

Effects of Liquid Anti-Stripping Additives on Rheological Properties of Performance Grade Binders

Zahid Hossain¹⁺, Musharraf Zaman², and Kenneth R. Hobson³

Abstract: This study presents a testing protocol for evaluating the viscoelastic properties of selected performance grade (PG) binders using a dynamic mechanical analyzer (DMA). It also presents the effects of amine-based liquid anti-stripping additives on the binders' rheological properties. Out of total 183 samples tested, 51 samples for three PG binders (PG 64-22, PG 70-28, and PG 76-28) were tested to establish the DMA-based testing protocol. The remaining samples were tested to obtain rheological data of the PG 64-22 binder with different dosages of two anti-stripping (AS) additives. Test results of the DMA were validated by comparing with those obtained from a dynamic shear rheometer (DSR). Test results show that the DMA can be used as an alternative tool for examining the viscoelastic behavior of binders. It was observed that the rutting factor [$G^*/\sin(\delta)$] of the binder decreased when the amount of AS additive was increased. The optimum dosage of either of these AS additives was found to be 0.50%. AS additives did not alter the mechanical workability and the linear viscoelastic limit of the binder. Also, a good correlation between the complex modulus of the PG 64-22 binder and the dynamic modulus of the corresponding mix was observed.

Key words: Anti-stripping additive; Complex modulus; DMA; Sweep test; Viscoelastic.

Introduction

Major asphalt concrete (AC) pavement distresses such as rutting, cracking, and stripping can be assessed by using the rheological characteristics of asphalt binders [1]. For example, stripping in AC pavements occurs when the bond between asphalt binder and aggregate is broken in presence of moisture. To address premature failures of bonds, amine-based liquid anti-stripping (AS) additives are often used in hot mix asphalt (HMA) pavements [2, 3].

Performance Grade (PG) binders are generally tested at high and intermediate temperatures using a dynamic shear rheometer (DSR) as per AASHTO T 135 [4]. Although DSRs are widely used in the PG grading of asphalt binders, it has some inherent limitations with respect to test conditions and reproducibility [5, 6]. For example, the DSR selects the PG grade of an asphalt binder based on a loading frequency of 1.59Hz rather than capturing its behavior for a larger frequency range. The repeatability and the reproducibility issues can be challenging for polymer-modified binders. These issues can be resolved by following the ASTM D3244 guidelines to some extent [5]. A dynamic mechanical analyzer (DMA) can be a viable device to validate rheological characteristics obtained from a DSR. However, no guidelines or specifications are available for rheological characterizations of PG binders using a DMA.

As noted earlier, AS additives are added with binders to reduce premature bond failure in asphalt pavements. It is reported that out

of 82% agencies that treat their asphalt mixes for premature bond failure, 56% use liquid amines, 15% use either liquid amines or lime, and 29% use lime [7]. Several liquid AS additives are certified by Oklahoma Department of Transportation (ODOT) [3]. These AS additives can be added with binders at different stages: at refineries, at distribution centers, or at HMA plants as a batch or continuous process [8]. The preferred method for adding these additives to an asphalt binder is to introduce it at the HMA plant. On the other hand, it is a common practice to test binders for their performance grades prior to the addition of AS additives [9]. Consequently, the rheological characteristics of a binder mixed with an AS additive remain unknown and the premature rut prediction in AC pavements may be underestimated in most cases. Moreover, the amount of AS additive can also change the rheological characteristics of a binder. Also, establishing a correlation between the complex modulus (G^*) of AS additive-modified binder and the dynamic modulus (E^*) of the corresponding mix would be useful for a better pavement design as currently such correlation does not exist.

The primary objective of this study is to generate rheological data of ODOT certified binders by using a DMA and to examine the influence of different dosages of AS additives. The optimum dosage of AS additive is then determined. This study also examines the mechanical workability, linear viscoelastic (LVE) limit, and temperature dependency of a binder mixed with different dosages of AS additives. Finally, it correlates the complex modulus (G^*) value of AS additive-modified binder with the dynamic modulus (E^*) value of a corresponding mix.

Overview of Previous Studies

To examine the viscoelastic behavior of an asphalt binder, it is necessary to understand its stress-strain response under different environmental and loading conditions [3, 10, 11]. It is desirable that the rheological properties of an asphalt binder be time-independent, which means that the rheological properties should remain unchanged if the asphalt binder is not subjected to any loading or

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environmental changes [12]. The Superpave specifications did not consider the effect possible thixotropic behavior (shear thinning) of a binder on its G^* and phase angle (δ) values [11]. The thixotropic network structure of binder can be destroyed or altered by repeated shearing due to addition of certain additives [13]. Clyne and Marasteanu [14] conducted strain controlled time sweep tests on long-term aged samples at intermediate temperatures to assess the fatigue behavior of nine PG binders certified in Minnesota. These researchers performed these tests with an oscillating stress of $500kPa$ applied at $1.59Hz$ by using a conventional DSR. These tests lasted from $15mins$ to $2.5hrs$. Test data and model parameters were then populated in tables of a rheological database. Loh et al. examined the mechanical workability of two neat binders (AC 10 and AC 20) by performing time sweep tests at their high critical temperatures [15]. It was reported that significant reductions in the G^* value were observed when the strain level decreased from 10 to 1%. However, none of these studies considered the influence of AS additives on the rheological properties of the binder.

As noted by several researchers [1, 3, 10, 16], it is important to perform specification-related dynamic testing of an asphalt binder within its LVE limit. The LVE limit of an asphalt binder is defined as the range of strain where the G^* value is at least 95% of the zero strain modulus [1]. Zhai et al. [17] conducted strain sweep tests on selected emulsified asphalt binders and reported that some had limited LVE regions (as low as 1% strain). Clyne and Marasteanu [14] also performed strain sweep tests on nine PG binders certified in Minnesota to obtain their LVE limits. These researchers observed that heavily polymer-modified binders showed sharper reduction in modulus with increasing strain. The sharp reduction of complex modulus with increase in strain indicates that under increased strain in the pavement, the materials may rut faster than binders that do not lose stiffness as quickly [14]. These researchers did not consider AS additives in their respective studies.

Temperature sweep tests on binders can be used to approximate the temperature at which a binder will satisfy the Superpave reflecting rutting resistance criteria. Selvaratnam et al. [2] and Gore [9] observed possible grade changes of selected PG binders due to the addition of two selected AS additives (ASA1 and ASA2). These researchers used DSRs to test binder samples in accordance with AASHTO T-315. Selvaratnam et al. [2] reported that the addition of ASA1 up to 0.75% and ASA2 up to 1.0% met the Superpave criteria. Gore [9] also reported that there was a slight change in the δ value (not more than 0.5°) due to the addition of ASA1 and ASA2. However, these researchers did not evaluate mechanical workability, LVE limits, and frequency dependency of AS additive modified binders.

