
Louisiana Transportation Research Center

Final Report 500

**Mechanistic Evaluation of Asphalt Mixtures
Containing Thiopave Additives**

by

Louay N. Mohammad, Ph.D.
Samuel B. Cooper, III, Ph.D., P.E.
Mostafa Elseifi, Ph.D., P.E.

LTRC and LSU



4101 Gourrier Avenue | Baton Rouge, Louisiana 70808
(225) 767-9131 | (225) 767-9108 fax | www.ltrc.lsu.edu

TECHNICAL REPORT STANDARD PAGE

1. Report No. FHWA/LA.12/500		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle Laboratory Evaluation of the Performance of HMA mixtures containing Thiopave additives		5. Report Date April 2016			
		6. Performing Organization Code LTRC Project Number: 736-99-1653 State Project Number: 10-5B			
7. Author(s) Louay Mohammad, Ph.D., Samuel B. Cooper, III, Ph.D., P.E. Mostafa Elseifi, Ph.D., P.E.		8. Performing Organization Report No.			
9. Performing Organization Name and Address Louisiana Transportation Research Center 4101 Gourrier Avenue Baton Rouge, LA 70809		10. Work Unit No.			
		11. Contract or Grant No. State Project Number: 736-99-1653 LTRC Project Number: 10-5B			
12. Sponsoring Agency Name and Address Shell Oil USA 910 Louisiana Street Houston, Texas 77002		13. Type of Report and Period Covered Final Report Period Covered: July 2009 – June 2010			
		14. Sponsoring Agency Code			
15. Supplementary Notes Conducted in Cooperation with the U.S. Department of Transportation, Federal Highway Administration					
16. Abstract The objective of this study was to compare the laboratory mechanistic properties of sulfur-modified warm mix asphalt (WMA) to conventional asphalt mixtures. Three mixtures, two hot mix asphalt (HMA) and one WMA, were prepared. The first mixture included an unmodified asphalt binder classified as PG 64-22, the second mixture contained a styrene butadiene styrene (SBS) elastomeric modified binder classified as PG 70-22, and the third mixture was a WMA that incorporated a sulfur-based mix additive and PG 64-22 binder. A suite of tests were performed to evaluate the rutting performance, moisture resistance, fatigue endurance, fracture resistance, and thermal cracking resistance of the three mixtures. Results of the experimental program showed that the rutting performance of sulfur-modified WMA was comparable or superior to conventional mixes prepared with polymer-modified and unmodified asphalt binders. Results of the modified Lottman test showed that the moisture resistance of the sulfur-modified mixture was comparable to conventional mixes. Additionally, fracture and fatigue properties, as measured by the semi-circular bend (SCB) and beam fatigue tests, show that the sulfur-modified WMA mixture possessed stiffer properties than that of a conventional polymer-modified mixture. Thermal stress restrained specimen test (TSRST) test results showed that the sulfur-modified WMA had a greater fracture stress than the polymer-modified mixture. However, there was no statistical significance between the average fracture temperatures for the mixes tested..					
17. Key Words Thiopave, Warm Mix, Sulfur, Mechanistic Properties			18. Distribution Statement Unrestricted. This document is available through the National Technical Information Service, Springfield, VA 21161.		
19. Security Classif. (of this report)		20. Security Classif. (of this page)		21. 52	
				22. Price	

Project Review Committee

Each research project will have an advisory committee appointed by the LTRC Director. The Project Review Committee is responsible for assisting the LTRC Administrator or Manager in the development of acceptable research problem statements, requests for proposals, review of research proposals, oversight of approved research projects, and implementation of findings. LTRC appreciates the dedication of the following Project Review Committee Members in guiding this research study to fruition.

LTRC Manager

Samuel B. Cooper, III, Ph.D., P.E.
Materials Research Manager

Members

Mark Bouldin, Shell USA
Richard May, Shell USA
Gary Fitts, Shell USA
Norm Pugh, Shell USA

Directorate Implementation Sponsor

Janice Williams, P.E.
DOTD Chief Engineer

Mechanistic Evaluation of Asphalt Mixtures Containing Thiopave Additives

by

Louay N. Mohammad, Ph.D.
Professor of Civil and Environmental Engineering
Director, Engineering Materials Characterization Research Facility

Samuel B. Cooper, III, Ph.D., P.E.
Materials Research Administrator
Louisiana Transportation Research Center

Mostafa Elseifi, Ph.D., P.E.
Assistant Professor
Department of Civil and Environmental Engineering
Louisiana State University

LTRC Project Number: 10-5B
State Project Number: 736-99-1653

conducted for

Louisiana Department of Transportation and Development
Louisiana Transportation Research Center

The contents of this report reflect the views of the author/principal investigator who is responsible for the facts and the accuracy of the data presented herein. The contents do not necessarily reflect the views or policies of the Louisiana Department of Transportation and Development or the Louisiana Transportation Research Center. This report does not constitute a standard, specification, or regulation.

April 2016

ABSTRACT

The objective of this study was to compare the laboratory mechanistic properties of sulfur-modified warm mix asphalt (WMA) to conventional asphalt mixtures. Three mixtures, two hot mix asphalt (HMA) and one WMA, were prepared. The first mixture included an unmodified asphalt binder classified as PG 64-22, the second mixture contained a styrene butadiene styrene (SBS) elastomeric modified binder classified as PG 70-22, and the third mixture was a WMA that incorporated a sulfur-based mix additive and PG 64-22 binder. A suite of tests were performed to evaluate the rutting performance, moisture resistance, fatigue endurance, fracture resistance, and thermal cracking resistance of the three mixtures. Results of the experimental program showed that the rutting performance of sulfur-modified WMA was comparable or superior to conventional mixes prepared with polymer-modified and unmodified asphalt binders. Results of the modified Lottman test showed that the moisture resistance of the sulfur-modified mixture was comparable to conventional mixes. Additionally, fracture and fatigue properties, as measured by the semi-circular bend (SCB) and beam fatigue tests, show that the sulfur-modified WMA mixture possessed stiffer properties than that of a conventional polymer-modified mixture. Thermal stress restrained specimen test (TSRST) test results showed that the sulfur-modified WMA had a greater fracture stress than the polymer-modified mixture. However, there was no statistical significance between the average fracture temperatures for the mixes tested.

ACKNOWLEDGMENTS

The financial support provided by Shell, Inc is greatly appreciated. The contents of this paper do not necessarily reflect the official views or policies of the Louisiana Department of Transportation and Development (DOTD) or the Louisiana Transportation Research Center (LTRC).

IMPLEMENTATION STATEMENT

This study compared the laboratory mechanistic properties of sulfur-modified warm mix asphalt (WMA) to conventional asphalt mixtures. Construction of field test sections of asphalt mixtures containing sulfur-modified additives alongside conventional asphalt mixtures are recommended to evaluate constructability, long term performance and environmental impacts. The implementation phase of this project shall provide an environmental assessment on the safety use of this technology on these field trials.

TABLE OF CONTENTS

ABSTRACT	iii
ACKNOWLEDGMENTS	v
IMPLEMENTATION STATEMENT	vii
TABLE OF CONTENTS	ix
LIST OF TABLES	xi
LIST OF FIGURES	xiii
INTRODUCTION	1
OBJECTIVE	3
SCOPE	5
METHODOLOGY	7
Background	7
Materials	8
Hot Mix Asphalt Mixture Design	10
Experimental Plan	12
DISCUSSION OF RESULTS	13
Rutting	13
Loaded Wheel Tester	13
Flow Number	13
Repeated Shear at Constant Height	14
Dynamic Modulus (54°C (77°F), 5 Hz)	15
Durability	15
Modified Lottman	15
Fatigue/Fracture Cracking	16
Semi-Circular Bend Fracture Test	16
Beam Fatigue Test	17
Dynamic Modulus (25°C (77°), 5 Hz)	18
Dissipated Creep Strain Energy	19
Low Temperature Cracking	20
Thermal Stress Restrained Specimen Test	20
Summary of the Results	20
CONCLUSIONS	23
RECOMMENDATIONS	25
ACRONYMS, ABBREVIATIONS, AND SYMBOLS	27
REFERENCES	29
APPENDIX A	31

Performance Testing	31
Loaded Wheel Tester (LWT).....	31
Flow Number (FN)	31
Repeated Shear at Constant Height (RSCH)	32
Semi-Circular Bend (SCB)	32
Modified Lottman	33
Beam Fatigue	34
Dissipated Creep Strain Energy (DCSE)	34
Thermal Stress Restrained Specimen Test (TSRST).....	35
Dynamic Modulus (E*).....	35

LIST OF TABLES

Table 1 Louisiana asphalt cement PG specification test results	9
Table 2 Wearing course job mix formula	11
Table 3 Test factorial	12
Table 4 Summary of test results.....	21

LIST OF FIGURES

Figure 1 Illustration of the laboratory preparation of sulfur-modified asphalt mixture materials.....	8
Figure 2 Mixture aggregate gradation curve.....	10
Figure 3 LWT test results	13
Figure 4 Flow number test results.....	14
Figure 5 Repeated shear at constant height test results	14
Figure 6 Dynamic modulus rutting parameter	15
Figure 7 Modified Lottman test results.....	16
Figure 8 Semi-circular bend test results	17
Figure 9 Fatigue stiffness vs. number of cycles.....	18
Figure 10 Number of cycles to failure (N_f) vs. microstrain.....	18
Figure 11 Dynamic modulus fatigue factor	19
Figure 12 Dissipated creep strain energy test results.....	19
Figure 13 Thermal stress restrained specimen test results.....	20
Figure A.1 The Hamburg-Type Loaded Wheel Tester (LWT)	31
Figure A.2 The semi-circular bending test	33
Figure A.3 Dissipated creep strain energy determination.....	35

INTRODUCTION

In the past few years, many highway agencies experienced a significant increase in construction bid prices. One major reason for this sharp increase is the rise in energy costs and the price of liquid asphalt cement, a petroleum product. While the price of asphalt has recently eased, economists widely agree that a sharp rebound in the price of petroleum products will take place as the US economy recovers from the current recession. Crude oil prices increased in 2009 from \$35 to \$80 a barrel confirming economists' forecast that a sharp rebound in the price of petroleum products will take place in the near future. As no slowdown in freight transportation growth is forecasted in the near future, it is imperative that innovative technologies that can improve the energy and resource efficiency of pavement construction operations be introduced to ensure continuous growth of the economy.

