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Using soybean-derived materials to rejuvenate reclaimed asphalt pavement (RAP) binders and mixtures

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Using soybean-derived materials to rejuvenate reclaimed asphalt pavement (RAP) binders and mixtures

by

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DEDICATION

I dedicate this dissertation to my family. My father, may Allah grant him the highest level of paradise, who spent his life working hard trying to give me a better life. My mother who encompasses me with love and to whom I go for help and advice. My wife Mariam who stood by me and encouraged me all the way through, and my children Hana, Mustafa, Sarah, and Farida who bring joy into my life and give meaning to everything.

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ABSTRACT

Over the past few years, the use of reclaimed asphalt pavement (RAP) has been growing consistently from 15% in 2009 to 20.3% in 2015. The desire to use higher amounts of RAP is inspired by the need to lower costs, conserve energy, and preserve the environment. Increasing asphalt prices, and limited supply of higher quality virgin aggregates, are strong motivations to use RAP as a replacement for the more expensive virgin asphalt and aggregates.

The main obstacle from using higher amounts of RAP is the aged and deteriorated properties of the RAP binder. With aging, asphalt binders suffer from oxidation which results in the conversion of part of the maltenes fraction to asphaltenes. Asphaltenes are primarily responsible for increasing the asphalt stiffness. The use of rejuvenators help restore the balance between the asphaltenes and maltenes, by adding more maltenes and/or improving the dispersion of asphaltenes.

Current rejuvenators that are available in the market are based on several materials including petroleum-based aromatic extracts, distilled tall oil, and other natural oils (i.e., organic oils). Bio-based rejuvenators have proven to be a better and safer alternative to petroleum-based rejuvenators containing aromatic compounds.

This research introduces a soybean-derived rejuvenator which is used to enhance the low temperature and fatigue properties of asphalt binders. During the first phase of the research, the effect of the rejuvenator is assessed by blending it with a neat PG58-28 and a polymer modified PG64-28 binders. Dynamic Shear Rheometer (DSR) and Bending Beam Rheometer (BBR) tests are conducted to characterize the rheological properties of the rejuvenated binders. Temperature-frequency sweeps are conducted and

complex shear modulus curves are constructed to compare between the control and the rejuvenated binders.

Dynamic modulus specimens are made using the rejuvenated PG58-28 and PG64-28 binders. The impact of the rejuvenator on both the dynamic modulus and phase angles is studied using master curves. A comprehensive statistical analysis using split-plot repeated measures (SPRM) is conducted to reveal statistical differences between the performance of the rejuvenator in both types of binders. The preliminary results indicate that the soybean-derived rejuvenator was successful at lowering both the high and low critical temperatures of both types of binders. The statistical analysis revealed that the extent of modification brought about by the rejuvenator was dependent on the binder type. The results of the dynamic modulus testing showed a consistent reduction in the dynamic modulus values and an increase in the phase angles with the use of the rejuvenator. A Fourier-transform Infrared study (FTIR) performed on the rejuvenated binders indicated that their aging behavior was similar to that of the control binders, indicating that the rejuvenator did not adversely impact the durability of the binders.

In the second phase of this research, a rejuvenated PG58-28 binders was blended with an extracted reclaimed asphalt pavement (RAP) binder. The fatigue behavior of the rejuvenated RAP binder is evaluated using linear amplitude sweep (LAS) testing. A significant increase in the fatigue life, particularly at low temperatures and increasing shear rate, is noted with the use of the rejuvenator. The rejuvenator was successful in lowering the performance grade of the stiff aged RAP binder to acceptable ranges. 100% RAP mixtures made and compacted into dynamic modulus and disk-compact tension (DCT) specimens were made using the neat PG58-28 and rejuvenated PG58-28 binders.

The DCT specimens containing the rejuvenator showed higher fracture energy at a test temperature of -6^{o}C which indicates better thermal cracking resistance. To assess the effect of blending efficiency, additional DCT specimens were prepared using extracted RAP binder blended with the rejuvenated PG58-28 binder. The RAP/rejuvenated PG58-28 blend was then remixed with the extracted RAP aggregate to simulate full blending. The DCT specimens prepared as such yielded even higher fracture energies indicating the significance of proper blending.

The thermal stability of the rejuvenated RAP binder was verified using thermogravimetric analysis (TGA). The mass loss due to thermal decomposition of the rejuvenated RAP binder was similar to that of the control binder. A study of the evolved gases using FTIR showed that the rate of mass loss of the rejuvenator can be inferred by comparing the FTIR spectra at different times.

CHAPTER 1. GENERAL INTRODUCTION

Using recycled materials in asphalt roads creates numerous benefits. Conserving energy, cutting down on harmful emissions, savings on materials and transportation costs, preserving the environment, reducing materials going to landfills, and not depleting the earth's natural resources are among a long list of benefits that can be achieved by recycling. Common recycled materials in asphalt mixtures include reclaimed asphalt pavement (RAP), recycled asphalt shingles (RAS), ground tire rubber (GTR), steel and blast furnace slag. Among these materials, RAP is considered the most common aiding the promotion of more cost-effective construction and maintenance activities. The percentage of reclaimed asphalt pavement (RAP) in asphalt mixtures has been growing consistently in the US from an average of 15.6 percent in 2009 to 20.3% in 2015 (Hansen and Copeland 2017).

1.1 Reclaimed asphalt pavements (RAP)

RAP is mainly produced from pavement milling operations and full-depth removal (NAPA 1996). During pavement rehabilitation projects, milling is used to grind a certain depth of the existing pavement to allow for a new pavement layer to be applied. Milling is done to maintain curbs, and structural clearance for bridges and over-passes. RAP often produced from milling has uniform properties, because it comes from the same pavement layer. Total pavement replacement involves a full-depth removal of the old pavement. RAP from full-depth removal operations is usually processed by crushing and sizing to provide consistent properties (NAPA 1996).

The Federal Highway Administration (FHWA) and the National Asphalt Pavement Association (NAPA) have been pushing towards more use of RAP in pavements. Any application of RAP is tied to the conditions that RAP material should meet or exceed the same standards as virgin materials and mixtures containing RAP should perform similar to or better than virgin mixtures. Using well-engineered RAP materials and mixtures with 50% RAP in the National Center for Asphalt Technology (NCAT) test track, satisfactory pavement performance was obtained in comparison to control test sections (West et al. 2012). As the amount of RAP increases, in high content RAP mixtures, strict quality control measures need to be followed to ensure consistency during mix production. The properties of the RAP material, including asphalt content and grade, aggregate quality, absorbance, and gradation, must be properly determined. Knowledge of the history of the milled pavement including performed maintenance, and failure mode can provide insight into the condition of the RAP material.

With increasing RAP content, it becomes necessary to use different techniques to ensure that the resulting mixture satisfies the desired performance levels. These techniques could include the use of softer virgin binders, utilizing warm mix technology, increasing asphalt content, and adding rejuvenators (Im et al. 2016). A nationwide survey conducted by the National Asphalt Pavement Association (NAPA) on the usage of RAP in the year 2015 revealed that states which reported using more than 20% RAP in asphalt mixtures have also reported using softer virgin binders and rejuvenators(Hansen and Copeland 2017).

The primary concern regarding using high amounts of RAP in asphalt mixtures is the excessive aging and stiffness of the RAP binder (Tran et al. 2012). The RAP binder is more susceptible to thermal cracking, fatigue failure, and reflective cracking. Asphalt is composed of two general fractions: asphaltene and maltene. Asphaltenes are high molecular weight solid particles which are largely responsible for the stiffness of asphalt. The asphaltenes form a colloidal suspension in the maltenes' phase. The maltenes phase contains low molecular weight constituents which keep the asphaltenes in suspension. As asphalt ages, part of the maltenes phase convert into asphaltenes. In the absence of sufficient maltenes to properly disperse the asphaltenes, they will tend to flocculate leading to higher viscosity and low creep rate. Aging takes place over the short and long terms. Short-term aging involves volatilization of the light end components in the maltenes during mixing and construction. Long-term aging occurs throughout the years of service of the pavement and is mainly attributed to the oxidation of the maltene fraction which is activated by both heat and ultraviolet radiation (Roberts et al. 1991).

1.2 Asphalt rejuvenation

Rejuvenators are added to RAP to partially or fully restore the physical and chemical properties of the aged RAP binder. Rejuvenators typically contain low molecular weight constituents which restore the balance between the asphaltene and maltene fractions in the binder. They help improve the dispersion of the asphaltene and prevent their agglomeration, hence reduce the binder's viscosity and enhance its stress relaxation ability.

It is important that rejuvenators blend properly with the RAP binder during mixing. Uniform blending between the rejuvenator and the RAP binder ensures that the full potential of the rejuvenator is achieved. A study into the use of rejuvenators in asphalt plants was conducted by Lee et al. (Lee et al. 1983) where the authors used a dye to enable them to visually detect the degree of blending of the rejuvenator. It was concluded that proper mechanical mixing can result in uniform diffusion of the rejuvenator into the RAP binder. In another study, a staged extraction method was used to collect the inner and outer layers of the asphalt film thickness separately(Carpenter and Wolosick 1980). The penetration values for both layers were monitored over a period of 100 days. Penetration values taken right after mixing shows the inner layer being more stiff than the outer layer. With time, however, the difference in penetration values between the outer and inner layer decreases indicating progressive diffusion of the rejuvenator into the RAP binder. The following four-step diffusion mechanism was suggested: 1) The rejuvenator forms a layer coating the outside surface of the RAP binder, 2) The rejuvenator begins to diffuse into the outer layers of the RAP binder until no rejuvenator is left on the outside surface, 3) The rejuvenator diffuses slowly from the outer layers into the linear layers of the RAP binder, and 4) Diffusion continues to occur over time until equilibrium is reached.

Currently available commercial rejuvenators are based on a variety of different materials that are derived from petroleum based aromatic extracts, distilled tall oil, and organic oils(Zaumanis et al. 2014). Bio-based rejuvenators have been introduced to offer a safer and more environmental friendly alternative to the aromatic rejuvenators which can pose health concerns. Mixtures containing 40% RAP were prepared successfully using organic natural oils(Hajj et al. 2013). Waste engine oil, waste vegetable oil, and waste vegetable grease have also been proposed as potential rejuvenators (Zaumanis et al. 2014). It was shown that organic-based rejuvenators can outperform petroleum-based rejuvenators (Zaumanis et al. 2014).

The effectiveness of a rejuvenator can be measured by its ability to improve the physical properties of an aged RAP binder. Rejuvenators typically lower both the critical high and low temperatures, increase fatigue life at intermediate temperatures, enhance low temperature thermal cracking resistance, and improve stress relaxation ability.

Several testing methods can be used to assess the binder performance including Dynamic Shear Rheometer (DSR) performance grading, temperature-frequency sweeps, linear amplitude sweeps, Multiple Stress Creep Recovery (MSCR), Bending Beam Rheometer (BBR) and rotational viscosity. Asphalt mixtures containing rejuvenators can be assessed by means of different tests, mainly, dynamic modulus testing, and disk-shaped compact tension (DCT) testing.

1.3 Organization of Dissertation

In this research, a soybean-derived rejuvenator is introduced where the effect of the rejuvenator on both a neat PG58-28 and a polymer-modified PG64-28 binders is first assessed. The effect of the rejuvenator on the rheological properties of each of the two binders is discussed in Chapter 2. Mixtures made with the rejuvenated binders are made and tested for dynamic modulus properties including modulus and phase angle values. A complex statistical analysis using split-plot repeated measures (SPRM) is presented where the effectiveness of the rejuvenator on the properties of both binders is evaluated. The durability of the rejuvenated binders is verified using Attenuated Total Reflection-Fourier Transform Infrared Analysis (ATR-FTIR).

Chapter 3 presents a more comprehensive analysis of the rheology of the rejuvenated binders. Complex shear modulus master curves are used to assess changes in stiffness and phase angles. A Glover-Rowe diagram is used to quantify the improvement in fatigue behavior due to rejuvenation. Black diagrams and Cole-Cole diagrams are used to provide more insight the viscoelastic properties of the rejuvenated binders. In Chapter 4, a PG58-28 binder blended with the soybean-derived rejuvenator is used to rejuvenate an extracted reclaimed asphalt pavement (RAP) binder. The performance grade of the rejuvenated RAP binder is determined and the reduction in stiffness and enhancement in low temperature performance is noted. The linear amplitude sweep (LAS) is conducted to further assess the fatigue improvement in the rejuvenated RAP binder. 100% RAP mixtures using the soybean-modified PG58-28 are made and compacted into dynamic modulus and disk-compact tension (DCT) specimens. The DCT specimens are tested at -6^{o}C, and the fracture energy is obtained. The effect of blending efficiency on the effectiveness of the rejuvenator is highlighted in Chapter 5. DCT specimens representing full blending conditions are prepared and the increase in fracture energy is noted. A study of the thermal stability of the rejuvenated RAP using Thermogravimetric analysis (TGA) is also given in Chapter 5. The mass loss with temperature for both the control and rejuvenated RAP is measured. Furthermore, a study of the evolved gases is done using FTIR and the collected spectrum is used to indicate the rate of mass loss of the soybean-derived rejuvenator. Finally, Chapter 6 summarizes the research with recommendations for future work.

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CHAPTER 2. INTRODUCING A SOYBEAN OIL DERIVED MATERIAL AS A POTENTIAL REJUVENATOR OF ASPHALT THROUGH RHEOLOGY, MIX CHARACTERIZATION AND FOURIER TRANSFORM INFRARED ANALYSIS

Modified from a paper published in Road Materials and Pavement Design

Mohamed Elkashef[a*], Joseph Podolsky[a], R. Christopher Williams[a], and Eric W. Cochran[b]

Abstract

The interest in rejuvenators has been growing rapidly in the past few years due to their ability to restore aged binders to their unaged state and the availability of aged recycled materials. The introduction of rejuvenators has made it possible to produce asphalt mixes with high recycled asphalt pavement (RAP) content. Typically, rejuvenators need to be added to the RAP bitumen in high dosages, more than 10%, to achieve the desired effect. In this work a new soybean-derived additive is introduced as a rejuvenator, at a percentage of 0.75% by weight of the bitumen. The effect of adding the soybean-derived rejuvenator on the rheological properties of both a performance grade (PG) 64-28 and a PG 58-28 bitumen is assessed using a dynamic shear rheometer (DSR), a bending beam rheometer (BBR), and a rotational viscometer. Dynamic modulus specimens for both the control and modified blends were prepared using a mixing and compaction temperature of 120°C, as well as a temperature of 140°C, and master curves were constructed using test results. The dynamic modulus data was further analyzed using a complex statistical technique which utilizes a split-plot repeated measure (SPRM) concept. It was noted that, at such a low dosage, the rejuvenator greatly improved the fatigue and low temperature properties of the tested asphalt binders. The dynamic modulus results revealed that the rejuvenator was successful in reducing asphalt binder

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stiffness, and that the extent of such a reduction depended largely on the asphalt grade. Additionally, the mixing and compaction temperature 120°C had the effect of the mix performing better at lower test temperatures than the specimens produced using a mixing and compaction temperature of 140°C. The aging characteristics of the rejuvenated binders was assessed using Fourier Transform Infrared-Attenuated Total Reflection (FTIR-ATR), which revealed similar aging behavior of both the control and modified asphalt binders, as indicated by the evolution of the carbonyl and sulfoxides indices.

2.1 Introduction

Rejuvenators have been successfully implemented to offset the high stiffness and low creep rate of aged RAP asphalt binder. Use of rejuvenators has resulted in considerable improvement to low-temperature properties of mixtures with high RAP content (Hajj et al. 2013; Shen et al. 2007; Zaumanis et al. 2014). The key to an efficient application of rejuvenators is to achieve an increase in the low-temperature performance without jeopardizing the overall mixture properties. The use of blending charts have been proposed as a tool to select an optimum rejuvenator dosage to avoid undesirable rutting problems that may occur as a result of higher dosages (Shen et al. 2007).

Aged asphalt binder can lose a great portion of its maltenes content as a result of oxidation leading to increased stiffness (Copeland 2011). Rejuvenators help replenish the maltenes content and rebalance the chemical composition of asphalt. They are added during mixing and gradually diffuse into the aged asphalt binder imparting softening characteristics (Carpenter and Wolosick 1980).

Other techniques have been adopted to allow using RAP in asphalt mixes, such as using a softer virgin binder, increasing the asphalt content, and utilizing warm-mix technology. These techniques however have been limited to mixtures with low RAP content (Im et al. 2016). Rejuvenators have proven to be very effective for mixtures with high RAP content. Over the past several years, research on rejuvenators has been growing rapidly. This research has been crucial for the use of mixtures with higher RAP contents, which would allow for additional cost savings, and considerable environmental benefits. A recent survey, conducted on the use of recycled materials in asphalt pavements, revealed that the average percentage of RAP in the US has only increased from 15% in 2009 to 20% in 2014 (Hansen and Copeland 2015). This percentage is expected to increase in the near future as researchers gain more understanding of the mechanism of rejuvenators and its interaction with aged asphalt binder.

The primary focus of most studies covering rejuvenators has been to assess their effect on the stiffness of aged asphalt binders and the low-temperature cracking resistance of the treated asphalt mixtures. It was concluded that rejuvenators successfully decrease aged asphalt binder stiffness and improve low-temperature cracking resistance of asphalt mixtures (Elseifi et al. 2011; Hajj et al. 2013; Zaumanis et al. 2013).

The relatively high viscosity that characterizes aged RAP binder results in poor mixing and compaction. A rejuvenator should be able to reduce the RAP binder's viscosity to ensure proper blending with the virgin binder and achieve uniform coating of both virgin and RAP aggregates. Through reducing the viscosity, the RAP binder becomes less stiff and can thus blend more easily with the virgin binder. The degree of blending between the RAP binder and the virgin binder determines to a large extent the performance of mixtures containing RAP, by increasing the effective percentage of RAP binder that contributes to the total asphalt content (Huang et al. 2005). Being able to reduce viscosity, rejuvenators can help achieve sufficient flow at lower mixing temperatures. The relationship between viscosity and temperature should be well understood. A good rejuvenator should be capable of lowering the viscosity to acceptable levels without the need for high dosages. High dosages of rejuvenators could lead to potential rutting, stripping and mix instability problems (Zaumanis et al. 2013).

It is important to study the chemical composition of both the binder and rejuvenator, as well as the interaction between them. A specific rejuvenator could work effectively for one binder but not another. A study conducted using aromatic extract rejuvenators concluded that they were more chemically compatible with a ABD (PG58-10) asphalt binder than a AAD (PG58-28) asphalt binder, leading to improved low temperature performance (Yu et al. 2014).

SARA fractionation is commonly used to detect changes in the different chemical fractions of asphalt due to aging and rejuvenation. Conversion of aromatics to asphaltenes was noted with aging with no significant change in resins or saturates, as revealed by a study using SARA (Yu et al. 2014). Subsequent addition of an aromatic extract rejuvenator resulted in an increase in saturates and aromatics content and a decrease in the asphaltenes.

Fourier Transform Infrared (FTIR) is used to characterize asphalt binders. Fourier Transform Infrared-Attenuated Total Reflection (FTIR-ATR) utilizes the concept of multiple internal reflection and evanescent waves to increase the sensitivity of measurement (Marsac et al. 2014). FTIR-ATR was used to determine the aging behavior of three different rejuvenators (Ongel and Hugener 2015) by comparing the evolution of carbonyl and sulfoxides functional groups. It was found that the carbonyl group barely existed in the unaged specimens and increases notably with aging for both the control and rejuvenated binders. The rate of increase in the carbonyl groups was higher in long-term aging (PAV) compared to short-term aging (RTFO). FTIR-ATR was also utilized to monitor the diffusion rate of the rejuvenator into the asphalt binder (Karlsson and Isacsson 2003). Both C=O and the C-H bonds were used to evaluate changes in the diffusion coefficient with temperature. A recent study involved studying mixtures prepared with 40% RAP with FTIR-ATR (Poulikakos et al. 2014). The oxidation level, as indicated by the carbonyl and sulfoxide groups, was found to be higher for softer asphalt binders compared to RAP extracted asphalt binders. It was suggested that difference in the oxidation level was due to the rate of diffusion of oxygen which was higher in case of lower viscosity/softer asphalt binders.

The production of soybean in the US constitutes about one third of the total world production. The state of Iowa is considered a substantial producer of soybean. The production of soybean in Iowa amounted to 14% of the US soybean output during a five-year period from 2010-2014, according to a recent report published by the Iowa soybean association(Iowa Soybean Association 2016).This huge production is processed in the form of either soybean meals or soybean oil. Soybean meals are largely consumed by the livestock industry while most of the soybean oil is used in the production of biodiesels. An estimated 20% of the soybean output is used to make biodiesel oil (Iowa Soybean Association 2016). The process of biodiesel oil production involves transesterification of the soybean oil in the presence of a catalyst(Ma and Hanna 1999). The abundancy of the soybean oil production in the US inspires the need to look for alternative applications other than biodiesel production.

Soybean acidulated soapstock (SAS), which is considered a rich source of soybean fatty acids, was used as a fluxing agent for four different asphalt binders(Seidel and Haddock 2014). Dosages ranging from 1% to 3% were added. The SAS modification resulted in a consistent decrease in the critical high temperature, as well as an increase in the phase angle. It was also concluded that the enhancement in performance at low temperature was dependent on the chemical composition of the binder. A recent study investigated the use of soybean oil as a warm-mix asphalt (WMA) additive, at dosages from 1-3%(Portugal et al. 2017). The study looked at the change in the mixing and compaction temperatures for both a neat and a polymer-modified binder. It was shown that an average reduction of 2.7^{o}C-3.4^{o}C was noted in the mixing and compaction temperatures for both types of binders.

Other than soybean oil, vegetable oils have been previously suggested as recycling agents or rejuvenators. Two-point bending tests performed on RAP mixtures modified with a vegetable oil based recycled agent showed improved fatigue performance and lower complex modulus (Mangiafico et al. 2016). Waste vegetable oil has been used to modify 100% RAP mixtures resulting in a reduced temperature performance grade(Zaumanis et al. 2014). Other bio-derived rejuvenators including distilled tall oil and cotton seed oil were also used to rejuvenate asphalt binders(Chen et al. 2014; Zaumanis et al. 2015).

2.2 Materials and Methods

Two asphalt binder grades were used in this study, namely PG 64-28 and PG 58-28 binders. The additive used will be referred to in a generic term as a soybean-derived additive. The soybean-derived additive was blended with the two binders PG 58-28 and

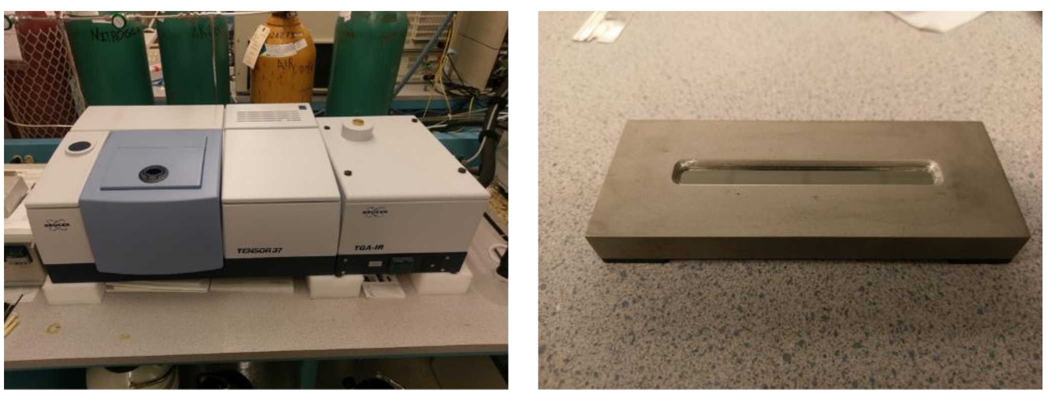
PG 64-28 at 0.75% by weight of the binder. Blending was done at a temperature of 140^{o}C ± 2^{o}C using a Silverson shear mill operated at 3000 rpm for one hour.

To assess changes in the Performance grade (PG) due to modification, dynamic shear rheometer (DSR) and Bending beam rheometer (BBR) tests were conducted according to AASHTO T315 and AASHTO T313, respectively. Testing was performed on both the control and modified PG 58-28 and PG 64-28 binders. Rolling Thin Film Oven (RTFO) aging was done according to ASTM D2872 at 163^{o}C for 85 minutes while PAV aging was performed on the RTFO aged binder according to ASTM D6521 for 20 hours at 100^{o}C and 2.1 MPa pressure.

The viscosity-temperature susceptibility (VTS) of the control and modified binders was studied by measuring the viscosity of the unaged control and unaged modified binders at different temperatures. For the viscosity measurements, a rotational viscometer was used according to AASHTO T316.

Dynamic modulus testing was conducted to evaluate the stiffness of both control and modified asphalt mixtures according to AASHTO T342. All test specimens for dynamic modulus testing were made using the same binder content and aggregate gradation, to preclude any effect of changes in the mix design. Mixing and compaction were done at a temperature of 120^{o}C, as well as a temperature of 140^{o}C, for both the control and modified bitumen to study the influence of the mixing and compaction temperature on the dynamic modulus. For each of the two binder grades, a total of four groups were prepared comprising the control and modified binders at mixing and compaction temperatures of 120°C and 140°C, making a total of eight groups. Three specimens were made for each of the eight test groups (24 specimens in total). Specimens were compacted using a Superpave gyratory compactor according to AASHTO T342. The specimen air void requirement was 7% ± 0.5%.

For FTIR-ATR testing a Bruker Tensor 37, Figure 2.1 (a), was used with an attenuated total reflection device shaped like a boat as shown below in Figure 2.1 (b). The ATR crystal is made out of germanium. The following settings were used for testing; resolution – 2cm^{-1}, sample scan time – 16 scans, saved data from 4000 to 855 cm^{-1}, scanner – 5kHz, aperture setting – 6mm, laser wavelength – 15800.36, and phase resolution – 32. There were three steps in specimen preparation; 1) specimens were prepared by pouring heated binder into 8mm DSR molds, 2) 8mm specimens placed into the boat and mixed with toluene, 3) boat placed in oven to evaporate toluene at 60°C for 5 minutes. Toluene was added to help dissolve the binder to better spread over the ATR crystal. Cleaning was done with toluene, q-tips and cotton swabs. The ATR boat device was used because of contamination concerns with toluene getting on the mirrors underneath the crystal.



(a) (b)

Figure 2.1. FTIR-ATR (a) FTIR – Bruker Tensor 37, and (b) ATR boat device

2.3 Results and Discussion

2.3.1 Binder testing

The control and modified binders were tested according to AASHTO T315 in order to determine their critical high temperature. The critical high temperature is determined from both unaged and RTFO aged specimens at $G^*/\sin\delta > 1$ kPa and $G^*/\sin\delta > 2.2$ kPa, respectively. The critical low temperature was determined using PAV aged specimens according to AASHTO T313. The results of both the critical high and low temperatures, along with the performance grade (PG), are shown in Table 2.1. The PG of the modified binder indicates a considerable change from the control binders for both binder grades; PG 64-28 and PG 58-28. A drop in the critical high temperature accompanied by a notable reduction in the critical low temperature was characteristic of the modified binders in comparison to the control binders. For both binder grades, the high temperature grade decreased by 18^{o}C whereas the low temperature grade decreased by 6^{o}C. A decrease in the high temperature grade denotes more susceptibility to rutting while a decrease in the low temperature grade marks more resistance to low-temperature cracking.

Table 2.1. Properties of control and modified binders

Binder	PG 58-28 Control	PG 58-28 Modified	PG 64-28 Control	PG 64-28 Modified
Unaged (High Temp.)	60.0	45.1	67.1	51.5
RTFO (High Temp.)	62.5	46.7	66.5	52.5
PAV (Low Temp.)	-29.9	-36.3	-29.0	-36.9
Performed Grade (PG)	PG58-28	PG40-34	PG64-28	PG46-34
Viscosity (Pa*s) at 135ºC	0.329	0.188	0.718	0.381
Viscosity (Pa*s) at 150ºC	0.172	0.143	0.385	0.250
Viscosity (Pa*s) at 165ºC	0.107	0.125	0.230	0.193
Viscosity temperature susceptibility (VTS)	-3.04	-1.14	-2.69	-1.71
Mass loss (%)	0.82	0.99	1.01	1.00

To further study the effect of modification, the rutting parameter $G^*/\sin\delta$ obtained using DSR measurements at a frequency of 10 rad/s was plotted against temperature as shown in Figure 2.2. It is obvious that the addition of the soybean additive caused a decrease in the rutting parameter signaling an increase in rutting susceptibility. This was true for both binder grades.

A similar plot, as Figure 2.2, was drawn to examine the fatigue parameter $G^*\sin\delta$ as shown in Figure 2.3. According to Superpave criteria, the critical intermediate temperature is reached when the value $G^*\sin\delta$ is equal to 5 MPa. A notable decrease in the lower critical intermediate temperatures occurs with modification which means that modified binders are more resistant to low temperature cracking than the control binders. The modified PAV aged PG 64-28 binder showed a better improvement in low temperature resistance compared to the PAV aged PG 58-28 binder. The effect of the soybean additive was more pronounced in the case of the PG 64-28 binder compared to the PG 58-28 binder. This dependency of performance on the binder grade was only true for thermal cracking, e.g. low temperature performance, whereas rutting resistance, e.g. high temperature performance, did not show such notable dependency.

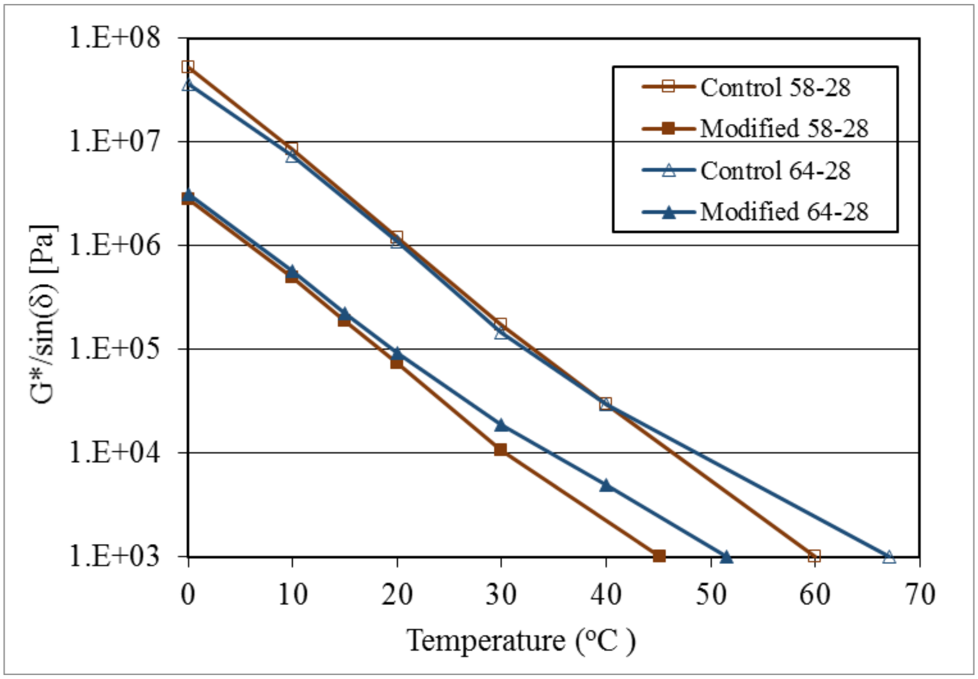


Figure 2.2. Variation of G*/sinδ parameter with temperature

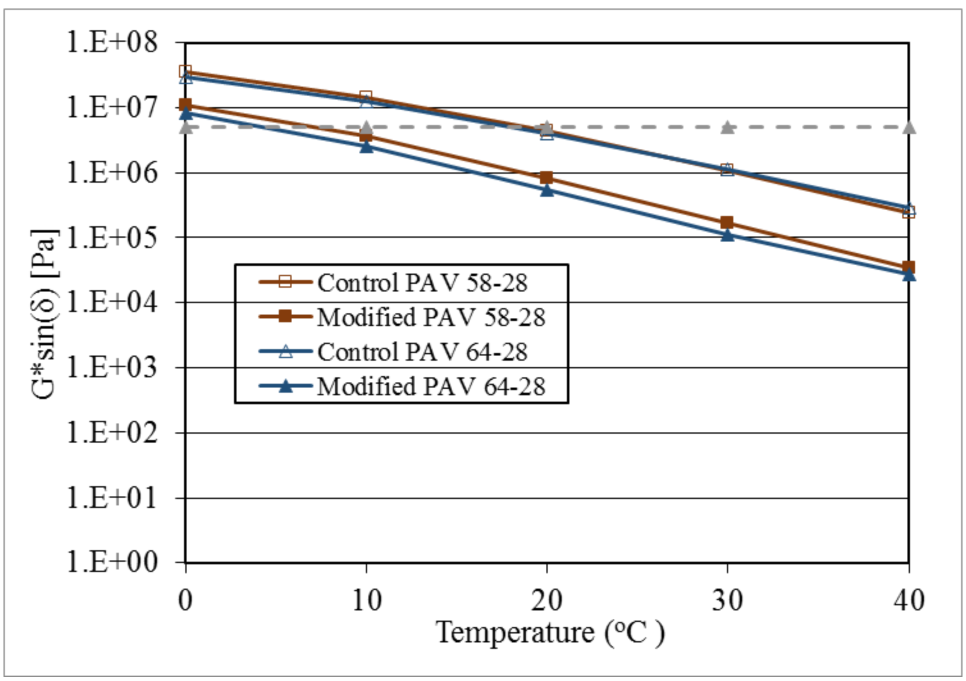


Figure 2.3. Variation of G*sinδ parameter with temperature

2.3.2 Viscosity-temperature susceptibility

The rate of change of the consistency of asphalt binder with temperature determines its temperature susceptibility. Binders with high temperature susceptibility exhibit very low viscosity at high temperatures leading to mixing and compaction problems. Additionally, such binders become very stiff at low temperatures and thus prone to low temperature cracking. For those reasons, high temperature susceptibility is considered to be problematic. To assess the temperature susceptibility, the viscosity temperature susceptibility parameter (VTS) has been used by many researchers due to its simple formulation *(Raouf and Williams 2010)* for formulating binders. Other parameters such as the penetration index (PI) and penetration viscosity number (PVN) have also been reported as good indicators of temperature susceptibility *(Zaumanis et al. 2013)*. VTS is defined as the slope of the least-square best fit line between log-log viscosity and log temperature according to Equation 2.1:

$$\boldsymbol{VTS} = \frac{\boldsymbol{log}[\boldsymbol{log}(\boldsymbol{\eta_1})] - \boldsymbol{log}[\boldsymbol{log}(\boldsymbol{\eta_2})]}{\boldsymbol{log}(\boldsymbol{T_2}) - \boldsymbol{log}(\boldsymbol{T_1})} \qquad [2.1]$$

where $\boldsymbol{T_1}$ and $\boldsymbol{T_2}$ are temperatures of bitumen in Rankine at known points and $\boldsymbol{\eta_1}$ and $\boldsymbol{\eta_2}$ are the corresponding viscosities in cp. The measured VTS values for more than 50 commonly used binders in the United States during the 1960's ranged between 3.36 and 3.98 (Puzinauskas 1967; Rasmussen et al. 2002). Figure 2.4 shows the viscosity versus temperature for both PG 64-28 and PG 58-28 control and modified binders. For both control and modified binders, the relationship between log temperature and log-log viscosity proved to be of a linear form as expressed by Equation 2.1. It is obvious that the viscosity decreases with modification for both binders. It is also interesting to note that the decrease in viscosity is more pronounced at lower temperatures. The use of modified binder would allow for lower mixing and compaction temperatures compared to the control binder. The VTS values calculated from Equation 2.1 are given in Table 2.1. The modified binders demonstrated a considerably lower temperature susceptibility indicating much less change in viscosity with temperature, compared to the control binders.

