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# Performance evaluation of polymer modified asphalt binders utilizing soybean-derived materials

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**Performance evaluation of polymer modified asphalt binders utilizing soybean-derived materials**

by

**Conglin Chen**

A dissertation submitted to the graduate faculty  
in partial fulfillment of the requirements for the degree of  
**DOCTOR OF PHILOSOPHY**

Major: Civil Engineering (Civil Engineering Materials)

Program of Study Committee:  
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The student author, whose presentation of the scholarship herein was approved by the program of study committee, is solely responsible for the content of this dissertation. The Graduate College will ensure this dissertation is globally accessible and will not permit alterations after a degree is conferred.

Iowa State University

Ames, Iowa

2018

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This work is dedicated to my parents, my parents in law, and my husband,

*Dongfeng Chen, Yan Zhao, Xiaolin Zhang, Demei Liu, and Yang Zhang*

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## ABSTRACT

Polymer modified asphalt binders have been widely used in the construction of flexible pavement over the past few decades. Due to the economic and environmental concerns of using the traditional petroleum-derived polymers, there is a demand for developing sustainable alternatives that can replace the petroleum-derived polymers for use in asphalt pavements. Triglyceride molecules from vegetable oils have been considered as important renewable resources, which can be used as biomonomers and be polymerized into bioadvantaged polymers with similar properties to petroleum-derived monomers and polymers. In this research, non-food soybean oil is selected as a starting point to produce bioadvantaged polymers because it is the most affordable and abundant locally produced vegetable oil in the United States. The polymerized soybean oil has rubbery properties and can be used as an alternative to petroleum-derived butadiene in the styrenic block copolymers. In the laboratory, the bioadvantaged polymer poly(styrene-block-acrylated epoxidized soybean oil) (PS-PAESO) with various polystyrene molecular weights and contents are successfully produced through reversible addition-fragmentation chain transfer (RAFT) polymerization. Their modification effects in asphalt binders are investigated and evaluated via laboratory testing. The testing results are used in the response surface modeling (RSM) for the development of prediction models with the intent to optimize the formulation of the biopolymer for asphalt pavement applications in warm climate regions. The testing results show the great potential of using biopolymers as sustainable alternatives to commercial styrene-butadiene polymers as it improves the neat asphalt binder's stiffness, elasticity, and rutting resistance at the same polymer dosage levels. The study on economic and environmental implications of biopolymers demonstrate that they are more cost-effective, environmentally friendly, and safer to produce

than petroleum-derived styrenic polymers. Using biopolymers in asphalt modification has shown great success, however, there has been no literature so far discussing the use of acrylated epoxidized soybean oil (AESO) alone as an additive in asphalt binders, while many relevant researchers have conducted studies of using bio-based oil in asphalt binders. To study the modification effects of AESO in asphalt binders, laboratory produced AESO and commercially available AESO are used at various concentration levels in the neat asphalt binder, and their performances are evaluated through a comprehensive binder investigations including rotational viscosity, performance grading, rheological, aging susceptibility, high temperature storage stability testing, etc. The results reveal that AESO is able to be used as a modifier in asphalt performance modifications by softening the asphalt binder and reducing the binder's stiffness. Furthermore, laboratory produced AESO performs superior to commercial AESO in terms of low temperature properties and fatigue life at the same dosage level without showing any separation problems. The findings also show that sufficient high dosage level of laboratory produced AESO can dramatically change the rheological properties of the neat asphalt binder with significant improvements on the resistance to fatigue damage and thermal cracking. Overall, the preliminary laboratory investigations on using soybean-derived polymers and additives in asphalt modifications have shown the feasibility of turning non-food soybean oil into more useful and valuable new materials. The results presented in this work may provide insights into the asphalt modifications using soybean-derived modifiers.

## CHAPTER 1. GENERAL INTRODUCTION

Polymer modified asphalt binders are often used in the construction of flexible pavements under high traffic volume and extreme weather conditions to enhance their performance and/or extend their in-service longevity [1–3]. Even though the price of polymer modified asphalt binder is higher than that of conventional neat asphalt binders, the long-term economic benefits of utilizing polymer modified asphalt binders are considerable [4]. Due to the shortage and fluctuating prices of petroleum-derived polymers, there is a demand to develop cost-effective, sustainable, and environmentally friendly bio-derived polymers that could be used as sustainable alternatives in asphalt paving industry [5–7]. Bio-based oil and renewable additives that can be derived from biomass materials are currently one of the top focus areas for pavement researchers. Vegetable oils such as soybean oil, sunflower oil, castor oil, palm oil, safflower oil, linseed oil, and canola oil are important renewable resources and commonly used as biofeedstocks to synthesize biopolymers through polymerization techniques [8–10]. At Iowa State University, bioadvantaged polymers were successfully synthesized using a biomonomer derived from soybean oil. The applications of using bioadvantaged polymers and additives in asphalt pavement can have a significantly positive impact in the asphalt industry.

### 1.1. Modifiers in asphalt

In general, there are three types of polymers that are commonly used in asphalt pavement applications including thermoplastic elastomers (e.g. styrene-butadiene (SB), styrene-butadiene-styrene (SBS), styrene-butadiene rubber (SBR), and styrene-isoprene-styrene (SIS)) and plastomers (e.g. polyethylene (PE), ethylene-vinyl acetate (EVA), and polypropylene (PP)) [11–14]. The rheological properties of the neat asphalt binders can be significantly changed by using polymers or additives [15]. After adding polymers or additives, the performance such as stiffness,



flexibility, elasticity, and stress relaxation of asphalt binder can be improved [16]. The concentrations for using additives or polymers for asphalt modification are usually 3 to 7% by weight of the modified binders [2,17–19]. In order to achieve homogeneous blends, high temperature and high shear speed are usually required when blending these aforementioned polymers with asphalt binders.

Among the wide variety of polymers, SBS and SBR are two of the most common polymers used in asphalt modification practices [17,20,21]. Because they can effectively bump the high temperature performance grade of neat asphalt binders by increasing the stiffness, which improves the asphalt binder's resistance to rutting [21]. Meanwhile, the styrenic block copolymers can entangle with the asphalt molecule to develop an effective elastic network during asphalt modification, and thereby improved elastic properties can be achieved with enhanced resistance to rutting and fatigue cracking [21].

SB and SBS are block copolymers that consist of two different monomers: styrene and butadiene. They are reacted and chained together to form a copolymer through polymerization with properties of both materials. In the copolymer, polystyrene is the hard domain that provides the stiffness, and polybutadiene is the soft and rubbery domain that offers elasticity when cooperating with asphalt [21]. Butadiene, as one of the most important feedstocks for producing SB and SBS polymers, is a co-product in the production of ethylene from crude oil [7]. As shale gas feedstocks become more dominant in the production of ethylene, the production of butadiene keeps decreasing in the United States (U.S.) that may lead to the shortage of butadiene supply [6,22,23]. Additionally, the commercially available polymers and additives used in asphalt modification are mostly inorganic and petroleum based, which has drawn environmental concerns [24,25]. Due to these existing problems, there is a need to develop bioadvantaged polymers or

additives that can be used as sustainable alternatives in asphalt modification with similar or better modification effects.

## 1.2. Bioadvantaged polymer

Bioadvantaged polymers are known as polymers that are produced directly from biofeedstocks (e.g. corns or soybeans) to plastics through chemical polymerization techniques. Bioadvantaged polymers can be used as potential substitutes for petroleum-derived materials [26]. Vegetable oils such as soybean, sunflower, castor, palm, safflower, linseed, and canola oils are commonly used as biofeedstocks to chemically synthesize biopolymers [8,9]. They are also known as triglyceride oils and recognized as important renewable resources due to the special chemical structure. Triglyceride is one of the main compositions in vegetable oils that consists of three fatty acid chains connected by one glycerol center [8,27–29]. They can be polymerized into polymers with flexible and rubbery properties to replace the petroleum-derived butadiene in styrenic copolymers. In this research, non-food soybean oil was chosen to be used as biofeedstocks due to its local availability in the Midwest of the U.S. However, the unsaturated fatty acids in triglycerides are not active enough for polymerization [30]. To improve the activity, epoxidation reaction can be applied to modify the C=C double bonds in triglycerides to yield epoxidized soybean oil (ESO) [30–32]. Since the reactivity is improved, they can be easily functionalized and/or polymerized. Biomonomer AESO and biopolymer PAESO have been successfully produced by using ESO following by acrylation reaction and reversible addition-fragmentation chain transfer (RAFT) polymerization [31,33]. Furthermore, AESO was also used to be copolymerized with styrene to produce poly(styrene-AESO) and poly(styrene-AESO-styrene) that can be used in asphalt modification and substitute SB and SBS via RAFT polymerization [6,34].

### 1.3. Soybean-derived monomer

There have been extensive research studies focusing on the use of soybean oil as biofeedstocks to yield soybean-based materials, because it is one of the most affordable and abundant vegetable oil in the U.S. In industry, soybean oil is commonly used as AESO through epoxidation of soybean oil and acrylation of ESO [30–32]. The AESO monomers can be subsequently stored and used as surface coating materials or polymerized to thermoset biopolymers for adhesives and asphalt modification [30–32]. In the study of biopolymer PS-PAESO, the asphalt binder performance test results have shown the great potential of using biopolymers as alternatives to petroleum-derived polymers. However, there is no literature about the use of AESO alone as an additive in asphalt modification. Currently, researchers focus on exploring the benefits of using bio-based oil in the pavement industry. In general, it was found that bio-oil is capable to decrease the stiffness of the neat asphalt binder as improving the binder's resistance to fatigue and thermal cracking at intermediate and low temperatures [35–38]. Additionally, polymerization of the monomer was determined to occur automatically in asphalt modification under air and heat conditions by significantly changing the rheological properties of the neat asphalt binder [39]. Therefore, conducting the study on the evaluation of using AESO in asphalt modification will be beneficial to determine if AESO can be used in asphalt performance modification and to examine if polymerization of AESO can occur during asphalt blending process through rheological characterizations.

### 1.4. Organization of dissertation

The objectives of this research are to evaluate and determine the effectiveness of bio-derived polymers or additives in asphalt modification, and how they affect the performance of neat asphalt binder due to modification through a comparison with commercially available counterparts. This

dissertation consists of six chapters: a general introduction, four technical articles, and conclusions and recommendations for future research. Chapter 1 gives a general introduction about the commonly used modifiers in the asphalt industry, why bio-derived materials are needed in asphalt modification, and the bio-derived polymers and additives used for this research. Chapter 2 demonstrates the development of bioadvantaged polymer, the economic and environmental benefits of the bioadvantaged polymers, and the modification effects of using bioadvantaged polymers PS-PAESO with different polystyrene parameters in the asphalt binder. Chapter 3 introduces utilizing response surface modelling to optimize the formulation of PS-PAESO polymer based on the modified binders' performance grading results and the verification of the prediction models. The possibility of using biomonomer AESO in asphalt modification is demonstrated in Chapter 4 through a full asphalt binder investigation including viscosity, temperature-frequency sweep, bending beam rheometer, linear amplitude sweep, and storage stability testing. In Chapter 5, the rheological properties and the effects of aging on AESO modified binders at various concentration levels are investigated. Finally, the general conclusions with recommendations for further work are presented in Chapter 6.

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**CHAPTER 2. PRELIMINARY INVESTIGATION OF BIOADVANTAGED POLYMERS  
AS SUSTAINABLE ALTERNATIVES TO PETROLEUM-DERIVED POLYMERS  
FOR ASPHALT MODIFICATION**

Modified from a paper published in *Materials and Structures*<sup>1</sup>

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### 2.1. Abstract

Due to recent volatility in the petroleum market, the possibility of using sustainable alternative materials as substitutes has gained great interest and viability. The purpose of this research is fourfold: to demonstrate how bioadvantaged polymers are produced using non-food soybean oil and showcase their economic and environmental value; to evaluate how they perform rheologically in asphalt against commonly used petroleum-derived polymers; to optimize the formulation of the bioadvantaged polymer for warm climate regions pavement applications based on the grading results, and to verify the modification effects of optimized bioadvantaged polymer by running performance grade tests. The study on economic and environmental implications demonstrated that poly(styrene-acrylated epoxidized soybean oil) (PS-PAESO) is more cost-effective, environmentally friendly, and safer to produce than SB polymer. The commercially produced petroleum-derived styrene-butadiene (SB) diblock polymer was used for comparison, while the laboratory produced bioadvantaged polymers were targeted at 1.25 MDa molecular weight of PS-

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PAESO diblock copolymers that consist of PAESO with various polystyrene (PS) molecular weights and contents. The effectiveness and rheological performance of the polymer modified asphalt binders were evaluated through binder investigations. Rheology test results indicated that the bioadvantaged polymers improved the stiffness, elasticity, and rutting resistance of the neat asphalt binder. Best-fit prediction models were developed through response surface modeling to optimize the PS-PAESO formulation in terms of PS content and molecular weight and the models were verified to be highly accurate based on the grading results. It was found that lower polystyrene content in PS-PAESO polymer could be beneficial in the improvement of critical high temperatures.

## 2.2. Introduction

Flexible pavement designs for high traffic volume and extreme weather conditions must meet special requirements for asphalt binder rheological properties [1]. Since rheological performance of asphalt binders relate directly to field performance, materials such as polymers were developed and used as modifiers in asphalt binder so asphalt mixes (consisting of the asphalt binder and aggregate/stone) could meet the needs for higher traffic volumes and extreme weather conditions, i.e. very high temperatures [2–4]. Polymers help modify asphalt rheological properties such that there is improved performance against rutting, fatigue, and thermal susceptibility, while increasing adhesion between asphalt binder and the aggregate. Polymers also provide improved resistance to low temperature thermal cracking [4,5]. Due to these advantages from polymer incorporation in asphalt binder, there is a substantial decrease in maintenance and rehabilitation applications because the increased use of polymer modified binders (PMBs) in the asphalt paving industry minimizes deterioration and increases in-service longevity of pavements [6,7].

### 2.2.1. Historical use of PMBs

Polymers commonly used over the past few decades in the asphalt industry include thermoplastic elastomers (e.g. styrene-butadiene (SB), styrene-butadiene-styrene (SBS), styrene-butadiene rubber (SBR), and styrene-isoprene-styrene (SIS)) and plastomers (e.g. polyethylene (PE), ethylene-vinyl acetate (EVA), and polypropylene (PP)) [2, 9–11]. The earliest use of natural and synthetic polymers can be found in patents dating from 1843 [10]. A patent detailing the use of 1% by weight of latex from the balata plant in an asphalt paving mixture was granted to Samuel Whiting in 1873. A French asphalt paving company constructed rubberized asphalt roads in 1902 [9]. After World War II, PMBs gained attention in European countries such as Britain and France. Test sections using PMBs were constructed in Britain and France and papers on the use of PMBs were published in Eurobitume conferences starting in 1978 [7]. In North America, polychloroprene latex began to be used in road paving for bitumen modification in the 1950s [10]. In 1965, the first commercial SBS product was developed in the United States (U.S.) [12]. In the following ten years, US departments of transportation (DOT) such as the Utah DOT, Kentucky DOT, Alabama DOT, Colorado DOT, and Texas DOT were using PMBs in constructing test road sections. In their reports, the application of different polymers (e.g. SBS, SBR, SB, and EVA) in test road sections showed substantially improved rutting resistance, reduced fatigue cracking, and mitigated thermal cracking [9, 13–15].

### 2.2.2. Economics of polymer modified asphalt binder

Although there are benefits of using PMBs, economics and environmental concerns still play a major role in the selection of paving technology [7, 11, 16]. The price of PMBs is higher than that of conventional neat asphalt binder on a per liquid ton, however, the long-term economic benefits of using PMBs cannot be ignored. To evaluate the overall long-term economic efficiency

of PMB roadways, Buncher and Rosenberger [17] did investigations on the field performance and economic values of 84 pairs of PMB and unmodified hot-mix asphalt (HMA) roadways in the U.S. and Canada by life cycle cost analysis. According to their study, the initial cost during construction for a PMB roadway is approximately 2-6% higher than the cost of a conventional neat asphalt binder roadway [17]. This difference in cost is offset by the reduction in maintenance costs (e.g. resurfacing and structural overlay) in the following 10 to 34 years as a PMB roadway maintenance costs are 19.9-62.1% lower than the maintenance costs for a conventional neat asphalt binder roadway over the same time span [17]. As a result, through life-cycle cost analysis, the total life-cycle cost saving from a PMB roadway is 6.5-15.5% lower than from a conventional neat asphalt binder roadway for high volume facilities [17]. Along with the advantages of better resistance to distresses and extended service life, increased interest in polymers for asphalt modification has also been observed in the research community and the paving industry [18].

### **2.2.3. Need for bioadvantaged polymers**

Among the wide variety of polymers used for modifying asphalt binder, thermoplastic elastomers, SB and SBS have proved to be the most commonly used and most successful polymers for asphalt binder modification followed by SBR [5, 19, 20]. They are petroleum-derived thermoplastic elastomers as the primary ingredient of making these polymers: butadiene, which is a co-product in the production of ethylene from crude oil [21]. Global Business Intelligence Research [22] reported that butadiene demand in the U.S. was 1.9 million tons with about 330 kilotons imported from foreign producers in 2012. They also predicted the demand of butadiene will keep climbing and the amount of imports will hit approximately 530 kilotons by 2020 [22]. Butadiene is a co-product that is obtained from liquid feedstocks (i.e. crude oil) with ethylene production. Ever since the U.S. shale gas boom occurred, gas feedstocks have become more

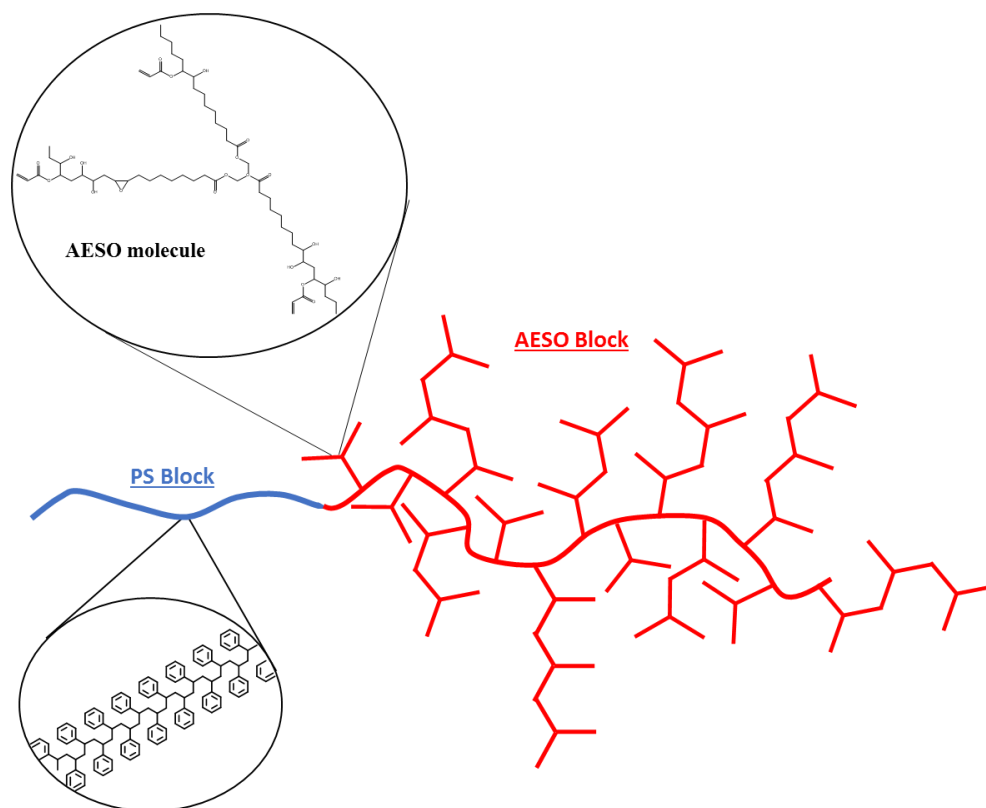
dominant in the production of ethylene that does not yield butadiene as a co-product, thus decreasing the amount of butadiene produced in the U.S. This may make the U.S. more dependent on butadiene imports [23]. Due to the increased reliance on shale gas for producing ethylene, butadiene shortages may occur and cause price fluctuations of petroleum-derived polymers in the chemical industry [24]. Because roadways are one of the largest applications of butadiene, butadiene shortages and price fluctuations of petroleum-derived polymers offer an opportunity for producing bio-derived and bioadvantaged polymers as alternatives in asphalt modification.

#### **2.2.4. Bioadvantaged polymers derived from soybean oil**

Bio-derived polymers are also known as bio-based and bioreplacement polymers, which are produced by upgrading complex molecules from nature such as trees, plants, and animals to simple monomers that chemically match monomers derived from petroleum through synthetic biology and advanced catalysis [25–27]. Whereas, bioadvantaged polymers refer to polymers that are produced directly from biofeedstocks (e.g. corn or soybeans) and can be produced to plastics through chemical polymerization techniques as potential substitutes for petroleum-derived materials [27]. Instead of making the raw complex molecules into simple monomers, it is far more cost-effective to use them directly in the production of bioadvantaged polymers by polymerization [27].

Vegetable oils (e.g. linseed oil, corn oil, cottonseed oil, and soybean oil) are biodegradable, renewable, cost-effective, and less toxic than crude oil, which makes them viable and important raw biomonomer resources to be chemically synthesized into bioadvantaged polymers [21, 23]. Vegetable oils are composed of triglyceride molecules that consist of three fatty acid chains and a glycerol backbone, therefore, with some chemical modifications they can be synthesized into a rubbery component to replace the petroleum-derived butadiene in block copolymers [28–30]. Non-

food soybean oil is one of the most abundant vegetable oils in the U.S. and was chosen to be the monomeric feedstock in this research. To improve the polymerization reactivity of the natural carbon-carbon double bonds in soybean oils, epoxidation (ring opening) method was conducted to produce epoxidized soybean oil (ESO) followed by acrylation of ESO to yield acrylated epoxidized soybean oil (AESO) [29, 31]. The bioadvantaged polymer is an AB diblock copolymer that consists of hard and stiff polystyrene domains and soft and rubbery domains of PAESO [23, 29]. The chemical structure of the poly(styrene-acrylated epoxidized soybean oil) (PS-PAESO) polymer is shown in Figure 2.1, which has a similar mechanism to SB polymer.



**Figure 2.1. Bioadvantaged polymer PS-PAESO chemical structure.**

In this research, the biomonomer AESO was copolymerized with styrene at different molecular weights and contents of polystyrene (PS) to optimize the PS-PAESO formulation and obtain equal or better performance than petroleum-derived block copolymers (*e.g.* SB and SBS) in asphalt

modification. The methods used to characterize the bioadvantaged polymers are presented and the modification effects of the bioadvantaged polymers on the asphalt binder rheology are shown and summarized. Using the results from grading at high and low temperatures, statistical surface regression modeling was done to develop prediction models for use in optimizing the formulation of the PS-PAESO. After the models were developed, one of the optimized formulations was created and used to modify the neat asphalt binder. This modified binder was then put through a binder grading investigation, and the models were verified. Lastly, this research presents the economic benefits and the environmental impacts from production up to use of PS-PAESO as an alternative to SB and SBS in the asphalt paving industry.

### **2.3. Objectives**

The main objectives of this research are as follows:

- To demonstrate how bioadvantaged polymers are produced using non-food soybean oil.
- To evaluate how laboratory produced bioadvantaged polymers perform rheologically in asphalt against commonly used petroleum-derived polymers.
- To optimize the formulation of the bioadvantaged polymer based on the performance grading results that can modify neat asphalt binder from PG 52-34 to PG 64-28 for warm climate regions pavement applications.
- To verify the modification effects of the optimized bioadvantaged polymers with proposed polystyrene parameters by running performance grade tests.

### **2.4. Development of bioadvantaged polymers for binder modification**

The raw materials needed for producing bioadvantaged polymer and the economic and environmental value of bioadvantaged polymer vs. traditional petroleum-derived polymer are demonstrated hereafter.

### 2.4.1. Materials used for production

Commercially available styrene was purchased and purified over basic alumina. The raw materials used as received in the reaction are ESO (contains 4000 ppm monomethyl ether hydroquinone as inhibitor), pyridine (catalyst, 99.8% purity), hydroquinone (inhibitor, 99% purity), and acrylic acid (contains 180-200 ppm MEHQ as inhibitor, 99% purity). AIBN (Azobisisobutyronitrile) as initiator, MEHQ (Methylhydroquinone, 99% purity), inhibitor remover, diethyl ether (ACS, grade), 2-phenyl-2-propyl benzodithioate (PPBD) as chain transfer agent (CTA), and sodium bicarbonate (white crystalline powder, certified ACS) were used as received without further purification. Chemical solvents used as reagents in the reaction are dioxane and toluene.

### 2.4.2. Production methods

The controlled/living free radical polymerization (CFRP) conducted to chemically synthesize the bioadvantaged polymers was reversible addition-fragmentation chain transfer (RAFT). Instead of using metal catalysts and initiators in traditional CFRP, i.e. Atom Transfer Radical Polymerization, that cannot be easily removed after polymers are formed, RAFT only requires organic chain transfer agents in the reaction, which is more environmentally friendly [29, 32]. Moreover, the polymer structure and polymer composition can be easily controlled and designed in RAFT and the desired molecular weight can be obtained in RAFT as well [23, 29]. These advantages are enabling RAFT to be a more widely used technique for polymer synthesis [33]. In this research, monomers (styrene and AESO), initiator (AIBN), CTA (PPBD) were mixed in solvent to synthesize PS-PAESO through RAFT polymerization [23, 34].

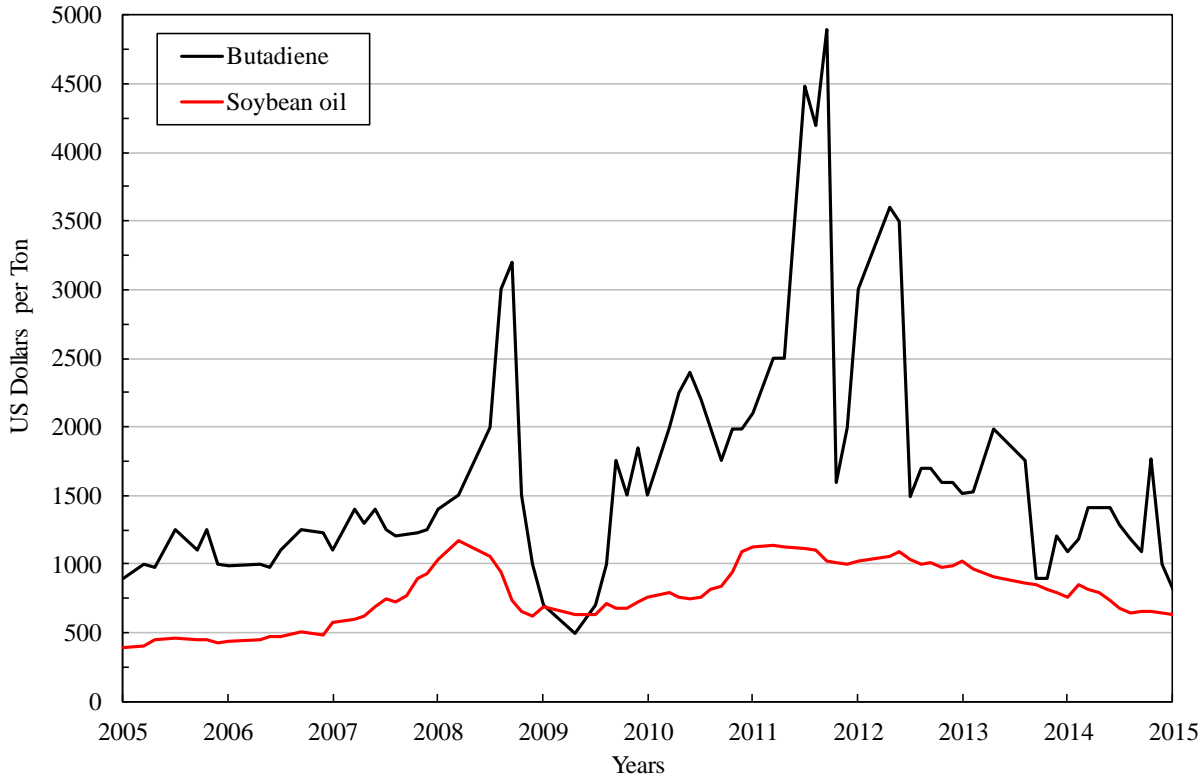


### **2.4.3. Economic and environmental implications of bioadvantaged polymers vs. Traditional petroleum-derived polymers in asphalt modifications**

The application of traditional petroleum-derived polymers can come with economic and environmental concerns [16]. The laboratory investigation was conducted to produce an economically competitive and environmental friendly alternative modifier for asphalt use. Besides the similar and even better modification effects of PS-PAESO, the bioadvantaged polymer is more environmentally friendly than the commercially available petroleum-derived SB polymer. As demonstrated, the petroleum-derived butadiene is produced as a co-product of the ethylene production from the steam cracking process that requires cracking temperatures between 790.0 to 830.0°C [35]. To compare with the AESO production, the reaction temperature is at 95.0°C [29], which indicates at least 90% heat energy savings. Currently, the U.S. is the only significant butadiene importer, butadiene needs to be stored under pressure as a liquefied or compressed gas during transportation that may cause safety issues [35] and has a transport cost of about \$300/ton. The supply chain of AESO mainly depends on non-food uses of soybean oil, which can be supplied domestically and shipped at ambient temperatures and pressure. Furthermore, the decomposition of petroleum-derived butadiene in nature is a lengthy process with toxic by-products that could deteriorate soils, pollute rivers, and poison animals [36]. Fu et al. [37] studied relevant environmental degradation properties of AESO. They conducted a soil burying experiment with AESO-based polymers and reported the degradation rate increases with increased AESO content in the polymer due to the biodegradability of AESO [37]. Therefore, the PS-PAESO bioadvantaged polymer is more biodegradable than commercial SB and SBS petroleum-derived polymers.

Soybean oil was chosen as a starting point to synthesize the bioadvantaged polymers since it is the most abundant locally produced vegetable oil in the U.S. In 2015, the U.S. was first in world

soybean production with 107 million metric tons (3.93 billion bushels) and the U.S. exported 43% of its total production [38]. Annually, about 80% of soybean oil is used for human food, 6% is used for animal feed, and 14% serves non-food uses like soaps, lubricants, and coating [36]. The idea of utilizing non-food soybean oil to copolymerize bioadvantaged polymers is turning the oil into more useful and valuable new materials [39]. On the contrary, global butadiene production is approximately 9 million metric tons where over 95% is produced as a by-product [35]. The use of natural gas instead of crude oil has tightened supplies of butadiene and influenced the price [40]. The price of SB or SBS polymers and the bioadvantaged polymer PS-PAESO mainly depends on the market prices of butadiene and soybean oil. Figure 2.2 presents a price comparison between butadiene and soybean oil in the past ten years [41–43]. This data illustrates the great economic potential of bioadvantaged polymers as alternatives with lower and more stable prices than that of traditional petroleum-derived polymers.



**Figure 2.2. Price comparison between butadiene and soybean oil from 2005 to 2015.**

### **2.5. Evaluation process of bioadvantaged polymers for use in asphalt binder modification**

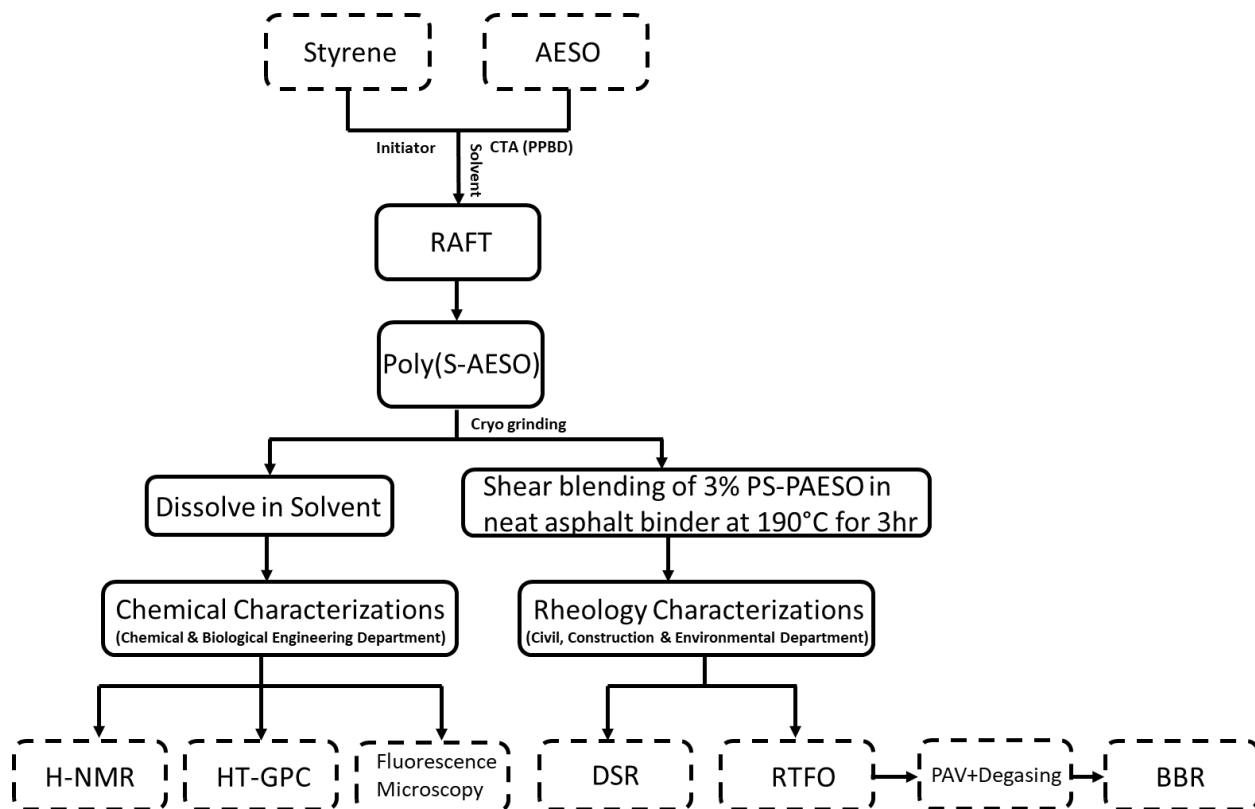
The expected-synthesized bioadvantaged polymers (PS-PAESO) were laboratory produced 1.25 MDa molecular weight (targeted molecular weight) of PS-PAESO with various PS molecular weight and contents at different lengths of reaction duration. The bioadvantaged polymers were used to modify a soft neat asphalt binder PG 52-34 from a Canadian crude source. The PS-PAESO modified blends were prepared at a dosage of 3% by weight of total blends [21, 23]. The modified blend codes with corresponding PS-PAESO bioadvantaged polymer polystyrene parameters are shown in Table 2.1. Shear blending was performed by utilizing a Silverson L4RT-A shear mixer with a square-hole high shear screen. All modified blends were shear blended at 3000 rpm shear rate and at blending temperature of 190°C for 3 hours according to previous research studies [21,

23]. For comparison purposes, the commercially available Kraton D1118 (polystyrene-block-polybutadiene diblock copolymer) polymer with 31% PS content was used to modify the same neat asphalt binder and shear blended by following the same blending procedure at the same dosage level for evaluation of modification effects [21, 44].

The laboratory produced bioadvantaged polymers were each partitioned into two portions. One portion was used for determining the analytical chemistry of the polymer, while the other portion was used to evaluate the polymer modification effects in a neat asphalt binder. The grading results of the bioadvantaged polymer modified asphalt blends used for statistical optimization are discussed in Section 2.6 and an optimized formulation of bioadvantaged polymer produced for verification through grading is presented in Section 2.7. The overall laboratory test plan is presented in Figure 2.3.

**Table 2.1. List of the different bioadvantaged polymers with their corresponding modified blend codes utilized for shear blending.**

Polystyrene Content, %	Polystyrene molecular weight, kDa			PS-PAESO diblock copolymer		Chemical reaction length, hr
	10	20	30	Molecular weight, MDa	PDI	
30	–	–	Blend 9	0.98	2.06	4
30	–	–	Blend 10	1.22	1.834	5
20	Blend 1	–	–	1.25	1.73	8
25	Blend 2, Blend 3	Blend 8	Blend 11,	1.24	1.76	8
30	Blend 4, Blend 5, Blend 6	–	Blend 12, Blend 13	1.26	1.72	8
35	Blend 7	–	–	1.25	1.75	8
30	–	–	Blend 14	1.29	1.69	9
30	–	–	Blend 15	1.49	1.63	10
30	–	–	Blend 16	1.63	1.52	11
30	–	–	Blend 17	1.76	1.49	12



**Figure 2.3. Overall test plan for bioadvantaged polymer (PS-PAESO).**

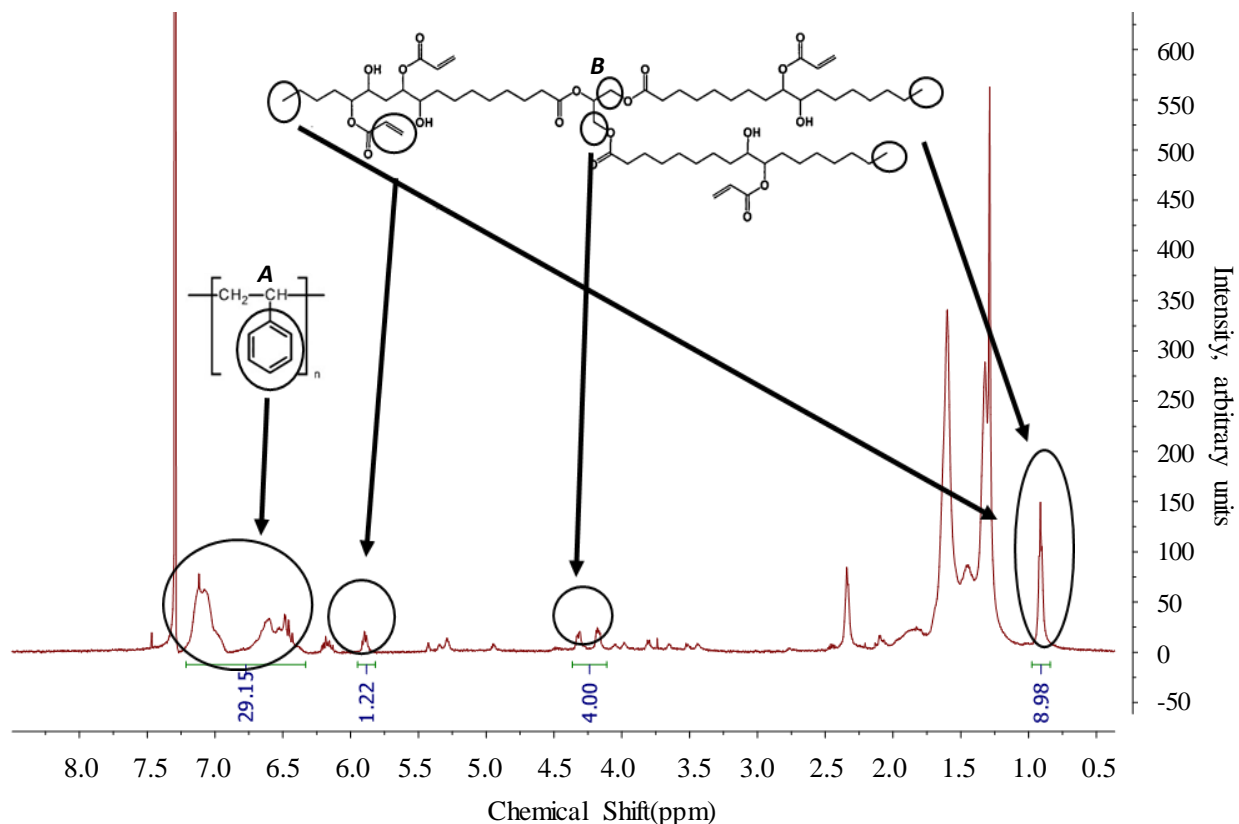
### 2.5.1. Chemical characterization of bioadvantaged polymer

Optimization of a block copolymer's formulation depends on the molecular weight parameter of the PS block and the PS contents used in the PS-PAESO diblock copolymer. The PS block composition will influence polymer phase solubility, morphology, and the molecular weight of the PAESO block for asphalt modification [29]. To chemically characterize the PS block for PS-PAESO polymer, H-NMR and HT-GPC were performed.

#### 2.5.1.1. Hydrogen nuclear magnetic resonance (H-NMR)

The H-NMR was conducted for quantifying the percentage of PS in the block copolymer and also the amount of residual terminated PS within the polymer by using a 600 MHz Bruker Avance III spectrometer. Deuterated chloroform (CDCL<sub>3</sub>) was used as solvent to dissolve the polymers. The actual effective PS content can be obtained from the NMR test results spectrum graph. An

example for quantifying PS content and PS composition within PS-PAESO polymer is shown in Figure 2.4. Letter “A” shows the aromatic hydrogens present in the styrene repeat unit and letter “B” shows the glycerol’s hydrogens present in the AESO’s backbone. The arrows pointing to the peaks in the circles represent the specific amount of hydrogens that can be integrated in each functional site, which can also be used to calculate the composition of the PS-PAESO polymer.