Since the 1970s, attempts have been made to use sulfur as a binder extender in order to reduce the amount of asphalt binder required in the mixture and to improve the mix mechanistic characteristics [1]. However, the concept of using sulfur in hot-mix asphalt (HMA) materials was abandoned in the 1980s after environmental and safety problems were encountered during installation and doubts about the cost viability of the modification were expressed [2]. Segregation of the additive from the binder was also reported due to the large difference in density between sulfur and asphalt binder [3]. In spite of the installation difficulties, sulfur-modification was found effective in enhancing the fatigue performance and stiffness characteristics of the mixture as compared to conventional mixtures [4]. The idea reappeared in the late 1990s with the development of a new class of solid dust-free sulfur product known as Shell Thiopave[®]. Many of the safety problems encountered earlier appeared to have been solved, as long as the mixture is produced at a target mixing temperature of $140 \pm 5^{\circ}\text{C}$. Since warm-mix asphalt (WMA) is designed to reduce the mixing temperature during production by 16 to 55°C lower than with typical HMA, the use of sulfur in the production of WMA may offer the potential to reduce energy and asphalt consumption in the preparation of asphalt mixtures.

Conventional mixtures were prepared by mixing aggregate blends with two virgin binders: an unmodified asphalt binder classified as PG 64-22 and a polymer-modified binder classified as PG 70-22. Performance testing included evaluation of the rutting and fatigue performances of the produced mixtures using a suite of laboratory testing procedures.

OBJECTIVE

The objective of this study was to characterize the laboratory performance of conventional HMA mixtures and mixtures containing Thiopave additives through their fundamental engineering properties. Specific objectives included comparing the laboratory performance of conventional HMA wearing course mixtures to similar WMA mixtures that contain Thiopave additives.

SCOPE

The research team conducted a limited factorial to determine the optimum proportions of Thiopave additives. The loaded wheel tracking (LWT) and semi-circular bend (SCB) test were conducted as part of the screening factorial. The optimum percentage of Thiopave additives was determined to be 40 percent.

Three HMA mixtures meeting DOTD specification were designed and examined. The first mixture was a conventional wearing course mixture using PG70-22 polymer modified asphalt cement; the second mixture was a conventional wearing course using unmodified PG64-22; and the third mixture was a wearing course mixture containing a binder consisting of 60 percent PG64-22 unmodified asphalt cement and 40 percent Thiopave additives. The mixture performance tests that were conducted were the Modified Lottman Test, dissipated creep strain energy (DCSE), semi-circular bend (SCB), dynamic modulus (E^*), flow number, loaded wheel tracking (LWT), flexural bending fatigue, thermal stress restrained specimen test (TSRST) and repeated shear at constant height (RSCH). Triplicate samples were tested in all cases, excluding the LWT test where duplicate samples were tested.

METHODOLOGY

Background

Recent investigations of the new class of sulfur extended technologies were reported in the literature. Thiopave[®], usually added at a ratio ranging from 30 to 40 percent from the binder weight, consists of pre-treated solid pellets that melt at a temperature above 120°C, Figure 1(d). The pellets are pretreated in order to reduce the emissions of harmful pollutants, such as hydrogen sulphide gas, during production and to lower the mixing and compaction temperature required for the modified mixture. During mixing, part of the sulfur bonds with the binder at a high temperature and reduces its viscosity while improving its elongation characteristics. The remaining part of the sulfur precipitates as the mixture cools down and crystallizes as a coated aggregate binder. These crystalline particles stiffen the mixture and act as a strengthening agent at a high temperature resulting in an improved rutting resistance. Sulfur modification also acts as an extender to the binder in the mixture, resulting in a decrease in the required asphalt cement content in the mixture. Given the difference in the density between the two components, it is recommended to maintain the volume fraction of the binder phase unchanged in the modified mixture based on the following relationship [3]:

$$\text{Sulfur + Binder \%} = \frac{100AR}{100R - P_s(R - G_{binder})} \quad (1)$$

where,

Sulfur + Binder % = binder and sulfur content in the mixture;

A = Percentage of binder by weight in conventional mixture (%);

R = Sulfur to binder substitution ratio (1.90);

P_s = weight percentage of sulfur in the modified blend; and

G = specific gravity of the unmodified binder.

Strickland et al., (2008) evaluated the performance of sulfur-modified mixtures in the laboratory [3]. Rutting resistance of the prepared mixtures was evaluated using the Asphalt Pavement Analyzer (APA) test at 58°C and the mixture stiffness modulus was measured at a temperature ranging from -10 to 30°C. In addition, the low temperature performance was evaluated using the TSRST. Results of this analysis indicated that the rutting and stiffness modulus of the mixture has improved. In addition, using sulfur enhanced the elongation properties of the mix at a low temperature. A comprehensive experimental program also evaluated the moisture resistance and dynamic modulus of sulfur-modified asphalt mixtures [1]. Results showed that the sulfur-modified mixture had a lower tensile-strength ratio

(TSR) after curing but greater dynamic moduli for all combinations of test temperatures and frequencies.

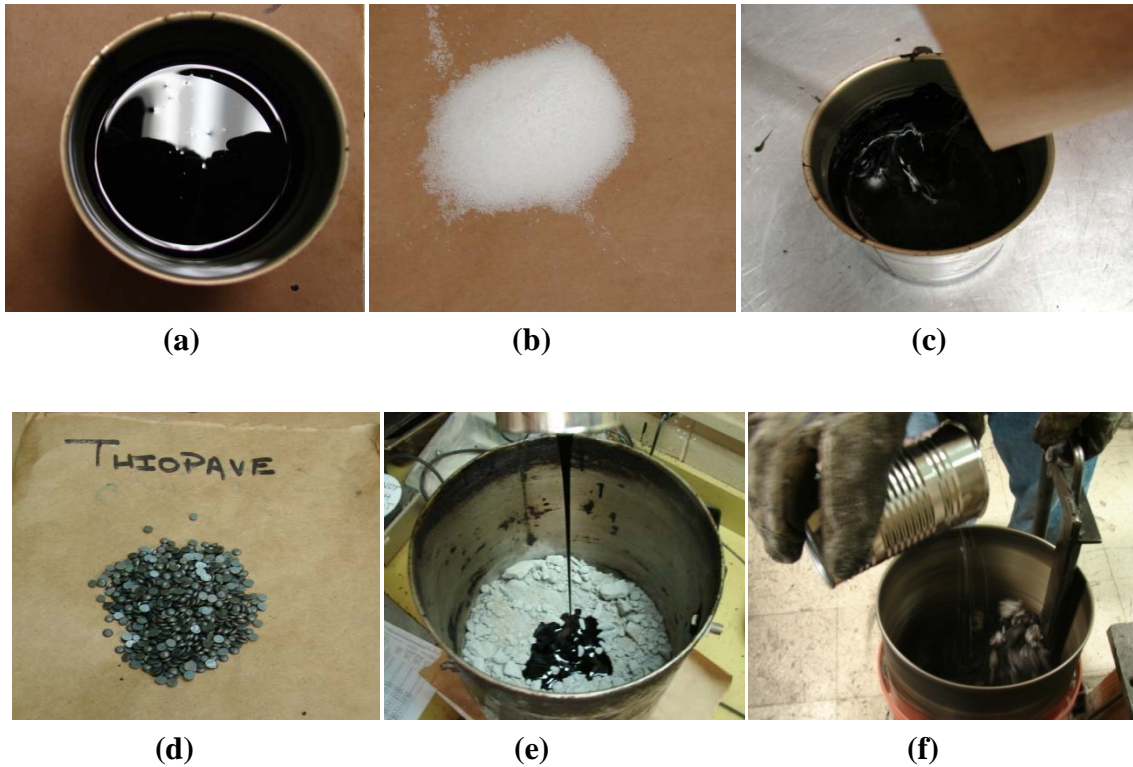


Figure 1

Illustration of the laboratory preparation of sulfur-modified asphalt mixture materials (a) Liquid Asphalt Binder, (b) Compaction Additive, (c) Blending Compaction Additive with the Asphalt Binder, (d) Pre-treated Thiopave Additive, (e) Heated Aggregate and Asphalt Binder in Mixing Bucket, (f) Pre-treated Thiopave Additive Blended with Heated Aggregate and Asphalt Binder

Materials

Two asphalt binders meeting the Louisiana specification for PG 64-22 and PG 70-22 (elastomeric polymer modified, M) were compared in this study, as shown in Table 1. In addition, the PG 64-22 binder was blended with 40 percent Thiopave additives. Special precautions were used, with respect to maximum temperature, when testing the binder containing Thiopave additives. Table 1 presents the properties of the asphalt cement used in this study, indicating that the PG 64-22 and PG 70-22(M) passed all specification requirements for their respective grading. The binder containing Thiopave additives could not be evaluated completely to determine the PG grading, due to emission concerns while conducting the rolling thin film oven (RTFO) and pressure aging vessel (PAV) aging procedures.