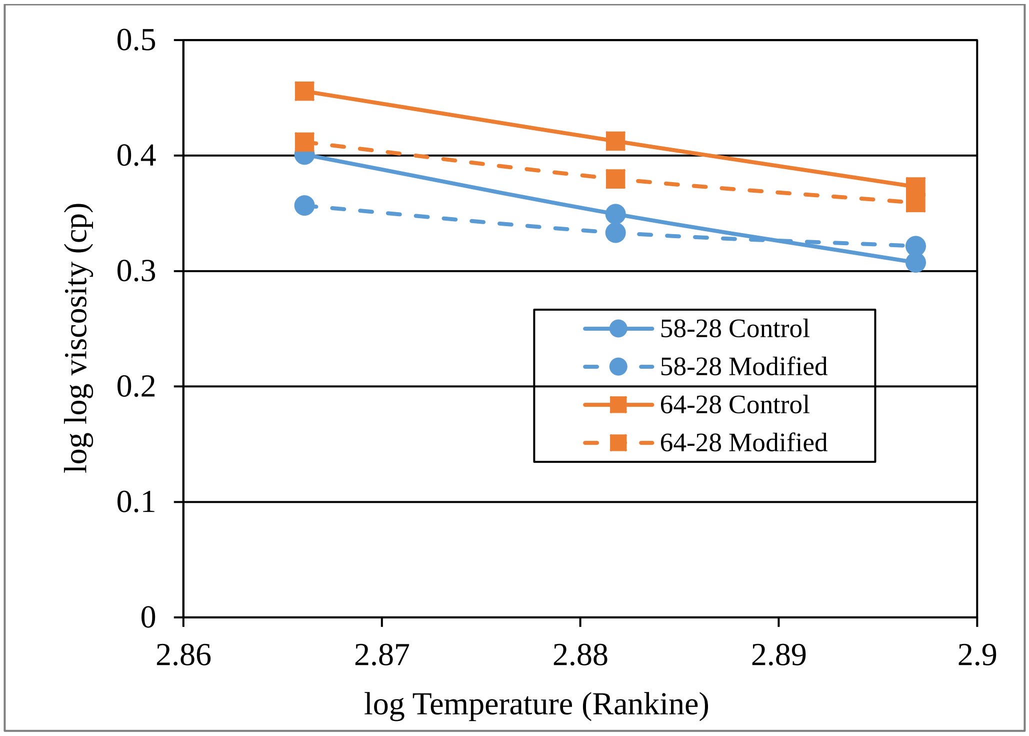


Figure 2.4. Relationship between viscosity and temperature

2.3.3 Dynamic modulus

The dynamic modulus is an important parameter which indicates the stiffness of asphalt concrete mixtures under dynamic loading. Dynamic modulus testing is performed over a range of temperatures and frequencies which simulates different environmental conditions and traffic loading. The work done under NCHRP Project 1-37A provided the basis for the development of the AASHTO Mechanistic-Empirical Pavement Design Guide for New and Rehabilitated Pavement structures which uses dynamic modulus, E*, of hot mix asphalt as a key input parameter for all three hierarchal levels of design

(NCHRP 2004). For level 1, E* is determined experimentally, whereas in both levels 2 and 3, the E* values are determined using the Witczak predictive equation. The E* test was introduced as a preferred Simple Performance Test (SPT), under NCHRP Project 9-19, and incorporated in the Superpave mix design procedure (Witczak et al. 2002). The dynamic modulus E* forms a key input parameter in AASHTOWare Pavement ME Design (AASHTO 2016).

The test setup shown in Figure 2.5 was based on the work done by Witczak (Witczak 2005). A compressive haversine load was applied with a frequency ranging from 25 to 0.01 Hz at different temperatures. The specimens prepared using PG 64-28 were tested at temperatures of 4^{o}C, 21^{o}C, and 37^{o}C, whereas those prepared with PG 58-28 were tested at temperatures of -4^{o}C, 4^{o}C, 21^{o}C and 28^{o}C. The specimens made using PG 58-28 binder were too soft at temperatures above 28^{o}C, and attempts to test them at a higher temperature were met with failure as the mounted brackets slipped off the face of the specimens while testing. The specimens were tested under the conditions of unconfined pressure and the strain was kept between 50 and 150 micro-strain to ensure that deformations are within the linear viscoelastic range of the material. To record the deformation, three LVDTs were placed at equal spacing around the circumference of the specimen and the average of all three readings was reported. The LVDTs were positioned on mounted brackets that were held in place using buttons glued to the face of the specimens.

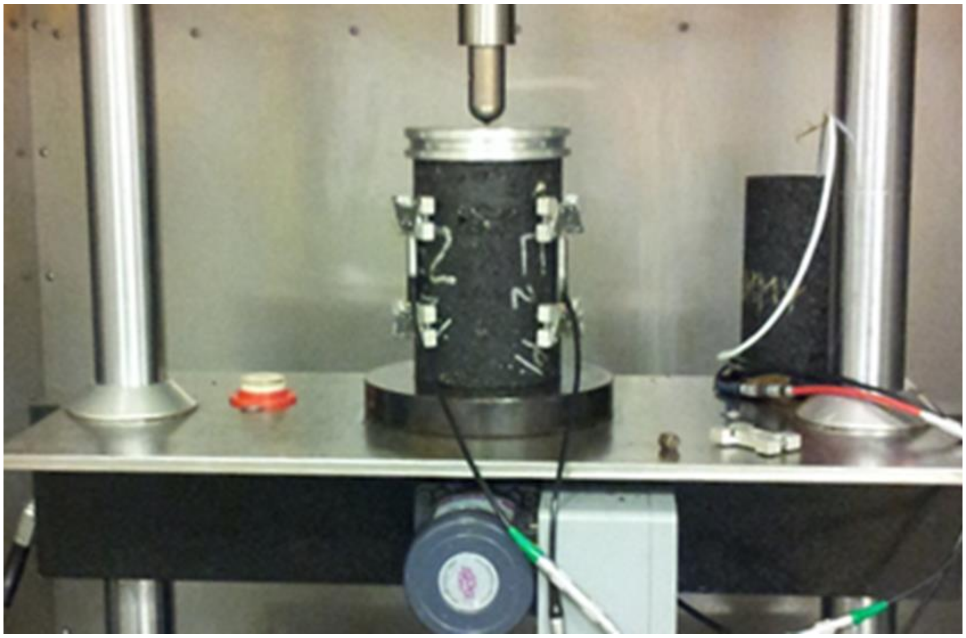


Figure 2.5. Test set-up for dynamic modulus

The dynamic modulus is expressed as the ratio between the maximum stress (σ_o) and maximum recoverable axial strain (ε_o) as outlined in (Witczak 2005)

A phase angle (φ) is defined which is used to evaluate the elasticity of the asphalt mix, where φ=0 denotes a purely elastic mix and φ=90° indicates a purely viscous mix. The construction of "master curves" using dynamic modulus data provides a very efficient way to characterize asphalt mixtures. The concept of time-temperature superposition is utilized to calculate asphalt stiffness across different temperatures and frequencies. Time-temperature superposition is based on the assumption that asphalt materials are rheologically simple and linearly viscoelastic at low strain measurements. Shift factors are used where the dynamic modulus data are shifted horizontally to plot a master curve at a selected reference temperature. Master curves typically follow a sigmoidal curve. A horizontal asymptote at low temperatures indicates a glassy modulus due to physical hardening of the asphalt. At intermediate and high temperatures, asphalt behaves as a Newtonian fluid with a constant slope indicating constant viscosity irrespective of the shear rate.

Shift factors (a_T) were calculated as the ratio between the reduced frequency at the reference temperature $(\omega_r)$and the frequency at the given temperature(ω), expressed as:

$$a_T = \frac{\omega_r}{\omega} \qquad [2.2]$$

A second-order polynomial relation expresses shift factors as a function of temperature, according to the following:

$$\log(a_T) = a_1 T^2 + a_2 T + a_3 \qquad [2.3]$$

where $a_1, a_2 and\ a_3$ are regression coefficients.

The sigmoidal model used to describe the dynamic modulus of asphalt mixtures is expressed as,

$$log|E^*| = \delta + \frac{\alpha}{(1+e^{\beta+\gamma(\log(t_r))})} \qquad [2.4]$$

where t_r is the reduced time of loading at the selected reference temperature, δ is the minimum value of E*, $\delta + \alpha$ is the maximum value of E*, and the parameters β and γ define the shape of the sigmoidal function.

The master curves for the mixtures prepared using PG 64-28 and PG 58-28 binders, at a reference temperature of 21^{o}C, are shown in Figures 2.6 and 2.7, respectively. For all mixtures, it is clear that the addition of the soybean additive caused a reduction in the dynamic modulus at all frequencies. However, the degree in reduction of the dynamic modulus was not constant along the entire range of the master curve, with more reduction taking place at lower frequencies, i.e. higher temperatures. The dynamic modulus values for both PG 64-28 and PG 58-28 control mixtures did not seem to vary significantly with changes in the mixing and compaction temperatures. The performance of PG 64-28 modified mixture, however, was noted to depend on the mixing and compaction temperature, with more reduction in dynamic modulus occurring at a mixing and compaction temperature of 120^{o}C compared to 140^{o}C. The effect of the mixing and compaction temperature was not as clear in the case of the mixtures using the modified PG 58-28. At high test temperatures, the effect of the mixing and compaction temperature on the dynamic modulus could not be assessed due to the wide variability in the results. It was also difficult, using the master curves alone, to compare between the efficiency of the soybean additive for the PG 64-28 and PG 58-28 mixtures. Based on the preceding master curve discussion, it was clear that despite the usefulness of the master curves in characterizing the control and modified mixtures, a more in-depth analysis is required to further study the performance of the soybean additive. The statistical analysis that follows will investigate the significance of each of the test parameters along with their interactions.

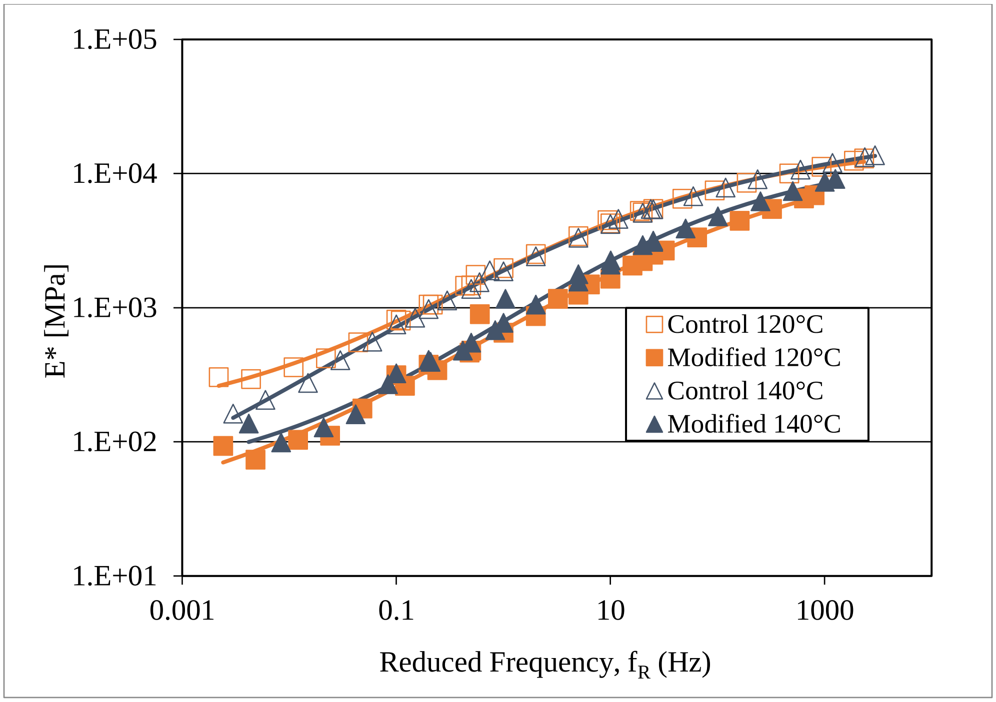


Figure 2.6. Master curve for mixes prepared with PG 64-28

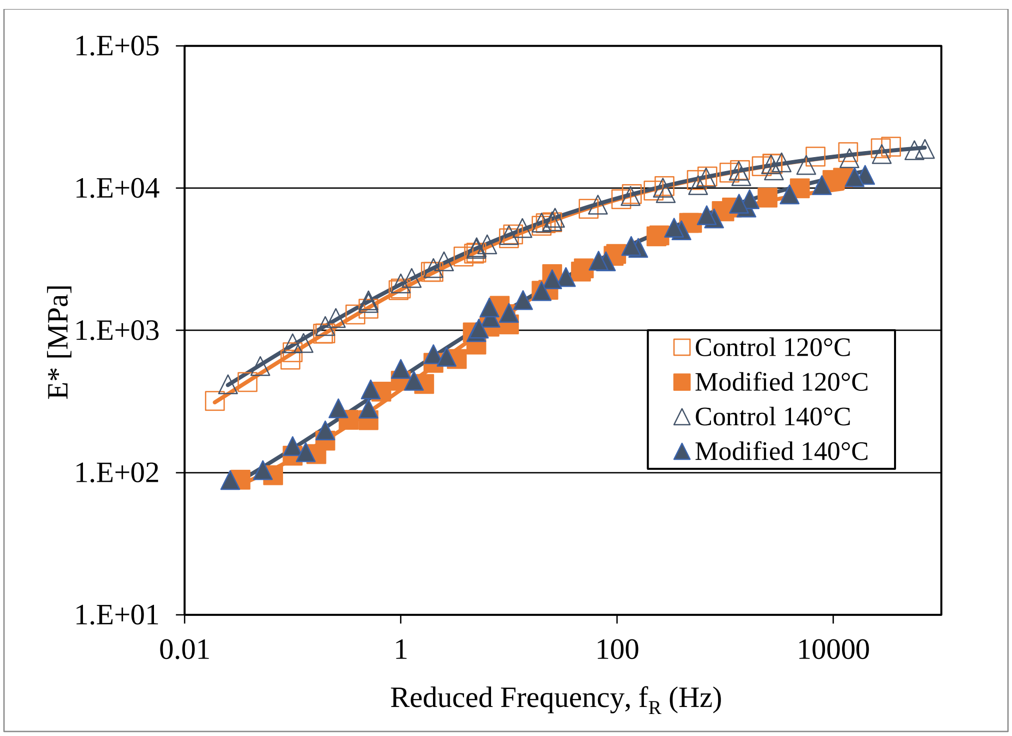


Figure 2.7. Master curves for mixes prepared with PG 58-28

2.3.4 Statistical analysis

The log-log scale used in the plotting of master curves makes it difficult to identify subtle differences between various specimen groups. To provide a detailed analysis and to quantify the differences between dynamic modulus values, a complex statistical analysis using analysis of variance (ANOVA) was performed. The analysis conducted involved more than a simple ANOVA analysis in that it utilized the concept of split- plot repeated measures (SPRM). The dynamic modulus test, in itself, is a repeated measure test since the same specimen is tested under a range of different temperatures and frequencies. A recent study has concluded that using SPRM isolates statistical errors which arises from reusing the same specimen for repeated testing (Buss et al. 2017). Such a statistical technique provides a clear advantage over common simplified statistical analyses that involve comparing data at a fixed temperature or frequency only. Using SPRM provides a full analysis that takes into account the interaction between the different experimental factors and isolates the error due to the variability of specimens that are treated the same.

The design of SPRM experiments involves dividing the experimental factors into whole plot and split plot factors. For the purpose of this analysis, the whole plot factors were identified as the main factors of interest, namely modification, mix temperature, and performance grade. Each of these whole plot factors comprised two levels; the modification factor included control and modified groups, the mix and compaction temperature factor included 120^{o}C and 140^{o}C, and the performance grade factor included PG 64-28 and PG 58-28. As for the split plot factors, these were identified as temperature and frequency, where the temperature factor included 4^{o}C and 21^{o}C, and the frequencies used were 0.1, 1, 2, 5, 10, 20 and 25 Hz. Data from -4°C, 28°C and 37°C were excluded as they were not common between specimens made of the two performance grade binders. The whole plot factors were combined at their different levels to create the whole plot groups, making a total of (2*2*2) 8 groups. Three specimens were tested at each group, for a total of 24 specimens. Each of the whole plot specimens were tested at the various test temperatures and frequencies.

As part of the SPRM design, it was important to isolate the error due to the variability in making the specimens, which could be due to the natural variability of the materials being used, slight differences in air voids, aggregate structure and binder absorption. In doing so, the specimens were defined as a separate factor so that variations among specimens could be determined and factored out of the analysis. The variations in specimens that are treated the same will constitute the sum of squares error term.

One of the fundamental assumptions for conducting an ANOVA analysis is that the variance between the specimen measurements within each group must be equal among all groups. To verify this assumption, a box-plot distribution of dynamic modulus values was plotted for the different test temperatures as shown in Figure 2.8. It was revealed that the variance in the dynamic modulus measurements was not the same for the different test temperatures, with the highest variance occurring at the lower test temperature. A log transformation of the dynamic modulus data proved to be very useful in providing a data set with roughly similar variances among different test temperatures, as shown in Figure 2.9.

An open-access statistical software "R" is used for the analysis. A summary of the p-values for the whole plot and subplot factors along with their interactions are shown in

Tables 2.2 and 2.3. The p-values are used as an indicator of the statistical significance of a given factor or factor interaction. Factors or factor interactions with p-values at or below a chosen alpha value are considered statistically significant. An alpha value of 0.05 represents 95% statistical difference at 95% confidence level. The factors or factor interactions with p-values below a chosen alpha value of 0.05 are highlighted.

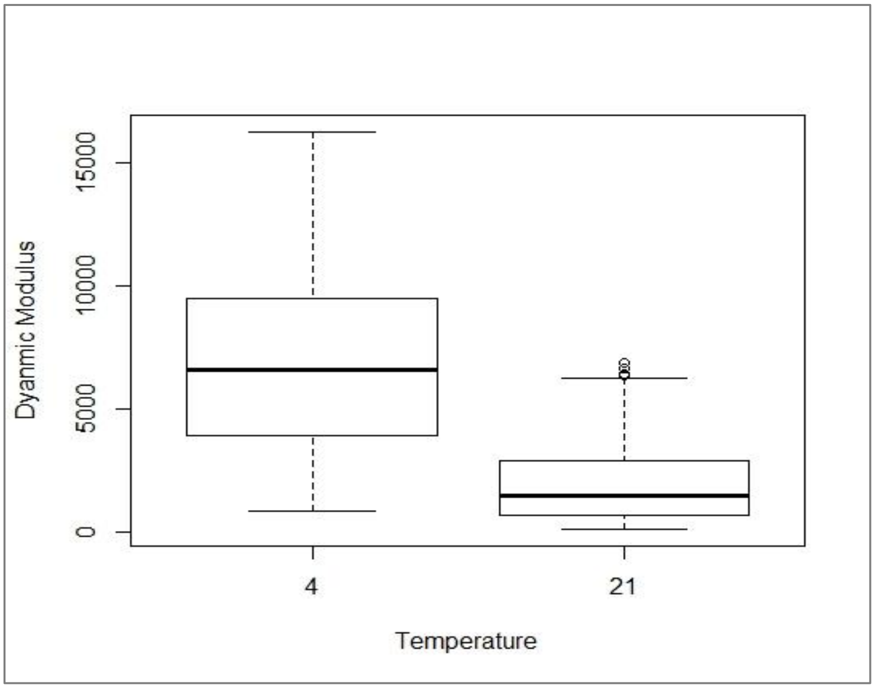


Figure 2.8. Box-plot distribution of the dynamic modulus with test temperature

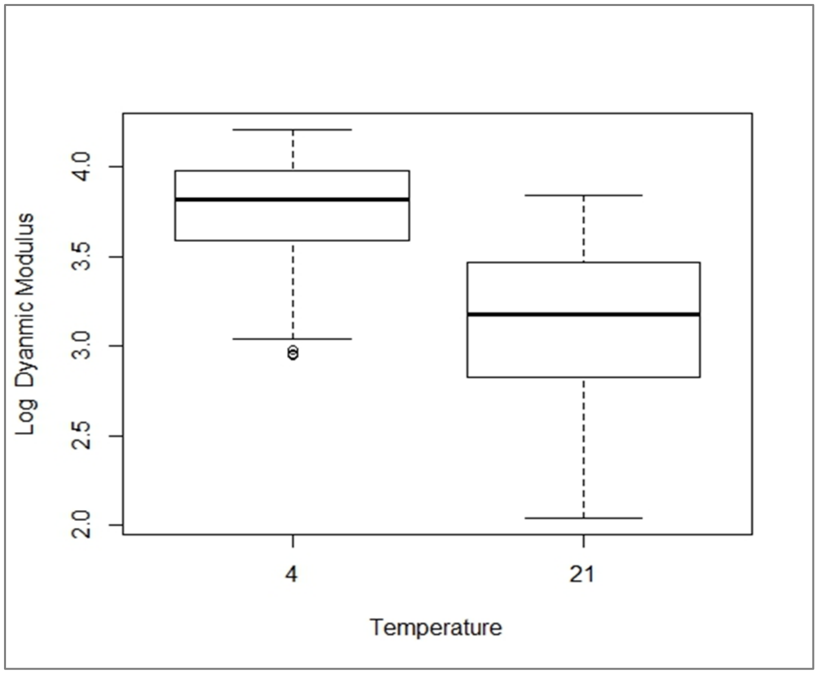


Figure 2.9. Box-plot distribution of log dynamic modulus with test temperature

Table 2.2. Summary of Whole Plot P-values for the ANOVA analysis

Whole plot factors	Df	Sum Sq	Mean Sq	F value	p-value
PG	1	0.255	0.255	6.09	0.025251
Modify	1	21.552	21.552	515.308	1.35E-13
MixTemp	1	0.314	0.314	7.512	0.014506
PG:Modify	1	0.746	0.746	17.833	0.000647
PG:MixTemp	1	0.008	0.008	0.181	0.675909
Modify:MixTemp	1	0.154	0.154	3.676	0.073221
PG:Modify:MixTemp	1	0.039	0.039	0.935	0.347971
Residuals	16	0.669	0.042		

Table 2.3. Summary of Sub Plot P-values for the ANOVA analysis

Sub plot factors	Df	Sum Sq	Mean Sq	F value	p-value
Temp	1	42.18	42.18	34218	<2E-16
Freq	8	32.77	4.1	3322.6	<2E-16
PG:Temp	1	0.23	0.23	185.16	<2E-16
Modify:Temp	1	0.28	0.28	227.63	<2E-16
MixTemp:Temp	1	0.02	0.02	16.342	6.89E-05
PG:Freq	8	0.13	0.02	13.625	<2E-16
Modify:Freq	8	0.99	0.12	100.34	<2E-16
MixTemp:Freq	8	0.01	0	0.764	0.63451
Temp:Freq	8	1.58	0.2	159.81	<2E-16
PG:Modify:Temp	1	0.12	0.12	95.998	<2E-16
PG:MixTemp:Temp	1	0.02	0.02	13.387	0.0003
Modify:MixTemp:Temp	1	0.01	0.01	4.169	0.04214
PG:Modify:Freq	8	0.07	0.01	7.335	7.85E-09
PG:MixTemp:Freq	8	0.01	0	1.143	0.3348
Modify:MixTemp:Freq	8	0	0	0.447	0.89165
PG:Temp:Freq	8	0.03	0	2.606	0.00923
Modify:Temp:Freq	8	0.08	0.01	8.531	2.31E-10
MixTemp:Temp:Freq	8	0	0	0.46	0.88377
PG:Modify:MixTemp:Temp	1	0	0	0.005	0.94543
PG:Modify:MixTemp:Freq	8	0	0	0.237	0.98354
PG:Modify:Temp:Freq	8	0.01	0	1.415	0.18995
PG:MixTemp:Temp:Freq	8	0.01	0	0.896	0.52048
Modify:MixTemp:Temp:Freq	8	0	0	0.431	0.90222
PG:Modify:MixTemp:Temp:Freq	8	0	0	0.409	0.91473
Residuals	272	0.34	0		

According to Table 2.2, the type of binder (PG), mixing and compaction temperature and the modification were all significant factors in determining the dynamic modulus. More precisely, differences in dynamic modulus values between groups of specimens using, for instance, different binder grades were statistically significant at a 95% confidence level. This was also true between groups of specimens made at different mixing temperatures, as well as between groups of specimens made with control and modified binders. In addition to the significance of the three whole plot main factors, the interaction between the binder type (PG) and the modification factors was also shown to be significant. This essentially means that that the extent of the effect of modification on the dynamic modulus is found to be significantly dependent on the binder grade. A plot of the mean of the log dynamic modulus, of the type shown in Figure 2.10, clearly demonstrates this finding where the lack of parallelism between the two lines is an indicator of the interaction between the two factors. From Figure 2.10, it can be seen that the drop in the mean of the log dynamic modulus as a result of modification was significantly larger in case of the PG 58-28 binder compared to the PG 64-28 binder. This finding leads one to believe that the efficiency of the soybean additive in reducing the dynamic modulus is dependent to a large extent on the binder grade and the binder's composition.

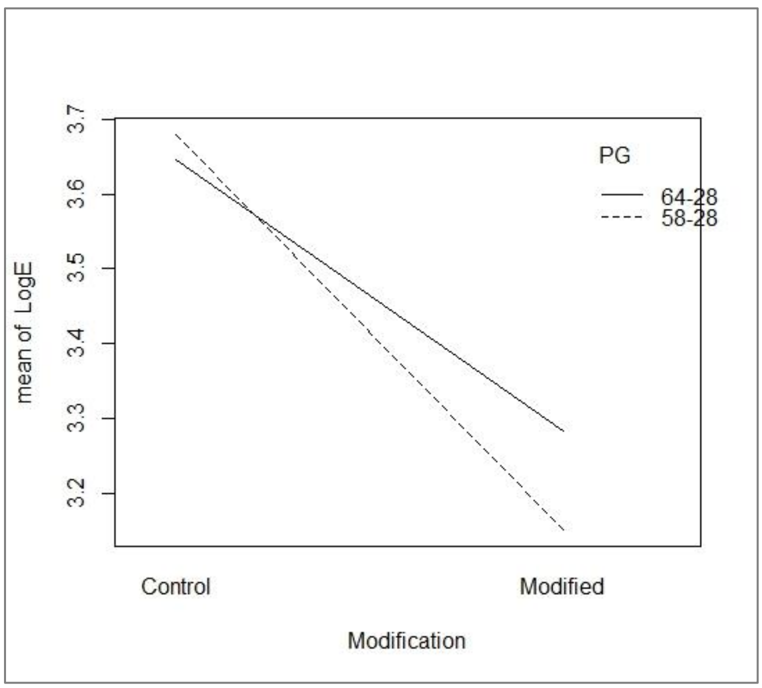


Figure 2.10. Interaction plot for PG and modification

According to Table 2.3, both the subplot factors, namely temperature and frequency were also found to be statistically significant, along with their two-way interaction with the whole plot factors. The analysis also revealed a number of three-way interactions between factors. An example of a three-way interaction is the interaction between PG, modification and temperature. This interaction is best explained through Figure 2.11 which plots the mean log dynamic modulus for both the control and modified binders at both test temperatures. It is shown that the degree of interaction between PG and modification varies with test temperature. More interaction is taking place between the two factors at the higher test temperature of 21^{o}C. This can be explained in terms of the PG of the two binders. Both binders have the same low temperature grade, which explains their roughly similar response to modification at low temperature whereas their response to modification deviates notably at high temperature due to the fact that their high temperature grades are different. This finding further illustrates that the degree in reduction of the dynamic modulus is binder grade and composition dependent, where the drop in dynamic modulus at both low and high temperature ranges is related to the low and high temperature binder grades, respectively.

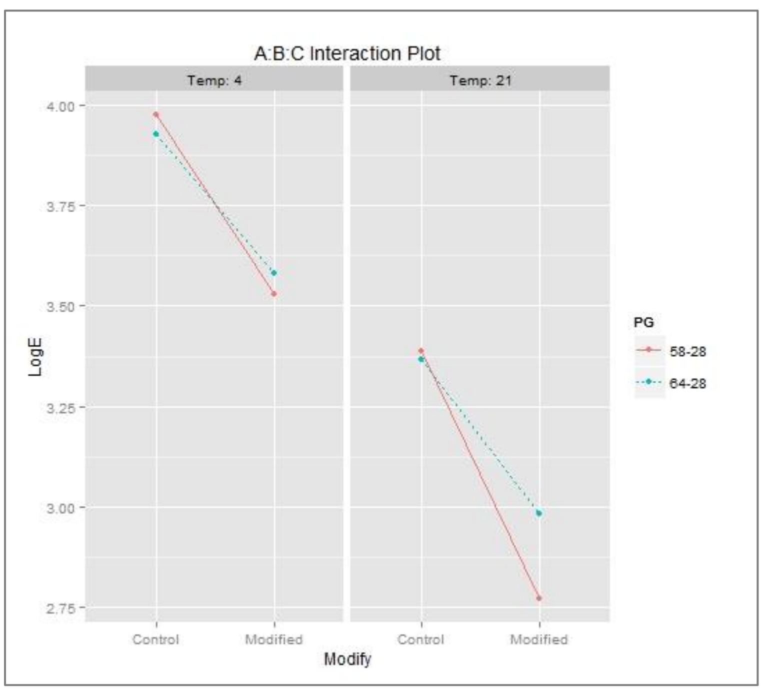


Figure 2.11. A plot of the three-way interaction between PG, modification and temperature

The analysis also revealed an interesting three-way significant interaction between mixing and compaction temperature, test temperature and modification. Figure 2.12 illustrates the interdependence of these three factors, where the lack of parallelism at test temperature 4^{o}C signifies more interaction between the modification and the mixing and compaction temperature compared to 21^{o}C test temperature. When tested at 4^{o}C, the drop in dynamic modulus of the specimens prepared at a mixing and compaction temperature of 120^{o}C was significantly larger than those specimens prepared at 140^{o}C. However, at the 21^{o}C test temperature, the effect of mixing and compaction temperature on the change in dynamic modulus upon modification was not as evident. This finding verifies the results from the master curve analysis where it was noted that the effect of the mixing and compaction temperature was insignificant at the higher test temperature.

