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13. Abstract
    Modifying asphalt binder is one of the primary methods of improving the performance of asphalt mixtures; the benefits include improved rutting resistance, cracking resistance, increased durability and stripping resistance. The addition of polymer, such as styrene-butadiene-styrene (SBS), is the most common method of modifying asphalt binders; however, chemical modifiers, extenders, hydrocarbons and anti-stripping additives are also employed to improve asphalt performance. A low viscosity isocyanate-based modifier for asphalt binders has been developed which claims to improve adhesion performance in the asphalt mix. The product crosslinks components in the liquid asphalt, and claims to reduce stripping of the aggregates from the binder and make a more flexible, sustainable pavement. This research intends to evaluate the effects of the additive on liquid asphalt and compacted asphalt pavements.

Evaluation of Isocyanate Asphalt Additive

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Abstract

Modifying asphalt binder is one of the primary methods of improving the performance of asphalt mixtures; the benefits include improved rutting resistance, cracking resistance, increased durability and stripping resistance. The addition of polymer, such as styrene-butadiene-styrene (SBS), is the most common method of modifying asphalt binders; however, chemical modifiers, extenders, hydrocarbons and anti-stripping additives are also employed to improve asphalt performance. A low viscosity isocyanate-based modifier for asphalt binders has been developed which claims to improve adhesion performance in the asphalt mix. The product crosslinks components in the liquid asphalt, and claims to reduce stripping of the aggregates from the binder and make a more flexible, sustainable pavement. This research intends to evaluate the effects of the additive on liquid asphalt and compacted asphalt pavements.

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Introduction

Isocyanates are a family of low molecular weight chemicals which are highly reactive. Often times they are used in rigid and flexible foams, fibers, paints and varnishes, and building insulation materials. Additionally, isocyanates are used in spray-on polyurethane products for commercial and industrial applications. They are used to protect wood, cement, steel, and provide protective coatings for boats, trucks, foundations and decks [1]. A low viscosity isocyanate-based modifier for asphalt binders has been developed which claims to improve adhesion performance in the asphalt mix. The product crosslinks components in the liquid asphalt, and claims to reduce stripping of the aggregates from the binder and make a more flexible, sustainable pavement. A request was made to the Louisiana Department of Transportation and Development (DOTD) materials lab to have the additive added to DOTD's approved materials list. The materials lab then requested that the Louisiana Transportation Research Center (LTRC) conduct research to evaluate the effects of the isocyanate additive on asphalt liquid and pavement.

Objective

The objective of this research was to evaluate the effects of the isocyanate asphalt additive on liquid asphalt cement and compacted asphalt concrete mixtures.

Scope

In order to analyze the effects that the additive has on asphalt cement and mixtures, performance grading and laboratory testing was conducted on control samples (samples with no additive), samples with the isocyanate (ISO) additive, and samples with the isocyanate additive as well as styrene-butadiene-styrene (SBS). One job mix formula was developed for this project and used for all of the mixtures. Once performance grading and laboratory testing took place, the results of each could be compared to the control sample results.

Methodology

Table 1 below describes each test mixture, and the names shown are used throughout all reported test results. It should be noted that the isocyanate and styrene-butadiene-styrene (SBS) are added as 1% and 2% by weight of the asphalt binder. The Control 70 and Control 76 asphalt binders are modified with SBS to achieve their respective performance grade (PG). One asphalt mix design was utilized throughout the entire testing regimen.

Table 1. Test specimen descriptions

Mixture Name	Description
Control 67	Conventional PG 67-22 Mixture
Control 70	Conventional PG 70-22 Mixture (SBS Modified)
Control 76	Conventional PG 76-22 Mixture (SBS Modified)
1% ISO	PG 67-22 Mixture w/ 1% Isocyanate additive
2 % ISO	PG 67-22 Mixture w/ 2% Isocyanate additive
1% ISO - 1% SBS	PG 67-22 Mixture w/ 1% Isocyanate additive & 1% SBS
2% ISO - 2% SBS	PG 67-22 Mixture w/ 2% Isocyanate additive & 2% SBS

Laboratory Experiments

Rotational Viscometer

The rotational viscometer is a test that measures the viscosity by analyzing the torque required to maintain a constant rotational speed of a cylindrical spindle while submerged in an asphalt binder sample at a constant temperature. The torque and speed are used to determine the viscosity of the binder in Pascal seconds. The test is run on original binder according to the Standard Method of Test for Viscosity Determination of Asphalt Binder Using Rotational Viscometer (AASHTO T 316). The binders in this study were run at 135° C.

