking is the most significant contributor to transverse cracking of pavements (Lamont Report, 1999).

In order to understand the difference, it is useful to briefly describe the mechanism leading to cracking. It is believed that thermal stresses causing cracking are due to constrained thermal strains. When the temperature drops, the pavement tends to contract its volume, following its thermal expansion/contraction coefficient; however, the layer underneath opposes some resistance due to friction, therefore thermal strains within the asphalt layer are not free to take place leading to co-active stresses proportional to the stiffness of the material. Since asphalt is a viscoelastic material, part of said stresses are dissipated through relaxation, but eventually they build up until they reach the strength of the material, leading to the formation of cracks to relieve these stresses. If the crack is caused by a one-time thermal stress condition that overcomes the material strength, the phenomenon is called “single-event thermal
cracking”. On the contrary, if the crack is caused by a series of thermal cycles, resulting in thermal stresses that never overcome the ultimate strength of the material, the phenomenon is classified as “thermal fatigue”.

Low-temperature cracking is associated with volumetric contraction that occurs as material experiences a temperature drop. At low temperatures, asphalt pavements behave as an elastic material and thermal stresses cannot be dissipated, thus leading to cracking (Ruth, 1977). Experience has indicated that the initial effect of low-temperature cracking on riding quality within approximately the first 3 years may be minor, but the intrusion of water often causes a volume change in the subgrade in the form of swelling in clays, densification in sands, or frost heave, resulting in adverse effects on the longitudinal profile. Also, a loss of structural integrity at crack locations can result in an extension of initial cracking, with sapling in the vicinity of these locations (Finn et al., 1976).

### 1.2. Development of Thermal Stresses and Strains

It is generally believed that thermal stress created by pavement restraint, as results of the rapid temperature drop at cold temperatures, causes thermal cracking. As the pavement contracts, stresses begin to build up within the asphalt pavement layers. If contraction occurs rapidly, the stresses can build and eventually exceed the stress relaxation ability or strength of the asphalt pavements. When this occurs, the pavement develops cracking as a way to relieve stress. Thermal cracking can result from one thermal cycle when a critically low temperature is encountered or from thermal cycling, where the temperature cycles up and down, but always remains above the critical low temperature. This purely thermally induced distress is referred to as “single event” thermal cracking. It is neither related to, nor considered to be, thermal fatigue cycling. The critical temperature at which this occurs depends on numerous variables such as the absolute minimum temperature, the nonlinear temperature-dependent coefficient of contraction, the glass transition temperature and etc.
Cracking caused by a single thermal cycle has been related to the asphalt binder stiffness at the temperature at which cracking occurs. In the Superpave® specification, this temperature corresponds to a creep stiffness of 300 MPa as measured using a Bending Beam Rheometer referred to as the limiting stiffness temperature. The limiting stiffness temperature is, therefore, defined as the pavement service temperature at which a certain stiffness value is reached after a specified loading time (Roberts et al., 1996).

1.3. Prediction of Asphalt Pavement Thermal Cracking

The prediction of asphalt pavement thermal cracking has been the subject of numerous studies that date back to the early 1960’s (Monismith and Secor, 1965). In many of these studies, attempts were made to introduce a procedure to predict pavement cracking based on the stress-strain-time–temperature relationship. A review of these procedures indicates that, in most cases, the mechanism of failure has been described based on a simplified concept that cracking will occur when the thermal stress build-up caused by a cooling rate reaches the strength of the asphalt mixture. A number of methods have been introduced throughout the years to model the viscoelastic behavior of asphalt binders and mixtures to estimate the accumulation of thermal stress during cooling cycles and predict the temperature at which cracking occurs (Haas, 1973; Ruth et al., 1982; Lytton et al., 1993).

Different models have been proposed in order to predict thermal stresses developing in an asphalt pavement and to predict the occurrence of thermal cracks. Originally, they relied on the measurement of asphalt mixture properties, but this approach requires complex and costly tests, therefore researchers focused on the estimation of mixture properties from aggregate and binder tests or, more lately, developed models based mainly on binder properties. In fact, although aggregate gradation and volumetric properties of the mixture have an important effect on the overall properties of the asphalt mix, thermal cracking is considered to be a binder-related distress, because of the temperature susceptibility of asphalt. These
models vary in their formulations of the viscoelastic response of asphalt binder and the representation of strength characteristics of asphalt binder. However, despite the variation in details, they all define failure by comparing thermal stress to strength.

Although the use of strength as the main criterion is dominant in the literature, researchers in a number of studies attempted to point out the importance of strain at failure and to describe deformation at break as an important criterion. Monismith and Secor (1965) presented results in the form of the failure envelop plotting strain at failure versus strength and commented that asphalt mixture failure can be defined, similar to polymeric materials, in a two-dimensional form including strain and stress at break.

Heukelom (1966) studied extensively the mechanism of asphalt binder failure and the role of deformation (or strain) in reaching the fracture point. Heukelom depicted that “fracture of asphalt binder always occurs after a certain deformation”. He also indicated that there is a strong relationship between fracture and rheology of asphalt binder and suggested the existence of a strong correlation between stiffness and deformation at break. This relationship was confirmed later by SHRP researches and was used as the basis of later studies.

Afterwards, research efforts have used thermo-visco-elastic analysis procedures in asphalt pavements using selected models and represented asphalt mixture rheological and failure properties (Hiltunen and Roque, 1994; Lytton et al., 1993). Roque, Buttler and Christensen have applied the concepts to develop a spreadsheet based software program to calculate thermal stresses during SHRP program (Christensen, 1993; Buttler and Roque, 1994). Bahia et al. (2002), refined these models by taking into account the stress and strain effect simultaneously to calculate thermal cracking temperature. This analysis method considered both the rheological properties and thermo-volumetric properties of asphalt binder.
1.4. Contributing Factors

There are several factors reported to affect low-temperature cracking in asphalt pavements. With the support of a large amount of research available on low-temperature cracking, the following factors are suggested to be of great importance: (Haas, 1988; Jung and Vinson, 1993)

1) Material Properties: Stiffness, Relaxation Modulus, Glass Transition, Thermal coefficient of contraction, Physical hardening

2) Environmental Conditions: Temperature, Cooling rate

3) Pavement Structure Aspects: Pavement geometry; width and thickness, base restraint conditions

Other factors, such as construction and asphalt pavement design factors have also been suggested as possibly significant variables. However, the most affecting factors seem to be the combination of environmental conditions, asphalt binder properties, layer thickness, and pavement age (Haas et al., 1987). By looking carefully at these factors, it can be understood that the most important factor is asphalt binder properties since the effect of other parameters can be reflected in the properties of asphalt binder. Due to this reason, researchers have been focusing on improvement of asphalt binder testings’ and performance in the last several decades.

2. Binder Characterization and Test for Low Temperature Cracking Properties

It is generally known that the behavior of asphalt pavement under low temperature conditions of induced stress is affected by the response of the asphalt binder. During the service life of the pavement, asphalt is exposed to low temperatures, which tend to alter the rheological behavior. Many researchers (Special Report 91-5, 1991) have agreed that asphalt binder is the dominant component for low-temperature performance of the asphalt pavement mixtures. Therefore, it is very important to study the
low temperature behavior of asphalt binder to obtain a better understanding of factors that affect the low temperature behavior of pavement.

Based on the concept that asphalt binder properties play the major role in cracking, several studies have focused on investigating the effect of rheological and other parameters of asphalt binder on low temperature performance. Techniques of characterizing asphalt binder and mixtures for low temperature cracking require simulation of field conditions which is somewhat difficult due to the relatively slow rate of loading induced by thermal shrinkage. A quantitative method is necessary in order to study the complex role of asphalt binder in the pavement and to relate its properties to low temperature cracking phenomenon.

Recognizing the limitation of the traditional asphalt binder characterization procedure in 1987, the Federal Highway Administration initiated a nationwide research program called the Strategic Highway Research Program, usually referred to as SHRP (Anderson et al., 1994). The final product of the SHRP research program was Superpave® (Superior Performance Asphalt Pavements) which presented as different performance grade tests (PG test). The Superpave® was designed to provide performance-related properties that can be related in a rational manner to pavement performance (McGennis, 1994).

NCHRP Project 9-10, “Superpave® Protocols for Modified Asphalt Binders,” was initiated to confirm whether the current Superpave® protocols are suitable for use with modified asphalt binders (Bahia et al., 2001). The conclusion drawn from reviewing the protocols was that the existing protocols cannot be used to fully characterize all asphalt binders modified with different additives. The main reason is that they are based on simplifying assumptions that cannot be reliably extended to modified binders. (Kim, 2008).

Several researchers have tried to capture the true low temperature performance of asphalt binder and correlate that with field performance. The next subsections will cover the background of development of these tests and properties that they measure to capture the asphalt binder low temperature performance.
2.1. Asphalt Binder Stiffness

The thermal stresses generated in pavement are known to depend mainly on the stiffness of the asphalt binder. The stiffness of the asphalt binder has a significant effect on the stiffness of the mixture. Penetration measurements at low temperatures were used by Shoor et al. (1966) to determine the low temperature behavior of paving grade. Heukelom (1966) related the asphalt stiffness to its penetration value. He also introduced the modified asphalt Penetration Index (PI), which is a measurement of the temperature susceptibility and is used to determine the asphalt stiffness at low temperatures. Hicks et al. (1993), found that the penetration of asphalt binder at 15 °C is a good indicator of the fracture temperature of the mixture during the SHRP binder validation study.

Doyle (1958) measured the ductility of various asphalts at 12.8 °C, regardless of sources, and observed extensive pavement cracking when the ductility dropped below 5cm. According to Traxler (1961), low ductility values are demonstrated by asphalt with a greater degree of complex flow. Welborn et al (1966), and Kandhal and Wenger (1975) reported a good correlation between the ductility and the shear susceptibility at 7 °C and 15.6 °C. In the study by Kandhal and Koehler (1984) of six experimental test sections in Pennsylvania indicated that lower ductility were associated with a higher incidence of load-associated longitudinal cracking.

Schweyer et al. (1977) have done considerable work on the use of the capillary rheometer and the development of several generations of the constant-stress rheometer which have been used to examine both asphalt stiffness and viscosity at low temperatures. Also Puzinauskas (1976) found that the low temperature viscosities of asphalt binder vary extremely over a wide range. This range increases with decreasing temperatures. Generally, poor correlation was registered between the consistency properties such as viscosity, penetration, or ductility. Furthermore, measurement at high or moderate temperatures cannot be used to predict the behavior of asphalt binders at subfreezing temperatures.
Majidzadeh and Schweyer (1967) studied the viscoelastic response of four asphalts in the temperature range of -9 °C to 5 °C using cylindrical specimens. At low temperatures such as -9 °C, the asphalt binders exhibited some instantaneous elastic deformation, which is represented by the spring in the Maxwell element. Subsequently, they studied (1968) the viscoelastic response of aged asphalt cements. Pink et al. (1980) used a Rheometric Mechanical Spectrometer (RMS) to make accurate low-temperature viscoelastic measurements on asphalt down to -94 °C. A dynamic master curve was developed to separate the effect of time and temperature. Button et al., also used the RMS to measure viscosity of asphalts from 0 ° to -46 °C. Thus, most of the predicting low-temperature cracking methods involve measured asphalt stiffness, predicted asphalt stiffness, or consistency and temperature susceptibility parameters that indirectly establish asphalt stiffness (Anderson et al., 1986).

A great deal of effort has been expended to correlate asphalt binder stiffness to observed low-temperature cracking for the concept of limiting stiffness that low-temperature cracking will occur when the asphalt stiffness reaches a certain value as a temperature and loading time (Hills et al., 1966; Readshaw, 1972; Gaw et al., 1974; Asphalt Institute Report, 1981). As a result of these reports, the recent asphalt binder specification has put the limit on the asphalt binder stiffness to control low-temperature cracking (SHRP report, 1993).

During the SHRP project, several studies have focused on developing a new device for measuring low temperature stiffness of binders. Finally, these studies led to the development a device to determine the properties and response of asphalt binders at low temperatures in the 1980’s (Anderson, 1990). This device was later modified and updated as part of the SHRP binder research (Bahia, 1992). The resulting machine was named the Bending Beam Rheometer (BBR). The testing procedure is given in AASTO TP1.

The data acquisition system of the BBR records the load and deflection test results and calculates two parameters: (1) Creep Stiffness, S(t), which is a measure of how the asphalt binder resists the creep
loading, and (2) m-value, which is a measure of the rate at which the creep stiffness changes with loading time.

The stiffness, $S(t)$, is a measure of the thermal stresses developed in the asphalt pavements as result of thermal contraction. Classic beam analysis theory is used to calculate the creep stiffness of the asphalt binder beam at 60 seconds loading time (McGennis et al., 1994). The BBR loads the beams for 240 s and report the stiffness values at loading times of 8, 15, 30, 60, 120 and 240 s. These values were chosen because they are fairly equally spaced on a logarithmic time scale. These data points, along with the following equation, are used to determine the shape of the stiffness (creep compliance) master curve for the asphalt binder (Equations (II-1)).

$$S(t) = A + B \log(t) + C [\log(t)]^2$$  

(II-1)

Where,

$S(t) =$ Asphalt Binder Stiffness

$T =$ Time (s)

$A,$ $B$ and $C =$ constants.

The slope of the stiffness curve, $m$, is a measure of the rate of stress relaxation by asphalt binder flow. The m-value indicates the rate of change of the stiffness, $S(t)$, with loading time. In other words, the m-value is the slope of the log creep stiffness versus log time curve at any time. Since the time dependency of asphalt binder varies, the shape of the stiffness master curve as well as the stiffness at 2 hr loading time are important to take into consideration. Therefore, the slope of the stiffness master curve is also used for specification purposes (Anderson, 1993).

The effect of these two specification parameters, $S(t)$ and m-value, on thermal cracking is analogous to the effect of $G^*$ and $\delta$ on rutting and fatigue cracking. As $S(t)$ increases, the thermal stresses developed in the pavement due to thermal shrinking also increase, and thermal cracking becomes more likely. On the
other hand, as the m-value decreases, so does the rate of stress relaxation. In other words, as the slope of
the asphalt binder stiffness curve flattens, the ability of the asphalt pavement to relive thermal stresses by
flow decreases. This again would increase the propensity of thermal cracking in the pavement.

2.2. Asphalt Binder Thermo-Volumetric Properties

Asphalt binders as one of the viscoelastic materials change their volume with variations in
temperature just like many other engineering materials. The amount of change is any direction is one third
of that in volume under the conditions of isotropic behavior and infinitesimal deformation, which are
assumed. The change in the volume of paving materials with temperature variation is one of the most
important properties for the prediction of thermally induced stresses and strains in pavements. However,
this thermal deformation property is not well understood in the care of asphalt paving materials. The
volume of asphalt binders and mixtures varies nearly linearly at temperatures higher than the glass
transition temperature, denoted by $T_g$. Within the range of temperatures where the glass transition occurs,
the volume changes in a nonlinear manner until the glass state is reached. Below $T_g$, the change in volume
resumes a linear trend but at a rate that is lower than the rate above the glass transition temperature. The
concept of collapse of free volume has been used successfully to explain this behavior for a variety of
amorphous materials. The concept has also been shown to work well for asphalt (Bahia and Anderson,
1993). An elaborate review of this topic is found elsewhere (Bahia, 1991). It was postulated that the
temperature dependency of rheological properties is related to the change in the volume of material. In the
modeling, however, thermal deformation is treated independently of the rheological properties.

2.2.1. Temperature Dependency of Asphalt Binder

The viscoelastic nature of asphalt as a paving material causes a strong temperature dependency of its
mechanical properties. The time-temperature superposition principle is a concept originally developed for
amorphous polymers and currently used to model asphalt mechanical behavior (SHRP A-369 report,
The principle originates from the observation that creep curves obtained for different temperatures, plotted in bilogarithmic scale, show the same shape. They can be translated along the horizontal loading time axis, in order to align them with a single curve (corresponding to a reference temperature) and form what is usually called the “master curve” of the material (Williams et al., 1955). Another way of looking at this concept is that loading time and temperature effects are independent and all relaxation times have the same temperature dependency. This is reflected in the fact that every point of a curve is translated by the same amount on the loading time axis, called “shift factor”, described by:

\[ a_T(T) = \frac{t_T}{t_0} \]  

(II-2)

\[ E(T, t_0 \cdot a_T(T)) = E(T_0, t_0) \]  

(II-3)

\[ \log(t_T) = \log(a_T(T)) + \log(t_0) \]  

(II-4)

where:

- \( E \) is the relaxation modulus (or other moduli, such as creep compliance or creep stiffness),
- \( a_T(T) \) is the shift factor corresponding to temperature \( T \),
- \( T \) is an arbitrary temperature,
- \( t_T \) is the loading time required to obtain a modulus equal to \( E \) at temperature \( T \),
- \( T_0 \) is the reference temperature,
- \( T_o \) is the loading time required to obtain a modulus equal to \( E \) at the reference temperature \( T_o \).

Logarithms of shift factors, when plotted against corresponding temperatures, show a linear trend. Materials complying with this behavior are called “thermo-theologically simple” and asphalt is classified among them. Shift factors can be described by the Williams-Landel-Ferry (WLF) equation (Williams et al., 1955):

\[ \log(a_T) = \frac{-C_1(T-T_o)}{C_2 + (T-T_o)} \]  

(II-5)
where $C_1$ and $C_2$ are constants depending on the material.

This unique characteristics of asphalt binders make them change from a fluid-like material with low stiffness to a solid-like glassy material with high stiffness within the normal range of their application temperature. In order to explain the dependency of flow properties of fluid-like materials on temperature, the concept that molecular mobility is a primary function of temperature was used for a long time and a large number of models were proposed to relate viscosity to temperature (Doolittle, 1951a). This concept, however, was found by some material scientists to be inadequate or too complicated to be used effectively to estimate the effects of temperature on flow properties (Doolittle, 1951b). Therefore, another approach was introduced that considered to be a primary function of the relative volume of molecules present per unit of free space, (i.e., “the fractional free volume”). The new concept that molecular mobility, and thus resistance to flow, is a function of free volume, led to the creation of the free volume concept that is widely accepted today and used to relate rheological properties of viscoelastic materials to temperature (Doolittle, 1951b and 1957).

2.2.2. Free Volume Concept

The free volume concept was used to explain the material properties and behaviors, and is in fact, behind the observation that the Williams-Landel-Ferry (WLF) equation and other free volume based relations cannot be used below the glass transition region (Fox and Flory, 1950; Williams et al., 1955). The concept assumes that the material is composed of free volume, $V_f$, and occupied volume, $V_o$. This theory presents the concept that the resistance to flow in a liquid depends upon the relative volume of molecules present per unit of free-space (Doolittle, 1951a). This study clearly showed that the free volume is directly related to the viscosity of the material and the viscosity can be used in special equation to estimate the free volume of the material (Doolittle, 1951a).
Furthermore, this concept was used to describe material glass transition phenomenon (Doolittle, 1951b). Based on this theory, during cooling from high temperatures, far above \( T_g \), the molecular adjustments, and therefore the collapse of free volume, is rapid and of the same order of magnitude as the temperature drop. As the temperature reaches the \( T_g \) region, however, the adjustments become slower, and if crystallization does not occur, a temperature is reached at which the collapse of free volume cannot occur within the experimental cooling time. The structural state of the material at the temperature is frozen-in and due to the continuous drop in thermal energy, that structural state deviates from thermodynamic equilibrium. Therefore, \( T_g \) is not an equilibrium transition; it originates from kinetic limitations on the rates of internal adjustments occasioned by changes in the material temperature (Fox and Flory, 1950). For this reason, it is an accepted fact that \( T_g \) is a function of the time scale of temperature change rate, rather than a true second-order transition (Kauzmann, 1948; McKenna, 1988).

The majority of asphalt researchers realize the importance of glass transition behavior and it is essential to take into account the effect of this phenomenon in calculating thermal stress build up. Although formulation that do not reflect the glass transition behavior have been accepted in the current specifications, the recent analytical methods take into account the glass transition behavior to have more reliable prediction of low temperature cracking.

2.2.3. The Glass Transition of Asphalt Binder

Similar to many amorphous polymers, the transition of asphalt binders from fluid to glassy behavior occurs within a relatively narrow temperature range called the glass transition region; the temperature at which this occurs is called the glass transition temperature, \( T_g \) (Kauzmann, 1948; Ferry, 1980). From a phenomenological point of view, the glass transition temperature is considered a second-order transition in the sense that first-order properties, such as volume, entropy, or enthalpy do not show discontinuity, but second order properties, such as thermal coefficient of expansion and heat capacity exhibit abrupt change (Fox and Flory, 1950; McKenna, 1988).
Asphalt binder exhibit glass transition behavior with significant changes in their thermal coefficients of expansion. The studies conducted by many researches clearly demonstrated that this class of amorphous materials show transitions that are, in many respects, similar to amorphous polymers and plastics (Wada and Hirose, 1960; Schmidt and Santucci, 1966; Majidzadeh and Schweyer, 1966; Anderson, 1971; Barral and Schmidt, 1964). Thermo-rheological studies of asphalt binders also revealed important findings about their $T_g$ behavior. The lack of fit of the WLF equation below the glass transition regions was reported in almost all rheological studies of asphalt binders (Dickinson and Witt, 1974; Pink and Merz, 1980). As a result, the use of different constants in the WLF equation above and below $T_g$ was suggested by some. In addition, the use of a different form of equation (Arrhenius function) was found by the SHRP research team to be more appropriate (Anderson et al., 1991).

These early studies revealed that $T_g$ is a strong function of the chemical composition of the asphalt. The more polar entities of asphalt (asphaltenes and aromatics) tend to reduce the strength of transition as measured by change in coefficient of thermal contraction/expansion (Wada and Hirose, 1960). The transition was observed to move to higher temperatures with an increase in these polar, more associated fractions. These studies showed that above $T_g$, $\alpha$ varies within a narrow range of $5.6$ to $6.2 \times 10^{-4}$ per °C, while it is about half the range below $T_g$ ($2.7$ to $3.3 \times 10^{-4}$ per °C) (Schmidt and Santucci, 1966).

Beside chemical composition, glass transition of asphalt binder can be explained using the concept of free volume. The total volume of the material is constituted by a fraction of occupied volume (i.e. volume of molecules and vibrational motion) and a fraction of free volume due to packing irregularities. Previous studies (Doolittle, 1951; Doolittle et al., 1957; Williams et al., 1955) showed how the internal mobility of amorphous glass-forming material is better related to the free volume, rather than the temperature. Following this principle, the WLF equation was derived. The WLF equation describes the temperature dependence of mechanical properties of viscoelastic materials.
When cooling the material from high temperatures, during the first stage (referred to as “liquid”), the magnitude of the molecular adjustments is significantly larger than the one of the reduction of the vibrational motion; therefore, the reduction of free volume follows linearly the temperature change. When reaching the glass transition region, the speed of the molecular adjustment becomes slower and after a certain temperature, called glass transition temperature $T_g$, the reduction of free volume cannot take place in the experimental time. The consequence is that further collapse of the material volume is due to the decrease of the vibrational motion of molecules, therefore the material is in a “glassy” meta-stable state (Bahia, 1991; Ferry, 1980). For this reason, the glass transition is not an equilibrium condition. It is a second order transition in which first order properties, such as enthalpy, entropy or volume, remain continuous but second order ones, like thermal coefficient and heat capacity show a marked discontinuity (Brandrup et al., 1999).

The glass transition temperature may be determined by several experimental techniques, but traditionally the most reliable method for determining the $T_g$ of an amorphous polymer is by estimating the temperature at which there is a change in its cubic thermal expansion coefficient- dilatometric method (Schmidt and Santucci, 1966). Usually this work is accomplished by measuring the specific volume change of a sample over a wide range of temperatures and then plotting the specific volume versus temperature. A typical example of this plot is shown in Figure II-1.
2.2.4. Physical Hardening

During the development of the Strategic Highway Research Program (SHRP) project (1994), in the early 1990s, researchers discovered a phenomenon occurring in asphalt binders at low temperatures, called physical hardening. Before that study, physical hardening was known and documented only for other amorphous materials, but it had mostly been ignored for asphalt binders.

