

IDEA

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Development of Renewable Polymers for Use in Asphalt Pavements

Final Report for
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Development of Renewable Polymers for Use in Asphalt Pavements

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EXECUTIVE SUMMARY

This report summarized findings from a National Cooperative Highway Research Program (NCHRP) Innovations Deserving Exploratory Analysis (IDEA) study 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 oils have been considered as important renewable resources, which 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 the construction at the National Center for Asphalt Technology (NCAT) Test Track section.

BACKGROUND

The rheological properties of the asphalt binder have a significant impact on asphalt pavement performance (Lianget 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). In order 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 (Isacson and Lu 1995). Due to the environmental 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 (Habib and Bajpai 2011, Salih et al. 2015, Grishchuk and Karger-Kocsis 2011). They can be polymerized into polymers with flexible and rubbery properties to replace the petroleum-derived butadiene in styrenic copolymers (Yan et al. 2016).

RESEARCH METHODOLOGY

The controlled radical polymerization chemistries such as atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT) were used in the presence of monomer acrylated epoxidized soybean oil (AESO) and styrene to synthesize the poly (Styrene-Acrylated Epoxidized Soybean Oil) (PS-PAESO) block polymers.

The modified asphalt blends were prepared by using biopolymers (PS-PAESO) and tested by following the Superior Performing Asphalt Pavements (Superpave) performance graded asphalt binder specifications. The primary tests performed on the modified asphalt blends were as follows:

- Dynamic shear rheometer (DSR) high temperature performance grades tests on unaged asphalt blends and the rolling thin-film oven (RTFO) tests on short-term aged modified asphalt blends
- RTFO short-term aging process on unaged modified asphalt blends
- Pressure aging vessel (PAV) long-term aging for the RTFO short-term aged residuals
- Bending beam rheometer (BBR) low temperature performance tests on the PAV long-term aging residuals

The mass losses of modified asphalt blends after the RTFO short-term aging were calculated. The master curves and the black diagrams were developed for both unaged and the RTFO short-term aged modified blends.

A single-factor analysis of variance (ANOVA) model was performed to assess the factors that could affect the rheological performance of the biopolymer modified blends. The least square means comparisons were performed using Tukey's honestly significant differences (HSD) test with $\alpha=0.05$. Response surface modeling was developed with the major factors and their interaction effects used to optimize the key influencing parameters for creating the prediction models. The JMP (version: Pro 12) statistical software was the computer program used for performing the analysis of variance and response surfacing modeling.

KEY FINDINGS

By evaluating the shear blending results of both unaged and the RTFO short-term aged modified asphalt blends, the biopolymers helped increase the critical high temperature of the neat asphalt binder to 0.3 to 7.0°C depending on the individual biopolymer trial blend compared to the neat asphalt binder. Furthermore, the majority of biopolymers used helped widen the continuous performance grade ranges and reduce the temperature susceptibility of the base asphalt binder. From the rheological test results, the biopolymers helped improve the rutting resistance and make the base asphalt binder more elastic in nature. In addition, the PS-PAESO with lower styrene content acted as a better biopolymer based on its benefits of critical high temperature.

IMPLEMENTATION READINESS AND BENEFITS

In the pavement area, there is a substantial increase in maintenance and rehabilitation applications that use polymer modified asphalt binders such as asphalt interlayers, thin lift overlays, and ultrathin overlays. The formulation of bio-based homopolymers and thermoplastic elastomers from vegetable oils (e.g., soybean oil) can be used as an economical and more sustainable alternative to styrene-butadiene block copolymers and rubbers with equal or better performance for asphalt pavement applications.

FUTURE WORK

Future research will focus on the field performance evaluation of the test track section that was paved with the biopolymer modified binder mixture. The asphalt binder and mixture samples collected from the field will be used for subsequent asphalt mixture performance testing and analysis for properties such as the dynamic modulus, flow number (F_N), Hamburg Steel Wheel (HSW), beam fatigue, and Disk-shaped Compact Tension (DCT) tests. Based on the evaluation of the produced asphalt mixture, the biopolymer formulation will be further optimized to achieve better performance in asphalt binders for future pavement applications.

Furthermore, the demonstration plot at the newly constructed NACT Test Track section will be closely monitored. After a two-year accelerated loading period, the field performance of the biopolymer modified asphalt mixture will be evaluated and compared to the control test track section that used the commercial counterpart. This will provide an overall evaluation of biopolymer application in asphalt pavement construction.

INTRODUCTION AND BACKGROUND

Flexible pavement designs for high traffic volume and extreme weather conditions must meet special requirements for asphalt binder rheological properties (Lianget al. 2016a). Since the rheological performance of asphalt binders relates directly to field performance, materials such as polymers were developed and used as modifiers in asphalt binders so asphalt mixes (consisting of the asphalt binder and aggregate/stone) could meet the needs of higher traffic volumes and extreme weather conditions (such as very high temperatures) (Chen et al. 2002, Liang et al. 2015, Moreno-Navarro et al. 2015). Polymers help modify asphalt rheological properties to improve performance against rutting, fatigue, and thermal susceptibility, while increasing adhesion between the asphalt binder and aggregate. Polymers also provide improved resistance to low temperature thermal cracking (Moreno-Navarro et al. 2015, Fernandes et al. 2008). Due to these advantages from polymer incorporation in asphalt binders, there is a substantial decrease in maintenance and rehabilitation applications needed. The increased use of polymer modified binders (PMBs) in the asphalt paving industry minimizes deterioration and increases in-service longevity of pavements (Pamplona et al. 2012, Isacsson and Lu 1995).

Polymers commonly used over the past few decades in the asphalt industry include thermoplastic elastomers (e.g., styrene-butadiene [SB], SBS, SBR, and styrene-isoprene-styrene [SIS]) and plastomers (e.g., polyethylene [PE], EVA, and polypropylene [PP]) (Chen et al. 2002, Lewandowski 1994, Yildirim 2007, Zhu et al. 2014). The earliest use of natural and synthetic polymers can be found in patents dating from 1843 (Yildirim 2007). A patent detailing the use of 1% latex by weight from the balata plant for an asphalt paving mixture was granted to Samuel Whiting in 1873. A French asphalt paving company constructed rubberized asphalt roads in 1902 (Lewandowski 1994). After World War II, PMBs attracted attention in European countries such as Britain and France. Test sections using PMBs were constructed in Britain and France and papers on the use of PMBs were published at Eurobitume conferences starting in 1978 (Isacsson and Lu 1995). In North America, polychloroprene latex was first used for bitumen modification in road paving in the 1950s (Yildirim 2007). In 1965, the first commercial SBS product was developed in the US (Legge 1987). During the following ten years, US departments of transportation (DOTs) in Utah, Kentucky, Alabama, Colorado, and Texas used PMBs in constructing test road sections. In their reports, the application of different polymers (e.g., SBS, SBR, SB, and EVA) in test road sections resulted in substantially improved rutting resistance, reduced fatigue cracking, and mitigated thermal cracking (Lewandowski 1994, Bahia et al. 1997, Harmelink 1992, Peterson and Anderson 1998).

Although there are benefits to using PMBs, economics and environmental concerns still play a major role in the selection of paving technology (Isacsson and Lu 1995, Zhu et al. 2014, Kowalski et al. 2016). The price of PMBs is higher than that of conventional neat asphalt binder on a per liquid ton basis, however, the long-term economic benefits of using PMBs cannot be ignored. To evaluate the overall long-term economic efficiency of PMB roadways, Buncher and Rosenberger (2005) investigated the field performance and economic costs of 84 pairs of PMB and unmodified hot-mix asphalt (HMA) roadways in the US and Canada by using life cycle cost analysis. According to their study, the initial cost of construction for a PMB roadway is approximately 2 to 6% higher than the cost of a conventional neat asphalt binder roadway. This difference in cost is offset by the reduction in maintenance costs (e.g., resurfacing and structural overlays) in the following 10 to 34 years. They found that PMB roadway maintenance costs are 19.9 to 62.1% lower than the maintenance costs for a conventional neat asphalt binder roadway over the same time span (Buncher and Rosenberger 2005). Their use of life-cycle cost analysis showed that for high volume facilities the total life-cycle cost saving from a PMB roadway is 6.5 to 15.5% lower than for a conventional neat asphalt binder roadway (Buncher and Rosenberger 2005). Along with the advantages of better resistance to distresses and extended service life, increased interest in

polymers for asphalt modification has also been observed in the research community and the paving industry (Von Quintus et al. 2007).

Among the wide variety of polymers used for modifying asphalt binders, thermoplastic elastomers (SB and SBS followed by SBR) have proved to be the most commonly used and most successful binder modification tools (Airey 2004, Fernandes et al. 2008, Wang et al. 2017). These thermoplastic elastomers with butadiene as the primary ingredient of making these polymers, which is known as petroleum-derived polymers because butadiene is a co-product in the production of ethylene from crude oil (Cascione et al. 2013). Global Business Intelligence Research reported that butadiene demand in the US was 1.9 million tons with about 330 kilotons imported from foreign producers in 2012 (Hydrocarbon Processing 2012). The report also predicted that the demand for butadiene will keep climbing and the amount of imports will hit approximately 530 kilotons by 2020. Butadiene is a co-product that is obtained from liquid feedstocks (i.e., crude oil) with ethylene production. Ever since the US shale gas boom occurred, gas feedstocks have become more dominant in the production of ethylene and do not yield butadiene as a co-product, thus decreasing the amount of butadiene produced in the US. This may make the US more dependent on butadiene imports (Williams et al. 2014). Due to the increased reliance on shale gas for producing ethylene, butadiene shortages may occur and cause price fluctuations of petroleum-derived polymers in the chemical industry (Bruijninx and Weckhuysen 2013). Because roadways are one of the largest applications of butadiene, butadiene shortages and price fluctuations of petroleum-derived polymers offer an opportunity for producing bio-derived and biobased polymers as alternatives in asphalt modification.

Bioderived polymers, also known as biobased and bioreplacement polymers, are produced by upgrading complex molecules from nature such as trees, plants, and animals to simple monomers that chemically match monomers derived from petroleum through synthetic biology and advanced catalysis (Duarte et al. 2012, Gosset 2009, Hernández et al. 2015). Biopolymers are polymers that are produced directly from biofeedstocks (e.g., corn or soybeans) as potential substitutes for petroleum-derived materials and can be synthesized to plastics through chemical polymerization techniques (Hernández et al. 2015). Instead of making the raw complex molecules into simple monomers, it is far more cost effective to use them directly in the production of biopolymers by polymerization (Hernández et al. 2015).

