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Performance of Asphalts Modified with Polyphosphoric Acid

Zahid Hossain, Andrew F. Braham, Gaylon Baumgardner

Final Report

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ABSTRACT

Among the three polymer additives approved by Arkansas Department of Transportation (ArDOT), styrene butadiene styrene (SBS) is the widely used co-polymer. Like many other states, Polyphosphoric Acid (PPA) is not an approved modifier in Arkansas. Even though ArDOT does not allow the use of PPA in asphalt, some suppliers may use it due to its economical advantages. The objective of this study was to find out short-term and long-term performance of asphalts modified with PPA. To evaluate the performance of PPA-modified binders, mechanistic, chemical and moisture susceptibility tests were conducted in laboratories on both asphalt binders and asphalt mixtures. To this end, base Performance Grade (PG) binders from two different crude sources were modified with different dosages of PPA along with its polymer counterpart, SBS. The mechanistic performance was evaluated by conducting Superpave tests, chemical properties were determined through acid detection and pH measurements, Fourier Transform Infrared Spectroscopy (FTIR) analysis, and saturates, aromatics, resins, and asphaltenes (SARA) analysis. Asphalt mixtures prepared from PPA- and SBS-modified binders and a selected aggregate were tested for moisture resistance, rutting, and creep behavior. Further, binders recovered from core samples obtained from old roadway sections (good and poor performing) were tested to ascertain if PPA had any adverse effects on them. The moisture susceptibility was predicted by employing the Surface Free Energy (SFE) technique. Superpave test results of asphalt binders suggest that PPA-modified binders are more rutting, fatigue cracking, and low temperature cracking resistant than PG 64-22 binders, but the use of Liquid Anti-Stripping Agents (LAA) may deteriorate the rutting performance. The SFE analysis did not show any significant negative effects on stripping potential of PPA-modified binder and aggregate systems. Asphalt mixture performance test data was found to be in agreement with the binder test data. The acid detection test method (AASHTO TP 78) is recommended to be a quick and easy test method for detecting the presence of PPA. Overall, there were no significant downsides to using PPA, but the PPA did not behave identically across asphalt binders from different sources. Findings of this study are expected to be helpful in revising the ArDOT specifications regarding PPA modification of asphalts.

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1. Introduction and Problem Statement

According to the 2014 Standard Specifications for Highway Construction of the Arkansas State Highway and Transportation Department (ArDOT), three types of Performance Grade (PG) binders (PG 64-22, PG 70-22, and PG 76-22) are approved to be used in highway construction projects in Arkansas. It further states that *PG 70-22 and PG 76-22 binders shall be production straight run binders that are modified by using either a SB, SBS or SBR to achieve the specified grade*. Although the ArDOT does not approve PPA as a modifier of asphalt binder, some suppliers may use it to get the desired Performance Grade (PG). This is mainly due to the potential economic advantages of polyphosphoric acid (PPA) over the approved polymers, refineries following market trends, or a combination of both. However, the performance of PPA-modified asphalt binders is still uncertain. For instance, suppliers can use approved modifiers to prepare a PG 76-22 from a PG 64-22, but they use PPA in a combination of styrene-butadiene-styrene (SBS) or styrene-butadiene (SB) to reduce the stiffness of the final product. However, PPA is a hydrophilic material; therefore PPA-modified asphalts may be susceptible to stripping. Another concern of PPA-modified asphalt is how the modified binder interacts with different liquid anti-stripping agents (LAAs) and various aggregates. Thus, it is very important to know how PPA may affect rheological and performance properties of the base binder, but it is also important to know whether PPA can be approved as an asphalt binder modifier for environmental conditions and aggregates in Arkansas.

2. Background and Literature Review

To achieve the objectives of this study, first a comprehensive literature review was conducted. The primary goal of doing a literature review was to gain knowledge about the methodology of PPA modification and mechanistic performance of PPA-modified asphalts. To this end, pertinent literature from well reputed journals and transportation agencies such as Transportation Research Record, Journal of Materials in Civil Engineering, Federal Highway Administration (FHWA), National Co-operative Highway Research Program (NCHRP), and Texas Transportation Institute (TTI) were reviewed.

The term Useful Temperature Interval (UTI) is used to identify the difference between the high and low temperature grading of an asphalt binder in the Superpave grading system. It depends upon the chemical compositions of the binder. As a crude source can be used to produce an asphalt binder of constant UTI, an asphalt producer desires to produce the asphalt binder with the widest UTI range. Baumgardner (2009) stated that to achieve an UTI higher than 92°C (e.g., 70+22=92 for a PG 70-22) neat binders must be modified by means of polymer(s) and/or chemical modifier(s). It is also stated that binders with a narrow UTI (e.g., 86°C or 89°C) might also require such modifications to meet the Superpave specifications. With PPA modification the same crude source is capable of producing PG 64-22, PG 70-22, and PG 76-22 binders. The later was affirmed by the researcher as a viable substitute of 3% SBS modified PG 64-22 asphalt binder.

Masson. J. F. (2008) described PPA as an oligomer of Phosphoric Acid (H_3PO_4). The basic compounds for the production of PPA are Phosphorus Pentoxide (P_2O_5) and Phosphoric Acid (H_3PO_4). It is sold on the basis of its calculated content of H_3PO_4 as for example 115%. Thus, PPA is available in various grades with percentages sometimes higher than 100% such as 105% or 115%. The 100 grade PPA (phosphoric acid) contains 72.4% P_2O_5, which is calculated from the formula weight ratio P_2O_5/H_3PO_4. Similarly, Pyrophosphoric Acid ($H_4P_2O_7$) contains 79.8% P_2O_5 as calculated from the ratio $P_2O_5/H_4P_2O_7$. The ratio of P_2O_5 contents provides the relative phosphoric acid content, which in this case is 79.8%/72.4% = 110%.

Pamplona et al. (2015) studied the effect of different proportions (0.0, 0.5, 1, 1.5, and 2%) of PPA on two 50/70 penetration grade asphalt binders of different chemical compositions. The chemical changes induced by the addition of PPA were determined by thin-layer

chromatography and the researchers found that the effects of PPA were influenced by the chemical composition of asphalt binder. It was reported that the effects of lower amounts of PPA on chemical composition were more significant than those of higher amounts. In regard to the percent recovery of the Multiple Stress Creep Recovery (MSCR) test, these researchers found that PPA seemed to be a very good modifier and higher proportions of PPA (1.5 and 2.0%) showed equivalent results. These researchers also reported that the effect of PPA decreased with an increase in temperature. Finally, these researchers analyzed Linear Amplitude Sweep test (LAS) test results to evaluate the fatigue characteristics of asphalt binders, and they suggested that asphalt binders became more resistant to fatigue cracking with the addition of PPA under both short- and long-term aging conditions.

Li et al. (2011) studied the effects of different modification types on the rheological and damage properties of asphalt binders modified with PPA and different polymers. The base binder of their study was PG 52-34, and was modified by 0.75% PPA, 0.3% PPA plus 1.0% styrene-butadiene-styrene (SBS) polymer, 2.0% SBS polymer only, and 0.3% PPA plus 1.1% Elvaloy polymer. Liquid phosphate ester was used as an anti-striping agent (ASA) at 0.5% (by the weight) to all modified binders except for the SBS only modifier. These researchers used Superpave DSR rheological tests for investigating high temperature PG grades of the modified binders, and found that when the properties of recovered binders from field mixes were considered, the PPA only and PPA plus SBS binder passed PG 70-XX, and SBS only and PPA plus Elvaloy binders passed PG 64-XX. They also found that at lower temperatures long-term aged recovered PPA plus Elvaloy and SBS only binders retained their -34^{o}C grades, but the PPA only and PPA plus SBS stiffened to have a low PG temperature of -28^{o}C. From the MSCR test results, the researchers found that the SBS plus PPA binder had the highest percent recovery among the four modified binders. The authors also mentioned that the polymer plus PPA modification was more resistant to fatigue cracking than the PPA only modification.

Kodrat et al. (2007) compared the effect of PPA-modified asphalt binders with straight and polymer-modified binders. The researchers studied binders from 19 different crude sources, and the PPA used to modify them contained 115% H_3PO_4. The tests performed by them to analyze the effects of PPA in asphalt binders were Superpave performance grades, extended bending beam rheometer, brittle state fracture and ductile state fracture. These investigators found that depending on the crude source, the high temperature grade property of asphalt is

significantly increased by the addition of 0.75% PPA while the low temperature grading properties remained largely unchanged. Moreover, the effect of PPA on the fracture properties in the brittle state and on the reversible aging process was found to be insignificant. Finally, these researchers recommended being cautious in using PPA-modified asphalt binders in areas where pavements would be susceptible to fatigue cracking because they have found that PPA may reduce the strain tolerance of asphalt in the ductile state.

Huang et al. (2008) studied the long-term aging characteristics of PPA-modified asphalt binders from three different asphalt sources under un-aged and PAV-aged conditions. The researchers used 1.5 % PPA of 105 grade (by the weight) to modify asphalt binders to carry out DSR, Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), and nuclear magnetic resonance (NMR) spectroscopy tests. The authors suggested that fatigue cracking and low temperature cracking of the pavement should be reduced because of the increment of the initial stiffness and low temperature flow properties of asphalts after long-term aging by the addition of PPA. Moreover, based on the results of NMR spectroscopy, the researchers were certain that the addition of PPA did not significantly change the internal structure of the asphalt binders by chemical reaction even after long term aging. Furthermore, from the NMR microscopy test results, the researchers affirmed that PPA reacts with residual water present in asphalt and as little as 0.073% of residual water is sufficient to hydrolyze 1.5% mass of PPA into orthophosphoric acid. Further, the researchers used a DSC device to evaluate thermal properties of unmodified and PPA-modified asphalt binders under oxidative aging conditions and reported that the locations, heights, and widths of the glass transition for PPA-modified asphalts were parallel to those of the unmodified asphalts.

Jafari et al. (2015) studied the effects of stress levels on creep and recovery behavior of modified asphalt binders. The researchers used one set of Rotational Thin Film Oven (RTFO)-aged PG 58-XX binders modified with 2%, 4% and 6% SBS, and another set of RTFO-aged PG 58-XX binders modified with 0.5%, 1% and 1.5% PPA to carry out MSCR tests. The authors stated that PPA-modified binders were less rutting resistant than the SBS-modified binders based on higher non-recoverable compliance (J_{nr}) values of PPA-modified binders at 12.8 kPa than SBS-modified binders. Moreover, they recommended adding a stress level of 12.8 kPa to the MSCR standard procedure to compare nonlinearity and rutting resistance of PPA-modified asphalt binders. Also, at high stress levels, PPA-modified binders did not exhibit their

viscoelastic properties, but the corresponding SBS-modified binders did, which convinced the researchers to state that even at 1.5% of PPA concentration could result in overly sensitive materials that would not be recommended for paving application. Finally, the authors recommended that at a temperature higher than the performance grade of the modified binders, the stress levels of lower than 3.2 kPa should be applied to avoid the negative recovery values of the PPA-modified binders.

Huang et al. (2011) studied the rheological and chemical properties of hydrated lime and PPA-modified asphalts. The researchers used 1.5% PPA and 10% hydrated lime (by weight) to modify three SHRP core asphalt binders as the base binders. The rheological properties of un-aged and PAV-aged binders were measured with a DSR at 30, 40, 58 and 64°C, and the chemical properties were determined by using an NMR spectroscopy test. These researchers found that the addition of PPA increased the rheological index substantially than the original neat asphalts. Moreover, the addition of PPA increased the asphalt binder's PG. However, further addition of hydrated lime to the PPA-modified asphalt binder changed the PG back to a lower grade. Furthermore, the researchers also found that addition of PPA increased the stiffness of the asphalt binder, but further adding hydrated lime with it reduced this stiffness. Based on NMR test results, the researchers reported that hydrated lime reacted with PPA in asphalt binder and formed solid calcium phosphate, which also supported the rheological results obtained from the DSR tests.

Baumgardner et al. (2005) described the mechanism of chemical modification of asphalt binder with PPA. They analyzed two sets of modified and unmodified asphalts from two crude sources, Saudi and Venezuelan, for chemical composition by asphaltene precipitation through thin layer chromatography (TLC), nuclear magnetic resonance (NMR), gel-permeation chromatography (GPC), and atomic force microscopy (AFM) tests. From the TLC test results, the researchers found that the asphaltene content increased from 9.1 to 14.7 % (by weight) by adding 1.2 % PPA to produce a PG 70-22 binder for the Saudi crude. On the other hand, for the Venezuelan binder, the asphaltene content increased from 10.5 to 14.9% (by weight) with the addition of 0.62% of PPA. The NMR analysis revealed that PPA preferentially reacted with the asphaltenic phase of the asphalt. Finally, these researchers implied that the PPA changed the chemical composition of the binder by changing saturates into asphaltenes.

