Development of Bio-Based Polymers for Use in Asphalt – Phase II

Final Report
April 2021

ASPHALT MATERIALS &
PAVEMENTS PROGRAM

IOWA STATE UNIVERSITY
Institute for Transportation

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16. Abstract

The opportunity to produce a high-value material derived from vegetable oil from the Midwest creates a tremendous economic opportunity to replace a dangerous and carcinogenic material in butadiene, which is derived from crude oil petroleum. The majority of butadiene is imported to use for subsequent production of polymers or is contained in polymers imported to the US. Development of the biopolymer technology for asphalt paving was sponsored by the Iowa Highway Research Board (IHRB) under a special funding mechanism for high-risk/high-potential-pay-off research. The biopolymers developed by Iowa State University were found to be an excellent alternative to the polymers currently used.

Since the conclusion of the first phase of this study in April 2014, a ton-per-day pilot plant was designed and built at Iowa State University's BioCentury Research Farm, west of Ames, at a cost of more than $6 million. The pilot plant was installed in late 2015, winterized for the 2015–2016 winter, and reopened in Spring 2016.

The research team worked since the completion of the Phase I IHRB project in getting the pilot plant working and correctly calibrated. The Bio-Polymer Processing Facility underwent rigorous troubleshooting and upgrades during 2016 and became capable of producing biopolymers in sufficient quantities to conduct field demonstration paving projects. Research done during this work led to optimized formulations of biopolymer and furthered the march toward the implementation of biopolymer for field demonstration projects.

Due to the high number of mix designs that include reclaimed or recycled asphalt pavement (RAP), the biopolymer was transformed with a rejuvenator into a liquefied state to perform easier and more efficient blending with neat binders. From this new biopolymer/rejuvenator combination, called BioMAG, one test section and two demonstration projects were paved at the National Center for Asphalt Technology (NCAT) Test Track at Auburn University in Alabama and two sites in Iowa. The section at the NCAT Test Track is performing well against rutting and cracking.

Currently, additional data are being collected about other distresses. For the two demonstration projects in Iowa, mix and binder were collected from the Altoona, Iowa site. Full mix and binder characterization have shown that BioMAG performs well in RAP mix designs and improves resistance against low temperature cracking and rutting.

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DEVELOPMENT OF BIO-BASED POLYMER FOR USE IN ASPHALT – PHASE II

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EXECUTIVE SUMMARY

This report summarizes findings from Phase II of an Iowa Department of Transportation (DOT) and Iowa Highway Research Board (IHRB) project to develop and demonstrate the application of bio-renewable polymers for use in asphalt pavements by utilizing soybean oil through chemical synthesis.

Triglyceride molecules from vegetable oil have been considered as important renewable resources that can be used as biomonomers and be polymerized into biopolymers with properties similar to petroleum-derived monomers and polymers. In this research, non-food soybean oil was selected as a starting point to produce biopolymers.

The modification effects and the effectiveness of the biopolymers were evaluated through a comprehensive asphalt binder investigation to optimize formulation of the biopolymers. Meanwhile, evaluation of the actual field performance of the biopolymer-modified asphalt mixture is ongoing via pavement construction at the National Center for Asphalt Technology (NCAT) Test Track at Auburn University in Alabama.

Furthermore, biopolymers were produced in combination with a rejuvenator for use in asphalt mix applications utilizing reclaimed or recycled asphalt pavement (RAP) and recycled asphalt shingles (RAS) in a semi-liquid state. The modification effects were documented through formulation for field trials. Field trials were conducted at two locations in Iowa, and mix performance was characterized for field produced mixes.

ABBREVIATIONS, ACRONYMS, AND INITIALISMS

ACS	American Chemical Society
AESO	acrylated ESO
AIBN	azobisisobutyronitrile
ANOVA	analysis of variance
APAI	Asphalt Paving Association of Iowa
BBR	bending beam rheometer
BCRF	BioCentury Research Farm
CFRP	controlled/living free radical polymerization
CMOD	crack mouth opening displacement
CTA	chain transfer agent
DCT	disc-shaped compact tension
DOT	Department of Transportation
DSR	dynamic shear rheometer
EHOSO	epoxidized high-oleic soybean oil
ESO	epoxidized soybean oil
EVA	ethylene-vinyl acetate
FHWA	Federal Highway Administration
GHG	greenhouse gas
HMA	hot-mixed asphalt
H-NMR	hydrogen nuclear magnetic resonance
HSD	honestly significant difference
HT-GPC	high temperature gel chromatography
HWT	Hamburg wheel tracking
IHRB	Iowa Highway Research Board
LED	light emitting diode
LVDT	linear variable deformation transducer
LVE	linear viscoelastic
MEHQ	methylhydroquinone
MSCR	multiple stress creep recovery
MW	molecular weight
NCAT	National Center for Asphalt Technology
PAEHOSO	poly acrylated epoxidized high oleic soybean oil
PAESO	poly AESO
PAV	pressure aging vessel
PDI	polydispersity index
PG	performance grade
PE	polyethylene
PP	polypropylene
PPBD	2-phenyl-2-propyl benzodithioate
PS	polystyrene
PS-PAESO	polystyrene-b-acrylated epoxidized soybean oil
RAFT	reversible addition-fragmentation chain transfer
RAP	reclaimed or recycled asphalt pavement
RAS	recycled asphalt shingle

RI	refractive index
RSM	response surface modeling
RTFO	rolling thin-film oven
SB	styrene-butadiene
SBR	styrene-butadiene rubber
SBS	styrene-butadiene styrene
SESO	sub-epoxidized soybean oil
SIS	styrene-isoprene styrene
THF	tetrahydrofuran
UTM	universal testing machine
VECD	viscoelastic continuum damage
WLF	Williams-Landel-Ferry

CHAPTER 1. INTRODUCTION

Background

The rheological properties of an asphalt binder have a significant impact on asphalt pavement performance (Liang et al. 2016a). Primary pavement distresses such as rutting at high temperature, thermal cracking at low temperature, and fatigue cracking due to repeated traffic loading are related to the rheological properties of the asphalt materials in pavement construction (Chen et al. 2002, Liang et al. 2015, Moreno-Navarro et al. 2015).

To improve the performance of asphalt binders, modifiers or additives such as styrene-butadiene styrene (SBS), styrene-butadiene rubber (SBR), and ethylene-vinyl acetate (EVA) have been used to modify asphalt (Isacsson and Lu 1995). Due to the environmental, safety, and economic concerns related to using petroleum-derived polymers, there is a rising demand for biopolymers that are sustainable, biodegradable, environmentally friendly, cost-effective, and less toxic than petroleum-derived polymers (Zhu et al. 2014, Kowalski et al. 2016).

Triglycerides are known as the most important renewable resources for producing biopolymers due to their special chemical structure that consists of three fatty acid chains connected by one glycerol center (Grishchuk and Karger-Kocsis 2011, Habib and Bajpai 2011, Salih et al. 2015). Triglycerides can be polymerized with flexible and rubbery properties to replace the petroleum-derived butadiene in styrenic copolymers (Yan et al. 2016).

Such high-value materials derived from vegetable oil can be produced within the Midwest US and create tremendous economic opportunity to replace a dangerous and carcinogenic material, such as butadiene, which is derived from crude oil petroleum. The majority of butadiene is imported to use for subsequent production of polymers or is contained in polymers imported to the US.

Development of the biopolymer technology for asphalt paving was sponsored by the Iowa Highway Research Board (IHRB) under a special funding mechanism for high-risk/high-potential-pay-off research. The biopolymers developed by Iowa State University were found to be an excellent alternative to the polymers currently used.

Since the conclusion of the first phase of this study in April 2014, a ton-per-day pilot plant was designed and built at Iowa State University’s BioCentury Research Farm, west of Ames, at a cost of more than $6 million. The pilot plant was installed in late 2015, winterized for the 2015–2016 winter, and reopened in Spring 2016.

The research team worked since the completion of the Phase I IHRB project in getting the pilot plant working and correctly calibrated. The Bio-Polymer Processing Facility underwent rigorous troubleshooting and upgrades during 2016 and became capable of producing biopolymers in sufficient quantities to conduct field demonstration paving projects.

This project is beneficial in demonstrating that the performance of the biopolymers developed meet expectations and have cost advantages. The outcome will be the development of a biopolymer that has cost and performance advantages for use on roads in Iowa. This project will also be beneficial in the development of new materials produced from Iowa feedstock materials (e.g., vegetable oil) and produced in Iowa.

This research has the potential to have a substantial impact on the Iowa economy through job creation, future tax revenue, and the export of a high-value specialty product, which has also shown success in numerous other applications, including adhesives, coatings, and packaging materials.

Project Goals and Objectives

The overall goals of this research were to develop and optimize the formulation of the biopolymer to maximize performance in asphalt modification and ensure the successful large-scale production of biopolymers in Iowa State University’s biopolymer pilot plant. In addition to these two areas of focus, the other main focus was to combine biopolymers with rejuvenators (in liquid form) for use with reclaimed or recycled asphalt pavement (RAP) and recycled asphalt shingle (RAS) mixtures and utilize this material for field demonstrations while characterizing binder and mix performance.

Achieving these goals will further the development and growth of biopolymer-modified asphalt mixtures and help enable the use of these mixtures throughout the US in the future.

The specific objectives of this research were as follows:

- Demonstrate how biopolymers are produced using non-food soybean oil
- Evaluate how laboratory-produced biopolymers perform rheologically in asphalt against the performance of commonly used petroleum-derived polymers
- Optimize the formulation of the biopolymer based on the performance grading results that can modify a neat asphalt binder from performance grade (PG) 52–34 to PG 64–28 for warm climate region pavement applications
- Verify the modification effects of the optimized biopolymers with proposed polystyrene (PS) parameters by conducting performance grade tests
- Produce 600 gallons of biopolymer from the biopolymer pilot plant and have the biopolymer-modified asphalt mixture paved on the National Center for Asphalt Technology (NCAT) Test Track at Auburn University in Alabama
- Formulate biopolymer/rejuvenator dosage combinations for use in field trials and perform mix characterization tests on the field-produced mixes from trials

Overall Project Experimental Plan

The use of polymers to improve asphalt performance is currently commonplace in the US, especially given the concerns about certain distresses (rutting, fatigue cracking, and thermal cracking at low temperatures). For this phase of the project, biopolymer evaluation was conducted through the creation of the various biopolymers considering the base asphalt and mix factors. The various biopolymers would all be blended the same way with the same binder and then put through a complete rheological characterization test plan. The test plan included collection of dynamic shear test results for both unaged and rolling thin-film oven (RTFO) short-term aged modified asphalt blends and bending beam rheometer test results for long-term aged binders to determine optimum amounts needed in the biopolymer to obtain maximum performance from polymer-modified asphalt.

After determining the optimized parameters for the biopolymer, trial-optimized biopolymers were produced, and rheological characterization results were verified with regression model and master curves, and black space diagrams were produced and analyzed. After this step was the production of 600 gallons of biopolymer from the biopolymer pilot plant with optimized PS parameters and placement of the biopolymer-modified asphalt mixture in pavement at the NCAT Test Track at Auburn University in Alabama.

Further research for this project entailed the development of a biopolymer and rejuvenator combination named BioMAG for mixtures utilizing RAP and switching the operation of the pilot plant over to produce this material. This material was then used to formulate dosages for three different field sections. Mix performance testing for the field-produced mix was then conducted for the three field sections (one at NCAT and two in Iowa).

Report Content/Overview

- Chapter 1 introduces background information and highlights the main goals and objectives of this study.
- Chapter 2 reviews past literature, summarizing information on polymer modifiers, RAP use in flexible pavement construction, current and past development of bio-advantaged polymers, and development of soybean-oil monomers.
- Chapter 3 covers the materials, production methods, and characterization methods of the biopolymer and biopolymer and rejuvenator combination used in this study.
- Chapter 4 presents the rheological results of the blends developed in this study using the biopolymer to formulate and verify optimized polystyrene parameters for the biopolymer.
- Chapter 5 describes the biopolymer pilot plant as well production of the biopolymer, BioMAG, for use in constructing field trial sections.
- Chapter 6 covers the mix performance of the field-produced mix from the field sections.
- Chapter 7 provides a summary of conclusions and recommendations for the future use of biopolymer and BioMAG in asphalt mixes.

CHAPTER 2. LITERATURE REVIEW

Polymer-modified asphalt binders are often used in the construction of flexible pavements for high traffic volume and extreme weather conditions to enhance pavement performance and/or extend their in-service longevity (Isacsson and Lu 1995, Pamplona et al. 2012, Liang et al. 2016b). 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 (Buncher and Rosenberger 2005).

With 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 can be used as sustainable alternatives in the asphalt paving industry (Cascione et al. 2013, Williams et al. 2014, Wang et al. 2016). 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 examples of renewable resources that are commonly used as biofeedstock to synthesize biopolymers through polymerization techniques (Sharma and Kundu 2006, Habib and Bajpai 2011, Lligadas et al. 2013). At Iowa State University, bio-advantaged polymers were successfully synthesized using a biomonomer derived from soybean oil. The applications using bio-advantaged polymers and additives in asphalt pavement can have a significantly positive impact in the asphalt industry.

Modifiers in Asphalt

In general, three types of polymers are commonly used in asphalt pavement applications: thermoplastic elastomers (e.g., styrene-butadiene [SB], SBS, SBR, and styrene-isoprene-styrene [SIS]), plastomers (e.g., polyethylene [PE], ethylene-vinyl acetate [EVA], and polypropylene [PP]) (Lewandowski 1994, Chen et al. 2002, Yildirim 2007, Zhu et al. 2014). The rheological properties of neat asphalt binders can be significantly changed by using polymers or additives (Cardone et al. 2014).

After adding polymers or additives, performance such as stiffness, flexibility, elasticity, and stress relaxation of the asphalt binder can be improved (Saboo and Kumar 2016). The concentrations for using additives or polymers for asphalt modification are usually 3% to 7% by weight of the modified binders (Airey 2004, Lu et al. 2011, Pamplona et al. 2012, Tarefder and Yousefi 2016). In order to achieve homogeneous blends, high temperature and high shear speed are usually required when blending these 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 (Airey 2004, Fernandes et al. 2008, Brown et al. 2009) 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 (Brown et al. 2009). On the other hand, the styrenic block copolymers can entangle with asphalt molecules 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 (Brown et al. 2009). 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 (Brown et al. 2009).

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 (Cascione et al. 2013). As shale gas feedstocks become more dominant in the production of ethylene, the production of butadiene keeps decreasing in the US. That may lead to the shortage of butadiene supply (Global Business Intelligence Research 2012, Bruijnincx and Weckhuysen 2013, Williams et al. 2014). Additionally, the commercially available polymers and additives used in asphalt modification are mostly inorganic and petroleum based, which has drawn environmental concerns (Seidel and Haddock 2014, Meadows et al. 2016). Due to these existing challenges, there is a need to develop bio-advantaged polymers or additives that can be used as sustainable alternatives in asphalt modification with similar or better modification effects.

Recycled Asphalt Material Use in Flexible Pavement Construction

The widespread use of RAP owes its inception to the increased price of petroleum following the energy crisis that occurred in the early 1970s. Since the late 1980s, almost two decades after the crisis, the incorporation of RAP reduced the amount of virgin asphalt binder used in asphalt mixtures and therefore helped keep the capital cost of pavements in check. For instance, in 2016, the utilization of recycled asphalt materials, including RAP, saved taxpayers more than $2.1 billion compared to the cost of traditional paving materials.

