AGING SUSCEPTIBILITY AND PERFORMANCE OF OIL MODIFIED ASPHALT BINDERS

By

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ABSTRACT

As oils are becoming more popular additives in asphalt binders as low temperature modifiers, there has been interest in the performance, especially the long-term aging, of oil modified asphalts. Research studies have reported widely varying effects of different types of oils on asphalt binders in terms of rheological and aging properties. This thesis is focused on characterizing the aging susceptibility or oxidation potential of commonly used oils to determine if the susceptibility is related to observed aging susceptibility of asphalt binders modified with oil and polymers. To accomplish this, two common oils, bio-oil and re-recycled engine oil bottoms (REOB), were aged in the PAV for several different intervals and then tested in a dynamic shear rheometer to detect changes in complex shear modulus and phase angle. Aging indices were calculated to normalize the magnitudes of change. Then 6 blends were prepared using bio-oil and REOB with combinations of polymers including SBS, Elvaloy, and PPA. Each oil was combined with each polymer combination to meet similar low-temperature performance grades. Two control blends, one containing SBS, the other a refinery produced PG 58-34 using an unknown quantity of Elvaloy, were prepared and obtained, respectively. Extended PAV aging was performed for 20-, 40-, and 60-hour cycles. Blends were then tested using frequency sweeps, elastic recovery tests, bending beam rheometer testing, and bitumen bond strength testing to evaluate the aging susceptibility on various performance metrics at different temperature levels.

Results show that bio-oil exhibits nonlinear and high aging susceptibility while the REOB exhibits no appreciable susceptibility to aging in terms of its complex shear modulus aging index and phase angle aging index. Testing of the modified asphalt blends yielded performance results that varied based on not only the aging susceptibility of the oil itself, but also of the polymer additives, as well as the interaction of the oil with the polymer. Blends containing the bio-oil performed better in the low temperature testing as compared to the blends with REOB, but the REOB blends showed better aging susceptibility results when measured at intermediate temperatures. Analysis of the results leads to conclude that aging of blends cannot be predicted from the aging of the oils, and there are significant interactions with polymers. Therefore, extended PAV aging is required to accurately define the long-term aging effects of these oil modifiers.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

Chapter 1: Introduction

1.1: Relevance and Common Modifiers

Today, in the United States, there are over 2.7 million miles of paved roads, 94% of which are paved with asphalt concrete [1]. As the performance demanded of our highways is ever increasing – we want our roads to last longer and provide a comfortable and safe surface to drive on - there has been increasing research in asphalt pavement enhancement. Modification of asphalt cements is a widely practiced method to enhance the performance of modern highways. Modification allows for the usage of lower quality asphalts, which are inexpensive to produce, but can be used in place of costly higher quality asphalts. As long as the cost to modify is cheaper than using unmodified, higher quality refinery asphalts, it is the choice method of meeting specifications today. The most common form of modification practiced is blending base asphalt binder with elastomers, polymers, and oils. However, there are many more types of modifiers available including: hydrocarbons, mineral fillers, antioxidants, antistripping additives, fibers, extenders, recycling agents and oxidants. The addition of these modifiers alters the rheological responses of the resulting homogenous blend with increased durability, mechanical, and chemical performance.

While issues related to rutting and fatigue have largely been solved through the usage of elastomer and polymer modification and modern analysis such as that provided in the Mechanistic Empirical Pavement Design Guide (MEPDG), low-temperature cracking has remained a prominent issue. Low-temperature cracks manifest as transverse cracks in the pavement. They form when the pavement cools quickly or reaches a very low temperature. The pavement's mechanism of failure in these conditions is thermal contraction. When the pavement contracts it is met with resistance due to the friction with the underlying base layers (typically aggregates). This causes internal tension that cannot be relieved via spatial translation of the pavement and so internal stresses begin to accumulate. When these stresses become larger than the local maximum tensile strength of the asphalt binder a crack forms. Due to there being larger resistance in the longitudinal direction than the transverse direction of the pavement, the cracks typically form in the transverse direction of the roadway and usually are uniformly spaced between each other, see **Figure 1**.

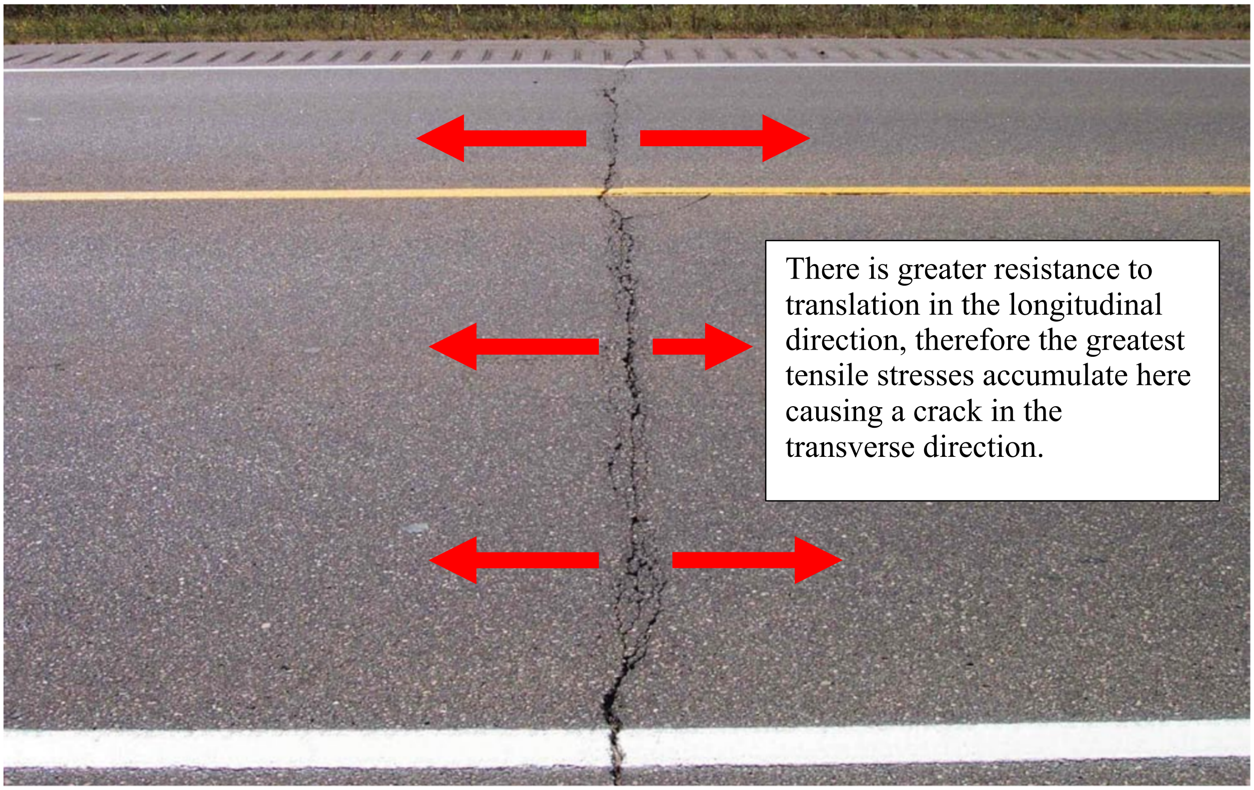
There is greater resistance to translation in the longitudinal direction, therefore the greatest tensile stresses accumulate here causing a crack in the transverse direction.

Figure 1: A transverse crack spanning the width of the highway [2].

To combat this issue with cracking, agencies are now recommending even lower performance grades (PG) in the northern, cooler parts of the United States, as low at -34ºC (-29.2ºF). To achieve these low PG grades, waste and byproduct oil modifiers such as bio-oil and re-recycled engine oil bottoms (REOB) have been blended with asphalts to create a product that is much more pliable and stress relaxing at lower temperatures. These oils are frequently combined with polymers as well to maintain or increase the stiffness and ability to recover from deformation.

1.2: Asphalt Chemistry and Aging Mechanisms

Asphalt's chemistry cannot be precisely defined as it is an organic material that is a byproduct of crude oil via a refining process known as fractional distillation. Because the nature of the material is dependent on source and refining technique, it is highly variable in its chemistry, but is made up of four primary constituents: saturates, aromatics, resins, and asphaltenes (**Figure 2**). Asphalt has often been described as a colloidal dispersion of asphaltenes into an oily matrix made up of the saturates, aromatics, and resins. The asphaltenes are stabilized in crude oils by natural resins that are act as surfactant agents. Asphaltenes and resins are responsible for the viscoelastic (time and loading dependent) properties of the asphalt at ambient temperatures [3].

Figure 2: The primary constituents of asphalt including: Saturates, Aromatics, Asphaltene, Resin, and Maltene.

The aging of asphalt can cause issues for pavements, especially for low-temperature performance of asphalts because of increased stiffness by embrittlement and reduced ability to relax stresses. This primary cause of aging is the oxidation of the asphalt and the rate at which this occurs is dependent on the composition of the asphalt and ambient temperature. When the asphalt oxidizes, the concentration of the polar functional groups increases, resulting in immobilization of molecules through intermolecular association [3], [4]. The increased molecular mass results in a loss of mobility to flow past one another, and therefore causes the embrittlement and inability to relax via molecular flow. Because, the various asphalt fractions have different reactivities towards oxidation, differences in concentration of the fractions will vary based on the age of the materials. In particular, during oxidative aging, a reduction in aromatics is observed while the resins and asphaltenes concentrations increase [5]. This is because oxidation causes the oils (maltene fraction – naphthene aromatic and saturates) to convert to resins, and the resins to convert to asphaltenes. As the ratio of asphaltene to maltene increases because of oxidation, the stiffness of the asphalt will increase [3], [6]. Ultimately, there are many mechanisms that cause asphalt age-related hardening including oxidation, loss of volatile fractions, changes in chemical structure such as polymerization, ultraviolet light, and heat [7].

1.3: Problem Statement

Asphalt and the materials used to modify it (oils or polymers) are made up of organic compounds which have varying potentials to oxidize. Previous work has shown that polymer modified asphalt blends have varying aging susceptibility depending on the concentration and type of oil and polymer modifiers used [8]. The usage of oils and polymers is therefore expected to change the aging susceptibility of asphalt blends. Currently, it is not known how to predict the change in aging susceptibility after modification and if the aging susceptibility of the oil modifiers themselves plays a major role in performance of the modified blends.

1.4: Hypothesis

The hypothesis of this study is that the aging susceptibility of the selected oils will play a major role in the aging susceptibility of the asphalt blends containing them.

1.5: Study Objectives

The study is focused on the following objectives:

1. Determine formulations to modify binder grades from PG 58-28 to achieve PG 58-34 using several commonly used oils and polymer additives.
2. Test the aging susceptibility of the oils used in modifying asphalt properties for low temperature cracking and compare oil aging with the aging of the blends containing the oils.
3. Determine if the various rheological properties used to measure performance-related properties can relate oils' aging with the blends aging and attempt to define a model.

1.6: Work Plan

Given the study objectives the following work plan was developed. There are two components to this study, oil testing, shown in **Table 1**, and blend testing, shown in **Table 2**.

Table 1: Oil testing work plan, including control variables and responses.

Control Variables		**Test**	**Response**
Oil	Bio-Oil (ANOVA-1055) REOB	Frequency Sweep	Complex Shear Modulus (G*) Phase Angle (°)
Aging Conditions	Unaged 8-Hour PAV 16-Hour PAV 24-Hour PAV		

Table 2: Blend testing work plan, including control variables and responses.

Control Variables		**Test**	**Response**
Asphalt PG	58-34	Frequency Sweep Elastic Recovery - DSR Bending Beam Rheometer Bitumen Bond Strength	Complex Shear Modulus (G*) Phase Angle (°) %Recovery Maximum Internal Shear Stress ΔTc Adhesion and Moisture Damage
Oil Type	Bio-Oil (ANOVA-1055) REOB		
Polymer Combinations	SBS Elvaloy + PPA PPA		
Aging Levels	Unaged 20-Hour PAV 40-Hour PAV 60-Hour PAV		

Chapter 2: Literature Review

In order to understand the state of the art in this topic and document what other researchers have reported, a detailed literature review was conducted. This chapter includes the summary of findings for five major studies conducted on this topic.

2.1: Differentiation of Bitumen According to the Refinery and Aging State Based on FTIR Spectroscopy and Multivariate Analysis Methods [9]

The objectives of this paper were to develop models for the characterization of bitumen based on the Fourier Transform Infrared Spectroscopy (FTIR) and a chemometrical evaluation of the spectral differences obtained using the FTIR. This information was used to accomplish two goals, create models to differentiate refinery sources of asphalts, and create additional models to differentiate between the age or oxidative state of the asphalts. The data also demonstrated that different relevant peaks within the spectra among the samples could identify whether the samples were aged or just from different refineries with reasonably high certainty.

The experiment involved the analysis of 36 paving grade bitumen samples of the grades 20/30, 30/45, 50/70, and 70/100 per EN 12591. Each of the samples are sourced from 10 different asphalt refineries in Germany, which were obfuscated for this experiment. The 36 different samples were aged in up to four different levels of aging. These levels of aging include: unaged, Rolling Thin Film Oven (RTFO) and Rotating Flask Test (RFT per EN 12607-3), and Pressure Aging Vessel (PAV) aged (per EN 14769). Some samples were RTFO/RFT aged two and three times to simulated intermediate and long-term aging. The final list of materials included samples that then were RTFO/PAV aged as well as RFT/PAV aged.

Samples for the FT-IR were prepared by dissolving the bitumen sample in cyclohexane at a mass ratio of 1:3. Once the samples were prepared, they were tested using a Perkin Elmer Spectrum Two FT-IR C96108 using attenuated total reflectance with multiple reflections using a Zinc Selenide crystal. The samples were pipetted onto the crystal and the cyclohexane solvent was allowed to dissolve for at least 15 minutes leaving a thin bituminous film on the crystal. This method allows for reduced noise in the measurements by reducing tiny air pockets between the sample and the crystal which would be detected and interfere with the reflections. Each sample was measured 3 times using 32 scans over a wave number range from 4,000 to 600 cm^{-1} with a resolution of 4 cm^{-1}. The obtained reflectance spectra were converted to absorbance spectra and irrelevant wave number ranges without any peaks were excluded from the analysis. From this, the relevant wave number ranges emerged – between 3,600 and 2,500 cm^{-1} and between 1,800 and 690 cm^{-1}. The data was then processed using Standard Normal Variate Transformation, determination of the first derivatives, Multivariate Analytical Methods, Factor Analysis, and Linear Discriminant Analysis.

This experiment produced the following conclusions regarding the two primary goals of differentiating asphalts based on refinery and aging state. First, bitumen can generally be differentiated on the basis of the refinery source using FT-IR produced spectra. The primary spectral peak used to differentiate the asphalt source were the aliphatic hydrocarbons with the symmetrical and asymmetrical stretching and bending vibrations of the methyl (CH_3) and the methylene (CH_2) groups found in the wave number ranges of 1,485 to 1,400 cm^{-1} and 1,400 to 1,357 cm^{-1}. For the carbonyl and sulfoxide compounds, differences between the samples from different refineries could be recognized but were not as pronounced as those produced by the aliphatic structures.

Secondly, bitumen can again be differentiated on the basis of the degree of aging. As the asphalt ages in the RTFO/RFT and PAV procedure the contents of the oxygen containing compounds increase as expected. This manifests in three primary spectral peaks correlated to the concentrations of carbonyl, sulfoxide, and hydroxy compounds found in the wave number ranges 1,730 to 1,670 cm^{-1}, 1,070 to 983 cm^{-1}, and 3,400 to 3,120 cm^{-1}, respectively. The aliphatic hydrocarbons are significant for the differentiation of unaged and short-term aged states. This emphasizes concerns about overlap between the structural differences of the bitumen at relatively short-term aged asphalts and asphalts from the different refineries (which also is based on the aliphatic structure). It is worth noting, however, age related changes of the aliphatic compounds were not consistent between refineries and therefore varies. Additionally, age related changes could be observed between the spectra recognized for aromatics and alkene compounds with a wave number at 960 cm^{-1}. It was observed that as the aromatics increase during aging, the alkene peak decreases.

This study verifies the legitimacy of investigating the changes in the primary oxygen containing compounds known as Hydroxy, Carbonyl, and Sulfoxide. These compounds have been shown to definitively predict the aging states of the asphalts relative to the respective refinery source. The relative rates of change between the concentrations of the oxidizing constituent components can be used to determine the aging susceptibility of the asphalts and perhaps the oils used in this thesis as well. The aging susceptibility of the asphalt and oil blends will be compared to their physical performance to determine the effects of aging on the various performance metrics.

2.2: Effects of Physio-Chemical Factors on Asphalt Aging Behavior [7]

The objectives of this paper were to evaluate the physical and chemical properties of asphalt at different aging times and temperatures. The properties of the asphalt binder were evaluated to determine the contents of saturates, aromatics, resins, asphaltenes, and determine the penetration, softening point, and molecular distribution of the asphalt. Gel Permeation Chromatography (GPC), Fourier Transform Infrared Spectroscopy (FTIR), Asphalt Constituents Fraction Analysis, and rheological tests were used to analyze the effects of asphalt from different crude oil sources on antiaging performance.

In general, there are two major pathways for oxidative aging, the conversion of aliphatic sulfide to sulfoxide (wave number 1,030 cm^{-1}), and benzylic carbon to carbonyl (wave number 1,700 cm^{-1}). Asphalt is a complex mixture of high molecular weight hydrocarbon molecules which contain the heteroatom nitrogen, sulfur, and trace metals such as vanadium and nickel. Due to this complex nature and mixture, the oxidation reaction of the asphalt is also very complicated and varies from source to source. Fractionation (ASTM D 4124-09) was used to separate asphalt into four primary fractions, asphaltene, saturates, aromatics, and resins to find trends in the change of proportions of these fractions among the various aging levels.

The experiment used three different asphalt crude sources from China aged at standard RTFO (AASHTO T240-08) and PAV (AASHTO R28-02) conditions to perform GPC (using a Waters 515 GPLC pump equipped with a Waters 410 differential refractometer), Fractionation, and FTIR (using a Nicolet 60 instrument).

The following conclusions were made for this experiment. First, at the various asphalt aging levels, the saturate contents remained relatively the steady while the contents of the aromatics and resins decreased. The aromatics and resins readily react with oxygen to produce asphaltenes, and hence its subsequent increase in content with aging. The changes in the chemical composition manifest in the degradation of the physical properties such as decreasing penetration and ductility while increasing the softening point. The molecular weight of the asphalt also increases as the dispersity decreases.

Secondly, the asphalt-aging reaction can be described by a first-order kinetics equation. Asphalts with large activation energies and low reaction rate coefficients have superior resistance to aging.

Finally, the aging mechanisms are again verified to be described by the two major pathways of the production of sulfoxide from aliphatic sulfide and carbonyl from benzylic carbon. Aging resistance can be ranked on the basis of wax content, fractional contents, and molecular weight while being in good agreement with rheological properties observed during aging.

This study again verifies the legitimacy of using FTIR to measure the contents of the oxygen containing products of sulfoxide and carbonyl. The contents of these constituents have been highly correlated to the oxidative aging of the asphalt in many studies beyond this one as well. This study, however, measured other properties such as the wax contents, and molecular weight as alternative measures of aging. These age-related metrics were then verified against the physical properties such as the complex modulus and phase angles in the same fashion that this thesis will use. This thesis, however, will expand on several of these experiments such as FTIR and physical performance using oil modified asphalts of which the oils may be able to alter the effects of aging on the asphalt blends.

2.3: Effect of Polymer and Oil Modification on the Aging Susceptibility of Asphalt Binders [8]

The objective of this study was to investigate the effects of bio-oil, re-refined wasted engine oil, and polymers and their interactions with each other on the aging susceptibility of asphalt binders. It investigates the rheological and chemical changes during lab simulated oxidative aging using several oils and polymers. After samples were aged, they were tested in a dynamic shear rheometer (DSR), and Bending Beam Rheometer (BBR) for rheological evaluation. Gel permeation chromatography and Fourier Transform Infrared Spectroscopy were used to compare the rheological responses to as to relate the chemistry to the stress related response observations. Results indicate that the aging susceptibility of modified asphalt binders is dependent on chemistry of the modifiers used. It was also found that certain combinations of polymers and oils yielded reduced aging susceptibility.