By then, two hardening phenomena of binders were known: oxidative aging and steric hardening. While the first one is mostly caused by irreversible chemical reactions between atmospheric oxygen and the polar groups of the asphalt, resulting in an increased stiffness (Peterson, 1984), the second one consists in a reversible thixotropic stiffening of the binder, due to the upsurge of a three-dimensional network of secondary bonds between the polar molecules (Brown et al. 1955, 1958; Ensley, 1973).

While developing the Bending Beam Rheometer test procedure, SHRP researchers (Bahia, 1991) showed that asphalts are subjected to another type of hardening when kept at temperatures lower or close to glass transition conditions. The origin of this phenomenon is well explained by the free volume theory.
(Ferry, 1980; Struik, 1978): physical hardening is a consequence of isothermal reduction of free volume at temperatures lower or close to the glass transition temperature (Figure II-2). The effect of such behavior is a general stiffening of the binder, with an increase of the elastic response, and, consequently, a reduced viscous stress relaxation aptitude.

![Figure II-2. Illustration of physical hardening as explained through the free volume concept (Tabatabaee, 2012).](image)

Below the glass transition temperature, asphalt binders are in a meta-stable condition due to the excess of internal energy. During the liquid phase of cooling, in fact, the reduction of volume follow the reduction of temperature and the material is in its thermodynamic equilibrium state. When glass transition occurs, the molecular adjustments become excessively slow to happen within the experimental time, so the internal energy of the material remains “frozen”. However, if the material is left in isothermal condition, the molecular adjustments take place, leading to a volume reduction and, as a consequence, to a change in mechanical properties of the material. This phenomenon is what is commonly called, for asphalt binders, physical hardening (Bahia, 1991). Its cause is the excess of internal energy of the material in its meta-stable condition. Physical hardening is generally considered to be fully reversible if the material is heated and left at a temperature higher than $T_g$ for a sufficient time.
From a microscopic point of view, as said, physical hardening is an isothermal reduction of the free volume of the material: this leads to a smaller volume and a more dense structural state, with stronger and more numerous secondary chemical bonds. At a macroscopic scale, the volume reduction is naturally reflected, while the stiffness is significantly increased, and the mechanical response is more elastic and less viscous.

An extensive study about the relationship between physical hardening and glass transition of asphalt binders has been conducted by Bahia (1991). He confirmed that what found by Struik (1978) can be applied to asphalt binders and that isothermal volume reduction and isothermal stiffening are strictly related and part of the same phenomenon. Moreover, Bahia discovered that in general the time necessary to reach thermodynamic equilibrium is proportional to the molecular weight.

Physical hardening rate, intended as the slope of the hardening shift factors against the logarithm of conditioning time, depends on the chemical composition of the binder, especially the amount of crystallizable wax and the length of molecular chains (SHRP A-369 report 1994; Bahia, 1991; Claudy et al., 1992). A study from the University of Calgary (Kriz et al., 2008) showed that even well above $T_g$ some residual hardening may persist, due to a partial crystallization of some components of the asphalt binder.

Within an asphalt mixture, bitumen is the component affected by physical hardening, therefore investigations mostly focus on this material, although it is showed that different mineral fillers and different volumetric properties of a mixture can influence the phenomenon (Romero et al., 1999). In particular, fracture properties rather than strength seem to be affected by physical hardening.

From an applicative point of view, the phenomenon becomes very important and critical for pavements in service at temperatures close to the glass transition temperature of the component bitumen. Because of the volume drop and the stiffness increase, thermal stresses generating within the pavement are more severe, whilst, as a consequence of the more markedly elastic behavior, the material is less
capable of dissipating those stresses through relaxation processes. All these factors can directly initiate cracking failures, or, by altering the rheological properties of the material, cause a discrepancy between the design and environmental parameters. In the perspective of the Superpave grading system, the effect of physical hardening can be assumed as a change in the PG grade of the binder, therefore the main basis of the mix design of the pavement is undermined.

2.2.5. Cooling Rate Dependency

Previous studies have postulated that low temperature cracking occurs at a temperature where the sum of accumulated increments of stress exceeds the strength of the asphalt (Christison et al., 1972; Hills et al., 1966). The magnitude of the incremental stresses depends on the rate of cooling, since this rate is equivalent to the loading time, which affects the amount of stress-relaxation that can occur by flow of the binder. It can be anticipated that low rates of cooling will lead to more stress relaxation and thus to lower cracking temperatures.

Attempts to see how the cooling rate works on the accumulated thermal stress and low temperature cracking have been made by many researchers. In the literature, it appears that the cooling arte were reported to range from 3 to 60 °C/hr (Janoo et al., 1993). It was found that the cracking temperature and tensile strength were not affected by cooling arte when it was equal or greater than 5 °C/hr. It was also indicated that the cooling rate has little or no effect on thermal contraction of asphalt mixes, which confirms the linear relationship between thermal shrinkage and temperature (Stoffels and Kwanda, 1996).

2.3. Asphalt Binder Fracture Properties

An extension of this procedure has been included in the AASHTO MP1a (2002), that is replacing the AASHTO M320. This new approach is based on the calculation of thermal stresses developing within the
pavement because of the restrained shrinkage caused by a thermal cycle, by using S(60 s) and m(60 s). Stresses are compared with the strength of the binder and the temperature at which they are equal is considered to be the limiting cracking temperature (See Figure II-3).

![Figure II-3. Thermal cracking criterion implemented in AASHTO MP1a (Anderson et al., 2001).](image)

Based on numerous fracture studies of composites, it is reasonable to expect that fracture properties of asphalt mixture are significantly influenced by the fracture properties of the asphalt binder. Consequently, fracture properties should be an important consideration in the specification of asphalt binder (Williams, 1987). Several studies of low temperature asphalt behavior also showed that there is a strong relationship between stiffness of asphalt binders and the amount of stretching they undergo until breaking (Heukelom, 1966). This observation suggests that the stiffness and strain at failure, as long as loading time and temperature are properly accounted for, can be used interchangeably (Anderson and Dongre, 1995). This result supports the use of limiting stiffness temperature as a criterion for low temperature thermal cracking (Mcleod, 1972; Readshwa, 1972). Typically, stiffer asphalt binders are more brittle and less stiff ones are more ductile. Unfortunately, creep stiffness as measured by the BBR is not enough to completely characterize the ability of some asphalt binders to stretch until breaking. For example, some asphalt binders exhibit high creep stiffness but can stretch farther before braking than
other ones. These types of binders would be allowed to have higher creep stiffness if it could be shown that they still displayed reasonably ductile behavior at low temperatures.

During the SHRP studies, this dilemma was solved by developing a device, called the Direct Tension Tester (DTT) that directly measured the failure strain for binders at very low temperatures (Anderson and Dongre, 1995). However, this test suffers from some problems such as repeatability and consistency due to its complicated preparation and testing process. Also the needs for a test sample with no constraint to allow stress-free shrinkage have led to unpopularity of this test (Bahia et al, 2012). Recently some researchers have used the Single-Edge Notched Bending (SENB) test, which is a fracture mechanics-based test commonly used in metal and other materials, to obtain the fracture properties of asphalt binders at low temperatures (Hore and Hesp, 2000; Hesp, 2003; Chailleux and Mouillet, 2006; Velasquez et al., 2011). Bahia et al., (2012) modified and improved the geometry of test to be similar to current BBR test geometry and they succeeded in evaluating the low temperature fracture properties of a broad range of asphalt binders. Figure II-4 shows a schematic of how the SENB test is performed and the parameters used for the calculation of fracture toughness (KIC) and fracture energy (Gf) (Velasquez et al., 2011; Bahia et al., 2012).

Typical result of the SENB testing system at low temperature grade of asphalt binder is shown in Figure II-5. The plot show clearly that this material has a ductile behavior and it goes under large
deformation before failure. It can be concluded that the ductile to brittle transition behavior of asphalt binders at low temperatures can be detected with the SENB system.

Figure II-5. Typical SENB result.

The result presented in Figure II-5, which correspond to a modified binder, plotted the force versus displacement which can be used to calculate different fracture properties such as failure energy and toughness. To determine the fracture properties of asphalt binder, an excel spreadsheet was developed by the research group to use SENB raw data to calculate certain parameters.

3. Binder Modification

When the produced asphalt does not meet the requirements, modification of the asphalt with additives has served as one of the cost-effective engineering solutions. Consequently, many researchers and designers, in order to create a failure-free pavement, have been motivated to specify modified asphalt binders. Observations in the field have shown the advantages of modified asphalt in delaying and preventing pavement distresses. As a corollary to this, the modification of asphalt binders has increased within the last decade because it provides the versatile properties needed to build better performing road.
Asphalt modification is expected to increase in the future because of the economic barriers involved in improving asphalts through refining processes and because of the logistical difficulties of using crudes that naturally produce better performing asphalt binders (Bahia, 1995). However, the use of various modifying techniques and additional materials has made the physical characteristics of the modified binders extremely complex and sometimes elusive (Bahia et al., 2001). As a result, a large number of studies have evaluated the rheological behavior of modified binders and discussed special testing methods or special characteristics of modified binder (Bahia et al., 1997, 2001). These studies have shown significant changes in rheological and failure behaviors of asphalt binders caused by using various modifiers.

3.1. Polymer Modification

The increasing demands of traffic on road building materials in recent years has resulted in a search for binders with improved performance relative to normal penetration grade asphalt binders. This effort to obtain improved binder characteristics has led to the evaluation, development and use of a wide range of bitumen modifiers which enhance the performance of the basic bitumen and hence the asphalt on the road (Nicholls, 1998). In recent years, there is a growing interest on asphalt modifications for use in high performance specialty pavements such as open-graded pavements (OGP) in which large gravels have been selectively utilized for creating open interconnected channels in the pavements (Bouldin, 1991).

Polymers are playing an increasingly important role in the asphalt industry and are the most technically advanced bitumen modifiers currently available. To achieve the goal of improving bitumen properties, a selected polymer should create a secondary network or new balance system within asphalt binders by molecular interactions or by reacting chemically with the binder. The strength, stiffness and adhesion of asphalt to gravel must be greatly improved to sustain the pavement performance. It is not surprising to witness various attempts to modify asphalt properties via chemical modification and/or
physical blending. The major efforts have been thus far directed to viscoelastic characterization of asphalt and rubbery materials (Collins et al., 1991).

Polymers can be classified into four broad categories, namely plastics, elastomers, fibres and additives/coatings. Plastics can in turn be subdivided into thermoplastics and thermosets (or thermosetting resins) and elastomers into natural and synthetic rubber. Globally, approximately 75% of modified binders can be classified as elastomeric, 15% as plastomeric, with the remaining 10% being either rubber or miscellaneously modified (Diehl, 2000).

Elastomers polymers exhibit the ability to recover to the initial condition after an applied load is removed. The elastomers, if mixed in an appropriate amount with asphalt, can confer their elastic properties to the modified binder, thus enhancing its elastic recovery capacities and, therefore, its resistance to permanent deformations. Within the elastomeric group, styrenic block copolymers have shown the greatest potential when blended with bitumen (Airey, 2003).

Plastomers are polymers that have high early strength under deformation, but they are less flexible than elastomers and tend to fracture under large strains. Additionally, plastomers deform more slowly than elastomers under an equivalent load. Plastomers when add to asphalt confer high rigidity to the binder and strongly reduce deformations under the load. Also, plastomers increase the viscosity of the asphalt (Read and Whiteoak, 2003).

PPA is a binder modifier used for improving both high and low temperature performance. The reported advantage of using PPA is that while the viscosity is significantly increased, the penetration of the binder remains approximately the same (Edwards et al., 2006). PPA has been used as a modifier alone or in combination with polymers. The intention of adding PPA to polymer modified binder is to reduce the polymer content leading to improved processing conditions, high temperature viscosity and storage stability (Daranga et al., 2009).
Polymer-modified binders obtained by mixing plastomeric or elastomeric macromolecular materials with traditional pure road asphalt binders have been available for more than 20 years. An ideal binder should have enhanced cohesion and very low temperature susceptibility throughout the range of temperatures to which it will be subject in service, but low viscosity at the usual temperatures at which it is placed. Its susceptibility to loading time should be low, whereas its permanent deformation resistance, breaking strength, and fatigue characteristics should be high. At the same time, it should have at least the same adhesion qualities (active and passive) as traditional binders. Lastly, its aging characteristics should be good, both for laying and in service (Brule, 1996). However, there has been growing uncertainty about the future supply of polymers to the fluctuation of prices in crude oil versus natural gas. This uncertainty has caused a need to find alternate modification techniques. Due to increasing costs associated with polymers, a number of low-cost asphalt modification and extension techniques have been presented to optimize cost and performance of conventional binders (Herrington, 1992; Morales et al., 2006; Rubab et al., 2011). Hence, different blends of binders with a large variety of materials have been studied to improve the binder properties and performance. In recent years oil modification has been introduced as a means to improve low temperature performance while maintaining the high temperature properties (Herrington, 1992; Villanueva et al., 2008; Rubab et al., 2011). Researchers have used a wide range of oils to enhance binder performance, specifically at low service temperature. The properties of the oils used vary significantly due to the variation of source (e.g. wood industry, oil refineries, etc.), composition, and refining techniques. Investigation of asphalt modification using these various kinds of oil has shown its potential improve binder properties for certain applications (Shi et al., 2001; Villanueva et al., 2008; Rubab et al., 2011). However, there are just limited studies that reports some effects of oil modification (Herrington et al., 1992; Villanueva and Zanzotto, 2008; Hesp and Raymond, 2011) but their structure and effect on asphalt binder are not fully known (Sarkanan and Ludwig, 1971; McCready and Williams, 2008; Hesp and Raymond, 2011). Therefore, investigating the characteristic and properties of different type of oils is critical and necessary for oil modification techniques.
3.2. Oil Modification

Lubrication has probably been known to humans since the invention of the motor and wheel. The use of petroleum substances, animal fat or vegetable oils for lubricating purposes since early ages has been well documented. Drastic increase in demand for lubricating oil motivated the industries to make a revolution in producing these oils. Nowadays, due to essential needs for lubricant oils throughout the world for various applications, numerous industries take part in producing these materials (Burdick and leffler, 1990; Honary and Richter, 2011). This trend causes the over production of these materials and pushes the industries to find other markets for lubricating oils.

In the past few years, lubricating oils have been used in asphalt industry to achieve some desirable properties for pavement materials. Researchers have used a wide range of oils to enhance binder performance, specifically at low service temperature (Shi et al., 2001; Villanueva et al., 2008; Rubab et al., 2011). The properties of the oils used vary significantly due to the variation of source (e.g. wood industry, oil refineries, waste lubrication oils, etc.), composition, and refining techniques. Besides technical advantage of using oils as an asphalt modifier, it can give more advantages from economical point of view and environmental concerns. For example, one type of these extenders is derived from car used oils. Waste lubrication oil can be an issue in near future while millions of people around the world owning and driving cars. These different oils can cause catastrophic environmental problems and concerns, which is why it is imperative to collect them for re-use or recycling. Therefore, using oil as a modifier for asphalt binder can be a good and economic alternative.

Although, extensive research has focused on the effect of different polymer modifiers on the properties of asphalt binder and their mechanism of effect, knowledge on the fundamental mechanisms of oil modification and appropriate selection criteria for achieving optimum characteristics is limited. A well-established principal in material science recognizes that the quality of the finished product in almost all final blends depends in material selection (Osswald and Menges, 1995; Baird and Collias, 1995).
Hence, a better understanding of the effect of oil modifiers at a fundamental level will help increase the quality of the final product.

As it mentioned earlier, there are large variety in selection of lubricating oils and information about their production and characteristic is vital for their usage in asphalt modification applications. The three main categories for lubricating oils are Petroleum-based, Bio-based and Refined waste oils. The next subsections will cover the production, characteristics and applications of these oils.

3.2.1. Petroleum-based Oils

The majority of petroleum lubricants base oils are produced through the refining and modification of crude oil. Crude oil, extracted from the earth, is a very complex mixture of various chemicals ranging in complexity from simple gaseous molecules to very high molecular weights components. Asphaltic components, for example, are very heavy materials left over after many of the lighter hydrocarbons are extracted from crude oil (Mikeska, 1986; Honary and Richter, 2011).

Based oils are derived from light and heavy crude, based on the type and sources where the crude petroleum is extracted. These oils are suitable for heavier petroleum derivatives like base oils for lubricants. This section will focus on hydrocarbon modifiers (aromatic, naphthenic, and paraffinic oils) which are produced from crude oils. The ability to produce these oils is highly crude source dependent. A high gravity crude, sweet crude, would be the most advantageous to produce hydrocarbon oils, since they yield high percentages of overhead fractions and low percentages of asphalt binder (Roberts et al., 1991). It is preferable to the refiner that the crude source does not contain sulfur, due to its corrosive nature.

Paraffinic Oils

The lube crude oil, which is reduced crude in which the light-end crudes have already been removed, is sent to the atmospheric distillation tower where the light ends are removed at temperature ranging from 15 to 345 °C. As the reduced crude is sent to the vacuum distillation tower, it is exposed to heat ranging
from 205 to 425 °C, which is the cut point. The gas oils are separated from the residuum, which will be further processed to produce asphalt products. In the vacuum tower the various viscosity oils are side streamed and are separated by their boiling point and viscosity range (Leffler, 1985; Burdick and leffler, 1990; Honary and Richter, 2011).

The paraffinic oils are captured at various viscosity and boiling ranges. Each product (fraction) has both an initial boiling point (IBP) and an end point (EP). The EP is the temperature at which 100% of the product is vaporized (Leffler, 1985). At this point the oil still contains both paraffinic and aromatic components. The oils are now separated by liquid/liquid extraction. An aromatic solvent preferentially dissolves the aromatic molecules, thus the solvent with the aromatics dissolved in it, readily separates itself from the rest of the compounds and the remaining would be the paraffinic oils (Leffler, 1985; Muraki, 1987; Honary and Richter, 2011).

The chemical of these mineral oils consist of hydrogen and carbon which is atoms of carbon and hydrogen bound together to form molecules of different structures. It is the arrangement of these atoms that determines whether the oil is aromatic, naphthenic, or paraffinic. The paraffinic structure is a straight or branched chain of hydrogen and carbon atoms (Muraki, 1987; Roberts et al., 1991). The paraffinic oil contains at least aromatic content of 18%, with a specific gravity of 0.874. The chemical structure of the paraffinic compound is shown in Figure II-6.

![Typical Paraffinic Structures](image)

**Figure II-6.** Chemical Structure of Paraffinic compound (Roberts et al., 1991).
Naphthenic Oils

After sending the reduced crude lube stock to vacuum distillation tower, the gas oils are separated from oils which contain naphthenic and aromatic molecules. The naphthenic oils are then either hydro treated or solvent extracted to remove the aromatic molecules. The hydro cracking of the oil breaks large molecules into smaller light molecules. The procedure is performed at a pressure of 3000 psi, with temperature ranging from 260 to 425 °C. The oil is mixed with hydrogen at 90 percent saturation, and is passed through a catalyst in pellet form. The hydrogen is then removed and the various ranges of naphthenic oils are separated in the fractioning tower based on their viscosity (Leffler, 1985; Honary and Richter, 2011).

The naphthenic oil can be either a simple or complex structure of rings which indicates the highest possible hydrogen/carbon ration in the asphalt molecules (Muraki, 1987; Roberts et al., 1991). The naphthenic oil has a lower specific gravity of 0.937 with an aromatic content 44%. A typical naphthenic structure is presented in Figure II-7.

![Typical Naphthenic Structures](image)

**Figure II-7.** Chemical Structure of Naphthenic compound (Roberts et al., 1991).
Aromatic Oils

The aromatic oils can be processed by either the paraffinic or naphthenic production processes. In processing either oil, the aromatic can either be separated out during solvent extraction or cracked into smaller molecules during hydro treating.

During solvent extraction an aromatic solvent is used to preferentially dissolve the aromatic molecules, thereby leaving behind the paraffins and naphthens. The extraction process uses a vessel with an internal mixing system. The solvent is fed into the column near the top and the stream is fed near the bottom of the vessel. As the solvent moves down the vessel it dissolves the aromatic molecules (extract), and the hydrocarbon, which rises to the top, is called raffinate (Leffler, 1985; Mikeska, 1986). The aromatic is then recovered by distillation. Based on the crude source, some aromatics may contain waxy components. If they do contain wax, it will be either removed through solvent extraction or by chilling the oil to solidify the waxy components.

In hydro treating, the aromatic molecules, which have the highest molecular weight, are broken down to create either paraffinic or naphthenic structures, depending on the base lube crude oil. The aromatic ring contains a stable six-carbon condensed, unsaturated ring (Mikeska, 1986; Roberts et al., 1991). The typical properties of the aromatic oil indicate that this oil has the highest specific gravity of 0.97 and the highest aromatic content of 70%. A typical aromatic structure is depicted in Figure II-8.

![Typical Aromatic Structures](image)

**Figure II-8.** Chemical Structure of Aromatic compound (Roberts et al., 1991).
3.2.2. Plant-based Oils

The increasing price and decreasing reserves of petroleum in the United States have generated development of substitutes for petroleum-based materials. In particular, asphalt has experienced a rapid increase in price in recent years and available quantities are likely to decline in the future. Therefore, the United States government is currently working to establish a more bio-based economy (Demirbas and Balat, 2006). A bio-based economy uses energy from renewable organic matter instead of fossil fuels. Bio-fuels and bio-oils have several advantages over petroleum products. Bio-based materials are renewable, environmentally friendly, provide energy security, and present a large economic opportunity for the United States (Demirbas and Balat, 2006).

The new policies toward bio-based economy have motivated administrators and researchers in pavement community to look for alternative bio-binders and extenders. Also increased environmental regulations for new drilling, dwindling existing resources, modifications to the refining process that maximize the fuel quantity while minimizing asphalt residue have increased the cost of asphalt in recent years. To address these challenging issues, pavement industries are seeking an alternative binder or extender to replace or reduce the petroleum-based asphalt used. The new asphalt binder should be eco-friendly and made from green technology. The sustainability approach taken by the highway industry has led different researchers to investigate new bio-based oils. Fini et al. (2010) researched the application and characterization of manure-based bio-oils in the asphalt industry. They reported that adding swine manure–based bio oil improved the low-temperature properties, but compromised the resistance to rutting at high temperatures. Williams et al. (2010) conducted a study on the utilization of fractionated bio-oil in asphalt. Three different sources of biomass (oak wood, switchgrass, and corn stover) were pyrolysed and fractionated to generate bio-binder. The study found considerable benefits of blending the bio-oil obtained from oak wood and switchgrass with traditional polymer-modified asphalt binders. Seidel and Haddock (2012) investigated the effect of Soy Fatty Acids as a modifier for asphalt binder. Their study suggested that Soy Fatty Acids have potential application as a fluxing agent for binders that are stiff and hard to mix.
(e.g., recycled asphalt binders). These researches depicts that there is significant potential of using bio-oils as new additives to asphalt binder and there is essential need to investigate these materials more comprehensively with specific focus on their characteristics.

According to the US Department of Agriculture, vegetable oils may be classified into three categories based on their production, use, and volume as (1) major oils, (2) minor oils, and (3) non-edible oils (Salunkhe et al., 1992). Major oils are those known for human or animal-feed consumption and often play important economic roles in the regions producing them. These include soybean, palm, sunflower, coconut, olive and etc. Minor oils are those used but in the smaller production scale in comparison with major oils. These oils have fatty acid profiles that could make them effective for industrial usage. They include niger, mango kernel, poppy, cocoa bean, grape seed and etc. Non-edible oils are the third group, and while the majority of oil plants are cultivated for food application, a number of non-edible oils exist. These are linseed, castor, tung, and tall, and are commercially grown for their unique chemical makeup. These non-edible oils are used in industrial applications such as in soaps, paints, varnishes, resins, plastics, and etc. Also their use is also being considered for industrial lubricants application (Honary and Richter, 2011).