Table 1
Louisiana asphalt cement PG specification test results

Property	Spec	PG 64-22	PG 64-22 +Thio	PG 70-22M
Test on Original Binder				
Dynamic Shear, $G^*/\sin(\delta)$, (kPa), AASHTO T315	1.30 ⁺ @ 64°C	1.92	2.79	—
Dynamic Shear, $G^*/\sin(\delta)$, (kPa), AASHTO T315	1.00 ⁺ @ 70°C	0.88	1.16	1.64
Dynamic Shear, $G^*/\sin(\delta)$, (kPa), AASHTO T315	1.00 ⁺ @ 76°C	—	—	—
Force Ductility Ratio (F2/F1, 4°C, 5 cm/min, F2 @ 30 cm elongation, AASHTO T300		N/A	N/A	N/A
Force Ductility, (4°C, 5 cm/min, 30 cm elongation, kg), AASHTO T300		N/A	N/A	0.31
Rotational Viscosity @ 135°C (Pa·s), AASHTO T316	3.0 ⁻	0.5	0.3	0.9
Tests on RTFO				
Dynamic Shear, $G^*/\sin(\delta)$, (kPa), AASHTO T315	2.20 ⁺ @ 64°C	3.25	N/A	—
Dynamic Shear, $G^*/\sin(\delta)$, (kPa), AASHTO T315	2.20 ⁺ @ 70°C	1.61	N/A	3.14
Dynamic Shear, $G^*/\sin(\delta)$, (kPa), AASHTO T315	2.20 ⁺ @ 76°C	—	—	1.65
Elastic Recovery, 25°C, 10 cm elongation, % AASHTO T301		N/A	N/A	65
Tests on (RTFO+ PAV)				
Dynamic Shear, @ 25°C, $G^*\sin(\delta)$, (kPa), AASHTO T315	5000 ⁻	2774	N/A	4615
BB Creep Stiffness, @ -12°C, (MPa), AASHTO T313	300 ⁻	234	N/A	196
Bending Beam, m-value @ -12°C, AASHTO T313	0.300 ⁺	0.312	N/A	0.317
BB Creep Stiffness, @ -18°C, (MPa), AASHTO T313	300 ⁻	—	—	—
Bending Beam, m-value @ -18°C, AASHTO T313	0.300 ⁺	—	—	—
Actual PG Grading		PG 64-22	N/A	PG 70-22M

N/A: Not available due to temperature concerns.

Hot Mix Asphalt Mixture Design

Superpave HMA mixtures meeting DOTD specification ($N_{\text{initial}} = 8$ -, $N_{\text{design}} = 100$ -, $N_{\text{final}} = 160$ -gyrations), were designed according to AASHTO TP28, “Standard Practice for Designing Superpave HMA” and Section 502 of the 2006 Louisiana Standard Specifications for Roads and Bridges [5]. In particular, the optimum asphalt cement content was determined based on volumetric (VTM = 2.5 - 4.5 percent, VMA \geq 12%, VFA = 68% -78%) and densification (% G_{mm} at $N_{\text{initial}} \leq 89$, % G_{mm} at $N_{\text{final}} \leq 98$) requirements. Siliceous limestone aggregates and coarse natural sand that are commonly used in Louisiana were included in this study. The three aggregate gradation blends evaluated in this study are presented graphically in Figure 2. In addition, limestone aggregates were tested to determine their aggregate consensus properties. The consensus properties test items included coarse aggregate angularity (CAA), fine aggregate angularity (FAA), flat and elongated (F&E) particles, and sand equivalency (SE).

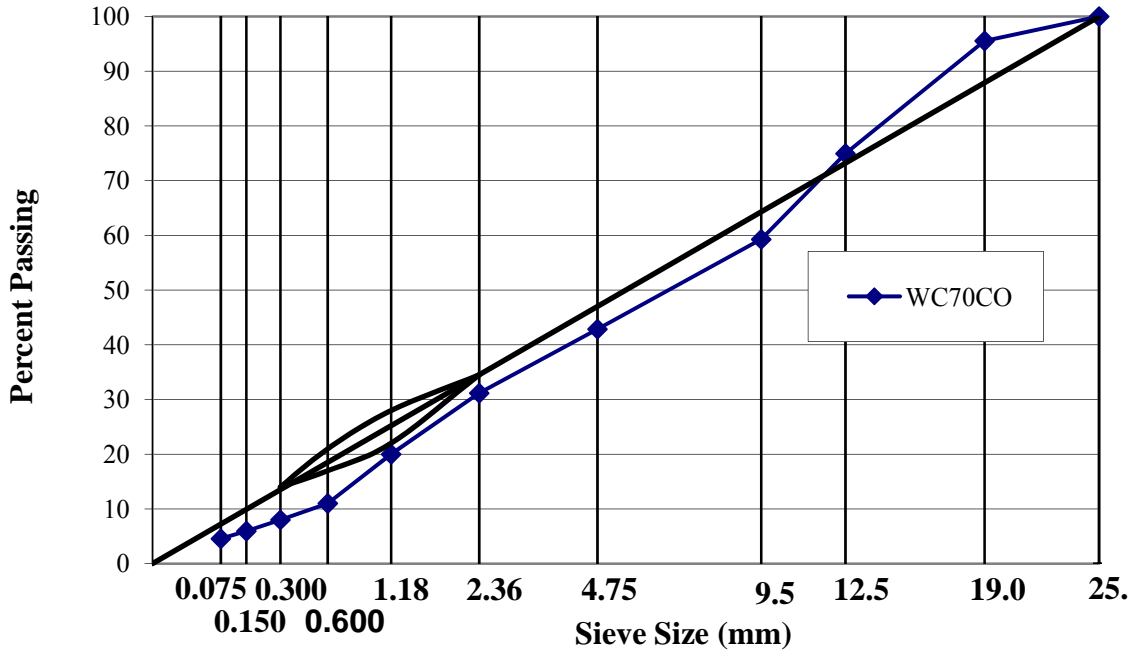


Figure 2
Mixture aggregate gradation curve

The job mix formulas for all mixtures considered in this study are summarized in Table 2. The design-optimum asphalt cement-binder content for the mixtures indicated is similar.

Table 2
Wearing course job mix formula

Mixture Designation		WC70CO	WC64CO	WC64SU
Mix Type		19.0 mm (3/4 in.) Superpave		
Aggregate	#67 LS	36%	36%	36%
	#78 LS	24%	24%	24%
	#11 LS	34%	34%	34%
	CS	6%	6%	6%
Binder type		PG 70-22M	PG 64-22	PG 64-22 +Thiopave+ KB2550
Binder Content, %		4.0	4.0	3.0*
% G _{mm} at N _{Ini}		87.0	87.0	87.0
% G _{mm} at N _{Max}		97.6	97.6	97.6
Design air void, %		3.7	3.7	3.7
VMA, %		13	13	13
VFA, %		68	68	68
Metric (U.S.) Sieve		Composite Gradation Blend		
37.5 mm (1½ in.)		100	100	100
25.0 mm (1 in.)		100	100	100
19.0 mm (3/4 in.)		96	96	96
12.5 mm (1/2 in.)		75	75	75
9.5 mm (3/8 in.)		59	59	59
4.75 mm (No. 4)		43	43	43
2.36 mm (No. 8)		31	31	31
1.18 mm (No. 16)		20	20	20
0.600 mm (No. 30)		11	11	11
0.300 mm (No. 50)		8	8	8
0.150 mm (No. 100)		6	6	6
0.075 mm (No. 200)		4.5	4.5	4.5

Note: LS: Limestone, CS: Coarse Sand, WC: Wearing Course, CO: Control, SU: Sulfur Modified, M: Elastomeric Polymer Modified,

*60/40KB: WMA with 60% PG 64-22 + 40% Thiopave® Additive.

Experimental Plan

An experimental factorial was developed in order to determine the mechanistic properties of the mixtures.

Table 3 shows the test factorial evaluated in this study. Notice that for the RSCH, beam fatigue, and TSRST, test samples for WC64CO were not evaluated.

Table 3
Test factorial

Mixture	Performance Test										
	Rutting				Durability	Fatigue Cracking					Low Temp Cracking
	LWT	FN	RSCH	E*@ 54°C	Lottman	ITS	SCB	Beam	E*@25°C	DCSE	TSRST
WC70CO	2	3	3	3	6	3	9	3	3	3	3
WC64CO	2	3	N/A	3	6	3	9	N/A	3	3	N/A
WC64SU	2	3	3	3	6	3	9	3	3	3	3

DISCUSSION OF RESULTS

Rutting

Loaded Wheel Tester

Figure 3 compares rutting performance of the three mixes evaluated in this study. This test predicts an acceptable rut performance for a mixture that achieves a maximum rut depth of 6.0 mm (0.2 in.) after 20,000 passes. As shown in Figure 3, mixture WC64CO had the largest rut depth at 20,000 cycles followed by WC64SU and WC70CO. It is noted that mixtures WC70CO and WC64SU exhibited a rut depth at 20,000 cycles that is less than or equal to 6.0 mm (0.2 in.). It is also noted that the WC64CO mixture failed the 6.0 mm (0.2 in) criteria used by DOTD.

