

Development of Bio-Based Polymers for Use in Asphalt

**Final Report
February 2014**

IOWA STATE UNIVERSITY
Institute for Transportation

Sponsored by
Iowa Highway Research Board
(IHRB Project TR-639)
Iowa Department of Transportation
(InTrans Project 11-423)

About the Institute for Transportation

The mission of the Institute for Transportation (InTrans) at Iowa State University is to develop and implement innovative methods, materials, and technologies for improving transportation efficiency, safety, reliability, and sustainability while improving the learning environment of students, faculty, and staff in transportation-related fields.

Disclaimer Notice

The contents of this report reflect the views of the authors, who are responsible for the facts and the accuracy of the information presented herein. The opinions, findings and conclusions expressed in this publication are those of the authors and not necessarily those of the sponsors.

The sponsors assume no liability for the contents or use of the information contained in this document. This report does not constitute a standard, specification, or regulation.

The sponsors do not endorse products or manufacturers. Trademarks or manufacturers' names appear in this report only because they are considered essential to the objective of the document.

Non-Discrimination Statement

Iowa State University does not discriminate on the basis of race, color, age, religion, national origin, sexual orientation, gender identity, genetic information, sex, marital status, disability, or status as a U.S. veteran. Inquiries can be directed to the Director of Equal Opportunity and Compliance, 3280 Beardshear Hall, (515) 294-7612.

Iowa Department of Transportation Statements

Federal and state laws prohibit employment and/or public accommodation discrimination on the basis of age, color, creed, disability, gender identity, national origin, pregnancy, race, religion, sex, sexual orientation or veteran's status. If you believe you have been discriminated against, please contact the Iowa Civil Rights Commission at 800-457-4416 or the Iowa Department of Transportation affirmative action officer. If you need accommodations because of a disability to access the Iowa Department of Transportation's services, contact the agency's affirmative action officer at 800-262-0003.

The preparation of this report was financed in part through funds provided by the Iowa Department of Transportation through its "Second Revised Agreement for the Management of Research Conducted by Iowa State University for the Iowa Department of Transportation" and its amendments.

The opinions, findings, and conclusions expressed in this publication are those of the authors and not necessarily those of the Iowa Department of Transportation.

Technical Report Documentation Page

1. Report No. IHRB Project TR-639	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle Development of Bio-Based Polymers for Use in Asphalt		5. Report Date February 2014	
		6. Performing Organization Code	
7. Author(s) R. Christopher Williams, Andrew Cascione, Eric Cochran, Nacu Hernandez		8. Performing Organization Report No. InTrans Project 11-423	
9. Performing Organization Name and Address Institute for Transportation Iowa State University 2711 South Loop Drive, Suite 4700 Ames, IA 50010-8664		10. Work Unit No. (TRAIS)	
		11. Contract or Grant No.	
12. Sponsoring Organization Name and Address Iowa Highway Research Board Iowa Department of Transportation 800 Lincoln Way Ames, IA 50010		13. Type of Report and Period Covered Final Report	
		14. Sponsoring Agency Code IHRB Project TR-639	
15. Supplementary Notes Visit www.intrans.iastate.edu for color pdfs of this and other research reports.			
16. Abstract <p>Asphalt binder is typically modified with poly type (styrene-butadiene-styrene or SBS) polymers to improve its rheological properties and performance grade. The elastic and principal component of SBS polymers is butadiene. For the last decade, butadiene prices have fluctuated and significantly increased, leading state highway agencies to search for economically viable alternatives to butadiene based materials. This project reports the recent advances in polymerization techniques that have enabled the synthesis of elastomeric, thermoplastic, block-copolymers (BCPs) comprised of styrene and soybean oil, where the "B" block in SBS polymers is replaced with polymerized triglycerides derived from soybean oil. These new breeds of biopolymers have elastomeric properties comparable to well-established butadiene-based styrenic BCPs.</p> <p>In this report, two types of biopolymer formulations are evaluated for their ability to modify asphalt binder. Laboratory blends of asphalt modified with the biopolymers are tested for their rheological properties and performance grade. Blends of asphalt modified with the biopolymers are compared to blends of asphalt modified with two commonly used commercial polymers. The viscoelastic properties of the blends show that biopolymers improve the performance grade of the asphalt to a similar and even greater extent as the commercial SBS polymers. Results shown in this report indicate there is an excellent potential for the future of these biopolymers as economically and environmentally favorable alternatives to their petrochemically-derived analogs.</p>			
17. Key Words asphalt—biopolymers—polymer-modified asphalt—soybean oil—styrenic block copolymers—styrene-butadiene-styrene		18. Distribution Statement No restrictions.	
19. Security Classification (of this report) Unclassified.	20. Security Classification (of this page) Unclassified.	21. No. of Pages 44	22. Price NA

DEVELOPMENT OF BIO-BASED POLYMERS FOR USE IN ASPHALT

**Final Report
February 2014**

Principal Investigator

R. Christopher Williams

Professor

Professor, Civil, Construction and Environmental Engineering, Iowa State University

Co-Principal Investigator

Eric Cochran

Associate Professor, Chemical and Biological Engineering, Iowa State University

Research Assistants

Andrew Cascione, Iowa State University

Nacu Hernandez, Iowa State University

Authors

R. Christopher Williams, Andrew Cascione, Eric Cochran, Nacu Hernandez

Sponsored by
the Iowa Department of Transportation and
the Iowa Highway Research Board
(IHRB Project TR-639)

Preparation of this report was financed in part
through funds provided by the Iowa Department of Transportation
through its Research Management Agreement with the
Institute for Transportation
(InTrans Project 11-423)

A report from
Institute for Transportation
Iowa State University
2711 South Loop Drive, Suite 4700
Ames, IA 50010-8664
Phone: 515-294-8103 Fax: 515-294-0467
www.intrans.iastate.edu

TABLE OF CONTENTS

ACKNOWLEDGMENTS	vii
EXECUTIVE SUMMARY	ix
Background	ix
Research Methodology	ix
Key Findings	x
Implementation Readiness and Benefits	x
Future Work	x
CHAPTER 1 INTRODUCTION	1
1.1 Problem Statement	1
1.2 Objectives	2
CHAPTER 2 LITERATURE REVIEW	3
2.1 Polymer-Modified Asphalt	3
2.2 Thermoplastic Elastomers	3
2.3 SBS and Asphalt Compatibility	5
2.4 Commercially Available SBS and SB Polymers	6
2.4 Polymers Synthesized from Vegetable Oils	6
CHAPTER 3 TEST PLAN AND PROCEDURE	8
3.1 Research Plan	8
CHAPTER 4 BIOPOLYMER SYNTHESIS	12
4.1 Chemical Modification of Soybean Oil	12
4.2 Synthesis of Thermoplastic Block Copolymers	13
CHAPTER 5 TEST RESULTS AND ANALYSIS	18
5.1 Characterizations of the Polymers	18
5.2 Evaluation of Asphalt Modified with Kraton Polymers	22
5.3 Evaluation of Asphalt Modified with the Biopolymers	25
CHAPTER 6 ECONOMIC ANALYSIS	30
CHAPTER 7 CONCLUSIONS AND RECOMMENDATIONS	31
REFERENCES	33

LIST OF FIGURES

Figure 1. Effects of polymer modification in asphalt binder (after Epps, J. A.).....	3
Figure 2. SBS polymer structure.....	4
Figure 3. Rheological testing of asphalt-polymer blends	11
Figure 4. A representative structure of a triglyceride	12
Figure 5. Conjugation of triglyceride molecule followed by two examples of AESO.....	13
Figure 6. RAFT polymerization mechanism	14
Figure 7. Molecular weight of polystyrene in RAFT reaction.....	15
Figure 8. Molecular weight of PS-PAESO in RAFT reaction.....	16
Figure 9. Molecular weight distribution of AESO, polystyrene (PS), and PS-PAESO.....	17
Figure 10. PS-PAESO diblock	18
Figure 11. PS-PAESO-PS triblock	18
Figure 12. Nuclear magnetic resonance spectra results of PS-PAESO-PS	19
Figure 13. Transmission electron microscopy image of PS-PAESO-PS.....	19
Figure 14. Differential scanning calorimetry results for PAESO and polystyrene blocks	20
Figure 15. Isothermal frequency scans of PS-PAESO-PS.....	21
Figure 16. Tensile strain (mm/mm) vs. load (MPa) for PS-PAESO-PS.....	21
Figure 17. Tensile strain (mm/mm) vs. tensile stress (MPa) for PS-PAESO-PS	22
Figure 18. Comparison of high temperature continuous performance grades.....	29
Figure 19. Comparison of low temperature continuous performance grades	29
Figure 20. Commodity costs comparison	30

LIST OF TABLES

Table 1. Biopolymer molecular weights and styrene contents	18
Table 2. DSR results for unaged asphalt modified with Kraton D1101	23
Table 3. DSR results for RTFO aged asphalt modified with Kraton D1101	23
Table 4. DSR results for unaged asphalt modified with Kraton D1118	24
Table 5. DSR results for RTFO aged asphalt modified with Kraton D1118.....	25
Table 6. BBR results for PAV aged asphalt modified with Kraton D1101 and D1118	25
Table 7. DSR results for asphalt modified with biopolymers.....	26
Table 8. DSR results for PAV aged asphalt modified with biopolymers	27
Table 9. BBR results for PAV aged asphalt modified with biopolymers	28

ACKNOWLEDGMENTS

The authors would like to thank the Iowa Highway Research Board for sponsoring this research as well as the Iowa Department of Transportation, the Asphalt Pavement Association of Iowa (APAI), and the members of the APAI for their participation as technical advisory committee members.

EXECUTIVE SUMMARY

Background

Asphalt binder used for high-performing pavements needs sufficient properties to resist cracking at low temperatures and rutting caused by shear forces from sustained loads at high temperatures. To produce an asphalt binder with these performance characteristics, the binder is commonly modified with elastomeric polymers to improve its rheological properties and lower its temperature susceptibility over a range of in-service pavement temperatures.

The most common elastomeric polymers used for asphalt modification are styrenic block copolymers (SBCs). SBCs are composed of blocks of polybutadiene and polystyrene to produce styrene-butadiene (SB) diblock polymers and styrene-butadiene-styrene (SBS) triblock polymers.

Recent advances in polymerization techniques have led to the development of elastomeric block copolymers produced with polystyrene and polymerized soy-derived triglycerides. While the past two decades of plant-oil based polymer research has yielded only thermosets, the newly produced polymers are thermoplastic elastomers that are processable at high temperatures.

Research Methodology

The thermoplastic elastomers were produced using a controlled radical polymerization technique to create the block copolymers.

Soybean oil triglycerides were first acrylated and epoxidized, creating acrylated epoxidized soybean oil (AESO). This process made them suitable to polymerize via controlled radical polymerization techniques, such as reversible addition-fragmentation chain-transfer polymerization (RAFT).

SBS-like triblock copolymers were then synthesized by polymerizing AESO and styrene monomer in the presence of a free radical initiator and a chain transfer agent to create polystyrene-*b*-polyAESO-*b*-polystyrene (PS-PAESO-PS). The polymerizing step was carried out under conditions effective to achieve a number-average degree of polymerization (N_n) for the thermoplastic block copolymer of up to 100,000 repeat units per molecule without gelation. Following the same process, SB diblock copolymers were also produced.

Laboratory Investigation

A laboratory investigation was conducted to characterize the PS-PAESO-PS and PS-PASEO biopolymers and to evaluate their effectiveness as a liquid asphalt modifier. Asphalt modified with the biopolymers was compared to asphalt modified with two commercially available Kraton polymers, D1101 (SBS) and SB D1118 (SB).

Key Findings

Rheology test results showed the biopolymer has the ability to widen the grade range of asphalt and reduce its temperature susceptibility. The base asphalt tested as a continuous PG 51.1-37.7 for a grade range of 88.8°C. Adding two percent D1101 to the base asphalt increased its continuous high PG to 57.2 without changing its -34 grade qualification on the low temperature side. Adding two percent PS-PAESO-PS to the base asphalt changed its continuous PG to 70.4-33.0 for a 103.4°C grade range. With the addition of two percent PS-PAESO, the base asphalt changed to a continuous PG of 69.1-32.8 for a 101.9°C grade range.

Thus, biopolymers significantly enhanced the performance properties of the base asphalt. By adding two percent of either biopolymer to an asphalt binder, the rutting resistance and temperature performance range of an asphalt pavement will improve.

Implementation Readiness and Benefits

Soybean oil is the world's most abundant vegetable oil and currently costs 40 percent less than butadiene. These lower costs will translate into lower costs of polymer-modified asphalt. Polymerized triglycerides are also intrinsically renewable, environmentally friendly, and safer to handle than butadiene.

With future implementation of the developed biopolymers, Iowa source materials (e.g., soybean oil) can be utilized to produce polymers for use in Iowa. This can create improved economic opportunities for soybeans resulting in economic value to Iowa and maintaining soil qualities through a balanced crop rotation with corn.

Future Work

Currently, at a polymer content of two percent, a base asphalt's low temperature PG may increase one grade, which may warrant the use a softer base asphalt to compensate for that effect. As additional data from asphalt-modification experiments become available, additional or improved polymer formulation designs may be developed. Future research can improve upon the biopolymers molecular architecture, styrene content, and molecular weight distribution.

A larger reactor has been purchased that is capable of making two kilogram samples, substantially larger than the approximately 100 gram samples produced in this study. In addition, a pilot plant is currently being designed that can produce even larger quantities of the biopolymers for future research.

Further work evaluating asphalt mixtures for rutting, low temperature cracking, and moisture susceptibility should be done while the pilot plant is being constructed. Based upon the evaluation of the mixture, an additional phase of research should include a field demonstration project that tests the performance of asphalt pavement containing terminally blended asphalt binder modified with the soy-based block copolymers.