**Figure 2.4. The NMR spectrum graph of PS-PAESO polymer.**

### 2.5.1.2. High temperature gel chromatography (HT-GPC)

The HT-GPC was performed to measure the molecular weight (MW) and polydispersity index (PDI) of the PS-PAESO polymer by using a Viscotek HT-GPC Module 350A equipped with a differential refractive index (RI) detector. The tests were conducted in tetrahydrofuran (THF) at 65°C. The HT-GPC provides quantitative analysis of the polymer to show polymerization control of processability and material properties, which is widely used in the polymer industry [45]. In

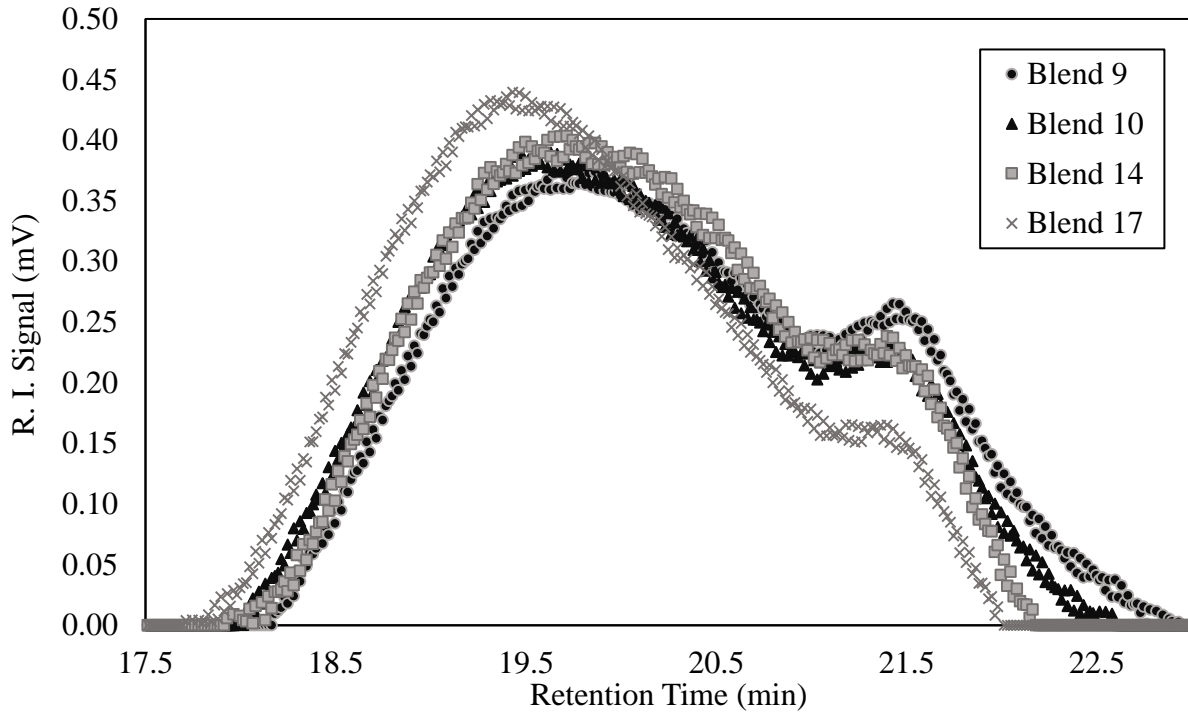
Figure 2.5, the HT-GPC trace of the PS-PAESO polymers (used in asphalt modification in Table 2.1) shows the growth of PS-PAESO molecular weight according to time. The molecular weight was calculated using poly(methyl methacrylate) standards.

Monodispersity in polymers produced by RAFT often signify a well-controlled polymerization. Moreover, lower PDIs are more desirable as polymer chains remain linear and less branched facilitating the solubility of the polymers in the asphalt binder. However, soybean based block copolymers produced by RAFT, have higher PDIs than other monomers due to the multiple sides of the AESO molecule that are available for polymerization. This feature enables branching of the polymer chains.

Another important property of polymers is their entanglement molecular weight. The entanglement molecular weight owns polymeric chains that are long enough to form one loop around themselves (also called a bridge). Polymers with molecular weights above their entanglement enhance the elasticity and recoverable behavior of the neat asphalt binder, when compared to lower molecular weight polymers.

Even though the PS-PAESO polymers (Table 2.1) were testified to have different molecular weight due to the chemical reaction length, all the diblock copolymers chosen for this study were entangled and achieved the minimum molecular weight for it to show entanglement in asphalt binder. Therefore, they can be used for asphalt modification with enhanced final mechanical and rheological properties of the asphalt blends and the different modification effects are not considered to be related to the PS-PAESO molecular weight.



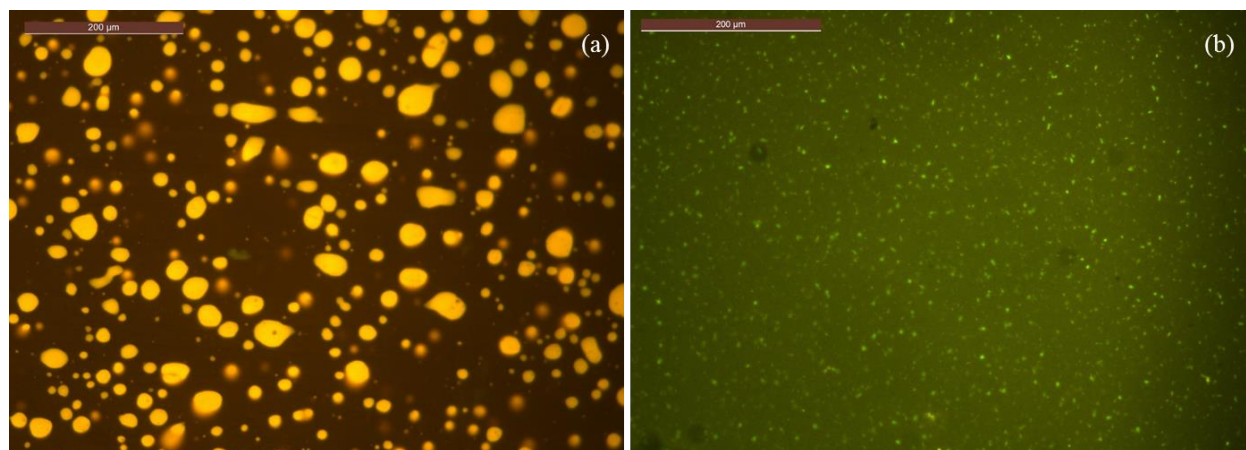


**Figure 2.5. High temperature gel chromatography of PS and PS-PAESO polymers.**

### 2.5.1.3. Fluorescence optical microscope

Glass film specimens were prepared by pouring a drop of heated modified asphalt binder onto the top of a glass plate and then covering the drop of heated asphalt with a smaller glass plate [46, 47]. After being covered, specimens were annealed in the oven for 15 min at 150°C to get rid of air bubbles and spread the material [36]. A Leica DM4000 B LED fluorescence optical microscope with a Leica DFC7000-T digital camera was used on the glass film specimens to observe the morphology of polymer modified binders. Figure 2.6 shows two fluorescence optical micrographs, one of a Kraton D1118 (SB) modified asphalt binder and one of a bioadvantaged polymer modified asphalt binder. They present different morphological conditions due to the distribution and fineness of the polymer in the asphalt matrix [48, 49]. In both images, shining spherical particles represents the swollen polymers by the aromatic compounds within the asphalt binder, while the dark phase represents the asphalt rich phase [5, 46, 50–53]. The scattered yellow particles, in

Figure 2.6 (a), are dispersed SB polymer in the neat asphalt binder after high speed shear blending and show a multiphase morphology that some of the polymer is only partially swollen by the asphalt binder with two co-continuous phases [54]. It also can be seen that the Kraton 1118D (SB) polymer dispersed coarsely due to the phase separation of butadiene with the neat asphalt binder [49]. In Figure 2.6 (b), the bioadvantaged polymer modified binder (Blend 1 in Table 2.1) displays a homogeneous morphology with finely dispersed particles, where phase separation does not occur with the neat asphalt binder [8, 50]. Similar homogeneous morphology was seen in the rest of the PS-PAESO modified blends through examination of micrographs. The examination indicated that PS content and molecular weight do not affect the dispersion and compatibility of the polymer in asphalt binder. Uniform dispersion allows the polymers to be entangled with asphalt molecules, and produce an increased elastic response with better compatibility between polymer and neat asphalt binder, which was also confirmed by rheological characterization [43, 45].



**Figure 2.6. Fluorescence optical micrographs of polymer modified asphalt blends (magnification=100x, scale bar=200μm): (a) the commercial Kraton D1118 (SB) polymer modified blends; (b) bioadvantaged polymer modified blends-Blend 1.**

## **2.5.2. Rheological characterization of bioadvantaged polymer modified neat asphalt binder**

Asphalt is a viscoelastic material whose rheological properties are related to test temperature and rate of loading. Asphalt binder should be fluid enough at mixing temperatures to be easily pumped during construction, while still being resistant to permanent deformation and thermal cracking during the service life of a pavement [56]. The rheological properties were characterized through use of a dynamic shear rheometer (DSR) and a bending beam rheometer (BBR) according to ASTM D6373-15 and AASHTO M320-10 with specimens tested in triplicate. The performance grade tests were performed at a wide range of temperatures and frequencies to determine the critical high temperatures and critical low temperatures that specifies the temperature range of an asphalt binder for a proper paving environment.

### ***2.5.2.1. Performance grading of asphalt blends***

To verify and determine the grade of the neat asphalt binder (PG 52-34) and modified blends, DSR testing (ASTM D7175-08 and AASHTO T315-10) was performed on both unaged and short-term aged asphalt blends for the high temperature grade and BBR testing (ASTM D6648-08 and AASHTO T313-10) was conducted on long-term aged blends for the low temperature grade. The short-term laboratory aging of neat asphalt binder and modified blends was performed by a rolling thin-film oven (RTFO) (ASTM D2872-12 and AASHTO T240-09). The long-term laboratory aging was performed on the asphalt binders in a pressure aging vessel (PAV) (ASTM D6521-13 and AASHTO R28-12) to expose the binders to high pressure and temperature (simulates long-term aging in a short amount of time). The grade of the commercially available Kraton D1118 (SB) modified neat asphalt binder was evaluated by following the same test approaches summarized above for comparison purposes.

### 2.5.2.1.1. Dynamic shear rheometer (DSR)

The DSR is usually conducted to characterize the viscous and elastic behavior of asphalt binder at high and intermediate temperatures for examining rutting resistance and high temperature susceptibility. The DSR measures the complex modulus ( $G^*$ , Pa) and phase angle ( $\delta$ , degree) of an asphalt binder which are both significantly influenced by temperature and loading frequency. The  $G^*$  measures the total deformation resistance of asphalt binder under repeated shear and the  $\delta$  represents the relative amount of recoverable and non-recoverable deformation of the viscoelastic asphalt binder [57].

The DSR test is conducted at an oscillation speed of 10 rad/s (1.59 Hz). The test is started at an initial testing temperature of 46.0°C, followed by subsequent testing in 6.0°C increments until a specimen fails. All unaged and RTFO short-term aged specimens were prepared by pouring heated asphalt binder into a 25mm diameter silicon mold and tested using 25mm diameter parallel plates. The critical high temperature can be obtained when the  $|G^*|/\sin(\delta)$  value of unaged specimen achieves 1.00 kPa and 2.20 kPa for unaged and RTFO short-term aged specimens, respectively. The critical high temperature test results of unaged and RTFO short-term aged blends are shown in Table 2.2. According to ASTM D6373-15, the high temperature performance grade is determined based on the lower value of the two high critical high temperatures of each blend as tabulated in Table 2.2 and along with its margin of error bar at 95% confidence intervals in Figure 2.7.

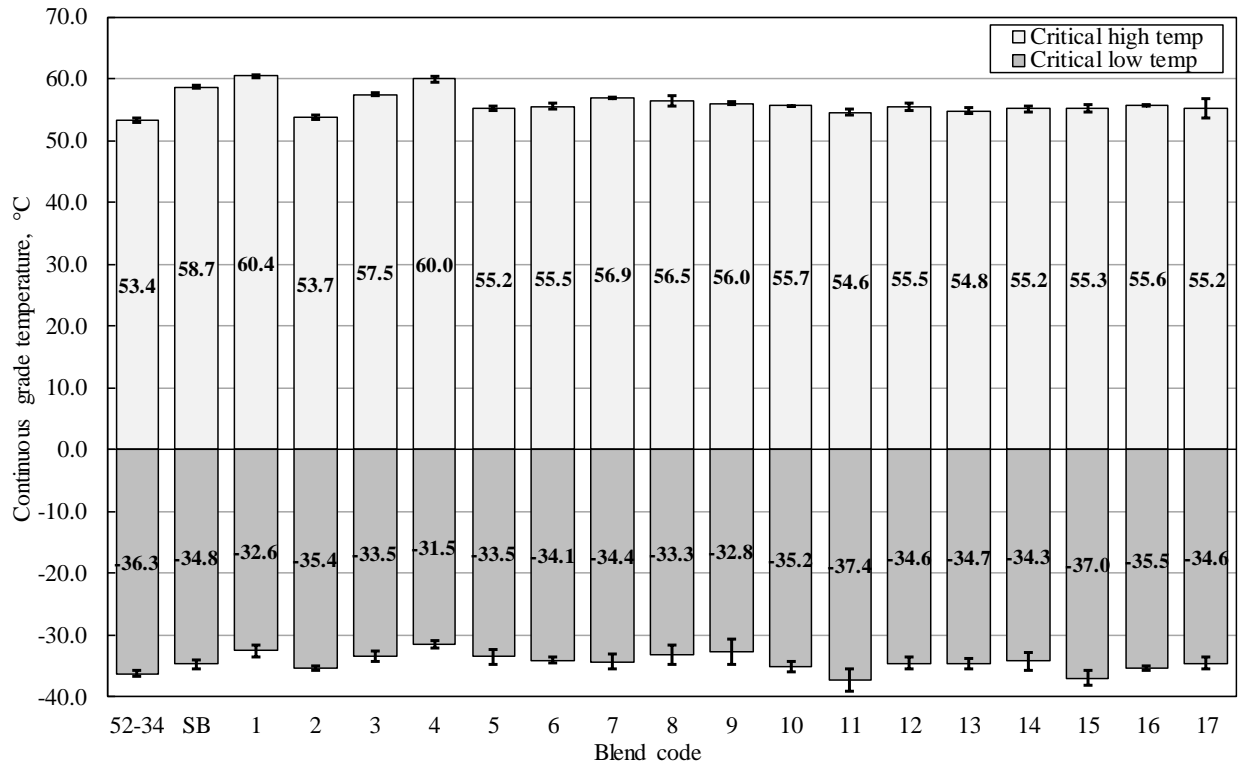
According to the DSR results, the neat asphalt binder has a critical high temperature of 53.4°C and was graded out at 52°C. An increase of critical high temperature can be observed for all bioadvantaged polymer modified asphalt binders when compared to the neat asphalt binder. Additionally, critical high temperatures of Blends 1, 3, 4, 7, 8, and 9 are very similar or higher

than that of the SB polymer modified binder with the same grade of 58°C. The best performing bioadvantaged polymers in terms of critical high temperature are shown in Blends 1 and 4, which contain PS with lower molecular weight and improve the critical high temperature by 6.6°C and 7.0°C above the critical high temperature of the neat asphalt binder, respectively. Critical high temperatures of Blends 1 and 4 are approximately 1.8°C higher than the critical high temperature of the SB polymer modified binder.

**Table 2.2. Critical high temperatures of unaged and RTFO short-term aged modified asphalt blends with corresponding high temperature performance grade.**

Blend code	Critical high temperature, °C		High temperature performance grade, °C
	Unaged	RTFO aged	
52-34	53.4*	53.7	52
SB	59.1	58.7*	58
1	60.7	60.4*	58
2	53.7*	56.3	52
3	57.5*	59.1	58
4	60.0*	62.0	58
5	56.8	55.2*	52
6	56.5	55.5*	52
7	56.9*	58.2	58
8	56.5*	56.9	58
9	56.5	56.0*	58
10	55.7*	57.8	52
11	56.7	54.6*	52
12	56.4	55.5*	52
13	56.8	54.8*	52
14	57.7	55.2*	52
15	57.3	55.3*	52
16	57.8	55.6*	52
17	56.9	55.2*	52

\*The final critical high temperature of the asphalt blends.



**Figure 2.7. Continuous performance grade ranges of the polymer modified asphalt blends and the neat asphalt binder.**

#### 2.5.2.1.2. Bending beam rheometer (BBR)

Low temperature thermal cracking occurs because the thermal stress applied on the asphalt mixture at low temperatures exceeds the asphalt mixture's tensile strength. Therefore, decreasing the low temperature susceptibility of the asphalt binder, lowering the asphalt binder stiffness, and enhancing the asphalt binder's ability to provide stress relaxation can be beneficial to minimize thermal cracking. The BBR is used to evaluate the low temperature properties of long-term aged polymer modified asphalt binders and the neat asphalt binder by measuring the center point deflection of the beam in 240 seconds. The stiffness (S) and creep rate (m-value) were determined at each loading time afterwards. The m-value is the rate of change for the creep stiffness with loading time, which indicates the stress relaxation of the asphalt binder. Based on the time-temperature superposition principle, the critical low temperature is determined where the m-value

is equal to 0.300 and/or S is equal to 300 MPa when measured at 60 seconds. Whichever result is more conservative is used for estimating the critical low temperature. The critical low temperature results are tabulated in Table 2.3 and along with their margin of error bars at 95% confidence intervals in Figure 2.7.

**Table 2.3. Critical low temperatures of long-term aged modified asphalt blends with corresponding low temperature performance grade and their continuous grade ranges.**

Blend code	Critical low temperature, °C	Low temperature performance grade, °C	Continuous grade range, °C
54-34	-36.3	-34	89.7
SB	-34.8	-34	93.4
1	-32.6	-28	93.0
2	-35.4	-34	89.1
3	-33.5	-28	91.0
4	-31.5	-28	91.5
5	-33.5	-28	88.7
6	-34.1	-34	89.6
7	-34.4	-34	91.3
8	-33.3	-28	89.8
9	-32.8	-28	88.8
10	-35.2	-34	90.9
11	-37.4	-34	92.0
12	-34.6	-34	90.1
13	-34.7	-34	89.4
14	-34.3	-34	89.5
15	-37.0	-34	92.3
16	-35.5	-34	91.1
17	-34.6	-34	89.8

The low temperature grade of the neat asphalt was -34°C because its critical low temperature was -36.3 °C (Figure 2.7 and Table 2.3). Additionally, 11 of the 17 bioadvantaged polymer modified blends were graded as -34 °C that was the same as the neat asphalt binder and the SB modified blends. In contrast, the other six bioadvantaged polymer modified blends increased the critical low temperature by 2.8°C to 4.8°C and graded out at -28°C. Therefore, six of the 17 bioadvantaged polymers were compromised on the low temperature grade.

The overall continuous performance grade range results were determined based on both the critical high temperature and critical low temperature of the modified asphalt blends. It indicates the temperature susceptibility of the asphalt binder and the working range of temperatures. The continuous grade range results summarized in Table 2.3 and Figure 2.7 show that 11 out of the 17 bioadvantaged polymer modified blends presented higher ranges than the neat asphalt binder and similar ranges to the SB modified binder. Thus, the majority of the formulated bioadvantaged polymers helped widen the continuous performance grade range and reduce the temperature susceptibility of the neat asphalt binder. It was noticed that PS-PAESO with lower PS content increases critical high temperature of the neat asphalt binder the most compared to the rest of PS-PAESO modified blends and reduces the temperature susceptibility of the neat asphalt binder with the closest continuous grade ranges to SB modified blends. For the purpose of this research, PS-PAESO polymer that can modify the neat asphalt binder to achieve increased critical high temperature with reduced temperature susceptibility superior to that of SB polymer modified asphalt binder for warm climate regions' applications is desirable.

*2.5.2.1.3. The effect of variable parameters in PS-PAESO on the properties of PMB/statistical analysis*

To verify whether the chemical reaction length of PS-PAESO polymer has any effects on the high and low temperature properties of the modified blends, statistical analysis was conducted on the results obtained from DSR and BBR. Therefore, two separate analyses of variances (ANOVA)s at a 95% confidence interval were conducted for the high temperature property by using the rutting parameter  $G^*/\sin\delta$  at various test temperatures and for low temperature properties of stiffness and m-value at different test temperatures, respectively. The statistical analysis was conducted on blends that have the same PS content (i.e. 30%) and molecular weight (i.e. 30kDa) but different chemical reaction lengths. They are Blend 9 (4hr), Blend 10 (5hr), Blend 12 (8hr), Blend 13 (8hr),



Blend 14 (9hr), Blend 15 (10hr), Blend 16 (11hr), and Blend 17 (12hr). The responses for the ANOVA are  $G^*/\sin\delta$ , stiffness, and m-value. In addition, factors examined within the ANOVA are chemical reaction length and test temperature.

The ANOVA table (Table 2.4) for high temperature property,  $G^*/\sin\delta$ , shows no statistically significant difference in the factor reaction length nor the interactive effect between length and test temperature. Whereas, there is statistically significant difference in test temperature as expected because the asphalt binder is a viscoelastic material with temperature-dependent behavior. The Tukey honestly significant difference (HSD) least square means difference test was performed on the tests results to better examine if there were differences between blends in terms of different reaction length levels as presented in Table 2.5. All levels of reaction length are connected by the same letter, which means there is no significant difference among these levels based on a 95% confidence interval. No statistically significant difference in reaction length was also found in the ANOVA tables and Tukey HSD least square means difference tables for responses of stiffness and m-value as shown in Table 2.4 and Table 2.5. As a result, the chemical reaction length of PS-PAESO does not affect the high and low temperature properties of the PS-PAESO modified blends.

The ANOVA on PS molecular weight and PS content were conducted on all 17 blends, because the chemical reaction length has been proved to have no effects on the high and low temperature properties of PS-PAESO modified blends. According to the ANOVA tables, two PS parameters were found to have significant effects on the high and low temperatures grading results at a 95% confidence interval. More importantly, PS content at the lower level of 20% is noted to be significantly different from the other three higher percentage contents (i.e. 25, 30, and 35%) and PS with higher molecular weight of 30kDa is considered to be significantly different from the other

two lower molecular weights (i.e. 10 and 20 kDa) based on the Tukey HSD least square means difference results presented in Table 2.6. Therefore, it can be inferred that lower PS content helps with high temperature performance while higher PS molecular weight has positive effects on low temperature performance in asphalt modifications.

**Table 2.4. ANOVA for  $G^*/\sin\delta$ , stiffness, and m-value with factors of chemical reaction length and test temperatures.**

Factor	DF	SS	MS	F Ratio	Prob>F
$G^*/\sin(\delta)_{(Unaged)}$					
Reaction length, hr	6	323.23	53.87	0.4980	0.7914
Testing temp, °C	5	488077.75	9615.55	902.3755	<.0001*
Reaction length*Testing temp	30	1055.53	35.18	0.3252	0.9818
Error	6	649.06	108.2		
C. Total	47	523785.82			<.0001*
R <sup>2</sup>	99.88				
$Stiffness_{(PAV\ aged)}$					
Reaction length, hr	6	1785.84	297.6	0.4816	0.8173
Testing temp, °C	1	156591.71	156591.7	253.3666	<.0001*
Reaction length*Testing temp	6	1163.89	194	0.3139	0.9253
Error	34	21013.5	618.0		
C. Total	47	186725.39			<.0001*
R <sup>2</sup>	88.75				
$m\text{-value}_{(PAV\ aged)}$					
Reaction length, hr	6	0.00160123	0.0002669	1.1747	0.3427
Testing temp, °C	1	0.05029231	0.0502923	221.3752	<.0001*
Reaction length*Testing temp	6	0.00217356	0.0003623	1.5946	0.1789
Error	34	0.00772417	0.000227		
C. Total	47	0.06570248			<.0001*
R <sup>2</sup>	88.24				

Note: *DF* degrees of freedom, *SS* sum of squares, *MS* mean square, statistically significant at  $\alpha < 0.05$ , \* means statistically significant difference.

**Table 2.5. Tukey HSD least square means difference of  $G^*/\sin\delta$ , stiffness, m-value for reaction length.**

Factor level of reaction length, hr		Least square mean
$G^*/\sin(\delta)_{(\text{Unaged})}$		
11	A	61.040883
10	A	60.187683
9	A	60.011250
8	A	59.986208
12	A	59.450717
5	A	54.357117
4	A	54.034917
Stiffness <sub>(PAV aged)</sub>		
9	A	170.16667
4	A	164.33333
5	A	162.85000
12	A	162.70000
10	A	156.61667
11	A	155.76667
8	A	151.85833
m-value <sub>(PAV aged)</sub>		
11	A	0.3515000
8	A	0.34275000
10	A	0.34066667
5	A	0.33833333
12	A	0.33816667
9	A	0.33300000
4	A	0.33200000

Note: Levels not connected by same letter are significantly different.

**Table 2.6. Tukey HSD least square means difference of critical high temperatures for the factor of PS content and critical low temperatures for the factor of PS molecular weight.**

Factor level of critical temperatures, °C		Least square mean
PS content, %		
20	A	60.175234
30	B	56.523518
35	B	56.375234
25	B	55.178809
PS molecular weight, kDa		
20	A	-32.51527
10	A	-33.69164
30	B	-35.91620

Note: Levels not connected by same letter are significantly different.

### 2.5.2.2. *Master curves and Black diagrams*

The  $G^*$  and  $\delta$  were measured and obtained by performing frequency sweeps at multiple temperatures using 8mm and 25mm diameter parallel plate specimens in a DSR. The range of the frequency sweep was between 1 to 100.0 rad/s at temperature stages of 20.0 to 30.0°C (8mm for lower temperatures at 5% strain rate) and 40.0 to 64.0°C (25mm for higher temperatures at 10% strain rate). The linear viscoelastic (LVE) regions of the materials were verified for the two plate sizes at the two temperatures ranges by performing strain sweep tests at the test temperatures using both plate sizes. For better evaluation of the materials resistance to shear deformation at different temperatures and frequencies, master curves and Black diagrams were developed for the neat asphalt binder, the SB modified binder, and all 17 different formulated bioadvantaged polymer modified binders. Blend 1 has the highest critical high temperature and the widest working range of temperatures in all PS-PAESO modified blends, which modified the neat asphalt binder from PG 52-34 to PG 58-28 and thereby can be used for warm climate regions pavement applications. Whereas, the PS-PAESO added in asphalt binder as Blend 7 performed close to the SB modified binder, because it helped improve critical high temperature of the neat asphalt binder by 3.5°C without affecting the low performance grade of the neat asphalt binder, i.e., kept the binder graded the same as the neat asphalt binder on the low temperature side. Therefore, Blend 1 was superior to SB modified binder in terms of critical high temperature and Blend 7 was the closest to the SB modified binder with the same low performance grade. For further analysis the rheological behavior of the aforementioned PS-PAESO blends, master curves and Black diagrams were constructed to compare against the neat asphalt binder and the SB modified binder.

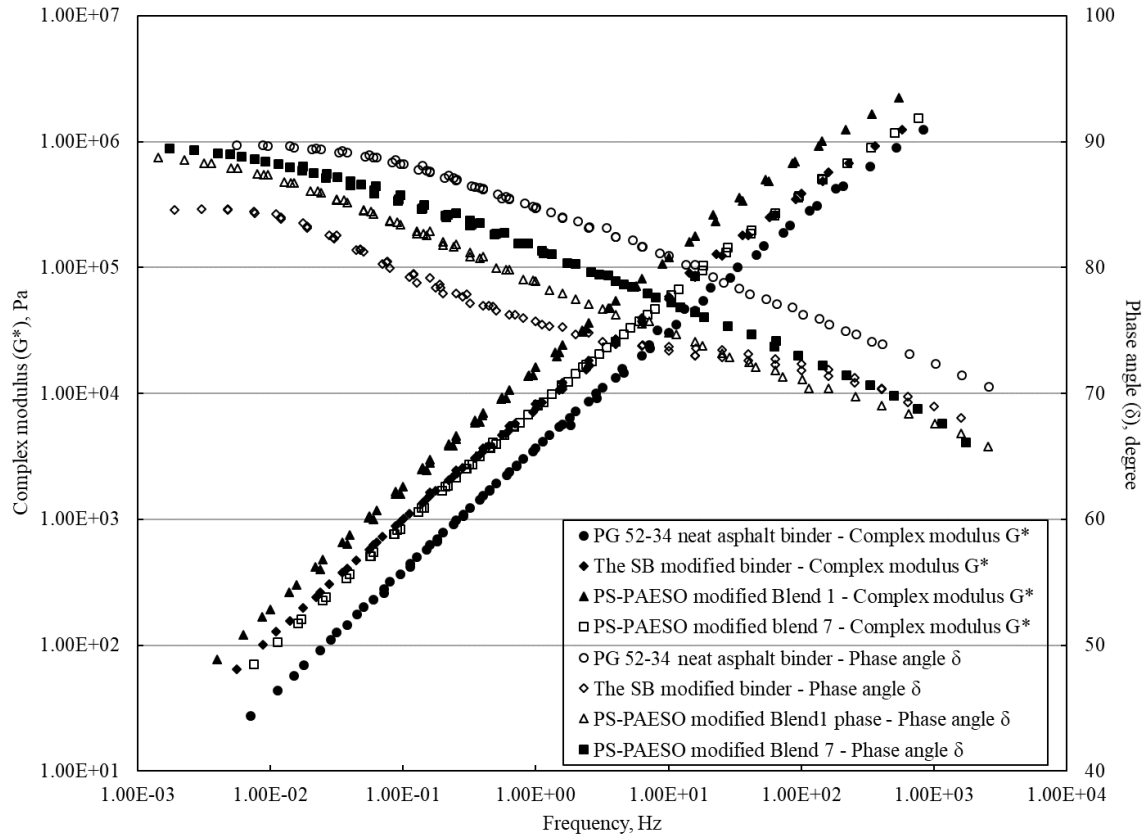
The master curves were developed by using an empirical time-temperature superposition principle known as the Williams-Landel-Ferry (WLF) equation at a reference temperature of

40.0°C [56]. The WLF equation is used to calculate the shift factors to shift the  $G^*$  and  $\delta$  at each frequency to create a smooth curve for comparing the rheological properties of the asphalt blends. The rheological properties of the neat asphalt binder and Blend 1 best-fit curves can be observed at high, intermediate, and low temperatures in Figure 2.8.

The commercial SB polymer and two PS-PAESO bioadvantaged polymers increase the  $G^*$  of the neat asphalt binder (Figure 2.8), which means these three polymers make the neat asphalt binder stiffer over the entire frequency range and temperature range. The modification effect of SB is more significant at low frequencies (higher temperatures) compared to the neat asphalt binder, which indicates pronounced improvement of rutting resistance through grade bumping by one performance grade at high temperature. However, the SB binder is noticed to have a slight increase at high frequencies (lower temperatures), meaning there is only a minor stiffening effect on the modified binder at lower temperatures by reducing critical low temperature within 2°C compared to the neat asphalt binder. A similar stiffening effect in the  $G^*$  master curve is observed for Blend 7 as compared to the SB binder due to overlapping occurring between their  $G^*$  master curves. Since the  $G^*$  master curve of Blend 1 is above both the SB and Blend 7 master curves over the entire frequency range, Blend 1 appears to be more resistant to rutting at high temperatures while less resistant to thermal cracking at low temperatures than the SB and Blend 7 modified binders. Compared to the neat asphalt binder, PS-PAESO in Blend 1 has significantly increased the  $G^*$  at high, intermediate, and low frequencies.

The viscoelastic behavior of the materials can be observed in the master curves by examining  $\delta$  against changes in frequency and temperature (Figure 2.8). There is phase angle reduction for commercial SB polymer modified binder and the two bioadvantaged polymer modified blends (Blend 1 and Blend 7) compared to the neat asphalt binder curve. In addition, the participation of

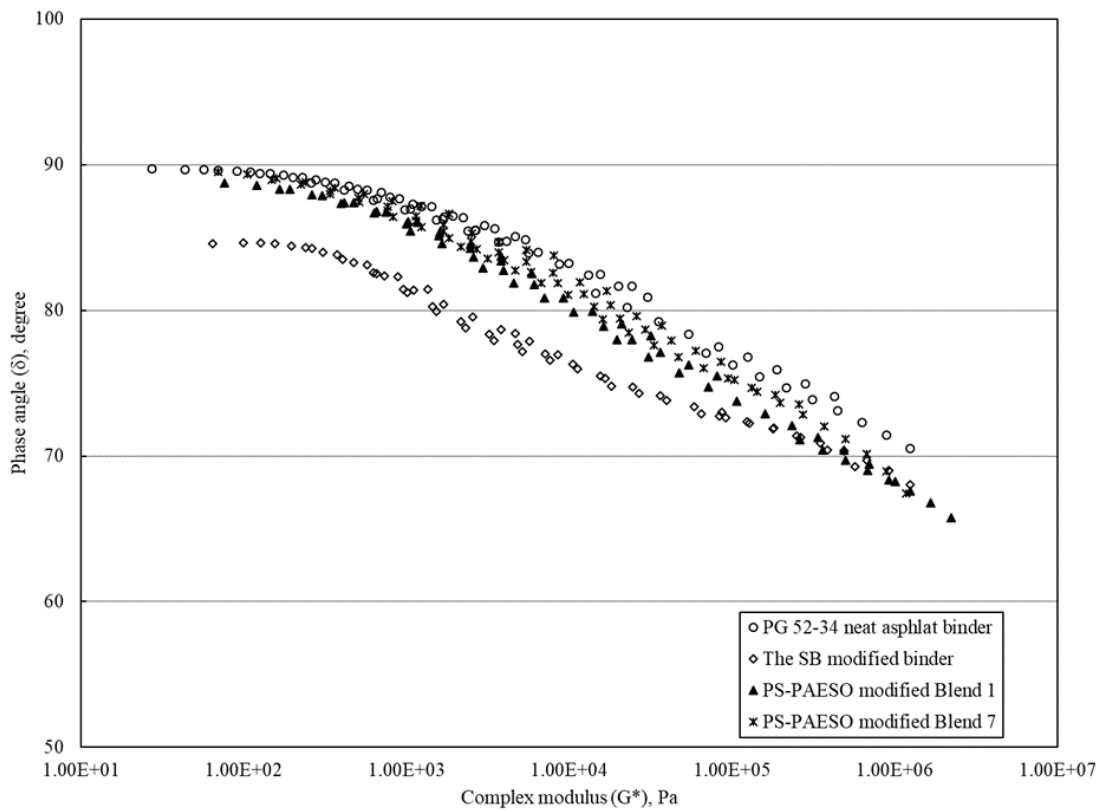
the bioadvantaged polymer in the neat asphalt binder results in a decrease of around 5 to 10 degrees in the phase angle for Blend 1 and a decrease between 2 and 5 degrees for Blend 7. This indicates improved elasticity when compared to the neat asphalt binder, which also means the bioadvantaged polymer makes the neat asphalt binder become more elastic in nature. The SB polymer significantly decreases the phase angle up to 10 degrees at intermediate frequencies (intermediate temperatures), but only slightly decreases the phase angle at higher and lower frequencies. The pronounced phase angle reduction of the SB modified binder indicates the elastic network formation in the neat asphalt binder where a plateau appears on the curve [6]. Compared to the SB modified binder, the biopolymer modified binder's phase angle decreases more evenly at intermediate and high frequencies. Both  $G^*$  master curves and the  $\delta$  master curves show the positive stiffening effect and the improvement of rutting resistance in the neat asphalt binder especially at high temperatures by using the bioadvantaged polymer. It is noted that PS-PAESO with lower PS content may have higher stiffening effects on the neat asphalt binder, thus improving resistance to rutting at higher temperatures, which is in agreement with the performance grade results.



**Figure 2.8.  $G^*$  Master curves and  $\delta$  master curves for the neat asphalt binder, SB modified binder, Blend 1, and Blend 7.**

The Black diagrams use both complex modulus ( $G^*$ ) and phase angle ( $\delta$ ) results and were developed for interpreting the modification effect of the polymers without depending on the shifting effect when constructing the master curves. The Black diagrams show that the curves present similar patterns with different amplitudes due to the polymer modification effects (Figure 2.9). The Black diagram curves of Blend 1 and SB modified binders show a shift towards lower phase angle compared to the neat asphalt binder. There is a pronounced modification effect of the SB modified binder at lower and intermediate stiffness values (low and intermediate  $G^*$ ), corresponding to higher temperatures and lower frequencies. Whereas there is no significant phase angle shift noticed for Blend 7 at lower and intermediate stiffness values, the curve is in between Blend 1 and the neat asphalt binder's curves. This shows that the PS-PAESO in Blend 7 does not

help with the improvement of neat asphalt binder's elasticity as much as the polymers used in Blend 1 and SB binder do. For Blend 1, the Black diagram curve shows a shift towards lower phase angles at higher stiffness values with lower temperatures and higher frequencies. In addition, at higher stiffness values with lower temperatures, both Blend 1 and Blend 7's curves overlap the SB modified one, which means they have similar modification effects on the neat asphalt binder at lower temperatures. The Black diagram curve of Blend 1 indicates the bioadvantaged polymer with lower PS content improves the elastic properties of the neat asphalt binder at lower and intermediate temperatures. However, the formulation of the PS-PAESO still needs to be optimized for improved modification effects.



**Figure 2.9. Black diagrams for the neat asphalt binder, SB modified binder, and Blend 1.**



## 2.6. Optimization of polystyrene content and molecular weight in polymer modified binder

To further improve the elasticity of the bioadvantaged polymer modified asphalt blends, statistical analysis and regression modeling were performed based on laboratory test results summarized in Section 4.2.1. Response surface modeling helps determine the functional relationship between the response and the independent variables, therefore, it helps to identify the optimum conditions that can improve product quality [58–61].

In this research, a response surface model was developed to estimate both the optimum PS content and molecular weight of the bioadvantaged polymer for maximizing the performance grade of the polymer modified binders. A second-order polynomial response surface model was developed and used as the initial full model as follows:

$$y = \beta_0 + \beta_1x_1 + \beta_2x_2 + \beta_3x_3 + \beta_{12}x_1x_2 + \beta_{13}x_1x_3 + \beta_{23}x_2x_3 + \beta_{11}x_1^2 + \beta_{22}x_2^2 + \beta_{33}x_3^2 + \varepsilon$$

where  $y$  is the response of the performance grading test results at high and low temperatures that relates to  $x_1, x_2$ , and  $x_3$  of the three major factors: PS molecular weight (kDa), PS content (%), and testing temperature ( $^{\circ}\text{C}$ ), respectively.  $\beta_0$  is the intercept,  $\beta_1 \dots \beta_{33}$  are coefficients and  $\varepsilon$  is the random error component. The fit quality of the polynomial model is expressed by the coefficient of determination,  $R^2$ .

Four initial response surface models were developed with respect to four test responses, which are  $G^*/\sin(\delta)$  with a limit of 1.0 kPa for unaged modified blends,  $G^*/\sin(\delta)$  with a limit of 2.2 kPa for the RTFO short-term aged modified blends, and  $m$ -value and stiffness of 0.300 and 300 MPa for the PAV aged modified blends, respectively. The step-wise regression was performed on the initial models of unmodified data, logarithm base 10 (Log10) transformed data, and root square transformed data to eliminate the non-significant variables with a confidence level of 95% until

the finalized models were obtained. The prediction models were selected from the finalized models by examining their residual plots that meet the normal distribution and have  $R^2$  values closest to 1.

Finalized prediction models for the high and low temperatures are summarized in Table 2.7 and their coefficient values are presented in Table 2.8. After combining the corresponding coefficient values (Table 2.8) with each prediction model, the optimum PS parameters in the PS-PAESO polymer can be determined with desirable modification effects. The predicted 1.25 MDa molecular weight of PS-PAESO bioadvantaged polymers with recommended PS molecular weight and PS content that could modify the neat asphalt binder PG 52-34 to be PG 64-28 are tabulated in Table 2.9. According to the proposed PS parameters, it is noted that lower PS molecular content (i.e. 5%) is able to increase the critical high temperature of the neat asphalt binder by two performance grades, but also reduces the low temperature performance grade by one grade. The PS molecular weight does not have much effect on the neat binder's high temperature performance grade because polymers with PS block that have molecular weights of 15, 20, 25, and 30 kDa at PS content of 5% have shown similar modification effects on critical high temperatures (Table 2.9). Even though PS molecular weight does not affect the critical high temperatures, it is important to note that there are minor effects of PS molecular weight on the low temperature side. In Table 2.9, it can be seen that the stiffness of the predicted blends decreases and the m-value increases as the molecular weight of PS increases from 15 to 30kDa at the same 5% PS content, which agrees with the findings concluded in Section 2.5.2.1. Due to the fact that the main objective of this research is to produce a polymer-modified asphalt binder with superior high temperature performance for warm climate pavement applications through use of the PS-PAESO bioadvantaged polymer, lower PS content was more of a priority in the formulation of the PS-PAESO according to the results presented.

**Table 2.7. Finalized prediction models for high and low temperatures.**

High temperature prediction models	
Unaged: $\left(\frac{G^*}{\sin\delta}\right) = 10^{(\beta_0 + \beta_1 \times x_1 + \beta_2 \times x_2 + \beta_3 \times x_3 + \beta_{11} \times x_1^2 + \beta_{22} \times x_2^2 + \beta_{33} \times x_3^2)}$	
RTFO aged: $\left(\frac{G^*}{\sin\delta}\right) = 10^{(\beta_0 + \beta_1 \times x_1 + \beta_2 \times x_2 + \beta_3 \times x_3 + \beta_{12} \times x_1 \times x_2 + \beta_{22} \times x_2^2 + \beta_{33} \times x_3^2)}$	
Low temperature prediction models	
Stiffness: $(stiffness) = 10^{(\beta_0 + \beta_1 \times x_1 + \beta_2 \times x_2 + \beta_3 \times x_3 + \beta_{22} \times x_2^2)}$	
m-value: $(m - value) = (\beta_0 + \beta_2 \times x_2 + \beta_3 \times x_3 + \beta_{11} \times x_1^2 + \beta_{22} \times x_2^2)^2$	

**Table 2.8. Regression coefficients of prediction models.**

Regression coefficient	Coefficient value	Regression coefficient	Coefficient value
$G^*/\sin(\delta)_{(Unaged)}$		$G^*/\sin(\delta)_{(RTFO\ aged)}$	
$\beta_0$	5.4062011	$\beta_0$	5.9536825
$\beta_1$	-0.035459	$\beta_1$	-0.022674
$\beta_2$	-0.051313	$\beta_2$	-0.083476
$\beta_3$	-0.097202	$\beta_3$	-0.089883
$\beta_{11}$	0.000833	$\beta_{12}$	0.0006269
$\beta_{22}$	0.0007587	$\beta_{22}$	0.0013052
$\beta_{33}$	0.0003658	$\beta_{33}$	0.0002742
$Stiffness_{(PAV\ aged)}$		$m-value_{(PAV\ aged)}$	
$\beta_0$	1.2166729	$\beta_0$	0.721626
$\beta_1$	-0.002152	$\beta_2$	0.0030204
$\beta_2$	-0.012236	$\beta_3$	0.0092462
$\beta_3$	-0.054661	$\beta_{11}$	0.00001688
$\beta_{22}$	0.0002663	$\beta_{22}$	0.00005379

**Table 2.9. Recommended polystyrene parameters in PS-PAESO bioadvantaged polymers with their predicted critical temperatures.**

Items	Values			
PolyStyrene MW, kDa	15	20	25	30
PolyStyrene Content,%	5	5	5	5
Critical high temp(unaged)	66	65.5	65.5	66.6
Critical high temp (RTFO aged)	69.5	67.5	66	64.3
Critical low temp@-18°C(m-value)	0.328	0.331	0.336	0.341
Critical low temp@-18°C(stiffness)	130	127	124	121
Critical low temp@-24°C(m-value)	0.268*	0.271*	0.275*	0.279*
Critical low temp@-24°C(stiffness)	277	270	263	257

\*The result value fails to meet the standard criteria.