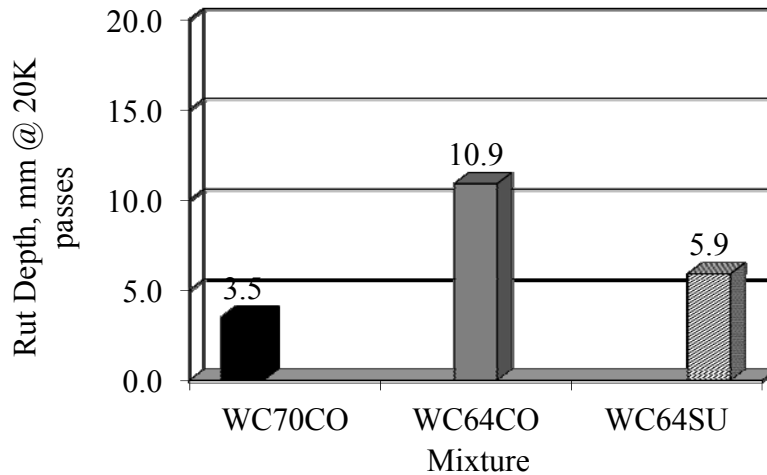


Figure 3
LWT test results

Flow Number

Figure 4 presents the FN for the three mixtures evaluated in this study. The FN is defined as the number of cycles at which tertiary flow occurs on a cumulative permanent strain versus number of cycles curve. It is noted that the greater the FN, the higher the mixture's resistance to permanent deformation. As shown in Figure 4, the sulfur-modified WMA mixture (WC64SU) outperformed both conventional mixtures including the polymer-modified mix in its resistance to permanent deformation.

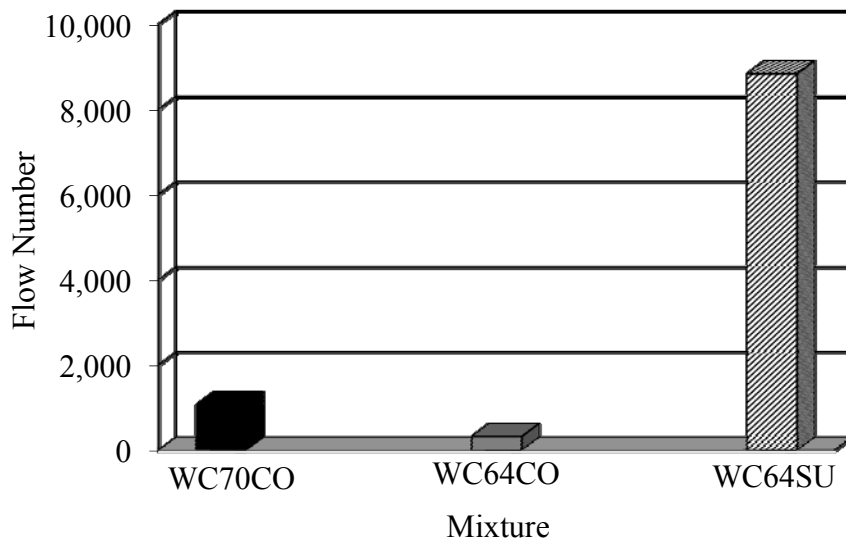


Figure 4
Flow number test results

Repeated Shear at Constant Height

Figure 5 presents the results of the RSCH test for the WC70CO and WC64SU mixtures. The permanent shear strain at 5,000 cycles is used to evaluate the mixtures' susceptibility to permanent deformation [19]. In this test, a lower permanent shear strain value is indicative of a reduced susceptibility to rutting failure. As shown in Figure 5, the sulfur-modified WMA mixture (WC64SU) had a lower permanent shear strain at 5,000 cycles than the conventional polymer-modified mixture (WC70CO).

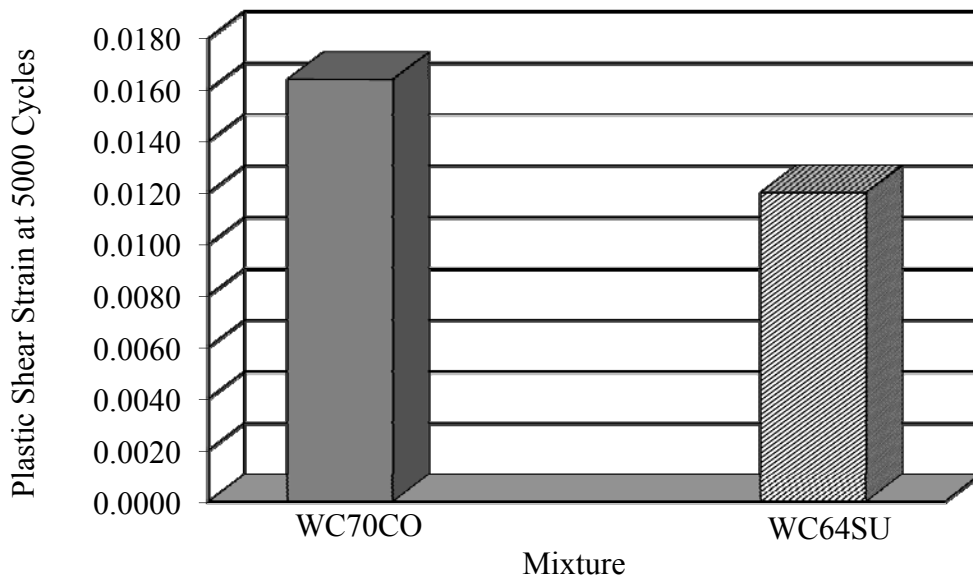


Figure 5
Repeated shear at constant height test results

Dynamic Modulus (54°C (77°F), 5 Hz)

The dynamic modulus results are analyzed to evaluate a rutting parameter. This parameter is typically achieved by dividing the E^* by the sine of the phase angle at 54°C (77°F) and 5 Hz. Figure 6 shows the comparison of the three mixtures evaluated in the lab study. The results show the addition of Thiopave additives resulted in a similar rut parameter to the WC64CO mixture.

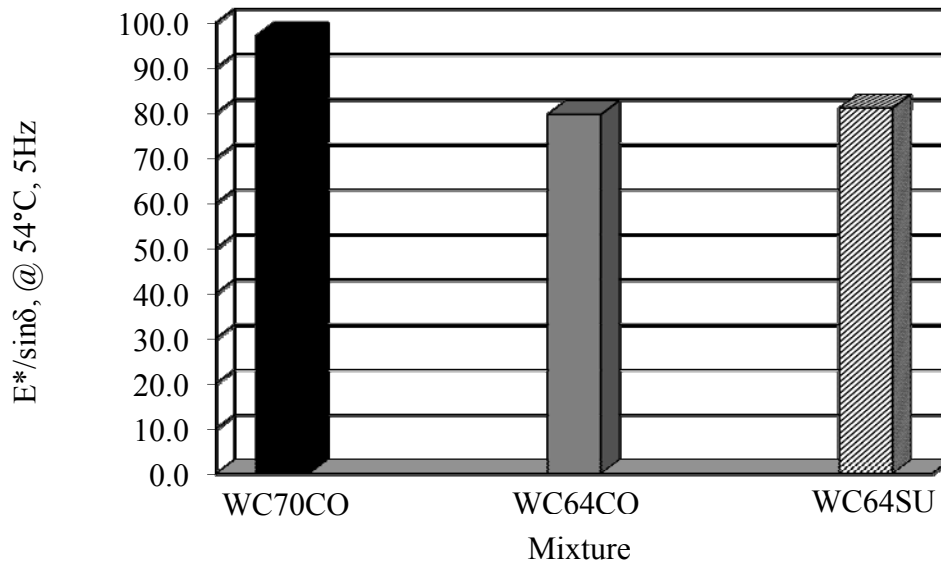


Figure 6
Dynamic modulus rutting parameter

These findings agree with other investigators, who have reported that the use of sulfur-modification improves the permanent deformation resistance of the mixture at high temperatures [3], [20]. The improved rutting performance is due to the stiffening effect of the sulfur crystals, which acts as a structuring agent for mixtures at high temperatures.

Durability

Modified Lottman

Figure 7 presents the moisture-resistance performance of the three mixtures based on the modified Lottman test results. While it appears from these results that the sulfur-modified WMA had a greater TSR than the conventional mixes, statistical analysis presented in the next section showed that this difference was not statistically significant. Considering that an 80 percent minimum TSR is necessary, the WC64CO mix would fail this requirement.

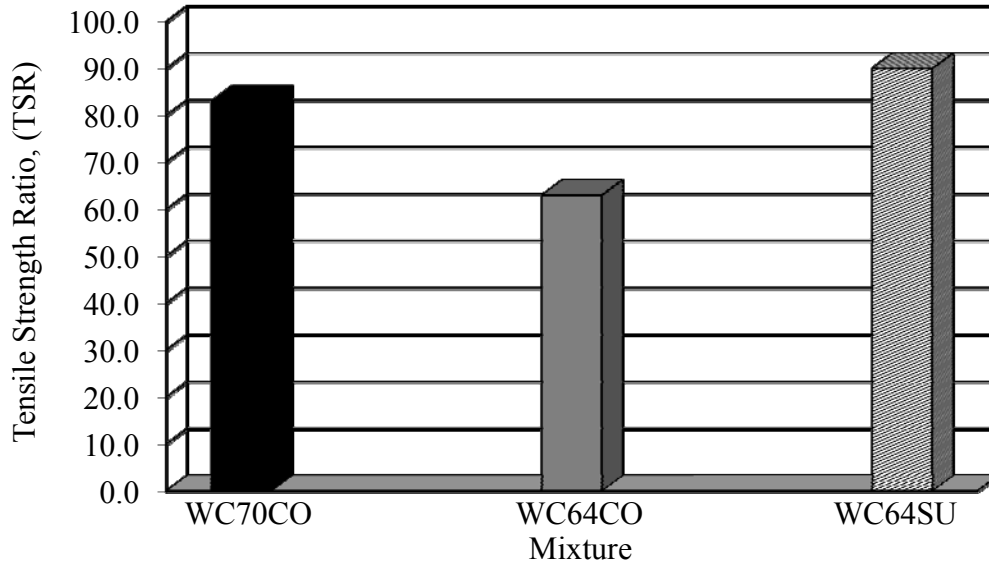


Figure 7

Modified Lottman test results

Fatigue/Fracture Cracking

Semi-Circular Bend Fracture Test

Figure 8 presents a comparison of the critical strain energy (J_c) data for the mixtures evaluated in this study. High J_c values are desirable for fracture-resistant mixtures. It is indicated that the fracture resistance of the conventional asphalt mixtures was greater than that of the sulfur-modified WMA mixture. Since a threshold of a minimum J_c of 0.65kJ/m^2 is typically used as a failure criterion for this test, it appears that mixtures WC64SU and WC64CO do not meet the cracking criterion set for this test. Given that cracking resistance is mainly controlled by the binder in the mixture, it is possible that the use of sulfur reduced the ductility and elongation properties of the binder at intermediate temperatures. However, a different cracking performance may be observed if a different rate of sulfur modification or a softer base asphalt was used as reported by past studies [21]. Given its stiff characteristics, the sulfur modified WMA mixture can be a candidate in a perpetual type or thick pavement structure or where a stiffer asphalt mixture is desirable.