CHAPTER 1 INTRODUCTION

1.1 Problem Statement

The performance of asphalt pavements at in-service temperatures depends on the grade of asphalt binder used in the paving mixture. In many cases, the characteristics of asphalt binder need to be altered to improve its rheological properties. Asphalt binder needs sufficient properties to resist cracking at low temperatures and rutting caused by shear forces from sustained loads at high temperatures. The physical properties of asphalt binder are typically modified with elastomeric polymers to produce an improved performance grade. The most common elastomeric polymers used for asphalt modification are styrenic block copolymers (SBC). SBCs are composed of blocks of polybutadiene and polystyrene to produce styrene-butadiene (SB) diblock polymers and styrene-butadiene-styrene (SBS) triblock polymers.

In 2008, there was a shortage of SB and SBS polymers for use in the asphalt industry. The shortage was due to a lack of global butadiene supply, the principal component of SBC grades for asphalt modification. Butadiene is a by-product of the production of ethylene, which is produced from the steam cracking process of petroleum based feedstocks. Steam cracker facilities can use either liquid petroleum products or gaseous products such as ethane, butane, or propane as the raw material to produce ethylene. The by-products that result from the steam cracking reaction depend on the composition of the raw material. Butadiene is only a by-product when liquid feeds, not gaseous feeds, are used as the raw materials.

As shale gas supplies become more abundant, crackers are more commonly using lighter petrochemical feeds such as ethane to produce ethylene and its by-products. However, using lighter feeds lowers butadiene production and tightens the supply (Foster 2011). This in-part led to the 2008 butadiene shortage as well as short term closure of some facilities. Although the butadiene supply has rebounded since then, it remains volatile and has been susceptible to rapid price increases. The butadiene market in the United States is particularly sensitive to global supply since butadiene is not substantially produced domestically but primarily imported from Asian and European countries.

As the asphalt industry continues to grow, it will increasingly need SBCs to modify asphalt binder. The global asphalt market is projected to reach 118.4 million metric tons by 2015, according to a January 2011 report by Global Industry Analysts, Inc. With increasing growth in the developing markets of China, India, and Eastern Europe, asphalt will be needed to construct their roadway infrastructure well into the next decade and beyond. The demand for asphalt, along with the need for improved asphalt pavement performance, will put pressure on butadiene supplies that have already experienced shortages. As a result, there is a growing need in finding sustainable and renewable SBC alternatives.

The successful synthesis of elastomeric SBCs requires a polymer like polybutadiene for its soft and rubbery properties. With the advent of new polymerization technologies that can produce polymers from biorenewable sources rather than petroleum, it may be possible to synthesize a

biopolymer from plant-based feedstocks that mimics the properties of polybutadiene. A bio-based alternative that could replace the petrochemically based polybutadiene in SBCs would help solve the economic and environmental concerns of using them.

Indeed, many advances have been made in this area, most notably in the production of vegetable-oil-based thermosets via both traditional cationic and free radical polymerization routes. Lu and Larock (2009) have shown that a variety of plant oils may be successfully polymerized via cationic polymerization into thermosets with a broad spectrum of physical properties and aesthetic appearances. While these thermoset materials may supplant a number of petrochemically-derived thermosets, the vast majority of commodity polymers, including SB and SBS, are thermoplastic materials that can be reheated and processed at high temperatures.

In laboratory studies, the research team has identified soybean oil as a viable renewable and biodegradable feedstock that can be polymerized into a material with similar properties as polybutadiene. This report documents the recent advances toward developing a formulation for a thermoplastic elastomer using the polymerized soybean oil as a replacement for butadiene. By replacing butadiene with the polymerized soybean oil in the SB and SBS block copolymer structure, this research has the potential to create a new class of renewable SB block copolymers that can be used for the asphalt industry as well as many others.

1.2 Objectives

This project supports the development of an innovative route to thermoplastic-elastomeric SBCs based largely on soybean oil, a renewable and biodegradable feedstock. The new class of SBCs contains a biopolymer derived from triglycerides in soybean oil that replaces the “B” block polymer (polybutadiene) in the block copolymer structure of SB and SBS. The efficacy these soy-based block copolymers as an alternative to the traditional polymer modifiers used in the asphalt industry are evaluated for this project. The objectives of this project are as follows:

- Identify the most promising polymerization chemistries for forming linear-chain polymers from vegetable oils.
- Synthesize soy-based biopolymers with blocks of polystyrene (PS) and polymerized soybean oil (PAESO) to create block copolymers with diblock (PS-PAESO) and triblock (PS-PAESO-PS) structures that use PAESO as a replacement for polybutadiene. Characterize the thermal, rheological, and morphological properties of these materials.
- Formulate blends of the diblock and triblock biopolymers with asphalt binder and quantitatively evaluate their influence on asphalt binder performance; compare these results with commercially available SB and SBS polymers.
- Evaluate the economics of the biopolymers as asphalt modifiers.

CHAPTER 2 LITERATURE REVIEW

2.1 Polymer-Modified Asphalt

Asphalt binder is commonly modified with polymers to improve its rheological properties in a paving mixture and to lower its temperature susceptibility over a range of in-service temperatures. Figure 1 compares the stiffness of a conventional asphalt binder to an ideal modified asphalt binder at different in-service temperatures. At high temperatures, polymer modification increases binder stiffness and elasticity, as a result of an increased storage modulus and a decreased phase angle. Both increasing the storage modulus and decreasing the phase angle improves rutting resistance of the pavement (Bahia and Anderson 1995). At low temperatures, polymer modification lowers creep stiffness of the asphalt which improves resistance to thermal cracking (Isacsson and Lu 1999).

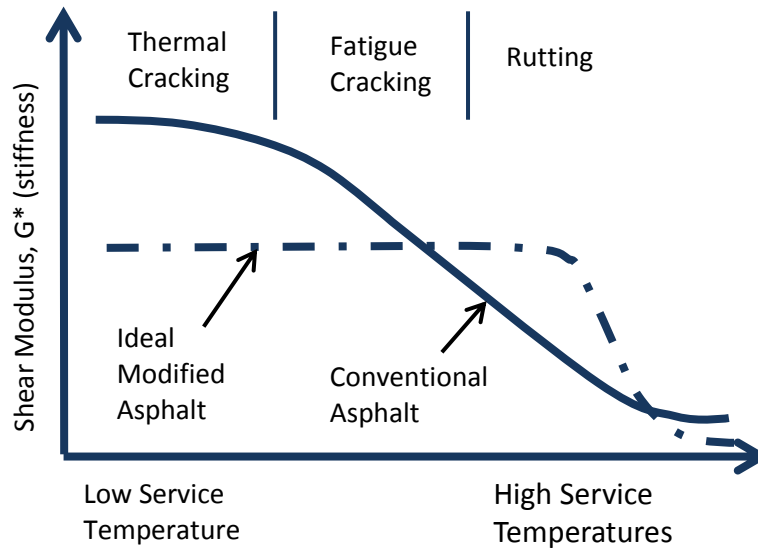


Figure 1. Effects of polymer modification in asphalt binder (after Epps, J. A.)

Polymers are very large molecules formed by linking together multiple small molecules called monomers. When a polymer consists of more than one repeating monomer unit, either in a random or block arrangement, it is termed a copolymer. The length of the polymer chain, monomer sequence, and chemical structure determine the physical properties of the resulting polymer. Polymers with blocks of repeating homopolymer chains are termed block copolymers (Oadian 1991).

2.2 Thermoplastic Elastomers

The most important block copolymer used in commercial practice is the ABA triblock (Hiemenz 2007). The A block is usually polystyrene, and the B block is an elastomer such as isoprene or butadiene. Such polymers are known as thermoplastic elastomers. SBS is the most widely used thermoplastic elastomer for asphalt modification. It is comprised of polystyrene-polybutadiene-

polystyrene chains that create an ordered morphology of cylindrical glassy polystyrene block domains within a rubbery polybutadiene matrix (Bulatovic et al. 2012). The polystyrene end-blocks provide strength to the polymer, while the polybutadiene mid-block gives the material its elasticity (Figure 2). SBS polymers are thermoplastic, meaning that they can be easily processed at high temperatures due to the linear nature of their chains. When heated above the polystyrene glass transition temperature (100°C), the crosslinked structure breaks down allowing the polymer to flow. Upon cooling, the rigid polystyrene end-blocks vitrify and act as anchors for the liquid rubbery domains by providing a restoring force when stretched (Fried 2008).

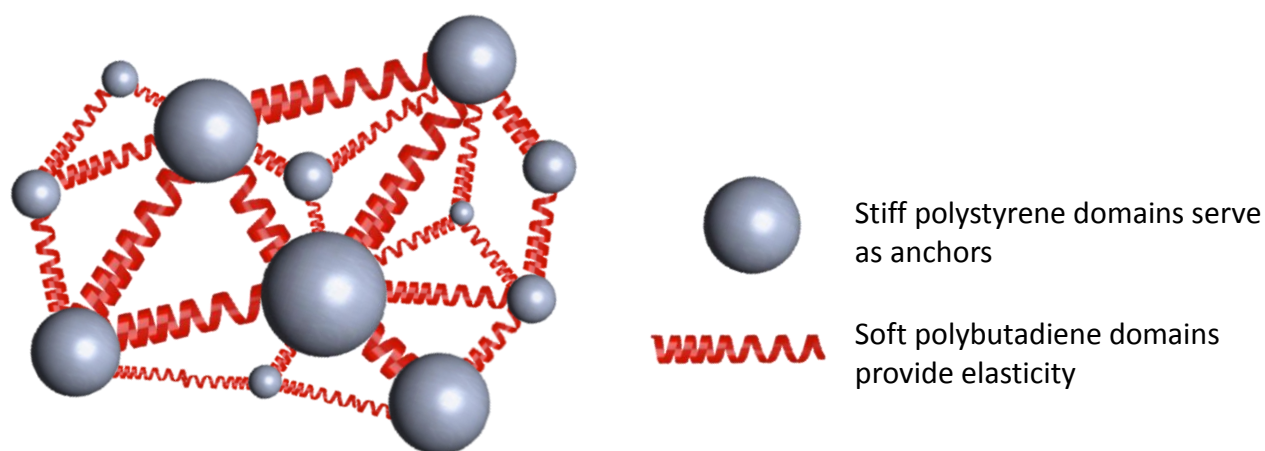


Figure 2. SBS polymer structure

The mechanism that allows SBS to possess the dual properties of thermoplasticity and elasticity in styrenic block copolymer arises from polymer thermodynamics and the chain architecture of the polymer. Flory-Huggins theory illustrates that nearly all polymers are mutually immiscible, due to the drastic loss of mixing entropy. The chemically dissimilar monomer sequences found in the block copolymers may be thought of conceptually as immiscible homopolymers bound covalently end-to-end. Due to this constraint, when a block copolymer phase separates, incompatible polymer types form meso-domains with a well-defined geometry dictated by the block composition and with a size governed by the overall molecular weight (Bates et al. 1999).

In a typical SBS elastomer, the styrene composition is about 10-30 wt% such that spherical or cylindrical styrene domains form in a matrix of butadiene. When the temperature is below the glass transition temperature of polystyrene ($T_g = 100^{\circ}\text{C}$), the polybutadiene matrix is liquid ($T_g < -90^{\circ}\text{C}$) but is bound between the vitreous polystyrene spheres, which serve as physical crosslinks. When the temperature is above the glass transition temperature of polystyrene, the entire elastomer system is molten and may be processed easily. Crosslinked poly(soybean oil) has been reported to have T_g values as low as -56°C (Yang et al. 2010). Comparatively, polybutadiene has a T_g of -90°C . Thus, the poly(soybean oil) is an excellent candidate to serve as the liquid component in thermoplastic elastomers based on styrenic block copolymers.

SBS is incorporated into asphalt binder, normally between 2 and 5 percent by weight of the total binder, through mixing and shearing at high temperatures to uniformly disperse the polymer. When blended with asphalt, the polymer swells within the asphalt maltene phase to form a continuous tridimensional polymer network (Lesuer 2009). At high temperatures, the polymer network becomes fluid yet still provides a stiffening effect that increases the modulus of the mixture. At low temperatures, a linked network within the asphalt redevelops without adversely affecting the low temperature cracking performance due to the elastic properties of the polybutadiene (Airey 2004). The resulting performance properties widen the working temperature range of the asphalt/polymer system.

2.3 SBS and Asphalt Compatibility

The differences in properties such as molecular weight, density, viscosity, and solubility coefficients between SBS and asphalt result in two distinct phases when using mechanical mixing to obtain SBS-modified asphalt (Sun et al., 2006). This can lead to thermodynamically unstable blends that have a tendency to segregate during hot storage (160°C). For polymers to impart desirable properties to asphalt binder, the binder and the polymer must be compatible. Incompatible asphalt-polymer blends lack a homogenous network of polymer chains throughout the blend, thereby reducing the polymer's effectiveness, and from a practical perspective, face handling issues.

Masson et al. (2003) showed that asphalt binder and polymer composition affect the stability of the blends. Asphalt binder consists of a complex system of hydrocarbon molecules that can be fractionated into asphaltene and maltene components (Hoiberg 1979). Asphaltenes are the heaviest components of the asphalt binder matrix and contribute to the stiffness of the asphalt, whereas maltenes are the lightest components and consist of compounds known as saturates, aromatics, and resins. The asphaltenes are dispersed throughout the maltene components in the asphalt matrix. Since the molecular weights of the polymeric chains are higher than or similar to those of the asphaltenes, they compete for the solvency of the maltene fraction and a phase separation may occur if there is an imbalance between the components (Fernandes et al. 2008). Therefore, it is recognized that asphalts with a lower asphaltene content and higher aromatics content are more compatible with SBS polymers (Alonso et al. 2010).