Daranga et al. (2009) investigated the storage stability and effects of mineral surfaces on PPA-modified asphalt binders. The researchers used three binders of varying grades to determine their chemical compositions, while they used two unmodified binders of known composition with two mineral fillers for determining the effect of mineral surface on asphalt binders. For the study of storage stability, the researchers used PG 58-22, SBS-modified PG 70-22 and Elvaloy-modified PG 64-22 binders further modified with 1% PPA (105 grade; by the weight of the binder). On the other hand, for detecting the influence of asphaltenes on rheological properties of PPA-modified asphalt binders, the researchers used PG 64-22 binder with 16% asphaltene content, and PG 58-22 binder with 9% asphaltene content. The researchers found that for a given binder, the higher the surface area to the volume ratio, the higher is the rate of oxidization. Moreover, from observing the pattern of reaction with PPA molecule and hydrogen bond formation, they concurred that the rate of oxidation of the modified asphalt binder did not depend on the addition of PPA, rather for some binders, it slowed it down. Finally, the researchers stated that the addition of mineral fillers increased the stiffness of the asphalt binder, whereas fillers with basic pH showed a tempering effect on the stiffness increment of the modified binder.

Shulga et al. (2012) investigated the effect of foaming on the performance of PPA-modified asphalt binders. The researchers used a Wirtgen WLB-10 laboratory foaming machine to foam two sets of base binders, namely, PG 64-22 and PG 64-16, of different asphaltene contents. PPA was used by the researchers to increase the PG of the base binders by one and two grades. The actual amount of PPA used in their study was 0.8% by wt. for the one-grade increase and 1.5% for the two-grade increase. The researchers performed Rotational viscosity, DSR, MSCR, LAS and Binder Bind Strength tests to evaluate the performance of PPA-modified foamed asphalt binders. They found that PPA did not have significant effects on the viscosity of the foamed asphalt binders. The DSR test results revealed that PPA did not change the true grade of the foamed binders. The researchers also found that PPA-modified foamed asphalt binders showed similar or better bond strength than the neat binders, which means that the PPA might have increased the bond between bitumen and aggregate. Finally, the LAS test results revealed that the fatigue life of the foamed asphalt binders increased with the amount of PPA.

Maine DOT (2013) published a report on field performance of a PPA-modified asphalt pavement. The field testing was performed on Route 1 in Perry where a pavement was constructed using a 12.5 mm mix. The base binder of the project was a PPA-modified PG 64-28

binder, and the results were compared with a pavement constructed with a neat PG 58-28 binder. The Automatic Road Analyzer (ARAN) data was used for evaluating the field performance of the constructed pavement. It was reported that visual observation did not find any pavement deterioration or distress in the PPA-modified pavement.

FHWA (2012) published a technical brief about the use and performance of PPA modified asphalts. The agency, in cooperation with Transportation Research Board and Minnesota DOT, organized a workshop to discuss using PPA as asphalt modifier. They found that when 3% or higher dosage of PPA is necessary to increase the PG of asphalt to two grades, the intermediate stiffness of the binder might increase. Also, the amount of PPA needed to increase the grade of asphalt depends upon the crude source. The agency stated that the extraction of binders modified with PPA could be hampered by stabilizing chemicals in the extraction solvent due to the presence of acid scavenging chemicals. Moreover, this report indicated that moisture damage potential of PPA-modified asphalt was very limited when the dosage level was between 1 and 1.5%. Finally, the report indicated positive field performance of PPA-modified asphalt binders in several states where the PPA dosage level was between 0.25 and 1.2%.

D'Angelo (2009) investigated the effects of PPA on asphalt binder properties from different crude sources namely Saudi and Venezuelan. The researcher used a combination of SBS polymer from different sources and PPA to modify PG 64-22 asphalt binders. This study also used different blending temperatures and speed to blend the polymer and PPA to investigate the difference in performance of the asphalt binders. It was found that the addition of 0.5% PPA increased the high temperature PG grade of the Venezuelan binder to one grade, whereas for the Saudi binder the same amount of PPA could not change the grade. Moreover, modified binders blended at lower temperatures showed significantly lower MSCR % Recovery values in the MSCR test than the modified binders blended at higher temperatures. Further, the addition of PPA also made the MSCR % Recovery value higher than the SBS-modified binders. Finally, this researcher used hydrated lime with PPA-modified asphalt to check for any negative interactions with PPA. The researcher found no negative effects on stripping resistance, but the stiffening effect of the PPA was found to be reduced to a small extent after the addition of lime.

Al-Qadi et al. (2014) investigated the effects of different additives and modifiers on the moisture susceptibility of asphalt concrete. The researchers used LAA and hydrated lime as ASA additives, and they used SBS and PPA as the modifiers. Four dosages (0.25, 0.5 0.75 and 1%) of the LAA were used to optimize the LAA content in asphalt mixes. Moreover, four LAA application methods (hydrated lime slurry, hydrated lime slurry with marination, dry hydrated lime to dry aggregate and dry hydrated lime with moist aggregate) were used for selecting the optimum hydrated dosage rate of hydrated lime. The researchers used 1.25% of PPA by weight of asphalt binder to bump the grade of PG 64-22 to a PG 70-22 binder. Moreover, they used 1.5% SBS with PG 64-22 binder to bump the grade to a PG 70-22 binder. For determining the moisture susceptibility they researchers performed Lottman test with five freezing and thawing cycles, Hamburg wheel tracking test and fracture test using semi-circular bend (SCB). The researchers also used SFE to characterize the adhesion and cohesion energy of asphalt binders with various additives and modifiers. The SFE values showed that LAA had the highest work of adhesion, and work of cohesion and compatibility ratio. However, the researchers found that PPA reduced the rutting resistance compared to the control mixture, and the mixture with PPA had the lowest fracture energy compared to the other modifiers. Finally, the researchers concluded that the addition of PPA resulted in greater vulnerability to moisture damage compared to the other additives and modifiers.

Yan et al. (2013) investigated the effects of PPA on chemical composition, physical properties, and morphology of asphalt binder. The researchers used three different penetration grade asphalts of 92, 85 and 63 to modify them with 105 grade PPA. The crude source of the first two binders was Saudi Arabia, whereas the third binder was from Chinese crude. The amount of PPA for modification was undisclosed in this study. The researchers performed softening point, penetration and ductility test to characterize the physical properties of the binders, whereas SARA analysis was done to characterize the chemical properties of the binders. For morphological analysis, the researchers followed the atomic force microscopy (AFM) technique. The researchers found that the physical performance and chemical composition of the binders depend largely on the crude source. The binder with a lower colloidal index is greatly influenced by PPA modification compared to the binder with a higher colloidal index. Finally, the researchers concluded that with the addition of PPA, the asphaltene fraction of the base binder increased and so did the viscosity of the modified asphalt binders.

Baldino et al. (2012) investigated the effects of PPA on low temperature rheological properties on neat and PPA-modified asphalt binders. The researchers used four penetration grade asphalt binders from three different crude sources: Venezuelan, Saudi Arabian, and Russian. Moreover, they used three different dosages (0.5, 1 and 1.5% by the weight) of PPA of 115 grade for modification of the asphalt binders. For rheological analysis, the scientists used a Dynamic Mechanical Analyzer (DMA) manufactured by Triton Technology, UK (TTDMA) for dynamic mechanical analysis, and the ring ball softening test to determine the softening temperature of the asphalt binder. The researchers found that the glass transition temperature of asphalt binders decreases with the addition of PPA. Moreover, the complex modulus (E^*) increased with the addition of PPA, whereas the stiffness also increased with the addition of PPA. Finally, the researchers stated that the effect of PPA on low temperature properties of asphalt binder depended on the chemical composition and crude source.

Xiao et al. (2014) investigated the high temperature rheological properties of asphalt binder modified four different polymer modifiers with or without PPA. Four polymers used in this study were SBS, oxidized polyethylene, propylene-maleic anhydride and -40 mesh ambient produced recycled crumb rubber. In this study, PPA was added with the polymer modified PG 70-22 binders. The PPA dosage rate was 0.5% by the weight of the asphalt binder. Two different DOT approved sources of asphalt binders were used in this study. The researchers found that using 0.5% PPA reduced the required polymer content to 1%. Moreover, the researchers found that the failing temperatures were higher with PPA-modified binders and the rutting factors in DSR test result were asphalt source dependent. Finally, the researchers concluded that the general viscoelastic behavior of the modified asphalt binders was dependent on the type of polymer used for modification.

Zhang et al. (2009) studied the influence of PPA, SBR, and sulfur on the physical properties, rheological properties, morphologies and storage properties of asphalt binders. The researchers used an AH-90 paving asphalt binder from China with a penetration grade of 90. The PPA was blended with the base binder by using a high shear mixer at a speed of 5000 r/min. For physical characterization, the researchers followed softening point test, penetration test, and for chemical analysis they used FTIR test results. The researchers found that PPA improved the high temperature physical and rheological properties. However, PPA had negative effects on the low temperature ductility, but the addition of SBR improved the ductile properties. Finally, the

researchers stated that the addition of sulfur improved the high temperature rheological properties of asphalt binder.

In short, as a summary to the literature review, existing literature suggests that PPA-modified asphalt binders are less rutting resistant than corresponding polymer-modified binders. But, fatigue resistance increases with the addition of PPA. Several researchers reported that the change in the binder grade by PPA modification is crude source dependent. Further, a low amount of PPA might yield favorable results and PPA modification gives better mechanistic results if PPA is used in combination with another polymer modifier. Finally, from the findings from the literature review and two surveys, the amounts of PPA used in this study were made.

3. Research Objectives

The principle objective of this study was to evaluate the short- and long-term laboratory performance of PPA-modified asphalt binders, with a secondary investigation of asphalt mixtures. Superpave binder tests were run on multiple asphalt binders and PPA dosage rates. The laboratory performance of the asphalt binders also included an evaluation of the chemical composition of the asphalt binders. Finally, selective asphalt mixture samples were prepared and tested in the laboratory binders for their mechanistic performance and moisture resistance. Based on the findings of this study, no negative effect of the selected levels of PPA was found in the performances of asphalt binders. However, the dosage rates and performance characteristics of the binder were found to be dependent on its crude source. Moreover, some admixtures such as LAA were found to be incompatible with PPA-modified asphalt binders. Thus, ArDOT may consider PPA as a potential modifier in additional to the existing co-polymers. However, it is recommended that tests to confirm compatibility with the asphalt binder source and any additives be performed before acceptance. This will require a revision of **Subsection 404.01 Design of Asphalt Mixtures (b) Design Requirements** of **Section 404 DESIGN AND QUALITY CONTROL OF ASPHALT MIXTURES**.

4. Research Methodologies

As discussed in Section 2, a comprehensive literature review was performed to gather information from published scientific articles regarding PPA-modification. After this literature review, two surveys were conducted to gain knowledge from two different perspectives, namely, the users (transportation agencies) and the producers (refineries). The first survey was conducted at the departments of transportation (DOTs), federal and other transportation agencies. The second survey was conducted to the certified asphalt binder suppliers in Arkansas.

This chapter provides a summary of two surveys conducted to gather the most updated knowledge regarding the state of the practice of the PPA modification. The first survey was conducted at the departments of transportation, federal agencies etc. to gather information on any guidelines, specifications, and concerns about using PPA to modify asphalt binder. The second survey was conducted to the certified asphalt binder suppliers in Arkansas.

4.1 Survey Neighboring States

Methodology of State Survey: The survey was conducted using a web based survey platform called "Survey Monkey," in which ten questions were uploaded for conducting the survey before sending out an e-mail invitation to the prospective respondents. Five polar (yes/no answer) questions as well as five descriptive questions were selected for the survey. The survey was then sent out to Transportation/Material specialists from departments of transportation, and federal agencies etc. Afterwards, responses of all questions were collected automatically using "survey monkey." There are twenty seven respondents for this survey as of May 25, 2015. Figure 4.1 shows the state highway agencies that responded to this survey. The section below contains a summary of the responses of 27 survey respondents. The total numbers of answers for a specific question might be lower than 27, as some might have chosen to not answer any specific question.

Allowing PPA-modified Asphalt Binder in Construction Projects: Among the 27 respondents, 17 agencies allow PPA to modify asphalt binder, whereas eight of them do not allow PPA. Figure 4.2 shows the respondents who answered this question. The green colored states answered they allowed PPA as an asphalt binder modifier, whereas the red colored states did not allow PPA.