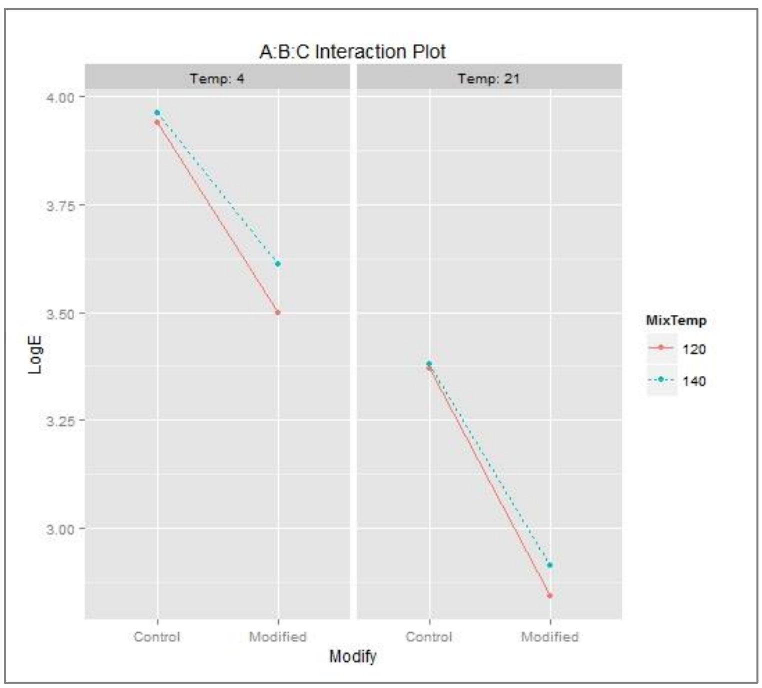


Figure 2.12. A plot of the three-way interaction between mixing temperature, modification and test temperature

2.3.5 FTIR-ATR

FTIR is used extensively to identify functional groups present in asphalt binders. Absorption/transmission peaks in an IR spectrum mark different vibrational frequencies of atomic bonds, which represent different functional groups. A study of the functional groups can reveal some useful information about aging of bitumen. An increase in carbonyls and sulfoxides chemical functional groups has been associated with an increase in viscosity and was noted to take place with aging (Herrington et al. 1994; Petersen and Glaser 2011).

FTIR-ATR uses attenuation of light internally reflected on a non-absorbing surface. The specimen is directly placed on the reflecting surface and absorbs the attenuated light, which penetrates a depth of only a few micrometers. The use of FTIR-ATR increases the sensitivity of measurement because multiple reflections lead to increased absorbance.

FTIR has been used to characterize aging in bitumens using the sulfoxides and carbonyls functional groups. The peaks at wavenumbers 1030 cm^{-1} and ≈1740 cm^{-1} represent the sulfoxides and carbonyls, respectively. Due to the differences in thickness between samples, the absolute peak values cannot be used as a measure of aging evolution. The sulfoxide and carbonyl peak values are however normalized against reference aliphatic functional groups, which do not significantly change with aging. The peaks at wavenumbers ≈1377 cm^{-1} and ≈1466 cm^{-1} representing methyl (CH_3) and ethyl (CH_2) groups, respectively, are usually taken as reference. Carbonyl and sulfoxides indices are calculated as follows:

$$I_{CO} = {}^{V_{CO}}\!/_{V_r} \qquad [2.5]$$

$$I_{SO} = {}^{V_{SO}}/_{V_r} \qquad [2.6]$$

where, I_{CO}: Carbonyl index, I_{SO}: Sulfoxide index, V_{CO}: Carbonyl peak value (Height or area), V_{SO}: Sulfoxide peak value (Height or area), V_r: Ethyl + Methyl peak values.

Calculating the peak areas was shown to be a good indicator of the aging indices (Marsac et al. 2014). In this study, the carbonyl peak area was calculated between wavenumbers 1753 cm^{-1} and 1660 cm^{-1}, the sulfoxide peak area between wavenumbers 1047 cm^{-1} and 966 cm^{-1}, and the ethyl and methyl peak areas between wavenumbers 1525 cm^{-1} and 1350 cm^{-1}, as outlined in the French MLPC Method No. 69 (Mouillet et al. 2009).

Figures 2.13 and 2.14 show the absorption FTIR spectra for the unaged, RTFO, and PAV control PG58-28 and PG64-28 binders. All spectra show distinct peaks that are typical of asphalt binders. An interpretation of the important peaks that appear in the spectra are provided in Table 2.4.

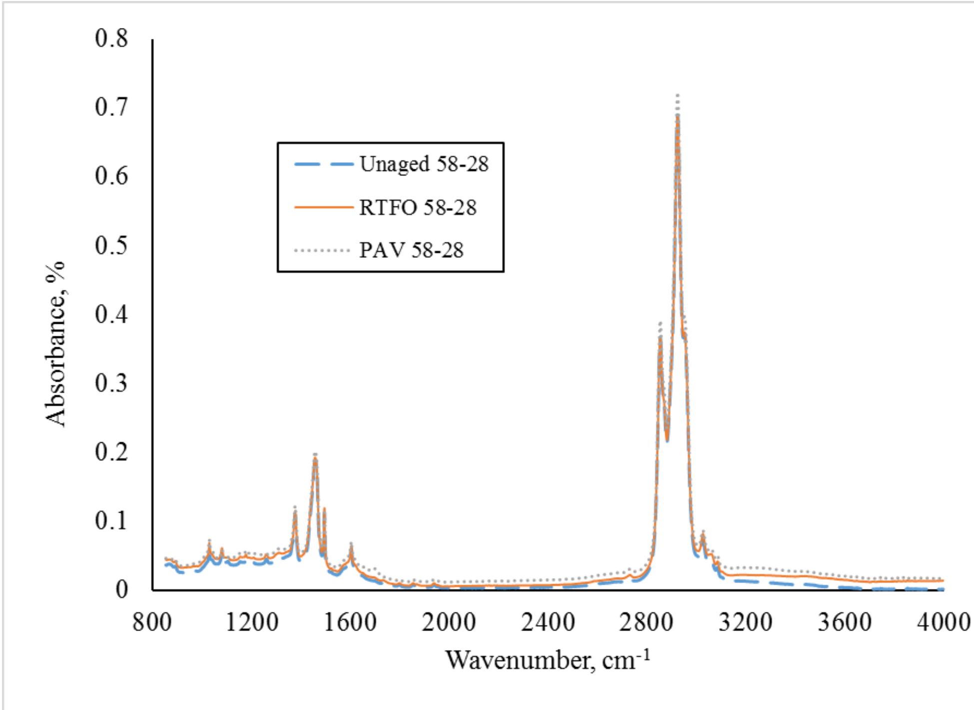


Figure 2.13. FTIR spectrum for the control PG58-28

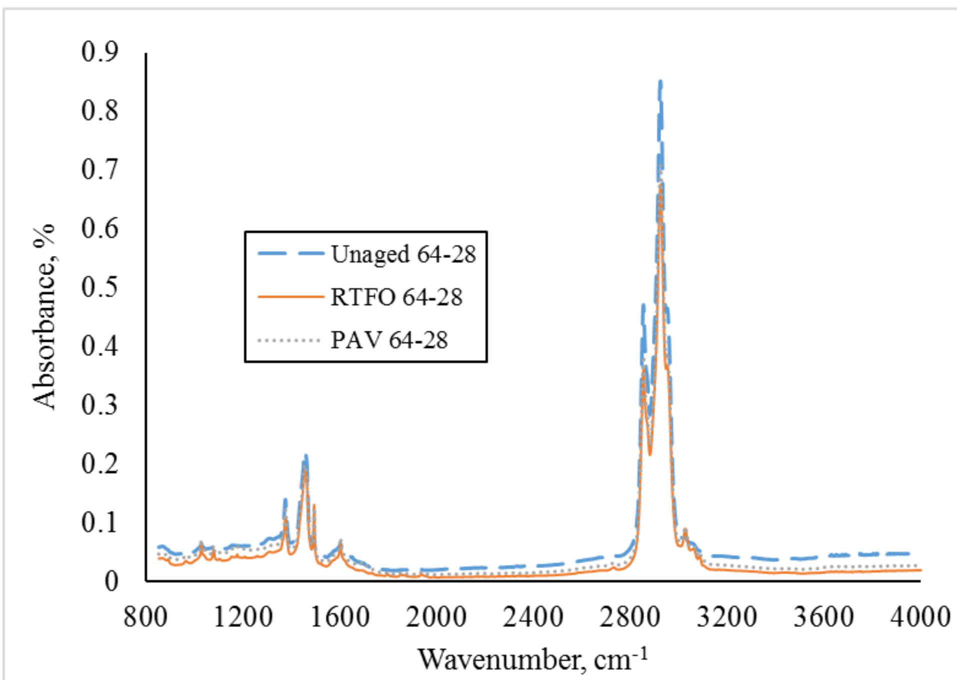


Figure 2.14. FTIR spectrum for the control PG64-28

Table 2.4. Interpretation of functional groups appearing in the FTIR spectra

Functional group	Absorption wavenumbers (cm^{-1})
Carbonyls	1741 (stretch)
Aromatic and Heteroaromatic rings	1604 (ring stretch)
Sulfoxides	1030 (stretch)
Methyl (aliphatic)	2955-2871 (stretch), 1456-1377 (bend)
Ethyl (aliphatic)	2924-2853 (stretch), 1496 (bend)

The FTIR spectra for the modified PG58-28 and modified PG64-28 are shown in Figures 2.15 and 2.16, respectively. Apart from the peaks in Table 2.4, an additional peak at 1155 cm^{-1} appears in the spectra for the modified binders, which is attributed to the ester moiety that is part of the soybean additive. It is also observed that the carbonyl peak increases significantly with the addition of the soybean additive owing to the ester bond that is present in the soybean additive structure.

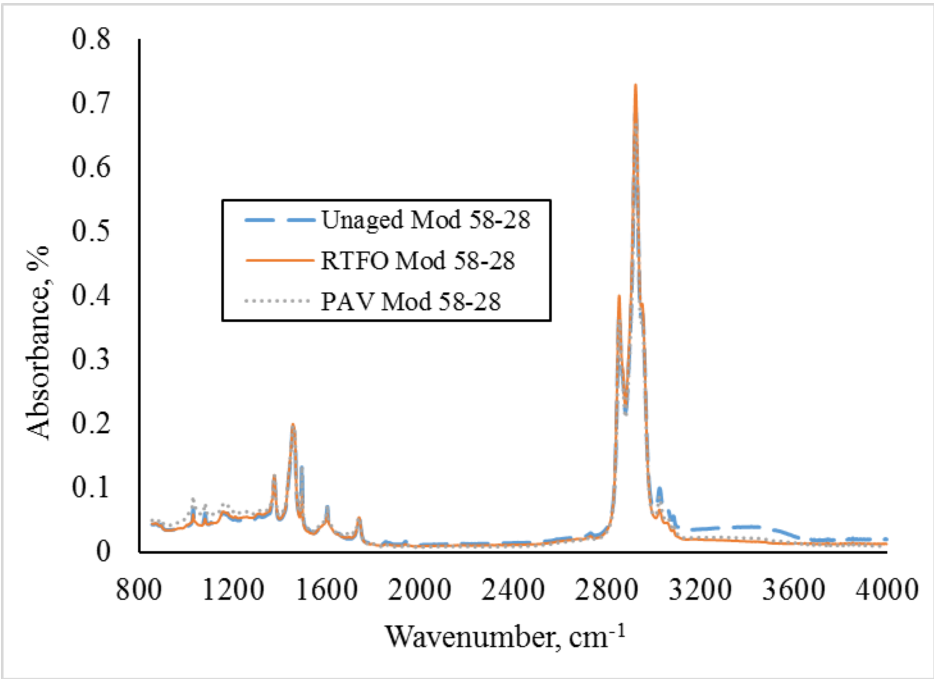


Figure 2.15. FTIR spectrum for the modified PG58-28

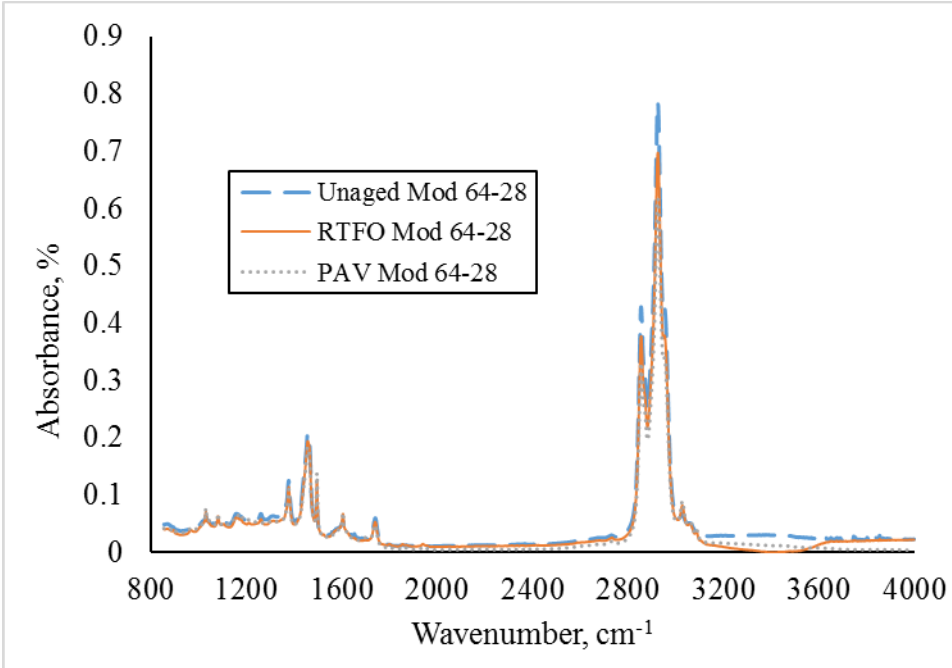


Figure 2.16. FTIR spectrum for the modified PG64-28

The carbonyl and sulfoxide indices were calculated according to Equations 2.5 and 2.6, using the peak areas as detailed above. A plot of both indices is provided in Figures 2.17 and 2.18. As expected, the carbonyl index is shown to increase with aging. The evolution rate of the carbonyl index was comparable for both control and modified binders which indicate that the addition of the soybean additive did not influence the aging behavior of the binder. The sulfoxide index showed a similar increase with aging for the PG58-28 binder, however a drop in the sulfoxide index was noted at later stages of aging for the PG64-28 binder. The drop was noted for both control and modified binders. Such drop in the sulfoxides index is not uncommon as decomposition of sulfoxides under severe aging conditions have been previously reported (Herrington 1995; Ouyang et al. 2006).

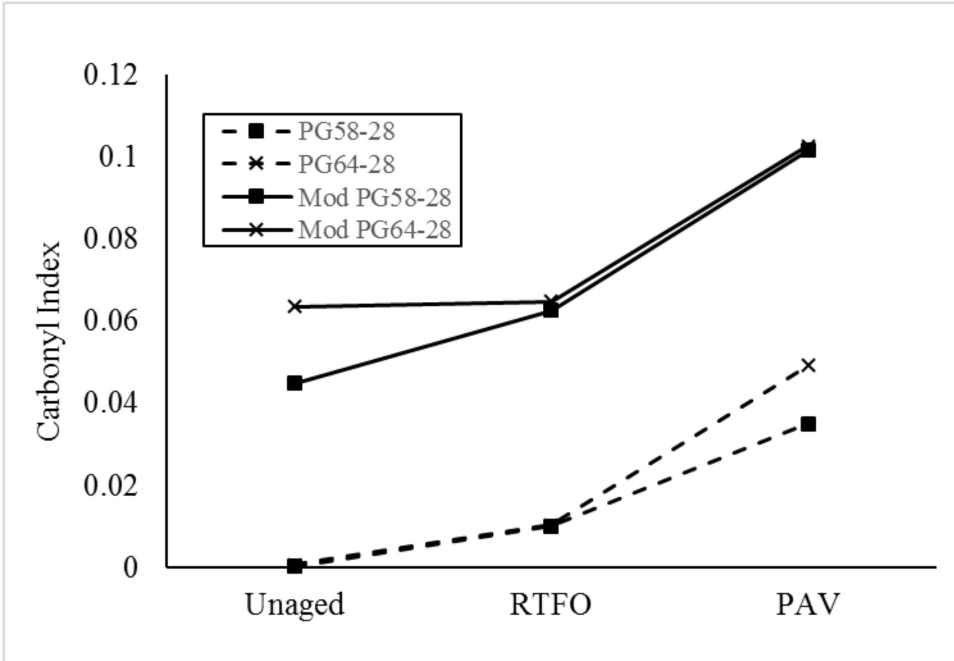


Figure 2.17. The change in carbonyl index with aging

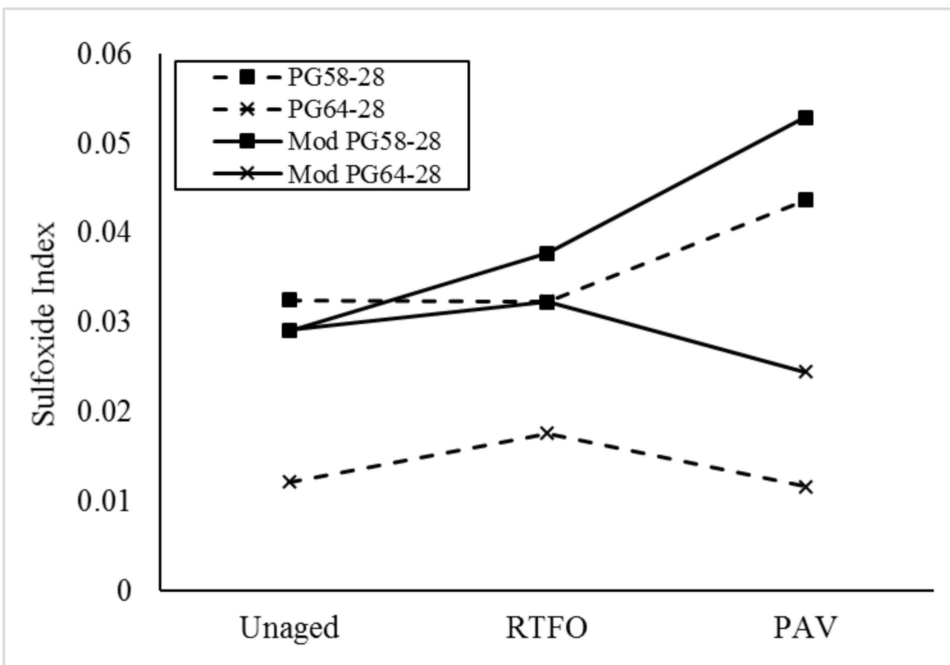


Figure 2.18. The change in sulfoxide index with aging

2.4 Summary and Conclusions

In this paper, a soybean-derived additive was investigated as a potential rejuvenator. The effect of adding a 0.75% rejuvenator by weight of binder on the rheological properties of both a PG58-28 and a PG64-28 was studied. The rejuvenator resulted in an improvement in the low temperature performance of both asphalt binders. The performance efficiency of the rejuvenator was shown to be dependent on the performance grade (PG) of the asphalt binder. In this case, the enhancement in fatigue resistance upon addition of the rejuvenator was more for the PG64-28 compared to the PG58-28. The use of rejuvenator also led to an increase in the rutting susceptibility, which could be controlled by careful selection of the rejuvenator content.

Rotational viscometer testing revealed that the soybean modified binders had much lower viscosity values as compared to the control binders at all test temperatures. The reduction in viscosity was greater at low temperatures, which promotes applying lower mixing temperatures when using the modified asphalt binders. It was also apparent that the modified binders had less viscosity-temperature susceptibility compared to the control binders.

Asphalt mixtures prepared using the modified binders at two different mixing and compaction temperatures, namely 120^{o}C and 140^{o}C, were tested for dynamic modulus, and compared against mixtures made with control binders. The constructed master curves showed a reduction in dynamic modulus with the soybean modification at both mixing temperatures. The effect on dynamic modulus at low test temperatures was however more prominent at the mixing temperature of 120^{o}C, in particular for the PG64-28 mixtures.

A comprehensive statistical analysis was performed to further analyze the effect of the different factors on the dynamic modulus. It was shown that the performance grade (PG), the mixing and compaction temperature, and modification were significant parameters in determining the dynamic modulus. The statistical analysis also verified that the performance of the soybean additive is dependent on the asphalt binder. Furthermore, it was revealed that the effect of the mixing and compaction temperature was significant at low test temperatures only, but not at high test temperatures.

FTIR-ATR was used to characterize aging in both the control and modified asphalt binders. It was noted that the carbonyl and sulfoxide functional groups were shown to increase with aging. Studying the evolution of these two functional groups, it was concluded that the modification did not cause any significant influence on the aging behavior of the asphalt binders.

In conclusion, the soybean-derived additive has proven to be very efficient in modifying the rheological properties of asphalt binders and the dynamic modulus of asphalt mixtures. It is remarkable to note that such effect of the soybean additive was achieved at a very small dosage of 0.75%, compared to dosages that can exceed 12% with commercially available rejuvenators. An even lower dosage can be used to reduce the negative impact of lowering rutting resistance, while still improving the low temperature fatigue performance considerably.

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CHAPTER 3. PRELIMINARY EXAMINATION OF SOYBEAN OIL DERIVED MATERIAL AS A POTENTIAL REJUVENATOR THROUGH SUPERPAVE CRITERIA AND ASPHALT BITUMEN RHEOLOGY

Modified from a paper published in Construction and Building Materials

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Abstract

The increased use of recycled asphalt materials in bituminous mixtures has led to increasing interest in rejuvenators. Rejuvenators are primarily used to restore the rheological properties of aged bitumens to their unaged state. In this work, the effect of adding a soybean-derived biomaterial at a 0.75% by mass of bitumen to a polymer modified PG64-28 and a neat PG58-28 is studied. Dynamic Shear Rheometer, Bending Beam Rheometer, and Rotational Viscometer are used to characterize the bitumens rheology. The effect of aging on the longevity of the soybean additive is examined. It was revealed that this material is a viable candidate as a rejuvenator. At such low dosage, it had a remarkable effect on the fatigue and low temperature properties of both bitumens. It also led to a notable decrease in the complex shear modulus accompanied by an increase in the phase angle, which is essentially reversing the effect of aging.

3.1 Introduction

In the past years, the interest in using reclaimed asphalt pavement (RAP) has been growing rapidly. This rise in interest is motivated by a number of reasons including a desire to reduce cost, preserve the environment, and conserve energy. With the increasing bitumen prices and dwindling supply of higher quality virgin aggregate, there is a compelling need to use larger amount of less expensive RAP to replace the more expensive virgin bitumen and aggregates. Despite the need to use higher proportions of RAP, a recent survey, conducted on the use of recycled materials in asphalt pavements, revealed that the average percentage of RAP in the US has only increased from 15% in 2009 to 20% in 2014 (Hansen and Copeland 2015). Such reluctance to use more RAP in asphalt pavements stem from the fact that the aged RAP bitumen has undesirable high stiffness and low creep rate, which makes it susceptible to low temperature thermal cracking (Yu et al. 2014). Accordingly, using higher percentages of RAP produces very stiff mixes which are difficult to field compact, and can result in unexpected premature failure (Copeland 2011).

Several techniques are being implemented to allow for the use of RAP in asphalt mixes, including mixing with a softer virgin bitumen, using higher asphalt content mixtures, and using warm-mix technology to minimize the short-term aging effect and to lower asphalt absorption (Im et al. 2016). These techniques are suitable for lower RAP content mixtures, however they failed to allow for the use of higher RAP content. For instance, the use of softer virgin bitumen would compensate the aging of the RAP bitumen for low RAP content mixes but its effect on high RAP content mixes would be insignificant (West et al. 2013). In this regard, rejuvenators have shown to be a very attractive alternative in that they can lead to higher RAP content. Rejuvenators have proven to be very efficient in restoring the aged bitumens to their original state. With the increase in popularity of hot-in-place pavement recycling (HIR), rejuvenators are becoming even more important. In HIR, old pavements are heated and milled in place before being mixed with virgin aggregates, virgin bitumen, and a rejuvenator.

Asphalt is composed of four distinct chemical fractions, namely asphaltenes, resins, aromatics, and saturates. Resins, aromatics, and saturates are collectively referred to as maltenes. The high molecular weight asphaltenes forms a colloidal suspension in low molecular weight maltenes. The asphaltene content has a great influence on asphalt viscosity. In a recent study, increasing the asphaltene content by addition of propane deasphaltene tar (PDA) resulted in a noticeable increase in the penetration index, a similar effect was also noted with aging (Firoozifar et al. 2011). Apart from the asphaltene content, the resins also plays an important role since they act as dispersing agents to the asphaltenes. The ratio of resins to asphaltenes is an important parameter that controls the degree of dispersion of asphaltenes and accordingly the asphalt viscosity (Bitumen 1995).

Rejuvenators are chemical or bio-derived additives which typically contain a high proportion of maltenes, which serves to replenish the maltene content in the aged bitumen that has been lost as a result of oxidation (Copeland 2011). The addition of maltenes helps rebalance the chemical composition of the aged bitumen, which contain high percentage of asphaltenes. Rejuvenators are added during mixing and are believed to diffuse within the aged bitumen imparting softening characteristics. The rejuvenator initially coat the outside of the RAP aggregates before they gradually seep into the aged bitumen layer until they diffuse through the film thickness (Carpenter and Wolosick 1980).

A number of studies have investigated the performance of rejuvenated bitumens and resulting asphalt mixtures. The main focus of these studies was to investigate the effect of rejuvenators on the stiffness of the aged bitumen and the low temperature cracking resistance of the produced asphalt mixtures (Elseifi et al. 2011; Hajj et al. 2013; Zaumanis et al. 2013). It has been concluded that rejuvenators successfully reduce the aged bitumen stiffness and notably improve the low temperature cracking resistance of the resulting mixture (Mogawer et al. 2013; Tran et al. 2012). The selection of the rejuvenator dosage was found to have a great influence on the effectiveness of the treatment (Shen et al. 2007). It was suggested that blending charts could be used to obtain an optimum dosage that meets the requirements of the bitumen specifications. Determining the proper dose is crucial since a higher dosage may cause undesirable excessive softening of the bitumen, which may lead to performance problems such as rutting. The rejuvenated bitumen properties can be determined through extraction of the aged bitumen, blending with the rejuvenator, and subsequent testing. Such technique, however, assumes perfect blending between the rejuvenator and the aged bitumen, which does not necessarily reflect actual conditions. During actual mixing, the rejuvenator might not diffuse fully through the aged asphalt film thickness.

The performance of mixes which involve RAP is controlled to a large extent by the degree of blending between the RAP bitumen and the virgin bitumen in addition to the effective percentage of RAP bitumen which contribute towards the total asphalt content(Huang et al. 2005). Through the use of rejuvenators, the RAP bitumen becomes less stiff and can thus blend more easily with the virgin bitumen.

Aged RAP bitumens are characterized as having a high relative viscosity. The high viscosity can lead to poor mixing and compaction, hence the study of the rejuvenator’s effect in reducing the viscosity is very important. Achieving low viscosity ensures that the bitumen has sufficient flow to properly blend with the virgin bitumen and to uniformly coat both virgin and RAP aggregates. It is equally important for the rejuvenator to be able to lower the RAP bitumen viscosity to acceptable levels without the need for high dosages. High dosages of rejuvenators could lead to potential rutting, stripping and mix instability problems (Zaumanis et al. 2013). The study of the temperature-viscosity dependence of the rejuvenated aged bitumen is also important because high mixing temperatures could damage the bitumen so it is advantageous to have an effective rejuvenator which would promote low mixing temperatures at a low dosage.

Rejuvenators vary greatly according to their chemical composition and origin. Numerous research efforts have been directed to assessing the performance of commercially available rejuvenators, as well as proposing new materials to act as rejuvenators. Materials derived from distilled tall oil, petroleum based aromatic extract, and organic oil have been successfully applied as rejuvenators (Zaumanis et al. 2014). Organic oil bio-derived rejuvenators have been presented as a more safe alternative to the carcinogenic aromatic oil rejuvenators (Hajj et al. 2013). Organic oils have been successfully used by the Florida Department of Transportation (FDOT) for mixes that contain 40% RAP. Two trial sections were constructed on I-95 using 0.75% of the organic oil by weight of RAP in 2009. Other DOTs have reported using organic oil at varying RAP contents such as the Texas DOT with 35% RAP and 5% RAS, and the New York City DOT with 20% RAP (Hajj et al. 2013). A study conducted by Zaumanis et al. (Zaumanis et al. 2014) investigated the performance of six different rejuvenators including waste engine oil, distilled tall oil, waste vegetable oil, waste vegetable grease, organic oil, and aromatic extract. The study was performed on mixes using 100% RAP, with a 12% rejuvenator dosage by mass of RAP bitumen. It was shown that organic-based rejuvenators were more efficient in lowering the low temperature performance grade (PG) of the rejuvenated bitumen compared to petroleum-based rejuvenators. It was also shown that none of the rejuvenators significantly reduced the high temperature PG, which indicates that with the use of an appropriate rejuvenator dosage, rutting should not be a concern. All of the six rejuvenators seemed to work efficiently at this dosage except for waste engine oil which did not meet the low temperature grade and resulted in high mass loss, which indicates volatility and increased aging susceptibility.

A number of studies have addressed the issue of durability of rejuvenated asphalt. In the work done by Shen et al. (Shen et al. 2007), mixtures containing 48% RAP and 12.5% rejuvenator, by mass of RAP bitumen, were evaluated for rutting in an asphalt pavement analyzer (APA) and for moisture sensitivity using indirect tensile strength (ITS) tests. It was shown that the performance of the rejuvenated mixes was better than the control RAP mixes prepared with a softer virgin bitumen. A recent study investigated the long-term aging behavior of rejuvenated bitumen prepared using five different rejuvenators (Mohammadafzali et al. 2015). It was revealed that the long-term aging effect differed greatly among rejuvenators. Two of the rejuvenators, namely aromatic extract and a water-based emulsion from naphthenic crude, caused slowing down of the aging rate compared to virgin bitumens while the other three, namely petroleum neutral distillate, oil-based bio-rejuvenator and a polyol ester pine, accelerated aging. Study of long-term cracking and fatigue resistance of rejuvenated mixes was performed on full-depth asphalt pavement specimens (Mohammadafzali et al. 2015). The long-term aging was simulated using an Accelerated Pavement Weathering System (APWS). APWS simulates real weather conditions including rain, sunshine and temperature fluctuations. The Texas Overlay Test, as described in TEX-248-F (Designation 2009), was performed to assess fatigue and cracking resistance for specimens subjected to 0, 1000, and 3000 hours of APWS aging. The results indicated that the rejuvenated mixes showed better fatigue and reflective cracking resistance compared to the virgin mixes. It was shown that rejuvenated asphalt mixtures showed better performance in terms of fatigue and reflective cracking compared to virgin asphalt mixtures, even after 3000 hours of APWS aging (Mohammadafzali et al. 2015).

The effectiveness of the rejuvenator is also related to the bitumen's chemical composition. A specific rejuvenator could work effectively for one bitumen but not another. Two bitumens from different crude sources, namely AAD (PG 58–28) and ABD (PG 58–10) from the Federal Highway Administration's Material Reference Library, were rejuvenated using aromatic extract rejuvenators (Yu et al. 2014). The effect of rejuvenation on the low temperature grade was more pronounced on the ABD bitumen compared to the AAD bitumen, which was attributed to a better chemical interaction between the rejuvenator and the bitumen.

The changes in the chemical composition of the bitumen as a result of aging and rejuvenation can be examined using SARA fractionation. PAV aging of a virgin bitumen, followed by SARA fractionation, revealed conversion of aromatics to asphaltenes with no significant change in resins or saturates (Yu et al. 2014). Addition of aromatic extract rejuvenator caused an increase in the content of saturates and aromatics accompanied by a reduction in the asphaltenes proportion. The chemical composition of the rejuvenated bitumen did not exactly mirror that of the virgin bitumen but the overall effect of the rejuvenation process was to introduce chemical changes that helped restore the virgin bitumen properties.