Several polymer parameters determine how a polymer will be effective in asphalt modification; these include chain architecture, composition, and the molecular weight distribution. Lu and Isacsson (1997) compared branched SBS polymer to linear SBS polymer-modified asphalt. They concluded that linear SBS polymers displayed a finer dispersion in modified asphalt which results in a lower phase separation during hot storage. Masson et al. (2003) concluded that the lower stability of branched SBS in asphalt was not necessarily due to its branched structure but its high molecular weight. SBS modified asphalt studies have reported linear SBS polymers to have molecular weights between 130,000 to 170,000 daltons and radial SBS polymers to have molecular weights between 210,000 to 350,000 daltons.

SBS copolymers should also meet several requirements to be compatible with asphalt: they should be rich in butadiene (generally 60-70%) and the molecular weight of the styrene fraction must exceed 10,000 daltons to obtain polystyrene rich domains (Lewandowski 1994).

The interaction between asphalt and SB is different from that with SBS (Martinez-Estrada et al. 2010). Maltenes have a more favorable interaction with the polybutadiene block compared with the PS block due to maltenes swelling the polybutadiene block and not the polystyrene block. In contrast, asphaltenes are incompatible with both polybutadiene and polystyrene. Therefore, interactions between asphalt and SB are more favorable than interactions between asphalt and SBS since SB only has one polystyrene block compared to the multiple end blocks of SBS. However, SBS is more commonly used for asphalt modification due to its ability to form an elastic network through physical entanglements in the polymer rich phase.

2.4 Commercially Available SBS and SB Polymers

Commercially available SBS and SB copolymers used for modifying asphalt binders in the United States are supplied by Kraton Performance Polymers, Inc. (Kraton). D1101 and D1118 are commonly used grades of Kraton for asphalt modification. D1101 is a clear, linear triblock copolymer (SBS), and D1118 is a clear, diblock copolymer (SB). Other SB and SBS polymers are produced by LG Chem, Korea Kumho Petrochemical Co., Taiwan Synthetic Rubber Corporation (TSRC), and others.

2.4 Polymers Synthesized from Vegetable Oils

Vegetable oils have been considered as monomeric feedstocks for the plastics industry for over 20 years. Polymers from vegetable oils have obtained increasing attention as public policy makers and corporations alike have been interested in replacing traditional petrochemical feedstocks due to their environmental and economic impact.

To date, moderate success has been achieved through the application of traditional cationic and free radical polymerization routes to vegetable oils to yield thermoset plastics (i.e., plastics which, once synthesized, permanently retain their shape and are not subject to further processing). For example, a variety of polymers, ranging from soft rubbers to hard, tough plastics were made by using cationic copolymerization of vegetable oils, mainly soybean oil (SBO), using boron trifluoride diethyl etherate (BFE) as initiator (Andjelkovic et al. 2006, Pfister & Larock 2010). Soybean oil-based waterborne polyurethane films were synthesized with different properties ranging from elastomeric polymers to rigid plastics by changing the polyol functionality and hard segment content of the polymers (Lu et al. 2005, Lu et al. 2011). Moreover, soybean oil was used to synthesize different bio-based products such as sheet molding composites, elastomers, coatings, foams, etc. (Zhu et al. 2006). Bunker et al. synthesized pressure sensitive adhesives using mini-emulsion polymerization of acrylated methyl oleate, a monoglyceride derived from soybean oil (Bunker et al. 2002, Bunker et al. 2003). The polymers produced were comparable to their petroleum counterparts. Zhu et al. generated an elastic network based on acrylated oleic methyl ester through bulk polymerization using ethylene glycol as the crosslinker, obtaining a high molecular weight linear polymer using mini-emulsion

polymerization (Zhu et al. 2006). Lu et al. created thermosetting resins synthesized from soybean oil that can be used in sheet molding compound applications by introducing acid functionality onto the soybean and reacting the acid groups with divalent metallic oxides or hydroxides, forming the sheet (Lu et al. 2005). Bonnaillie et al. created a thermosetting foam system using a pressurized carbon dioxide foaming process of acrylated epoxidized soybean oil (AESO) (Bonnaillie et al. 2007).

Uncontrolled chain branching and crosslinking is inevitable by using these conventional polymerization routes due to the multifunctional nature of triglycerides, multiple initiation sites along the chain backbone, and chain transfer/termination reactions. While these thermoset materials may indeed supplant a number of petrochemically-derived thermosets, the vast majority of commodity polymers are highly processable thermoplastic materials. There is thus a need to develop highly processable thermoplastic and elastomeric polymers from vegetable oils with a wide range of applications and physical properties.

CHAPTER 3 TEST PLAN AND PROCEDURE

3.1 Research Plan

The research plan included the following specific tasks:

1. Synthesize soy-based styrenic block copolymers, with blocks of polymerized styrene (PS) and polymerized acrylated epoxidized soybean oil (PAESO), through the use of reversible addition-fragmentation chain transfer (RAFT). Triblock copolymers will contain outer blocks of polystyrene with an interior block of PAESO to form PS-PAESO-PS. Diblock copolymers will contain a block architecture of PS-PAESO.
2. Characterize the thermal, rheological, and morphological properties of the block copolymers.
3. Formulate blends of PS-PAESO-PS and PS-PAESO with bitumen and quantitatively evaluate their influence on asphalt performance; compare these results with commercially available SBS and SB block copolymers.
4. Evaluate the economics of soy-based polymers as bitumen modifiers.

Specific details of each task are outlined below.

Task 1: PS-PAESO-PS copolymers via RAFT polymerization

Reversible addition-fragmentation chain transfer (RAFT) polymerization was applied to acrylated epoxidized soybean oil, comprised predominantly of triglyceride mixtures. The distinctive feature of this chemistry is that it allows the design of the molecular architecture of the resultant polymers such that they are predominantly non-crosslinked linear or lightly branched chains. The chains behave as elastomers/rubbers at room temperature, but reversibly melt, and are susceptible to common processing techniques at elevated temperatures. RAFT has received a great deal of attention with respect to petrochemical feedstocks, but it has not been successfully applied to biofeedstocks such as soybean oil. The success of the technology on vegetable oils such as soybean oil is surprising, as conventional radical polymerization typically brings the polymerization of triglycerides into thermoset materials. RAFT successfully controls the polymerization of triglyceride so that it terminates at a desired molecular weight and block composition and produces thermoplastic polysoybean oil.

RAFT polymerization limits the number of initiation sites and drastically reduces the rate of polymer-to-polymer chain transfer and termination reactions, and also introduces the capability to produce custom chain architectures such as block copolymers (BCPs) and statistical copolymers. This degree of control is superior to that offered by other controlled radical polymerization methods — that is, polymers of higher molar mass may be obtained over a shorter period of time with less rigorous purification.

Task 2: Characterize the thermal, rheological, and morphological properties of the block copolymers.

Initial experiments during the project focused on the establishment of a reproducible procedure for the preparation of PS-PAESO-PS materials. In these experiments, reactions were allowed to progress for 12 hr, and gel permeation chromatography (GPC) was used to assess the degree of polymerization. In successful polymerizations, polymerization kinetics were assessed and fine-tuned such that polyAESO compounds with minimal polydispersity and of targeted molecular weight were produced. As structure-property relationships for the different PS-PAESO-PS systems were catalogued, composition and molecular weight ranges that were best suited as bitumen modifiers were rationally identified.

Presented in this report, are test results of two biopolymers (PS-PAESO-PS and PS-PAESO) that were developed specifically for this project as asphalt modifiers. These two materials represent the culmination of over fifty preliminary polymerizations that solidified our understanding of the reaction kinetic data and the processing parameters required to reproducibly synthesize polymers of designated composition and molar mass. As more data from asphalt-modification experiments become available, additional or improved formulation designs may be developed. The final soy-based block copolymers developed for the project were subjected to the following of characterization techniques with a focus on the symmetric PS-PAESO-PS triblock copolymers.

Thermal Characterization: Differential scanning calorimetry (DSC) was used to assess the glass transition temperature of each material and also its thermal stability.

Spectroscopy: Hydrogen-1 Nuclear Magnetic Resonance (^1H -NMR) was used to show the spectra of the PS-PAESO-PS triblock.

Rheology: Master curves were developed from oscillatory shear testing in a temperature-controlled parallel plate rheometer. These data serve as a “fingerprint” for structural information, indicate the processability of the material, are strongly correlated to their performance as asphalt modifiers, and serve as a direct point-of comparison with commercially available SBS materials.

Tensile Elongation: The PS-PAESO-PS materials were hot-pressed into “dogbones” for tensile elongation experiments yielding stress-strain curves. These experiments provided direct measurements of the strength, toughness, and (reversible) elasticity of these materials. These data also served as a direct point-of-comparison with the SBS family.

Transmission Electron Microscopy (TEM): The PS-PAESO-PS specimens were stained with OsO₄ (Os will attach selectively to double bonds on the polyAESO domains), and imaged to gain a real-space image of how PS domains are distributed within the polyAESO matrix.

Task 3: Blended PS-PAESO-PS polymers with asphalt binders and rheological testing

The PS-PAESO-PS and PS-PAESO biopolymers were blended with asphalt binder to evaluate the rheological properties of the biopolymer-asphalt blend. Two commercially available Kraton polymers were also blended with the same asphalt binder to compare the biopolymer-modified asphalt to commercially used polymer asphalt modified. The two Kraton polymers selected for the study were D1101 (SBS triblock) and D1118 (SB diblock).

A soft asphalt from Flint Hills Resources' Pine Bend Refinery in Rosemount, Minnesota graded as a PG XX-34 was used as the base asphalt. All asphalt-polymer blends were prepared in the laboratory with a Silverson L4RT shear mixer at 3000 rpm and 180°C. For each polymer-asphalt batch, 500 grams of asphalt was poured into a 1 quart aluminum can. Polymer was added to each can at two percent by total weight of the asphalt-polymer blend. The high shear mixing process was carried out for 1.5 hours.

A control batch of asphalt binder was also prepared to compare the properties of the base asphalt to the polymer-asphalt blends. It was processed following the same procedure as the polymer-asphalt batches where a 1 quart can of the base asphalt was mixed in the shear mixer at 180°C for 1.5 hours. In total, five polymer-asphalt batches were prepared; they are as follows:

- XX-34 base asphalt processed in shear mill
- XX-34 + SBS Kraton D1101
- XX-34 + SB Kraton D1118
- XX-34 + PS-PAESO-PS
- XX-34 + PS-PAESO

The subsequent rheological testing of the blends is outlined below in Figure 3 and will follow the American Association of State Highway and Transportation Officials (AASHTO) M 320 testing for determining the performance grade of the modified asphalt binders. The polymer-asphalt blends were tested a dynamic shear rheometer (DSR) at high and intermediate temperatures and tested in a bending beam rheometer at low temperatures (BBR). A rolling thin film oven (RTFO) and pressure aging vessel (PAV) were used to conduct simulated aging of the blends representative of the aging of binders that occurs during production of asphalt mixtures and the in-situ aging, respectively.

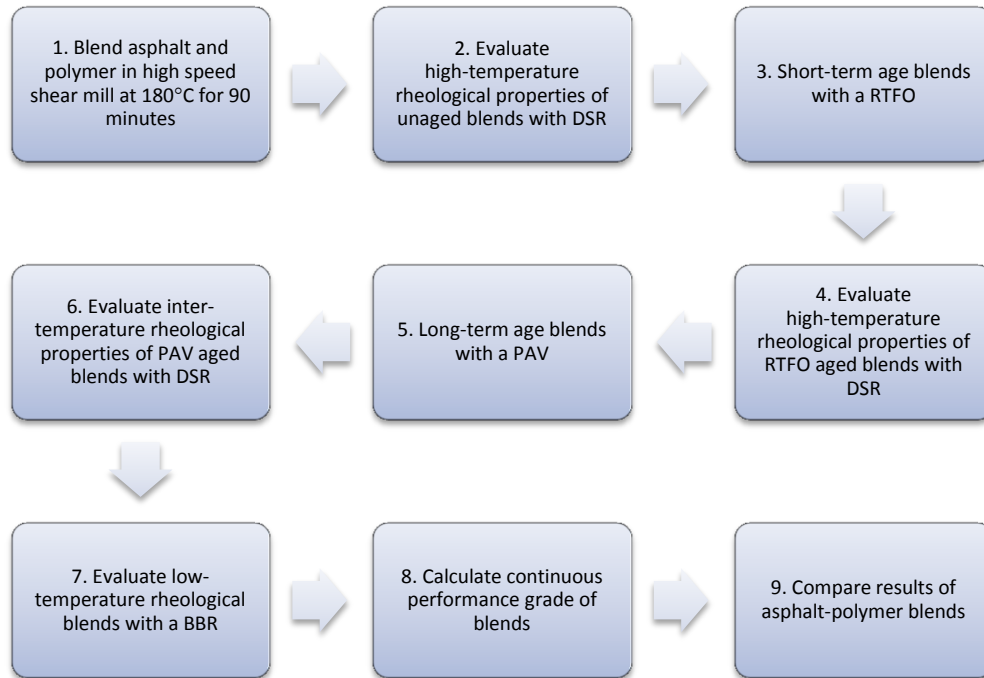


Figure 3. Rheological testing of asphalt-polymer blends

Task 4: Economic evaluation of soy-based polymers as bitumen modifiers

An economic analysis of the raw material costs for the biopolymers will be benchmarked to typical raw material costs for SBS polymers used in the asphalt paving industry.