In recent years, however, sustainability has been the driving force for the incorporation of RAP into new asphalt pavements. The sustainability in the context of pavements is a framework that focuses on social, environmental, and economic needs rather than merely focusing on only the capital costs. The use of RAP can decrease the depletion of non-renewable resources, including fossil fuels and aggregates, and help with the decrease of greenhouse gas (GHG) emissions.

It is worth highlighting that, in the US in 2012, about 1,324 million tons of crushed aggregate worth $12 billion was manufactured, of which about 82% was used in road construction and maintenance (Van Dam et al. 2015). Also, the total GHG emissions due to all highway and street construction was estimated at 117 million tons CO_{2e} in 2008 (Van Dam et al. 2015). Therefore, RAP can have a huge positive effect on the sustainability of pavements if incorporated into asphalt mixtures appropriately.

Driven largely by sustainability gains, the use of RAP has been attracting a large number of researchers and practitioners (Noureldin and Wood 1987). Although there are many justifiable reasons for replacing virgin aggregates with RAP in asphalt mixtures, many problems associated with the incorporation of this material into asphalt mixtures still exist. RAP is generally obtained by milling asphalt concrete pavements at the end of their service lives. The asphalt binder in RAP generally has a poor relaxation ability owing to its oxidation occurring throughout the service life of an asphalt concrete pavement. Therefore, when RAP is incorporated into an unaged asphalt mixture, the resulting composite mixture becomes stiffer and more brittle. A myriad of rejuvenators have been produced to restore the properties of RAP binder to address this drawback (Zaumanis et al. 2014).

Bio-advantaged Polymer

Bio-advantaged polymers are known as polymers that are produced directly from biofeedstock (e.g., corn or soybeans) into plastics through chemical polymerization techniques. Bio-advantaged polymers can be used as potential substitutes for petroleum-derived materials (Hernandez et al. 2014). Vegetable oils such as soybean, sunflower, castor, palm, safflower, linseed, and canola oils are commonly used as biofeedstocks to chemically synthesize biopolymers (Sharma and Kundu 2006, Habib and Bajpai 2011). They are also known as triglyceride oils and are recognized as important renewable resources due to their 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 (Grishchuk and Karger-Kocsis 2011, Habib and Bajpai 2011, Salih et al. 2015, Yılmaz et al. 2017). 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 biofeedstock due to its local availability in the Midwest. However, the unsaturated fatty acids in triglycerides are not active enough for polymerization (Yan et al. 2016). To improve the activity, epoxidation reaction can be applied to modify the C=C double bonds in triglycerides to yield epoxidized soybean oil (ESO) (Zhang et al. 2015, Yan et al. 2016, Cochran et al. 2018). Since the reactivity is improved, the unsaturated fatty acids can be easily functionalized and/or polymerized.

Biomonomer acrylated ESO (AESO) and biopolymer poly AESO (PAESO) have been successfully produced by using ESO followed by acrylation reaction and reversible addition-fragmentation chain transfer (RAFT) polymerization (Cochran et al. 2018). 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 (Cascione et al. 2011, Williams et al. 2014).

In later studies, it was found that using high oleic soybean oil as the biofeedstock could produce a polymer with fewer side chains due to having less C=C double bonds, and therefore fewer reactive sites for polymerization to occur. The resulting product is poly (acrylated epoxidized high oleic soybean oil) or PAEHOSO. This change also assisted in controlling the polymerization by reducing the rate at which the polymer would cross-link and form a thermoplastic gel. The reaction must be stopped in a narrow window, when the molecular weight has become large enough, but the material still has thermoplastic behavior. The increased level of control made the scaling of the production of the polymer much easier.

Soybean-Derived Monomer

Given it is one of the most affordable and abundant vegetable oils in the US, extensive research studies have focused on the use of soybean oil as biofeedstock to yield soybean-based materials. In industry, soybean oil is commonly used as AESO through epoxidation of soybean oil and acrylation of ESO (Zhang et al. 2015, Yan et al. 2016, Cochran et al. 2018). The AESO monomers can be subsequently stored and used as surface coating materials or polymerized to thermoset biopolymers for adhesives and asphalt modification (Zhang et al. 2015, Yan et al. 2016, Cochran et al. 2018).

In the study of biopolymer polystyrene-b-acrylated epoxidized soybean oil (PS-PAESO), the asphalt binder performance test results have shown great potential for 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 are focusing on exploring the benefits of using bio-based oil in the pavement industry.

In general, it was found that bio-oil is capable of decreasing the stiffness of the neat asphalt binder in improving the binder's resistance to fatigue and thermal cracking at intermediate and low temperatures (Fini et al. 2012, Sun et al. 2016, Fini et al. 2017, Lei et al. 2017). 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 (Chung et al. 2015). 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 the asphalt blending process through rheological characterizations.

CHAPTER 3. DEVELOPMENT OF BIO-POLYMERS AND MONOMERS FOR ASPHALT MODIFICATION

The raw materials needed for producing biopolymer and the economic and environmental value of biopolymer vs. traditional petroleum-derived polymer are documented in this chapter.

Materials Used for Production

The raw soybean materials used were ESO and, later, epoxidized high-oleic soybean oil (EHOSO). EHOSO was found to decrease the number of reactive sites during the polymerization process leading to less branching and more control over the polymerization. Commercially available styrene was purchased and purified over basic alumina. The raw materials used in the polymerization reaction were ESO (containing 4,000 ppm monomethyl ether hydroquinone as an inhibitor), pyridine (catalyst with 99.8% purity), hydroquinone (inhibitor with 99% purity), and acrylic acid (containing 180–200 ppm methylhydroquinone [MEHQ] as inhibitor with 99% purity). Azobisisobutyronitrile (AIBN) served as the initiator. MEHQ (with 99% purity as an inhibitor remover), diethyl ether (American Chemical Society [ACS] grade), 2-phenyl-2-propyl benzodithioate (PPBD) (as a chain transfer agent [CTA]), and sodium bicarbonate (white crystalline powder, certified ACS) were used without further purification. Chemical solvents initially used as reagents in the reaction were dioxane and toluene. Subsequently, sub(partially) epoxidized soybean oil was found to be a successful and low cost solvent with improved health, safety, and environmental parameters.

Polymerization Techniques

The controlled/living free radical polymerization (CFRP) conducted to chemically synthesize the biopolymers was 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 CTAs in the reaction, which is more environmentally friendly (D’Agosto 2008, Hernández et al. 2015). Moreover, the polymer structure and composition can be easily controlled and designed in RAFT, and the desired molecular weight (MW) can be obtained in RAFT as well (Williams et al. 2014, Hernández et al. 2015). These advantages have made RAFT more widely used for polymer synthesis (Rudin and Choi 2013).

In this research, monomers (styrene and AESO), an initiator (AIBN), and CTA (PPBD) were mixed in solvent to synthesize PS-PAESO through RAFT polymerization (Williams et al. 2014, Cochran et al. 2018). The final product of PS-PAESO is presented in Figure 1a (PS-PAESO polymer) and 1b (PS-PAESO polymer after cryogrinding under liquid nitrogen with smaller polymer particles for better blending compatibility).

Figure 1. (a) PS-PAESO polymer and (b) PS-PAESO polymer after cryogrinding

Conceptualization of BioMAG

After making the change to using EHOSO as the monomer, the use of the soybean oil was explored as a solvent to be used during the polymerization. It was found that sub-epoxidized soybean oil (SESO) worked well for this task, and the resulting material was a blend of approximately 50% SESO and 50% PAEHOSO. This material is referred to as BioMAG.

SESO is soybean oil, and namely the triglyceride molecule that has gone through a partial epoxidation process. This results in only one or two of the C=C double bonds being epoxidized. Having fewer reactive sites on the molecules has shown favorable performance when blended into asphalt. It is hypothesized that the SESO molecule reacts to asphaltene molecules adding a long fatty acid chain. This addition improves the miscibility of the asphaltenes with the maltenes and leads to a de-aggregation of the asphaltene clusters.

The addition of BioMAG to asphalt has two-fold benefits. The PAEHOSO increases the elastic recovery and decreases the rutting potential, while the SESO improves the low temperature performance causing a widening of the PG temperature range. It has been found that the PAEHOSO interacts with SBS polymers, so the use of both SBS and BioMAG leads to superior performance. The few reactive sites on the PAEHOSO can react to the C=C double bonds on the polybutadiene chain, leading to a much larger polymer with increased elasticity as illustrated in Figure 2.

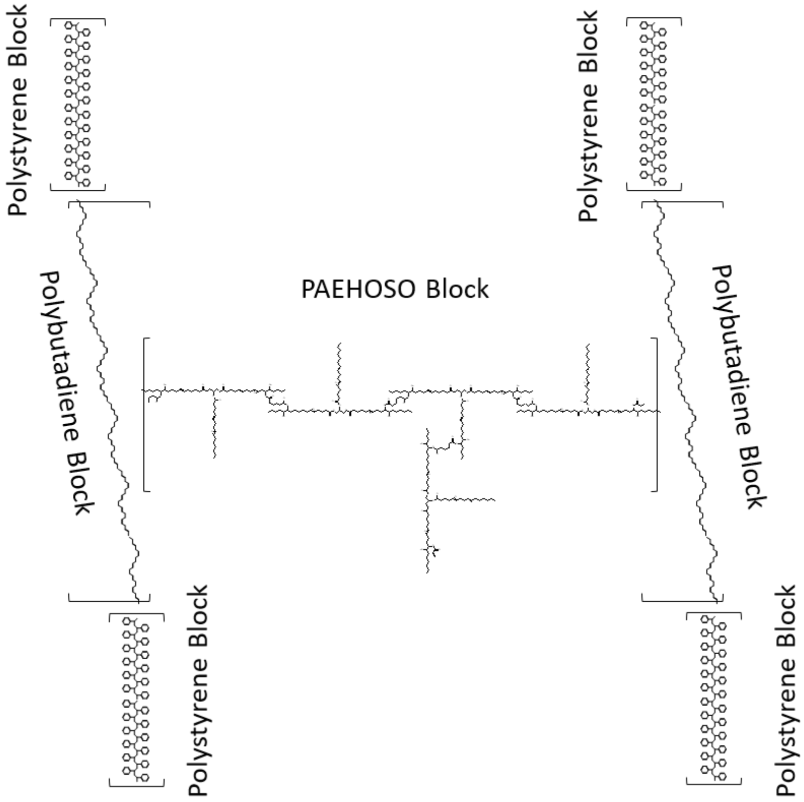


Figure 2. PAEHOSO reaction to the C=C double bonds on the polybutadiene chain

Chemical Characterization of PS-PAESO and BioMAG

Optimization of a block copolymer's formulation depends on the MW parameter of the PS block and the PS contents used in the PS-PAESO diblock copolymer. The PS block composition influences polymer phase solubility, morphology, and the MW of the PAESO block for asphalt modification (Hernández et al. 2015). To chemically characterize the PS block for the PS-PAESO polymer, hydrogen nuclear magnetic resonance (H-NMR) and high temperature gel chromatography (HT-GPC) were performed.

Hydrogen Nuclear Magnetic Resonance (H-NMR)

The H-NMR was conducted by using a 600 MHz Bruker AVANCE III spectrometer to quantify the percentage of PS in the block copolymer and also the amount of residual terminated PS within the polymer. Deuterated chloroform ($CDCL^3$) was used as a 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 the PS-PAESO polymer is shown in Figure 3.

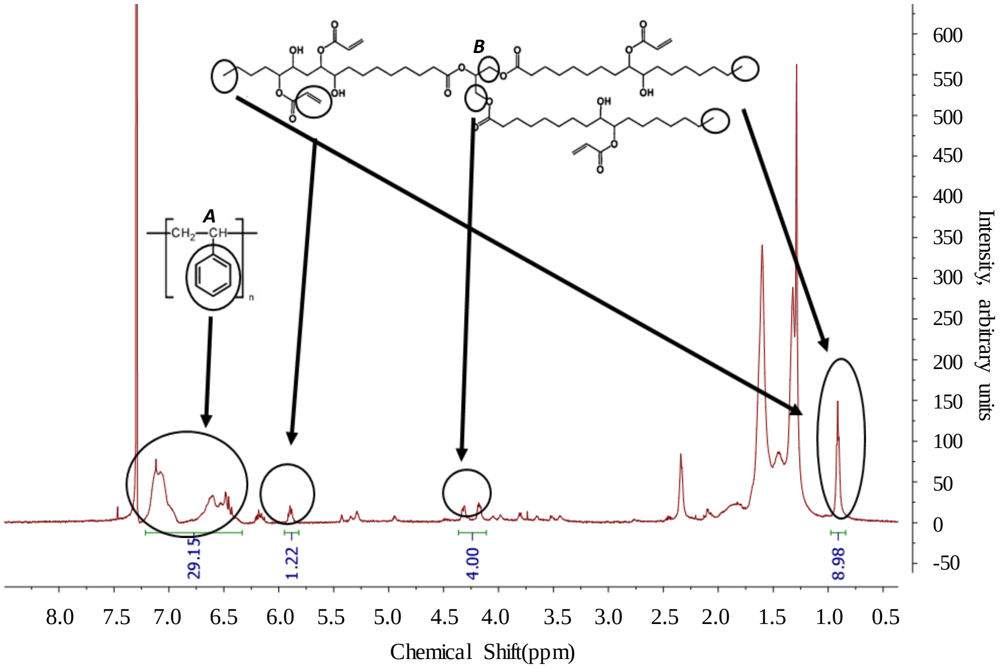
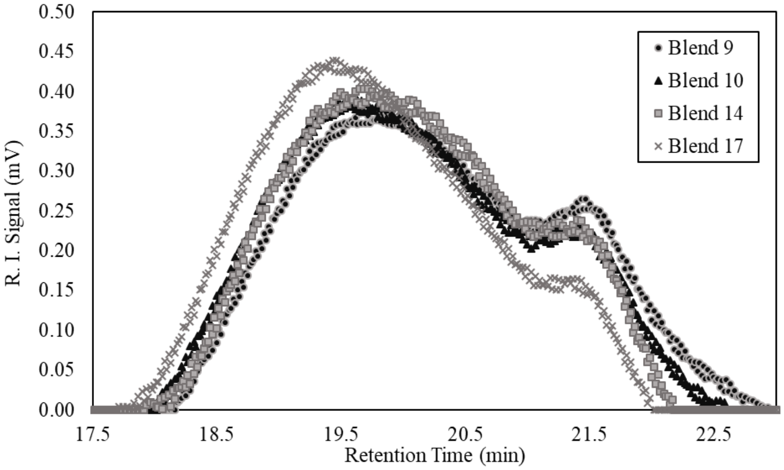


Figure 3. NMR spectrum graph of PS-PAESO polymer

The letter A shows the aromatic hydrogens present in the styrene repeat unit, and the letter B shows the glycerol hydrogens present in the AESO's backbone. The arrows pointing to the peaks in the circles represent the specific amounts of hydrogen that can be integrated into each functional site, which can also be used to calculate the composition of the PS-PAESO polymer.

High Temperature Gel Chromatography (HT-GPC)

The HT-GPC was performed to measure the MW and polydispersity index (PDI) of the PS-PAESO polymer by using a Viscoteck 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, which is widely used in the polymer industry, provides quantitative analysis of the polymer to show polymerization control of processability and material properties (Räntzsch et al. 2016). In Figure 4, the HT-GPC trace of the PS-PAESO polymers (used in asphalt modification as shown in Table 1 in the next chapter) shows the growth of PS-PAESO molecular weight according to retention time.