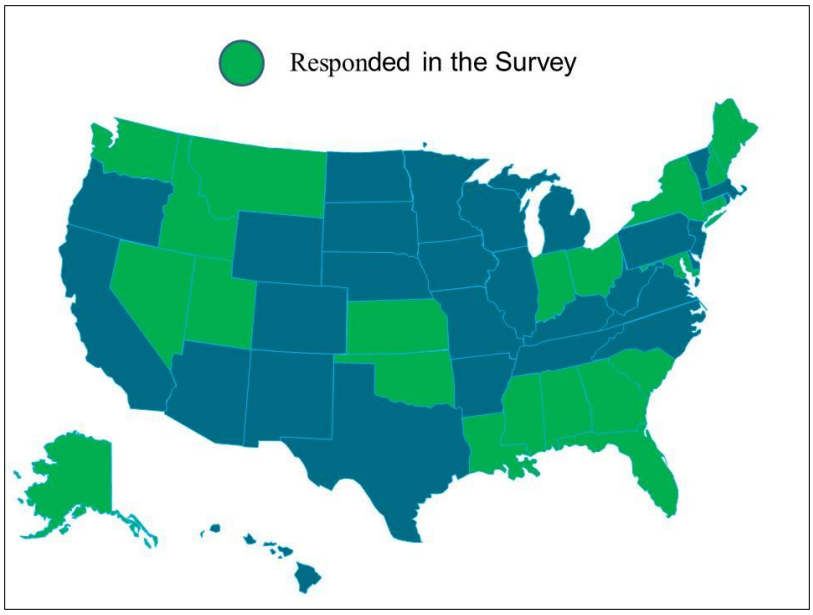

Figure 4.1: Respondents of State Survey.

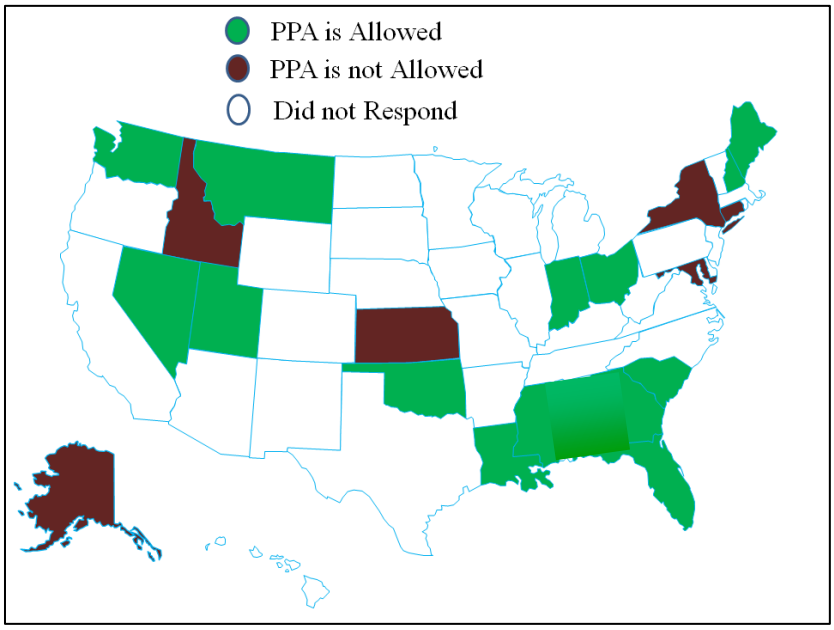

Figure 4.2: States Allowing PPA as a Modifier in Asphalt Binder.

Specifications of Using PPA for Binder Modification: Six DOTs of Ohio, Florida, Alabama, South Carolina, Georgia and Mississippi have specifications of using PPA to modify asphalt binders. The specification of Mississippi DOT states that PPA can be used at 0.75% to enhance the physical properties of the base binder to meet the requirements for PG 67-22 binders. Moreover, PPA may be used at a low dosage rate of 0.5% and as a catalyst or a mixing agent in

the production of performance grade PG 76-22 binders. The specification also strictly states that, PPA can never be used to adjust the physical properties of the binder to a full binder grade. The DOTs of Georgia, South Carolina, and Florida allow a maximum of 0.5% PPA per weight of the binder to modify the neat asphalt binders, whereas the DOTs of Alabama and Ohio allow PPA in the amounts of 0.2% and 1%, respectively. Figure 4.3 shows the states that have specification about PPA modification among the respondents of this survey.

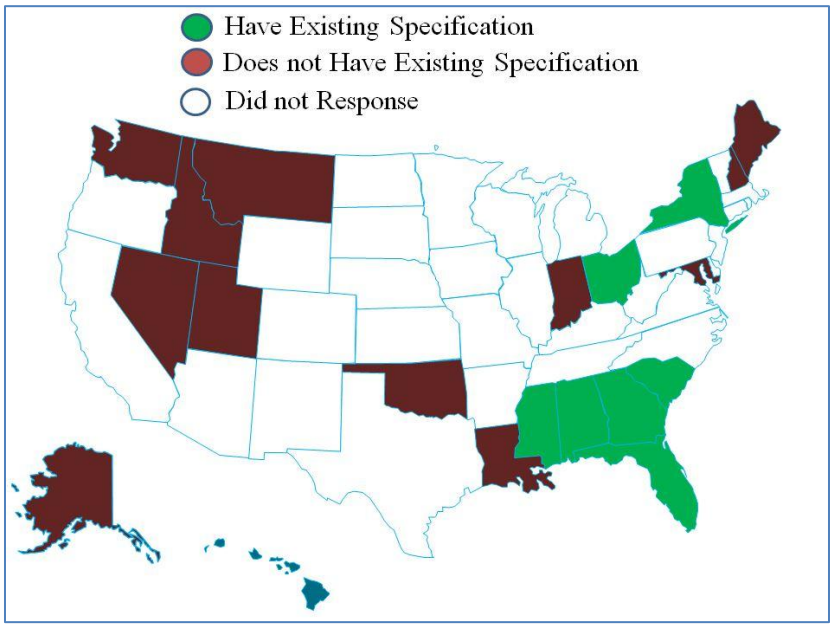

Figure 4.3: Existing Specifications Regarding PPA Modification.

Concerns of Using PPA-modified Asphalt Binders: A total of 16 DOTs expressed their concerns of using PPA-modified asphalt binders, whereas ten DOTs said they were not concerned about it. Figure 4.4 shows the graphical representation of the highway agencies' concerns in this regard.

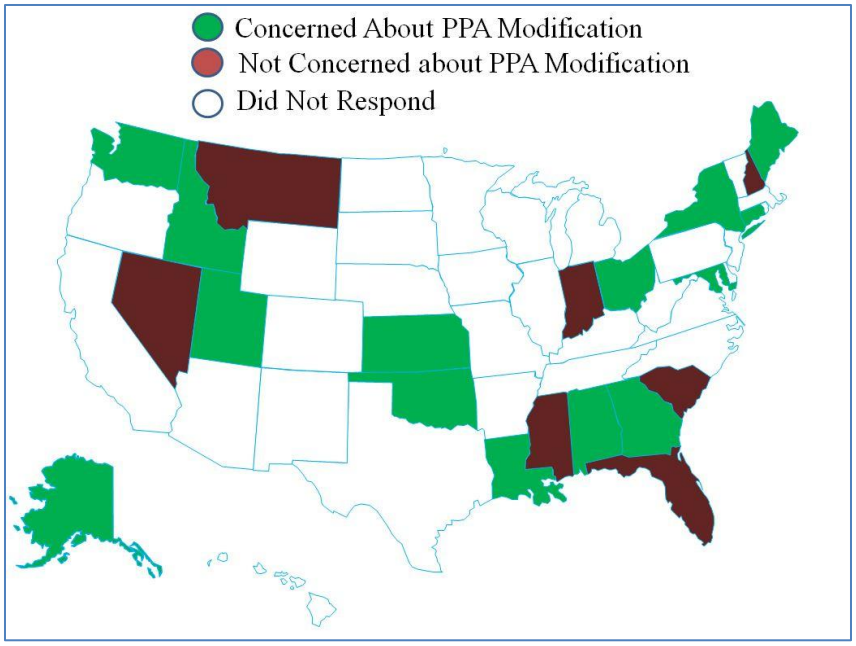

Figure 4.4: Concerns on Using PPA in Asphalt Binders.

Using PPA-modified Asphalt Binders in Last Five Years: Among the 27 respondents, 14 agencies used PPA-modified asphalt binders in their pavements, whereas eleven agencies said they did not use any PPA-modified asphalt binders. Figure 4.5 shows the map of the respondents.

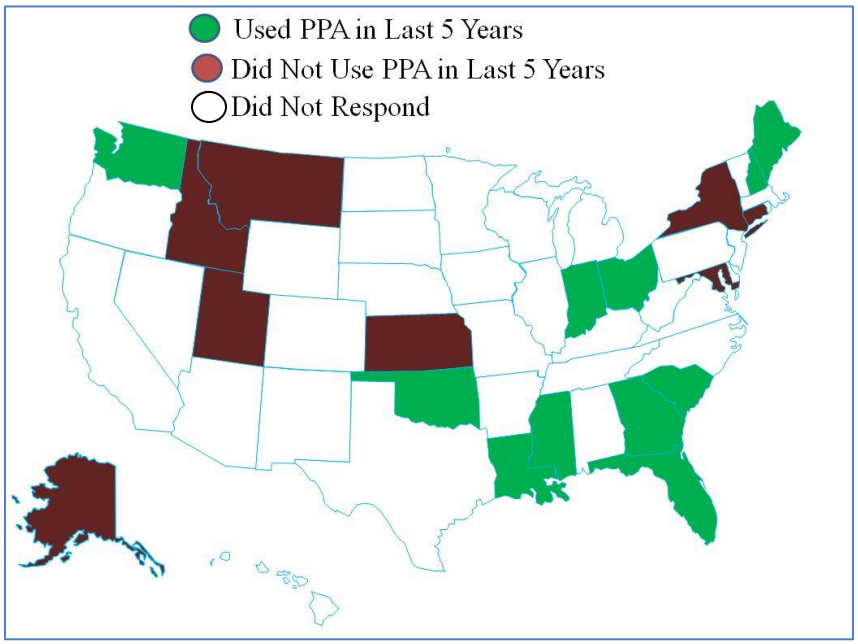

Figure 4.5: Using PPA-modified binders in Last Five Years.

Do Contractors Notify when They Use PPA-modified Asphalt Binders? Almost half of the respondents said that the contractors do not notify them when they use PPA-modified asphalt binders. Figure 4.6 shows the contractors' notifying patterns regarding the use of PPA-modified asphalt binders.

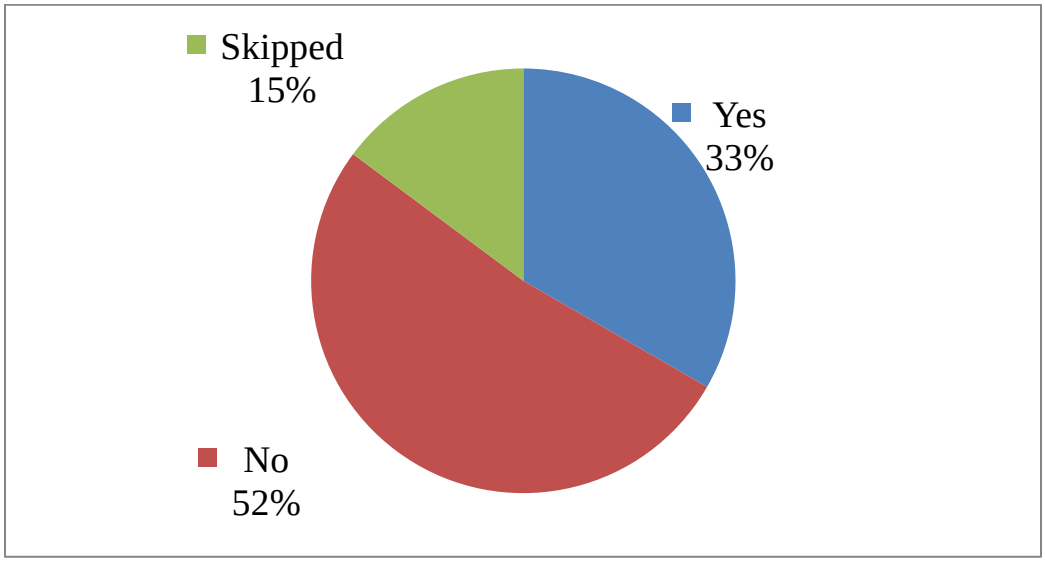

Figure 4.6: Response Whether Contractors Notify when PPA-modified Asphalt Binders is Used.

Ongoing Research Projects on PPA-modified Asphalt Binders: A total of three DOTs, namely, Maine, Oklahoma and New York, currently have ongoing projects to evaluate the performance of PPA-modified asphalt binders. The name of the projects currently ongoing in New York is "Determining Binder Flushing Causes in New York State." The other two projects currently being worked on in Maine and Oklahoma go by the names of "Field Test of a Polyphosphoric Acid (PPA) Modified Asphalt Binder on Rt. 1 in Perry," and "Performance of Asphalt Binders Modified with Polyphosphoric Acid (PPA)."