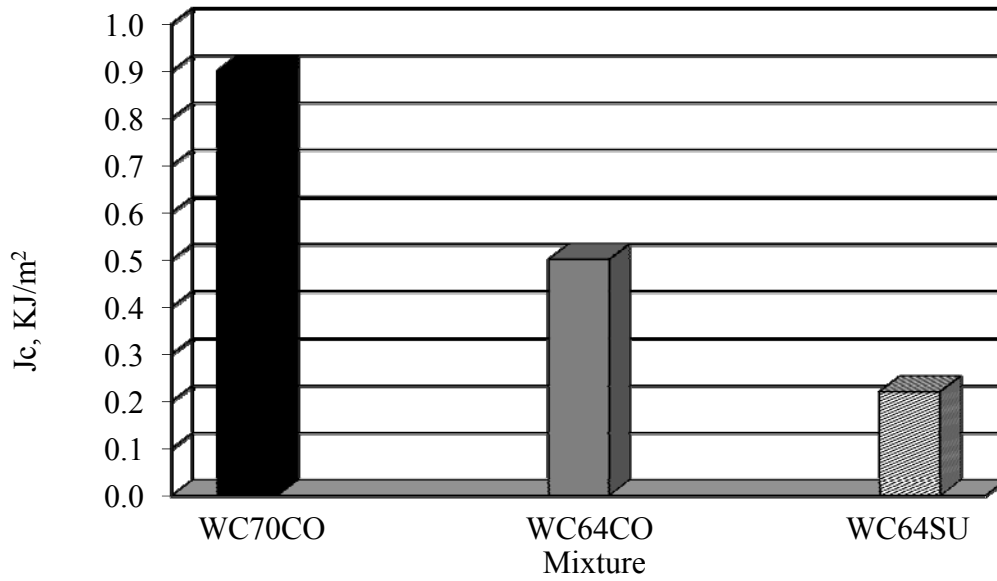


Figure 8
Semi-circular bend test results

Beam Fatigue Test

Figure 9 shows the results of the fatigue stiffness. The mixture containing Thiopave additives resulted in higher initial stiffness but failed sooner than the conventional mixture at all strain levels. This result is expected due to the stiffening properties of the sulfur additives. Figure 10 illustrates the relationship between the number of cycles to failure and the strain level applied to the specimen; mixture WC64CO was not tested in fatigue. (As shown in Figure 10, the polymer-modified mix (WC70CO) had a flatter slope at higher strain levels, which indicates that the modified mixture will exhibit a greater fatigue life at a higher bending strain). Other investigators have also reported that the average fatigue life of conventional mixtures is longer than sulfur-modified mixes at high strain levels [1]. This may be caused by the stiffening effect of the sulfur additive due to the crystallization of the sulfur particles during mixing. The results from this test are consistent with that observed from the SCB test. Given its stiffness properties, the higher modulus of sulfur modified mixtures will reduce the magnitude of strain induced in the pavement.

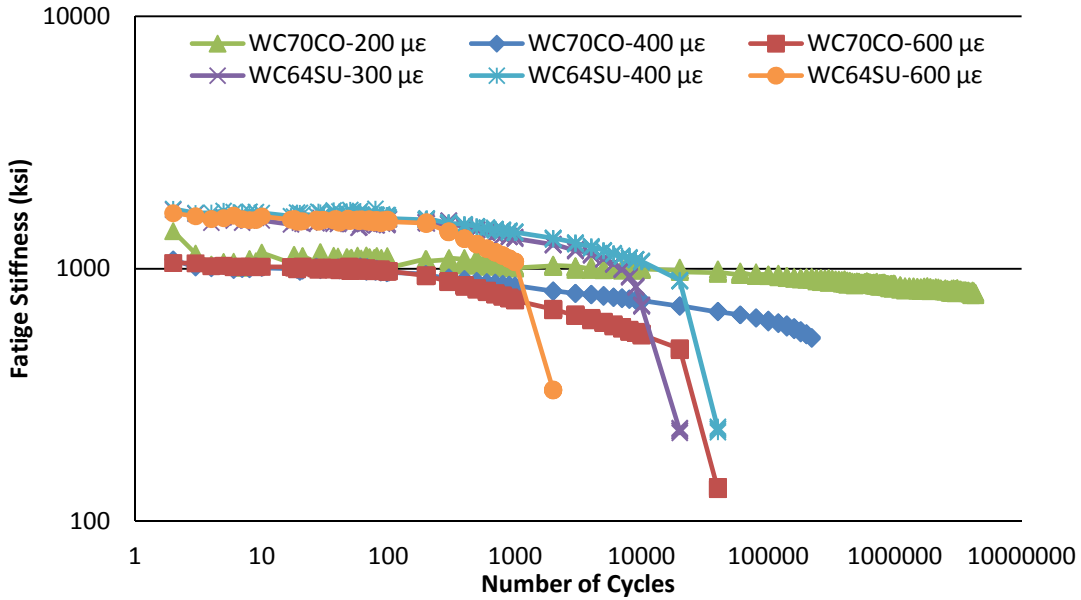


Figure 9
Fatigue stiffness vs. number of cycles

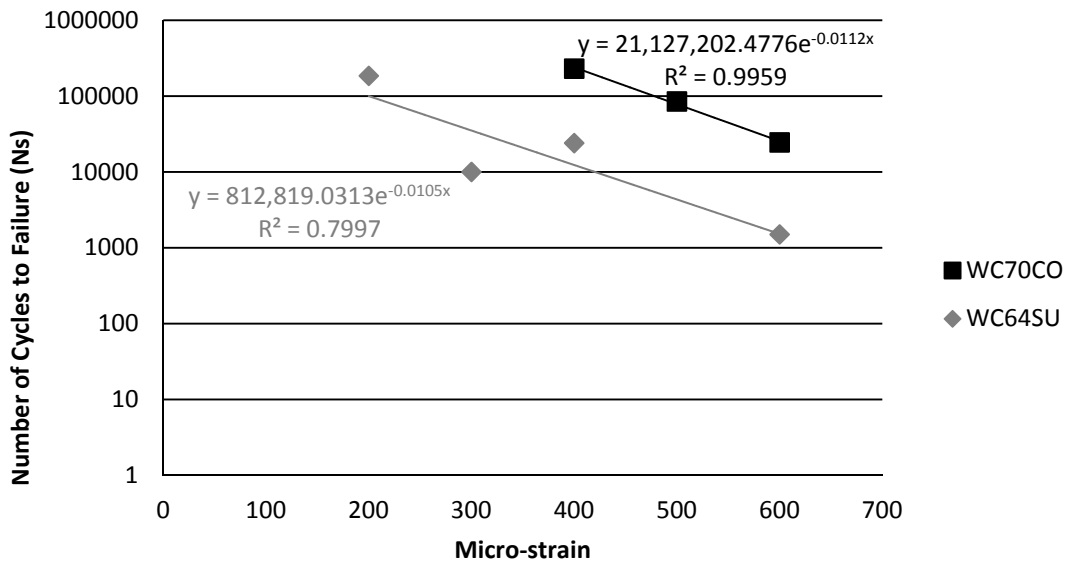


Figure 10
Number of cycles to failure (N_f) vs. microstrain

Dynamic Modulus (25°C (77°), 5 Hz)

The results from the dynamic modulus test were analyzed to determine the fatigue properties of the mixtures. Figure 11 shows the results of this analysis. The figure shows the mixture containing Thiopave additives had a much higher fatigue factor than the conventional

mixtures, indicating that the mixture containing Thiopave has a lower fatigue resistance than the conventional mixtures.