Vegetable oils (e.g., from linseed, corn, cottonseed, and soybean) are biodegradable, renewable, cost effective, and less toxic than crude oil, which makes them viable and important raw biomonomer resources to be chemically synthesized into biopolymers (Cascione et al. 2013, Williams et al. 2014). Vegetable oils are composed of triglyceride molecules that consist of three fatty acid chains and a glycerol backbone; therefore, with some chemical modifications they can be synthesized into a rubbery component to replace the petroleum-derived butadiene in block copolymers (Raquez et al. 2010, Hernández et al. 2015, Zhang et al. 2015). Non-food soybean oil is one of the most abundant vegetable oils in the US and was chosen to be the monomeric feedstock in this research. To improve the polymerization reactivity of the natural carbon-carbon double bonds in soybean oils, the epoxidation (ring opening) method was used to produce epoxidized soybean oil (ESO), followed by acrylation of ESO to yield acrylated epoxidized soybean oil (AESO) (Liu et al. 2015, Hernández et al. 2015). The biopolymer is an AB diblock copolymer that consists of hard, stiff polystyrene domains and soft, rubbery domains of PAESO (Williams et al. 2014, Hernández et al. 2015). The chemical structure of the polystyrene-acrylated epoxidized soybean oil (PS-PAESO) polymer shows similar mechanisms to SB polymers in FIGURE 1.

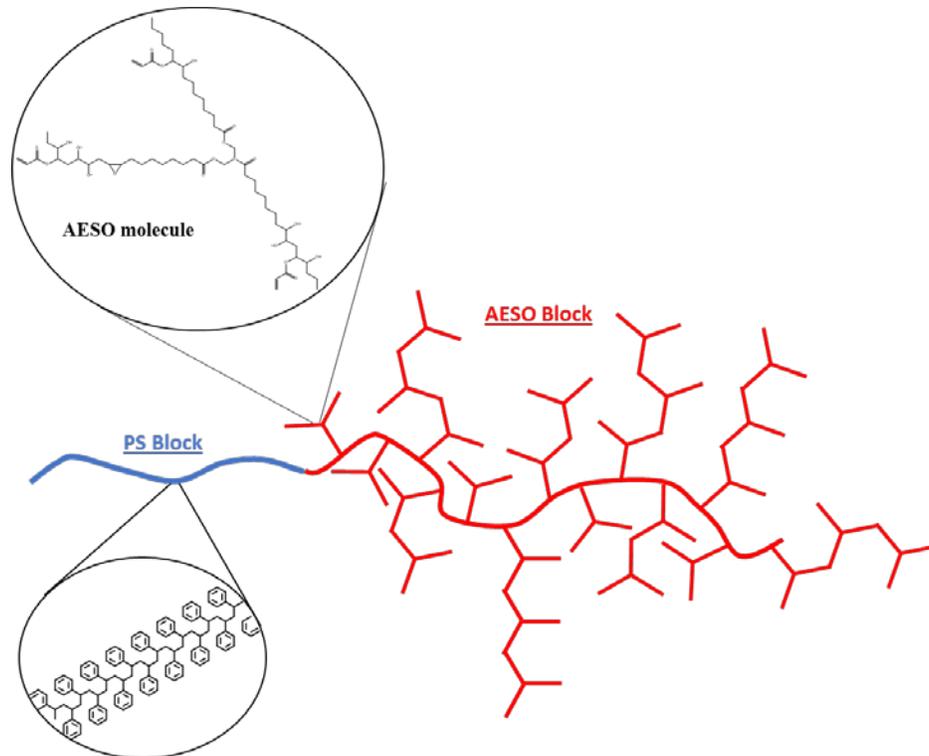


FIGURE 1 Biopolymer PS-PAESO chemical structure.

TECHNICAL OBJECTIVES

The overall objectives of this research are to develop and optimize the formulation of the biopolymer to maximize its performance in asphalt modification, and to ensure the successful large-scale production of biopolymer in the biopolymer pilot plant. Achieving both objectives will all for the development of biopolymer modified asphalt mixtures for field performance evaluation in the future.

The specific objectives of this research are listed below:

- Demonstrate how biopolymers are produced using non-food soybean oil.
- Evaluate how laboratory produced biopolymers perform rheologically in asphalt against commonly used petroleum-derived polymers.
- Optimize the formulation of the biopolymer based on the performance grading results that can modify neat asphalt binder from performance grade (PG) 52–34 to PG 64–28 for warm climate regions pavement applications.
- Verify the modification effects of the optimized biopolymers with proposed polystyrene parameters by running performance grade tests.
- Produce 600 gallons of biopolymer from the biopolymer pilot plant and have the biopolymer modified asphalt mixture paved in the NCAT Test Track in Alabama.

DEVELOPMENT OF BIOPOLYMERS 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 project.

MATERIALS USED FOR PRODUCTION

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

POLYMERIZATION TECHNIQUES

The controlled/living free radical polymerization (CFRP) conducted to chemically synthesize the biopolymers was reversible addition-fragmentation chain transfer (RAFT). Instead of using metal catalysts and initiators in traditional CFRP (i.e., atom transfer radical polymerization) that cannot be easily removed after polymers are formed, RAFT only requires organic chain transfer agents in the reaction, which is more environmentally friendly (Hernández et al. 2015, D'Agosto 2008). Moreover, the polymer structure and composition can be easily controlled and designed in RAFT and the desired molecular weight can be obtained in RAFT as well (Hernández et al. 2015, Williams et al. 2014). 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 (Cochran et al. 2014, Williams et al. 2014). The final product of PS-PAESO is presented in FIGURE 2a, and the biopolymer is shown in FIGURE 2b after cryogrinding under liquid nitrogen with smaller polymer particles for better blending compatibility.



FIGURE 2 (a) PS-PAESO polymer and (b) PS-PAESO polymer after cryogrinding.

MODIFIED BLENDS PREPARATION AND EXPERIMENTAL PLAN

The expected synthesized biopolymers (PS-PAESO) were laboratory produced at 1.25 MDa molecular weight (targeted molecular weight) of PS-PAESO with various PS molecular weights and contents at different lengths of reaction duration. The biopolymers were used to modify a soft neat asphalt binder PG 52-34 from a Canadian crude source. The PS-PAESO modified blends were prepared at a dosage of 3% by weight of total blends (Cascione et al. 2013, Williams et al. 2014). The modified blend codes with corresponding PS-PAESO biopolymer polystyrene parameters are shown in TABLE 1.

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 3000 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 (Cascione et al. 2013, Dorokhova et al. 2012).

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 3.

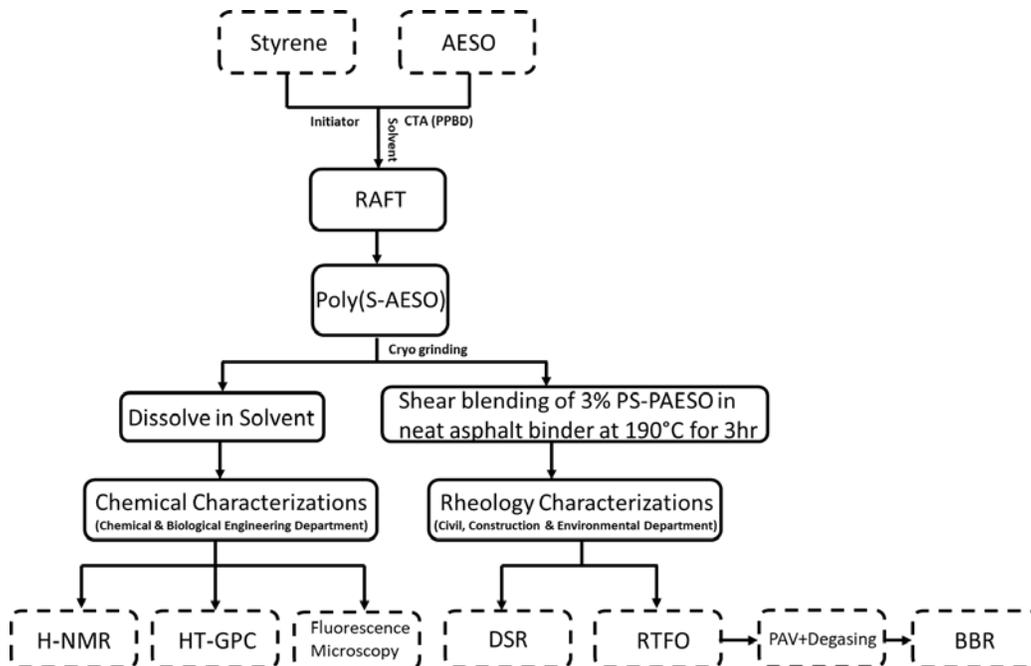


FIGURE 3 Overall test plan for biopolymer (PS-PAESO).

TABLE 1 Different Biopolymers with their Corresponding Modified Blend Codes Utilized for Shear Blending

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

CHARACTERIZATIONS OF BIOPOLYMER AND BIOPOLYMER MODIFIED ASPHALT BINDERS

Chemical Characterization of Biopolymer

Optimization of a block copolymer's formulation depends on the molecular weight parameter of the PS block and the PS contents used in the PS-PAESO diblock copolymer. The PS block composition will influence polymer phase solubility, morphology, and the molecular weight of the PAESO block for asphalt modification (Hernández et al. 2015). To chemically characterize the PS block for 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 PS-PAESO polymer is shown in FIGURE 4.

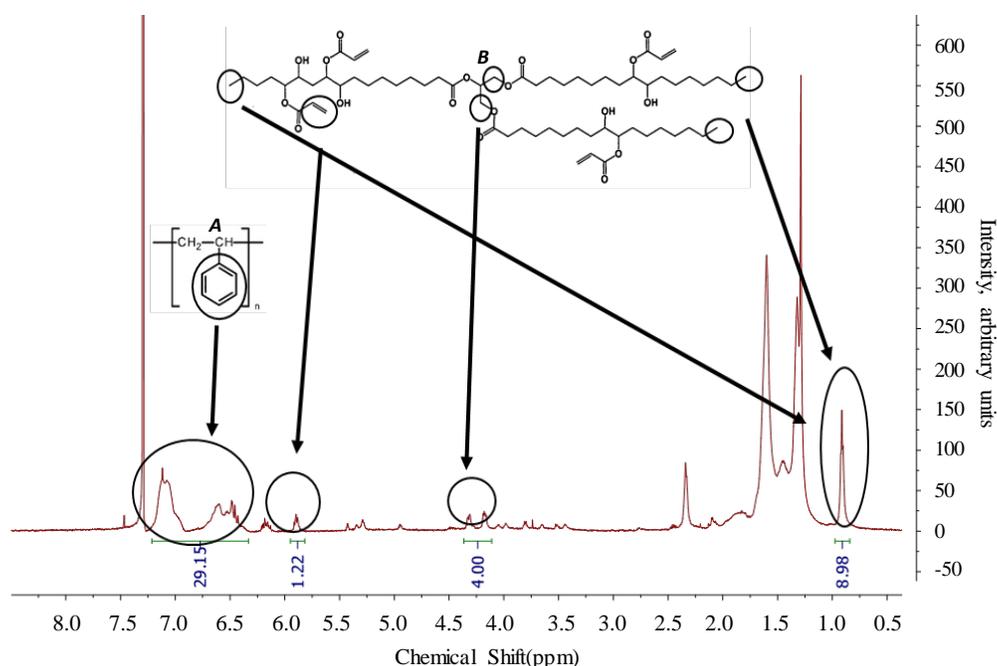


FIGURE 4 NMR spectrum graph of PS-PAESO polymer.