This study uses only one base binder a Flint Hills refinery produced PG 64-22. Polymers and elastomers included SBS (styrene-butadiene-styrene) and polyethylene, while bio-oil and re-refined waste engine oil (RWEO) were used as the oil modifiers. The combinations included the base binder, the base binder with only polymers, the base binder with only oils, the base binder with each polymer and each oil, and combinations with both polymers and each oil. The blends were aged using the Rolling Thin Film Oven procedure (AASHTO T 240) and Pressure Aging Vessel procedure (AASHTO R 28) at 20- and 40-hour aging levels.

The results of this experiment on the various metrics are as follows. First, adding only polymers to the base binder the G^* (complex modulus) aging index was lower than the aging index of the unmodified base binder. These differences in the aging index were the highest when tested at high temperature. The blend containing both polymers demonstrated the lowest aging index for this test. The author concluded these results show that polymers can have a significant impact on the aging susceptibility of the blend.

GPC was used to verify these results at the chemical level. When comparing the 40-hour aged, unmodified binder to the unaged, unmodified binder, the asphaltene peak increased significantly in size and shifted to an earlier elusion time. This can be caused by the production of more asphaltene from naphthene and polar aromatics, an increase in the size of the asphaltene structures as a result of increasing asphaltene interactions after aging, or from both of these causes simultaneously. As such, an increase was observed in these large molecules after aging. However, when polymers were added to the blends, a decrease in the amount of large molecular asphalt constituent sizes was observed. It is theorized that this suggests that's the polymers have the ability to reduce the amount of the aging the asphalt experiences. This finding is in agreement with the rheological responses observed in the aging index.

Secondly, the addition of both oils causes a decrease in the overserved stiffness of the polymer modified binders before and after aging. GPC analysis of these oil and polymer modified blends reveals that the molecular size distribution is not significantly affected before and after aging. These results are thought to indicate that the addition of the bio-oil and RWEO do not affect the aging susceptibility of the base binder. It was found that blends containing the polymers and the RWEO showed the least aging susceptibility compared to the unmodified base binder. The rheological responses at intermediate temperatures agree with the rankings of the creep-stiffness aging indices. At high temperatures lower aging indices were observed for all polymer modified binders. As for the binders with polymers and oils, the results varied.

Further GPC analysis of the polymer/elastomer and oil modified blends shows that the presence of polymers and RWEO decreased the change in the average molecular weight of the blends after 40 hours of PAV aging. Additionally, PAV aging significantly increased the carbonyl content for all of the blends, where it increased most drastically in the unmodified base binder even when compared to the polymer-only modified blends. An explanation proposed by the author suggests this might be caused by the microstructural interactions between the asphalt and polymer decreasing the exposure of the asphalt components to oxygen. It was also observed that the effect of aging on polymer-only modification is greater than on oil-only modified blends. The carbonyl area aging index indicated that the effect of oil modification can only be observed when oils are blended with a polymer for this specific base binder. Modified blends showed higher aging susceptibility when using the carbonyl area aging index. The results for the bio-oil blends were in agreement with rheological responses and molecular size distribution. Positive effects were noted for blends containing the RWEO in DSR, BBR, and GPC results. These results indicate that intramicellar association between the asphalt binder and the modifiers is a major contributing factor to aging susceptibility and oxidative embrittlement. Also, as carbonyl groups increase as products of oxidation during aging, the asphalt and additives compatibility decreases.

Finally, it is noted that sulfoxide production has been used as a measure of asphalt aging. However, from this study it was found that some blends oxidized rapidly to form sulfoxide, but the oxidation continued even after the sulfoxide production stopped due to the exhaustion of the aliphatic sulfide. At this stage, carbonyl begins to form more rapidly. This is because sulfide sulfur acts as an internal oxidation-reduction inhibitor to limit the formation of the carbonyl from a peroxy intermediate. Once the sulfur source is exhausted, the carbonyl formation can continue unhindered. It is also mentioned that the paper did not include sulfur quantification for the blends so the quantification of sulfoxide using FTIR cannot explain (by the means of the growth of sulfoxide) to the overall aging of the binders.

This paper is foundational to this thesis as many of the same experimental methods will be used to quantify the oxidation of the oil and polymer modified asphalts in this thesis. It also serves to offer comparative techniques to analyze the data with. It also suggests that the primary metric used to determine the oxidation status of the blends should be the carbonyl area aging index. The main difference between this thesis and this paper is the additional testing of the oils themselves, both rheologically and by FTIR analysis. The oxidation of and response of the oils will be measured and used to further understand the rheological responses observed in the long-term aging susceptibility of oil and polymer modified asphalt blends.

2.4: Effect of Extended Aging on Asphalt Materials Containing Re-Refined Engine Oil Bottoms [10]

The objectives of this study were to investigate the binder and mixture performance of REOB modified blends at varying concentrations up to 15%. The main goals to accomplish this objective involved evaluating the effectiveness of extended high-temperature oven aging (EHTOA) of various REOB-modified mixtures and binders, and to investigate the physical hardening potential of REOB-modified binders after EHTOA.

In order to do this, four asphalt binders containing concentrations of REOB at 0%, 2.5%, 6%, and 15% were prepared. Chemical variety and respective properties were kept within comparable limits by using the same base binder, a PG 58-28 in the 3 blends containing REOB. Blending was done using two different methods. The first approach was used to create the 2.5% REOB blend by direct dilution from the original base binder. The blend containing 15% REOB was made by adding 20% by mass of a PG 100+ material and then diluting the blend with 15% REOB. The blend containing 6% REOB was done using a similar method, except a 64-22 was diluted with REOB to soften it to a PG 58-28. At this point the authors suggest that extended long-term pressure aging vessel (PAV) aging has been criticized as being “disconnected” from field service aging dynamics. To address this claim, laboratory mixture aging was instead used to investigate the effects of aging of REOB-modified asphalt in the presence of aggregates and RAP. The experiment was limited to a single mix design, aggregate type, and RAP source – used in a concentration of 22% (by asphalt binder replacement). The mixtures were designed to meet the following properties:

- Voids in mineral aggregate (VMA): 14.5%
- Design Air Voids: 3.8%
- Asphalt content by weight of mixture: 4.5%
- Maximum theoretical specific gravity (Gmm): 2.754

- Voids filled with asphalt (VFA): 73.8%
- Performance specimen air voids: 6.5% to 7.5%
- Virgin aggregate type: Diabase

Mixtures were then short-term oven aged, long-term oven aged, and extended high-temperature oven aged while still loose mixtures. After aging, binders were extracted and recovered using trichloroethylene. The recovered binders were tested in the bending beam rheometer (BBR) (AASHTO T 313) and extended BBR testing, as well as intermediate temperature performance testing using the double-edge notched tension (DENT) test (AASHTO TP 113). The DENT test approximates the ductile strain tolerance in the form of crack-tip opening displacement, an indicator of fatigue performance. The mixture tests included asphalt mixture performance testing (AMPT) (AASHTO TP 79) and fatigue testing using the AMPT cyclic fatigue test (AASHTO TP 107). Low temperature properties of the mixtures were obtained using the thermal stress restrained specimen test (TSRST) (AASHTO TP 10).

The results showed that for the high temperature PG (HTPG) of the extracted binders the HTPG increased by more than 1 PG grade as aging increased from STOA to LTOA, and then from LTOA to EHTOA. The 2.5% REOB binder after STOA and LOTA showed a slightly lower HTPG than the blend containing 0% REOB. This was the case until EHTOA. The HTPG results are shown below in **Table 3**. The results of the low-temperature testing are shown in **Table 4** where the addition of REOB sometimes improved the low-temperature PG (LTPG) versus the control blend, but almost always yielded worse ΔTc performance (more negative).

Table 3: Summary of HTPG for extracted and recovered REOB-modified asphalt from three oven-aging levels

Binder	Material 0% REOB	 2.5% REOB	 6% REOB	 15% REOB
STOA HTPG (°C)	75.3	72.7	74.4	76.1
LTOA HTPG (°C)	82.0	79.5	80.4	82.5
EHTOA HTPG (°C)	91.4	95.3	98.2	98.4

NOTE: REOB percentages are slightly lower because of the presence of 22% RAP binder in the recovered materials.

Table 4: Summary of low-temperature testing results for extracted and recovered REOB-modified asphalt from three oven-aging levels

Binder	Parameter	Material 0% REOB	 2.5% REOB	 6% REOB	 15% REOB
STOA	BBR LTPG	−25.2	−28.4	−23.8	−24.0
	BBR ΔT_c	−2.5	−2.7	−5.4	−8.2
	Extended BBR LTPG	−23.9	−26.7	−23.9	−19.0
	Extended BBR ΔT_c	−3.3	−2.2	−4.2	−11.8
LTOA	BBR LTPG	−28.4	−28.3	−24.9	−24.9
	BBR ΔT_c	−1.4	−2.5	−3.3	−8.2
	Extended BBR LTPG	−23.6	−25.9	−22.5	−20.3
	Extended BBR ΔT_c	−3.3	−2.5	−5.8	−11.5
EHTOA	BBR LTPG	−25.1	−21.2	−13.7	−15.6
	BBR ΔT_c	−3.1	−6.8	−12.6	−15.9
	Extended BBR LTPG	−20.2	−13.7	−8.7	1.7
	Extended BBR ΔT_c	−5.6	−15.5	−17.6	−28.3

NOTE: Temperatures are in degrees Celsius. REOB percentages are slightly lower because of the presence of 22% RAP binder in the recovered materials.

DENT results indicated that when mixtures were modified with more than 2.5% REOB, the strain tolerance for the mixtures decreased at all aging levels. Furthermore, the strain tolerance for EHTOA mixtures decreased by as much as 30% as the concentration of REOB in the mixtures increased. The authors suggest this finding indicates accelerated deterioration of the mixtures with aging and increased concentrations of REOB.

The results of the dynamic modulus and phase angle, as expected, increased the dynamic modulus and decreased the phase angle as aging increased. Using an evaluation space that related the width of the relaxation spectra (γ) with the inflection point frequency (-β/γ) for mixtures. The inflection point frequency corresponds to the maximum phase angle and is expected to decrease with increasing age, whereas an increase in the width of the relaxation spectra corresponds to a flattening of the master curve (which indicates longer times are required to relax stresses). The results met expectations and demonstrated that with increasing age γ became larger, and -β/γ decreased. The 0% control blend underwent flattening of the master curve as well, but with relatively smaller changes in the -β/γ parameter compared to the blends containing REOB. The blends containing 2.5% and 6% REOB caught up to the 0% blend in terms of flattening after increasing aging, suggesting that REOB accelerates the oxidation process. The worsening behavior was observed to a much higher degree in the blend containing 15% REOB after LTOA. AMPT cyclic fatigue testing showed that as aging levels increased for the mixtures, the programmed microstrain decreased, but the cycles to failure at the programmed microstrain decreased. In other words, as aging of the REOB blends increased, the strain required to fail decreased and occurred at a number of cycles to failure similar to that of the lesser aged material.

The TSRST fracture temperature showed no consistent change with different amounts of REOB at STOA and LTOA aging levels. Fracture temperatures became warmer with increased aging for the mixtures but were not sensitive to the amount of REOB in the mixture. However, at EHTOA, the cracking temperature of the mixtures with 6% REOB and 15% REOB were increased more than the 0% mixture. The author suggests that this aging procedure may be useful for detecting mixtures with higher concentrations of REOB. The thermal stresses tended to decrease with REOB-modified mixtures. STOA mixtures showed no significant differences in fracture stresses, while at LTOA, mixtures containing 2.5% and 6% REOB increased the fracture stress relative to the control mixture, while the 15% mixture decreased the fracture stress. Finally, at EHTOA, all REOB mixtures showed a decrease in fracture energy relative to the control where the mixture containing 15% REOB showed a substantial decrease in fracture energy.

In conclusion, it appears that the addition of REOB is detrimental to asphalt binder performance with increasing age. It was shown that ΔTc dramatically decreases with increasing REOB concentration and age. This has been correlated to worsening low-temperature performance by various other studies. Dynamic modulus and phase angle testing showed again that as REOB concentration and age increased, mixtures showed greater rates of change in mechanical response indicating increased relative aging susceptibility to the control mixture. Fatigue resistance decreased with age as expected via the AMPT cyclic fatigue test, fracture temperature and stress tests demonstrated that the addition of REOB was detrimental to mixture strength especially as temperature increased. ΔTc has shown up in several studies now to be an effective indicator of low-temperature performance especially for mixtures containing REOB. The results of the study are directly applicable to the mixture testing component of this thesis using the semi-circular bend (SCB) test. REOB mixtures will be expected to perform worse with increasing age. This thesis will attempt to further investigate the oils by testing them alone at various aging levels. This will help verify whether the aging susceptibility of the oils has an effect on the rheological and mechanical performance of oil-modified mixtures.

2.5: Investigation of the Effect of Oil Modification on Critical Characteristics of Asphalt Binders [11]

The work in this document regarding oil modification of asphalt is extensive, therefore this review is not exhaustive of the work, but rather will extract relevant aspects to this thesis. The goal of this study was to investigate the effects of oil modification on the rheological properties of asphalt binder. Low temperature and high temperature properties were examined. Ultimately, it was found that oils vary in their effects of the rheological performance of asphalt. It was observed that for all oils that were used in the study, the low-temperature performance was improved but could be attributed to a softening effect from the addition of the oil. The effects of oil on thermally induced stresses and strains was also investigated. It was again found that oil modification has potential to improve cracking resistance of asphalt during thermal cycles.

In this study two base asphalts were selected from two different sources, a Flint Hills PG 64-22 with a relatively high asphaltene content, and a Valaro PG 64-22 with a relatively low asphaltene content. The binders were modified with several different oils including a petroleum aromatic (PA), three different paraffinic petroleum oils, three different bio-oils, and two different refined waste oils. Two of the three bio-oils are plant derived liquids, and one of the refined waste oils is from a motor oil, while the other refined waste oil is from waste cooking oil. The oils were blended with the neat asphalt binders at dosages selected to decrease the PG by one grade, so the high-temperature PG was within 58°C + 1°C. Several tests were performed including the determination of the high, intermediate, and low PG, the glass transition temperature (Tg), the multiple stress creep and recovery test (MSCR), frequency sweep testing, linear amplitude sweep testing (LAS), single edge notched beam testing (SENB), and bitumen bond strength (BBS) testing.

The findings concluded that for oil-modified asphalt binders, the addition of the oils significantly changes the rheological responses at different temperatures and frequencies. The oils all reduced the stiffness of the asphalt which subsequently negatively impacts the high temperature PG as well as improve the low-temperature performance. The rutting parameters |G*|/sinδ (complex shear modulus divided by the sine of the phase angle) and Jnr (the non-recoverable creep compliance) showed worsening performance with the addition of the oils. Additionally, analysis of relaxation modulus curves indicated that oil modification caused very little deviation from the base binder master curve at high and intermediate temperatures and loading times. The glassy modulus, on the other hand, was significantly lower when compared to the base asphalt at all aging levels. The author suggests this indicates that at the dosages of oil used in the study, oil modification can improve low temperature properties with a relatively unequitable decrease on the high temperature properties. In other words, the benefit to the low temperature performance is greater than the related performance loss at high temperature.

The low temperature performance was characterized by the glass transition temperature and the creep and relaxation properties as measured by the BBR. The BBR results showed that adding oil reduced the modulus observed at low temperature. This is because the oil introduced a relatively softer fraction to the asphalt structure, hence the detrimental effects to the high temperature PG. The oil also decreased the glass transition temperature and increased the m-value (the rate of stress relaxation) due to the oil's lower molecular weight and higher free volume relative to the asphalt. These properties increase the molecular mobility of the asphalt and oil blend manifesting in increased temperature sensitivity and time dependency. SENB failure stress and strain testing results demonstrated that some of the oils can improve cracking resistance at low temperatures.

The SENB results also revealed a linear relationship between oil content and log stiffness. This linear relationship can be extended to the m-value and phase angle.

The author also suggests that oil modification affected the aging susceptibility of the asphalt binder, where the effects and their magnitudes were dependent on the type of oil used. The differences in aging susceptibility were attributed to the composition of the oil which in turn interacted with different compounds within the base asphalt. Age-related hardening increased in bio-oil modified asphalts while a decrease in the age-related hardening was observed for the refined waste oil modified asphalts.

Fatigue and moisture damage showed some oils were beneficial for improving cracking and moisture sensitivity while others showed no benefit or deteriorated the properties. The conditioning of samples in water did not cause a significant reduction in the pull-off strength, and in most cases the strength remained almost constant when accounting for variability between samples. In the case with one of the bio-oils and both refined waste oils, the wet pull-off strength was about 0.5 MPa on average greater than the dry pull-off strength. However, in all cases the pull-off strength for oil-modified asphalts were nearly half that of the unmodified asphalt binder. The author attributed this loss in adhesion to the lower stiffness of the oil-modified blends, and that the stiffness and viscosity of the blends plays a role in the propensity of the asphalt blend to strip from the aggregate. The author also sites two studies (by Kantipong and Bahia, and Bahia et al.) which found that asphalts with high stiffness and viscosity better resist displacement by moisture relatively to those with low stiffness and viscosity. This is cited to be the case because stiff asphalts typically contain chemical compositions that include higher concentrations of polar functional groups which can provide resistance to stripping. Furthermore, all dry and all but one wet BBS test exhibited cohesive failure (failure within the binder itself, rather than cleanly separating from either the aggregate or metal pull-off stub).

While this study did not include polymers as a modifier in the oil-modified asphalt blends, its findings are still useful to segregate the resultant effects contributed by the oils from those contributed by the polymers used in this (my) thesis. This study also mentions varying aging susceptibility as a result of the various oil modifiers. This means that both polymers (as mentioned in a previous literature review by Li et al [8] and oils contribute to the aging susceptibility of the base asphalt, and therefore resultant rheological and mechanical performance. Finally, this work also quantifies the effects of oil modification on the pull-off tensile strength (adhesion/cohesion) in both wet and dry conditions, concluding that the oil-modification is detrimental to pull-off strength and typically has a higher pull-off strength when tested in the wet condition for some oils. These conclusions will be further tested in my thesis by testing many of these properties in asphalts modified by both polymers and oils and the related aging susceptibility of these modifiers on the rheological and mechanical performance.

2.6: Summary of Findings from Literature Review

The review of the studies listed in this chpater leads to the follwing findings:

1. Asphalts can be differentiated using FT-IR spectra and on the basis of the degree of aging. The primary spectral peak used to determine the degree of aging are the aliphatic hydrocarbon groups found in the wave number ranges of 1,485 to 1,400 cm^{-1} and 1,400 to 1,357 cm^{-1}. The carbonyl and sulfoxide compounds, however, showed differences between the samples from different sources, but were not as pronounced as those produced by the aliphatic structures. As the asphalt ages in the lab or the in the field the contents of the oxygen containing compounds increases. This manifests in three primary spectral peaks correlated to the concentrations of carbonyl, sulfoxide, and hydroxy compounds found in the wave number ranges 1,730 to 1,670 cm^{-1}, 1,070 to 983 cm^{-1}, and 3,400 to 3,120 cm^{-1}, respectively. In addition, age related changes could be observed between the spectra recognized for aromatics and alkene compounds with a wave number at 960 cm^{-1}. It was also observed that as the aromatics increased during aging, the alkene peak correspondingly decreased. [7], [9]

2. Asphalt Constituents Fraction Analysis, and rheological tests can be used to analyze the aging performance of asphalt from different crude oil sources. At the various asphalt aging levels, the saturate contents remained relatively steady while the contents of the aromatics and resins decreased. The changes in the chemical composition manifest in the degradation of the physical properties such as decreasing penetration and ductility while increasing the softening point. The molecular weight of the asphalt also increases as the dispersity decreases.