The stiffness of a HMA mix decreases as the loading time increases or the loading frequency decreases. The dynamic modulus (E^*) value of a HMA mix can reduce as much as ten-fold when the loading frequency is reduced from 10 to $0.01Hz$. The corresponding G^* value of the binder exhibits a similar frequency dependency [18]. Accordingly, the traffic speed on newly constructed asphalt pavements can significantly influence its rutting potential. A pavement section experiencing slower traffic at early stage is expected to experience higher rutting damage. Frequency sweep tests can be conducted on asphalt binder to simulate this condition.

DMA's have been used by polymer and food processing industries

for the last several years [19]. Lately, some researchers have used a DMA to examine the fatigue and healing characteristics of asphalt mastic and specially designed HMA mixtures [20]. Hossain and Zaman [21] analyzed a neat PG 64-22 binder using a DMA. That study, however, did not include any AS additive.

Material, Equipment, and Test Methodology

Materials

An unmodified PG 64-22 binder and two styrene-butadiene-styrene (SBS) modified (PG 70-28 and PG 76-28) binders, all collected from a local refinery in Oklahoma, were used to establish the DMA testing protocol. The PG 64-22 binder was then mixed with different dosages of ASA1 and ASA2, and its mechanical workability and rheological characteristics were examined by conducting time, temperature, strain, and frequency sweeps tests.

The atomic composition of the selected PG 64-22 binder has been reported to have 92% carbon, 6.7% hydrogen, 0.63% nitrogen, and 0.67% sulfur [22]. The viscosity of the PG 64-22 binder was found to be $134mPa-s$ at ODOT's recommended mixing temperature ($163^\circ C$). Selected amine based AS additives are organic compounds with a functional group containing a nitrogen (N) atom with a lone pair (valence electron) and at least one hydrogen (H) atom replaced with an alkyl or aryl group (hydrocarbons) (Figs. 1(a)-1(c)). These AS additives are surfactants with a lyophobic amine group which are highly surface active [22]. The "head" groups of a surfactant tend to diffuse through the lyophilic surface of the binder, while the lyophilic hydrocarbon chain ("tail" group) still remains in the asphalt binder (Fig. 1(d)). Thus, an AS additive acts as a bridge between the asphalt binder and the aggregate surface which resist the action of water. Depending on the asphalt grade and aggregate type, ASA1 is added to asphalt in the amount of 0.2-0.8% by the weight of the binder [24]. The recommended dosage of ASA2 is 0.5 to 1.0% [8]. Both of these AS additives are commercial products.

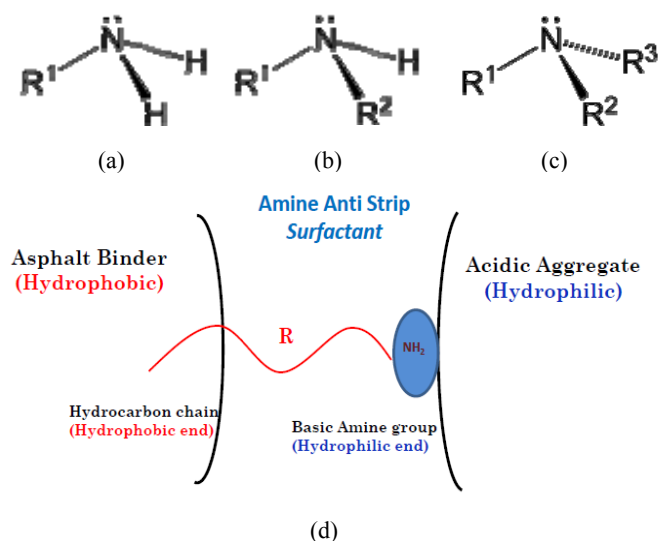
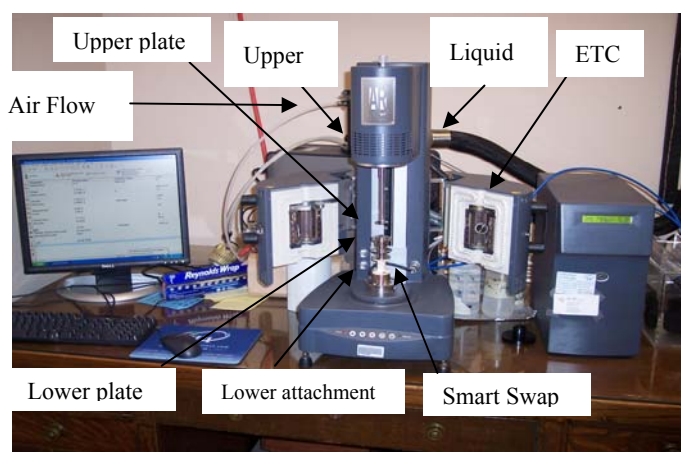


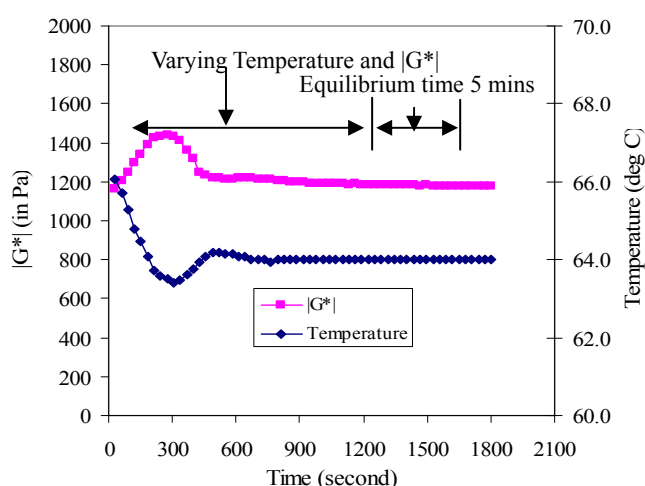
Fig. 1. Functional Group of Asphalt Binder and Amine-Based Liquid Anti-Stripping and Surface Modification (a) Primary Amine, (b) Secondary Amine, (c) Tertiary Amine, and (d) Surface Modification of Acidic Binder with Amine Anti-Stripping Agent [22, 23].

Table 1. Properties of Anti-Stripping Additives Used in This Study [8, 24].

Name of Additive	ASA1	ASA2
Dosage	0.2-0.8%	0.5-1.0%
Physical State	Brown to Dark Brown Liquid	Brown to Dark Brown Liquid
Viscosity	225cps at 25°C	350cps at 25 °C
Flash Point	> 149 °C	> 200 °C
Boiling/Condensation	> 150 °C	> 150 °C
Melting/Freezing	< 0 °C	< 0 °C
Density	0.95g/cm ³ at 25 °C	1.03g/cm ³ at 25 °C
Solubility	Partially Soluble in Cold Water	Partially Soluble in Cold Water
Storage Temperature	32 to 38 °C	Below 48.9 °C
pH	13 at 22 °C	12.2 at 22 °C
Specific Gravity	0.99 to 1.03	1.02
Vapor Density	>1	>1
Solubility in Water	Slight	Partially Soluble in Cold Water
Composition	Bis-Hexamethylenetriamine > 30%, Aminoethylethanolamine (AEEA) > 1%, and the Rest Is Unknown, If Any.	Alcohol Ethoxylate (33%), Fatty Amine Derivative (25%), Distillate Residues (19%), Polyamines (18%), and Fatty Acid (5%)



(a)



(b)

Fig. 2. AR2000ex Rheometer (DMA) Used in the Current Study (a) DMA and (b) Thermal Equilibrium of the DMA.