The popularity of bio-oils and bio-fuels over the past few years has resulted in a significant investment of public and private capital for the development of non-edible alternative crop oils. Additionally, the attention given to the negative health effects of petroleum based oils has re-invigorated the development by major US seed companies of special varieties of oilseeds. The Association for Advancement of Industrial Crops (AAIC) has a list of several alternative industrial crops that its member is working on. Most noteworthy are crops like Cuphea, Camelina, canola, castor, peanut and pennycress, among those being investigated by the oil crop divisions of AAIC (Honary and Richter, 2011).

The basic structure of fats and oils is an molecule between glycerol and three fatty acids. Depending on the length of the carbon chain making up the fatty acid, the resulting fat can either be liquid (Oil) or
solid. Since glycerol is capable of bonding with three molecules of fatty acids, the result is referred to as triglyceride (Figure II-9).

![Chemical Structure of Triglyceride](image)

Figure II-9. Chemical Structure of Triglyceride (Honary and Richter, 2011).

A triglyceride, also called triacylglycerol (TAG), is a chemical compound formed from one molecule of glycerol and three fatty acids. The structure of glycerin is shown in Figure II-10. Also Fatty acids contain a chain of carbon atoms combined with hydrogen (forming hydrocarbon).

![Chemical Structure of Glycerin](image)

Figure II-10. Chemical Structure of Glycerin (Honary and Richter, 2011).

Vegetable oils have many advantages and some shortcomings when considered for use in industrial applications. Most importantly, unless modified, they lack oxidation stability. Oxidative stability of vegetable oils is dependent on the position and degree of unsaturation of fatty acids that are attached to the glycerol molecule. Also it should be mentioned that the longer the fatty acid carbon chain, the higher
the viscosity and melting point. Double bonds within the carbon chain lower the viscosity and melting point significantly.

Generally, longer chains have a higher viscosity and shorter chains have a lower viscosity. Carbon chains of 25 carbons or more are in the range of base oils for lubricating oils. It should be noted that carbon chains of lower numbers have higher flammability and lower boiling point (Honary and Richter, 2011).

3.2.3. Refined Waste Oils

Nowadays, you will find some type of oils is being used in some applications such as factories, cars, homes, etc everywhere. These oils after being used will be recollected and if they won’t be reused, it can cause serious logistic and natural problems due to limited storage capacity. Therefore, consumption of reused oil can be beneficial from different aspects such as financial advantages, nature preservation, reducing pollution and etc. The main types of these oils are waste lubricating oil, waste motor oil and waste cooking oil. This subsection briefly discusses the potential of using these materials as asphalt binder modifiers and extenders.

Worldwide, motor vehicles and industrial machines require millions of gallons of lubricating oil. Also, with millions of people around the world owning and driving cars, waste lubrication oil is inevitable. The used lubricating oil generates waste disposal problem because improperly disposed of used oil may contaminate the environment. Used oil can cause catastrophic environmental hazards and concerns, which is why it is imperative to collect the waste oil for re-use or recycling. These reasons have motivated researchers to use these materials for different applications. Villanueva et al. (2008) studied the addition of used lubricating oils in two different air-blown asphalts at concentrations ranging from 1 to 10 percent. This study concluded that used lubricating oils can be used as softening additives without sacrificing the grade span although some disadvantages were reported as well. Rubab et al. (2011) investigated the chemical aging in asphalt binder modified with Engine Oil Residue (EOR). They
reported that EOR is an economical modifier used to increase the Superpave grade span of asphalt binders but EOR significantly increase both the rate of oxidation.

Furthermore, according to the U.S. Environmental Protection Agency (2011), approximately 3 billion gallons of waste cooking oil are collected annually from restaurants and fast food establishments in the United States. Waste cooking oil can be polymerized to use as an additive in asphalt binder. Wen et al., (2012) conducted a study about laboratory evaluation of waste cooking oil–based asphalt. This study showed that addition of refined waste cooking oil with traditional asphalt binder reduced the PG of the base binder, indicating an increased resistance to thermal cracking, but reduced resistance to rutting. However, due to the unknown history of used oil and the possibility of the contamination of material, it is not obvious whether used oil is able to improve the asphalt binder characteristics to a consistency level appropriate for construction purposes and pavement performance and, at the same time, to optimize the chemical characteristics with regard to durability. Therefore, this type of materials needs be investigated more comprehensively to assure their beneficial effects for asphalt pavements.
III. Materials and Methods

1. Binder Materials

The test matrix included conventional asphalts and oil modified binders. Two asphalt binders commonly used in the Mid-west region of the United States were selected in this study: Flint Hills (FH) PG 64-22, which has a relatively high asphaltenes content, and Valero PG 64-22 (labeled by producers PG 64-16), which has a relatively low asphaltenes content. These neat binder samples were obtained from the asphalt binder producers, and were received in five-gallon pails. The neat binders were used as the base for preparation of modified binders.

Since the rheological properties of asphalt binders change with time due to aging processes during construction and service such as oxidation and volatilization, properties are evaluated at different aging conditions in specifications to simulate behavior over the entire service life. Current asphalt binder specifications consider three levels of aging: a) original binder, which represents the asphalt stored before mixing with aggregates; b) short term-aged binder, or binder aged during the mixing and compaction process; and c) long term-aged binder, which is the binder aged after several years of service life in the pavement.

Laboratory aging of the binder if performed to achieve conditions that are closer to actual field conditions. Current specifications consider two laboratory procedures specially designed to simulate the aging of the binders. Rolling Thin Film Oven (RTFO) simulates short term aging (Roberts et al., 1996). A specific amount of asphalt cement (35 g) is poured into a bottle, which is placed into an oven at 163 °C for 85 min (ASTM D 2872, AASHTO T240). The oven is designed with a rotating rack that allows continuous exposure of fresh asphalt. An air jet is used to inject air inside the orifice of the bottle for further oxidation. The aging of the binders with the RTFO test represented the aging that happens in the
binder during the mixing and compaction of asphalt mixture samples. In this research, material is RTFO-aged prior dynamic rheological test for PG High temperature criteria to be evaluated from high temperature aspect of view.

The Pressure Aging Vessel (PAV) (Roberts et al., 1996) simulates the long term aging during five to ten years of in-service asphalt pavements. A 50 g sample of RTFO aged binder is poured into a pan, which is placed inside a pressure vessel at 100 °C and 2070 kPa for 20 hr (ASTM D 6521, AASHTO PP1). Durability related failures such as fatigue and thermal cracking are the primary distresses associated with aged pavements, therefore the low temperature creep and relaxation properties measured by the BBR are evaluated after the binder has been long term aged in the PAV. In this study the asphalt binders were subjected to short-term and long-term aging, using the RTFO and PAV to represent service conditions from immediately after construction to 5-10 years in-service.

Oil modification of asphalts is not a new phenomenon, but interest in this technique has increased considerably due to the need to improve asphalt pavements low temperature performance. Oils used in the asphalt industry are often classified as petroleum based, bio-based, refined used oils and others, with the most commonly used being the petroleum based.

1.1 Asphalt Sample Modification

Two complete full factorial test matrices for binder modification were completed. In the first test matrix, the neat binder (Flint Hills) and the nine oil modified versions of that binder were tested. Table III-1 summarize the properties of these materials.
Table III-1. Material used for Binder Testing.

<table>
<thead>
<tr>
<th>Description</th>
<th>Base Binder</th>
<th>Oil Modifiers</th>
<th>Aging Levels</th>
<th>Mixing Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Flint Heal &amp; Valero PG 64-22</td>
<td></td>
<td>Original (OB), RTFO, PAV</td>
<td>High Shear (HS)</td>
</tr>
<tr>
<td>Viscosity, cSt @ 40 °C</td>
<td>Petroleum-Aromatic (PA) 2036</td>
<td>Petroleum-Paraffinic (PP-1) 92.2</td>
<td>Petroleum-Paraffinic (PP-2) 290</td>
<td>Petroleum-Paraffinic (PP-3) 48000</td>
</tr>
<tr>
<td>API Gravity</td>
<td>9.5</td>
<td>15</td>
<td>26</td>
<td>16.8</td>
</tr>
<tr>
<td>Density, gr/cm³ @ 15 °C</td>
<td>1.00</td>
<td>0.96</td>
<td>0.89</td>
<td>0.95</td>
</tr>
<tr>
<td>Flash Point, °C</td>
<td>215</td>
<td>215</td>
<td>300</td>
<td>345</td>
</tr>
<tr>
<td>Refine Waste (RW-1)</td>
<td>Bio-Oil (BO-1) N/A</td>
<td>Bio-Oil (BO-2) N/A</td>
<td>Bio-Oil (BO-3) 90.9</td>
<td>N/A</td>
</tr>
<tr>
<td>N/A</td>
<td>20</td>
<td>19</td>
<td>N/A</td>
<td>65.3</td>
</tr>
<tr>
<td>Flash Point, °C</td>
<td>N/A</td>
<td>N/A</td>
<td>0.91</td>
<td>32.8</td>
</tr>
<tr>
<td>Refined Waste (RW-2)</td>
<td>Refined Waste (RW-2) N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table III-1 summarizes the material used in this study including modifiers, aging levels and blending conditions. To avoid being biased, it was decided to use another base binder and oil combination for application to the modeling phase of the research. It should be mentioned that BO-1 and BO-2 are from plant liquid and the origin of RW-1 and RW-2 are waste motor oil and waste cooking oil respectively.

Two replicates were tested for each binder. In the case of good repeatability, the average of the two replicates was used for the analysis of results. Acceptable repeatability was assumed when the differences between the two replicates were lower than 10%. In the case of larger differences between replicates, a third replicate was run.
The limiting factor for selection of the dosage of oil modifier was the loss of high temperature performance grade due to a decrease in stiffness resulting from the introduction of the oil modifier. Loss of high temperature performance with the use of oil modifiers has been reported in the literature (Villanueva and Zanzotto, 2008; Hesp and Raymond, 2011). The maximum oil possible that resulted in the loss of only one high temperature performance grade was selected. The targeted grades include 58 °C grade +1 °C for each neat binder. Final modifier quantities for blending of modified binders were identified that resulted in in similar high-temperature Performance Grade (PG) relative to the base binder. After several trials blends to determine the relationship between percent modifier and high-temperature grade, blends were produced to exhibit grades within + 1 °C of one another. The required percentage of each modifier and resulting grade can be seen in Table III-2.

**Table III-2.** Percent modifier used to get same high-temperature grade for oil modified binders with FH base.

<table>
<thead>
<tr>
<th>Oil Modifier</th>
<th>Content (% wt)</th>
<th>True Grade (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA</td>
<td>10</td>
<td>58.60</td>
</tr>
<tr>
<td>PP-1</td>
<td>6</td>
<td>58.43</td>
</tr>
<tr>
<td>PP-2</td>
<td>9</td>
<td>58.55</td>
</tr>
<tr>
<td>PN</td>
<td>7</td>
<td>59.07</td>
</tr>
<tr>
<td>BO-1</td>
<td>5</td>
<td>59.87</td>
</tr>
<tr>
<td>BO-2</td>
<td>6</td>
<td>58.58</td>
</tr>
<tr>
<td>BO-3</td>
<td>4</td>
<td>59.45</td>
</tr>
<tr>
<td>RW-1</td>
<td>5</td>
<td>58.22</td>
</tr>
<tr>
<td>RW-2</td>
<td>4</td>
<td>58.64</td>
</tr>
</tbody>
</table>
In order to further investigate the oil modification effect, four different oils (one from each category) were selected for use at the same concentration to provide another means of comparison. Therefore, in the second test matrix, materials selected for this part consisted of a neat binders plus different binder-modifier combinations as follows:

- Base neat binders; Flint Hills (FH) which is a PG 64-22.
- Four modifier types; Aromatic oil (PA), Paraffinic oil (PP-3), Bio-oil based oil (BO-1), Refined Waste Oil (RW-1).
- One level of modification; 5%.

The added amount of oil was fixed at 5% to be able to compare the oil effect on low temperature performance and thermal stresses equally.

### 1.2 Modification Process

In general, for the case of liquid asphalt binders and oil, the liquid-liquid mixing action taking place during the blending process is characterized by two phases, the continuous (major) phase and the dispersed or distributed (minor) phase. The physical phenomenon that dominates each phase is a “distributive” mixing process, although at certain shear levels a “dispersive” mixing process will also take place simultaneously (Osswald and Menges, 1995; Baird and Collias, 1995; Tadmor and Gogos, 2011; Osswald and Ortiz, 2006).

Distributive mixing refers to processes that reduce the macro-scale non-uniformity of the distribution of the minor component into the major medium without disturbing the initial droplet size of the minor component. Distributive mixing of compatible liquids is usually characterized by the distribution of the droplets or secondary phase within the matrix. In this mechanism of mixing, the distribution is achieved
by imposing large strains, thus is highly dependent on the viscosity ratio \((\phi)\) of the two phases, defined as \(\eta_2/\eta_1\), with 2 being the minor component.

Minor phase droplets in the major matrix tend to stay or become spherical due to the natural tendencies of the droplet to maintain the lowest possible surface to volume ratio. However, a flow field within the mixer applies stress to the droplets, causing them to deform and break up to smaller sizes, a process referred to as “dispersion”. The phenomenon of dispersion happens simultaneously with the distributive mixing process, repeatedly breaking up droplets until the deviatoric stresses of the flow field can no longer overcome the surface tension of the new droplets formed (Osswald and Menges, 1995; Baird and Collias, 1995). During dispersive mixing the imposed strain is not as important as the imposed stress which causes the minor phase droplet break-up.

Although extensive research has focused on the effect of different polymer modifiers on the properties of asphalt binder and their mechanism of effect (Morales, 2006; Masson, 2009), knowledge on the fundamental mechanisms of oil modification and appropriate blending process for achieving optimum characteristics is limited. A well-established principal in material science recognizes that the quality of the finished product in almost all final blends depends in part to how well the materials were mixed (Osswald and Menges, 1995; Baird and Collias, 1995). Hence, a better understanding of the mixing process of oil modifiers will help achieve optimum processing conditions and increase the quality of the final product. Thus, further exploration was focused on the appropriate mixing process of oil modification through various blending procedures and its implications for low temperature performance of oil modified asphalt binders as subsection of this study.

1.2.1. Mixing Processes

The ability to apply intense shear and shorten mixing cycles gives the high shear mixers broad appeal for applications that require immiscible fluids to be formulated into emulsions, or high viscosity liquids to
be dispersed and distributed into a liquid medium. In this study, a Ross 100-L High Shear Laboratory Mixer was used. The schematic figure of the device is shown in Figure III-1(a). The rotor/stator generator of the batch High Shear Mixer is generally positioned 2-3 head diameters from the bottom of the can. To ensure adequate dispersion of heavier liquids, the rotor/stator generator may be located in the center of the can. The head used in this study is a “Disintegrating Head” as shown in Figure III-1(b). The Disintegrating Head is excellent for general purpose mixing, fast droplet size reduction of heavier liquids, and producing vigorous flow in the material (Charless Ross and Son Company, 2009). This type of rotor and head has the capability of producing speed ranging from 0-10,000 rpm. The speed in this study was held constant at approximately 5000 rpm, the maximum possible without material spillage. In this high shear mixing unit, the rotor includes a single set of four blades. As the rotating blades pass each opening in the stator, they mechanically shear liquid droplets and expel material at high velocity into the surrounding mix, creating intense hydraulic shear. At the same rapid rate at which material is expelled, more is drawn into the bottom of the rotor/stator generator, promoting a continuous and rapid flow (Charless Ross and Son Company, 2009). This process is shown in Figure III-1(c).

Conventional low-shear mixer with radial-flow turbines was used to impose low shear mixing conditions, with the speed controlled in the range of 600-700 rpm. Since time of blending may potentially play an important role on the quality of final blend, different blending times were used. During the blending process, samples were extracted from the blend at 15 and 30 min intervals to investigate the blending time effect, up to 120 min. Longer mixing times were deemed impractical. Mixing temperature was also carefully selected, as mixing at low temperatures may not give the homogenous blend due to high viscosity of major phase (base binder) and at very high temperatures excessive binder aging may become a limiting issue (Charles Ross & Son Company, 2009). Therefore, a mixing temperature of 150±5 °C was selected as a balanced temperature in which the phase viscosities were sufficiently low.
The limiting factor for selection of the dosage of oil modifier was the amount of loss of high temperature performance grade due to decrease in stiffness resulting from the introduction of the oil modifier. Loss of high temperature performance with the use of oil modifiers has been reported in the literature. Thus it was decided to select the maximum oil possible without resulting in the loss of a high temperature performance grade. Based on trial and error, a 5% dosage was deemed appropriate for both oil types. Continuous high temperature performance grading results are presented in Figure III-2. It is seen that 5% aromatic oil (AM) had a less significant effect of the PG, while the addition of 5% paraffinic oil (PF) caused a drop to levels only slightly lower than a PG 64.
At the selected dosage the added oil does not have significant effect on high temperature performance of the modified binders, thus any improvement at the low end of service temperatures will not be at the expense of loss of high temperature performance. Furthermore, at high service temperatures blending deviatoric stress levels seem to be of limited significance, as low shear and high shear blending do not show significant difference in terms of high temperature performance, with only slightly higher softening associated with high shear blending.

1.2.2. Miscibility and Dispersive Mixing Mechanisms

To investigate the effect of shear stress on the characteristic of the final blend, the Bending Beam Rheometer test was conducted on the oil modified binders. The degree of miscibility, as previously discussed, have important implications for the mechanical, physical, rheological, and optical properties of the resulting blend (Baird and Collias, 1995; Tadmor and Gogos, 2011), mechanical performance tests were performed at low service temperatures using the BBR. The purpose was to determine if the
dispersive mechanism using high shear mixing translates into measurable performance improvement at low service temperatures. Figure III-3 shows only the summary of some stiffness results of BBR testing.

Figure III-3 shows that oil modifiers decreased the creep stiffness at all temperatures. The decrease in stiffness was more prominent when high shear blending was used, indicating that the effect of the
higher blending stress on droplet breakdown and homogenization results in a more significant softening of the binder at low service temperatures. Lower stiffness can potentially improve binder performance at low temperature by decreasing the binder’s ability to build-up thermal stress.

To better quantify the effect of oil modification on binder creep stiffness, the change in stiffness was expressed as the ratio of the percent change of stiffness to the base binder stiffness ($\frac{\Delta S}{S_o}$). The percent change in m-value was also calculated as the ratio of the absolute value of the difference of m-values to the m-value of the base binder ($\frac{|\Delta m|}{m_o}$). The calculated $\frac{\Delta S}{S_o}$ and $\frac{|\Delta m|}{m_o}$ values are shown in Figure III-4.

(a) Aromatic Oil

(b) Paraffinic Oil

Figure III-4. The Effect of Oil Modification on Low Temperature Properties.
The highest percent change in properties occurs when blends are made at high shear conditions for both aromatic and paraffinic oil modifications. Figure III-4 depicts that the effect of blending type is more significant on the stiffness, while m-value changed similarly for both low shear and high shear blending. The overall results confirm that oil modification is a shear-dependent process as increasing blending deviatoric stress enhances miscibility of oil in the binder, improving the low temperature properties of all oil modified asphalt binders by further breaking down oil droplets and homogenizing at a much finer level than achieved by simple low shear blending.

Furthermore, the effect of the added shearing stress during oil blending on glass transition behavior is studied as well. The resultant thermal curves can be used as a means of determining changes in the material structure and morphology through comparison of measured Tg and thermal behavior. The effect of the added shearing stress during oil blending is shown in Figure III-5.
Figure III-5 shows that incorporating 5% oil modifier into the base asphalt decreased the $T_g$ of the binder, for all oil types and blending procedures, although the extent of change varied. Shear stress levels during blending seem to have significantly affected the final blend properties, as indicated by the higher change in $T_g$ compared to low shear blends. These results indicate that the high deviatoric stress imposed to oil droplets during high shear mixing have led to a finer breakdown of droplets, resulting in a blend homogenized at a much finer scale, leading to greater variation at the micro-scale properties of the blend (Van der Zande and Van den Broek, 1998). Better dispersion of oil droplets results in better mixing quality and hence achieving $T_g$ values closer to that of the oil additive. Lower glass transition in an asphalt binder can also be indicative of lower potential for thermal cracking as the ductile-brittle transition is shifted down to lower temperatures (Turner and Branthaver, 1997).

The results indicate that by increasing the imposed deviatoric shear stress during blending by using high shear mixers, the decrease in base binder $T_g$ was more than double the decrease resulting from oil blended a low shear levels. The close dependency of the $T_g$ results on blending shear stress level indicates the existence of a dispersive blending mechanism. The $T_g$ results are not displayed for the sake of brevity.
The dispersive blending takes place at higher applied stress levels in addition to the underlying distributive mixing process, breaking up the liquid droplets and achieving well-dispersed and distributed blends at a much finer level. It is expected that the improvement in low temperature properties of the oil modified asphalt binder would result in reduced pavement low temperature cracking due to the general reduction in binder stiffness, increase of m-value, and decreasing of the glass transition temperature.

In dispersive mixing another important factor for achieving a homogenized blend is the residence time (mixing time). Sufficient blending time is necessary to insure that all droplets have broken down to their minimum possible size for the applied deviatoric stress state, and achieve a completely homogenized final blend. To investigate this factor samples were taken from the high shear aromatic modified asphalt binder blend at 15-min increments up to one hour and then the samples were taken every 30 min. Rheological measurements were taken at two temperatures for each sample to determine if there was significant change over the 2 hr period of blending time. Figure III-6 shows the summary of these results of DSR testing.

![Figure III-6](image-url)
In Figure III-6, the residence time, is observed to only slightly change $|G^*|/\sin \delta$ values as blending time increased. It can be seen that after half an hour blending, the high temperature properties of the blend showed the similar values in constant range. This slight change in magnitude is not significant enough to justify longer and less practical blending periods and may in fact be due to oxidative aging from continued blending at high temperatures. Based on the results it was determined that equilibrium mixing time was achieved in the first 30 min. At the equilibrium mixing time the mixed product has acquired a specific droplet and droplet-size distribution that will not continue to change significantly, no matter how long the mixing process continues (Charles Ross & Son Company, 2009). Thus it is believed that the binder-oil blend approaches full homogenization and maximum droplet breakdown during the initial 30 min of blending.

Based on the literature review and these results, it is believed that by imposing the higher stress and strain state to the system one may achieve ideal blend properties from the oil modification, maximizing performance gains. Thus in the present study the blending conditions are set to use high shear conditions for 30 min.

2. Materials Testing Procedures

Recognizing the limitation of the traditional asphalt binder characterization procedure in 1987, the Federal Highway Administration initiated a nationwide research program called the Strategic Highway Research Program, usually referred to as SHRP (Anderson et al., 1994). The final product of the SHRP research program was Superpave® (Superior Performance Asphalt Pavements). The Superpave® was designed to provide performance-related properties that can be related in a rational manner to pavement performance (McGennis, 1994).
2.1 High Temperature PG Test

The Dynamic Shear Rheometer (DSR) was introduced in 1993 by Superpave® as a tool to measure the mechanical characteristics of the binder. This device provided a useful method to evaluate the capability of the binder to resist rutting. The principle used with the DSR is to apply sinusoidal, oscillatory stresses or strains over a range of temperatures and loading frequencies to a thin disc of bitumen, sandwiched between the two parallel plates of the DSR. Anderson et al. (1994) assumed that rutting is caused by the total dissipated energy as calculated from the strain-stress curve.

\[
W_i = \pi \cdot \tau_0^2 \cdot \frac{1}{G^*} \cdot \frac{1}{\sin \delta}
\]  

(III-1)

Where:

\( W_i \) = total energy dissipated at the ith cycle

\( \tau_0 \) = maximum stress applied

\( G^* \) = complex modulus

\( \delta \) = phase angle.

\( |G^*|/\sin \delta \) was introduced as the rutting parameter. Equation III-1 shows that increasing the rutting parameter \( |G^*|/\sin \delta \) causes dissipated energy to decrease and, as a consequence, more rutting to occur. The Superpave® specification parameter \( |G^*|/\sin \delta \) was identified as the term to be used for high-temperature performance grading of paving asphalts in rating the binders for their rutting resistance.