Polymers Other Than PPA to Modify Asphalt Binders: From the responses collected in the survey it is quite imminent that SBS is the most popular polymer modifier, which is used by seventeen state highway agencies. The closest to SBS in terms of popularity amongst the twenty seven respondents is SBR with ten users. Other polymers used by the DOTs to modify asphalt binders are SB, GTR, Elvaloy, Crumbed Rubber (CRM) and aromatic oil. Figure 4.7 shows the popularity of these polymers among the 27 respondents in this survey.

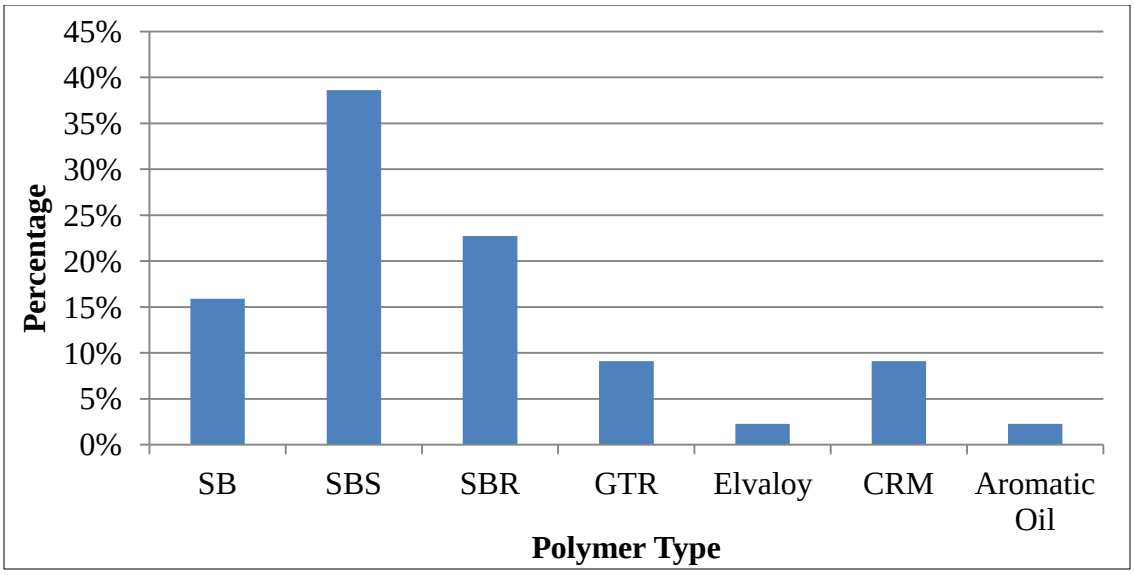

Figure 4.7: Popularity of Different Polymers Other Than PPA for Modifying Asphalt Binders.

Incompatible Aggregate or Liquid Anti-stripping Agents (LAA): The only aggregate that the respondents voiced their concerns while using them with PPA is limestone. Oklahoma DOT stated that amine based LAA have the tendency to drop the true high temperature grade of the asphalt binder, whereas phosphate based LAA drops the true grade less than the others.

Additional Information about PPA Modification: The respondent from the Utah Department of Transportation said that the asphalt binder modification depended largely on the crude source, and the refineries did not always notify them about modification so they do FTIR testing to monitor any use of PPA or other polymers.

4.2 Survey Certified Asphalt Binder Suppliers in Arkansas

For the same purpose of gathering state of the art information regarding PPA modification of asphalt binder, a separate survey was completed to certified asphalt binder suppliers in Arkansas. The survey was sent to the asphalt binder suppliers listed in Table 4.1.

Methodology of Survey Certified Asphalt Binder Supplier in Arkansas: Ten questions were finalized before sending the survey to the respondents. This survey was also conducted using the web based survey platform called “Survey Monkey,” where the survey questions were uploaded. An email invitation consisting of the URL of the survey and a message describing the purpose of the survey was sent to each prospective survey participant. There were only three responses. The

following section in this chapter consists of the responses of the three respondents to the ten questions.

Motivation of Using PPA: The first respondent stated that the combination of PPA with polymer provides a cost effective mean of providing modified asphalt binder that meets the needs of the public. However, the second respondent stated that they use PPA just to follow the market.

Table 4.1: Certified Asphalt Binder Suppliers in Arkansas

Supplier Name	**Location**
APAC-Central, Inc.	Catoosa, OK
APAC-Missouri, Inc.	Springfield, MO
Asphalt Terminals & Transportation, LLC.	Muskogee, OK
Calumet Lubricants Company	Shreveport, LA
Calumet Specialty Products Partners, LP	Muskogee, OK
Coastal Energy Corporation	Miller, MO
Coastal Energy Corporation	Willow Springs, MO
Ergon Asphalt and Emulsion, Inc.	Memphis, TN
Ergon Asphalt and Emulsion, Inc.	Vicksburg, MS
Heartland Asphalt Materials	Memphis, TN
Heartland Asphalt Materials	New Madrid, MO
HollyFrontier Refining & Marketing LLC	Catoosa, OK
Hunt Southland Refining Company	Sandersville, MS
Hunt Southland Refining Company	Vicksburg, MS
Lion Oil Company	El Dorado, AR
Lion Oil Company	Muskogee, OK
Marathon Petroleum Corporation	Memphis, TN
NuStar Marketing LLC (NuStar Energy LP)	Catoosa, OK
Phillips 66	Granite City, IL
Valero Marketing & Supply Company	Ardmore, OK

Moreover, they also stated that they don't believe the final product quality and performance using PPA matches that of elastomeric polymers and they will not use PPA at all if possible. The third respondent answered that their refinery used PPA as a crosslinking agent when modifying asphalt with Elvaloy polymers, and the PPA dosage is typically at a rate between 0.15% and 0.30%. When used with SBS, PPA is used to reduce polymer concentration for a given PG. This not only reduces cost but also improves rotational viscosity and makes some highly modified binders easier to handle in the field. The third responder also stated that they currently do not use PPA alone in modifying binders, but there are some cases where it would be beneficial.

Mixing Protocol for PPA modification: As a response to the mixing protocol, the first respondent said that they mix PPA after crosslinking near production temperature in line using a static mixer. The final cure takes place in storage tank over a few hours. The second respondent answered that they use a small batch tank where the asphalt is pumped (320 – 240^{o}F) and the PPA is added. The third respondent stated that PPA is added to modify binders at typical storage temperatures (290 - 320^{o}F). The mixing time is dictated by the size of the tank and the viscosity of the base binder. In some instances, PPA is blended at the rack as the truck is loaded.

Preferable PPA Grade for Modification Purpose: The first respondent said they use 105 grade PPA for asphalt modification purposes. The second respondent stated that to meet a PG 64-22V (MSCR grading) specification they typically require 1.25% PPA. The third respondent answered that they use both 105 and 115 grades of PPA, at dosage rates ranging from 0.15% to 1.0%.

Concerns from the Users Regarding PPA Modification: The first respondent said that the users need to be knowledgeable and informed such as the concentration limit and verify mix compliances. The second respondent answered that where anti-strips are present, the PPA is removed from the system, and they are aware of a number of projects in different states that failed due to the resulting asphalt being too soft after the acid or amine reactions take place. Moreover, this respondent also stated that there are a number of states that do not allow the use of PPA and many states limit the use of PPA. The third respondent stated they had not heard of any concerns with the performance of PPA used in any projects, and the vast majority of binders they supplied in some states included a combination of PPA and SBS in modified binders. The respondent also mentioned that some of the states that they routinely supply binders completely

forbid the use of PPA. Furthermore, the respondent shared one of his/her experiences regarding PPA modification where a customer added a non-PPA compatible warm mix additive to the asphalt without the refinery's knowledge. He/she also stated that certain warm mix additives will negate the effects of the PPA and the reaction will also negate the effects of the warm mix additive.

Other Additives Used with PPA: As an answer to this query, the first respondent mentioned that they used SBS and crosslinker to obtain the desired elasticity. The second respondent stated that they did not use any other modifier with PPA, whereas the third respondent answered that they used SBS and Elvaloy with PPA.

Significance of Crude Source for PPA Modification: The first respondent stated that the supplier must confirm the suitability when the source changes. The second respondent answered that the asphalt (crude) source is critical to any formulation. For example, if the refinery performs a caustic wash on the crude oil in their process, this would nullify the benefits of PPA and effectively remove it from the system. Finally, the third respondent stated that asphalt binders from certain crude sources cannot be modified well with PPA.

Additional Information Regarding PPA Modification: The first respondent stated that the FHWA has done a considerable amount of work on PPA-modified asphalt binders, and they should be consulted for additional technical information. The second respondent stated that he is dubious about the long-term properties of liquid asphalt when PPA is used as opposed to elastomers. The respondent prefers the MSCR specifications when a polymer curve is included, which requires the use of an elastomer with or without the addition of PPA. Moreover, the respondent's opinion is that PPA meets the AASHTO specification, but its use compromises the quality or performance. Thus, there are risk factors involved with some systems that can compromise the quality of a project.

4.3 Test Plan

From these surveys, important information such as PPA dosage rates, compatible admixtures, market culture, and information on aggregate compatibility were collected. From the findings of the literature review, responses from survey participants, expertise of the industry partner (Paragon Technical Service, Inc.), and in discussions with the ArDOT TRC research panel

members, a detail test plan of the study was developed. A summary of the research methodology is presented in Figure 4.8. At first, the unmodified and modified asphalt binders were collected from Paragon Technical Services, Inc. Selected PPA-modified asphalt binders were further modified with LAA to evaluate their performance properties. The LAA were blended with hand-blending technique previously implemented by the research group (Hossain et al. 2015)

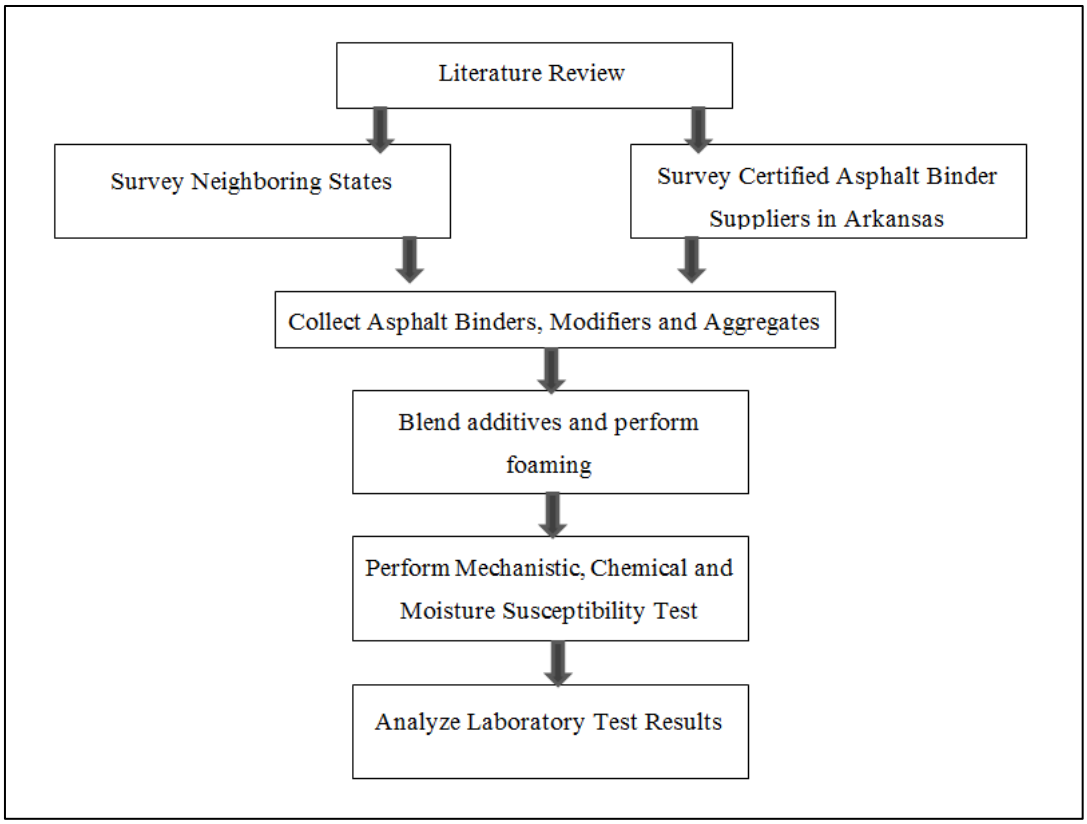

Figure 4.8: Summary of Research Methodology.