At 22°C, p^H values of ASA1 and ASA2 were found to be 13 and 12.2, respectively. Some additional chemical and mechanical properties of these AS additives are presented in Table 1.

Equipment

The DSR used in this study is designed to permit testing of asphalt according to the AASHTO standards for binder testing in a stress controlled mode. Besides verifying the grading (pass or fail) of a binder sample at a pre-defined temperature, this DSR is also capable of determining PG grading, linearity, and temperature calibration of an asphalt binder. Once parameters for these tests are set, templates are created. On the other hand, the DMA is designed to perform sweep tests (time, strain, temperature, and frequency) of an asphalt binder. In addition to the testing parameters for a particular sweep test, the measuring head geometry and dimension, and material density are entered as inputs. Reusable oscillation procedure files containing the test specifications are then created.

A DMA can determine many rheological properties of an asphalt binder, including: storage modulus, viscous modulus (or loss modulus), complex modulus, damping, creep, stress relaxation, glass transition, and softening point [20]. Tests relevant to these properties can be performed as a function of temperature, frequency or time in a constant (or step fashion), or under a fixed rate. It has also been reported that a DMA is the most sensitive of all thermal analytical techniques [22]. However, many of these features are out of scope of this paper.

The DMA used in this study is a fifth-generation commercial rheometer [19]. Fig. 2(a) shows the DMA assembly, including an environmental testing chamber (ETC) capable of maintaining a temperature ranging from -150 to 400°C [19]. The maximum heating/cooling rate in the ETC is 24°C/min, and the accuracy of the temperature is $\pm 0.1^\circ\text{C}$. To attain rapid cooling and to maintain an equilibrium temperature for a binder sample, the ETC is connected to a liquid nitrogen supply which does not react with the asphalt binder being tested. Both unaged and rotational thin film oven (RTFO) aged binder samples were tested in accordance with AASHTO T 315. These requirements were maintained by inputting the specifications in the software of the DMA. The thermal equilibrium for a binder sample in the ETC chamber of the DMA was determined as per AASHTO T 315. The sample was tested at a constant speed of 1.59Hz for 30mins. The G^* value versus the testing

time was plotted in Fig. 2(b), and the thermal equilibrium was found to be three minutes. To be on a conservative side, a five-minute thermal equilibrium was maintained at all testing temperatures.

Additionally, a rotational viscometer (RV) was used to measure viscosity of the binder as per AASHTO T 316 test method. Short-term aging of the binder was simulated in a RTFO as per AASHTO T 240. To simulate long-term aging of the binder, a pressure aging vessel (PAV) was used and AASHTO R 28 was followed. A bending beam rheometer (BBR) was used to evaluate the low temperature resistance of the same binder with 0.5% ASA1, and AASHTO T 313 was followed.

Mixing Additives

Three selected percentages of each AS additive (0.25, 0.50, and

0.75% for ASA1, and 0.50, 0.75, and 1.00% for ASA2) were mixed with the PG 64-22 binder. While mixing an AS additive with the PG 64-22 binder, ODOT's test specifications "OHD L-36: Method of Test for Retained Strength of Bituminous Paving Mixtures," were followed [3]. Before mixing, the binder was heated for two hours at 145°C. After pouring the AS additive in the heated binder, it was manually stirred for 30s. The mix (AS additive and binder) was then kept in a pre-heated oven at 145°C for an hour, and the sample was stirred for 30s at ten minutes interval. The binder was then kept overnight for further testing.

Test Methodology in the DMA

The test matrix for the current study is shown in Table 2. Out of total 183 binder samples, 51 samples were tested for establishing the

Table 2. Binder Test Matrix (a) DMA Testing Protocol Establishment and Validation, (b) Superpave Rutting Factor and Phase Angle Determination, (c) Sweep Tests, and (d) Fatigue and Thermal Cracking.

(a)							
Procedural and Validation Purpose	Binder Type	Sample Loading Temp (°C)		Testing Temp (°C)	No. of DMA Tests	No. of DSR Tests	
Thermal Equilibrium	PG 64-22	58		64	3	-	
Rutting Factor	PG 64-22	58		64	3	3	
Rutting Factor	PG 70-28	64		70	3	3	
Rutting Factor	PG 76-22	70		76	3	3	
Temperature Dependency	PG 64-22	DMA: 52; DSR: 52 to 67 @ 3°C interval		58 to 73 @ 3°C	3	18	
DSR Fine Tuning	PG 76-28	70, 76, 85 (for DSR)		76	-	9	
Total Number of Tests:					15	36	
(b)							
Purpose	Binder Type	AS Agent	Dosage (by Weight %)	Testing Temp (°C)	No. of DMA Tests		
Rutting Factor	PG 64-22	ASA1	0.25, 0.50, and 0.75	64	9		
Rutting Factor	PG 64-22	ASA2	0.50, 0.75, and 1.0	64	9		
Total Number of Tests:					18		
(c)							
Binder Type	AS Agent	Dosage (by Weight %)	Sweep Type and Number of Tests on DMA				No. of Tests on DMA
			Time ^a	Strain ^b	Temperatue ^c	Frequency ^d	
PG 64-22	ASA1	0.00	3	3	3	3	12
		0.25	3	3	3	3	12
		0.50	3+6 ^f	3	3	3	18
		0.75	3	3	3	3	12
	ASA2	0.00	-	-	-	-	-
		0.50	3	3	3	3+12 ^g	24
		0.75	3	3	3	3	12
		1.00	3	3	3	3	12
Total Number of Tests:					102		
(d)							
Binder Type	AS Agent	Dosage (by Weight %)		No. of DSR Test	No. of BBR Test		
PG 64-22	ASA1	0.00		3	3		
		0.50		3	3		
Total Number of Tests:					12		

a Testing temperature = 64°C; strain = 12%, and frequency = 10rad/s, time = 15mins;

b Testing temperature = 64°C; strain = 0.1 to 51.1%, and frequency = 10rad/s.

c Testing temperature = 58 to 73°C @ 3°C; strain = 12%, and frequency = 10rad/s.

d Testing temperature = 64°C; strain = 12%, and frequency = 0.15 to 15.15rad/s.

f 6 samples were tested to determine the influence of storage time.

g 12 samples were tested at 4.4, 21.1, 37.8, and 54.4°C to compare G* binder with E* of mixes.

DMA protocol. The remainders of samples were tested to characterize rheological properties of PG 64-22 binder with different dosages of AS additives.