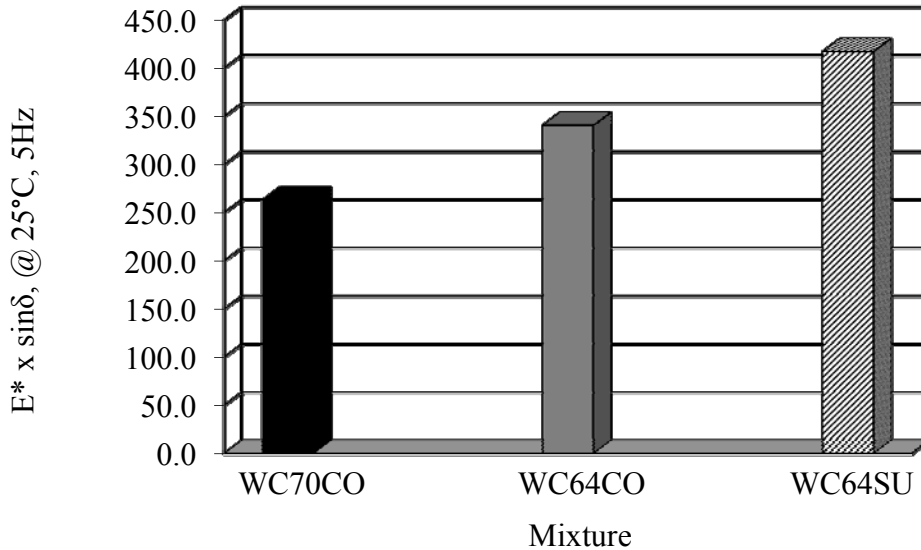


Figure 11
Dynamic modulus fatigue factor

Dissipated Creep Strain Energy

Figure 12 presents the mean DCSE values for the mixtures evaluated in this study. Mixtures that exhibit lower DCSE values are more susceptible to cracking than mixtures having higher values. As shown in this figure, the WC70CO mixture had the highest DCSE values and is, therefore, less prone to cracking at the tested temperature of 10°C (50°F). However, all mixtures met the 0.75 KJ/m³ cracking criterion set for this test [15].

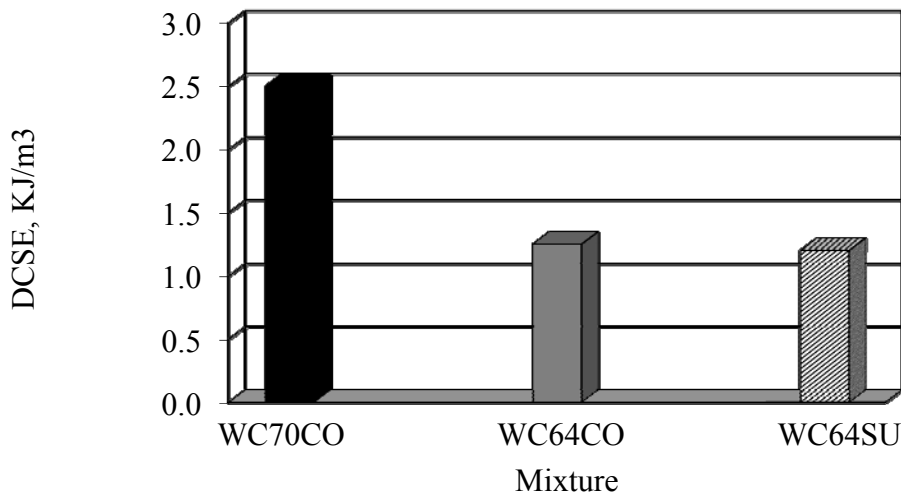


Figure 12
Dissipated creep strain energy test results

Low Temperature Cracking

Thermal Stress Restrained Specimen Test

Figure 13 presents the results of the thermal stress restrained specimen test; mixture WC64CO was not tested. As shown in Figure 13, mixture WC70CO had a lower fracture temperature than mixture WC64SU. However, statistical analysis presented in the next section showed that this difference was not statistically significant. The difference in fracture temperature may be caused by the stiffening effect of the sulfur on the binder, which reduced its ductility and its ability to dissipate the applied stress at low temperatures. This may also indicate that the glass transition temperature of the binder increased due to the sulfur modification, which increased the critical temperature at which fractures were observed.

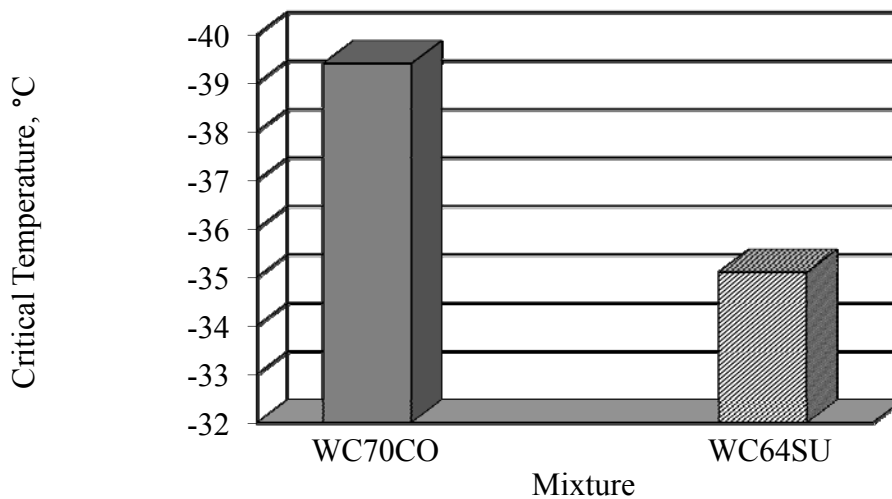


Figure 13

Thermal stress restrained specimen test results

Summary of the Results

Laboratory test results were statistically analyzed and grouped using the analysis of variance (ANOVA) procedure provided in the Statistical Analysis System (SAS) program. A multiple comparison procedure with a significance level of 5 percent was performed for the means. The results of the statistical grouping were reported with the letters A, B, C, D, and so forth. The letter A was assigned to the highest mean followed by the other letters in appropriate order. A double (or more) letter designation, such as A/B, indicates that the difference in the means is not clear-cut, and that the results could fall in either category.

Table 4 summarizes the statistical ranking of the laboratory test results for the three mixture types considered in the LTRC study. In general, WC64SU exhibited improved high temperature performance when compared to WC64CO and WC70CO. It is noted that WC64SU exhibited reduced intermediate temperature performance as indicated by the SCB test. However, there was no statistical difference between WC64SU and WC64CO for the DCSE test. TSRST results showed that WC64SU had greater fracture stress than WC70CO. There was no statistical significance between the average fracture temperatures for the mixes tested.

Table 4
Summary of test results

MIX ID	Moisture Resistance	Rutting			Fatigue	Fracture		Low Temperature	
	TSR	LWT	RSCH	Fn	Beam Fatigue	DSCE	J _c	TSRST (Fracture Temp)	TSRST (Fracture Stress)
WC64CO	A ¹	B ¹	N/A	C	N/A	B	B ¹	N/A	N/A
WC70CO	A	A	A	B	A	A	A	A	B
WC64SU	A	A	A	A	B	B	C ¹	A	A

1. Indicates failed criterion

CONCLUSIONS

Mechanistic properties of warm mix asphalt mixtures containing Thiopave additives were determined and compared to conventional hot mix asphalt mixtures. A suite of tests were performed to evaluate the rutting performance, moisture resistance, fatigue endurance, fracture resistance, and thermal cracking resistance of the three mixtures using the Hamburg type loaded-wheel tester, the flow number test, the repeated shear at constant height (RSCH) test, the modified Lottman test, the beam fatigue test, the dynamic modulus, the semi-circular bending test (SCB), the dissipated creep strain energy (DCSE) test, and the thermal stress restrained specimen test (TSRST).

Results of the LWT, RSCH, and FN tests showed that the rutting performance of the sulfur-modified WMA mixture was comparable to the conventional mixtures prepared with polymer-modified and unmodified asphalt binders.

Results of the modified Lottman test showed that the sulfur-modified WMA had comparable moisture resistance to the conventional mixes.

Fracture and fatigue properties showed that the sulfur-modified WMA mixture exhibited reduced fatigue and fracture resistance when compared to the other mixtures. This is due to the stiffening of the mixture provided by the sulfur modifier. Given its stiff characteristics, the sulfur-modified mixture can be a candidate in a perpetual type or thick pavement structure or where a stiffer asphalt mixture is desirable.

TSRST results showed that the sulfur-modified WMA mixture had a greater fracture stress than the polymer-modified mixture. However, there was no statistical significance between the average fracture temperatures for the mixes tested.

RECOMMENDATIONS

This study compared the laboratory mechanistic properties of sulfur-modified warm mix asphalt (WMA) to conventional asphalt mixtures. Based on the results of this laboratory study, it is recommended that field trials of asphalt mixtures containing sulfur-modified additives be conducted to evaluate long term performance as well as environmental impact. A possible source of a field trial is the Louisiana Accelerated Loading Facility.

ACRONYMS, ABBREVIATIONS, AND SYMBOLS

AADTT	Average annual daily truck traffic
AASHTO	American Association of State Highway and Transportation Officials
ASTM	American Society for Testing and Materials
ATM	Asphalt treated mixture
APA	Asphalt pavement analyzer
CA	Coarse aggregate
CAA	Coarse aggregate angularity
CS	Coarse sand
DOTD	Department of Transportation and Development
DSCE	Dissipated Creep Strain Energy
E*	Dynamic Modulus
EE	Elastic energy
FA	Fine aggregate
FAA	Fine aggregate angularity
FE	Fracture energy
F&E	Flat and elongated
FHWA	Federal Highway Administration
FN	Flow number
FWD	Falling weight deflectometer
GR	Granite
HMA	Hot mix asphalt
HMAC	Hot mix asphalt cement
ITS	Indirect tensile strength
JMF	Job mix formula
LAPA	Louisiana Asphalt Pavement Association
LFWD	Light falling weight deflectometer
LS	Limestone
LTRC	Louisiana Transportation Research Center
LVDT	Linearly variable differential transducer
LWT	Loaded wheel tracking
MEPDG	Mechanistic Empirical Pavement Design Guide
MTS	Material Testing System
NCHRP	National Cooperative Highway Research Program
NV	Novaculite
PAV	Pressure Aging Vessel