Asphalt binders from two different sources were used to evaluate their mechanistic, chemical and moisture susceptibility of the PPA- and LAA-modified binders. These properties were compared with those of SBS-modified binders. For mixture performance tests, selected types of binders from one source were used. The asphalt binder was a Canadian crude source, and it was supplied by Ergon Asphalt and Emulsions, Inc. Memphis, TN. The second binder was an Arabian crude source, which was a combination of "*sweet and sour crudes*," and it was supplied by Marathon Petroleum Corporation, Catlettsburg, KY. The second crude source was selected purposely so that a different amount of PPA was needed to increase its PG grade from PG 64-22 to PG 70-22. For each binder, three different dosages of PPA were used to modify the

neat binder. One of the PPA-modified binders from each binder source was foamed to evaluate its performance as a Warm Mix Asphalt (WMA). Along with PPA, SBS was used as a modifier to compare properties of PPA- and SBS-modified binders. Details of sample modifications and nomenclatures are shown in Table 4.2. As shown in this table, a known compatible LAA named Kao Gripper® X2 (0.5% by weight; samples S1B4 and S2B4) from Kao Specialties Americas, LLC was included in the test plan, as suggested by Paragon's Chemist. All binder samples except the foamed binders presented in Table 4.2 were blended in Paragon's laboratory. The foamed asphalt binders were prepared by using "The Foamer" available at the ArDOT Materials Laboratory.

Table 4.2: Details of Sample Nomenclature

Base Binder	Crude Source	Refinery	Modification	Final Performance Grade	Sample Nomenclature
PG 64-22	Canadian	Ergon Asphalt & Emulsions, Inc., Memphis, TN	-	PG 64-22	S1B1
			0.25% PPA	Softer than PG 70-22	S1B2
			0.5% PPA	PG 70-22	S1B3
			0.5%PPA, 0.5% LAA	PG 70-22	S1B4
			0.5% PPA (Foamed)	PG 70-22	S1B5
			0.75% PPA	Harder than PG 70-22	S1B6
			2% SBS	PG 70-22	S1B7
			2% SBS, 0.5% PPA	PG 76-22	S1B8
	Arabian	Marathon Petroleum Corporation, Catlettsburg, KY	-	PG 64-22	S2B1
			0.5% PPA	Softer than PG 70-22	S2B2
			0.75% PPA	PG 70-22	S2B3
			0.75%PPA, 0.5% LAA	PG 70-22	S2B4
			0.75% PPA (Foamed)	PG 70-22	S2B5
			1% PPA	Harder than PG 70-22	S2B6
			2% SBS	PG 70-22	S2B7
			2% SBS, 0.75% PPA	PG 76-22	S2B8

From the findings of literature review and survey results, it was also determined that some highway agencies were concerned about the performance of several LAAs present in the market. Since PPA is an acid, a possible compatibility issue between PPA and LAA develops. At present, ArDOT allows LAAs from four particular suppliers, namely, Akzo Nobel Surface Chemistry LLC, Arr-Maz Custom Chemical, MeadWestvaco (MWV) Specialty Chemicals (currently called Ingevity), and PreTech Industries, Inc. LAAs produced by these suppliers were used to further modify (hand blend) PPA-modified PG 70-22 binders and tested in the A-State laboratory. As recommended by the manufacturers, the following dosage levels were used in this study: (i) 0.5% AD-here® HP Plus™ from Akzo Nobel, (ii) 0.5% PermaTac Plus® from Arr-Maz, (iii) 0.5% Evotherm® M1 from Ingevity, and (iv) 0.5% PaveGrip® from PreTech. The nomenclatures used for the LAA modified samples are shown in Table 4.3.

Table 4.3: Nomenclatures of LAA Modified Binders

Base Binder	LAA	Nomenclature
S1B3	Pavegrip	S1B4-Pavegrip
	PermaTac Plus	S1B4-PermaTac
	Adhere HP Plus	S1B4-Adhere
	Evotherm M1	S1B4-Evotherm
S2B3	Pavegrip	S2B4-Pavegrip
	PermaTac Plus	S2B4-PermaTac
	Adhere HP Plus	S2B4-Adhere
	Evotherm M1	S2B4-Evotherm
S1B1	Pavegrip	S1B1+Pavegrip
	PermaTac Plus	S1B1+PermaTac
	Adhere HP Plus	S1B1+Adhere
	Evotherm M1	S1B1+Evotherm
S2B1	Pavegrip	S2B1+Pavegrip
	PermaTac Plus	S2B1+PermaTac
	Adhere HP Plus	S2B1+Adhere
	Evotherm M1	S2B1+Evotherm

4.4 Test Methods

4.4.1 Asphalt Binder Rheological Tests

Penetration Test

Penetration test of asphalt binder is the measurement of the depth of penetration of a standard needle into the asphalt binder. The test is performed in accordance with AASHTO T 49. The test procedure includes melting and cooling the asphalt binder to room temperature. A standard penetration needle is allowed to penetrate into the binder for a period of 5 seconds. The depth of penetration is measured in units of 0.1 mm and recorded as penetration number. The total weight allowed to penetrate into the asphalt binder is 100g. Figure 4.9 shows a penetration test device.

Figure 4.9: Penetration Test Device.

Rotational Viscosity (RV) Test

The RV test was performed in accordance with AASHTO T 316. Figure 4.10 shows a DV-II+ Pro rotational viscometer (RV) from Brookfield Engineering Inc. in which the test was

performed. The RV test is performed to measure the viscosity of asphalt binders at higher temperatures. In this study RV test was done from 135 to 180 °C at a 15° C interval.

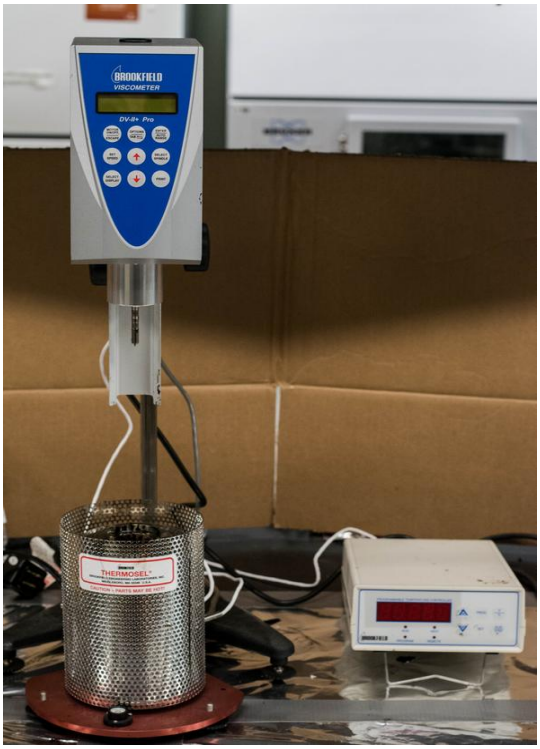

Figure 4.10: RV Test Device.

The viscosity of asphalt binder is the measure of the workability, pumpability, and mixability of the asphalt binder. At first, the asphalt binder sample is heated until fluid and 10 gm of asphalt binder is poured into the sample chamber. The temperature is set to the desired temperature by using a temperature controller and it is kept for 30 minutes to bring it to the set temperature. At that temperature, the motor is turned on to rotate the spindle at a constant speed of 20 RPM. The amount of torque required maintaining the constant speed (20 RPM) of the cylindrical spindle is used to estimate the viscosity of the binder. After 10 minutes of temperature equilibrium, 3 separate readings are taken at 1 min interval. The Superpave specification for unaged asphalt binder is that the viscosity of the binder should be $\leq$ 3 Pa.s at 135°C.

Dynamic Shear Rheometer (DSR) Test

The dynamic shear rheometer (DSR) test is performed to characterize the viscous and elastic behavior of asphalt binder at high and intermediate service temperatures. The DSR measures the

complex shear modulus (G*) and phase angle (δ) of asphalt binders at desired temperatures and frequency of loading. The G* is the measure of the total resistance of the binder to deformation when repeatedly sheared whereas, the δ is the measure of elasticity of the binder. The lower the values of δ, the more elastic the binder is, whereas a higher value indicates viscous binder.

Figure 4.11 shows an Anton Paar MCR 302 DSR machine which was used in this study. In the DSR test, a thin binder sample is sandwiched between two circular plates where the lower plate is fixed and the upper plate oscillates back and forth at a certain frequency, creating a shearing action. According to AASHTO T 315, the test frequency is 10 radians per second (1.59 Hz). The test is performed according to AASHTO T 315 in different aging conditions, namely, unaged, RTFO-aged and PAV-aged, of the binders. For unaged and RTFO-aged binders, the primary measurement according to the Superpave specification is the rutting parameter, which is calculated by taking the ratio of G* and sinδ (i.e., G*/sinδ). On the other hand, the DSR test for PAV-aged binders calculates fatigue factor at intermediate temperatures by multiplying G* and sinδ (i.e., G*•sinδ).

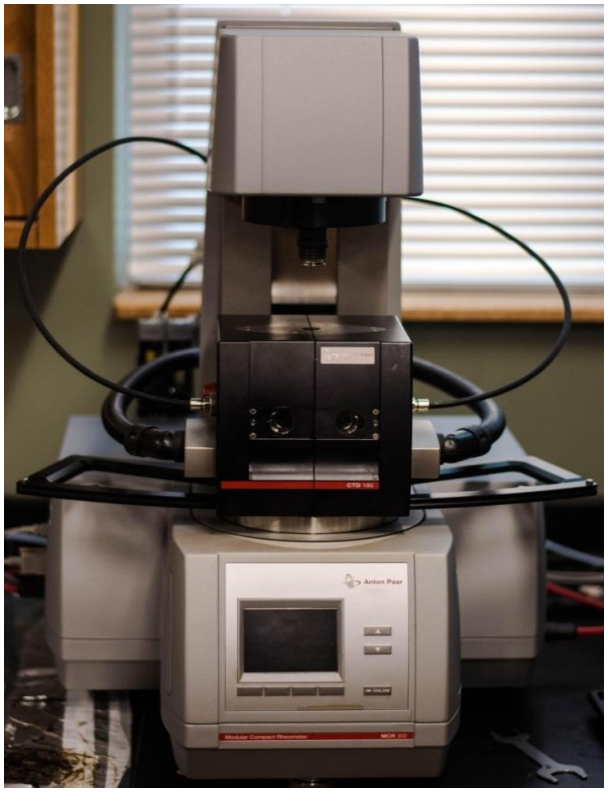

Figure 4.11: Dynamic Shear Rheometer.

The Superpave specifications with respect to the DSR test results for unaged, RTFO-aged and PAV-aged binders are shown in Table 4.4.

Table 4.4: Superpave Specification for Rutting and Fatigue Factor

Material	Value	Test Temperature (^{o}C)	Specification
Unaged binder	G*/sinδ	High Service	≥ 1.0 kPa (0.145 psi)
RTFO-aged binder	G*/sinδ	High Service	≥ 2.2 kPa (0.319 psi)
PAV-aged binder	G*•sinδ	Intermediate Service	≤ 5000 kPa (725 psi)

Bending Beam Rheometer (BBR) Test

The BBR test is performed to measure low temperature stiffness and stress relaxation properties of asphalt binders. These parameters indicate asphalt binders' resistance to low temperature cracking. Apart from that, BBR test also provides the low service temperature of the PG grading. From the BBR test, creep stiffness and the slope of the master stiffness curve, referred to as "m-value", at 60 s is measured. The test is performed in accordance with AASHTO T 313. A typical BBR device is shown in Figure 4.12. The Superpave specifications for BBR test are shown in Table 4.5.

For the test, degassed PAV-aged binders are used to prepare a 0.246 x 0.492 x 5.000 inch (6.25 x 12.5 x 127 mm) solid asphalt beam. This beam is loaded at its midpoint in a simply supported set-up where the two supports are 4.02 inches (102 mm) apart and the load is 0.22 lb (100 g). The beam deflection is measured at 8, 15, 30, 60, 120 and 240 seconds. A stiffness master curve is plotted for these points. From the curve, slopes are drawn at 8, 15, 30, 60, 120 and 240 seconds to calculate the "m" values. The test is performed at a 10°C higher than the expected the low service temperature. To simulate the low service temperature, the time-temperature superposition principle is used.

Figure 4.12: Bending Beam Rheometer (BBR).

Table 4.5: Superpave Specification for BBR Test

Parameter	Test Temperature (^{o}C)	Specification
"m-value" at 60 second	Low Service Temperature +10^{o}C	$\geq$ 0.300
Stiffness at 60 seconds	Low Service Temperature +10^{o}C	$\leq$ 300 MPa

Rotational Thin Film Oven (RTFO)

The RTFO oven simulates short term aging of asphalt binders for use in DSR test as well as for PAV-aging. The RTFO oven uses high temperature and air pressure to simulate the aging phenomenon that happens to asphalt binders during the heating and storage inside of a mixing plant. Figure 4.13 shows an RTFO oven used for this study. The RTFO-aging of asphalt binders is done according to AASHTO T 240. At first, 35 gm asphalt binder is poured into cleaned and

preheated RTFO glass bottles. The glass bottles are then placed into the RTFO sample rack which rotates at a speed of 15 rpm. The test temperature is 163°C and the aging time is 85 minutes. During the test, 244 in^3/min (4 L/min) air flows into each sample bottles.