Rutting factor

The heated binder was poured into silicon rubber molds to prepare test samples (Fig. 3(a)). Samples were then allowed to cool down for an hour. A Microsoft® window-based software “AR Instrument Control” networked with the testing unit was used to monitor and control the DMA. Immediately after attaching the measuring system, a standard three-minute rotational mapping of the equipment was carried out to obtain baseline data for the correction of torque. The ETC was then closed and the chamber temperature was raised to the sample loading temperature, which was 6°C below the testing temperature. Once the sample loading temperature maintained its equilibrium condition for two minutes, the upper plate was lowered to the zero-gap position. The ETC was opened, the upper plate was raised, and a sample was placed onto the lower plate. After placing the sample on the lower plate, the ETC was closed and the upper plate was lowered to the testing gap of 1.05mm. The ETC was then opened and a trimmer was used to trim the bulged portion of the sample, as shown in Fig. 3(b). Depending upon the sample loading temperature and binder grade, multiple rounds of trimming was necessary to obtain desired test samples (Figs. 3(c) and 3(d)).

Following the trimming, the ETC was closed, the upper head was lowered to the geometry gap of 1mm, and a five-minute thermal equilibrium was maintained at the testing temperature. The binder specimen was then pre-conditioned for one minute by pre-shearing with a loading frequency of 1.59Hz and a strain level of 12%. The purpose of the pre-shearing was to remove any historical load associated with sample preparation, storage, handling, and loading. Following the pre-shearing, a three-minute time sweep test was conducted with a strain level of 12%, and a frequency level of 1.59Hz. Data was collected every nine seconds. The last ten datasets were used to evaluate the $G^*/\sin(\delta)$ value. The post-test temperature was set to 100°C as an aid to clean the plates and prepare the equipment for the next test.

Sweep Tests

Time Sweep — In a time sweep test, a binder sample was loaded at 58°C. The temperature was raised to the testing temperature of 64°C, and the thermal equilibrium was maintained for five minutes. At 64°C, a 30-second pre-shearing was performed at a strain level of 5% and a frequency level of 1.59Hz. The test was conducted at a constant strain of 12% and a constant frequency of 1.59Hz, over a period of 15mins.

Strain Sweep — In a strain sweep test, a frequency of 1.59Hz was kept constant while the oscillation amplitude was increased in some progression. The sample was loaded at 58°C. After maintaining the thermal equilibrium for the testing temperature, the sample was pre-sheared for one minute at a strain level of 0.15% and a frequency level of 1.59Hz. During the testing phase, the sample was subjected to strains ranging from 0.15 to 51.15%.

Temperature Sweep — In a temperature sweep test, the frequency and the oscillation amplitude were kept constant, while the

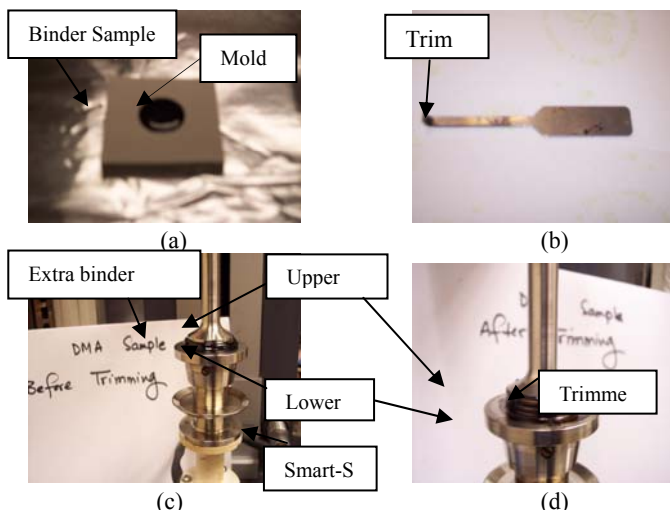


Fig. 3. (a) Binder Sample on Silicon Rubber Mold, (b) Trimmer for DMA, (c) Sample in DMA before Trimming, and (d) Sample in DMA after Trimming.

temperature was increased in some progression. The effect of high temperatures on the PG 64-22 binder was examined for a range of temperature from 58 to 73°C with increments of 3°C. Samples were loaded and trimmed at 58°C, followed by a 30-second pre-shearing at a strain level 1% and a frequency level of 1.59Hz. During the temperature sweep test, the thermal equilibrium was maintained at each data collection point. Samples were tested using a progression going from low temperatures to high temperatures.

Frequency Sweep — It is known that several factors including aggregate type and characteristics, compaction effort, binder type, and binder content contribute to the E^* value of a mix. For simplicity, frequency sweep tests on RTFO-aged binder samples (0 and 0.5% ASA2) were tested to correlate G^* values of binders with E^* values of corresponding mixes. In a frequency sweep test, the loading frequency ranged from 25 to 0.1Hz. Samples were pre-conditioned at a frequency of 25Hz and a temperature of 4.4°C. Samples were then tested at 4.4, 21.1, 37.8, and 54.4°C. At each testing temperature, a five-minute thermal equilibrium was maintained.

Results and Discussions

Validation of DMA Protocol

Test results obtained from the DMA are compared with those from the DSR (Fig. 4). It is seen that all three unaged asphalt binders satisfy the Superpave reflecting rutting factor of 1kPa at their high critical temperatures. The value of δ is close to 90° for the PG 64-22 binder, whereas it is as low as 51° for polymer modified PG 76-28 binder. From Figs. 4(a) and 4(b) it is observed that the test results ($G^*/\sin(\delta)$ and δ values) for PG 64-22 and PG 70-28 binders obtained from the DMA match well with those from the DSR. However, the DMA gives significantly higher $G^*/\sin(\delta)$ value for the polymer-modified PG 76-22 binder.

Student's t-tests (paired two-sample) were performed to compare the test results obtained from the DMA and the DSR to see if the differences had any statistical significance. It showed that at 95%

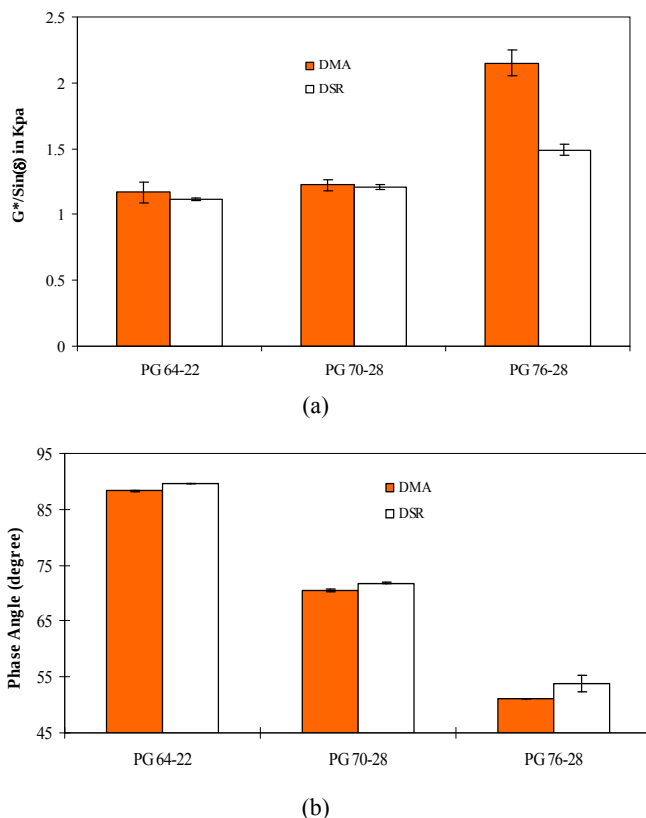


Fig. 4. Test Results of Selected PG Binders at High Grade Temperatures Using DMA and DSR (a) $G^*/\sin(\delta)$ and (b) δ Values (Note: Each Data Point Is the Average of Three Replications, and Vertical Bars Denote $\pm$ One Standard Deviation of the Population).

