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Use of Bioadvantaged Materials for Use in Bituminous Modification

Conglin Chen

Iowa State University, conglin@iastate.edu

Joseph H. Podolsky

Iowa State University, podolsky@iastate.edu

Nacú B. Hernández

Iowa State University, nacu23@iastate.edu

See next page for additional authors

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Abstract

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Keywords

Bitumen modification, biopolymers, green, sustainable

Disciplines

Materials Chemistry | Transportation Engineering

Comments

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Authors

Conglin Chen, Joseph H. Podolsky, Nacú B. Hernández, Austin Hohmann, R. Christopher Williams, and Eric W. Cochran

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Use of bioadvantaged materials for use in bituminous modification

Conglin Chen ^a, Joseph H. Podolsky ^{a,*}, Nacu Hernandez ^b, Austin Hohmann ^b,
R. Christopher Williams ^c, Eric W. Cochran ^d

^aIowa State University, Department of Civil, Construction, and Environmental Engineering, 174 Town Engineering, Ames, Iowa, 50011, USA

^bIowa State University, Department of Chemical, and Biological Engineering, 3125 Sweeny Hall, Ames, Iowa, 50011, USA

^cIowa State University, Department of Chemical, and Biological Engineering, 490 Town Engineering, Ames, Iowa, 50011, USA

^dIowa State University, Department of Chemical, and Biological Engineering, 1035 Sweeny Hall, Ames, Iowa, 50011, USA

Abstract

Historically, the use of “green” materials around the world has been limited due to their higher production costs when compared to petrochemical derived materials. However, due to the recent volatility and increasing price of petroleum derivatives, there is a growing demand for the use of environmentally friendly materials. One of the most commonly used materials for bitumen modification are poly(styrene-block-butadiene-block-styrene) (SBS) type polymers. Recently, Iowa State University Chemical Engineering Department was able to synthesize thermoplastic elastomers using acrylated epoxidized soybean oil (AESO), a bioadvantaged replacement of butadiene, and styrene with the use of controlled radical polymerization techniques. Initial rheological tests conducted on the bitumen-polymer blends have shown that the biopolymers improve the complex shear modulus of the bitumen to a similar and even greater extent as the commercially available SBS polymers.

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Keywords: Bitumen modification; biopolymers; green; sustainable

* Corresponding author. Tel.: +1-515-294-4419; fax: +1-515-294-4975.

E-mail address: podolsky@iastate.edu

1. Introduction

Historically, the use of “green” materials, materials produced partially or entirely from renewable natural resources other than petroleum, around the world has been limited due to their higher production costs when compared to petrochemical derived materials. However, due to the recent volatility and increasing price of petroleum derivatives, there is a growing demand for the use of environmentally friendly materials. Two different approaches have emerged for the creation of these materials. The first one termed “bioreplacement”, in which fields like: synthetic biology and catalysis collaborate are used to produce petrochemical monomers from sugars and lignocellulosic feedstocks that do not require new ways of producing the polymers we know today. For example, the use of metabolic engineering to harvest monomers as: butadiene, isoprene, styrene, etc., from genetically modified bacteria.

In recent history the supply of butadiene, a byproduct of the steam cracking in the production of ethylene, has been consistently decreasing due to a novel method of producing ethylene from natural gas. This method yields no butadiene, thus decreasing the amount of butadiene in the market and consequently increasing its price (Romagosa and Corun 2008). This phenomenon has created an excellent opportunity for the use of bioadvantaged materials as a replacement for petroleum based rubbers, such as the styrene-butadiene-styrene (SBS) type thermoplastic elastomers (TPEs). SBS triblock copolymers are made up of styrene-butadiene-styrene polymer chains that create an ordered cylindrical morphology composed of glassy polystyrene block domains within a rubbery polybutadiene matrix (Williams et al. 2014). Styrenic based TPEs, particularly those from Kraton® are used in a wide range of applications, such as: footwear, packaging, pressure sensitive adhesives, packaging materials, bitumen modification, electronics, etc. Of these applications, the use of SBSs as bitumen modifiers is one of the largest and most forgiving in terms of material properties (Cochran et al. 2013, Cochran et al. 2014). SBSs type polymers are added as modifiers to bitumen to increase a pavement’s service life by improving the resistance to rutting at high temperatures and thermal cracking at low temperatures. According to a 2011 report by Global Industry Analysts, Inc. the global bitumen market will have reached approximately 119 million metric tons by the end of this year (Cochran et al. 2013, Cochran et al. 2014). Being the bitumen paving industry the largest end-use market of bitumen. With the ever-increasing growth in global population and with the emerging economies bitumen will be indispensable to build the future roadway infrastructures. This demand for bitumen creates a prime opportunity for the use of bioadvantaged materials as bitumen modifiers.