The United States produces about one third of the world soybean output (Iowa Soybean Association 2016).The State of Iowa is considered one of the big producers of soybean in the US, according to a recent report published by the Iowa Soybean Association. (Iowa Soybean Association 2016).This substantial production mainly is used in making soybean meal or soybean oil. Soybean meals are largely consumed by the livestock industry while most of the soybean oil is used in the production of biodiesel fuel. An estimated 20% of the soybean output is used to make biodiesel oil (Iowa Soybean Association 2016). The process of biodiesel oil production involves transesterification of the soybean oil in the presence of a catalyst(Ma and Hanna 1999). The abundancy of the soybean oil production in the US inspires the need to look for alternative applications other than biodiesel production.

A number of previous studies have used soybean oil derived materials in asphalt. Soybean acidulated soapstock (SAS), which is considered a rich source of soybean fatty acids, was used as a fluxing agent at dosages from 1-3%(Seidel and Haddock 2014). There was a consistent decrease in the critical high temperature with the SAS modification. An enhancement in the low temperature was also observed. Another recent study used soybean oil as a warm-mix asphalt (WMA) additive, with dosages from 1-3%. It was concluded that a reduction in the mixing and compaction temperature of 3.4oC was attained at a dosage of 1% (Portugal et al. 2017).

This paper presents a soybean-derived rejuvenator that is capable of achieving significant changes in the binder rheology at low dosages. These rheological changes are sustained with aging. This addresses a major drawback of currently available rejuvenators that require high dosages. Having a rejuvenator that is effective at low dosages provides a very economically viable alternative. This is in addition to the fact that using higher percentages of rejuvenators poses concerns regarding durability and the extent of chemical and physical changes of the original binder(Zaumanis et al. 2013).

3.2 Materials and Methods

Two asphalt bitumen grades are used in this study, namely PG64-28 and PG58-28. The PG64-28 bitumen is a polymer modified bitumen whereas the PG58-28 is a neat bitumen. The additive used will be referred to in a generic term as a soybean derived additive(Williams et al. 2016) . The control bitumens are modified by blending 0.75% of the additive by mass of the total bitumen blend using a shear mill at 140^{o}C ±2^{o}C and 3000 rpm for one hour. The blends as well as the control bitumen were then subjected to different aging conditions, namely Rolling Thin Film Oven (RTFO), and Pressure Aging Vessel (PAV).

To assess the high and low temperature performance of both the control and modified bitumens, Dynamic Shear Rheometer (DSR) and Bending Beam Rheometer (BBR) tests were conducted according to AASHTO T315 and AATHTO T313, respectively. Tests were done on unaged, RTFO aged, and PAV aged bitumens. Rolling Thin Film Oven (RTFO) aging was done according to ASTM D2872 at 163^{o}C for 85 minutes while PAV aging was performed on the RTFO aged bitumen according to ASTM D6521 for 20 hours at 100^{o}C and 2.1 MPa pressure. The viscosity of the unaged control and unaged modified bitumens were measured using a rotational viscometer according to AASHTO T316.

To further investigate the effect of the soybean derived additive on the rheological properties of asphalt, a frequency sweep using a DSR was done on the unaged, RTFO aged, and PAV aged bitumens. The frequency sweep covered a range of frequencies extending from 0.6 to 100 rad/s at temperatures of 0, 10, 20, 30 and 40^{o}C, using a controlled strain of 1%. An 8-mm diameter and 2-mm gap geometry was used for all samples. This agrees with widely accepted recommendations to use the 8-mm diameter geometry for temperatures up to 40^{o}C(Alavi et al. 2015; Haghshenas 2016). For comparison reasons, the tests were repeated using a 25-mm diameter and 1-mm gap geometry for the unaged and RTFO aged samples. However, the 25-mm geometry resulted in erroneous high phase angles, possibly due to inaccuracies of torque measurements at low test temperatures. Hence, the results of the 25-mm diameter geometry were discarded and only the results from the 8-mm diameter geometry is shown here. Master curves were generated at a reference temperature of 20^{o}C.

For all of the above tests, replicates of three samples were measured at each testing condition and the average values are reported.

3.3 Results and Discussion

3.3.1 Master Curves

The performance of asphalt bitumens can be characterized with the aid of “master curves” which are constructed using the time-temperature superposition principle. Asphalt is viewed as a linear viscoelastic material at low strains with a temperature-dependent behavior. At high temperatures, asphalt behaves as a Newtonian fluid where the viscosity is constant regardless of the shear rate whereas at low temperatures a limiting modulus, referred to as glass modulus, is reached due to physical hardening effects. The time-temperature superposition allows calculation of asphalt stiffness over a wide range of temperatures and frequencies, using limited range measurements. Shift factors are calculated and used to shift the modulus values, at various temperatures, horizontally to plot a master curve of the material at a reference temperature. The shift factor (a_T) defines the ratio between the reduced frequency at the reference temperature $(\omega_r)$and the frequency at the desired temperature(ω), expressed as:

$$a_T = \frac{\omega_r}{\omega} \quad [3.1]$$

A number of models were proposed to calculate the shift factors, including Williams-Landel-Ferry (WLF) and Arrhenius models. For the purpose of this study, a second order polynomial relation that expresses log (a_T) in terms of temperature was used(Kutay and Jamrah 2013):

$$\log(a_T) = a_1 T^2 + a_2 T + a_3 \quad [3.2]$$

where $a_1, a_2 and\ a_3$ are regression coefficients. The variation of log(a_T) with temperature, as obtained using equation 3.2, is shown in Figures 3.1 and 3.2 for both PG58-28 and PG64-28 binders, respectively.

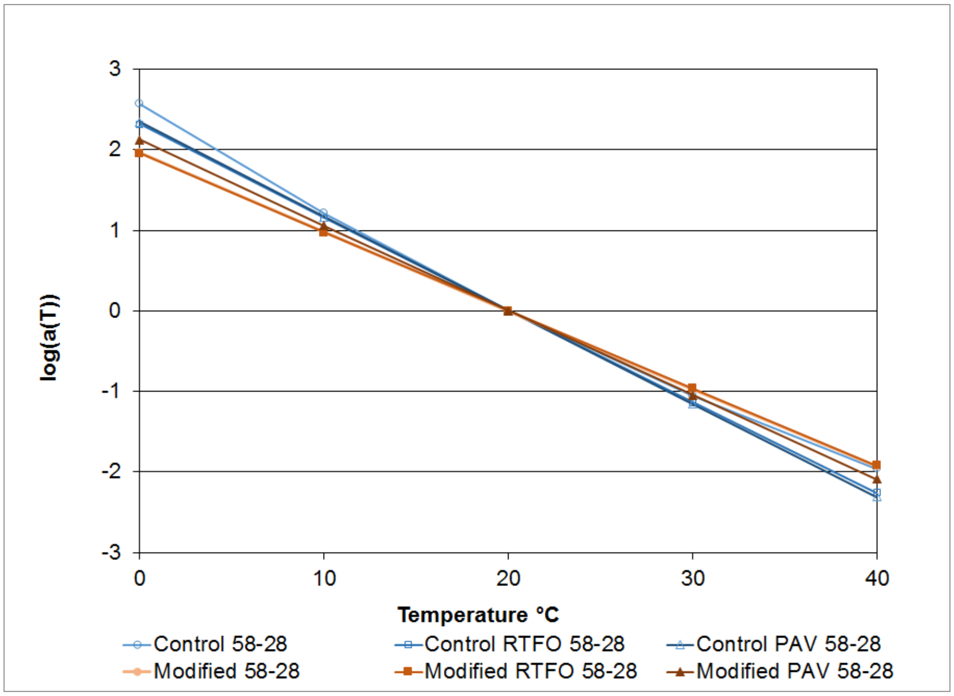

Figure 3.1. log (a_T) with temperature for PG58-28 binders

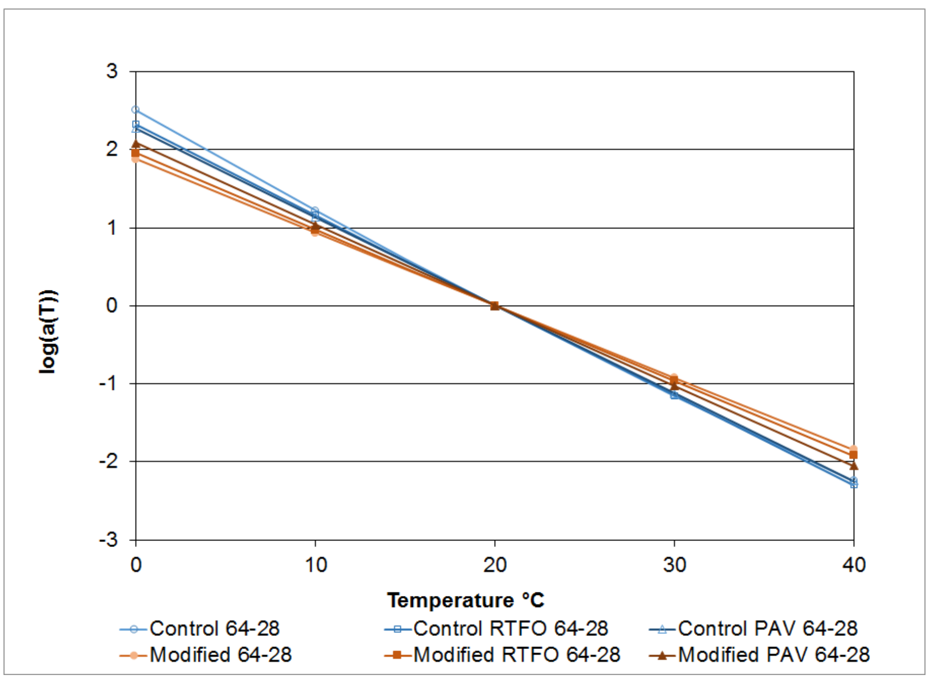

Figure 3.2. log (a_T) with temperature for PG64-28 binders

The sigmoidal model has been used to describe the dynamic modulus of asphalt mixtures. Recently, it has been successfully applied by many researchers to model asphalt bitumens (Yao et al. 2012). The sigmoidal model can be used to represent the complex shear modulus of the bitumen G^* in the following form:

$$log|G^*| = \delta + \frac{\alpha}{(1+e^{\beta+\gamma(\log(t_r))})} \quad [3.3]$$

where t_r is the reduced time of loading at the selected reference temperature, δ is the minimum value of $G*$, $\delta + \alpha$ is the maximum value of $G*$, and the parameters β and γ define the shape of the sigmoidal function.

Figures 3.3 and 3.4 compare the G* master curves at the reference temperature of 20^{o}C for the PG64-28 and PG58-28 bitumens, respectively. It is obvious that the addition of the soybean modifier resulted in a reduction in the complex shear modulus at both high and low temperature ranges. The drop in the complex shear modulus was more significant in the low and intermediate temperature ranges, which is advantageous in terms of enhancing the fatigue and low-temperature thermal cracking resistance of the bitumen. The same trend was observed at all different aging stages of the two bitumen grades. The impact of the rejuvenator, at such low dosage, was substantial to the extent that the behavior of the PAV modified bitumen was comparable to the original unaged bitumen.

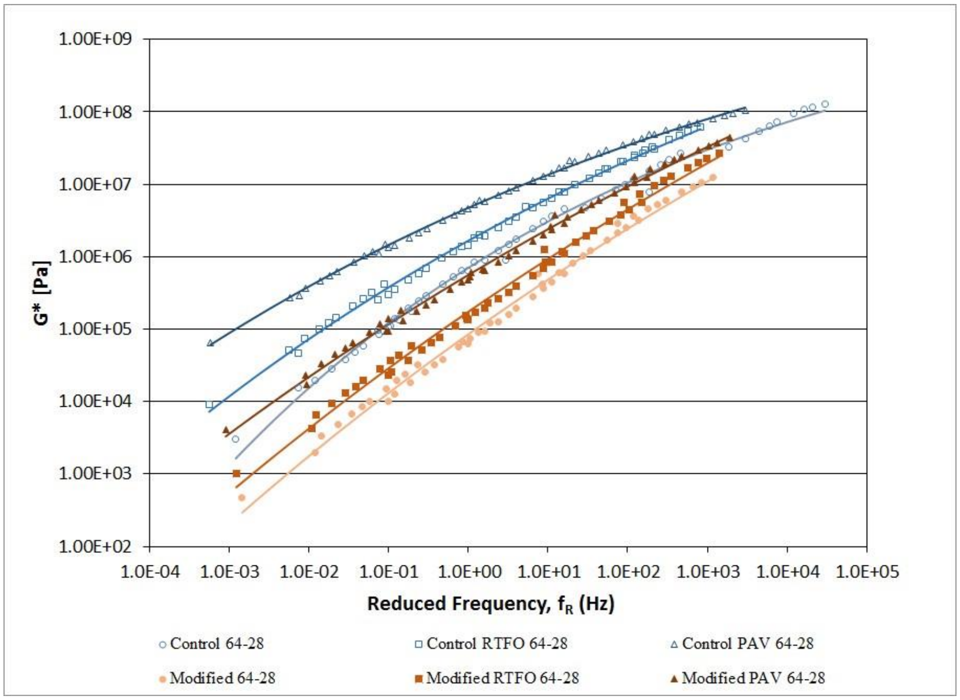

Figure 3.3. Master curves for the control and modified PG64-28 bitumens

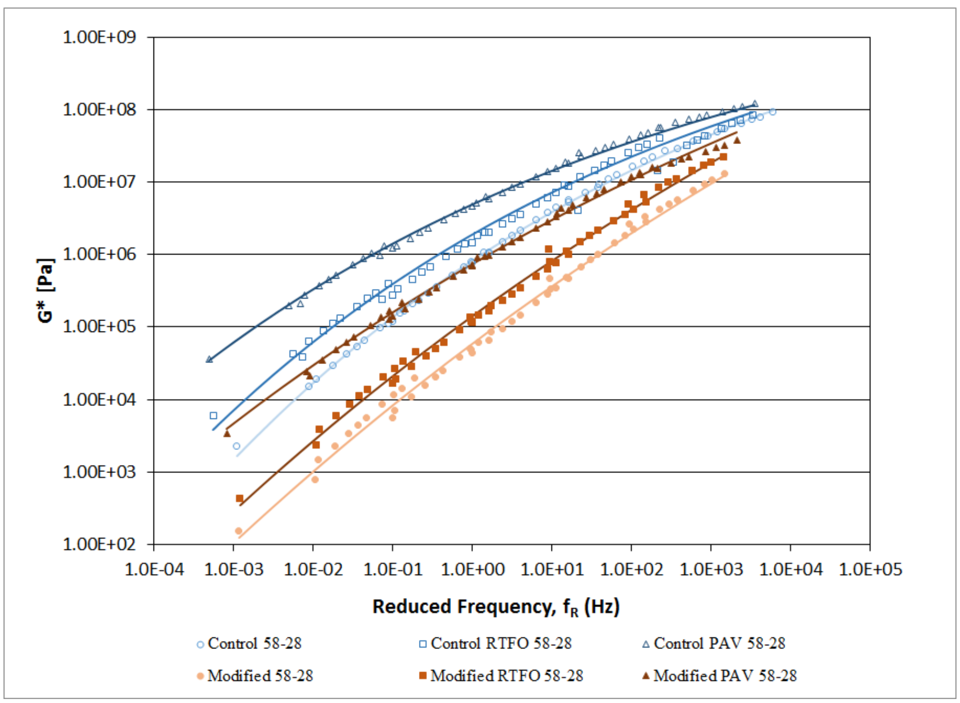

Figure 3.4. Master curves for the control and modified PG58-28 bitumens

From the master curves, it can be concluded that the presence of the rejuvenator did not influence the aging characteristics of the bitumens. As expected, aging caused a distortion in the shape of the master curve indicating notable changes in the chemistry of the aged asphalt. Upon aging the master curve becomes flatter resulting in a decrease in temperature susceptibility. Aging also led to an upward shift in the master curve denoting an increase in the complex shear modulus. These changes that were associated with aging were noted for both the aged modified and aged control bitumens.

The shift factors obtained from the time-temperature superposition were used to generate phase angle master curves, as shown in Figures 3.5 and 3.6. The addition of the rejuvenator resulted in an increase in the phase angle in all cases. For both unaged bitumens, PG64-28 and PG58-28, the increase in phase angles was more pronounced at higher frequencies, corresponding to lower temperatures. With aging, both the modified and unmodified bitumens showed a decrease in phase angle, however the overall decrease in phase angle was higher in case of the modified bitumen. Nevertheless, the PAV aged modified bitumen still exhibited a notably higher phase angle compared to the PAV aged unmodified bitumen.

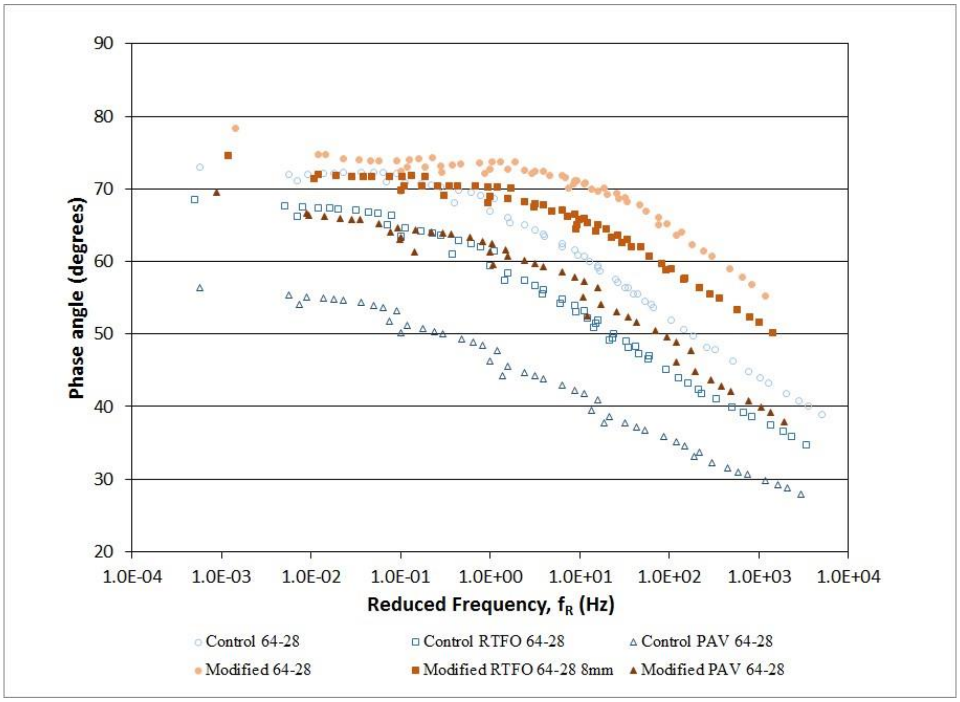

Figure 3.5. Phase angle master curve for the PG64-28 bitumen

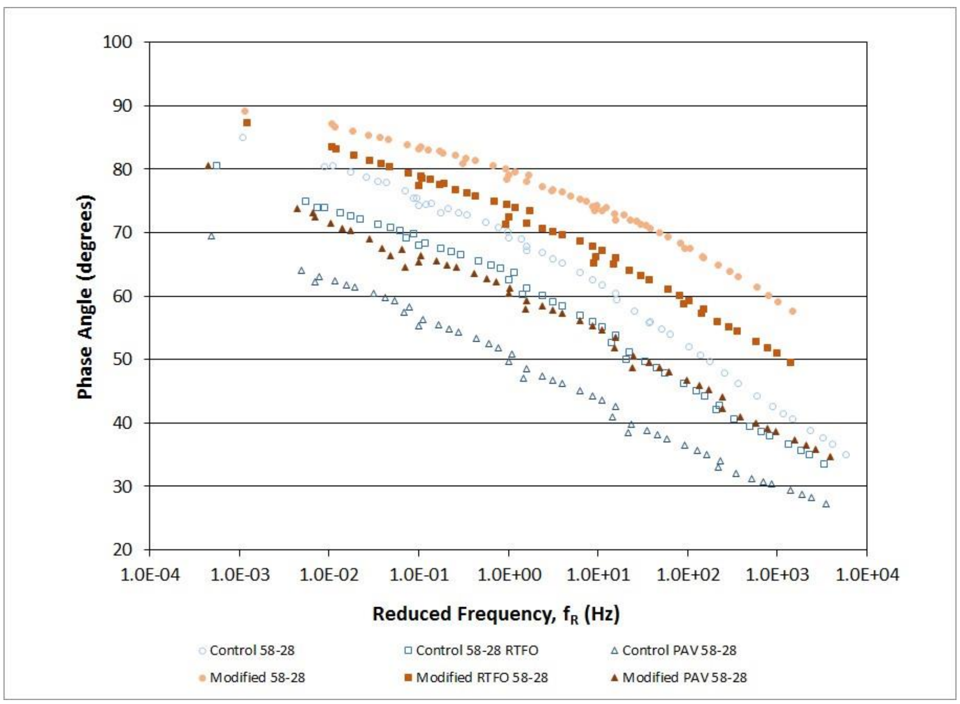

Figure 3.6. Phase angle master curve for the PG58-28 bitumen

3.3.2 Rutting and Fatigue resistance

The rutting and fatigue resistance of the control and modified bitumens were assessed according to the bitumen specifications as given in AASHTO M320. The rutting parameter G*/sinδ, determined from the DSR measurements at a frequency of 10 rad/s, was plotted with temperature in Figure 3.7. The G*/sinδ parameter decreased with the addition of the soybean additive, indicating more susceptibility to rutting. Both bitumen grades showed very similar magnitudes of reduction in rutting with modification, where the rutting parameter dropped down to 7-10% of its original value.

In addition to the frequency sweep described above, the bitumens were tested according to AASHTO T315 to determine their critical high temperatures. The critical high temperatures for the unaged and RTFO aged bitumens corresponding to G*/sinδ>1 kPa and G*/sinδ>2.2 kPa are shown in Table 3.1.

Table 3.1. Properties of control and modified bitumens

Bitumen	PG58-28 Control	PG58-28 Modified	PG64-28 Control	PG64-28 Modified
Unaged (High Temp.),ºC	60.0	45.1	67.1	51.5
RTFO (High Temp.),ºC	62.5	46.7	66.5	52.5
PAV (Low Temp.),ºC	-29.9	-36.3	-29.0	-36.9
Performed Grade (PG)	58-28	40-34	64-28	46-34
Viscosity (Pa*s) at 135ºC	0.329	0.1875	0.7175	0.3808
Viscosity (Pa*s) at 150ºC	0.172	0.1425	0.385	0.250
Viscosity (Pa*s) at 165ºC	0.107	0.125	0.2292	0.1933
Mass loss (%)	0.82	0.99	1.01	1.00

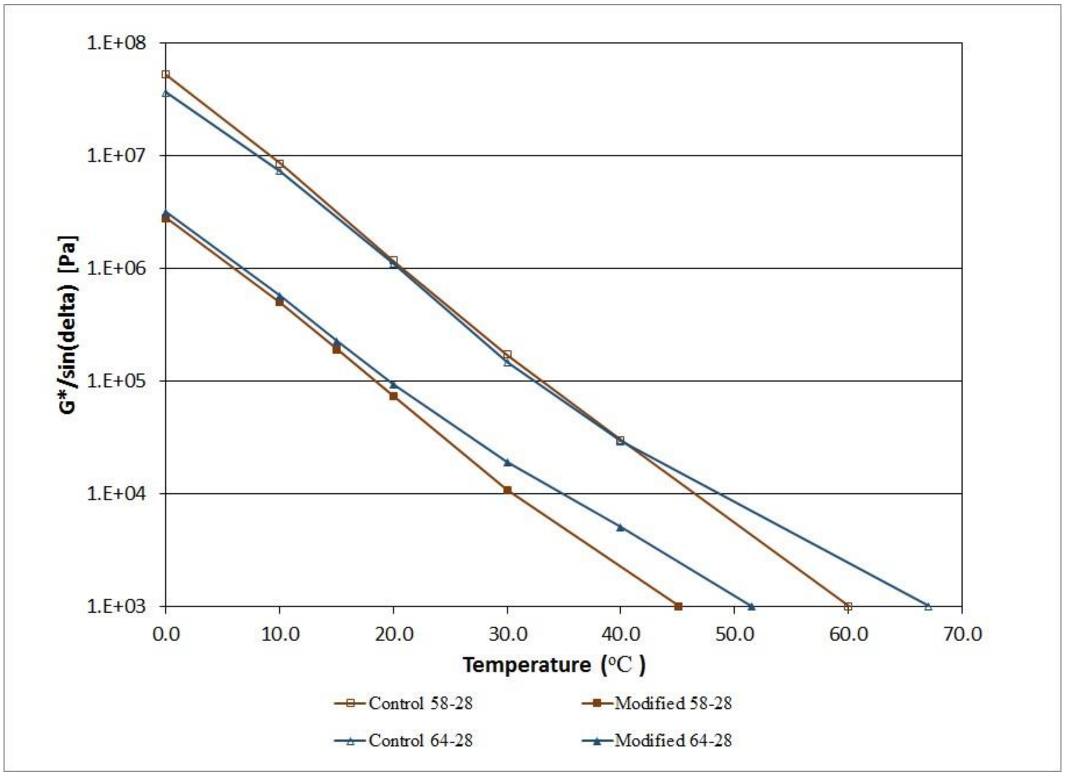

Figure 3.7. Variation of G*/sinδ parameter with temperature

The fatigue potential, measured by G*sinδ, was plotted against temperature as shown in Figure 3.8. Superpave specifies a G*sinδ of less than 5 MPa as a critical intermediate temperature. The modified bitumens showed a notable increase in fatigue resistance, as indicated by the lower critical intermediate temperatures noted. It is interesting to note however that the modified PAV 64-28 showed more resistance to fatigue than the modified PAV 58-28 even though both the control PAV PG64-28 and control PAV PG58-28 exhibited similar fatigue resistance. From these results, it can be inferred that the presence of the soybean additive had the effect of reducing the rate of aging in the polymer modified PG64-28 as compared to the neat PG58-28. So, it can be fairly said that the degree of improvement in fatigue properties depended on the type of bitumen where in this case the polymer modified PG64-28 showed greater improvement.

The exact reason for this type of behavior is not clear though, and a rigorous chemical analysis maybe required to reveal the nature of the interaction between the additive and the bitumen. Another important factor which may have had an effect is the interaction between the polymer and the additive. It should be noted however that the dependency of performance on the bitumen type was only true for fatigue, whereas rutting did not show such dependency.

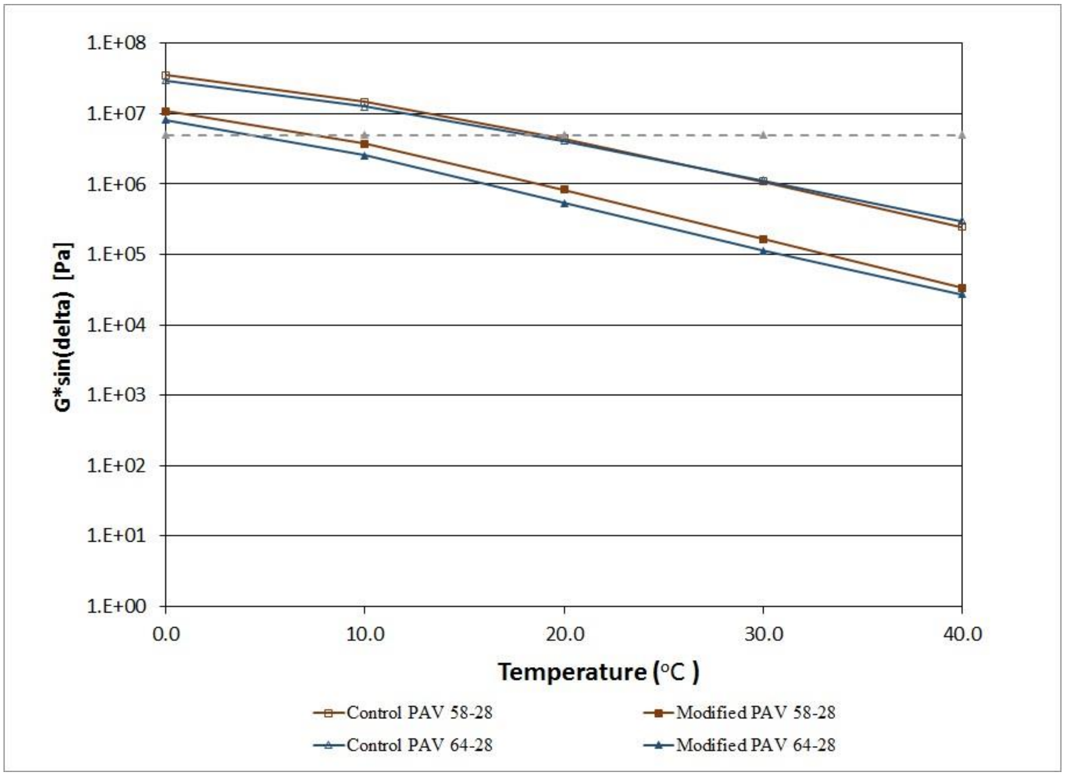

Figure 3.8. Variation of G*sinδ parameter with temperature

To determine the critical low temperature of the PAV aged bitumens, tests were performed according to AASHTO T313. The results of the BBR testing is shown in Table 3.1, with the modified bitumens showing a significant reduction in critical low temperature. The overall Performance Grade (PG) of the modified bitumen, as shown in Table 3.1, indicates a significant change from the control bitumen.

The viscosity of the blend containing the soybean derived additive showed a noticeable decrease in viscosity at the different temperatures, indicating that the additive was successful in reducing the intermolecular interactions between the asphalt molecules. Of particular importance is the mass loss of the modified bitumens was comparable to that of the control bitumens, as shown in Table 3.1, which gives clear evidence to the thermal stability of the soybean additive.

It is worth noting that such considerable change in the rheological properties was achieved by the addition of only 0.75% of the additive, which signifies its substantial effect. The dosage of the additive can be carefully controlled to achieve the required final properties of the blend.

3.3.3 Black diagrams

Since the properties of asphalt bitumens can only be fully described through both the dynamic modulus and phase angles, black diagrams were constructed to visually correlate between the two parameters. Black diagrams show the variation of the phase angle with the dynamic modulus. Unlike master curves, black diagrams simply plot the measured data without the need to do model fitting or shifting, hence inaccuracies in modeling is minimized. For this reason, black diagrams are found to be a very useful tool for analysis that is independent of temperature and frequency effects. Typically, black diagrams give a smooth curve that shows an increase in phase angle with decreasing complex shear modulus. At phase angles approaching 90^o, the curve forms an asymptote signifying Newtonian behavior. The curve intercepts the Y-axis at the glass modulus at 0^o phase angle.

The black diagram for the PG58-28 control and modified bitumens at the different aging conditions is shown in Figure 3.9. It is clear that the curves for the modified bitumens were shifted to the right of the control bitumens' curves, denoting a reduction in stiffness accompanied by an increase in the phase angle. This observation was true at all aging stages. The amount of shift was the same for all aging states, which indicates that the rejuvenator's impact on the bitumen properties was not influenced by aging. Such observation attests to the longevity of the rejuvenator and its prolonged effect on the bitumen. Figure 3.10 shows the black diagram of PG64-28 control and modified bitumens. It can be observed that there is a notable improvement in performance between the modified PAV bitumen and the control PAV bitumen. This observation points to the fact that the soybean additive had a positive effect on reducing the aging mechanism in the modified bitumen, as evidenced by the fatigue results in Figure 3.8 above.