Molecular weight was calculated using poly (methyl methacrylate) standards

Figure 4. High temperature gel chromatography of PS and PS-PAESO polymers

Monodispersity in polymers produced by RAFT often signifies a well-controlled polymerization. Moreover, lower PDIs are more desirable as polymer chains remain linear and less branched, which facilitates 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 MW. The entanglement MW contains polymeric chains that are long enough to form one loop around themselves (also called a bridge). Polymers with MWs above their entanglement weight enhance the elasticity and recoverable behavior of the neat asphalt binder when compared to lower MW polymers.

Even though the PS-PAESO (as shown in Table 1 in the next chapter) were thought to have different MWs due to the chemical reaction length, all the diblock copolymers chosen for this study were entangled and achieved the minimum MW needed to show entanglement in the asphalt binder. Therefore, these diblock copolymers can be used for asphalt blend modification with enhanced final mechanical and rheological properties of the blends, and the different modification effects are not considered to be related to the PS-PAESO MW.

CHAPTER 4. RHEOLOGICAL CHARACTERIZATION AND STATISTICAL ANALYSIS OF PS-PAESO MODIFIED ASPHALT BINDERS

Modified Blends Preparation and Experimental Plan

The expected synthesized biopolymers (PS-PAESO) were laboratory produced at 1.25 MDa molecular weight (targeted MW) of PS-PAESO with various PS MWs and contents at different lengths of reaction duration. The biopolymers were used to modify a soft neat asphalt binder, which was a 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 (Cascione et al. 2013, Williams et al. 2014). The modified blend codes with corresponding PS-PAESO biopolymer polystyrene parameters are shown in Table 1.

Table 1. Different biopolymers with their corresponding modified blend codes utilized for shear blending

	Polystyrene molecular weight, kDa			PS-PAESO diblock copolymer		Chemical reaction length, hr
Polystyrene Content, %	10	20	30	Molecular weight, MDa	PDI	
30	–	–	Blend 9	0.98	2.06	4
30	–	–	Blend 10	1.22	1.83	5
20	Blend 1	–	–	1.25	1.73	8
25	Blends 2 & 3	Blend 8	Blend 11	1.24	1.76	8
30	Blends 4, 5, & 6	–	Blends 12 & 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

A Silverson L4RT-A shear mixer with a square-hole high shear screen was used to perform shear blending. All modified blends were shear blended at a 3,000 rpm shear rate and at a blending temperature of 190°C for 3 hours in accordance with blends prepared in previous research studies (Cascione et al. 2013, Williams et al. 2014). 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 using the same blending procedure at the same dosage level to evaluate the modification effects (Dorokhova et al. 2012, Cascione et al. 2013).

The laboratory-produced biopolymers 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 biopolymer-modified asphalt blends used for statistical optimization and an optimized formulation of biopolymer produced for verification through grading are presented here. The overall laboratory test plan is presented in Figure 5.

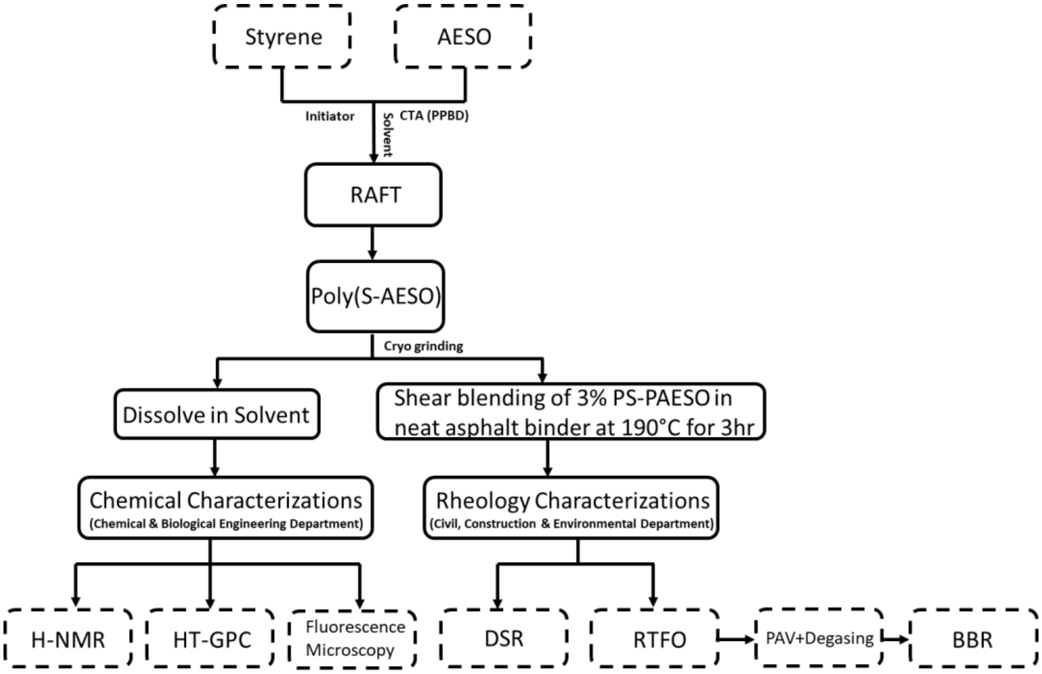


Figure 5. Overall test plan for biopolymer (PS-PAESO)

Asphalt is a viscoelastic material whose rheological properties are related to test temperature and rate of loading. An 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 pavement service life (Brown et al. 2009). 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 M 320-10 with specimens tested in triplicate. The performance grade tests were performed at a wide range of temperatures and frequencies to determine the critical high and low temperatures that specify the temperature range of an asphalt binder for a proper paving environment.

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 (Handle et al. 2016, Grossegger et al. 2018). After being covered, the specimens were annealed in the oven for 15 min at 150°C to remove air bubbles and allow the material to spread (Valverde et al. 2008). A Leica DM4000 B light emitting diode (LED) fluorescence optical microscope with a Leica DFC7000-T digital camera was used with the glass film specimens to observe the morphology of the polymer-modified binders. Figure 6 shows two fluorescence optical micrographs, one of a Kraton D1118 (SB)-modified asphalt binder and one of a biopolymer-modified asphalt binder.

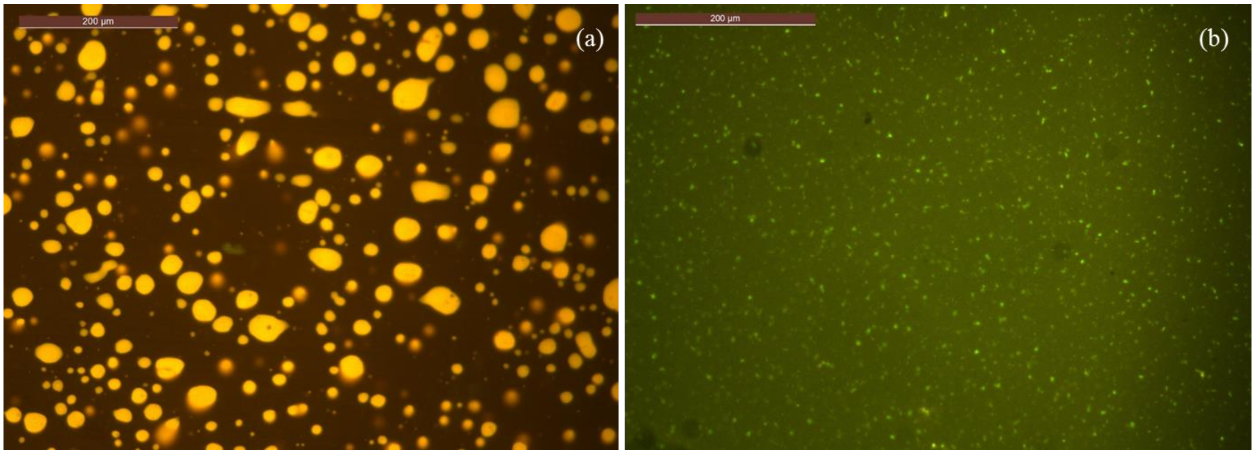


Figure 6. Fluorescence optical micrographs of polymer-modified asphalt blends (magnification=100x, scale bar=200μm): (a) commercial Kraton D1118 (SB) polymer-modified blends and (b) biopolymer-modified blends-Blend 1

The micrographs present different morphological conditions due to the distribution and fineness of the polymer in the asphalt matrix (Wen et al. 2002, Nassar et al. 2012). In both images, shining spherical particles represent the swollen polymers as shown by the aromatic compounds within the asphalt binder, while the dark phase represents the asphalt rich phase (Fernandes et al. 2008, Alonso et al. 2010, Liang et al. 2016a, tur Rasool et al. 2017). The scattered yellow particles in Figure 6a are dispersed SB polymers in the neat asphalt binder after high speed shear blending and reflect a multiphase morphology that shows some of the polymer is only partially swollen by the asphalt binder with two co-continuous phases (Merusi et al. 2014). It can also be seen that the Kraton 1118D (SB) polymer was dispersed coarsely due to the phase separation of butadiene with the neat asphalt binder (Merusi et al. 2014).

In Figure 6b, the biopolymer-modified binder (Blend 1 in Table 1) displays a homogeneous morphology with finely dispersed particles, where phase separation does not occur with the neat asphalt binder (Lu et al. 2011, tur Rasool et al. 2017). Similar homogeneous morphology was seen in the rest of the PS-PAESO-modified blends through examination of the micrographs. The examination indicated that PS content and MW do not affect the dispersion and compatibility of the polymer in the asphalt binder. Uniform dispersion allows the polymers to be entangled with asphalt molecules and produce an increased elastic response with better compatibility between the polymer and neat asphalt binder. This finding was also confirmed by rheological characterization.

Performance Grading of Modified Asphalt Binders

To determine and verify the grade of the neat asphalt binder (52-34) and modified blends, DSR testing (ASTM D7175-08 and AASHTO T 315-10) was performed on both unaged and short-term aged asphalt blends for the high temperature grade and BBR testing. ASTM D6648-08 and AASHTO T 313-10 testing was conducted on long-term aged blends for the low temperature grade. The short-term laboratory aging of the neat asphalt binder and the modified blends was performed using a RTFO (ASTM D2872-12 and AASHTO T 240-09). The long-term laboratory aging was performed on the asphalt binders in a pressure aging vessel (PAV) (ASTM D6521-13 and AASHTO R 28-12) to expose the binders to high pressure and temperature (simulating long-term aging in a short amount of time). The grade of the commercially available Kraton D1118 (SB)-modified neat asphalt binder was evaluated for comparison purposes by following the same test approaches.

Dynamic Shear Rheometer (DSR)

The DSR test is usually conducted to characterize the viscous and elastic behavior of asphalt binder to determine rutting resistance and high temperature susceptibility at high and intermediate temperatures. The DSR test measures the complex modulus (G*, Pa) and phase angle (δ, degree) of an asphalt binder, which are both significantly influenced by temperature and loading frequency. The G* measures the total deformation resistance of the asphalt binder under repeated shear, and the δ represents the relative amount of recoverable and non-recoverable deformation of the viscoelastic asphalt binder (Gama et al. 2016).

The DSR test is conducted at an oscillation frequency 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 25 mm-diameter silicon mold and were tested using 25 mm diameter parallel plates. The critical high temperature can be obtained when the $|G^*|/\sin(\delta)$ value of an 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.

Table 2. Critical high temperatures of unaged and RTFO short-term aged modified asphalt blends with corresponding high temperature performance grade

Blend	Critical high temperature, °C Unaged	Critical high temperature, °C RTFO aged	High temperature performance grade, °C
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	52
8	56.5*	56.9	52
9	56.5	56.0*	52
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

According to ASTM D6373-15, the high temperature PG is determined based on the lower value of the two high critical high temperatures of each blend as tabulated in Table 2 and along with its margin of error bar at 95% confidence intervals in Figure 7.

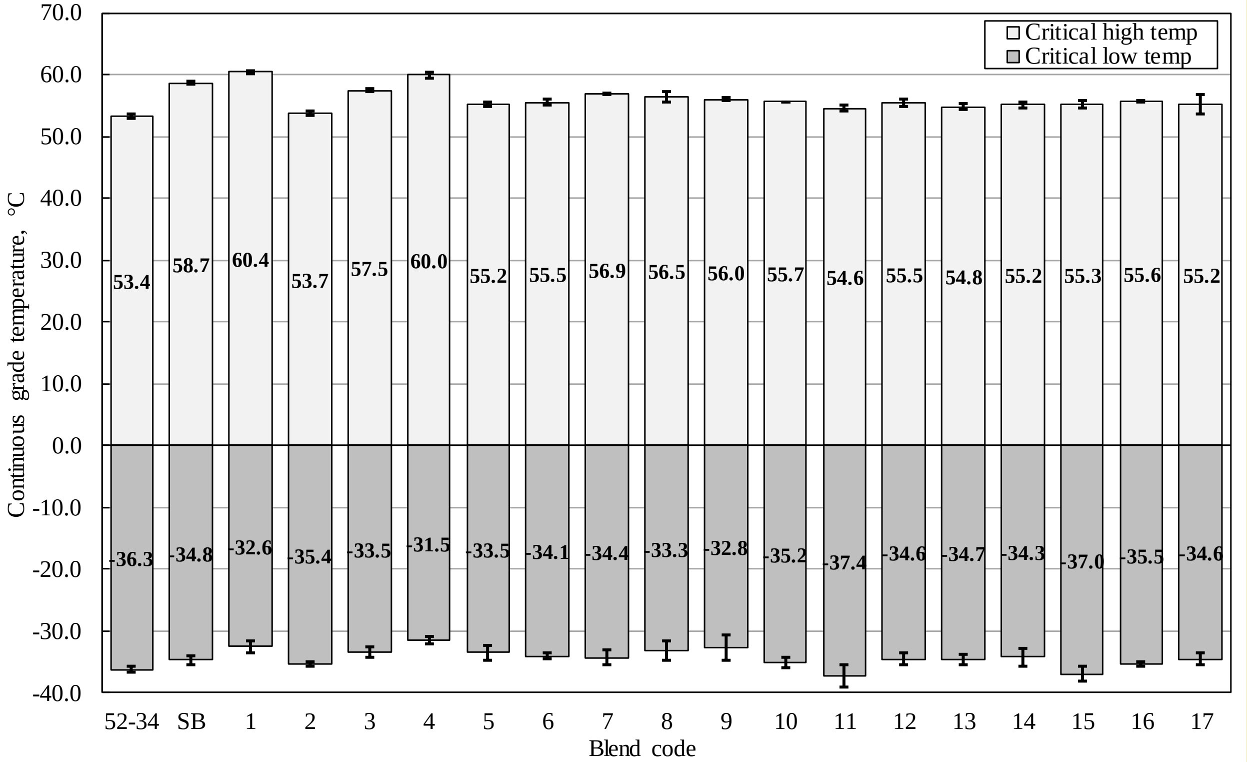


Figure 7. Continuous performance grade ranges of the polymer modified asphalt blends and the neat asphalt binder

According to the DSR test results, the neat asphalt binder had a critical high temperature of 53.4°C and was graded out at 52°C. Increased critical high temperature could be observed for all biopolymer-modified asphalt binders when compared to the neat asphalt binder. Additionally, critical high temperatures of Blends 1, 3, 4, and 7 were very similar or higher than that of the SB polymer-modified binder with the same grade of 58°C. The best performing biopolymers in terms of critical high temperature were shown in Blends 1 and 4, which contain PS with a lower MW 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 were approximately 1.8°C higher than the critical high temperature of the SB polymer-modified binder.

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 in minimizing 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 at 240 sec. 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 sec. The more conservative result is used for estimating the critical low temperature. The critical low temperature results are tabulated in Table 3, along with their margin of error bars at 95% confidence intervals in the previous Figure 7.