   Asphalt oxidation reactions can be described by a first-order kinetics equation. Asphalts with large activation energies and low reaction rate coefficients have superior resistance to aging. The aging mechanisms are described by the two major pathways of the production of sulfoxide from aliphatic sulfide and carbonyl from benzylic carbon. Aging resistance can be ranked on the basis of wax content, fractional contents, and molecular weight while being in good agreement with rheological properties observed during aging. [7]

Adding polymers to asphalt binders can change the aging rates as measured by the G^* (complex shear modulus) aging index. These differences in the aging index between binders with and without polymers are the highest when measured at high temperatures. The addition of both oils and polymers can cause a decrease in the overserved stiffness of the polymer modified binders before and after aging. GPC analysis of oil and polymer modified blends reveals that the molecular size distribution is not significantly affected by adding these additives neither before nor after aging. The effect of aging on polymer-only modification is different than on oil-only modified blends. Sulfoxide production can be used as a measure of asphalt aging. However, some studies show that some blends oxidized rapidly to form sulfoxide, but the oxidation continued even after the sulfoxide production stopped due to the exhaustion of the aliphatic sulfide. At this stage, carbonyl begins to form more rapidly. This is because sulfide sulfur acts as an internal oxidation-reduction inhibitor to limit the formation of the carbonyl from a peroxy intermediate. Once the sulfur source is exhausted, the carbonyl formation can continue unhindered. [8]

3. Adding oils reduces the stiffness modulus measured at low temperatures. This is because the oil introduced a relatively softer fraction to the asphalt structure, hence the detrimental effects to the high temperature performance grade. Oils can also decrease the glass transition temperature and increase the m-value (the rate of stress relaxation) due to the oil’s lower molecular weight and higher free volume relative to the asphalt. It appears that oils can

increase the molecular mobility of the asphalt and oil blend manifesting in increased temperature sensitivity and time dependency. Differences in aging susceptibility of the low temperature properties are attributed to the composition of the oil which in turn interacted with different compounds within the base asphalt. Age-related hardening increased in bio-oil modified asphalts while a decrease in the age-related hardening was observed for the refined waste oil modified asphalts. [11]

4. The findings from the literature review indicate that the cumulative effect of oils and polymers blended with asphalt is not well understood, and the cause of observed differences in aging due to the use of various oils is a complex phenomenon that requires further research. The findings also show that measuring the aging index as determined from ratio of various rheological properties is a good approach to study this complex phenomenon and for determining its impact on the performance of modified asphalt binders.

The next chapters of this thesis include detailed descriptions of the objectives for the study and work plan. They also include the analysis of the results collected and the findings of this study.

Chapter 3: Objectives, Materials, and Testing Methods

This chapter covers the details of the different phases of this study and explains the testing methods used.

3.1: Objectives and Phasing

In order to fully capture the effects of oil additives on asphalt binders several phases of testing are required to measure the effects on the rheology and aging susceptibility.

Phase 1 – Objectives and Methods:

- Determine the aging/oxidation susceptibility of the oils themselves by measuring the rheological response of the viscous and elastic components.

The first phase of testing will measure and quantify the aging susceptibility of the oil modifiers via physical analysis. The physical analysis will involve the measurement of the complex shear modulus and phase angle of two primary oil additives at the aforementioned aging levels. These parameters are known to be sensitive in the detection of aging. The oils are tested in a dynamic shear rheometer (DSR) at 0°C using 25mm parallel plate geometry with a 250µm gap. The oscillatory shear strain responses will give an indication of the aging susceptibility.

Phase 2 – Objectives and Methods:

- Measure changes in rheological response of the viscous and elastic components due to aging to determine the susceptibility of the blends to aging/oxidation.
- Because oils may affect the adhesiveness of the asphalt and oil blend, the BBS test will be used to determine the effects on adhesion and moisture susceptibility of the blends, a primary point of failure in oil modified binders.

The second phase of testing will further examine aging susceptibility by mixing the various oils and several common polymers with a base asphalt binder. Again, there will be a physical analysis. The objective of this phase of the study is to quantify the rheological effects of the blends by measuring complex modulus, phase angle, elastic recovery, stiffness and m-value, and adhesion. This testing will help identify trends in aging susceptibility which may change based on aging duration.

3.2: Performance Metrics of Pavements

Enhanced performance of these modified asphalts manifests in several measured properties some of which that are highly correlated to real world performance. These metrics of performance are standardized by the American Society for Testing and Materials (ASTM) and the American Association of State Highway and Transportation Officials (AASHTO) and typically include the following metrics:

High Temperature Performance Grade (Complex Shear Modulus and Phase Angle) (AASHTO T 315) – The high temperature PG is defined as the minimum temperature between the temperature in which the unaged binder’s |G*|/sinδ is equal to 1 kPa at 12% strain and the temperature in which the rolling thin film oven (RTFO) aged binder’s |G*|/sinδ is equal to 2.2 kPa at 10% strain in a Dynamic Shear Rheometer (DSR) [12]. G^* is known as the complex shear modulus which relates complex shear stress and complex shear strain, where the complex shear stress is applied as an oscillation in time at a particular amplitude and angular frequency. In response to the applied stress there will be a resultant complex shear strain which will also oscillate at an angular frequency that lags the applied stress by a phase angle, δ. The complex shear modulus is determined by the relationship between the storage modulus, G', and the loss modulus, G'' which characterizes the amount of energy stored in a strained medium and lost due to damping, respectively. The ratio of the loss modulus to the storage modulus is known as the loss factor and is used to quantify the ability to damp energy. This relationships between complex shear modulus, storage modulus, loss modulus, and phase angle are shown in the following equations:

$$G^* = G' + iG''$$

$$i = \sqrt{-1}$$

$$Loss\ Factor = \frac{G''}{G'} = \tan\delta$$

Elastic Recovery (AASHTO TP 123 Method B) – This test measures the amount of strain recovered at a fixed strain. There are two versions of this test, including the Binder Yield Energy Test (BYET) and the DSR-Elastic Recovery (DSR-ER) test. The yield energy can be used to identify the relative performance of different materials in terms of resistance to fatigue or extreme loading damage.

The DSR-ER test serves as an alternative to the ductility test (AASHTO T 51) and elastic recovery test (ASTM D6084). It should be noted that the relationship between ductility and elastic recovery to pavement performance is not known and there is no clear evidence that having higher ductility or higher elastic recovery improves pavement performance [13]. This test can, however, can detect relative aging and oxidation presenting in the form of increased maximum stress exerted by the DSR to achieve the test defined required strain of 277.78% at a strain rate of 2.315%/s. This response is of use if strain is the failure criteria of interest.

Low Temperature Performance Grade (AASHTO T 313) – The low temperature performance grade is defined as the minimum between the critical temperatures based on the stiffness and relaxation of the asphalt binder. The critical stiffness temperature is defined as the continuous temperature at which the asphalt's stiffness is 300 MPa after 60 seconds of loading at 980 mN in the Bending Beam Rheometer (BBR) testing apparatus after 1-hour of conditioning time in an ethanol alcohol bath. The relaxation (m-value) critical temperature is defined as the continuous temperature at which the asphalt's m-value is 0.300 after 60 seconds of loading in the same conditions described above for the stiffness. Asphalt binders can be either stiffness-controlled or relaxation-controlled which is defined as the difference between the stiffness and relaxation critical temperature (ΔTc), respectively. If the difference is negative, the binder is said to be relaxation controlled, otherwise it is stiffness-controlled. This just means that whichever parameter is controlling is the critical performance limiting property and defines the low temperature PG. ΔTc is used as a metric to quantify the magnitude of difference in the controlling properties. For low temperature performance, asphalt binders must have an appropriate relaxation relative to its stiffness. In other words, you can have a very stiff binder perform well as long as it can relax accumulated shrinkage stresses due to thermal contraction quickly enough. The same can be said vice versa as well, a binder with low stiffness will not require a high relaxation because it will not accumulate stresses quickly enough to cause failure in tension causing cracking. There have been proposals to cap this magnitude of difference at a ΔTc of -5.0ºC [14], [15] as a limitation on this phenomenon for desirable field performance.

Bitumen Bond Strength (Pull of Tensile Strength) (AASHTO T 361) – The bitumen bond strength (BBS) test is used to quantify the tensile force needed to remove a pull-off stub that is bonded to an aggregate substrate with asphalt binder. Samples are prepared in both wet and dry conditions. After conditioning, a pneumatic load is applied to a pull-off stub using an ASTM D4541 Type IV adhesion tester until failure. The test is used to quantify the bonding properties of the asphalt binder and the compatibility between aggregate types and asphalt binders. The pull-off tensile strength is measures over a variety of environmental conditions and curing times to provide information about the bond strength at the interface between the substrate and asphalt binder.

3.3: Binder Formulation and Testing Summary

Initially, the oils of study that would later be mixed in the asphalts were tested in the DSR for mechanical properties. These oils included a bio-oil (ANOVA-1055, a Cargill supplied proprietary vegetable oil-based product, that has been chemically modified for improved asphalt compatibility and optimized around the useful temperature range), and re-refined engine oil bottoms (REOB). The oils were then aged in the pressure aging vessel (PAV) at 8-, 16-, and 24-hours at 100°C. A frequency sweep procedure was customized to be able to measure the extremely viscous fluids accurately. The procedure performed the frequency sweep from 0.1 to 10 Hz at 10% strain collecting 100 data points at step of 0.1 Hz per measurement. The testing temperature was 0°C. The DSR was equip with the 25mm parallel plate spindle and the testing gap was set to 250µm. The oils were then tested using this procedure at the unaged and aged conditions described above for their complex modulus and phase angle at several frequencies. A summary of this phase is outlined in **Table 5.**

Table 5: Phase 1 factors and testing summary.

Oil Testing and Analysis			
Oils	**Aging Condition**	**Test**	**Response**
Bio-Oil (ANOVA-1055) REOB	Unaged 8-Hour PAV 16-Hour PAV 24-Hour PAV	Frequency Sweep	Complex Modulus (G*) Phase Angle (°)

Six different formulations were selected containing various dosages of the bio-oil and REOB, with varying dosages of SBS, Elvaloy (a proprietary terpolymer developed by DuPont) and Poly-phosphoric Acid (PPA), or just PPA. Two "blends" will serve as a control group; one of which contains SBS and sulfur (a cross-linker), and another refinery produced PG 58-34 asphalt containing an unknown quantity of Elvaloy polymer. These formulations were selected to determine the effects of the oil's aging susceptibility on one base asphalt modified with several different common polymers. The controls were selected as a baseline to compare to as they have not been modified with oils. All of the formulations were designed to meet relatively similar high and low temperature performance grades. The exact formulations, and continuous performance grades as measured following AASHTO T 315 are shown in **Table 6**.

All blends, other than the refinery control blend, were prepared and mixed at low shear for 90 minutes at 150°C ± 10°C. The blends were then rolling thin film oven (RTFO) aged following AASHTO T 240, and PAV aged for 20-, 40-, and 60-hours at 100°C following AASHTO R 28. Then they were tested for several viscoelastic and mechanical properties after aging including: frequencies sweeps following the first portion of the linear amplitude sweep specification AASHTO TP 101, DSR-ER following AASHTO TP 123 method B, BBR testing following AASHTO T 313, and Bitumen Bond Strength (BBS) testing following AASHTO T 361. A summary of factors and tests is presented below in **Table 7**. Since the specification for the BBS test is vague about curing temperatures and conditions, the dry testing was performed with an application temperature of 150°C, and a minimum of 1 hour of conditioning at 26°C before testing. The wet BBS testing was also performed with a 150°C application temperature, but then cured for 96 hours in a water bath at 40°C. After the 96 hours of conditions, samples were allowed to return to room temperature for 1 hour before testing, which was recorded to be 20°C. Otherwise, the test was performed to specification.

Table 6: Summary of formulations and standard PG Grading.

		Binder Designation							
		Blend BO-1	**Blend BO-2**	**Blend BO-3**	**Blend R-4**	**Blend R-5**	**Blend R-6**	**Blend C-7**	**Blend C-8**
Binder Formulation, % Total Binder Weight	**PG 58S-28 Base Asphalt**	**93.75%**	**94.80%**	**96.50%**	**89.50%**	**90.80%**	**93.50%**	-	-
	PG 52S-34	-	-	-	-	-	-	**96.85%**	-
	Contractor Supplied PG 58-34	-	-	-	-	-	-	-	**100%**
	SBS (Concentrate 6% SBS + 94% 58S-28) (Kraton 243)	**3.00%**	-	-	**2.50%**	-	-	-	-
	SBS (Kraton 243 Pellets)	-	-	-	-	-	-	**3.00%**	-
	Bio Oil (APG 1055)	**3.25%**	**4.00%**	**3.00%**	-	-	-	-	-
	REOB	-	-	-	**8.00%**	**8.00%**	**6.00%**	-	-
	Sulfur	-	-	-	-	-	-	**0.15%**	-
	Elvaloy (4170)	-	**1.00%**	-	-	**1.00%**	-	-	-
	PPA	-	**0.20%**	**0.50%**	-	**0.20%**	**0.50%**	-	-
	Total	**100.00%**	**100.00%**	**100.00%**	**100.00%**	**100.00%**	**100.00%**	**100.00%**	**100.00%**
Original Binder	**G*/sin(d) (> 1.0 kPa) @ 58°C**	-	2.280	1.345	-	1.51	1.52	2.380	1.365
	G*/sin(d) (> 1.0 kPa) @ 64°C	1.408	1.210	0.661	1.603	0.798	0.745	1.280	0.764
	G*/sin(d) (> 1.0 kPa) @ 70°C	0.794	-	-	0.877	-	-	-	-
	Pass/Fail Temperature (°C)	67.6	65.8	60.5	68.7	61.9	61.5	66.4	61.2
RTFO Residue	**G*/sin(d) (> 2.2 kPa) @ 58°C**	-	5.445	3.05	-	3.88	3.52	6.130	3.3
	G*/sin(d) (> 2.2 kPa) @ 64°C	3.544	2.830	1.475	3.470	1.99	1.67	3.265	1.835
	G*/sin(d) (> 2.2 kPa) @ 70°C	1.964	-	-	1.915	-	-	-	-
	Pass/Fail Temperature (°C)	68.8	66.3	60.7	68.6	63.1	61.8	67.8	62.2
PAV Residue	**Cr. St, Mpa (< 300 Mpa) @ -18°C**	108.5	105	120	95.8	107	102	128	108
	Cr. St, Mpa (< 300 Mpa) @ -24°C	272	248	266	181.5	234	227	259	243
	S(60) Pass/Fail Temp.	-24.6	-25.3	-25.4	-28.7	-27.1	-27.5	-25.2	-26.5
	m-value (>0.300) @ -18°C	0.392	0.377	0.378	0.3565	0.359	0.366	0.352	0.386
	m-value (>0.300) @ -24°C	0.319	0.333	0.317	0.2975	0.312	0.31	0.312	0.336
	m(60) Pass/Fail Temp.	-25.6	-28.5	-25.7	-23.7	-25.5	-25.1	-25.7	-28.3
	Pass/Fail Temperature (°C)	-34.6	-35.3	-35.4	-33.7	-35.5	-35.1	-35.2	-36.5
True PG Grade		67.6 - 34.6	65.8 - 35.3	60.5 - 35.4	68.6 - 33.7	61.9 - 35.5	61.5 - 35.1	66.4 - 35.2	61.2 - 36.5

Table 7: Phase 2 factors and testing summary.

Asphalt and Oil Blend Testing							
Base Asphalt		**Oil Type**	**Polymer**	**Designation**	**Aging Levels**	**Test**	**Response**
Experimental Group	58S-28	Bio-Oil (Cargill ANOVA-1055)	SBS	BO-1	Unaged 20-Hour PAV 40-Hour PAV 60-Hour PAV	Frequency Sweep	Complex Shear Modulus (G*) Phase Angle (°)
			Elvaloy + PPA	BO-2		ER-DSR	%Recovery Maximum Internal Shear Stress
			PPA	BO-3			
		REOB	SBS	R-4		BBR	ΔTc
			Elvaloy + PPA	R-5			
			PPA	R-6		BBS (Unaged Only)	Adhesion and Moisture Damage
Control Group	52S-34	-	SBS	C-7			
	58-34	-	Elvaloy	C-8			

Chapter 4: Results

This Chapter covers the details of the results collected for the two phases of this study. The first part includes the analysis of testing results of oils and the second is focused on the blends testing results. A brief summary of findings for each testing procedure are provided at the end of each section.

4.1: Oil Testing Results

After the oils were PAV-aged at the various aging levels (8-, 16-, and 24-hours) and tested in the Dynamic Shear Rheometer (DSR) using a frequency sweep as described in the methods and materials section, the aging index was calculated for each the bio-oil and the re-recycled engine oil bottoms (REOB) using the following equation:

$$Aging\ Index = \frac{G^*_{aged}}{G^*_{unaged}}.$$

4.1.1: Bio-Oil Testing Results

A plot of the log Complex Shear Modulus (G*) vs. log frequency is shown below in **Figure 3** for the bio-oil**.** Note that points were collected every 0.1 Hz although only discrete major points are shown to keep the charts readable; this format is maintained throughout the rest of the report for all charts where frequency is plotted on a logarithmic scale. It is immediately apparent that the bio-oil ages non-linearly with respect to the complex shear modulus. In other words, as the oil ages the complex shear modulus becomes larger (indicating increasing stiffness) at an increasing rate with time. Within the 24-hour aging period, the complex shear modulus did not asymptote towards any constant value, indicating that the aging process could continue if more time was allowed for aging. It is uncertain from these results to what degree this aging could theoretically continue. It is also worth noting that these results were collected 0°C, so the effect on the modulus of the oils at greater temperatures at reasonably short aging durations is far less likely to be impacted to as severe of a degree as is shown in these results. The purpose, however, of testing at this temperature was to be able to detect the changes associated with oxidative aging in the DSR, and these results confirm that the bio-oil is susceptible to aging.

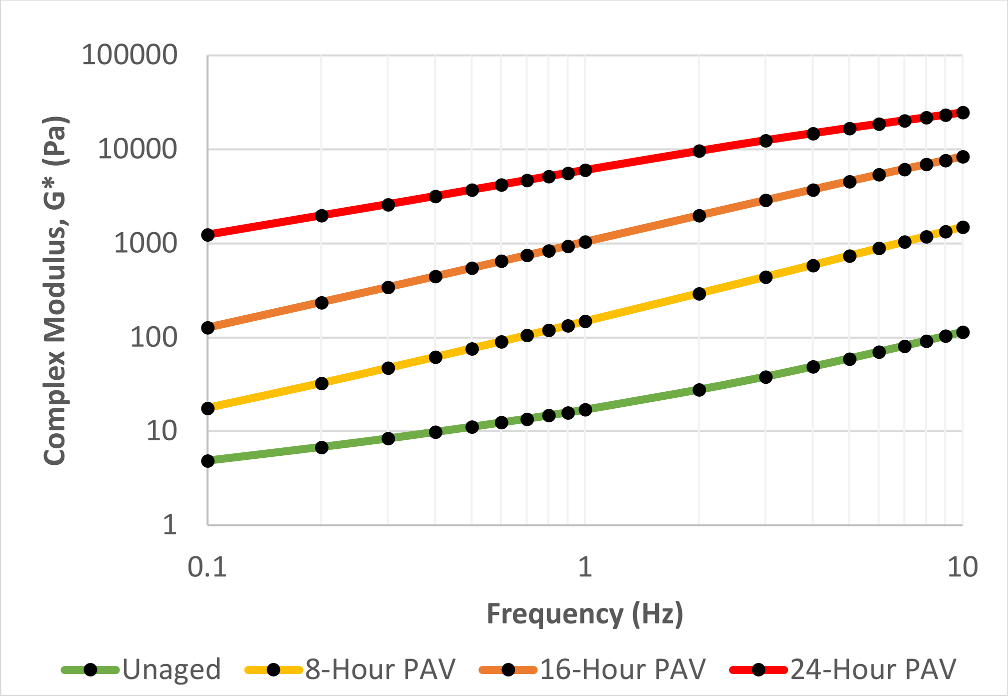

Figure 3: Log G vs Log Frequency for Bio-Oil at different aging levels.*

Examining the same results using the aging index further illustrates the increasing impact on the complex shear modulus and is shown below in **Figure 4**. This chart makes the aging susceptibility quantifiable relative to the unaged modulus at the various frequencies. As the oil ages, the aging index at any given frequency significantly increases with age. Also, as the oil ages, the maximum aging index shifts towards a lower frequency (the blue arrows on the chart). From the raw data, the peak aging index shifted from 10 Hz to 4.8 Hz after moving from the 8-hour PAV age to the 16-hour PAV age, then from 4.8 Hz to 1.2 Hz after moving from the 16-hour PAV age to the 24-hour PAV age. This shift in peak aging index suggests that the effect of aging on the bio-oil is dependent on both frequency and stiffness. The same data used in the first two plots was then plotted again in **Figure 5**, this time as a function of the PAV age instead of the frequency in order to illustrate the frequency dependence of the bio-oil.