The Superpave® parameter for rutting resistance is obtained by testing the asphalt binder using a DSR. Since asphalt binders are isotropic incompressible materials, the extensional properties can be calculated from the shear properties. A cylindrical asphalt sample is sandwiched between two plates, one fixed and one oscillating, as shown in Figure III-7. Torque is applied to the oscillating plate. The
temperature and stress level of testing can be adjusted according to the expected pavement temperatures and vehicle speeds.

Figure III-7. Dynamic Shear Rheometer Setup (Delgadillo, 2008).

The principle used with the DSR is to apply sinusoidal, oscillatory stresses or strains over a range of temperatures and loading frequencies to a thin disc of bitumen, which is sandwiched between the two parallel plates of the DSR. In general, two testing (plate) geometries are used with the DSR, namely an 8 mm diameter plate with a 2 mm testing gap and a 25 mm diameter plate with a 1 mm testing gap. The selection of the testing geometry is based on the operational conditions with the 8 mm plate geometry generally being used at low and intermediate temperatures (-5–40 ºC) and the 25 mm geometry at high temperatures (40–90 ºC).

Since the properties of asphalt change with temperature, the testing temperature for characterizing the binder must be the same temperature as the temperature experienced by the binder in the field. The pavement temperature depends on environmental factors like the weather and solar radiation. For this reason, pavement temperatures vary for different locations. Pavement temperatures in Florida are higher than pavement temperatures in Minnesota, for example. This means that stiffer binders will be needed in Florida than in Minnesota. The temperatures that are more relevant for rutting characterization are the summer temperatures. Permanent deformation is more critical when the asphalt is softer during the hot
season. Therefore, PG high temperature test were conducted at 58 °C and 64 °C (the base binder and oil modified binder HT PG grade).

The original and RTFO aged binder samples were poured into small silicone molds of 25 mm diameter and approximately 2 mm height. The sample was taken from the silicone mold and placed on the bottom plate of the DSR, which was kept at a temperature around 45 °C. The top plate was then lowered, squeezing the sample down to the required thickness, (1 mm), and the edges were trimmed. After this, the chamber was placed on the testing fixture, and the temperature conditioning began. After the desired temperature was reached and had become steady (after approximately 10 min), the loading began.

2.2 Intermediate Temperature PG Test

Fatigue cracking in asphalt pavements is caused by repetitive traffic loading. There are two mechanisms of fatigue cracking in asphalt pavements: top-down and bottom-up (Huang, 2004). Bottom-up cracks initiate at the bottom of the asphalt surface or asphaltic base layer as a result of high strains associated with flexure and propagate to the surface. Bottom-up cracking is the most common form of fatigue cracking. Top-down cracks initiate at the surface under the wheel path and propagate downward. Top-down cracking leads to longitudinal cracks in the wheel path whereas bottom-up cracking leads to an inter-connected network of cracks, often referred to as alligator cracking. Fatigue damage is a distress mechanism observed in asphalt binder at moderate to low temperatures.

The Dynamic Shear Rheometer (DSR) is a common device used to evaluate asphalt binder properties, including fatigue resistance. In DSR testing of asphalt binders, a cylindrical specimen is placed between two parallel plates as depicted previously in Figure III-7. Rheometers are designed to test materials with a fluid or soft consistency which tend to flow under their own self weight (Lakes, 2009), making it a good instrument for measuring the fatigue resistance of binders due to its semi-solid behavior at the intermediate temperatures used for fatigue testing. Additionally, DSRs allow for fine control and
measurement of torque, displacement, and temperature. The ability to precisely measure and control temperature, torque and deflection angle is critical when testing asphalt binders due their high temperature and loading amplitude/rate sensitivity. Based on the Superpave specification, the testing for fatigue is conducting on the PAV aged material to simulate the pavement service life.

2.3 Low Temperature PG Test

In the current Superpave specification, these parameters from Bending Beam Rheometer (BBR) test are used to evaluate the binder rheological characteristic at low temperatures. From this test, apparent stiffness, $S$, is determined at a loading time of 60 s. From the same data the slope of the log stiffness versus log time, the $m$-value, is also calculated at 60 s. The temperature at which $S(60) \leq 300$ MPa and $m(60) \geq 0.3$ is specified as the critical temperature +10 °C. These limits were established based on data from previous studies as well as the data obtained by SHRP (Bahia and Anderson, 1994).

Thermo-mechanical properties of the base and oil modified asphalt samples were measured using the Bending Beam Rheometer to evaluate the low temperature properties of oil modification based on the ASTM D6648 and AASHTO T 313. Test were performed at temperatures of -12 °C, -18 °C, -24 °C to cover a wide range of low temperatures conditions as well as attempting to target test temperatures below and above the binder T$_g$. The measurements of creep stiffness and the $m$-value of asphalt binder beams were conducted after one hour isothermal conditioning. Since low-temperature thermal cracking occurs during the service life of the pavement, it is recommended to do this test on PAV aged materials.

2.4 Glass Transition (T$_g$) Test

The dilatometric cells and expansion measuring capillary tube, illustrated in Figure III-8, are used in this study. The tester was modeled after the dilatometer used during the SHRP program. The determination of T$_g$ is based on volumetric changes in the contents of the cell, measured as the fluid
surrounding the sample moves up or down the capillary tube in response to temperature change. Each point representing the height of the liquid in the capillary tube was then converted into specific volume and plotted against temperature (Bahia and Anderson, 1993).

![Schematic figure of T<sub>g</sub> test Device](image)

**Figure III-8.** Schematic figure of T<sub>g</sub> test Device (Nam and Bahia, 2009).

Currently, no formal standard for this device is available and therefore the test was performed following a modified version of the procedure developed by Bahia and Nam (2004). The binder sample is prepared by pouring 10 g of hot asphalt into a circular silicone rubber mold with a diameter of 40 mm and a height of 8.0 mm shown in **Figure III-9**. In this study, the system was further modified by using a very precise pressure transducer to measure the changes in alcohol column height.

![Silicon mold and dilatometric cell](image)

**Figure III-9.** Silicon mold (left) and inside of dilatometric cell (right).
The dilatometric cell is made of aluminum, and it is connected to a vertical capillary tube with its top end open. The assembly is filled with ethyl alcohol, and no air bubble must be trapped inside in order to avoid misleading measurements of volume. To achieve this, the insertion of the samples into the cell and the closing of the assembly is carried out inside a container filled with ethyl alcohol. At the base of the tube a pressure transducer is placed to measure the changes of height of the liquid every 5 seconds. Since the measurements are particularly sensitive to many factors, each cell was accurately calibrated in order to take into account the thermal contraction and expansion of the equipment and the liquid. Changes in the volume of the sample can be measured by knowing the diameter (i.e. 1 mm) of the capillary tube and the change of liquid height.

The temperature change rate (cooling rate) was fixed for all tests at 1 °C/min. This rate was chosen for practical and economic reasons, but also confirms what had been used in previous studies (Schmidt and Santucci, 1966; Majidzadeh and Schweyer, 1966; Anderson, 1971; Jongepier and Kuilman, 1970; Bahia and Anderson, 1993; Nam, 2001; Ojo et al., 2008). The temperature of the dilatometer cells was controlled by placing it in a specially designed chamber that was cooled by liquid nitrogen and heated by an electrical heater. The test temperature range was fixed between 30 °C to -50 °C for all binders and thermal-volumetric properties of the binders including the glass transition temperature (T_g) and thermal coefficients of contraction above T_g (liquid state- α_l) and below T_g (glassy state- α_g) were reported after each test. These results are also used in the theoretical calculation of the asphalt binder stress and strain buildup.

Assessing Superpave tests lead to development of new tests based on the failure and damage concept. Significant amount of researches have been focused on the developing new test procedures at different range of temperatures to replace or complete the current PG tests. Some of these tests are used in this study to investigate the effect of oil modification on asphalt binder from damage point of view as well.
2.5 Multiple Stress Creep and Recovery (MSCR) Test

The repeated creep test is proposed as a method of separating the dissipated energy and estimating the resistance to accumulation of permanent strain for asphalt binders. The RCR test was developed during the NCHRP 9-10 project. Bahia et al. (2001) recommended the repeated creep recovery test (RCR) using the dynamic shear rheometer (DSR) to evaluate the resistance of asphalt binders to permanent deformation at high temperatures. The NCHRP 9-10 project recommend a shear stress in the range of 30 Pa to 300 Pa for 100 cycles at a rate of 1 s loading time followed by a 9 s unloading time (Bahia et al., 2001).

The MSCR test was developed to reduce the number of samples at each stress level and it is the following development of RCR test. The test uses 1 s creep loading followed by 9 s recovery for the following stress levels: 25, 50, 100, 200, 400, 800, 1600, 3200, 6400, 12800, 25600 Pa at 10 cycles for each stress level. The test starts at the lowest stress level and increase to the next stress level at the end of every 10 cycles, with no rest periods between creep and recovery cycles or changes in stress level. (D’Angelo et al., 2007). D’Angelo selected two stress levels, 0.1 kPa and 3.2 kPa, upon correlation between binder and mixture rutting results for performing the MSCR test. Ten cycles are run for each stress level for a total of 20 cycles. Figure III-10 shows the typical results from MSCR test.
The average non-recoverable strain for the 10 creep and recovery cycles is then divided by the applied stress for those cycles yielding the non-recoverable creep compliance \(J_{nr}\). \(J_{nr}\) for 0.1 kPa is calculated by divided the strain after 10 cycles to 0.1 kPa. Equations (III-2) and (III-3) show the calculation method for \(J_{nr}\) at 0.1 kPa (AASHTO TP 70).

\[
J_{nr}(0.1, N) = \frac{\varepsilon_{10}}{0.1} \quad \text{for } N = 1 \text{ to } 10 \tag{III-2}
\]

\[
J_{nr0.1} = \frac{\sum_{n=1}^{10} [J_{nr}(0.1, N) \varepsilon_{10}]}{10} \quad \text{for } N = 1 \text{ to } 10 \tag{III-3}
\]

where,

\(\varepsilon_{10} = \varepsilon_{r} - \varepsilon_{o}\)

\(\varepsilon_{r}\) = strain value at the end of the recovery portion (i.e., after 10.0 s) of each cycle strain

\(\varepsilon_{o}\) = initial strain value at the beginning of the creep portion of each cycle.
The definition for the $J_{nr}$ at 3.2 kPa is analogous. The $J_{nr}$ parameter was suggested as a measure of the binder contribution to mixture permanent deformation (D’Angelo et al., 2006).

### 2.6 Frequency Sweep test

To investigate the effect of oil modification more in depth, frequency sweep tests were conducted for different level of aged binders with and without oil modification in DSR machine. Complex modulus master curve were constructed to determine the rheological behavior over a large range of loading times and temperatures. Master curves of the modified asphalts along with the base binder are compared in this study. The frequency sweep tests were performed under controlled 1% strain loading conditions using frequencies from 0.1 rad/s to 100 rad/s, with the 8-mm diameter and 2000 µm testing gap geometry at 4, 16, 28, 40, 52 and 64 °C respectively.

Direct measurements of rheological properties of the extender oils were taken to support definition of fundamental reasons to explain the effects of oil modification on modified binder rheological properties. Due to the low viscosity and stiffness of the material the Bob and Cup geometry was selected as the most suitable geometry to perform rheological measurements. **Figure III-11** shows this fixture.

![Bob and Cup Fixture](image)

*Figure III-11. Bob and Cup Fixture.*
The concentric cylinder rheometer is a common instrument that operates in a different range of temperature for collecting data used for many engineering materials with low viscosity. When the bob rotates at a constant speed and the cup is stationary, the instrument measures the torque required to maintain a constant angular velocity of the bob. The opposing torque comes from the shear stress exerted on the bob by the fluid. This is the principal used in this device to measure the rheological properties of low viscosity materials such as oils. More specific information regards this fixture can be found in Steffe, (1996).

2.7 Linear Amplitude Sweep (LAS) Test

Many researchers showed that a poor correlation exist between the currently used fatigue parameter G*sinδ and field performance data. The SHRP approach for fatigue criteria lacks the ability to characterize actual damage resistance (Bahia, et al. 2001). Furthermore, this specification does not account for pavement structure or traffic loading as the measurement is made at one, low strain level over very few cycles of loading. When this specification was developed, it was speculated that binder in pavements function mostly in the linear viscoelastic regime. However, subsequent research has proven this is not the case (Bahia, et al. 2001).

To solve the limitations of the current specification, recently the Linear Amplitude Sweep (LAS) test has been proposed as an alternative for PG test. The LAS test consists of cyclic loading in the DSR and utilizes the same testing geometry as PG test. However, in the LAS test, load amplitudes are systematically increased to accelerate damage. In addition to amplitude sweep loading, the LAS test includes a frequency sweep test prior to the amplitude sweep to obtain an undamaged material response used in viscoelastic continuum damage modeling. The frequency sweep is conducted at a small load amplitude of 0.1% strain to avoid inducing damage. Figure 2 provides a schematic of the amplitude sweep loading. Loading begins with 100 cycles of sinusoidal loading at 0.1% and 10 Hz frequency. Loading
proceeds in 1% strain step increments. Each strain step consists of 100 cycles of loading at 10 Hz frequency (Hintz, 2012).

2.8 Single Edge Notched Beam (SENB) test

Binders fracture properties were tested using SENB fracture test. The SENB test follows ASTM E399 standard and assumes that linear elastic fracture mechanics (LEFM) conditions hold. The SENB geometry adds a notch to the beams made using common BBR molds which the notched beams can be prepared by making a notch of 3 mm (i.e., corresponding to 20-25% of beam depth) in the wide side (i.e., 12.7 mm) of the BBR mold side-beams. The SENB tests include tests run during an hour conditioning period at -12 °C temperature (the Low temperature grade of base binders) at a constant displacement rate of 0.01 mm/sec. The purpose of this test is to determine the effect of oil modification on change in fracture properties as measured by the SENB. The extent of this change and its potential importance is assessed and explained using these results.

2.9 Bitumen Bond Strength (BBS) test

In asphalt mixtures, moisture damage is defined as the loss of stiffness and strength due to moisture exposure under mechanical loading and manifests itself in a phenomenon referred to as stripping. The reduction of the pavement integrity due to moisture damage plays an important role in other types of distresses, such as rutting, fatigue cracking, and raveling (Cho and Kim, 2010). There are three main mechanisms by which moisture can degrade an asphalt mixture: (a) loss of cohesion within the asphalt binder or mastic, (b) adhesive failure between aggregate and asphalt (i.e., stripping), and (c) degradation of the aggregate (Copeland et al., 2007).

Bond strength is a critical parameter in evaluating a binder’s ability to resist moisture damage. A simple test performed directly on the asphalt-aggregate interface can more effectively evaluate the
influence of water in both cohesive and adhesive strength, leading to a better understanding of the moisture sensitivity of asphalt mixtures. Recently, such a test method, called the Bitumen Bond Strength (BBS) test, was introduced (Youtcheff and Aurilio, 1997; Kanitpong and Bahia, 2003; Moraes et al., 2011).

In this study, the Bitumen Bond Strength Test (BBS) (Figure III-12), was used to evaluate the asphalt-aggregate bond strength and moisture damage. Moraes et al. (2011) investigated the feasibility of the BBS test for moisture damage characterization and results from these studies indicated that the BBS is a reliable test to investigate the moisture sensitivity of the material.

![Figure II-12: Bitumen Bond Strength (BBS) test equipment (Moraes et al., 2011).](image)

As indicated in Figure III-12, the BBS device is comprised of a portable pneumatic adhesion tester, pressure hose, piston, reaction plate and a metal pull-out stub. To start the test, the piston is placed over the pull-out stub and the reaction plate is screwed onto it. Then, a pressure hose is used to introduce compressed air to the piston. During the test, a pulling force is applied on the specimen by the metal stub. Failure occurs when the applied stress exceeds the cohesive strength of the asphalt binder or the bond strength of the asphalt-aggregate interface (i.e., adhesion).
IV. Evaluation of Oil Modification Effect on the Performance

Overview

It is well documented in the literature that oil modification has a softening effect on asphalt binder and thus it has been used to increase the workability of asphalt binder. However, detailed knowledge and understanding of the mechanisms of effect of the oil on the asphalt binder through a wide range of temperatures is lacking. In this chapter, neat and oil modified binders were evaluated by conducting different performance test at different temperatures to address the aforementioned deficiencies in the current state of knowledge.

1. High Temperature Performance

1.1 PG High Temperature Test

Research from the Strategic Highway Research Program (SHRP) suggested the use of complex modulus ($G^*$) and phase angle ($\delta$) as the index of properties related to the performance of the asphalt binders and using $|G^*|/\sin\delta$ to evaluate the high temperature performance of asphalt. In this section, $|G^*|/\sin\delta$ is used as an indicator of high temperature performance for material in the first test matrix. The results for original binders are shown in Figure IV-1.
Figure IV-1 shows that adding oil to asphalt binder decreases the high temperature properties, as expected. Also, the high temperature target for all type of oils was satisfied at 58 °C, and the optimum oil content was determined to reduce the neat binder high temperature grade by one 6°C grade increment. This figure depicts that the effect of different oils will be different on mechanical properties of the binder at high temperatures. It can found from Figure IV-1 that the RW-1 oil is the most effective one, reducing one grade with the addition of only 4 percent. Meanwhile, the aromatic oil is the least effective oil which needs to use 10 percent to reach optimum percentage. It should be mentioned that the purpose of oil modification is mainly enhancement of low-temperature performance. However, it is desirable that at the selected dosage, added oil does not have significant effect on high-temperature performance of the modified binder, thus any improvement at the low end of service temperatures will not be at the expense of significant loss of high temperature performance. In the next figure, the effect of different oil dosages on asphalt binder high temperature performance at original level of aging is shown.
Figure IV-2. Summary of HT PG data for different oil percentages.

Figure IV-2 shows the effect of increasing oil content on the high temperature performance of original asphalt binder. The effect on high-temperature performance of binder becomes stronger with an increase in oil content. These results confirm that the effect of different types of oils can be different. For
example, as shown in Figure IV-2 that at 5% oil content, bio-oil is reducing the G*/sin\(\delta\) of neat binder 25% more than the aromatic oil. Also this figure depicts that there may be an exponential relationship between oil content and stiffness of oil modified binders. This possible relationship will be more investigated and explained in the later chapter.

Furthermore, the PG test were done on the RTFO aged of neat and oil modified binders to investigate the oil modification effect on aging. The DSR test was run on the optimum oil content for oil modified binders and their G*/sin\(\delta\) was determined at 58 °C and 64 °C, as was done for the original binder. Figure IV-3 shows the summary of these results.

![Figure IV-3. Summary of HT PG data for RTFO aged binders.](image)

Figure IV-3 confirms that the selected optimum oil content for oil modified binders also satisfies the criteria for RTFO binders (shown with a dashed line) at 58 °C. In order to investigate the oil modification effect more comprehensively and avoid being biased, combination of VA base binder and some of the oil were tested at high and low temperature too. The results for original binders with VA base binder are shown in Figure IV-4.
**Figure IV-4.** Summary of HT PG data for original binders with VA base binder.

*Figure IV-4* shows that the optimum oil content is different for the same oil type but with different base binder. This figure depicts that the effect of oil modifiers are very similar for both base binder and they only have slight different optimum percentages. It can found from *Figure IV-4* that adding oil to asphalt binder would decrease the high temperature properties as it was shown for FH base binder as well.

Furthermore, comparison *Figure IV-3* with *Figure IV-1* can reveal that the aging susceptibility of neat binder will be changed due to the incorporation of oil additives. This matter is discussed further in the next figure. In *Figure IV-5*, in order to calculate the aging susceptibility of oil modified binders, the ratio of $|G^*|/\sin\delta$ of RTFO-aged binder to that of the unaged binder (referred to as “Aging Index” herein) was calculated for the binders, as shown in the figure below. The aging index is important because it shows the aging susceptibility of the material, in practical terms it provides insight into the development of stiffness at different periods of pavement service life. If a material has higher aging susceptibility, it will gain stiffness faster through the time and its properties would deteriorate in faster pace. Therefore, typically materials with less aging susceptibility are more desirable.
These results show that age hardening is changed when the binder is modified with oil additives and the aging effect of different oils are not the same. The difference in aging index for different oils comes from their different chemical components. The bio-oils demonstrate the most aging susceptibility among other types, this result is related to the higher volatile content in bio-oils. Figure IV-5 indicates that neat binder age hardening remained constant when the binder is modified with aromatic or naphthenic oil while it is increased when it is modified with paraffinic oils. The least aging susceptibility was observed for refined waste oils as both types used caused a decrease in aging susceptibility relative to the base binder. This may be attributed to the fact that these materials add some fractions to the asphalt medium which is not part of the normal low molecular weight fraction of conventional asphalt binders, thus the presence of these new compounds improves the aging susceptibility of the composite material. Also, RW-1 oil is refined motor oil that assumes has less aging susceptibility due to its original function. It should be mentioned that these aging indices are influenced by both extender oil concentration and extent of aging.

Figure IV-5. The Ratio of $|G^*|/\sin\delta$ of RTFO-aged to unaged Binder.
1.2 Multiple Stress Creep and Recovery (MSCR) Results

The Multiple Stress Creep and Recovery (MSCR) test was developed as a replacement for the existing AASHTO M-320 high-temperature binder test. The results from the MSCR test may also be used as an alternative to various PG plus tests used to assess rutting resistance of binders. In addition to characterizing fundamental properties, the MSCR is an easy-to-use performance-related test. Equipment for testing of the binders was focused on the existing dynamic shear rheometer (DSR). In its final shape, according to AASHTO TP70 standard “Standard Method of Test for Multiple Stress Creep Recovery (MSCR) Test of Asphalt Binder Using a Dynamic Shear Rheometer (DSR)” or American Society for Testing and Materials standard (ASTM D 7405), the test consists of 10 cycles of 0.1 kPa stress creep and recovery, followed immediately by another 10 cycles of 3.2 kPa stress creep and recovery. Each cycle consists of one second of loading and 9 seconds of recovery upon instantaneous unloading. The non-recoverable creep compliance, $J_{nr}$, and the percent recovery, $R\%$, are two of the parameters calculated from the measured strain under different stress cycles (D’Angelo et al., 2007). However, latest researches suggested to use 30 number of cycles and also include 10 kPa stress level to the current test procedure to increase the accuracy of the results (Bahia et al., 2011; Golalipour, 2011).

MSCR test was conducted for neat and oil modified binders and $J_{nr}$ and percent recovery reported for each binder at different stress levels. The non-recoverable compliance ($J_{nr}$) for 0.1 kPa is calculated by divided the strain after 30 cycles to 0.1 kPa. Equations (IV-1) and (IV-2) show the calculation method for $J_{nr}$ at 0.1 kPa (AASHTO TP 70).

$$J_{nr}(0.1, N) = \frac{\varepsilon_{10} - \varepsilon_0}{0.1} \quad (IV-1)$$

$$J_{nr0.1} = \frac{\text{SUM}[J_{nr}(0.1,N)]}{10} \quad \text{for } N = 1 \text{ to } 30 \quad (IV-2)$$

where,

$$\varepsilon_{10} = \varepsilon_r - \varepsilon_0$$
ε_r = strain value at the end of the recovery portion (i.e., after 10.0 s) of each cycle strain
ε_o = initial strain value at the beginning of the creep portion of each cycle.

The definition for the J_{nr} at 3.2 kPa and 10 kPa are analogous. Also R% is calculated based on following equations at 0.1 kPa in MSCR test (AASHTO TP 70):

\[
ε_r(0.1, N) = \frac{(ε_1 - ε_{10}) \times 100}{ε_1} \quad \text{for } N = 1 \text{ to } 30 \quad (IV-3)
\]

\[
R_{0.1} = \frac{SUM[ε_r(0.1, N)]}{10} \quad \text{for } N = 1 \text{ to } 30 \quad (IV-4)
\]

where,

ε_{10} = ε_r - ε_o

ε_1 = ε_c - ε_o

ε_c = strain value at the end of the creep portion (i.e., after 1.0 s) of each cycle strain
ε_r = strain value at the end of the recovery portion (i.e., after 10.0 s) of each cycle strain
ε_o = initial strain value at the beginning of the creep portion of each cycle.