confidence level ($p = 0.05$) the $G^*/\sin(\delta)$ and δ values for PG 64-22 and PG 70-28 binders from the DMA and the DSR did not differ significantly. In the case of the PG 76-28 binder, however, the t-test results ($p = 0.05$) suggested that there were significant differences in the mean $G^*/\sin(\delta)$ and δ values obtained from these two pieces of equipment. The $G^*/\sin(\delta)$ values for the PG 76-28 binder obtained from the DSR and the DMA are 1.49 and 2.15 kPa, respectively. Possible reasons for the differences in the G^* and δ values are discussed below.

Some difficulties were encountered in conducting the DSR tests for the PG 76-28 binder. Naturally, PG 76-28 is a much stiffer and more viscous binder than the other two. During the initial trial on the DSR, the δ value for the PG 76-28 binder was found to be relatively higher (63.7° from the DSR tests compared to 51.2° from the DMA tests) than expected, which led to lower $G^*/\sin(\delta)$ values. This could be due to the fact the parallel plates might not have been in smooth contact with the sample due to the presence of minute air bubbles. As shown in Fig. 5, taking additional measures, namely extra trimmings and raising the sample loading temperature reduced the δ value by 15%, thus providing more reliable results from the DSR.

Fig. 6 shows a comparison of the $G^*/\sin(\delta)$ and δ values obtained from the DSR and the DMA for the PG 64-22 binder at temperatures ranging from 58 to 73°C at 3°C interval. Each data point in the chart represents the average value of three tests, and the vertical line at each point represents the error bar. It is evident that δ

values obtained by using the DMA fit very well with those obtained from the DSR throughout the range of testing temperatures. The $G^*/\sin(\delta)$ values obtained from the DMA also match well with those from the DSR at temperatures of 61°C and higher. Although the mean $G^*/\sin(\delta)$ value from the DMA at 58°C differs from that obtained from the DSR, the Student's t-test results show that the difference does not have any statistical significance at 95% confidence.

Effect of Anti-Stripping Additives

Both ASA1 and ASA2 reduced the $G^*/\sin(\delta)$ values of the PG 64-22 binder (Fig. 7(a)). The higher the dosage level of an AS additive, the lower the $G^*/\sin(\delta)$ value, which means lower rutting resistance. Selvaratnam et al. [2] and Gore [9] observed similar behavior for some selected PG binders tested in their studies. ASA1 seems to have a higher influence in the reduction of $G^*/\sin(\delta)$ values than ASA2. This observation is supported by the viscosity data of ASA1 and ASA2 which 225cps for the former and 350cps for the latter at 25°C. Binder samples with 0.75% ASA1 and 1.0% ASA2 failed the Superpave reflecting rutting criterion. An addition of either AS additive makes the binder a more liquid-like material, which is observed in their corresponding δ values (Fig. 7(b)). When an AS additive is added, the primary amines present in these additives (aka surface active agents) react with the carboxylic acids present in the binder and form corresponding salts that also act as AS additives. As mentioned earlier, these AS additives are more viscous than the neat binder. The decrease in the viscosity of the modified binder increases the diffusivity of the amine groups in the AS additive through the binder to the surface. As viscosity of the binder decreases, its elastic modulus (G') also decreases but δ value increases. Consequently, the complex modulus (G^*) of asphalt binder decreases, and so does the rutting factor ($G^*/\sin(\delta)$).

It is also important to note that any amount up to 0.50% ASA1 or 0.75% ASA2 can be blended with this PG 64-22 binder without jeopardizing the Superpave acceptance criterion. However, a 4 and 6% reduction in rutting resistance is expected in case of 0.25 and 0.50% ASA1. On the other hand, a 1 and 6% reduction in rutting resistance is predicted in case of 0.5 and 0.75% ASA2. The reductions in rutting resistance in case of 0.75% ASA1 and 1.0% ASA2-modified binders are 22 and 9%, respectively.

Sweep Test Results

Mechanical workability: The mechanical working effects for the PG 64-22 binder with different dosages of AS additives were evaluated by performing 15-min time sweep tests at the high critical temperature. As expected, δ values for these binders remained constant throughout the testing period. However, a slight increase in G^* values, representing marginal rheopectic or anti-thixotropic behavior, was observed. This behavior might be due to the fact that the hydrophilic suspended particles in asphalt binder form a lattice structure throughout the asphalt binder which causes an increase in viscosity and thus, hardening. Moffat [25] also reported similar behavior for the Canadian Tar Sand bitumen in viscosity measurements.

It is expected that keeping the binder at elevated temperature for

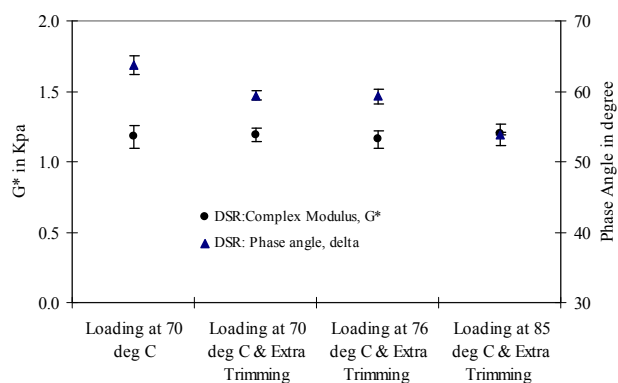


Fig. 5. Variation G^* and Values of PG 76-28 Binder with Higher Sample Loading Temperature and Extra Trimming Efforts While Using DSR (Note: Vertical Lines Represent Standard Deviation).

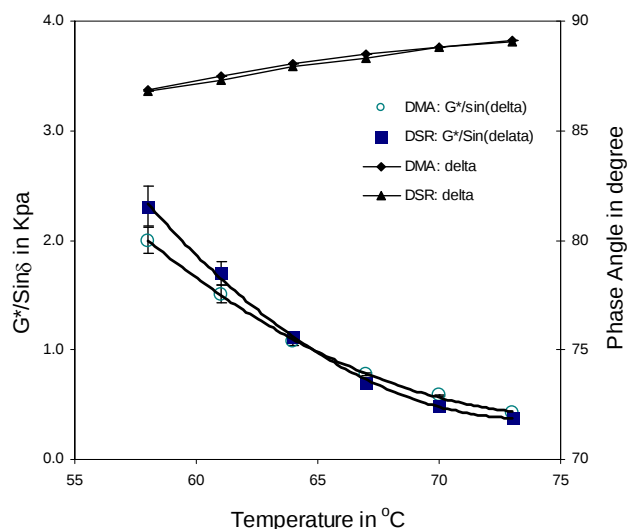


Fig. 6. Validation of DMA Results for a Wide Range (Near High PG) of Temperature.

an extended period of time may affect the binder stiffness. At the same time, the storage time of the AS additive may influence the binder stiffness. To evaluate the effect of storage time (two years in an air-conditioned room at 22°C) of ASA1, PG 64-22 binder samples were tested at 64°C. The $G^*/\sin(\delta)$ value of the binder with 0.5% ASA1 was found to be 1.01 kPa, which was only 0.03 kPa lower than its fresh counterpart. Therefore, it is expected that the functionality of ASA1 will remain the same if it is stored for such short-period of time.