Table 3. Critical low temperatures of long-term aged modified asphalt blends with corresponding low temperature performance grade and their continuous grade ranges

Blend	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. Additionally, 11 of the 17 biopolymer-modified blends were graded as -34°C, which was the same grade as the neat asphalt binder and the SB-modified blends. In contrast, the other six biopolymer-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 biopolymers were compromised on the low temperature grade.

The overall continuous PG range results were determined based on both the critical high and low temperatures of the modified asphalt blends. This indicated the temperature susceptibility of the asphalt binder and the working range of temperatures. The continuous grade range results were summarized in Table 3 and Figure 7.Figure 7. Continuous performance grade ranges of the polymer modified asphalt blends and the neat asphalt binder

Table 3 shows that 11 of the 17 biopolymer-modified blends presented higher ranges than the neat asphalt binder as well as similar ranges to the SB-modified binder. Thus, the majority of the formulated biopolymers helped widen the continuous PG range and reduce the temperature susceptibility of the neat asphalt binder. It was noted that the PS-PAESO with a lower PS content increased the critical high temperature of the neat asphalt binder the most compared to the rest of PS-PAESO-modified blends and reduced the temperature susceptibility of the neat asphalt binder with comparable continuous grade ranges as the SB-modified blend.

For the purpose of this research, the most desirable PS-PAESO polymer can modify the neat asphalt binder to achieve an increased critical high temperature with reduced temperature susceptibility superior to that of the SB polymer-modified asphalt binder for applications in warm climate regions.

Master Curves and Black Diagrams

The G* and δ were obtained and measured by performing frequency sweeps at multiple temperatures using 8 mm- and 25 mm-diameter parallel plate specimens in a DSR. The range of the frequency sweep was between 1.0 to 100.0 rad/s at temperature stages of 20.0 to 30.0°C (8 mm for lower temperatures at 5% strain rate) and 40.0 to 64.0°C (25 mm 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 temperature ranges by performing strain sweep tests at the test temperatures using both plate sizes.

For better evaluation of the material 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 biopolymer-modified binders. Blend 1 had the highest critical high temperature and the widest working range of temperatures of all the PS-PAESO-modified blends, which modified the neat asphalt binder from PG 52-34 to PG 58-28, and thereby can be used for pavement applications in warm climate regions.

Meanwhile, the PS-PAESO added in the asphalt binder as Blend 7 performed similarly to the SB-modified binder, because it helped improve the 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., it kept the binder graded the same as the neat asphalt binder on the low temperature side. Therefore, Blend 1 was superior to the SB-modified binder in terms of critical high temperature, and Blend 7 was the closest to the S-modified binder with the same low PG.

For further analysis, the rheological behaviors 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 (Brown et al. 2009). The WLF equation is used to calculate the shift factors needed to shift the G* and δ 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 are shown at high, intermediate, and low temperatures in Figure 8.

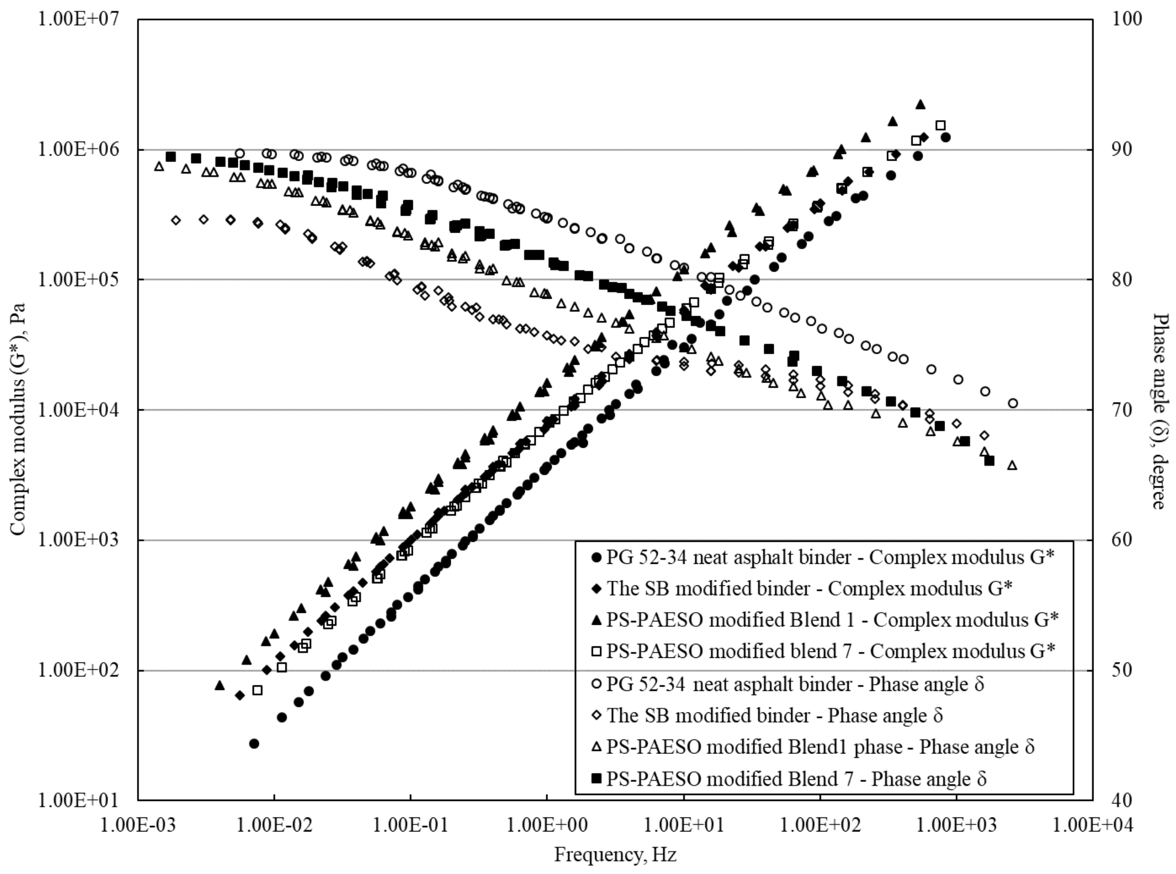


Figure 8. Master curves and δ master curves for the neat asphalt binder, SB-modified binder, Blend 1, and Blend 7

The black diagrams use both complex modulus (G*) and phase angle (δ) results and were developed to interpret 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 as shown in Figure 9.

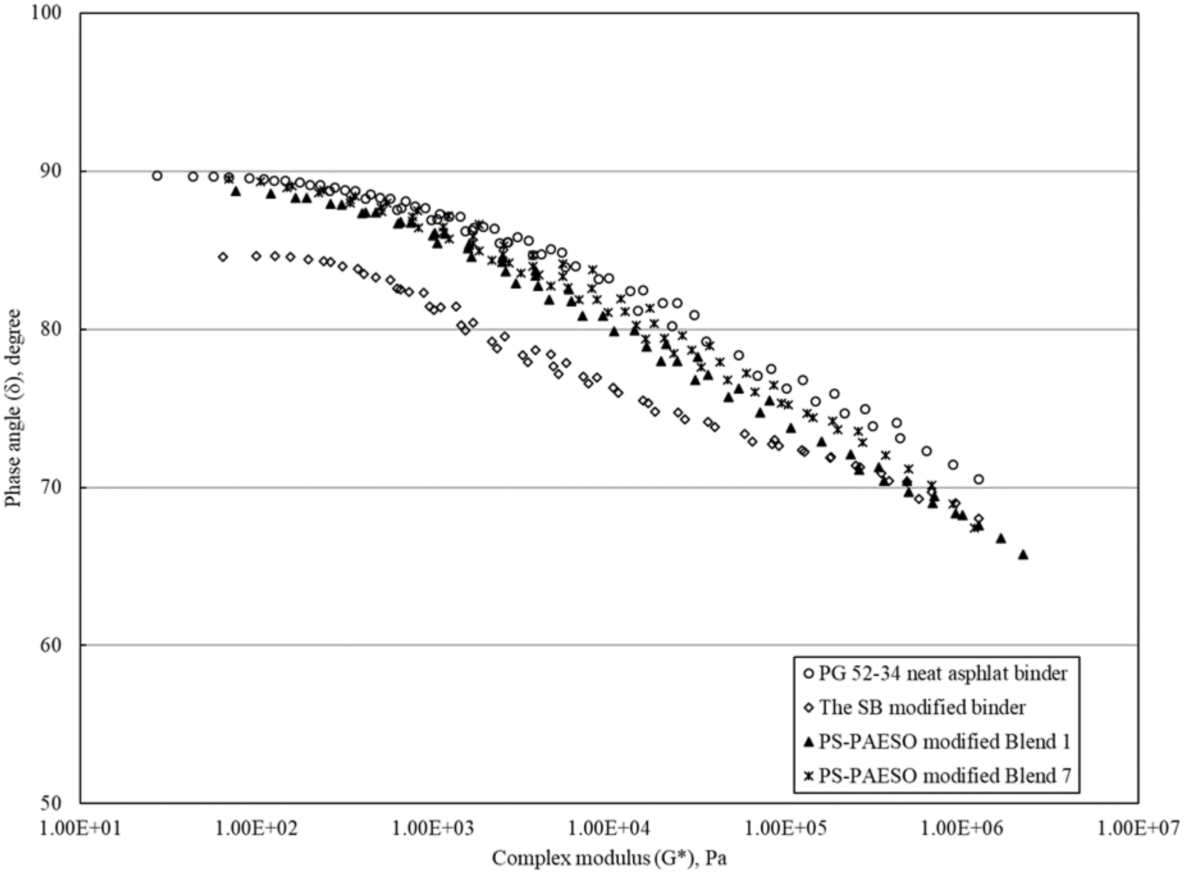


Figure 9. Black diagrams for the neat asphalt binder, SB-modified binder, and Blend 1

The black diagram curves of Blend 1 and the SB-modified binders show a shift toward a 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. While there is no significant phase angle shift noticed for Blend 7 at the lower and intermediate stiffness values, the curve appears 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 the neat asphalt binder's elasticity as much as the polymers used in Blend 1 and the SB binder do. For Blend 1, the black diagram curve shows a shift toward lower phase angles at higher stiffness values with lower temperatures and higher frequencies. In addition, at higher stiffness values with lower temperatures, both the curves for Blend 1 and Blend 7 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 that the biopolymer 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.

Statistical Analysis of PS-PAESO

Effect of Varied Parameters in PS-PAESO on the Properties of PMB

To verify whether the chemical reaction length of the PS-PAESO polymer has any effect on the high and low temperature properties of the modified blends, a statistical analysis was conducted on the results obtained from DSR and BBR. Therefore, two separate analyses of variances (ANOVAs) at a 95% confidence interval were conducted for the high temperature property by using the rutting parameter G*/sinδ at various test temperatures and for low temperature properties of stiffness and m-values at different test temperatures, respectively. The statistical analysis was conducted on blends that have the same PS content (i.e., 30%) and MW (i.e., 30 kDa) but different chemical reaction lengths. They were Blend 9 (4 hr), Blend 10 (5 hr), Blend 12 (8 hr), Blend 13 (8 hr), Blend 14 (9 hr), Blend 15 (10 hr), Blend 16 (11 hr), and Blend 17 (12 hr). The responses for the ANOVA are G*/sinδ, stiffness and m-value. Additional factors examined within the ANOVAs were chemical reaction duration and test temperature. The ANOVA table (Table 4) for high temperature property, G*/sinδ, shows no statistically significant difference in the factor reaction length nor the interactive effect between length and test temperature.

Table 4. ANOVA for G*/sinδ, stiffness, and m-value with factors of chemical reaction length and test temperatures

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

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

As expected, there was a statistically significant difference in test temperatures because the asphalt binder is a viscoelastic material with temperature-dependent behavior. The Tukey honestly significant difference (HSD) least square means test was performed on the test results to better examine if there were differences between blends in terms of different reaction durations, as presented in Table 5.

Table 5. Tukey HSD least square means difference of G*/sinδ, stiffness, m-value for reaction duration

Factor level of reaction duration, hr		Least square mean
G*/sin(δ) **(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 **(PAV aged)**		
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 **(PAV aged)**		
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

Levels not connected by same letter would be significantly different

All levels of reaction duration 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 found in the ANOVA tables and Tukey HSD least square means difference tables for responses of stiffness and m-value as shown in Tables 4 and 5. As a result, the chemical reaction duration of PS-PAESO does not affect the high and low temperature properties of the PS-PAESO-modified blends.

The ANOVA on PS MW and PS content were conducted on all 17 blends, because the chemical reaction duration was proven to have no effects on the high and low temperature properties of the PS-PAESO-modified blends. According to the ANOVA tables, two PS parameters were found to have significant effects on the high and low temperature grading results at a 95% confidence interval. More importantly, a PS content at the lower level of 20% was found to be significantly different from the other three higher percentage contents (i.e., 25%, 30%, and 35%) and a PS with a higher MW of 30 kDa was considered to be significantly different from the other two lower MWs (i.e., 10 and 20 kDa) based on the Tukey HSD least square means difference results presented in Table 6.

Table 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

Levels not connected by same letter are significantly different

From the results, it can be inferred that a lower PS content helps with high temperature performance, while a higher PS MW has positive effects on low temperature performance in asphalt modifications.

Response Surface Modeling

In many cases, performing a full experimental design plan is very time consuming and expensive. To avoid this problem, a partial experimental design plan was generated, and prediction models were developed using the measured results through response surface modeling (RSM) to optimize the formulation of the polymer. Thus, 17 PS-PAESO polymers with a target MW of 1,250 kg/mol, consisting of PAESO with various PS MWS and contents, were produced. These PS-PAESO formulations were then used to modify the base binder at the same dosage, and the modified binders were subsequently put through a full binder investigation following ASTM D6373-15 and AASHTO M 320-10 criteria (defined as the critical high and low temperatures for determination of the modified blends grade). The grading results obtained from laboratory testing were then used for polymer formulation optimization via RSM.

The main objective of this part of the study (i.e., optimization of PS parameter MW and content in PS-PAESO for better performing modified asphalt binders) could be achieved through the development of a new statistical approach using RSM that employs these binder performance test results. The secondary objective was 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 region pavement applications with a 3% polymer content dosage and perform equal to 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 such as polystyrene MW, polystyrene content, and test temperature) on the test responses of the polymer-modified asphalt binder's critical high and low temperatures (i.e., G*/sin(δ) for unaged and short-term aged blends, stiffness, and m-value) were investigated. To assess the accuracy of the predicted equations obtained from RSM, the recommended PS parameters with predicted critical temperatures and verified grade results on the recommended PS-PAESO polymer produced are presented. The overall research process is summarized in Figure 10.