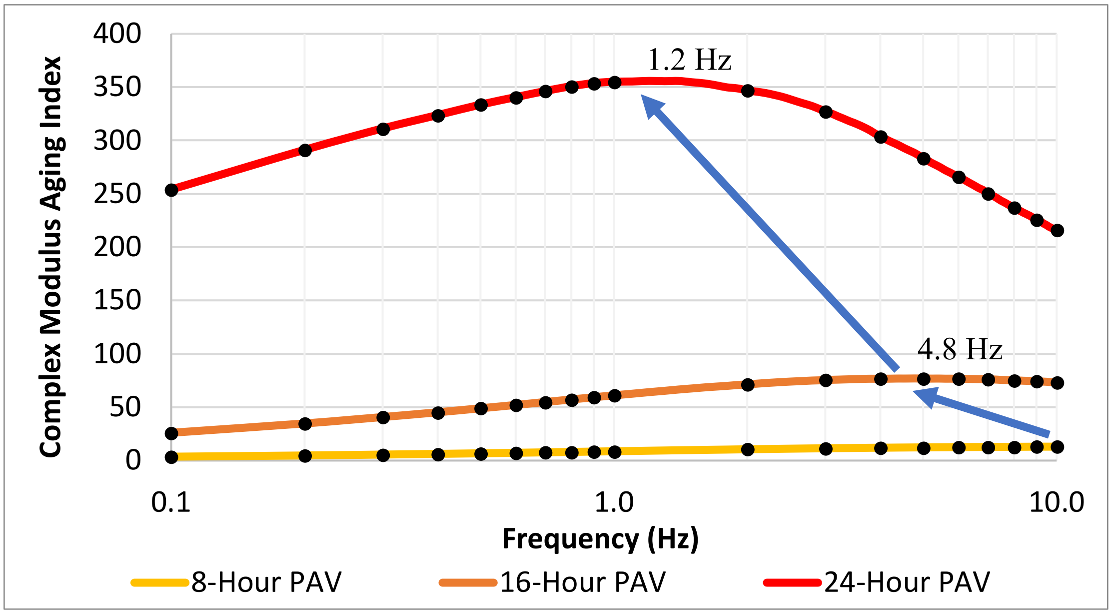

Figure 4: Complex Modulus Aging Index vs. Frequency for Bio-oil.

From **Figure 5**, this shifting behavior of the peak aging index can be seen visually as the intercepts between the different frequencies progressing to higher PAV ages. Each intercept at a particular PAV age means that for the given intercepting frequencies, the aging susceptibility of the complex moduli are equal. This intercepting behavior is only noted for the 10 Hz frequency. Since frequencies are plotted for each decade, this means that the aging susceptibility is less apparent at increasing frequencies and that the asymptotic behavior in aging index occurs somewhere between 1 and 10 Hz. Indeed, this is the case as was presented in **Figure 4** with the corresponding aging index shifting to lower frequencies as a function of age. Interestingly, the aging susceptibility of the 10 Hz curve falls below that of the 0.1 Hz curve after approximately 21-hours of PAV aging. To further investigate why this may be, the phase angles were plotted vs. frequency in **Figure 6**.

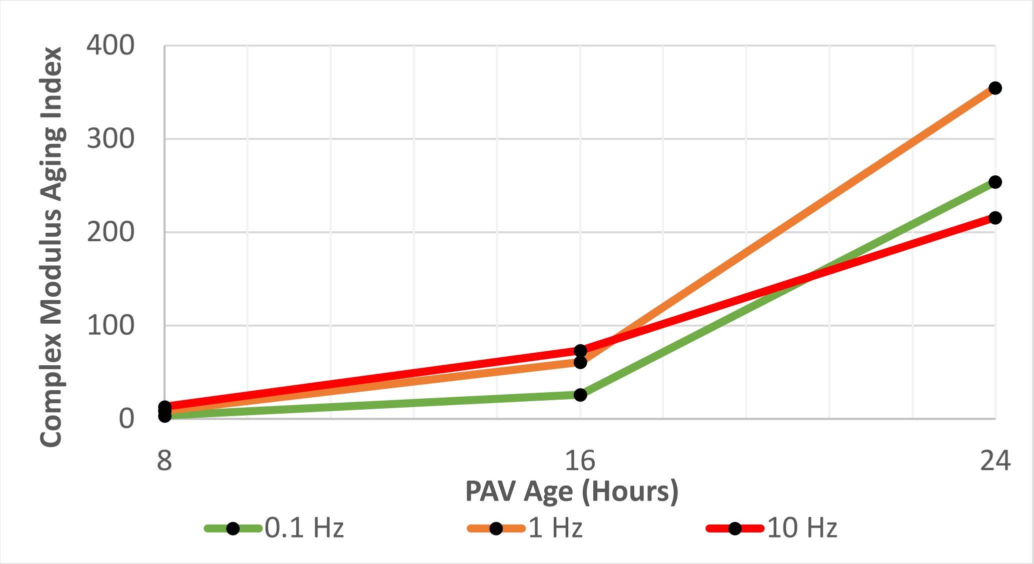

Figure 5: Complex Shear Modulus Aging Index vs. PAV age for 3 decades of frequencies.

Figure 6, like the complex modulus, shows that the phase angle is also susceptible to aging in a non-linear manner. Interestingly, the bio-oil becomes more "fluid-like" from the unaged condition until the 8-hour PAV condition (for some frequencies) and then more elastic at 24-hours of PAV aging. This is not due to variance in responses, because two replicates were tested and showed the most variance in the unaged condition (COV less than 3.5% for all points), and the least in the aged conditions (COV typically less than 1%). The behavior is further modeled in **Figure 7**. This phenomenon could indicate the breakdown of some of the chemical structures of the bio-oil after aging and oxidation or be due to reaching some resonant frequencies (shown as the intersection of the 8- and 16-hour PAV curves at ~0.35 Hz) in the oil. Whatever the case may be, the reasoning is outside of the scope of this study and is a potential topic for further investigation. Furthermore, strangely, this increase in phase angle with initial aging did not correspond to a decrease in the observed complex modulus, with similarly measured phase angles representing more than one complex modulus depending on the age. This notion of chemical change or breakdown seems to further be validated as the aging conditions increased to 16- and 24-hours of PAV aging. At these ages, the phase angles begin to decrease with age, initially depending to the frequency (greater than ~0.4 Hz shows this), but then at 24-hour aging, the entire curve was shifted below that of the unaged bio-oil. This decrease in phase angle corresponds to an increased elastic response as is typically expected to be observed with oxidation of viscoelastic organic materials. I believe that this initial increase and subsequent decrease in phase angle with increasing aging corresponds to an initial breakdown of some chemical structure of the bio-oil followed with the formation and accumulation of larger more rigid structures. Further chemical analysis of the bio-oil would be required to confirm this hypothesis. This does not, however, fully explain why (for frequencies greater than ~0.4 Hz) the complex shear modulus increases with age and can be completely different in magnitude for a specified phase angle between differently aged samples.

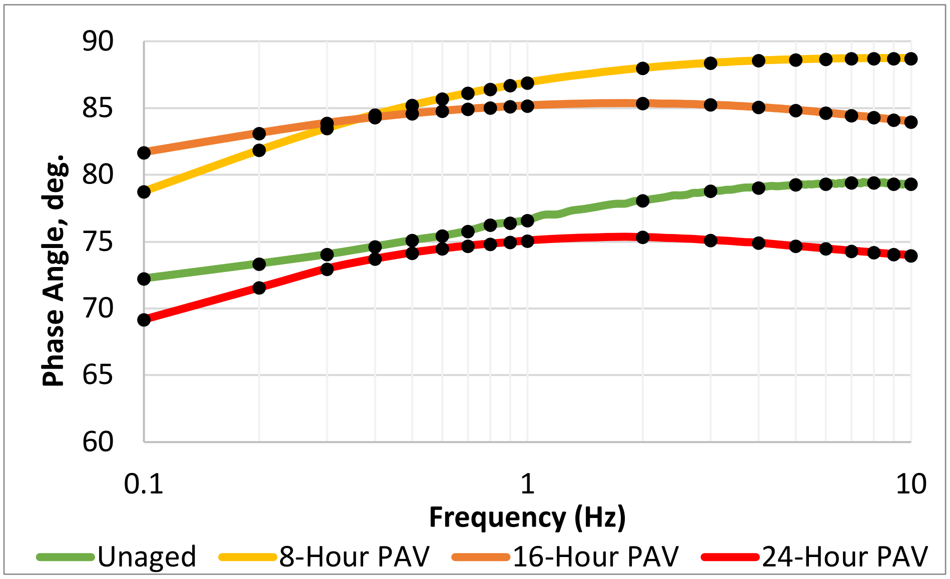

Figure 6: Phase angle vs frequency for bio-oil at various aging conditions.

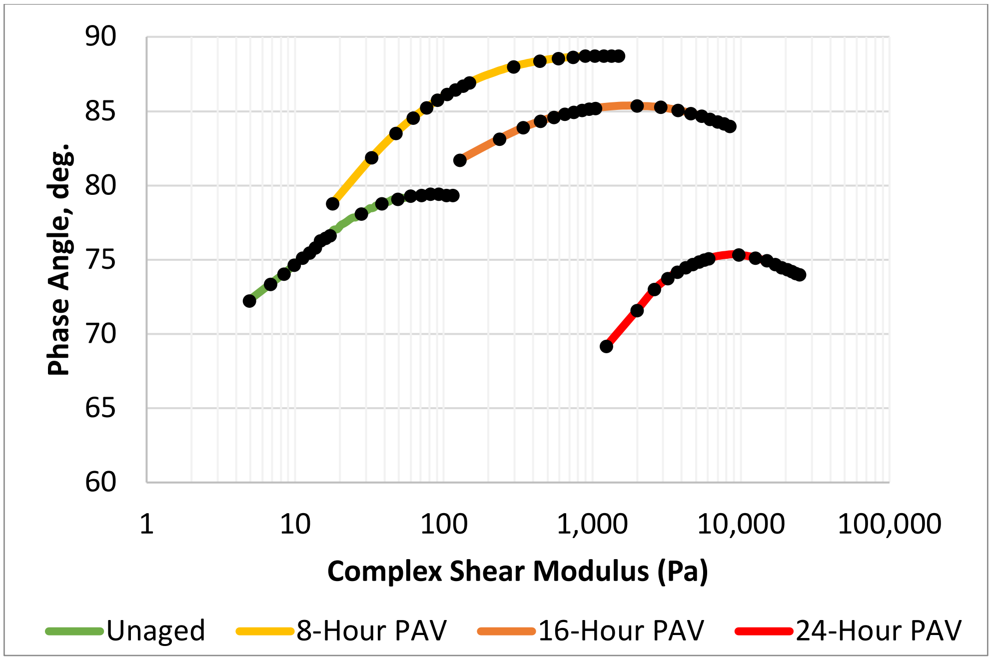

Figure 7: Complex shear modulus versus phase angle for bio-oil.

To quantify the aging susceptibility of the phase angle for bio-oil, the aging index was plotted versus the frequency for the aged conditions relative to the unaged condition and is shown in **Figure 8**. Below about 0.35 Hz, for the range of the frequencies tested, the aging susceptibility of the bio-oil at 8-hour PAV aging is lower than that at 16-hours of PAV aging. After 0.35 Hz, the 8-hour PAV aged bio-oil shows relatively unchanging aging susceptibility, while the 16-hour aged bio-oil shows decreasing aging susceptibility (as the curve approached 1.0). After 24-hours of PAV aging, the bio-oil again showed increased (absolute) aging susceptibility, reaching a minimum value around 0.3-0.4 Hz and then increasing beyond this frequency. This increased aging susceptibility behavior is expected at higher frequencies for relatively aged organic viscoelastic materials such as asphalt, because greater rigidity is observed with shear-thickening materials.

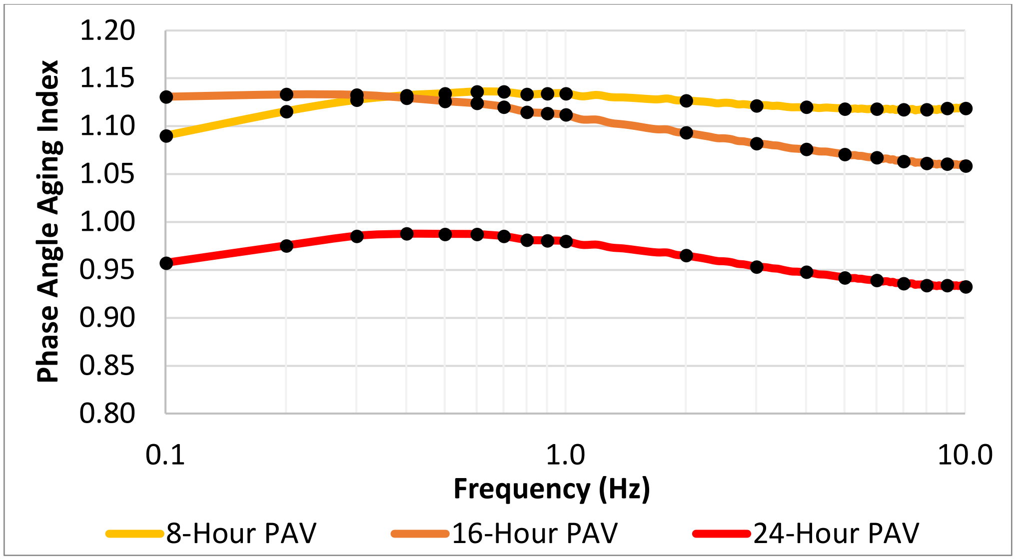

Figure 8: Phase angle aging index versus frequency for bio-oil.

Finally, the phase angle was plotted vs PAV age, rather than frequency, and is shown in **Figure 9**. Particularly of interest, is the PAV age at which the phase angle is insensitive to age or equal to 1.0 on the plot. This plot shows that this point of insensitivity for the 3 decades of frequencies initially occurs at an increased PAV age, and then decreases non-linearly with age as the frequency increases. These behaviors indicate that the aging susceptibility of the phase angle is dependent on both the frequency tested and the level of aging of the bio-oil. Several key parameters discussed are presented numerically in **Table 8** below.

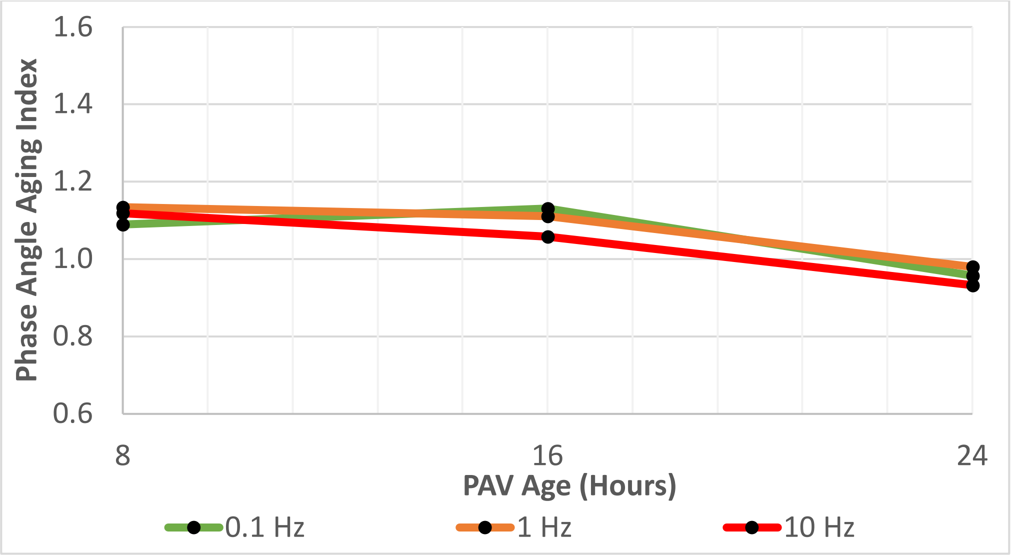

Figure 9: Phase angle aging index versus PAV age for bio-oil.

Table 8: Summary aging indices for bio-oil.

Summary						
Frequency (Hz)	**Complex Modulus Aging Index**			**Phase Angle Aging Index**		
	8-Hour	**16-Hour**	**24-Hour**	**8-Hour**	**16-Hour**	**24-Hour**
0.1	3.64	26.06	254.09	1.09	1.13	0.96
1.0	8.73	61.17	355.11	1.13	1.11	0.98
10.0	13.08	73.50	216.05	1.12	1.06	0.93

4.1.2: Re-recycled Engine Oil Bottoms (REOB) Testing Results

A plot of the log Complex Shear Modulus (G*) vs. log frequency is shown below in **Figure 10** for the REOB. Completely conversely to the bio-oil tested, the REOB displayed no appreciable sensitivity to aging for any of the aging conditions tested. The same behavior was observed in the phase angle in **Figure 11**. When the same data was plotted in **Figure 12** and **Figure 13** as an aging index and then zoomed-in on there are noticeable differences between aging conditions. These differences, however, are not appreciable for any sort of performance characterization and are easily within the variance of the test which allows for up to 10% variance in tested values. This insensitivity to aging is thought to be due to the presence of anti-oxidants since this is a component of recycled engine oil and engine oils use many anti-oxidants to prevent changing properties in the engine oil which would be detrimental to its performance.

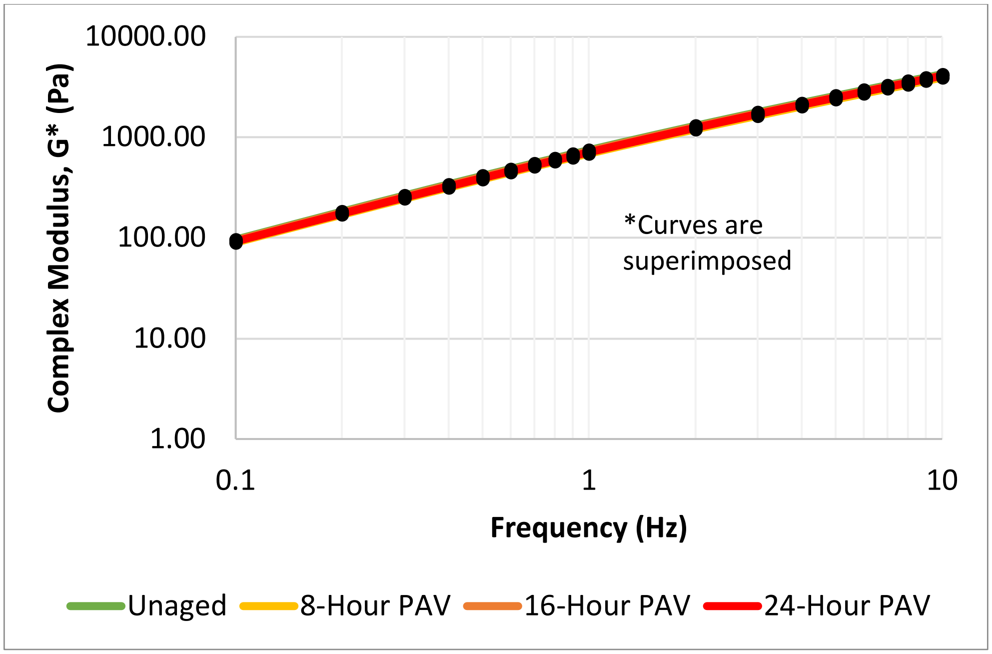

Figure 10: Complex shear modulus versus frequency for REOB.