Dynamic Shear Rheometer

The dynamic shear rheometer (DSR) is used to characterize the viscous and elastic behavior of asphalt binders at medium to high temperatures. Testing was done on original, rolling thin-film oven (RTFO) aged binder and pressure aging vessel (PAV) aged binder samples following the Standard Method of Test for Determining the Rheological Properties of Asphalt Binder Using a Dynamic Shear Rheometer (AASHTO T 315) procedures. Binders from this study are tested at temperatures starting at 64°C, increasing every 6°C increments until specification failure, where it is assigned a performance grade (PG). The DSR also gives the continuous grade, also known as the true grade, where the device calculates exact temperature at specification failure. DOTD specifications for DSR require test results, $G^*/\sin(\delta)$, of original binders to be a minimum of 1 kPa, RTFO aged binders to be a minimum of 2.2 kPa, and PAV aged binders to be a maximum $G^* x \sin(\delta)$ of 5000 kPa.

Multiple Stress Creep Recovery

The Standard Method of Test Multiple Stress Creep Recovery (MSCR) of Asphalt Binder Using a Dynamic Shear Rheometer (AASHTO T 350) test method is used to determine the presence of elastic response in asphalt binder under shear creep and recovery at two stress levels at a specified temperature. For PG asphalt binders, the specified temperature will typically be the high temperature. Asphalt binder is conditioned using the Rolling Thin-Film Oven (RTFO) Test (AASHTO T 240), and a sample of the conditioned sample is tested using T 315. The sample is tested at two stress levels followed by recovery at each stress level. The stress levels are 0.1 kPa and 3.2 kPa. The creep portion of the test is

1-second, followed by a 9-second recovery. Ten creep and recovery cycles are tested at each stress level.

Ductility

The Standard Method of Test for Ductility of Asphalt Materials (AASHTO T 51) was used to determine the ductility of a bituminous material measured by the distance to which it will elongate before breaking when two ends of a briquette specimen of the material are pulled apart at a specified speed and a specified temperature. The test is made at a temperature of 25 ± 0.5°C and with a speed of 5 cm/min ± 5.0%.

Bending Beam Rheometer

The bending beam rheometer (BBR) test applies a static stress to a beam of asphalt and measures the strain rate to derive the stiffness of the beam. The BBR test is conducted on binder that has been subjected to both short-term aging (rolling thin film over) and long-term aging (pressure-aging vessel). The Standard Method of Test for Determining the Flexural Creep Stiffness of Asphalt Binder Using the Bending Beam Rheometer (AASHTO T 313) test method is utilized to provide the low temperature stiffness and relaxation properties of asphalt binders. These parameters give an indication of an asphalt binder's ability to resist low temperature cracking. An additional test criterion is the "m-value": this value is the tangent of the creep curve at 60s load time. This provides an indication of the ability of a binder to dissipate stresses or relax.

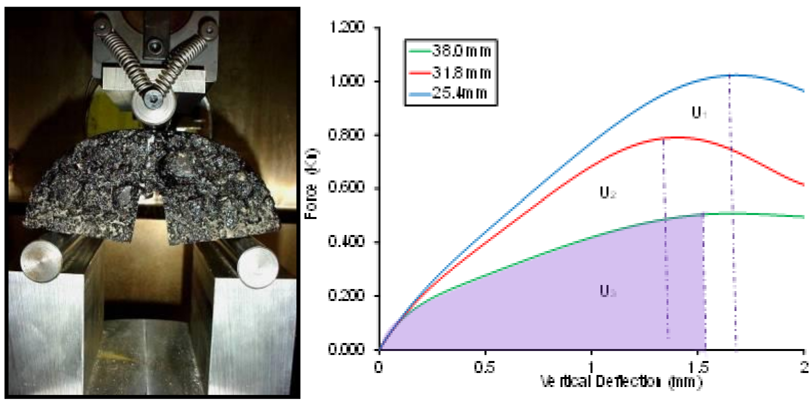
Semi-Circular Bend Test (SCB)