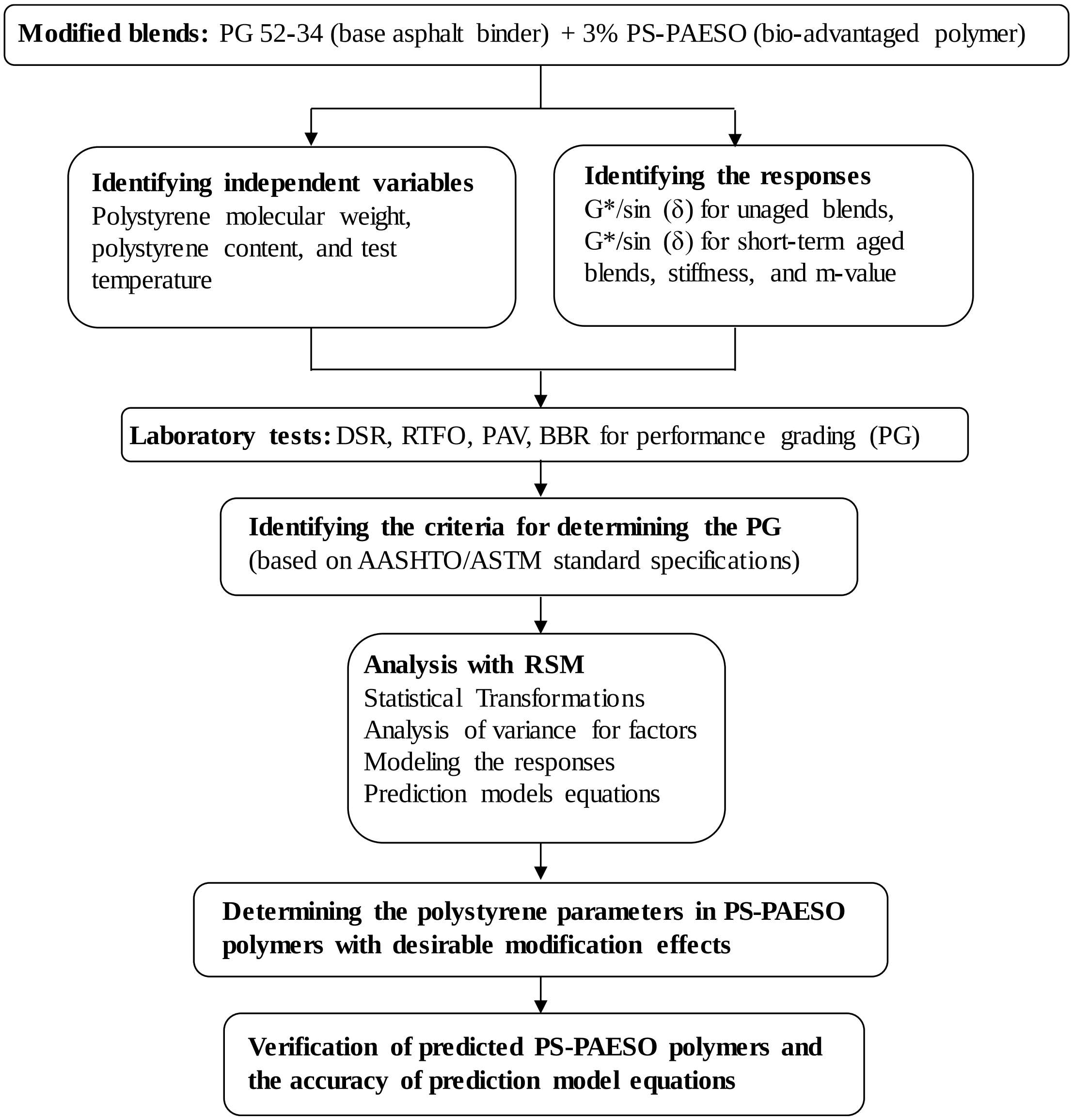


Figure 10. Overall optimization process

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 MW, polystyrene content, and test temperature) were selected to develop the initial response surface model to find the functional relationship through a stepwise regression process using 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 1.

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33}\ 1 x_3^2 + \varepsilon \qquad (1)$$

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 MW (kg/mol), polystyrene content (%), and test temperature (°C), respectively. β_0 is the intercept, $\beta_1 \ldots \beta_{33}$are the coefficients, and ε 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(δ) of unaged modified blends, G*/sin(δ) of RTFO short-term aged modified blends, and m-value and stiffness of PAV aged modified blends. The stepwise regression was performed on the initial models of unmodified data, Log10 transformed data, and SQRT transformed data. The regression was performed to eliminate the least important variable that had the highest p-value compared to the rest of the variables until the finalized model was obtained using only statistically significant variables with a confidence level of 95% or higher.

Four initial response surface models were developed with respect to four test responses, which are G*/sin (δ) with a limit of 1.0 kPa for unaged modified blends, G*/sin (δ) 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, respectively, for the PAV aged modified blends. The stepwise 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 met the normal distribution and had R^2 values closest to 1.

Finalized prediction models for the high and low temperatures are summarized in Table 7, and their coefficient values are presented in Table 8.

Table 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 8. Regression coefficients for prediction models

Regression coefficient	Coefficient value	Regression coefficient	Coefficient value
G*/sin(δ) (Unaged)		**G*/sin(δ) (RTFO aged)**	
β0	5.4062011	β0	5.9536825
β1	-0.035459	β1	-0.022674
β2	-0.051313	β2	-0.083476
β3	-0.097202	β3	-0.089883
β11	0.000833	β12	0.0006269
β22	0.0007587	β22	0.0013052
β33	0.0003658	β33	0.0002742
Stiffness (PAV aged)		**m-value (PAV aged)**	
β0	1.2166729	β0	0.721626
β1	-0.002152	β2	0.0030204
β2	-0.012236	β3	0.0092462
β3	-0.054661	β11	0.00001688
β22	0.0002663	β22	0.00005379

After combining the corresponding coefficient values (Table 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 MW of PS-PAESO biopolymers with recommended PS MW and PS content that could modify the neat asphalt binder PG 52-34 to be PG 64-28 are tabulated in Table 9.

Table 9. Recommended polystyrene parameters in PS-PAESO biopolymers 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

According to the proposed PS parameters, it is noted that a lower PS molecular content (i.e., 5%) is able to increase the critical high temperature of the neat asphalt binder by two PGs, but also increases the low temperature performance by one grade. The PS MW does not have much effect on the neat binder's high temperature performance grade because polymers with a PS block that have MWs of 15, 20, 25, and 30 kDa at a PS content of 5% have shown similar modification effects for critical high temperatures (Table 9). Even though PS MW does not affect the critical high temperature, it is important to note that there are minor effects of PS MW on the low temperature side. In Table 9, it can be seen that the stiffness of the predicted blends decreases and the m-value increases as the PS MW increases from 15 to 30 kDa at the same 5% PS content, which agrees with the findings previously presented in this chapter.

Because the main objective of this part of the research was to produce a polymer-modified asphalt binder with superior high temperature performance for pavement applications through use of the PS-PAESO biopolymer, a lower PS content was more of a priority in the formulation of the PS-PAESO given the results.

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 in analyzing the relationship between polystyrene parameters and responses in the developed surface plots. In multiple surface plots, two independent variables, PS content, and PS MW, were plotted on the x and y axes, and the response was plotted on the z axis, as shown in Figure 11.

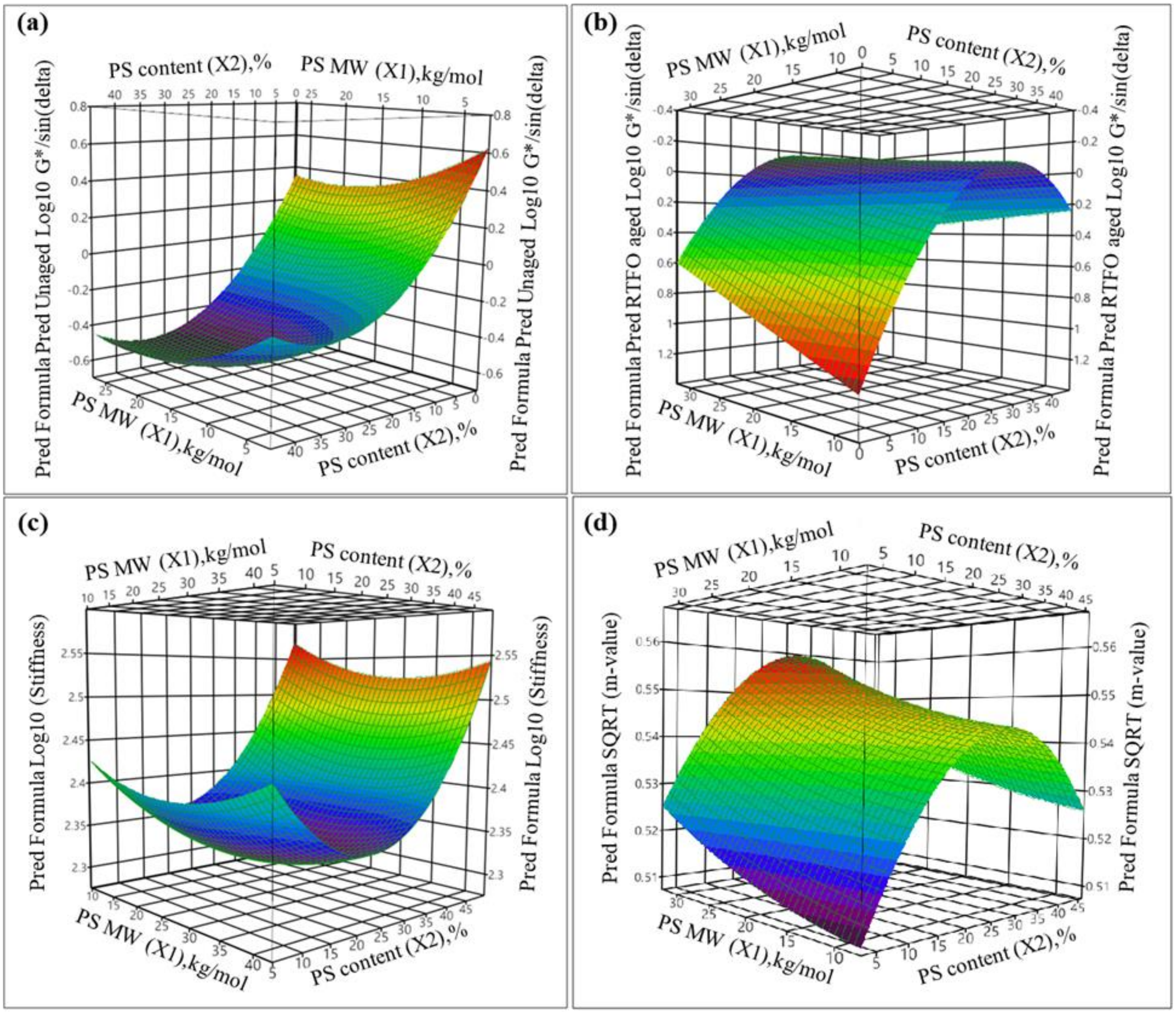


Figure 11. Surface plots of responses: (a) unaged Log10 (G*/sin(δ)), (b) RTFO aged Log10 (G*/sin(δ)), (c) PAV aged Log10 (stiffness), and (d) PAV aged SQRT (m-value) for responses versus polystyrene parameters

To achieve a PG 64-28, the polymer-modified blends needed to pass 64.0°C for high temperature grading (via G*/sin(δ)) and pass at a test temperature of -18°C for low temperature grading (via stiffness – S and the m-value). In Figure 11a, at a constant polystyrene MW, an increase in the Log10 (G*/sin(δ)) value results in a decrease of polystyrene content, while a change in the polystyrene MW exerts minimal effects on Log10 (G*/sin(δ)) values. To meet the criteria for passing the unaged asphalt binder criteria of G*/sin(δ) 1.0 kPa, the Log10 (G*/sin(δ)) 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 Log10 (G*/sin(δ)) surface plot as well in Figure 11b. The polystyrene content should be less than 10% to achieve the RTFO aged Log10 (G*/sin(δ)) need to be greater than 2.2 kPa criteria.

An increase in polystyrene content from 5% to 45% results in Log10 (stiffness) value changes from higher to lower to higher at a constant polystyrene MW as shown in Figure 11c. 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 preferred.

In Figure 11d, at a constant polystyrene MW, the highest SQRT (m-value) was obtained at an intermediate polystyrene content between 25 and 30%. In terms of polymer composition, polystyrene is the hard and stiff domain that provides strength to the polymer (Williams et al. 2014). 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 (Airey 2003, Airey 2004, Williams et al. 2014). Achieving a higher critical high temperature so that the modified binder can be used for pavement applications is preferred, but not to the detriment or decrease of the low temperature grade within this research. As a result, a lower polystyrene content with increasing polystyrene MW (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 the previous Table 9.

Biopolymer Formulation Verification

To verify the accuracy of the prediction model equations, one of the PS-PAESO bio-advantaged polymer formulations in Table 9 was produced: 1,250 kg/mol PS-PAESO, with a polystyrene MW 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 using high- and low-temperatures grade tests. The same high speed and high temperature shear blending procedure previously summarized was conducted to prepare the modified blends. Unaged and RTFO short-term aged modified binder specimens were prepared using a 25 mm-diameter silicon mold and tested in triplicate by using 25 mm-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 the 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 the 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 was estimated. The overall PG for the recommended polymer-modified asphalt binder follows the estimated PG, which was PG 64-28. These results indicated that the prediction models are highly accurate; however, the other three PS-PAESO polymer formulations in Table 9 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 12.

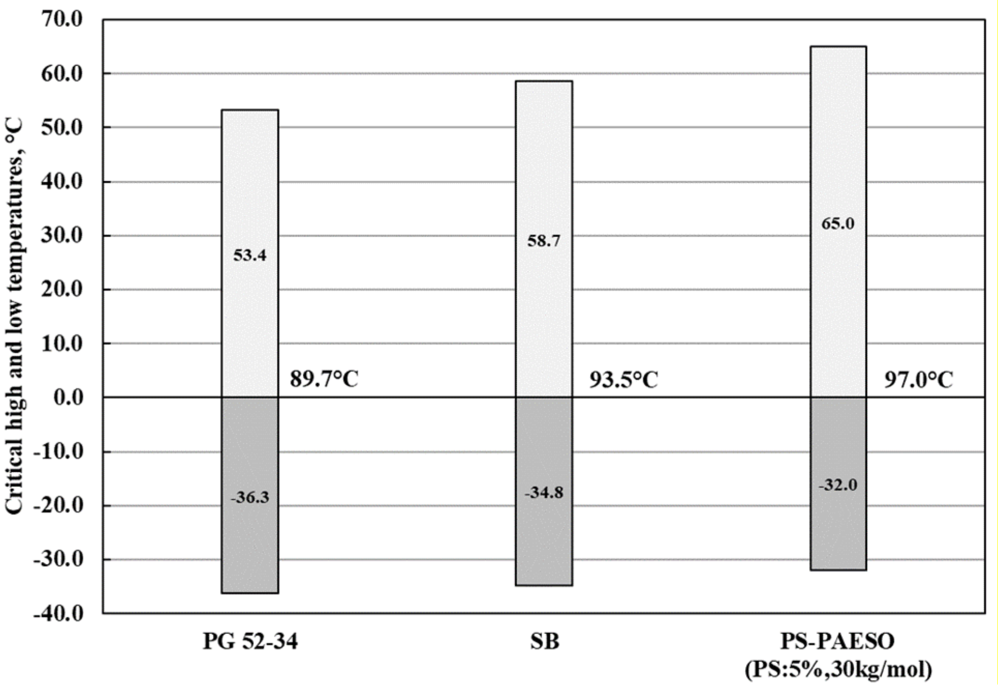


Figure 12. Critical high and low temperature comparisons for the base asphalt binder, SB-modified blends, and PS-PAESO-modified blends with calculated continuous grade ranges next to the bars

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 test. However, the continuous grade range for the biopolymer was 97.0°C, which was superior to the SB polymer (93.5°C) and the PG 52-34 base asphalt binder (89.7°C), as shown next to the bars in Figure 12.

CHAPTER 5. BIOPOLYMER PILOT PLANT, DOSAGE FORMULATION, AND CONSTRUCTION OF TEST SECTIONS

As part of this research project, a biopolymer pilot plant capable of producing 10 tons of polymer per week was built just west of Iowa State University at its BioCentury Research Farm as shown in Figure 13.