Figure 4.13: Rotational Thin Film Oven (RTFO).

Pressure Aging Vessel (PAV)

The PAV simulates long term aging of asphalt binders (7 to 10 year period). The PAV aging is done in accordance with AASHTO R 28. Figure 4.14 shows the PAV device used for this study. The aging process is conducted at various temperatures namely, 90, 100 and 110°C depending on the climatic condition. For this study a 100°C aging temperature was selected. Moreover, the aging process takes 20 hours. The required air pressure for PAV aging is 300 psi (2.07 MPa).The PAV-residues are used for DSR tests for measuring the fatigue factor and BBR test to measure the low temperature cracking properties of asphalt binder. However, for using the PAV residues for direct tension test (DTT), it is recommended to degas the sample in a vacuum degassing oven. Other than DTT, the degassing activity is optional. Figure 4.15 shows a vacuum degassing oven used in this study. The degassing process is done at temperature of 170°C for a period 30 minutes.

Figure 4.14: Pressure Aging Vessel (PAV).

Figure 4.15: Vacuum Degassing Oven.

4.4.2 Chemical Performance Tests

FTIR Spectroscopy

FTIR analysis is a common and quick technique to identify the functional groups present in asphalt binders. It is commonly used in the asphalt industry to identify the presence of any specific functional group in asphalt binders (Yildrim, 2007; Masson et al., 2001; Diefendefer, 2006; Fernandez-Berridi et al., 2006). The principle behind FTIR spectrum analysis could be explained by the Planck-Einstein relation (Equation 4.1).

$$E = h\,\nu = h\,c/\lambda = h\,c\,\bar{\upsilon} \qquad 4.1$$

In Equation 4.1, E is the energy, h is Planck's constant, c is the speed of light and $\bar{\upsilon}$ is the wavenumber, which is inversely proportional to the wavelength. According to this principle, when a given molecule absorbs energy a range of mechanical motion including symmetrical and asymmetrical stretching, rocking, wagging scissoring and twisting is possible when photons with discrete energy are present. This enables the mapping of the absorption bands in the FTIR spectrum. Figure 4.16 shows the stretching and bending vibrations of atoms due to absorption of infrared radiation. If one considers the incident infrared radiation intensity as "Io" and the intensity of the beam after the interaction of the sample as "I", the ratio "I" and "Io" is a function of the frequency of light, which gives the spectrum. This spectrum could be specifically three types, namely transmittance, reflectance and absorbance. The multiple vibration type occurring instantaneously creates a very complex absorption spectrum. This picture of spectrum is dependent on the functional group present in the sample which changes the value of "I" after the interaction of infrared radiation. The FTIR device detects this intensity of light with the help of a detractor after the infrared interact with the sample. A working principle of FTIR is shown in Figure 4.17. For this study, a Nicolet 8700 spectrometer was used, and the FTIR spectrum was analyzed using Thermo Electron's OMNIC software.

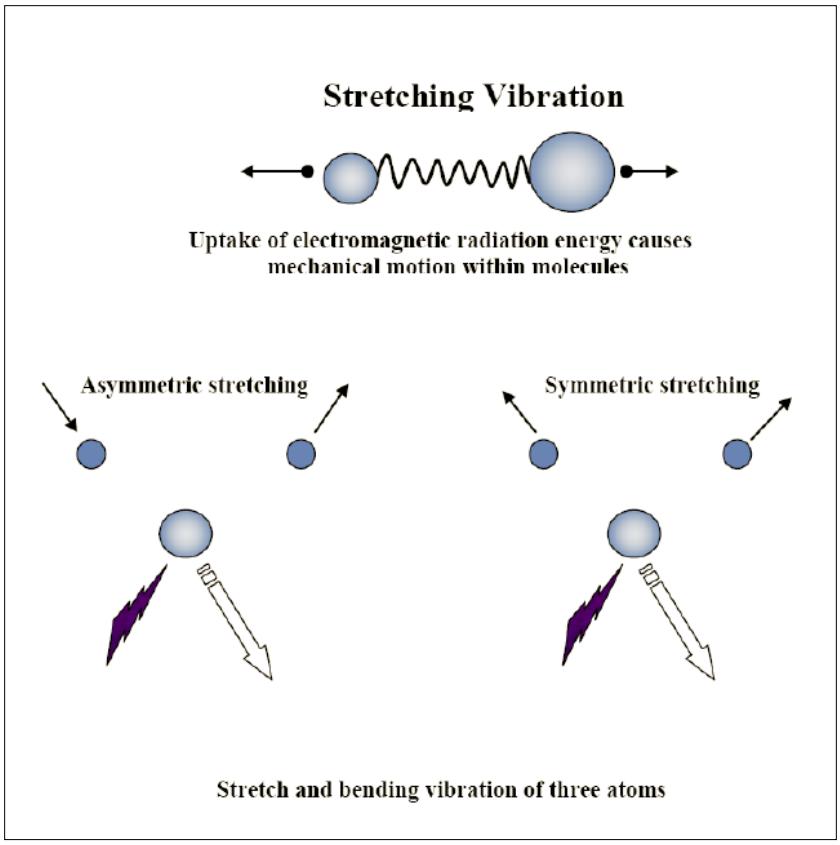

Figure 4.16: Stretching and Bending Vibrations of Atoms due to Absorption of Infrared Radiation.

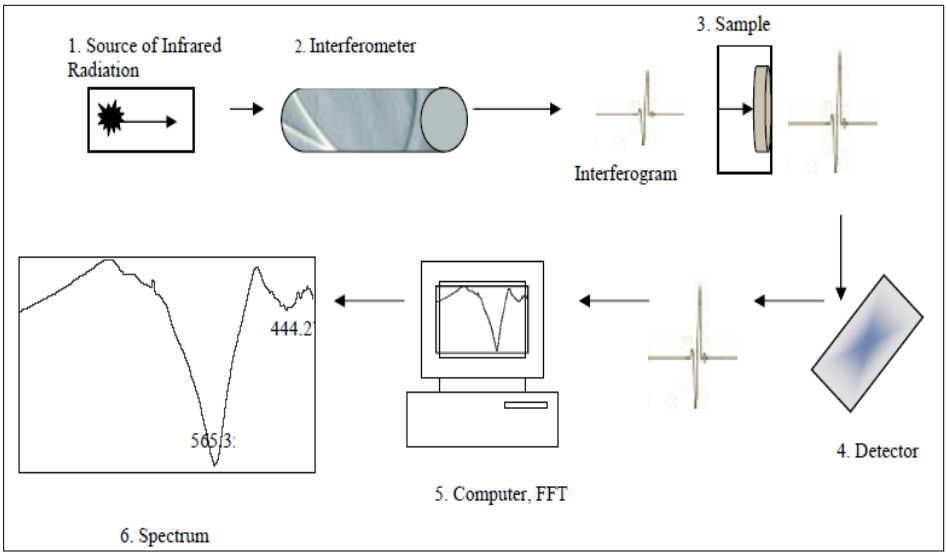

Figure 4.17: Experimental Set-up for FTIR Spectroscopy.

Sample preparation is a very important step of FTIR test, as improper sample preparation could change or alter the spectrum (Nasrazadani et al., 2010). There are various methods of

sample preparation of asphalt binder testing. One of the methods is the Attenuated Total Reflectance (ATR) method and the other one is transmission FTIR method. The former method is suggested by AASHTO T 302-05 to quantify the polymer content in asphalt binders. In this method, 10 gm of heated asphalt binder is placed over a wax paper which is cut to the size slightly larger than the face of an ATR crystal. Care has to be taken so that sufficient material is placed on the crystal so that the entire face is covered. The desired thickness of asphalt binder over the wax paper is 1 mm. Before running the test, the paper with asphalt binder is allowed to cool down for a sufficient period of time.

In the transmission FTIR method, 10 gm of heated asphalt binder is placed on wax paper. Over the wax paper, approximately 100 mg of potassium bromide (KBr) is pressed in a 13 mm die of about 10000 psi for two minutes to achieve a solid KBr pallet.

Apart from the aforementioned sample preparation techniques disposable Real Crystal IR cards is also used by researchers for FTIR sample preparation technique. This is a very recent technique to accommodate samples such as asphalt binders. The IR card contains a circular aperture which enables transmitting IR microporous substrate. For preparing the samples, at first asphalt binder is heated to 163 °C to make it fluid. One drop of the fluid binder is placed on the side of the IR card crystal aperture, which is spread over the crystal by a clean glass slide. The sample must be thin enough for the source to pass through. After preparing the sample, it is allowed to cool down sufficiently before running any test. For this study, KBr IR cards of 9.5 mm aperture size from International Crystal Labs were used. Figure 4.18 shows an empty IR card and a prepared sample for FTIR test.

For this study, a KBr beam splitter from a spectrum range of 350 to 7400 cm^{-1} was used. The samples were run over 50 scans at 4 cm^{-1} resolution for 30 seconds. The test was done at a relative humidity under 5%. At first, the IR spectrum was taken of an empty IR card for background, over which the samples were tested. The data analysis was performed by the OMNIC software, which provides the absorbance and wavenumber data for a sample. The data was plotted with the help of the MS Excel tool.

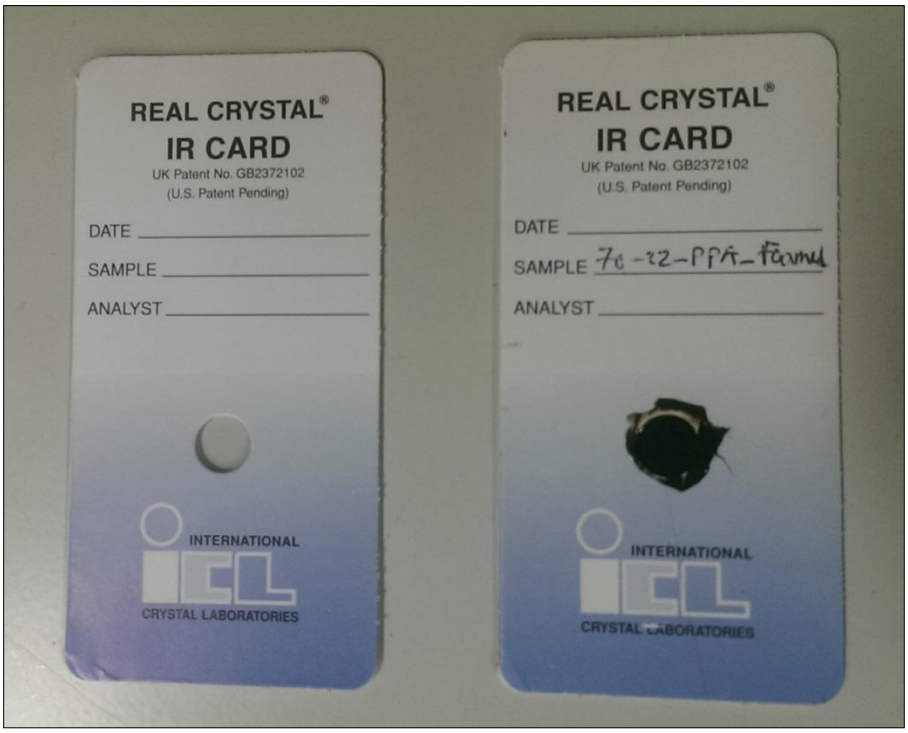

Figure 4.18: An Empty IR card (Left) and a Sample Ready for FTIR Test (Right).

Acid Detection Test

To detect the presence of phosphorus or PPA in asphalt binder, a qualitative test titled acid detection test was done. The test result shows the presence or absence of PPA by a visible color change in the reagents used for the test. The test is performed in accordance with AASHTO TP 78. The reagents needed for this test are ammonium molybdate, antimonyl tartrate, 1 n sulfuric acid, ascorbic acid and butyl alcohol. Typical positive and negative results of acid detection test is shown in Figure 4.19 (Figure 19a is a negative test, and Figures 4.19b and 4.19c are positive test).