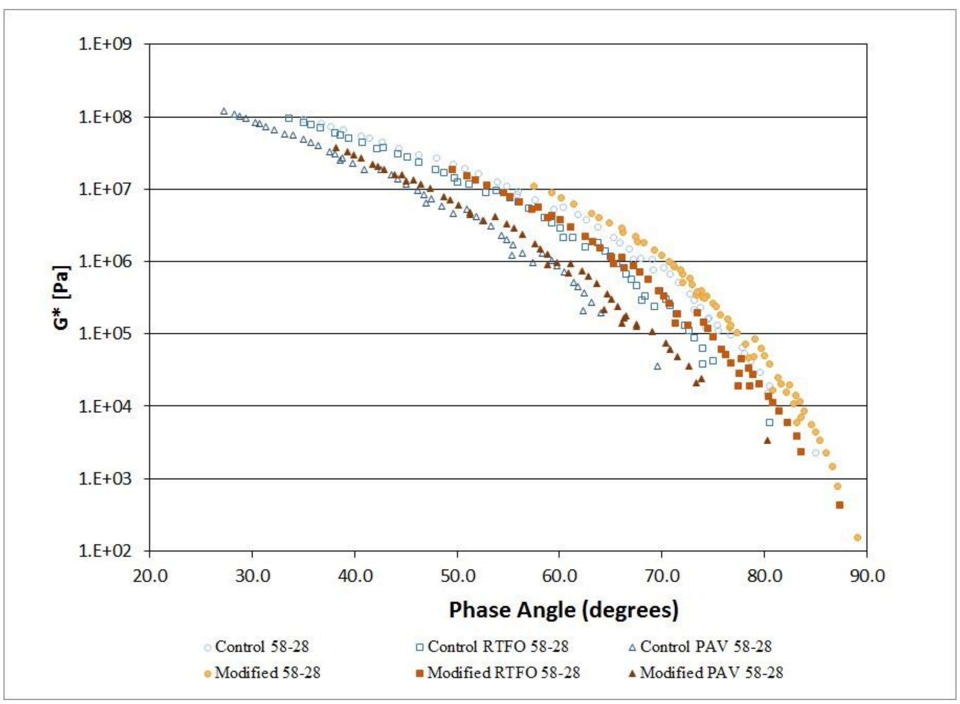

Figure 3.9. Black diagram for PG58-28 bitumens

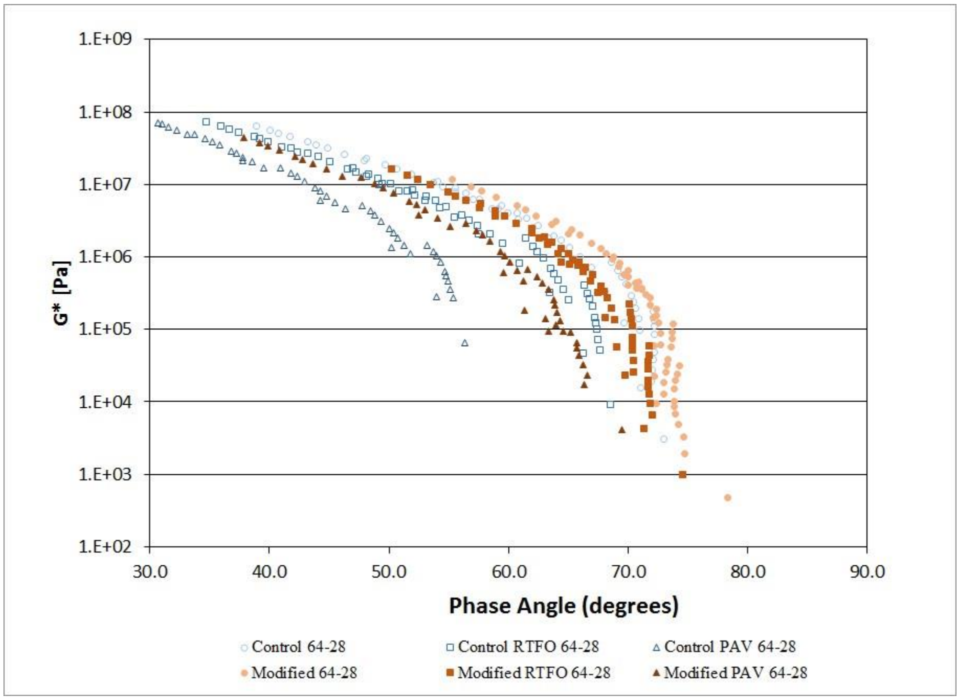

Figure 3.10. Black diagram for PG64-28 bitumens

Black diagrams are also used to confirm that no phase separation between the rejuvenator and the asphalt bitumen is taking place with temperature. A smooth curve with no discontinuities mean that the material is rheologically simple, which indicates that the material is homogenous and no phase transition is occurring with temperature (Airey 2002). In this respect, black space diagrams can also be used to verify the validity of the time-temperature superposition principle which is essentially based on the assumption of the material being rheologically simple and linearly visco-elastic. The black diagrams for all the modified bitumens were smooth with no overlaps or sharp discontinuities, suggesting that the rejuvenator did not show any phase separation from the bitumen at any of the test temperatures, and confirming the validity of the time-temperature superposition used to construct the master curves above.

3.3.4 Glover-Rowe diagrams

The Glover-Rowe parameter was introduced to assess fatigue cracking of bitumen at low temperatures. This parameter was first introduced by Glover (Glover et al. 2005) and was then found to correlate well with bitumen ductility measurements made by Kandhal (Kandhal 1977). Such correlation was based on Glover's fatigue parameter obtained using DSR measurements at 15^{o}C and 0.005 rad/s. According to Kandhal's work, the onset of cracking is marked by 5cm ductility and significant damage takes place when the material reaches 3cm ductility. The Glover-Rowe parameter was used to define a damage zone outlining the two stages of damage, namely damage onset and significant cracking. The damage thresholds are defined according to the equations: $G^* * {cos\delta^2}/{sin\delta} = 180\ kpa$ for damage onset and $G^* * {cos\delta^2}/{sin\delta} = 450\ kpa$ for significant damage. These equations are based on a test temperature of 15^{o}C and a test frequency of 0.005 rad/s.

Recognizing the excessively long time of testing at such a slow loading rate of 0.005 rad/s, it was suggested to use frequency sweeps conducted at temperatures above and below 15^{o}C to obtain G* and δ at a temperature of 15^{o}C and a frequency of 0.005 rad/s using the principle of time shifts (Anderson et al. 2011).

In this study, the results of the DSR frequency sweeps covered an extended range of temperatures from 0 to 40^{o}C so it was possible to calculate time shifts at an intermediate reference temperature of 15^{o}C. Using these time shifts, a sigmoidal function fit was obtained to represent a master curve at 15^{o}C. The value of G* and δ, at 15^{o}C and 0.005 rad/s were plotted along with the Glover-Rowe parameters as shown in Figure

3.11. The lower and upper Glover-Rowe bounds defines a damage zone where the former represents the onset of damage and the latter represents significant cracking.

Figure 3.11 shows the change in the state of the bitumen with aging in comparison to the Glover-Rowe damage lines. Generally, aging is shown to push the bitumen closer to the damage lines. At PAV aging, the PG64-28 bitumen crossed the onset damage line into the damage zone marking crack initiation. The PG58-28 did not fall into the damage zone after PAV aging, however it was very close indicating that a limited additional time of PAV aging would have rendered it damaged. The use of the soybean additive brought about a considerable reduction in the complex shear modulus and an increase in the phase angle, which is opposite to the effect of aging. With the addition of the soybean additive, the modified bitumen was pushed away from the damage lines indicating an enhanced ability to withstand additional time of PAV aging without failure. It is interesting to note that the rate of aging of the modified PG64-28 bitumen was less than the control PG64-28, whereas this was not the case for the PG58-28 bitumen. This finding confirms with both the results from the fatigue parameter and black diagram. The soybean additive works in a way to render the polymer modified PG64-28 bitumen less susceptible to aging, and hence increases its fatigue resistance.

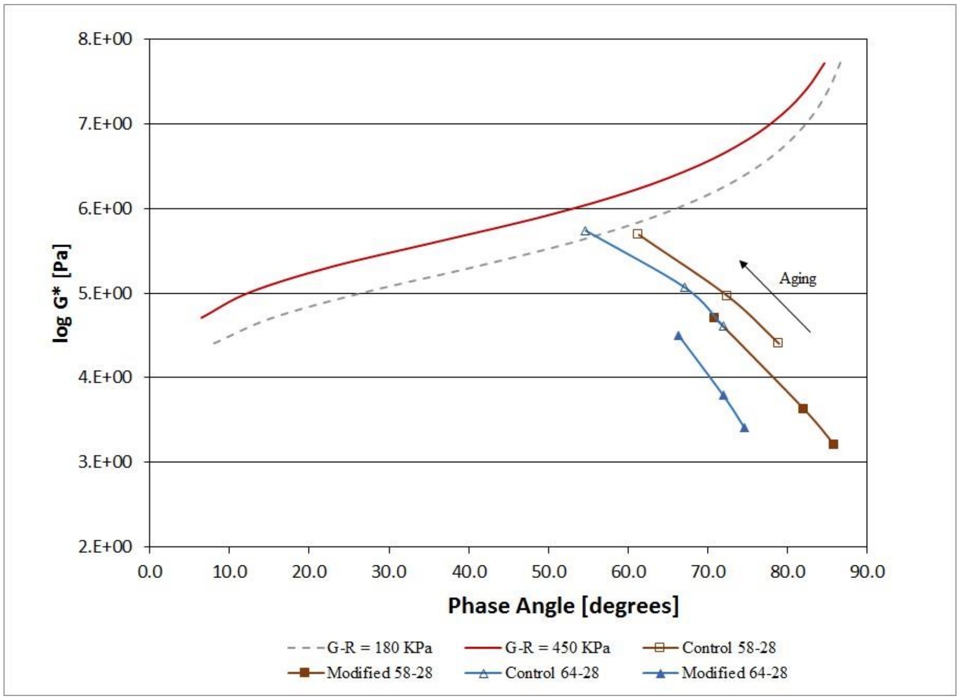

Figure 3.11. Glover-Rowe diagram

3.3.5 Cole-Cole diagram

Another widely-used diagram that serves as a mean of bitumen characterization is the modified Cole-Cole plot, which shows the elastic complex shear modulus (G’) versus the viscous complex shear modulus (G’’). The plot provides a simple visual tool to describe the relationship between the elastic and viscous behavior of a bitumen. A straight line defined by G’=G” is usually superimposed on the plot to provide more insight on the significance of the data. This line acts as a boundary line where data points lying to its left indicate prevalence of the viscous properties whereas data points on its right indicates a shift towards a more elastic behavior. Figures 3.12 and 3.13 present the Cole-Cole diagram for both PG58-28 and PG64-28 bitumens, respectively. At high temperatures, the viscosity portion of the complex shear modulus is dominant. As the temperature decreases, the bitumen starts to lose some of its viscous characteristics in favor of the elastic behavior. Eventually, the overall behavior is dominated by the elastic mechanism at low temperatures. The aged bitumens show more elastic behavior compared to the unaged bitumens at all test temperatures. The addition of the soybean into the control bitumens adds more viscosity, mainly due to its effect on increasing the phase angle. All the tested bitumens exhibited an almost linear relationship in the Cole-Cole diagram which essentially means that no structural changes were evident with the addition of the soybean additive.

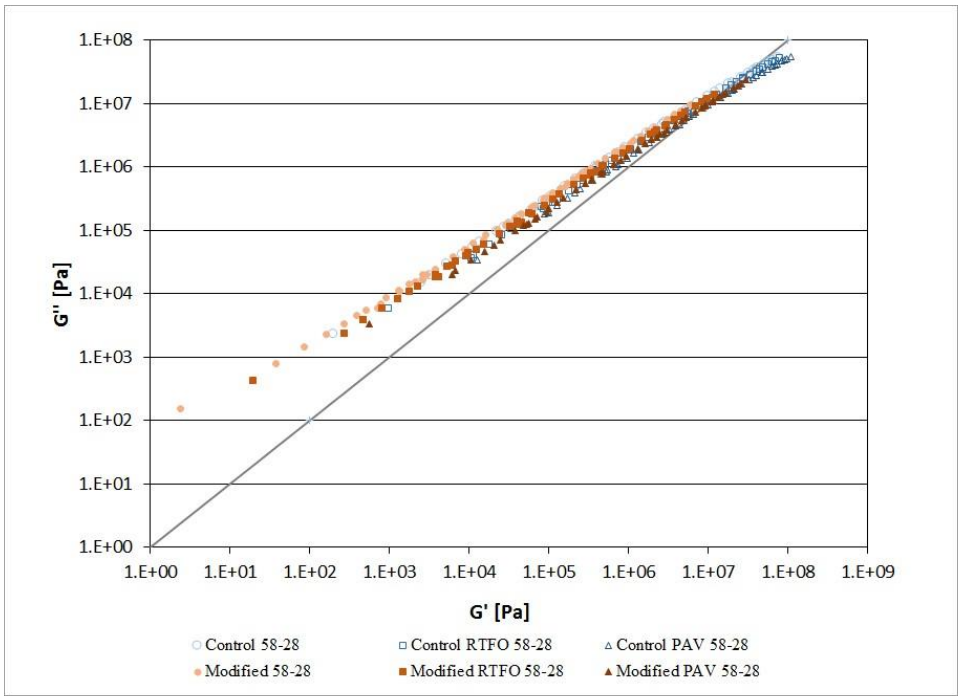

Figure 3.12. Cole-Cole diagram for PG58-28

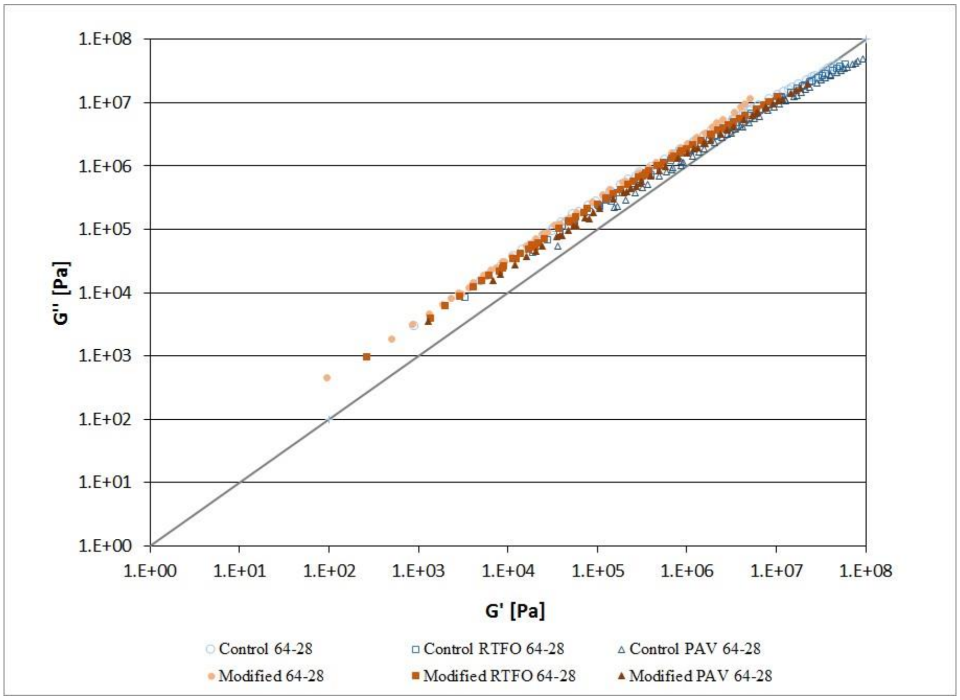

Figure 3.13. Cole-Cole diagram for PG64-28

3.4 Summary and Conclusions

In this work, a bio-derived soybean material was added to both a polymer modified PG64-28 and a neat PG58-28 bitumens at a low dosage of 0.75% by mass. DSR was used to conduct a frequency sweep on both the control and modified bitumens at further stages of aging, namely unaged, RTFO and PAV aged. The data from the frequency sweeps were used to construct master curves for the different bitumens. Comparison of the master curves showed a considerable reduction in the complex shear modulus accompanied by an increase in phase angle with the addition of the soybean derived material. These changes were evident for both types of bitumens. Further analysis of the modified bitumens was done to determine the Performance Grade using a DSR and BBR. It was noted that a considerable improvement in fatigue and low temperature performance was achieved with the soybean additive. This improvement was maintained even after the modified bitumen was subjected to PAV aging. In one case, the modified PAV 64-28 bitumen even showed a reduced aging rate compared to the control PAV 64-28 bitumen. The mass loss of the modified bitumens were comparable to those of the control bitumens, which attests to the thermal stability of the biomaterial used. The black diagrams for the modified bitumens showed a continuous plot with no discontinuities implying no phase separation with temperature.

The Glover-Rowe parameters were used to assess the non-load induced cracking potential of the bitumens. Based on this model, it was found that the control PAV aged bitumens either cracked as with the PG64-28 bitumen or was close to cracking as with the PG58-28 bitumen. However, the addition of the soybean derived biomaterial greatly enhanced the cracking resistance of the bitumens, as suggested by the Glover-Rowe model, which would allow for additional hours of aging without cracking. Using a Cole-Cole diagram, it was shown that the biomaterial increased the viscosity of the bitumen at all temperatures.

In summary, the soybean derived biomaterial used was successful in introducing notable changes to the rheology of both a polymer modified and a neat bitumen, at a very low dosage of 0.75%. This is considered a significant effect when compared to the regular dosages used for commercial rejuvenators which usually exceeds 12%. With such significant performance, an even lower dosage can be designed to tailor the properties of the blend without greatly sacrificing the rutting resistance. The next phase of this work would involve testing the biomaterial on aged RAP bitumen to further verify its rejuvenating ability.

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CHAPTER 4. IMPROVING FATIGUE AND LOW TEMPERATURE PERFORMANCE OF 100% RAP MIXTURES USING A SOYBEAN-DERIVED REJUVENATOR

Modified from a paper published in Construction and Building Materials

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Abstract

One of the major obstacles towards higher mixture percentages of reclaimed asphalt pavements (RAP) is its greater susceptibility to failure under low temperatures and fatigue loading. Rejuvenators offer a very attractive solution by partially or fully restoring the aged properties of the RAP binder. In this research, a soybean-derived rejuvenator is used to modify a PG58-28 binder at 6% and 12% by weight. The soybean-modified PG58-28 and a neat PG58-28 are blended with an extracted RAP binder. Changes in the rheological properties of the different blends are assessed using performance grading (PG), temperature-frequency sweep and linear amplitude sweep (LAS) testing. RAP mixtures made of 100% RAP with the addition of neat PG58-28 or soybean-modified PG58-28 were used to prepare dynamic modulus and disk-shaped compact tension (DCT) specimens. The binder testing results clearly indicate that the soybean rejuvenator has a significant impact on the both the low and high temperature properties of the RAP binder. Such improvement was not attainable by using the neat PG58-28 alone. The soybean rejuvenator also showed sustained durability with aging. The LAS results indicated a significant increase in the fatigue life of the soybean rejuvenated RAP binder. Results of dynamic modulus testing did not reveal significant differences between the various mixtures. The fracture energy of the mixtures prepared

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with the soybean rejuvenator were higher than the control mixtures as revealed by DCT test results.

4.1 Introduction

Over the past several years, there has been an increasing interest in reclaimed asphalt pavement (RAP) owing to the increase in virgin binder and aggregate costs and RAP being readily available. Environmental concerns over binder production as well as the declining supply of good virgin aggregates are also strong reasons in favor of more RAP usage. The current low trends in using RAP, which did not exceed 20% RAP in new mixtures during the year 2014, is attributed to the deteriorated properties of the RAP binder (Hansen and Copeland 2015). Aged RAP binder exhibits high stiffness and low stress relaxation ability as a result of excessive oxidation (Yu et al. 2014). Additionally, high RAP content mixtures tend to be difficult to field compact and can lead to unexpected premature failure (Copeland 2011).

A number of techniques have been devised to mitigate the effect of RAP including adding a softer virgin binder, increasing the asphalt content, and utilizing warm-mix technology to lessen the effect of short-term aging and lower asphalt absorption (Im et al. 2016). These techniques seem to be appropriate for mixtures with low RAP content however they fail to provide satisfactory results with increasing RAP content (West et al. 2013). Rejuvenators have provided the impetus for researchers to further investigate mixtures with increasing RAP content. Rejuvenators are added to aged binders to help partially or fully restore their aged properties to its original state.

During aging, the maltenes fraction in the asphalt is converted to the more viscous asphaltenes fraction by means of oxidation. Asphaltenes, with higher molecular weight, tend to form a colloidal suspension in the lower molecular weight maltenes. Asphaltenes is largely responsible for the viscosity of asphalt materials (Firoozifar et al. 2011). An increase in asphaltenes due to aging result in high stiffness and low creep rate. Rejuvenators reverse the effect of aging by either providing more maltenes to balance the excess amount of asphaltenes, or by allowing better dispersion of asphaltenes (Elseifi et al. 2011). Several studies have examined the low temperature properties and stiffness of aged binders upon rejuvenation (Elseifi et al. 2011; Zaumanis et al. 2015). It was shown that rejuvenators improve low temperature cracking resistance and reduce the aged binder stiffness. A number of rejuvenators have been proposed including petroleum based aromatic extracts, distilled tall oil, and organic oil (Zaumanis et al. 2014).

The durability of rejuvenators is crucial to their proper usage. Softening agents containing volatile compounds can only provide a temporary reduction in stiffness to aid compaction. Upon volatilization of these compounds, the softening agents can no longer provide additional enhancement to the mixture. Rejuvenators need to have a prolonged effect on the asphalt mixture properties. In a recent study, the long-term aging performance of five different rejuvenators was studied (Mohammadafzali et al. 2015). It was shown that the studied rejuvenators differ greatly in terms of their durability performance. Some rejuvenators improved the aging rate compared to the virgin binders whereas others accelerated aging. The chemistry of the interaction between the rejuvenator and the binder is also very important. A recent study showed that an aromatic extract rejuvenator worked effectively for a PG58-10 and not as effectively with a PG58-28 binder(Yu et al. 2014).

Cracking induced by fatigue is considered a primary mode of distress in asphalt pavements. The viscoelastic properties of the asphalt binder determine to a great extent the fatigue performance of asphalt mixes (Bahia et al. 2001). The fatigue resistance of binders is currently characterized using the fatigue parameter, $G^* * sin\delta$. This parameter is determined using a Dynamic Shear Rheometer (DSR) measurements at 1% strain rate, as per AASHTO T315, to ensure that the binder remains within the linear viscoelastic region. Such approach has failed to capture the performance of binders under destructive loading which results in accumulated damage (Bahia et al. 2001). The Time sweep (TS) test was introduced based on the work done on NCHRP Project 9-10 (Bahia et al. 2001; Bonnetti et al. 2002). The TS test is conducted using a DSR on an RTFO+PAV aged binder with an 8-mm-diameter geometry. In this test a repeated cyclic load is applied under constant strain rate until failure. Failure is typically marked by a 50% drop in G* (Kim et al. 1997). The choice of the constant strain rate at which to run the test is determined to reflect the pavement structure and traffic conditions. A major drawback of the TS test is the uncertainty in testing time and the fact that it can take several hours to perform. Additionally, such elongated testing time may cause steric hardening of the binder, which could skew the results (Planche et al. 2004). Recently, the Linear amplitude sweep test (LAS) was introduced as an efficient test to characterize fatigue in binders (Johnson et al. 2009). Similar to the TS test, the LAS test uses an 8-mm-diameter and a 2-mm gap geometry, to apply a repeated cyclic load to the binder sample. In the LAS test however, an increasing strain rate is applied to induce accumulated damage. In a recent study that investigated the use of six different recycling agents on the fatigue life of 100% RAP mixtures, LAS testing was used to evaluate the number of cycles to failure for all rejuvenated blends (Zaumanis et al. 2015). It was concluded that the bio-derived recycling agents were superior to the petroleum based recycling agents. The bio-derived recycling agents increased the number of cycles to failure in the RAP binder to a level comparable to that of the virgin binder. In another study, LAS testing was used to assess the fatigue performance of a RAP binder blended with both a soft and a stiff virgin binders at both 20% and 50% RAP binder content. It was shown that the fatigue life increased with higher amounts of RAP binder. It was also concluded that using a softer binder in lieu of a stiff binder led to better performance compared to increasing the stiff virgin binder content (Willis et al. 2012).

Using RAP can have a great impact on the low temperature cracking potential of asphalt mixtures. Hence, it is important to assess the low temperature properties of mixtures prepared with RAP. The disk-shaped compact tension (DCT) is one of the commonly used tests to assess low temperature cracking resistance (Wagoner et al. 2005). The DCT test gives the fracture energy, in J/m^2, for a crack to propagate through a notched specimen under a displacement-controlled tensile loading. A comprehensive study that correlated fracture energy to field performance showed that a fracture energy between 350-400 J/m^2 marks a sufficient resistance against thermal and reflective cracking (Buttlar et al. 2010). Minimal occurrence of transverse cracking was found in mixtures with fracture energies above 400 J/m^2 (Buttlar et al. 2010). A recent investigation that looked into the effect of different percentages of recycled materials into asphalt mixtures was conducted at Iowa State University and the University of Illinois Urbana-Champaign (Williams et al. 2011). This study looked at low temperature performance of eight different mixtures, containing various percentages of RAP and recycled asphalt shingles (RAS), used in the construction of Illinois Tollway (I-90). DCT testing done at -12^{o}C revealed that the fracture energy decreased with the addition of recycled materials, with the specimens containing 50% recycled materials failing to meet the minimum threshold of 350 J/m^{2} (Williams et al. 2011). DCT testing was also used to assess the effect of aging on the low temperature fracture behavior of asphalt mixtures (Braham et al. 2009). It was concluded that fracture energy decreased consistently with longer hours of aging. With aging, an increase in the peak load was noted followed by a steep drop in the load resulting in an overall less area under the load-displacement curve hence less fracture energy.

Previous studies have shown that the soybean-derived additive was successfully applied to reduce the stiffness and enhance the low temperature properties of both a polymer modified PG 64-28 and a neat PG 58-28 binders (Elkashef et al. 2017). Fourier transform Infrared-Attenuated total reflection (FTIR-ATR) analysis has verified the durability of the binders rejuvenated with the soybean-derived additive by examining changes in the carbonyl and sulfoxide indices with aging. In this work, the soybean-derived additive is used to modify RAP binders and to prepare 100% RAP mixtures.

4.2 Materials and Methods

A PG58-28 and a soybean-derived rejuvenator was used for this study. The reclaimed asphalt pavement (RAP) used in this study was milled from pavements in the State of Iowa, USA. The RAP was crushed to a nominal maximum aggregate size of 12.5 mm, and dried in an oven at 110^{o}C. The RAP gradation is given in Table 4.1. The RAP binder content was determined to be 5.1% using an ignition oven. Extraction of the RAP binder was performed as per ASTM D2172-Method A- using toluene as a solvent.

Subsequent recovery of the RAP binder was done by the aid of a rotary evaporator as specified in ASTM D5404. A nitrogen blanket was pumped over the binder solution continuously to eliminate any oxidation of the RAP binder resulting from the recovery process. In the determination of the PG of the RAP binder, the extracted RAP binder was considered already RTFO aged and hence was used directly to determine the RTFO critical high temperature. The RAP binder was however PAV aged before testing for the critical low temperature using a Bending Beam Rheometer (BBR).

Table 4.1: RAP gradation

Sieve Size (in.)	Sieve Size (mm)	Percent passing
3/4	19	100
1/2	12.5	91
3/8	9.5	82
#4	4.75	57
#8	2.36	42
#16	1.18	26
#30	0.6	14
#50	0.3	12
#100	0.15	10
#200	0.075	8

The PG58-28 binder was initially blended with the soybean rejuvenator at a dosage of 6% and a 12% by weight. The prepared blends were then mixed with the extracted RAP binder at a ratio of 1:5 by weight, resulting in an effective rejuvenator dosage rate of 1% and 2% by total weight of binder respectively. This ratio was selected to match with the proportions of the binder in the tested asphalt mixtures. A control blend was prepared by mixing the RAP binder with a neat PG58-28 at the same ratio. Hence the binder characterization phase is comprised of four different binders as follows; RAP binder, RAP binder+ PG58-28, RAP binder+ 6% modified PG58-28 and RAP binder+ 12% modified PG58-28.

To evaluate the performance grade of the different binders, DSR and BBR tests were performed as per AASHTO T315 and AASHTO T313, respectively. Rolling thin Film Oven (RTFO) aging was done in accordance with ASTM D2872 at 163^{o}C for 85 minutes. PAV aging was conducted on the RTFO aged binder as per ASTM D6521 for a duration of 20 hours at 100^{o}C and 2.1 MPa pressure.

A temperature-frequency sweep was performed for both the RTFO and RTFO+PAV aged binders using a DSR. For the RTFO aged binders, a 25-mm diameter and a 1-mm gap geometry was used, whereas an 8-mm diameter and a 2-mm gap geometry was used for the RTFO+PAV aged binders. A temperature range that extends from 10^{o}C to 34^{o}C at 6^{o}C increments was used for the RTFO+PAV aged binders with frequencies that ranged from 0.6 to 100 rad/s. The same frequency range was used for the RTFO aged binders but with temperatures that ranged from 46^{o}C to HTPG+6^{o}C for the soybean-modified binders and 70^{o}C to HTPG+6^{o}C for the other binders. HTPG stands for the high temperature PG of the specific binder. The Christensen-Anderson-Marasteanu (CAM) model was used to construct master curves at a reference temperature of 70^{o}C for the RTFO aged binders and 22^{o}C for the RTFO+PAV aged binders.

Linear amplitude sweep (LAS) testing was done on RTFO+PAV aged binder using a DSR with an 8-mm-diameter and a 2-mm gap geometry as per AASHTO TP 101.

Dynamic modulus specimens were made using a mixing and compaction temperature of 140^{o}C. A Superpave gyratory compactor was used to compact the specimens which were designed to have a total binder content of 6% and a target air void of 4%. Three specimens were prepared for each test group. Dynamic modulus testing was conducted according to AASHTO T342, at 4^{o}C, 21^{o}C, and 37^{o}C. The specimens measured 100mm in diameter and 150mm in height. To ensure that the deformation remains within the linear viscoelastic range, the axial strain was kept between 50 and 150 micro-strain. Deformations were recorded using the average reading of three LVDTs placed around the circumference of the specimen. The LVDTs were attached to the specimen using mounted brackets and buttons glued to the specimen face. The sigmoidal model was used to construct master curves at a reference temperature of 21°C.

The disk-shaped compact tension (DCT) test was conducted according to ASTM D7313 to evaluate the low temperature cracking resistance of the mixtures. Testing was performed on lab-compacted samples with a binder content of 6% and a target air void content of 4%.

4.3 Results and discussion

4.3.1 Performance grading (PG) and ΔT_c

The binders were tested in accordance with AASHTO T315 to determine their critical high temperatures. The specification criteria used to determine the critical high temperature were $G^*/\sin\delta > 1$ kPa and $G^*/\sin\delta > 2.2$ kPa for both the unaged and RTFO aged binders, respectively. The extracted RAP binder was not RTFO-aged as it was considered short-term aged. Hence, it was tested as is to determine its RTFO critical high temperature. Accordingly, there was no unaged data for the extracted RAP binder. The PG results are shown in Table 4.2. The RAP binder was shown to be considerably aged with a very high critical temperature of 108.6°C. The critical high temperature of the RAP binder was reduced by almost 30 degrees, when blended with the 6% modified PG58-28. This large reduction in the critical high temperature caused the binder to drop down by 5 PGs, which is quite a significant drop. In comparison, the mere addition of the neat PG58-28 to the RAP binder led to a drop of only one PG. It is also important to note that there was no significant mass loss associated with the soybean additive, which attest to its thermal stability.

The critical intermediate temperature was also determined using PAV aged binders, as shown in Table 4.2. The critical intermediate temperature was based on the criterion G* x sinδ < 5000 kPa. A slight drop in the RAP binder's critical intermediate temperature was noted with the use of the neat PG58-28. The soybean-modified PG58-28 had a much more notable effect on the critical intermediate temperature.

The critical low temperature of the PAV aged binders was determined according to AASHTO T313, and the results are displayed in Table 4.2. The soybean-modified RAP binder showed a significant decrease in the critical low temperature compared to the pure RAP binder. This decrease in the critical low temperature resulted in a one PG and a two PG drop with the addition of a 6% and 12% modified PG58-28 respectively. Compared to the effect of the neat PG58-28 which had almost no impact on the critical low temperature, it can be fairly concluded that the soybean modification was largely successful in enhancing the low temperature properties of the RAP binder.

Table 4.2. Binder Properties

Binder	RAP	RAP+ PG58-28	RAP+ 6% Modified PG58-28	RAP+ 12% Modified PG58-28
Unaged (High Temp.), ºC	NA	105.6	78.4	76.2
RTFO (High Temp.), ºC	108.6	99.9	76.5	73.9
PAV (Intermediate Temp.), ºC	29.9	28.3	24.6	23.2
PAV (Low Temp.), ºC	-10.8	-11.9	-20.2	-22.3
Performance Grade (PG)	106-10	100-10	76-16	70-22
ΔT_{c}, ºC	-9.7	-9.2	-6.6	-5.5
Mass loss (%)	NA	0.4	0.4	0.5

The BBR test provides a plot of the stiffness of the tested beam with time. The value of the stiffness and the slope of the stiffness curve at a time of 60 seconds are referred to as S and m respectively. The parameter ΔT_c was recently introduced as a measure to assess the non-load thermal cracking potential of binders(Anderson et al. 2011). ΔT_c is readily calculated from the BBR results, as the difference between the continuous grade temperatures at S=300 MPa and m=0.3 as per ASTM D7643. Earlier work has shown that the parameter ΔT_c is related to aging where a decrease in that parameter is noted as the binder loses its ability to undergo stress relaxation (Anderson et al. 2011; Glover et al. 2005). Aged binders were shown to exhibit a strong m-controlled behavior, where the low temperature properties become largely limited by the m-value. The critical low temperature of an m-controlled binder is dictated by its m-value. Hence the temperature at which m=0.3 is significantly higher than that at which S=300, leading to large negative values for ΔT_c. From Table 4.2, the RAP binder showed a very low value of ΔT_c indicating that stress relaxation is greatly hindered by the excessive oxidation that accompanied aging. Mixing the RAP binder with unmodified PG58-28 binder does not significantly improve its stress relaxation ability. However, an increase in the parameter ΔT_c is obvious with the addition of the soybean-modified PG58-28. Nevertheless, all tested binders showed m-controlled behavior.