Bioadvantaged polymers are made from natural renewable resources which are can be completely biodegradable, and non-toxic as alternatives to petroleum-based polymers (Lukkassen and Meidell 2007). An ideal source of natural renewable material used for producing bioadvantaged polymers are vegetable oils. The makeup of vegetable oils is usually triglycerides, formed by three unsaturated fatty acids (FAs) connected by a glycerol center (La Scala and Wool 2005). Functionalization of the unsaturated fatty acyl chain in FAs through epoxidation, followed by acrylation can be used to produce different components of bioadvantaged polymers (Rus 2010).

Recently, the department of Chemical Engineering at Iowa State University was able to synthesize thermoplastic elastomers using acrylated epoxidized soybean oil (AESO), a bioadvantaged replacement of butadiene, and styrene with the use of controlled radical polymerization techniques, such as Atom Transfer Radical Polymerization (ATRP) and Reversible Addition Fragmentation Chain Transfer Polymerization (RAFT). Controlled radical polymerization introduces the capability of producing custom chain architectures such as block copolymers. Thus, it is possible to synthesize poly(styrene-block-AESO-block-styrene) triblock copolymers with similar physical properties as their petroleum counterparts. Initial rheological tests conducted on the bitumen-polymer blends have shown that the biopolymers improve the complex shear modulus of the bitumen to a similar and even greater extent as the commercially available SBS polymers, even when using 1% less polymer by weight (Hernandez et al. 2014, Williams et al. 2014).

2. Experimental Section

2.1. Materials

Bitumen from Flint Hills Resources Pine Bend Refinery in Rosemount, Minnesota with a XX-34 PG grade was used as the base. The bioadvantaged polymer modifiers (PS-PAESO and PS-PAESO-Cl) were synthesized via RAFT polymerization and were used without further modification (Cochran *et al.* 2014).

2.2. Blending

A total of 18 blends with 13 different bioadvantaged polymers (PS-PAESO and PS-PAESO-Cl) were tested, each polymer had a different styrene molecular weight (MW) and/or polystyrene content (%), as shown in Table 1. All biopolymers and one Kraton D1118 SB polymer were shear blended with the PG XX-34 at a rate of 3% by weight of the binder, using a Silverson L4RT-A high shear mixer with the square-hole high shear screen head. The shear blending process was performed at 190 °C with a shear rate of 3000 RPM for 3 hours without the use of any cross-linking agent.

Table 1. List of the different bioadvantaged polymers with their corresponding bitumen blend codes utilized for shear blending.

Styrene Content, %	Styrene Molecular Weight, kDa			Reaction Length, hr
	10	20	30	
30			Blend 9	4
30	–	–	Blend 10	5
20	Blend 1		–	
25	Blend 2, Blend 3	Blend 8	Blend 11, Blend 12*,	8
30	Blend 4, Blend 5, Blend 6		Blend 13, Blend 14	
35	Blend 7		–	
30		–	Blend 15	9
30	–		Blend 16	10
30			Blend 17	11
30			Blend 18	12

*Note: Blend 12 is PS-PAESO-Cl

2.3. Experimental Plan

The purpose of this research is to investigate and evaluate the rheological properties of the unaged, short-term aged and long-term aged bioadvantaged polymer blends against the control binder (PG XX-34) according to Superpave specifications. To address the objectives of this study, performance grading was conducted through the following test methods:

- AASHTO T 315-10: Determining the Rheological Properties of Bitumen Binder Using a Dynamic Shear Rheometer (DSR),
- AASHTO T 240-13: Effect of Heat and Air on a Moving Film of Bitumen Binder (Rolling Thin-Film Oven Test),
- AASHTO R 28-12: Accelerated Aging of Bitumen Binder Using a Pressurized Aging Vessel (PAV), and
- AASHTO R 49-09: Determination of Low- Temperature Performance Grade (PG) of Bitumen Binders.