CHAPTER 4 BIOPOLYMER SYNTHESIS

4.1 Chemical Modification of Soybean Oil

Soybean oil is the most abundant vegetable oil, which accounts for almost 30% of the world's vegetable oil supply. It is particularly suitable for polymerization, because it possesses multiple carbon-carbon double bonds that allow for modifications such as conjugation, epoxidation of the double bonds, etc. Soybean oils are mixtures of triglycerides (a representative structure appears in Figure 4), containing a number of double bonds that may serve as candidates for polymerization.

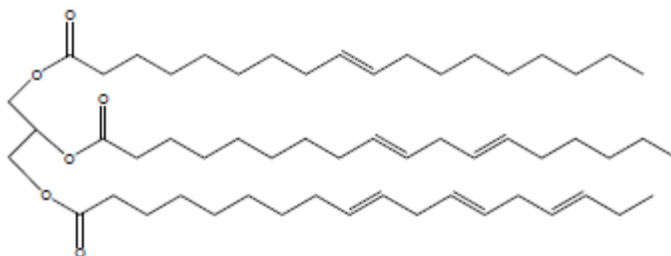


Figure 4. A representative structure of a triglyceride

In unprocessed oils these are located in the middle of the alkyl chains, and have only limited reactivity towards propagation reactions due to steric hindrance and unfavorable stability of the free radical. This reactivity improves dramatically when the double bonds are conjugated (Li et al. 2001, Henna et al. 2007, Valverde et al. 2008, and Robertson et al. 2010). Evidently, this may be readily achieved to nearly 100% conversion with homogeneous Rh catalysis (Larock et al. 2001).

A conjugated triglyceride may contain one or more conjugated sites. For instance, a conjugated triglyceride may contain a single conjugated site per triglyceride. Alternatively, each fatty-acid chain of the triglyceride may contain one or more conjugated sites. Exemplary conjugated triglycerides are shown in Figure 5. Acrylation of soybean oil is achieved by epoxidation of the soybean oil's carbon-carbon double bonds, followed by acrylation of the epoxy rings to yield acrylated epoxidized soybean oil (AESO) monomer which is radically polymerizable and used as the monomer for the block copolymer polymerizations.

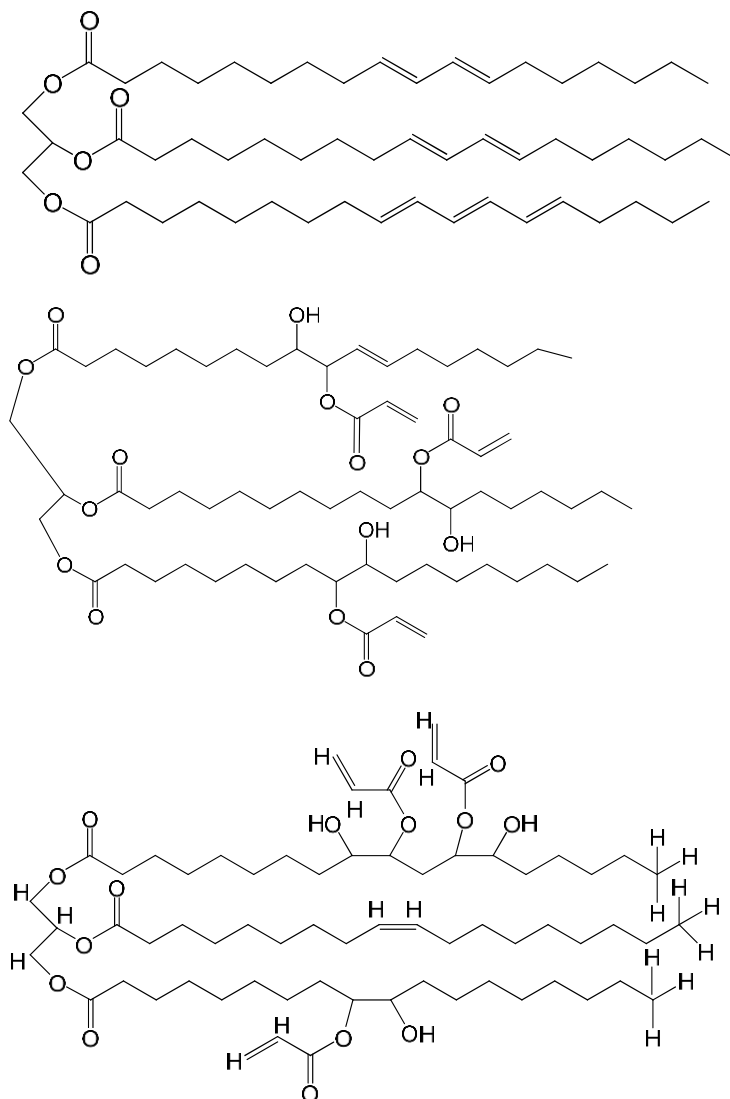


Figure 5. Conjugation of triglyceride molecule followed by two examples of AESO

4.2 Synthesis of Thermoplastic Block Copolymers

A radically polymerizable triglyceride monomer (AESO) was polymerized with polystyrene via reversible addition-fragmentation chain-transfer (RAFT) polymerization, in the presence of a free radical initiator and a chain transfer agent, to form a thermoplastic block copolymer. The polymerizing step was carried out under conditions effective to achieve a number average degree of polymerization (N_n) for the thermoplastic block copolymer of up to 100,000 repeat units per molecule without gelation.

RAFT polymerization is a type of living polymerization or controlled polymerization, utilizing a chain transfer agent (CTA). Conventional RAFT polymerization mechanism consists of a sequence of addition-fragmentation equilibria, as shown in Figure 6 (Moad et al. 2006).

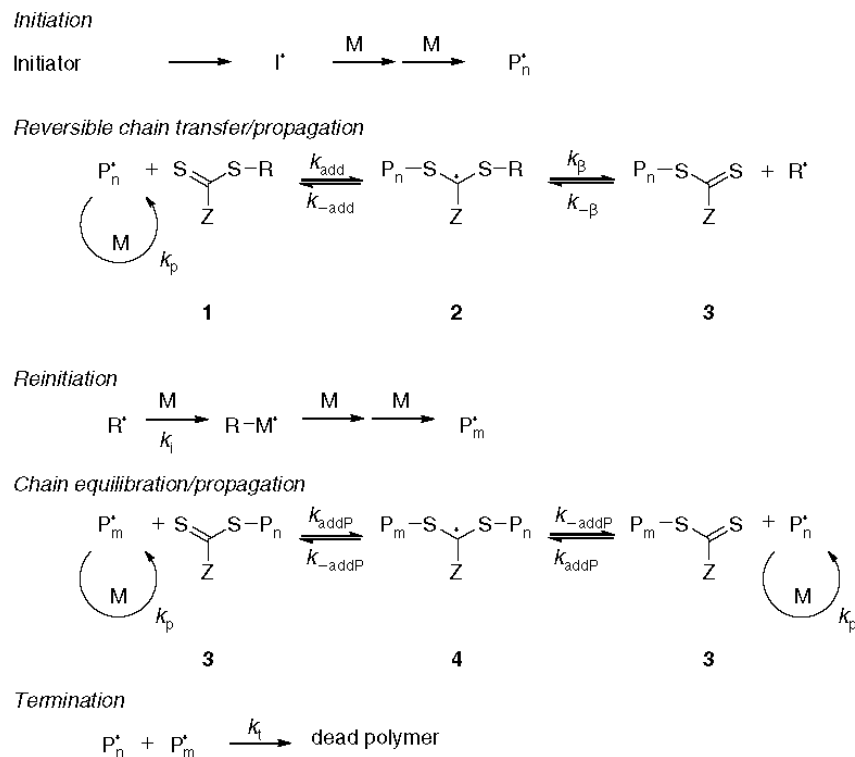


Figure 6. RAFT polymerization mechanism

The RAFT polymerization reaction starts with initiation. Initiation is accomplished by adding an agent capable of decomposing to form free radicals; the decomposed free radical fragment of the initiator attacks a monomer yielding a propagating radical (P_n^{\bullet}), in which additional monomers are added producing a growing polymer chain. In the propagation step, the propagating radical (P_n^{\bullet}) adds to a chain transfer agent (CTA), such as a thiocarbonylthio compound ($\text{RSC}(\text{Z})=\text{S}$), (1), followed by the fragmentation of the intermediate radical (2) forming a dormant polymer chain with a thiocarbonylthio ending ($\text{P}_n\text{S}(\text{Z})\text{C}=\text{S}$), (3) and a new radical (R^{\bullet}). This radical (R^{\bullet}) reacts with a new monomer molecule forming a new propagating radical (P_m^{\bullet}). In the chain propagation step, (P_n^{\bullet}) and (P_m^{\bullet}) reach equilibrium and the dormant polymer chain (3) provides an equal probability to all polymers chains to grow at the same rate, allowing polymers to be synthesized with narrow polydispersity. Termination is limited in RAFT, and, if occurring, is negligible. Targeting a specific molecular weight in RAFT can be calculated by multiplying the ratio of monomer consumed to the concentration of the CTA used by the molecular weight of the monomer.

To synthesize the soy-based block copolymers, AESO was purchased from Fisher Scientific and was used as received. High-performance liquid chromatography (HPLC)-grade toluene was purchased from Fisher Scientific and used without further purification. Styrene was purchased from Fisher Scientific and purified over basic alumina followed by three freeze-pump-thaw cycles. RAFT synthesis was performed in a similar manner to the procedure described by Moad et al. (Moad et al. 2006, Moad et al. 2009). Briefly, azobisisobutyronitrile (AIBN) was used as

the initiator. 1-phenylethyl benzodithioate was used as the chain transfer agent (CTA), and was synthesized according to established procedures (Moad et al. 2006, Moad et al. 2009).

Reversible Addition-Fragmentation Chain Transfer Polymerization (RAFT) of Styrene

Monomer (styrene), initiator, CTA, and solvent were mixed under argon in a round-bottomed flask with various mass ratios of monomer: solvent, 1:5 molar ratio of initiator to CTA, and 10:1 molar ratio of monomer to CTA. The reaction flask was bubbled with argon for 30 minutes to remove oxygen from the system before the temperature was increased. The reaction was run at 100 °C and the reaction time varied according the desired molecular weight (M_n). The molecular weight (number average) increase of the styrene homopolymer as a function of time is shown in Figure 7.

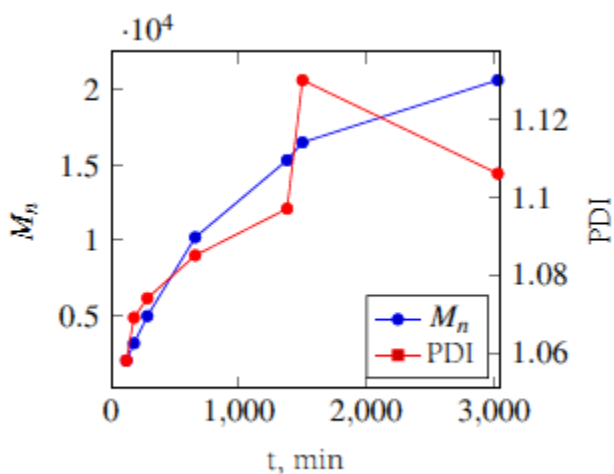


Figure 7. Molecular weight of polystyrene in RAFT reaction

RAFT of Acrylated Epoxidized Soybean Oil

Monomer (AESO), initiator, CTA, and solvent (1,2-dioxane) were mixed under argon in a 100 mL round-bottomed flask with various mass ratios of monomer: solvent, 1:5 molar ratio of initiator to CTA, and 10:1 molar ratio of monomer to CTA. This monomer to CTA ratio represents an excess of CTA compared to a typical RAFT synthesis. In a typical RAFT reaction, a N:1 ratio would yield polymers with an average of N repeat units. In RAFT polymerization of AESO, however, the multifunctional character of the AESO monomer tends to crosslink, which is mitigated by the use of excess CTA, as described herein. The reaction flask was bubbled with argon for 30 minutes to remove oxygen from the system before the temperature was increased. The reaction was run at 70 °C and the reaction time varied according the desired molecular weight (M_n).

*Synthesis of P(Styrene-*b*-AESO)*

For synthesis of P(styrene-*b*-AESO), AESO monomer dissolved in toluene (or dioxane) was transferred to the reaction vessel containing the styrene homopolymer. The reaction proceeded for 5-6 hours, and the product was cooled down and precipitated three times in excess methanol and water. M_n was monitored as a function of time for the diblock copolymer (Figure 8). The product was stirred in a 2:1 volume ratio of methanol to ethanol solution to remove unreacted AESO monomer. The final product was vacuum dried for 24 hours at room temperature. In Figure 9, the gel permeation chromatography (GPC) curves show a decrease in elution time (increase in molecular weight) from the AESO monomer, to polystyrene homopolymer (PS), and to the diblock copolymer (PS-PAESO).