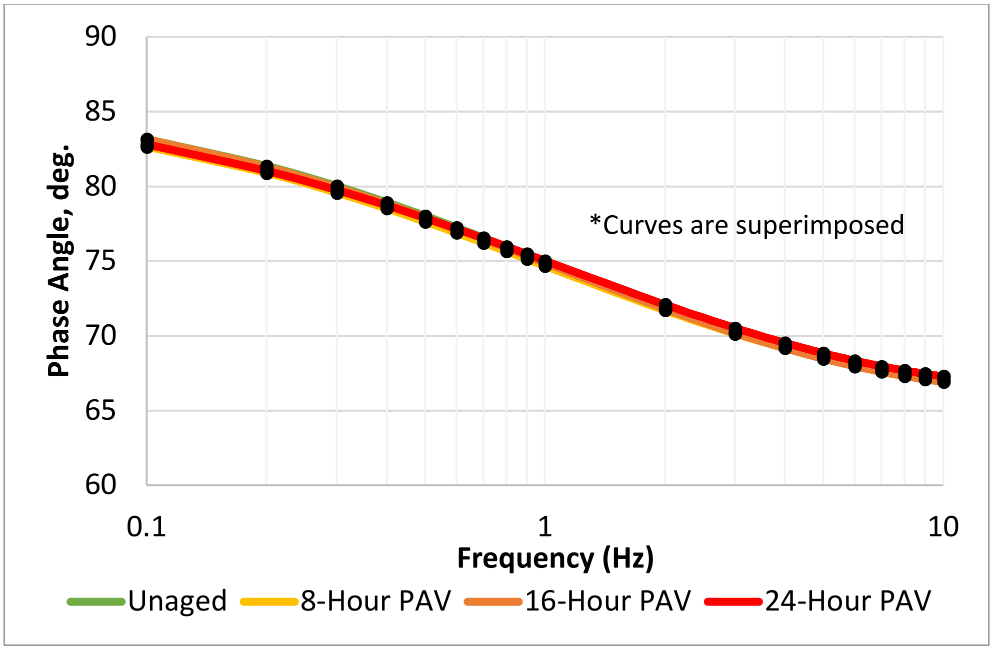

Figure 11: Phase angle versus frequency for REOB at several aging conditions.

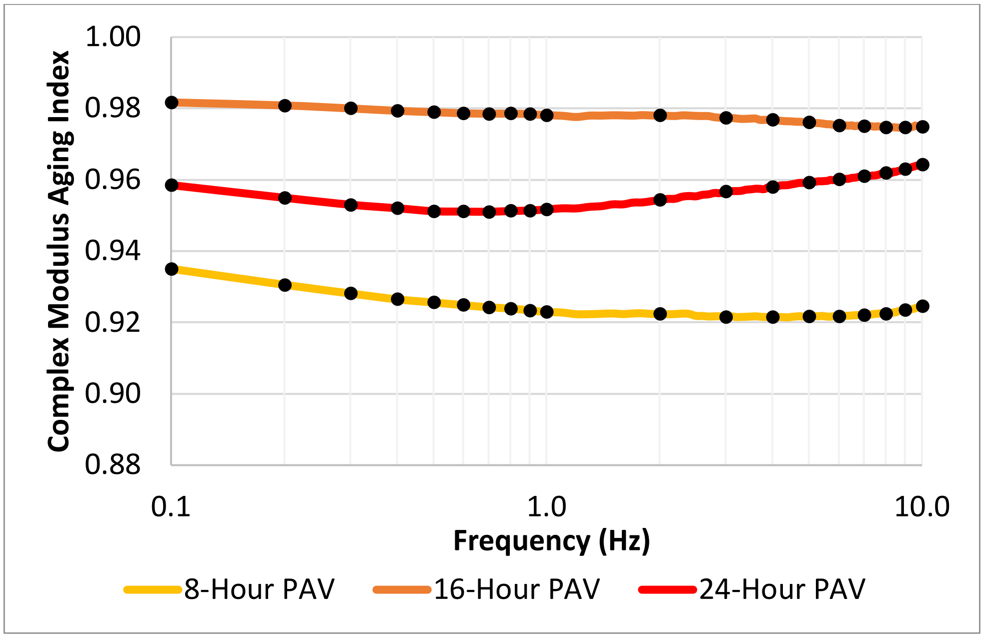

Figure 12: Complex shear modulus aging index versus frequency for REOB at several aging conditions.

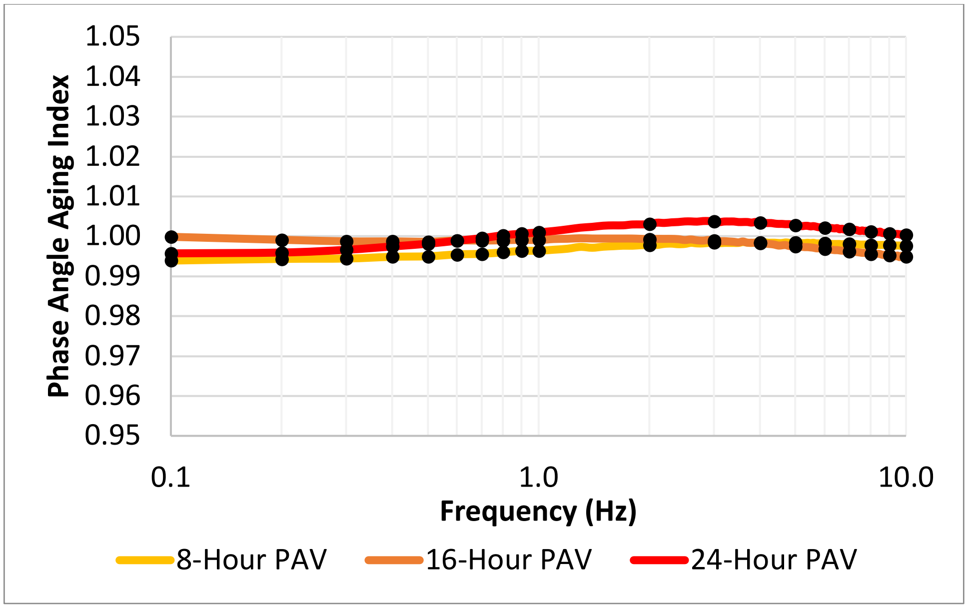

Figure 13: Phase angle aging index versus frequency for REOB at several aging conditions.

Finally, the aging indices for the complex shear modulus and phase angle were plotted in **Figure 14** and **Figure 15** as a function of PAV age for 3 decades of frequency, and to no surprise, there is no appreciable difference in aging index as a function of PAV age, with all curves essentially flat. Therefore, it is concluded that the REOB shows not only no dependence on age for its mechanical properties, but also no appreciable sensitivity to frequency for the ranges and ages tested. As was done for the bio-oil, **Table 9** summarizes key parameters discussed numerically.

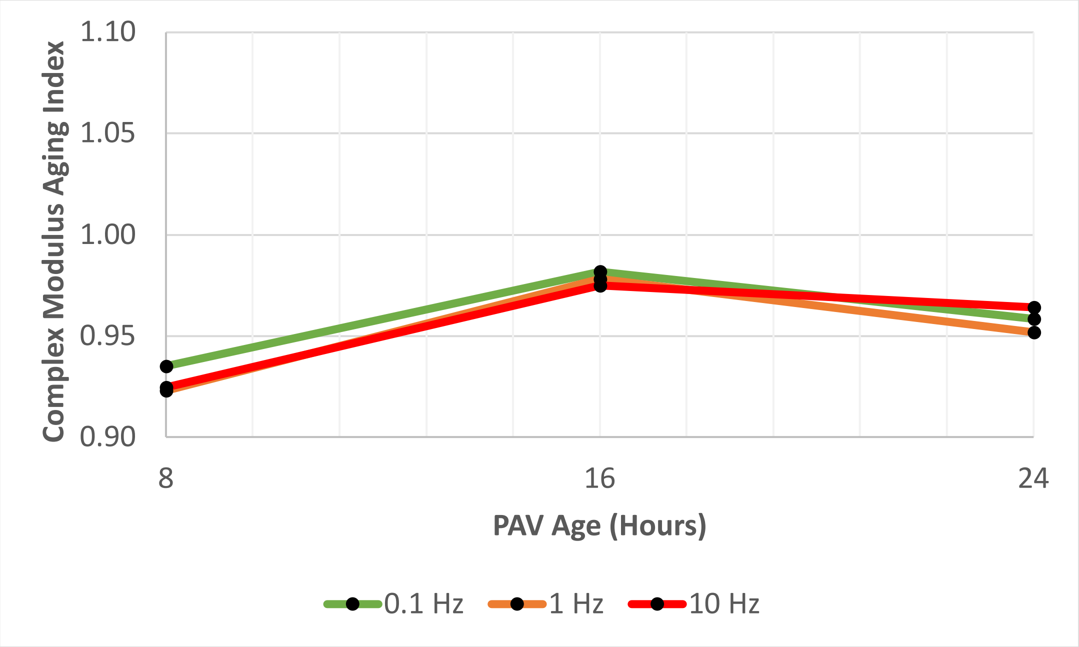

Figure 14: Complex shear modulus aging index versus PAV age for REOB at 3 decades of frequency.

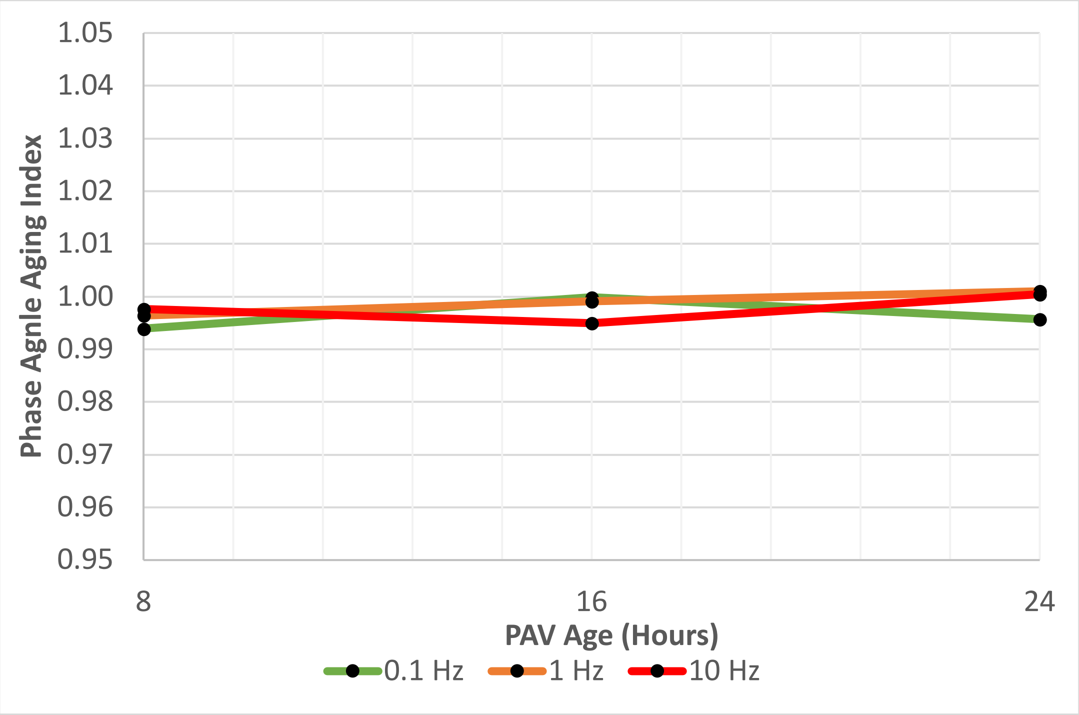

Figure 15: Phase angle aging index versus PAV aging for REOB at 3 decades of frequency.

Table 9: Summary aging indices for REOB.

Summary						
Frequency (Hz)	**Complex Modulus Aging Index**			**Phase Angle Aging Index**		
	8-Hour	**16-Hour**	**24-Hour**	**8-Hour**	**16-Hour**	**24-Hour**
0.1	0.94	0.98	0.96	0.99	1.00	1.00
1.0	0.92	0.98	0.95	1.00	1.00	1.00
10.0	0.92	0.97	0.96	1.00	0.99	1.00

4.2: Oil and Polymer Modified Asphalt Blend Testing Results

After the blends were prepared as described in section 3.3: Binder Formulation and Testing Summary, **Table 6** and aged at 20-, 40-, and 60-hours in the PAV, they were tested in the dynamic shear rheometer for the various PG+ properties described in **Table 7**: Phase 2 factors and testing summary. Similarly as was done for the oil testing results, an aging index was calculated for the various testing responses and is defined as follows:

$$Aging\ Index = \frac{Testing\ Response\ of\ Interest_{Aged}}{Testing\ Response\ of\ Interest_{Unaged}}.$$

The results of these tests are presented in the following subsections.

4.2.1: Frequency Sweep Testing Results

As was done for the oils in the first phase, aging index for complex shear modulus were plotted versus PAV age for all the blends and is shown in **Figure 16**. Blend BO-1 shows relatively linear aging susceptibility for all ages and frequencies with a greater increase in susceptibility at lower frequencies. Blends BO-2 and BO-3 displayed some nonlinearity after about 40-hours of PAV aging. Like blend BO-1, blend R-4 shows relatively linear aging susceptibility for all ages and frequencies with a greater increase in susceptibility at lower frequencies. This linear behavior is likely to be attributed to the fact that both of these blends contain similar quantities of SBS. Because bio-oil is susceptible to aging and REOB is not, this would likely explain the observed difference in magnitude of aging susceptibility between the blends, where BO-1 shows a higher aging susceptibility. Interestingly, blends R-5 and R-6 seem to asymptote their aging susceptibility after about 40-hours of PAV aging for all frequencies, again with the lower frequencies showing the greatest magnitude of aging effects. With the exception of blend BO-1 and BO-2 at 60-hours PAV age (barely), all blends including the control blends exhibited an aging index of under 40 for all frequencies.

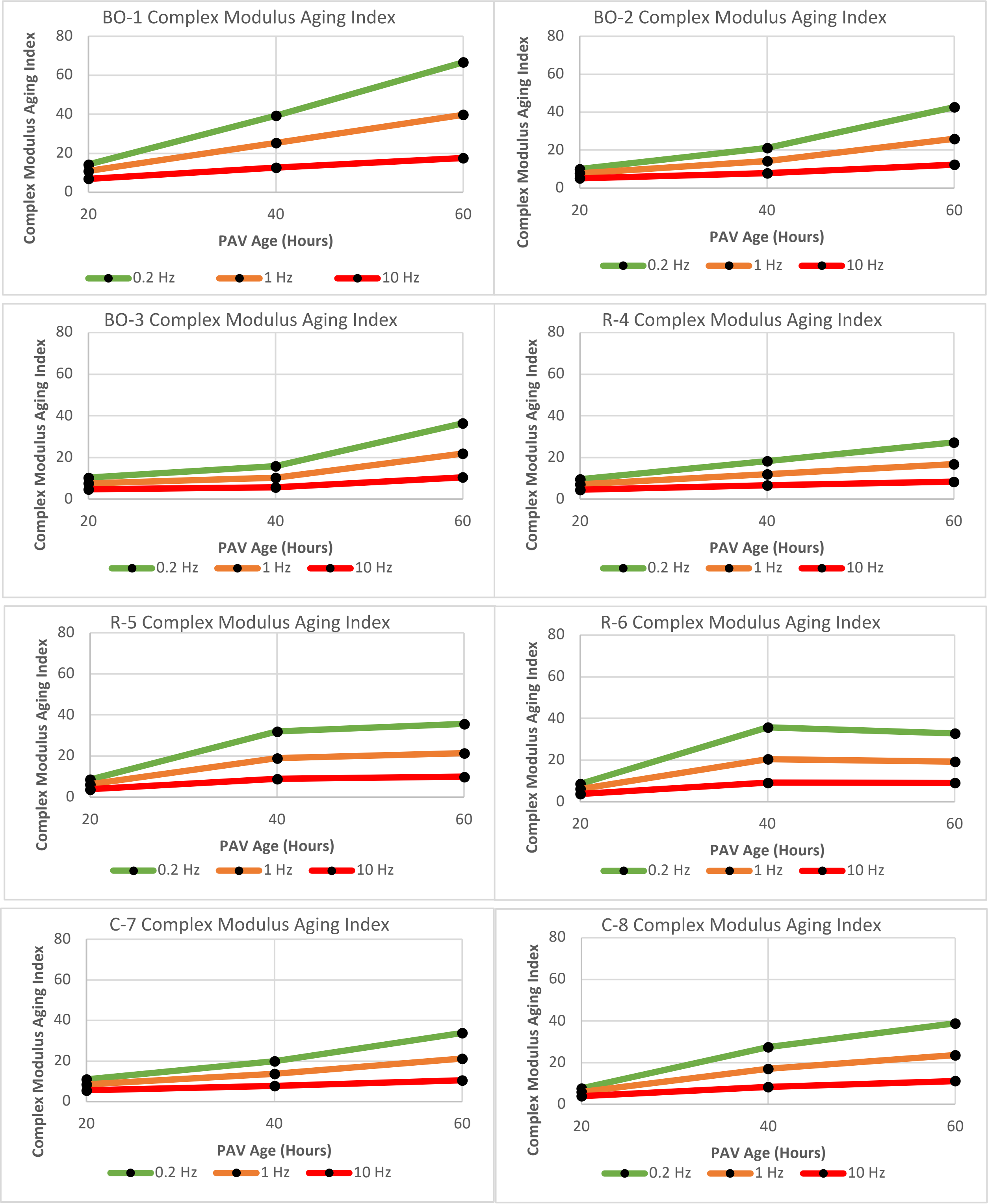

Figure 16: Summary of complex shear modulus aging indices for all blends.

The results for the blends containing bio-oil at 1 Hz were selected and are presented in **Figure 17**. 1 Hz was selected because it is a reasonable middle ground for the frequency of traffic loading between low and high speeds. What is immediately apparent is that blend BO-1 has a noticeably higher aging susceptibility at all aging durations compared to blends BO-2, BO-3, C-7, and C-8. This susceptibility to oxidation becomes more apparent at higher aging durations as well, while the other blends compared in this figure maintain relatively similar aging indices as they age. This behavior indicates that the polymer modifier used seems to have a much higher susceptibility to aging than the bio-oil and is one explanation for the increased aging susceptibility for blend BO-1 since blends BO-2 and BO-3 also contain similar quantities of oil (3.25%, 4.00%, and 3.00% respectively).

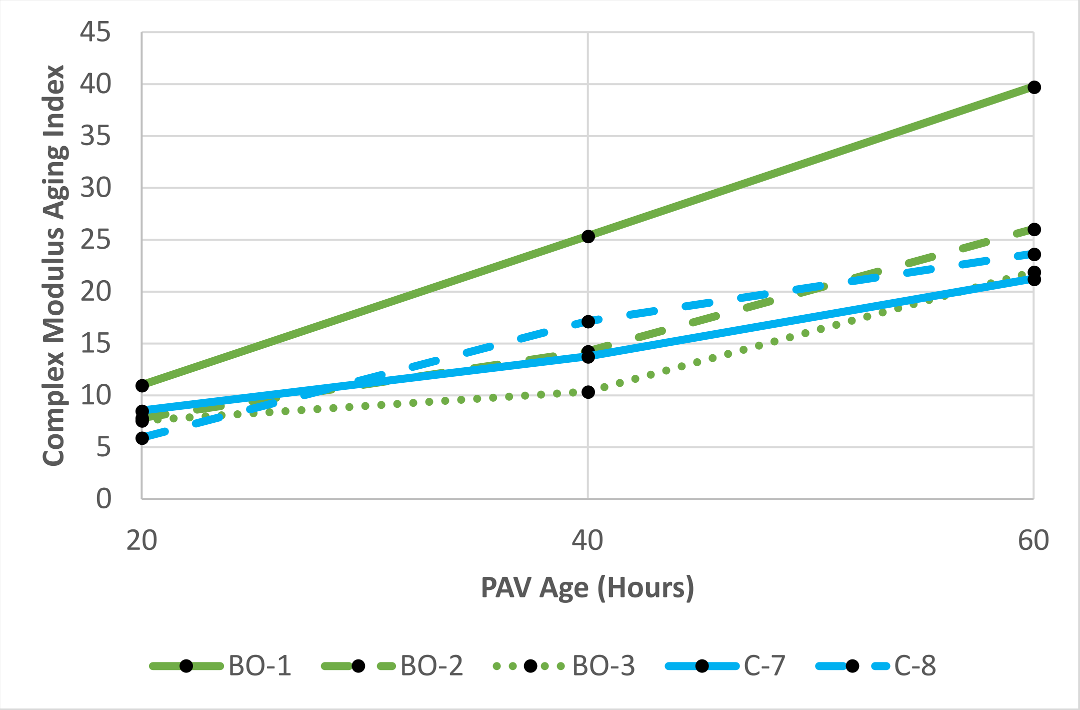

Figure 17: Complex shear modulus aging indices at 1 Hz for blends containing bio-oil and both control blends.

To confirm the aging susceptibility of the SBS being the cause of the substantial difference in aging susceptibility of blend BO-1, another plot containing the results of the REOB containing blends versus PAV age was constructed and is shown in **Figure 18**.