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 amount of hydrogens 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 molecular weight (MW) and polydispersity index (PDI) of the PS-PAESO polymer by using a Viscotek HT-GPC Module 350A equipped with a differential refractive index (RI) detector. The tests were conducted in tetrahydrofuran (THF) at 65°C. The HT-GPC, 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 5, the HT-GPC trace of the PS-PAESO polymers (used in asphalt modification in TABLE 1) shows the growth of PS-PAESO molecular weight according to time. The molecular weight was calculated using poly (methyl methacrylate) standards.

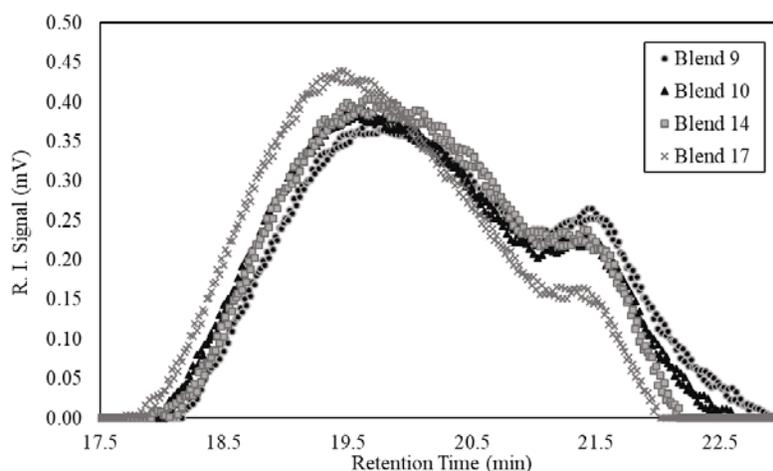


FIGURE 5 High temperature gel chromatography of PS and PS-PAESO polymers.

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

Even though the PS-PAESO (TABLE 1) were thought to have different molecular weights due to the chemical reaction length, all the diblock copolymers chosen for this study were entangled and achieved the minimum molecular weight needed to show entanglement in the asphalt binder. Therefore, they 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 molecular weight.

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. 2017). 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. 2007). A Leica DM4000 B LED fluorescence optical microscope with a Leica DFC7000-T digital camera was used on the glass film specimens to observe the morphology of 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. They present different morphological conditions due to the distribution and fineness of the polymer in the asphalt matrix (Nassar et al. 2012, Wen et al. 2002).

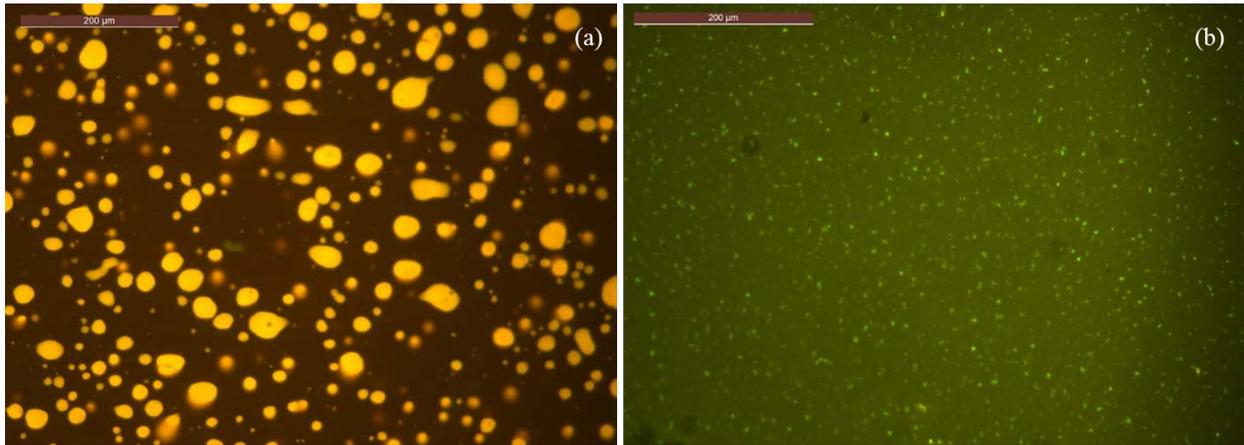


FIGURE 6 Fluorescence optical micrographs of polymer modified asphalt blends (magnification=100x, scale bar=200μm): (a) commercial Kraton D1118 (SB) polymer modified blends and (b) biopolymer modified blends-Blend 1.

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 (tur Rasool et al. 2017, Fernandes et al. 2008, Liang et al. 2016b, Alonso et al. 2010). The scattered yellow particles, in FIGURE 6 (a), 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. 2013). It also can 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. 2013). In FIGURE 6 (b), 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 (tur Rasool et al. 2017, Lu et al. 2011). 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 molecular weight do not affect the dispersion and compatibility of the polymer in asphalt binder. Uniform dispersion allows the polymers to be entangled with asphalt molecules, and produce an increased elastic response with better compatibility between the polymer and neat asphalt binder. This finding was also confirmed by rheological characterization.

RHEOLOGICAL CHARACTERIZATION OF BIOPOLYMER MODIFIED ASPHALT BINDERS

Asphalt is a viscoelastic material whose rheological properties are related to test temperature and rate of loading. Asphalt binder should be fluid enough at mixing temperatures to be easily pumped during construction, while still being resistant to permanent deformation and thermal cracking during the service life of a pavement (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 M320-10 with specimens tested in triplicate. The performance grade tests were performed at a wide range of temperatures and frequencies to determine the critical high and low temperatures that specify the temperature range of an asphalt binder for a proper paving environment.

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 T315-10) was performed on both unaged and short-term aged asphalt blends for the high temperature grade and BBR testing (ASTM D6648-08 and AASHTO T313-10) was conducted on long-term aged blends for the low temperature grade. The short-term laboratory aging of neat asphalt binder and the modified blends was performed by a rolling thin-film oven (RTFO) (ASTM D2872-12 and AASHTO T240-09). The long-term laboratory aging was performed on the asphalt binders in a pressure aging vessel (PAV) (ASTM D6521-13 and AASHTO R28-12) to expose the binders to high pressure and temperature (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 summarized above.

Dynamic Shear Rheometer (DSR)

The DSR 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 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 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 speed of 10 rad/s (1.59 Hz). The test is started at an initial testing temperature of 46.0°C, followed by subsequent testing in 6.0°C increments until a specimen fails. All unaged and RTFO short-term aged specimens were prepared by pouring heated asphalt binder into a 25mm diameter silicon mold and were tested using 25mm diameter parallel plates. The critical high temperature can be obtained when the $|G^*|/\sin(\delta)$ value of unaged specimen achieves 1.00 kPa and 2.20 kPa for unaged and RTFO short-term aged specimens, respectively. The critical high temperature test results of unaged and RTFO short-term aged blends are shown in TABLE 2.

TABLE 2 Critical High Temperatures of Unaged and RTFO Short-Term Aged Modified Asphalt Blends with Corresponding High Temperature Performance Grade

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

*The final critical high temperature of the asphalt blends

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

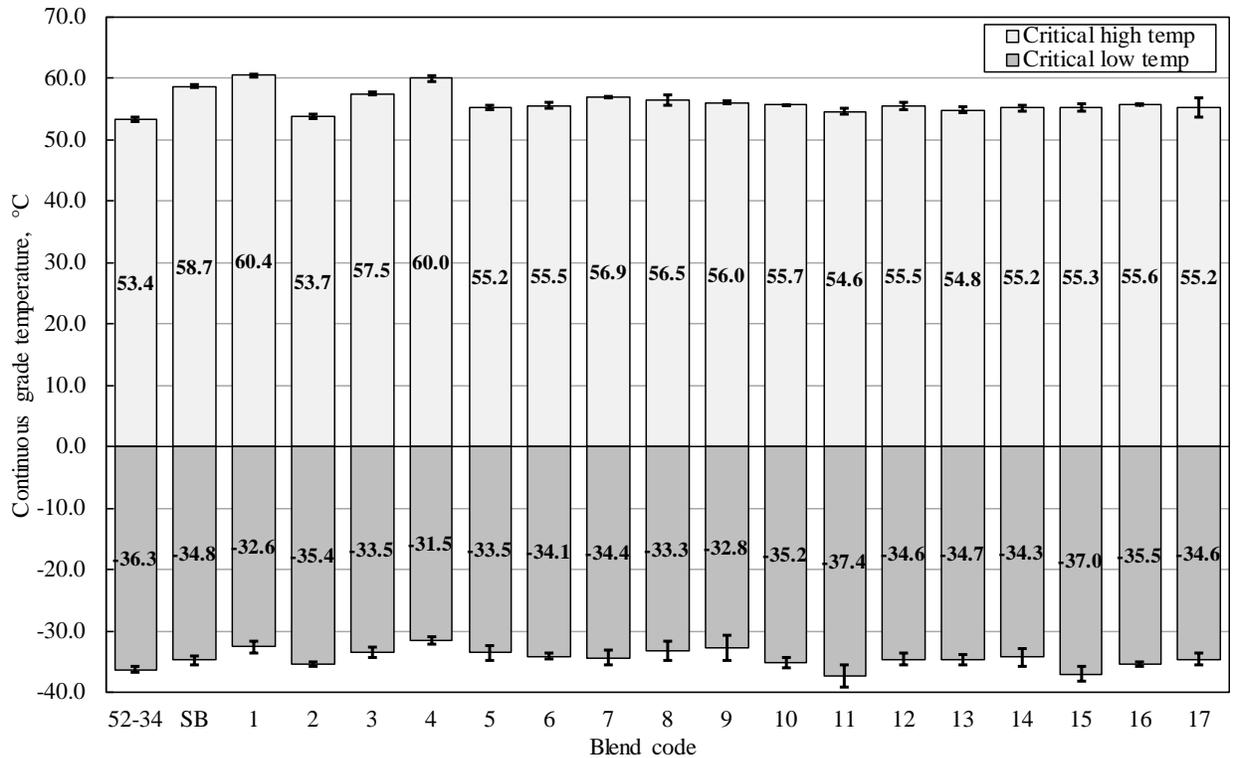


FIGURE 7 Continuous performance grade ranges of the polymer modified asphalt blends and the neat asphalt binder.

According to the DSR results, the neat asphalt binder has a critical high temperature of 53.4°C and was graded out at 52°C. Increased critical high temperature can be observed for all biopolymer modified asphalt binders when compared to the neat asphalt binder. Additionally, critical high temperatures of Blends 1, 3, 4, 7, 8, and 9 are very similar or higher than that of the SB polymer modified binder with the same grade of 58°C. The best performing biopolymers in terms of critical high temperature are shown in Blends 1 and 4, which contain PS with a lower molecular weight and improve the critical high temperature by 6.6°C and 7.0°C above the critical high temperature of the neat asphalt binder, respectively. Critical high temperatures of Blends 1 and 4 are approximately 1.8°C higher than the critical high temperature of the SB polymer modified binder.