## 2.7. Performance grade of optimized bioadvantaged polymer in asphalt binder

For the purpose of testing the predicted PS-PAESO bioadvantaged polymers' modification effects, high and low temperatures performance grading was conducted on one of the predicted optimized bioadvantaged polymers that was PS-PAESO with PS molecular weight of 30 kDa and a 5% PS content.

The modified blends were prepared by following the same shear blending procedures previously presented. The DSR testing was conducted on the unaged and RTFO short-term aged bioadvantaged polymer modified binder specimens in triplicate by using 25mm diameter parallel plates. The tests started at an initial test temperature of 46°C and increased in 6°C increments until each specimen failed. Critical high temperatures of 67.0°C and 65.0°C were determined for the unaged and RTFO aged modified binder from the DSR performance grade reports, respectively. The results are very close to the predicted values with only 0.4°C and 0.7°C difference from the predicted critical high temperatures of 66.6°C and 64.3°C as shown in Table 2.9. The m-value of the modified binder failed at the testing temperature of -24°C that resulted the low temperature performance grade was graded out at -28°C due to the time-temperature super position principle. The overall performance grade of the predicted polymer modified binder was PG 64-28 based on the performance grade tests, which is the same performance grade of the predicted result. The same grade between the tested and predicted results shows the high accuracy of the prediction models. For further model verification, all the predicted optimized PS-PAESO polymer formulations need to be produced for rheology testing.

A bioadvantaged polymer pilot plant has been built to determine the technical feasibility of producing bioadvantaged polymers. Industrial production of AESO products presents a few challenges in stability and polymer processing. The major concern is stability of the AESO

monomer after production. The acrylates on the AESO monomer are highly reactive and it is essential to maintain stability for good reproducibility. AESO polymer's (PAESO or PS-PAESO) main challenge is conversion of AESO monomer during the polymerization. Conversion greatly affects the polymer's molecular network (depending on reaction parameters) and its processing. Research on these challenges are ongoing and they will be evaluated in future studies.

## 2.8. Conclusions and recommendations

In this research, bioadvantaged polymers derived from non-food soybean oil at various polystyrene molecular weights and polystyrene contents were successfully synthesized by using the RAFT polymerization technique. The chemical characterization of bioadvantaged polymer was assessed by conducting H-NMR and HT-GPC. The morphology of polymer modified asphalt binders was examined by using a fluorescence optical microscope. The image of bioadvantaged polymer modified binder displayed homogeneous morphology with finer dispersion of polymer particles than the commercial SB polymer did in asphalt modification.

Furthermore, a laboratory investigation was also conducted to evaluate the bioadvantaged polymer modification effects in neat asphalt binder and to compare with the commercially available SB and neat asphalt binder. 18 groups of polymer modified asphalt blends (including 17 different bioadvantaged polymers modified asphalt blends and one commercial SB polymer modified blends) were prepared by modifying a neat asphalt PG 52-34 at a dosage rate of 3% by total weight of the blends using high speed shear blending. All bioadvantaged polymers helped increase the critical high temperature of the neat asphalt binder from 53.4 to 53.7-62.0°C. Two of the blends (1 and 4) outperformed the SB polymer modified blends and were approximately 1.8°C higher for the critical high temperature, which means the bioadvantaged polymer has the ability to improve rutting resistance of the neat asphalt binder. However, the bioadvantaged polymers did

not substantially improve the resistance to thermal cracking due to the fact that the critical low temperatures were increased. Eleven out of the seventeen bioadvantaged modified blends widened the neat asphalt binder's grade range and were close to the SB polymer modified binder's range, which shows that the bioadvantaged polymer is able to improve (widen) temperature susceptibility.

The statistical analysis for evaluating the effect of changing factors (i.e. chemical reaction length, PS content, and PS molecular weight) in PS-PAESO on the PS-PAESO modified asphalt binders grading results demonstrated that chemical reaction length was not a significant factor. However, statistical analysis did prove that PS parameters do play a significant role in affecting the properties of the modified blends. Furthermore, it was also shown that lower PS content helped improve the critical high temperature more while higher PS molecular weight was shown to slightly improve the critical low temperature more.

According to the  $G^*$  and  $\delta$  master curves, the best performing bioadvantaged polymer modified binder in terms of critical high temperature showed a trend of increasing  $G^*$  and decreasing  $\delta$  compared to the neat asphalt binder, which presents the positive stiffening effect and the improvement of rutting resistance in the neat asphalt binder at high temperatures. The elasticity improvement of the neat asphalt after modification can also be observed in the Black Space diagrams. The rheological performance test results indicated that there is great potential from the use of bioadvantaged polymers as sustainable alternatives to traditional petroleum based polymers in asphalt modification with similar or even better modification effects at the same polymer dosage level.

Four bioadvantaged polymers with optimized formulations of polystyrene molecular weight and polystyrene content that can modify a neat asphalt binder from PG 52-34 to PG 64-28 for warm climate regions pavement applications were estimated using the developed response surface

models based on the high and low temperatures performance grades. One of the optimized bioadvantaged polymer formulations with polystyrene molecular weight of 30 kDa and polystyrene content of 5% was produced and the modified binder was tested rheologically to verify the accuracy of the developed response surface models. The critical high temperatures of the optimized polymer modified asphalt binder was 67.0°C for the unaged binder and 65.0°C for the RTFO aged binder which were both within 1.0°C of the estimated temperatures of 66.6°C and 64.3°C, respectively. The similarities between the critical high temperature results and determined grades of the tested and estimated results show that the developed formulation models work well. In the future, the other three optimized bioadvantaged polymer formulations should be produced to provide further verification of the prediction models. In addition, it would be advantageous to investigate if it is possible to optimize PAESO parameters to further make PS-PAESO even more cost-efficient, as well as improve performance in polymer modified asphalt binders. After all optimized PS-PAESO bioadvantaged polymers are produced in the future, the Multiple Stress Creep Recovery and storage stability tests will be conducted on all bioadvantaged polymers and SB polymer modified asphalt binders for characterization and comparison.

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**CHAPTER 3. DETERMINATION OF THE OPTIMUM POLYSTYRENE  
PARAMETERS USING ASPHALT BINDER MODIFIED WITH POLY(STYRENE-  
ACRYLATED EPOXIDIZED SOYBEAN OIL) THROUGH RESPONSE SURFACE  
MODELLING**

Modified from a paper published in *Road Materials and Pavement Design*<sup>1</sup>

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### 3.1. Abstract

This paper reported on the modification effects of soybean oil-based block bio-advantaged copolymers, poly(styrene-*block*-acrylated epoxidized soybean oil) (PS-PAESO) using polymerized AESO (PAESO) married with various polystyrene molecular weights and polystyrene contents, in the base asphalt binder through performance grade testing. Best-fit prediction models were developed through response surface modelling (RSM) using the grading results to maximize the modification effects of PS-PAESO in the base binder by optimizing the polystyrene parameters. The optimized formulation of PS-PAESO with 5% polystyrene content and 30 kg/mol polystyrene molecular weight was produced and blended with the base asphalt binder, which modified the base asphalt binder from PG 52-34 to PG 64-28 as estimated by the prediction models that could be used for warm climate regions pavement applications. This result verified the high accuracy of the prediction models, and showed that the optimized PS-PAESO formulation performed superior to the commercial poly(styrene-*block*-butadiene) (SB) in asphalt modification at the same dosage in terms of critical high temperature.

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### 3.2. Introduction

Soybean oil is one of the most abundant oils in global vegetable oil production [1,2]. It possesses multiple carbon-carbon double bonds (C=C) that allow for modification, which makes it particularly suitable for polymerization as biomonomers (biological monomers) in the polymer industry [3,4]. Due to the low reactivity of these double bonds in vegetable oils (i.e. soybean oil), soybean oil needs to be epoxidized and reacted with acrylic acid to yield acrylated epoxidized soybean oil (AESO) that has very active double bonds for polymerization [5–8]. Then AESO can be polymerized and synthesized into a rubbery component to replace butadiene in block copolymers (e.g. poly(styrene-block-butadiene) (SB) and poly(styrene-block-butadiene-block-styrene) (SBS)) with similar properties [3,4,7].

In previous research, soybean oil-based block bio-advantaged copolymers, poly (styrene-block-acrylated epoxidized soybean oil) (PS-PAESO), have been successfully synthesized in the laboratory [3,7,9–11]. When used for modification they have shown improved elasticity and reduced the temperature susceptibility of the base asphalt binder to equal and/or better performance than the same base asphalt binder modified with commercial SB polymer at the same dosage levels [3,7,9–11]. Previous research done by Cascione et al.[9] and Williams et al. [7] at Iowa State University found that the optimum dosage of PS-PAESO was 3% by weight of the modified blends, and that the blend procedure needed to maximize the modification effects of PS-PAESO polymer must be set at high speed (i.e. 3000rpm) and high temperature (i.e. 190°C) for 3 hours shear blending using a base asphalt binder with performance grade of 52-34. Recent research conducted by Chen et al. [11] investigated the modification effects of different PS-PAESO polymers with a target of 1250 kg/mol molecular weight PS-PAESO diblock copolymer consisted of PAESO with various polystyrene (PS) molecular weight and molecular content. The chemical

characterizations on PS-PAESO polymers were performed by using a hydrogen nuclear magnetic resonance (H-NMR) and high temperature gel chromatography (HT-GPC) to identify if the polymer's molecular weight, PS content, and polydispersity met the polymer design target as a process of quality control/ quality assurance [11]. Furthermore, morphology conditions of PS-PAESO modified asphalt binder were examined against commercial SB polymer modified asphalt binder through a fluorescence optical microscope [11]. The fluorescence optical micrographs presented different morphological conditions between SB and PS-PAESO modified binders as PS-PAESO modified binders showed a homogenous morphology with finer polymer particles distribution while SB presented a multiphase morphology with coarsely distributed polymer [11]. This indicated PS-PAESO polymer had better compatibility with base asphalt binder and was able to be entangled with asphalt molecules with an increased elastic response, which was confirmed by rheological characterizations [11]. The master curves for complex shear modulus and phase angle and Black diagrams were produced for examining the viscoelastic behavior of polymer modified binders under a wide range of frequencies and temperatures [11]. The rheological curves presented the positive stiffening effect and increase of elasticity with additional PS-PAESO over the testing frequency range [11]. Additionally, studied economic and environmental implications of PS-PAESO biopolymer versus commercial petroleum-based SB polymer indicated that there was great value in using PS-PAESO with lower heat generation during production, lower and more stable prices (\$0.92/lb of PS-PAESO vs. \$1.05/lb SB), safer to transport, less toxic, and more biodegradable than commercial petroleum-based polymers [10,11]. These aforementioned findings showed great potential in using PS-PAESO polymer as a sustainable modifier alternative to petroleum-based polymer in asphalt performance modification with desirable modification effects and environmental and economic benefits. However, it is necessary to optimize the

formulation of PS-PAESO polymer for this research to maximize the performance of polymer modified binder.

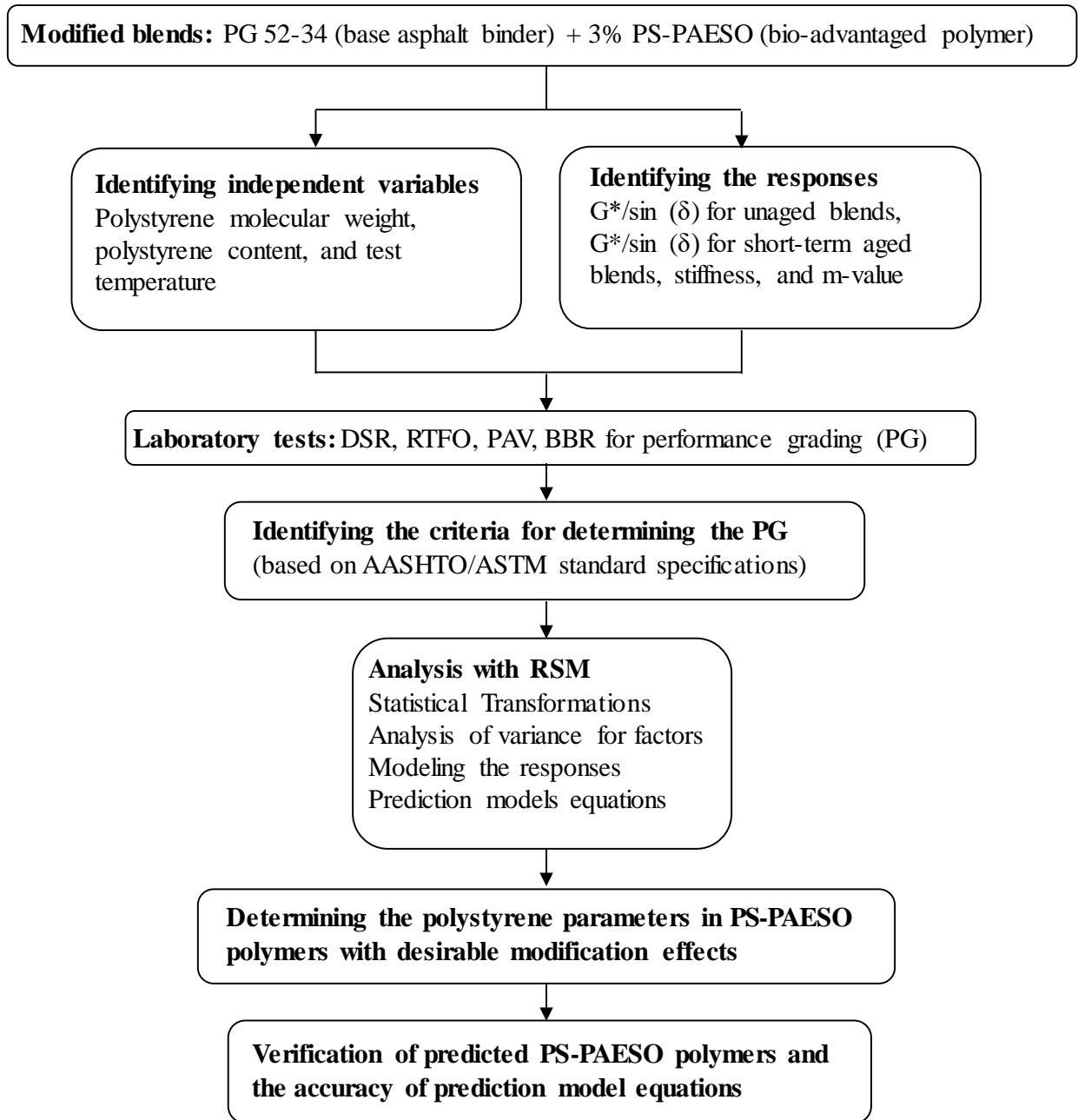
In many cases, performing a full experimental design plan is very time-consuming, and expensive. To solve this problem, a partial experimental design plan was done and prediction models were developed using the measured results through response surface modelling (RSM) to optimize the formulation of the polymer. Thus, seventeen PS-PAESO polymers with target molecular weight of 1250 kg/mol consisting of PAESO with various polystyrene (PS) molecular weights and contents were produced. These PS-PAESO formulations were then used to modify the base binder at the same dosage, and subsequently the modified binders were put through a full binder investigation following ASTM D6373-15 and AASHTO M320-10 criteria (defined as the critical high and low temperatures for determination of the modified blends grade). The grading results obtained from laboratory testing were used hereafter for polymer formulation optimization via RSM.

RSM is a combination of techniques from both mathematics and statistics. It helps in identifying factors that produce the best response or satisfy process specifications with fewer experiments and also helps to identify optimum conditions that improve product quality by giving a suitable model for the unknown relationship between the responses and the independent variables [12–15]. RSM has many applications in research and has been shown to be very effective in the optimization of machining techniques in mechanics [16], chemical reactions in material science [17,18], water treatment in environmental science [19,20], and torrefaction conditions in biomass [21]. Furthermore, the use of RSM has been used in past asphalt research. RSM was used for predicting asphalt pavement properties [22], evaluating the effect of lime content and grading on the stripping potential and the Tensile Strength Ratio (TSR) of Stone Matrix Asphalt (SMA) and



hot mix asphalt (HMA) [14,23,24], determining optimum binder content of warm mix asphalt (WMA) [25], optimizing the fracture toughness characteristics in asphalt mixtures in terms of low temperature cracking performance [26], and developing relationships between independent factors (i.e. temperature and frequency) and HMA permanent deformation [15]. These applications of RSM in different fields of engineering illustrate that RSM can be used as a beneficial modelling tool in statistical analysis and prediction.

The main objective of this study (i.e. optimization of PS parameters molecular weight and content in PS-PAESO for better performing modified asphalt binders) can be achieved through the development of a new statistical approach using response surface modelling (RSM) using these binder performance test results. The secondary objective is to showcase that PS-PAESO can, when its formulation is optimized, modify a PG 52-34 base asphalt binder to a PG 64-28 polymer modified binder for warm climate regions pavement applications with a 3% polymer content dosage and perform equal and/or better than the commercial SB polymer in terms of critical high temperature and continuous grade range. Thus, the interaction effect of the independent variables (experimental factors) (i.e. polystyrene molecular weight, polystyrene content, and test temperature), on the test responses of polymer modified asphalt binder's critical high and low temperatures (i.e.  $G^*/\sin(\delta)$  for unaged and short-term aged blends, stiffness, and m-value) will be investigated. In order to assess the accuracy of the predicted equations obtained from RSM, the recommended PS parameters with predicted critical temperatures and testified grade results on the produced recommended PS-PAESO polymer will be presented. The overall research process is summarized in Figure 3.1.



**Figure 3.1. The overall research process.**

### 3.3. Experimental materials

#### 3.3.1. Asphalt binder and polymer types

The base asphalt binder used for this research was procured from a Canadian crude source and was graded out to be PG 52-34. To compare performance, a commercially available petroleum-

derived SB di-block) polymer was used for asphalt modification. The bio-advantaged polymers used for asphalt modification are laboratory produced PS-PAESO polymers with target molecular weight of 1250 kg/mol that consists of PAESO block and PS block with different polystyrene parameters as shown in Table 3.1.

**Table 3.1. List of the different PS-PAESO polymers for asphalt modification with corresponding modified asphalt blends codes.**

Polystyrene Content, %	Polystyrene Molecular Weight, kg/mol			Chemical Reaction Length, hr
	10	20	30	
30	–	–	Blend 9	4
30	–	–	Blend 10	5
20	Blend 1	–	–	8
25	Blend 2, Blend 3	Blend 8	Blend 11,	8
30	Blend 4, Blend 5, Blend 6	–	Blend 12, Blend 13	8
35	Blend 7	–	–	8
30	–	–	Blend 14	9
30	–	–	Blend 15	10
30	–	–	Blend 16	11
30	–	–	Blend 17	12

### 3.3.2. Development of PS-PAESO

#### 3.3.2.1. Production materials

Styrene was purified over basic alumina. Other raw materials used as received in the reaction are ESO (contains 4000 ppm monomethyl ether hydroquinone as inhibitor), pyridine (catalyst, 99.8% purity), hydroquinone (inhibitor, 99% purity), and acrylic acid (contains 180-200 ppm MEHQ as inhibitor, 99% purity). AIBN (Azobisisobutyronitrile), MEHQ (Methylhydroquinone, 99% purity), inhibitor remover, diethyl ether (ACS, grade), and sodium bicarbonate (white crystalline powder, certified ACS) were used as received without further purification. Chemical solvent used as reagents in the reaction are dioxane and toluene.

### **3.3.2.2. Production Methods [27,28]**

The reaction was initiated when ESO was mixed with pyridine (catalyst) and hydroquinone (inhibitor) in a flask. Toluene and acrylic acid were added to the mixture and then diethyl ether and sodium bicarbonate were added to the solution as a purification process when the reaction was completed. A vacuum oven was used to dry the material overnight until the final product, AESO, was obtained. A controlled/living free radical polymerization (CFRP) was utilized in this research to synthesize PS-PAESO polymers through reversible addition-fragmentation chain-transfer (RAFT). Biomonomer AESO was polymerized with polystyrene in the condition of a free radical initiator and a chain transfer agent (CTA). Compared to traditional CFRP, the polymer structure, composition, and molecular weight can be easily controlled and designed using RAFT.

### **3.3.2.3. Chemical characterization of PS-PAESO [11]**

H-NMR spectroscopic analysis on the produced PS-PAESO polymers was performed on by using a 600 MHz Bruker Avance III spectrometer. The actual effective PS contents can be obtained from the H-NMR spectrum graph. A HT-GPC was used to measure molecular weight and molecular weight distribution of the PS-PAESO polymer. The results from HT-GPC provide important information for predicting the processability, material properties, and quantitative analysis of a polymer. The compatibility between polymer and asphalt binder and dispersity of the polymer within asphalt binder were examined using a fluorescence microscope with high intensity light to illuminate specimens on a sample glass slide to produce magnified and lightened images. The specific results can be found in previously published research [11].

### **3.3.3. Sample preparation and experimental testing plan**

All modified blends were prepared by using PS-PAESO bio-advantaged polymer and commercial SB polymer at 3% by weight of the total modified blends [7,9]. The bio-advantaged

polymer was blended at  $190\pm 5^{\circ}\text{C}$  for three hours at 3000 rpm using a shear mixer [7,9]. After the modified blends were produced, material was reserved for testing in a dynamic shear rheometer (DSR) to acquire the unaged critical high temperature. Additional material was poured into glass containers and blown with consistent air in a rolling thin-film oven (RTFO) to determine the volatility of the material and simulate binder aging during hot mix asphalt (HMA) production and construction [29]. Enough material from the short-term aged blends was reserved for DSR testing to obtain the short-term aged critical high temperature. The remaining short-term aged material from the blends was placed in trays and exposed to pressure at high temperature to simulate long term binder aging during HMA service life so the subsequent material blends could be tested again in a DSR for fatigue cracking specification purposes as well as a bending beam rheometer (BBR) test to attain critical low temperatures [29].

All tests mentioned were conducted for evaluating the bio-advantaged polymer modification effects on the performance grading results of the modified blends. The Superpave (Superior performing asphalt pavements) performance grading system binder tests were conducted by following the ASTM/AASHTO standard specifications listed below:

- ASTM D7175-08 (AASHTO T315-10): Standard Test Method for Determining the Rheological Properties of Asphalt Binder Using a Dynamic Shear Rheometer,
- ASTM D2872-12 (AASHTO T240-09): Standard Test Method for Effect of Heat and Air on a Moving Film of Asphalt (Rolling Thin-Film Oven Test),
- ASTM D6521-13 (AASHTO R28-12): Standard Practice for Accelerated Aging of Asphalt Binder Using a Pressurized Aging Vessel (PAV),

- ASTM D6648-08 (AASHTO T313-10): Standard Test Method for Determining the Flexural Creep Stiffness of Asphalt Binder Using the Bending Beam Rheometer (BBR), and
- ASTM D6373-15 (AASHTO M320-10): Standard Specification for Performance Graded Asphalt Binder.

The DSR measures the viscous and elastic properties of the asphalt binder at high and intermediate temperatures to determine the material's resistance to permanent deformation (rutting) and fatigue cracking. From testing, the two main parameters acquired are the complex modulus ( $G^*$ ) and the phase angle ( $\delta$ ), which are measured at multiple temperatures at one frequency (1.59 Hz or 10 rad/sec). The complex modulus is the total resistance of the binder to deformation under repeated shearing stress, which consists of the storage modulus ( $G'$ ) and the loss modulus ( $G''$ ). The two components are related to the amount of energy stored and lost in a specimen's material during each testing cycle, respectively. The phase angle is between 0-90 degrees and is defined as the time lag between the applied stress and the resulting strain. Because asphalt binder is considered a viscoelastic material, the time lag is larger at higher temperatures as the binder is more viscous in nature, while at low temperatures it is smaller as the binder is more elastic in nature [29–31]. In this research, the DSR tests were only conducted for evaluating the asphalt binder rutting resistance at high temperatures. For polymer-modified binder a high complex modulus and a low phase angle is most desired, which implies a much stiffer asphalt binder. For asphalt modification, polymers are expected to increase the elasticity of the base asphalt binder that indicates the improvement of permanent deformation resistance [32]. Rheological master curves and Black diagrams were generated by using the complex modulus and

phase angle collected from frequency sweep tests by using a DSR and the results were presented in previous published research [11].

At low temperatures, asphalt binder behaves like an elastic solid, however, it may become too brittle and crack when the stress exceeds the material's capacity. The BBR measures low temperature stiffness and failure properties of asphalt binder that has been PAV aged, a process that simulates long-term in-service aging and hardening of the asphalt binder. In the BBR test, deflection and load are measured as an asphalt binder beam deflects under a constant loading at the prescribed test temperatures. The time-temperature superposition principle is used to shorten laboratory testing time and is built into the design of the BBR equipment and test. To achieve time-temperature superposition an offset of 10.0°C is used. Parameters obtained from the test are creep stiffness and m-value at 60 seconds, which represent the resistance of asphalt binder to creep loading and change in stiffness (fatigue cracking), respectively. Performing both DSR and BBR tests offer a wide range of temperatures for understanding the stiffness of asphalt binder [29,31,34,35].

### **3.4. Statistical transformations of data and response surface modelling**

A response surface model was developed to estimate the optimum polystyrene parameters of the bio-advantaged polymer PS-PAESO needed for maximizing the performance at both high temperature and low temperatures for the polymer modified asphalt blends by using the laboratory performance grade test results of the modified blends. The factors that had significant effects on the modified binders' grading results were identified through analyses of variances (ANOVA)s at a 95% confidence interval in previous research, which were test temperature, polystyrene molecular weight, and polystyrene content [11]. Therefore, these three significant factors were used as independent variables in RSM.

### 3.4.1. Statistical transformations

In order to obtain the most reliable and appropriate prediction model, the residuals of the finalized models were first examined in the non-transformed state (unmodified) and transformed states. The residual plot evaluation is important because it demonstrates how well the test data fits the prediction model that meets the normality assumption [36]. The statistical transformations help change the shape of a distribution or relationship with the variables. The transformations selected for evaluation and comparison were the logarithm base 10 (Log10) transformed state and square root (SQRT) transformed state that can substantially help reduce skewness of the residuals, yield approximately equal spread, and produce a nearly linear or additive relationship [37]. The fit model of standard least square calculations were performed to test the overall significance of independent variables and their interactive effects at each state of regression model by the ANOVA F-test. Additionally, the  $R^2$  (coefficient of determination) values for each finalized regression model should be examined as well due to its reflection of the model's accuracy and variability. The  $R^2$  value indicates the percentage of the variability in the dependent variable that can be explained by the model. The  $R^2$  value is between 0 to 1; when  $R^2$  value approaches 1 the regression model fits the actual data better than if it were to approach 0 [13].

### 3.4.2. Response surface modelling (RSM)

Based on the laboratory test results, the critical high and low temperatures of the bio-advantaged polymer modified blends were used as responses. The effects of independent factors (i.e. polystyrene molecular weight, polystyrene content, and test temperature) were selected to develop the initial response surface model to find the functional relationship through a step-wise regression process by the standard least squares approach.



The initial full model allows the formulation of a second-order polynomial model to describe the process, which includes three first-order model linear effects, three cross product factors (interactive terms), and three second-order quadratic items as shown in Equation. (3.1).

$$y = \beta_0 + \beta_1x_1 + \beta_2x_2 + \beta_3x_3 + \beta_{12}x_1x_2 + \beta_{13}x_1x_3 + \beta_{23}x_2x_3 + \beta_{11}x_1^2 + \beta_{22}x_2^2 + \beta_{33}x_3^2 + \varepsilon \quad (3.1)$$

where  $y$  is the response of the testing results which relates to  $x_1$ ,  $x_2$ , and  $x_3$  of the three major factors: polystyrene molecular weight (kg/mol), polystyrene content (%), and test temperature ( $^{\circ}\text{C}$ ), respectively.  $\beta_0$  is the intercept,  $\beta_1 \dots \beta_{33}$  are coefficients and  $\varepsilon$  is the random error component. The fit quality of the polynomial model is expressed by  $R^2$ .

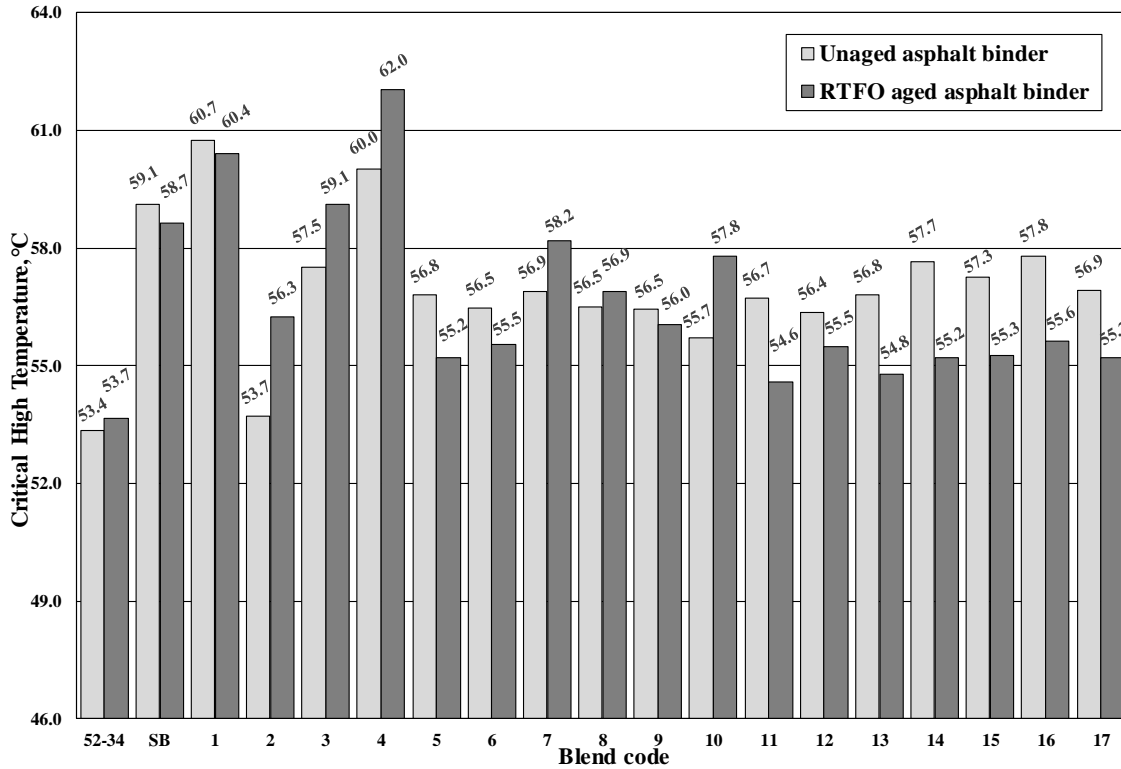
In each response surface model, the four responses are  $G^*/\sin(\delta)$  of unaged modified blends,  $G^*/\sin(\delta)$  of RTFO short-term aged modified blends, and m-value and stiffness of PAV aged modified blends. The step-wise regression was performed on the initial models of unmodified data, Log10 transformed data, and SQRT transformed data to eliminate the least important variable that had the highest p-value than that of the rest variables until the finalized model was obtained with only statistically significant variables with a confidence level of 95% [38].

### 3.5. Results and discussions

#### 3.5.1. Dynamic shear rheometer results

The DSR tests were performed on unaged and RTFO short-term aged bio-advantaged polymer modified asphalt blends by following ASTM D7175-08 and AASHTO T315-10. According to Superpave standard specifications, the high temperature performance grades were determined on both unaged and RTFO short-term aged DSR results, with the lower of the two critical high temperatures values being chosen as the high temperature performance grade. Furthermore, the specification requires that the high temperature grade criteria for unaged asphalt binder is 1.0 kPa for  $G^*/\sin(\delta)$  and for RTFO short-term aged asphalt binder is 2.2 kPa for  $G^*/\sin(\delta)$ .

The critical high temperatures for unaged modified blends are shown in Figure 3.2. The critical high temperatures of bio-advantaged polymer modified blends vary between 53.7°C and 60.7°C. Since the base asphalt binder has a critical high temperature of 53.4°C, all of the modified blends have higher critical high temperatures. The positive results in unaged critical high temperatures of modified blends indicate rutting resistance improvement of the neat asphalt binder and also imply the bio-advantaged polymers make the base asphalt binder stiffer after modification. The critical high temperatures for RTFO short-term aged modified blends are shown in Figure 3.2. After the RTFO short-term aging process, some of the blends increased the critical high temperature while others decreased 1.0-2.0°C. The temperature variation after the aging process may be the result of different bio-advantaged polymer structures and components that induced different formations of branched networks within the base asphalt binder or aging and testing variability. By following the standard specification, the finalized critical high temperatures of the modified blends are higher than the base asphalt binder that indicate positive modification effects from the PS-PAESO polymer on the high temperature grade.



**Figure 3.2. Critical high temperature for unaged and RTFO aged binders.**

### 3.5.2. High temperature grade prediction model

The analysis of variance (ANOVA) tables were obtained and analyzed for the response surface models at each state (untransformed data, Log10 transformed data, and square root transformed data) through the step-wise regression process by the standard least squares approach. The critical high temperature results shown in Figure 3.2 were used as the responses in each initial full model, respectively. Three finalized models in unmodified, Log10 transformed state, and SQRT state were compared by examining the residuals, with the one closest to having a normal distribution and equal standard deviation being selected as the model for predicting the optimum PS-PAESO polystyrene parameters.

### 3.5.2.1. Unaged prediction model

For the unaged modified blends results, the residuals from the final models of the three states were compared as shown in Figure 3.3. After transformation, the residuals of Log10 transformed state followed the normal distribution and met the equal standard deviation condition with a high  $R^2$  value of 99.0% and the smallest standard deviation of 0.077 among the three states. The ANOVA table and the corresponding coefficient values table of the final Log10 transformed state model are shown in Tables 2 and 3. The finalized prediction model for unaged modified blends DSR results (high temperature)  $G^*/\sin(\delta)$  is presented in Equation (3.2).

$$\left(\frac{G^*}{\sin\delta}\right) = 10(\beta_0 + \beta_1 \times x_1 + \beta_2 \times x_2 + \beta_3 \times x_3 + \beta_{11} \times x_1^2 + \beta_{22} \times x_2^2 + \beta_{33} \times x_3^2) \quad (3.2)$$

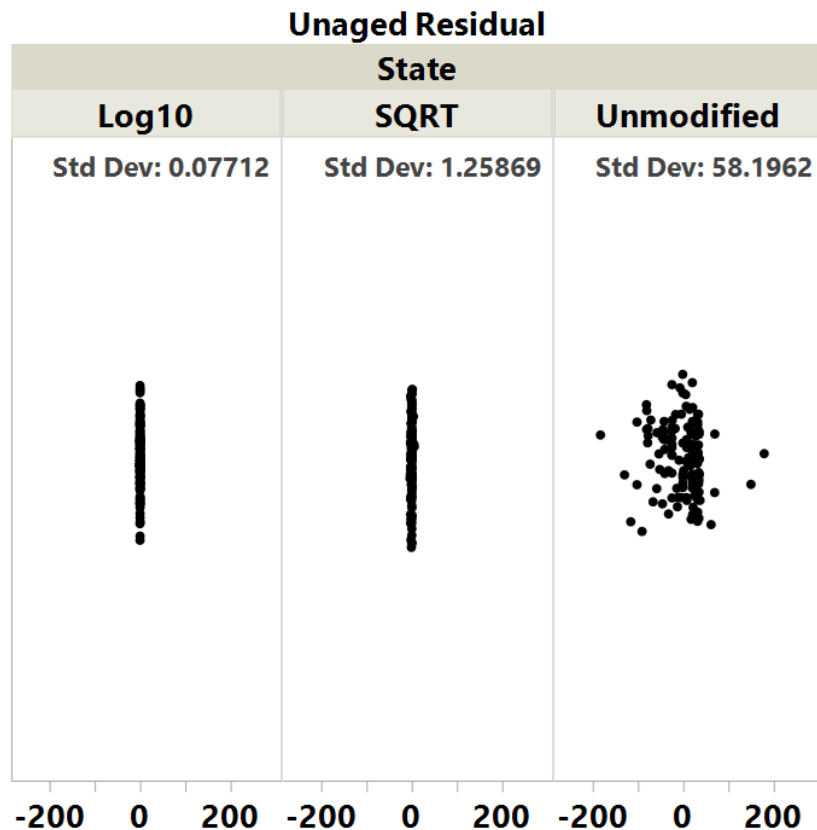


Figure 3.3. Residual comparisons with standard deviations of unaged polymer modified blends  $G^*/\sin(\delta)$  values.

### 3.5.2.2. *RTFO aged prediction model*

For comparison of the RTFO short-term aged DSR results at unmodified state, Log10 transformed state, and SQRT transformed state, the finalized models residuals were examined as the example shown in Figure 3.3. The Log10 transformed state model had the smallest standard deviation of 0.090 with a 99.0% R<sup>2</sup> value, and smallest spread of residuals, and thus was selected as the final prediction model. The ANOVA table and the corresponding coefficient values table of the final Log10 transformed state model are shown in Table 3.2 and Table 3.3. The finalized prediction model's equation is presented in Equation. (3).

$$\left(\frac{G^*}{\sin\delta}\right) = 10^{(\beta_0 + \beta_1 \times x_1 + \beta_2 \times x_2 + \beta_3 \times x_3 + \beta_{12} \times x_1 \times x_2 + \beta_{22} \times x_2^2 + \beta_{33} \times x_3^2)} \quad (3)$$

**Table 3.2. ANOVA of Log10 transformed model for unaged, RTFO modified blends DSR test  $G^*/\sin(\delta)$  values and PAV aged modified blends BBR test stiffness values, and SQRT transformed model for PAV aged modified blends BBR test m-value.**

Independent Variable	DF	SS	MS	F Ratio	Prob>F
$G^*/\sin(\delta)_{(Unaged)}$					
PS MW,kg/mol_X1	1	0.0431506	0.043151	6.9226	0.0096*
PS content,%_X2	1	1.2256559	1.225656	196.6300	<0.0001*
Test Temp,°C_X3	1	4.1770890	4.177089	670.1236	<0.0001*
X1^2	1	0.0383756	0.038376	6.1565	0.0144*
X2^2	1	0.6335020	0.633502	101.6317	<0.0001*
X3^2	1	0.3651306	0.365131	58.5773	<0.0001*
R <sup>2</sup>	99.27	-	-	-	-
Std Dev of Residuals	0.07712	-	-	-	-
$G^*/\sin(\delta)_{(RTFO\ aged)}$					
PS MW,kg/mol_X1	1	0.1734077	0.173408	20.3664	<0.0001*
PS content,%_X2	1	1.1465881	1.146588	134.6646	<0.0001*
Test Temp,°C_X3	1	3.5717483	3.571748	419.4949	<0.0001*
X1*X2	1	0.1093027	0.109303	12.8374	0.0005*
X2^2	1	1.7921634	1.792163	210.4861	<0.0001*
X3^2	1	0.2051615	0.205161	24.0958	<0.0001*
R <sup>2</sup>	99.00	-	-	-	-
Std Dev of Residuals	0.09014	-	-	-	-
Stiffness <sub>(PAV aged)</sub>					
PS MW,kg/mol_X1	1	0.0488737	0.048874	16.1880	<0.0001*
PS content,%_X2	1	0.0705068	0.070507	23.3534	<0.0001*
Test Temp,°C_X3	1	3.5495883	3.549588	1175.702	<0.0001*
X2^2	1	0.0796086	0.079609	26.3681	<0.0001*
R <sup>2</sup>	90.50	-	-	-	-
Std Dev of Residuals	0.0541	-	-	-	-
m-value <sub>(PAV aged)</sub>					
PS content,%_X2	1	0.0488737	0.048874	16.1880	<0.0001*
Test Temp,°C_X3	1	0.0705068	0.070507	23.3534	<0.0001*
X1^2	1	3.5495883	3.549588	1175.702	<0.0001*
X2^2	1	0.0796086	0.079609	26.3681	<0.0001*
R <sup>2</sup>	76.52	-	-	-	-
Std Dev of Residuals	0.01604	-	-	-	-

Note: *DF* degrees of freedom, *SS* sum of squares, *MS* mean square, statistically significant at  $\alpha < 0.05$ .