Figure 13. Iowa State University's vegetable-based biopolymer pilot plant facility

This effort was vital in determining the technical and economic feasibility of producing the biopolymers to use in asphalt modification.

In Fall 2018, the biopolymer pilot plant successfully produced the biopolymers on a large scale after plant calibration and trial runs. Subsequently, 600 gallons of biopolymer (first generation of BioMAG) were transferred to East Alabama Paving Co., Inc. to blend the biopolymer and produce the biopolymer-modified asphalt mixture for paving the NCAT Test Track section in Alabama. The test track paving was a success for this research project as shown in Figure 14, given it proved that the biopolymer could be produced on a large scale and blended into an asphalt binder at asphalt mix facilities currently doing paving.

Figure 14. NCAT Test Track paving and compaction using biopolymer-modified asphalt mixture

The NCAT test also demonstrated that the biopolymer-modified asphalt mixture can be easily compacted and paved in a manner similar to other commercial polymer-modified asphalt mixtures in construction.

The test section built at NCAT is located in W10 as shown in Figure 15.

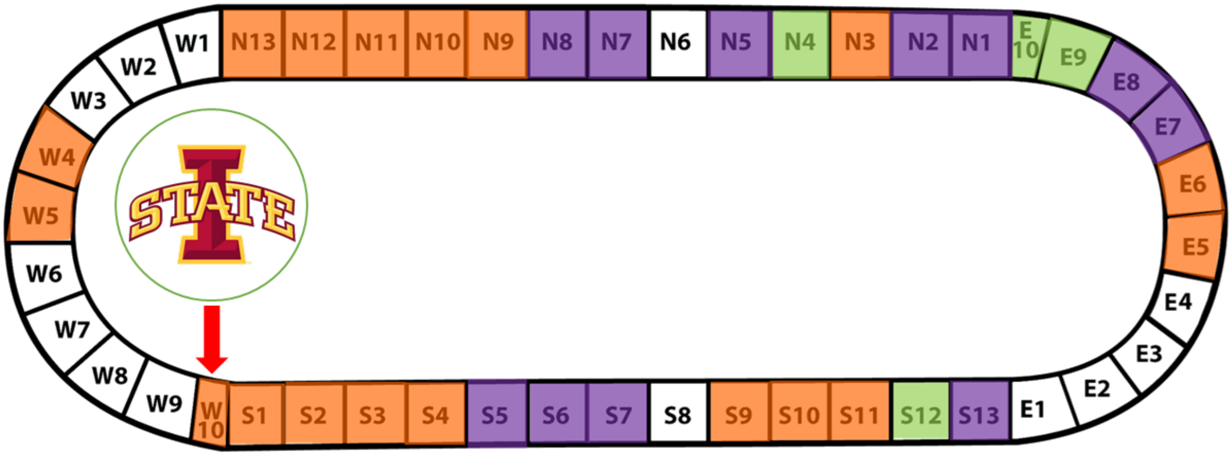


Figure 15. Location of first generation BioMAG test section at NCAT Test Track placed in 2018

After 14 years of simulated wear from heavily loaded semi-trailers in a three-year period, less than 3 mm of rutting was experienced by the test section.

Section E5A was used as the control section for comparison. The control and BioMAG sections' PG results are shown in Table 10 after blending and after being extracted and recovered from the field-produced mixes.

Table 10. Rheological results from blended and field extracted and recovered control and BioMAG test sections at NCAT

Sample	PG High Temp. (°C)	PG Low Temp. (°C)	Continuous Grade Range (PG High Temp. - PG Low Temp.), (°C)	ΔT_c	MSCR %, 3.2, kPa-1	High Temp. PG (°C)
E5A Virgin	76	-22	98	-2.6	**59.9**	64E
E5A Extracted	88	-16	104	-7.3	**58.7**	64E
W10 Virgin	70	-16	86	-3	**29.5**	64H
W10 Extracted	88	-16	104	-6.6	**59.9**	64E

PG = performance grade, MSCR = multiple stress creep recovery

Just after blending the BioMAG (W10 Virgin) does not perform as well as the control (E5A Virgin). However, after the field mix is produced and the binder is extracted and recovered, the BioMAG group (W10 Extracted) performs similarly to the control (E5A Extracted) in terms of elastic recovery and even performs better in terms of ΔT_c (a measure of how resistant the binder is to thermal cracking).

Two additional demonstration projects have been completed since the NCAT Test Track project. The first project was an overlay on NE 80th Street in Altoona, Iowa, as shown in Figure 16, for about a 1-mile length of roadway that used 600 tons of hot-mixed asphalt (HMA).

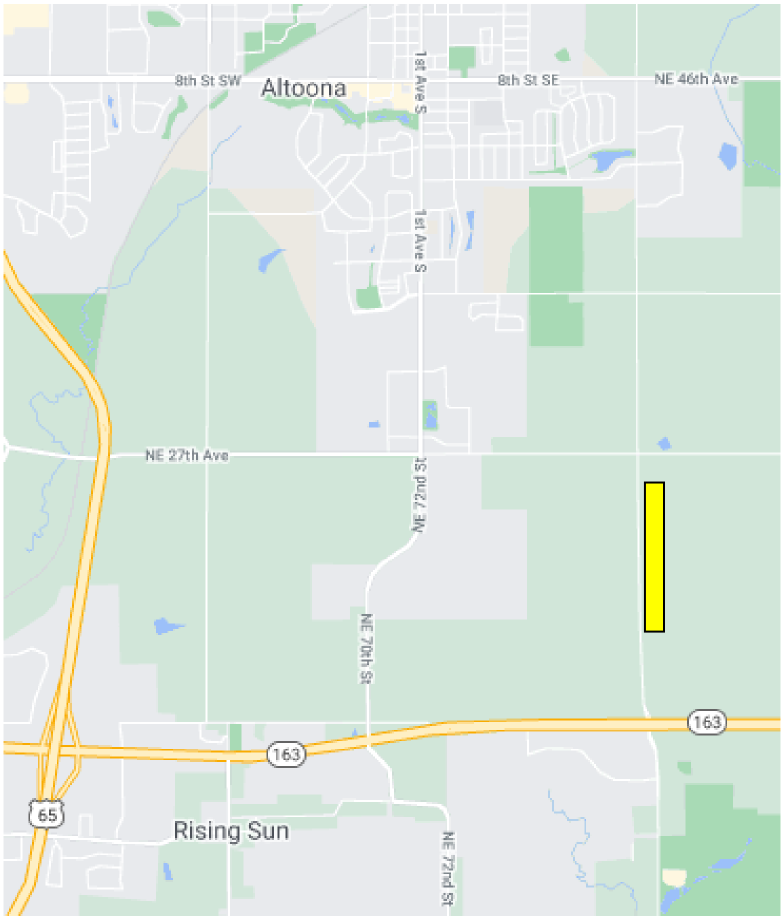


Figure 16. Altoona demonstration project location

The mix design used 20% RAP and a dense-graded limestone aggregate gradation and was designed for high traffic. Aggregates from different sources, each at different percentages, were blended (see Table 11) to achieve a desirable aggregate blend (see Figure 17).

Table 11. Gradation and percentages of aggregates used for developing the combined gradation

Aggregate Type	Percentage in Blend	Aggregate Gradation for Each Aggregate Type										
		1"	3/4"	1/2"	3/8"	#4	#8	#16	#30	#50	#100	#200
3/4" W Chip	10	100	98	62	33	6	3	2.5	2.3	2	1.7	1.5
3/8" W Chip	30	100	100	100	92	23	3.5	2.5	1.8	1.7	1.6	1.5
Man. Sand	30	100	100	100	100	96	66	36	18	7	3.5	2.5
Nat. Sand	10	100	100	100	100	96	83	64	41	15	2	0.7
RAP	20	100	100	96	93	71	54	41	29	16	11	9.1

W = washed, Man. = manufactured, Nat. = natural, RAP = reclaimed asphalt pavement

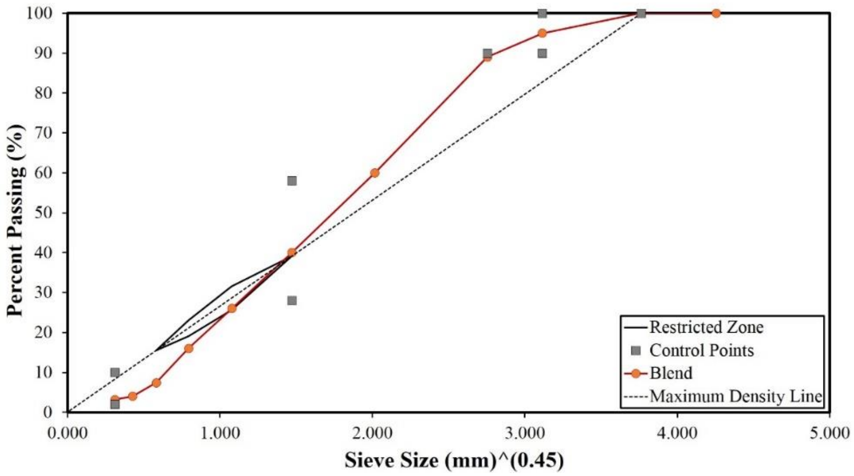


Figure 17. Combined aggregate gradation used for preparing asphalt mixtures in the asphalt plant

The asphalt binder formulation began with a polymer-modified asphalt graded at 58-28H. The continuous grade of this base asphalt was 65.4-31.0 with a ΔTc of -1.6 and 34.8% elastic recovery at 58°C. This binder was selected due to the favorable interactions between SBS and PAEHOSO. The goal of the formulation was to maintain the PG 58-28H grade after the RAP was included, effectively offsetting the negative impact of the RAP on the performance of the pavement.

More than 30 different blends were created in the laboratory to explore the impacts of changing doses or other variables. The final outcome was the base binder with 5.0% BioMAG, 1.2% SESO, and 0.13% sulfur by weight of the neat binder. Note, BioMAG is comprised of 50% SESO, so it could also be reported as 2.5% PAEHOSO, 3.7% SESO, and 0.13% sulfur. The resulting asphalt blend data is shown in Table 12, where BMH is the base binder, -F is the field sampled asphalt, and -FE is the field sampled HMA where the binder has been removed by extraction and recovery with toluene by distillation, and the BMH-FE binder includes the RAP binder from the mix.

Table 12. Altoona demonstration project asphalt blend data

Binder ID	Formulation	RAP	PG	Delta Tc	Mass Loss	MSCR 58c
BMH	58-28H (2.11% SBS + Sulfur)	N/A	64-28(65.4-31.0)	-1.6	0.10%	34.81%, Jnr=0.9387
BMH-F	58-28H (2.11% SBS + Sulfur) + 5.00% BIOMAG + 1.20% SESO + 0.13% Sulfur %bnb	N/A	64-28(64.2-33.3)	-3.4	0.16%	36.05%, Jnr=1.1584
BMH-FE	58-28H (2.11% SBS + Sulfur) + 5.00% BIOMAG + 1.20% SESO + 0.13% Sulfur %bnb	20% RAP	64-28(66.2-30.8)	-2.2	N/A	42.82%, Jnr=0.8138

The final outcome (BMH-FE) shows that the formulation was succesful in preserving the PG58-28H grade, and the elastic performance was improved by the addition of PAEHOSO. There were some complications during the blending procedure in the field. Given this was a new product, the blending was performed in a tanker truck with agitation to minimize any risk involved for the contractor. Due to this inefficient blending technique, the results were not as good as they could have been using an integrated blending system.

The next demonstration project was at the BioCentruy Research Farm, an Iowa State University owned facility, just west of Ames, Iowa, as shown in Figure 18.

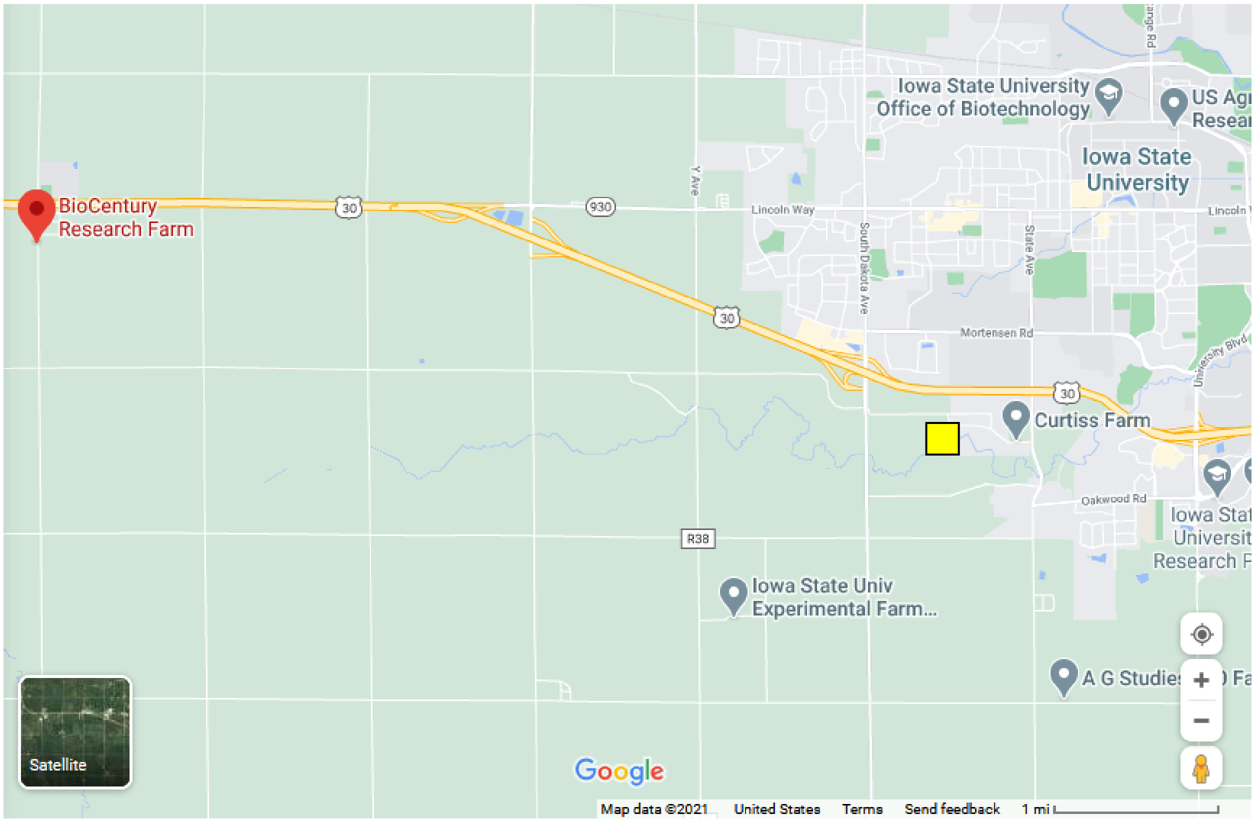


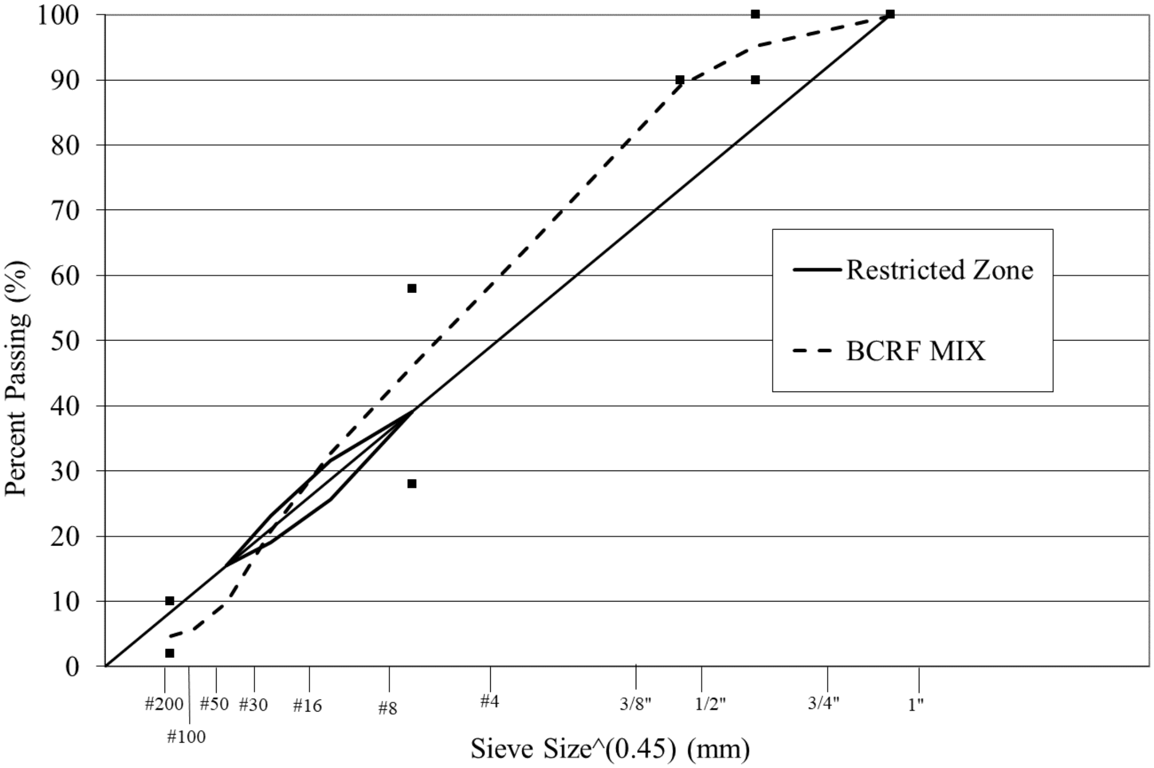
Figure 18. BioCentury Research Farm demonstration project location