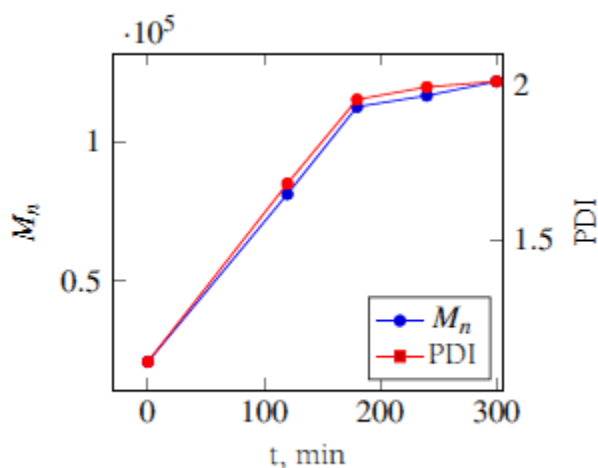


Figure 8. Molecular weight of PS-PAESO in RAFT reaction

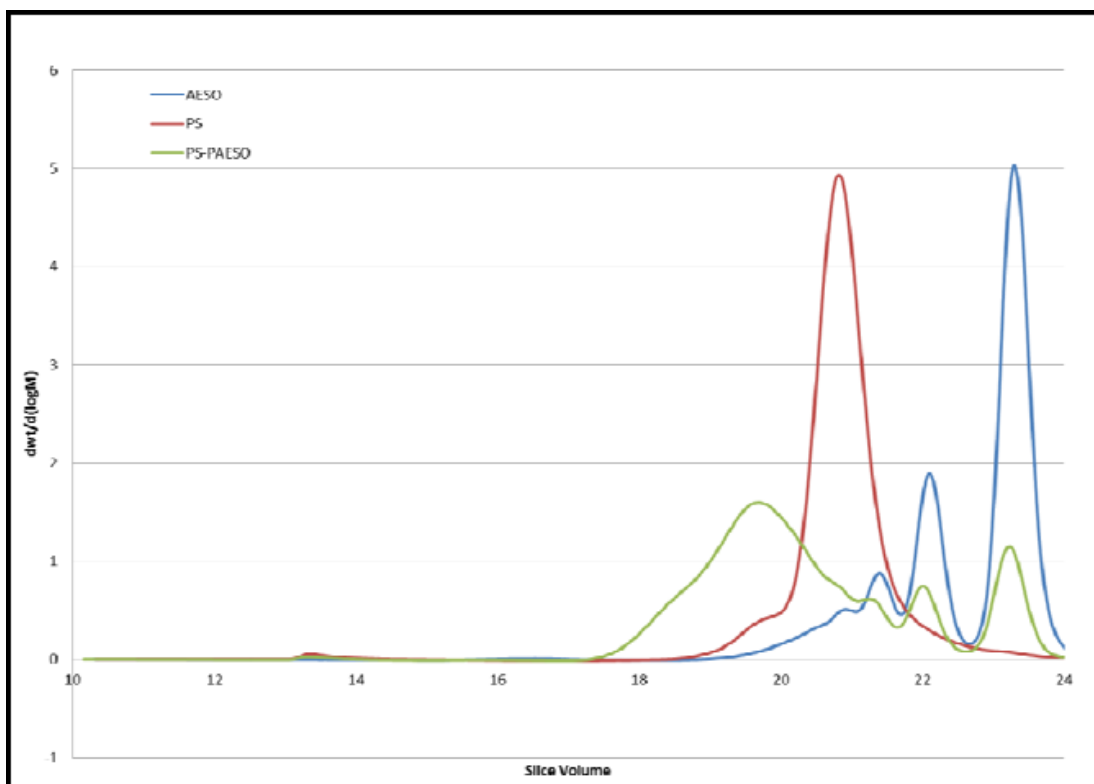


Figure 9. Molecular weight distribution of AESO, polystyrene (PS), and PS-PAESO

*Synthesis of P(Styrene-*b*-AESO-*b*-Styrene)*

For P(styrene-*b*-AESO-*b*-styrene), the P(styrene-*b*-AESO) diblock was redissolved in toluene (or dioxane), styrene, and AIBN. The reaction vessel was bubbled with argon for 1 hour and the reaction proceeded for 1-2 hours at 70°C. The final product was precipitated two times in excess methanol and water. The product was then stirred in a 2:1 volume ratio of methanol to ethanol solution for 15 minutes to remove the unreacted AESO monomer. The product was filtered and vacuum dried at room temperature for 24 hours.

Reaction Time

RAFT reaction times were varied according the desired molecular weight (M_n) (see Figure 8). Most reactions were stopped after 24 hours. M_n of poly(styrene-*b*-AESO) was also monitored as a function of time, as shown in Figure 6. The GPC curves in Figure 9 show a decrease in elution time (increase in molecular weight) from the monomer, to homopolymer, to the diblock can be seen. After the addition of the final styrene block, the final product p(styrene-*b*-AESO-*b*-styrene) was subjected to different characterization techniques.

CHAPTER 5 TEST RESULTS AND ANALYSIS

5.1 Characterizations of the Polymers

The final soy-based, thermoplastic, elastomeric, block copolymers are presented in Figures 10 and 11. The PS-PAESO diblock is shown in Figure 10, and the PS-PAESO-PS triblock is shown in Figure 11.



Figure 10. PS-PAESO diblock



Figure 11. PS-PAESO-PS triblock

The PS-PAESO and PS-AESO-PS block copolymers were subsequently characterized for their molecular weight and polydispersity index using gel permeation chromatography (GPC) and for their polystyrene content using hydrogen-1 nuclear magnetic resonance $^1\text{H-NMR}$ (Table 1). The results show 33 percent styrene in the PS-PAESO diblock and 49 percent styrene in the PS-PAESO-PS triblock. $^1\text{H-NMR}$ results are presented in Figure 12.

Table 1. Biopolymer molecular weights and styrene contents

	M.W.^a	PDI^b	%Styrene^c	1st ^d	2nd ^e
PAESO	29,500	1.39	0	-	-
PS-PAESO	40,980	1.34	33	13,900	-
PS-PAESO-PS	53,300	1.84	49	13,900	12,200

^aTotal molecular weight of block copolymer

^bPolydispersity

^cPercent styrene in block copolymer

^dMolecular weight of styrene in first block

^eMolecular weight of styrene in second block

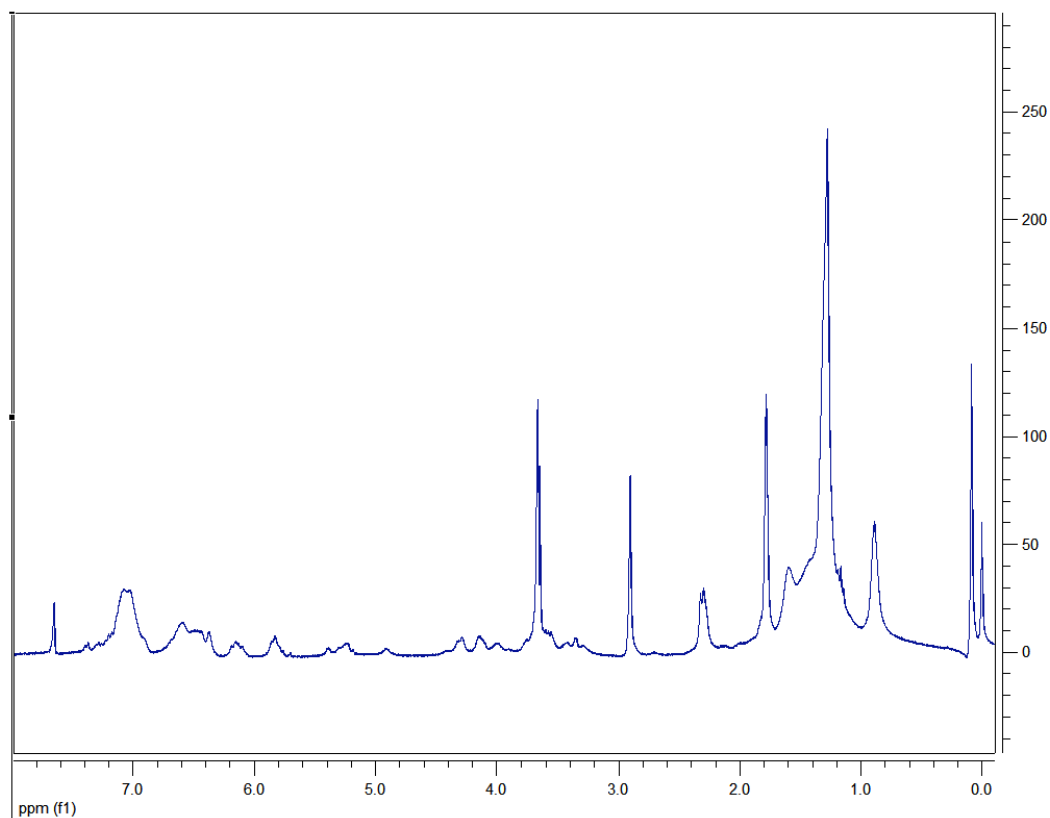


Figure 12. Nuclear magnetic resonance spectra results of PS-PAESO-PS

Figure 13 is a transmission electron microscopy (TEM) image of a PS-PAESO-PS sample. The image shows a semi-ordered structure where the black islands are the styrene (hard) blocks and the lighter regions are the AESO (soft) blocks.

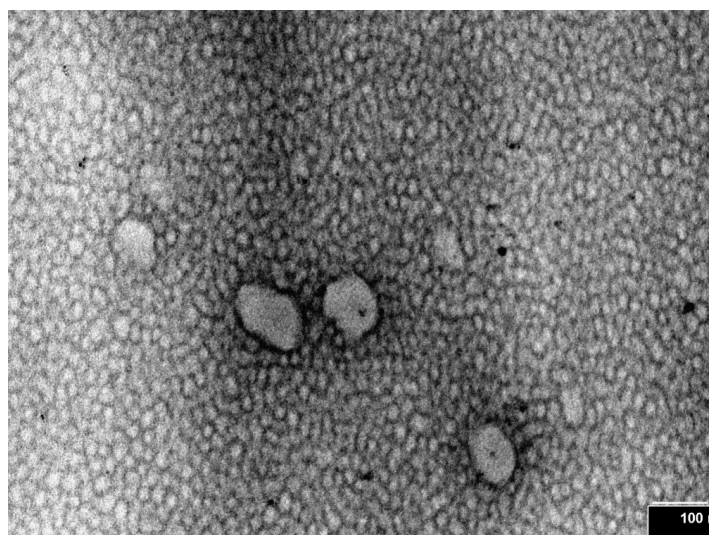


Figure 13. Transmission electron microscopy image of PS-PAESO-PS

DSC testing provided a glass transition temperature for the PAESO and polystyrene blocks (Figure 14). The lower curve in the figure represents the PAESO block and the upper curve represents the polystyrene block. The glass transition of the PAESO is at -10°C ; no apparent glass transition is present for the polystyrene block.

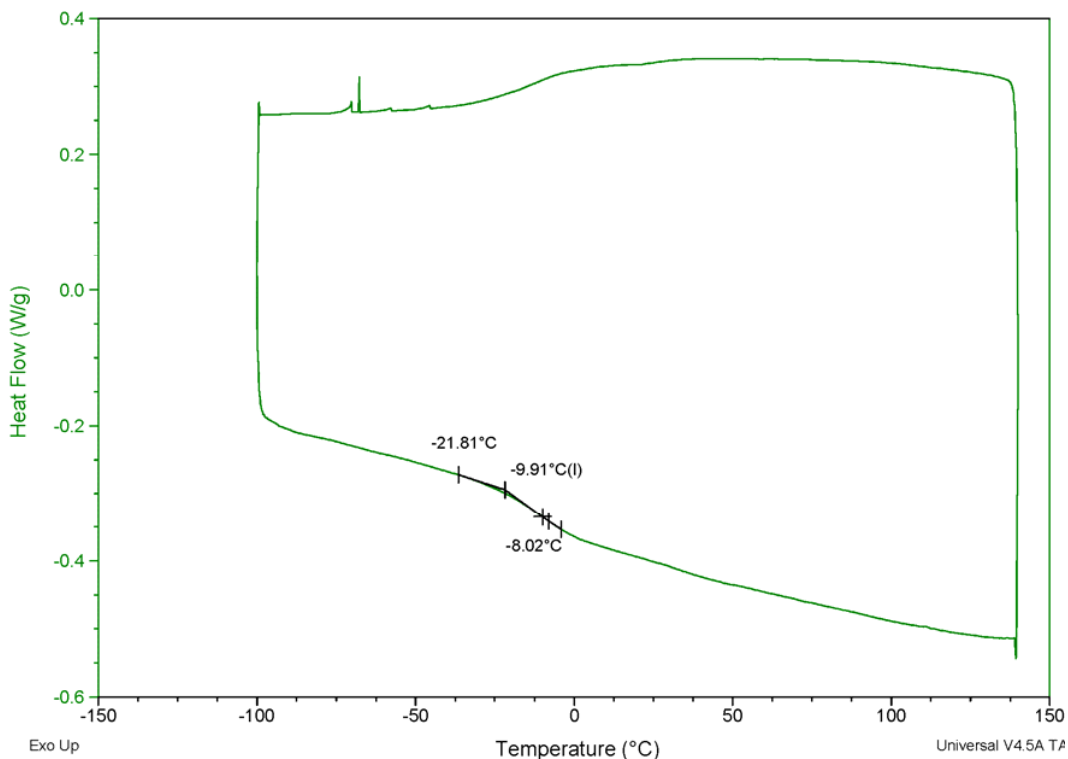


Figure 14. Differential scanning calorimetry results for PAESO and polystyrene blocks

Isothermal frequency scans with a frequency range of 0.1-100 rad/s were conducted on the PS-PAESO-PS biopolymer within the linear viscoelastic regime using a strain of 2.5%. The initial temperature was set to 120°C , and the final temperature was set to 220°C . Temperature was changed in 20°C decrements, allowing 3 minutes as an equilibration time. The elastic modulus, G' , shows no apparent change with change in frequency or temperatures below about 200°C . The rheology results are shown in Figure 15.