Bending Beam Rheometer (BBR)

Low temperature thermal cracking occurs because the thermal stress applied on the asphalt mixture at low temperatures exceeds the asphalt mixture's tensile strength. Therefore, decreasing the low temperature susceptibility of the asphalt binder, lowering the asphalt binder stiffness, and enhancing the asphalt binder's ability to provide stress relaxation can be beneficial to minimize thermal cracking. The BBR is used to evaluate the low temperature properties of long-term aged polymer modified asphalt binders and the neat asphalt binder by measuring the center point deflection of the beam in 240 seconds. The stiffness (S) and creep rate (m-value) were determined at each loading time afterwards. The m-value is the rate of change for the creep stiffness with loading time, which indicates the stress relaxation of the asphalt binder. Based on the time-temperature superposition principle, the critical low temperature is determined where the m-value is equal to 0.300 and/or S is equal to 300 MPa when measured at 60 seconds. 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 FIGURE 7.

The low temperature grade of the neat asphalt was -34°C because its critical low temperature was -36.3°C (FIGURE 7 and TABLE 3).

TABLE 3 Critical Low Temperatures of Long-Term Aged Modified Asphalt Blends with Corresponding Low Temperature Performance Grade and their Continuous Grade Ranges

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

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 performance grade 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 summarized in TABLE 3 and FIGURE 7 show that 11 out 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 performance grade 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 to 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 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 8mm and 25mm diameter parallel plate specimens in a DSR. The range of the frequency sweep was between 1 to 100.0 rad/s at temperature stages of 20.0 to 30.0°C (8mm for lower temperatures at 5% strain rate) and 40.0 to 64.0°C (25mm for higher temperatures at 10% strain rate). The linear viscoelastic (LVE) regions of the materials were verified for the two plate sizes at the two temperatures ranges by performing strain sweep tests at the test temperatures using both plate sizes. For better evaluation of the materials resistance to shear deformation at different temperatures and frequencies, master curves and black diagrams were developed for the neat asphalt binder, the SB modified binder, and all 17 different formulated biopolymer modified binders. Blend 1 has 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 SB modified binder with the same low performance grade. 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 can be observed at high, intermediate, and low temperatures in FIGURE 8.

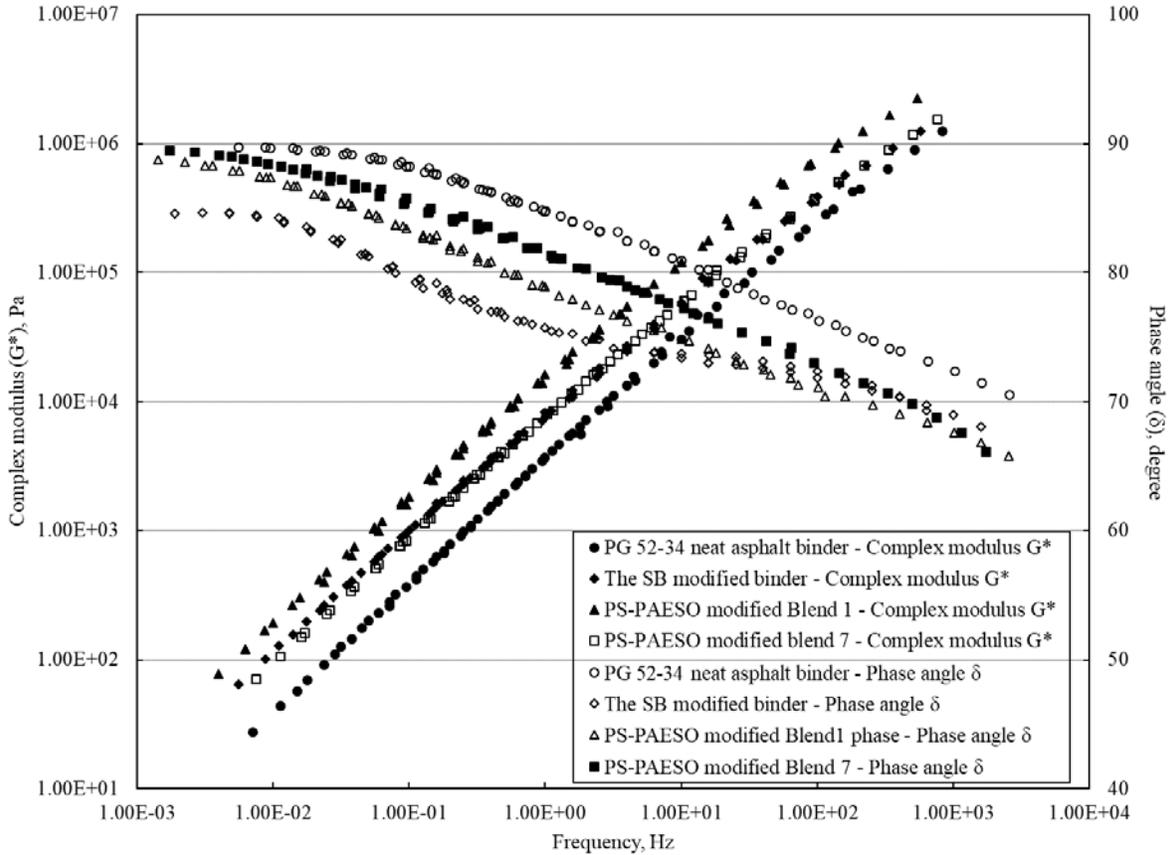


FIGURE 8 Master curves and δ master curves for the neat asphalt binder, SB modified binder, Blend 1, and Blend 7.

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 (FIGURE 9).

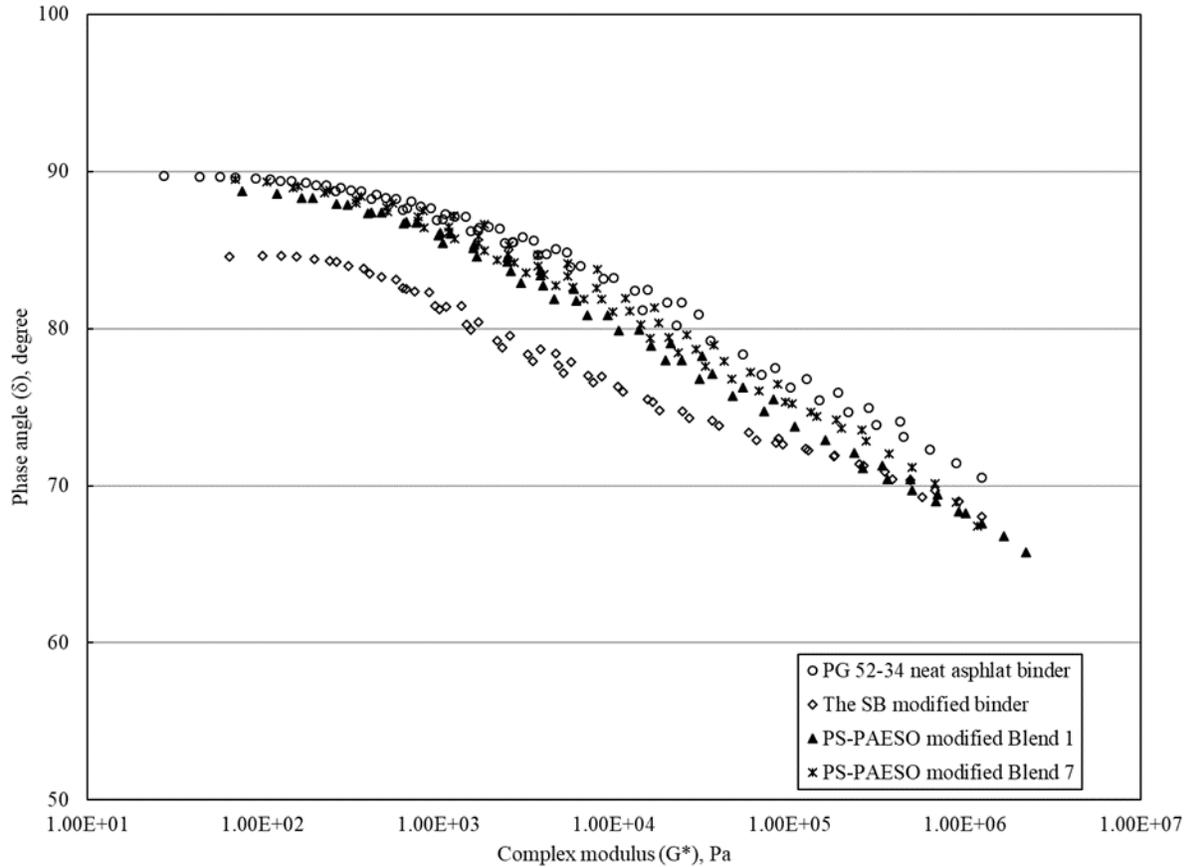


FIGURE 9 Black diagrams for the neat asphalt binder, SB modified binder, and Blend 1.

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 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 AND RESPONSE SURFACE MODELING

THE EFFECT OF VARIABLE PARAMETERS IN PS-PAESO ON THE PROPERTIES OF PMB/STATISTICAL ANALYSIS

To verify whether the chemical reaction length of PS-PAESO polymer has any 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 $G^*/\sin\delta$ at various test temperatures and for low temperature properties of stiffness and m-value at different test temperatures, respectively. The statistical analysis was conducted on blends that have the same PS content (i.e., 30%) and molecular weight (i.e., 30kDa) but different chemical reaction lengths. They are Blend 9 (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 $G^*/\sin\delta$, stiffness, and m-value. Additional factors examined within the ANOVA are chemical reaction length and test temperature.

The ANOVA table (TABLE 4) for high temperature property, $G^*/\sin\delta$, shows no statistically significant difference in the factor reaction length nor the interactive effect between length and test temperature.

TABLE 4 ANOVA for $G^*/\sin\delta$, Stiffness, and m-value with Factors of Chemical Reaction Length and Test Temperatures

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

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

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

TABLE 5 Tukey HSD Least Square Means Difference of $G^*/\sin\delta$, Stiffness, m-value for Reaction Length

Factor level of reaction length, hr	Least square mean	
$G^*/\sin(\delta)$ (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

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

All levels of reaction length are connected by the same letter, which means there is no significant difference among these levels based on a 95% confidence interval. No statistically significant difference in reaction length was 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 length of PS-PAESO does not affect the high and low temperature properties of the PS-PAESO modified blends.