The semi-circular bend (SCB) test characterizes the fracture resistance of hot-mix asphalt (HMA) mixtures based on fracture mechanics principals, and the critical strain energy release rate, also called the critical value of J-integral, or J_c. Figure 1 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, 31.8 mm, and 38.0 mm were selected and a test temperature of 25°C. The semi-circular specimen is loaded monotonically until fracture failure occurs under a constant cross-head deformation rate of 0.5 mm/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:

$$Jc = -\left(\frac{1}{b}\right)\left(\frac{dU}{da}\right)$$

where,
b = sample thickness, mm;
a = the notch depth, mm; and
U = the strain energy to failure, kN-mm.

Figure 1. Semi-circular bending test



Hamburg Loaded Wheel Tester (LWT)

Rutting performance of the mix was assessed by the Standard Method of Test for Hamburg Wheel-Track Testing of Compacted Hot Mix Asphalt (AASHTO T 324). This test is considered a torture test that produces damage by rolling a 703-N (158-lb.) steel wheel across the surface of a specimen that is submerged in 50°C water for 20,000 passes at 56 passes a minute. The specifications allow for a rut depth of 10 mm at 20,000 passes at 50ºC for the low volume wearing course.

Modified Lottman Test

The Standard Method of Test for Resistance of Compacted Asphalt Mixtures to Moisture-Induced Damage (AASHTO T 283) test was utilized to analyze the moisture susceptibility of the test specimens. The test method covers preparation of specimens and the measurement of the change of diametral tensile strength resulting from the effects of water saturation and accelerated water conditioning, with a freeze–thaw cycle, of compacted asphalt mixtures. The results may be used to predict long-term stripping susceptibility of the asphalt mixture and evaluate liquid antistripping additives that are added to the asphalt binder.

Discussion of Results

Binder-Performance Grading

Table 2 below displays the rotational viscometer results for all of the binder samples. The Control 67 binder had a viscosity of 550 mPa·s, the Control 70 had a viscosity of 1058 mPa·s, and the Control 76 had a viscosity of 2050 mPa·s. The data shows that the viscosity of the 1% ISO and 2% ISO samples have an identical viscosity of 687.5 mPa·s. The addition of the isocyanate increased the viscosity but had no significant effect on the viscosity of the binder. When the SBS was incorporated into the ISO modified binders, the viscosity of the binder increased closer to the typical viscosity range for PG 70-22 and PG 76-22 asphalt binders. Also note, all of the modified binders pass the viscosity requirement of 3000 mPa·s.

Table 2. Rotational viscometer results

Rotational Viscometer (mPa·s)	
Mixture	**Avg**
Control 67	550
Control 70	1058
Control 76	2050
1% ISO	687.5
2% ISO	687.5
1% ISO - 1% SBS	825
2% ISO - 2% SBS	1308

Table 3 shows the effect that the isocyanate modifier and the addition of SBS has on the asphalt binder grade. The 1% ISO and 2% ISO samples have a continuous grade similar to the Control 70. The 1% ISO-1% SBS sample had a continuous grade more representative of a PG 76 and the 2% ISO-2% SBS sample had a continuous grade typically found in a PG 82. It can be concluded that the addition of isocyanate increases the binder's high performance grade, and the addition of isocyanate and SBS further increases the high performance grade of the asphalt binder.