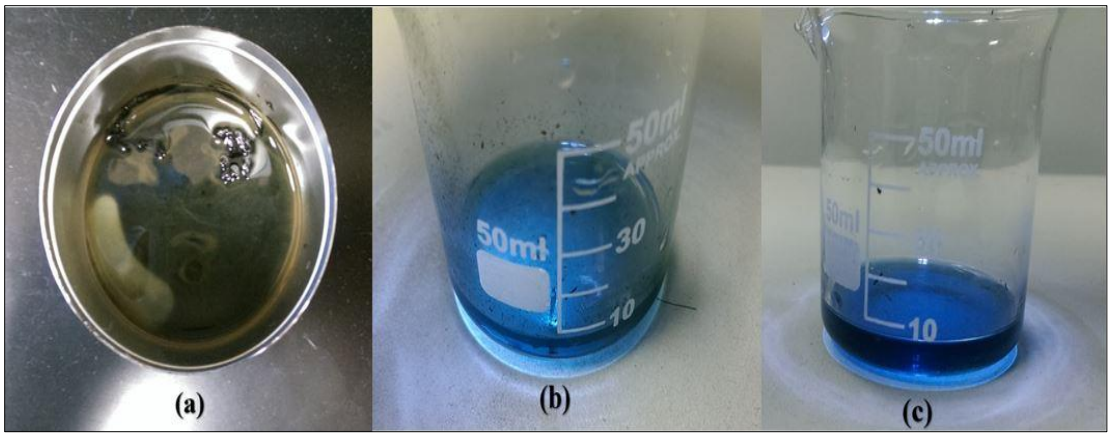

Figure 4.19: Acid Detection Test Results.

SARA Analysis

The SARA analysis was intended for determining the percentages of certain families of chemical constituents in the tested asphalt binders. The SARA analysis was performed in accordance with "ASTM D 4124-09: Standard Test Method of Separating Asphalt into Four Fractions". In this method, the test specimen was put into reflux with n-heptane for at least three hours. To start a reflux, an asphalt specimen weighing 2.00±0.30g was taken in a round bottom flask. For each gram of asphalt specimen, 100mL of n-heptane (HPLC grade) was added to it. A stirring magnet was put into the flask. A Leibig condenser was fitted to the opening of that flask. The assembly was fastened with a clamp and set on a heating bath containing sand smaller than the size of the US standard Sieve No. 20. The heating bath was then placed on a hot plate and the temperature was set at 200±50°C and the stirring was set at 300±50 rpm. This reflux operation caused the highly polar fractions (i.e. asphaltenes) to precipitate. Although the standard, ASTM D 4124-09, recommended using iso-Octane, it was not capable enough to entirely dissolve the specimen in reflux. Therefore, n-heptane was used to get the entirely dissolved specimen. The other three constituents (saturates, aromatics, and resins) got dissolved in n-heptane. The mixture of those three fractions is typically termed as maltenes. Maltenes were loaded onto a chromatographic column of activated alumina (pH 9-10) of particle size 50-200 μm and allowed to elute under gravity. The individual fraction came out in a sequence as saturates, aromatics and resins. The non-polar saturates came out first with n-heptane elution. The naphthene aromatics fraction was eluted with a consecutive application of toluene and toluene:methanol (50:50) solvents. A UV light of 366 nm wavelength was shined onto the column to monitor the advancement of the

aromatics fraction. A fluorescent band was progressing down. After collecting the entire fluorescent band, the polar aromatics or the resins started to elute. The resins fraction was completely collected lastly with trichloroethylene. All the eluted fractions were completely dried using a rotary evaporator and were reported as the percent fraction of the original sample. Sometimes a drying with chloroform was required to escape all the solvents out of the eluted fractions.

Moisture Susceptibility Measurement by Surface Free Energy (SFE) Technique

Apart from the mixture tests, moisture susceptibility can also be measured by the surface science-based SFE techniques. In the SFE method, cohesive energy of asphalt binder is calculated and the adhesive forces between asphalt binders and aggregates are calculated. Researchers have used the SFE technique to measure the compatibility between the asphalt binder and aggregates to quantify the vulnerability of the asphalt-aggregate compatibility to moisture damage. In this study, the Sessile Drop (SD) method has been used as it is simple, less time consuming and involves easy sample preparation techniques. In the SD method, static contact angles of asphalt binders and aggregates are measured by an Optical Contact Analyzer (OCA) device. Figure 4.20 shows the OCA device used in this study.

Figure 4.20: Optical Contact Analyzer (OCA) Device.

In the SD technique, one drop of probe liquid is dropped on the asphalt binder sample which is coated over a thin glass slide and subsequently the shape of the drop is automatically analyzed by the software connected to the OCA device. For one drop, more than 100 contact angles on each side of the drop are measured in this technique to get a very precise measurement. The volume of the drop is regulated and the same drop volume is used for all the samples. To determine the contact angle of asphalt binder a very smooth and thin surface of asphalt is created on a thin glass slide. The sample preparation procedure for a SD test is described below:

- At first, asphalt binders are heated at a temperature of 163 °C until they are fluid enough to spread over a solid surface.
- A glass slide of 57 mm x 70 mm x 1.5 mm is wrapped on all four sides with scotch tape to the desired sample outline. The glass slide is cleansed by quickly run through a flame before coating with the tape to make sure it is free from any particles or charges.
- With the help of a trimmer, a very small amount of asphalt binder is placed over one of the sides of the taped area.
- Another glass slide is quickly pressed and moved starting from the asphalt drop over the taped area to spread the asphalt binder evenly and smoothly over the surface of the glass slide.
- The tapes are removed after the asphalt binder has been cooled down sufficiently.

Figure 4.21 shows an asphalt binder sample ready for an OCA test. Beside asphalt binder samples, contact angles of aggregate samples were also measured using the SD method for this study.

Figure 4.21: An Asphalt Binder Sample Ready for OCA Test.

The sample preparation technique for an aggregate sample is briefly described below:

- Cutting of the rock samples: Rock samples are cut to thin and acceptable sizes before doing any types of cleaning or polishing. The rocks are cut in thin slices where the cut thickness varying from 0.25 to 0.5 inches. Figure 4.22 shows a typical rock sample after cutting.

Figure 4.22: A Typical Rock Sample After Cutting.

- Cleaning and polishing of the sample: After cutting, the samples are washed with water to remove any visible material present on the surface and cleansed using a paper towel. After cleaning, the testing surface of the sample is polished by silicon carbide grits. When the polishing is finished, the samples are washed with soap and warm distilled water. After this initial cleaning, the samples are cleansed further by hexane, which is applied to the sample by a saturated paper towel.
- Drying: After cleaning, the samples are dried at 105 °C for 12 hours. Then the sample is cooled to room temperature in a desiccator with anhydrous calcium sulfate crystal.

4.4.3 Asphalt Mixture Tests

Evaluation of Rutting and Stripping of Asphalt (ERSA) Test

The ERSA Test is used for testing the rutting and moisture-susceptibility of hot mix asphalt (HMA). It determines the susceptibility of premature failure of HMA caused by weakness in the aggregate structure, inadequate binder stiffness, or moisture damage. This test method aims to measure the rut depth and the number of passes to failure. In order to perform this test, a saw-cut slab from laboratory-compacted HMA specimen or a core from a compacted pavement is needed. The thickness of the cylindrical specimen can be from 38 mm (1.5 in) to 100 mm (4 in) and the diameter of 150 mm (6 in). For each test, two samples are needed, which are shown in Figure 4.23. The specimen has to be submerged in a water bath of 40^{o}C to 50^{o}C. The ERSA Tracking machine has a moving wheel of 203.2 mm (8 in) and 47 mm (1.85 in) wide steel which goes along the specimen. From a specification standpoint, it is essentially identical to the Hamburg Wheel Test. The wheel has a load of 158 lbs (703 N), and it should make 52 passes across the specimen per minute with a maximum speed of 0.305 m/s. The machine is limited to running 20,000 cycles. Arkansas specifications (Section 407) for surface courses require a maximum rut depth of 8.000 mm (0.314 inches) at 8,000 cycles for an APA style wheel tracking tests. Since the University of Arkansas is utilizing the ERSA tester, the maximum cycle value of 8,000 cycles and a maximum rut depth of 8.0 mm (0.324 inches) are utilized. The gradation of the specimen, which is caused by the wheel, is measured.

Figure 4.23: Left and Right ERSA Samples to Perform Test.

Dynamic Modulus in IDT configuration

IDT Dynamic Modulus is a modification of the standard for measuring dynamic modulus according to AASHTO T 342. While AASHTO standard uses cylindrical specimens, IDT dynamic modulus uses disc specimens, which are the same in shape as the ones used in creep compliance tests (AASHTO T 322). The basis for using this configuration as a tool for measuring IDT dynamic modulus was proposed by Kim et al. (2004) based on the mathematical formulation developed by Hondros (1959). The test basically consists of applying loads at varying frequencies (from 25 Hz to 0.1 Hz) at different temperatures (from -10^{o}C to 54^{o}C). A basic test setup is shown in Figure 4.24.

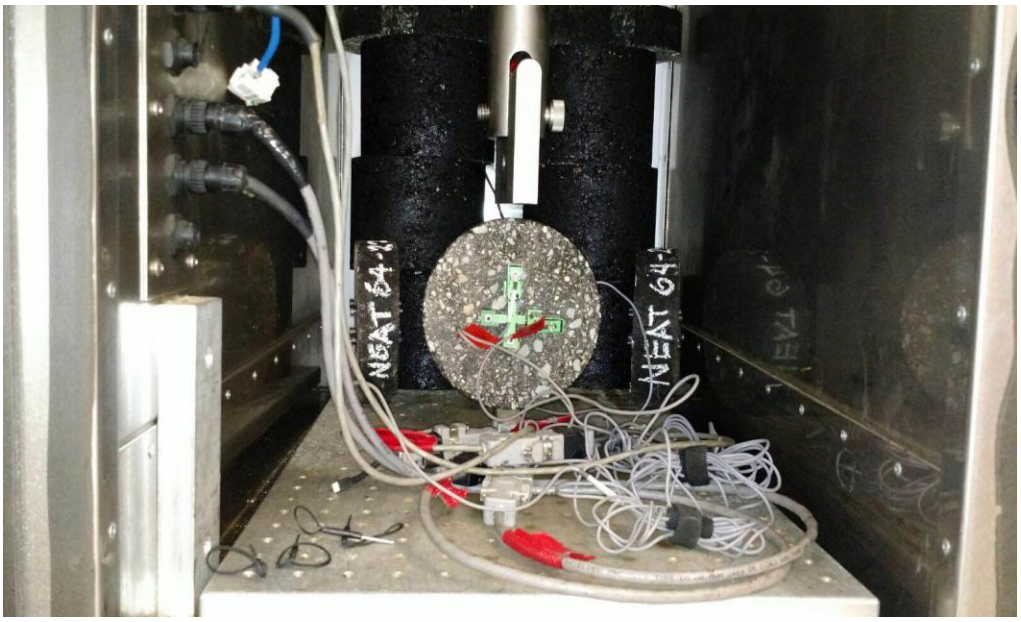

Figure 4.24: Dynamic Modulus in IDT Configuration.

Uniaxial Dynamic Modulus

In order to measure the Dynamic Modulus of an asphalt concrete sample, a dynamic load is applied at different frequencies: 0.1 Hz, 0.5 Hz, 1.0 Hz, 5 Hz, 10 Hz, and 25 Hz. Each of these frequencies as tested at five different temperatures: -10°C, 4°C, 21°C, 37°C, and 54°C. The amplitude of the load is recorded as well as the vertical deformation of the specimen using three extensometers. Then, the ratio of the amplitudes of vertical stress to vertical strains is computed in order to obtain the value of dynamic modulus for each combination of frequency and temperature following AASHTO T 62-07 (AASHTO, 2014). Specimens of 100 mm (4 in.) diameter and 150 mm (6 in.) tall were used, as seen in Figure 4.25.

Semi-Circular Bend (SCB) Fracture Test

Semi-Circular Bend (SCB) Test determines the fracture energy and fracture toughness at low temperatures of asphalt mixtures by its semi-circular geometry. The geometry is a half disc with a notch, as seen in Figure 4.26. To perform the test two samples are needed per test. Three replicates per binder were prepared. From each of these, a slice from the center of the specimen was obtained. This slice, which should be 25 mm (1 in.) thick, 150 mm (6 in.) diameter, and

notch's length 15 mm (0.6 in.) and 1.5 mm (0.06 in.) width, is cut in a half where one half is tested at -24^{o}C and the other half at -10^{o}C. The loading rate applied was 0.03 mm/min (0.012 in/min), as per AASHTO TP 105-13 (AASHTO, 2013).

Figure 4.25: Uniaxial Dynamic Modulus.

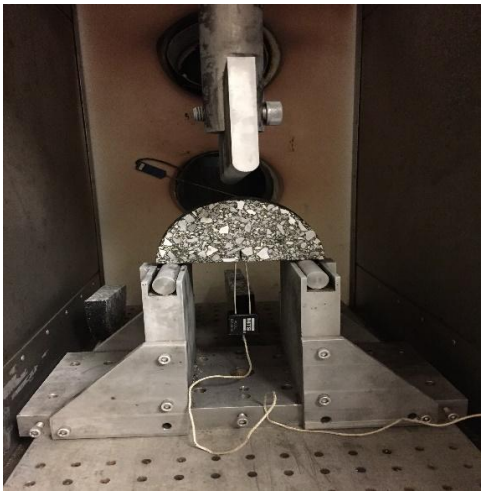

Figure 4.26: SCB Test.