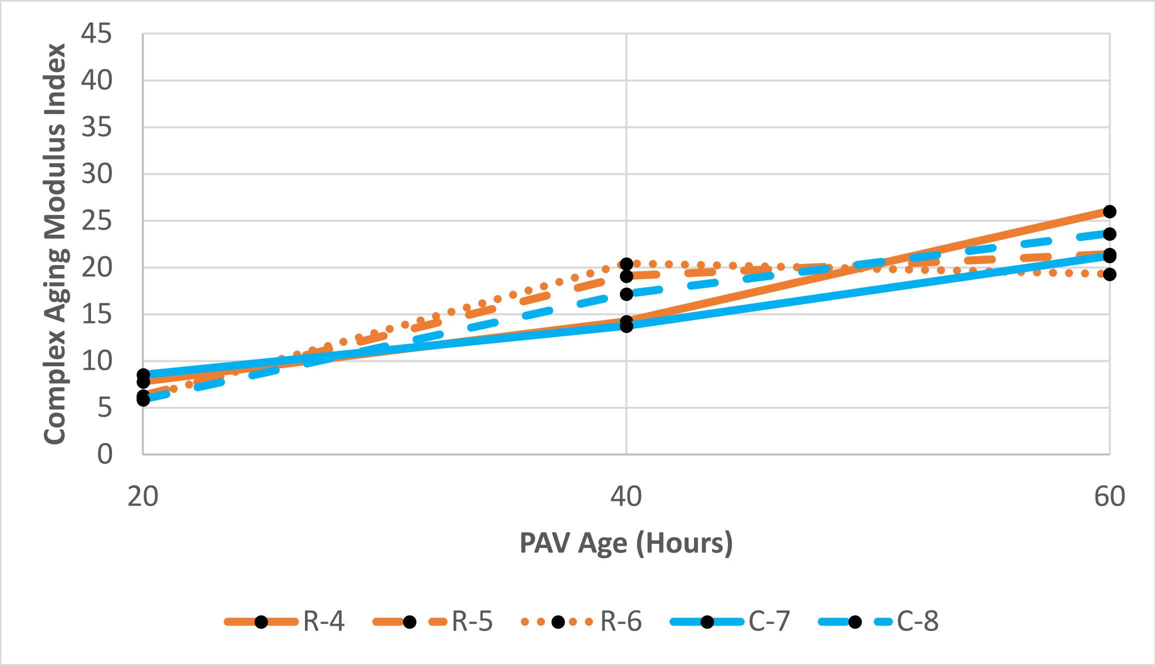

Figure 18: Complex modulus aging indices at 1 Hz for blends containing REOB and both control blends.

This figure mostly debunks that the SBS must be the cause of the extreme aging susceptibility noted in blend BO-1, since blend R-4 also contains SBS, but did not show any appreciably significant difference in the aging index compared to the other REOB blends and controls. Compared to the blends containing Elvaloy and PPA though (R-5 and R-6), the aging index did not level off after 40-hours, thus making the contribution of aging susceptibility from the SBS still plausible. Therefore, there must be some negative combinatorial effects associated with combining this bio-oil with asphalt blends containing SBS. This behavior can further be seen in **Figure 19**.

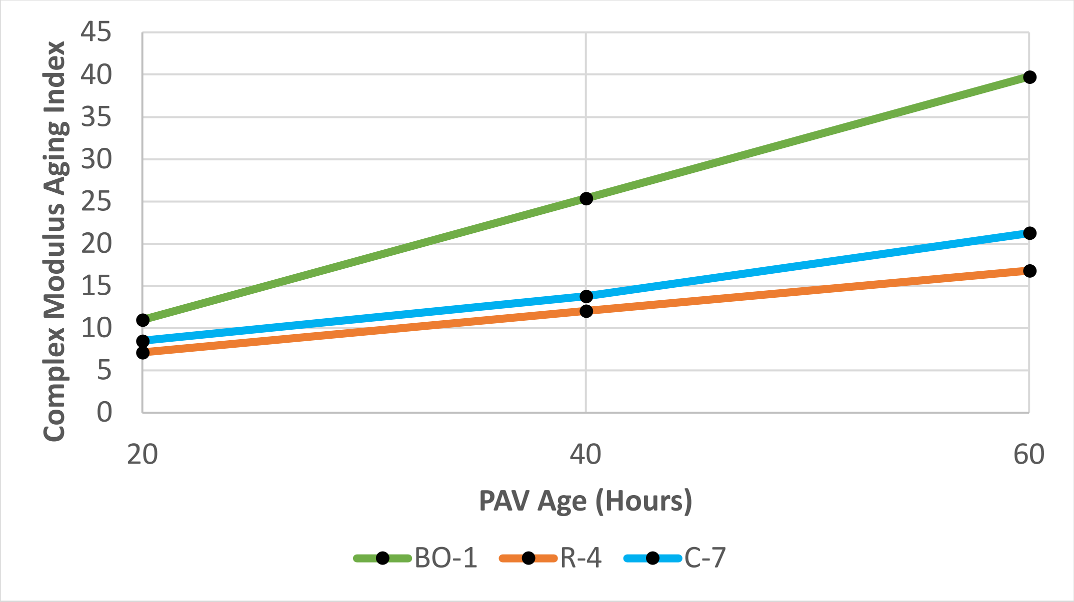

Figure 19: Complex shear modulus aging index at 1 Hz for blends BO-1, R-4, and C-7 which contain SBS.

Furthermore, since phase 1 results concluded that REOB does not show any appreciable aging susceptibility up to 20-hours of PAV aging unblended (more oxidative exposure compared to when blended with asphalt), the aging susceptibility associated with blends containing REOB are likely to be associated to the aging susceptibility of the polymer and base asphalt only. Counterintuitively, blends R-5 and R-6, show higher aging susceptibility (again referring to **Figure 18**) shortly after 20-hours of PAV aging and up to 40-hours of PAV aging when compared to the control blends and blend R-4, which contains SBS. However, after 40-hours of PAV aging, the aging indices for these two blends level off and remain relatively stable around an index of 20 with additional aging. The control blends, and REOB blend containing SBS (R-4) show behaviors of aging susceptibility that is not yet (if ever) ready to become asymptotic.

In the same spirit of analysis used for **Figure 18**, **Figure 20** plots the blends containing Elvaloy and PPA (BO-2 and R-5) against the control that is most similar in composition (C-8), containing only Elvaloy. Blend BO-2 shows the least aging susceptibility up until nearly 60-hours of PAV aging and then begins to show the most susceptibility with an apparent transition to a more rapid change in aging index after 40-hours of PAV aging. Blend R-5 begins to asymptote just after 40-hours of PAV aging and blend C-8 appears to increase relatively linearly with PAV age. This seems to indicate a positive combinatorial effect with blends containing REOB, Elvaloy and PPA at extended aging.

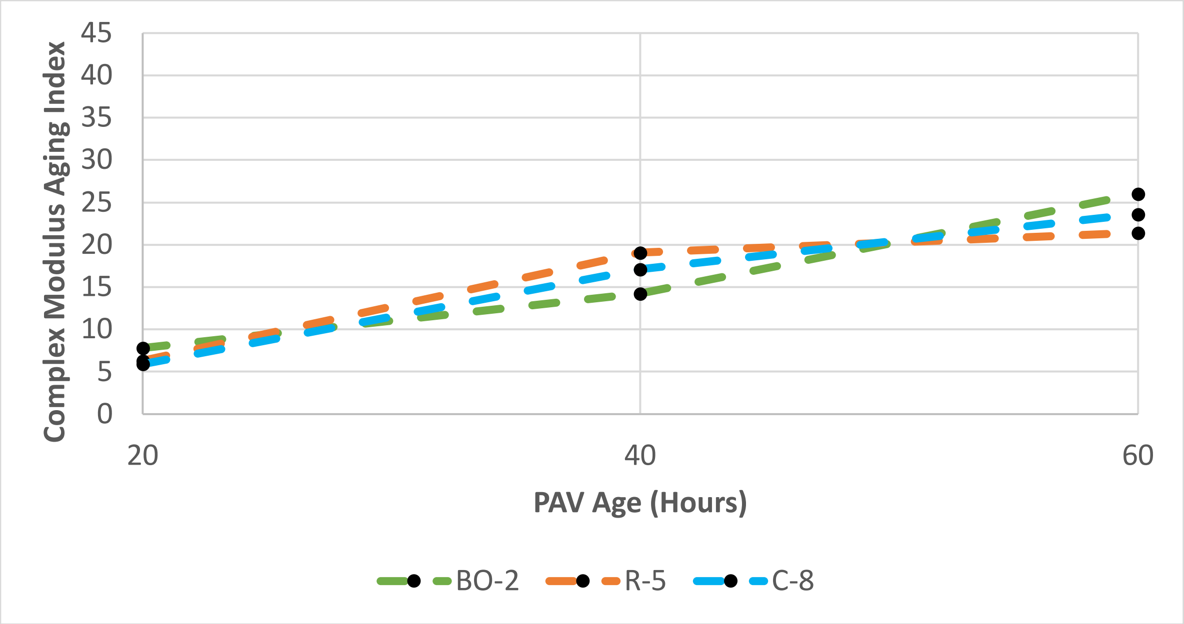

Figure 20: Complex shear modulus aging index at 1 Hz for blends BO-2 and R-5, which contain Elvaloy and PPA, and C-8 which contains only Elvaloy.

Again, to compare the aging affects between the blends containing only an oil and PPA, blends BO-3, R-6, C-7 and C-8's aging indices are plotted versus PAV age as shown in **Figure 21**.

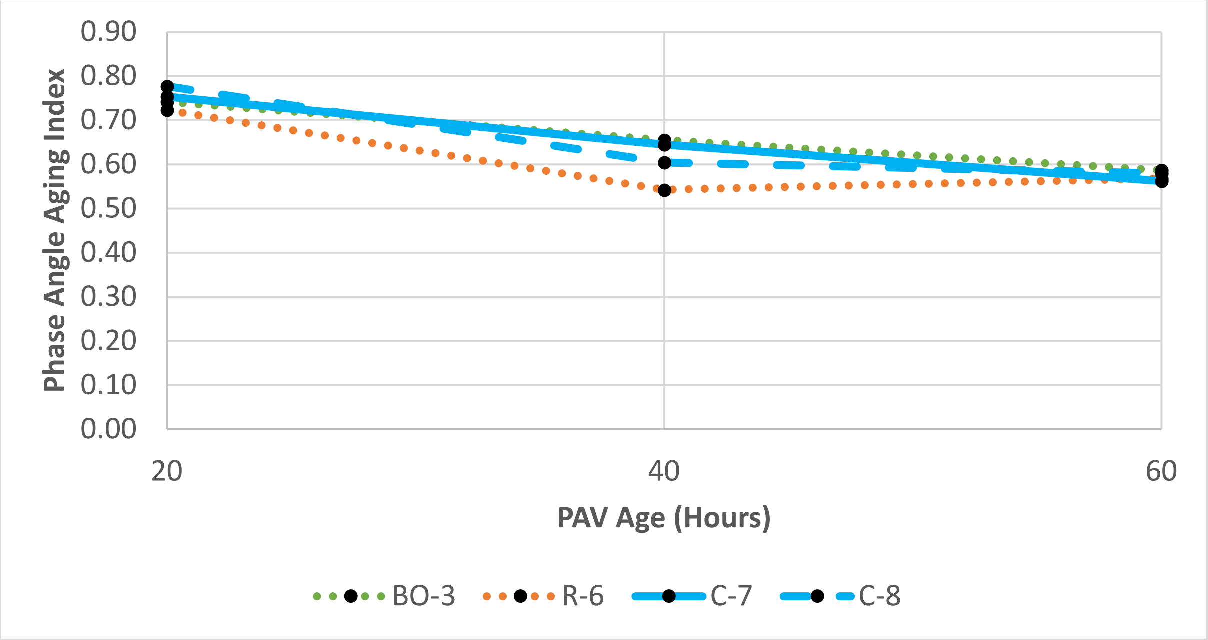

Figure 21: Complex shear modulus aging index at 1 Hz for blends BO-3 and R-6, which contain PPA, and C-7 and C-8 which contains SBS and Elvaloy respectively.

Again, the REOB blend containing only PPA exhibits an asymptote after about 40-hours of PAV aging. The blend containing bio-oil (BO-3), shows the reverse behavior an appears to accelerate in its aging susceptibility after about 40-hours of PAV aging. Ultimately, though, all of the blends displayed roughly the same final complex shear modulus aging index of about 20-24 times that of the unaged binder properties.

Finally, the phase angles are investigated for aging susceptibility, again at 1 Hz frequency, and versus the PAV age. These are summarized in a similar fashion as was done for the complex modulus aging indices, first by oil type in **Figure 22**, and then by polymer type in **Figure 23**.

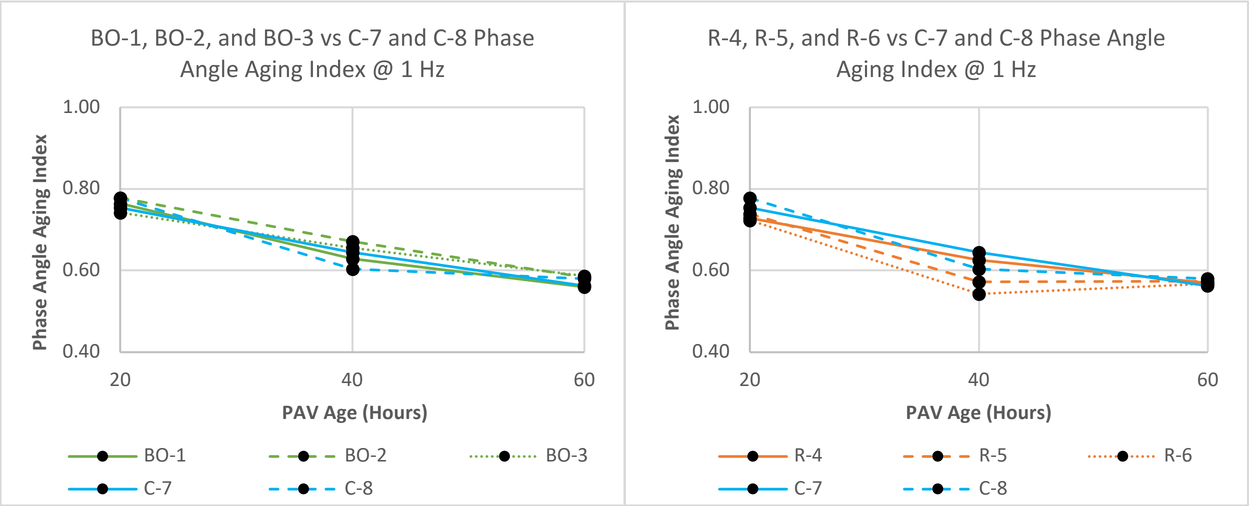

Figure 22: Phase angle aging indices by oil type.

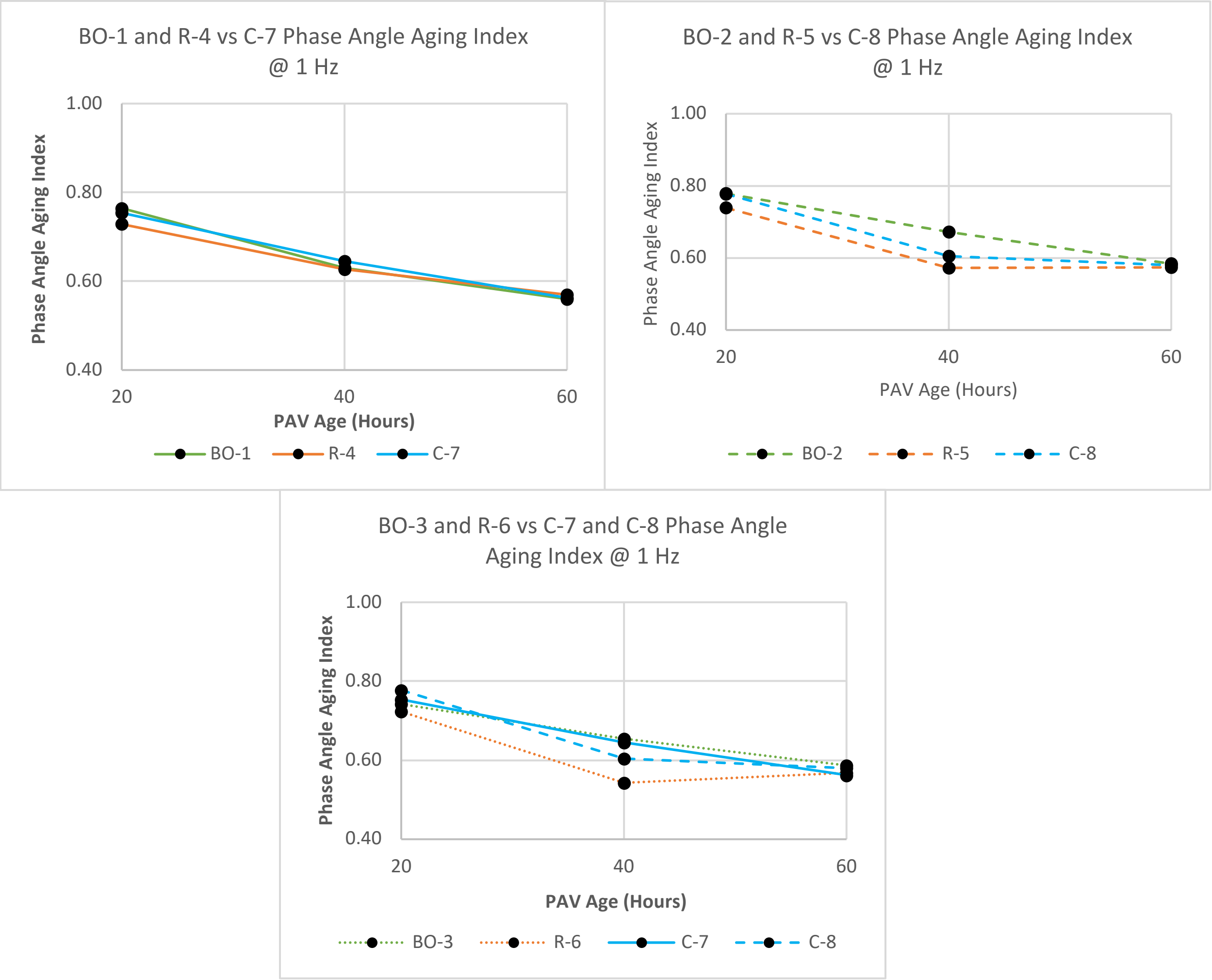

Figure 23: Phase angle aging indices by polymer type

Interestingly, the phase angle aging indices seem to follow very similar trends among the various blends, with REOB showing the greatest influence around 40-hours of PAV aging, but then recovering some of those losses as the blend continued to age towards 60-hours. The bio-oil blends showed the least susceptibility to aging versus the control blends in terms of the phase angle aging index. Therefore, it is postulated that the phase angle aging index likely mostly depends on the age of the asphalt. Since previous work has focused on the varying aging susceptibility among sources, multiple bitumen sources were not tested to verify this. After 60-hours of aging, all blends exhibited approximately 60% of their originally measured unaged phase angles.

4.2.2: Frequency Sweep Conclusion Summary

- There appears to be negative combinatorial effects to the complex shear modulus aging index associated with combining bio-oil with asphalt blends containing SBS. This blend, BO-1, showed the highest susceptibility to aging.
- There appears to be positive combinatorial effects to the complex shear modulus aging index with blends containing REOB, Elvaloy and PPA at extended aging. Blends R-5 and R-6 showed asymptotic behavior in complex shear modulus aging indices after about 40-hours of PAV aging.
- Lower testing frequencies show the greatest effects of aging susceptibility for all oil and polymer types.
- Blends containing SBS showed the greatest sensitivity to aging depending on the oil type used in the blend, with bio-oil showing the greatest sensitivity, REOB showing the least, and the control showing slightly higher sensitivity than when compared to the REOB blend.