Table 3. Original asphalt binder grades

DSR/Grading (Original Binder)		
Mixture	**Avg. Phase Angle**	**Continuous Grade**
Control 67	87.3	67
Control 70	78.7	75.6
Control 76	68.7	83.1
1% ISO	86.94	73.28
2% ISO	86.52	74.14
1% ISO - 1% SBS	84.9	76.4
2% ISO - 2% SBS	82.84	84.02

Table 4 below displays the binder grades of the short-term aged binders. The test results show that the addition of the isocyanate additive increased the grade of the short-term aged binder. The addition of 1% ISO additive increased the continuous grade from 68 found in the Control 67 sample to a PG 72. The 2% ISO and the 1%ISO-1% SBS had identical grades and they increased the binder grade to a PG 76. Finally, the 2% ISO-2% SBS had the most effect on the binder grade and they increased the binder grade to a PG 82.

Table 4. Short-term aged binder grades

DSR/Grading (RTFO)		
Mixture	**Avg. Phase Angle**	**Continuous Grade**
Control 67	82.4	68.2
Control 70	73.8	75.7
Control 76	65.5	79.4
1% ISO	84.5	72.25
2% ISO	80.35	75.85
1% ISO - 1% SBS	79.85	75.85
2% ISO - 2% SBS	73.05	86.5

Table 5 below displays the binder results of the long-term aged binders. All of the test samples had were tested at 26.5º C. The data shows that the addition of the isocyanate and the SBS did not affect the intermediate temperature stiffness of the asphalt binder when compared to the Control 67.

Table 5. Long-term aged binder grades

DSR/Grading (PAV)		
Mixture	**Avg. Phase Angle**	**Avg. G***
Control 67	44.2	5760
Control 70	44.4	5090
Control 76	46.8	4630
1% ISO	45.5	5755
2% ISO	44.35	5355
1% ISO - 1% SBS	44.2	5595
2% ISO - 2% SBS	39.95	5685

Figure 2 below displays the results of the multiple stress creep recovery test. The graph shows the J_{nr}, which is the non-recoverable creep compliance, plotted against the percent recovery for each test sample at the 3.2 kPa stress level. The curve shown on the graph is used to signify if the binder has high elasticity or poor elasticity. The data points above the curve have high elasticity and points below the curve have poor elasticity. The data shows that only the Control 76 and the 2% ISO-2% SBS samples had high elasticity. It appears that the binders lack elasticity without the addition of SBS.

Figure 2. Multiple stress creep recovery results

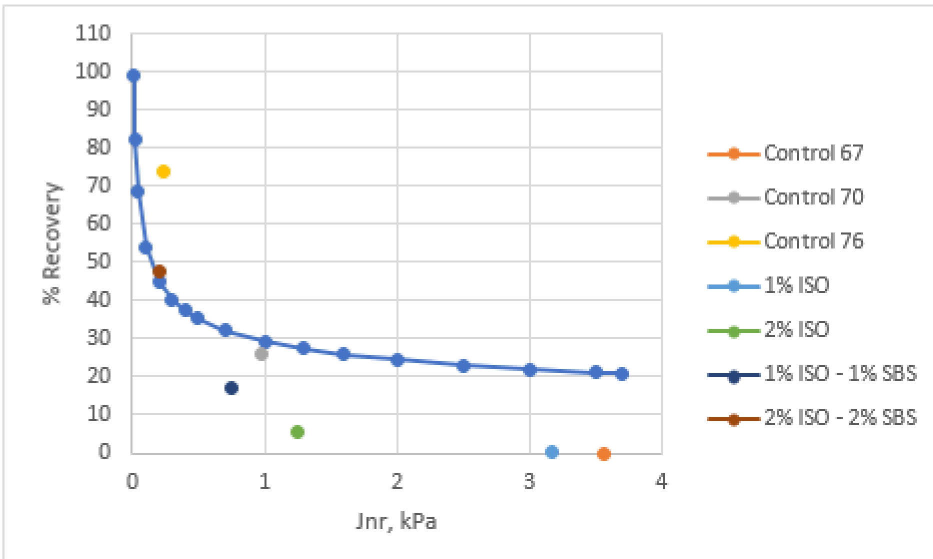


Table 6 below displays the ductility results for the test samples. The Control 70 and Control 76 samples were not tested. The control 67, 1% ISO, and 2% ISO all had a ductility of 150 cm; the 1% ISO - 1% SBS sample had a similar ductility of 146 cm; and the 2% ISO - 2% SBS had a large reduction in the ductility with 73 cm.