The definition for the R% at 3.2 kPa and 10 kPa are analogous. The MSCR procedure was performed for the oil modified binders, following the procedure described in chapter 3. As previously discussed, the J_{nr} parameter is suggested as a measure of the binder contribution to mixture permanent deformation and the R% is believed to have some effect on rutting resistance as well (D’Angelo et al., 2007; Golalipour, 2011). The Figure IV-6 shows the summary of these results.
Figure IV-6. The MSCR summary results for neat and oil modified binders at their PG temperature.

Figure IV-6 shows that oil modification has damaging effect on rutting resistance since it is reducing the stiffness of the binder. Also it can be seen that some of bio-oils show slightly better rutting performance by having lower \( J_{nr} \) values in comparison with others. The other important point that can be
observed is that oil modification does not have any effect on percent recovery. Modifiers such as polymers significantly increase the recovery by forming cross-linked high-elasticity networks across the binder. Thus the percent recovery has been used to indicate the presence of elastomer modification to their effect on elasticity. However, these results indicate that the oil modification is not affecting recovery and thus the mode of its effect is different from polymer modification.

Another important factor that can be calculated from MSCR test is $J_{\text{nr}}$-diff. This parameter is an indicator of stress sensitivity (AASHTO TP 70). This is an important matter because it depicts the nonlinearity level of the material behavior and rutting in modified asphalt binders that can be highly dependent on stress level. Therefore, $J_{\text{nr}}$-diff was calculated between 0.1 kPa and 3.2 kPa as well as between 3.2 kPa and 10 kPa. Figure IV-7 shows the summary of these results.

![Figure IV-7](image)

**Figure IV-7.** Stress sensitivity of $J_{\text{nr}}$ compared between different stress levels.

It is clearly seen that comparing the higher stress levels (3.2 kPa and 10 kPa) yields a much higher percent difference, thus capturing a higher degree of stress sensitivity in the binder behavior than was apparent by only testing at the standard lower stress levels. Figure IV-7 depicts that the oil modification does not have significant effect on non-linearity of the material at low stress levels, however it significantly increases the stress sensitivity at higher stress levels in comparison with neat binder. It can
also be seen that the $J_{in}$ diff values for neat binder and oil modified are similar at low stress levels. This similarity confirms previous research which concluded that the extender oil material demonstrates linear behavior at these stress levels. (Mooney, 1995; Honary and Richter, 2011). It should be mentioned that PP-2, RW-1 and RW-2 oils also show higher non-linearity degree in comparison with neat binder at lower stress levels.

2. Intermediate Temperature Performance

Pavements are thought to be most susceptible to fatigue damage during springtime. During thawing of snow and ice in the spring, granular layers underlying the asphalt surface become saturated. Saturation reduces load carrying capacity, leading to high stresses and strains in the asphalt layer(s) (Huang, 2004). Therefore, fatigue testing of asphalt pavements is typically conducted at intermediate temperatures corresponding to spring conditions.

2.1 Intermediate Temperature PG Test (Dynamic Shear Rheometer)

Fatigue cracking typically occurs at intermediate pavement temperatures. The fatigue cracking parameter, $|G*| \cdot \sin \delta$, was determined on the assumption that fatigue cracking is a strain controlled phenomenon. The SHRP researches considered fatigue as a strain controlled phenomenon because it is common case in thin pavements. The current Superpave specification for binder fatigue resistance was developed under the assumption that a softer, more elastic binder will reduce fatigue cracking. The specification places a maximum limit of 5,000 kPa on $|G*| \cdot \sin \delta$, (where $|G*|$ is the complex shear modulus and $\delta$ is the phase angle), measured at a strain amplitude of 1% and frequency of 10 rad/sec in the DSR. Table IV-1 shows the summary of these results for oil modified binders.
Table IV-1. Intermediate temperature results for oil modified binders.

<table>
<thead>
<tr>
<th>Asphalt type</th>
<th>Oil Modifier type</th>
<th>Intermediate temperature (PAV aged)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Temp. °C</td>
</tr>
<tr>
<td>FH (PG 64-22)</td>
<td>N/A</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>PA</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>PP-1</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>PP-2</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>PN</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>BO-1</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>BO-2</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>BO-3</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>RW-1</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>RW-2</td>
<td>19</td>
</tr>
</tbody>
</table>

These results confirm that based on the current PG criteria, all neat and modified binders are passing the fatigue limit at their intermediate temperature. Also it can be seen in this table that the \(|G^*|\sin\delta\) values for these binders are in the similar range. Some of the oil like RW-1 and RW-2 are reducing the stiffness of the binder at the PAV aging level which is beneficial for fatigue life based on the Superpave assumptions.
2.2 Linear Amplitude Sweep (LAS) Test (Dynamic Shear Rheometer)

The LAS is used to evaluate the ability of an asphalt binder to resist fatigue damage by applying cyclic loading at increased amplitudes in order to accelerate damage. The LAS test protocol consists of two steps: in the first step the rheological properties are measured while the damage characteristics of the binder are measured in the second step. For comprehensive fatigue characterization of asphalt materials, a model relating applied load and fatigue life is often derived. Obtaining such a model allows for consideration of pavement structure (i.e., applied load amplitude) and traffic (i.e., number of cycles to failure). Asphalt binder demonstrate a well-defined relationship between load amplitude and fatigue life ($N_f$) as follows (Monismith, et al., 1970):

$$N_f = A \gamma^B$$  \hspace{1cm} (IV-5)

where,

$\gamma$ = load amplitude

$A, B$ = material dependent properties.

A schematic of Equation (IV-5) is provided in Figure IV-8 (Hintz, 2012).
In this research, the same approach as Viscoelastic Continuum Damage Mechanics (VECD) used to analyze the LAS data for this study. The damage intensity corresponding to a 35% decrease compared to the initial $|G^*|\cdot \sin \delta$ was selected as the failure criteria, in accordance to recommendations made in AASHTO TP 101. Since the intermediate temperature grade of the base binders was 25 °C, it was decided to run all LAS tests at this temperature to be able to compare improvement or deterioration of the modified binder response in comparison to the base binders. LAS analysis results in a fatigue life power law as a function of strain amplitude. The summary of the results in terms of cycles fatigue failure for 2.5% and 5.0% strain amplitude are shown in Figure IV-9.

![Figure IV-9. Number of failure value in LAS test at different strain level conducted at 25C.](image)

The results show that the most of the oil additives increase the fatigue life and improve the fatigue resistance at different strain levels. These data confirm that the oil modification has a possible potential of improving the fatigue resistance. The PP-1 paraffinic oil modified binder shows the best performance and it is followed by PN, RW-1 and BO-1 oils. On the other hand, the performance of the BO-2, PP-2 and RW-2 oil modifications of the FH-based binder deteriorated compared to the base binder LAS performance.
3. Low Temperature Performance

3.1 Low Temperature PG Test (Bending Beam Rheometer)

Mechanical performance tests were performed at low-service temperatures using the Bending Beam Rheometer to determine if the change in stiffness at high temperature resulting from adding oil to asphalt medium translates into measurable performance improvement at low service temperatures. Figure IV-10 shows the BBR test results for PAV aged neat and modified binders.

Figure IV-10. BBR creep results at different temperatures for neat and modified binders.
It can be inferred from Figure IV-10 that introducing oil into asphalt can decrease the stiffness and increase the m-value significantly; these changes are beneficial to improve low temperature performance of asphalt binder. It can be seen that except aromatic oil modifier, all other extenders improve the low temperature performance by one grade as both stiffness and m-value criteria at -18 °C are satisfied. Although the aromatic oil decreased the high temperature performance grade by one grade, it did not improve low temperature performance grade due to failure of the stiffness criterion. This can be explained by the high aging susceptibility of this material which resulted in significant aging after PAV long term aging effect, consequently increasing the stiffness significantly. Also, this effect of aging becomes more clear for BO-1 oil which has the highest aging index among all the oils. This oil has the lowest stiffness at high temperature but at low temperature, it ranked 8th among the tested binders due to its high level of age hardening. However, this type of oil has one of the highest m-values, indicating a rapid rate of modulus relaxation, which is highly important for stress relaxation due to thermal contraction.

Another important factor to be considered is the effect of temperature. It can be seen in Figure IV-10 that by increasing temperature by 6°C, the binders stiffness increasing significantly. This type of behavior is more apparent for BO-1 modified oil which its stiffness increased by double when the temperature drops from -18 °C to -24 °C. This indicates that when temperature drops sharply, the thermal stress of this oil also will increase sharply, which makes pavement tend to crack more easily. It is expected that the improvement in low temperature properties of the oil modified asphalt binder would result in reduced pavement low temperature cracking due to the general reduction in binder stiffness and increase of m-value. In order to compare the effect of oil modification on low temperature properties more clearly, some of the oils were selected to show in Figure IV-11.
Figure IV-11. Effect of oil modification on BBR creep stiffness and m-value results at different temperatures.

The trend of change of the BBR creep stiffness and m-value with temperature is shown in Figure IV-11. Figure IV-11 clearly shows a trend similar to that observed at higher temperatures, in which
introducing oils into the asphalt binder decreased the stiffness, as well as increasing the m-value significantly. Both of these changes are believed to be beneficial in terms of the low temperature performance of binder. Addition of the paraffinic petroleum oils, PP-1 and PP-2, and the refined waste oils (RW) had the most significant effect on reduction of the creep stiffness of binder more significantly than the other three kinds of oil. However, considering m-value, the PP-1 and BO-1 oils are observed to result in the highest improvement in the rate of modulus relaxation.

To investigate the effect of base binder on low temperature properties, some oil combinations with VA base binder are also tested and the BBR test results are presented in Figure IV-12.
Figure IV-12 shows that the effect of oil modifiers are quite similar for both base binders. It can be seen in Figure IV-12 that introducing oil into asphalt decreases the stiffness and increases the m-value significantly and the ranking of oil modifiers are almost the same as FH base. It can be seen that except aromatic oil modifier, the rest improves the low temperature performance by one grade and they are satisfying both stiffness and m-value criteria at -18 °C.

Although, the aromatic oil decreased the high temperature performance grade by one grade, it couldn’t improve the low temperature grade as it failed the stiffness criteria. This can be explained by aging susceptibility of this material which was high and due to long term aging effect, its stiffness increased significantly and it didn’t pass the criteria. Also, this effect of aging becomes more clear for BO-2 oil which has the highest aging index among all the oils. This oil has the lowest stiffness at high temperature but at low temperature, similar the effects on stiffness were less severe as it ranked near the middle relative to other modifiers. This difference in behavior is related to the relatively high level of age hardening for binders modified with this material. This results showed that the aging susceptibility can be a very important factor in low temperature properties and thus, it was decided to conduct the BBR test on
original binder and calculate aging index as described in the high temperature section for selected materials. The BBR test was conducted at -12 °C and -18 °C for unaged samples of four oil modified binders (one from each category) plus neat binder and the aging index was calculated for all of them. **Figure IV-13** presents the aging index for these binders at low temperature for PAV-aged to unaged condition.

![Figure IV-13](image)

**Figure IV-13.** The Ratio of stiffness of PAV-aged to unaged Binder.

These results show that age hardening is changed when the binder is modified with oil additives and the aging effect of different oils are not the same. These results are in agreement with results presented in **Figure IV-5** for aging index of RTFO-aged materials. As it can be seen in **Figure IV-13**, the bio-oils demonstrate the highest aging susceptibility this is an indication of the higher volatile content in this oil. The least aging susceptibility was observed for refined waste oil. The ranking of the aging susceptibility for these materials at PAV-aged level is the same as RTFO-aged confirming that aging susceptibility is a material characteristic and it will affect in the same trend at different aging levels and temperatures.
2.2 Low Temperature Fracture Test (Single Edged Notched Beam)

Asphalt binder low temperature fracture behavior was evaluated using the Single Edged Notched Beam (SENB) device. The SENB test was conducted for neat and oil modified binders at -12 °C which corresponds to the low temperature grade of the neat binder, thus enabling comparison to the fracture properties of neat and oil modified binders. Since the thermal cracking issue is the target, the SENB test was conducted on the PAV material to be able to simulate real field conditions. The fracture load was determined as the peak load occurring during the test, and the fracture deformation was the corresponding deformation at the peak load. The fracture energy was measured as the area under the load-deformation curve up to the point of failure. Depending on the binder type and test temperature, failure can occur at the peak load or at a lower load after the peak. Figure IV-14 shows the summary of the SENB results for neat and oil modified binders.

![Graph showing filtered maximum load for different binders](image-url)
Figure IV-14. Maximum load and toughness parameters calculated from SENB test at -12 °C.

Figure IV-14 depicts that oil modification does not significantly improve the maximum load that the binder can take in the fracture mode due to the fact that oil modified binder has less stiffness. This also cause the lower toughness of oil modified binder in comparison with the neat binder. However, the important parameters regarding fracture behavior is the maximum displacement and total energy which shows binder ductile behavior and tolerance against failure. Summary of the measured parameters are shown in Figure IV-15.
Figure IV-15 shows that adding oil to neat binder decreased low-temperature stiffness and increased the strain tolerance. It is observed that the oil additives extended the post peak fracture resistance, and significantly increased deformation to failure. Fracture load did not change significantly with oil modification but the total failure energy and displacement at maximum load increased significantly.
However, some of the oils could not improve the fracture properties and that is believed to be due to their higher aging susceptibility. Since the SENB test was conducted on the PAV-aged material, the stiffness of some oil modified binders increased tremendously and that affects their ductile behavior.

In general, these results indicate a possible improvement in low-temperature performance by adding some types of oil modifiers (generally refined waste and paraffinic petroleum based) due to the fact that oil modification decrease stiffness of the binder and improve its ductile behavior. Therefore, a number of oil modification is concluded to be a good candidate to use to improve the low temperature properties. However, the type of the oil should be selected optimally such as to limit the adverse effect on high temperature performance and aging susceptibility.

4. Rheological Properties

To have a complete characterization of the asphalt binder, as a viscoelastic material, asphalt binder must be tested over a wide frequency range (loading times) and temperatures related to actual traffic loads and pavement temperatures. By expressing this behavior with a mathematical model, the responses can be reduced to a limited number of variables. Furthermore the mathematical model allows calculating the response of binders at loading times and temperatures other than those directly measured. The mathematical model of an asphalt binder could also be used for the prediction of pavement performance. Therefore, frequency sweep test for oil modified binder as well as neat one was employed, and the complex modulus master curves of results are generated at the reference temperature of 28 °C based on the time-temperature superposition principle. Time-temperature superposition (TTS, also frequency-temperature superposition) is a well-known procedure frequently applied, either to determine the temperature dependence of the rheological behavior of a material or to expand the time or frequency regime at given temperature at which the material behavior is studied. The master curve is fitted using the following equation (Anderson et al., 1994):
\[ G^* = G_e^* + \frac{G_g^* - G_e^*}{[1 + (f_c / f^-)^{k}]}^{m_e/k} \]  

(IV-6)

Where:

- \( G_e^* \) = Equilibrium Complex Modulus when frequency tends to zero
- \( G_g^* \) = Glassy Complex Modulus when frequency tends to \( \infty \)
- \( f_c \) = location parameter
- \( f^- \) = Reduced Frequency
- \( k, m_e \) = Shape parameters.

**Figure IV-16** shows a typical master curve and the rheological parameters including glassy moduli, \( G^*_g \), crossover frequency, \( \omega_c \) or crossover time, \( t_c \), and rheological index, \( R \). Because different asphalt binders can show different master curve shapes, these parameters could be used to characterize asphalt binders.
The glassy modulus, $G^*$, is the value that the complex modulus or stiffness modulus approaches at low temperatures and high frequencies or short loading time (normally 1 GPa). The steady-state viscosity, $\eta_0$, is indicative of the steady-state of the asphalt binder which is asphalt specific. The frequency at a given temperature where $\tan \delta = 1$ is the crossover frequency, $\omega_c$. At this point, the storage and loss moduli are equal. The crossover frequency can be considered a hardness parameter that indicates the general consistency of asphalt at the selected temperature and is asphalt specific. The crossover frequency is the reciprocal of the crossover time, $\omega_c = 1/ t_c$. Finally the difference between the glassy modulus, $G^*$, and the complex shear modulus at the crossover frequency, $G^*(\omega_c)$ is the rheological index (R). The rheological index, which is asphalt specific, is directly proportional to the width of the relaxation spectrum and indicates the rheological type (Anderson et al., 1994).

In the construction of a master curve, using time-temperature superposition or method of reduced variable, data is first collected over a range of temperatures and frequencies. A standard reference temperature must be selected. Generally, when analyzing viscoelastic data for asphalt binders, a reference temperature between 25 °C to 30 °C is used. The data at all temperatures is shifted horizontally, with respect to time of loading, until the curves merge into a single smooth function. The shifting may be done based on any of the viscoelastic functions. In this study the William-Landall-Ferry (WLF) shift factors were applied to construct the master curve. The WLF Equation is described by the following relationship:

$$\log \alpha(T)d = [-C_1 (T-T_d)]/[C_2 + (T-T_d)]$$

(IV-7)

Where:

$\alpha(T)d$ = the horizontal shift factor relative to the reference temperature, $T_d$
$T$ = the test temperature in C or K
$T_d$ = the reference temperature from which the data is shifted, in C or K
$C1$ and $C2$ = empirically determined constants.
In Equation (IV-7), the C1 and C2 are material dependent fitted constants. Summary of neat and oil modified binders master curves are shown in Figure IV-17.

**Figure IV-17.** Summary of master curve results for neat and oil modified binders.
Figure IV-17-a shows the typical fitting results of master curve for asphalt binder. The complex modulus curves of original neat and oil-modified binders are shown in Figure IV-17-b. Despite the constraint on the fitting of the shift factors, R-squared values are well above 98% for all neat and oil modified binders. These results clearly depict the difference in rheological properties of neat binder in comparison with oil modified binders. Also it can be seen that different oils has different effect on master curve of binder. Figure IV-17-b shows that BO-2 and RW-2 oils have most significant effect on binder behavior and it affects the high and low temperature properties more significant than other type of oils meanwhile the PA oil has the least effect on the master curve and has highest complex modulus among other oil modified binders as it was shown in previous sections as well. Furthermore, it can be understood from oil modified binders master curves that the most apparent effect of the oil is on the stiffness of the binder and temperature susceptibility. As it is shown in Figure IV-17-b, all oils decrease the stiffness of the asphalt binder by reducing the complex modules values and increase the slope of the master curve which represent the higher temperature susceptibility. Another point that can be raised is that the difference between complex modulus of neat and oil modified binders is larger at high temperature rather than low temperature which means some of oils may not be as effective at low temperature as they damage the high temperature properties. This point should be carefully considered in selecting different oil types for different application.

As it was discussed previously, aging effect is one of the important factor that should be paid attention to when investigating the oil modification influence. To investigate the effect of oil modification on aged asphalt binder rheological behavior, RTFO-aged sample of oil modified binders were tested for each oil modifier at optimum concentration. To explore the change in the properties of asphalt binder, master curve of oil modified binders at short term aging level were constructed. Figure IV-18 shows the summary of these results for oil modified binders.
It can be seen in Figure IV-18 that regardless of aging level, the effect of oil modification on base binder is apparent. However, the results depict that the difference between neat binder with oil modified binders is reduced in comparison with unaged results. This can be related to the fact that oil modifiers usually increasing the aging susceptibility of the material and causing faster stiffening rate upon aging. Also, the effect of aging appears to reduce the values of slope and intercept of the fitting function of the temperature shift factors; this shows that the aged binder is less temperature susceptible than unaged one. RW-1 oil shows the most change compare to neat one rather other oils and this may be explained by type of this material. RW-1 is refined waste motor oil and this type of product has usually low aging and temperature susceptibility. This factor may counted as a bonus for oil modifier since this material can be less temperature sensitive which has been one of the concern about asphalt binders. It should be noted that in general, all of oil modified binders express very similar rheological behavior at their optimum concentration.
Comparing Figure IV-17-b and Figure IV-18 can give an indication of aging index discussed earlier in this chapter. The results show that the aging index value is higher at high temperatures and as temperature decreases this value decreases too. Therefore, material shows higher aging index value at higher temperature rather than low temperature at the same aging level. It can be seen in the master curve that the difference at high temperature is larger value and as the temperature approached toward the low temperatures, this gap gets smaller. However, this trend is not the same for different oil modified binders since they show different aging and temperature susceptibility. Furthermore, the aging index values would significantly increase if the aging level goes from RTFO to PAV.

Moreover, to investigate the effect of oil content on asphalt binder rheological behavior, different percentage of oil contents were used for each oil. To explore the change in the properties of asphalt binder, master curve of oil modified binders at different percentages were constructed. Figure IV-19 shows the summary of these results for RW-1 oil modified binders.

**Figure IV-19.** Summary of master curve results for aromatic oil modified binders at different concentration.
It can be seen from Figure IV-19 that with the increasing of the oil content, the complex modulus master curve shift to down gradually and the complex modulus become smaller in the whole frequency zone. Typically, the properties shown in high frequency (low frequency) present the properties of binder at low temperature (high temperature). Therefore, it can be inferred from this figure that oil can damage the high temperature performance but improve low temperature performance, and with the increasing of the oil content, this effect will become more significant. These results confirm that the main oil additive effects on asphalt binder are reducing the stiffness and increasing the temperature susceptibility of these materials.

5. Moisture Sensitivity and Damage

Investigating the moisture damage in asphalt binders and evaluating the right combination of materials that are resistant to moisture is important to prevent pavement degradation. The asphalt binder characteristics can influence both the adhesion of the asphalt-aggregate system and the cohesion of the binder. The properties of the asphalt binder that can influence the asphalt-aggregate bond are the chemistry of the asphalt (e.g., polarity and constitution), viscosity, film thickness, and surface energy (Bahia et al., 2007; Xiau et al., 2007). The cohesive strength of the asphalt in the presence of moisture is also influenced by the other factors such as chemical nature of the binder and processing techniques.

The aggregate surface and pull-out stubs are cleaned completely to remove moisture and dust which could affect adhesion. After cleaning process, the pull-out stubs and the aggregate plates are heated in the oven at 145 °C for a minimum of 60 min to remove absorbed water on the aggregate surface and provide a better bond between the asphalt binder and the aggregate. In this study, the granite was selected as aggregate type for this test. Then stubs are removed from the oven and an asphalt binder sample is placed immediately on the surface of the stub for approximately 10 s. Then, the aggregate plate is removed from the oven and the stub with the asphalt sample is pressed into the aggregate surface firmly until the stub
reaches the surface and no excess of asphalt binder is observed to be flowing. The stubs need to be pushed down as straight as possible and twisting needs to be avoided to reduce the formation of trap air bubbles inside the sample and to minimize stresses. **Figure IV-20** shows the picture of some BBS prepared samples.

![Figure IV-20](image)

**Figure IV-20.** BBS prepared samples before testing.

Before testing, dry samples are left at room temperature for 24 hr. For wet conditioning, samples are first left at room temperature for 1 hour to allow for the aggregate-binder-stub system to reach a stable temperature. Then, samples are submerged into a water tank at 40°C for the 96 hr conditioning time. After conditioning time is completed, samples are kept at room temperature for 1 hr before testing (AASHTO TP-91). **Figure IV-21** shows the summary of BBS pull-off strength results for neat and oil modified binders.
The average pull-off strength was calculated from four replicates. As shown in the Figure IV-21, the conditioning of specimens in water did not cause a significant reduction in strength and, in most cases, the pull-off strength stayed almost constant by taking into account the variability of the test results. These results clearly show that the pull-off strength of oil modified binders were decreased in comparison with the neat one and this is related to the lower stiffness. The stiffness and viscosity of the asphalt binder does play a role in the propensity of the asphalt mixture to strip. It has been reported that asphalts with high stiffness and viscosity resists displacement by moisture better than those that have low stiffness and viscosity (Kanitpong and Bahia, 2003). Asphalts with high stiffness usually carry high concentration of polar functionalities that provide more resistance to stripping (Bahia et al., 2007). Although most of binder pull-off strengths stayed constant after condition in the water, some of them showed improvement in the results. It is very interesting to see that PP-1, PP-2, BO-3, RW-1 and RW-2 oils improved the pull-off strength after 96 hr conditioning in the water. The chemical interaction between the asphalt binder and the aggregate is critical in understanding the capability of binders to resist moisture damage. These results may be explained by the theory that the chemical interaction is still going on between oil and base binder which leads to better performance after condition. Also, aging effect can be significantly critical in this
matter since materials were kept in the water bath at 40 °C for four days and that may cause oil modified binders to age and gain some stiffness which results in higher pull-off strength.