**Table 3.3. Regression coefficients of prediction models for unaged, RTFO aged modified blends DSR test  $G^*/\sin(\delta)$  values, PAV aged modified blends BBR test stiffness values and m-value.**

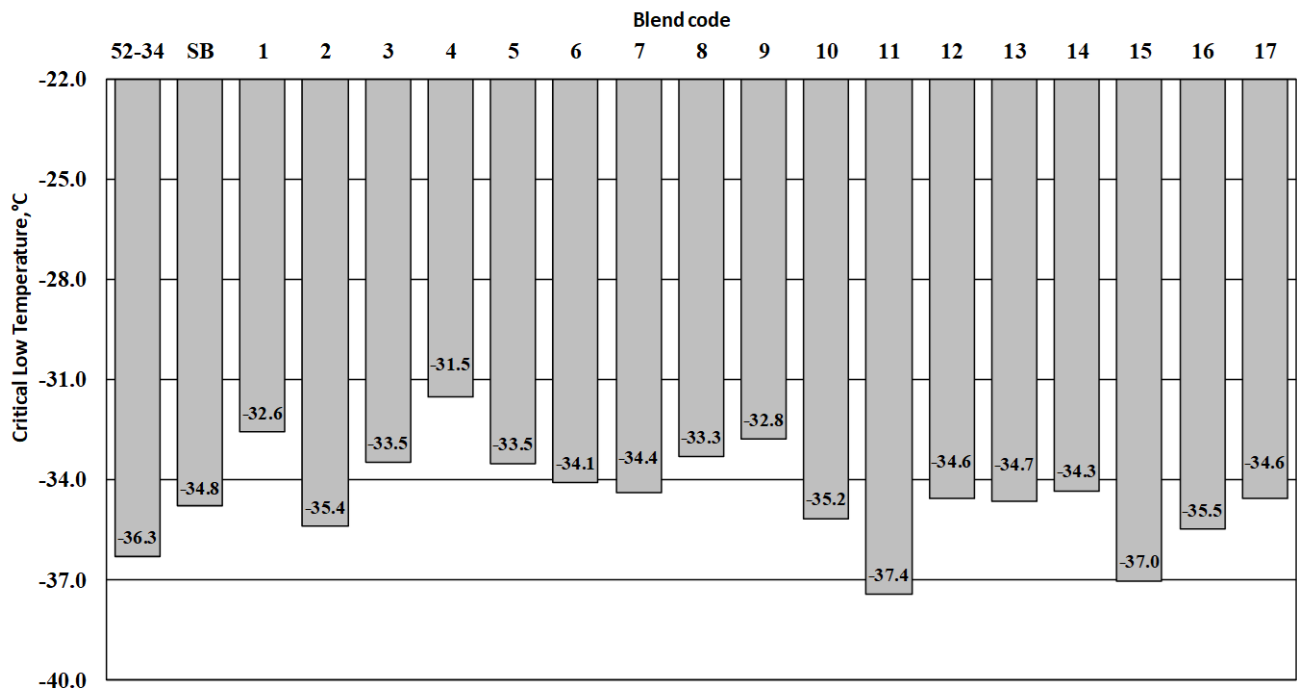
Regression coefficient	Coefficient value	Standard Error	t Ratio	Prob>  t
$G^*/\sin(\delta)_{(Unaged)}$				
$\beta_0$	5.4062011	0.132	40.96	<.0001*
$\beta_1$	-0.035459	0.013477	-2.63	0.0096*
$\beta_2$	-0.051313	0.003659	-14.02	<.0001*
$\beta_3$	-0.097202	0.003755	-25.89	<.0001*
$\beta_{11}$	0.000833	0.000336	2.48	0.0144*
$\beta_{22}$	0.0007587	7.526e-5	10.08	<.0001*
$\beta_{33}$	0.0003658	4.779e-5	7.65	<.0001*
$G^*/\sin(\delta)_{(RTFO\ aged)}$				
$\beta_0$	5.9536825	0.175453	33.93	<.0001*
$\beta_1$	-0.022674	0.005024	-4.51	<.0001*
$\beta_2$	-0.083476	0.007193	-11.60	<.0001*
$\beta_3$	-0.089883	0.004388	-20.48	<.0001*
$\beta_{12}$	0.0006269	0.000175	3.58	0.0005*
$\beta_{22}$	0.0013052	0.00009	14.51	<.0001*
$\beta_{33}$	0.0002742	5.586e-5	4.91	<.0001*
Stiffness <sub>(PAV aged)</sub>				
$\beta_0$	1.2166729	0.049357	24.65	<.0001*
$\beta_1$	-0.002152	0.000535	-4.02	<.0001*
$\beta_2$	-0.012236	0.002532	-4.83	<.0001*
$\beta_3$	-0.054661	0.001594	-34.29	<.0001*
$\beta_{22}$	0.0002663	5.187e-5	5.13	<.0001*
m-value <sub>(PAV aged)</sub>				
$\beta_0$	0.721626	0.014255	50.62	<.0001*
$\beta_2$	0.0030204	0.000752	4.02	<.0001*
$\beta_3$	0.0092462	0.000473	19.56	<.0001*
$\beta_{11}$	0.00001688	3.951e-6	4.26	<.0001*
$\beta_{22}$	-0.00005379	1.541e-5	-3.49	0.0007*

Note: statistically significant at  $\alpha < 0.05$ .

### 3.5.3. Bending beam rheometer results

By following the ASTM D6648-08 and AASHTO T313-10 test procedures, the critical low temperature results were obtained by performing the bending beam rheometer tests on the modified

blends after the PAV long-term aging process. The criteria for the critical low temperature are based on two parameters: the stiffness and the m-value at a loading time of 60 seconds in a BBR. The critical low temperature is determined using the limiting criteria of the stiffness being less than or equal to 300 MPa or the m-value being greater than or equal to 0.300. The low temperature grade of the base asphalt binder used in this study was graded at  $-34^{\circ}\text{C}$ . The critical low temperature results obtained from BBR testing are summarized in Figure 3.4.



**Figure 3.4. Critical low temperature for modified blends.**

Based on the critical low temperature results, the blends that have temperatures lower than  $-34^{\circ}\text{C}$  and are graded as  $-34^{\circ}\text{C}$ , while the blends that have temperature higher than  $-34^{\circ}\text{C}$  but lower than  $-28^{\circ}\text{C}$  are graded as  $-28^{\circ}\text{C}$ . The results in Figure 3.4 indicate most of the bio-advantaged polymers used did not substantially improve the low temperature performance grade compared to the base asphalt binder. Therefore, the bio-advantaged polymers were generally compromised on the low temperature grade by as much as  $4.8^{\circ}\text{C}$  (blend 4) but did improve by  $1.1^{\circ}\text{C}$  (blend 11)



while they all improved the high temperature grade. The PS-PAESO polymer performed like most of the polymers use in asphalt modification in terms of comprising on stiffness and low temperature grade. When there is an improvement on the properties of the base asphalt binder by polymer modification, there would always compromise some other performance of the modified asphalt binder [39–42]. However, the continuous grade ranges listed in Table 3.4 indicate the bio-advantaged polymers are able to widen the working temperature ranges of the base asphalt binder. Eleven of the seventeen blends have higher continuous grade ranges than the base asphalt binder and eight of the seventeen blends have continuous grade ranges very close to the commercially available SB polymer, which indicate the bio-advantaged polymers have positive effects on reducing the temperature susceptibility of the base asphalt binder.

**Table 3.4. Continuous PG ranges of polymer modified blends.**

Blend code	Continuous Grade Range, °C
52-34	89.7
SB	93.4
1	93.0
2	89.1
3	91.0
4	91.5
5	88.7
6	89.6
7	91.3
8	89.8
9	88.8
10	90.9
11	92.0
12	90.1
13	89.4
14	89.5
15	92.3
16	91.1
17	89.8

### 3.5.4. Low Temperature Grade Prediction Model

Response surface modelling was developed for estimating the optimum polystyrene parameters based on the critical low temperature results. The same procedures used in developing the high temperature grade prediction models were used for determining and examining the appropriate prediction models on the low temperature side. The critical low temperature depends on stiffness and m-value from the BBR tests, thus, two prediction models were determined corresponding to these data parameters.

#### 3.5.4.1. Stiffness prediction model

The BBR stiffness data was used as the response in the initial full model. After the step-wise regression process and the examination of the residuals, the finalized model selected for the bio-advantaged polymer modified blends was the Log10 transformed state model with a  $R^2$  value of 91.0% and the smallest standard deviation of the residuals in comparison with the other two states. The ANOVA table and the corresponding coefficient values are shown in Table 3.2 and Table 3.3. The finalized prediction model is shown in Equation (3.4).

$$(\text{stiffness}) = 10^{(\beta_0 + \beta_1 \times x_1 + \beta_2 \times x_2 + \beta_3 \times x_3 + \beta_{22} \times x_2^2)} \quad (3.4)$$

#### 3.5.4.2. m-value prediction model

The m-value data obtained from the BBR test was used as the response for developing the models. The finalized model selected for the PAV long-term aged modified blends was the SQRT transformed state model with a 76.5%  $R^2$  value and the residuals followed a normal distribution. The ANOVA table and the corresponding coefficient values are presented in Table 3.2 and Table 3.3. The final prediction model is shown in Equation (3.5).

$$(\text{m} - \text{value}) = (\beta_0 + \beta_2 \times x_2 + \beta_3 \times x_3 + \beta_{11} \times x_1^2 + \beta_{22} \times x_2^2)^2 \quad (3.5)$$

### 3.5.5. Estimated optimum polystyrene parameters & verification

Each of the prediction models needs to be combined with corresponding coefficient values in the tables to obtain their respective prediction model equations. The prediction model equations can estimate the optimum polystyrene parameters in the PS-PAESO polymer needed to achieve the most desirable performance grade of the polymer modified blends. Therefore, the four prediction models need to be used in combination to meet criteria according to the Superpave standard specifications as summarized here:

- setting Eq. (3.2) equal to 1.0 (kPa), which is the  $G^*/\sin(\delta)$  critical limit for high temperature rutting deformation of unaged asphalt binder;
- setting Eq. (3.3) equal to 2.2 (kPa), which is the  $G^*/\sin(\delta)$  critical limit for high temperature rutting deformation of the RTFO short-term aged asphalt binder;
- setting Eq. (3.4) equal to or less than 300 (MPa), which is the stiffness critical limit for low temperature thermal cracking of the PAV long-term aged asphalt binder, and
- setting Eq. (3.5) equal to or greater than 0.300, which is the m-value critical limit for low temperature thermal cracking of the PAV long-term aged asphalt binder.

The recommended bio-advantaged polymers of 1.25 MDa molecular weight PS-PAESO with estimated polystyrene molecular weight and polystyrene content that could modify the PG 52-34 base asphalt binder to be PG 64-28 for warm climate regions pavement applications with corresponding estimated test results are summarized in Table 3.5.

**Table 3.5. Recommended polystyrene parameters in PS-PAESO bio-advantaged polymers with their estimated critical temperatures.**

Items	Values			
PolyStyrene MW, kg/mol	15	20	25	30
PolyStyrene Content,%	5	5	5	5
Critical high temp(unaged)	66	65.5	65.5	66.6
Critical high temp (RTFO aged)	69.5	67.5	66	64.3
Critical low temp(PAV aged)	-30.8	-31.1	-31.5	-32.0
Critical low temp@-18°C(m-value)	0.328	0.331	0.336	0.341
Critical low temp@-18°C(stiffness)	130	127	124	121
Critical low temp@-24°C(m-value)	0.268*	0.271*	0.275*	0.279*
Critical low temp@-24°C(stiffness)	277	270	263	257

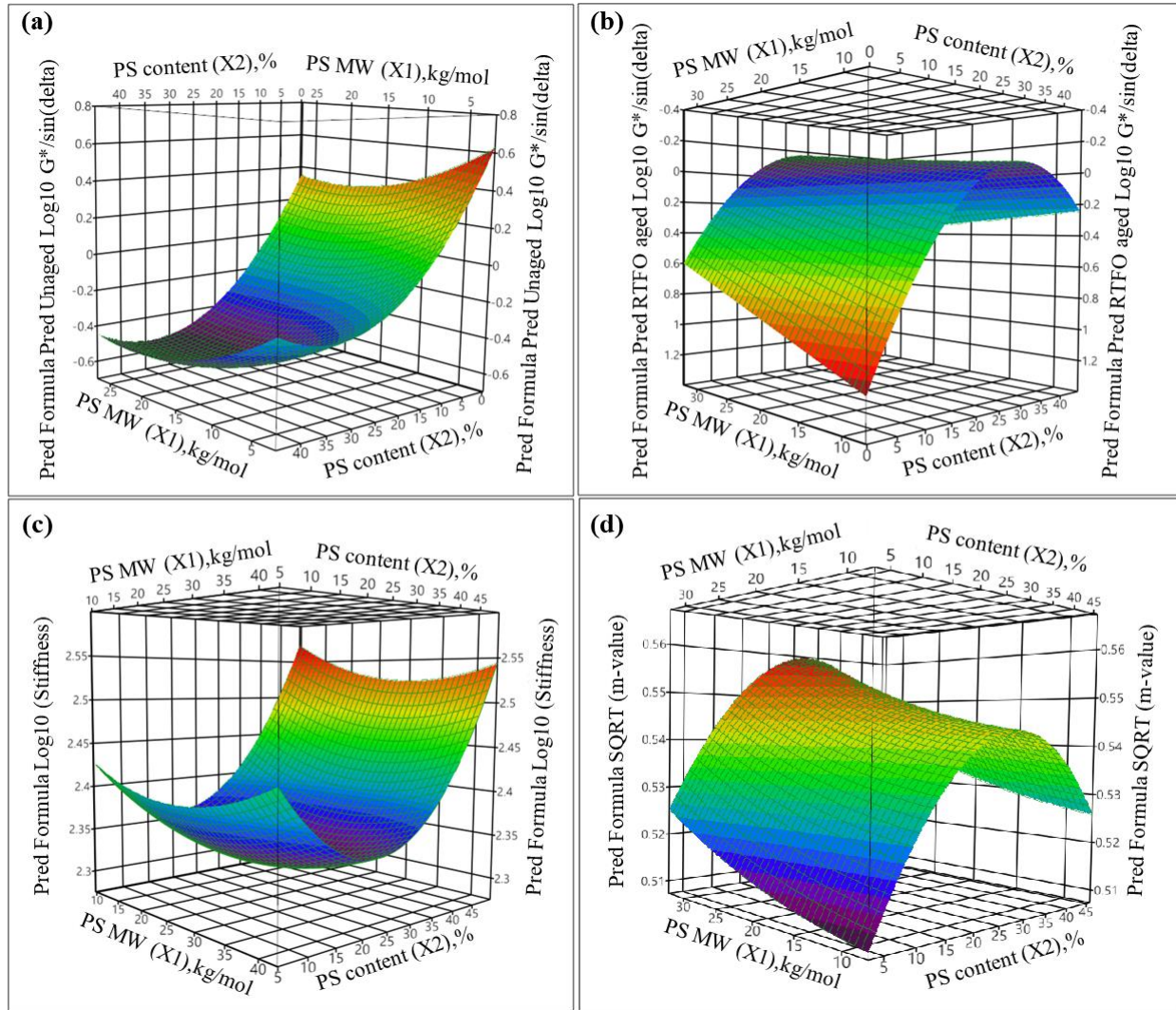
Note: values with \* fail to meet the criteria.

Surface plots were developed to further examine the relationship between independent variables and responses by using the four finalized prediction models. Due to the fact that test temperature had the greatest effect on the asphalt binder rheological performance for both high and low temperature performance grading, the respective critical test temperatures were chosen to be constant for analyzing the relationship between polystyrene parameters and responses in the developed surface plots. In multiple surface plots, two independent variables, polystyrene content (PS content) and polystyrene molecular weight (PS MW), were plotted in the x and y axes and the response was plotted in z axis as shown in Figure 3.5.

To achieve PG 64-28, the polymer modified blends need to pass 64.0°C for high temperature grading (via  $G^*/\sin(\delta)$ ) and pass at a test temperature of -18°C for low temperature grading (via stiffness and the m-value). In Figure 3.5 (a), at a constant polystyrene molecular weight, an increase in  $\text{Log}_{10}(G^*/\sin(\delta))$  value results in a decrease of polystyrene content while a change in the polystyrene molecular weight causes minimal effects to  $\text{Log}_{10}(G^*/\sin(\delta))$  values. To meet the criteria for passing the unaged asphalt binder criteria of  $G^*/\sin(\delta)$  1.0 kPa, the  $\text{Log}_{10}(G^*/\sin(\delta))$

value needs to be higher or equal to 0, therefore, the polystyrene content is suggested to be less than 10%. The same trend was observed in the RTFO aged  $\text{Log}_{10}(G^*/\sin(\delta))$  surface plot as well in Figure 3.5 (b). The polystyrene content should be less than 10% to achieve the RTFO aged  $\text{Log}_{10}(G^*/\sin(\delta))$  to be greater than 2.2 kPa criteria.

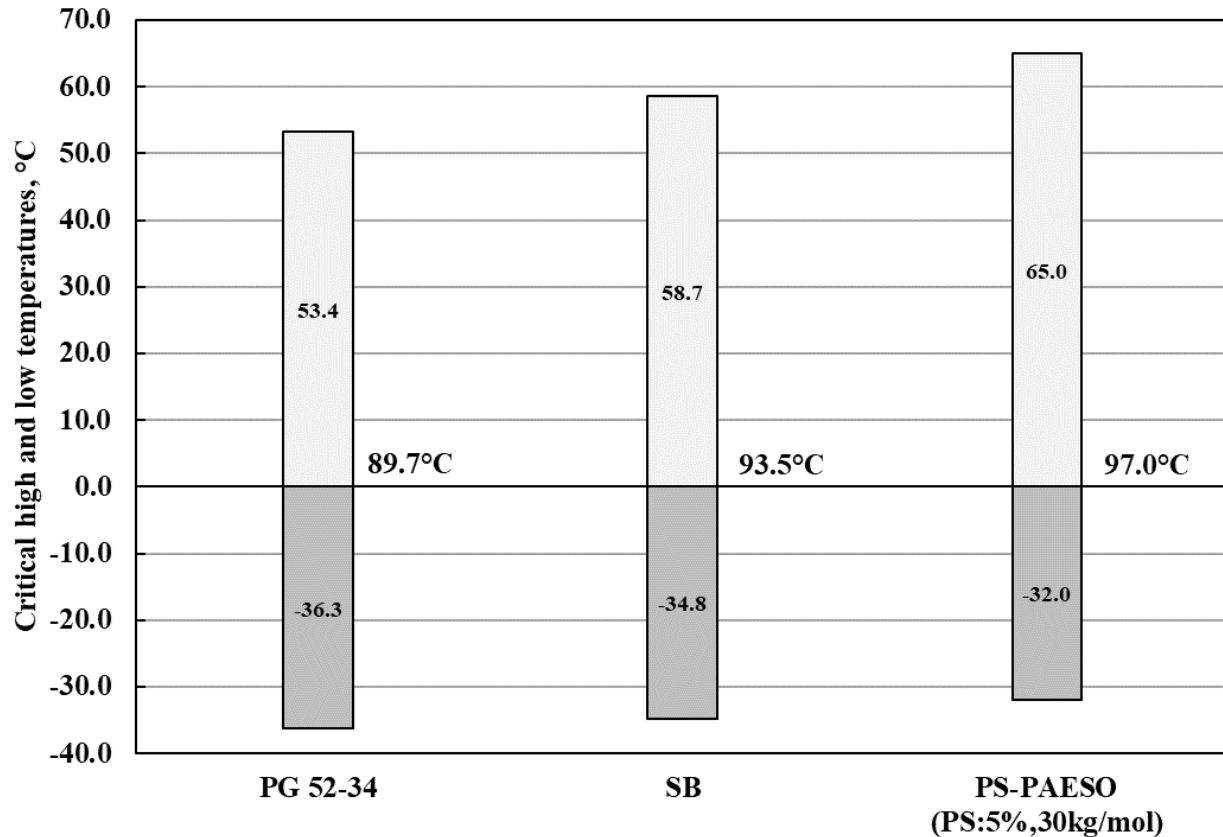
An increase in polystyrene content from 5% to 45% results in changes of  $\text{Log}_{10}$  (stiffness) values from higher to lower to higher at a constant polystyrene molecular weight as shown in Figure 3.5 (c). However, higher polystyrene content is not recommended for the high temperature grade surface plots because only lower polystyrene contents could meet the criteria of 1.0 and 2.2 kPa for unaged and RTFO aged binder grading. Therefore, lower polystyrene contents are inferred. In Figure 3.5 (d), at a constant polystyrene molecular weight, the highest SQRT (m-value) was obtained at an intermediate polystyrene content between 25-30%. In terms of polymer composition, polystyrene is the hard and stiff domain that provides strength to the polymer [7]. When the polymer is blended with an asphalt binder, the polystyrene domain will increase the stiffness of the base asphalt binder as the polystyrene content in the polymer increases [7,43,44]. Achieving a higher critical high temperature such that the modified binder can be used for warm climate regions pavement application is preferred but not to the detriment, or decrease in the low temperature grade within this research. As a result, lower polystyrene content with increasing polystyrene molecular weight (from 15 to 35 kg/mol) can improve the values of SQRT (m-value) from about 0.51 to 0.53. It can be concluded that the analysis of surface plots matches the estimated test results and suggested polystyrene parameters in Table 3.5.



**Figure 3.5. Surface plots of responses: (a) unaged Log10 ( $G^*/\sin(\delta)$ ), (b) RTFO aged Log10 ( $G^*/\sin(\delta)$ ), (c) PAV aged Log10 (stiffness), and (d) PAV aged SQRT (m-value)) for responses versus polystyrene parameters.**

To verify the accuracy of prediction model equations, one of the PS-PAESO bio-advantaged polymer formulations in Table 3.5 was produced 1250 kg/mol PS-PAESO with polystyrene molecular weight of 30 kg/mol, and polystyrene content of 5% was blended with the same base asphalt binder. The asphalt modification effects from the optimized PS-PAESO formulation with the base asphalt binder were examined by high and low temperatures grade tests. The same high speed and high temperature shear blending procedure was conducted to prepare the modified

blends as summarized in Section 3.3.3. Unaged and RTFO short-term aged modified binder specimens were prepared using a 25mm diameter silicon mold and tested in triplicate by using 25mm diameter parallel plates in a DSR. An initial test temperature was set at 46.0°C with increasing increments of 6.0°C until each specimen failed. It was found that the critical high temperature of unaged specimen was 67.0°C (only 0.4°C higher than the estimated one). For the RTFO aged specimen, the critical high temperature of 65.0°C was determined and it was 0.7°C higher than estimated one. The critical low temperature was -32.0°C for the polymer modified binder and it was graded out at -28°C, which is the same as estimated. The overall performance grade for the recommended polymer modified asphalt binder follows the estimated performance grade which is PG 64-28. The results indicate the prediction models are highly accurate, however, the other three PS-PAESO polymers formulations in Table 3.5 need to be produced and tested to further verify the accuracy of the prediction models. The grading results were also compared with the base asphalt binder and the SB polymer modified blends as shown in Figure 3.6. The optimized PS-PAESO significantly increased the critical high temperature of the base asphalt binder and it performed better than the commercial SB polymer at the same dosage level in terms of rutting resistance but not as well for the critical low temperature. However, the continuous grade range for the biopolymer was 97.0°C and is superior to the SB polymer (93.5°C) and the PG 52-34 base asphalt binder (89.7°C) as calculated next to the bars in Figure 3.6.



**Figure 3.6. Critical high and low temperatures comparison for the base asphalt binder, SB modified blends, and PS-PAESO modified blends with calculated continuous grade ranges next to the bars.**

### 3.6. Economics & process repeatability

Polymers have been used as modifiers in asphalt binder to improve rheological performance and widen the continuous grade range for heavy traffic loadings and adverse climate conditions [45]. The increase of neat asphalt binder elasticity helps improve the resistance to permanent deformation at high temperature and thermal cracking at low temperature [44,46]. Two of the most commonly used polymers in asphalt modification are styrenic block copolymers (SBC); SBS tri-block copolymer and SB di-block copolymer [43,46,47]. The main component of SB and SBS is butadiene that is a by-product from the steam cracking process of liquid petroleum-based feedstocks [9]. As shale gas supplies become more abundant, crackers are more commonly using



gas petrochemical feeds, which lowers butadiene production and tightens the supply [48]. The shortage of butadiene has induced the highly volatile and increasing price of SBS and SB polymers since 2008 [49]. Furthermore, the United State is the only significant butadiene importer and butadiene has to be stored and transported under pressure as a liquefied or compressed gas that will increase the cost along with safety issues as well [50]. Therefore, there is a growing demand for finding sustainable and cost-competitive alternatives to replace butadiene in SBCs.

Vegetable oils consist of triglyceride molecules that contain three fatty acids and a glycerol backbone, which can be synthesized into a rubbery component with similar properties to butadiene used in SBCs. Vegetable oils such as linseed oil, corn oil, cottonseed oil, and soybean oil are all suitable and ideal candidates to be biomonomers in polymerization. In this research, non-food soybean oil was chosen as a starting point to be a monomeric feedstock to synthesize the bio-advantaged polymers. This is because soybean oil is the most abundant locally-produced vegetable oil in the US and leads the world soybean production with 43% annual export of total production [51]. Turning non-food soybean oil into bio-advantaged polymers is producing a new market and in the process making non-food soybean oil into a more useful and valuable new material that is 12.4% lower in cost to produce than commercial SB.

### **3.7. Conclusions and recommendations**

In this research, the PS-PAESO bio-advantaged polymers produced with polystyrene and polymerized soybean oil-derived triglycerides were laboratory synthesized using PAESO married with different polystyrene parameters through RAFT polymerization. A full binder investigation was conducted on the polymer modified blends, which showed positive modification effects from PS-PAESO addition to rutting resistance, continuous performance grade ranges, and elasticity of the base asphalt binder. In comparison with a commercial SB polymer, PS-PAESO bio-advantaged

polymer is capable of increasing the critical high temperature and widening the continuous performance grade range to similar or higher extents (1.0°C to 2.0°C) at the same polymer dosage level with a lower production and selling price.

A new approach of using response surface modelling to optimize the polystyrene parameters in PS-PAESO bio-advantaged polymer formulation was developed based on the high and low temperature performance grade results. The prediction models indicated that polystyrene content, not polystyrene molecular weight in PS-PAESO have more influence on high temperature performance grades, where smaller amount of polystyrene content in PS-PAESO polymer make the base asphalt binder more resistant to rutting. Based on the prediction model equations, several formulations with 5% polystyrene content and varied polystyrene molecular weights were proposed and one was produced for verification purposes. The formulation used for verification (e.g. PAESO with 30 kg/mol polystyrene molecular weight and 5% polystyrene content) when blended with the based asphalt binder had critical high temperature results for unaged and short-term aged were 0.4°C, and 0.7°C higher than the estimated ones, while the critical low temperature model gave the same results as measured. The overall performance grade of the recommended polymer modified blends was PG 64-28 as estimated, which significantly increased the rutting resistance of the base asphalt binder. The response surface modelling developed models were shown to be highly accurate and able to optimize the PS-PAESO formulation used at the same dosage as commercially produced styrene-butadiene polymer in asphalt modification. The suggested polystyrene parameters obtained from response surface modelling could potentially become a starting point for synthesizing other vegetable oil-based bio-advantaged polymers with similar chemical properties of PAESO in the styrenic block copolymers for asphalt modification. In addition, the response surface modelling methodology illustrated in this research could be used

to analyze other variables for related asphalt characterization in future works. It is also recommended that in the future, the other three formulations be produced and used for model verification.

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## CHAPTER 4. LABORATORY INVESTIGATION OF USING ACRYLATED EPOXIDIZED SOYBEAN OIL (AESO) FOR ASPHALT MODIFICATION

Modified from a paper published in *Construction and Building Materials*<sup>1</sup>

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### 4.1. Abstract

This investigation examines the modification effect of using two types of acrylated epoxidized soybean oil (AESO) in asphalt binder at various concentration levels. The effects of AESO on rheological performance of neat asphalt binder were evaluated by employing rotational viscosity (RV), dynamic shear rheometer (DSR), and bending beam rheometer (BBR) tests. The results indicate that AESO has positive softening effects on decreasing the stiffness of asphalt binder, thereby reduces viscosity and lowers mixing and compaction temperatures. Moreover, laboratory produced AESO (LabAESO) performs superior to commercial available AESO (ComAESO) in terms of low temperature properties and fatigue life at the same concentration level and shows no separation. These findings suggest that a sufficiently high level of LabAESO is necessary in asphalt modification to dramatically affect rheological properties, and therefore enhance the neat asphalt binder's resistance to fatigue damage at intermediate temperatures and thermal cracking for cold regions pavement applications. Overall, LabAESO shows the potential to be used in asphalt modification with desirable performance improvement, and economic and environmental benefits.

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## 4.2. Introduction

Flexible pavements using asphalt binder have encountered various pavement distresses due to increased traffic volume and adverse environmental factors throughout history [1–4]. The most critical pavement distresses in flexible pavements are permanent deformation at high temperatures, fatigue cracking at intermediate temperatures, and thermal cracking at low temperatures [1–3,5,6]. Additionally, oxidative aging of asphalt binder in hot mix asphalt is considered another major issue to pavement performance. Aging causes the asphalt binder in asphalt mixtures to be more viscous at high temperatures and more brittle at low temperatures. Thus, aging accelerates the development of pavement failures and shortens the design life of the pavement [3,4,7]. An appropriate stiffness of asphalt binder is desired to achieve a certain rutting resistance at service temperatures, while at the same time the asphalt binder must be fluid enough to allow for pumping and mixing with aggregates [3,8]. To enhance pavement performance and extend longevity of the roadways, polymer modified binders have been widely used in flexible pavement.

Polymers or additives used to modify asphalt to achieve a better performance are mostly inorganic and petroleum based, which has drawn concerns about environmental and economic problems [9,10]. To solve these problems, more sustainable alternatives for asphalt performance modification such as bio-based polymers derived from vegetable oils have facilitated research in industrial applications due to their benefits of inherent degradability, low toxicity, universal availability, and economic potential [10–15].

Vegetable oils commonly used as monomers in polymerizations are soybean oil, sunflower oil, castor oil, palm oil, safflower oil, linseed oil, and canola oil [11,16,17]. They are important renewable resources for biopolymers and are recognized as triglyceride oils that consist of three fatty acid chains connected by one glycerol center [11,18,19]. Triglyceride oils can be polymerized

into biopolymers with flexible and rubbery properties due to the long fatty acid chains [16]. These fatty acids with carbon double bonds (C=C) are also known as unsaturations, which can be modified to attach functional groups such as converting C=C to epoxy groups through an epoxidation reaction, which is recognized as one of the most effective modification methods [11–13,20]. Since the epoxy groups are very reactive, they can be easily functionalized with other groups [11–13,20]. In industry, soybean oil is commonly used as acrylated epoxidized soybean oil (AESO) through epoxidation of soybean oil (ESO) and acrylation of ESO [11–13,20]. Then AESO monomers can be subsequently stored and used by themselves as surface coating materials or be polymerized to obtain thermoset biopolymers or bio-copolymers [11–13,20].

Since soybean oil is one of the most affordable and abundant vegetable oils in the United States (U.S.), there have been extensive research studies focused on the use of soybean oil as a biofeedstock to yield acrylated epoxidized soybean oil (AESO) monomer used in the production of industrial thermoset biopolymers such as coatings, inks, plasticizers, adhesives, and asphalt modifiers [10,17,19,21]. Biopolymers synthesized from triglyceride oil monomers have rubbery and flexible properties which enable them to be used as alternatives to petroleum-based polymers in asphalt modification [16,22]. Promising performance, environmental, and economical benefits of using biopolymers that were polymerized from the biomonomer AESO in asphalt modification have been shown in previous research conducted by Williams et al., Cascione et al., and Chen et al. [23–26]. According to their research studies, AESO was laboratory copolymerized with styrene to produce poly(styrene-block-acrylated epoxidized soybean oil) (PS-PAESO) diblock copolymer and poly(styrene-block-acrylated epoxidized soybean oil-block-styrene) (PS-PAESO-PS) triblock copolymer for asphalt performance modification [23–25]. Both diblock and triblock biopolymers were found to be beneficial in increasing elasticity, improving rutting resistance, and decreasing

temperature susceptibility of the neat asphalt binder at a polymer concentration level of 3% [23–25]. They also performed superior to a commercial petroleum-based styrene-butadiene (SB) polymer in terms of rutting resistance experienced in warm climate regions when used at the same concentration level [23–25]. Current research is focusing on the production of AESO and biopolymers using AESO at commercial scale to conduct hot mix asphalt (HMA) performance testing and forthcoming demonstration-paving projects using biopolymer modified asphalt binders. The synthesis of AESO-based biopolymers has been very successful and their modification effects in asphalt binder have shown great potential in past and current research, however, there is no literature about the use of AESO itself as an additive in asphalt modification.

This research focuses on the modification effect of using two types of AESO in asphalt binder and provides an understanding of how the concentration level of AESO affects the neat asphalt binder performance as well. The modification effects of AESO modified binders were evaluated by Superpave performance grading specifications and rheological properties data for both high and low temperatures that were obtained from rotational viscometer (RV), dynamic shear rheometer (DSR), and bending beam rheometer (BBR). The effects of additional AESO in neat asphalt binder on the resistance of fatigue damage and thermal cracking at intermediate and lower temperatures were evaluated by employing Linear Amplitude Sweep (LAS) tests and BBR tests, respectively. The separation tendency with the additional AESO at different concentration levels was determined by storage stability tests on all AESO modified binders. Therefore, the potential of using AESO for asphalt performance modification was studied and reported through the aforementioned asphalt binder laboratory investigation.

### 4.3. Objective and scope

The objectives of this research are as follows:

- To explore the possibility of using AESO in asphalt modification.
- To evaluate the modification effect of using AESO as an additive in asphalt binder by Superpave specifications for performance grading.
- To assess the effects of various concentration levels (low, intermediate, and high) of AESO on the performance of the neat asphalt binder including viscosity, rheological properties at high and low temperatures, fatigue life, and storage stability.
- To compare the modification effects on the neat asphalt binder by using laboratory produced AESO (LabAESO) versus commercially available AESO (ComAESO) and to make recommendations.

### 4.4. Materials and methods

#### 4.4.1. Experimental materials and material preparation

This research focuses on the modification effects of using laboratory produced AESO (LabAESO) and commercially available AESO (ComAESO) at various concentrations in asphalt binders. The PG 64-22 asphalt binder obtained from a U.S. Midwest supplier (Canadian crude source) was utilized as the neat asphalt binder and served as the control group to make comparisons with the AESO modified binders. The properties of the PG 64-22 asphalt binder are shown in Table 4.1. The commercially available AESO was purchased from Sigma-Aldrich and used as received. The properties of LabAESO and ComAESO are presented in Table 4.2 and are shown visually in Figure 4.1. The main difference between LabAESO and ComAESO is the acrylate functionality of the monomer. The acrylate functionality represents the number of acrylate groups per triglyceride molecule. The AESO monomers with different acrylate functionality levels have

different triglyceride molecule structures with different absorbance to light spectrum, which leads them to be shown in different colors (Figure 4.1) and physical properties (Table 4.2). Additionally, different acrylate functionality may also affect the performance of the AESO monomer in asphalt modification differently. Controlling the acrylate groups in the molecule with lower acrylate functionality could reduce the branches of the molecule and thereby makes the monomer or polymer more linear in structure, which may cause better reactions to occur between the monomer and asphalt binder and enables the monomer to show entanglement behavior in modified binders. Therefore, LabAESO monomer with lower functionality was expected to have better compatibility with the neat asphalt binder with polymer entanglement behavior in modified binder compared to that of the high functionality ComAESO.

Additive or polymer concentration levels higher than 7% are not commonly used in asphalt modification. To better understand the use of AESO and to identify the potential of using AESO in asphalt binder modification, concentrations of low (3%), intermediate (9%), and high (15%) by total weight of the modified binders were selected to prepare the modified blends in this research according to a previous trial-blending study. Two blends at each concentration level were produced to verify the stability of the material in asphalt modification. Twelve modified binders were produced by shear blending using a Silverson L5M-A shear mixer. The neat binder was heated up in a 140°C oven until it was thoroughly heated and sufficiently fluid to pour. The neat binder was then transferred to a heating mantle until reaching the shear blending temperature. AESO was added into the binder when the binder's temperature was at  $145\pm 5^\circ\text{C}$  and the shear blending was performed at 3000 rpm for 60 min to ensure the AESO was distributed homogeneously in the asphalt binder. During the blending process, it was noticed that AESO was easily mixed into the

neat binder showing no signs of physical separation after blending was finished. The blending protocol was designed based on a previous trial-blending study.

**Table 4.1. Properties of PG 64-22 neat asphalt binder.**

Aging status	Instrument	Properties	PG64-22
Unaged binder	RV	Viscosity at 135°C (Pa·s)	0.408
	DSR	G*/sinδ at 64°C (kPa)	1.268
RTFO aged residue	RTFO	Mass loss at 163°C (%)	0.565
	DSR	G*/sinδ at 64°C (kPa)	4.296
RTFO+PAV aged residue	DSR	G* sinδ at 25°C (kPa)	2959
	BBR	Stiffness at -12°C (MPa)	210
	BBR	m-value at -12°C	0.318

Note: RTFO means Rolling Thin Film Oven; PAV means Pressure Aging Vessel; RV means Rotational Viscometer; DSR means Dynamic Shear Rheometer; BBR means Bending Beam Rheometer.

**Table 4.2. Properties of Laboratory produced AESO and commercially available AESO.**

	LabAESO			ComAESO		
Acrylate functionality	1.3			2.6		
Molecular weight, g/mol	1044			1200		
Viscosity, Pa*s	Shear speed, rpm			Shear speed, rpm		
	10	30	50	10	30	50
at 65°C	0.925	0.923	0.920	0.895	0.870	0.866
at 85°C	0.345	0.330	0.327	0.300	0.285	0.280
at 105°C	0.175	0.151	0.148	0.145	0.122	0.119
at 125°C	0.125	0.085	0.081	0.093	0.064	0.060
at 145°C	0.105	0.058	0.052	0.075	0.042	0.038



**Figure 4.1. Physical conditions of commercial available AESO (ComAESO on the left) and laboratory produced AESO (LabAESO on the right).**

#### **4.4.2. Laboratory testing**

##### **4.4.2.1. Brookfield viscosity test**

Viscosity is the ratio between the applied shear stress and the shear rate, which measures the resistance of a liquid material to flow (measured in Pascal-second, Pa\*s). The viscosity of the asphalt binders were tested and obtained using a Brookfield rotational viscometer. The viscosity testing was done using a SC4-21 spindle at the following test temperatures of 135°C, 150°C, 165°C, and 180°C with a speed of 20 rpm according to AASHTO T 316-10. The rotational viscosity measurements were collected after 15-min of waiting time for temperature equilibration followed by a 3-min waiting time to stabilize the viscosity at the specific test speed and three viscosity readings were generated at 1-min intervals for each test temperature. Duplicate tests were done for each asphalt binder.

##### **4.4.2.2. Dynamic shear rheometer (DSR) test**

The high and intermediate temperature performance grades of all asphalt binders were determined by conducting DSR testing at a frequency of 10 rad/s using an Anton Paar MCR 302 DSR according to AASHTO T 315-10. The high temperature performance grades were done on unaged and Rolling Thin Film Oven (RTFO) aged binders using a 25 mm diameter parallel plate with a 1 mm testing gap, while the intermediate temperature performance grades were done on Pressure Aging Vessel (PAV) aged binders using an 8 mm diameter parallel plate with a 2 mm testing gap. The RTFO aging process was conducted on the unaged binders by aging the material under heat and air at oven temperature of 163°C for 85 min to mimic short-term aging caused by plant mixing by following AASHTO T240-09. The mass loss of the asphalt binder after RTFO aging was also calculated according to AASHTO T240-09. The PAV aging process was performed on RTFO residue and the RTFO aged material was aged in a sealed vessel at 2.10 MPa pressure

and 100°C for 20h to simulate long-term aging during a pavement's service according to AASHTO R 28-12. The test was done in triplicate for each asphalt binder and the average values are reported.

The frequency sweep test using a DSR was conducted on the unaged asphalt binders to evaluate the effect of AESO on the neat binder's rheological properties by following AASHTO T 315-10. The strain sweep test was done to verify that the strain rate used for testing binder specimens at each temperature was within the linear viscoelastic range. All asphalt specimens were tested at frequency ranges between 0.1 to 100 rad/s at various test temperatures from 10°C to 64°C. For the lower test temperatures, 10°C, 20°C, and 30°C, an 8 mm parallel plate with a 2 mm gap was selected to perform the frequency sweep tests at a 0.5% strain rate. While a 25 mm parallel plate with a 1 mm gap was used for the frequency sweep tests at a 5% strain rate for the higher test temperatures of 40°C, 46°C, 52°C, 58°C, and 64°C. The complex shear modulus ( $G^*$ ) and phase angle ( $\delta$ ) values of each asphalt binder were obtained at each testing frequency and temperature.

#### **4.4.2.3. Bending beam rheometer (BBR) test**

The low temperature performance grade was calculated based on the creep stiffness and m-value obtained from BBR testing on PAV aged binders. The asphalt binder beams (125mm (length) x 12.5mm (width) x 6.25mm (thickness)) were prepared in silicon molds and the tests were conducted by following AASHTO T313-10. The center deflection of the beam was measured continuously over 240s by applying a constant load. The stiffness and m-value at 60s of testing time were collected at the testing temperature of 10°C above minimum pavement temperature from the BBR testing, which represented the material's values at 7200s at the minimum pavement temperature according to the time-temperature equivalency principle [27,28]. In this research, the BBR test was conducted at two test temperatures of -12°C and -18°C. Beams for each asphalt binder's group were run in triplicate and the mean values are reported.



#### 4.4.2.4. Linear amplitude sweep (LAS) test

The LAS test was conducted on the PAV aged asphalt binders at intermediate test temperatures under cyclic loading with a linearly accelerated load amplitudes using a DSR by following AASHTO TP 101-14. The test was designed to assess the fatigue life of the material under continuous damage by determining the damage parameters. All PAV aged asphalt binders were tested by using an 8mm parallel plate with a 2mm gap setting in the DSR. To include the critical intermediate temperatures of all asphalt binders (Table 4.3), the LAS test was conducted at temperatures of 16°C, 19°C, 22°C, and 25°C [6]. The test was done in triplicate for each asphalt binder and the average value was reported.

The LAS test involves two types of testing. A frequency sweep test is performed on the specimen to determine the parameter  $\alpha$  for the damage analysis. Moreover, the undamaged material rheological properties can be obtained at an applied load of 0.1% strain over a frequency range of 0.2 Hz to 30 Hz during the frequency sweep test. Then a strain sweep test is conducted to accelerate fatigue damage on the specimen using oscillatory shear at 10 Hz frequency with a linearly increasing strain from 0.1% to 30% for 3100 loading cycles. The LAS test was designed according to the Viscoelastic Continuum Damage (VECD) principle and the material's ability to fatigue damage can be calculated by following Equations (4.1)-(4.6) according to AASHTO TP 101-14.

The damage accumulation in the specimen over time from the frequency sweep and strain sweep results is calculated by following the Equation (4.1) below:

$$D(t) \cong \sum_{i=1}^N [\pi \gamma_0^2 (C(t_i) - C(t_{i-1}))]^{\frac{\alpha}{1+\alpha}} (t_i - t_{i-1})^{\frac{1}{1+\alpha}} \quad (4.1)$$

where  $D(t)$  is damage intensity over testing time  $t$ ;  $t$  is the testing time (in second);  $\gamma_0$  is strain (%);

$C(t) = \frac{|G^*|(t)}{|G^*|_{initial}}$ , which is the ratio of the complex modulus (in MPa) at any testing time  $t$  and the

initial complex modulus at undamaged condition; and  $\alpha=m^{-1}$  in which m is the best-fit straight line slope of log storage modulus versus frequency.

The C(t) and D(t) values at a specific testing time can be calculated and be used to fit the power law Equation (4.2) below:

$$C(t) = C_0 - C_1 D(t)^{C_2} \quad (4.2)$$

where  $C_0=1$  and  $C_1$  and  $C_2$  are curve fitting coefficients.