4.2.3: Elastic Recovery (DSR-ER) Testing Results

Beginning this analysis, the aging indices for %recovery and maximum stress were calculated and then plotted versus PAV age. **Figure 24** shows the %recovery aging indices by oil types compared to the control blends, and **Figure 25** shows the maximum induced stress to achieve the required strain aging indices. In the case of elastic recovery, it is assumed that a higher %recovery with higher maximum shear stresses is a good property for intermediate temperatures. This means the binder is able to recover more strain even after an application of high stress, but this does not say anything about the fatigue life as an effect of aging since this test uses only one loading cycle. In this analysis, a higher aging index for %recovery with a simultaneously high aging index for maximum stress is therefore assumed to be good in terms of mechanical performance, but bad in terms of aging susceptibility.

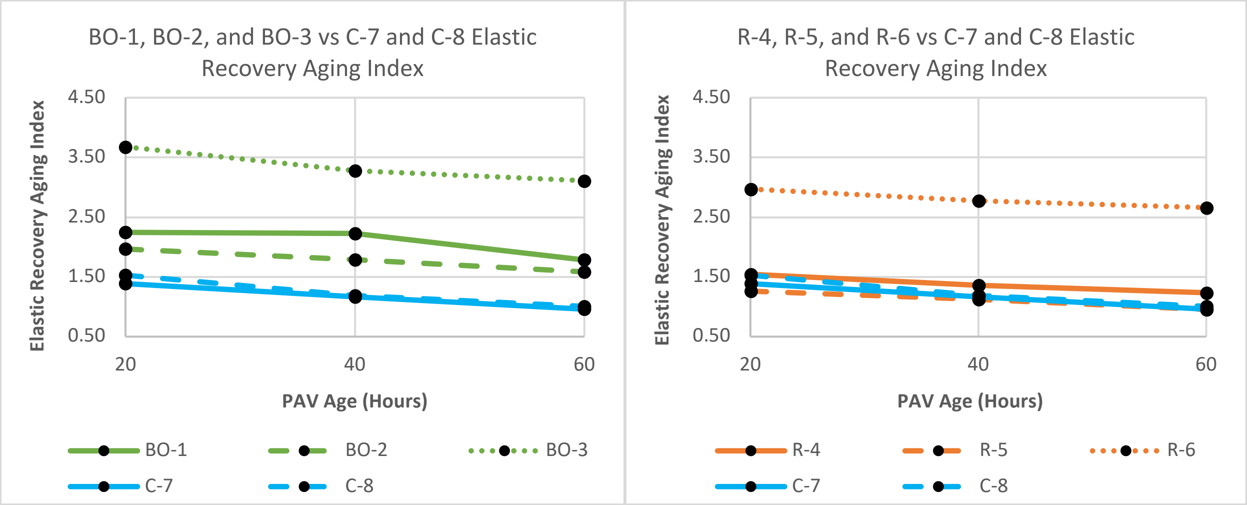

Figure 24: Elastic recovery (%recovery) aging index versus PAV age by oil type.

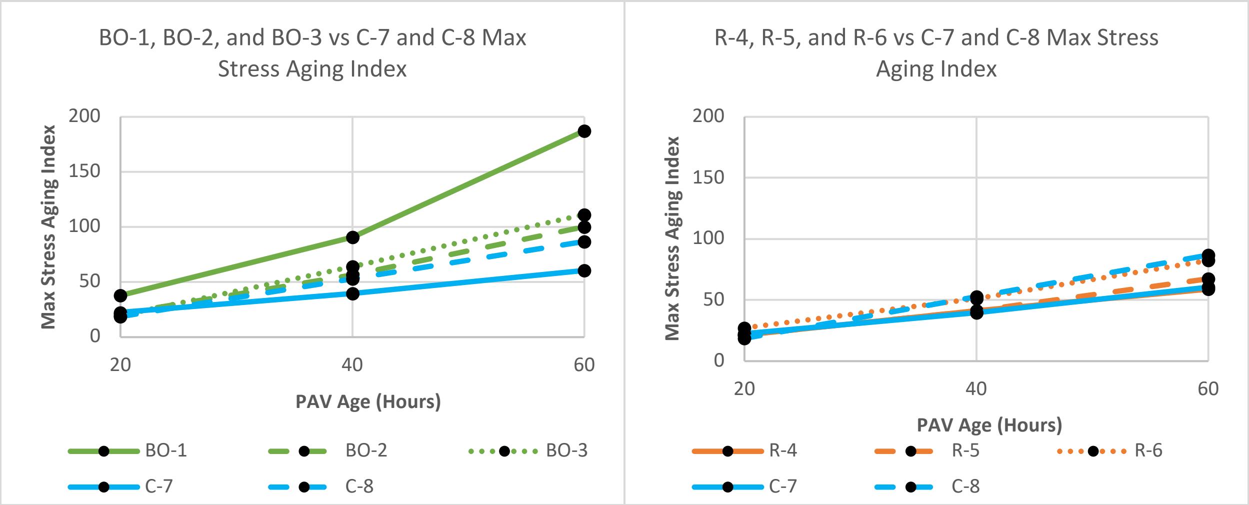

Figure 25: Maximum induced shear stress aging index versus PAV age by oil type.

The bio-oil containing blends showed approximately 50% greater %recovery aging susceptibility when compared to the controls with the exception of blend BO-3, containing only PPA, which was 200% greater. This suggests that PPA without additional Elvaloy shows greater %recovery aging susceptibility, and this is again confirmed with blend R-6, which is a REOB blend containing only PPA. Therefore, PPA shows a greater response to aging in terms of elastic recovery and this can be seen in **Figure 26**.

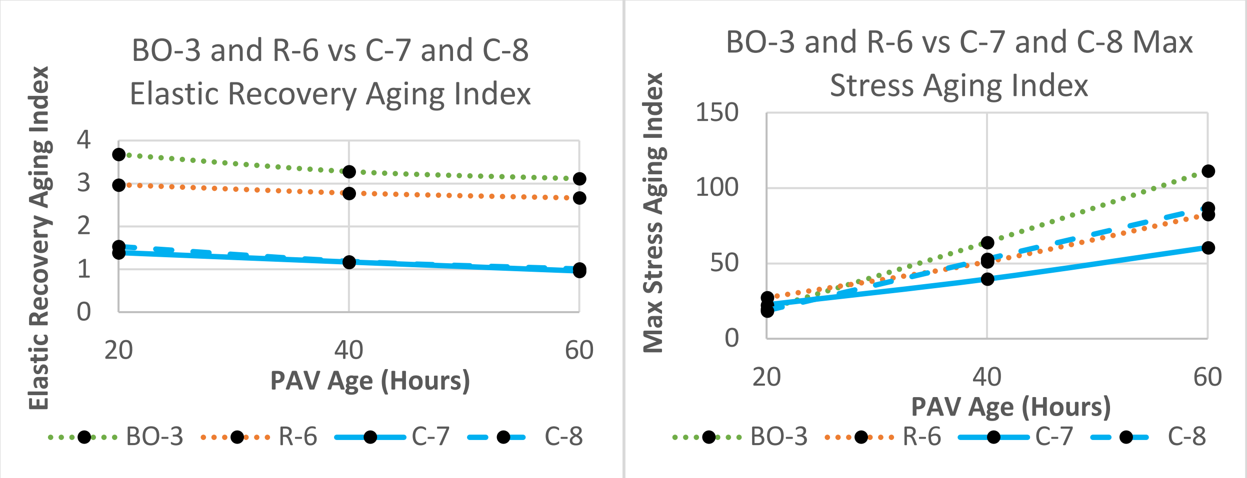

Figure 26: Elastic recovery and maximum internal shear stress aging susceptibility for blends BO-3 and R-6, containing only PPA, versus C-7 and C-8, containing Elvaloy and PPA.

To further investigate this, it can be seen in the maximum stress plots that the blends containing PPA did not show any relatively significant susceptibility. In fact, only blend BO-1 showed significant susceptibility to aging in terms of maximum stress. This means that the blends containing only PPA exhibit superior recovery performance at relatively high shear stresses, but very high %recovery aging susceptibility for all PAV ages.

The blend BO-1, containing bio-oil and SBS, also shows consistent relatively high %recovery performance with PAV age. With increasing PAV aging, the %recovery aging susceptibility remains the 2nd highest but reaches the highest maximum internal shear stress at 60-hours of all of the blends. This means that bio-oil with SBS (BO-1) shows consistent improved elastic recovery performance relative to the unaged blend even at very high internal shear stresses at intermediate temperatures. This, however, means it exhibits very high aging susceptibility in terms of maximum internal shear stress. These results are consistent with the observed complex shear modulus aging index for blend BO-1 in the previous section, which exhibited the highest susceptibility to aging, and therefore a correspondingly high complex shear modulus at increased age. This is also true for blend R-4 and C-7, both of which also contain SBS, but exhibit the lowest maximum internal shear stress aging susceptibility which is consistent with the observed complex shear modulus aging indices observed in the previous section. The observed effect on the maximum internal shear stress aging indices, however, is not quite as profound as it is for the complex shear moduli for blends R-4 and C-7. These observations are shown below in **Figure 27**. Compared to the SBS blend containing bio-oil, BO-1, blend C-7 and R-4 showed very little aging susceptibility in terms of %recovery.

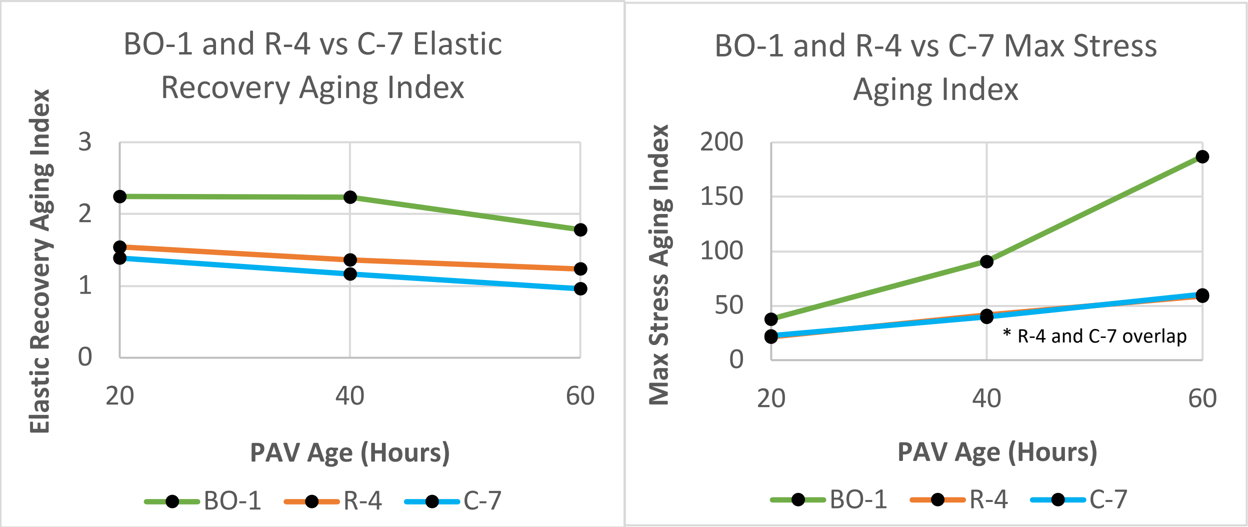

Figure 27: Elastic recovery and maximum internal shear stress aging susceptibility for blends BO-1 and R-4, versus C-7, all containing SBS.

Further investigating the effects of the polymers on aging susceptiblity with the different oils, aging susceptibility plots for blends containing Elvaloy and PPA are shown in **Figure 28**. Again, the blend containing the aging susceptible bio-oil, exhibits a greater %recovery susceptibility to aging compared to the blends containg REOB, and no oil. This also manifests in the observed maximum stress. Intestingly, the REOB blend containing SBS, R-4, the REOB blend containg Elvaloy and PPA, R-5, and both control blends, C-7 and C-8, after 60-hours of PAV aging exhibited nearly no observable difference in %recovery aging susceptibility from the unaged blends. In other words, the effects of long term aging on these blends in terms of %recovery is minimal.

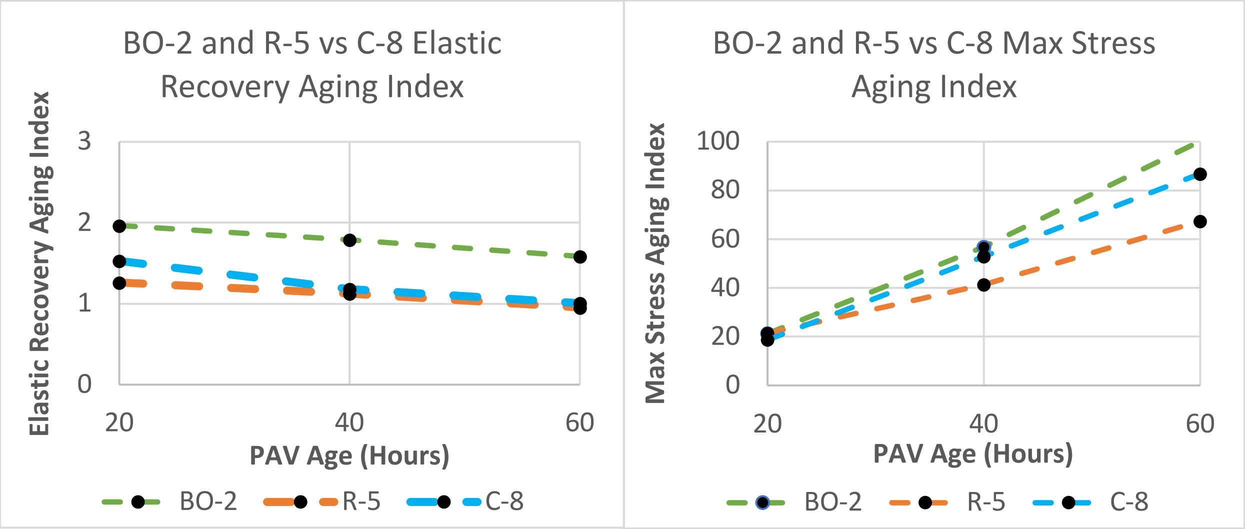

Figure 28: Elastic recovery and maximum internal shear stress aging susceptibility for blends BO-2 and R-5, containing Elvaloy and PPA, versus C-8, containing Elvaloy.

4.2.4: Elastic Recovery Conclusion Summary

- In the case of elastic recovery, it is assumed that a higher %recovery with higher maximum shear stresses is a good property for intermediate temperatures. This means the binder is able to recover more strain even after an application of high stress, but this does not say anything about the fatigue life as an effect of aging since this test uses only one loading cycle.
- PPA without additional Elvaloy shows greater %recovery aging susceptibility for both oil types at all PAV ages.
- Blends containing only PPA exhibit superior recovery performance at relatively high shear stresses, but very high %recovery aging susceptibility for all PAV ages.
- Bio-oil with SBS (BO-1) shows consistent improved elastic recovery performance relative to the unaged blend even at very high internal shear stresses at intermediate temperatures. This, however, means it exhibits very high aging susceptibility in terms of maximum internal shear stress. These results are consistent with the observed complex shear modulus

aging index for blend BO-1 in the previous section, which exhibited the highest susceptibility to aging, and therefore a correspondingly high complex shear modulus at increased age.

- Compared to the SBS blend containing bio-oil, BO-1, blend R-4 and C-7 showed very little aging susceptibility in terms of %recovery for all PAV ages.
- The REOB blend containing SBS, R-4, the REOB blend containg Elvaloy and PPA, R-5, and both control blends, C-7 and C-8, after 60-hours of PAV aging exhibited nearly no observable difference in %recovery aging susceptibility from the unaged blends. In other words, the effects of long term aging on these blends in terms of %recovery is minimal.

4.2.5: Bending Beam Rheometer (BBR) Testing Results

ΔTc has been shown in literature to be a good indicator of aging susceptibility of oil-modified binders. ΔTc is the calculated difference between the stiffness critical temperature and the m-value critical temperature. A negative ΔTc value means the relaxation rate, or m-value, determines the low temperature performance grade. A positive ΔTc means stiffness determines the low temperature performance grade. An increasingly more negative ΔTc would indicate that the m-value becomes more and more controlling of the low temperature grade determination. Binders with a highly negative ΔTc have been implicated in a few projects with high rates of cracking. An accepted limit on ΔTc has not been fully implemented for asphalt binders, but a minimum ΔTc of -5.0 °C has been suggested in literature [16]. This proposed limitation suggests relaxation rate is the primary mechanism responsible for low-temperature cracking performance.

In this study, all blends, including the controls, had ΔTc values that became more negative with increasing PAV age as can be seen in **Table 10**. Therefore, to analyze the results in a meaningful way, the difference in ΔTc was taken from the next lowest aging condition beginning with 40-hour PAV aging as follows:

$$Relative\ Incremental\ Change\ in\ \Delta\mathrm{Tc} = \Delta\mathrm{Tc}_i - \Delta\mathrm{Tc}_p$$

$$where\text{: } \Delta\mathrm{Tc}_i = \Delta\mathrm{Tc}\text{ for the PAV age of interest}$$

$$\Delta\mathrm{Tc}_p = \Delta\mathrm{Tc}\text{ for the PAV age prior to the }\Delta\mathrm{Tc}\text{ at the PAV age of interest.}$$

The results for all of the blends are shown below in **Figure 29**.

Table 10: Table of Critical Temperatures and ΔTc values for all blends.

Binder	Age	m(60) Critical Temp (℃)	S(60) Critical Temp (℃)	ΔTc
Blend BO-1	**20 Hour PAV**	-35.6	-34.6	0.9
	40 Hour PAV	-32.2	-33.4	-1.2
	60 Hour PAV	-29.0	-32.6	-3.6
Blend BO-2	**20 Hour PAV**	-38.5	-35.3	3.2
	40 Hour PAV	-34.9	-34.0	0.9
	60 Hour PAV	-31.0	-32.8	-1.8
Blend BO-3	**20 Hour PAV**	-35.7	-34.9	0.8
	40 Hour PAV	-31.9	-33.0	-1.1
	60 Hour PAV	-26.5	-31.2	-4.7
Blend R-4	**20 Hour PAV**	-33.7	-38.7	-5.0
	40 Hour PAV	-29.3	-36.4	-7.0
	60 Hour PAV	-23.1	-35.6	-12.5
Blend R-5	**20 Hour PAV**	-35.5	-35.9	-0.4
	40 Hour PAV	-29.9	-35.1	-5.2
	60 Hour PAV	-22.7	-35.1	-12.4
Blend R-6	**20 Hour PAV**	-35.1	-36.1	-1.0
	40 Hour PAV	-29.7	-34.4	-4.8
	60 Hour PAV	-24.1	-31.9	-7.8
Blend C-7	**20 Hour PAV**	-35.7	-35.2	0.5
	40 Hour PAV	-31.1	-34.4	-3.3
	60 Hour PAV	-24.7	-33.4	-8.7
Blend C-8	**20 Hour PAV**	-38.3	-35.6	2.8
	40 Hour PAV	-33.2	-34.7	-1.5
	60 Hour PAV	-28.5	-34.0	-5.4

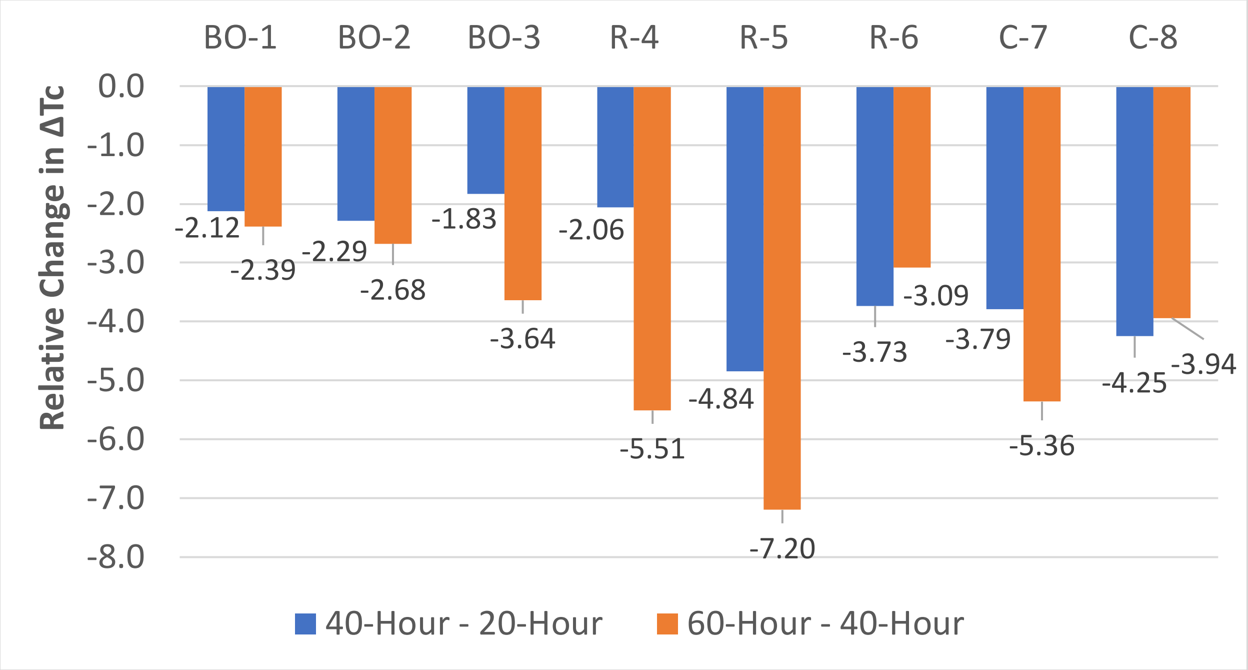

Figure 29: Relative incremental change in ΔTc.