Furthermore, it is very important to look at the failure type for oil modified binder at both dry and wet condition. In the dry condition, all the binders showed the cohesive failure which is very typical failure in this condition. Cohesive failure happens due to the rupture of bonds between molecules in the asphalt film. On the other hand, adhesive failure happens due to rupture of bonds between molecules of different phases on the interface of the two materials. The effect of moisture on the performance of the pavement can be the result of the combination of both mechanisms. After 96 hr of conditioning in the water, all of the binders showed cohesive failure except BO-3 oil modified binders which showed failure in stub. Figure IV-22 shows pictures of these failures.

![Figure IV-22. Pictures of BBS failures types.](image)

Based on the failure of BO-3 oil modified binders, the improvement of this binder is questionable since the failure happened as stub failure not cohesive or adhesive. Different factors can cause this failure such as not hot enough rocks or stubs, wrong sample preparation, chemical reaction between this oil and water, etc. However, the results for four oils (PP-1, PP-2, RW-1 and RW-2) showed improvement after water conditioning and the their failure types was cohesive for both dry and wet conditions.
In order to remove any possible confounding effects due to the effect of different stiffness on the cohesive strength, it was decided to use a procedure recommended by Moraes et al. (2012) by normalizing the results to iso-stiffness condition.

Frequency sweep test data was used to calculate the complex modulus of different binder at the typical range of temperatures in the laboratory (25 °C). At this temperature, an oscillatory strain of 1% was applied at 1.59Hz frequency to obtain a measure of complex modulus |G*| within the linear viscoelastic range of the material. Considering the iso-testing temperature of asphalt binders and by interpolating between the frequency sweep test temperatures, the |G*| is equal to 1 MPa was chosen as iso-stiffness of each asphalt binder to perform the analysis. Using the equations below presented for dry (Equation IV-8) and wet (Equation IV-9) conditioning to estimate Pull-off Tensile Strength (POTS) at the iso-stiffness condition at the determined iso-stiffness temperatures (Moraes et al., 2012).

\[ \Delta POTS = 1.14 \Delta G^* \]  
\[ \Delta POTS = 0.82 \Delta G^* \]

where

\[ \Delta POTS = POTS_{Iiso-Temp} - POTS_{Temp} \]
\[ \Delta G^* = |G^*|_{Iiso-Temp} - |G^*|_{Temp} \]

In equations above, the data for G* at testing temperature (25 °C) was obtained using master curve data. By performing this analysis procedure, the pull-off strength at iso-stiffness condition for both dry and wet conditions were calculated and the results are shown in **Figure IV-23**.
Figure IV-23. BBS pull-off strength for neat and oil modified binders for dry and wet condition at iso-stiffness state.

Figure IV-23 shows very similar trend to experimental results and it can be seen that most of the binder do not show significant difference between dry and wet condition results. Also, these results confirm that the PP-1, PP-2 and RW-1 oils are improving the moisture resistance of base binder and they can be very good options to modify asphalt binder in the area with cold temperatures and excessive rains and snows. To show the effect of water on the bond strength of an asphalt-aggregate system better, moisture sensitivity was also evaluated by means of POTS due to immersion of the asphalt-aggregate system in water for the conditioning time.

$$\text{Loss of bond strength (\%)} = \frac{(\text{POTS}_{\text{dry}} - \text{POTS}_{\text{wet}})}{\text{POTS}_{\text{dry}}}$$  \hspace{1cm} (IV-10)

Using the equations above presented for evaluation of change in pull-off strength due to conditioning (Moraes et al., 2012), the results were calculated and presented in Figure IV-24.
Figure IV-24 shows the change in strength of bonding in the material after 96 hr of water conditioning at 40 °C. Since the standard criteria for coefficient of variation for this test is 10%, it can be concluded that most of these binders did not show any significant change due to water conditioning. However, it is shown that PP-1, PP-2 and RW-1 oil modified binders still show improvement after normalizing the data for iso-stiffness condition. This result can be explained due to the fact that the chemical composition of paraffinic oil has more polarity and that can help significantly for moisture damage. The RW-1 improvement can be related to its function as motor oil that typically they are hydrophobic and the effect of water on them is very minimal. These three binders can be a very good candidate for cases that needed moisture resistance.
V. Investigation of Oil Effect on Viscoelastic and Thermal Properties of Asphalt Binder

Overview

Thermally induced cracking of asphalt pavement continues to be a serious issue in cold climate regions as well as in areas which experience extreme daily temperature differentials. Improving binder low temperature fracture and stiffness properties continues to be a subject of particular concern. Therefore, in this chapter, the oil effect on viscoelastic and thermal properties of asphalt binder is investigated.

In the first section, different rheological results of oil modified binders are captured and tried to explain the results in regarding the oil properties. The second part is dedicated to thermal properties and how oil modification would affect them. Therefore, this chapter focuses on investigating the effect of low temperature behavior of oil modified asphalt binder on the thermal stress and strain build-up due to thermal cycles. Furthermore, using developed analytical procedure, the strain and stress prediction of oil modified binder is conducted. Defining a failure criteria and the effect of aging are another main parts of this chapter.

Introduction

There is widespread recognition that asphalt binders play a key role in mixture behavior and pavement performance. Accumulated stress in asphalt binder, as a consequence of low temperature conditions, is believed to be mainly responsible for the thermal cracking of asphalt pavements. There have been attempts to introduce modifiers to improve low temperature properties of asphalt binders. One of these modifiers which get a lot of attention is oil additive. Although several researchers have tried to investigate the rheological properties of oil modified binders, most of them focused on the performance
part and not studying the fundamental effect of this additive on the asphalt binder molecular structure. Therefore, there is an essential need to look how this material effect the binder.

1. Oil Effect on Properties of Asphalt Binder Viscoelastic Properties

1.1 High and Low temperature Properties

In this section of study, materials in second test matrix were used to investigate the oil modification effect on asphalt binder properties when the same percentage of different oils are used. DSR test were conducted for the neat and oil modified binders likewise the previous chapter. Figure V-1 shows the results of high temperature PG grade for all three binders at both original and RTFO aged levels.
Figure V-1. High temperature performance grade values for neat and modified binders.

Figure V-1 shows that at the same oil content, the aromatic oil reduce the stiffness of neat binder more than paraffinic oil and the refined waste motor oil is the most effective one in reducing the stiffness. It can be seen that by adding 5% paraffinic oil, the PG grade of modified binder would remain at 64 °C meanwhile adding the same amount of other oils cause one degrade of binder high temperature PG. This result can be related to the oil properties which depends on molecular structure and free volume. It can be said that RW-1 oil decrease the base binder stiffness more significantly rather than the other oils. This result can be in alignment with studies in material science which present that for enhancing the stiffness, the free volume should be minimized (Tsuie et al., 2006). Moreover, it can be found from Figure V-1 that this trend will remain the same even after aging. It can be seen that the RTFO aged binders shows similar trend that RW-1, BO-1, aromatic and paraffinic oils have more significant effect in reducing the stiffness respectively. To explore the effect at low temperatures, BBR tests were conducted for PAV aged of neat and modified binders. Figure V-2 presents the summary of these results.
Figure V-2 depicts that the raking of the stiffness stayed the same as high temperature results. This results indicate that all these binders fail the PG criteria at -18 °C except the RW-1. It can be seen that RW-1 oil has better effect in reduction of asphalt binder stiffness rather than all the other oils and just by adding 5% of that, the binder passes the stiffness criteria at -24 °C. It should be mentioned that the difference between aromatic oil modified binder stiffness with paraffinic one is reduced and this can be related to their different aging susceptibility. Aromatic oil may have more volatile components in its molecular structure and this cause more age hardening and hence a higher increase in stiffness. This statement is also correct about BO-1 oil since its stiffness increased more than any other oil modified binders after long term aging.

1.2 Rheological Properties

To get the whole picture of the oil rheological properties in comparison with the asphalt binder, the frequency sweep test is needed to conduct for these materials. Therefore, frequency sweep test for oils as well as neat binder was employed, and the complex modulus master curves of results are generated at the
reference temperature of 28 °C based on the time-temperature superposition principle (TTSP). Master curves constructed based on the frequency sweep test results are shown in Figure V-3.

It can be seen from Figure V-3 that slope of oil curve is significantly steeper than the asphalt binder. This indicates that the temperature susceptibility of oil material is higher than binder and adding oil to asphalt binder will increase the molecular mobility and temperature susceptibility as it was seen in the experimental data. Typically, the properties shown in high frequencies represent the properties of material at low temperature and properties at low frequencies exemplify high temperature. It can be seen in the figure that there is significant difference between oil and binder results at low frequencies which means enormous difference in stiffness at this range. Therefore, it can be inferred from this figure that oil can damage the high temperature performance by reducing the stiffness but improve low temperature performance. Figure V-3 shows that the PA and PP-3 master curves are similar and the BO-1 and RW-1 are close to each other as well. This means that these oil should have similar effect on asphalt binder which was shown in high and low temperature results that BO-1 and RW-1 depicts similar data at 5%.
2. Oil Effect on Thermal Volumetric Properties of Asphalt Binder

2.1 Glass Transition and Thermal Coefficients

Researchers findings indicate one of the results of increasing in free volume is an increase in molecular mobility and hence the temperature susceptibility of the material would be altered (Meijer and Govaert, 2005). To investigate this more in details, it is decided to perform glass transition test for neat binder and oils. To be able to run the \( T_g \) test for oil material, some minor details of the \( T_g \) sample preparation process was changed to accommodate its fluidity. To estimate the glass transition temperature, the traditional approach is to fit an asymptote to the high temperature portion of the relation and another asymptote to the low-temperature portion. The slope of the first asymptote represents the coefficient of thermal contraction above \( T_g \), called \( \alpha_l \), while the slope of the second is the coefficient of contraction below the \( T_g \), called \( \alpha_g \). The intersection of the two linear asymptotes is \( T_g \). A typical example of this plot is shown in Figure II.1.

The following hyperbolic equation, which has been used to fit binder thermo-volumetric properties (Bahia and Anderson, 1993), was applied to the neat binder and oils data, and found to be effective to fit to our test data.

\[
\nu = C_v + \alpha_g (T - T_g) + R(\alpha_l - \alpha_g) \ln\{1 + \exp[(T - T_g) / R]\}
\]  

(V-1)

Where:

\( \nu \) = specific volume change in ml/g

\( C_v \) = a constant, having no physical significance

\( T_g \) = the glass transition temperature

\( \alpha_g \) = slope of lower asymptote of the \( \nu \) versus Temperature curve

\( \alpha_l \) = slope of upper asymptote of the \( \nu \) versus Temperature curve

\( R \) = a parameter representing the curvature between asymptotes.
Using the above equation, glass transition parameters were calculated for neat binder as well as aromatic and paraffinic oils. Table V-1 shows the summary of these results.

Table V-1. \(T_g\) results for neat binder and oil additives.

<table>
<thead>
<tr>
<th>Material</th>
<th>(T_g) (°C)</th>
<th>(R)</th>
<th>(\alpha_l)</th>
<th>(\alpha_g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat Binder</td>
<td>-10.00</td>
<td>8.06</td>
<td>8.18E-04</td>
<td>3.84E-04</td>
</tr>
<tr>
<td>PP-3 Oil</td>
<td>-36.70</td>
<td>9.12</td>
<td>1.08E-03</td>
<td>2.57E-04</td>
</tr>
<tr>
<td>PA Oil</td>
<td>-28.20</td>
<td>15.37</td>
<td>1.27E-03</td>
<td>3.95E-04</td>
</tr>
</tbody>
</table>

As Table V-1 shows, the coefficient of contraction above the \(T_g\) temperature, \(\alpha_i\), is very different between the binder and the oils. Due to the fact that BO-1 and RW-1 oils are soluble in alcohol, it was not possible to run \(T_g\) test on these oils by themselves. As it was expected, the \(\alpha_i\) of the oil additives is significantly higher than the neat binder which represent higher temperature susceptibility. This result indicate that the oil additive has more molecular mobility due to possible presence of more free volume in its structure and that will cause its higher temperature susceptibility. Also the \(T_g\) temperature of oil additive is much lower than the asphalt binder which is related to their chemical component. Although it should be mentioned that the glass transition temperature of oils in this calculation may not be very accurate due to the very large transition area of the oils and the small lower asymptote. To explore this effect in more depth, the \(T_g\) test was performed for oil modified binders as well. Figure V-4 compares the \(T_g\) and \(\alpha_i\) of unaged modified binders with neat binder.
Figure V-4. $T_g$ results for neat and modified binders.

Figure V-4 shows that the $T_g$ of oil modified binders were decreased due to the contribution of oil component in asphalt medium. Also it can be seen that the $\alpha_l$ was increased for all oil modified binders in comparison with neat binder which indicates increasing the temperature susceptibility (time dependency).
of the material. This observation confirms that oil introduction to asphalt medium can result in asphalt stiffness reduction and lower $T_g$ temperature. It is interesting to see that $T_g$ temperature of PP-3 oil is lower than the PA one although their ranking for other properties was reverse. This can be explained due to the fact that glass transition temperature is affected different factors such as chemical component which can be very different for these two oils. Figure V-4 shows also that RW-1 has the lowest $T_g$ and highest $\alpha_t$ which means RW-1 is the most effective oil so far regarding low temperature properties. Furthermore, increase in free volume will alter the molecular mobility which affects the temperature susceptibility of the material. Higher temperature susceptibility will show itself in thermal coefficient of contraction as well as m-value. Figure V-5 shows the m-value parameters for neat and oil modified binders.

![Figure V-5. BBR m-value results at different temperatures.](image)

Figure V-5 shows that the oil modification increases the m-value of neat binder at the wide range of low temperatures due to change in chemical component and free volume. Hence, the time dependency of material is in increased as well. Also, it can be seen that the aromatic oil has more significant effect on m-value rather than paraffinic one and the ranking of the oil modified binders are the same as viscosity. RW-1 oil modified binder shows the best results for m-value and it almost passes -24 °C criteria as well. Another important point is that the temperature susceptibility of the oil modified binders are different. For
example, RW-1 shows the least temperature susceptibility since its m-value does not change dramatically due to the change in temperature from -18 °C to -24 °C meanwhile this change is more significant for BO-1 oil. This can be very good characteristic for RW-1 oil modified binder in comparison with the rest.

2.2 Physical Hardening

The time dependent hardening of asphalt binders has been recognized and studied in asphalt binders extensively. Time dependent hardening was observed near the glass transition temperature of asphalt binders during the Strategic Highway Research Program (SHRP) contract A002-A and was referred to as “physical hardening” by the researchers (SHRP A-369 report 1994; Bahia, 1991; Claudy et al., 1992). It was shown that this phenomenon causes an increase in the asphalt binder stiffness when stored at a constant low temperature.

Although many researchers agree upon the effects of physical hardening, there is some disagreement about the exact mechanism responsible for this phenomenon as well as the temperature range in which physical hardening occurs (Bahia, 1991; Bahia and Anderson, 1991, 1992, 1993; SHRP A-369 report 1994). Studies by Doolittle (1951a, b) showed that the internal mobility of amorphous materials is better related to the free volume rather than temperature. Based on this concept, Struik (1978) described the occurrence of physical hardening to be the consequence of isothermal reduction of free volume at temperatures close to the glass transition temperature. However, in the asphalt community, some researchers have reported on the dependence of the hardening rate on the chemical composition of the asphalt binder and some other attributed this phenomenon to the rate of collapse of inter-molecular “free volume” in the binder, as described by Struik for amorphous materials (Struik, 1978; Bahia, 1991; Bahia and Anderson, 1993).

Since oil modification may affects both free volume and chemical component of the asphalt binder, it is necessary to look into physical hardening for oil modified binders. Therefore, it was decided to study
the oil effect on physical hardening. Material from both test matrix 1 and 2 were stored at -12 °C, -18 °C and -24 °C for 72 hr and the stiffness and m-value of BBR beams were measured at 1, 4, 24, 48 and 72 hr intervals. In this section, first the results from first test matrix which includes all the oils at their optimum percentages are shown and the main effect of oil on physical hardening will be discussed. Afterwards, to look more deeply in relationship between oil characteristics and physical hardening phenomenon, the results of oil modified binders from second test matrix are discussed to investigate the physical hardening for different oils at the same percentage. Figure V-6 shows the physical hardening results of BBR beams for neat and oil modified binders at -12 °C.

(a) Stiffness change trends at isothermal condition
Figure V-6 shows that the stiffness of the asphalt binder is increasing when it kept at isothermal condition and this change in stiffness reducing by increasing time span. Moreover, the m-value of the binders are decreasing over time when they being kept at the same low temperature for long time. These results are in accordance with Struik studies as well that he showed that physical hardening causes an increase in stiffness and a reduction of the stress relaxation capacity in amorphous materials like asphalt binders (Struik, 1978). Also, it is interesting to see that after 48 hr, the stiffness and m-value change curves are almost getting to the plateau and it can be seen that the stiffness value and m-value are getting constant almost after 48 to 72 hr. To investigate the effect of oil modification on the physical hardening more clearly, it is needed to calculate the change in stiffness and m-value at different condition time in comparison with 1 hr standard measurement. This calculation helps to compare the changes due to physical hardening between neat binder and oil modified binders. Figure V-7 shows the physical
hardening effect on stiffness value changes of BBR beams at different temperatures for neat and oil modified binders.

(a) Stiffness percent change at -12 °C

(b) Stiffness percent change at -18 °C
Figure V-7. BBR stiffness physical hardening percent changes at different isothermal conditions for oil and neat modified binders.

The results show that the increase is very sharp at the beginning of isothermal condition and then it is reduced until it flattens. Figure V-7 depicts that oil modification is increasing the physical hardening in comparison with neat binder. It is shown in Figure V-7 (a) that the neat binder has the lowest percent change in stiffness and BO-2 shows the worst behavior in this regard. The most similar behavior to neat binder belongs to BO-1 oil modified binder which shows almost the same trend at lower temperatures such as -18 °C and -24 °C. Figure V-7 (b) and (c) show that there is a trend for binders in changing stiffness due to conditioning at different temperatures. The interpretation of this trend is that the stiffening phenomenon becomes faster when testing temperature is decreased. This may be in agreement with the concept that physical hardening is driven by the excess of free volume (i.e. internal energy) when cooling the binder below or close to $T_g$. Thus, a possible explanation is that, when quenching the binder from room temperature, a lower temperature implies a wider deviation from the thermodynamic equilibrium. Furthermore, it can be said that the reason for decreasing the stiffness change slope after 48 hr is due the
fact that binder is reaching its equilibrium and the molecular structure finds its stable configuration and the change is free volume is minimizing. It should be mentioned that the results depicts that the physical hardening happening below and above the glass transition temperature as it was reported by other researchers as well (Anderson and Marasteanu, 1999).

In order to see the direct relationship between oil type and physical hardening, material from second test matrix were tested for physical hardening at three temperatures and different conditioning time the same as previous part. **Figure V-8** shows the physical hardening effect on stiffness value and m-value changes of BBR beams at different temperatures for neat and 5% oil modified binders at -12 °C.

![Stiffness percent change at -12 °C](image)
Figure V-8 shows that the physical hardening effect is different for different oils even at the same oil content and the stiffness change rate is larger for oil modified binders than the base one. Figure V-8 (a) depicts that the ranking of physical hardening is not the same as the other oil modified properties. This reveals that the physical hardening is affected different factors including free volume, chemical components, etc. Other interesting result is related to the change in m-value due to isothermal conditioning. Figure V-8 (b) shows that all the oil modified binder except PP-3 decreasing the m-value reduction due to physical hardening and this can be very important for thermal cracking. Since m-value is the capability of the material to relax the stresses, it is critical to have higher m-value at long winter to avoid cracking problems.

In general, these results confirm that oil modification alter physical hardening of the base binder and this effect should be considered in order to estimate the effectiveness of oil modification. The results depict that adding oil to asphalt medium causes increase in the stiffness of asphalt binder in long period of
isothersmal conditioning and this effect can be different for different oils. Also, the data shows that oil modification can decrease the m-value loss due to the physical hardening effect.

All of these results may be explained by free volume theory. The Free volume concept indicate that amorphous materials consists of volume occupied by molecules and inter-molecular free volume. The free volume concept is not new idea and it has been the focus of thousands of researches in material science. The idea that the resistance to flow in a liquid depends upon the relative volume of molecules present per unit of free-space is a concept that is intuitively acceptable.

Doolittle (1951) explained that the viscosity and the resistance of material against flow is directly related to the free space in material structure. He also indicated that the free volume has a direct effect on glass transition behavior of the material. Consequently, this concept was used by many researchers to explain material behavior such as temperature dependency. Different studies indicated that the increase in free volume will result in an increase of molecular mobility and hence the temperature susceptibility of the material would increase (Bondi, 1951; Argon and Bessonov, 1977). Furthermore, it has been shown that how the damping and creep properties of the material depend on aging properties, that is, on the preceding decrease in free volume (Struik, 1977; Heijber, 1978). Following the prove of direct relationship between free volume and molecular mobility, it was found that relaxation modulus in polymers are connected with molecular mobility, and therefore we shall consider what types of molecular motion are possible in the glassy state, and how these motions manifest themselves in the mechanical behavior (Heijber, 1978).

In general, oil modification results show that by adding oil additive to asphalt medium, the stiffness of the material decreases meanwhile the temperature susceptibility increases. Also, it was shown that oil modification decreases the glass transition temperature and it has an effect on physical hardening by increasing the rate of hardening at different range of low temperatures. It appears that oil modification may have an effect on free volume of asphalt binder and introducing oil additive to asphalt binder
medium may increase the free volume. However, this study does not have any direct measurement of free volume due to the complexity of the asphalt binder molecular structure and it can be beneficial to investigate this concept for oil modification more in depth and details in future.

3. Thermal Stress and Strain Analysis for Asphalt Binder

Investigating the effect of oil modification on thermal stress and strain of asphalt binder is significantly critical to select appropriate material to avoid premature thermal cracking in pavements. The mechanism of failure has been described based on the idea that cracking will occur when the thermal stress build-up reaches the strength of asphalt material. In order to calculate the stress and strain build-up accurately, it is needed to conduct several test at low temperatures to cover all the aspects of thermal cracking. Due to the fact that thermal cracking happens during the service life of pavement, all the tests for this part were conducted on the PAV-aged material to simulate the real field condition. The following analytical process is used in this study to predict thermal stresses due to cooling cycle for oil modified binders.
Figure V-9. Summary of analytical method used to predict thermal stresses.

In this method, BBR and \( T_g \) results of oil modified binders used to numerically predict stress induced by thermal cycles. Stiffness in BBR results were used to construct stiffness master curve to convert to relation modulus (Marasteanu, 2002). Master curves were obtained for two purposes: first, to compare the stiffness and the corresponding relaxation modulus master curves and, second, to calculate thermal stresses. All the calculations were performed with Excel spread sheets developed by the author. The stiffness master curves were generated by fitting the Christensen–Anderson–Marasteanu (CAM) model to
the BBR stiffness data obtained at two temperatures (Marasteanu, 2002). Note that (creep) stiffness is the simple inverse of the fundamental viscoelastic creep compliance function. The version of the CAM model for stiffness is as follows:

\[ S(t) = S_{\text{glassy}} [1(t/t_c)^w]^{-w/v} \]  

Where:

- \( S(t) = \text{Stiffness at time } t \)
- \( S_{\text{glassy}} = 3 \text{ GPa } \)
- \( t_c = \text{crossover time} \)
- \( w,v = \text{shape parameters in the model.} \)

The curve fitting was done in the log (stiffness) versus log (time) domain, and the results were converted back to stiffness and time domains. The reference temperature was the higher of the three test temperatures for each binder, which was also equal to the corresponding PG low-temperature of neat binder. Plots of the required analysis to calculate the stiffness master curves at -12 °C are shown in Figure V-10.