The damage intensity of D(t) at failure  $D_f$  is calculated by using the C at the peak shear stress as Equation (4.3) below:

$$D_f = \left( \frac{C_0 - C_{at\ peak\ stress}}{C_1} \right)^{\frac{1}{C_2}} \quad (4.3)$$

The cycle numbers to fatigue failure ( $N_f$ ) can be calculated by using Equation (4.4) below:

$$N_f = A(\gamma_{max})^{-B} \quad (4.4)$$

where  $\gamma_{max}$  is the maximum expected binder strain at the numbers of cycle to fatigue failure; and A and B are coefficients for the model and can be calculated using Equations (4.5) and (4.6) below:

$$A = \frac{f(D_f)^k}{k(\pi C_1 C_2)^\alpha} \quad (4.5)$$

$$B = 2\alpha \quad (4.6)$$

where  $f$  is the frequency at 10 Hz, and  $k=1+(1-C_2)\alpha$ .

#### 4.4.2.5. Storage stability test

The storage stability test was performed following ASTM D7173-11 to determine the separation tendency of polymer modified asphalt binder. The test is commonly known as the cigar tube test (CTB) as an aluminum tube (25mm diameter and 140mm height) is used to hold the material during storage. In this research, the tubes were filled with  $50\pm 0.5$ g of AESO modified asphalt binders and sealed. The tubes were stored vertically in an oven at  $163\pm 5^\circ\text{C}$  for 48h and

were transferred to a freezer set at a temperature of  $-10\pm 10^{\circ}\text{C}$  for a minimum of 4h until the material solidified thoroughly. Each tube with the solidified binder was cut into three portions of equal length. The center section was discarded, while the top and bottom portions were saved for rheological testing. The complex shear modulus ( $G^*$ ) and phase angle ( $\delta$ ) of the material from the top and bottom portions were obtained by DSR test using a 25mm diameter parallel plate with a 1mm gap at a test temperature of  $60^{\circ}\text{C}$  through a frequency sweep test (1.0 to 100 rad/s) at 5% shear strain. The separation index ( $I_s$ ) of  $G^*$  and  $\delta$  were calculated by using the logarithm of the ratio between  $G^*$  of the top and the bottom and  $\delta$  of the top and bottom at the test temperature of  $60^{\circ}\text{C}$  and test frequency of 10 rad/s [8,29]. The storage stability of the material was evaluated by how close the  $I_s$  value is to zero. The binder with a  $I_s$  value closer to zero indicates there is less potential for the binder to have separation [8,29]. The percent separation was determined by using the  $G^*/\sin\delta$  value at 10 rad/s following Equation (4.7) below [30]:

$$\%Separation = \frac{\left(\frac{G^*}{\sin\delta}\right)_{max} - \left(\frac{G^*}{\sin\delta}\right)_{avg}}{\left(\frac{G^*}{\sin\delta}\right)_{avg}} \quad (4.7)$$

where  $\left(\frac{G^*}{\sin\delta}\right)_{max}$  is the higher value between the top and bottom tube portions and  $\left(\frac{G^*}{\sin\delta}\right)_{avg}$  is the average value of the two portions.

## 4.5. Results and discussions

### 4.5.1. Rotational viscosity (RV)

#### 4.5.1.1. Viscosity and statistical analysis

The viscosity tests were performed on the unaged neat asphalt binder and all AESO modified asphalt binders. Viscosity results are presented in Table 4.3. It can be observed that the addition of AESO decreased the viscosity of the modified PG 64-22 asphalt binder. The viscosity of modified binders with additional AESO decreased as testing temperature increased from  $135^{\circ}\text{C}$  to

185°C, which indicated AESO was successfully incorporated in the neat asphalt binder by reducing the intermolecular interaction of the asphalt molecules [31].

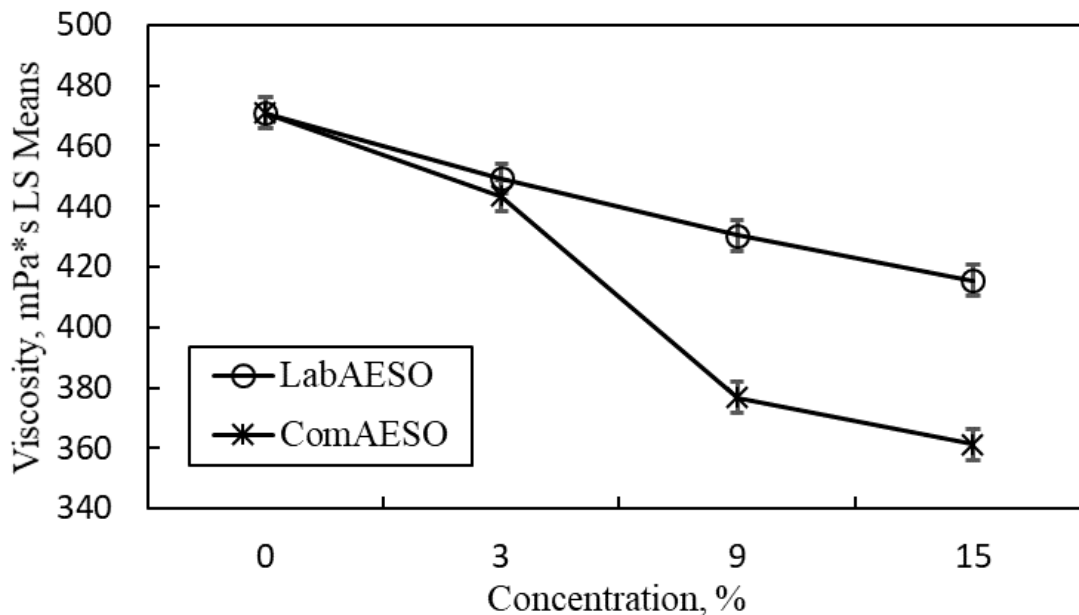
Statistical analysis of AESO modified asphalt binders' viscosity was conducted to examine how the factors of AESO types, concentration levels, and their interactions affect the response (material's viscosity at test temperature of 135°C with 20 rpm shear speed) by means of analyses of variance (ANOVA). The viscosity testing results at 135°C was used for the statistical analysis because it was used as a typical testing temperature to evaluate the mixability and workability of asphalt binder [9,32]. The order of testing was randomized and 48 data points were collected on all materials for statistical analysis. Figure 4.2 presents the plot of least square means values with margin of error bars at 95% confidence intervals for each binder's viscosity as the concentration increases. It was noticed, as the concentration level of AESO increased, the viscosity reducing effect became more significant in viscosity values, which indicated AESO was acting like a fluxing agent in asphalt modification [9]. The use of AESO in asphalt modification softened the neat binder, therefore increased the mobility of the asphalt binder's intermolecular interaction, which resulted in the reduction of viscosity [9,31]. More reduction in viscosity was observed on the ComAESO modified asphalt binders due to the lower viscosity of ComAESO compared to the LabAESO's (Table 4.2). Furthermore, a more pronounced reduction in viscosity was found in the blends with 9%ComAESO concentration level (20% viscosity reduction of the neat asphalt binder). The AESO types and the four levels of concentration were shown to be statistically significantly different based on the viscosity values at a 95% confidence interval by the ANOVA. The interaction effects of AESO types and levels of concentration were examined by a Tukey honestly significant difference (HSD) least square means difference test at a 95% confidence interval, as presented in Table 4.4. It was noticed that the 3%LabAESO group was not different

from the 3%ComAESO group in terms of viscosity values. The groups of 9%LabAESO, 15%LabAESO, 9%ComAESO, and 15%ComAESO were significantly different from each other and are significantly different from the neat asphalt binder (with 0%LabAESO and 0%ComAESO) and 3%LabAESO and 3%ComAESO as well. The groups with 15% concentration level of LabAESO and ComAESO reduced the neat asphalt binder's viscosity the most among all the concentration levels. Specifically, the 15%LabAESO reduced the neat asphalt binder's viscosity approximately 12% and the 15%ComAESO reduced the viscosity around 23% as compared to the neat binder's.

Viscosity is an indicator of the flow characteristics, which is also related to the mixing and compaction temperatures for HMA construction [32,33]. The asphalt blends need to be fluid enough for pumping and handling during mixture production and the paving process, therefore the material's workability and mixability are required to be evaluated by the rotational viscosity test [32,33]. The viscosity results presented above showed that increasing AESO concentration resulted in reducing the viscosity of the neat asphalt binder, which indicated an appreciable 3°C to 5°C decrease in mixing and compaction temperatures in construction with additional 15% AESO as shown in Figure 4.3. However, the viscosity reducing effect resulted in decreasing the stiffness of the neat asphalt binder and thereby might decrease the resistance to permanent deformation at higher temperatures.

**Table 4.3. Properties of control and modified binders.**

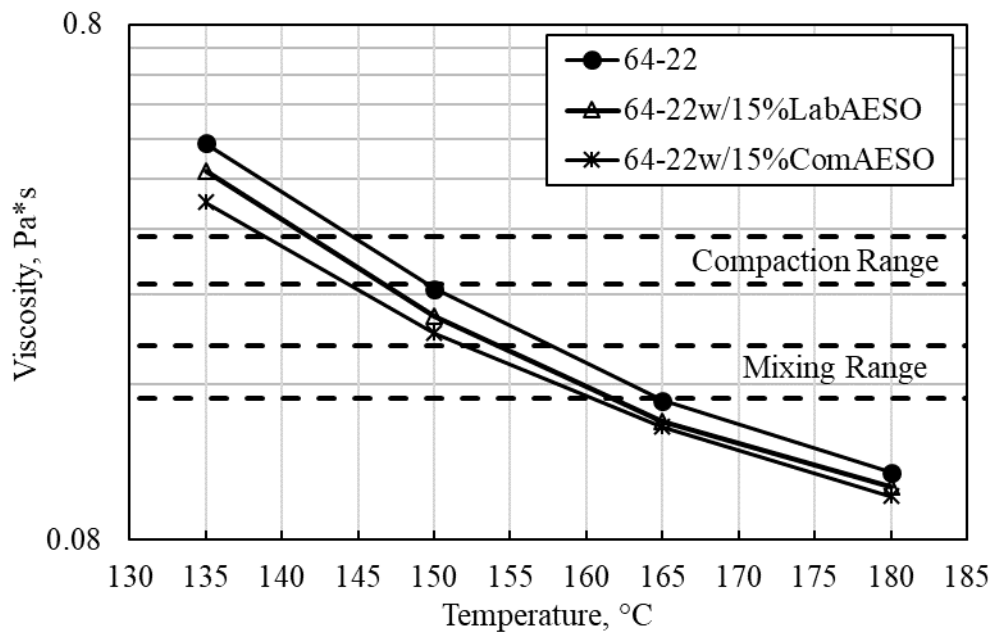
Blends	PG 64-22	PG 64-22 w/ 3%LabA ESO	PG 64-22 w/ 9%LabA ESO	PG 64-22 w/ 15%LabA ESO	PG 64-22 w/ 3%ComA ESO	PG 64-22 w/ 9%ComA ESO	PG 64-22 w/ 15%ComA ESO
Unaged (High Temp.), °C	66.6	64.4	61.3	58.8	64.4	63	60.4
RTFO (High Temp.), °C	67.6	66	61.4	59.3	66.9	66.4	65.4
PAV (Intermediate Temp.), °C	23.8	22.4	15.3	14.7	19.9	18.1	17.9
PAV (Low Temp.), °C	-23.8	-23.9	-25.7	-28.2	-23.0	-23.3	-24.4
Performance Grade (PG)	64-22	64-22	58-22	58-28	64-22	58-22	58-22
Mass loss at 163°C, %	0.565	0.598	0.676	0.960	0.758	0.847	0.852
Viscosity (Pa*s) at 135°C	0.471	0.449	0.430	0.415	0.443	0.377	0.361
Viscosity (Pa*s) at 150°C	0.245	0.238	0.229	0.217	0.237	0.223	0.201
Viscosity (Pa*s) at 165°C	0.149	0.158	0.148	0.136	0.150	0.150	0.133
Viscosity (Pa*s) at 180°C	0.108	0.119	0.113	0.101	0.111	0.121	0.097

**Figure 4.2. Viscosity least square means plot for effect of AESO at 135°C.**

**Table 4.4. Tukey HSD least square means different of viscosity for group names.**

Level		Least sq mean
0%, LabAESO	A	470.83
0%, ComAESO	A	470.83
3%, LabAESO	B	449.17
3%, ComAESO	B	443.33
9%, LabAESO	C	430.42
15%, LabAESO	D	415.42
9%, ComAESO	E	376.67
15%, ComAESO	F	361.25

Note: Levels not connected by the same letter are significantly different.



**Figure 4.3. Mixing and compaction temperatures for 15% AESO modified binders and PG 64-22 binder.**

#### 4.5.1.2. Viscous-flow activation energy

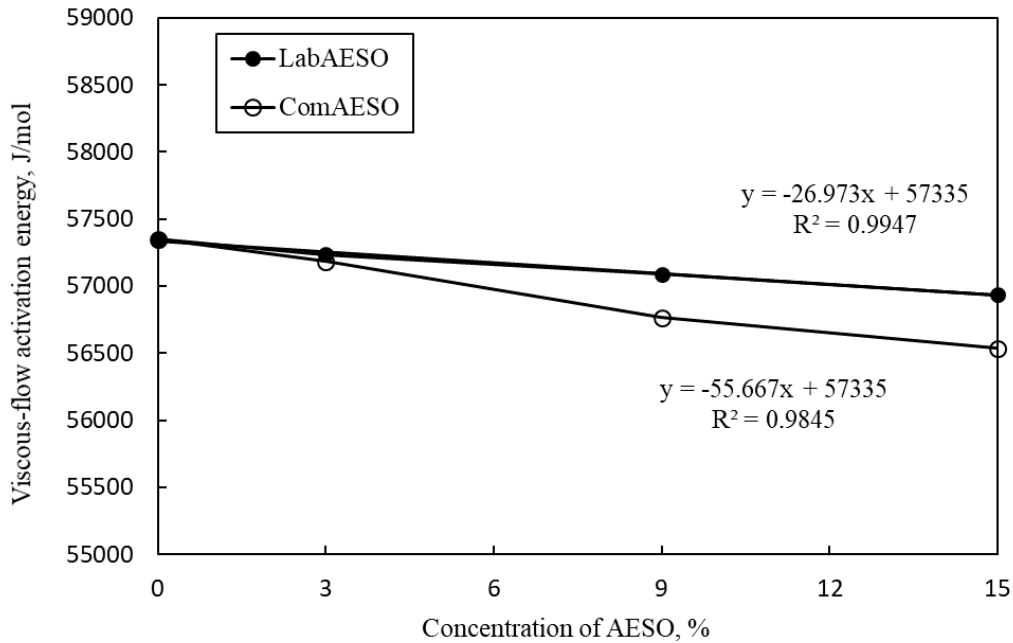
The activation energy can be used to indicate the temperature dependency or independency of the asphalt binder viscosity and it was first introduced by Henry Eyring [34]. The activation energy of viscous flow represents the force that is needed to move fluid particles and the intermolecular energy that must be overcome [35,36]. The temperature susceptibility of the modified blends can

be evaluated by examining the relationships between the activation energy for flow and the levels of polymer concentration using the Arrhenius equation as follows:

$$\ln \eta = \ln A + \frac{E_f}{RT} \quad (4.8)$$

where  $\eta$  is the apparent viscosity of the asphalt binder,  $T$  is temperature in K,  $A$  is a constant,  $E_f$  is the activation energy for flow, and  $R$  is the universal gas constant (8.314 J/(mol K)). The viscosity for all asphalt binders at test temperatures 135°C to 180°C were obtained using a rotational viscometer and the activation energy for flow was calculated by following the Arrhenius equation above. The effect of AESO on activation energy for flow was presented in Figure 4.4. The activation energy decreased as the AESO concentration increased for both AESO materials, which meant adding AESO could be beneficial to temperature susceptibility and represents a strong temperature independency effect [37–39]. This meant that the higher the level of AESO concentration in the neat asphalt binder, the less sensitive the neat asphalt binder became to temperatures changes [35]. The addition of AESO in the neat asphalt binder might spread the asphalt molecules further apart and thereby less activation energy was needed for flow [37]. In comparison with LabAESO, ComAESO had a more pronounced improvement on the temperature susceptibility of the neat asphalt binder. At the 15% AESO concentration level, the activation energy of the neat asphalt binder changes from 57348.9 J/mol to 56935.0 J/mol for LabAESO and from 57348.9 J/mol to 56537.3 J/mol for ComAESO. The activation energy for flow had also been shown to be related to compaction effort [35]. According to the study by Salomon and Zhai [35], lower activation energy for flow required lower compaction effort, which means the easier the compaction becomes for asphalt mixes at the same temperature. Therefore, AESO in asphalt modification could decrease the temperature susceptibility of the neat asphalt binder and lower the compaction effort of HMA.





**Figure 4.4. The effect of AESO concentration levels on activation energy for flow of asphalt binders.**

#### 4.5.2. Performance grade (PG)

The performance grade of all asphalt binders was evaluated and determined based on the Superpave asphalt binder specification as outlined by AASHTO M 320-10. The rutting parameter  $G^*/\sin\delta$  of the asphalt binders was obtained through DSR tests at a frequency of 10 rad/s on both unaged and RTFO short-term aged materials by following AASHTO T 315-10. The critical high temperatures were determined by the specification criteria of  $G^*/\sin\delta \geq 1$  kPa for unaged materials and  $G^*/\sin\delta \geq 2.2$  kPa for RTFO aged materials, whereby the lower critical high temperature of the two should be used for the high temperature performance grade.

As the test results present in Table 4.3 and Figure 4.5, the critical high temperatures of the unaged and RTFO aged neat asphalt binder decreased with the addition of both LabAESO and ComAESO. However, the reduction on the critical high temperatures with additional ComAESO did not have as much effect as the LabAESO did at the same concentration level. It was observed

that the RTFO short-term aging process had stiffening effects on all asphalt binders by increasing the critical high temperatures of the unaged binders. As shown in Figure 4.5, ComAESO modified binders had higher critical high temperatures after RTFO aging compared to that of LabAESO modified binders, which indicated additional ComAESO made the neat asphalt binder more susceptible to short-term aging effects as the concentration level increased. Additionally, ComAESO might be more susceptible to aging effects as compared to LabAESO at the same concentration level. However, further effects of AESO on aging are needed to be investigated in a future study. According to the overall critical high temperature results, it can be inferred that adding AESO made the neat asphalt binder more susceptible to permanent deformation at high temperatures by decreasing the critical high temperature of the neat asphalt binder. This matched the findings in the viscosity analysis that additional AESO softened the neat asphalt binder with the reduction of neat asphalt binder's viscosity in Section 4.5.1.1.

The mass loss after the RTFO aging process was calculated to evaluate the thermal stability of the modified blends. In Table 4.3, the mass loss increased as the AESO concentration level increased. This indicated that there was a loss of volatile fractions in the modified binders, however, the mass loss values satisfied the Superpave mass loss requirement (i.e. less than 1%). Therefore, the mass loss results confirmed the thermal stability of the AESO materials and AESO was not considered as a volatile material for asphalt binder modification.

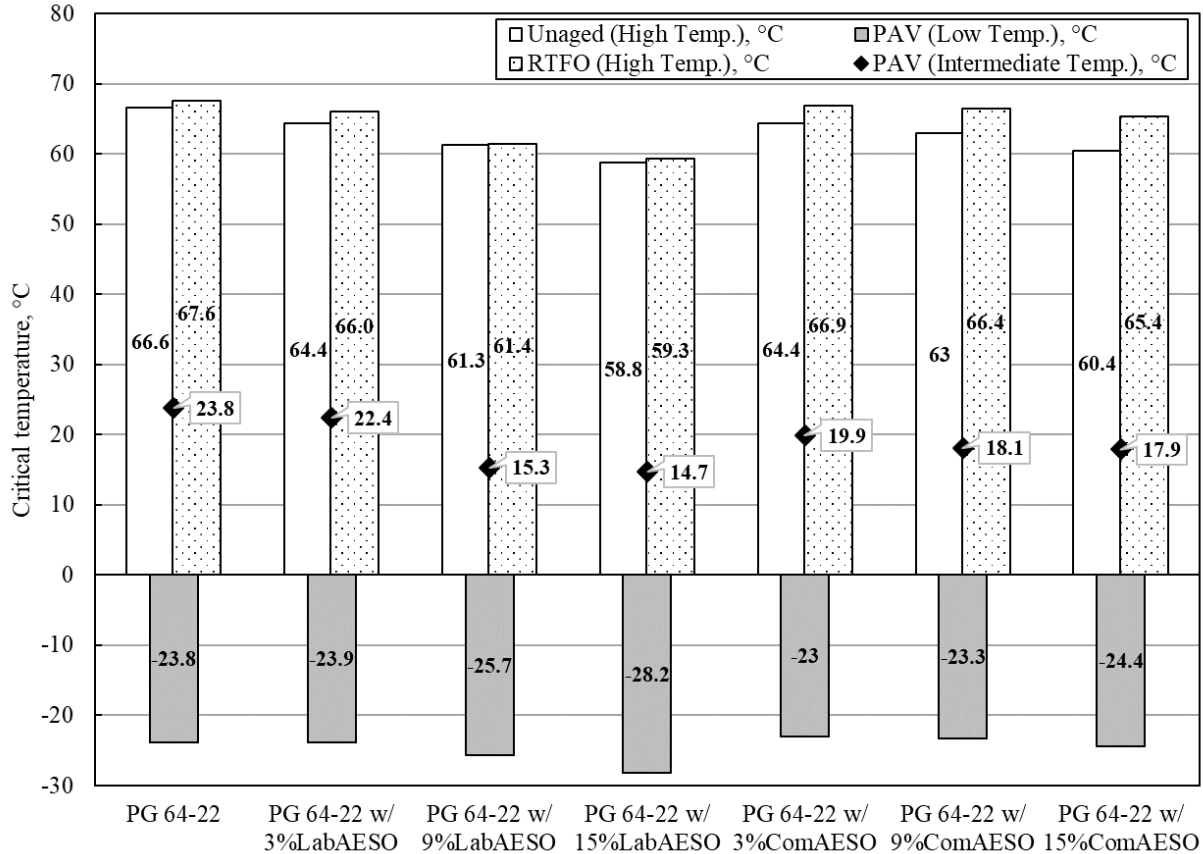
The critical intermediate temperatures for the asphalt binders were measured via DSR testing on PAV long-term aged materials and were determined based on the criteria of  $G^* \cdot \sin \delta \leq 5000$  kPa as summarized in Table 4.3 and shown in Figure 4.5. A drop in the critical intermediate temperature was found when both AESO was blended into the neat asphalt binder. A more pronounced effect on critical intermediate temperature was noticed on the 9% and 15% LabAESO

modified binders. Thus, both AESO materials could be beneficial in fatigue resistance, while LabAESO had a more notable effect on improving the resistance to fatigue as it decreased the critical intermediate temperature more significantly when sufficient concentration was added to the neat asphalt binder.

The critical low temperatures of the asphalt binders were measured by conducting the BBR test on PAV aged materials following AASHTO T313-10. The results in Table 4.3 and Figure 4.5 showed that LabAESO decreased the critical low temperature of the neat asphalt binder as the LabAESO concentration level increased. The 15%LabAESO modified asphalt binder decreased one low temperature grade of the neat asphalt binder from  $-22^{\circ}\text{C}$  to  $-28^{\circ}\text{C}$ . However, ComAESO was noticed to slightly decrease the neat asphalt binder's critical low temperature without changing its low temperature performance grade. It can be concluded that LabAESO helped with critical low temperature of the neat asphalt binder and was able to decrease one grade of the neat asphalt binder by adding sufficient concentration, which also meant LabAESO improved the neat asphalt binder's resistance to thermal cracking at low temperatures. The overall performance grade of AESO modification are summarized in Table 4.3.

It was important to note that neither LabAESO nor ComAESO could change the performance grade of the neat asphalt binder at lower level concentration such as 3%. The intermediate concentration level 9% for both LabAESO and ComAESO only affected the high temperature performance grade by lowering it one grade while it did not help with low temperature grade. At a high concentration level of 15%AESO, ComAESO modified binder performed similar to the 9%ComAESO modified binders on the performance grade. In comparison, the 15%LabAESO helped with reducing the low temperature grade by one grade and thereby changed the performance

grade of the neat asphalt binder from PG 64-22 to PG 58-28, an often-used asphalt binder for asphalt pavements in the Midwestern United States.



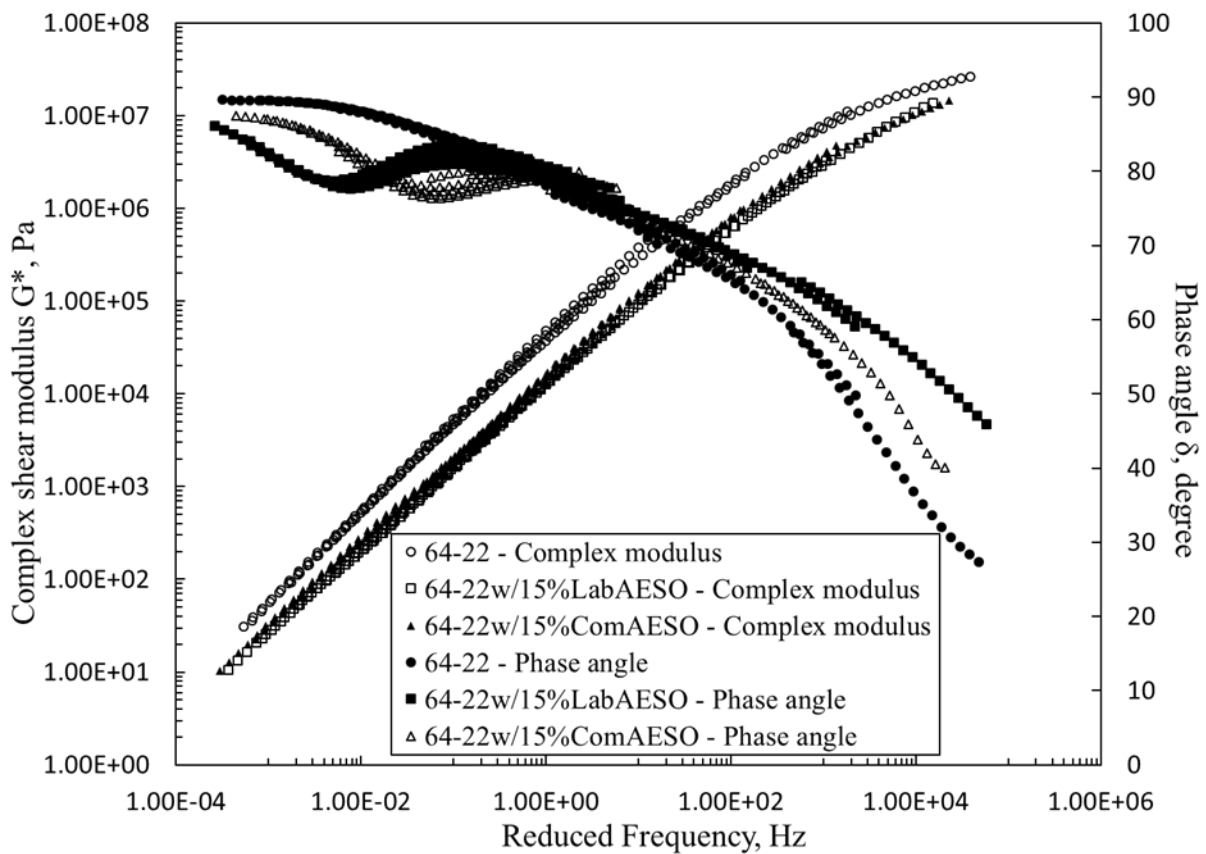
**Figure 4.5. The critical high, intermediate, and low temperatures for AESO modified binders and PG 64-22 binder.**

### 4.5.3. Master curves

Master curves for neat asphalt binder and AESO modified binders were developed by using the Williams-Landel-Ferry (WLF) equation at a reference temperature of 40°C. The rheological parameters of complex modulus and phase angle obtained from frequency and temperature sweep tests were shifted at each frequency to achieve a smooth curve by following the time temperature superposition principle. The rheological behavior of each material at different temperatures and frequencies can be easily observed and compared from the best-fit curves.

In the complex shear modulus master curves, all AESO modified binders showed lower curves with smaller complex modulus values compared to the neat asphalt binder's that indicated the softening effect with additional AESO. It was also noticed that the complex modulus of the AESO modified binder became even smaller when the concentration level increased as shown in Figure 4.6. The stiffness reducing effect of AESO was noticed on the overlapped AESO modified binders' curves with a reduction of complex modulus over the entire frequency region, which indicated the decrease of critical high temperature with more susceptibility to rutting than that of the neat asphalt binder. In the analysis of phase angle master curves as shown in Figure 4.6, it was noticed that AESO affected the phase angle of neat asphalt binder differently at high, intermediate, and low frequencies. A reduction of phase angle with lower phase angle master curves was observed after modification with the presence of a phase angle plateau for a low frequency (high temperature) zone. This meant that with higher amounts of AESO drastically changed the rheological curve shape of the neat asphalt binder with the development of a polymer elastic network, and this is represented by a plateau that is a typical of a polymer modified asphalt binder [8,40–43]. The plateau presented the changes of phase angle that dropped and arose again to approach to  $90^\circ$  as the testing temperature increased, which indicated better elastic recovery behavior at high testing temperatures and entanglement behavior of modified asphalt binder [2,40,41,43,44]. This plateau is also an indicator of well-blended polymer modified asphalt binder behavior that showed better interaction between polymer and asphalt binder with positive effects on decreasing the thermal susceptibility of the neat asphalt binder [40,41,43–45]. However, increased phase angle values were observed for high concentration AESO modified binders at intermediate and high frequency zones compared to the neat asphalt binder. 15%ComAESO modified binder showed a  $10^\circ$  improvement in phase angle value while 15%LabAESO modified binder presented a significant

phase angle value improvement of approximately  $20^\circ$  at high frequency and low temperature, which indicates they were more viscous and less stiffer compared to the neat asphalt binder. A more viscous behavior of modified binders indicated better ability to dissipate stresses through the flow of asphalt molecule at intermediate and high frequencies (intermediate and low temperatures) regions, which suggested there is substantial improvement against low temperature thermal cracking and fatigue cracking at intermediate temperature when sufficient amount of LabAESO was used [7,9,28,46,47].



**Figure 4.6. Complex modulus and phase angle master curves for 15%LabAESO modified binder, 15%ComAESO modified binder, and neat asphalt binder.**

#### 4.5.4. Low temperature properties

Low temperature thermal cracking of pavements occurs due to the thermal stress accumulation in the asphalt mixture [9,28,48]. Asphalt binders with low stiffness and the ability to relax under high stress are preferred as they are less susceptible to thermal cracking at low temperature [32,48]. Low temperature properties of the asphalt binders, creep stiffness ( $S$ ) and creep rate ( $m$ -value), were measured and obtained by creep tests over 240s using a BBR. The creep stiffness reflects the flexibility of the material and the  $m$ -value indicates the stress relaxation ability of the material at a certain test temperature [46,48]. The requirements for asphalt binder to prevent thermal cracking are the creep stiffness must be less than or equal to 300 MPa and the  $m$ -value must be greater than or equal to 0.300 according to the Superpave specification. The creep stiffness and  $m$ -value of the asphalt blends were calculated at a loading time of 60s at temperatures of  $-12^{\circ}\text{C}$  and  $-18^{\circ}\text{C}$  as shown in Figure 4.7.

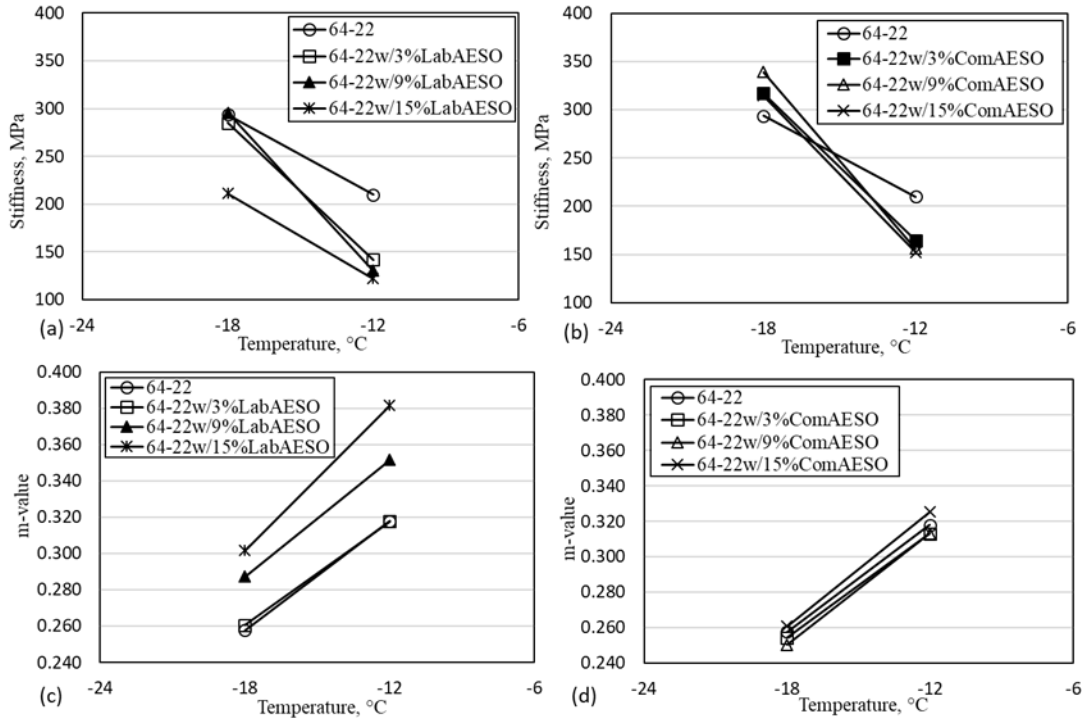
The effect of LabAESO on the stiffness of neat asphalt binder can be observed in Figure 4.7 (a). The lower and intermediate concentrations of LabAESO (3% and 9%) had similar effect on reducing the stiffness of the neat asphalt binder as they decreased the neat binder's stiffness by about 70 MPa at a temperature of  $-12^{\circ}\text{C}$ . However, there was no reduction of stiffness observed on 3% and 9% LabAESO blends at a test temperature of  $-18^{\circ}\text{C}$ , which indicated the effect of LabAESO on low temperature performed differently at different temperatures when the addition of LabAESO in the neat asphalt binder was at a lower or intermediate concentration level. This can also be inferred that 3% and 9% LabAESO were only able to increase the flexibility of neat asphalt binder at testing temperature of  $-12^{\circ}\text{C}$  with a slightly lower critical low temperature than that of the neat asphalt binder. To further reduce the creep stiffness at a lower testing temperature of  $-18^{\circ}\text{C}$ , higher concentration of LabAESO was necessary in the modification. As expected, the

15%LabAESO considerably reduced the stiffness of the neat asphalt binder at both  $-12^{\circ}\text{C}$  and  $-18^{\circ}\text{C}$  around 90 MPa. The results indicated sufficient concentration of LabAESO was needed for enhancing low temperature performance by decreasing one grade of the neat asphalt binder's low temperature performance grade, and thereby reducing the possibility of thermal cracking at a lower testing temperature of  $-18^{\circ}\text{C}$ . In Figure 4.7 (a) and Figure 4.8 (a), LabAESO modified blends were found to meet the stiffness requirement at both test temperatures. For m-value, it can be seen that the m-value increased when the concentration level of LabAESO increased as shown in Figure 4.7 (c). The m-value decreased as test temperatures went down from  $-12^{\circ}\text{C}$  to  $-18^{\circ}\text{C}$  as expected. However, only the 15%LabAESO modified binder was able to relax under stress and pass the m-value criteria at  $-18^{\circ}\text{C}$ , which agreed with the rheology analysis in the master curves that the 15%LabAESO had the most viscous behavior at low temperatures. It can be concluded that LabAESO improved the flexibility of the neat asphalt binder and decreased the neat asphalt binder's susceptibility to thermal cracking at low temperature. Furthermore, high concentration level of LabAESO was needed to significantly enhance the low temperature properties of the neat asphalt binder. However, the ComAESO was found not to be effective on low temperature properties of the neat asphalt binder at lower temperatures. It can be seen in Figure 4.7 (b) that lower, intermediate, and higher ComAESO concentration levels (3%, 9%, and 15%) had similar softening effects on the neat asphalt binder's stiffness at  $-12^{\circ}\text{C}$  by reducing stiffness value about 40 MPa. Whereas, increase of stiffness was noticed at temperature of  $-18^{\circ}\text{C}$  on ComAESO modified blends, which failed to meet the stiffness requirement at that test temperature. The m-value of all ComAESO modified blends was found to be followed the same trend of the neat asphalt binder when test temperature changed (Figure 4.7 (d)), which met the requirement at -

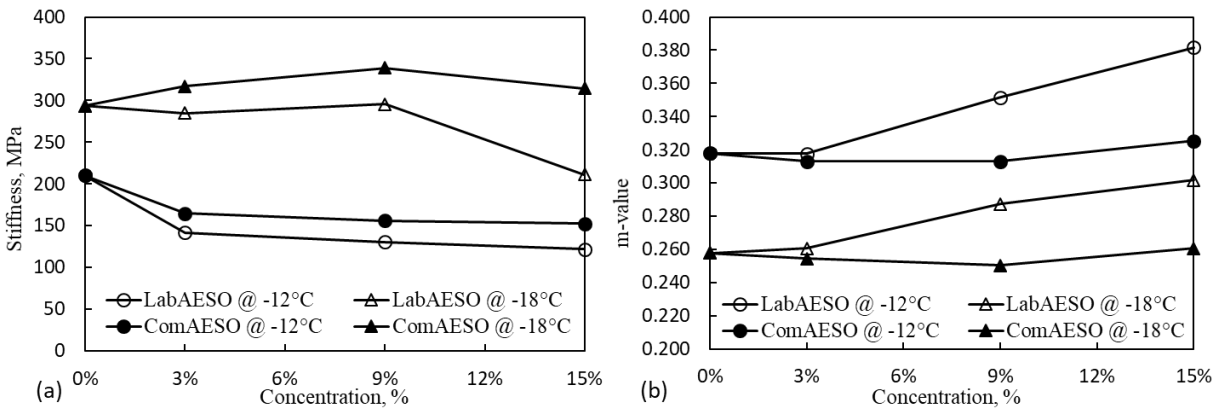


12°C, but failed at -18°C and thereby they were graded the same as the neat asphalt binders at low PG.

The changes of stiffness and m-value with increasing of AESO concentration level at test temperatures of -12°C and -18°C can be observed in Figure 4.8 (a). At test temperature of -12°C, the stiffness of the neat asphalt binder decreased when the concentration levels of AESO increased, while LabAESO had more softening effect on the neat asphalt binder compared to that of the ComAESO as the line of LabAESO was below the ComAESO's in Figure 4.8 (a). However, when the test temperature went down to -18°C, it was noticed that the intermediate concentration level (9%) for both AESO was the threshold at which the neat asphalt binder needed to break through to get benefit from AESO on the low temperature properties. It was clear that concentration level above 9% significantly dropped the stiffness of neat asphalt binder as seen from the pronounced stiffness reduction observed for the 15%LabAESO modified binder. The effect of AESO at different concentration levels on m-value can be easily observed in Figure 4.8 (b). For both test temperatures, LabAESO was found to considerably increase the m-value as the concentration level increases, while the effect of ComAESO on m-value was negligible as the results shown in Figure 4.8 (b). Overall, the 15%LabAESO modified binder had the lowest stiffness with the highest m-value. These results indicated that the LabAESO helped with stress relaxation and was better able to dissipate stresses when a sufficient concentration of LabAESO was added, thus reducing the susceptibility of the neat asphalt binder to thermal cracking at low temperatures.



**Figure 4.7. Effect of AESO on asphalt binder creep stiffness (S) and creep rate (m-value) versus temperature.**



**Figure 4.8. Effect of AESO concentration levels on asphalt binder low temperature properties.**

**4.5.5. Fatigue damage resistance**

The LAS test was performed to estimate the material’s resistance to accelerated fatigue damage under cyclic loading with increasing amplitudes at intermediate temperatures. The comparisons of fatigue life values ( $N_f$ ) of all the asphalt binders at strain levels of low (2.5%), intermediate (5%

and 7%), and high (10%) at different test temperatures are presented in Figure 4.9 (a)-(d). It was seen that modified asphalt binder with 15% LabAESO had the highest fatigue life among all asphalt binders at all test temperatures. At low strain level, no significant fatigue life differences were observed, especially at lower temperatures. All binders' fatigue life decreased steeply when the strain level increased, which indicated that all the binders were more susceptible to higher levels of traffic. Moreover, as the test temperature decreased, reduced fatigue life was observed for all blends due to the binders becoming stiffer at lower temperatures. However, the binder with 15% LabAESO had the highest fatigue life and the lowest strain susceptibility compared to other blends. This also was in agreement with the grading and viscosity results, because the addition of AESO softened the neat asphalt binder, thus making the neat asphalt binder less stiff at lower temperatures and improved its fatigue life at intermediate temperature.

To better correlate the cycles to fatigue failure in the field, a strain rate of 5% was chosen to present the fatigue life of the material corresponding to 1000 microstrains in asphalt mixture [1,6,49]. The different concentration effect of LabAESO and ComAESO on fatigue life of the neat asphalt binder could be easily evaluated from the LAS test results with various intermediate temperatures at strain levels of 5% as show in Figure 4.10. For all binders, the fatigue life increased when temperature increased. The six modified blends had higher fatigue life with additional AESO in the binder, which means using AESO in asphalt modification could be beneficial to fatigue life at intermediate temperatures due to the softening effect of adding AESO. The neat asphalt binder had a critical intermediate temperature of 23.8°C, thus the fatigue life of neat asphalt binder significantly dropped as the testing temperature decreased as presented in Figure 4.10. A similar fatigue life trend could be observed for lower AESO concentration level (3% LabAESO and 3% ComAESO) with a slightly improvement compared to that of the neat asphalt binder as test

temperature increased from 16°C to 25°C. Furthermore, more pronounced increase in LabAESO modified binders' fatigue life was observed at lower test temperatures of 16°C and 19°C compared to the other two higher test temperatures. This could be inferred that LabAESO helped improved the fatigue cracking resistance of the neat asphalt binder at lower intermediate temperatures, which agrees with the intermediate temperature performance grading results of LabAESO modified binders in Table 4.3 and Figure 4.5 by significantly reducing the critical intermediate temperature of the neat asphalt binder. For intermediate and high concentration levels of 9% and 15% LabAESO, the fatigue life of the neat asphalt binder over the entire test temperature range was consistently increased by approximately 100% and 290%, respectively. However, the fatigue life of 15% ComAESO modified binder only increased by around 147% at the test temperature range as compared to that of the neat asphalt binder. Additionally, it was also observed that the 9% ComAESO binder had improvement in fatigue life at higher temperatures of 22°C and 25°C, but improvement slowed down at lower temperatures of 16°C and 19°C.