4.3.2 Complex shear modulus master curves

Temperature-frequency sweeps results can be used to fully characterize asphalt binders over a wide range of frequencies and temperatures using the concept of time-temperature superposition. time-temperature superposition principle defines shift factors which are used to transform properties at a given frequency and test temperature to an equivalent reduced frequency at a reference temperature. Shift factors are calculated using the Williams-Landel-Ferry (WLF) equation as given by:

$$log\alpha_T = -\frac{C_1(T-T_o)}{C_2+(T-T_o)} \quad [4.1]$$

where α_T = shift factor; T_o = reference temperature, T= test temperature, and the parameters C1 and C2 are dependent on the reference temperature.

Once shift factors are determined, the reduced frequency, ω_r ,can be obtained from the test frequency, ω, using

$$\alpha_T = \frac{\omega_r}{\omega} \quad [4.2]$$

The Christensen-Anderson-Marasteanu (CAM) model is considered very effective in describing the rheological behavior of asphalt within the linear viscoelastic region(Kim 2008). The CAM model is expressed as follows(Marasteanu and Anderson 1996):

$$|G^*| = G_g \left[1 + \left(\frac{\omega_c}{\omega}\right)^{\nu}\right]^{-w/\nu} \quad [4.3]$$

where G^*= complex shear modulus, G_g = glassy modulus, ω_c = crossover frequency, and both w and ν are model parameters. w defines the rate at which the complex modulus curve reaches an upper and lower asymptote. ν is equal to log(2)/R, where R is the rheological index. The rheological index is the difference between the glassy modulus and the modulus at the crossover frequency.

Figures 4.1 and 4.2 shows the complex shear modulus master curves for both the RTFO aged and the RTFO+PAV aged for all binders at a reference temperature of 70°C and 22°C, respectively. It is evident that the soybean modification had a much more significant effect on reducing the RAP binder's complex shear modulus compared to the mere blending of the neat PG58-28 binder. This notable impact on the complex shear modulus, brought about by the soybean modification, was still evident after PAV aging. In comparison, the effect of the unmodified virgin binder PG58-28 was significantly diminished upon PAV aging. This result could potentially mean that the soybean modification resulted in a better aging resistance. With soybean modification, the reduction in the complex shear modulus of the RTFO+PAV aged RAP binder remained significant at low and intermediate frequencies. At very high frequencies denoting very low temperatures, the complex shear modulus of the soybean modified RAP binder was no longer significant from that of the RAP binder. This is typical of asphalt materials as the master curves tend to converge to an asymptote at very high frequencies.

The shape of the master curves, as described in part by the rheological index, R, can be used as an indication of aging. Upon aging, master curves show a more gradual transition from viscous to elastic behavior which results in a flatter shape. A study of both Figures 4.1 and 4.2, clearly shows that the master curves of all binders get flatter with PAV aging. Figure 4.2 however show that the two soybean-modified RAP binders did not show as much flatness compared to the other two binders, namely pure RAP and RAP blended with PG58-28. This observation also supports the notion that the soybean modification improves the aging resistance of the binders.

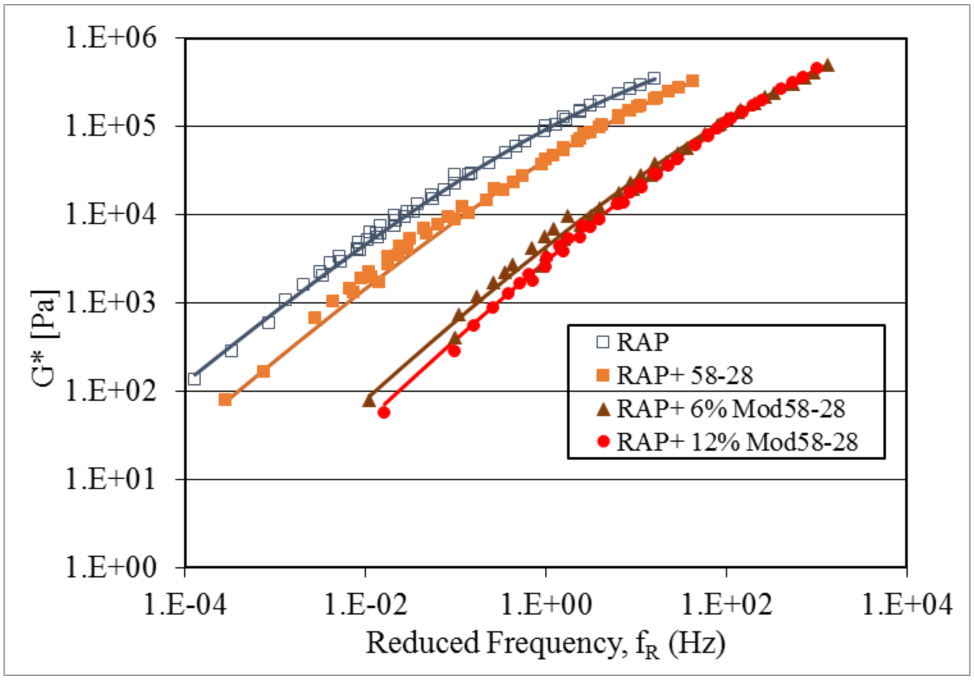

Figure 4.1. Complex shear modulus master curves for RTFO aged binders at 70ºC

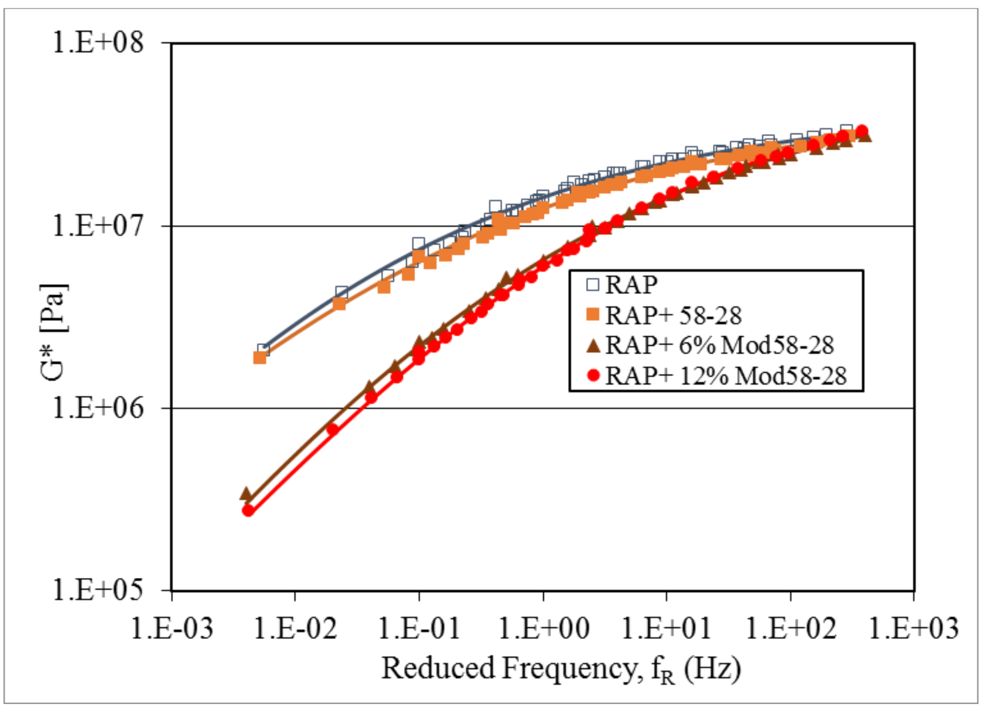

Figure 4.2. Complex shear modulus master curves for PAV aged binders at 22ºC

The shift factors, obtained from the fitting of the complex shear modulus master curves, were used to develop phase angle master curves as shown in Figures 4.3 and 4.4

for both RTFO and RTFO+PAV aged binders, respectively. The soybean modification resulted in an increase in the phase angle at all frequencies. This trend was seen for both RTFO and RTFO+PAV aged binders. An increase in the phase angle marks a more viscous behavior. A shift towards viscous behavior enhances stress relaxation and ultimately improves fatigue resistance.

The crossover frequency, defined as the frequency at a phase angle of 45^o, marks the transition between viscous and elastic behavior. The behavior is predominantly viscous for frequencies below the crossover frequency whereas a change into a dominant elastic behavior is seen for frequencies above the crossover frequency. A study of both Figures 4.3 and 4.4 show that the crossover frequency undergoes many orders of magnitude increase due to soybean modification. The RAP binder initially shows a very low crossover frequency, which decreases even further with PAV aging. Such a low crossover frequency renders the behavior of RAP binder predominantly elastic. Addition of the unmodified PG58-28 slightly increases the crossover frequency of the blend. The use of the soybean modified PG58-28, however, brings about a considerable increase in the crossover frequency.

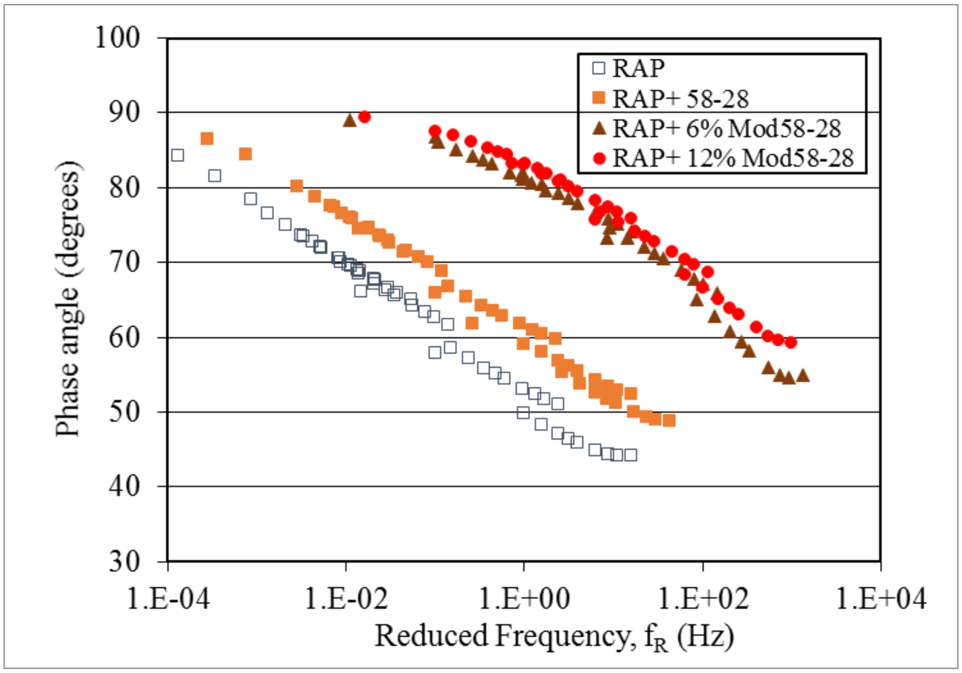

Figure 4.3. Phase angle master curves for RTFO aged binders at 70°C

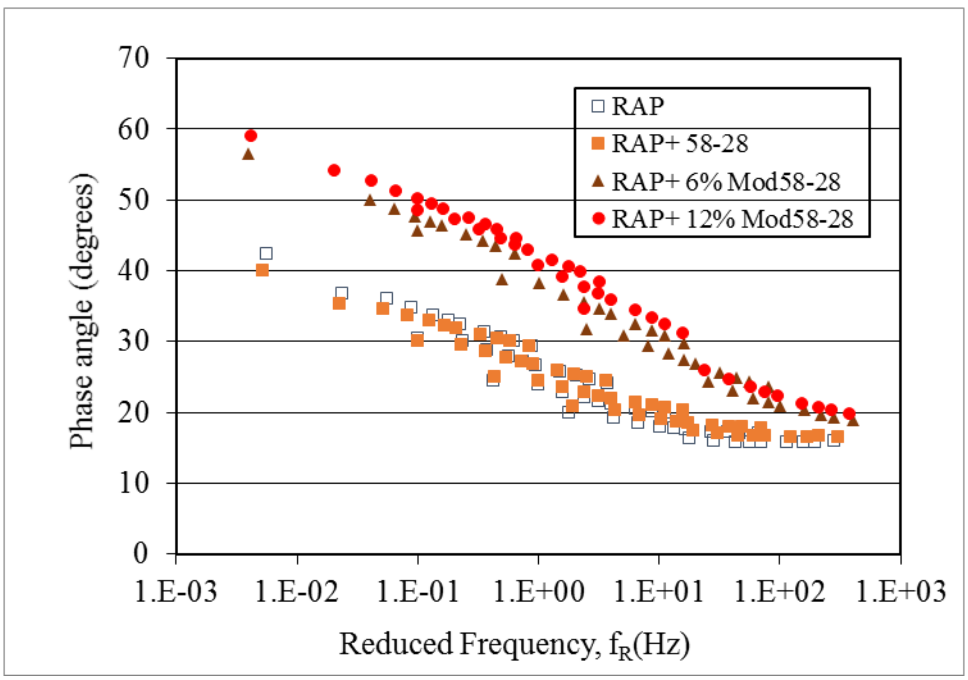

Figure 4.4. Phase angle master curves for PAV aged binders at 22°C

4.3.3 Linear Amplitude Sweep (LAS) test

The LAS test is based on the principle of Viscoelastic Continuum Damage (VECD). VECD defines damage in terms of a damage parameter. This damage parameter quantifies the amount of damage relative to the undamaged properties. The undamaged properties are determined by applying a frequency sweep at a low strain rate of 0.1% prior to the application of the strain amplitude ramping procedure. A constant frequency of 10 Hz is applied with an increasing strain rate from 0.1% to 30%. Testing is done on RTFO+PAV aged binder using an 8-mm diameter and a 2-mm gap geometry. The LAS test is efficient in that the total duration of the test, including the initial frequency sweep, do not exceed 20 minutes. VECD analysis is used to transform the results into an estimate of the fatigue life at different constant strain amplitudes.

VECD is based on Schapery's work potential theory which establishes a relationship between damage and work performed as given by (Schapery 1984):

$$\frac{dD}{dt} = \left(\frac{dW}{dD}\right)^{\alpha} \text{ [4.4]}$$

where t is time, W is work performed, D is damage intensity, and α is a material constant related to the rate at which damage occurs.

To determine α, the following equation is used

$$\alpha = 1 + \frac{1}{m} \text{ [4.5]}$$

where m is the slope of the log-log plot of storage modulus versus frequency. This plot is obtained using the initial frequency sweep.

The dissipated work (W) under strain-controlled conditions is expressed as:

$$W = \pi\gamma_o|G^*|sin\delta \text{ [4.6]}$$

where γ_o is shear strain, G^* is complex modulus, and δ is phase angle.

An expression is developed, using the above relationships, to calculate the damage intensity (D) as a function of time. The test results data is then used to determine the accumulation of damage intensity throughout the loading history.

A power law was suggested to fit a relationship between $|G^*|sin\delta$ and the damage intensity, D, in the form of (Hintz et al. 2011):

$$|G^*|sin\delta = C_o - C_1(D)^{C_2} \text{ [4.7]}$$

where C_o is the value of $|G^*|sin\delta$ during the 0.1% strain amplitude step, C_1 and C_2 are model coefficients.

Substituting Equation 4.7 into Equation 4.4 and integrating, an expression defining the number of cycles to failure (N_f) can be derived in the form of (Kim et al. 2006):

$$N_f = A(\gamma_{max})^{-B} \text{ [4.8]}$$

where the coefficients A and B are defined as:

$$A = \frac{f(D_f)^k}{k(\pi I_D C_1 C_2)^\alpha} \text{ [4.9]}$$

$$B = 2\alpha \text{ [4.10]}$$

where $k = 1 + (1 - C_2)\alpha$, I_D is the initial value of $|G^*|$ at 1% strain, *f* is the loading frequency of 10Hz, and D_f is the damage intensity at failure, defined as 35% reduction in C_o.

Using Equation 4.8, an estimate of the number of cycles to failure can be obtained for a given strain rate, γ_{max}.

In this work, the LAS test is conducted at three different temperatures, 25°C, 28°C, and 31°C. These temperatures covered the range of fatigue/intermediate critical temperatures for all binders, as given in Table 4.2.

A log-log plot of the number of cycles to failure versus strain rate gives a straight line with an A intercept and a slope equals to -B. Such plots are shown at the various test temperatures in Figures 4.5-4.7. An increase in the coefficient B, which depends solely on the parameter α, indicates a higher rate of deterioration at higher strain rates. As expected, the RAP binder with a steeper slope, thus larger B, showed considerable deterioration and loss of fatigue life with increasing strain rate. The RAP binder rejuvenated with the soybean-modified PG58-28 at both 6% and 12% dosage showed considerable improvement with increasing shear strain rates. These rejuvenated binders did not exhibit a drastic loss in fatigue resistance with increasing shear strain rates as observed in both the RAP binder and the RAP binder blended with the unmodified PG58-28. This trend was true at all test temperatures.

The effect of rejuvenation was more prominent at strain rates of 5% and above. At a strain rate of 2.5%, the difference between the RAP binder blended with PG58-28 and the rejuvenated RAP binders was not significant. In fact, the RAP binder blended with PG58-28 showed slightly better performance at low strain rates. A strain rate of 5% was found to correlate best with fatigue in mixtures as measured by the energy ratio test(Tran et al. 2012). The energy ratio test involves three different tests namely resilient modulus, creep compliance, and indirect tensile strength. It was found that the dissipated creep strain energy at failure obtained from the energy ratio test correlated best with the cycles to failure from the linear amplitude sweep test at 5% strain rate(Tran et al. 2012). Cracked sections in pavements studied under the long-term pavement performance (LPPT) program showed close correlation to 4% strain (Hintz et al. 2011). Hence a comparison based on 5% strain is more in line with field performance. A 5% binder strain corresponds to a value of 1000 microstrain in the pavement layer (Hintz et al. 2011).

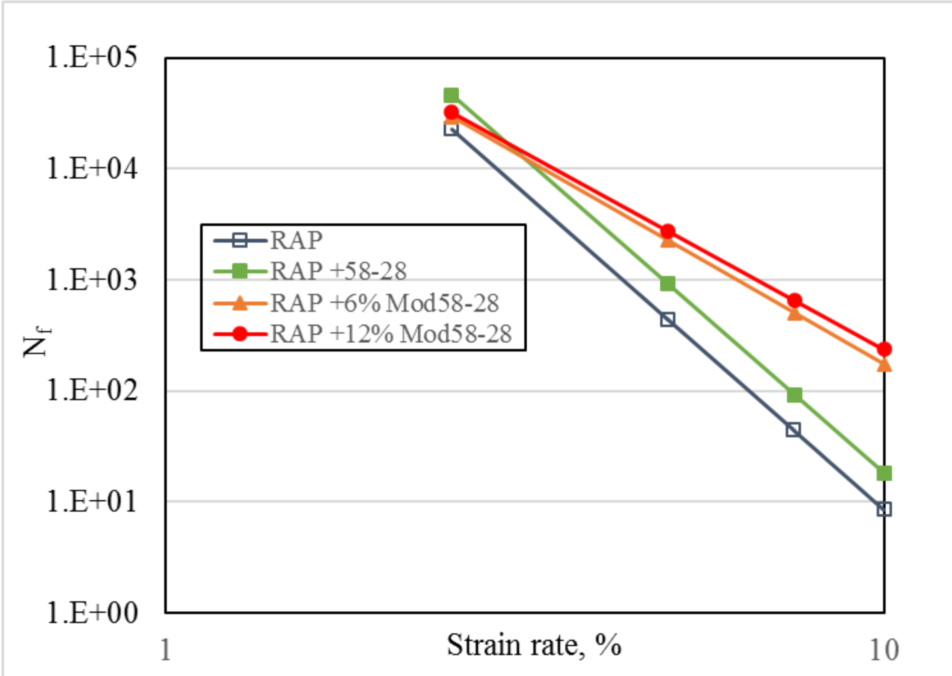

Figure 4.5. Cycles to failure at test temperature of 31°C

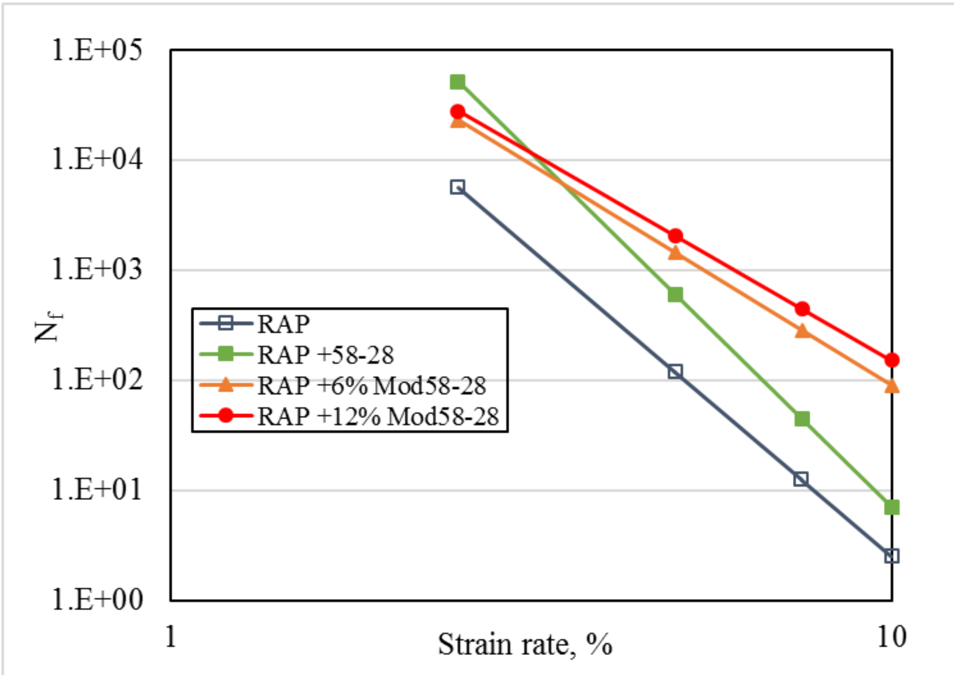

Figure 4.6. Cycles to failure at test temperature of 28°C

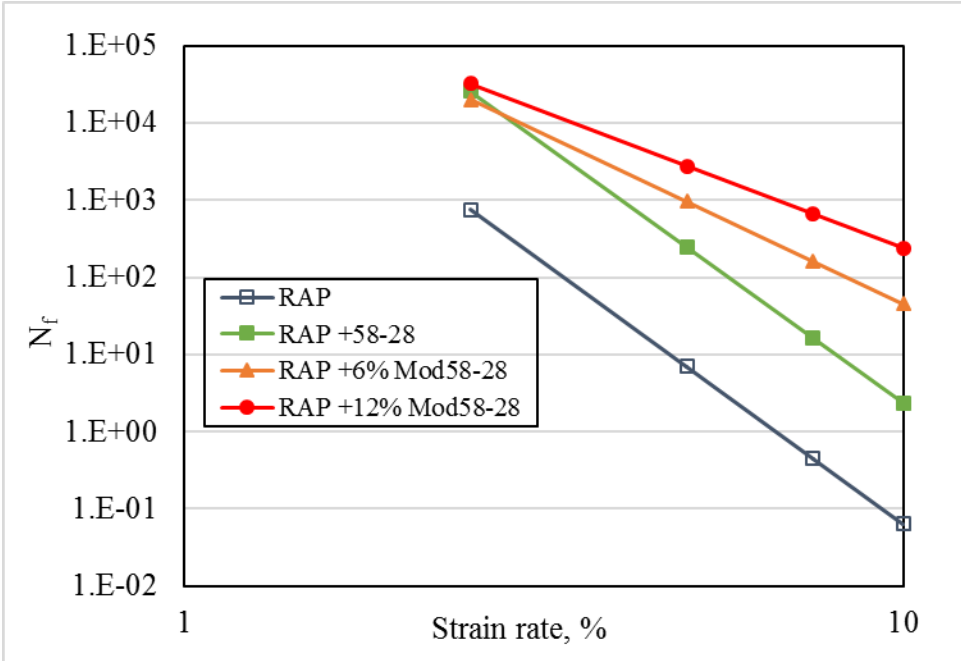

Figure 4.7. Cycles to failure at test temperature of 25ºC

Figure 4.8 shows a plot of the cycles to failure measured at 5% strain rate for all binders at three different test temperatures. The impact of rejuvenation on fatigue life was more pronounced at lower temperatures. It is evident that the improvement attained with the addition of the rejuvenator is more prominent with decreasing temperatures. As the temperature decreased from 31 to 25, the RAP binder showed considerable reduction in fatigue performance compared to the rejuvenated RAP binders. These results provide evidence of the improved fatigue resistance of the rejuvenated binders.

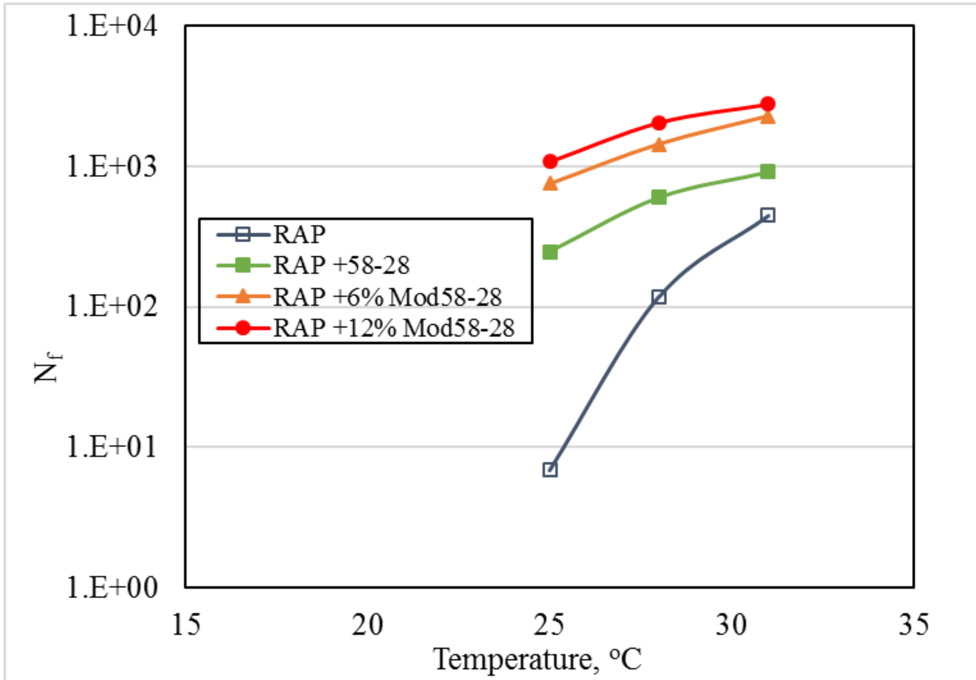

Figure 4.8. Cycles to failure at a strain rate of 5%

4.3.4 Dynamic modulus

Dynamic modulus (E*) testing measures the stiffness of asphalt mixtures over a wide range of frequencies and temperatures, which relates to different environmental conditions and traffic loading. The E* test was developed during NCHRP project 9-19 (Herrington 1995; Witczak et al. 2002) and is now considered a key input parameter in AASHTOWare Pavement ME Design (AASHTO 2016). The test proposed by Witczak (Witczak 2005) applies a compressive haversine load at a frequency ranging from 25 to 0.01 Hz at different temperatures.

In this work, the tested specimens were prepared using RAP mixtures with the addition of virgin PG58-28 and soybean-modified PG58-28 at 6% and 12% dosage. Mixing and compaction were done at 140°C. Three specimens were prepared at each test mixture, making a total of nine specimens

The sigmoidal model was used to fit the dynamic modulus test data to construct master curves for the asphalt mixtures. The sigmoidal model is expressed as,

$$log|E^*| = \delta + \frac{\alpha}{(1+e^{\beta+\gamma(\log(t_r))})} \qquad [4.11]$$

where t_r is the reduced time of loading at the selected reference temperature, δ is the minimum value of $E*$, $\delta + \alpha$ is the maximum value of $E*$, and the parameters β and γ define the shape of the sigmoidal function.

The dynamic modulus master curves for all mixtures, at a reference temperature of 21^{o}C, are shown in Figure 4.9. The shift factors obtained from fitting the sigmoidal model were used to construct phase angle master curves as shown in Figure 4.10. The differences between the dynamic modulus master curves did not follow a clear trend that matched with the binders' performance grade results. Hence it was not possible to assess the impact of the soybean rejuvenator on the dynamic modulus of the tested mixture. The dynamic modulus measures the stiffness of the asphalt mixture and is affected by the air content, aggregate gradation, asphalt content, in addition to the binder's viscosity. Accordingly, differences in the binder's viscosity may not be as obvious. All mixtures had an air void content of 4% so the dynamic modulus values should be expected to increase with low air voids(Yu and Shen 2012). On the other hand, the RAP had a fine gradation which tend to decrease the dynamic modulus(Daniel and Lachance 2005). Another important factor is the degree of blending between the RAP binder and the virgin binder during actual mixing which determines the actual reduction in the total binder's stiffness. The dynamic modulus results include the effect of all the above factors and hence it was difficult to isolate the binder's effect. Moreover, a study on RAP mixtures conducted at the University of Minnesota revealed that the conditions of the dynamic modulus testing may affect the results of mixtures containing high RAP content (Li et al. 2008). The study suggested that microcracks could develop in the specimen when tested at low temperatures, due to the stiffness of the RAP binder. These microcracks affect the specimen's performance at high temperature testing, leading to lower observed stiffness.

A more representative test to assess the impact of the soybean modification is the disk-shaped compact test (DCT). Unlike the dynamic modulus test, the DCT test measures fatigue cracking at higher loading capacity and a lower test temperature. Fatigue cracking is critical to mixtures prepared with RAP. The next section presents the results of the DCT test performed on both the control and modified mixtures.

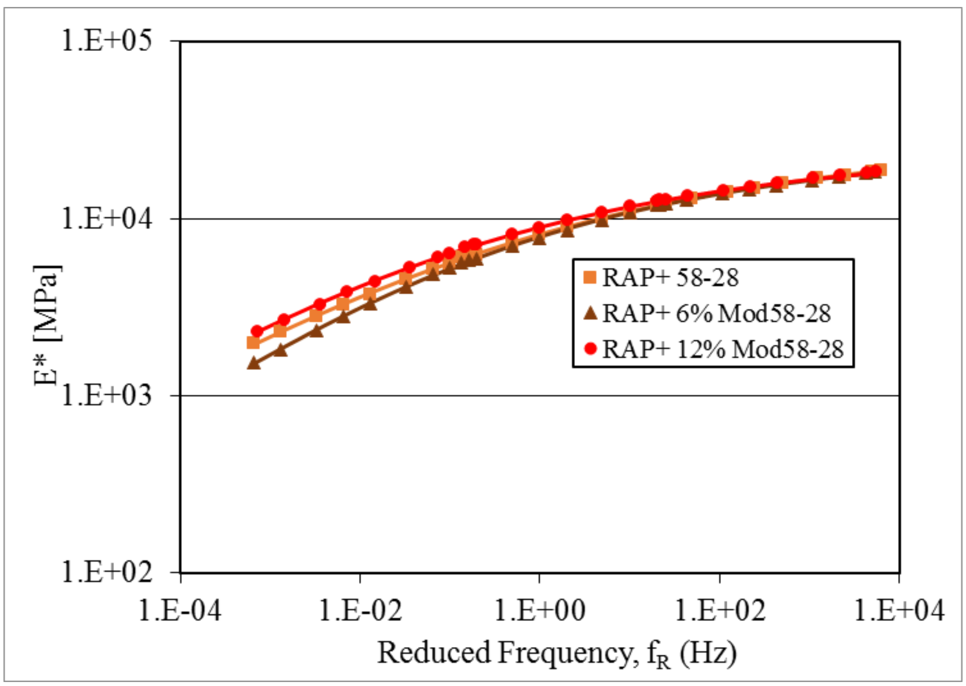

Figure 4.9. Dynamic modulus master curves for asphalt mixtures

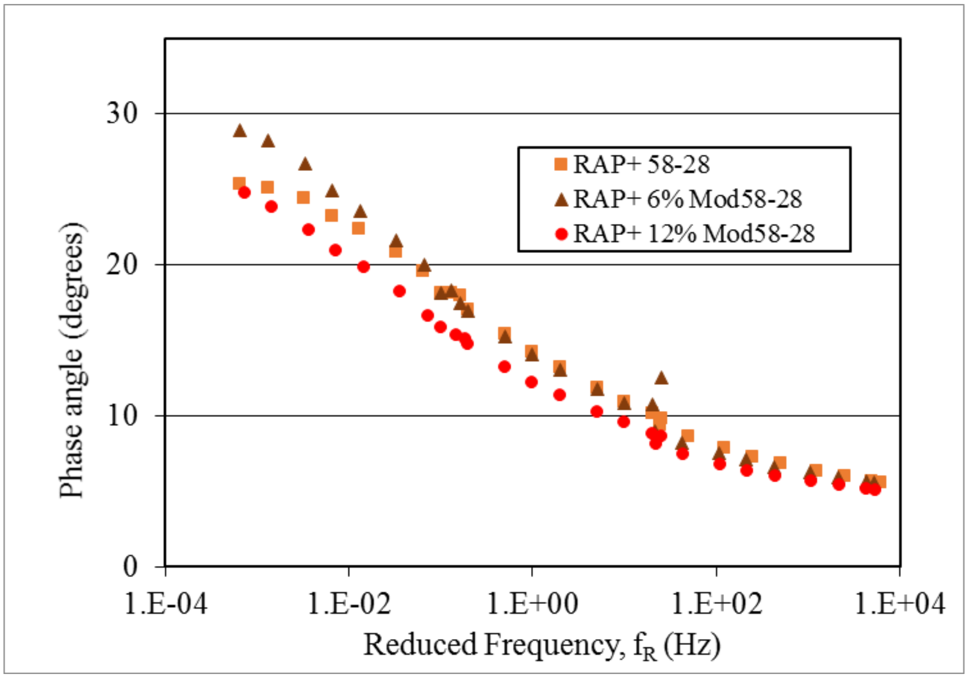

Figure 4.10. Phase angle master curves for asphalt mixtures

4.3.5 Disk-shaped compact tension (DCT)

RAP mixtures with the addition of either a virgin PG58-28 or a 12% soybean-modified PG58-28 were prepared. For each of the two test mixtures, a total of five replicate specimens measuring 50mm in thickness and 150mm in diameter were prepared as per ASTM D7313. A notch 1.5-mm wide is cut along the diameter of the specimen. A flat surface is cut perpendicular to the notch as per the specimen dimensions specified in ASTM D7313. The specimens were conditioned at the desired test temperature of -6^{o}C in a refrigerator for 3 hours prior to testing. The instrument loading rods were inserted into dual openings cored into the specimen. The loading rods are used to pull the specimen apart at a rate of 1mm/min. The crack mouth opening displacement (CMOD) is monitored using a clip gauge extensometer. Upon testing, a seating load of 0.1 kN was first applied to ensure the specimen is tightly held in place. The fracture energy constitutes the amount of work needed to crack a unit area. The work done is calculated by measuring the area under the load-displacement curve. The fractured area is taken as the product of the specimen thickness and the ligament length.