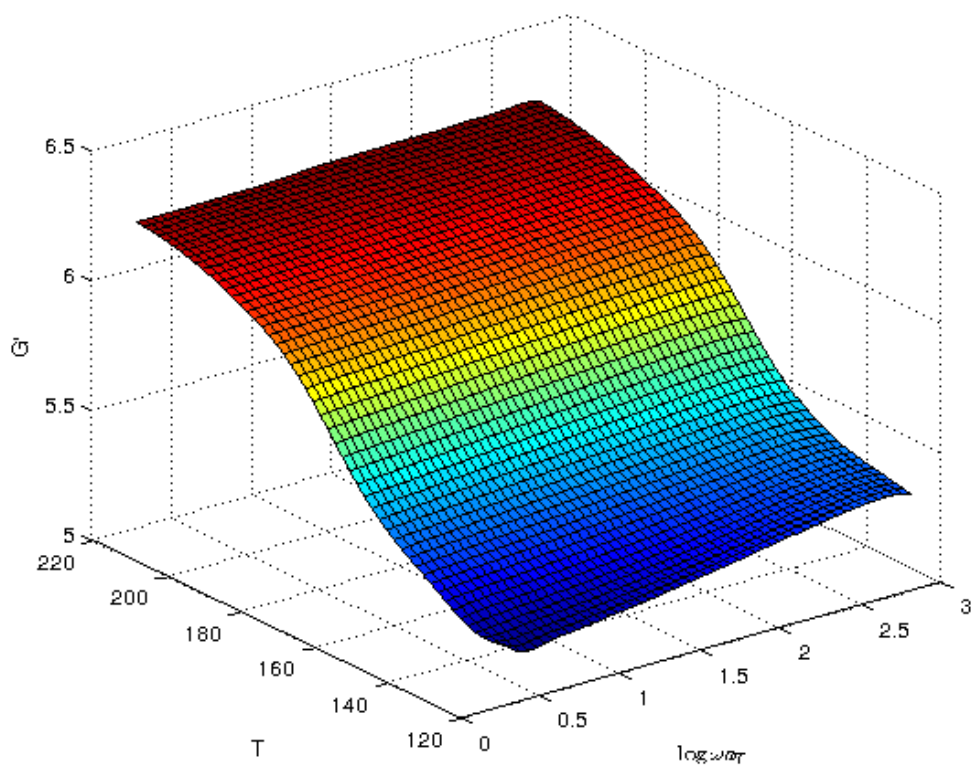


Figure 15. Isothermal frequency scans of PS-PAESO-PS

Tensile testing was performed in an Instron 5569 using a speed of 60 mm/minute (Figure 16). The results show that the maximum stress that can be applied to the RAFT synthesized triblock copolymer was about 1.3 MPa (Figure 17).

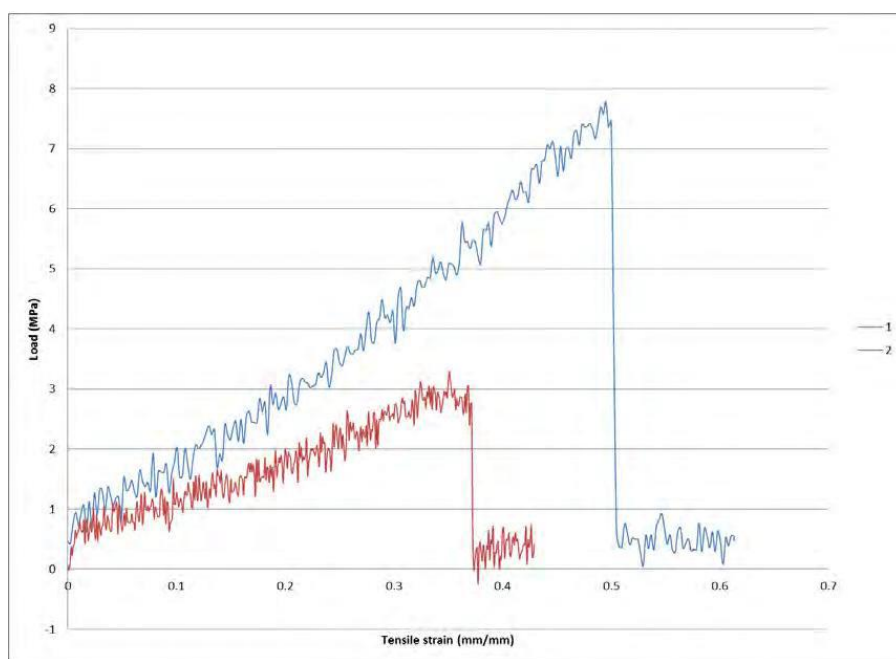


Figure 16. Tensile strain (mm/mm) vs. load (MPa) for PS-PAESO-PS

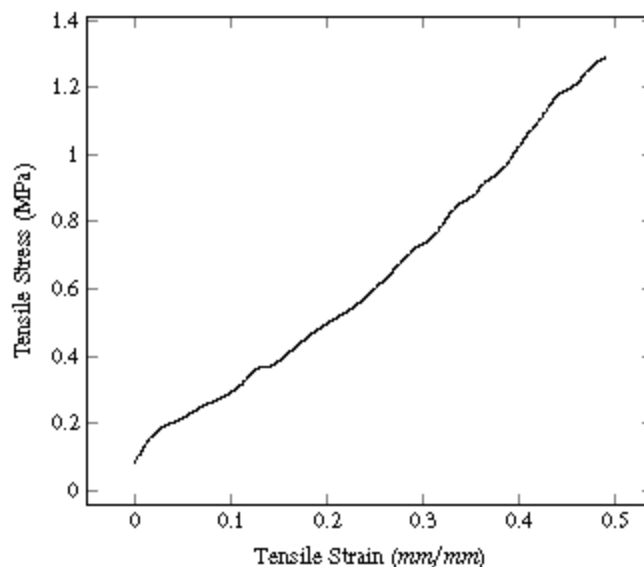


Figure 17. Tensile strain (mm/mm) vs. tensile stress (MPa) for PS-PAESO-PS

The characteristics of the soy-based polymers as presented in this chapter, demonstrate they should be suitable as an asphalt modifier. In addition to asphalt, they may also be used in various applications for other industries, such as viscosity modifiers for consumer care products, adhesives, sealants, rubber compositions, products for the automobile industry, footwear, packaging, products for consumer electronics, etc.

5.2 Evaluation of Asphalt Modified with Kraton Polymers

Prior to evaluating blends of asphalt with the soy-based block copolymer, the XX-34 base asphalt was blended with Kraton D1101 SBS triblock and Kraton D1101 SB diblock at different percentages of polymer. The high PG failing temperature for each blend was evaluated using the DSR. The high performance grade (PG) temperature of an asphalt represents the temperature in degrees Celsius where the phase angle (δ) divided by the complex shear modulus (G^*) is equal to 1kPa for unaged binders and 2.2kPa for rolling thin film oven aged binders. Lower phase angles increase the elastic component of an asphalt binder, and higher complex shear modulus values increase the stiffness of the material. Thus, the higher the PG failure temperature of an asphalt binder, the greater its ability will be to resist pavement rutting from vehicular loading.

In Table 2, the DSR results show the unaged XX-34 base asphalt contained a continuous high PG of 51.09. Kraton D1101 SBS polymer was then added to the base asphalt at levels of 1, 2, 3, 4, and 5 percent, to evaluate how the percentage of D1101 would change the PG of the binder. As expected, the continuous high PG increased as the polymer content increased. Similar results were obtained for the RTFO aged D1101 polymer-asphalt blends (Table 3).

Table 2. DSR results for unaged asphalt modified with Kraton D1101

Temp	Measurement	Base Asphalt	w/ 1% Kraton D1101	w/ 2% Kraton D1101	w/ 3% Kraton D1101	w/ 4% Kraton D1101	w/ 5% Kraton D1101
46°C	G* (Pa)	2023	2816	4500	5152		
	δ (degrees)	86.36	84.05	79.40	76.44		
	G*/sin(δ) (kPa)	2.03	2.83	4.58	5.30		
52°C	G* (Pa)	879	1205	1962	2361	3560	4790
	δ (degrees)	87.75	85.85	81.85	79.38	64.64	60.63
	G*/sin(Δ) (kPa)	0.88	1.21	1.98	2.40	3.94	5.50
58°C	G* (Pa)		569	928	1141	1946	2703
	δ (degrees)		87.01	83.48	81.44	68.8	64.77
	G*/sin(δ) (kPa)		0.57	0.93	1.15	2.09	2.99
64°C	G* (Pa)				588	1076	1532
	δ (degrees)				82.36	71.78	68.65
	G*/sin(δ) (kPa)				0.59	1.13	1.65
70°C	G* (Pa)					614	902
	δ (degrees)					75.8	70.50
	G*/sin(δ) (kPa)					0.64	0.96
PG Failing Temp (°C)		51.09	53.67	57.42	59.45	65.59	69.7

Table 3. DSR results for RTFO aged asphalt modified with Kraton D1101

Temp	Measurement	Base Asphalt	w/ 1% Kraton D1101	w/ 2% Kraton D1101	w/ 3% Kraton D1101	w/ 4% Kraton D1101	w/ 5% Kraton D1101
46°C	G* (Pa)	5449	7038	9619	11395		
	δ (degrees)	81.66	78.49	73.95	70.27		
	G*/sin(δ) (kPa)	5.51	7.18	10.01	12.11		
52°C	G* (Pa)	2250	2998	4276	5230	6944	8541
	δ (degrees)	84.13	81.33	77.59	74.14	67.80	62.57
	G*/sin(δ) (kPa)	2.26	3.03	4.38	5.44	7.50	9.62
58°C	G* (Pa)	994	1349	1973	2475	3359	4516
	δ (degrees)	86.09	83.87	81.03	78.36	73.11	65.74
	G*/sin(δ) (kPa)	1.00	1.36	2.00	2.53	3.510	4.95
64°C	G* (Pa)				1198	1653	2442
	δ (degrees)				82.06	77.11	70.00
	G*/sin(δ) (kPa)				1.21	1.70	2.60
70°C	G* (Pa)						1331
	δ (degrees)						73.61
	G*/sin(δ) (kPa)						1.39
PG Failing Temp (°C)		52.38	54.45	57.22	59.20	61.89	65.60

Tables 4 and 5 show the DSR results of the unaged and RTFO aged XX-34 base asphalt modified with Kraton D1118 SB polymer, respectively, at polymer contents of 1, 2, 3, 4, and 5 percent. The D1118 polymer did not increase the grade of the base asphalt as much as the D1101 polymer. For example, when 5 percent D1118 polymer was blended with the base asphalt, the continuous grade of the base asphalt increased to 62.2°C; whereas when 5 percent D1101 polymer was blended with the base asphalt, the continuous grade of the base asphalt increased to 65.6°C. The high PG temperatures for the D1101 modified asphalt was expected since SBS is known to have a greater ability than SB to form an elastic network of physical chain entanglements in the polymer rich phase of an asphalt-polymer blend.

Table 4. DSR results for unaged asphalt modified with Kraton D1118

Temp	Measurement	Base Asphalt	w/ 1% Kraton D1118	w/ 2% Kraton D1118	w/ 3% Kraton D1118	w/ 4% Kraton D1118	w/ 5% Kraton D1118
46°C	$ G^* $ (Pa)	2023	2674	3170	4745		
	δ (degrees)	86.36	83.89	81.14	75.27		
	$G^*/\sin(\delta)$ (kPa)	2.03	2.69	3.21	4.91		
52°C	$ G^* $ (Pa)	879	1162	1438	2242	2229	2870
	δ (degrees)	87.75	85.73	83.54	77.96	75.86	72.95
	$G^*/\sin(\delta)$ (kPa)	0.88	1.17	1.45	2.29	2.299	3.00
58°C	$ G^* $ (Pa)		546	689	1102	1126	1488
	δ (degrees)		87.14	85.49	80.80	77.34	74.26
	$G^*/\sin(\delta)$ (kPa)		0.55	0.69	1.12	1.15	1.55
64°C	$ G^* $ (Pa)				565	601	812
	δ (degrees)				82.42	78.04	74.57
	$G^*/\sin(\delta)$ (kPa)				0.57	0.61	0.84
Failing Temp (°C)		51.09	53.37	55.03	59.12	59.51	62.30

Table 5. DSR results for RTFO aged asphalt modified with Kraton D1118

Temp	Measurement	Base Asphalt	w/ 1% Kraton D1118	w/ 2% Kraton D1118	w/ 3% Kraton D1118	w/ 4% Kraton D1118	w/ 5% Kraton D1118
46°C	$ G^* $ (Pa)	5449	7233	8100	10065		
	δ (degrees)	81.66	78.39	75.76	72.06		
	$G^*/\sin(\delta)$ (kPa)	5.51	7.38	8.36	10.58		
52°C	$ G^* $ (Pa)	2250	3091	3575	4666	5079	6319
	δ (degrees)	84.13	80.74	77.60	73.72	72.2	68.68
	$G^*/\sin(\delta)$ (kPa)	2.26	2.13	3.66	4.86	5.34	6.78
58°C	$ G^* $ (Pa)	994	1418	1695	2271	2540	3231
	δ (degrees)	86.09	83.05	79.90	76.07	73.96	70.22
	$G^*/\sin(\delta)$ (kPa)	1.00	1.43	1.72	2.34	2.64	3.43
64°C	$ G^* $ (Pa)				1142	1311	1731
	δ (degrees)				78.84	76.43	72.41
	$G^*/\sin(\delta)$ (kPa)				1.16	1.35	1.82
Failing Temp (°C)		52.38	54.74	56.02	58.65	59.67	62.20

The low temperature creep stiffness and the m-value of the base asphalt and Kraton polymer-asphalt blends were evaluated using a bending beam rheometer (BBR) (Table 6). Three percent Kraton D1101 and D1118 each increased the continuous low temperature PG only by about three degrees which kept the low PG at -34°C.