Table 6. Ductility results

Ductility (cm)	
Control 67	150
1% ISO	150
2% ISO	150
1% ISO - 1% SBS	146
2% ISO - 2% SBS	73

Table 7 below displays the results of the bending beam rheometer test. The results of the test show that the low temperature grade for five of the mixtures is -16; however, they were very close to a -22. The results for the four modified mixtures are similar to the Control 67 as the data indicates that the isocyanate additive and SBS did not have an impact on the low temperature grade.

Table 7. Bending beam rheometer results

BBR (PAV)			
Mixture	**Avg Stiffness**	**Avg mValue**	**Low Temp. PG grade**
Control 67	199.5	0.299	-16
Control 70	201	0.298	-16
Control 76	164	0.31	-22
1% ISO	199.5	0.2985	-16
2% ISO	151	0.3055	-22
1% ISO - 1% SBS	180.5	0.2965	-16
2% ISO - 2% SBS	106.1	0.298	-16

Semi-Circular Bending Test

The semi-circular bending test was conducted at an intermediate temperature to determine the cracking resistance of the mixtures. The critical strain energy (J_c) is presented in Figure 3. The specifications require a minimum J_c of 0.5 kJ/m^2. The 2% ISO mixture failed to meet the minimum J_c requirement. The 1% ISO-1% SBS sample had a J_c of 0.46. For the purposes of this specification, the value of 0.46 would round up to 0.5 and the sample would be considered to pass specification. The remainder of the test samples met the minimum requirement with the 2% ISO-2% SBS sample displaying the most resistance to cracking with a J_c of 0.62. The 1% ISO sample performed nearly as well as the Control 76, and outperformed the Control 70 and Control 67 samples.

Figure 3. Semi-circular bend test results

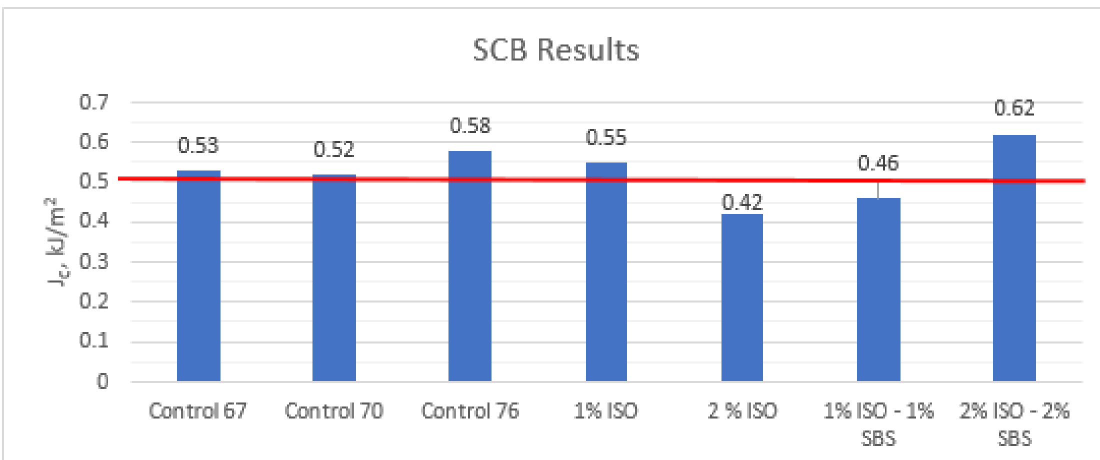
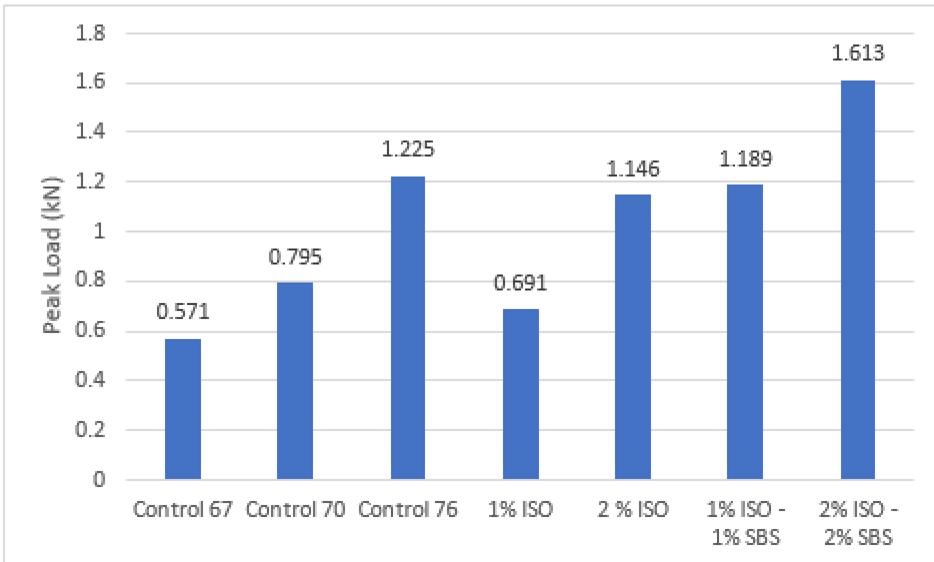