The ANOVA on PS molecular weight and PS content were conducted on all 17 blends, because the chemical reaction length has been proved to have no effects on the high and low temperature properties of PS-PAESO modified blends. According to the ANOVA tables, two PS parameters were found to have significant effects on the high and low 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 higher molecular weight of 30kDa was considered to be significantly different from the other two lower molecular weights (i.e., 10 and 20 kDa) based on the Tukey HSD least square means difference results presented in TABLE 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

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

Therefore, it can be inferred that a lower PS content helps with high temperature performance, while a higher PS molecular weight 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 modelling (RSM) to optimize the formulation of the polymer. Thus, 17 PS-PAESO polymers with a target molecular weight of 1250 kg/mol consisting of PAESO with various polystyrene (PS) molecular weights and contents were produced. These PS-PAESO formulations were then used to modify the base binder at the same dosage, and subsequently the modified binders were put through a full binder investigation following ASTM D6373-15 and AASHTO 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 study (i.e., optimization of PS parameters molecular weight and content in PS-PAESO for better performing modified asphalt binders) can be achieved through the development of a new statistical approach using response surface modelling (RSM) that employs these binder performance test results. The secondary objective is to showcase that PS-PAESO can, when its formulation is optimized, modify a PG 52-34 base asphalt binder to a PG 64-28 polymer modified binder for warm climate regions pavement applications with a 3% polymer content dosage and perform equal and/or better than the commercial SB polymer in terms of critical high temperature and continuous grade range. Thus, the interaction effect of the independent variables (experimental factors such as polystyrene molecular weight, polystyrene content, and test temperature) on the test responses of the polymer modified asphalt binder's critical high and low temperatures (i.e., $G^*/\sin(\delta)$ for unaged and short-term aged blends, stiffness, and m-value) will be investigated. In order to assess the accuracy of the predicted equations obtained from RSM, the recommended PS parameters with predicted critical temperatures and verified grade results on the produced recommended PS-PAESO polymer will be presented. The overall research process is summarized in FIGURE 10.

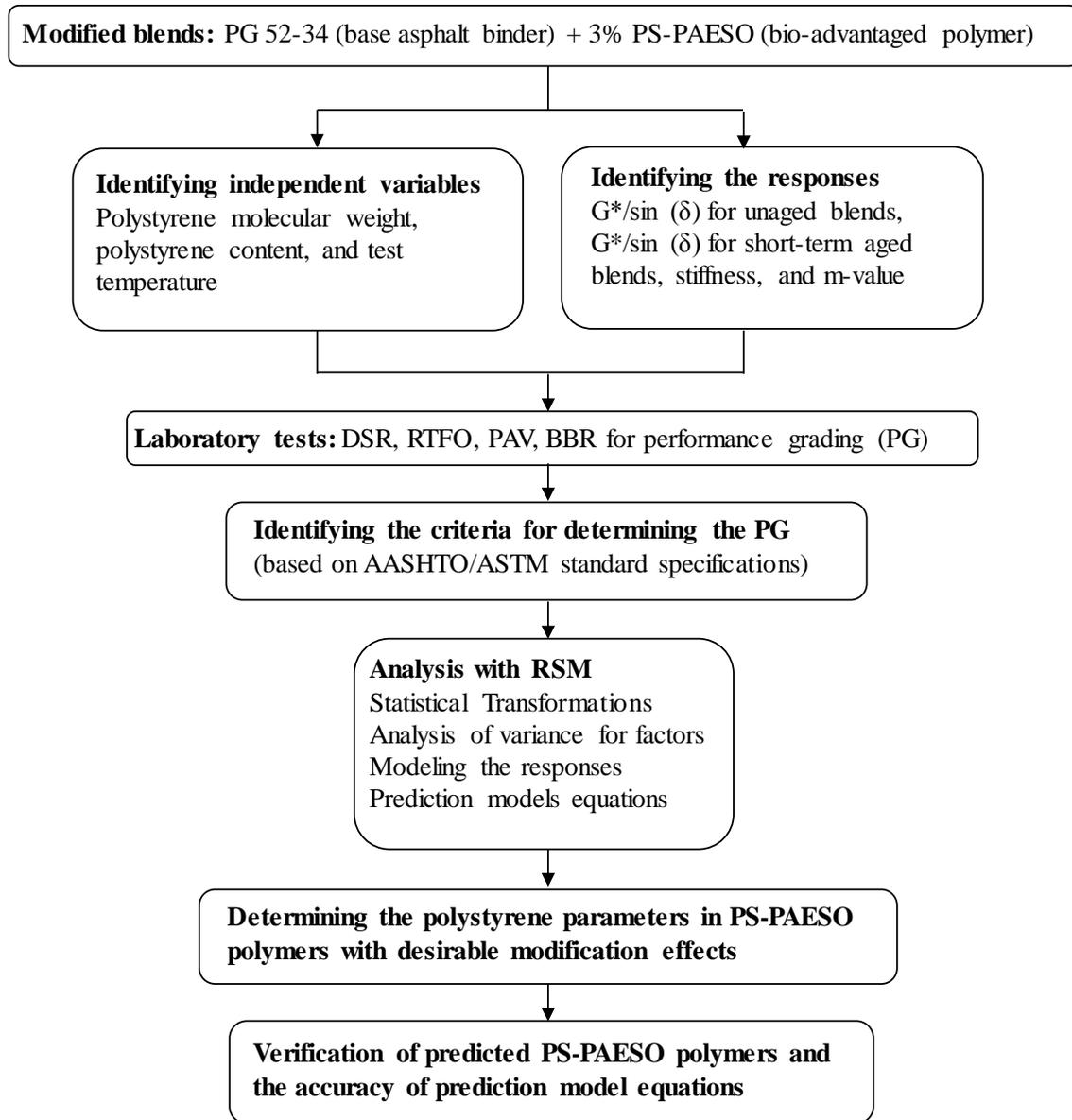


FIGURE 10 Overall optimization process.

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 molecular weight, 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 below.

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

where y is the response of the testing results which relates to x_1 , x_2 , and x_3 of the three major factors: polystyrene molecular weight (kg/mol), polystyrene content (%), and test temperature ($^{\circ}\text{C}$), respectively. β_0 is the intercept, $\beta_1 \dots \beta_{33}$ 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 $G^*/\sin(\delta)$ of unaged modified blends, $G^*/\sin(\delta)$ of RTFO short-term aged modified blends, and m-value and stiffness of PAV aged modified blends. The 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 with the rest of the variables until the finalized model was obtained using only statistically significant variables with a confidence level of 95%.

Four initial response surface models were developed with respect to four test responses, which are $G^*/\sin(\delta)$ with a limit of 1.0 kPa for unaged modified blends, $G^*/\sin(\delta)$ with a limit of 2.2 kPa for the RTFO short-term aged modified blends, and m-value and stiffness of 0.300 and 300 MPa for the PAV aged modified blends, respectively. The 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 meet the normal distribution and have R^2 values closest to 1.

Finalized prediction models for the high and low temperatures are summarized in TABLE 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 of 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 molecular weight of PS-PAESO biopolymers with recommended PS molecular weight and PS content that could modify the neat asphalt binder PG 52-34 to be PG 64-28 are tabulated in TABLE 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 performance grades, but also reduces the low temperature performance by one grade. The PS molecular weight does not have much effect on the neat binder's high temperature performance grade because polymers with a PS block that have molecular weights of 15, 20, 25, and 30 kDa at PS content of 5% have shown similar modification effects on critical high temperatures (TABLE 9). Even though PS molecular weight does not affect the critical high temperatures, it is important to note that there are minor effects of PS molecular weight on the low temperature side. In TABLE 9, it can be seen that the stiffness of the predicted blends decreases and the m-value increases as the molecular weight of PS increases from 15 to 30kDa at the same 5% PS content, which agrees with the findings in Section 4.2.1. Because the main objective of this research is to produce a polymer-modified asphalt binder with superior high temperature performance for warm climate pavement applications through use of the PS-PAESO biopolymer, a lower PS content was more of a priority in the formulation of the PS-PAESO according to the results presented.

Surface plots were developed to further examine the relationship between independent variables and responses by using the four finalized prediction models. Due to the fact that test temperature had the greatest effect on the asphalt binder rheological performance for both high and low temperature performance grading, the respective critical test temperatures were chosen to be constant for analyzing the relationship between polystyrene parameters and responses in the developed surface plots. In multiple surface plots, two independent variables, polystyrene content (PS content) and polystyrene molecular weight (PS MW), were plotted in the x and y axes and the response was plotted in the z axis as shown in FIGURE 11.

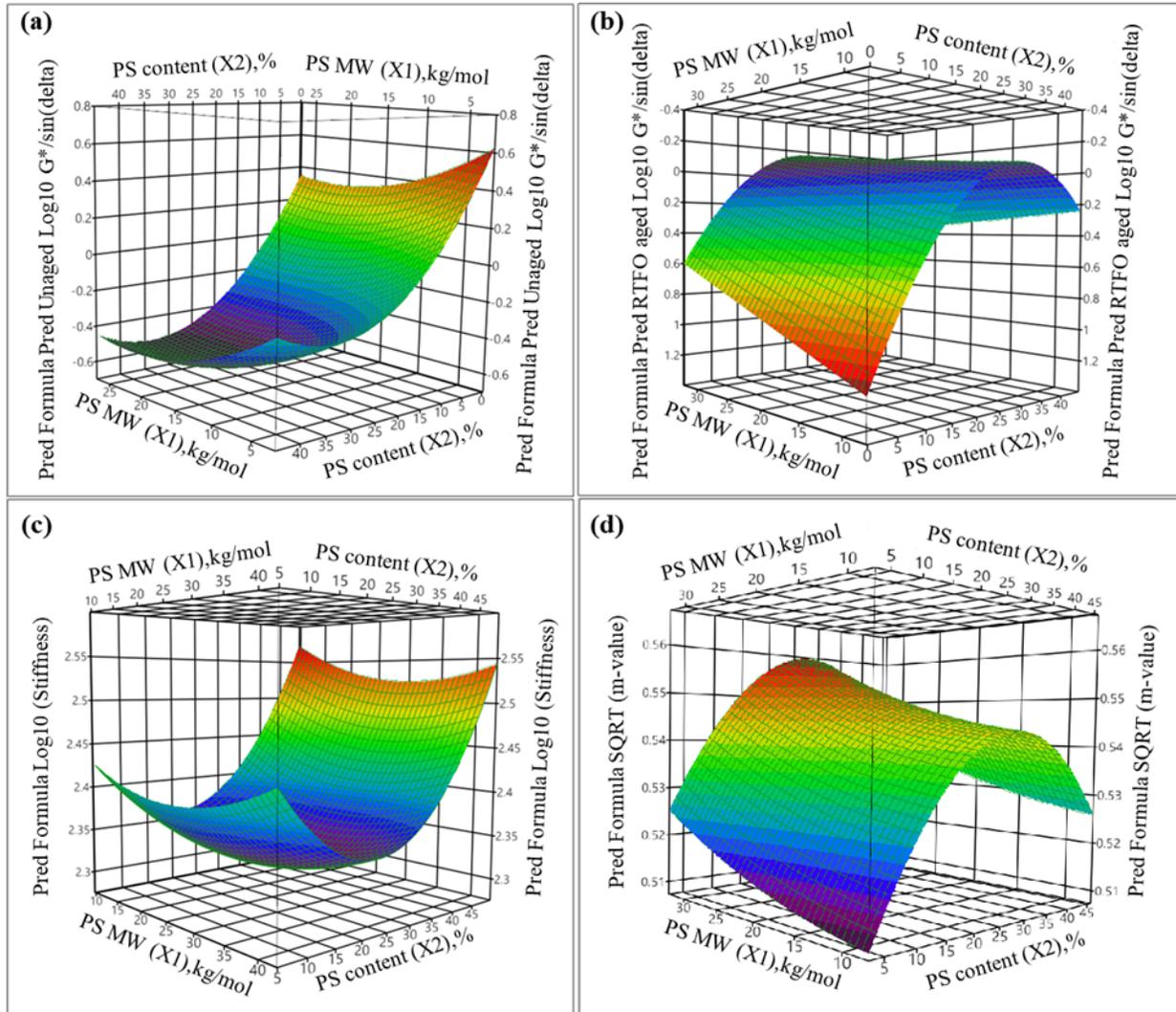


FIGURE 11 Surface plots of responses: (a) unaged $\text{Log}_{10} (G^*/\sin(\delta))$, (b) RTFO aged $\text{Log}_{10} (G^*/\sin(\delta))$, (c) PAV aged Log_{10} (stiffness), and (d) PAV aged SQRT (m-value) for responses versus polystyrene parameters.