This project was to pave the parking lot at the facility. The existing parking lot was gravel. Some of the gravel was removed and a subbase was prepared. A base course of HMA was placed using an unmodified PG64-22S with 25% RAP. The surface course used a formulated polymer-modified asphalt with SBS polymer and BioMAG and included 18% RAP. The individual aggregate gradations as well as the blend gradation are shown in Table 13 and Figure 19.

Table 13. Gradation and percentages of aggregates used for developing the combined gradation

Aggregate Type	Percentage in Blend	Aggregate Gradation for Each Aggregate Type										
		1"	3/4"	1/2"	3/8"	#4	#8	#16	#30	#50	#100	#200
3/4" Crushed LC	25	100	99	82	68	42	25	16	12	10	8	7
3/8" CL Chip LC	21	100	100	100	92	23	3.5	2.5	1.8	1.7	1.6	1.5
Man. Sand	17	100	100	100	100	96	68	38	20	7.5	3.5	2.5
Nat. Sand	19	100	100	100	100	98	87	69	40	8	0.6	0.2
RAP	18	100	100	98	93	77	61	48	36	23	15	12

LC = limestone crushed, CL = clean, Man. = manufactured, Nat. = natural, RAP = reclaimed asphalt pavement



BCRF = BioCentury Research Farm

Figure 19. Combined aggregate gradation used for preparing asphalt mixtures in the asphalt plant

The goal of this asphalt binder formulation was to drop the low temperature by one grade to achieve at PG58-28H after the RAP was included. The base asphalt for this project was an unmodified PG64-22S. In this project, a newer blending procedure was used and referred to as a master batching process. This is when the SBS polymer is added to the asphalt in high concentrations while being mixed in; then, the high concentrate is diluted with the unmodified base asphalt to a lower polymer concentration and the other additives are blended in. This process increases the interactions between the polymers while at a high concentration leading to a better elastic network that forms. The final outcome of the formulation was 2.1% SBS, 5.0% BioMAG, 1.2% SESO, and 0.13% sulfur. The resulting asphalt blend data is shown in Table 14.

Table 14. BioCentury Research Farm asphalt formulation

Binder ID	Formulation	RAP	PG	Delta Tc	Mass Loss	MSCR 58c
	64-22S	N/A	64-22(66.2-23)	-0.4	0.19%	N/A
BCRF-F	64-22S + 2.11% SBS + 5.00% BIOMAG + 1.20% SESO + 0.13% Sulfur %bnb	N/A	64-28(69.6-30.5)	0.3	0.10%	59.63%, Jnr=0.4006
BCRF-FE	64-22S + 2.11% SBS + 5.00% BIOMAG + 1.20% SESO + 0.13% Sulfur %bnb	18% RAP	70-28(71.8-29.9)	0.1	N/A	48.58%, Jnr=0.3861

The final outcome achieved better performance than was expected, reaching a PG58-28V with the RAP binder included. Note that the additive doses were the same for the Altoona project and for the NCAT Test Track, but, here, the elastic recovery is significantly higher due to the master batching procedure. The low temperature was able to be reduced from -23.0°C to -29.9°C, even with the inclusion of RAP, while also improving the high temperature performance. This illustrates the unique benefit of using BioMAG and blending it in an integrated manner at the facility.

CHAPTER 6. MIX PERFORMANCE OF FIELD PRODUCED MIX FROM TEST SECTIONS

Asphalt Mixture Performance Characterization for Altoona and BioCentury Research Farm Projects

Dynamic modulus is a simple performance test that, to some extent, enables the prediction of rutting in asphalt mixtures (Brown et al. 2009, Goh et al. 2011). Dynamic modulus performance for asphalt mixtures is determined by applying sinusoidal loading and calculating the result by dividing peak-to-peak stress by peak-to-peak strain. Dynamic modulus represents an asphalt mixture’s resistance against deformation at low to high frequencies and low to high temperatures (Brown et al. 2009).

According to Li and Williams (2012), who developed a more practical method for performing dynamic modulus tests, five temperatures and six frequencies conventionally used for performing this test can be replaced with three test temperatures and nine frequencies. Such replacement saves resources and considerably decreases the testing duration. Therefore, due to the mentioned advantages of this method, all the dynamic modulus tests were performed at three temperatures (4°C, 21°C, and 37°C) and nine frequencies (25 Hz, 20 Hz, 10 Hz, 5 Hz, 2 Hz, 1 Hz, 0.5 Hz, 0.2 Hz, and 0.1 Hz). Before applying the frequency sweeps, the specimens were conditioned for at least three hours at each test temperature to reach thermal equilibrium (Arabzadeh and Guler 2019).

Dynamic modulus and phase angle master curves for asphalt-based materials can be constructed using many different methods (Yusoff et al. 2011). For example, a sigmoidal function (Equation 2) as developed by Pellinen and Witczak has been used for the prediction of dynamic modulus values of asphalt-based materials.

$$\log(|E^*|) = \delta + \frac{\alpha}{1+e^{\beta+\gamma\log\left(\frac{1}{f_r}\right)}} \qquad (2)$$

where: $|E^*|$ is dynamic modulus in MPa, δ is minimum modulus value in MPA, $\delta + \alpha$ is maximum modulus value in MPa, β and γ are parameters describing the sigmoidal function shape, and f_r is reduced frequency in Hz at the reference test temperature (e.g., 21°C in this research).

Podolsky et al. (2018a) recently proposed a new model, Equation 3, that can determine the phase angle master curves with high accuracy. This equation is an enhanced version of the models developed by Booji and Thoone (Booij and Thoone 1982) and Yang and You (2015).

$$\delta(f_r) \approx c\frac{\pi}{2}\,\frac{\alpha\gamma}{\left(1+e^{\beta-\gamma\log f_r}\right)^x}\,e^{(\beta-\gamma\log f_r)} \qquad (3)$$

where: $\delta(f_r)$ is the phase angle in radians and C and X are parameters introduced to the already existing models (Booij and Thoone 1982, Yang and You 2015) by Podolsky et al. (2018a). Based on the findings of Podolsky et al. (2018a), the shape parameters (α, β, γ, and δ) and the C and X parameters were determined through the minimization of square errors calculated for the predicted and measured values of log $|E^*|$ and δ.

The dynamic modulus test was performed on both the control and BioMAG asphalt mixtures for the Altoona project to determine the influence of the BioMAG asphalt binder in changing the values of the phase angle and dynamic modulus. The dynamic modulus test was not conducted on the mixture obtained from the BioCentury Research Farm project, as the mixture for this project was used for paving a parking lot where no considerable volume of traffic was expected.

After performing dynamic modulus tests on the Altoona mixtures, the specimens were subjected to a push-pull fatigue test to evaluate the traffic load-associated fatigue cracking resistance. For the push-pull fatigue test, the specimens were cut from both ends to achieve a height of 130 ±5 mm, and then glued to the loading platens (AASHTO TP 107-18). The testing temperature selected for performing the fatigue test was around 21°C. A fingerprint test was run on each specimen to determine and maintain the machine compliance factor, a unitless number that had to be maintained between 5 and 15. The target on-specimen strains selected for this test ranged from 250 to 500µƐ. To achieve these levels of strain, a universal testing machine (UTM) applied a haversine wave loading at a frequency of 10 Hz while using feedback loops of the linear variable deformation transducer (LVDT) deformations to remain within the desired strain range. Measuring the change in length of the actuator LVDT, rather than the LVDTs mounted on the specimens, was the reason for maintaining the machine compliance factor between 5 and 15 for each push-pull fatigue test (Aurangzeb et al. 2012).

The dynamic modulus and phase angle data, together with data acquired from the push-pull test, were used with the Beta version of the FlexMAT program that was under development by the asphalt research team of North Carolina State University for the Federal Highway Administration (FHWA). This program enabled the development of pseudostiffness (C) versus damage parameter (S) curves. To determine the fatigue performance of the Altoona mixtures procured from an asphalt plant, the relationship between the C and S values was modeled using Equation 4.

$$C = 1 - C_{11}S^{C_{12}} \tag{4}$$

where: C_{11} and C_{12} are the coefficients of the model. It is known that the relationship between the C and S is representative of a fundamental material property as it is independent of the testing temperature, loading mode, and loading amplitude (Etheridge et al. 2019).

The fatigue life, represented as loading cycles to failure (N_f), of each mixture type at each strain level was calculated based on 50% reduction in the C value, so that that the number of cycles to failure at each strain level (ε_0) could be predicted using Equation 5.

$$N_f = K_1\left(\frac{1}{\varepsilon_0}\right)^{K_2} \tag{5}$$

where: K_1 and K_2 are the material constants representing the intercept and slope of the equation, respectively (Hafeez et al. 2013).

The Hamburg wheel tracking (HWT) test is a loaded wheel test that has been used to evaluate rutting and moisture stripping resistance of asphalt mixtures since the 1970s (Asphalt Institute 2014). This test can be conducted in dry and wet conditions. In this research, following AASHTO T 324 -16, the test was performed in the wet condition to evaluate the influence of the BioMAG binder on resistance to both types of mentioned distress, i.e., rutting and moisture stripping. The data obtained from the HWT test were then plotted to determine the rutting slopes, stripping slopes, and stripping inflection points (as included in Figure 22 later in this chapter).

The disc-shaped compact tension (DCT) test has been used as a test method for characterizing the thermal cracking resistance of asphalt mixtures (Wagoner et al. 2005). The test is conducted according to ASTM D7317-13 and is performed under a displacement-controlled tensile loading mode, which causes propagation of cracks in the ligament area of a notched asphalt concrete specimen (Wagoner et al. 2005) . The crack propagation quantified through measuring the crack mouth opening displacement (CMOD) is recorded during the test (Wagoner et al. 2005).

In this study, the DCT test was performed at -18°C, since the low temperature grade of the asphalt binder used was -28°C. Fracture energy (previous Equation 4) and peak load, the parameters calculated for the DCT test, were obtained through the analysis of load-CMOD data acquired from this test. It is believed that the presence of RAP decreases the fracture energy (Behnia et al. 2011). Therefore, to evaluate the influence of the BioMAG asphalt binder, the fracture energies of the control and BioMAG mixtures were calculated and then compared.

Evaluation of Asphalt Mixtures' Master Curves for the Altoona Project

The master curves constructed for asphalt mixtures at a reference temperature of 21°C are presented in Figure 20. Master curves constructed for asphalt mixture specimens fabricated at 7% air void content: (a) phase angle and (b) dynamic modulus

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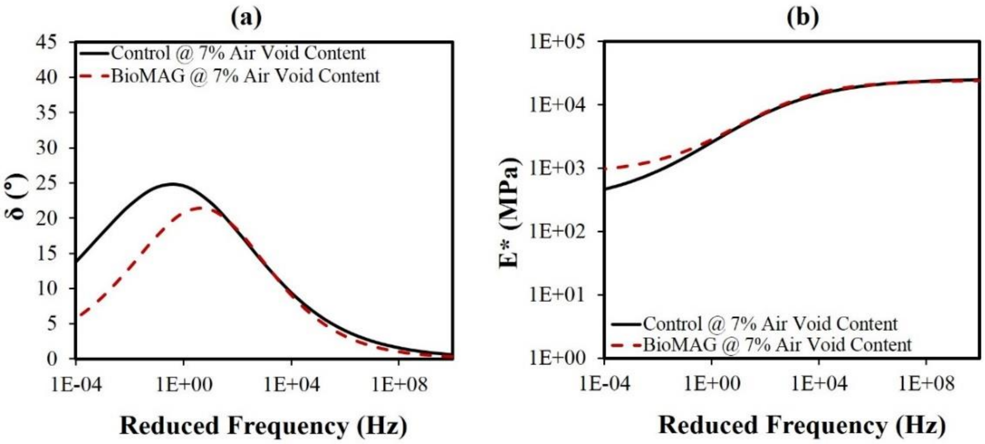

Figure 20. Master curves constructed for asphalt mixture specimens fabricated at 7% air void content: (a) phase angle and (b) dynamic modulus

Greater phase angle values, or higher relaxation capability, is indicative of better resistance of an asphalt mixture against cracking (Brown et al. 2009). Greater dynamic modulus values are indicative of higher resistance of a mixture to deformation because of its higher stiffness (Brown et al. 2009). As can be seen in the previous Figure 20a, at lower frequencies, or higher temperatures, the phase angle values of the BioMAG asphalt mixture become smaller than those of the control asphalt mixture. Such behavior can be attributed to the presence of PAEHOSO, as this polymer-based additive increases the resistance of an asphalt mixture to deformation (e.g., rutting) at higher temperatures by producing a polymer network consisting of large polymers. It is postulated that the SESO, by decreasing and de-aggregating the asphaltene particle size (Podolsky et al. 2018b), allows an increased penetration of BioMAG asphalt binder into the permeable voids of aggregates and therefore provides a stronger bond at the aggregate-asphalt binder interface resulting in smaller deformations and smaller phase angle values at higher temperatures. However, adhesion tests should be performed to verify this hypothesis.

In an asphalt mixture, the inflection point (e.g., the peak of the phase angle master curve [Sias et al. 2013]) is indicative of transition from a more viscous to a more elastic behavior. Aggregates are responsible for the elastic behavior and asphalt binder is responsible for the viscous behavior (Sias et al. 2013). As can be seen in Figure 20a, the peak of the phase angle curve for the BioMAG asphalt mixture is shifted to higher frequencies. Such a shift is indicative of an increase in the viscous behavior of the asphalt binder that is due to presence of the SESO.