DSR testing is performed at an oscillation speed of 10 rad/sec (1.59 Hz) with 25 mm parallel plates on unaged and short-term aged bitumen and 8 mm parallel plates on long-term aged bitumen according to AASHTO T 315-10.

However, 8 mm plate geometry testing will not be shown in this study due to lack of material needed for testing at low temperature in the BBR. The DSR tests aim at characterizing the viscous and elastic behavior of bitumen at high and intermediate temperatures to predict rutting resistance and fatigue cracking susceptibility. The DSR measures the shear complex modulus (G^* , Pa) and phase angle (δ , degrees) of bitumen. G^* is the measurement of the total resistance of bitumen to deformation in shear when exposed to repeated loads. Whereas, δ represents the relative amount of recoverable and non-recoverable deformation of the viscoelastic bitumen as a δ of 0° represents a fully elastic material and 90° represents a completely viscous material. This test provides the high temperature grade for both the unaged and short-term aged control bitumen and bioadvantaged polymer blends. A continuous grade is determined for unaged bitumen based on the value of $|G^*|/\sin(\delta)$ equal to 1.00kPa, whereas, for short-term (RTFO) aged bitumen $|G^*|/\sin(\delta)$ should be equal to 2.20kPa. Additionally this test makes it possible to characterize rheology through examination of master curves and black diagrams.

The RTFO test is conducted to simulate aging during the manufacture and construction of HMA pavements according to AASHTO T 240-13. There are two main purposes for performing this test. One is to provide an aged bitumen for further testing and the second is to determine the mass of volatiles that would be lost during the manufacture and construction of HMA pavement in the field, of which 1% mass loss is the limit. The second purpose of this test will not be elaborated upon in the Results and Discussion section as the control bitumen and all the bioadvantaged polymer blends had mass loss lower than the required 1% mass loss. The PAV is conducted according to AASHTO R 28-12 and simulates the effects of long-term aging on bitumen that happens over the course of several years in the field. Based on an investigation conducted by Bahia and Anderson (Bahia and Anderson 1995), the PAV simulates the field aging of in-service HMA pavement during the first 5-10 years of pavement’s service life.

The BBR was used to determine the low temperature susceptibility, thermal cracking potential, and the low temperature performance grade of bitumen according to AASHTO R 49-09. The BBR is designed to measure how much bitumen deflects or creeps under a constant load at a constant low temperature, which is related to the pavement critical low temperature. The test was performed using the material that had been aged in both the RTFO and PAV.

3. Results and Discussion

Based on the Superpave standard specifications, the high temperature performance grades were determined on unaged and short-term aged (RTFO aged) of the control bitumen (PG XX-34), the bioadvantaged polymer blends with the unmodified bitumen and the Kraton SB diblock polymer modified based unmodified bitumen. The test results are shown in Figure 1 (a). Blend 0 is the results from the control bitumen (PG XX-34). According to standards discussed in section 2 the high temperature performance grade is determined based on the lower of the two high critical temperature values of each bitumen group.

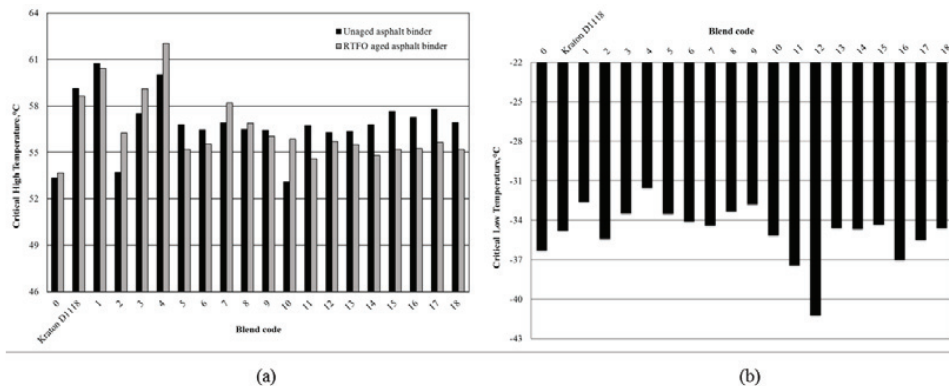


Fig. 1. Critical Temperatures of Blends and Base Bitumen (a) unaged and short-term (RTFO), and (b) long-term aged (PAV).