Linear Viscoelastic Limits: Fig. 8 presents the effect of strain on the G^* values for the PG 64-22 binder with different amounts of ASA1 and ASA2. It is evident that the G^* value remained constant for all binder types up to a strain level of 51%. For this PG 64-22 binder, the LVE behavior was exhibited up to a strain level of 51% as 95% of $G^*_{\epsilon=0}$ (G^* corresponding to zero strain) was not achieved at that point. This behavior is observed because the PG 64-22 binder behaves like a Newtonian fluid above 50°C [16].

Temperature Dependency: The $G^*/\sin(\delta)$ and δ values for the ASA1-mixed binder are plotted against the testing temperatures in Fig. 9(a). As expected, the $G^*/\sin(\delta)$ value decreased and the δ value

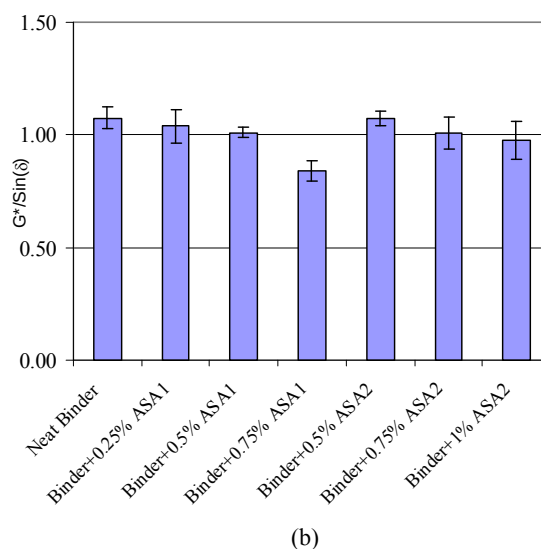
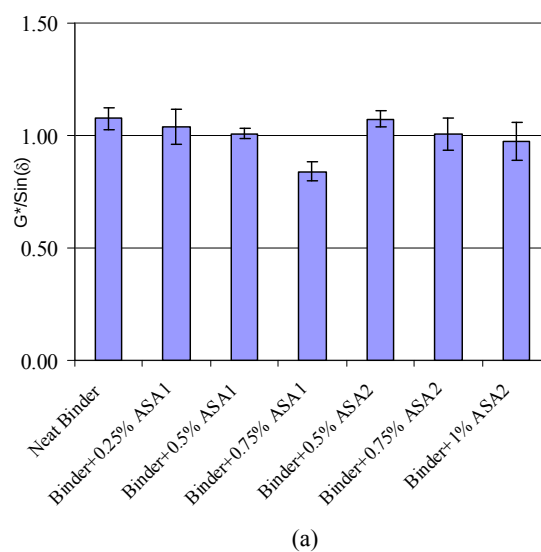


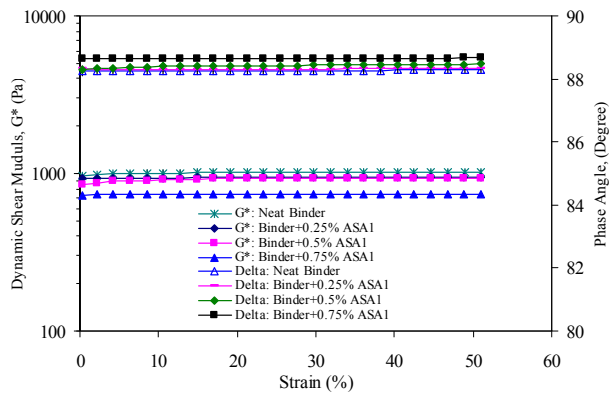
Fig. 7. Effect of Anti-Stripping Agents on $G^*/\sin(\delta)$ of PG 64-22 Binder (a) ASA1 and (b) ASA2.

increased with increasing temperature. This is because at a low temperature, the asphaltenes (n-heptane insoluble material) in asphalt binder are able to form a compact structure, whereas at high end of the testing temperature they disperse as free particles [26, 27]. It is also observed that the higher the dosage of ASA1, the lower the $G^*/\sin(\delta)$ value and the higher the δ value. Similar behavior was observed for ASA2-mixed binder (Fig. 9(b)). This could be due to the decrease in the number of polar molecules in the asphalt binders resulting in a decrease in the intermolecular forces.

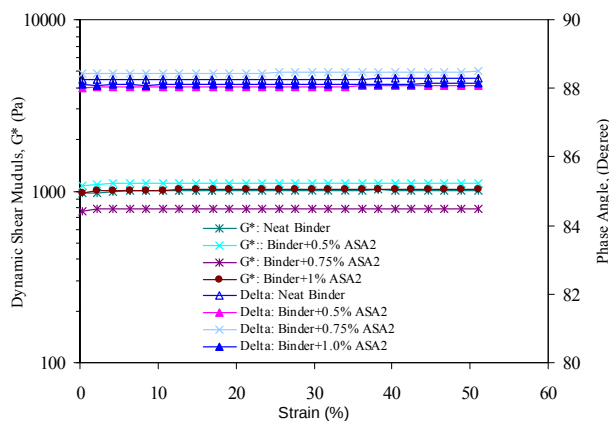
The horizontal dotted lines in Figs. 9(a) and 9(b) represent the Superpave specified limiting value (1.0 kPa). Temperatures for each binder type that meets the Superpave criterion for unaged condition are presented in Table 3. Similar observations were made by Selvaratnam et al. [2], who reported $G^*/\sin(\delta)$ values RTFO-aged samples; the limiting high critical temperatures were found to be higher than unaged condition. Taking the minimum of unaged and RTFO-aged limiting temperatures, the high critical temperatures of the PG 64-22 binder with AS additives were calculated and are reported

Table 3. True High PG Grade for Each Binder Type.