The relationships between damage intensity (D) and integrity parameter (C) of the asphalt binders at test temperature of 25°C and strain level of 5% are presented in Figure 4.11. The C value represents the integrity level of the material such as the value of one means the highest integrity as in the undamaged state of the material and zero indicates completely damaged material in the failure state [32]. It was observed that the neat asphalt binder had the lowest curve with the least integrity. However, the C value increased with increasing AESO concentration. A significant increase of C value was found for the 15% LabAESO modified binder such that 15% LabAESO outperformed the rest of the binders.

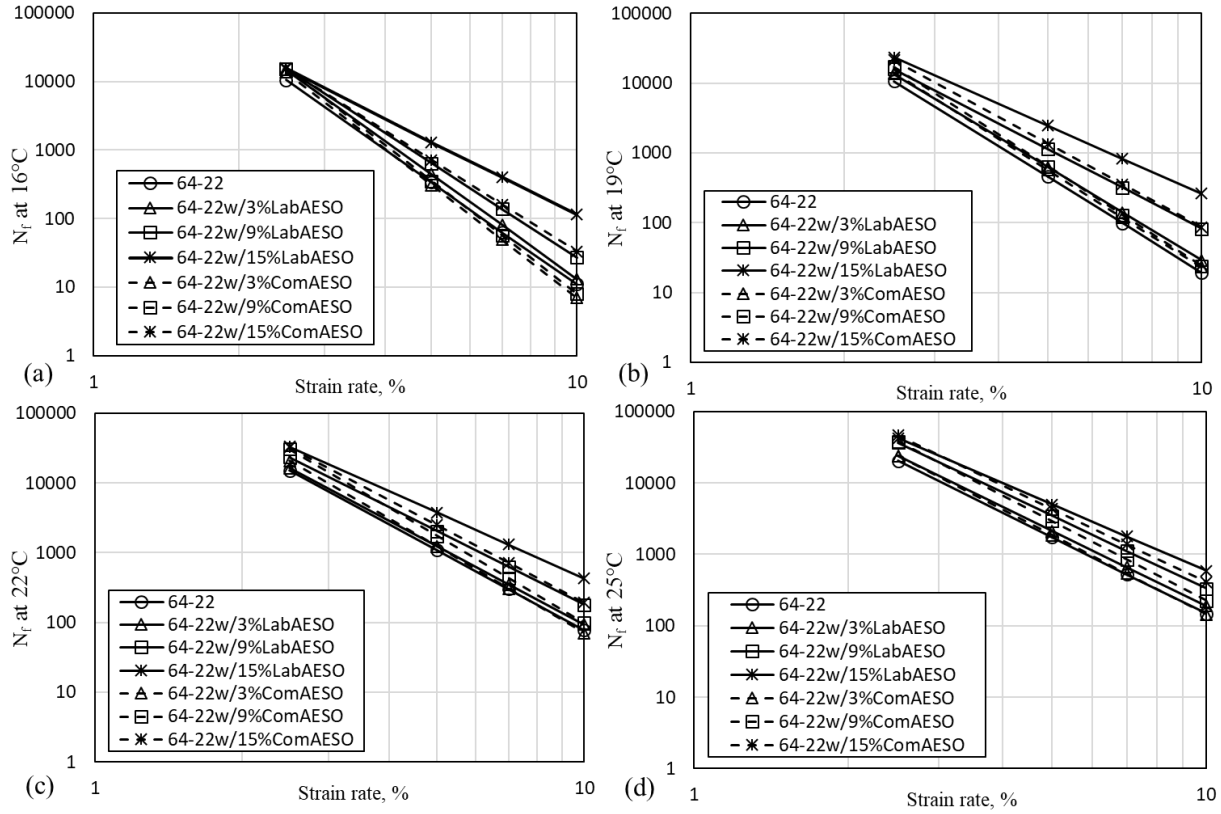


Figure 4.9. Effect of AESO on fatigue life at different test temperatures and strain levels.

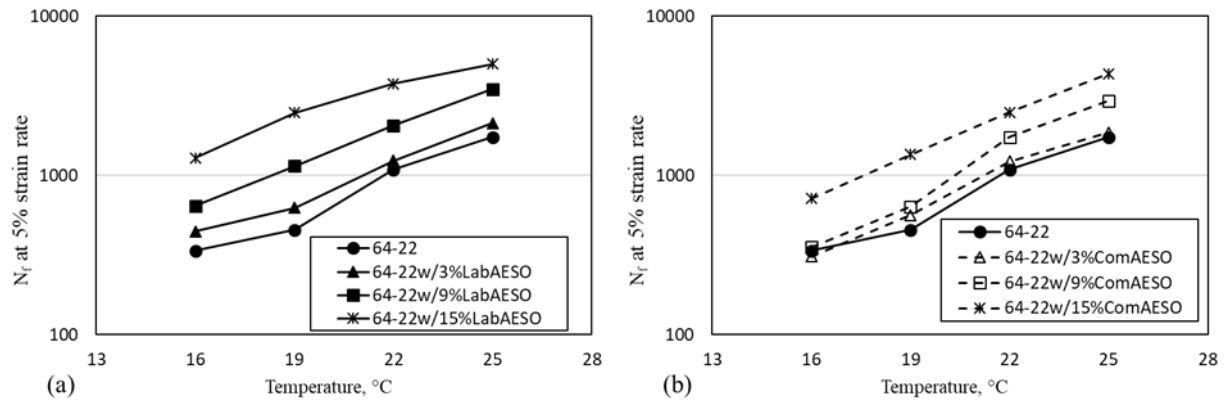
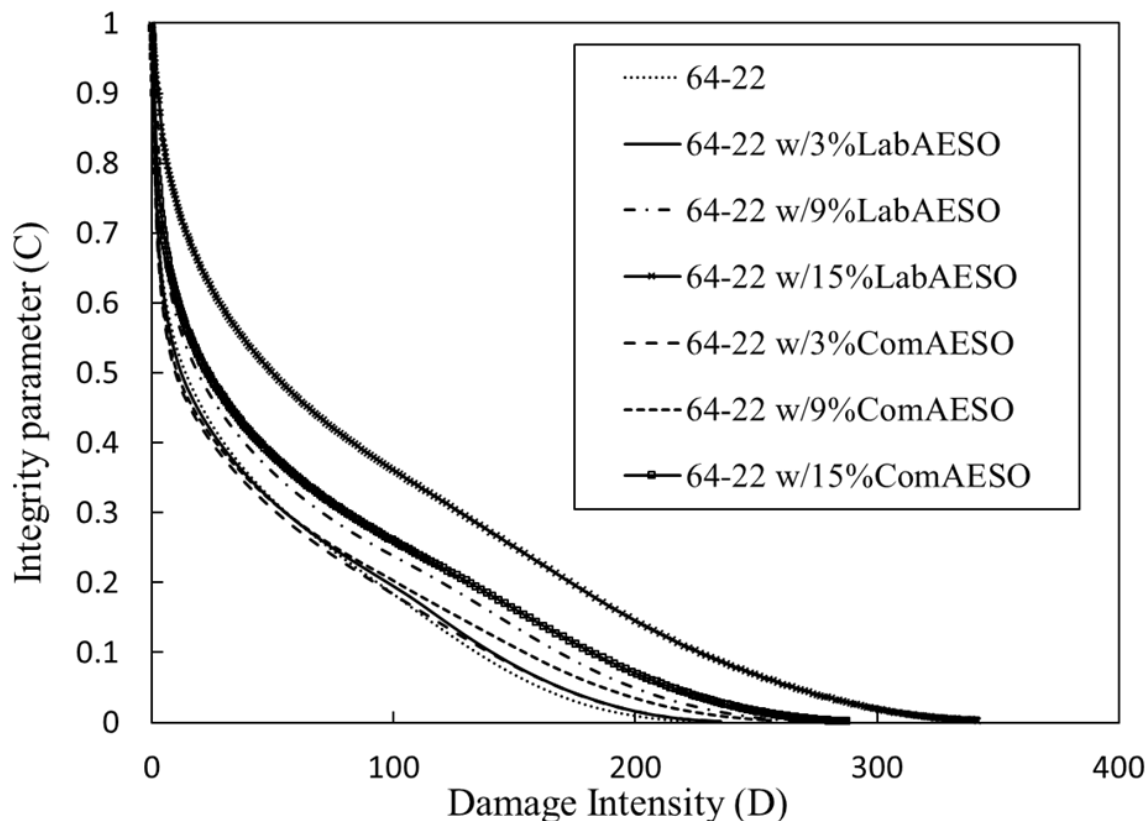


Figure 4.10. Effect of AESO on fatigue life at 5% strain rate.



**Figure 4.11. Effect of AESO on the VECD damage curve.**

#### 4.5.6. Storage stability

The degree of separation on the modified binders was determined based on their rheological properties (i.e. complex shear modulus and phase angle) in this research using the binders under storage conditions from the CTB test. The effects of AESO concentration levels and types of AESO on the degree of separation in the modified binders were evaluated as shown in Table 4.5. It can be seen that the percentage of separation increased gradually as the concentration level of LabAESO increased. The percent separation was about 7.9%, 8.6%, and 9.1% for the LabAESO concentration levels of 3%, 9%, and 15%, respectively. According to standard specifications, the deviations of top and bottom comparison larger than 10% represent phase separation, and it is considered to be incompatible issue between the additives and the neat asphalt binder. The percent separation of the three LabAESO concentration levels were all below 10%, and thereby LabAESO

was not considered to affect the high temperature storage stability of the neat asphalt binder [29]. However, the percent separation for ComAESO modified binder increased significantly to about 12% when the concentration level reached 9% and 15%, which exceeded the requirement for phase separation. It can be inferred that ComAESO had stability and compatibility issues with the neat asphalt binder when additional intermediate or high concentration levels of ComAESO were added into the neat binder.

The complex shear modulus and phase angle comparisons of the binders' top and bottom sections at test temperature of 60°C and test frequency of 10 rad/s are shown in Figure 4.12. It was noticed that all AESO modified blends had higher complex modulus at the top than the bottom (Figure 4.12 (a)), which could be caused by the density difference between the AESO and neat asphalt binder. It was noted that the complex modulus difference between the top and bottom of the LabAESO modified blends at three concentration levels seemed to be constant, while that difference for the ComAESO modified blends increased as the concentration level increased. For the phase angle comparison (Figure 4.12 (b)), it can be seen that all binders had closer phase angle values between top and bottom than that of the complex modulus. The observations on the differences between top and bottom of  $G^*$  and  $\delta$  could be quantified by using the  $I_s$  value as tabulated in Table 4.6. The  $G^*$ - $I_s$  values of LabAESO modified binders were close to one to another with a slight increase when the LabAESO concentration level increased from 3% to 15%. However, the  $G^*$ - $I_s$  of ComAESO presented a dramatic increase as the concentration level increased from 3% to 9%. In comparison with the  $G^*$ - $I_s$  values of LabAESO and ComAESO, LabAESO was found to be a better additive for asphalt modification with less potential to separate in high temperature storage even with a high concentration level of 15%. The similar  $I_s$  value trend on LabAESO and ComAESO was noticed in  $\delta$ - $I_s$  as well. Additionally,  $\delta$ - $I_s$  values on all modified

binders were noted to be closer to zero than  $G^*$ - $I_s$  values. This can be inferred that the complex modulus seemed to be the limiting factor that showed the phase separation of the AESO modified binders.

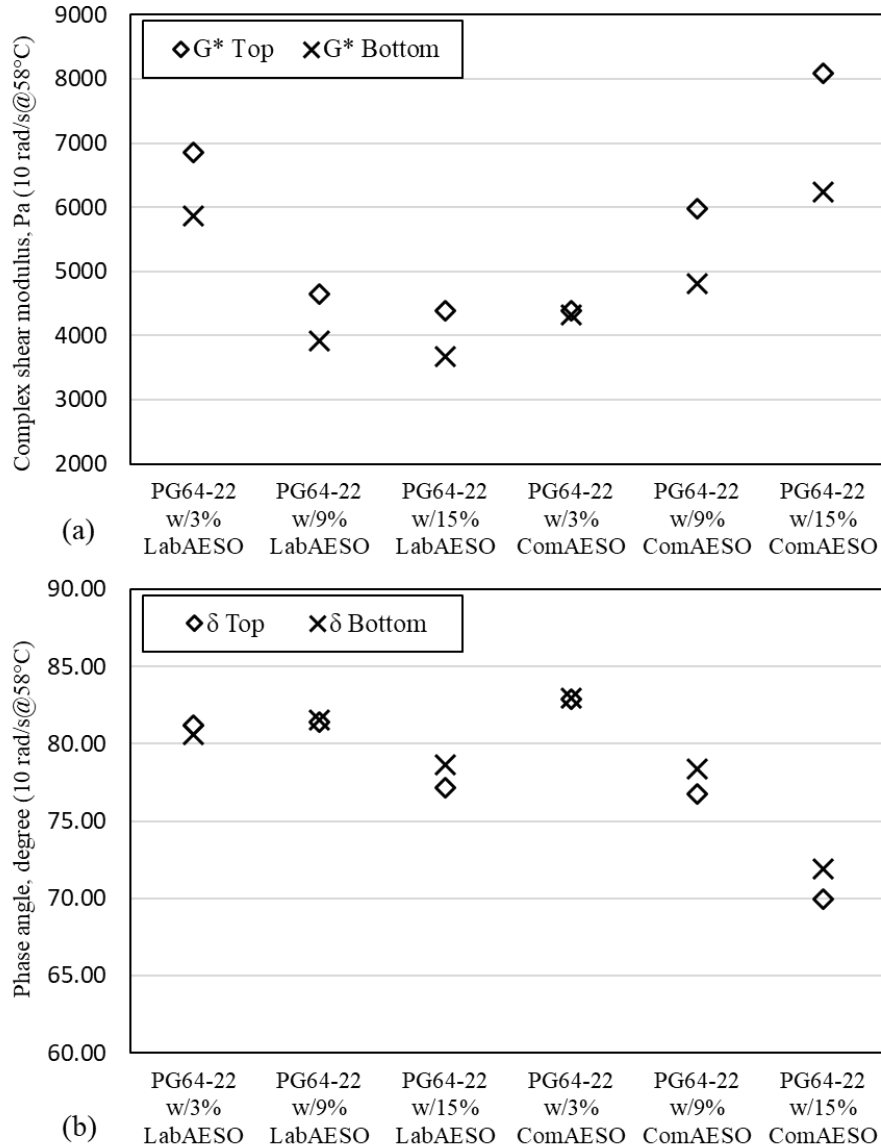
**Table 4.5. Effect of AESO concentration levels on asphalt binder separation.**

Blends	$G^*/\sin(\delta)@(10\text{rad/s})$		Ave	%Sep (<10%)
	Top	Bottom		
PG64-22 w/3% LabAESO	5.928	6.944	6.436	7.9
PG64-22 w/9% LabAESO	4.709	3.964	4.337	8.6
PG64-22 w/15% LabAESO	4.503	3.749	4.126	9.1
PG64-22 w/3% ComAESO	4.416	4.350	4.383	0.8
PG64-22 w/9% ComAESO	6.141	4.852	5.497	11.7
PG64-22 w/15% ComAESO	7.603	5.927	6.765	12.4

**Table 4.6. The  $G^*$  and  $\delta$  separation index ( $I_s$ ) of AESO modified binders at 60°C and 10 rad/s.**

Blends	$G^*@(10\text{rad/s})$			$\delta@(10\text{rad/s})$		
	Top	Bottom	$I_s$	Top	Bottom	$I_s$
PG64-22 w/3% LabAESO	6851	5859	0.068	81.23	80.62	0.003
PG64-22 w/9% LabAESO	4641	3921	0.073	81.38	81.55	-0.001
PG64-22 w/15% LabAESO	4390	3676	0.077	77.13	78.65	-0.008
PG64-22 w/3% ComAESO	4382	4317	0.006	82.88	82.97	0.000
PG64-22 w/9% ComAESO	5978	4809	0.095	76.78	78.35	-0.009
PG64-22 w/15% ComAESO	8094	6236	0.113	69.93	71.88	-0.012





**Figure 4.12. Complex modulus and phase angle comparisons of the AESO modified binders after storage at a test temperature of 60°C.**

#### 4.6. Conclusions

In this research, the possibility of using AESO for asphalt modification and the modification effects with various concentration levels of AESO were examined and determined through laboratory investigation. According to the performance evaluation of AESO modified binders, the key findings were summarized as follows:

- Both types of AESO had positive softening effect on the neat asphalt binder with reduction of viscosity, which resulted in the benefits of decreased mixing and compaction temperatures. The activation energy values indicated asphalt binder with additional AESO decreased temperature susceptibility and lowered the compaction effort needed to produce HMA.
- AESO (LabAESO and ComAESO) was found to have negative effect on critical high temperatures due to the reduction of viscosity. In contrast, the softening effect of AESO helped with intermediate and low temperature performance grades. However, only LabAESO at higher (15%) concentration level was noted to be the most beneficial on low and intermediate performance grades.
- Reduction of stiffness was observed on AESO modified binders in complex shear modulus master curves. AESO's phase angle master curves showed less thermal susceptibility with the presence of a rubbery behavior plateau at low frequencies and high temperatures. Higher phase angle values were noticed at intermediate and high frequency ranges, which indicated the improvement to fatigue damage and thermal cracking at intermediate and low temperatures due to the more viscous behavior the modified binder presented. A sufficient high concentration of AESO was needed for asphalt modification to present more drastic effects on rheological curves.
- Asphalt binder's low temperature properties (creep stiffness and creep rate) indicated that 15%LabAESO had higher stress relaxation and better ability to dissipate stresses, and thereby reduced the neat asphalt binder's susceptibility to thermal cracking.
- Positive effects on fatigue damage with additional AESO in neat asphalt binder showed increased fatigue life when the concentration level increased. Additionally, sufficient

high LabAESO concentration was recommended for significant improvement of neat asphalt binder's fatigue life.

- LabAESO at three concentration levels were found to have no separation issue, while ComAESO did not have good stability and compatibility with the neat asphalt binder with higher percent separation at intermediate and high concentration levels.

Furthermore, the complex modulus was found to be the limiting factor that causing the potential for separation in high temperature storage stability.

To conclude, it was found that AESO had positive effects on reducing the stiffness of the neat binder, and LabAESO showed beneficial effects on the resistance to fatigue damage and thermal cracking of the neat asphalt when sufficient high concentration level was added. The findings indicated that LabAESO performed superior to ComAESO in terms of fatigue life and low temperature properties at the same concentration level without separation issue. Therefore, it was suggested that LabAESO could be used as a fluxing agent to reduce the stiffness, to increase fatigue life, and to improve susceptibility to thermal cracking by increasing thermal stress relaxation of the neat asphalt binder for pavement applications in cold regions such as the Midwestern United States. Further research should be conducted to evaluate how short-term and long-term aging affect AESO modified binders at various concentration levels. To better understand the interaction between AESO and the neat asphalt binder, analytical chemical testing must be conducted in a future study.

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**CHAPTER 5. RHEOLOGICAL PROPERTIES AND EFFECTS OF AGING ON  
ACRYLATED EPOXIDIZED SOYBEAN OIL MONOMER-MODIFIED ASPHALT  
BINDER**

Modified from a paper published in *Road Materials and Pavement Design*<sup>1</sup>

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### 5.1. Abstract

This investigation examines the rheological properties and effects of aging on laboratory produced acrylated epoxidized soybean oil (AESO) monomer (LabAESO) and commercially available AESO (ComAESO) modified asphalt binders at various concentration levels. The rheological curves show that the polymerization of AESO occurs during blending with the polymer and that the entanglement characteristic curvature appears gradually as AESO concentration level increases. The findings indicated that sufficiently high level of LabAESO is necessary to affect the neat asphalt binder's rheological properties as shown in Van Gurp-Palmen curves, master curves, and Black diagrams. The research results revealed that AESO monomer has shown great potential to be used as a modifier in asphalt performance modification. Additionally, LabAESO works better on reducing aging susceptibility than ComAESO, and that is shown clearly with increasing dosage levels of LabAESO and ComAESO.

### 5.2. Introduction

Asphalt binder is a by-product from crude oil refining process and has been used for thousands of years in adhesive, sealant, and pavement binder applications [1]. Each year, pavement

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construction consumes the vast majority of asphalt binder due to its adhesive properties, ability to coat aggregates and its special rheological behavior [2]. As asphalt binder is a viscoelastic material, its rheological properties change along with loading rate and temperature. It is preferred to have asphalt binder fluid enough for pumping and mixing at high temperatures while stiff enough to provide strength and prevent permanent deformation at high service temperature and less elastic to dissipate stress for thermal cracking at low service temperature [2,3]. Therefore, asphalt binder plays an important role in the performance of flexible pavement and the rheological properties are proved to have close relationships to the field performance [4].

Polymers or additives are used to improve the overall performance of asphalt binder by increasing the stiffness and flexibility with higher resistance to thermal and aging susceptibility and thereby substantially improve pavement performance and extend the service life of asphalt mixtures [4,5]. The modification effects make significant changes on the rheological properties of neat asphalt binder such as viscosity, complex modulus, and phase angle, therefore, they are able to efficiently enhance the neat asphalt binder's performance [4]. However, there are always challenges when using polymers or additives for modification, which include high temperature susceptibility, poor aging resistance, and compatibility issues [6]. Besides these challenges, there are always economic and environmental concerns. To solve these problems, renewable additives, agents, and polymers were investigated and studied by researchers for modification purposes instead of using inorganic and petroleum-based polymers.

Bio-based oil and renewable additives that can be derived from biomass materials are currently one of the top focus areas for researchers in pavement industry. Sun et al. [7] conducted comprehensive laboratory investigations on the chemical compositions of bio-oil that was derived from waste cooking oil and its performance in asphalt binder. The chemical results showed that no

chemical reaction occurred between the bio-oil and the base asphalt binder after blending. According to the performance test results, the bio-oil was able to decrease the softening point and viscosity, and increase the penetration and ductility of the base binder with no signs of separation. It was noticed that the bio-oil had negative effects on the binder's resistance to deformation and the elastic recovery. However, it showed positive effects on the base binder's resistance to thermal cracking at low temperatures. Lei et al. [8] used bio-oil derived from wood plants as additives in asphalt binder and found that the bio-oil significantly enhanced the neat asphalt binder's performance at intermediate and low temperatures by lowering the stiffness and increasing the stress relaxation of the base binder. They also developed a new partition method to study the mechanism of oil-modified binders. The results indicated that the large and the medium molecular size contents correlates well with the low and intermediate temperatures performance, respectively. They concluded that the oil modifiers showed positive effects on the performance of low and intermediate temperatures due to the decrease of large and medium molecular size contents. Fini et al. [9,10] conducted performance testing on a blend of bio-binder produced from the thermochemical conversion of swine manure and base asphalt binder. With this partial bio-binder, the low temperature properties were improved whereas adverse effects on the high temperature grade were observed. Their study also showed that bio-oil materials from different source materials had different rates of susceptibility to aging effect.

Seidel and Haddock [11] studied the rheological properties of asphalt binder modified using soybean acidulated soapstock that is a renewable vegetable-based asphalt additive from soybean fatty acids. Their test results indicated that with additional soybean fatty acids asphalt binder became softer, less stiff, and reduced viscosity, which could be used as a fluxing agent for stiff binder with improved workability and low temperature performance. Aging is considered to be

one of the most serious causes behind asphalt pavement deterioration due to the hardening of asphalt binder [12]. Thus, it is necessary to evaluate the aging susceptibility of modified binders through laboratory testing. Xu et al. [13] conducted investigations on the application of wood lignin as a modifier in asphalt modification. They found wood lignin caused stiffening effect that resulted in rutting resistance improvement at high temperatures. Moreover, it was noticed that wood lignin had positive effects on anti-aging of modified binder and it could be used as anti-oxidants with economic and environmental benefits. However, negative effects on low temperature performance and fatigue life of lignin modified binder were noted. Podolsky et al. [14] researched the effects of aging on rejuvenated vacuum tower bottom using several bio-derived rejuvenating agents and found that all renewable agents were able to reduce the stiffness of vacuum tower bottom due to aging. They also noted the hydrogreen affected phase angle differently than the linseed oil materials in phase angle master curves. Thus, the choice of materials dose matter and can affect aging susceptibility.

At Iowa State University, bio-based polymers were successfully synthesized using an acrylated epoxidized soybean oil (AESO) monomer [15–18]. The biopolymer's modification effects showed improvement against rutting and reduced temperature susceptibility, which performed superior to commercial petroleum-based polymers [15–18]. Furthermore, polymerization of monomer was able to occur automatically in asphalt modification under air conditioning during high temperature blending with increased melting temperature, tensile strength, and rutting resistance of the neat asphalt binder according to Chung et al. [20]. Polymers produced during the blending of monomer within asphalt is noted to be an innovative approach with rheological property changes and improvement of compatibility [21]. The synthesis of AESO-based biopolymers is very successful and its modification effects in asphalt binder have shown great potential, however, no literature

was found to use AESO monomer itself as additives in asphalt modification. Previous investigation on using laboratory produced AESO monomer modified asphalt binder had shown beneficial effects on softening the neat asphalt binder with reduced mixing and compaction temperatures. Moreover, laboratory produced AESO also shows the positive effects on fatigue life at intermediate temperatures and thermal cracking at low temperatures at high concentration level with no storage stability issue.

In this research, we propose that oxidative polymerization of AESO can occur during asphalt blending when the asphalt component is exposed to air, which causes asphalt performance modification, and thereby changes the rheological properties of neat asphalt binder. The rheological properties of AESO modified binders were examined through Van Gorp-Palmen (vGP), master curves, and Black diagrams over a wide range of testing frequencies and testing temperatures. Furthermore, aging effects will be evaluated through rheological parameters (i.e. complex shear modulus and phase angle) for comparisons between unaged and aged materials obtained from dynamic shear rheometer (DSR) testing. The overall results will provide a comprehensive understanding of how AESO monomer affects asphalt binder's rheological properties after modification and how the aging conditions affect the rheological behavior of AESO modified asphalt binders.

### 5.3. Objective and scope

The objectives of this research are as follows:

- To examine the effects of various concentration levels of AESO on rheological properties of neat asphalt binder.
- To evaluate the effects of aging on various concentration levels of AESO modified asphalt binders.

- To compare the modification effects of laboratory produced AESO (LabAESO) versus commercial available AESO (ComAESO) in terms of rheological properties and aging susceptibility.

## 5.4. Materials and methods

### 5.4.1. Experimental materials and material preparation

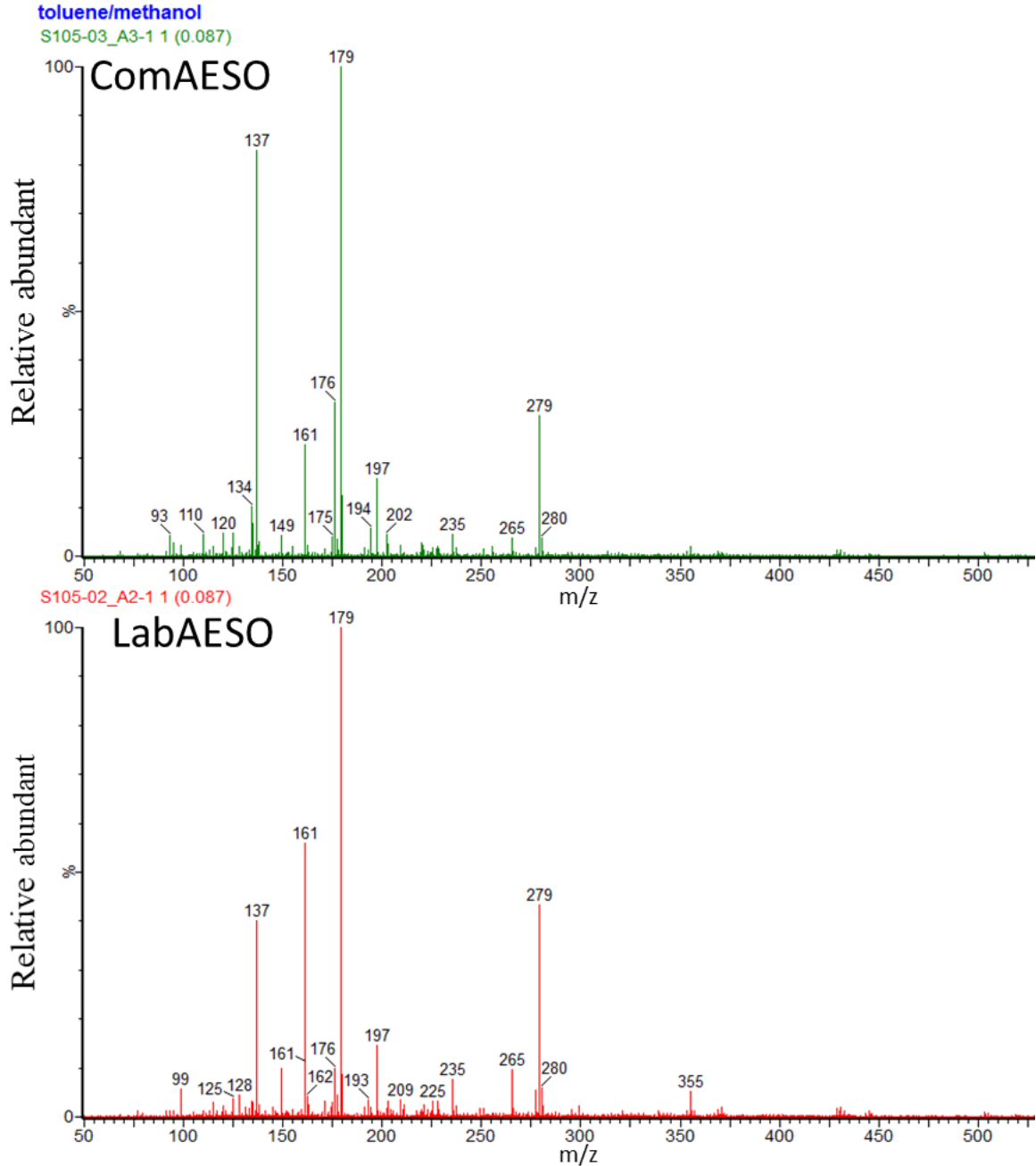
This research focused on rheological characterization and aging sensitivity of two types of AESO modified binders at various concentration levels in asphalt binders. The neat asphalt binder used as the control group, was a PG 64-22 procured from a U.S. Midwest binder supplier (Canadian crude source) with properties shown in Table 5.1. The two types of AESO monomer used for asphalt modification are laboratory produced AESO (LabAESO) and commercial available AESO (ComAESO) that was purchased from a reputable supplier and used as received. The chemical structure of AESO can be found in O'Donnell et al. [22] and Sotoodeh-nia et al [23]. Both AESOs have similar molecular weights (i.e. LabAESO 1044 g/mol and ComAESO 1200 g/mol) but with different acrylate functionality of 1.3 for LabAESO and 2.6 for ComAESO. The acrylate functionality is defined as the number of acrylate groups in each triglyceride molecule, which relates to the structure of the molecule. The ion distributions corresponding to their relative abundance in each type of AESO were collected and are shown in the mass spectrum gained through atmospheric pressure solids analysis probe with time-of-flight mass spectrometry (ASAP-TOFMS) in Figure 5.1. The mass spectrum showed that both AESOs consist of the same molecule but differ in their relative abundance. This means that both AESO contain the same ions in the molecule but the ions showed up with different intensities due to the differences in acrylate functionality. Additionally, lower functionality means better control in the acrylate groups with

the reduction of branches in the molecule, therefore, they are expected to have different effects in asphalt binder.

AESO concentration levels of low (3%), intermediate (9%), and high (15%) by total weight of binder were selected to prepare the modified blends. Modified blends at each concentration level for each type of AESO material were prepared in duplicate to ensure the same modification effects. Shear blending was conducted by blending AESO into the neat asphalt binder using a Silverson L5M-A shear mixer. The AESO modified blends were prepared by high-speed shear blending at 3000 rpm and blending temperature of  $145 \pm 5^\circ\text{C}$  for 60 min. The blending procedure was determined based on previous trial blends at different blending temperatures and durations to maximize the modified binder's performance.

**Table 5.1. Properties of PG 64-22 neat asphalt binder.**

Aging status	Properties	PG64-22
Unaged binder	Viscosity at $135^\circ\text{C}$ (Pa·s)	0.408
	$G^*/\sin\delta$ at $64^\circ\text{C}$ (kPa)	1.268
RTFO aged residue	Mass loss at $163^\circ\text{C}$ (%)	0.565
	$G^*/\sin\delta$ at $64^\circ\text{C}$ (kPa)	4.296
RTFO+PAV aged residue	$G^* \sin\delta$ at $25^\circ\text{C}$ (kPa)	2959
	Stiffness at $-12^\circ\text{C}$ (MPa)	210
	m-value at $-12^\circ\text{C}$	0.318



**Figure 5.1. ASAP-TOFMS mass spectrum of LabAESO and ComAESO.**

#### 5.4.2. Laboratory testing

##### 5.4.2.1. Performance grade (PG)

The AESO modified binders were graded according to the Superpave Performance Grading (PG) requirements defined in AASHTO M 320. A Dynamic Shear Rheometer (DSR) was used to

determine the critical high temperature and critical fatigue temperature of the asphalt binder by following AASHTO T315-10 and AASHTO TP 101-14, respectively. A Bending Beam Rheometer was used to obtain the stiffness and m-value of the asphalt binder according to AASHTO T313-10. The short-term aging was performed using a Rolling Thin Film Oven at 163°C for 85 min according to AASHTO T240-09 and the long-term aging was conducted using a Pressure Aging Vessel (PAV) at 100°C for 20h under 2.10 MPa pressure following AASHTO R28-12. All tests were done in triplicate and the average values were reported.

#### **5.4.2.2. Rheological testing (DSR)**

The temperature-frequency sweep test using the DSR was conducted on the unaged asphalt binders to evaluate the effect of AESO on the neat binder's rheological properties by following AASHTO T 315-10. A strain sweep test was done to verify whether the strain rate used for specimens at each test temperature kept the tested asphalt binder within the linear viscoelastic range. All asphalt specimens were tested at frequency ranges between 0.1 to 100 rad/s at various test temperatures from 10°C to 64°C. For lower test temperatures of 10°C, 20°C, and 30°C, the 8 mm parallel plates with a 2 mm gap was selected to run the frequency sweep test at 0.5% strain rate. While the 25 mm parallel plates with a 1 mm gap was used for frequency sweep test at 5% strain rate for higher test temperatures of 40°C, 46°C, 52°C, 58°C, and 64°C. The complex shear modulus ( $G^*$ ) and phase angle ( $\delta$ ) values of asphalt binder were obtained at each tested frequency and temperature.

The temperature sweep test was performed at various test temperatures of 40°C, 46°C, 52°C, 58°C, and 64°C on unaged, Rolling Thin Film Oven (RTFO) aged, and PAV aged asphalt binders with a strain rate of 5% at 10 rad/s using 25 mm parallel plates with a 1 mm gap in a DSR according to AASHTO T315-10. The test was conducted to evaluate the aging effects on the asphalt binders'



rheological properties. Ten data points of complex modulus and phase angle at each test temperature were measured and collected for all asphalt blends. Tests were done in triplicate for each material and the mean values were calculated and used for comparisons. The aging sensitivity of the modified blends were evaluated by calculating the aging index (AI) of the complex modulus obtained from the DSR test at a test temperature of 58°C and frequency of 10 rad/s using Equations (5.1) and (5.2) presented below [24]:

$$AI_{RTFO} = \frac{G^*_{RTFO \text{ aged binder}}}{G^*_{\text{unaged binder}}} \quad (5.1)$$

$$AI_{PAV} = \frac{G^*_{PAV \text{ aged binder}}}{G^*_{\text{unaged binder}}} \quad (5.2)$$

## 5.5. Results and discussions

### 5.5.1. Performance grade (PG)

The performance grade of all asphalt binders was verified and determined by following the Superpave specifications. The results are presented in Table 5.2. With additional AESO, the critical high temperature of the neat asphalt binder decreased, which means AESO might have negative effects on resistance to rutting. However, the softening effect of AESO was noticed to be beneficial in the binder's stiffness at intermediate and low temperatures with lower PG. It was also found that 15%LabAESO modified binder decreased the critical low temperature of the neat asphalt binder from -23.8°C to -28.2°C, which lowered the PG from PG -22 to PG -28. Moreover, 15%LabAESO reduces the critical intermediate temperature by 9.1°C, which significantly improves the potential to resist fatigue cracking at intermediate service temperatures. It was also noted that the AESO types showed different effects on the asphalt binder's useful temperature interval (UTI) span as the AESO concentration level increased. As the LabAESO increased from low to intermediate to high concentration, the UTI span of the binder decreased from 86°C to 80°C

then increased up to 86°C. However, the UTI span of the binder decreased from 86°C to 80°C with additional intermediate and high concentrations of ComAESO. The UTI span results indicated that low concentration level of AESO was not able to change the UTI span of neat asphalt binder. The softening effect of AESO at intermediate concentration level decreased the UTI span of the neat asphalt binder by lowering the high temperature performance grade. At high concentration level, only LabAESO was able to present enough softening effect on lowering both high and low performance grades of the neat asphalt binder to widen the UTI span to 86°C. It is important to note that aging may have more effects on ComAESO modified binders, because ComAESO modified binders before and after RTFO aging process shows about 2.5°C, 3.4°C, and 5°C temperature differences as the concentration level increases while the LabAESO modified binders and neat asphalt binder only show less than 2°C temperature increase due to the aging effect. It can be inferred that LabAESO may be less susceptible to aging effect compared to the ComAESO at the same concentration level. Additionally, sufficient high concentration of LabAESO may have positive effect on reducing the aging effect of the neat asphalt binder. Further investigation on aging effects were conducted and presented in Sections 5.5.4 and 5.5.5.

**Table 5.2. Properties of control and modified binders.**

Blends	PG 64-22	PG 64-22 w/ 3%LabAESO	PG 64-22 w/ 9%LabAESO	PG 64-22 w/ 15%LabAESO	PG 64-22 w/ 3%ComAESO	PG 64-22 w/ 9%ComAESO	PG 64-22 w/ 15%ComAESO
Unaged (High Temp.), °C	66.6	64.4	61.3	58.8	64.4	63	60.4
RTFO (High Temp.), °C	67.6	66	61.4	59.3	66.9	66.4	65.4
PAV (Intermediate Temp.), °C	23.8	22.4	15.3	14.7	19.9	18.1	17.9
PAV (Low Temp.), °C	-23.8	-23.9	-25.7	-28.2	-23.0	-23.3	-24.4
Performance Grade (PG)	64-22	64-22	58-22	58-28	64-22	58-22	58-22
Useful Temperature Interval, °C	86.0	86.0	80.0	86.0	86.0	80.0	80.0
Mass loss at 163°C, %	0.565	0.598	0.676	0.960	0.758	0.847	0.852

### 5.5.2. Van Gulp-Palmen (vGP) curve & Black diagram

Van Gulp-Palmen (vGP) curves were generated to identify the phase separation tendency and to verify the applicability of the time-temperature superposition principle (TTSP) on asphalt blends [25,26]. The vGP curve examines the relationships between complex shear modulus as x-axis and phase angle as y-axis at various testing temperatures and frequencies. The continuity and smoothness of the curve represent the condition of the material's superposition and the effectiveness of the TTSP on the material [25,27,28]. The curve includes the information about the distribution condition of the molecular weight, the plateau modulus, and the polydispersity [25,29–31]. Moreover, the shape of the curve helps identify the structure of the polymer (such as linear polymers or nonlinear polymers) added for asphalt modification [31]. The validity of TTSP and tendency of phase separation were examined by vGP curves on the AESO modified asphalt binders for further rheological property analysis of the modified blends. The vGP curves of all asphalt binders are shown in Figure 5..