From these results, it is apparent that the oil type is the dominant factor controlling low temperature performance. The compatibility of the polymer additives with the oil type seem to affect the magnitude of the relative change. All blends containing bio-oil show the least amount of relative change and magnitude in ΔTc with increasing PAV age. For all 3 bio-oil blends, the ΔTc never fell below -5.0, indicating strong low temperature performance even at high aging levels, and low aging susceptibility for low temperature cracking performance. REOB blends exhibit the worst compatibility except with PPA, where its relative change in magnitude is similar to that of the bio-oil blend containing PPA, BO-3, at high aging intervals. Blends R-4 and R-5, containing SBS and a combination of Elvaloy and PPA respectively, fell below the proposed threshold of -5.0 ΔTc after 40-hours of PAV aging, and continued to fall to about -12.5 ΔTc.

Furthermore, the REOB containing blends performed even worse than the oil-free control blends. This would suggest very poor long-term aging performance of REOB containing blends, and a very high aging susceptibility at low service temperatures. These results would further suggest that it would be better to not use REOB at all if low temperature performance is a critical performance metric for a pavement design if it is to be believed that highly negative ΔTc values correlate to poor low-temperature pavement performance. Therefore, the compatibility of the oil type with the polymer additive and/or the aging susceptibility of the oils themselves, appears to be the contributing factor to the aging susceptibility of the ΔTc value for the blends. In this case if aging susceptibility of the oil is the factor assumed to determine ΔTc performance, then it appears as though an oil with high complex shear modulus aging index, such as the bio-oil, performs better than an oil that has low or no complex shear modulus aging susceptibility, such as the REOB.

4.2.6: Bending Beam Rheometer Conclusion Summary

- ΔTc has been shown in literature to be a good indicator of aging susceptibility of oil-modified binders.
- An accepted limit on ΔTc has not been fully implemented for asphalt binders, but a minimum ΔTc of -5.0 °C has been suggested in literature [16]. This proposed limitation suggests relaxation rate is the primary mechanism responsible for low-temperature cracking performance.
- In this study, all blends, including the controls, had ΔTc values that became more negative with increasing PAV age as can be seen in **Table 10**.
- The oil type is the dominant factor controlling low temperature performance. The compatibility of the polymer additives with the oil type affects the magnitude of the relative change at extended ages.

- For all 3 bio-oil blends, the ΔTc never fell below -5.0, indicating strong low temperature performance even at high aging levels, and low aging susceptibility for low temperature cracking performance.
- It would be better to not use REOB at all if low temperature performance is a critical performance metric for a pavement design if it is to be believed that highly negative ΔTc values correlate to poor low-temperature pavement performance.
- If the aging susceptibility of an oil is the factor assumed to determine ΔTc performance, then it appears as though an oil with high complex shear modulus aging index, such as the bio-oil, performs better than an oil that has low or no complex shear modulus aging susceptibility, such as the REOB.

4.2.7: Bitumen Bond Strength Testing Results

Samples were prepared for both dry and wet conditioning as described in section 3.3: Binder Formulation and Testing Summary. Pull of tensile strength was then plotted as an average of 4 replicate tests per sample for each blend for both conditions so conditioning conditions could be evaluated between blends. These results are plotted in **Figure 30**, error was calculated using 90% confidence using the following equation:

$$Error\ (90\%\ confidence) = 1.645 * \frac{\sum \sigma_i}{\sqrt{n}}$$

$$where\ \sigma_i = standard\ deviation\ of\ the\ samples$$

$$and\ n = number\ of\ replicates.$$

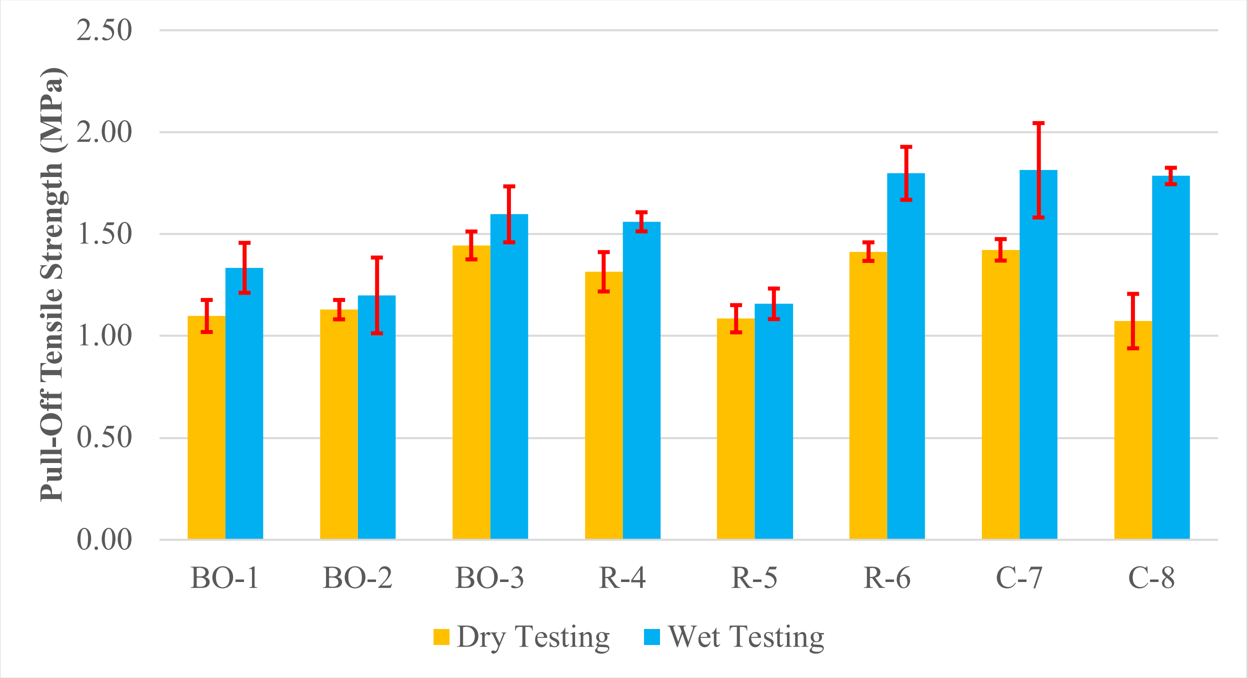

Figure 30: Dry and wet pull of tensile strength results from BBS testing for all blends.

Overall, for all samples, the pull-off tensile strength varied within a range of 1 MPa ± 0.75 MPa for both the wet and dry curing conditions. Blends BO-1 and BO-2 showed very little difference in pull-off tensile strength while BO-3 showed slightly more pull-off strength. This same trend can be attributed to good compatibility of the bio-oil and REOB with PPA, because blend R-6 confirms this. REOB blends tended to show better compatibility with SBS and PPA when the pull-off strength is compared to that of the bio-oil blends containing SBS and PPA, BO-1 and BO-3. The control blend C-7 with SBS, showed one of the highest dry pull-off strengths, only rivaled by blend BO-3 and R-6 for both wet and dry conditions. Wet testing conditions showed generally increased pull-off tensile strengths compared to dry conditioning. This is likely attributed to extended curing time and a slightly cooler testing temperature of 20°C versus 26°C between the wet and dry testing, respectively. Accounting for the testing temperature differences and the variability between samples, none of the blends show any particular detrimental performance to pull-off tensile strength.

4.2.8: Bitumen Bond Strength Conclusion Summary

- For all samples, the pull-off tensile strength varied within a range of 1 MPa ± 0.75 MPa for both the wet and dry curing conditions.
- There appears to be good compatibility in Blends BO-3 and R-6, containing only PPA polymer with bio-oil and REOB, respectively, and blend R-4, containing REOB and SBS.
- Compared to the control blends, all oil-containing blends exhibited similar pull-off tensile strengths in the dry conditions. The control blends showed the highest relative pull-off strength compared to the oil containing blends after wet conditioning. This indicates that the oils have a detrimental effect on moisture susceptibility of the blends.
- Wet testing conditions showed generally increased pull-off tensile strengths compared to dry conditioning. This is likely attributed to extended curing time and a slightly cooler ambient room testing temperature of 20°C for wet testing versus 26°C for dry testing.

Chapter 5: Summary of Findings and Conclusions

5.1: Summary of Findings

The findings presented in this section summarize the findings made at the end of each testing section.

1. Phase 1 of this study first investigated the aging susceptibility of the oil modifiers themselves used in asphalt blends to increase low temperature performance. It was discovered that the bio-oil, ANOVA 1055, exhibited nonlinear high aging/oxidative susceptibility in terms of its complex shear modulus aging index. REOB on the other hand showed no appreciable aging/oxidative susceptibility in terms of its complex shear modulus aging index. The phase angle aging indices also showed non-linear behavior for the bio-oil and again no appreciable change for the REOB. This lack of aging susceptibility in the REOB is thought to be due to the presence of anti-oxidants which are often used in engine oils from which REOB is derived. Because the oils showed variable aging sensitivity, blends were produced to see if the aging susceptibility of the oil itself had any effect on the intermediate and low temperature properties of the asphalt blends containing both polymers and oils.

2. After blends were produced with various polymers and quantities of oils to achieve similar low-temperature PG grades, they were tested for aging susceptibility using frequency sweeps, elastic recovery tests, and BBS tests at intermediate temperatures, and BBR tests at low temperatures. The frequency sweeps showed that for all blends aging susceptibility was most prominent when tested at lower frequencies. Higher frequencies tended to show more similar aging susceptibilities. Bio-oil which showed aging susceptibility, also caused

blends containing SBS to have far more pronounced effects on the complex shear modulus aging susceptibility. REOB on the other hand which showed no appreciable aging susceptibility, caused blends containing Elvaloy and PPA to exhibit asymptotic behavior in terms of complex shear modulus aging susceptibility after about 40-hours of PAV aging. Blends containing SBS showed the greatest sensitivity to aging depending on the oil type used in the blend, with bio-oil showing the greatest sensitivity, REOB showing the least, and the control showing slightly higher sensitivity than when compared to the REOB blend.

3. Elastic recovery results were interpreted as good when higher %recovery was associated with higher maximum shear stress at intermediate temperatures. This implies that a binder with these properties is able to recover more strain even after an application of high stress, since this test is strain controlled. This response, however, says nothing about the fatigue life. Blends containing PPA but no Elvaloy exhibited increased %recovery aging susceptibility for both oil types at all PAV ages occurring at relatively high shear stresses. Bio-oil with SBS (BO-1) shows consistent improved elastic recovery performance relative to the unaged blend even at very high internal shear stresses at intermediate temperatures. This, however, means it exhibits very high aging susceptibility in terms of maximum internal shear stress. These results are consistent with the observed complex shear modulus aging index for blend BO-1, which exhibited the highest susceptibility to aging, and therefore a correspondingly high complex shear modulus at increased age. Compared to the SBS blend containing bio-oil, BO-1, blend R-4 and C-7 showed very little aging susceptibility in terms of %recovery for all PAV ages. The REOB blend containing SBS, R-4, the REOB blend containg Elvaloy and PPA, R-5, and both control blends, C-7 and C-8, after 60-hours of PAV aging exhibited nearly no observable difference in %recovery

aging susceptibility from the unaged blends. In other words, the effects of long term aging on these blends in terms of %recovery is minimal.

4. ΔTc has been shown in literature to be a good indicator of aging susceptibility of oil-modified binders. An accepted limit on ΔTc has not been fully implemented for asphalt binders, but a minimum ΔTc of -5.0 °C has been suggested in literature [16]. This proposed limitation suggests relaxation rate is the primary mechanism responsible for low-temperature cracking performance. In this study, all blends, including the controls, had ΔTc values that became more negative with increasing PAV age. The oil type is the dominant factor controlling low temperature performance. For all 3 bio-oil blends, the ΔTc never fell below -5.0, indicating strong low temperature performance even at high aging levels, and low aging susceptibility for low temperature cracking performance. It would be better to not use REOB at all if low temperature performance is a critical performance metric for a pavement design if it is to be believed that highly negative ΔTc values correlate to poor low-temperature pavement performance. If the aging susceptibility of an oil is the factor assumed to determine ΔTc performance, then it appears as though an oil with high complex shear modulus aging index, such as the bio-oil, performs better than an oil that has low or no complex shear modulus aging susceptibility, such as the REOB.

5. The bitumen bond strength (BBS) test is used to quantify the tensile force needed to remove a pull-off stub that is bonded to an aggregate substrate with asphalt binder. The test is used to quantify the bonding properties of the asphalt binder and the compatibility between aggregate types and asphalt binders. The pull-off tensile strength is measures over a variety of environmental conditions and curing times to provide information about the bond

strength at the interface between the substrate and asphalt binder. For all samples, the pull-off tensile strength varied within a range of 1 MPa ± 0.75 MPa for both the wet and dry curing conditions. There appears to be good compatibility in Blends BO-3 and R-6, containing only PPA polymer with bio-oil and REOB, respectively, and blend R-4, containing REOB and SBS. Compared to the control blends, all oil-containing blends exhibited similar pull-off tensile strengths in the dry conditions. The control blends showed the highest relative pull-off strength compared to the oil containing blends after wet conditioning. This indicates that the oil type may have a detrimental effect on moisture susceptibility of the blends. Wet testing conditions showed generally increased pull-off tensile strengths compared to dry conditioning. This is likely attributed to extended curing time and a slightly cooler ambient room testing temperature of 20°C for wet testing versus 26°C for dry testing.

Therefore, ultimately, it appears as though the aging susceptibility of asphalts depends on the aging susceptibility of the oils themselves, the aging susceptibility of the polymers themselves, and the compatibility between the oil and polymer additive package. In some cases, certain properties exhibited increased aging susceptibility when the oil was susceptible to aging, and other times this aging phenomenon was beneficial as was seen in the BBR testing results for ΔTc. Depending on the critical design requirements, each oil has its advantages for certain responses.

5.2: Conclusions

Based on the summary of findings, the following conclusions can be states:

1. Oils have significantly different aging susceptibilities and their aging susceptibility is not a good predictor of blends' aging.
2. There are significant interactions between oils and polymers that controls the aging of the blends. Therefore, aging of blends is necessary for reliable determination of blends' performance.
3. There appears to be negative effects on adhesion of blends containing oils as compared to the control blends after wet conditioning. This should be further investigated to avoid damage problems.

5.3: Recommendations for Further Studies

Based on the scope of this study, there are recommendations for further study that would be beneficial to this research. They are as follows:

1. Why does the phase angle for the bio-oil increase with age relative to the unaged condition up to 16-hours in the PAV, then decrease below that of the unaged condition at 24-hours PAV as would be normally expected to occur? This is particularly unusual because the complex shear modulus observed is generally much greater for the same phase angle between ages, even with observed variance in acquired data between replicates.
2. As an extension to the first point, Fourier Transform Infrared Spectroscopy (FTIR) and/or Gel Permeation Chromatography (GPC) should be used to determine the chemical nature of the aging reaction in the bio-oil. Subsequently, this could also be performed on the blends used in this study to determine what aspects of the asphalt, polymer, and oil are aging, and at what rates to better understand the combined aging/oxidation.

3. Other oils should be tested as well. Oil producing companies research and develop new products all of the time, with varying properties that they decide will likely work best with asphalt. These oils should be tested for aging susceptibility, and whether or not the aging susceptibility of the oil and polymers as a whole have significant impacts on performance properties of asphalt blends. This is important because the aging and oxidation and subsequent breakdown of asphalt properties is the main cause of observed pavement failures.

References

[1] "Engineering Overview," *National Asphalt Pavement Association*. [Online]. Available: http://www.asphaltpavement.org/index.php?option=com_content&view=article&id=14&Itemid=33. [Accessed: 01-Oct-2018].

[2] Office of Materials and Road Research Pavement Management Unit, "Mn/DOT Pavement Distress Identification Manual," no. July, 2011.

[3] R. Moraes and H. Bahia, "Developing Simple Indices for Cracking Resistance of Asphalt Binders at Intermediate and Low Temperatures." Transportation Research Record, 2018.

[4] Y. Ruan, R. R. Davison, and C. J. Glover, "Oxidation and viscosity hardening of polymer-modified asphalts," *Energy and Fuels*, vol. 17, no. 4, pp. 991–998, 2003.

[5] R. Moraes and H. U. Bahia, "Effect of Mineral Filler on Changes in Molecular Size Distribution of Asphalts During Oxidative Aging," *Road Mater. Pavement Des.*, vol. 0629, no. November, pp. 1–18, 2015.

[6] N. Dehouche, M. Kaci, and K. A. Mokhtar, "Influence of Thermo-Oxidative Aging on Chemical Composition and Physical Properties of Polymer Modified Bitumens," *Constr. Build. Mater.*, vol. 26, no. 1, pp. 350–356, 2012.

[7] H. Liu, P. Hao, H. Wang, and S. Adhikair, "Effects of Physio-Chemical Factors on Asphalt Aging Behavior," *J. Mater. Civ. Eng.*, vol. 26, no. 1, pp. 190–197, 2014.

[8] Y. Li, R. Moraes, E. Lyngdal, and H. Bahia, "Effect of Polymer and Oil Modification on the Aging Susceptibility of Asphalt Binders," *Transp. Res. Rec. J. Transp. Res. Board*, vol. 2574, no. 2574, pp. 28–37, 2016.

[9] S. Weigel and D. Stephan, "Differentiation of bitumen according to the refinery and ageing state based on FTIR spectroscopy and multivariate analysis methods," *Fuel*, vol. 208, pp. 655–661, 2017.

[10] D. J. Mensching, A. Andriescu, C. Decarlo, X. Li, and J. S. Youtcheff, "Effect of Extended Aging on Asphalt Materials Containing Rerefined Engine Oil Bottoms," *Transp. Res. Board TRB 2017 Annu. Meet.*, pp. 1–18, 2017.

[11] A. Golalipour, "Investigation of the Effect of Oil Modification on Critical Characteristics of Asphalt Binders." ProQuest, 2013.

[12] ASTM, "Standard Test Method for Determining the Rheological Properties of Asphalt Binder Using a Dynamic Shear Rheometer (ASTM D 7175-08)," *Annu. B. Am. Soc. Test. Mater. ASTM Stand.*, no. C, pp. 1–16, 2013.

[13] AASHTO, "Standard Method of Test for Measuring Asphalt Binder Yield Energy and Elastic Recovery Using the Dynamic Shear Rheometer (AASHTO TP 123-16)," pp. 1–9, 2016.

[14] R. M. Anderson, G. N. King, D. I. Hanson, and P. B. Blankenship, "Evaluation of the Relationship between Asphalt Binder Properties and Non-Load Related Cracking," *J. Assoc. Asph. Paving Technol.*, vol. 80, pp. 615–663, 2011.

[15] T. Bennert, "Asphalt Binder and Mixture Properties Produced with REOB Modified Asphalt Binders," in *FHWA Asphalt Binder Expert Task Group*, 2015.

[16] T. Bennert, C. Ericson, D. Pezeshki, and R. Corun, "Fatigue Performance of Re-Refined Engine Oil Bottom–Modified Asphalt," *Transportation Research Record: Journal of the Transportation Research Board*, vol. 2574, no. 2574. pp. 1–16, 2016.