DSR results indicated the base bitumen had a critical high temperature of 53.4 °C. When comparing the base bitumen to the bioadvantaged polymer blends an increase on the critical high temperature can be seen. Moreover, the best performing bioadvantaged polymer blends used were the polymers with a lower styrene molecular weight: blend 1 and blend 4, both of which have a styrene molecular weight of 10 kDa. These two blends have approximately a 1.8 °C higher critical high temperature than the Kraton SB polymer modified bitumen blend (58.7 °C). Several of the bioadvantaged polymer blends such as: blend 2, blend 3, blend 4, blend 7, blend 8, and blend 10, increased the critical high temperature 1-2 °C after RTFO aging, whereas, the other blends decreased 1-2 °C after RTFO aging. However, it is difficult to discern why certain bioadvantaged polymers blends increase the critical high temperature while others decrease the critical high temperature after short-term aging. Further investigation needs to be done towards this topic of interest.

According to AASHTO R 49-09, the criteria for the critical low temperature of a bitumen specimen is based on two parameters: the stiffness and the m-value at a loading time of 60 seconds in the BBR test. The limiting criteria are if the stiffness is greater than 300 MPa or the m-value is less than 0.300. The low temperature performance grade of the base bitumen used in the study was graded out at -34 °C since its critical low temperature tested at -36.3 °C. In this case, the majority of bioadvantaged polymer blends do not show improvement in the low temperature performance as shown in Figure 1 (b). From the results most of the bioadvantaged polymer blends increased the critical low temperature by 1-2 °C higher than the base bitumen's critical low temperature. Therefore, the polymer modified bitumen blends were not affected by the addition of the bioadvantaged polymers and are still considered as a -34 °C performance grade. Nonetheless, some of the bioadvantaged polymers had bigger effects on the critical low temperature as they decreased the low temperature grade from -34 °C to -28 °C; such as blend 1, blend 3, blend 4, blend 5, blend 8, and blend 9. However, from the continuous performance grade ranges in Table 2, most of the bioadvantaged polymer blends were higher than the control bitumen's range and were close to the commercial Kraton SB polymer's range. Thus, the majority of the bioadvantaged polymers are helping reduce the temperature susceptibility of the base bitumen.

Table 2. Continuous performance grade ranges of the polymer modified bitumen and the base bitumen.

Blend Code	Continuous Grade Range, °C
0	89.7
Kraton D1118	93.4
1	93.0
2	89.1
3	91.0
4	91.5
5	88.7
6	89.6
7	91.3
8	89.8
9	88.8
10	88.2
11	92.0
12	96.9
13	90.1
14	89.4
15	89.5
16	92.3
17	91.1
18	89.8

The master curves were developed using the William, Landel and Ferry (WLF) equation to calculate the most appropriate factors to shift the experimental complex modulus at each testing frequency. By comparing the overlapped best fit curves, the rheological properties of each modified bitumen can be observed at higher, intermediate, and lower temperatures for both unaged and short-term aged bitumen. The data was obtained through DSR testing on unaged modified and RTFO aged modified bitumen at temperatures between 20 °C and 58 °C

(20 °C, 30 °C, 46 °C, and 58 °C) at frequencies between 0.1Hz to 100.0Hz at 31 points. Since complex modulus (G^*) cannot be the only parameter deciding the rheological properties of bitumen, the phase angle (δ) should also be taken into account. Black diagrams were also developed by using both phase angle (δ) and complex modulus (G^*) of unaged and short-term aged modified bitumen to describe the rheological behavior of a modified bitumen against that of the control bitumen. Figure 2 shows the master curves (a) and the black diagrams (b) of unaged and short-term aged Blend 1 against the control bitumen. Blend 1 was chosen for display purposes as Blend 1 was by far the best performing of the bioadvantaged polymer blends.