It was observed from Figure 5. (a) that the curve of the neat asphalt binder was smooth and continuous, which represents good superposition and the effectiveness of the TTSP in the entire test temperature range [25,27,31]. The phase angle of the neat asphalt binder increased roughly from  $27^\circ$  to  $90^\circ$  while the complex shear modulus decreased, which indicates the asphalt binder lost its elasticity and became more viscous as test temperature increased from  $10^\circ\text{C}$  to  $64^\circ\text{C}$ . LabAESO modified blends showed similar curves to the neat asphalt binder as presented in Figure 5. (b) and (c) without any phase separation being observed. However, a very slight phase separation was noted on the ComAESO modified blends (Figure 5. (d) and (e)) compared to the LabAESO modified blends, which means LabAESO was more compatible with the neat asphalt binder with a better interaction effect and the modified blends were more homogeneous in comparison with

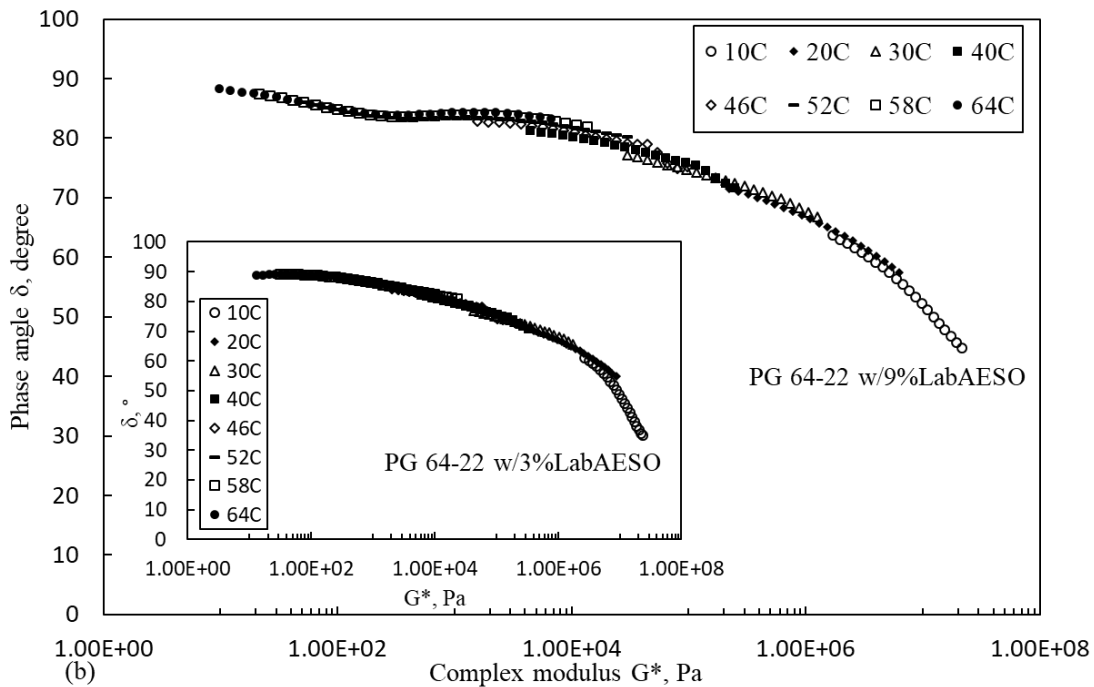
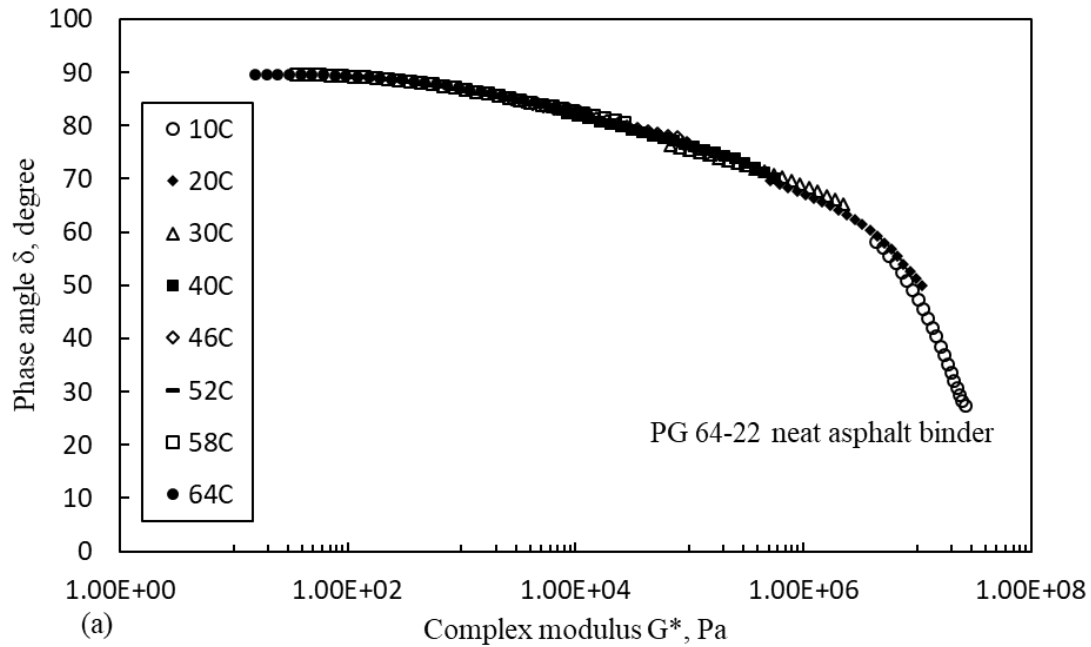
ComAESO modified blends [25,32]. For both AESO materials' modified binders, there was a change of curve shape at higher testing temperatures when 9% of AESO was added (Figure 5. (b) and (d)). The appearance of this special curvature became wider and more obvious (Figure 5. (c) and (e)) as higher concentration of AESO (i.e. 15%AESO) was added. A better display of the curvature for 15%LabAESO and 15%ComAESO modified asphalt binders was presented in Figure 5.3. This unique curvature showed interesting changes in phase angle for the blends. The phase angle dropped to a minimum value then rises again and approaches 90°, while the complex modulus decreased. The characteristic curvature was an indicator of polymer entanglement behavior with the asphalt molecules during modification, which represents AESO was acting like a linear polymer in asphalt modification and the molecular weight was distributed evenly in the neat asphalt binder without phase separation [25,31,33,34]. It was possible to assume that the oxidative polymerization of AESO monomer occurred independently within the presence of some asphalt components and air at the blending temperature, and thereby the neat asphalt binder was modified properly with notable changes in rheological properties [19]. However, the product of AESO polymerization in asphalt binder and changes of chemical components of the modified blends are still needed to be investigated in future studies.

The plateau modulus ( $G_N^0$ ) is known as the most fundamental parameter to identify the entanglement behavior of molecules in a viscoelastic behaving material [35]. It is defined as the stiffness of the materials when the phase angle is at its lowest (the most elastic response) [31,36]. When  $G_N^0$  appears, it is indicating the storage modulus ( $G'$ ) dominates over the loss modulus ( $G''$ ), and thereby the  $|G^*|$  is getting close to the value of  $G'$  at the minimum value of phase angle ( $\delta$ ). This can be expressed as Equation (5.3) below [31,35]:

$$G_N^0 = \lim_{\delta \rightarrow 0} |G^*(\delta)| \quad (5.3)$$

By the means of vGP-plot, the  $G_N^0$  can be easily observed and determined with the presence of a unique curvature as shown in Figure 5.3. In modified asphalt binder, the curvature presents the elastic-recovery behavior due to the entanglement of the polymer as mentioned above. Therefore, the  $G_N^0$  represents the total resistance to shear force when the asphalt binder shows the most elasticity at high temperatures. The  $G_N^0$  for 15%LabAESO and 15%ComAESO modified binders were 176 Pa and 1100 Pa, approximately. Since 15%ComAESO modified asphalt binder had higher  $G_N^0$  with smaller phase angle compared to 15%LabAESO modified asphalt binder (Figure 5.3), the 15%LabAESO modified asphalt binder presents more viscous behavior at higher temperatures, which is in agreement with the discussions on grading results.

The Black diagrams are the vGP plots with reversed axes. More drastic entanglement could be observed in the Black diagrams shown in Figure 5.4. It was observed that as the concentration increased, more entanglement was noticed with a higher magnitude curvature for both AESO modified blends at higher temperatures and lower frequencies. The rubbery-like behavior at phase angle of  $75^\circ$  to  $85^\circ$  was noticed for the AESO modified blends when the stiffness of the blends were about 100 to 1000 kPa. For the ComAESO modified blends, the same rubbery elastic phase angle range was found for stiffness values between 1000 and 10000 kPa. This means even though the rubbery responses are similar for LabAESO and ComAESO modified blends, the nature of the ComAESO modified binder is stiffer than the LabAESO modified binder at higher test temperatures.



**Figure 5.2. The vGP curves of neat asphalt binder PG 64-22 and AESO materials modified asphalt binders: (a) PG 64-22 neat asphalt binder, (b) PG 64-22 neat asphalt binder modified with 3 and 9% LabAESO, (c) PG 64-22 neat asphalt binder modified with 15%LabAESO, (d) PG 64-22 neat asphalt binder with 3 and 9% ComAESO, and (e) PG 64-22 neat asphalt binder with 15%ComAESO.**

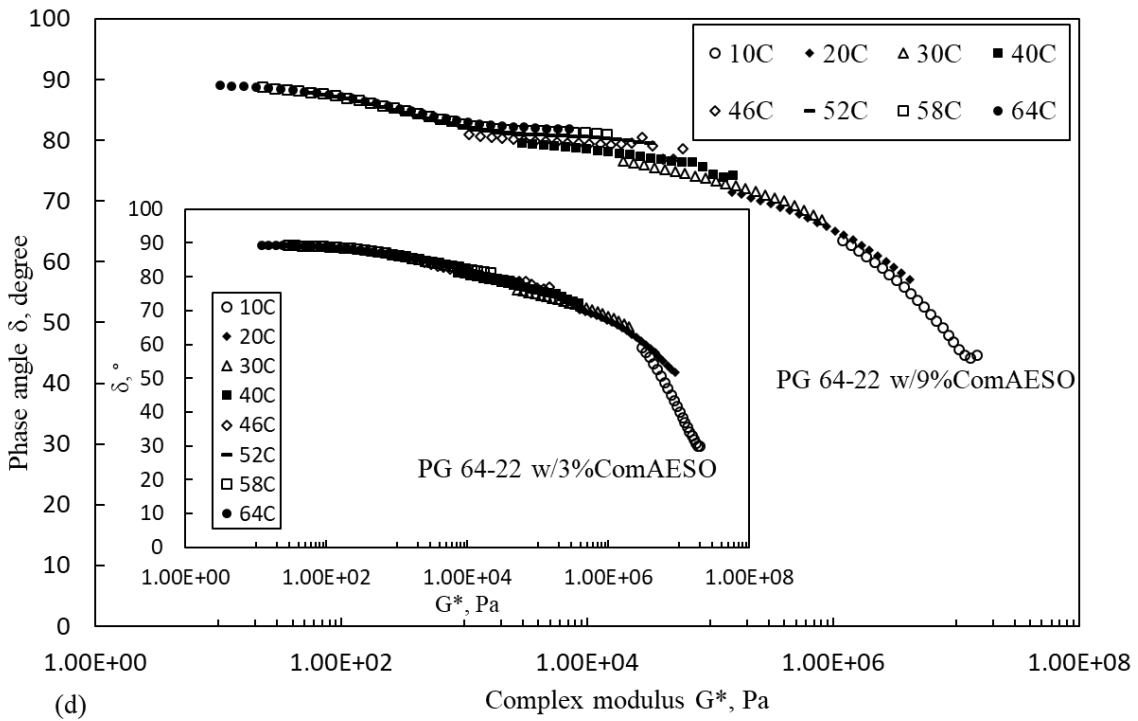
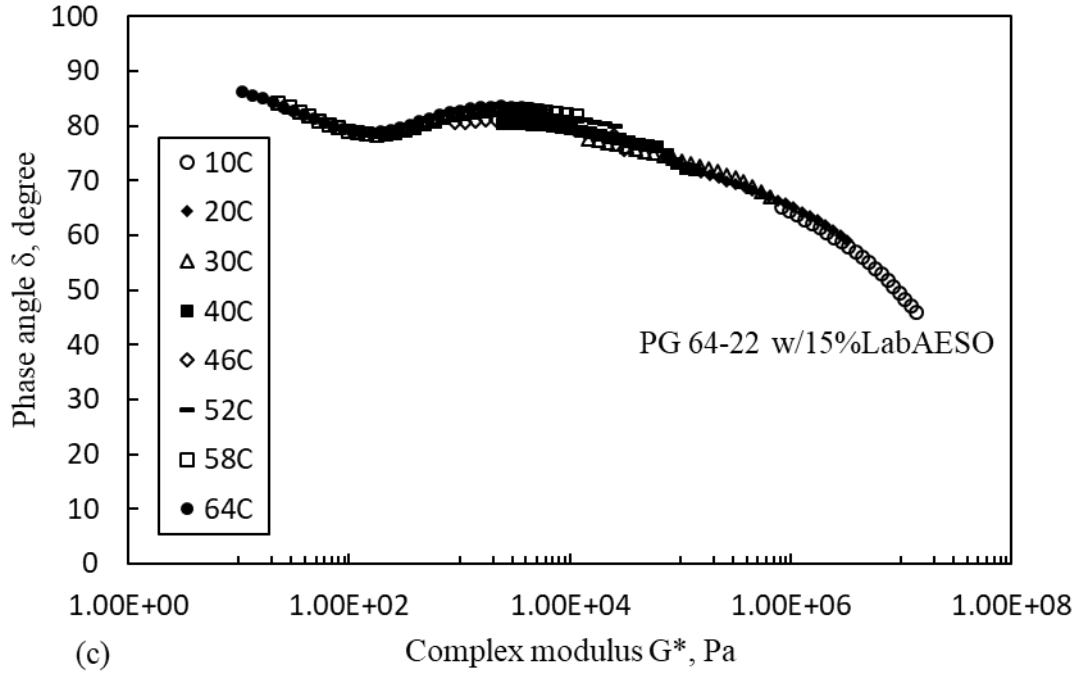


Figure 5.2. (Continued)



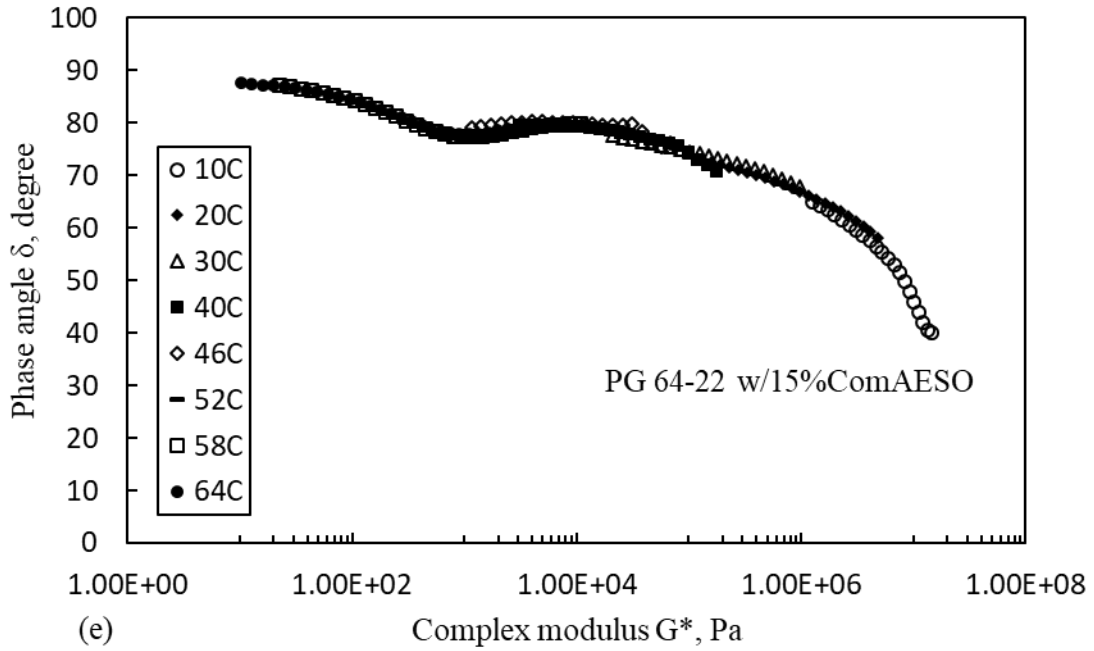


Figure 5.2. (Continued)

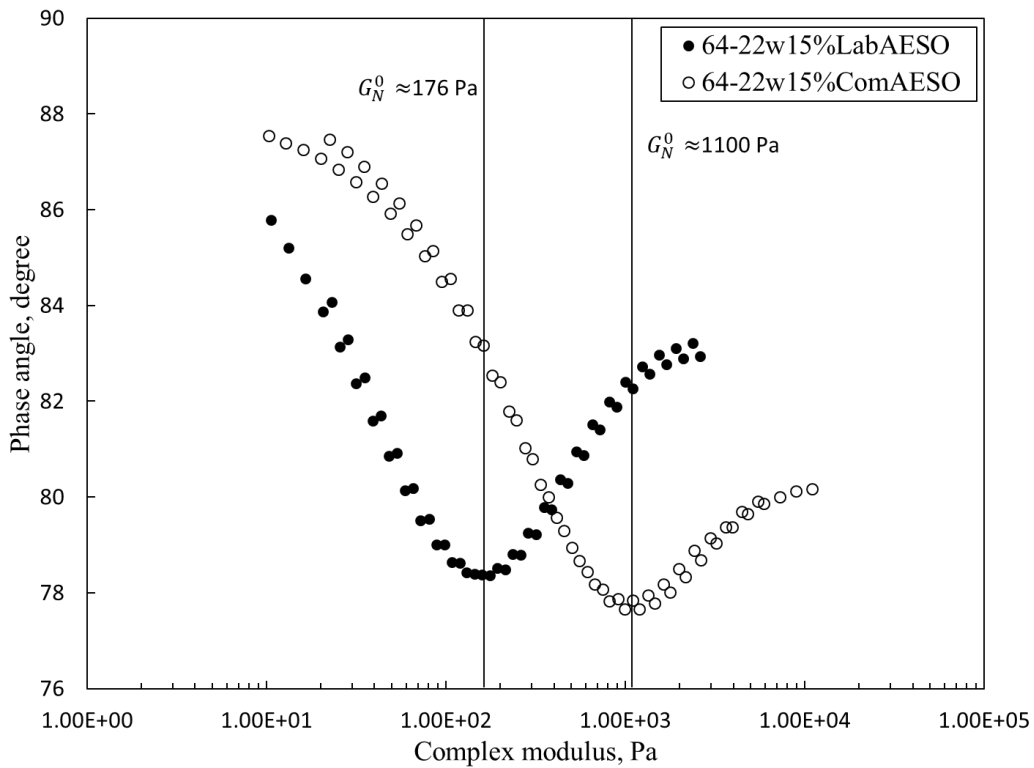
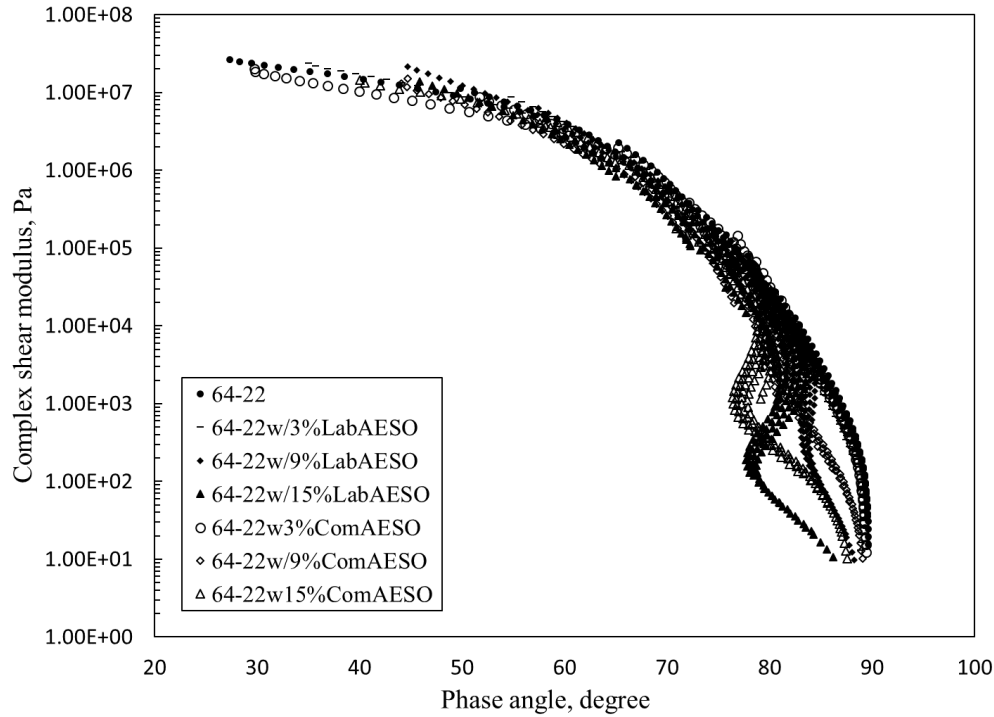


Figure 5.3. The vGP curves for 15%LabAESO and 15%ComAESO modified asphalt binders with the plateau modulus  $G_N^0$ .



**Figure 5.4. Black diagrams of LabAESO and ComAESO modified blends.**

### 5.5.3. Master curves

The complex modulus and phase angle master curves and Black diagrams were constructed to investigate the rheological properties of the neat asphalt binder and AESO modified asphalt binders [12,28]. The applicability of TTSP was verified by evaluating the vGP curves of all the binders in Section 5.5.2, thereby the rheological master curves were generated by using the TTSP at a reference temperature of 40°C. In TTSP, shift factors are needed to be identified at various test temperatures to shift the tested modulus values horizontally to obtain a continuous smooth curve at the reference temperature [37,38]. From the master curve, the viscoelastic behavior of the materials over a wide range of testing temperatures and frequencies was estimated and compared easily [12,28–30]. Shift factors were calculated by using the Williams-Landel-Ferry (WLF) equation as below:

$$\log \alpha_T = -\frac{C_1(T-T_R)}{C_2+(T-T_R)} \quad (5.4)$$

where  $\alpha_T$  is the horizontal shift factor,  $T_R$  is the reference temperature (°K),  $T$  is the test temperature (°K), and coefficients of  $C_1$  and  $C_2$  are the empirical constants based on the reference temperature. The reduced frequency was calculated according to the shift factor as Equation (5.5) hereafter:

$$\alpha_T = \frac{\omega}{\omega_T} \quad (5.5)$$

where  $\omega$  is the reduced frequency (Hz) and  $\omega_T$  is the frequency used in test (Hz).

The Christensen-Anderson-Marasteanu model (CAM model) was applied to characterize the rheological properties of modified asphalt binders and the master curves obtained from CAM model presented better comparisons for the neat and modified asphalt binders [37,39]. The CAM model is a modified and improved model from the Christensen-Anderson (CA model) for reliable performance evaluation, which is more suitable, effective, and precise in describing the viscoelastic behavior of the material influenced by temperature and frequency [40–44]. The CAM models for complex shear modulus  $G^*$  are expressed as Equation (5.6) below:

$$G^*(\omega) = G_g \left[ 1 + \left( \frac{\omega_c}{\omega} \right)^v \right]^{-\frac{w}{v}} \quad (5.6)$$

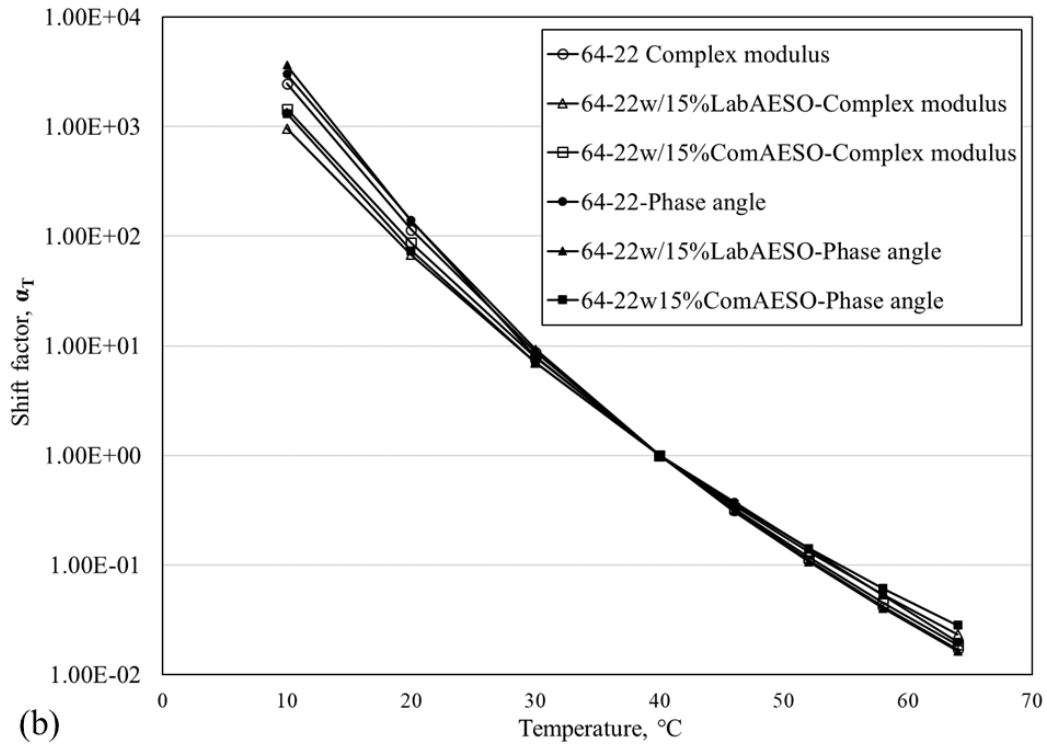
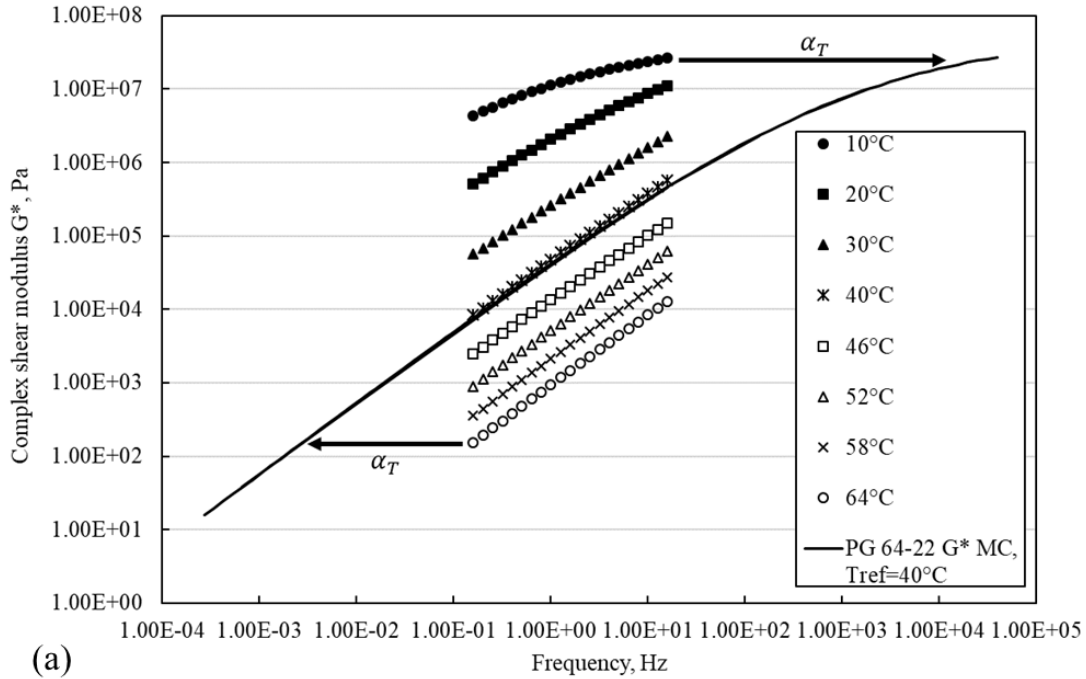
where  $G^*(\omega)$  is the complex modulus at reduced frequency (Pa),  $G_g$  is the glassy modulus (Pa),  $\omega_c$  is the crossover frequency (location parameter),  $\omega$  is the reduced frequency (Hz),  $w$  and  $v$  are shape parameters.  $v$  is equal to  $\text{Log}(2)/R$ , where  $R$  is the rheological index (shape factor).

The complex modulus  $G^*$  master curves and phase angle master curves for all asphalt binders used in this research were constructed as a function of reduced frequency at the reference temperature of 40°C by employing the equations listed above. The effects of AESO in asphalt binder modification were observed by comparing AESO modified master curves to the neat asphalt binder's master curves. An example of how tested data at different frequencies and temperatures were shifted by using shift factors is presented in Figure 5.5 (a). The  $G^*$  master curves of all AESO modified asphalt binders presented lower modulus values than the neat asphalt binder's curve over

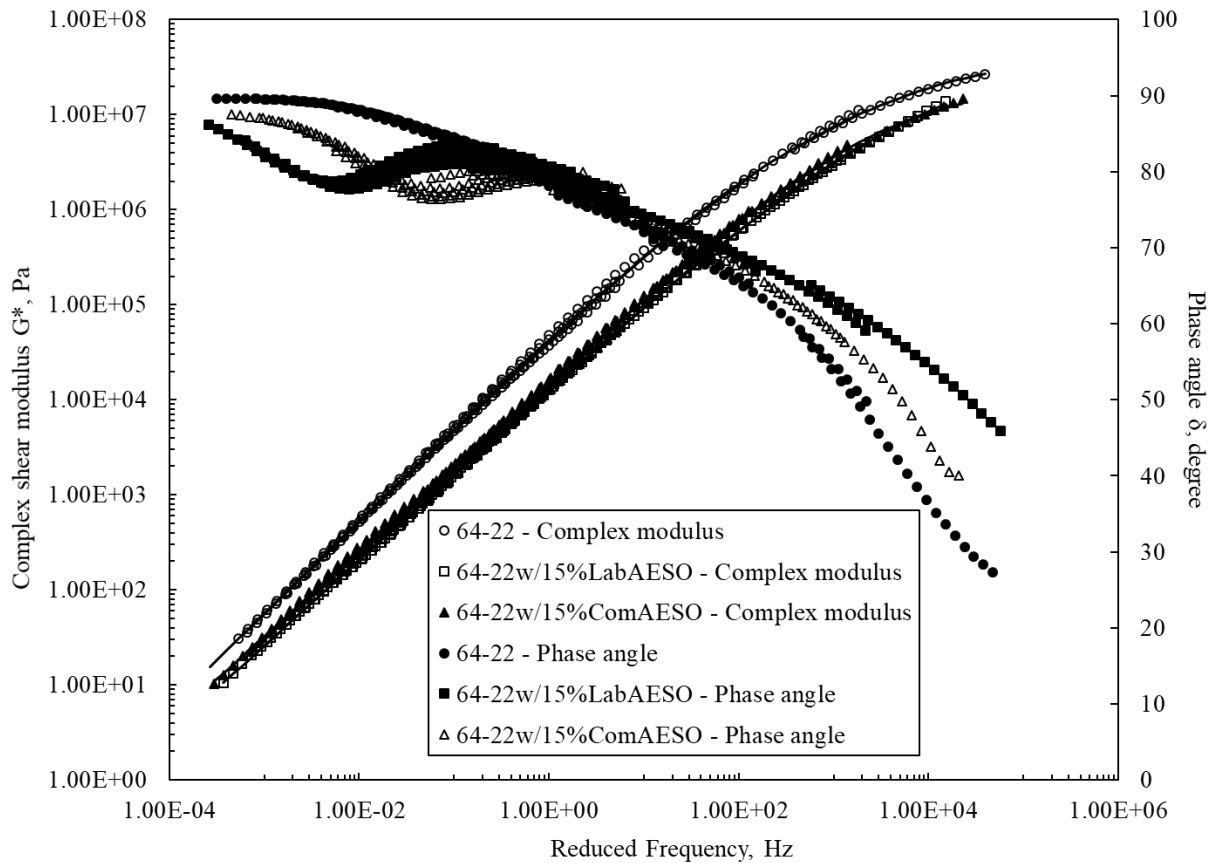
the entire frequency ranges (temperature ranges). The lower complex modulus values of AESO modified blends indicate stiffness reduction of the neat asphalt binder, which also means both critical high temperatures and rutting resistance were reduced at high temperatures while the neat asphalt binder's resistance to fatigue cracking at intermediate temperature and low-temperature thermal cracking was enhanced [41,45]. These findings from master curves match the conclusions drawn from the results in the performance grade. However, differences between the master curves were hardly observed due to the curves overlapping at a low concentration level (i.e. 3%) of AESO. At intermediate AESO concentration level (i.e. 9%), the modified blends' softening tendency appeared as a lower master curve with reduced modulus. The shift factors at different test temperatures for the neat asphalt binder and 15%AESO modified binders are shown in Figure 5.5 (b). The master curves of higher AESO concentration level modified blends (i.e. 15%LabAESO and 15%ComAESO) are presented in Figure 5.6. The softening effect of AESO materials in asphalt modification was observed through the modulus reduction at intermediate frequencies (intermediate temperatures). Furthermore, it was noted (Figure 5.6) that the 15%ComAESO modified blends had slightly higher modulus values than the 15%LabAESO modified blends. This indicates that the 15%ComAESO modified blends had slightly higher molecular mass components compared to the 15%LabAESO modified blends, which is in agreement with the chemical makeup of ComAESO, as it has a slightly higher molecular weight than LabAESO [32].

In phase angle master curves, a phase angle curve shape change is noticed at low frequencies (high temperatures), while an increase of phase angle is found at high frequencies (low temperatures) compared to the neat asphalt binder. As shown previously in the  $G^*$  master curves, more effects were observed in the phase angle master curves at high concentration levels of AESO.

In Figure 5.6, the plateau in the phase angle master curves for both the 15% AESO modified blends indicated that there was a decrease in thermal susceptibility of the neat asphalt binder from AESO modification [32]. The plateau also showed a rubber-like behavior for the modified blends over a broader range of temperatures, which indicates that there was a better interaction between asphalt and the additive, and that they are highly compatible [32]. The plateau of 15% LabAESO appeared at the frequency range of  $10^{-4}$  to  $10^{-1}$  Hz with phase angle rubbery response of  $78^{\circ}$  to  $88^{\circ}$ , while the 15% ComAESO had plateau at the frequency range of  $10^{-3}$  to 1 Hz with phase angle rubbery response of  $75^{\circ}$  to  $85^{\circ}$  (Figure 5.6). According to the results, it was inferred that even though the plateau of 15% LabAESO and 15% ComAESO modified blends were similar in width, the 15% LabAESO modified blend showed a rubbery response at higher temperatures with less rubbery behavior than the 15% ComAESO. As shown in Figure 5.6 there was a slight increase of phase angle values from both the 15% AESO modified blends at intermediate frequencies (intermediate temperatures) and a more pronounced phase angle increase at high frequencies. At high frequency and low temperature zone (Figure 5.6), 15% LabAESO modified blends presented a significant increase in phase angle values compared to 15% ComAESO modified blends and the neat asphalt binder with an increase of approximately  $20^{\circ}$  as compared to the neat asphalt binder. This increase in phase angle indicated that the 15% LabAESO made the neat asphalt binder more viscous and enhanced stress relaxation, thereby improved the resistance to thermal cracking at low temperature and fatigue resistance at intermediate temperature. To conclude, sufficient concentration level of AESO was necessary to enhance the additive effect with beneficial effects on fatigue and thermal cracking.



**Figure 5.5. Development of master curve and shift factor plot: (a) shifting PG 64-22 neat asphalt binder  $G^*$  data using shift factor ( $\alpha_T$ ); (b) shift factors at testing temperatures on all binders.**



**Figure 5.6. Complex modulus  $G^*$  and phase angle  $\delta$  master curves for 15%LabAESO modified binder, 15%ComAESO modified binder, and neat asphalt binder.**

#### 5.5.4. Aging effects

Figure 5.7 showed the variations of complex modulus and phase angle due to the aging effects. After the aging process, all asphalt binders showed improved stiffness and elasticity through increased complex modulus and reduced phase angle, respectively. Thus, the aging process stiffened the binders and made the binders more elastic, especially after PAV aging (long-term aging process). It was also seen that the asphalt binder's stiffness and viscoelasticity varied with the change of test temperature due to temperature-dependent behavior of the material. When test temperature increased, all blends (i.e. unaged, RTFO aged, and PAV aged binders) became softer and more viscous with decreased complex modulus and increased phase angle.

The complex modulus of RTFO aged binder was approximately twice as large as the complex modulus of the unaged binder for the neat and LabAESO modified binders. However, the complex modulus of the RTFO aged ComAESO modified binder was three to four times higher than the complex modulus of the unaged ComAESO modified blends. This was also observed for the PAV aged binders, the complex modulus of the PAV aged neat and LabAESO modified asphalt binder was approximately ten times larger than that of the unaged blends, while PAV ComAESO modified blends are about fifteen to twenty-three times larger than the complex modulus of the unaged blends. This indicated that LabAESO had a lower stiffening effect on the neat binder compared to ComAESO at the same concentration level. It was also observed from both types of AESO modified blends that the modified binder became less stiff at higher concentration of AESO in asphalt binder. This occurred for the unaged, RTFO aged, and PAV aged results. After RTFO and PAV aging processes, the 15%LabAESO modified binder was found to have the lowest curves in both aging conditions with the smallest complex shear modulus values at each test temperature compared to the rest of the binders. Therefore, 15%LabAESO modified binder had the lowest stiffness behavior with the highest susceptibility to permanent deformation at high temperatures, which was in agreement with the findings from Section 5.5.3. However, 15%LabAESO was also shown to enhance the thermal relaxation and fatigue resistance, which is in agreement with the grading results.

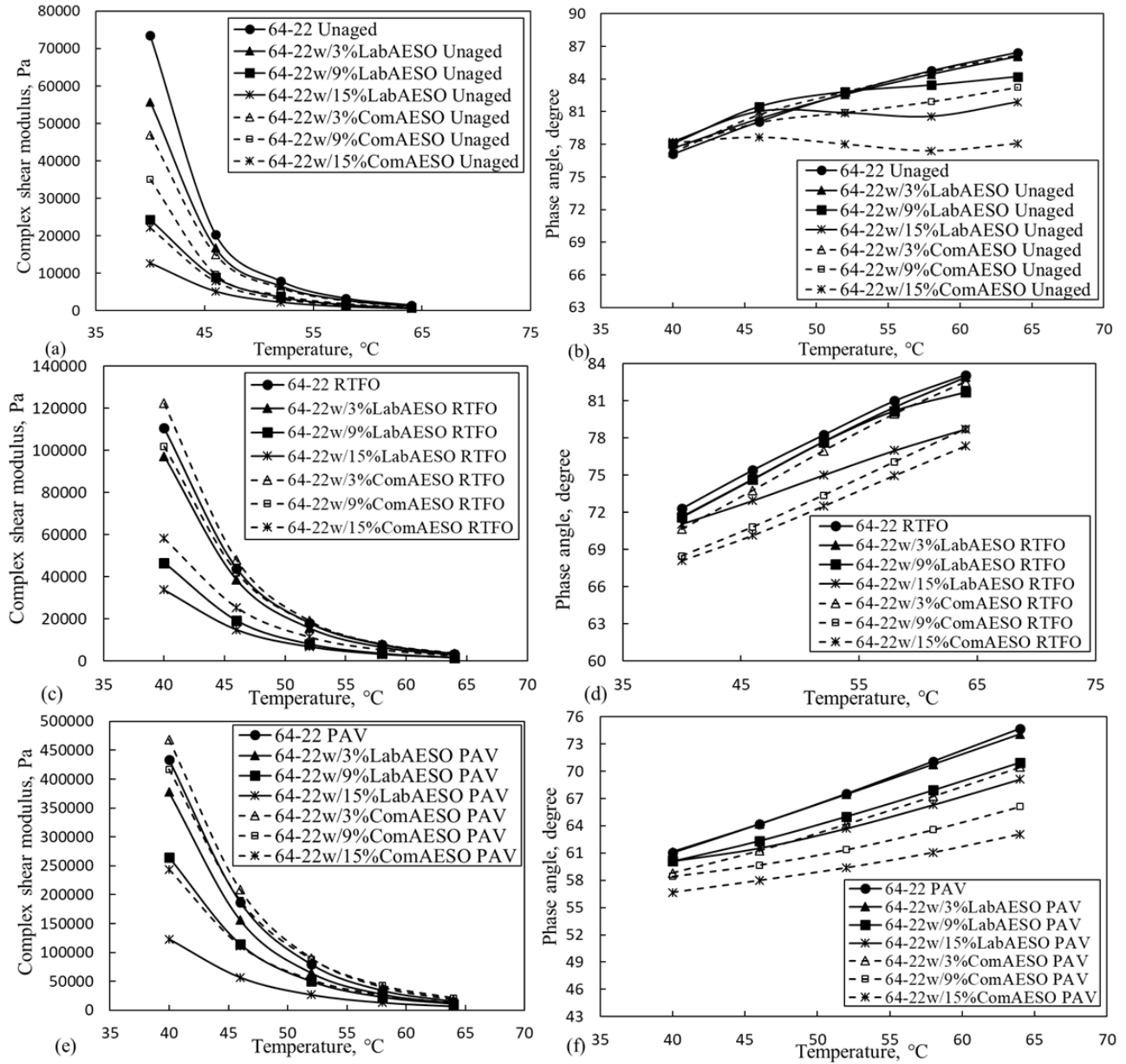
For phase angle values, a reduction of  $5^{\circ}$  to  $10^{\circ}$  after RTFO short-term aging and  $10^{\circ}$  to  $15^{\circ}$  reduction after PAV long-term aging process were noticed. Reduced phase angle was more pronounced at lower test temperatures, while this effect was opposite for phase angle at higher test temperature for all blends after aging. Both AESO types decreased the phase angle values of the neat asphalt binder, while ComAESO modified blends had lower phase angle values at each test



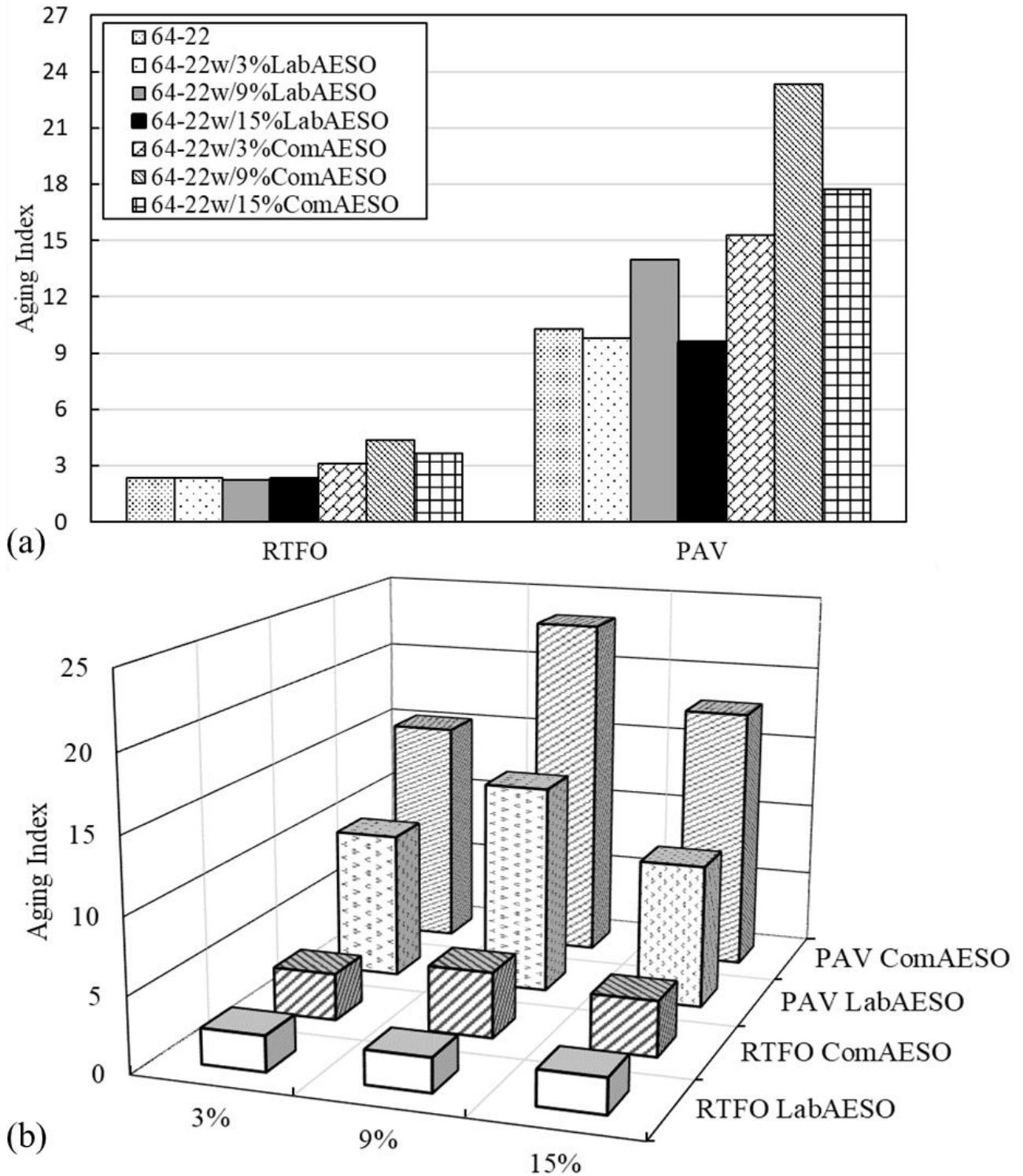
temperature as compared to LabAESO modified blends at the same concentration level in unaged, RTFO aged, and PAV aged states. Thus, both AESO materials were able to increase the elasticity of the neat asphalt binder, however, ComAESO had a more pronounced effect on improving the elasticity of the neat asphalt binder by reducing the phase angle more than that of LabAESO. According to the rubbery-like behavior found in the vGP curves and Black diagrams of the AESO modified blends in Figure 5.7 (b), it was observed that the curvatures of 15%ComAESO and 15%LabAESO followed the same trend. The trend showed the phase angle increased first, then decreased to a minimum value, and then rose again for test temperatures from 40°C to 64°C. These curvatures were in agreement with the AESO modified binders' rheological behavior of phase angle master curves in Figure 5.6 at low frequency and higher temperatures. However, this rubbery response of the binders disappeared after the aging process (Figure 5.7 (d) and (f)) on all modified blends, as the phase angle values gradually increased as the test temperature increased.