To achieve PG 64-28, the polymer modified blends needed to pass 64.0°C for high temperature grading (via $G^*/\sin(\delta)$) and pass at a test temperature of -18°C for low temperature grading (via stiffness and the m-value). In FIGURE 11 (a), at a constant polystyrene molecular weight, an increase in $\text{Log}_{10} (G^*/\sin(\delta))$ value results in a decrease of polystyrene content, while a change in the polystyrene molecular weight exerts minimal effects on $\text{Log}_{10} (G^*/\sin(\delta))$ values. To meet the criteria for passing the unaged asphalt binder criteria of $G^*/\sin(\delta)$ 1.0 kPa, the $\text{Log}_{10} (G^*/\sin(\delta))$ value needs to be higher or equal to 0, therefore, the polystyrene content is suggested to be less than 10%. The same trend was observed in the RTFO aged $\text{Log}_{10} (G^*/\sin(\delta))$ surface plot as well in FIGURE 11 (b). The polystyrene content should be less than 10% to achieve the RTFO aged $\text{Log}_{10} (G^*/\sin(\delta))$ need to be greater than 2.2 kPa criteria.

An increase in polystyrene content from 5% to 45% results in Log_{10} (stiffness) values changes from higher to lower to higher at a constant polystyrene molecular weight as shown in FIGURE 11 (c). However, higher polystyrene content is not recommended for the high temperature grade surface plots because only lower polystyrene contents could meet the criteria of 1.0 and 2.2 kPa for unaged and RTFO aged binder grading. Therefore, lower polystyrene contents are preferred. In FIGURE 11 (d), at a constant

polystyrene molecular weight, the highest SQRT (m-value) was obtained at an intermediate polystyrene content between 25–30%. In terms of polymer composition, polystyrene is the hard and stiff domain that provides strength to the polymer (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 (Williams et al. 2014, Airey 2003, 2004). Achieving a higher critical high temperature so that the modified binder can be used for pavement applications in warm climate regions 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 molecular weight (from 15 to 35 kg/mol) can improve the values of SQRT (m-value) from about 0.51 to 0.53. It can be concluded that the analysis of surface plots matches the estimated test results and suggested polystyrene parameters in TABLE 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: 1250 kg/mol PS-PAESO, with a polystyrene molecular weight of 30 kg/mol and polystyrene content of 5%, was blended with the same base asphalt binder. The asphalt modification effects from the optimized PS-PAESO formulation with the base asphalt binder were examined by using high and low temperatures grade tests. The same high speed and high temperature shear blending procedure summarized previously was conducted to prepare the modified blends. Unaged and RTFO short-term aged modified binder specimens were prepared using a 25mm diameter silicon mold and tested in triplicate by using 25mm diameter parallel plates in a DSR. An initial test temperature was set at 46.0°C with increasing increments of 6.0°C until each specimen failed. It was found that the critical high temperature of 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 performance grade for the recommended polymer modified asphalt binder follows the estimated performance grade which was PG 64-28. These results indicated that the prediction models are highly accurate, however, the other three PS-PAESO polymers 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.

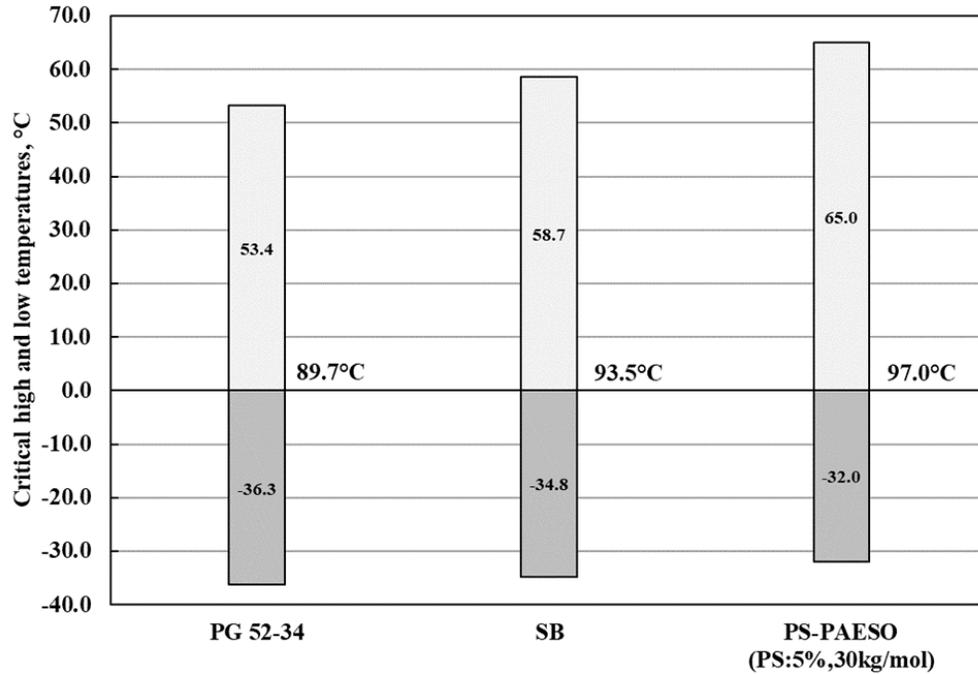


FIGURE 12 Critical high and low temperature comparisons for the base asphalt binder, SB modified blends, and PS-PAESO modified blends with calculated continuous grade ranges next to the bars.

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 calculated next to the bars in FIGURE 12.

COST COMPARISONS OF BIOPOLYMERS AGAINST PETROLEUM-BASED POLYMERS IN HMA

When evaluating the biopolymers, it is necessary to examine the material costs and the return. To do this, the costs for the raw materials were presented in FIGURE 13 with labor needed to produce the biopolymer included. For comparison purposes, FIGURE 13 displays the main components needed to make the final products—SB and PS-PAESO and their costs per lb.

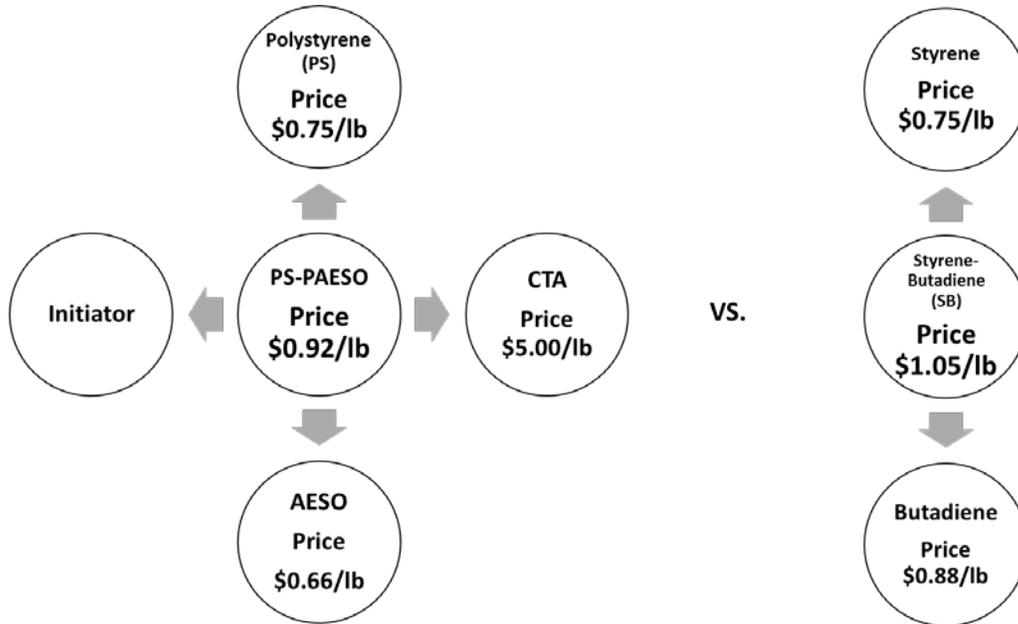


FIGURE 13 Cost comparison of PS-PAESO versus SB by (\$/lb or \$/kg).

As shown in FIGURE 13, the PS-PAESO final cost is \$0.92/lb or \$2.02/kg, while SB costs \$1.05/lb or \$2.31/kg.

Past research has proven that to achieve the same PG for both high and low temperatures using the biopolymer (PS-PAESO) as a neat bitumen modified with SB, only 2% of PS-PAESO by weight of the bitumen needs to be used versus 3% of the SB by weight of the bitumen for a polymer modification (Williams et al. 2014). An example comparing the difference in initial cost for road construction is shown in TABLE 10.

TABLE 10 Breakdown of HMA Cost per Lane Mile with PS-PAESO and SB

Description	SB Modified HMA	PS-PAESO Modified HMA
ESAL Design	1.5 Million	1.5 Million
HMA Thickness (in.)	6.5"	6.5"
Aggregate	Price/ton	Price/ton
HMA Aggregate Price/ton based on ESAL Level	\$29.83	\$29.83
HMA tonnage, tons/inch	396.00	396.00
Bitumen Type	Price/ton	Price/ton
PG XX-34	\$550.00	\$550.00
Bitumen Modification Cost	\$63.00	\$40.36
PG XX-34 w/polymer modification	\$596.50	\$573.98
HMA Price, per ton (including 5% AC)	\$58.16	\$57.04
HMA Cost/lane mile	\$149,703.84	\$146,820.96

Note: The prices of aggregates are based on the bid prices from the Iowa DOT. The neat asphalt binder price is based on the price of PG XX-34 supplied by Flint Hills in Minnesota.

The pricing of the aggregates used is based on the bid prices from the Iowa DOT while the bitumen price is based on the price of PG XX-34 supplied by Flint Hills in Minnesota. As shown in the following table, a cost saving of \$2,882.88 per lane mile is realized when the biopolymer PS-PAESO is used rather than SB.

BIOPOLYMER PILOT PLANT AND CONSTRUCTION OF AN NCAT TEST TRACK SECTION

As part of this research project, a biopolymer pilot plant capable of producing 10 tons of polymer per week has been built at Iowa State University as shown in FIGURE 14. This effort is vital in determining the technical and economic feasibility of producing the biopolymers that will be utilized in bitumen modification.



FIGURE 14 Iowa State University's vegetable-based biopolymer pilot plant facility.