![Stiffness Mater Curve](image-url)
Figure V-10. Summary of stiffness master curve constructed for 5% PA modified binder.

Figure V-10 shows that the fitted master curve and the temperatures used for BBR testing. It can be seen that the fitting curve is in a good agreement with experimental data and there is no significant deviation. Stiffness master curve can show the viscoelastic behavior of asphalt binder at low temperatures and the trend of temperature effect on asphalt properties. Figure V-11 shows the comparison of these data for PAV-aged of neat and oil modified binders.

Figure V-11. Stiffness master curve for neat and oil modified binder.
It is shown in Figure V-11 that after adding oil, the stiffness of binder is decrease significantly, and with the reduced time increasing, the stiffness of all asphalt binders are increased. These changes can make the thermal stress of oil modified binder is smaller than neat asphalt when temperature drops which can reduce the risk of low temperature cracking. Comparing these results, it can be concluded that oil modification can affect the stiffness significantly but the degree of influence varies with the type of oil. For example, comparing the stiffness of BO-1 oil modified asphalt and PA oil modified asphalt in Figure V-11, indicate that the stiffness of BO-1 oil modified asphalt is smaller than PA oil modified asphalt and this difference is getting more significant by increasing reduced time. This means that BO-1 may show less stress build-up since the stiffness master curve has a significant effect on stress build-up of asphalt binder due to thermal cycles. The most significant oil modification effect on stiffness belongs to RW-1 oil modified binder which showed quit distinctive results in previous sections in comparison with other oils. This binder has shown one of the best performances in regards of low temperature results and probably has the most beneficial effect on neat binder.

The experimental creep compliance data should be converted to relaxation modulus for the next step of analysis. There are two main modeling techniques that could be used to fit rheological data collected for viscoelastic materials. The first technique uses mechanical analogue in which response is modeled in terms of the basic material behaviors: elastic, plastic, and viscous. Each of these basic responses can be given a mechanical analogue such as a spring, a dashpot, or a slider. Various configurations of springs and dashpots in series or parallel can be used to model viscoelastic behavior. The combination of generalized Maxwell and generalized Kelvin-Voigt model known as Burger model is among the most widely used mechanical analogues for asphalt material. The other technique is using the phenomenological models in which a selected mathematical formulation is fitted to the data and the values of the parameters in the formulation are derived based on the statistical fitting routines.

The advantage of mechanical analogue modeling is that the mathematical derivatives and integrals have been fully developed and thus closed-form solutions could be utilized. In addition, physical
meanings could be given to the model parameters such as the spring elastic modulus, the dashpot viscosity, and the relaxation time of the combination of them. Mathematical formulations such as the Prony series can fit such models like Burger model and simplify the solutions of conversions and integrals. Therefore, the experimental creep compliance data were converted to relaxation modulus by using the Prony series algorithm, which numerically solves the convolution integral where $E(t)$ is the relaxation modulus and $D(t)$ is the creep compliance. The converted data were then fitted with CAM model for relaxation modulus, which is identical to Equation (V-2) except that $S$ is replaced by $E$. The relaxation modulus master curves for 5% PA oil modified asphalt binder is shown in Figure V-12.

![Figure V-12. Relaxation Modulus Master Curve of 5% PA modified binder.](image)

As expected, $S$ and $E$ are almost identical at very short times, where the slopes of $S(t)$ and $E(t)$ on a double logarithmic scale are close to zero. As the time increased, $E(t)$ became increasingly smaller than $S(t)$. The slopes of log $E(t)$ and log $S(t)$ versus log(t) were simply calculated as the first derivative of the corresponding fitted models.

The literature review of the failure properties of asphalt binders and mixtures, indicate that for many viscoelastic materials failure can occur, not only by reaching the strength, but also by reaching failure strain (known as ductility as well). Strain at failure is an indication of brittleness or ductility of materials, which is considered an important failure property. It is believed that this failure property is as important
as strength in many engineering applications and the strain at failure can be very sensitive to temperature and strain rate. It is therefore needed to take into consideration the effect of temperature on strain and strain rate of oil modified binders to have a comprehensive picture of their behavior at low temperatures.

The relationship between temperature variation and induced stress free deformation is a requirement in the prediction of thermally induced stresses and strains. Thermal deformation of elastic materials is nearly a linear function of temperature in the temperature range of interest. For asphalt materials however, since there exists glass transition and it is a fact that glass transition temperature is usually within the temperature range of interest, a linear approximation of the thermal deformation is no longer appropriate. Better modeling of the nonlinear relationship between the temperature and the deformation is essential. Due to the nature of the glass transition of viscoelastic materials, the curve of thermal deformation versus temperature exhibits a nearly dual-linear shape. Glass transition test was conducted for all the material at PAV-aged condition and these results were incorporated to make strain temperature curve for modified binders. Figure V-13 shows the summary of $T_g$ results for neat and modified binders at PAV aging level.

![Figure V-13. Summary of $T_g$ results for neat and oil modified binders at PAV aging level.](image)

The results presented in Figure V-13 shows that the aging would decrease the $T_g$ of asphalt binder. This can be explained with change in chemical components of asphalt binder like the asphaltenes and
resins fractions. During the oxidative aging process, the glass transition behavior of the neat binder is
dominated by the aromatic and resins fraction. In chemical terms, aging leads first to a decrease in
aromatic content and subsequent increase in resin content, together with a higher asphaltene content leads
to decrease in $T_g$ (Wei et al., 1996). Subsequently, the analytical method that discussed earlier is used to
calculate the thermal strain build-up by integrating glass transition test data. Figure V-14 shows the
summary results of this process for 5% PA modified binder as an example.

Figure V-14. Summary of analytical method used for 5% PA modified binder for $T_g$ results.
The same analytical process was done for the rest of oil modified binder to be able to compare the effect of different oils on thermal strain build up for modified asphalt binders. Figure V-15 shows the summary of these results for all neat and oil modified binders.

![Figure V-15. Summary of analytical method used for strain induced due to thermal cycles.](image-url)
As can be seen in Figure V-15, the thermal strain results for different oil modified binders are significantly different from each other and the base binder. The strain curve of the base binder is higher than the all oil modified binders which shows that the base binder is very susceptible to thermal cracking at low temperatures. Although the oil content was 5% for all oils, it can be seen that there is significant difference in their behavior. PP-3 oil modified binders shows the most strain induced values due to thermal cycles and the RW-1 has the lowest one. Higher value for thermal strain is not desirable because if the strain of material increases fast due to thermal cycles, it will reach its strain tolerance faster and it will crack sooner. The material which shows the least thermal strain has better ductile behavior and this gives this material the capability of more deformation under thermal cycles. There results confirm that this analytical method is capable of detecting differences in thermal and rheological behavior of different oil modified binders and it can be used to calculate thermal stresses and strains.

4. Measuring Stress and Strain at Failure for Asphalt Binder

The asphalt binder failure properties can be measured using the SENB as introduced in previous chapters. The failure stresses obtained in this test are considered as the strength of the oil modified binders. To have a better evaluation of failure properties, the samples for neat and oil modified binders were tested at three temperatures similar to the BBR results. Three replicates for each oil modified asphalt were tested at each temperature, and the results of SENB parameters are shown in Figure V-16.
(a) Maximum load

(b) Toughness
Figure V-16. Summary of SENB failure test for neat and oil modified binders.

Figure V-16 presents the summary of SENB test results at three temperatures for the base and oil modified binders. As shown in Figure V-16-a, the maximum load that sample tolerated is increasing with lowering of the testing temperature. This trend is logical since the stiffness of the material is increasing by going to lower temperatures, and it would be harder to break the material. This is also valid for the
trend of KIC parameter shown in the Figure V-16-b. The toughness of the materials show increase with decreasing the temperature. However, this increase in maximum load and toughness is different for different oil modified binders and is related to the temperature susceptibility. It can be seen that maximum load is increasing significantly from -18 °C to -24 °C for some of the materials and this may affect the thermal cracking behavior of them.

In general, two important results from SENB test should be considered in terms of resistance of binders to cracking: maximum displacement and fracture energy. These two parameters are directly related to failure behavior of asphalt binders and they depict material cracking potential due to thermal cycles. Maximum displacement is a critical parameter since it represents level of ductile behavior of asphalt binders. Higher maximum deflection indicates a more ductile behavior under thermal cycles before it reaches its strain tolerance. It is shown in Figure V-16-c that this parameter decreases by lowering the temperature. This is related to the fact that at lower temperatures, materials gaining more stiffness and their behavior changes from ductile to brittle. This trend can be seen in Figure V-16-c for all neat and oil modified binders. However, the results depict that oil modification has significant positive effect on the ductile behavior of base binder. It can be seen that most of oil modified binders show improvement of maximum displacement at lower temperatures which is very beneficial in avoiding premature thermal cracking. The second important factor is total failure energy. This parameter shows the amount of energy that should be applied to the sample until it breaks. To select the better material in terms of fracture properties, the more fracture energy is desirable since it means that the material would tolerate more amount of stress or strain before its total failure. As presented in Figure V-16-d oil modification increases the failure energy and makes binder more suitable for low temperature applications.

Equation (V-3) and (V-4) were used to calculate the stress and strain at failure based on the principles of a three point flexural beam.
\[ \sigma_f = \frac{3PL}{2bd^2} \]  

(V-3)

\[ \varepsilon_f = \frac{6Dd}{L^2} \]  

(V-4)

where:

\( \sigma_f \) = Stress in outer beam at midpoint, (MPa)

\( \varepsilon_f \) = Strain in the outer surface, (mm/mm)

P = load at a given point on the load deflection curve, (N)

L = Support span, (mm)

B = Width of test beam, (mm)

d = Depth of tested beam, (mm)

D = maximum deflection of the center of the beam, (mm).

Table V-2 includes a summary of the results of SENB data analysis for failure stress and strain for neat and oil modified binders. The results show that the failure strain decreases by lowering the test temperature meanwhile the failure stress is increasing. The rate of these changes are different for neat and oil modified binders, and the temperature effect can be significant for some of the binders. The RW-1 oil modified binders show the highest strain and stress failure in comparison with the neat and other oil modified binders.
Table V-2. Summary of SENB failure stress and strain for neat and oil modified binders.

<table>
<thead>
<tr>
<th>Temp C</th>
<th>PAV-aged</th>
<th>SENB Test</th>
<th>Calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Binder</td>
<td>Max Load (N)</td>
<td>Displacement at Max Load (mm)</td>
</tr>
<tr>
<td>-12</td>
<td>Neat</td>
<td>3.05</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>5% PA</td>
<td>2.38</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>5% PP-3</td>
<td>2.37</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>5% BO-1</td>
<td>1.84</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>5% RW-1</td>
<td>1.37</td>
<td>0.66</td>
</tr>
<tr>
<td>-18</td>
<td>Neat</td>
<td>3.20</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>5% PA</td>
<td>3.60</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>5% PP-3</td>
<td>2.99</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>5% BO-1</td>
<td>3.32</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>5% RW-1</td>
<td>2.32</td>
<td>0.36</td>
</tr>
<tr>
<td>-24</td>
<td>Neat</td>
<td>3.37</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>5% PA</td>
<td>4.30</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>5% PP-3</td>
<td>3.82</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>5% BO-1</td>
<td>3.67</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>5% RW-1</td>
<td>3.69</td>
<td>0.21</td>
</tr>
</tbody>
</table>

4.1 Viscoelastic Approach

As previously discussed, the SENB failure energy, $G_f$, includes energy dissipation due to formation of crack surfaces and also due to viscoelastic creep; the fraction of each component is dependent on material properties and test conditions. In order to determine the proportions of each energy dissipation mechanism, Tabatabaee and Bahia (2013) introduced the concept of pseudo-strain to analytically determine the time-independent failure energy. Analysis of viscoelastic materials using pseudo-variables is based on the application of the “elastic-viscoelastic correspondence principle”. Use of this principle allows the separation of the time-dependency from the constitutive equations describing the deformation of viscoelastic materials (Lakes, 2009; Kim, 2009), as well as fracture behavior in time-dependent materials (Schapery, 1984).
Using the approach described in Tabatabaee and Bahia (2013), the loading curves for the studied binders were transformed to their corresponding pseudo-elongation curves. The pseudo-elongation curves enabled the calculation of Time-independent strain energy \( (G_{TI}) \) as the area under load-pseudo-elongation curve normalized to the ligament area. The difference between the time-independent strain energy and the total failure energy is taken to represent energy dissipated through creep and viscous flow, referred to as “time-dependent failure energy” in this study. An example of this transformation is shown in Figure V-17 at -12°C, for the neat binder.

**Figure V-17.** Example of pseudo-deformation transformation of SENB load-deformation curve for neat binder at -12 °C.

Figure V-17 shows clearly that part of sample deformation is due to time-independent behavior. This result depict that the load values is not affected by viscoelastic analysis and this new approach helps only to differentiate between time-dependent and time-independent deformation and to calculate the ratio of elastic (time independent) part to viscous (time dependent) part and explore the nature of the ductile behavior of material under the SENB test conditions. Using the pseudo-deformation procedure the total failure strain of the studied binders were analyzed at -12 °C, allowing for a clear comparison between different oil modified binders as shown in terms of time-independent and total deformation at failure in Figure V-18.
Figure V-18. Time-independent and Total displacement at failure plotted for neat and oil modified binders at -12 °C.

Figure V-18 shows that the neat binder has the lowest pseudo-deformation at failure, which depicts the lowest time-independent strain tolerance. The comparison depicts that although the total behavior of these binders varies, their time-independent deformation at failure almost stays the same as the neat binder. This means that the failure strain ranking of all binders is almost the same. Furthermore, The results in terms of ratio of time-independent strain to total strain are shown in Figure V-19.
Figure V-19. Ratio of time-independent to total strain plotted for neat and oil modified binders at -12 °C.

Figure V-19 indicates that the PA oil has the highest ratio of pseudo strain which depicts the highest time-independent behavior that represent more elastic behavior. The RW-1 oil modified binder has lowest pseudo strain ratio which represents higher viscous behavior and thus the most ductile behavior. This analysis is helpful to explore the ductile behavior of oil modified binders under the SENB test and reveals the reason for large displacement of some of these binders.

Tabatabaee and Bahia (2013) showed that the comparison of binder failure energy components to mixture fracture performance indicate that there is no significant difference between the strength of the relationship between binder and mixture cracking resistance if the binder total failure energy is used, or just the time-independent component. Although breakdown of the failure energy into specific components for derivation of fracture mechanics parameters is of academic and research interest, it does not appear to be necessary for material comparison and rankings. The results of this study confirm these earlier findings and, therefore, it may be better to include the whole material behavior for failure criteria rather than only fraction of that.
4.2 Aging Effect

Aging of asphalt binders is induced by chemical and/or physical changes during the production of the pavement and throughout its service life. The process is usually accompanied by stiffening of the binders, which in general influences the deterioration of asphalt pavements. The most important modes of pavement failure that are significantly affected by aging are traffic loading induced fatigue cracking, thermally induced cracking, and moisture induced raveling (Lu and Isacsson, 2000). The chemical change that occurs in asphalt binders due to oxidative aging results in an increase of both viscous and elastic properties of the binder. Therefore, aged asphalt binder sustains high shear stress with deformation (high elastic stiffness), and it is unable to relax the stress through viscous flow (Jung, 2006). As a result, the pavement has a higher susceptibility to fatigue and thermal cracking. Therefore, the aging susceptibility of the material is important and critical factor in material behavior specifically at low temperatures.

As previously discussed, some of the oils increasing the aging index of neat binder which results in the significant stiffness increase and may cause some problems for low temperature performance. Therefore, it was decided to investigate the effect of aging on failure properties of oil modified binders. The SENB failure test was conducted for neat and oil modified binder at RTFO-aged and PAV-aged level at -12 °C. These results would help to look at the effect of aging on failure energy, $G_f$, and other failure properties from SENB test. Figure V-20 presents the summary of SENB results for neat and oil modified binders at two level of aging.
(a) Maximum load

(b) Toughness
Figure V-20. Summary of SENB failure test for neat and oil modified binders.

Figure V-20 presents the summary of SENB test results at two aging level for the base and oil modified binders. As it is shown in Figure V-20-a, the maximum load that sample tolerated is increasing by increasing aging level from RTFO to PAV. This trend is logical since the stiffness of the material is increasing by going to higher aging level and it would be harder to break the material. This is also valid...
for the trend seen in the Figure V-20-b. The toughness of the materials show increase with increasing the aging level. However, this increase in maximum load and toughness is different for different oil modified binders and that is related to the aging susceptibility. This characteristic of asphalt binder discussed extensively in this study and it is mentioned that the material with lower aging susceptibility is more ideal.

It is shown in Figure V-20-c that the maximum displacement would decrease by increasing the aging. This is related to the fact that at higher aging level, materials gaining more stiffness and their behavior changes from ductile to brittle. This trend can be seen in Figure V-20-c for all neat and oil modified binders. Also, it is presented in Figure V-20-d that oil modification increases the failure energy and makes binder more suitable for low temperature applications even after different aging levels. However, it is shown that aging may not be desirable for failure properties due the fact that increasing in aging level would decrease the flexibility of the material to deform under the load and this may decrease the failure energy as well.

5. Failure Criteria

The last step of this process is calculating thermal stress build up by using results from first section. For nonlinear viscoelastic materials, Schapery’s theory (1969) is capable of characterizing the mechanical nonlinearity. Because in solving stress problems, the analytical approach is rarely successful due to the difficulties in finding the infinite integral of the integrand, numerical procedures were developed to solve the following equation of the constitutive relationship (Zeng, 1997).

\[
\sigma(t) = \int_0^t E(\xi - \xi') \frac{\alpha(t')}{\tau} d\tau \\
\xi(t) = \int_0^t \frac{dt'}{\alpha(t')} [T(t')] 
\]
where:

- $\sigma(t)$ = Stress Buildup Function
- $t$ = present time
- $\tau$ = past time, a time variable ($0 \leq \tau \leq t$)
- $\xi$ = reduced time
- $\xi(t)$, a reduced time variable
- $E$ = the relaxation modulus
- $\alpha_T$ = the temperature shift factor
- $\varepsilon$ = strain.

In order to compute the stress using Equation (V-6) for the known strain and/or temperature histories, it is necessary to firstly compute the temperature dependent reduced time in Equation (V-5). Using a code in the MATLAB, the stress build up due to thermal cycle were calculated both for neat and oil modified binders. It should be mentioned that in this analysis the same strain rate as SENB test was used to be able to compare the results at the same condition. Figure V-21 shows the calculated stress build-up in this analysis.

Figure V-21. Summary of stress build up analysis for neat and oil modified binders.
The results show that the oil-modified binders have a better performance regards to stress build up phenomenon at cooling process in comparison with neat binder. It can be seen in Figure V-21 that the PA oil shows better performance than PP-3 oil and this can be related to its lower strain in T_g test and lower relaxation modulus. The thermal stress evolution is directly related to the relaxation modulus evolution; therefore, it appears that the m-value must play an important role in thermal stress accumulation. However, these results also indicated that the development of thermal stresses was significantly controlled by stiffness and to a smaller magnitude by m-value. Figure V-21 depicts that the RW-1 oil modified binders shows the lowest stress build-up due to thermal cycles that is ideal for a binder used in the pavement in cold region. However, this figure cannot tell the whole story about thermal cracking behavior of these materials at low service temperatures. Figure V-21 shows only stress build-up for the materials but it does not show how the failure of the material will happen. Therefore, it is needed to combine these results with Table V-2 data to define the failure point for each material and see if the failure happens due to stress or strain tolerance. Figure V-22 presents the results for failure stress and strain of the neat and RW-1 oil modified binder as an example.
The intersection of failure stress or strain line with build-up stress or strain is failure temperature which asphalt binder will crack due to thermal cycles. The neat binder results show that the failure temperature for stress criteria is around -12 °C meanwhile the strain criteria set the cracking temperature for -9 °C. Figure V-22 shows that RW-1 oil is improving both stress and strain criteria of base binder. For RW-1 oil modified binders, the cracking temperature would be around -30 °C based on the stress criteria but in the strain criteria, the cracking temperature is almost -14 °C. These results confirm that the RW-1 oil modification is improving the cracking properties of neat binder significantly. Also, it should be mentioned that for the RW-1 oil modified binder, the limiting criteria is failure strain not the stress. This result confirm that oil modification can be a very good candidate to improve the low temperature performance and properties of asphalt binder. The RW-1 oil incorporation to asphalt binder only for 5% results in almost 5 degree improvement in cracking temperature. Summary of cracking temperature of all oil modified binders in both criteria are shown in Figure V-23.
Figure V-23. Cracking temperature based on the stress and strain failure criteria for neat and oil modified binders.

Figure V-23 shows that oil modification is capable of improving the cracking resistance of asphalt binder even at low concentrations. The best performance of oil modified binder belongs to RW-1 oil modified binder as it expected from other test results. The important point that should be emphasized here is that the results reveal that the strain criteria is controlling factor for oil modified binders cracking temperatures. These results confirm that oil modifiers can be a promising material to use to improve pavement cracking issues in the cold regions besides the fact some of these materials are refined waste material that has low cost and usage of them will benefit the green mission of the countries.
VI. Prediction of Oil Modified Binder Performance Grade Properties

Overview

In this chapter, a model is proposed to predict the properties of oil modified binder based on the properties of its constituents. This model is relatively simple one based on the rheological properties of asphalt binder and oil. The hypothesis used for developing the model in this dissertation is that there is a linear relationship between oil content and rheological properties of oil modified binders. Furthermore, introducing the classification system as a criteria for oil modifiers is another main objective of this chapter.

Introduction

To effectively predict responses of the oil modified asphalt pavements due to different traffic loads and environmental conditions, the oil modification of asphalt binder should be characterized over a wide range of temperatures and loading times. Performance models for oil modified binders can lead to better selection of oil additive for asphalt modification and consequently achieve a better pavement performance. This is very important for cold climate conditions like those in the northern United States and Canada, where the asphalt pavement is the dominant component in performance of asphalt pavements.

1. Define a Relationship

There are some difficulties in characterizing viscoelastic materials such as asphalt binders. One difficulty is that properties of asphalt binders change over time (aging), and these changes might be different for various types of asphalt binder. Another difficulty is that the behavior of asphalt binder
should be characterized over a wide range of temperatures and loading times or frequencies. Finally, characterization of asphalt binder should address pavement distresses directly. The PG binder system, developed by the SHRP, considers these requirements with cyclic and creep tests over a wide range of temperatures and loading times on original and laboratory aged asphalt binders. Therefore in the present study it was deemed essential to investigate the relationship different properties with oil additive contents.

1.1 Performance Grade at High Temperatures

The first step for modeling of oil modified binders is to find the relationship between oil content and oil modified binder properties. To investigate the oil effect on high temperature performance of binders, different dosages of oils were introduced into the binder to prepare and test the oil modified binders for high temperature performance at 64 °C and 58 °C (grade temperature of the base and modified binders) with the DSR. The |G*/sin\(\delta\)| parameter and the continuous grading temperature are calculated according to ASTM D 7643-10 were selected for use as indicators of high temperature performance. The results for original binders are shown in Figure VI-1.

![Figure VI-1](image-url)  

(a) The relationship between oil content and (a) the G*/sin\(\delta\) rutting parameter at 64 °C, and (b) True PG Temperature for FH base.

In Figure VI-1, it can be seen that a semi-log relationship exists between oil content and the high temperature performance grade properties. Furthermore, it is observed that true performance grade has a
strong linear relationship with oil content and all R-squared values are higher than 98%. The next step is to find an appropriate model to be able to fit the experimental data. To validate this relationship and avoiding being biased with one base binder, the PH high temperature tests were conducted for VA base with other oils at different concentrations. **Figure VI-2** shows the summary of these results for PA and BO-2 oil.