The AIs of complex modulus for the two types of AESO modified blends were calculated and compared in terms of RTFO aging and PAV aging effects as shown in Figure 5.8 (a). The effects of AESO concentration level on the AIs can be observed in Figure 5.8 (b). According to the results, LabAESO modified blends had similar AI to that of the neat asphalt after RTFO aging. On the contrary, ComAESO blends had higher AI, where the AI of the neat asphalt binder increased approximately 34%, 89%, and 58% for concentration levels of 3%, 9%, and 15%. Due to the PAV aging, there was a more pronounced aging effect for all binders. However, ComAESO modified binders showed the highest AIs in both aged conditions compared to the rest of the binders. It was noticed that the intermediate concentration of 9%AESO binders was the threshold that had the highest AIs with the most susceptibility to aging effect for both AESO blends in RTFO and PAV aged conditions as the AESO concentration level increased. Whereas, LabAESO modified blends

with low 3% and high 15% concentration levels had relatively smaller AIs compared to that of the neat asphalt binder. After PAV aging, the 15% LabAESO binder was found to be the least sensitive blend to the effect of aging because of having the lowest AI for all binders. Based on this result, it was inferred that a sufficient amount of AESO concentration level was needed to achieve desirable performance and to make the binder less sensitive to aging. The AIs results also indicated that LabAESO was less sensitive to aging than ComAESO when used in asphalt modification.



**Figure 5.7. Comparisons of neat asphalt binder with AESO modified blends: (a) stiffness, unaged; (b) phase angle, unaged; (c) stiffness, RTFO aged; (d) phase angle, RTFO aged; (e) stiffness, PAV aged; (f) phase angle, PAV aged.**



**Figure 5.8. Aging index comparisons of complex modulus for neat asphalt binder and AESO modified blends at 58°C: (a) AI versus aged conditions; (b) AI versus AESO concentration level.**

### 5.5.5. Statistical analysis on aging results

To further analyze the effects of different aging conditions on asphalt binders' rheological properties, the complex shear modulus and phase angle measured from DSR tests in Section 5.5.4 were used to conduct statistical analysis. Two analyses of variance (ANOVA)s were generated to examine the effects from the factors of AESO type, concentration level, and aging condition on the responses of binders' complex modulus and phase angle. Ten data points at each testing temperature and aging condition of each asphalt binder were collected from triplicate tested samples. Thus, a total of 3600 data points were used for statistical analysis with random sample testing orders employed. The distribution of residuals and equal error standard deviations on complex shear modulus and phase angle values were verified to meet the normality assumption. Therefore, complex shear modulus data was transformed using Log10 transformation to meet the normality for the variance across the temperatures, and the Log10 of complex modulus data was used for statistical analysis. The statistical significant results are presented in the following sections.

#### 5.5.5.1. *Complex shear modulus*

The least square means values of Log10 complex modulus with standard error bars for two AESO types modified binders is shown in Figure 5.9. It was clear that LabAESO modified binders had lower complex modulus than the ComAESO modified binders, which means LabAESO had more softening effects with lower stiffness value. A Student's t-test was conducted to showcase if there were statistical differences between AESO types at a 95% confidence interval. The results indicated LabAESO was statistically different from ComAESO as presented in Table 5.3.

The interaction between AESO type and aging condition was examined using a least square plot of Log10 complex modulus with standard error bars as presented in Figure 5.10. It was clear

to observe that aging affected the stiffness of both AESO materials modified binders by significantly increasing the complex modulus of unaged binders especially after PAV long-term aging condition. It was also observed that LabAESO modified binders appear to have lower stiffness with smaller complex shear modulus across the overall aging conditions compared to that of ComAESO modified binders, which means LabAESO modified binders were more susceptible to rutting with a lower critical high temperature compared to ComAESO modified binders. A lower complex shear modulus increasing rate of LabAESO was noticed from unaged condition to RTFO aging conditions than that of ComAESO, where ComAESO modified binder was more susceptible to aging than LabAESO modified binder. A Tukey honestly significant difference (HSD) least square means difference test was conducted to see if there were statistical differences between AESO types due to aging condition at a 95% confidence interval as shown in Table 5.4. It was noticed that AESO modified binders were different from one to another because of the aging conditions. Within each aging condition, LabAESO modified binder was considered to be different from ComAESO modified binder except for AESO modified binders at unaged condition, which occurs due to different aging susceptibilities from ComAESO and LabAESO. Furthermore, higher stiffness values were observed for ComAESO modified binder than LabAESO modified binder at each aging condition in terms of least square means.

Figure 5.11 displays the interaction of AESO type, concentration level, and aging condition in a plot of least square means values of Log10 complex shear modulus. It was clear to see that both AESO types reduce the complex modulus of the neat asphalt binder (0%) and that the binder became less stiff as the concentration level increased. It was also noticed that LabAESO had a more pronounced effect on stiffness reduction compared to that of ComAESO on asphalt binder at the same concentration level. The stiffening effects of aging are visually shown in the plot for

each AESO modified binder at a certain concentration level as the complex shear modulus increased with increased aging. Through observation the increasing rate of complex shear modulus before and after aging process, LabAESO modified binders at each concentration level had similar or smaller rate compared to the neat asphalt binder's, however, ComAESO modified binders presented steeper slopes with higher increasing rate than that of neat asphalt binder for all concentration levels and across aging. This indicated ComAESO modified binders were more susceptible to aging effects in comparison with the neat and LabAESO modified binders, which agrees with the findings in the examination of AESO type and aging condition interaction in Figure 5.10 and Table 5.4. The significant differences of interaction in terms of AESO types, concentration level, and aging condition were examined through a Tukey HSD test as presented in Table 5.5. Modified binders using the same AESO type at the same concentration level but in different aging conditions were connected by different letters, which means they are significantly different from one to another due to the aging effects. Increased least square means values were also observed from RTFO short-term aging and PAV long-term aging results, which means aging increased the stiffness of the binder. In unaged condition, neat asphalt binder was noticed to have the highest complex modulus. However, 3%ComAESO modified binder had a slightly higher complex modulus than that of neat asphalt binder after RTFO short-term aging. This means that the 3%ComAESO binder's stiffness was higher than the neat asphalt binder's due to the aging effects and that it was more susceptible to aging than the neat asphalt binder's. This effect was also observed for the 3%ComAESO and 9%ComAESO modified binders with higher complex modulus obtained after PAV long-term aging condition compared to that of the neat asphalt binder. While, 15%LabAESO had the lowest complex modulus values across all aging conditions and

showed significant differences compared to the rest of the binders in each aging condition in terms of complex shear modulus performance.

**Table 5.3. Student's t-test and One-way ANOVA results on AESO type based on the complex modulus ( $\text{Log}_{10}(G^*)$ ) and phase angle ( $\delta$ ) values.**

Factor	DF	SS	MS	F Ratio	Prob>F
<b>Log<sub>10</sub>(G*)</b>					
AESO type	1	11.6038	11.6038	24.4312	<.0001*
Error	3598	1708.8944			
C. Total	3599	1720.4981			
<b><math>\delta</math></b>					
AESO type	1	2258.99	2258.99	34.9783	<.0001*
Error	3598	232368.48			
C. Total	3599	234627.47			

Note: *DF* degrees of freedom, *SS* sum of squares, *MS* mean square, statistically significant at  $\alpha < 0.05$ , \* means statistically significant difference.

**Table 5.4. Complex shear modulus ( $G^*$ ) and phase angle ( $\delta$ ) Tukey HSD least square means difference for AESO type by aging condition.**

Level		Least sq. mean
<b>G*</b>		
ComAESO,PAV aged	A	4.8888116
LabAESO,PAV aged	B	4.7191857
ComAESO,RTFO aged	C	4.2293883
LabAESO,RTFO aged	D	4.0639614
ComAESO,Unaged	E	3.7442470
LabAESO,Unaged	E	3.7386571
<b><math>\delta</math></b>		
LabAESO, Unaged	A	81.851683
ComAESO, Unaged	A	81.549167
LabAESO, RTFO aged	B	76.913360
ComAESO, RTFO aged	C	75.238493
LabAESO, PAV aged	D	66.160000
ComAESO, PAV aged	E	63.384500

Note: Levels not connected by same letter are significantly different; Levels connected by different letters but overlapping are not significantly different.



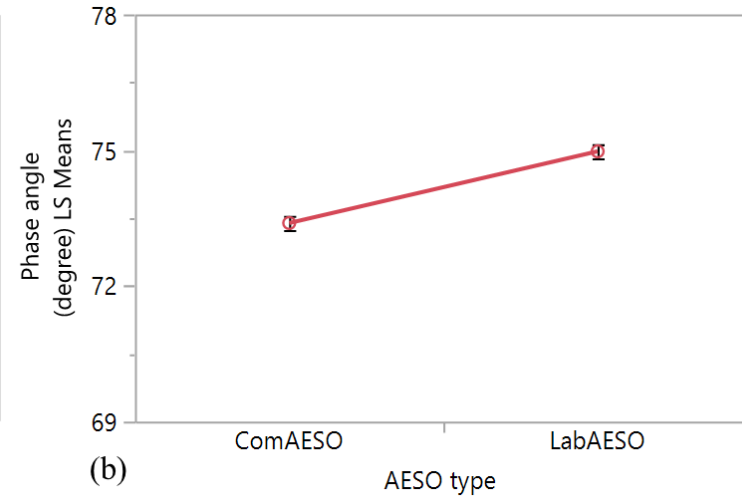
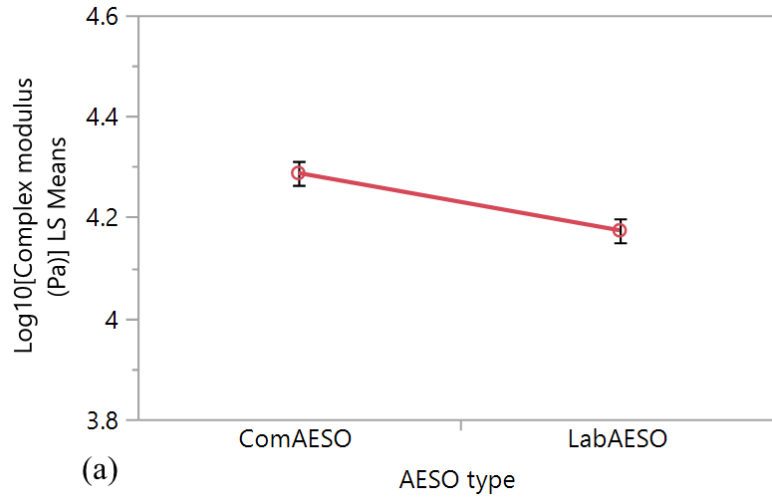


Figure 5.9. Least square mean plot of (a) Log10 complex modulus vs. AESO type and (b) phase angle versus AESO type.

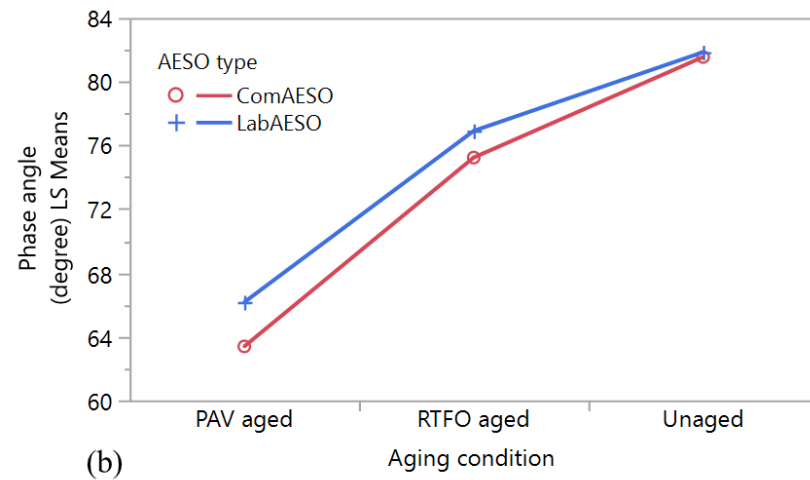
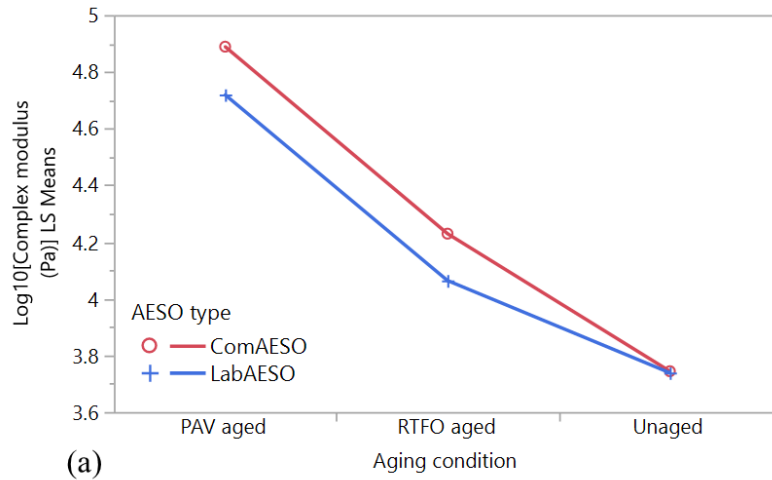
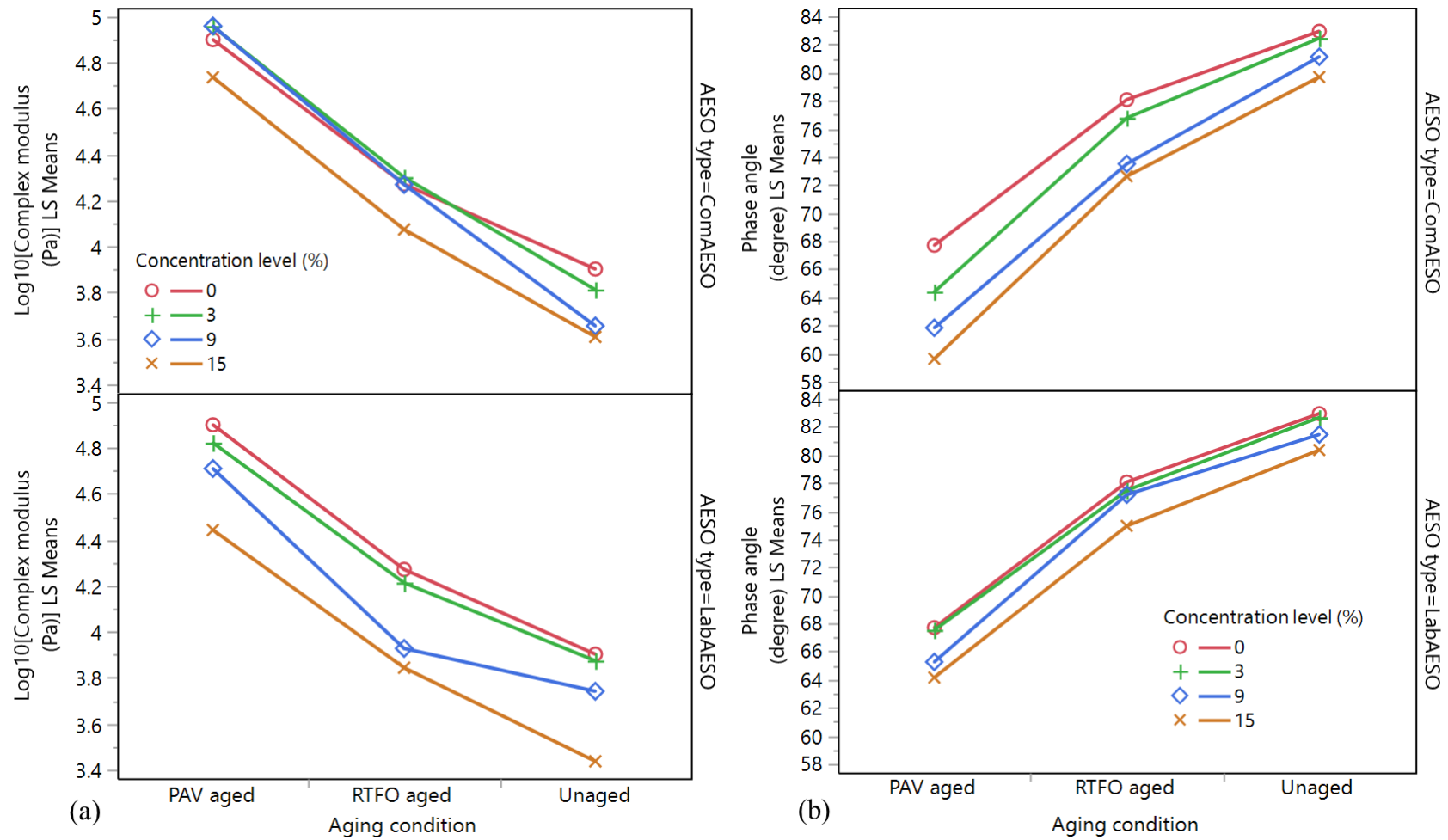


Figure 5.10. Least square means plot for interaction effects of aging condition and AESO type to (a) Log10 complex modulus and (b) phase angle.



**Figure 5.11. Least square means plot of (a) complex modulus for interaction effects of aging condition, AESO types, and concentration level and (b) phase angle for interaction effects of aging condition, AESO types, and concentration level.**

**Table 5.5. Complex shear modulus Tukey HSD least square means difference for AESO type by concentration level and aging condition.**

Level		Least sq. mean
9%ComAESO,PAV aged	A	4.9597798
3%ComAESO,PAV aged	A	4.9578338
0%LabAESO,PAV aged	A B	4.9008261
0%ComAESO,PAV aged	A B	4.9008261
3%LabAESO,PAV aged	A B	4.8224443
15%ComAESO,PAV aged	B	4.7368068
9%LabAESO,PAV aged	B	4.7105227
15%LabAESO,PAV aged	C	4.4429496
3%ComAESO,RTFO aged	C D	4.3014399
0%LabAESO,RTFO aged	C D E	4.2713607
0%ComAESO,RTFO aged	C D E	4.2713607
9%ComAESO,RTFO aged	C D E	4.2702157
3%LabAESO,RTFO aged	D E	4.2131146
15%ComAESO,RTFO aged	E F	4.0745368
9%LabAESO,RTFO aged	F G	3.9276119
0%LabAESO,Unaged	F G	3.9026486
0%ComAESO,Unaged	F G	3.9026486
3%LabAESO,Unaged	F G	3.8739511
15%LabAESO,RTFO aged	G H	3.8437582
3%ComAESO,Unaged	G H I	3.8124127
9%LabAESO,Unaged	G H I	3.7414679
9%ComAESO,Unaged	H I	3.6548566
15%ComAESO,Unaged	I J	3.6070701
15%LabAESO,Unaged	J	3.4365607

Note: Levels not connected by same letter are significantly different; Levels connected by different letters but overlapping are not significantly different; Blends with 0% LabAESO and ComAESO are the neat asphalt binder PG 64-22.

#### 5.5.5.2. Phase angle

From the full statistical analysis shown in the ANOVA table, all factors and their interactions were shown to have statistically significant effects on the response of phase angle values at a 95% confidence interval. Figure 5.9 presents the least square means plot of phase angle with standard error bars for two types of AESO. It was observed that LabAESO had a slightly higher phase angle value about 75° compared to ComAESO phase angle value of around 73° based on the overall data, which means LabAESO modified binders had a more viscous effect to that of ComAESO.

Moreover, they are considered significantly different from each other according to the Student's t-test as shown in Table 5.3.

The interaction effects of aging condition and AESO type is shown in Figure 5.10. Both AESO modified binders showed that the phase angle decreased with aging. LabAESO modified binders seemed to be less susceptible to the RTFO short-term aging process compared to ComAESO modified binders because the rate of phase angle changing was lower for LabAESO modified binders between unaged to RTFO conditions. ComAESO modified binders were also found to be more susceptible to aging with a slightly higher decrease rate shown as steeper slope line between RTFO and PAV aging conditions compared to the LabAESO modified ones. Therefore, LabAESO was considered to be less susceptible to overall aging effects in comparison with ComAESO. The differences between AESO types based on different aging conditions were examined by using a Tukey HSD test. The results indicated there was no significant difference between the unaged LabAESO and ComAESO modified binders. However, RTFO and PAV aging conditions made both LabAESO and ComAESO modified binders significantly different from each other, which means they had different susceptibility to aging effects. From the results, ComAESO modified binders showed more aging effects with the biggest drop of phase angle especially after long-term aging as the least square mean value shows in Table 5.4.

Figure 5.11 clearly presents how the interactions of aging condition, AESO type, and concentration level affected the phase angle performance. Evident aging effects could be observed in Figure 5.11 for both AESO modified binders at each concentration level showed more elastic behavior by reducing the phase angle values. For LabAESO modified binders, 3% concentration level barely changed the phase angle of the neat asphalt binder (0% concentration level), and 9% concentration level decreased the phase angle by a few degrees. 15% LabAESO had more effects

on the elastic nature of the neat asphalt binder compared to the low and intermediate concentration levels. From the LabAESO modified binders aging lines, the slopes were similar to the slopes seen from the neat binder with aging. This means that LabAESO might have similar aging susceptibility to that of the neat asphalt binder. Whereas, ComAESO was noticed to affect the elastic nature of the neat asphalt binder with slightly lower phase angle values compared to that of LabAESO modification effects at unaged condition. Aging seemed to have more impact in changing the ComAESO modified binders' phase angle with considerable reduction of phase angle values as compared to the neat asphalt binder as the concentration level increased. Steeper slopes of aging lines between RTFO and PAV aging conditions indicated long-term aging had more aging effects on ComAESO modified binders. Overall, ComAESO modified binders were more susceptible to aging effects with more elastic effects on neat asphalt binder compared to that of LabAESO modified binders.

The significant differences between blends with different AESO types at various concentration levels based on different aging conditions were examined by conducting a Tukey HSD test using least square mean differences as the results presented in Table 5.6. As expected, the same modified binders (same types of AESO at same concentration level) showed statistically significant differences due to different aging conditions. In unaged condition, asphalt binders at low (3%) concentration level of LabAESO and ComAESO presented no significant differences to the neat asphalt binder. However, AESO modified binders with intermediate (9%) and high (15%) concentration levels were significantly different from the neat asphalt binder (0%AESO) in terms of phase angle performance. No differences were noticed between LabAESO and ComAESO when the concentration levels were at intermediate (9%) or high (15%). Whereas, there was no difference between the 9%LabAESO modified binders and low (3%) concentration level of AESO

modified binders. Moreover, 15%ComAESO was significantly different from all the unaged binders because it had the most elastic behavior. For RTFO aged binders, neat asphalt binder (0%), low (3%) concentration level, and 9%LabAESO modified binders were found to drop the phase angle by a few degrees due to the aging effect and were found to be not statistically significant different from one to another. The 15%LabAESO was considered to be different from the neat asphalt binder, 3% and 9% LabAESO modified binders with a smaller phase angle value, but not as elastic as the ComAESO at intermediate and high concentration levels. It was important to note that ComAESO with intermediate and high concentration levels were not found to be different from each other, but were the most sensitive to aging effects with the smallest phase angle values causing these two binders to be significantly different from all the other binders. Increased sensitivity to aging was seen for ComAESO after the long-term PAV aging process. The PAV aged binder of 3%ComAESO and PAV aged AESO binders at intermediate and high concentration levels were found to be significantly different from the PAV aged neat asphalt binders except for 3%LabAESO modified binders. This indicated that an increase in the AESO concentration level could increase the aging effects by dropping the phase angle values, while ComAESO was more sensitive to aging effects compared to LabAESO at the same concentration levels.

**Table 5.6. Phase angle Tukey HSD least square means difference for AESO type by concentration level and aging condition.**

Level		Least sq. mean
0%ComAESO,Unaged	A	82.943133
0%LabAESO,Unaged	A	82.943133
3%LabAESO,Unaged	A B	82.661200
3%ComAESO,Unaged	A B C	82.444533
9%LabAESO,Unaged	B C D	81.452133
9%ComAESO,Unaged	C D	81.125467
15%LabAESO,Unaged	D E	80.350267
15%ComAESO,Unaged	E	79.683533
0%LabAESO,RTFO aged	F	78.071373
0%ComAESO,RTFO aged	F	78.071373
3%LabAESO,RTFO aged	F	77.476133
9%LabAESO,RTFO aged	F	77.166733
3%ComAESO,RTFO aged	F	76.769133
15%LabAESO,RTFO aged	G	74.939200
9%ComAESO,RTFO aged	H	73.498400
15%ComAESO,RTFO aged	H	72.615067
0%LabAESO,PAV aged	I	67.703733
0%ComAESO,PAV aged	I	67.703733
3%LabAESO,PAV aged	I	67.524667
9%LabAESO,PAV aged	J	65.261067
3%ComAESO,PAV aged	J	64.384467
15%LabAESO,PAV aged	J	64.150533
9%ComAESO,PAV aged	K	61.827667
15%ComAESO,PAV aged	L	59.622133

Note: Levels not connected by same letter are significantly different; Levels connected by different letters but overlapping are not significantly different; Blends with 0% LabAESO and ComAESO are the neat asphalt binder PG 64-22.

## 5.6. Conclusions

Within this research, polymerization of AESO monomer was done through shear blending in asphalt binder within the presence of air to create modified asphalt binder. Rheological properties and effects of aging on AESO modified asphalt binders at different AESO concentration levels were investigated through laboratory testing, with the major findings summarized.

The vGP and Black diagrams showed a noticeable characteristic curvature for AESO modified binders indicating that AESO when used at high concentrations levels caused polymer

entanglement behavior within the asphalt binder. The smooth and continuous curves in vGP and Black diagrams indicated no phase separation with additional AESO and represented the effectiveness of time-temperature superposition principle in the entire test temperature ranges. Rheological master curves showed that there was a reduction of stiffness with additional AESO in the asphalt binder over the entire frequency and temperature ranges. Less thermal susceptibility of AESO modified binders was noted with increasing AESO concentration in the master curves. LabAESO presented more viscous behavior at low temperatures and high frequencies.

Aging conditions increased the stiffness and elasticity of all unaged asphalt binders blends. In comparison with ComAESO modified binders and the neat asphalt binder, LabAESO was the least susceptible to aging, especially after the long-term aging process. Furthermore, the phase angle rubbery response of AESO modified binders at intermediate and high concentration levels disappeared with increased aging. The aging index results also indicated that with a sufficiently high level of LabAESO, not only was the fatigue and low temperature performance improved, but also that susceptibility to aging was reduced for the neat asphalt binder. The statistical analysis specified there were significant differences between the modification effects from LabAESO and ComAESO in terms of complex modulus and phase angle. The statistical analysis also confirmed that ComAESO was more susceptible to aging effect than LabAESO.

In summary, the polymerization of AESO monomer occurred automatically within asphalt binder and air, and that polymer entanglement behavior appeared in rheological curves at higher testing temperatures. The aging results indicated ComAESO presented higher susceptibility to aging effects when compared to LabAESO at the same concentration level. For both AESO modified binders at intermediate and high concentration levels, the rubbery response in phase angle values disappeared due to aging effects. In comparison with the ComAESO, LabAESO at



high concentration level was found to have significantly positive effects on decreasing the stiffness and reducing aging susceptibility of the neat asphalt binder. Further chemical investigation should be conducted to verify the polymerization product of AESO in asphalt binder after shear blending, and the changes to chemical components after AESO modification are needed to be studied and investigated as well. Additionally, AESO should be added to different types of asphalt binder for further investigation. The performance investigation of AESO in asphalt mixtures is also recommended in future studies.

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## CHAPTER 6. CONCLUSIONS AND RECOMMENDATIONS

### 6.1. Bioadvantaged polymer poly(styrene-*block*-acrylated epoxidized soybean oil) (PS-PAESO)

The bioadvantaged polymer PS-PAESO derived from non-food soybean oil was introduced in the first two papers. The PS-PAESO diblock copolymers at various polystyrene molecular weights and polystyrene contents were successfully produced in the laboratory using the RAFT polymerization technique. The H-NMR and HT-GPC were conducted to identify the percentage of PS in the block copolymer and molecular weight of the polymer, respectively.

A fluorescence optical microscope was performed to examine the morphology of polymer modified asphalt binder. In comparison to the polymer dispersion of the commercial SB diblock copolymer, the images of PS-PAESO polymers showed homogeneous morphology with finely dispersed polymer particles. The uniform dispersion allowed the polymers to be entangled with asphalt molecules, and produce an increased elastic response with better compatibility between the polymer and neat asphalt binder.

To investigate how PS-PAESO polymers affected the performance grading and rheological properties of the neat asphalt binder, seventeen different PS-PAESO polymers at a polymer dosage of 3% by weight of the total binder were blended into a neat asphalt binder (PG 52-34) individually at high temperature and by high shear speed blending. A commercially available SB polymer was also used for modification as a comparison. The grading results showed that all PS-PAESO polymers helped increase the critical high temperature of the neat asphalt binder from 53.4 to 53.7-62.0°C. Two of the blends (1 and 4) outperformed the SB polymer modified blends and were approximately 1.8°C higher for the critical high temperature, which means the bioadvantaged polymer has the ability to improve rutting resistance of the neat asphalt binder. However, the

bioadvantaged polymers did not substantially improve the resistance to thermal cracking due to the fact that the critical low temperatures were increased. Eleven out of the seventeen bioadvantaged modified blends widened the neat asphalt binder's grade range and were similar to the SB polymer modified binder's range, which indicated that the bioadvantaged polymer was capable of improving (widening the continuous grade range) the resistance to temperature susceptibility of the base asphalt binder.

Statistical analysis was conducted to identify if the changing factors (i.e. chemical reaction length, PS content, and PS molecular weight) in PS-PAESO polymers had significant effect on PS-PAESO modified binders' grading results. According to the statistical analysis, the chemical reaction length of synthesizing PS-PAESO was not a significant factor that affecting the grading results. Whereas, PS parameters were shown to have significant effects on the grading results. Furthermore, it was also shown that lower PS content helped improve the critical high temperature, while higher PS molecular weight was shown to slightly improve the critical low temperature.

Temperature-frequency sweep tests were conducted using a DSR, and the data were utilized to develop the  $G^*$  master curves,  $\delta$  master curves, and Black Space diagrams for analysis of the rheological properties. According to the  $G^*$  and  $\delta$  master curves, the best performing bioadvantaged polymer modified binder in terms of critical high temperature showed a trend of increasing  $G^*$  and decreasing  $\delta$  compared to the neat asphalt binder, which presents the positive stiffening effect and the improvement of rutting resistance in the neat asphalt binder at high temperatures. The elasticity improvement of the neat asphalt after modification can also be observed in the Black Space diagrams. The rheological performance test results indicated that there is great potential from the use of bioadvantaged polymers as sustainable alternatives to traditional

petroleum based polymers in asphalt modification with similar or even better modification effects at the same polymer dosage level.

In many cases, performing a full experimental design plan is time-consuming and expensive. To solve this problem, a partial experimental design plan was done, and prediction models were developed using the grading results obtained from laboratory tests through response surface modelling (RSM) to optimize the formulation of the PS-PAESO polymer.

The prediction models indicated that polystyrene content, not polystyrene molecular weight in PS-PAESO had more influence on high temperature performance grades, where a smaller amount of polystyrene content in PS-PAESO polymer made the base asphalt binder more resistant to rutting. Based on the prediction model equations, several formulations with 5% polystyrene content and varied polystyrene molecular weights were proposed and one was produced for verification purposes.

The formulation used for verification was PAESO with 30 kg/mol polystyrene molecular weight and 5% polystyrene content. The critical high temperature results of modified binder for unaged and short-term aged binders were 0.4°C, and 0.7°C higher than the estimated ones, while the critical low temperature model gave the same results as measured. The overall performance grade of the recommended polymer modified blends was PG 64-28 as estimated, which significantly increased the rutting resistance of the base asphalt binder.

The response surface models developed were shown to be highly accurate and able to optimize the PS-PAESO formulation used at the same dosage as commercially produced styrene-butadiene polymer in asphalt modification. The suggested polystyrene parameters obtained from response surface modelling could potentially become a starting point for synthesizing other vegetable oil-



based bio-advantaged polymers with similar chemical properties of PAESO in the styrenic block copolymers for asphalt modification.

### **6.2. Soybean-derived monomer acrylated epoxidized soybean oil (AESO)**

The third and fourth papers focused on the full binder investigation of using AESO in asphalt modification. The objectives of conducting this investigation were to explore the possibility of using AESO in asphalt modification and the modification effects of laboratory-produced AESO and commercially available AESO at various dosages in asphalt binder. The performance of AESO modified binders was evaluated through the rotational viscosity, DSR, BBR, LAS, and storage stability tests.

According to the viscosity results, both AESO sources softened the neat asphalt binder by reducing its viscosity. This indicated that AESO was beneficial by decreasing mixing and compaction temperatures and thus improve the workability of the neat asphalt binder. The activation energy values calculated from the viscosity data revealed that the asphalt binder with additional AESO would decrease the temperature susceptibility and lower the compaction effort needed to produce HMA.

In terms of grading results, both AESO sources were found to have negative effect on critical high temperatures due to the reduction of viscosity. In contrast, the softening effect of the AESO helped with intermediate and low temperature performance grades. However, only LabAESO at a higher (15%) concentration level was noted to be the most beneficial on low and intermediate performance grades.

In rheological master curves, reduction of stiffness was observed on AESO modified binders in complex shear modulus master curves. AESO's phase angle master curves showed less thermal susceptibility with the presence of a rubbery behavior plateau at low frequencies and high

temperatures. Higher phase angle values were noticed at intermediate and high frequency ranges, which indicated the improvement to fatigue damage and thermal cracking at intermediate and low temperatures due to the more viscous behavior that the modified binder presented. A sufficient high concentration of AESO was needed for asphalt modification to present more drastic effects on rheological curves.

To further investigate the rheological behavior of the AESO modified asphalt binders, the Van Gurp-Palmen (vGP) and Black diagrams were developed as well. The vGP and Black diagrams showed a noticeable characteristic curvature for AESO modified binders indicating that AESO, when used at high concentrations levels, caused polymer entanglement behavior within the asphalt binder. The smooth and continuous curves in vGP and Black diagrams indicated no phase separation with additional AESO and represented the effectiveness of the time-temperature superposition principle in the entire test temperature ranges. Rheological master curves showed that there was a reduction of stiffness with additional AESO in the asphalt binder over the entire frequency and temperature ranges. Less thermal susceptibility of AESO modified binders was noted with an increasing AESO concentration in the master curves. LabAESO presented more viscous behavior at low temperatures and high frequencies.

How the AESO affected the rheological properties ( $G^*$  and  $\delta$ ) of the neat asphalt binder was evaluated through temperature sweep testing using a DSR. The overall results indicated the aging conditions increased the stiffness and elasticity of all unaged asphalt binders blends. In comparison with ComAESO modified binders and the neat asphalt binder, LabAESO was the least susceptible to aging, especially after the long-term aging process with a PAV. Furthermore, the phase angle rubbery response of AESO modified binders at intermediate and high concentration levels disappeared with increased aging. The aging index results also indicated that with a sufficiently

high level of LabAESO, not only was the fatigue and low temperature performance improved, but also that susceptibility to aging was reduced for the neat asphalt binder. The statistical analysis identified there were significant differences in the modification effects between LabAESO and ComAESO in terms of complex modulus and phase angle. The statistical analysis also confirmed that ComAESO was more susceptible to aging than LabAESO.

The modified binders' creep stiffness and creep rate values were collected from BBR tests at low testing temperatures. The asphalt binder's low temperature properties (creep stiffness and creep rate) indicated that 15% LabAESO had higher stress relaxation and better ability to dissipate stresses, and thereby reduced the neat asphalt binder's susceptibility to thermal cracking. The positive effects on fatigue damage with additional AESO in the neat asphalt binder were also noticed through the LAS test. The fatigue life of the neat asphalt binder was increased as the AESO concentration level increased. Additionally, sufficient high LabAESO concentration was recommended for significant improvement of neat asphalt binder's fatigue life.

The high temperature storage stability of the AESO modified binders were evaluated by performing the DSR tests on the top and bottom 1/3 of the materials in the cigar tubes at a testing temperature of 60°C. The results showed that LabAESO at three concentration levels were noticed to have no separation issue, while ComAESO did not have good stability and compatibility with the neat asphalt binder with higher percent separation at intermediate and high concentration levels. Furthermore, the complex modulus was found to be the limiting factor that causes the potential for separation in high temperature storage stability.

### 6.3. Future research

Future work should focus on the performance evaluation of hot mix asphalt (HMA) using bioadvantaged polymer modified binders and AESO modified binders. This study showed that

bioadvantaged polymers are able to increase the critical high temperature, to increase the resistance of rutting, and to decrease the temperature susceptibility of the neat asphalt binder. The asphalt binder test results also revealed the great potential of utilizing derived and advantaged bioadvantaged polymers as sustainable alternatives to traditional petroleum derived polymers in asphalt modification with similar or even better modification effects at the same polymer dosage level. Therefore, it is important to demonstrate how the polymer modified binders would affect the performance of asphalt mixtures in a wide range of climatic and environmental conditions beginning with high temperature performance tests. The dynamic modulus testing, flow number testing, and Hamburg Wheel Track testing could be done on the control mixtures (neat asphalt binder), bioadvantaged polymer modified asphalt mixtures, and commercial polymer modified asphalt mixtures to characterize the stiffness and permanent deformation resistance of the mixtures. Additionally, low temperature cracking susceptibility and fatigue performance tests are also recommended to conduct.

Furthermore, the use of AESO at sufficient high concentration level presented significant improvement on the fatigue and thermal cracking resistance. It was also noted that AESO was able to decrease the viscosity of the neat asphalt binder, and thereby increase the workability of the asphalt binder during mixing with aggregates. To characterize the AESO modified asphalt mixtures performance in fatigue and low temperature cracking susceptibility, Semi-Circular Bending Geometry testing, disk-shaped compact tension geometry testing, and four-point bending beam apparatus testing are recommended.

The overall asphalt mixtures performance tests that are recommended to conduct in the future research by following the ASTM/AASHTO standard specifications are listed below:

- AASHTO T342-11: Determining Dynamic Modulus of Hot Mix Asphalt (HMA).
- ASTM D7313-13: Standard Test Method for Determining Fracture Energy of Asphalt – Aggregate Mixtures Using the Disk-Shaped Compact Tension Geometry.
- AASHTO T324-04: Hamburg Wheel-Track Testing of Compacted Hot Mix Asphalt (HMA).
- AASHTO T-283-14: Resistance of Compacted Hot Mix Asphalt (HMA) to Moisture-Induced Damage.
- ASTM D6931-12: Standard Test Method for Indirect Tensile (IDT) Strength of Bituminous Mixtures.
- AASHTO T321-07: Determining the Fatigue Life of Compacted Hot Mix Asphalt (HMA) Subjected to Repeated Flexural Bending.
- AASHTO TP105-13: Determining the Fracture Energy of Asphalt Mixtures Using the Semicircular Bend Geometry (SCB).

According to the asphalt mixtures performance evaluation, demonstration paving test sections are recommended for construction in this research. Therefore, the actual performance of the road section using the biopolymer modified asphalt binder can be monitored and compared to the control test section.

In the current research, the modification effects of bioadvantaged polymers and the biomonomer additives in asphalt binders were evaluated through asphalt binder performance testing. Further work on the investigations of how the polymer and additive chemically affect the neat asphalt binder should also be conducted. For example, Fourier Transform Infrared (FTIR)

could be conducted to determine how the polymer or additive affect the functional groups of the asphalt binder and could also be used to identify how aging process changes the functional groups of the unaged modified binders. Additionally, the effectiveness of the polymer may vary due to the base asphalt binders contain different chemical fractions of asphalt. Therefore, it is necessary to use the polymer or additive with base asphalt binders from different sources. SARA (Saturates/Aromatics/Resins/Asphaltenes) fractionation is also encouraged to conduct on the different base asphalt binders and polymer modified binders, thus the changes in chemical composition due to modifications or aging can be examined in comparisons.