The DCT test results are shown in Table 4.3 below. The average fracture energy of the mixtures made with the soybean rejuvenated RAP binder was on average higher than that of the control mixtures. A t-test conducted on the data resulted in a p-value of 0.3. The large p-value is attributed to the high variability nature of the DCT testing, which is very sensitive to the notch size and specimen dimensions. The coefficient of variation in the results were similar for both types of mixtures. The average fracture energy of the control mixture did not pass the minimum threshold of 400 J/m^2 (Buttlar et al. 2010), whereas the mixtures rejuvenated with the soybean additive exceeded that minimum.

Table 4.3. DCT results for the tested mixtures

Mixture type	Average fracture energy (J/m^2)	Coefficient of variation
RAP+ 58-28	377	0.17
RAP+ 12% Mod58-28	424	0.18

4.4 Summary and Conclusions

In this study, a soybean-derived rejuvenator was used to modify a PG58-28 at a dosage of 6% and 12% by weight of binder. The soybean-modified binder was then blended with an extracted RAP binder at a ratio of 1 part modified PG58-28 to 5 parts RAP, resulting in an effective rejuvenator dosage of 1% and 2% by weight of the binder blend respectively. A control blend was prepared by mixing the neat PG58-28 with the RAP binder at the same ratio. The critical high and low temperatures of the RAP binder dropped significantly with the use of the soybean rejuvenator. The RAP binder changed from a PG106-10 to a PG76-16 using the 6% modified PG58-28 and to a PG70-22 with the 12% modified PG58-28. In comparison, the control blend, using the neat PG58-28, merely changed the RAP binder to a PG100-10. Hence, the neat binder acting alone had insignificant impact on the critical temperatures of the RAP binder. This means that the soybean rejuvenator is largely responsible for any changes in the critical temperatures.

At intermediate temperatures, the linear amplitude sweep (LAS) test results showed a considerable improvement in the fatigue life of the PAV-aged binders upon adding the soybean-derived rejuvenator. This effect was higher for the lower test temperature of 25^{o}C compared to that of 31^{o}C. Even though LAS results serve as a good indication of the fatigue life of asphalt mixtures, future work will include fatigue testing on rejuvenated RAP mixtures to verify the findings of LAS results.

The binder master curves showed a consistent decrease in stiffness and an increase in phase angle with the soybean-derived rejuvenator. Such increase remained significant following PAV aging of the binders. Hence, it can be concluded that the rejuvenation effect was sustained with PAV aging which attests to the durability of the rejuvenator. On the other hand, the PAV-aged control blend did not show significant differences from the PAV-aged RAP binder.

Dynamic modulus specimens were prepared using 100% RAP mixtures blended with a neat PG58-28, a 6% soybean-modified PG58-28 and a 12% soybean-modified PG58-28. Both the dynamic modulus and phase angle master curves did not reveal any differences between the various mixtures. It was not clear whether this result was due to incomplete blending between the RAP binder and the virgin binders. Another possible explanation would be that the dynamic modulus values represent a lot of contributions from various properties of the mixture, so the binder effect may not be clearly discerned.

Disk-shaped compact tension (DCT) specimens were prepared using 100% RAP mixtures blended with a neat PG58-28 and a 12% soybean-modified PG58-28. The specimens made with the soybean rejuvenated mixture showed a higher fracture energy compared to the other set of specimens.

Based on this study, the soybean-derived rejuvenator was proven successful in enhancing the fatigue and low temperature properties of the extracted RAP binders as well as 100% RAP mixtures. Future research will investigate ways to improve blending between the RAP binder and the rejuvenator during actual mixing to better enhance mixture properties.

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CHAPTER 5. THERMAL STABILITY AND EVOLVED GAS ANALYSIS OF REJUVENATED RECLAIMED ASPHALT PAVEMENT (RAP) BITUMEN USING THERMOGRAVIMETIRC ANALYSIS-FOURIER TRANSFORM INFRARED (TGA-FTIR)

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Abstract

Several reports exist on the use of natural-oil based materials as rejuvenators to restore the properties of aged binders. More specifically, regarding their ability to enhance the binders' low temperature properties and to reduce their stiffness. The extent of blending between a rejuvenator and a RAP binder impacts the efficiency of the rejuvenator. In this research, a PG58-28 binder modified with a soybean-derived rejuvenator at 12% by weight, is added to an extracted RAP binder at a ratio of 1:5 resulting in a rejuvenator dosage rate of 2% by total weight of binder. The performance grade (PG) of the rejuvenated RAP binder is determined using both Dynamic Shear Rheometer (DSR) and Bending Beam Rheometer (BBR). The low temperature fatigue cracking of the rejuvenated RAP binder is assessed using the Glover-Rowe parameter through DSR testing. Mixtures made of 100% RAP aggregates are prepared, with the addition of a neat PG58-28 and a soybean-modified PG58-28, and their fracture energy is determined using disc compact tension (DCT) testing. To assess the degree of blending, mixtures representing full blending condition were prepared using extracted RAP binder blended with PG58-28 and soybean-modified PG58-28, and mixed with the extracted RAP aggregate. These mixtures were tested using DCT. The thermal stability of the rejuvenator and the binders is determined using thermogravimetric analysis (TGA). The

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evolved gases from the TGA analysis are analyzed using Fourier Transform Infrared (FTIR) to chemically characterize the rejuvenator and the binders.

5.1 Introduction

Recently, reclaimed asphalt pavement (RAP) has been the subject of extensive research since it offers an environmental friendly and economically viable alternative to offset the increasing binder and aggregate costs. However, the aged properties of RAP binders preclude application of high content RAP mixtures. The use of RAP in new mixtures was limited to only 20% by weight during the year 2014 [1]. RAP binder undergoes excessive oxidation leading to high stiffness and low stress relaxation ability [2]. High RAP content mixtures also can be difficult to field compact which might lead to unexpected premature failure [3].

Addition of a softer virgin binder, using higher binder content, and employing warm-mix technology are among a number of techniques to allow for the use of RAP in asphalt mixtures [4]. However, none of these techniques seem to be effective for mixtures containing high RAP content [5]. The introduction of rejuvenators has paved the way for using higher percentages of RAP in asphalt mixtures. Rejuvenators can help partially or fully restore aged binders' properties to their original state.

Binder aging is characterized by a change of the maltenes fraction into asphaltene through oxidation. The amount of asphaltene is related to the viscosity of asphalt [6]. An increase in asphaltene with aging cause the binder to exhibit high stiffness and a low creep rate. Rejuvenators recreates the balance between the asphaltene and maltene by providing more maltenes and/or by allowing better dispersion of the asphaltenes [7].

Improvement in the low temperature properties and stiffness of rejuvenated aged binders have been verified by a number of studies [7, 8]. Several rejuvenators derived from petroleum based aromatic extracts, distilled tall oil, and organic oils have been successfully implemented [9] . A recent study investigated the fatigue behavior of neat and polymer modified binders rejuvenated with a soybean-derived material using Glover-Rowe fatigue diagram [10]. Aging was shown to push the binders closer to the damage lines, while rejuvenation had a restoring effect moving the binders away from the damage lines. The use of the soybean-derived rejuvenator caused a reduction in the complex shear modulus and an increase in the phase angle, which was opposite to the effect of aging. The rate of aging was also noted to decrease upon rejuvenation in the case of the polymer modified binder [10].

The disk compact tension (DCT) test is commonly used to evaluate the low temperature performance of mixtures containing RAP [11]. The fracture energy, in J/m2, measured through the DCT test can be used as an indication of field performance. A comprehensive study that involved DCT testing on cores taken from different pavements revealed that a fracture energy between 350-400 J/m2 was indicative of sufficient thermal and reflective cracking resistance [12]. A fracture energy above 400 J/m^2 was obtained for pavements with minimal transverse cracking. Accordingly, it was concluded that a minimum fracture energy of 400 J/m2 is required to ensure adequate low temperature performance [12]. The DCT was also used to assess mixtures made with varying percentages of RAP and recycled asphalt shingles (RAS) [13]. It was shown that the presence of recycled materials lowered the fracture energy of the mixtures. Another study looked into the effect of aging on low temperature behavior through DCT testing [14]. It was shown that the fracture energy decreased consistently with aging.

Thermogravimetric analysis (TGA) is used to determine mass loss as a function of temperature. TGA can either be done in an inert environment using nitrogen or in an oxidative environment using air. An inert environment does not allow for combustion to occur. TGA under nitrogen has been previously used to characterize asphalt binders with different asphaltene contents [6]. A relation between the asphaltene content and the decomposition temperatures of asphalt was noted. The thermal stability decreased with more asphaltene content resulting in a lower char yield [6]. In a recent study, TGA of binder blends containing re-refined vacuum tower bottoms (RVTB) was performed under nitrogen and air to assess changes in the thermal stability [15]. The binders were heated under nitrogen until the mass loss reached a plateau at around 600^{o}C. Air was then introduced and the temperature raised to 800^{o}C to burn off the remaining constituents. The remaining mass referred to as ash was less than 2%. No significant changes in the thermal stability was noted between the neat binder and the binder blended with 9% RVTB. TGA was also used to characterize binders modified with styrene-butadiene-styrene polymer and tall oil pitch [16]. It was concluded that the modified binders were thermally stable at the mixing and compaction temperatures of asphalt concrete pavements. Recently, TGA was coupled with mass spectrometry to study chemical changes in aged binders [17]. The TGA analysis was performed under a flow of argon up to a temperature of 900^{o}C. It was noted that char yield decreased from 17% to 6% with aging.

Natural oils have been successfully used as bio-derived alternatives to petroleum-based rejuvenators containing carcinogenic aromatic extracts [9]. Distilled tall oil, cotton seed oil, vegetable oil, and soybean oil are examples of materials previously used to make rejuvenators [8, 18]. Soybean oil holds great potential due to the abundant production of soybeans in the United States. The United States is responsible for about one third of the world soybean production [19]. Most of the soybean output goes into the livestock industry to make soybean meal, or is used to make soybean oil which is then converted into biofuel through transesterification [20].

Several studies have used soybean oil in asphalt modification. Soybean acidulated soapstock (SAS), a rich source of soybean fatty acids, was introduced as a flux agent [21]. SAS at a dosage rate of 1-3% led to a decrease in the critical high temperature and an enhancement in the low temperature properties. Soybean oil was also used as a warm-mix asphalt additive to reduce the mixing and compaction temperature by 3.4°C with 1% dosage [22]. In a recent study, a soybean-derived rejuvenator have been successfully used to lower the stiffness and improve fatigue performance of a neat PG58-28 and a polymer modified PG64-28 binders with sustained durability as verified by Fourier transform Infrared-Attenuated total reflection (FTIR-ATR) [23]. The ability of the soybean-derived rejuvenator to improve the fatigue and low temperature cracking resistance of 100% RAP mixtures was shown through dynamic modulus testing, linear amplitude sweep testing and binder master curves [24]. In this work, the thermal stability of RAP binders rejuvenated with soybean-derived material is assessed as well as the degree of blending between the virgin binder and RAP binder in the rejuvenated RAP mixtures.

5.2 Materials and Methods

The binder used in this study is a neat PG58-28. A soybean-derived material is used as a rejuvenator. Reclaimed asphalt pavement (RAP) was milled from pavements in the State of Iowa, USA. The RAP had a nominal maximum aggregate size of 12.5 mm and a binder content of 5.1%.

The extraction of the RAP binder was conducted as per ASTM D2172-Method A- using toluene. A rotary evaporator was then used to evaporate out the toluene and recover the RAP binder as per ASTM D5404. The recovery process was performed under a nitrogen blanket to prevent further oxidation of the binder. The recovered RAP binder was tested using a Dynamic Shear Rheometer (DSR) to determine their RTFO high critical temperature. PAV-aged RAP binder was tested using a Bending Beam Rheometer (BBR) to determine their low critical temperature.

The soybean rejuvenator was added to the PG58-28 binder at a dosage of 12%. A neat PG58-28 and the 12% modified PG58-28 were then blended with the extracted RAP binder at a ratio of 1:5, resulting in an effective rejuvenator dosage of 0% and 2%, respectively. A pure RAP binder was also used as a control.

For performance grade evaluation, DSR and BBR tests were conducted as per AASHTO T315 and AASHTO T313, respectively. Short-term aging using a Rolling Thin Film Oven (RTFO), was done according to ASTM D2872 at 163^{o}C for 85 minutes. Long-term aging using PAV was conducted on the RTFO aged binder as per ASTM D6521 for a duration of 20 hours at 100^{o}C and 2.1 MPa pressure.

To assess fatigue using the Glover-Rowe parameter, DSR testing was done at a temperature of 44.7^{o}C and a frequency of 10 rad/s. The Glover-Rowe damage lines were plotted and the condition of the various binders at different aging conditions were marked on the Glover-Rowe diagram.

To evaluate low temperature cracking resistance, the Disc Compact Tension (DCT) test was conducted in accordance with ASTM D7313 at a temperature of -6^{o}C. DCT specimens measuring 50mm in thickness and 150mm in diameter were used. Three samples were prepared and tested for each mixture at the desired test temperature and the average fracture energy was reported. Specimens were conditioned at the test temperature for 2 hours prior to testing. The load was applied using loading rods inserted into two holes cored into the specimen, at rate inducing a crack mouth opening displacement (CMOD) of 1 mm/min.

Thermogravimetric analysis (TGA) was performed using a Netzsch STA449 F1 instrument to assess the thermal stability of the studied binders, namely RAP, RAP+PG58-28 and RAP+ 12% modified PG5-28. TGA was also conducted on the soybean-derived rejuvenator to determine its thermal decomposition behavior. A 5-mg sample was placed in an alumina crucible and an internal mass balance allowed recording changes in mass with temperature. The instrument also provided differential scanning calorimetry (DSC) data. A reference crucible made of alumina was used and the difference in heat flow needed to keep the sample crucible at the same temperature as the reference crucible was recorded. DSC data can be used to identify endothermic and exothermic events taking place during the heating process. DSC data was retrieved and used to further analyze the thermal behavior of the soybean-derived rejuvenator.

To provide some insight on the chemical composition of the binders and the rejuvenator, the evolved gases from the TGA run was analyzed using Fourier Transform

Infrared (FTIR). The TGA instrument is connected to a Bruker Tensor 37 FTIR instrument. An FTIR spectrum was acquired every 15 seconds so a complete analysis of the evolved gases can be obtained. FTIR is useful to identify different functional groups within the sample. The FTIR spectra of the rejuvenator can be studied and a comparison between the chemical composition of the unrejuvenated and rejuvenated binders can be made.

5.3 Results and Discussion

5.3.1 Performance Grading

The performance grades of the control RAP binder as well as the rejuvenated RAP binders were determined and are listed in Table 5.1. The critical high temperature was obtained using DSR testing in accordance with AASHTO T315 as per the criteria $G^*/\sin\delta > 1$ kPa and $G^*/\sin\delta > 2.2$ kPa for both the unaged and RTFO aged binders. No unaged result is available for the extracted RAP binder since it was considered RTFO aged. The RAP binder failed at a high temperature of 108.6^{o}C. No appreciable drop in the critical high temperature was noted with the addition of the neat PG58-28. However, the modified PG58-28 resulted in a reduction in the critical high temperature from 108.6^{o}C to 73.9^{o}C. A similar reduction in the critical low temperature was noted from -10.8^{o}C to -22.3^{o}C. The overall effect of the 12% modified PG58-28 was to bring down the PG of the RAP binder from PG106-10 to PG70-22.

Table 5.1: Rheological properties of tested binders

Binder	RAP	RAP+ PG58-28	RAP+ 12%Modified PG58-28
Unaged (High Temp.), ºC	NA	105.6	76.2
RTFO (High Temp.), ºC	108.6	99.9	73.9
PAV (Low Temp.), ºC	-10.8	-11.9	-22.3
Performance Grade (PG)	106-10	100-10	70-22
Mass loss (%)	NA	0.4	0.5

The mass loss values show that there was no considerable mass loss difference due to the addition of the soybean-derived rejuvenator, which points to its thermal stability. A more thorough analysis of the thermal stability of the rejuvenator will be given by the TGA results.

5.3.2 ΔT_c parameter

The PAV low temperature shown in Table 5.1 is the minimum temperature at which both the stiffness and m-value from the BBR test satisfy the conditions set forward in ASTM D7643. Recently, there has been a lot of interest in studying both the stiffness and m-value property independently and in relation to one another [25]. Aged binders have shown to exhibit more deterioration in their m-values [26]. With aging, the difference between the temperature at the limiting stiffness S=300MPa ($T_{c,S}$) and the temperature at the limiting m-value m=0.4 ($T_{c,m}$) starts to increase. To provide more insight into the low temperature properties, the values of both $T_{c,S}$ and $T_{c,m}$ are plotted in Figure 5.1. It is seen that the addition of the PG58-28 did not affect the values of both temperatures significantly. The addition of the soybean rejuvenator caused a decrease in both temperatures. However, there was more drop in the value of $T_{c,m}$ compared to the value of $T_{c,S}$ upon the addition of the rejuvenator. As explained earlier, aged binders suffer from a largely reduced m-value which significantly lower their stress relaxation properties. The effect the rejuvenator has on the value of $T_{c,m}$ clearly illustrates its ability to restore the stress relaxation properties of the aged binder. The difference between $T_{c,S}$ and $T_{c,m}$ was defined as ΔT_c [25]. The ΔT_c parameter for the RAP, RAP+ PG58-28 and the RAP+12% modified PG5-28 binders was calculated as -9.7°C, -9.2°C and -5.5°C. A more negative ΔT_c value is characteristic of an aged binder. The ΔT_c was improved significantly with the soybean rejuvenator.

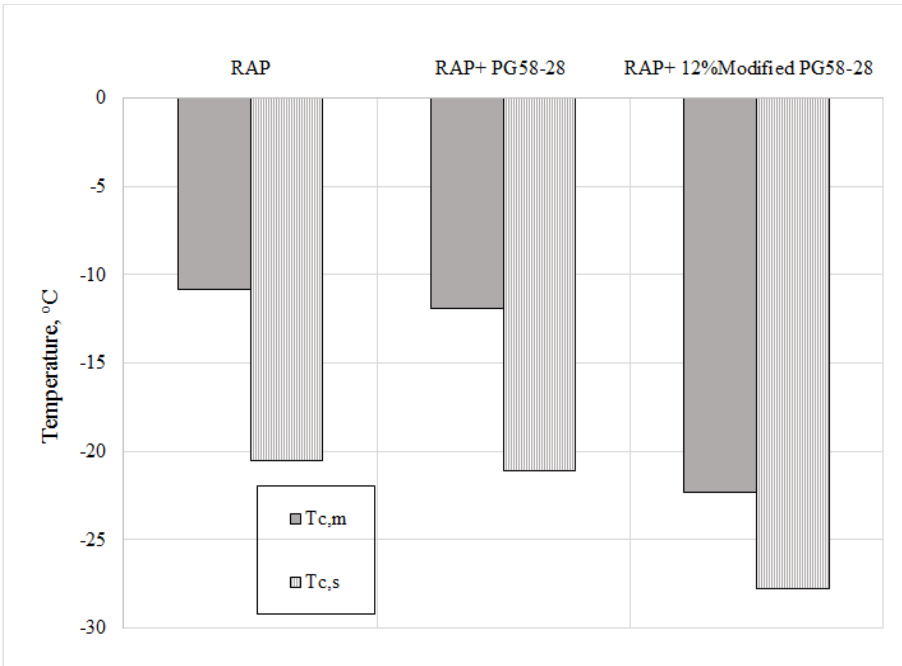

Figure 5.1. Values for $T_{c,S}$ and $T_{c,m}$ for the tested binders

5.3.3 Rutting and Fatigue parameters

Figure 5.2 shows the variation of the rutting parameter, $G^*/\sin\delta$, with temperature for all three binders. The data shown in Figure 5.2 was obtained using DSR testing at a frequency of 10 rad/s using RTFO-aged binders. Unaged binders could not be assessed since there was no unaged data for the RAP binder. Additionally, the critical high temperature, shown in Table 5.1, was limited by the RTFO-aged binder rutting performance. For RTFO-aged binders, rutting performance is considered acceptable when the measured rutting parameter is above 2.2KPa, as specified by AASHTO T315.

RAP binders, being very stiff, typically have high resistance against rutting. With the addition of the rejuvenator, the stiffness drops and so does the rutting resistance. The rejuvenated RAP binder showed acceptable rutting resistance up to a temperature of 73.9°C.

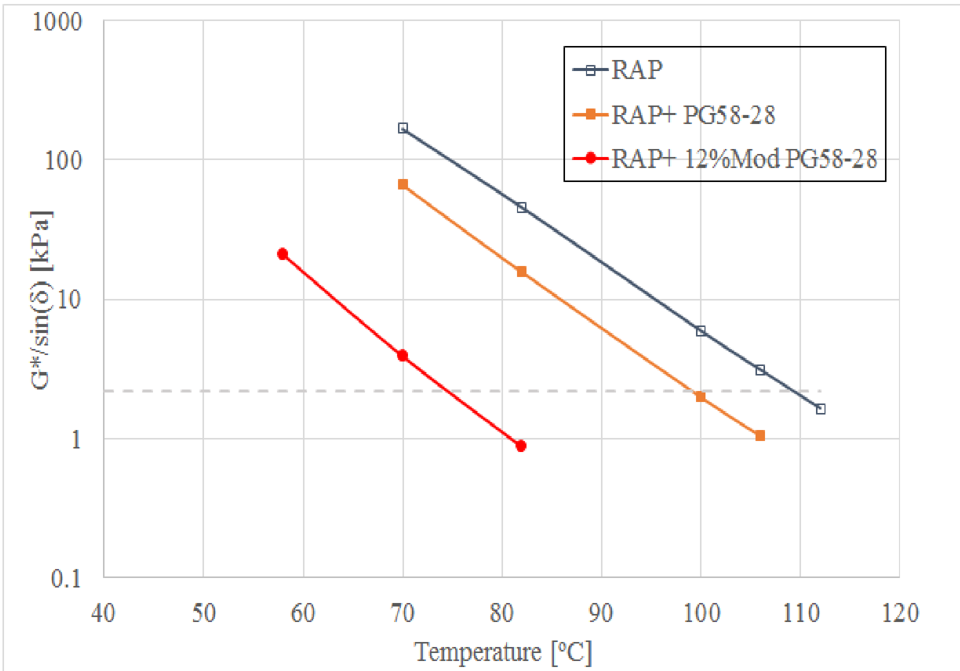

Figure 5.2. Variation of G*/sinδ parameter with temperature

The fatigue parameter G* sinδ examines the fatigue performance at intermediate temperature. The critical intermediate temperature is defined as the value when G*sinδ = 5000 kPa as per AASHTO T315. Figure 5.3 shows the variation of G* sinδ with temperature. The rejuvenated RAP binder shows a lower critical intermediate temperature compared to both the control RAP binder and the RAP binder blended with the PG58-28. The fatigue parameter for the rejuvenated binder however increases relative to the other two binders below a temperature of around 18°C. This is largely due to the increase in phase angle with the addition of the rejuvenator.

The fatigue parameter G*sinδ adopted by Superpave is a measure of energy dissipation. A lower fatigue parameter indicates less energy dissipated in the form of cracks and deformation. This parameter however has been scrutinized recently specifically due to its insensitivity to aging [26]. A recently developed parameter, namely the Glover-Rowe parameter, will be used to further study the fatigue performance and aging characteristics of the binders in the next section.

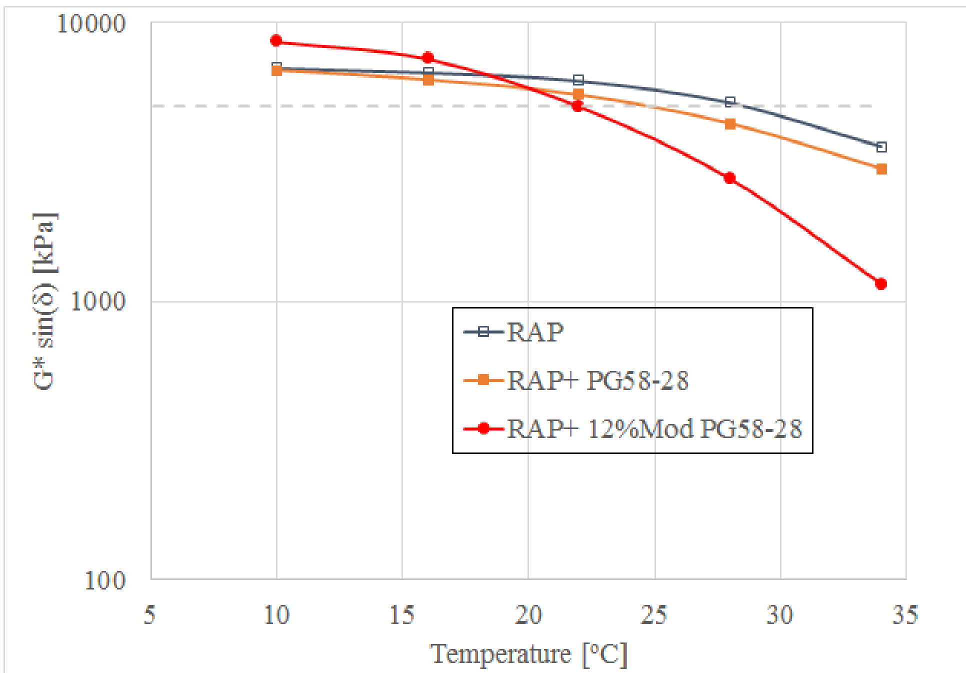

Figure 5.3. Variation of G* sinδ parameter with temperature

5.3.4 Glover-Rowe Parameter

The Glover-Rowe Parameter has been recognized as a valuable tool to investigate fatigue in bitumen. The parameter was based on the work done by Glover [26] who initially introduced the parameter in the form of $G'/\left(\eta'/_{G'}\right)$ where G' is the storage modulus and $\eta'$is the dynamic viscosity. Glover's fatigue parameter was found to correlate well with ductility measurements made by Kandhal [27]. The fatigue parameter was later simplified in the form of $G^* * \omega * {cos\delta^2}/{sin\delta}$. The parameter can be calculated using DSR measurements at 15^{o}C and 0.005 rad/s, where the data correlated best with ductility and field performance. Two damage zones were identified denoting the onset of cracking and significant damage. The damage zones are defined in terms of the fatigue parameter per the equations: $G^* * {cos\delta^2}/{sin\delta} = 180\ kpa$ for damage onset and $G^* * {cos\delta^2}/{sin\delta} = 600\ kpa$ for significant damage. Since it is impractical to perform DSR testing at the shear rate of 0.005 rad/s, it was proposed to run the testing at a temperature of 44.7^{o}C and a frequency of 10 rad/s [25].

DSR testing was performed on the RTFO aged and the RTFO+PAV aged binders at a temperature of 44.7^{o}C and a frequency of 10 rad/s. The complex shear modulus and the phase angle for each of the binders at the respective aging condition were noted and marked on the Glover-Rowe fatigue diagram in Figure 5.4. The Glover-Rowe damage lines were also plotted indicating onset of damage and significant damage. For all binders, PAV aging cause a shift towards the upper left corner of the diagram denoting higher stiffness and lower phase angles. For the RAP binder, the deteriorated condition of the binder was evident by its proximity to the significant damage line. The diagram predicts the PAV-aged RAP binder to show significant signs of fatigue cracking if used as is. Blending the RAP binder with a PG58-28 did not considerably improve its fatigue resistance. The PAV-aged RAP binder blended with PG58-28 is still destined to total failure under fatigue, as suggested by the diagram. Using the soybean-derived rejuvenator clearly improved the fatigue cracking resistance of the RAP binder. The rejuvenator helped reduce the stiffness as well as increase the phase angle hence shifting the RAP binder away from the damage zone. It is also worth noting that the rate of damage with

PAV aging was lower with the rejuvenated RAP binder compared to the pure RAP binder and the RAP binder blended with the neat PG58-28.

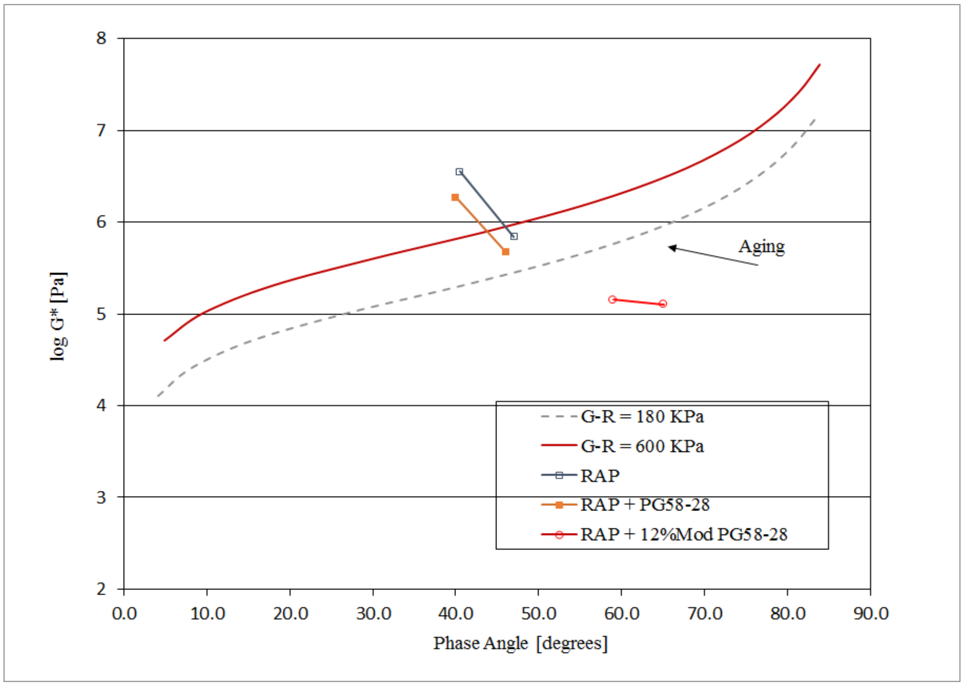

Figure 5.4. Glover-Rowe diagram

5.3.5 Disk-shaped compact tension (DCT)

DCT specimens were prepared using 100% RAP aggregate mixed with virgin binder. The RAP aggregate, having a 5.1% binder content, was mixed with virgin binder to bring the binder content to a total of 6%. Two groups of specimens were made using neat PG58-28 and 12% modified PG58-28 as virgin binders. During actual mixing, the virgin binder does not fully blend with the RAP binder. Hence, these specimens represented real/partial blending conditions. To assess full blending condition, RAP binder was first extracted and recovered from the RAP aggregate. The RAP binder was then blended with the virgin binder; neat PG58-28 or 12% modified PG58-28. The resulting blend was then remixed with the recovered bare RAP aggregate and compacted to produce two additional groups of DCT specimens representing full blending conditions. In total, four groups of specimens were prepared and tested, to assess the difference in performance between the neat PG58-28 and the 12% modified PG58-28 considering both real/partial and full blending with the RAP binder. Testing for all specimens was done at -6^{o}C. All mixtures were prepared with a total binder content of 6% and a target air void content of 4%. Mixing and compaction was done at a temperature of 140^{o}C.