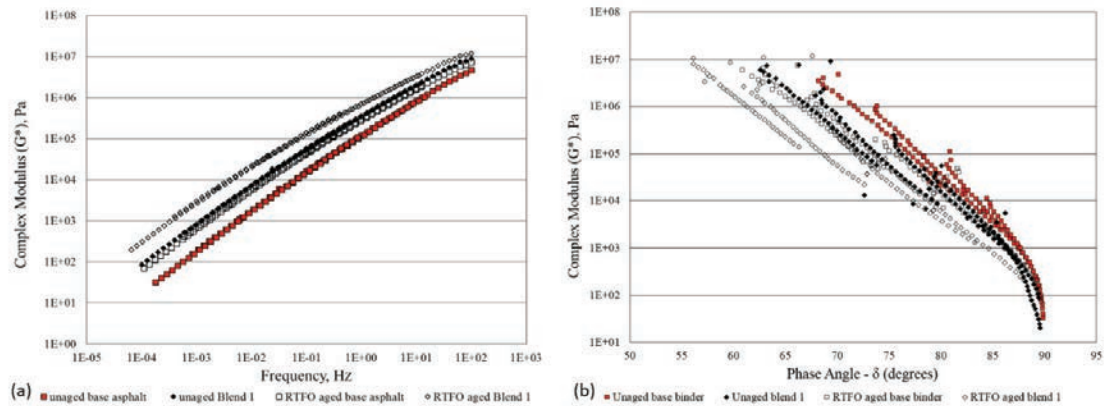


Fig. 2. Unaged and Short-term Aged Rheology of Blend 1 & Base Bitumen (a) Master Curves, (b) Black Diagrams.

Comparing the unaged base bitumen master curves to the short-term aged master curves in Figure (a), it is observed that with aging the bitumen becomes stiffer at higher, intermediate and lower temperatures. This is the case for both the control bitumen and bioadvantaged polymer blend (Blend 1). However, as can be seen from Figure 2(a), Blend 1 is much stiffer at higher temperatures (lower frequencies) than the control bitumen at higher temperatures for both age categories, but the difference in stiffness is not as great at lower temperatures between the two groups.

According to the black diagrams in Figure 2(b), it can be observed that at high stiffness values (high G^*), corresponding to lower temperatures and higher frequencies, the black diagram curves show a shift towards lower phase angles for Blend 1 which indicate the hardening and aging due to polymer modification. At lower temperatures a phase angle shift of 5 to 10 degrees is observed for unaged bitumen between the control and Blend 1, while a phase angle shift of 10 to 15 degrees is observed between the control bitumen and Blend 1 after short-term aging. This shift in phase angle is also seen at higher temperatures (low stiffness – G^*), but is much smaller – 1 to 3 degrees. This shows that the bioadvantaged polymer used in Blend 1 is making the control bitumen more elastic in nature. From these observations and the results seen in Figure 1 and Table 2 it can be assumed that PS-PAESO with lower molecular weight and lower styrene content acts as a better bioadvantaged polymer.

Based on the rheology test results gathered in this study, prediction modeling can be performed through statistical regression modeling. Modeling can help in developing a formula that can help predict the recommended bioadvantaged polymer chemical components (styrene molecular weight and styrene content) that will provide sufficient improvement of elasticity for the modified blends at high temperature. Future studies will be conducted on verifying the predicted bioadvantaged polymers (PS-PAESO) rheological performance in bitumen.

In addition with this work, a bioadvantaged polymer pilot plant capable of producing 10 tons of polymer per week has been built at the Iowa State University, see Figure 3. This effort is key in determining the technical and economical feasibility of producing the bioadvantaged polymers that will be utilized in bitumen modification.



Fig. 3. Iowa State University's vegetable based bioadvantaged polymer pilot plant facility.

4. Cost comparison of bioadvantaged polymers against petroleum-based polymers in HMA

When evaluating the bioadvantaged polymers, it is necessary to examine the costs put into the material and the return. To do this, the costs for the raw materials, and labor needed to produce the bioadvantaged polymer were tabulated. For comparison purposes Figure 4 displays the main components needed to make the final products – Styrene Butadiene (SB) and Polystyrene Polyacrylated Epoxidized Soybean Oil (PS-PAESO) and their costs per lb. As shown in Figure 4, PS-PAESO final cost is at \$0.92/lb or \$2.02/kg, while SB is \$1.05/lb or \$2.31/kg.