Binder Type	Unaged Condition Limiting Temperature (°C)	RTFO-aged Condition Limiting Temperature (°C)	True High PG Temperature (°C)	Pass/Fail?
Neat PG 64-22	65.0	66.0	65.0	Pass
PG 64-22 + 0.25% ASA1	64.3	65.5	64.3	Pass
PG 64-22 + 0.50% ASA1	64.1	64.7	64.1	Pass
PG 64-22 + 0.75% ASA1	62.7	64.5	62.7	Fail
PG 64-22 + 0.50% ASA2	64.8	65.1	64.8	Pass
PG 64-22 + 0.75% ASA2	63.4	64.7	63.4	Fail
PG 64-22 + 1.0% ASA2	63.2	64.2	63.2	Fail



(a)

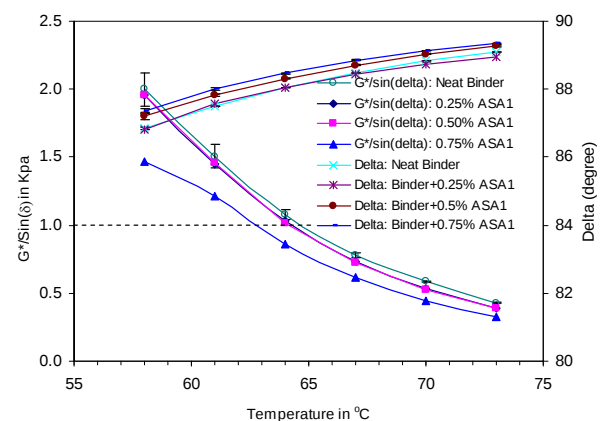


(b)

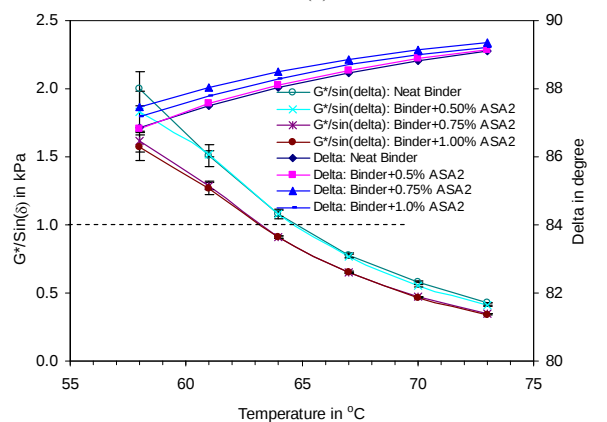
Fig. 8. Strain Sweep Test Data of PG 64-22 Binder at 64°C (a) ASA1 and (b) ASA2 (Note: Each Line Represents a Data Combination of Three Replications of Test).

in Table 3. The true high critical temperature for the neat PG 64-22 binder was found to be 65°C. Correlating with limiting values of Superpave specified rutting factors (1.0kPa for unaged and 2.2kPa for RTFO-aged conditions), the optimum dosage of both ASA1 and ASA2 was found to be 0.50%.

Loading frequency dependency: To correlate the G^* value of the binder with the E^* value of a corresponding surface mix (ODOT Insoluble S4), frequency sweep tests were conducted on RTFO-aged PG 64-22 binder samples with and without 0.5% ASA2. Binder samples were tested at 4.4, 21.1, 37.8, and 54.4°C at loading frequencies ranging from 25 to 0.1Hz at each temperature. Once the sample had reached the required test temperature, a strain controlled oscillating torque was applied and the sample was preconditioned



(a)



(b)

Fig. 9. Temperature Effects on Anti-Stripping-Modified PG 64-22 Binder (a) ASA1 and (b) ASA2.

for one-minute at 25Hz. This set of frequency sweep tests were performed in a step fashion. The *first step* was designed to conduct the test in the frequency range of 25 to 5Hz, and test data was recorded at 5-Hz interval. A *second step* was added to continue the test for a loading frequency ranging from 1 to 0.1Hz, and test data was recorded for loading frequencies of 1, 0.5, and 0.1Hz. Samples were tested at temperatures going from coldest to warmest. Testing at a given temperature started with the highest frequency of loading and proceeded to the lowest.

The mix data used in this study was obtained from a related study [22]. The nominal maximum aggregate size of this mix was 19mm with a binder content of 5.3%. The dynamic modulus (E^*) value of

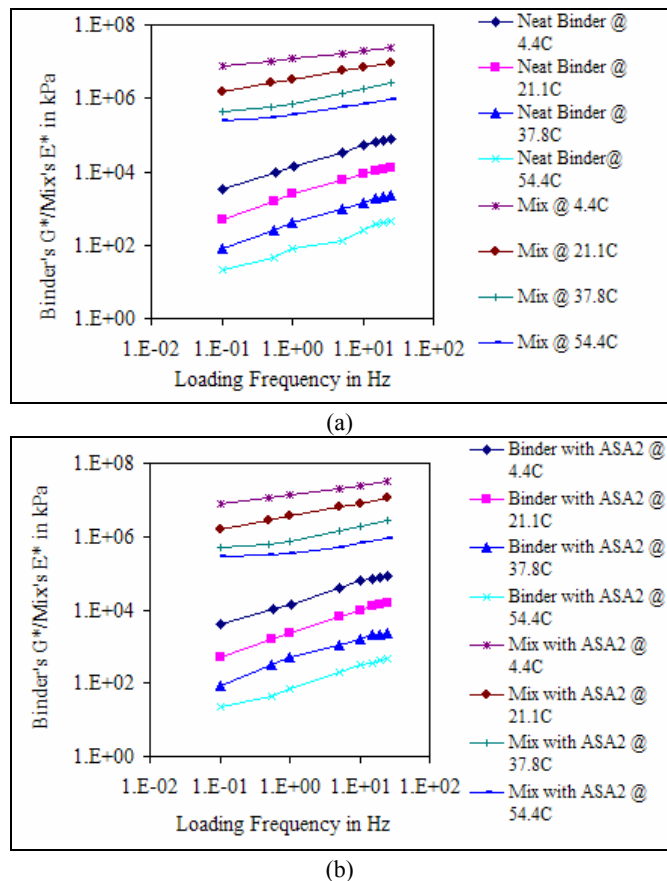


Fig. 10. Binder's Complex Modulus versus Mix's Dynamic Modulus versus Over a Range of Temperatures (a) with no Anti-Stripping Agent and (b) with 0.5% ASA2 (Note: Dynamic Modulus Data is Obtained from [22]).

Table 4. Model Parameters for Correlation between Binder's Complex Modulus (G^*) and Mix's Dynamic Modulus (E^*).

Binder Type	Frequency (Hz)	Power Model, $E^* = A(G^*)^N$		
		A	N	R^2
PG 64-22	25	9813.9	0.7033	0.975
	10	18661	0.6441	0.995
	5	22150	0.6312	0.987
	1	13289	0.7063	0.984
	0.5	18617	0.6774	0.975
	0.1	14927	0.5556	0.711
PG 64-22 +0.5%ASA2	25	13015	0.6927	0.998
	10	12484	0.6924	0.998
	5	11944	0.7029	0.997
	1	14071	0.7076	0.967
	0.5	18221	0.6843	0.964
	0.1	40641	0.6116	0.949

the mix was evaluated in accordance with the AASHTO TP 62 test method. The mixing and compaction temperatures for the mix were 163 and 149°C, respectively. Isotherms of G^* and E^* for the tested binder and mix samples are shown in Figs. 10(a) and 10(b). The test results indicate that ASA2 does not appear to have any significant effect on the E^* value. As expected, testing temperature had significant influence on both G^* and E^* values. Also, the loading

frequency exhibited significant influence on both the G^* value of the binder and the E^* value of the mix. The G^* value of the binder reduced as much as 18-fold when the loading frequency reduced from 10 to 0.1 Hz, and the E^* value of the corresponding mix reduced as much as five-fold. The E^* value of the mix was found to be a power function ($E^* = A(G^*)^N$) of the G^* value of the binder. Model parameters A and N for the established correlations are shown in Table 4. A good correlation ($R^2 = 0.98$ or higher) was observed for loading frequencies ranging from 0.5 to 25 Hz.