The DCT test results for both real blending and full blending conditions are shown in Table 5.2. In general, the average fracture energy of the mixtures prepared with the rejuvenated PG58-28 binder was higher than the mixtures prepared using the neat PG58-28. Regardless of the blending condition, the fracture energy of the RAP mixtures made with the neat PG58-28 were lower than the minimum threshold of 400J/m^2 required to provide adequate transverse cracking performance [12]. The difference between the real blending and full blending conditions for these mixtures was not discernable due to the fact that the low temperature performance grades of the pure RAP binder and the RAP binder modified with neat PG58-28 were not distinctly different as shown in Table 5.1.

Typically, DCT testing is done at a temperature which is 10^{o}C higher than the binder’s low temperature performance grade (PG). Noting that the low temperature performance grade of the RAP + 12% modified PG58-28 blend was -22^{o}C as shown in Table 5.1, one would expect the mixtures prepared with the rejuvenated PG58-28 to provide satisfactory performance up to a test temperature of -12^{o}C. However, the DCT results under real blending conditions show that these mixtures barely exceeded the minimum threshold of 400J/m^2 at a test temperature of -6^{o}C. When full blending condition was achieved, the fracture energy of these mixtures increased to 528 J/m^2.

Partial or improper blending can cause non-uniform distribution of the rejuvenator throughout the aged RAP binder. This non-uniform blending creates spots of unrejuvenated stiff RAP binder which acts as stress concentration regions leading to reduced fracture energy. The large coefficient of variation noted with the real blending mixes could be an indication of non-uniform blending as indicated above.

The results clearly indicate that the degree of blending can have a major impact on the performance of the rejuvenated RAP mixtures. It is thus of paramount importance to ensure a high degree of blending so that the full potential of the rejuvenator is achieved. A comprehensive study into the way the rejuvenator is added and mixed with the RAP mixtures is important to ensure proper blending.

Table 5.2: DCT results for the tested mixtures at -6^{o}C

	Real blending		Full blending	
Mixture Type	Average fracture energy (J/m^2)	Coefficient of variation	Average fracture energy (J/m^2)	Coefficient of variation
RAP + PG58-28	377	0.17	379	0.07
RAP + 12% Mod PG58-28	424	0.18	528	0.06

5.3.6 Thermogravimetric analysis (TGA)

TGA was conducted for all three binders to assess changes in their mass with temperature. The binders were heated from 50^{o}C to 1000^{o}C at a rate of 20^{o}C/min. Nitrogen was used as a purging gas at a flow rate of 20 ml/min to prevent combustion until a temperature of 550^{o}C was reached. At this temperature, the purging gas was then changed to a 50:50 mixture of oxygen and nitrogen at a total flow rate of 20 ml/min. The use of oxygen helped promote combustion of the remaining asphalt constituents beyond a temperature of 550°C.

The TGA curves for all three binders are shown in Figure 5.5. All curves show four distinct regions. The initial region showing minimal mass loss. The end of this region is marked by the initial decomposition temperature which is hereby defined as the temperature where the mass loss reached a value of 2%. The second region shows a consistent mass loss denoting thermal decomposition of asphalt constituents. A third region which starts around 540°C exhibits a near horizontal plateau indicating no further mass loss. The fourth and last region represents the combustion of the remaining carbonaceous constituents upon the addition of oxygen.

Figure 5.6 shows the first derivative of the TGA curve, referred to as the derivative thermogravimetric (DTG) curve. DTG provides information about the rate of change of mass loss with temperature, and can be used to identify the temperature at which this rate reaches a maximum. The region in the DTG curve where the rate of mass loss was nearly zero corresponds to the part of the TGA curve where negligible mass loss was occurring. The thermal decomposition region showed an increasing rate of mass loss up to a temperature of 470-480°C where the rate of mass loss was maximized. Beyond this temperature, the rate of decomposition starts to drop down until it reaches a near zero value at about 540°C where no significant mass loss was taking place. The addition of oxygen at a temperature of 550°C triggered further mass loss because of combustion. The combustion process resulted in two more mass loss peaks at around 600-620°C and 700°C.

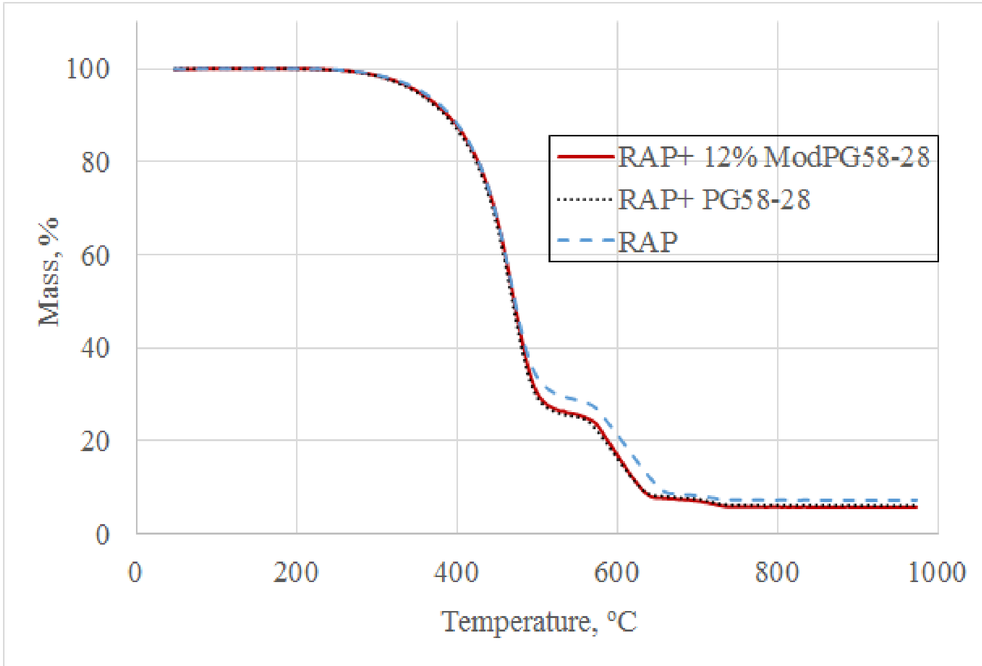

Figure 5.5. TGA curves of studied binders

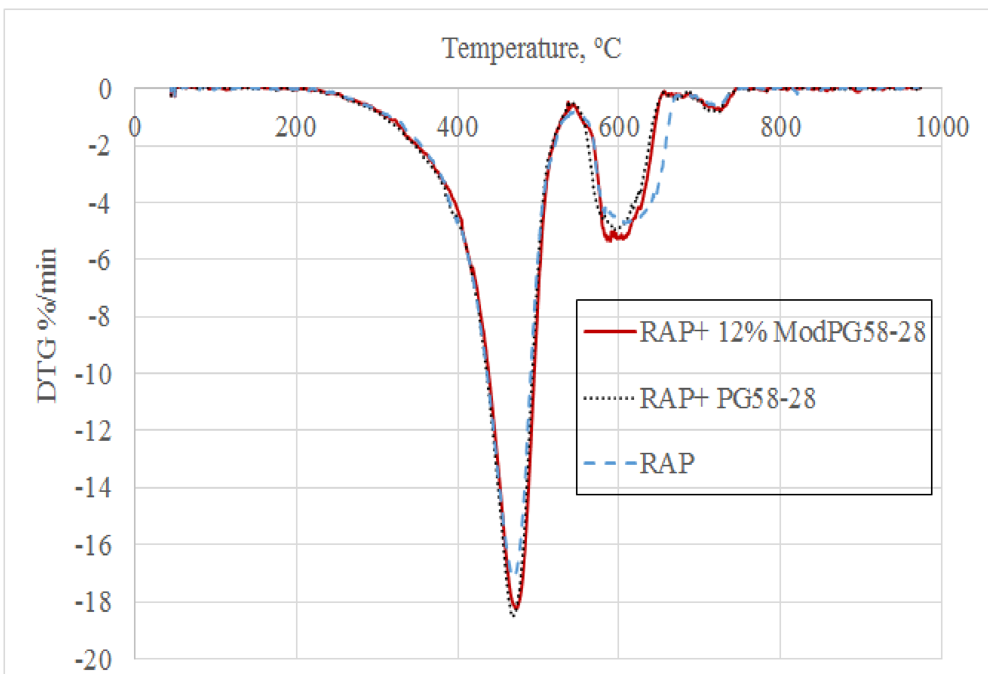

Figure 5.6. DTG curves of studied binders

Table 5.3 shows the initial decomposition temperature (IDT), char yield percentage, and percentage residue for all three binders, obtained from the TGA curves. The char yield is the mass remaining at a temperature of 550°C, and the percentage residue is the remaining percentage of asphalt material at the end of the analysis. A study of the parameters in Table 5.3, as well as a comparison of the TGA curves, clearly indicate that the RAP binder shows the highest thermal stability among all three binders. This result confirms with the fact that aged binders have a large portion of asphaltene which are thermally stable at high temperatures. The increased thermal stability is evidenced by the high initial decomposition temperature, as well as the high percentage of char yield and residues. Adding a softer binder, PG58-28, lowers the initial decomposition temperature by a few degrees, from 316°C to 309°C, as given by Table 5.3.

More importantly is the effect of the soybean-modifier on the TGA curve, DTG curve and the TGA parameters. The TGA results point to the fact that the addition of the soybean rejuvenator does not seem to impact the binders' thermal stability. The TGA and DTG curves of the soybean rejuvenated binder does not deviate much from the RAP+ PG58-28 binder. It is also important to note that there was no sign of thermal decomposition of the rejuvenator at normal asphalt mixing and compaction temperatures.

Table 5.3: TGA results of the studied asphalt binders

	IDT (°C)	Chair yield (%)	Residue (%)
RAP	316	30	7
RAP + PG58-28	309	26	6
RAP + 12% Mod PG58-28	309	26	6

To assess the thermal stability of the pure soybean-derived rejuvenator. TGA was conducted on a 5-mg sample of pure rejuvenator placed in an alumina crucible under the same conditions described above. The TGA and DTG plots are shown in Figure 5.7. The TGA curve shows good thermal stability up to a temperature of around 300°C. Following this temperature, the rejuvenator starts to thermally decompose at an increasing rate. An abrupt mass loss is observed from 370°C -400°C where more than 60% of the soybean-derived rejuvenator is lost. The DTG curve shows a peak mass loss at around 390°C. The entire sample was thermally degraded at the end of the temperature program leaving no residue behind.

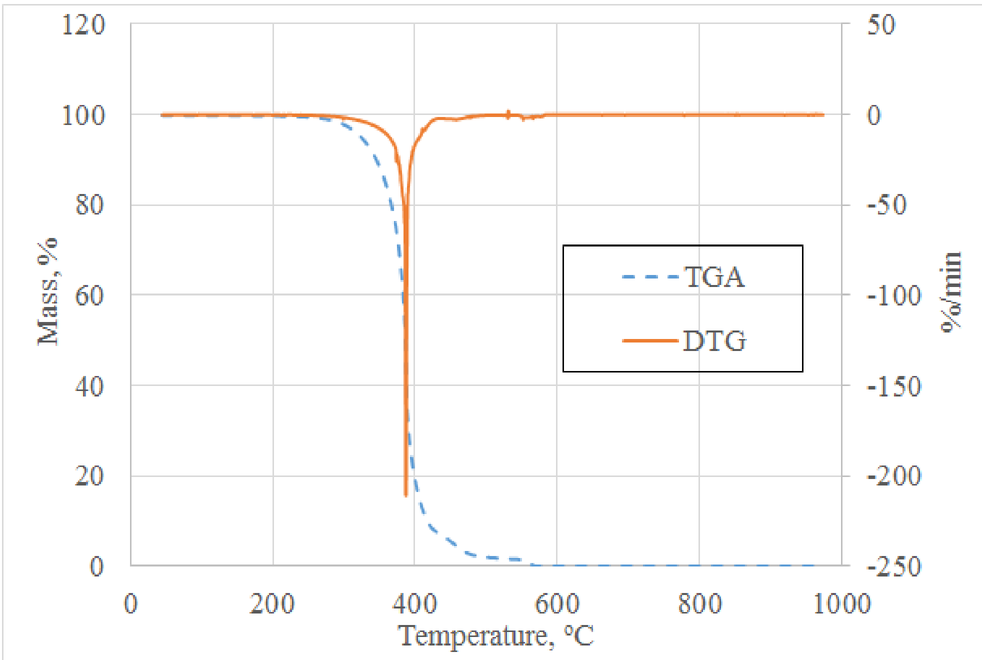

Figure 5.7. TGA and DTG curves of the soybean-derived rejuvenator

Figure 5.8 provides a DSC curve for the soybean-derived rejuvenator. Positive and negative peaks on this plot indicate exothermic and endothermic events, respectively. The DSC curve shows two distinct exothermic events. The first event around 390°C relates to the thermal decomposition of the rejuvenator. The sharpness of this peak is an indication of the homogeneity of the rejuvenator sample. The second peak around 580°C denotes the combustion of the sample under oxygen.

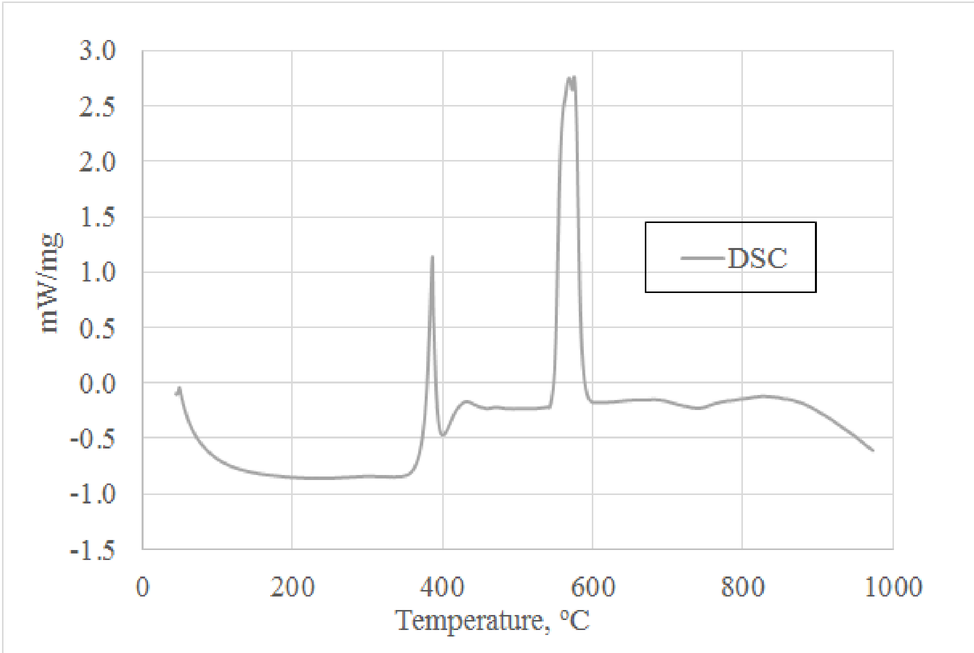

Figure 5.8. DSC curve of the soybean-derived rejuvenator

5.3.7 FTIR analysis

An FTIR spectrum can be collected for the evolved gases from the TGA analysis. The FTIR spectrum for the gases produced during the TGA analysis of the soybean-derived rejuvenator at a temperature of 390°C is shown in Figure 5.9. This temperature corresponds to the maximum mass loss of the rejuvenator as determined earlier from the TGA results. The FTIR spectrum of the soybean-derived rejuvenator shows a distinct peak at 1736cm^{-1} which corresponds to the C=O stretch in the ester moiety present in the rejuvenator's structure. The ester moiety is also characterized by the peaks at 1015cm^{-1} and 1153cm-^{1} which correspond to the C-O stretch.

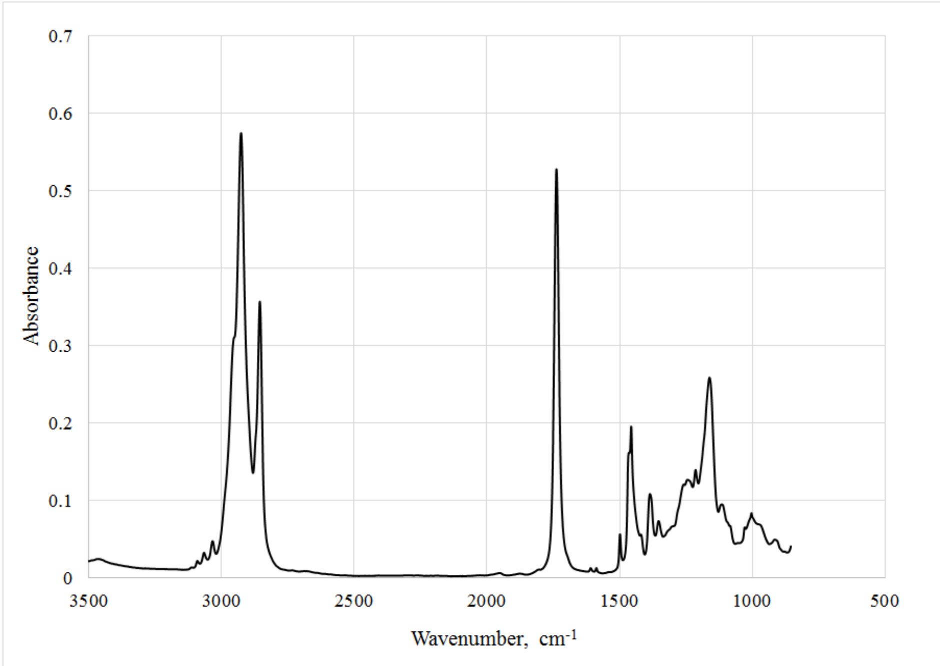

Figure 5.9. FTIR Spectrum for the rejuvenator at 390°C.

The FTIR spectra obtained for the evolved gases from the three different binders at 390°C are shown in Figure 5.10. The peak at 2930cm^{-1}, which corresponds to the C-H stretch in the alkane hydrocarbon structure, was used to normalize the three spectra. The characteristic peaks of the rejuvenator appear in relatively high intensity in the rejuvenated RAP binder. These peaks are absent or are of negligible intensity in the other two binders that did not contain the rejuvenator.

The FTIR spectra can also serve as an indication of the rate of mass loss of the rejuvenator. This is done by comparing the relative intensities of the rejuvenator's characteristic peaks; ester peaks, in the rejuvenated binder. To illustrate this, the FTIR spectra for the three binders at a temperature of 500°C are displayed in Figure 5.11. At this temperature, the rate of mass loss of the rejuvenator is considerably lower than at 390°C, as per the TGA results. The characteristic peaks of the rejuvenator at 1736cm^{-1}, 1015cm^{-1}, and 1153cm^{-1} are barely discernable in the spectra in Figure 5.11. The is because only a small amount of the rejuvenator is still evolving at this temperature. Hence, the relative intensity of the rejuvenator's peaks in the binder can provide a clue about the rate at which the rejuvenator is thermally decomposing at a given temperature.

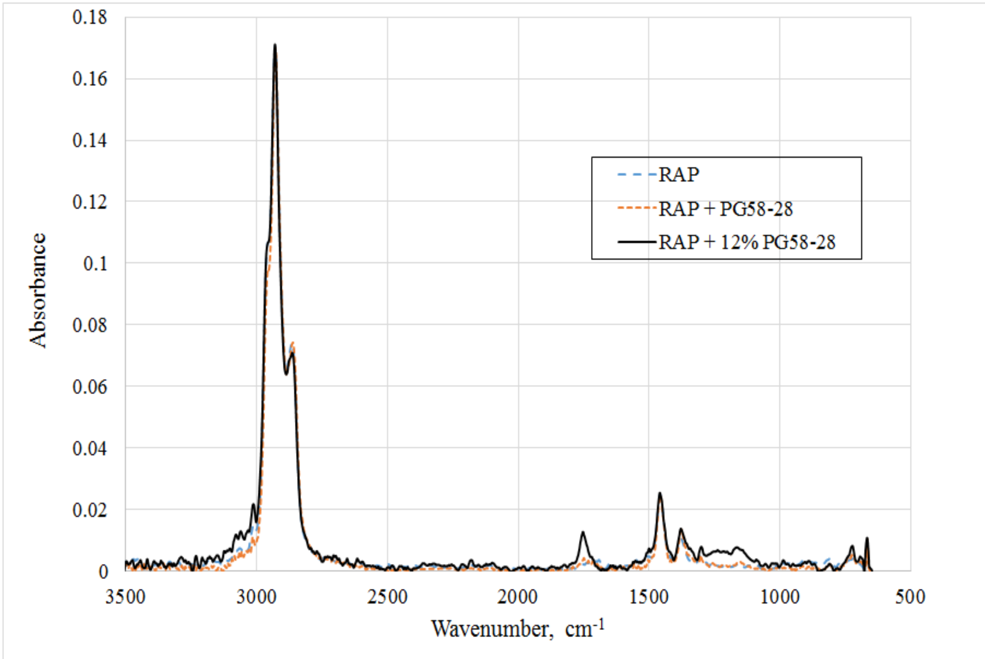

Figure 5.10. FTIR Spectrum at 390°C.

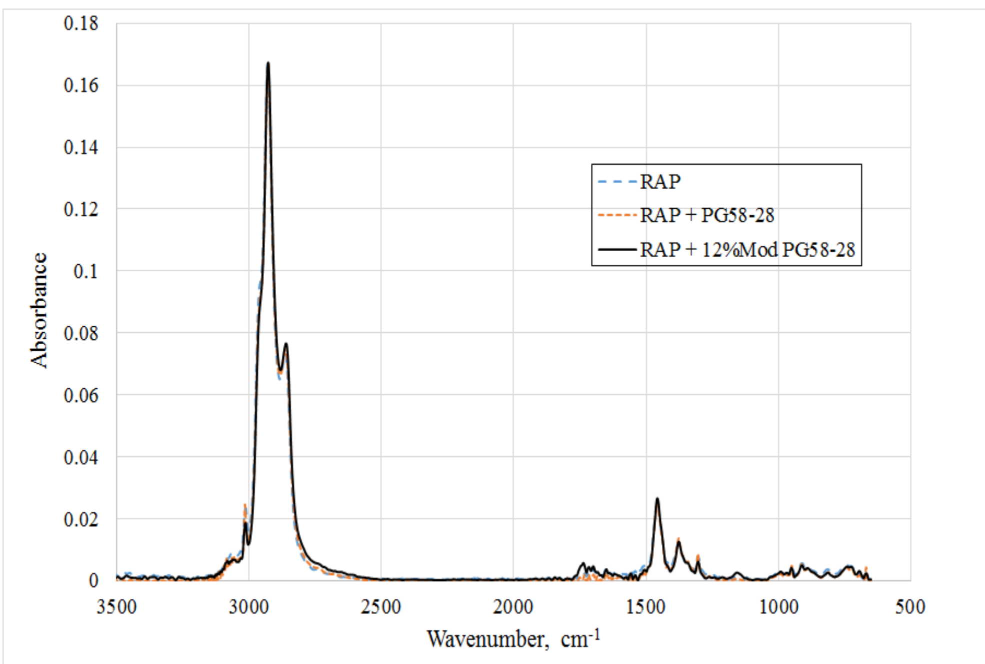

Figure 5.11. FTIR Spectrum at 500°C.

5.4 Summary and Conclusions

The work done in this paper aimed at investigating the impact of using a soybean-derived rejuvenator on the properties and thermal stability of a RAP binder. Rejuvenated RAP mixtures prepared with 100% RAP aggregate were also assessed based on their DCT fracture energy results. The effect of blending was also highlighted.

The use of the soybean-derived rejuvenator clearly brought down the RAP binder performance grade to acceptable working ranges. The highly stiff RAP with a PG of 106-10 was changed to a PG70-22 with the addition of the 12% soybean-modified PG58-28, for a 2% rejuvenator dosage of the total binder. No significant mass loss was noted due to the addition of the soybean-derived rejuvenator.

The Glover-Rowe parameter showed considerable improvement in the fatigue cracking resistance for the rejuvenated RAP binder. The rate of aging of the rejuvenated RAP binder was lower than that of the control RAP binder, as suggested by the Glover-Rowe diagram.

The DCT results showed improvement in the fracture energy with the use of the soybean-derived rejuvenator. Such improvement was more pronounced when the full blending condition was achieved. The real blending condition showed less increase in fracture energy owing to the partial blending between the virgin binder and the RAP binder.

The TGA results verified the thermal stability of the rejuvenated RAP binder. The soybean-derived rejuvenator did not show any signs of premature thermal decomposition. The TGA curve for the rejuvenated RAP binder showed very similar resemblance to the control RAP and the RAP binder blended with PG58-28. FTIR analysis of the evolved gases revealed that the rejuvenator has characteristic peaks which can serve as an indication of the rate of its thermal decomposition within the asphalt binder.

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CHAPTER 6. GENERAL CONCLUSIONS

6.1 Rejuvenation of a neat and a polymer modified binders

A soybean-derived additive was introduced as a rejuvenator to enhance the low temperature and fatigue properties of binders. At a dosage of 0.75% by weight of binder, both a neat PG58-28 and a polymer modified PG64-28 were rejuvenated to improve their low temperature performance. The efficiency of the rejuvenator was seen to relate to the performance grade of the binder. The PG64-28 showed better improvement in fatigue compared to the PG58-28. Rutting susceptibility was however increased by the addition of the rejuvenator, which could be controlled by adjusting the dosage rate of the rejuvenator. The rejuvenator led to a reduction in viscosity promoting less compaction energy.

Temperature-frequency sweep testing was done using a DSR. The results of the temperature-frequency sweeps were used to develop complex shear modulus master curves for both the control and rejuvenated binders at different stages of aging, namely unaged, RTFO-aged, and PAV-aged. The rejuvenated binders showed a consistent drop in the complex shear modulus and an increase in the phase angle at the different aging stages. The extent of the change in the complex shear modulus values and phase angles was maintained with aging denoting that the rejuvenator had a sustained effect on the binders.

Black diagrams were constructed for the rejuvenated binders using a DSR and smooth plots were obtained indicating no phase separation between the rejuvenator and the binders with changes in temperature. It was shown that the rejuvenated binders showed better fatigue cracking resistance with aging compared to the control binders using the Glover Rowe parameter.

Dynamic modulus specimens prepared at two different mixing and compaction temperatures, namely 120°C and 140°C, were tested at different temperatures and frequencies. The resulting dynamic modulus values were lowered considerably for mixtures containing the rejuvenator, at all test temperatures and frequencies. The results of a split-plot repeated measures (SPRM) statistical analysis showed that the lower mixing and compaction temperature of 120°C yielded more reduction in dynamic modulus at low test temperatures, particularly for the PG64-28 binder.

The durability of the rejuvenated binders was assessed using a FTIR-ATR by noting the increase in the carbonyl and sulfoxide functional groups with aging. The rate of increase in the carbonyl and sulfoxide indices was similar in both the control and rejuvenated binders, indicating that the rejuvenator did not have any adverse impact on the durability of the binders.

6.2 Rejuvenation of a reclaimed asphalt pavement (RAP) binder

In this phase of the research, a soybean-derived rejuvenator was blended with a neat PG58-28 at 6% and 12% by weight of binder. The blend was then used to rejuvenate an extracted RAP binder at a ratio of 1 part modified PG58-28 and 5 parts RAP. A neat PG58-28 was blended with RAP at the same ratio, yielding a control blend. The results indicate that the performance grade of the RAP binder was brought down from a PG106-10 to a PG76-16 and PG70-22 when blended with the 6% rejuvenated PG58-28 and the 12% rejuvenated PG58-28, respectively.

Linear amplitude sweep (LAS) testing was done to assess the fatigue performance of the rejuvenated RAP binder at different temperatures and strain rates. The fatigue life of the rejuvenated RAP binder was significantly increased especially at lower test temperatures and higher strain rates.

Complex shear modulus master curves revealed a consistent decrease in stiffness and increase in phase angle for the rejuvenated RAP binder. This impact on the stiffness and phase angle was maintained after PAV aging, which attests to the durability of the rejuvenator.

The fatigue cracking resistance of the rejuvenated RAP binder was greatly enhanced as revealed by the Glover-Rowe diagram. The rate of aging of the rejuvenated RAP binder was shown to be lower than that of the pure RAP binder.

6.3 100% RAP mixtures

6.3.1 Dynamic modulus

100% RAP mixtures were made by adding a neat PG58-28, a 6% soybean-modified PG58-28 and a 12% soybean-modified PG58-28. The dynamic modulus test did not capture the differences between the binders. The dynamic modulus test results did not follow a clear trend that matched with the binder results. The dynamic modulus test reflects various mixture properties; hence the contribution of the binder may not be as clearly discernable. Partial blending between the RAP binder and the virgin binder could possibly have influenced the dynamic modulus test results.

6.3.2 Disk-shaped compact tension (DCT)

100% RAP mixtures blended with a neat PG58-28 and a 12% soybean modified PG58-28 were made and compacted into disk-shaped compact tension (DCT) specimens and subsequently prepared for testing. The DCT specimens were tested at -6^{o}C. The specimens containing the rejuvenator resulted in a fracture energy of 377 J/m^2 compared to a fracture energy of 424 J/m^2 for the control specimens. DCT specimens simulating full blending conditions were prepared by extracting the RAP binder and pre-blending it with the virgin binders before re-mixing the blend with the bare extracted aggregate. Specimens made as such showed a fracture energy of 379 J/m^2 for the control mixtures and 528 J/m^2 for the rejuvenated mixtures. The increase in fracture energy of the rejuvenated mixtures from 424 J/m^2 to 528 J/m^2 shows that the full potential of the rejuvenator can better be achieved if full blending is obtained.

6.4 Thermal stability of rejuvenated RAP binder

The thermal stability of the rejuvenated RAP binder was verified by the results of the RTFO mass loss and by the TGA results. The addition of the rejuvenator did not result in any signs of premature thermal decomposition. The TGA curve of the rejuvenated RAP binder was very similar to that of the RAP binder blended with neat PG58-28. FTIR analysis of the evolved gases revealed that the rejuvenator has characteristic peaks which can serve as an indication of the rate of its thermal decomposition within the asphalt binder.

6.5 Future Research

Future work should include more testing to further characterize the rejuvenated mixtures. This study revealed that the rejuvenator could lead to a reduction in the rutting susceptibility of binders. Even though aged RAP binders tend to be very stiff and show high rutting resistance. Mixtures prepared with rejuvenated RAP binders must be tested against rutting to ensure satisfactory rutting performance. Hamburg Wheel Track Testing could be done on both control and rejuvenated 100% RAP mixtures to assess rutting resistance. RAP mixtures containing different dosages of the rejuvenator could be prepared and tested for rutting. An optimum rejuvenator dosage can thus be selected based on the mixtures performance. Another important factor, which is related to field performance, is the effect of moisture on mixtures prepared using the rejuvenator. Moisture susceptibility testing, as specified in AASHTO T 283, can be conducted to assess the resistance of rejuvenated RAP mixtures against moisture ingression. 100% RAP mixtures containing the rejuvenator at various dosages should be prepared and tested using indirect tensile strength to determine their tensile strength ratios.

Moreover, there is a need for incorporating the rejuvenator in field projects where the actual performance of both untreated and treated test sections can be compared. An extensive study should be undertaken where the rejuvenator should be incorporated in the construction of road sections. The performance of the rejuvenated test sections should be monitoring throughout an extended period. Pavement coring will need to be made after one year to assess the condition of the treated sections. Extraction and recovery should be done to characterize the rejuvenated binders. Other tests including DCT should also be performed to assess the low temperature properties of the rejuvenated binder.

The interaction between the binder and the rejuvenator should also be examined more thoroughly. The current study showed that the properties of the binder, including performance grading, influences the effectiveness of the rejuvenator. A study that involves adding the rejuvenator to different binders with varying stiffness should be conducted to determine the chemical and rheological changes that occur. The chemical nature of these changes could be assessed through a number of different analytical characterization tools including chromatography and mass spectrometry.