Table 6. BBR results for PAV aged asphalt modified with Kraton D1101 and D1118

		Base Asphalt		w/ 3% Kraton D1101		w/ 3% Kraton D1118	
Temp	Measurement	PAV Aged		PAV Aged		PAV Aged	
-24°C	Stiffness (MPa)	182	-	245	244	245	237
	m-value	0.346	-	0.310	0.306	0.311	0.307
-30°C	Stiffness (MPa)	479	-	520	489	492	495
	m-value	0.271	-	0.239	0.241	0.244	0.235
Continuous Low Grade (°C)		-37.68		-34.71		-34.78	

5.3 Evaluation of Asphalt Modified with the Biopolymers

PS-PAESO and PS-PAESO-PS were blended with the base asphalt to determine how the biopolymers affected the base asphalt's PG. Each biopolymer was added to the base asphalt at a polymer content of 2 percent. (The biopolymers were not evaluated in the asphalt at multiple contents similarly to the Kraton polymers, due to limited laboratory production capabilities. Since the completion of this study, a larger reactor has been purchased which allows for larger

biopolymer production capacity.) The blends were compared to the base asphalt as well as the base asphalt processed in the shear mill without polymer. The results in Table 7 highlight the high heat levels that occur during shear mill processing which cause the asphalt to age, resulting in a 2.5 to 3 degree increase of the high PG temperature. Although a continuous high PG of 51.09°C was measured in the base asphalt with the DSR, 53.64°C should be used as the base asphalt PG for a proper comparison to respective polymer-modified asphalt blends since all polymer-asphalt blends were processed in a shear mill.

When 2 percent PS-PAESO diblock was added to the base asphalt, the base asphalt's continuous high PG increased from 53.64°C to 69.08°C. The PS-PASEO-PS triblock at 2 percent increased the continuous high PG to 70.4°C. Both PG values are higher than the asphalt modified with 2 percent D1101 and D1118, which were 57.22°C and 55.03°C respectively. The higher PG values in the biopolymer-modified asphalt are a result of a lower phase angle and higher shear modulus value than the Kraton polymer-modified asphalt.

Table 7. DSR results for asphalt modified with biopolymers

Temp	Measurement	Base Asphalt		Base Asphalt processed in shear mill w/o polymer		Base Asphalt w/ 2%PS-PAESO		Base Asphalt w/ 2%PS-PAESO-PS	
		Unaged	RTFO Aged	Unaged	RTFO Aged	Unaged	RTFO Aged	Unaged	RTFO Aged
46°C	G* (Pa)	2023	5449	2843	8219				
	δ (degrees)	86.36	81.66	84.37	79.35				
	G*/sin(δ) (kPa)	2.027	5.51	2.857	8.362				
52°C	G* (Pa)	879	2250	1214	3383	9599	18900	11250	21275
	δ (degrees)	87.75	84.13	86.03	82.24	73.92	67.98	73.12	67.56
	G*/sin(δ) (kPa)	0.88	2.26	1.216	3.414	9.988	20.39	11.76	23.02
58°C	G* (Pa)		994	557.2	1494	4323	8646	5100	9893
	δ (degrees)		86.09	87.26	84.55	77.01	71.39	76.34	70.85
	G*/sin(δ) (kPa)		1.00	0.5579	1.501	4.436	9.124	5.248	10.48
64°C	G* (Pa)					2012	4043	2384	4680
	δ (degrees)					79.85	74.90	79.40	74.34
	G*/sin(δ) (kPa)					2.04	4.19	2.43	4.86
70°C	G* (Pa)					983	1941	1157	2233
	δ (degrees)					82.24	78.23	82.11	77.72
	G*/sin(δ) (kPa)					0.99	1.98	1.17	2.29
76°C	G* (Pa)							583	1094
	δ (degrees)							84.44	80.76
	G*/sin(δ) (kPa)							0.59	1.11
PG Failing Temp (°C)		51.09	52.38	53.64	55.26	69.82	69.08	71.42	70.42

The asphalt properties from DSR testing at intermediate pavement temperatures on PAV aged blends are presented in Table 8. The intermediate PG temperature is calculated as the temperature in degrees Celsius where the complex shear modulus multiplied by the phase angle equals 5000 kPa. Lower intermediate PG temperatures indicate an asphalt binder has a greater ability to deform without building up large stresses. A more compliant material will help reduce structural fatigue cracking in pavements. The biopolymers increased the intermediate PG temperatures four to six degrees Celsius. The PS-PAESO-PS modified asphalt contained a lower continuous PG intermediate temperature (12.96°C) than the PS-PAESO modified asphalt (15.11°C). The main factor contributing to this difference was the larger G^* value component in the PS-PAESO modified asphalt. Although both PS-PAESO and PS-PAESO-PS asphalt blends possess similar elastic properties at intermediate temperatures as evident from the phase angles, the presence of the second polystyrene block in the PS-PAESO-PS may be contributing the polymers ability to form a network of physical entanglements throughout the asphalt binder to create a more compliant material at intermediate temperatures.

Table 8. DSR results for PAV aged asphalt modified with biopolymers

		Base Asphalt	Base Asphalt processed in shear mill w/o polymer	Base Asphalt w/ 2%PS-PAESO	Base Asphalt w/ 2%PS-PAESO-PS
Temp	Measurement	PAV Aged	PAV Aged	PAV Aged	PAV Aged
22°C	$ G^* $ (Pa)	8.22E+05		3.24E+06	2.49E+06
	δ (degrees)	57.71		43.42	43.77
	$G^*/\sin(\delta)$ (kPa)	694.5		2228	1725
19°C	$ G^* $ (Pa)	1.35E+06		4.80E+06	3.72E+06
	δ (degrees)	55.17		41.42	41.77
	$G^*/\sin(\delta)$ (kPa)	1110		3177	2476
16°C	$ G^* $ (Pa)	2.20E+06	2.47E+06	7.08E+06	5.49E+06
	δ (degrees)	52.51	50.26	39.37	39.77
	$G^*/\sin(\delta)$ (kPa)	1748	1894	4490	3510
13°C	$ G^* $ (Pa)	3.61E+06	3.93E+06	1.03E+07	8.07E+06
	δ (degrees)	49.61	47.49	37.39	37.76
	$G^*/\sin(\delta)$ (kPa)	2746	2900	6248	4937
10°C	$ G^* $ (Pa)	5.80E+06	6.21E+06		1.18E+07
	δ (degrees)	46.7	44.68		35.75
	$G^*/\sin(\delta)$ (kPa)	4216	4366		6884
6°C	$ G^* $ (Pa)	9.13E+06	9.76E+06		
	δ (degrees)	43.73	41.78		
	$G^*/\sin(\delta)$ (kPa)	6310	6495		
PG Failing Temp (°C)		8.78	9.02	15.11	12.96

After intermediate temperature testing, the long-term aged biopolymer-asphalt blends from the PAV were evaluated for their low temperature properties (Table 9). When the base asphalt was processed in the shear mill without polymer, the creep stiffness increased and the m-value decreased at low temperatures which resulted in a higher critical cracking temperature. The critical cracking temperature is the temperature at which an asphalt binder's creep stiffness is greater than 300 MPa or m-value is less than 0.300. Both the creep stiffness and m-value are determined from BBR testing after 60 seconds of loading. Adding two percent biopolymers to the base asphalt resulted in the critical cracking temperature increasing from -36.3°C to -32.8°C for the PS-PAESO modified asphalt and -33.0°C for the PS-PAESO-PS modified asphalt.

Table 9. BBR results for PAV aged asphalt modified with biopolymers

		Base Asphalt		Base Asphalt processed in shear mill w/o polymer		Base Asphalt w/ 2%PS-PAESO		Base Asphalt w/ 2%PS-PAESO-PS	
Temp	Measurement	PAV Aged		PAV Aged		PAV Aged		PAV Aged	
-18°C	Stiffness (MPa)	-	-	-	-	117	-	128	-
	m-value	-	-	-	-	0.360	-	0.336	-
-24°C	Stiffness (MPa)	182	-	190	223	267	279	271	274
	m-value	0.346	-	0.319	0.327	0.291	0.280	0.296	0.290
-30°C	Stiffness (MPa)	479	-	444	479	471	-	-	-
	m-value	0.271	-	0.261	0.267	0.214	-	-	-
Continuous Low Grade (°C)		-37.68		-36.34		-32.83		-33.02	

A PG temperature grade comparison of the base asphalt, asphalt modified with Kraton polymers, and asphalt modified with the biopolymers, is shown in Figures 18 and 19. The charts highlight the differences among base asphalt modified with different polymers at two percent. The D1101 and D1118 polymers increased the high PG temperature approximately one grade, from 51.1°C to 57.2°C and 55.0°C, respectively. For the biopolymers, when two percent PS-PAESO was added to the base asphalt, the high PG temperature increased from 51.1°C to 69.1°C; and when two percent PS-PAESO-PS was added to the base asphalt, the high PG temperature increased to 70.4°C. These increases equate to approximately three grade bumps and demonstrate the effectiveness of the biopolymers. By adding two percent of either biopolymer to the base asphalt, the increase in high temperature PG will enhance the rutting resistance of an asphalt pavement.

While the biopolymers were more effective than the Kraton polymers at increasing the high temperature performance grade, the biopolymers increased the low temperature PG of the base asphalt one grade while the Kraton polymers did not (Figure 2). This increase in the low temperature PG caused the asphalt binder to be more susceptible to low temperature cracking at -34°C. The benefit of adding two percent Kraton polymers was increasing the high PG temperature one grade without changing the low PG. Thus, the Kraton polymers were effective in reducing the temperature susceptibility of the base asphalt. (The Kraton modified asphalt samples that were tested for low temperature properties contained three percent polymer, not two

percent polymer. Since additional polymer will increase the low temperature PG, the extra 1% polymer in these samples should not affect the analysis.)

Therefore, the biopolymers were more effective than the Kraton polymers in increasing the high temperature, but not as effective in retaining the low stiffness modulus of the base asphalt. Adding two percent of either biopolymer to the base asphalt, increased the low temperature PG one grade (from -34 to -28C). Even so, adding two percent PS-PAESO-PS increased the grade range (the high PG minus the low PG) from 88.8 to 103.4 which substantially increases the performance temperature range of the base asphalt.

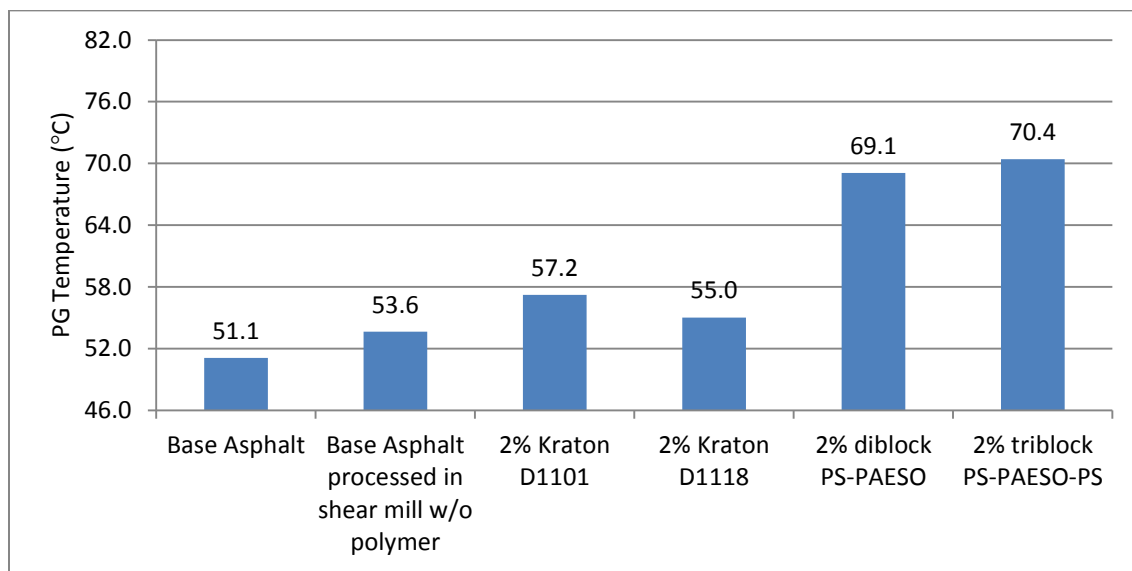


Figure 18. Comparison of high temperature continuous performance grades

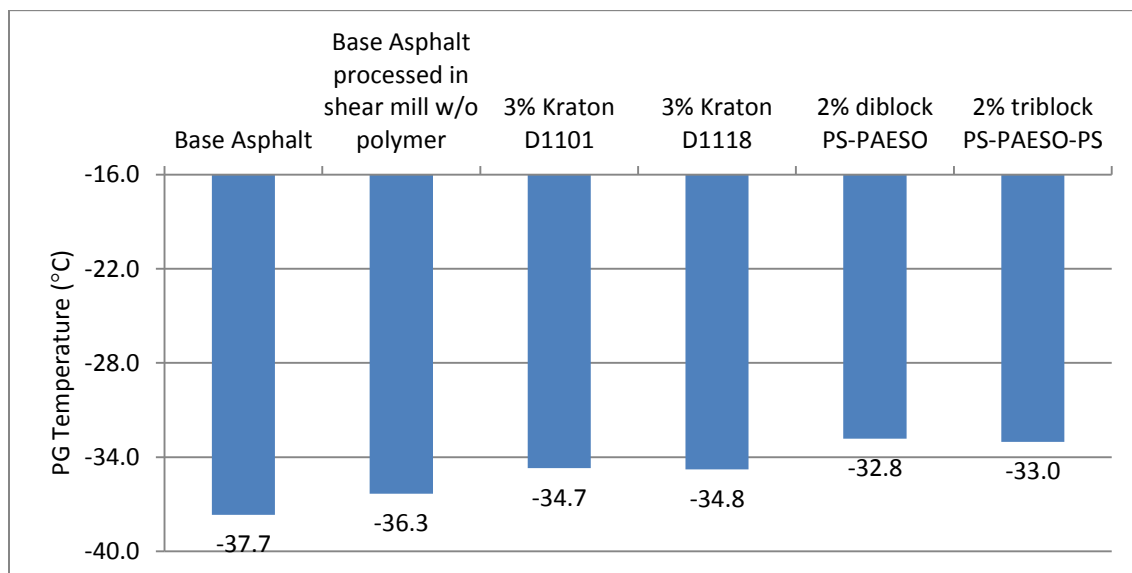


Figure 19. Comparison of low temperature continuous performance grades

CHAPTER 6 ECONOMIC ANALYSIS

The most significant cost in manufacturing SBS polymers is the price of butadiene. For the last decade butadiene has been subject to large price fluctuations from crude oil price increases and global market shifts in supply and demand. Butadiene supply has been tightening due to the abundance of shale gas supplies. Since shale gas has become more available, lighter petrochemical feeds such as ethane have been more commonly used as a feedstock at cracking facilities to produce ethylene and its co-products that include butadiene. However, butadiene is only a co-product when heavier liquid feeds, not lighter feeds, are used. The effects this has had on the price of butadiene over the last several years are shown in Figure 20.