The presence of SESO and PAEHOSO also increases the dynamic moduli at higher temperatures, which is again an indication of increased resistance to rutting (Figure 20b). However, at lower temperatures, or higher frequencies, the modification of the asphalt binder with PAEHOSO and SESO does not result in a considerable change (see Figure 20). Therefore, to draw more a more robust conclusion regarding the behavior of these asphalt mixtures at higher frequencies, it would be more appropriate to test the low-temperature cracking properties of the control and BioMAG asphalt mixtures.

Evaluation of Low Fatigue Cracking Resistance of Altoona Mixtures

The modification of the asphalt binder with the BioMAG (or the combination of PAEHOSO and SESO) for the Altoona project resulted in the improvement of fatigue resistance in the asphalt mixtures. Figure 21 shows an example of reduction in modulus of asphalt mixtures with respect to number of cycles at a constant amplitude strain mode of 350 μƐ.

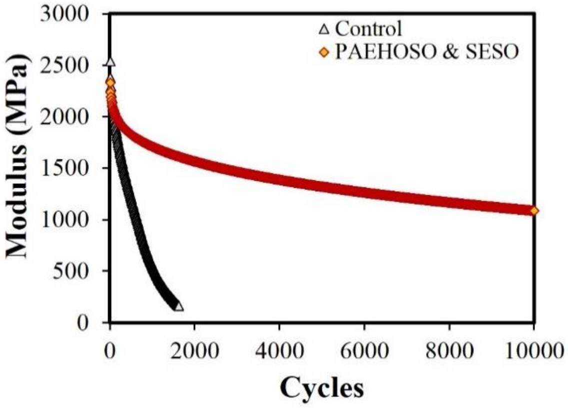

Figure 21. Example of reduction in moduli with respect to number of cycles

Both of the curves shown are representative of the existence of uniform strain fields within the specimens. According to Lundstrom et al. (2004), who conducted a study on the influence of asphalt mixture stiffness on fatigue failure, an S-shaped curve indicates the non-uniformity of the strain field formed within a specimen. Therefore, it would be fair to state that the test setup used for evaluating the fatigue performance was selected, assembled, and computer-controlled appropriately.

Figure 22 presents the damage characteristic curves obtained based on the viscoelastic continuum damage (VECD) theory.

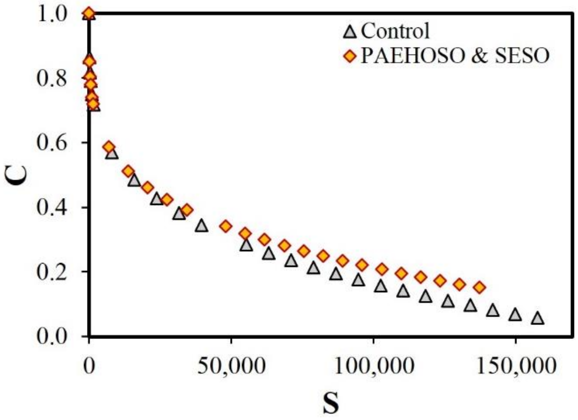

Figure 22. Fatigue behavior based on viscoelastic continuum damage theories

The C values calculated for the Altoona mixture are greater than that of the control. This can be explained through the increased elastic recovery of the asphalt binder because of the presence of PAEHOSO. Although the asphalt binder modified for the Altoona project also contained SESO, the dominant influence of PAEHOSO dwarfed the influence of SESO on reducing the C values.

Figure 23 shows the relationship between the microstrain level and fatigue life (N_f) calculated based on 50% reduction in pseudostiffness.

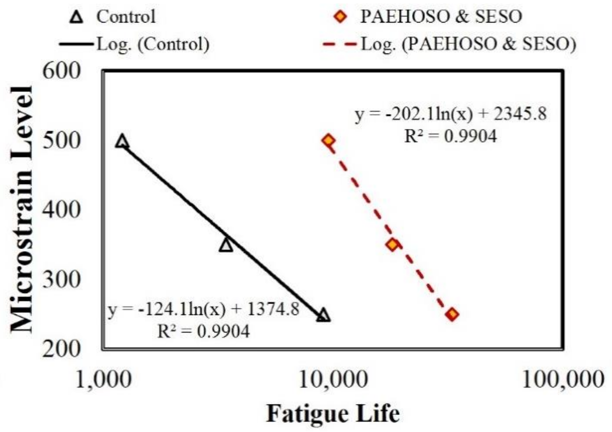

Figure 23. Relationship between strain level and fatigue life

The results obtained by performing the fatigue test on the Altoona mixtures indicate a tremendous improvement in fatigue performance. In addition to the positive effect of SESO, the PAEHOSO polymer, being a thermoplastic elastomer, helped with increasing fatigue resistance. Many other researchers, including Saboo et al. (2018), have proven that the modification of asphalt binders with elastomers increases their fatigue life. According to Figure 23, at a strain level of350 μℇ, for example, the modification of the asphalt binder with the SESO and PAEHOSO increases the N_f from 3,430 to 18,100 cycles, and that is an increase of about 430% in the fatigue life.

Evaluation of Low Temperature Cracking Resistance of Altoona Mixtures

RAP, due to having an aged/oxidized binder, causes reduction in fracture energy as well as brittleness in asphalt mixtures (Cong et al. 2016). It is known that an asphalt mixture with lower fracture energy exhibits more transverse (low-temperature) cracking (Dave et al. 2016). Figure 24 illustrates the behavior of two specimen types evaluated for resistance against low temperature cracking using DCT.

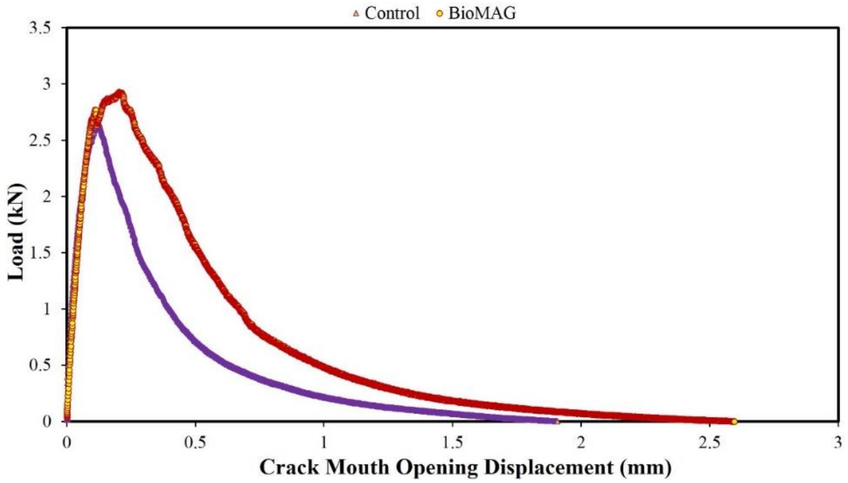

Figure 24. Data obtained from DCT test and plotted for two different specimen types

Also, to provide more information, all of the data obtained from this test are summarized and presented in Table 15.

Table 15. Fracture energies and peak loads calculated from DCT test results

Specimen Type	Fracture Energy (J/m^2)		Maximum Load (kN)	
	Avg.	SE	Avg.	SE
Control	355	26	2.73	0.03
BioMAG	468	28	2.94	0.16

Avg = average, SE = standard error

As is evident, the presence of SESO restores the relaxation capability of the BioMAG asphalt mixture that can be proved by the area increased under the curve (see Figure 24) due to presence of SESO or the greater value of fracture energy (see Table 15).

These results are in accordance with the findings of Huang et al. (2015) who proved the enhancement in thermal properties of RAP binders modified with a vegetable-oil based rejuvenator. According to Figure 24 and Table 15, there is not a significant difference between the peak loads of the control and BioMAG specimens. This lack of difference can be attributed to the fast-loading rate used in the DCT test (Li et al. 2008). However, the significant increased displacement of the BioMAG asphalt mixtures is proof for the increased ductility in this mixture.

According to a national pooled fund study, a part of which was conducted by researchers at Iowa State University, the passing criterion for low-temperature cracking resistance of an asphalt mixture is a minimum fracture value of 400 J/m^2 (Marasteanu et al. 2012). Therefore, the mixture containing 20% RAP, and not modified with PAEHOSO and SESO, would not be acceptable.

Evaluation of Asphalt Mixtures' Resistance Against Moisture Damage and Rutting

The slopes of the lines drawn on the linear regions of HWT data (see Figure 25) are indicative of rutting and stripping behavior of an asphalt mixture.

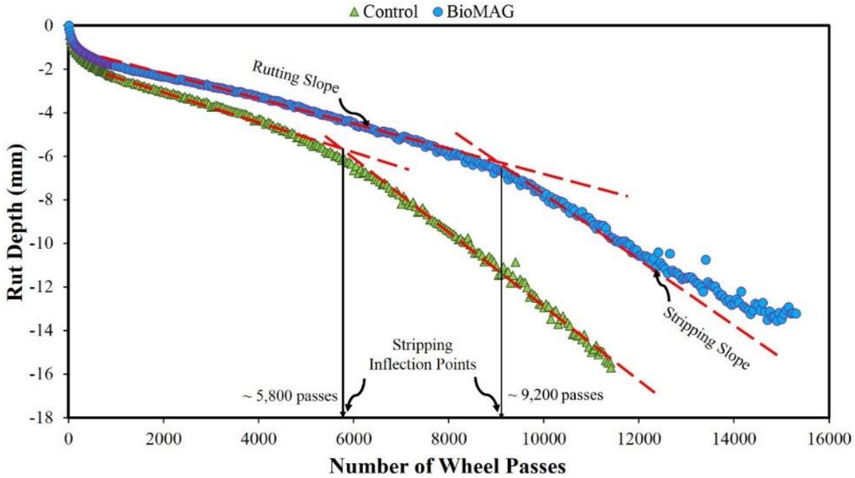

Figure 25. Data obtained from HWT test, analyzed and plotted for two different specimen types

The steeper (more negative) these slopes, the less resistance of an asphalt mixture to rutting and moisture damage. Therefore, the asphalt mixture containing no PAEHOSO and SESO is more prone to rutting and stripping (see Figure 25 and Table 16).

Table 16. Rutting and stripping test results

Specimen Type	Rutting Slope		Stripping Slope		Stripping Inflection Point (No. of Passes)	
	Avg.	SE	Avg.	SE	Avg.	SE
Control	- 0.56	0.03	-3.50	0.23	6,391	626
BioMAG	- 0.28	0.04	-2.17	0.16	10,010	919

Avg = average, SE = standard error

The superior elastic recovery of the asphalt binder used in the BioMAG asphalt mixture can justify the enhanced resistance to rutting and is all due to the presence of PAEHOSO.

The enhanced moisture resistance of the BioMAG asphalt mixture can be attributed to the decreased work of adhesion between water and the asphalt binder due to the presence of PAEHOSO and SESO, which are different types of epoxidized soybean oil. The epoxidized soybean oils have been successfully used as a hydrophobicity enhancement agent for increasing the water repellency of bio-based and polymer-based materials (Zhang et al. 2010). Therefore, due to such enhanced hydrophobicity, there would be a lower tendency for water to remain at the aggregate-binder interface, resulting in the mitigation of moisture damage by increasing the adhesion of the asphalt binder to aggregates in BioMAG asphalt mixtures.

The superior performance of the BioMAG asphalt mixture can be indicative of the appropriateness of the amount of PAEHOSO and SESO used for the modification of the asphalt binder. Otherwise, overdosing an asphalt mixture with rejuvenators increases the stripping potential (Zaumanis et al. 2013).

CHAPTER 7. CONCLUSIONS AND FUTURE WORK

The PS-PAESO diblock copolymers at various polystyrene MWs and polystyrene contents were successfully produced in the laboratory using the RAFT polymerization technique. The H-NMR and HT-GPC tests were conducted to identify the percentage of PS in the block copolymer and MW of the polymer, respectively. A fluorescence optical microscope was used to examine the morphology of the 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 produced an increased elastic response with better compatibility between the polymer and the neat asphalt binder.

To investigate how PS-PAESO polymers affected the performance grading and rheological properties of the neat asphalt binder, 17 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 bio-advantaged polymer has the ability to improve rutting resistance for the neat asphalt binder more than the SB-modified binder does. However, bio-advantaged polymers did not substantially improve resistance to thermal cracking, due to the fact that their critical low temperatures increased. Eleven of the 17 bio-advantaged-modified blends widened the neat asphalt binder’s grade range and had ranges similar to that of the SB polymer-modified binders, which indicated that the bio-advantaged polymer was capable of improving (widening the continuous grade range) and 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 MW) in PS-PAESO polymers had a significant effect on PS-PAESO-modified binder grading results. According to the statistical analysis, the chemical reaction length of synthesizing PS-PAESO was not a significant factor that affected the performance 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 MW 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 G* master curves, δ master curves, and black space diagrams for analysis of the rheological properties. According to the G* and δ master curves, the best performing bio-advantaged polymer-modified binder in terms of critical high temperature showed a trend of increasing G* and decreasing δ 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. Through RSM several formulations of PS-PAESO were optimized and one of the optimized formulations was used to verify the RSM model equations.

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

At this point in time, demonstration projects were about to take place as the pilot plant was operational. However, due to costs and the idea that most mix designs contain RAP, the biopolymer was now formulated as BioMAG, which is a 50/50 combination of PAEHOSO and SESO, where SESO is a rejuvenator and PAEHOSO is the polymer to account for the stiffening of the mix due to RAP inclusion. In this form, the bioiolymer/rejuvenator combination is in liquid form and not pelletized, so it is much easier and efficient to blend into a binder.

From this material, one test section was paved at NCAT in Alabama in 2018 and two demonstration projects were paved in Iowa (at the BioCentury Research Farm west of Ames and in Altoona) in Summer and Fall of 2019. The BioMAG test section at NCAT has performed well against rutting and cracking. Additional data were still being collected from the test track as well as from the two demonstration projects in Iowa.

From the demonstration project in Altoona, asphalt binder and loose asphalt mixture samples were procured from the terminal and the plant to perform quality control, investigate the additional influence of BioMAG on mitigating the undesired effects of RAP, and predict the behavior of the BioMAG mixture in the field.

From mix and binder characterization, BioMAG was found to remedy the influence of RAP and created a comparable binder to that of the control binder, PG 58-28H with no RAP, based on multiple stress creep recovery (MSCR) and low-temperature performance grading using the BBR.

Low-temperature mix results showed that the BioMAG could have superior low-temperature cracking resistance compared to that of the control mix. This was shown by a 25% increase in the fracture energy due to the presence of PAEHOSO and SESO.

The BioMAG mixtures, when tested with the HWT device, resulted in better rutting resistance, e.g., the rutting slopes of the BioMAG asphalt mixtures were almost half of those obtained from the control mixtures.

The BioMAG asphalt binder enhanced the stripping resistance of the mixture. This was shown by the increase of the stripping slope (from -3.5 to -2.17) and the stripping inflection point (from 6,391 to 10,010 cycles), up to 38% and 36%, respectively.

Much was learned from the execution of the demonstration projects, and many useful industry connections were made with contractors and terminal suppliers.

It was shown that, with ideal blending conditions, the asphalt binder can reach very high levels of performance by improving the elastic behavior and decreasing the thermal cracking potential at the same time. Even under less-than-ideal blending conditions, the BioMAG blends were able to meet the goals of the formulation.

In the future, additional demonstration projects will be completed with even greater amounts of RAP, and the projects will be performed in more diverse climates and conditions throughout the nation.

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