Figure 4 below displays the average peak load on the 25.4 mm SCB test specimen. The data shows that the 2% ISO-2% SBS sample had the highest peak load, the Control 76 had the second highest peak load, and the 2% ISO and 1% ISO-1% SBS samples had similar peak loads.

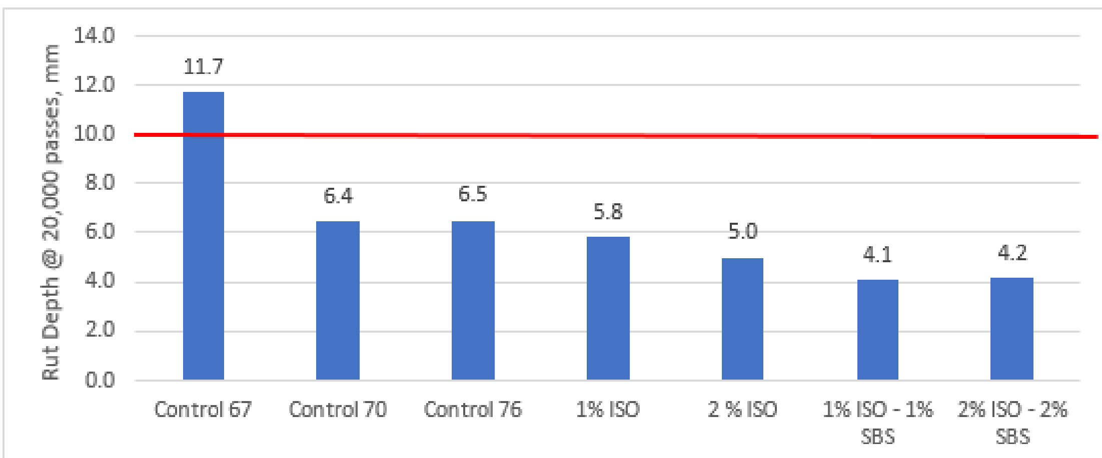
Figure 4. Peak load at 25.4-mm notch depth



Hamburg Loaded Wheel Test

Rutting is a significant concern for asphalt roadways in Louisiana, therefore the mixtures are subjected to the Hamburg loaded wheel test to characterize behavior in response to cyclic rolling loads. Figure 5 presents the LWT data generated for this report. The specifications for low volume roadways call for a maximum rut depth of 10 mm at 20,000 passes. The Control 67 sample is the only sample that failed to meet the specification. The data shows that the 1% ISO-1% SBS and the 2% ISO-2% SBS samples performed the best with rut depths of only 4.1 mm and 4.2 mm after 20,000 passes. The 1% ISO and 2% ISO both performed well with rut depths of 5.8 mm and 5.0 mm respectively.