PG	Performance graded
PLS	Porous limestone
PSPA	Portable Seismic Pavement Analyzer
RAP	Reclaimed asphalt pavement
RLT	Repeated load triaxial
RTFO	Rolling Thin Film Oven
RY	Rhyolite
SBS	Styrene Butadiene Styrene
SCB	Semi-circular bend
SCT	Static compression test
SE	Sand Equivalency
SGC	Superpave gyratory compactor
SS	Sandstone
T _F	Film thickness
TI	Toughness index
TSR	Tensile strength ratio
TSRST	Thermal Stress Restrained Specimen Test
USW	Ultrasonic Surface Wave
WMA	Warm mix asphalt

REFERENCES

1. Timm, D; Tran, N; Taylor, A; Robbins, M; and Powell, B. "Evaluation of Mixture Performance and Structural Capacity of Pavements Using Shell Thiopave®." *Phase I: Mix Design, Laboratory Performance Evaluation and Structural Pavement Analysis and Design*. NCAT Report 09-05, Auburn, AL, 2009.
2. Deme, I; and Kennedy, B. "Use of Sulfur in Asphalt Pavements." Paper presented at the 5th International Symposium on Pavement Surface Characteristics, Roads and Airfield, Toronto, CA, 2004.
3. Strickland, D; Colange, J; Martin, M; and Deme, I. "Performance Properties of Sulphur Extended Asphalt Mixtures with Modified Sulphur Pellets." International Society of Asphalt Pavement, 2008.
4. Kennedy, T.W; Haas, R; Smith, P; Kennepohl, G.A; and Hignell, E.T. "Engineering Evaluation of Sulphur-Asphalt Mixtures." *Transportation Research Record 659*. Transportation Research Board, National Research Council, Washington, D.C., 1997.12-17.
5. *Louisiana Standard Specifications for Roads and Bridges*, Louisiana Department of Transportation and Development, Baton Rouge, Louisiana, 2006.
6. AASHTO, American Association of State Highways and Transportation Officials. "Hamburg Wheel-Track Testing of Compacted Hot-Mix Asphalt (HMA)." AASHTO Designation 324, Washington D.C., 2007.
7. Bonaquist, R.F; Christensen, D.W; and Stump, W. "Simple Performance Tester for Superpave Mix Design: First-Article Development and Evaluation." National Cooperative Highway Research Program (NCHRP) Report 513, Transportation Research Board, National Research Council, Washington, D.C., 2003.
8. AASHTO, American Association of State Highways and Transportation Officials. "AASHTO TP7 Standard Test Method for Determining the Permanent Deformation and Fatigue Cracking Characteristics of Hot Mix Asphalt (HMA) Using the Simple Shear Test (SST) Device." AASHTO TP7, Washington D.C., 2001.
9. Wu, Z; Mohammad, L.N; Wang, L.B; Mull, M.A. "Fracture Resistance Characterization of Superpave Mixtures Using the Semi-Circular Bending Test." *Journal of ASTM International*, Vol. 2, No. 3., 2005.
10. AASHTO, American Association of State Highways and Transportation Officials. "Standard Method of Test for Resistance of Compacted Asphalt Mixtures to Moisture-Induced Damage." AASHTO T 283-03, Washington D.C., 2003.
11. AASHTO, American Association of State Highways and Transportation Officials. "Standard Method of Test for Determining the Fatigue Life of Compacted Hot-Mix

- Asphalt (HMA) Subjected to Repeated Flexural Bending.” AASHTO T 321, Washington D.C., 2007.
12. Witczak, M.W. “Laboratory Determination of resilient Modulus for Flexible Pavement Design.” Research Results Digest, National Cooperative Highway Research Program (NCHRP) Report 1-28A, Transportation Research Board of the National Academies, No. 285. 2004.
 13. AASHTO, American Association of State Highways and Transportation Officials. “Creep Compliance and Strength of Hot-Mix Asphalt.” AASHTO T322, Washington D.C., 1993.
 14. Roque, R; Birgisson, B; Zhang, Z; Sangpetngam, B; and Grant, T. “Implementation of SHRPP Indirect Tension Tester to Mitigate Cracking in Asphalt Pavements and Overlays.” Final Report Submitted to Florida Department of Transportation, University of Florida, Gainesville, May 2002.
 15. Roque, R; Birgisson, B; Drakos, C; and Dietrich, B. “Development and Field Evaluation of Energy-Based Criteria for Top-Down Cracking Performance of Hot-Mix Asphalt.” *Journal of the Association of Asphalt Paving Technologists*. Vol. 73, Baton Rouge, Louisiana, 2004.
 16. Alshamsi, K.S. “Development of Mix Design Methodology for Asphalt Mixtures with Analytically Formulated Aggregate Structures.” Ph.D. Dissertation, Louisiana State University and Agricultural and Mechanical College, Baton Rouge, Louisiana, May, 2006.
 17. AASHTO, American Association of State Highways and Transportation Officials. “Standard Test Method for Thermal Stress Restrained Specimen Tensile Strength.” AASHTO TP 10, Washington D.C., 1993.
 18. AASHTO, American Association of State Highways and Transportation Officials. “Standard Test Method for Determining Dynamic Modulus of Hot-Mix Asphalt (HMA).” AASHTO TP 62, Washington D.C., 2003.
 19. Sousa, J; Solaimanian, M; and Weissman, S. “Development and Use of the Repeated Shear Test (Constant Height): An Optional Mix Design Tool.” SHRP-A-698, Strategic Highway Research Program, National Research Council, Washington, D.C., 1994.
 20. Taylor, A; Tran, N; May, R; Timm, D; Robbins, M; and Powell, B. “Laboratory Evaluation of Sulfur-Modified Warm Mix.” *Journal of the Association of Asphalt Paving Technologists*, Vol. 79, pp. 403-442., 2010.
 21. Lee, D.Y. “Modification of Asphalt and Asphalt Paving Mixtures by Sulfur Additives.” *Industrial & Engineering Chemistry Product Research and Development*, Vol. 14, No. 3, 1975, pp. 171-177.

APPENDIX A

Performance Testing

Loaded Wheel Tester (LWT)

Rutting performance of the mix was assessed using a Hamburg-type LWT, manufactured by PMW, Inc. of Salina, Kansas. This test is considered a torture test that produces damage by rolling a 703N (158 lb.) steel wheel across the surface of a slab that is submerged in 50°C (122°F) water for 20,000 passes at 56 passes a minute; see Figure A.1. A maximum allowable rut depth of 6 mm (0.24 in.) at 20,000 passes at 50°C (122°F) was used as a failure criteria.



Figure A.1
The Hamburg-Type Loaded Wheel Tester (LWT)

Flow Number (FN)

The flow number test was used to assess the permanent deformation characteristics of paving materials by applying a repeated dynamic load for several thousand repetitions on a cylindrical asphalt sample. The FN is defined as the starting point, or cycle number, at which tertiary flow occurs on a cumulative permanent strain curve obtained during the test. This test uses a loading cycle of 1.0 second in duration, and consists of applying a 0.1-second haversine load followed by a 0.9-second rest period [7]. Permanent axial strains are recorded throughout the test. The test was conducted at an effective temperature T_{eff} and stress level of 54°C (129.2°F) and 207 kPa (30 PSI), respectively. This test is applicable to laboratory prepared specimens 100 mm (3.9 in.) in diameter and 150 mm (5.9 in.) in height for mixtures with nominal maximum size aggregate less than or equal to 37.5 mm (1.5 in.).

Repeated Shear at Constant Height (RSCH)

The RSCH test is used as an indicator of accumulated permanent deformation. This test was conducted according to AASHTO TP7 Procedure F. It is a controlled stress test that applies haversine shear stress pulses to a cylindrical specimen. The shear stress amplitude is applied with a maximum shear stress of 68 kPa (9.9 PSI) for a loading time of 0.1 second and a rest period of 0.6 seconds. A varying axial load is applied automatically during each cycle to maintain the specimen at constant thickness or height. Repetitive loading is applied for a total of 5,000 repetitions or until 5 percent permanent shear strain is reached by the sample. The primary response variable from this test is the cumulative permanent shear strain at the end of testing [8].

Semi-Circular Bend (SCB)

Fatigue cracking potential was assessed using the SCB test developed by Wu et al.[9]. This test characterizes the fracture resistance of HMA mixtures based on fracture mechanics principals, the critical strain energy release rate, also called the critical value of J-integral, or J_c . Figure presents the three-point bend load configuration and typical test result outputs from the SCB test. To determine the critical value of J-integral (J_c), semi-circular specimens with at least two different notch depths need to be tested for each mixture. In this study, three notch depths of 25.4 mm (1.0 in.), 31.8 mm (1.3 in.), and 38 mm (1.5 in.) were selected based on an a/r_d ratio (the notch depth to the radius of the specimen) between 0.5 and 0.75. The test temperature was selected to be 25°C (77°F). The semi-circular specimen is loaded monotonically till fracture failure under a constant cross-head deformation rate of 0.5 mm/min (0.02 in/min) in a three-point bending load configuration. The load and deformation are continuously recorded and the critical value of J-integral (J_c) is determined using the following equation (9):

$$J_c = \left(\frac{U_1}{b_1} - \frac{U_2}{b_2} \right) \frac{1}{a_2 - a_1} \quad (2)$$

where,

b = sample thickness;

a = the notch depth; and

U = the strain energy to failure.