Selection of Rheometer

It is recognized that although advanced DSRs might be capable of performing these sweep tests, the DSR used in the present study is not equipped with such features. As mentioned earlier, having the flexibility of adding multiple steps in one test provides some competitive advantages to the DSR in terms of efficiency. Enhanced efficiency was clearly observed for the frequency sweep tests (from 25 to 0.1 Hz) in which the *first step* involved collection of data at 5-Hz interval, while the *second step* involved collection of data at 0.5-Hz interval. Temperature sweep tests demonstrated similar efficiencies. A DMA-based temperature sweep test (58 to 70°C, at 3°C interval) is far more efficient than its DSR counterpart. As noted earlier, a 5-min thermal equilibrium time was sufficient for the DMA, compared to the recommended 10 mins equilibrium time for the DSR. Overall, a DSR is found to be more convenient for binder verification and grading, as templates for the associated AASHTO specifications can be readily used. It worth noting that the purpose of this comparison is to highlight the strengths and weaknesses of both pieces of equipment for a given testing situation, not to promote one over the other.

Optimum Dosage of Anti-Stripping Additive

The optimum dosage of an AS additive depends on both rheological characteristics of an asphalt binder and performance of the asphalt mix. In addition to rutting factor, other rheological characteristics such as fatigue factor and low temperature cracking resistance govern the acceptable dosage level. As noted earlier, to fulfill the Superpave specified rutting criterion, the maximum dosage level of both ASA1 and ASA2 was found to be 0.5% by weight of the binder.

To examine the Superpave specified fatigue and thermal cracking criteria, limited laboratory tests were conducted in this study. To evaluate the fatigue resistance, pressure aging vessel (PAV)-aged PG 64-22 binder samples with and without 0.5% ASA1 were tested at its intermediate temperature (25°C) using a DSR. The fatigue factor ($G^* \sin(\delta)$) of neat PG 64-22 binder was found to be 2,855 kPa and that of the ASA1-modified binder was found to be 2,810 kPa. Both of these values are within the acceptable Superpave specifications (less than or equal to 5,000 kPa), and ASA1 found to reduce the fatigue potential of a pavement. Similarly, bending beam rheometer (BBR) test results at -12°C on PAV-aged samples showed that 0.5% ASA1 decreased the stiffness, $S(t)$, of neat PG 64-22 binder from 195 to 184 MPa, which passed the Superpave criterion ($S(t)$ should be no more than 300 MPa). As expected, the m-value, denoting rate of stress relaxation, of ASA1-modified binder increased from 0.316

to 0.320, which satisfied the Superpave criterion (m-value should be at least 0.300).

The bond strength of the same PG 64-22 and AS additives was studied as part of a related study and reported in Hossain et al. [22]. In that study, an increase in bond strength was reported for the same PG 64-22 binder when either of these AS additives was added. The bond strength was estimated by evaluating the tensile strength ratio (TSR) for asphalt mixes with ASA2 and surface free energy (SFE) for binder with ASA1. The TSR increased from 0.56 to 0.89 when 0.5% ASA2 was added. Because of the nature of that project, locally available high moisture susceptible granite aggregates were used in the control mix. The TSR was determined as per AASHTO T 283, except for the sample curing procedure which was same as the corresponding mix design procedure (AASHTO R 30). The ODOT follows this modified curing procedure and uses a TSR value of 0.8 or higher for acceptable mixes [22, 26]. While evaluating the SFE of the same PG 64-22 binder, it was reported that the corresponding values of the SFE component of the control binder and the same binder with 0.5% ASA1 are 11.2 and 15.4 ergs/cm², respectively [22]. This represents a 37% increase from the control binder. An increase in SFE indicates increased resistance against moisture damage in pavement [25, 27]. Thus, the optimum dosage for both AS additives was selected as 0.5% (by weight of the binder).

Conclusions and Recommendations

This study presents rheological data of three locally available PG binders in Oklahoma using a dynamic mechanical analyzer. The mechanical workability, linear viscoelastic limit, and temperature and frequency dependency on a PG 64-22 binder mixed with two anti-stripping (AS) additives namely, ASA1 and ASA2, were examined. Based on the analyses of laboratory test data, the following conclusions can be drawn:

- The DMA was found to be an effective and efficient tool for examining the viscoelastic properties of unmodified PG 64-22 and low polymer modified binder such as PG 70-28.
- A thermal equilibrium time of five minutes was sufficient for the DMA, when testing PG binders at high temperatures. In comparison, the recommended thermal equilibrium time for the DSR was much longer (ten minutes).
- Based on the Superpave reflecting rutting factor of unaged and RTFO-aged PG 64-22 binder, the maximum allowable dosage of ASA1 and ASA2 was found to be 0.5% for the tested PG 64-22 binder.
- Anti-stripping additives did not have any influence on the mechanical workability of the PG 64-22 binder
- Neither ASA1 nor ASA2 altered the linear viscoelastic limit of the PG 64-22 binder. No noticeable drop of G* was observed up to a strain level of 51%.
- Anti-stripping additives stored (up to two years at 22°C) in an air-conditioned facility did not degrade the functionality of anti-stripping additives.
- The high critical temperature for the PG 64-22 binder found to be 65°C, but it degraded when a liquid anti-stripping additive was mixed with the binder. The corresponding reduction of the high PG temperature was 2.3 and 1.8°C in case of 0.75% ASA1 and 1.0% ASA2-mixed binder, respectively.

- Frequency sweep tests data at various testing temperatures showed loading frequency had significant influence on the G* values of a binder. The G* value reduced as much as 18 folds when the loading frequency was reduced from 10 to 0.1Hz. Similarly, the E* value of the corresponding mix reduced as much as five folds.
- Good correlations between the G* values of the binder and the E* values of the mix were established. The dynamic modulus of the mix was found to be a power function of the complex modulus of the binder ($E^* = A(G^*)^N$). The anti-stripping additive did not seem to show any significant influence on the E* value of the mix.

Based on the findings and limited scope of the current study, additional laboratory testing is needed to validate the testing protocol for a high polymer modified asphalt binder such as PG 76-28, subjected to short-term and long-term aging. Also, additional frequency sweep tests on binders mixed with other AS additives (i.e., hydrated lime) could be conducted at various temperatures and time-temperature superposition could be used to obtain their master curves. Furthermore, dynamic mechanical analyses of asphalt mastic and mixture samples with and without anti-stripping additives could be conducted to predict the fatigue life of a pavement.

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