Figure 5. Hamburg loaded wheel test results



Modified Lottman Test

Moisture susceptibility is also a concern for asphalt mixtures in Louisiana. In order to analyze the potential long-term stripping susceptibility of the modified asphalt pavements, the modified Lottman test was conducted. As seen in Figure 6 below, all of the test samples passed the minimum tensile strength ratio of 80%. It can be seen that the Control 70 sample outperformed all of the ISO/SBS modified samples, and the Control 76 sample outperformed all of the ISO/SBS modified samples with the 2% ISO being the only exception. Of the ISO/SBS modified samples the 2% ISO performed the best, while the 1% ISO-1% SBS performed the next best.

Figure 6. Modified Lottman test results

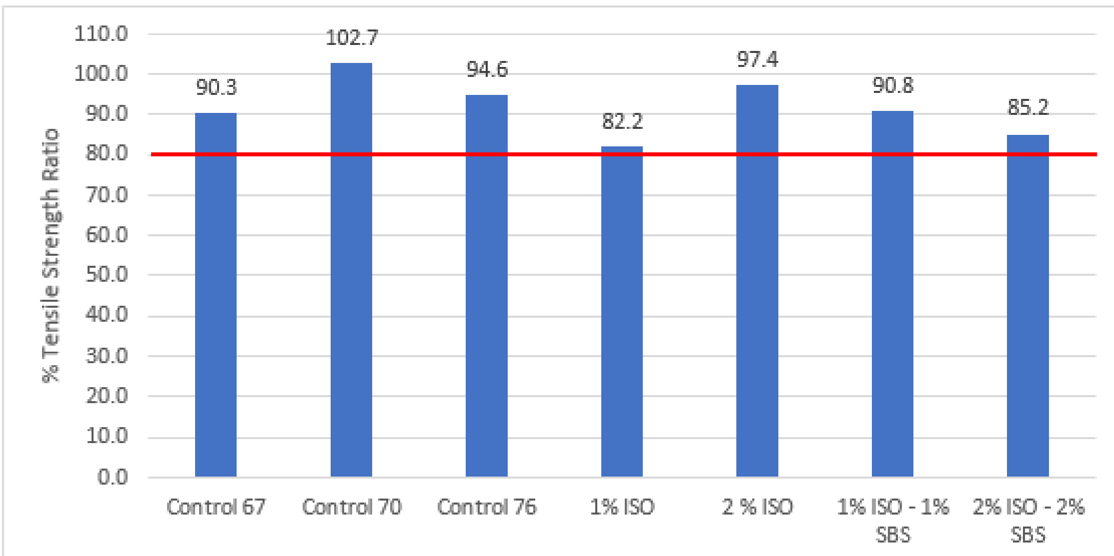
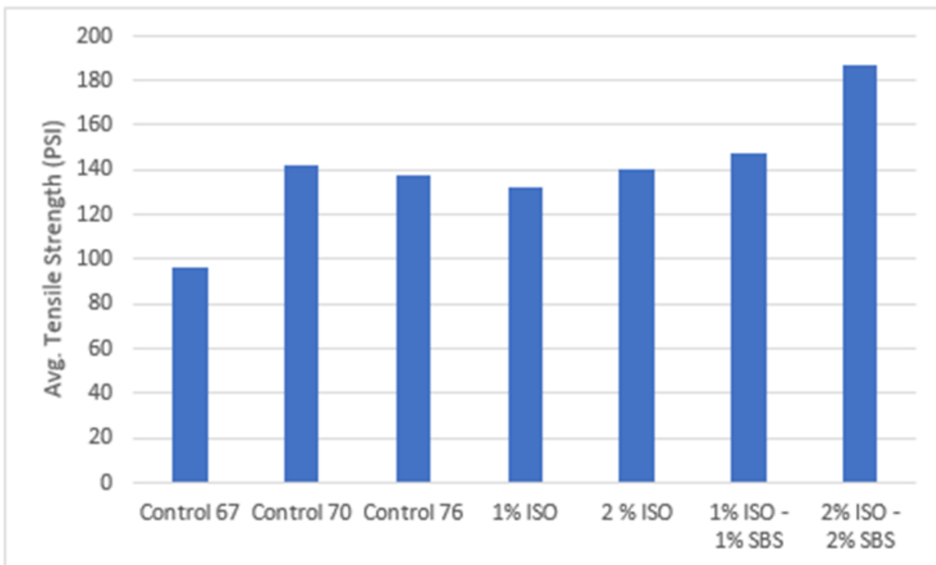