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 were transferred to Eastern Alabama Paving to blend the biopolymer and produce the biopolymer modified asphalt mixture for paving the test track section at NCAT. The test track paving was a success for this research project as shown in FIGURE 15, as it proved that the biopolymer could be produced on a large scale and blended into an asphalt binder at asphalt facilities currently doing paving. Additionally, the NCAT test also demonstrated that the biopolymer modified asphalt mixture can be compacted easily and paved in a manner similar to other commercial polymer modified asphalt mixtures in construction.



FIGURE 15 NCAT Test Track paving and compaction using biopolymer modified asphalt mixtures.

SUMMARY AND CONCLUSIONS

Biopolymer production at both the laboratory and pilot plant scales has proved successful in this research project. In the laboratory, the PS-PAESO diblock copolymers at various polystyrene molecular weights and polystyrene contents levels were successfully produced in the laboratory using the RAFT polymerization technique. The H-NMR and HT-GPC were conducted to identify the percentage of PS in the block copolymer and molecular weight of the polymer, respectively.

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

To investigate how PS-PAESO polymers affected the performance grading and rheological properties of the neat asphalt binder, 17 different PS-PAESO polymers at a polymer dosage of 3% by weight of the total binder were individually blended into a neat asphalt binder (PG 52-34) 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 their critical high temperature was approximately 1.8°C higher, which meant the biopolymer has the ability to improve rutting resistance of the neat asphalt binder. However, the biopolymers did not substantially improve the resistance to thermal cracking because the critical low temperatures were increased. Eleven of the 17 biopolymer modified blends widened the neat asphalt binder's grade range and were similar to the SB polymer modified binder range,

which indicated that the biopolymer was capable of improving (widening the continuous grade range) the base asphalt binder's resistance to temperature susceptibility.

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

Temperature-frequency sweep tests were conducted using a DSR and the resulting data were utilized to develop the 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 biopolymer modified binder in terms of critical high temperature showed a trend of increasing G^* and decreasing δ compared to the neat asphalt binder, which displayed the positive stiffening effect and improvement of rutting resistance at high temperatures. The elasticity improvement of the neat asphalt after modification can also be observed in the Black Space diagrams. The rheological performance test results indicated that there is great potential for the use of biopolymers as sustainable alternatives to traditional petroleum based polymers in asphalt modification, with similar or even better modification effects at the same polymer dosage level.

In many cases, performing a full experimental design plan is time consuming and expensive. To deal with this problem, a partial experimental design plan was prepared. Prediction models were developed using the grading results obtained from laboratory tests through RSM to optimize the formulation of the PS-PAESO polymer.

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

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

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

According to the results obtained from cost comparisons, the production of biopolymer was \$0.13/lb or \$0.29/kg cheaper than that of SB polymer and a cost saving of \$2882.88 per lane mile was realized when using the biopolymer PS-PAESO over that of SB based on previous research.

Additionally, the biopolymer pilot plant successfully produced a biopolymer for use in paving trials. This biopolymer was transferred to Alabama and used for paving a test track section at NCAT. The use of biopolymer modified asphalt mixture for paving has proved that the biopolymer polymerization reaction could be scaled up from a laboratory to the pilot plant. The successful use of biopolymer asphalt mixture in paving construction also proved that the biopolymer could be blended at existing asphalt facilities and the mixture can be easily mixed and compacted as are other commercial polymer modified binders in mixtures.

Future research will focus on the field performance evaluation of the test track section that was paved with the biopolymer modified binder mixture. The asphalt binder and mixture samples collected from the field will be used for subsequent asphalt mixture performance testing and analysis for properties such as the dynamic modulus, flow number (F_N), Hamburg Steel Wheel (HSW), beam fatigue, and Disk-shaped Compact Tension (DCT) tests. Based on the evaluation of the produced asphalt mixture, the biopolymer formulation will be further optimized to achieve better performance in asphalt binders for future pavement applications.

REFERENCES

- Airey, G. D. 2003. Rheological Properties of Styrene Butadiene Styrene Polymer Modified Road Bitumens. *Fuel*, Vol. 82, No. 14, pp. 1709–1719.
- Airey, G. D. 2004. Styrene Butadiene Styrene Polymer Modification of Road Bitumens. *Journal of Materials Science*, Vol. 39, No. 3, pp. 951–959.
- Alonso, Sergio, Luis Medina-Torres, Roberto Zitzumbo, and Felipe Avalos. 2010. Rheology of Asphalt and Styrene-Butadiene Blends. *Journal of Materials Science*, Vol. 45, No. 10, pp. 2591–2597.
- Bahia, Hussain U., Dario Perdomo, and Pamela Turner. 1997. Applicability of Superpave Binder Testing Protocols to Modified Binders. *Transportation Research Record: Journal of the Transportation Research Board*, No. 1586, pp. 16–23.
- Brown, E. R., P. S. Kandhal, F. L. Roberts, Y. R. Kim, D-Y. Lee, and T. W. Kennedy. 2009. *Hot Mix Asphalt Materials, Mixture Design and Construction*. Third Edition. National Asphalt Pavement Association, Research and Education Foundation, Lanham, MD.
- Bruijninx, Pieter C. A. and Bert M. Weckhuysen. 2013. Shale Gas Revolution: An Opportunity for the Production of Biobased Chemicals? *Angewandte Chemie-International Edition*, Vol. 52, No. 46, pp. 11980–11987.
- Buncher, Mark and Carlos Rosenberger. 2005. Understanding the True Economics of Using Polymer Modified Asphalt through Life Cycle Cost Analysis. *Asphalt*, Vol. 20, No. 2, pp. 28–30.
- Cascione, Andrew A., Nacú B. Hernández, Eric W. Cochran, and R. Christopher Williams. 2013. Investigation of Asphalt Modified with Biopolymers Derived from Soybean Oil. Paper presented at the 5th European Asphalt Technology Association Conference, June 3–5, Braunschweig, Germany.
- Chen, J., M. Liao, and H. Tsai. 2002. Evaluation and Optimization of the Engineering Properties of Polymer-Modified Asphalt. *Journal of Failure Analysis and Prevention*, Vol. 2, No. 3, pp. 75–83.
- Cochran, Eric W., Ronald Christopher Williams, Nacu B. Hernandez, and Andrew A. Cascione. 2014. Thermoplastic elastomers via reversible addition-fragmentation chain transfer polymerization of triglycerides. U.S. Patent No. 20,140,343,192.
<https://www.google.com/patents/WO2014189939A3?cl=en>.
- D'Agosto, Franck. 2008. Handbook of RAFT Polymerization. *Macromolecular Rapid Communications*, Vol. 29, No. 11, pp. 934–935. <https://doi.org/10.1002/marc.200800209>.
- Dorokhova, T. N., L. R. Lyusova, A. A. Popov, L. S. Shibryaeva, and S. G. Karpova. 2012. Investigation of Physico-Chemical Properties and Structural Parameters of Diene-Vinyl Aromatic Thermoplastic Elastomers as a Polymeric Base of Adhesive Compositions. *Polymer Science Series D*, Vol. 5, No. 3, pp. 141–44.
- Duarte, Ana Rita C., Simone S. Silva, João F. Mano, and Rui L. Reis. 2012. Ionic Liquids as Foaming Agents of Semi-Crystalline Natural-Based Polymers. *Green Chemistry*, Vol. 14, No. 7, pp. 1949–1955.
- Fernandes, Mônica Romero Santos, Maria Madalena Camargo Forte, and Leni Figueiredo Mathias Leite. 2008. Rheological Evaluation of Polymer-Modified Asphalt Binders. *Materials Research*, Vol. 11, No. 3, pp. 381–386.
- Gama, Dennyale Alves, José Manoel Rosa, Tomas Jeferson Alves De Melo, and John Kennedy Guedes Rodrigues. 2016. Rheological Studies of Asphalt Modified with Elastomeric Polymer. *Construction and Building Materials*, Vol. 106, pp. 290–295.
- Gosset, Guillermo. 2009. Production of Aromatic Compounds in Bacteria. *Current Opinion in Biotechnology*, Vol. 20, No. 6, pp. 651–658.
- Grishchuk, S. and J. Karger-Kocsis. 2011. Hybrid Thermosets from Vinyl Ester Resin and Acrylated Epoxidized Soybean Oil (AESO). *Express Polymer Letters*, Vol. 5, No. 1, pp. 2–11.

- Grossegger, Daniel, Hinrich Grothe, Bernhard Hofko, and Markus Hospodka. 2017. Fluorescence Spectroscopic Investigation of Bitumen Aged by Field Exposure Respectively Modified Rolling Thin Film Oven Test. *Road Materials and Pavement Design*, Vol. 19, No. 4, pp. 992–1000.
- Habib, Firdous and Madhu Bajpai. 2011. Synthesis and Characterization of Acrylated Epoxidized Soybean Oil for UV Cured Coatings. *Chemistry and Chemical Technology*, Vol. 5, No. 3, pp. 317–326.
- Handle, Florian, Josef Füssl, Susanna Neudl, Daniel Grossegger, Lukas Eberhardsteiner, Bernhard Hofko, Markus Hospodka, Ronald Blab, and Hinrich Grothe. 2016. The Bitumen Microstructure: A Fluorescent Approach. *Materials and Structures*, Vol. 49, No. 1–2, pp. 167–180.
- Harmelink, Donna. 1992. *Special Polymer Modified Asphalt Cement*. Interim Report. Colorado Department of Transportation, Denver, CO.
<https://www.codot.gov/programs/research/pdfs/1992/polymer.pdf>.
- Hernández, Nacú B., Mengguo Yan, R. Christopher Williams, and Eric W. Cochran. 2015. Thermoplastic Elastomers from Vegetable Oils via Reversible Addition-Fragmentation Chain Transfer Polymerization. In *Green Polymer Chemistry: Biobased Materials and Biocatalysis*, Chapter 12, pp. 183–99. American Chemical Society, Washington, DC.
- Hydrocarbon Processing/Gulf Publishing Company LLC. 2012. US Shale Gas Boom Poised to Weaken Domestic Butadiene Market—Study. *Hydrocarbon Processing*.
<http://www.hydrocarbonprocessing.com/news/2012/10/us-shale-gas-boom-poised-to-weaken-domestic-butadiene-market-study>.
- Isacson, U. and X. Lu. 1995. Testing and Appraisal of Polymer Modified Road Bitumens—State of the Art. *Materials and Structures*, Vol. 28, No. 3, pp. 139–159.
- Kowalski, Karol J., Jan Krol, Piotr Radziszewski, Raquel Casado, Victor Blanco, Domingo Perez, Victor M. Vinas, Yvan Brijsse, Mia Frosch, Duy Michael Le, and Matt Wayman. 2016. Eco-Friendly Materials for a New Concept of Asphalt Pavement. *Transportation Research Procedia*, Vol. 14, pp. 3582–3591.
- Legge, Norman R. 1987. Thermoplastic Elastomers. *Rubber Chemistry and Technology*, Vol. 60, No. 3, pp. 83–117.
- Lewandowski, L. H. 1994. Polymer Modification of Paving Asphalt Binders. *Rubber Chemistry and Technology*, Vol. 67, No. 3, pp. 447–480.
- Liang, Ming, Peng Liang, Weiyu Fan, Chengduo Qian, Xue Xin, Jingtao Shi, and Guozhi Nan. 2015. Thermo-Rheological Behavior and Compatibility of Modified Asphalt with Various Styrene-Butadiene Structures in SBS Copolymers. *Materials and Design*, Vol. 88, pp. 177–185.
- Liang, Ming, Shujun Liu, Weiyu Fan, Xue Xin, Hui Luo, and Baodong Xing. 2016a. Rheological and Chemical Characterization of Deoiled Asphalt Modified with FCC Slurry. *Materials and Structures*, Vol. 49, No. 9, pp. 3607–3617.
- Liang, Ming, Yong Hu, Xiangjun Kong, Weiyu Fan, X. Xin, and Hui Luo. 2016b. Effects of SBS Configuration on Performance of High Modulus Bitumen Based on Dynamic Mechanical Analysis. *Kemija u Industriji*, Vol. 65, No. 7–8, pp. 379–384.
- Liu, Kunwei, Samy A. Madbouly, and Michael R. Kessler. 2015. Biorenewable Thermosetting Copolymer Based on Soybean Oil and Eugenol. *European Polymer Journal*, Vol. 69, pp. 16–28.
- Merusi, Filippo, Felice Giuliani, Sara Filippi, and Giovanni Polacco. 2013. A Model Combining Structure and Properties of a 160/220 Bituminous Binder Modified with Polymer/Clay Nanocomposites. A Rheological and Morphological Study. *Materials and Structures*, Vol. 47, No. 5, pp. 819–838.
- Moreno-Navarro, F., M. Sol-Sánchez, and M. C. Rubio-Gámez. 2015. The Effect of Polymer Modified Binders on the Long-Term Performance of Bituminous Mixtures: The Influence of Temperature. *Journal of Materials & Design*, Vol. 78, pp. 5–11.
- Nassar, I. M., K. I. Kabel, and I. M. Ibrahim. 2012. Evaluation of the Effect of Waste Polystyrene on Performance of Asphalt Binder. *ARPN Journal of Science and Technology*, Vol. 2, No. 10, pp. 927–935.