In contrast, polymerized triglycerides, such as those found in soybean oil, are intrinsically renewable, are environmental friendly, and may also be shown to exhibit biodegradability. The research presented in this report indicates the elastomeric properties of soybean oil polymer appear to be competitive with modern commodities such as polybutadiene (synthetic rubber). Furthermore, the cost of the soybean oil monomer has become highly competitive in recent years. As shown in Figure 20, soybean oil as a biomonomer is more economical than butadiene monomer feedstocks (e.g., a ton of soybean oil costs less than \$1,000, whereas a ton of butadiene has cost up to \$3,500). The lower raw materials costs of soybean oil translate into lower costs of polymer-modified asphalt. The handling of vegetable oils in producing the bioelastomers and subsequent linking with styrene is also much safer and has less impact on the environment. Thus, the novel soy-based, thermoplastic, elastomeric, block copolymers provide a cost-effective, environment-friendly, viable alternative for the conventional petrochemically-derived polymeric SBS and SB. With future implementation of the developed biopolymers, Iowa source materials (e.g., soybean oil) can be utilized to produce polymers for use in Iowa. This can create improved economic opportunities for soybeans resulting in economic value to Iowa and maintaining soil qualities through a balanced crop rotation with corn.

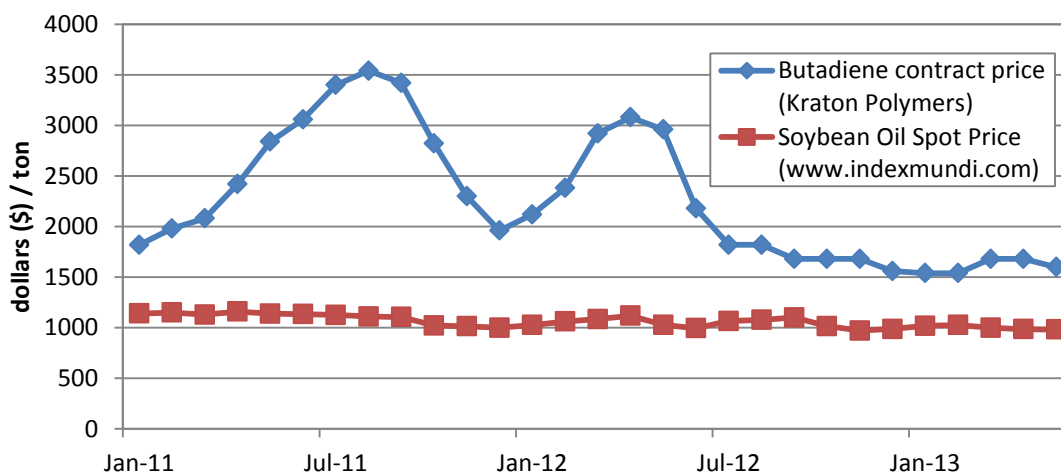


Figure 20. Commodity costs comparison

Preliminary simulations estimate PAESO will cost about \$2000 per ton as compared with \$3200 per ton for polybutadiene. Further, the storage and handling of PAESO is less than polybutadiene.

CHAPTER 7 CONCLUSIONS AND RECOMMENDATIONS

Recent advances in polymerization technology have led to the development of elastomeric block copolymers produced with polystyrene and polymerized soy-derived triglycerides. While the past two decades of plant-oil based polymer research has yielded only thermosets, the produced polymers are highly processable thermoplastics. They were produced by first polymerizing acrylated, epoxidized triglyceride molecules in soybean oil to yield PAESO. SBS-like triblock copolymers were then synthesized by replacing the “B” block (typically polybutadiene) in the ABA triblock structure with PAESO to create polystyrene-*b*-polyAESO-*b*-polystyrene (PS-PAESO-PS). Styrene and AESO monomer were polymerized using reversible addition-fragmentation chain-transfer polymerization (RAFT), in the presence of a free radical imitator and a chain transfer agent, to form the block copolymers. The polymerizing step was carried out under conditions effective to achieve a number average degree of polymerization (N_n) for the thermoplastic block copolymer of up to 100,000 without gelation. Following the same process, SB diblock copolymers were also produced using polystyrene and polyAESO.

A laboratory investigation was conducted to characterize the PS-PAESO-PS and PS-PASEO biopolymers and to evaluate their effectiveness as a liquid asphalt modifier. Asphalt modified with the biopolymers was compared to asphalt modified with two commercially available Kraton polymers, D1101 (SBS) and SB D1118 (SB). Rheology test results showed the biopolymer has the ability to widen the grade range of asphalt and reduce its temperature susceptibility. The base asphalt tested as a continuous PG 51.1-37.7 for a grade range of 88.8°C. Adding two percent D1101 to the base asphalt increased its continuous high PG to a 57.2°C without changing its -34°C grade qualification on the low temperature side. Adding two percent PS-PAESO-PS to the base asphalt changed its continuous PG to a 70.4-33.0 for a 103.4°C grade range. With the addition of two percent PS-PAESO, the base asphalt changed to a continuous PG of 69.1-32.8 for a 101.9°C grade range. Thus, biopolymers significantly enhanced the performance properties of the base asphalt. By adding two percent of either biopolymer to an asphalt binder, the rutting resistance and temperature performance range of an asphalt pavement will improve.

Currently, at a polymer content of two percent, a base asphalt's low temperature PG may increase one grade, which may warrant the use a softer base asphalt to compensate for that effect. As additional data from asphalt-modification experiments become available, additional or improved polymer formulation designs may be developed. Future research can improve upon the biopolymers molecular architecture, styrene content, and molecular weight distribution.

A larger reactor has been purchased that is capable of making two kilogram samples, substantially larger than the approximately 100 gram samples produced in this study. In addition, a pilot plant is currently being designed that can produce even larger quantities of the biopolymers for future research. Further work evaluating asphalt mixtures for rutting, low temperature cracking, and moisture susceptibility should be done while the pilot plant is being constructed. Based upon the evaluation of the mixture, an additional phase of research should include a field demonstration project that tests the performance of asphalt pavement containing terminally blended asphalt binder modified with the soy-based block copolymers.

REFERENCES

- Airey, G. D. 2004. Styrene butadiene styrene polymer modification of road bitumens. *Journal of Materials Science* 39:951-959.
- Alonso, S., M-T. Luis, R. Zitzumbo, and F. Avalos. 2010. Rheology of asphalt styrene-butadiene blends. *Journal of Materials Science* 45:2591-2597.
- Andjelkovic, D. D., L. Fengkui, and R. C. Larock. 2006. Novel Polymeric Materials from Soybean Oils: Synthesis, Properties, and Potential Applications. *ACS Symposium Series* 921:67-81.
- Bahia, H.U. and D.A. Anderson. 1995. The SHRP binder rheological parameters: why are they required and how do they compare to conventional properties. *Transportation Research Board*. Record No. 1488: 32-39. Washington D.C.
- Bates, F. S., and G. H. Fredrickson. 1999. Block copolymers-designer soft materials. *Physics Today* 52(2):32-38.
- Bonnaillie, L. M., and R. P. Wool. 2007. Thermosetting Foam With a High Bio-Based Content From Acrylated Epoxidized Soybean Oil and Carbon Dioxide. *Journal of Applied Polymer Science* 105(3):1042-52.
- Bunker, S., C. Staller, N. Willenbacher, and R. Wool. 2003. Miniemulsion Polymerization of Acrylated Methyl Oleate for Pressure Sensitive Adhesives. *International Journal of Adhesion and Adhesives* 23(1):29-38.
- Bulatovic, V. O., V. Rek, and K. J. Markovic. 2012. Polymer modified bitumen. *Materials Research Innovations* 1:1-6.
- Bunker, S., and R. P. Wool. 2002. Synthesis and Characterization of Monomers and Polymers for Adhesives from Methyl Oleate. *Journal of Polymer Science Part A: Polymer Chemistry* 40(4):451-58.
- Epps, J.A. 1986. Asphalt Pavement Modifiers. *Civil Engineering Magazine* April.
- Fernandes, M. R. S., M. M. C. Forte, and L. F. M. Leite. 2008. Rheological Evaluation of Polymer-Modified Asphalt Binders. *Materials Research* 11(3):381-386.
- Foster, J. 2011. Lighter feeds in US steam crackers brings new attitude toward on-purpose butadiene, propylene prospects. *Platts Special Report: Petrochemicals* 1-6.
- Fried, J. R. 2008. *Polymer Science and Technology*. Second edition. Upper Saddle River, NJ: Prentice Hall.
- Henna, P. H., D. D. Andjelkovic, P. P. Kundu, and R. C. Larock. Biobased Thermosets from Free Radical Copolymerization of Conjugated Linseed Oil. *Journal of Applied Polymer Science* 104:979-985.
- Hiemenz, P. C., and T. P. Lodge. 2007. *Polymer Chemistry*. Second edition. Raton, FL: CRC Press.
- Isacson, U., and X. Lu. 1999. Characterization of bitumens modified with SEBS, EVA and EBA polymer. *Journal of Materials Science* 34:3737-3745.
- Larock, R. C., X. Dong, S. Chung, K. Reddy, and L. E. Ehlers. 2001. Preparation of Conjugated Soybean Oil and Other Natural Oils and Fatty Acids by Homogeneous Transition Metal Catalysis. *Journal of the American Oil Chemists' Society* 78:447-453.
- Lesueur, D. 2009. The colloidal structure of bitumen: consequences on the rheology and on the mechanisms of bitumen modification. *Advances in Colloid and Interface Science* 145:42-82.

- Lewandowski, L. H. 1994. Polymer modification of paving asphalt binders. *Rubber Chemistry and Technology* 76(3):447.
- Li, F., M. V. Hanson, and R. C. Larock. 2001. Soybean Oil-Divinylbenzene Thermosetting Polymers: Synthesis, Structure, Properties and their Relationships. *Polymer* 42(4):1567-1579.
- Lu, J., K. Shrikant, and R. P. Wool. 2005. New Sheet Molding Compound Resins From Soybean Oil. I. Synthesis and Characterization. *Polymer* 46(1):71–80.
- Lu, X., and U. Isacson. 1997. Compatibility and storage stability of styrene-butadiene-styrene copolymer modified bitumens. *Materials and Structures* 30:618-626.
- Lu, Y., and R. C. Larock. 2009. Novel Polymeric Materials from Vegetable Oils and Vinyl Monomers: Preparation, Properties and Applications. *ChemSusChem* 2:136-147.
- Lu, Y., Y. Xia., and R. C. Larock. 2011. Surfactant-Free Core-Shell Hybrid Latexes From Soybean Oil-Based Waterborne Polyurethanes and Poly(Styrene-Butyl Acrylate). *Progress in Organic Coatings* 71(4):336–42.
- Martinez-Estrada A., A. E. Chavez-Castellanos, M. Herrera-Alonso, and R. Herrera-Najera. 2010. Comparative Study of the Effect of Sulfur on the Morphology and Rheological Properties of SB and SBS modified asphalt. *Journal of Applied Polymer Science* 115:3409-3422.
- Masson, J.-F., P. Collins, G. Robertson, J. R. Woods, and J. Margeson. 2003. Thermodynamics, Phase Diagrams, and Stability of Bitumen-Polymer Blends. *Energy & Fuels* 17:714-724.
- Moad, G., E. Rizzardo, and S. H. Thang. 2006. Living Radical Polymerization by the Raft Process- a First Update. *Australian Journal of Chemistry* 59:669–92.
- Moad, G., E. Rizzardo, and S. H. Thang. 2009. Living Radical Polymerization by the Raft Process-a Second Update. *Australian Journal of Chemistry* 62(11):1402–72.
- Odian, G. 1991. *Principles of Polymerization*. Third edition. New York: John Wiley and Sons, Inc.
- Pfister, D. P., and R. C. Larock. 2010. Thermophysical properties of conjugated soybean oil/corn 30 stover biocomposites. *Bioresource Technology* 101(15):6200–06.
- Robertson, M. L., K. Chang, W. M. Gramlich, and M. A. Hillmyer. 2010. Toughening of Polylactide with Polymerized Soybean Oil. *Macromolecules* 43:1807-1814.
- Valverde, M., D. Andjelkovic, P. P. Kundu, and R. C. Larock. 2008. Conjugated Low-Saturation Soybean Oil Thermosets: Free-Radical Copolymerization with Dicyclopentadiene and Divinylbenzene. *Journal of Applied Polymer Science* 107:423-430.
- Yang, L., C. Dai, L. Ma, and S. Lin. 2010. Conjugation of soybean oil and its free-radical copolymerization with acrylonitrile. *Journal of Polymers and the Environment* 19:189-195
- Zhu, L., and R. P. Wool. 2006. Nanoclay Reinforced Bio-Based Elastomers: Synthesis and Characterization. *Polymer* 47(24):8106–15.