Figure 7 below displays the average tensile strength of the unconditioned test specimens. The data shows that the 2% ISO-2% SBS had the highest average tensile strength while the Control 70, Control 76, 1% ISO, 2% ISO, and the 1% ISO-1% SBS had similar average tensile strengths.

Figure 7. Average tensile strength of unconditioned samples



Conclusions

The objective of this research was to evaluate the effects of an isocyanate asphalt additive on liquid asphalt and compacted asphalt pavements. Based on the results presented, the following conclusions may be drawn:

- The results of the rotational viscometer show that the viscosity increased with the addition of the isocyanate, and increased even more with the addition of the SBS. All of the modified binders had an acceptable viscosity.
- The addition of the isocyanate and SBS increased binder stiffness at high temperatures.
- The addition of the isocyanate and SBS had no impact on the intermediate and low temperature properties of the asphalt binder.
- According to the MSCR test, the Control 76 and 2% ISO-2% SBS samples had high elasticity but the remainder of the test samples had poor elasticity.
- The Control 67, 1% ISO, 2% ISO and the 1% ISO-1% SBS samples had similar ductility; however, the ductility was significantly reduced for the 2% ISO-2% SBS sample.
- The 2% ISO mixture failed to meet the SCB cracking criteria for DOTD. The 2% ISO-2% SBS sample displayed the most resistance to cracking with a J_c of 0.62. The 1% ISO sample performed nearly as well as the Control 76.
- All of the isocyanate and SBS modified mixtures passed the LWT rutting criteria. The 1% ISO-1% SBS and 2% ISO-2% SBS samples performed the best with rut depths of 4.1 mm and 4.2 mm. The 1% ISO and 2% ISO samples also passed specification easily with rut depths of 5.8 mm and 5.0 mm.
- All of the test samples passed the minimum tensile strength ratio of 80% required for the modified Lottman test. The Control 70 sample outperformed all of the ISO/SBS modified samples, and the Control 76 sample outperformed all of the ISO/SBS modified samples except for the 2% ISO sample. The 2% ISO performed the best of the four modified samples, while the 1% ISO performed the worst of the four.

Recommendations

Based on the findings of the research, the isocyanate additive seems to increase the stiffness of the asphalt binders and mixtures, but it must be used with SBS for it to have the elastic properties required to pass specification. The isocyanate used in conjunction with SBS increases cracking resistance, rutting resistance, and performs well against moisture susceptibility. Additionally, the additive combination does not adversely affect the low and intermediate temperature binder properties and increases the stiffness of the binder at high temperatures.

Acronyms, Abbreviations, and Symbols

Term	**Description**
AASHTO	American Association of State Highway and Transportation Officials
BBR	bending beam rheometer
cm	centimeter(s)
DSR	dynamic shear rheometer
FHWA	Federal Highway Administration
ft.	foot (feet)
HMA	hot mix asphalt
ISO	isocyanate
in.	inch(es)
J_c	critical strain energy release rate
DOTD	Louisiana Department of Transportation and Development
LTRC	Louisiana Transportation Research Center
LWT	loaded wheel test
lb.	pound(s)
m	meter(s)
mm	millimeter(s)
min	minute(s)
mPa	mega Pascal(s)
MSCR	multiple stress creep recovery
PAV	pressure aging vessel
PG	performance grade
RTFO	rolling thin film oven
s	second(s)
SBS	styrene-butadiene-styrene
SCB	semi-circular bend

References

[1] National Institute for Occupational Safety and Health, "cdc.gov," 23 April 2014. [Online]. Available: https://www.cdc.gov/niosh/topics/isocyanates/default.html. [Accessed 7 December 2021].