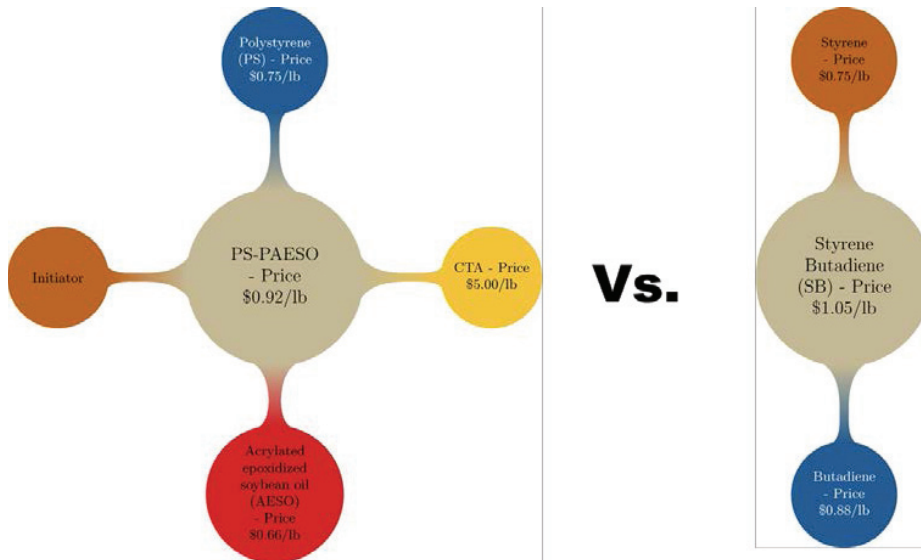


Fig. 4. Cost Comparison of PS-PAESO vs. SB by (\$/lb or \$/kg).

Past research has been proven that to get the same performance grade (PG) for both high and low temperature using the bioadvantaged polymer (PS-PAESO) as a neat bitumen modified with SB only 2% of PS-PAESO by weight of the bitumen need only be used versus 3% of the SB by weight of the bitumen for polymer modification (Williams *et al.* 2014). A comparison example of the difference in initial cost for road construction is shown in Table 3. The pricing of the aggregates used are based on the bid prices from the Iowa Department of Transportation (DOT), while the bitumen price is based on the price of PG XX-34 supplied by Flint Hills out of Minnesota. As shown from the table below a cost saving of \$2882.88 per lane mile is realized when using the bioadvantaged polymer PS-PAESO over that of SB.

Table 3. 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

5. Conclusion

Overall, this research shows that use of PS-PAESO as a bioadvantaged replacement of SB is possible. With further refinement of the PS-PAESO chemistry the possibility to perform if not equal but better than SB is possible. From this work the bioadvantaged polymers (PS-PAESO and PS-PAESO-Cl) helped increase the critical high temperature of the base bitumen from 53.35 °C to 53.71 °C–62.04 °C. The results displayed that the better performing bioadvantaged polymers were those with lower styrene molecular weight. They outperformed Kraton SB at the same dosage level and were 1.8 °C higher for the critical high temperature. For the critical low temperature, the bioadvantaged polymer modified blends were graded at the same temperature or higher than the base bitumen. Due to this result a loss of grade was seen at low temperature, and thus several of the bioadvantaged polymers did not improve binder resistance to thermal cracking.

However, 10 out of the 18 modified blends presented higher continuous grade ranges than the base bitumen and were close to the Kraton SB polymer's range, which resulted in reducing the temperature susceptibility of the base bitumen. Additionally, based on the observation from both master curves and black diagrams, all modified blends became stiffer especially at low frequencies and high temperatures due to the establishment of a rubber-elastic network within the modified blends, which means the bioadvantaged polymers improved the rutting resistance of bitumen and made the base bitumen more elastic in nature. Currently the price and timing is right for the commercialization of this technology as shown from the cost comparison to SB in section 4 and the improved performance of the base bitumen modified with the different PS-PAESO and PS-PAESO-Cl in section 3.

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