**Figure VI-2.** Summary of high temperature results for two kind of oil modified binders with VA base binder.
Figure VI-2 depicts that slope of oil content versus log G*/sinδ is linear for VA base as well and this linear line can fit to experimental data adequately. Statistical analysis confirmed that the best correlation is achieved with linear line and this gives the highest R² and lowest standard error of means (MSE) values. Moreover, it should be mentioned that this result indicate the slope of the line is almost the same for two temperatures but it is different for different oils.

1.2 Performance Grade at Low Temperatures

To investigate the relationship of oil modified binder properties at low temperature with oil content, the m-value and creep stiffness measures were plotted against oil content, as shown for the example of one base binder and four oil additives in Figure VI-3. The BBR results are plotted on a semi-log scale against the oil content to derive possible relationships between these two parameters for development of low temperature grade predictive equations. It can be seen in that under the semi-log coordinate system the relationship between oil content and stiffness and m-value show very good liner relationship, with all R-squared values higher than 94%. It is observed that by increasing the oil content, the stiffness of binder is decreasing and the m-value is increasing.

Figure VI-3. The relationship between oil content and low temperature performance of the modified binder with FH base at -12 °C: (a) Relationship between stiffness and oil content, (b) Relationship between m-value and oil content.
To explore the validity of this linear relationship for other base binder, BBR test was conducted for PAV aged materials at different concentrations for all four oils. However, to be concise, just the results of PA and BO-2 oil is shown in Figure VI-4. The BBR stiffness and m-value were recorded at different oil content for each of the binders at -12 °C.

Figure VI-4 depicts that this linear relationship between log stiffness versus oil content is also satisfactory and fits very well to the experimental data for VA base binder. Furthermore, it can be seen
that the linear line can fit to m-value data too. This may be indication that the oil modification is mostly physical interaction of binder and oils rather than the chemical one. It should be mentioned that by increasing the oil content, the stiffness of binder is decreasing and the m-value is increasing. Based on the current specification, this indicates that the oil modification is improving the low temperature properties of asphalt binder.

1.3 Rheological Properties

To investigate the oil percentage effect on asphalt binder rheological properties more in depth, two rheological parameters (R and $\omega_c$) which explains the behavior of the material were calculated for neat and oil modified binders at different oil contents. The rheological index (R) is the difference of the log of glassy modulus to the log of complex modulus at the crossover frequency. As the R increases, the master curve will become more flat, indicating a more gradual transition from purely elastic behavior to steady-state flow. A high rheological index also means an increased delayed elastic behavior. In addition, R could show the energy storage of the binder during deformation. Asphalt binders with higher R-values will store more energy during deformation than asphalts with lower R-values, at similar modulus or compliance levels. The crossover frequency can be thought of as a location parameter for the master curve, and is indicative of the overall hardness of a given binder. The lower the crossover frequency at a given temperature, the harder will be the asphalt. Figure VI-5 shows the summary of the oil percentage correlation with these parameters for aromatic and bio-based oils.
Figure VI-5. Rheological Parameters versus oil content.

Figure VI-5 depicts the effect of oil concentration on rheological index (R) and the cross over frequency (\(\omega_c\)) for two different oils. These results show that by increasing the oil content, rheological index will decrease which can be translated to sharper transition from purely elastic behavior to viscous condition. Also increase in R value can be related to the MSCR results that oil modified binders showed more permanent deformation and less recovery capacity. Furthermore, it can be seen that the cross over frequency is increasing by introducing more oil content to asphalt binder which means reduction in the material hardness. Overall, these results confirm that increasing oil percentage would result in stiffness reduction of asphalt binder and increase the temperature susceptibility. Also it can be found from above figure that the relation of oil content with rheological parameters is linear and the linear fit explains very well the oil content effect on asphalt binder properties.

2. Obtain the Oil Rheological Properties

The next step is to find an appropriate composite model to be able to fit to these experimental data. Therefore, literature review in composite materials were conducted to find the most applicable composite
models which represent the oil modified asphalt binder. During the literature, it was recognized the to be able to use composite models, viscoelastic properties of each component is needed. Therefore, it was decided to conduct the tests to obtain these properties for oil additives. By using Bob and Cup, the results for oils high temperature performance and frequency weep test data were captured. Figure VI-6 shows the summary of master curve results for all the oils.

![Figure VI-6. Master curve results for oil materials.](image)

**Figure VI-6** clearly shows the difference between different oil properties at intermediate and high temperature range. It can be seen that different oils depict different rheological behavior and this makes significant change in properties of different oil modified binders. Therefore, the oil data captured in this range of temperatures can be used directly for any calculations. However, due to the temperature and torque limitations of DSR, it was not possible to obtain low temperature properties for oils. In order to obtain stiffness and m-value amounts, it was needed to find an analytical solution rather than actual experiments. Therefore, the following approach is proposed to determine low-temperature properties of oils by using the master curve data. **Figure VI-7** shows the analytical solution to determine oil low temperature properties.
Figure VI-7 shows the process used to construct complex modulus master curve of oil and then convert that to stiffness master curve. In this method, choosing right temperatures and frequencies in frequency sweep test is very critical since the whole picture of oil behavior should be captured to be able
to determine its low temperature properties accurately. To better understand the process, Figure VI-8 present the results of this process for PA oil.

![Master curve fit](image-url)
Figure VI-8. Summary of proposed analytical solution results for PA oil.
Figure VI-8 shows the analytical process used to use complex modulus master curve of aromatic oil to construct stiffness master curve. As it can be seen in the Figure VI-8 (a), at first it is needed to construct complex modulus master curve based on the experimental results. Using WLF shift factors, the data at different temperatures were converged to the same line as reference temperature (28 °C). Then, the complex modulus master curve can be converted to complex creep compliance. In the next step, the results should converted from frequency domain to time domain. This part was done though using proper equations presented in Figure VI-8. The last part of this process is to convert the creep compliance master curve in time domain to stiffness master curve in tome domain. Finally, the stiffness and m-value at desired temperature at 60 s can be determined. In Figure VI-8(c), the red point is the indication of stiffness at -12 °C at 60 s for PA oil. This figure shows that the desired point to determine stiffness and m-value is in the range of captured properties by frequency sweep test and there is no need for extrapolation. The same process was applied for other oils as well to obtain their low temperature properties. The next step is to use neat binder and oils properties at high and low temperature to predict oil modified binder performance using composite models in the literature. These composite models were selected based on their description in the literature (Daniel and Ishai, 1994; Lakes, 2009). The summary of these models fitted to the experimental data of aromatic oil are presented in Figure VI-9.
Figure VI-9. Summary of composite models results.

Figure VI-9 shows that the composite models are not able to predict the experimental results very well. The closest model fitting to experimental data is Hirsch model but this model cannot follow the trend of oil modified binders at different oil percentages. These results show that although oil modified binder is composite material but the classic viscoelastic composite models cannot be fitted to its experimental data. Therefore, it was decided to develop a phenomenological model based on the experimental data and validate the model with other results.

3. Phenomenological Model Development

3.1 High Temperature Data

As it was shown earlier, the linear relationship seems to be adequate to fit to the experimental data of oil modified binders. Based on statistical analysis of various combinations, the following model (equation VI-1) was found to best describe the experimental high temperature data as a function of oil content.
\[
\log \left( \frac{G^*}{\sin \delta} \right)_{\text{Modified}} = \left( \frac{G^*}{\sin \delta} \right)_{\text{Neat}} - x \left( \frac{\log G^*/\sin \delta}_{\text{Oil}} \right)
\] (VI-1)

where:

- \(G^*\) = Complex shear modulus
- \(\delta\) = phase angle (°)
- \(x\) = Oil content.

Using neat binder and oil properties at high temperatures, the model was fitted to oil modified binder data, as shown in Figure VI-10. As it can be seen in this figure, the correlation of fitted results to the model is very well. It can be found that this model predicts the properties of oil modified binders at different temperatures very well. It should be mentioned that there is slight deviation between model prediction and experimental results for some of the oils, specifically at higher oil contents, as shown in Figure VI-10. However, overall the model is shown to be capable of successfully predicting the oil modified binders based on the log-linear relationship between properties and oil content, as an initial estimate to aid designers in selection of appropriate oil dosage for binder modification.

**Figure VI-10.** Relationship between experimental results and model prediction of oil modified binders.
To validate the model accuracy, the data for VA base binder and oil properties at high temperatures were used in the model to fit to PA oil modified binders data. The summary of these results presented in Figure VI-11.

![Figure VI-11. Summary of developed model results for PA oil with VA base binder at different concentration.](image)

As it can be seen in this figure, the correlation of fitted results to the model is very well. It can be found that this model predicts the properties of oil modified binders at high temperatures adequately. In the next step, RTFO-aged neat binder properties and original oil properties used to predict RTFO-aged oil modified performance at different high temperatures. For the sake of brevity, an example of the relationships developed for only BO-2 oil is shown here.
Figure VI-12. Summary of developed models results without aging effect. RTFO aged Material- G*/sin\( \delta \).

**Figure VI-12** shows that the model prediction has significant deviation from experimental results due to the aging effect. It was shown earlier in this document that each oil has different aging susceptibility and this shortcoming in the model should be addressed. Also it is found that by increasing the oil content, this deviation becomes more clear. Therefore, it was decided to try aging the oil using the standard RTFO procedure for asphalt materials and use the RTFO-aged oil data to predict oil modified binder data more precisely. Number of different oils were aged using standard procedure for RTFO aging (ASTM D 2872, AASHTO T240). The RTFO-aged neat and oil data were used in the model to predict the oil modified binders. However, this effort was unsuccessful and the model still was incapable of accurate prediction. As an example, the data for one of the oils are shown in **Figure VI-13**.
Figure VI-13. Summary of developed models results, RTFO aged Material- G*/sinδ, PP-1 Oil.

It is shown in Figure VI-13 that although the oil material was aged in standard procedure for the asphalt binder, the model prediction is still not accurate. The reason is that the procedure aging is specifically designed for materials like asphalt binder with high viscosity and stiffness and it is not properly working for oil materials with significant different properties than asphalt binder. Since the oil aged properties is not available due to limitation in experimental procedures, oil unaged properties should be used in the model. To solve this problem, it was decided to add aging effect parameter in the model. Based on the statistical analysis, it was found that the following model gives the best correlation with experimental results:

\[ y = b - a(x)^{\beta} \]  \hspace{1cm} (VI-2)

Where:

\[ \beta = \text{Aging factor: \text{Aging Index Modified Binder} / \text{Aging Index Neat Binder}} \]

\[ b = \text{Aged Neat Binder Properties} \]

\[ x = \text{Oil content} \]

\[ a = \text{Ratio of Aged Neat Binder to Oil Properties (i.e. log stiffness binder/log stiffness oil).} \]
The aging index in this model is being calculated the same way as explained earlier in this document. The aging factor in this model is places as the power of the oil content because in this way, it can take into account the increasing effect of aging by increasing the concentration. The new improved model is used to predict aged oil modified binder properties at high temperature and the results are presented in Figure VI-14.

**Figure VI-14.** Summary of improved model results for RTFO-aged BO-2 oil modified binders.

(a) Model without the aging factor

(b) Model with the aging factor
Figure VI-14 shows that without the aging factor, the model prediction would not be accurate. It can be seen that without aging factor, the prediction is deviating from the experimental results and this deviation is increasing by increasing the oil content. However, adding the aging factor will solve this issue and Figure VI-14 shows that the revised model can accurately predict the RTFO-aged properties of oil modified binders at different oil concentration.

However, this method is not very practical due to the fact that the data from unaged and aged neat and oil modified binder plus oil data is needed to put in the model and predict the oil modified binders results. An important and practical implication of the linear trends observed in first section of this chapter, is that only modification at a single oil content is necessary to estimate the high temperature grade for any other oil content without need of additional testing. Thus the linear function for estimation of high temperature grade, as shown in Equation (VI-3), can be calibrated with data from only a single oil content, in addition to the base binder grade.

\[
HT\, PG_{C\%\, oil} = HT\, PG_{Neat} - \left(\frac{C}{C_0}\right)(HT\, PG_{Neat} - HT\, PG_{C_0\%\, oil})
\]  

(VI-3)

where:

\(HT\, PG = \) High Temperature True Grade (°C)

\(C_0 = \) Oil content of trial modification

\(C = \) Oil content of target modification.

This approach is straightforward and practical, making the estimation of the effect of oil on asphalt binder a very efficient and cost effective process, and significantly reducing the number of necessary tests required for binder selection.
3.2 Low Temperature Data

As was discussed earlier in this study, different oil modifiers used in this study will result in varying degrees of aging susceptibility in the modified binder. In order to be able to incorporate the effect of aging in the predictive relationships, a number of BBR tests were conducted on unaged samples of oil-modified binders at different concentrations in addition to the previously measurements made at PAV-aged conditions. “Aging Indexes” were derived for both the neat and modified binders, as the ratio of the aged to unaged binder stiffness. Since the low temperature properties is the target of oil modification, the model should be able to predict material behavior at long term aging condition.

As directly measuring the rheological properties of the oils at the low temperatures of interest was not possible or practical using the BBR or DSR, an analytical procedure was used to estimate the stiffness and m-value at low temperatures by extending measurements made at high and intermediate temperatures and converting shear complex modulus to transient flexural creep stiffness, details of which are described in section 2 of this chapter. The resulting model is shown in Equation VI-4.

\[
\log (S_{(60)})_{\text{Modified}} = (S_{(60)})_{\text{Neat-Aged}} - \left[ \frac{(S_{(60)})_{\text{Neat-Aged}}}{(S_{(60)})_{\text{Oil}}} \right] x^\beta
\]  

\((VI-4)\)

where:

\[
\beta = \frac{\text{Aging Index of Oil Modified Binder}}{\text{Aging Index of Neat Binder}}
\]

\(x = \text{Oil content}\)

The aging parameter, \(\beta\), as the power of the oil content accounts for the observed increase in the effects of aging on stiffness as the oil contest increases. The model was used to predict aged oil modified binder properties at low temperature for BBR data for the example of the PA oil modified binders are presented in Figure VI-15. In the figure, model with aging coefficient is named as model-rev. This figure compares the effect of aging in model prediction and shows how significant the aging effect is for oil modified binders. This aging significance can be different for different type of oils and as it was shown in
previous chapters, some of the oils are more prone to aging. Hence, it is essential to take into account the aging effect in all model prediction for aged oil modified binders in this method.

As it was discussed in the previous part that this method is complicated and it needs some number of tests to be able to predict oil modified binders results accurately. Since oil modified binders show the similar linear trend at low temperatures to the high temperature results, the same approach can be taken here as well. For the low temperature S and m true grades a simple linear trend can be used to estimate the true grade at any oil concentration if the grade of a single oil content is known. Equation VI-5 shows the data needed to predict oil modified binder PG results. This process can significantly decrease the time and resources necessary to perform a large number of tests at low temperatures for every concentrations of oil.

\[
LT\ PG_{C\%\ oil} = LT\ PG_{Neat} - (\frac{C}{C_0})(LT\ PG_{Neat} - LT\ PG_{C_0\%\ oil})
\]  

(VI-5)

where:

\(LT\ PG\) = High Temperature True Grade (°C)

\(C_0\) = Oil content of trial modification

\(C\) = Oil content of target modification.
The analysis was performed for BO-1 oil at -12 °C and PP-1 and RW-1 at -18 °C using Equation VI-5. **Figure VI-16** shows the results for PA, PP-1 and RW-1 oil modified binders. These results confirmed that the new model is capable of predicting oil modified binder properties at wide range of temperatures by using only one concentration. This model is significantly beneficial since the contractor can use this model to predict the oil modified binders without using significant resources to test all the material and it is easy way to select the better material.

![Model Predicted log Stiffness vs Experimental measures log Stiffness](image)

**Figure VI-16.** Model results for PAV-aged oil modified binders.

### 4. Criteria for Oil Classification

One of the main objectives of this study is to develop a simple and effective system for oil classification that reflects effects of oil modification on PG grading of binders. The results presented in this chapter show that the effects of oils are simple and can mostly be described in terms of linear models in terms of relative effects on $G*/\sin\delta$, $S(60)$, and $m(60)$. The linear relationship also appears valid for the True grades corresponding to the $G*/\sin\delta$ of 2.2 kPa, $S= 300$ MPa, and $m=0.300$. It is therefore proposed that oil modifiers be classified and defined by three numbers, representing the true Grade (TG) temperature changes for 1 % addition of an oil modifier or extender. This index consisting of three values
can be called the “Oil Modification Index” (OMI) and can be simply defined by only testing a single modification content:

\[ \text{OMI} = (\text{°C Reduction in } G^*/\sin \delta \text{ TG}) - (\text{°C Reduction in } S(60) \text{ TG}) - (\text{°C Reduction in } m(60) \text{ TG}) \]

If the purpose of modification is improving the low temperature grade with minimal high temperature grade loss, the most favorable oil index would have the smallest magnitude for the first number in the OMI, and higher magnitudes for the second and third numbers. Such an OMI will define an oil that has a small effect on \( G^*/\sin \delta \text{ TG} \) (high temperature grade) and higher effects on \( S \) and \( m \) TGs (low temperature grades). The definition of the OMI is practical and offers a simple system for ranking and selection of oils for asphalt modification.

**Table VI-1** shows the OMI index for FH base binder with nine different oil types. Based on the results of this study, it appears that the only data required for assigning an OMI to an oil-binder combination is the performance grade testing of the modified binder at a single oil content and use the linear relationships discussed earlier to determine the amount needed to achieve the target grade change. Since there is a dependency on base asphalt, OMI values for any given oil will change as a function of based asphalt, thus OMI should be defined for each unique oil-base binder configuration.

**Table VI-1. Oil Modification Index for different oil modifiers.**

<table>
<thead>
<tr>
<th>Asphalt Base</th>
<th>Oil Type</th>
<th>ATG per 1% Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>FH</td>
<td></td>
<td>HTG-OB</td>
</tr>
<tr>
<td>PA</td>
<td></td>
<td>-0.7</td>
</tr>
<tr>
<td>PP-1</td>
<td></td>
<td>-1.2</td>
</tr>
<tr>
<td>PR-2</td>
<td></td>
<td>-0.8</td>
</tr>
<tr>
<td>PN</td>
<td></td>
<td>-0.9</td>
</tr>
<tr>
<td>BO-1</td>
<td></td>
<td>-1.1</td>
</tr>
<tr>
<td>BO-2</td>
<td></td>
<td>-1.1</td>
</tr>
<tr>
<td>BO-3</td>
<td></td>
<td>-1.5</td>
</tr>
<tr>
<td>RW-1</td>
<td></td>
<td>-1.4</td>
</tr>
<tr>
<td>RW-2</td>
<td></td>
<td>-1.7</td>
</tr>
</tbody>
</table>
From Table VI-1, it can be seen that this classification system can be used to define the appropriate oil for different functions. For example, if there is a need for oil to improve the m-value of base binder, the RW-1 and RW-2 can be good options. The RW oils (refined waste) shows the best overall performance in terms of the OMI index, as also supported by data presented earlier in this study. Similarly, PA, the petroleum based aromatic oil, can be identified as the least effective oil on the low temperature but this oil can be used as rejuvenator since it does not damage the high temperature as much as the others.
VII. Summary of Findings and Future Work

1. Summary of Findings

This study is focused on understanding the effect of oil modification on asphalt binder rheological properties and performance. In the previous chapters, the results of experimental data and analytical methods were presented. This was done to investigate the effect of addition of oils on high, intermediate and low temperature performance of asphalt binder. In addition to measuring the performance-based result of oil modified binders, the cracking properties of oil modified binders were investigated as well. To contribute to the current state of knowledge this study was focused on development of an understanding of oil modified binder behavior from a fundamental view and further implements these findings to develop models to predict the behavior of oil modified materials. Based on the results and analyses, the following findings are stated:

- Oil modification significantly alters asphalt binder rheological properties at different temperatures and frequencies. The results confirm that oil modification reduces the asphalt binder stiffness; Hence, it negatively impacts high temperature performance and improves low-temperature performance.

- Evaluation of low temperature performance as measured by the glass transition temperature and creep/relaxation behavior indicates that increasing blending deviatoric shear stress through use of high shear mixers can shift the blending process from simply “distributive”, to “distributive” and “dispersive”, the latter is more effective and favorable as it ensures droplet breakdown to smaller scales and homogenization at a much finer level, thus providing an improved degree of dispersion.
BBR results showed that adding oil reduced binder modulus at low service temperatures, with greater reduction achieved if high shear mixing was used.

- Adding oil to the asphalt medium will decrease its stiffness by introducing a softer fraction with different chemical components to the asphalt binder structure. This leads to detrimental effects on high temperature performance by reducing the stiffness, while improving the low temperature properties. Also, oil modification decreased the $T_g$ temperature and increased the m-value due to introduction of oil portion to asphalt medium which has lower molecular weight and higher free volume.

- Oil modification increases molecular mobility of asphalt binder and hence increases the temperature susceptibility and time dependency of the material.

- The Superpave rutting parameter ($|G^*|/\sin\delta$) and non-recoverable creep compliance ($J_{nr}$) were employed to evaluate the high temperature performance of binders. The results show that oil modification is detrimental to the high temperature performance.

- The oil modification affected the aging susceptibility of asphalt binder, with the effect being dependent on the type of oil. Differences were attributed to composition of various oil modifiers affecting different compounds within the base asphalt. An increase in age hardening is observed for the bio-oils while a decrease in age hardening is observed when the refined waste oils are added.

- Analysis of relaxation modulus master curves indicates that oil modification caused vary little deviation from the base binder master curve at high and intermediate temperatures/loading times, but demonstrated significantly lower glassy modulus values relative to the neat binder at all aging levels. Such results indicate that at the dosages used, oil modification can cause improvements of low temperature properties with less adverse effects on properties at higher service temperatures.
Fatigue and moisture damage data showed that some of oils are beneficial regarding the improvement the cracking and moisture sensitivity meanwhile some other did not change or deteriorated those properties.

A simple analytical method is proposed to calculate thermal stresses by using rheological and thermo-volumetric properties of oil modified binders. The results indicate the asphalt binder stiffness plays an important role to control stress build up due to temperature decrease. However, the controlling factor in cracking behavior of oil modified binders is strain tolerance.

SENB failure stress and strain results confirmed that some of the oils have a potential to improve the cracking resistance of base binder at low temperatures.

The results indicate that there is a linear relationship between oil content and log stiffness. Also further analysis indicates that this linear relationship can also be extended to m-value and phase angle.

A relatively simple model was developed to predict the properties of oil modified binders based on rheological properties of the modified binder components. The model was validated and included adjustments for aging effects as well.

The observed relationships were used to develop a practical oil ranking index called here the Oil Modification Index (OMI) which represents the changes in True Grade values for high and low temperature properties. The OMI is expected to be base binder specific and thus should be determined for any unique oil-base and binder combination.

The overall results show that oils vary in their impact on properties, but they all have a positive impact on low temperature properties and performance.
2. Conclusion

This study indicates that addition of oil modifier would change the rheological and thermal behavior of asphalt binder. Based on the results, it is concluded that oil modification can improve the low temperature properties of asphalt binder due to reducing the stiffness and increasing the relaxation modulus. The results also depict that oil modification has a positive effect on cracking resistance of asphalt binder at broad range of temperatures.

3. Recommendations for Future Work

This study suggests oil modification can significantly improve the low temperature performance and properties of asphalt binder. The following are the recommended areas of future research:

- Different combination of oil modifiers with other additives such as polymers, anti-stripping agent, etc.

- Further research on the oil modification mechanism and comparison with extensive mixture data needs to be performed.

- Further research on the validation of the experimental results with field data.
VIII. References


AASHTO T240 (2010). “Standard Method of Test for Effect of Heat and Air on a Moving Film of Asphalt Binder (Rolling Thin-Film Oven Test) ”, American Association of State Highway and Transportation Officials, Washington, D.C.