- Pamplona, Thaís F., Bruno de C. Amoni, Ana Ellen V. de Alencar, Ana Paula D. Lima, Nágila M. P. S. Ricardo, Jorge B. Soares, and Sandra de A. Soares. 2012. Asphalt Binders Modified by SBS and SBS/Nanoclays: Effect on Rheological Properties. *Journal of the Brazilian Chemical Society*, Vol. 23, No. 4, pp. 639–647.
- Peterson, C. and H. Anderson. 1998. *Interstate 70 Polymerized Asphalt Pavement Evaluation*. Unpublished report. Utah Department of Transportation, Salt Lake City, UT.
- Räntzsch, Volker, Manfred Wilhelm, and Gisela Guthausen. 2015. Hyphenated Low-Field NMR Techniques: Combining NMR with NIR, GPC/SEC and Rheometry. *Magnetic Resonance in Chemistry*, Vol. 54, No. 6, pp. 494–501.
- Raquez, J. M., M. Deléglise, M.-F. Lacrampe, and P. Krawczak. 2010. Thermosetting (Bio)Materials Derived from Renewable Resources: A Critical Review. *Progress in Polymer Science*, Vol. 35, No. 4, pp. 487–509.
- Rudin, Alfred and Phillip Choi. 2013. In Memoriam for Alfred Rudin (1924–2011). In *The Elements of Polymer Science & Engineering*, Third Edition. pp. xix–xx.
- Salih, Ashraf M., Mansor Bin Ahmad, Nor Azowa Ibrahim, Khairul Zaman Hj Mohd Dahlan, Rida Tajau, Mohd Hilmi Mahmood, and Wan Md Zin Wan Yunus. 2015. Synthesis of Radiation Curable Palm Oil-Based Epoxy Acrylate: NMR and FTIR Spectroscopic Investigations. *Molecules*, Vol. 20, No. 8, pp. 14191–14211.
- tur Rasool, Raqiqa, Shifeng Wang, Yong Zhang, Yue Li, and Guangtai Zhang. 2017. Improving the Aging Resistance of SBS Modified Asphalt with the Addition of Highly Reclaimed Rubber. *Construction and Building Materials*, Vol. 145, pp. 126–134.
- Valverde, Marlen, Dejan Andjelkovic, Patit P. Kundu, and Richard C. Larock. 2007. Conjugated Low-Saturation Soybean Oil Thermosets: Free-Radical Copolymerization with Dicyclopentadiene and Divinylbenzene. *Journal of Applied Polymer Science*, Vol. 107, No. 1, pp. 423–430.
- Von Quintus, Harold, Jagannath Mallela, and Mark Buncher. 2007. Quantification of Effect of Polymer-Modified Asphalt on Flexible Pavement Performance. *Transportation Research Record: Journal of the Transportation Research Board*, No. 2001, pp. 141–154.
- Wang, Peng, Ze-jiao Dong, Yi-qiu Tan, and Zhi-yang Liu. 2017. Effect of Multi-Walled Carbon Nanotubes on the Performance of Styrene–butadiene–styrene Copolymer Modified Asphalt. *Materials and Structures*, Vol. 50, No. 1, pp. 1–11.
- Wen, Guian, Yong Zhang, Yinxi Zhang, Kang Sun, and Yongzhong Fan. 2002. Improved Properties of SBS-Modified Asphalt with Dynamic Vulcanization. *Polymer Engineering and Science*, Vol. 42, No. 5, pp. 1070–1081.
- Williams, R. Christopher, Andrew A. Cascione, Eric W. Cochran, and Nacú B. Hernández. 2014. *Development of Bio-Based Polymers for Use in Asphalt*. Final Report. Iowa Highway Research Board, Iowa Department of Transportation, Ames, IA.
- Yan, Mengguo, Yuerui Huang, Mingjia Lu, Fang-Yi Lin, Nacú B. Hernández, and Eric W. Cochran. 2016. Gel Point Suppression in RAFT Polymerization of Pure Acrylic Cross-Linker Derived from Soybean Oil. *Biomacromolecules*, Vol. 17, No. 8, pp. 2701–2709.
- Yildirim, Yetkin. 2007. Polymer Modified Asphalt Binders. *Construction and Building Materials*, Vol. 21, No. 1, pp. 66–72.
- Zhang, Chaoqun, Mengguo Yan, Eric W. Cochran, and Michael R. Kessler. 2015. Biorenewable Polymers Based on Acrylated Epoxidized Soybean Oil and Methacrylated Vanillin. *Materials Today Communications*, Vol. 5, pp. 18–22.
- Zhu, Jiqing, Bjorn Birgisson, and Niki Kringos. 2014. Polymer Modification of Bitumen: Advances and Challenges. *European Polymer Journal*, Vol. 54, No. 1, pp. 18–38.

APPENDIX: RESEARCH RESULTS

PROGRAM INFORMATION

Program Steering Committee: NCHRP IDEA Program Committee

Project Title: Development of Renewable Polymers for Use in Asphalt Pavements

Task Number: IDEA 178

Start Date: July 1, 2014

Complete Date: Dec. 31, 2018

Product Category: New product development

Principal Investigator:

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PRODUCTION OF BIOPOLYMERS FOR ASPHALT MODIFICATION

The soybean-derived biopolymers were successfully produced through pilot-scale polymerization facilities and then were used for modification at an asphalt terminal to produce an asphalt mixture for use in a pavement with the desired performance.

WHAT WAS THE NEED?

Polymer modified asphalt binders have been widely used in the construction of flexible pavement over the past few decades. These binders were observed to enhance the overall performance of asphalt binders by increasing the stiffness and flexibility, especially on higher traffic volume roadways and under adverse environmental conditions. The styrene-butadiene (SB) and styrene-butadiene-styrene (SBS) polymers are the polymers most commonly used in asphalt modification due to their positive effects on the performance of the asphalt binders. Butadiene is the critical material needed to produce SB or SBS polymers, and it is co-produced from ethylene production using liquid crude oil feedstock. However, natural gas feedstocks cost less and thus have dominated in the production of ethylene since the shale gas boom occurred. Also, they do not yield butadiene as a co-product. This has caused tightening in the supply of butadiene that significantly influences the fluctuation in the market prices of SB or SBS polymers. Additionally, butadiene must be stored under pressure as a liquefied or compressed gas during transport, a requirement that may raise safety issues and incur additional transport costs. Due to the economic and environmental concerns around using these traditional petroleum-derived polymers, demand has increased for sustainable alternatives that can replace the petroleum-derived polymers for use in asphalt pavements.

WHAT WAS OUR GOAL?

The goal was to produce non-food source soybean-derived biopolymers through chemical polymerization techniques for use in neat asphalt binder performance modification, as well as in asphalt mixtures, to meet performance expectations.

WHAT DID WE DO?

The research team produced biopolymers with various polymer formulations to investigate their effects in asphalt modification. Chemical and rheological characterization of biopolymers and biopolymer modified asphalt binders were conducted to better understand the materials properties. The chemical characterizations were studied by conducting the hydrogen nuclear magnetic resonance (H-NMR), high temperature gel chromatography (HT-GPC), and other tests. The rheological properties of biopolymer modified binders were evaluated through a comprehensive asphalt binder testing program according to the AASHTO/ASTM test methods. The biopolymer modified asphalt binder testing results were subsequently used for statistical analysis and modelling to identify the significant polymer formulation parameters that affected the modification results and allowed researchers to optimize the biopolymer formulation for use in asphalt binders. A cost comparisons between the biopolymer and SB polymer were made to evaluate the economic benefits of biopolymer in the polymer production and the hot mix asphalt (HMA).



FIGURE 16 Biopolymer.

WHAT WAS THE OUTCOME?

The biopolymer formulation that performed best was selected and produced in the laboratory and the grading results confirmed its effectiveness in asphalt modification. The cost comparisons indicated that the biopolymer was able to save \$2882.88 per lane mile in the HMA than that of SB polymer. Additionally, the biopolymer pilot plant was able to produce more than 600 gallons of the biopolymer for paving an NCAT Test Track section. Production of the biopolymer at the pilot plant demonstrated the biopolymer polymerization reaction could be scaled up from the laboratory to the pilot plant level. The success of the biopolymer asphalt mixture paving construction proved that the biopolymer could be blended at existing asphalt blending and production facilities and the mixture can be mixed and compacted as easily as other commercial polymer modified binders in mixtures.



FIGURE 17 Construction of NCAT Test Track section using biopolymer modified asphalt mixtures.

WHAT IS THE BENEFIT?

The production of biopolymers proved the feasibility of using non-food source soybean oil as a bio-feedstock to generate polymers. The biopolymer can be used as the commercial counterpart to petroleum-derived polymers, working at the same dosage level and delivering similar or even better modification effects. These biopolymers are also sustainable, cost effective, and environmentally friendly. More important, the project team was able to produce biopolymers at a biopolymer pilot plant in a large enough quantity for demonstration paving trials. The overall research effort demonstrated the feasibility of implementing the biopolymer into construction practices.

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