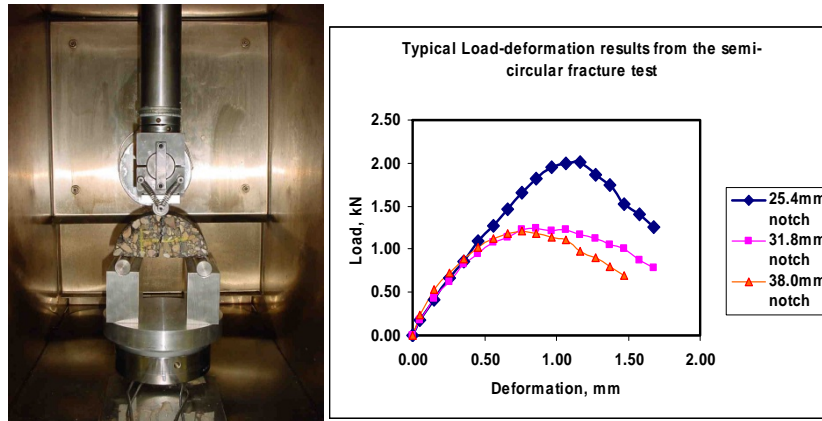


Figure A.2
The semi-circular bending test

Modified Lottman

The Modified Lottman test was used to evaluate the effect of saturation and accelerated water conditioning on compacted HMA samples utilizing freeze-thaw cycles. This method quantifies HMA mixtures' sensitivity to moisture damage, which is necessary to assure durability and long-lasting hot mix asphalt. Numerical values of retained indirect-tensile properties are obtained by comparing conditioned samples, samples subjected to vacuum saturation and freeze-thaw cycles, to unconditioned samples. "Unconditioned" samples are samples that are not saturated nor subjected to freeze-thaw cycles. For each mix used in the study, six – 150- (5.91) x 95-mm (3.7 in.) diameter samples were compacted with a Superpave gyratory compactor (SGC) to an air void content of 7 ± 0.5 percent. After compaction and air void determination, the six SGC samples were subdivided into two groups of three samples so that the average air void contents of the two subsets were approximately equivalent. The "unconditioned" sample subset was stored at room temperature for 24 ± 3 hours. Afterwards the "unconditioned" specimens were wrapped or placed in a heavy duty, leak-proof plastic bag and then placed in a $25 \pm 0.5^\circ\text{C}$ ($77 \pm 1^\circ\text{F}$) water bath for $2 \text{ hours} \pm 10$ minutes. The "unconditioned" specimens were then tested to determine the indirect tensile strength for each sample. The "conditioned" samples were placed in a freezer at -17.8°C (0°F) for 16 to 18 hours. After the freezing cycle, the conditioned samples were placed in a 60°C (140°F) water bath for 24 hours. Upon completion of the freeze/thaw cycle, the indirect tensile strength for the conditioned samples was determined. The average indirect tensile strength was determined for both conditioned and unconditioned samples by summing the test values and then determining the average value. The TSR is defined as the ratio of the conditioned to the unconditioned indirect tensile strength [10].

Beam Fatigue

Beam fatigue testing is used to characterize the fatigue properties of a mixture. This test was conducted according to AASHTO T321 protocol at 25°C (77°F). It is a strain-controlled test in which a beam 318 mm (15 in.) long by 63.5 mm (2.5 in.) wide by 50.8 mm (2.0 in.) high is subjected to 4-point bending. The strain level selected was selected such that failure does not occur prior to 10,000 cycles. The center deflection of the beam was continuously measured and used in the computation of the stiffness. Failure was defined as the load cycle at which the specimen exhibits a 50 percent reduction in stiffness. The number of cycles to failure (N_f) was used in the analyses. The reported test results were the average of three test samples [11].

Dissipated Creep Strain Energy (DCSE)

The DCSE threshold represents the energy that the mixture can tolerate before it fractures. The evaluation of DCSE of an HMA mixture involves two individual laboratory tests performed on the same specimen. The indirect resilient modulus (M_R) test and the indirect tensile strength (ITS) test were conducted at 10°C (50°F) on the same specimen to calculate the dissipated strain energy [12], [13]. Triplicate specimens of 150 mm (5.9 in.) in diameter and 50 mm (2.0 in.) in thickness were used. The test specimens were conditioned at 10°C (50°F) for four hours before a 200-cycle haversine load with 0.1 second loading period and 0.4 second rest period in each loading cycle was applied along the diametrical plane on the specimen. A conditioning loading sequence was applied before beginning the actual test in order to obtain uniform measurements in load and deformation. Then, a four-cycle haversine compressive load was applied and load and deformation data recorded continuously. The magnitude of the applied load should be such that it results in a deformation as close as possible to 100 microstrains. After one test was completed, the specimen was rotated 90 degrees and tested again. The resilient modulus was calculated from the average value of the two test results. Once the M_R test finished, the ITS test was then performed on the same specimen.

The DCSE calculation used in this study was introduced by Rogue et al. ([14], [15]) and later used by Alshamsi [14], [15],[16]. As indicated in Figure A.3, DCSE is defined as the fracture energy (FE) minus the elastic energy (EE). The fracture energy is defined as the area under the stress-strain curve up to the point where the specimen begins to fracture. As shown in Figure A.3, the area within the curve OA and X-axis (i.e., Area OAB) is the fracture energy. The elastic energy is the energy resulting in elastic deformation. Therefore, M_R , calculated from the resilient modulus test, is selected as the slope of the line AC and the area of triangle ABC is taken as the elastic energy (EE). The failure strain (ϵ_f), peak tensile strength (S_t) and fracture energy are determined from the ITS test. A rather clear picture of DCSE calculation is described below:

$$M_r = \frac{S_t}{\varepsilon_f - \varepsilon_0} \quad (3)$$

$$\varepsilon_0 = \frac{(M_R \times \varepsilon_f - S_t)}{M_R} \quad (4)$$

$$EE = \frac{1}{2} \times S_t \times (\varepsilon_f - \varepsilon_0) \quad (5)$$

$$DCSE = FE - EE \quad (6)$$

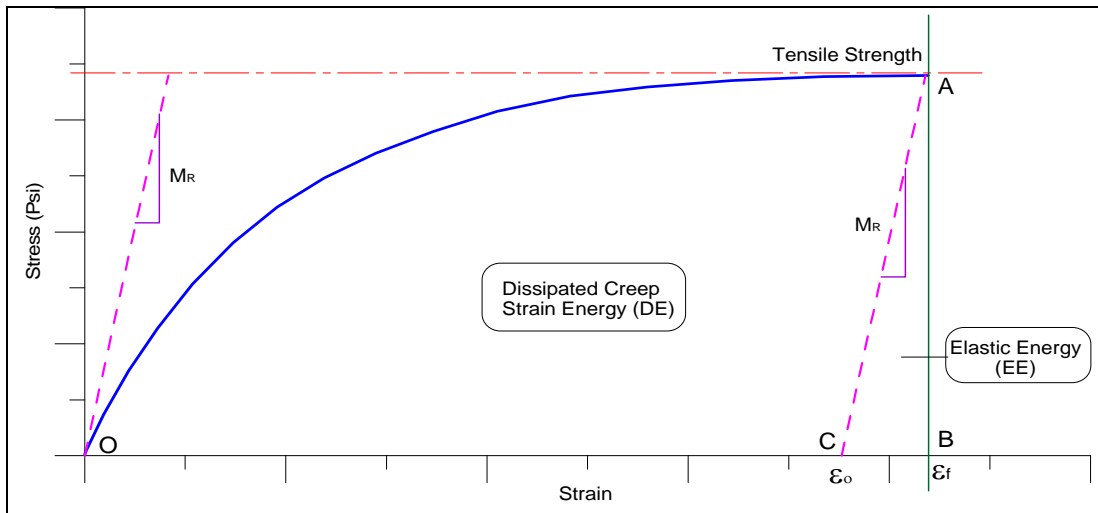


Figure A.3
Dissipated creep strain energy determination

Thermal Stress Restrained Specimen Test (TSRST)

This test was used to determine the tensile strength and fracture temperature of compacted bituminous mixtures by measuring the tensile load in a specimen which is cooled at a constant rate 10°C/hour (50°F/hour) while being restrained from contraction. The test was conducted in accordance with AASHTO TP-10 [17]. The samples tested for this study were compacted beams 254 mm (10 in.) long by 50.8 mm (2 in.) wide by 50.8 mm (2 in.) high.

Dynamic Modulus (E*)

Dynamic modulus describes the mixture's stiffness over a range temperatures and frequencies which could be encountered during performance. This test consists of applying a uniaxial sinusoidal (i.e., haversine) compressive stress to an unconfined or confined HMA cylindrical test specimen. The stress-to-strain relationship under a continuous sinusoidal loading for linear

viscoelastic materials is defined by a complex number called the “complex modulus” (E^*). The absolute value of the complex modulus, $|E^*|$, is defined as the dynamic modulus. The dynamic modulus is mathematically defined as the maximum (i.e., peak) dynamic stress (σ_0) divided by the peak recoverable axial strain (ε_0):

$$|E^*| = \frac{\sigma_0}{\varepsilon_0} \quad (7)$$

The dynamic modulus test consists of testing samples at 4.4, 20, 37.8, and 54.4°C (40, 70, 100 and 130°F) at loading frequencies of 0.1, 0.5, 1.0, 5, 10, and 25 Hz at each temperature for the development of master curves for use in pavement response and performance analysis. The haversine compressive stress was applied on each sample to achieve a target vertical strain level of 100 microns in an unconfined test mode. The test was conducted in accordance with AASHTO TP-62 [18].

This public document is published at a total cost of \$250. 42 copies of this public document were published in this first printing at a cost of \$250. The total cost of all printings of this document including reprints is \$250. This document was published by Louisiana Transportation Research Center to report and publish research findings as required in R.S. 48:105. This material was duplicated in accordance with standards for printing by state agencies established pursuant to R.S. 43:31. Printing of this material was purchased in accordance with the provisions of Title 43 of the Louisiana Revised Statutes.