IDT Creep Compliance and Indirect Tensile Strength

Creep compliance is defined as the time-dependent strain divided by the applied stress and indirect tensile strength is the strength shown by a specimen, which is subject to tension. The test

method will follow AASHTO T 322 specifications and will be conducted at the following temperatures: -10, 0, and 10^{o}C. Three replicates will be used and the specimen geometries will have a diameter of 6 in. (150 mm) and a 1.5 in. height (38 mm). The purpose of the test is to determine the tensile creep by the application of a static load of fixed magnitude along the diametrical axis of the specimen for the duration of 100 seconds. During the creep test, loads are selected to remain horizontal strain in the linear viscoelastic range, which is typically below 500 x 10^{-6} mm/mm. When the creep tests are finished at each temperature the tensile strength can be determined by applying a load to the specimen at a rate of 12.5mm of ram movement per minute. The vertical and horizontal deformation will be recorded on both ends of the specimens and the load until the load starts to decrease.

Checking Mix Design

In order to perform the mix design a binder of PG 64-22 was used combined with aggregates ½" Chips (11%), 3/8" VB Gr Chips (17%), Manufactured Sand (20%), 37% of ¼" Screening (37%), and Concrete Sand (15%). Mix design HM154-11 was used from APAC-Central (Arkhola) in Van Buren, AR.

Specific Gravity of Coarse Aggregate – AASHTO T 85

To perform the specific gravity of coarse aggregate, an amount of 2000 g coarse aggregate was used. Table 4.6 shows the results obtained for specific gravity for each aggregate.

Table 4.6: Specific Gravity of Coarse Aggregate

Aggregate	Mass, Oven dry specimen, A	Mass, saturated surface dry specimen, B	Mass, saturated sample in water, B	Sp. Gravity	Specific Gravity SSD	Apparent Specific Gravity	Absorption
½" Chips	1980.4	2029.1	1228.9	2.47	2.54	2.64	2.46%
3/8" VB Gr Chips	1980.3	2043.8	1228.2	2.43	2.51	2.63	3.21%
¼" Screening	1966.3	2032.6	1222.4	2.43	2.51	2.64	3.37%

Specific Gravity of Fine Aggregate – AASHTO T 84

To perform the specific gravity of fine aggregate, an amount of 1000 g of fine aggregate was used. Table 4.7 shows the results obtained for the specific gravity for each aggregate.

Table 4.7: Specific Gravity of Fine Aggregate

Aggregate	Mass, Oven dry specimen, A	Mass, Pycnometer + water, B	Mass, pycnometer + Specimen + Water, C	Mass, SSD specimen, S	Sp. Gr.	Sp. Gr. SSD	Apparent Sp. Gr.	Absorption
½" Chips	496.6	1273.6	1582.7	500.1	2.60	2.62	2.65	0.70%
3/8" VB Gr Chips	495.5	1263.6	1568.9	500.1	2.54	2.57	2.61	0.93%
Man Sand	496.3	1266.2	1576.4	500.0	2.61	2.63	2.67	0.75%
¼" Screening	496.2	1253.8	1561.7	500.0	2.58	2.60	2.64	0.77%
Concrete Sand	499.5	1272.1	1585.3	500.0	2.67	2.68	2.68	0.10%

*****These data were collected from the fine fraction of the coarse aggregate.

Bulk Specific Gravity (G_{mb}) – AASHTO T 166

Three replicates of 4500 g were used, which were compacted with 75 gyrations combined with amount of binder was 297.44 g. Three additional replicates of 4500 g were used, which were compacted with 115 gyrations. Tables 4.8 through 4.10 show the results for the bulk specific gravity.

Table 4.8: Bulk Specific Gravity (Gmb) at N_{design} of 75

Sample	A (Mass Dry, g)	B (Mass Sat. Air, g)	C (Mass in Water, g)	Gmb (A/(B-C)	Va
Replicate1	4807.10	4809.20	2743.40	**2.327**	**2.43**
Replicate2	4732.40	4733.70	2702.80	**2.330**	**2.29**
Replicate3	4732.30	4734.10	2704.10	**2.331**	**2.25**
Average	4757.27			**2.329**	**2.33**

Table 4.9: Bulk Specific Gravity (Gmb) at N_{max} of 115

Sample	A (Mass Dry, g)	B (Mass Sat. Air, g)	C (Mass in Water, g)	Gmb (A/(B-C)	Va	%G mm
Replicate1	4837.10	4838.20	2770.00	**2.339**	**1.93**	**0.98**
Replicate2	4886.50	4887.30	2793.20	**2.333**	**2.16**	**0.98**
Replicate3	4628.20	4629.80	2641.00	**2.327**	**2.42**	**0.98**
Average	4783.93			**2.333**	**2.17**	**0.98**

Bulk Specific Gravity (G_{mm}) – AASHTO T 209

Three additional replicates of 4500 g were used combined with an amount of binder 297.44 g. Table 8 shows the results of the bulk specific gravity (G_{mm}).

Table 4.10: Bulk Specific Gravity (Gmm)

Sample	A (Mass Dry, g)	C (Mass in Water, g)	Gmm (A/(A-C)
Replicate1	2792	1623.4	**2.389**
Replicate2	2642.5	1532.5	**2.381**
Average	2717.25		**2.385**

4.5 Field Performance Data Collection

It is imperative to collect field performance data such as roughness and rutting to check the current condition of the road network, the deterioration rate, or the necessity for maintenance by a highway agency. Almost all North American highway agencies are currently using automated methods for collecting pavement distress data. However, the process may vary among state agencies, the basic understandings are quite similar in how the data are collected. Two of the most prominent pavement distress parameters used by ArDOT are international roughness index (IRI) and rutting to characterize pavement distress. In fact IRI and rutting are the only two parameters ArDOT uses for rating pavements. The threshold values used by ArDOT for rating pavements based on IRI and rutting is shown in Table 4.11.

Table 4.11: Threshold Values of Pavement Distresses for ArDOT

	Scoring	Rating
IRI – Asphalt	000 – 060	Very Good
	060 – 095	Good
	095 – 170	Fair
	170 -	Poor
Rutting	0.000 – 0.125	Excellent
	0.125 – 0.350	Good
	0.350 – 0.500	Fair
	0.500 -	Poor

The pavement management section of ArDOT is responsible for collecting, processing, analyzing and reporting pavement performance data. ArDOT uses an Automated Road Analyzer (ARAN) to collect IRI and rutting data. Figure 4.27 shows an ARAN used by ArDOT

Figure 4.27: Automated Road Analyzer

The ARAN is used to monitor pavement performance data and pavement imageries on approximately 9500 centerline miles of roadways per year. Upon collection of these data, they are delivered to the ArDOT computer servers where they are referenced through the ArDOT geographic information system and processed with different analysis software (ArDOT, 2014). The pavement management division of ArDOT uses a multimedia highway information system (MMHIS) to report the data. Two hard drives containing the ARAN data were collected from ArDOT to collect pavement distresses. These data were analyzed by MMHIS software. Figure 4.28 shows a screenshot of MMHIS software.

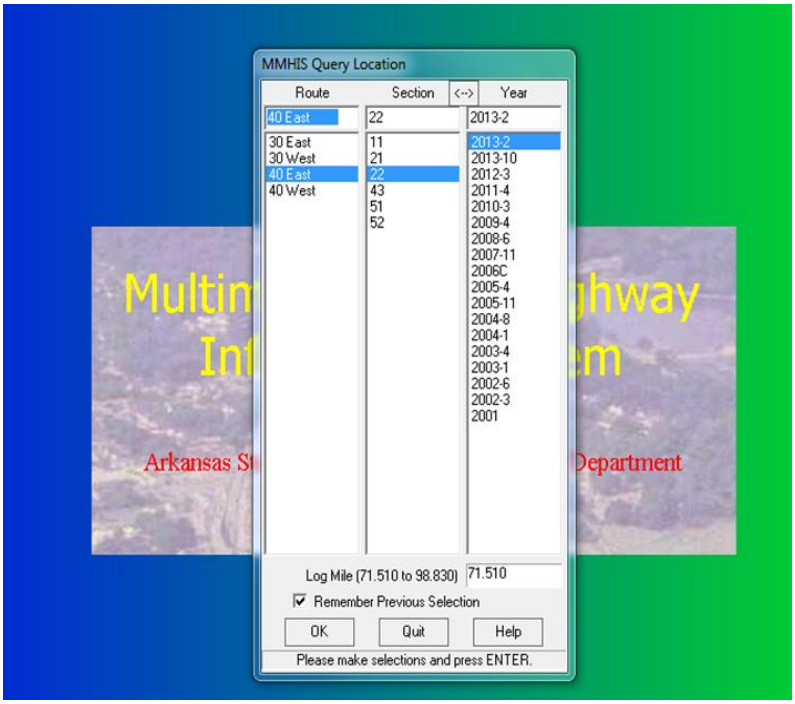

Figure 4.28: MMHIS Screenshot.

To check for any negative effects of PPA-modified asphalt binders, field data were collected from Arkansas Interstate system to verify if they contained PPA. The brief methodology of collecting field data is explained below:

Acid detection test was performed on the recovered binders from all ten sections of an ArDOT sponsored Technical Research Committee (TRC) project (TRC 1404). The sections from which the PPA-modified asphalt binder was detected were identified. Afterwards, the IRI and rutting data for that particular section was collected by using MMHIS software.

5 Data and Analysis

5.1 Binder Performance Tests

5.1.1 Penetration Test Results

Penetration test results, presented in Figure 5.1, reveal that Source 2 binders are harder than Source 1 binders at a room temperature of 25^{o}C. With the addition of PPA, the penetration values decrease. A similar trend is observed for the SBS modification. However, the decrease in penetration values for PPA-modified binder is proportional to the amount of PPA being used in the modification process. Furthermore, the PPA-modified PG 70-22 binder (S1B3 or S2B3) is softer than its SBS-modified counterpart (S1B7 or S2B7). The addition of the LAA, Kao Gripper™, softened the binders (i.e., increases penetration values), irrespective of source, as indicated in penetration values of S1B4 and S2B4, as presented in Figure 5.1. Finally, the increase in softness of the binder due to the addition of Kao Gripper™ is not prominent in the case of Source 2 binder.

As mentioned earlier, at a room temperature of 25^{o}C, the penetration values increased slightly in the case of Kao Gripper®. While comparing penetration values of other four LAAs-modified binders, an opposite trend was observed (Figure 5.2). The penetration values decreased due to the addition of AD-here® HP Plus, PermaTac Plus®, Evotherm®, or PaveGrip®. It is worth recalling that the base binder used for LAA modification was PPA-modified PG 70-22 binders (S1B3 and S2B3). Among these LAAs, Evotherm® showed the lowest penetration values, which was followed by PermaTac Plus®, PaveGrip®, and AD-here® HP Plus. Overall, LAAs did not have any adverse effects on the penetration grade of the binder.

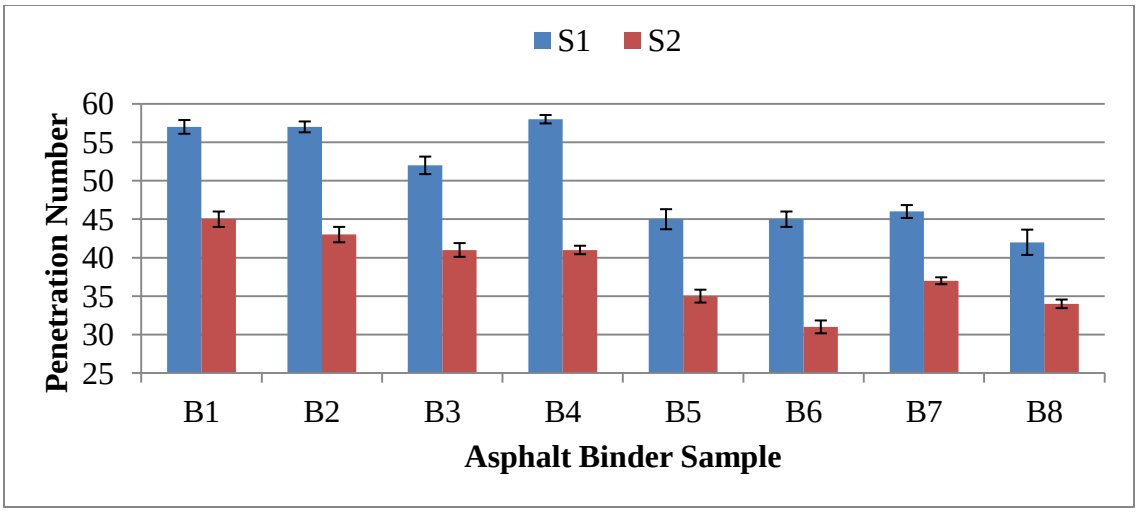

Figure 5.1: Penetration Test Results.

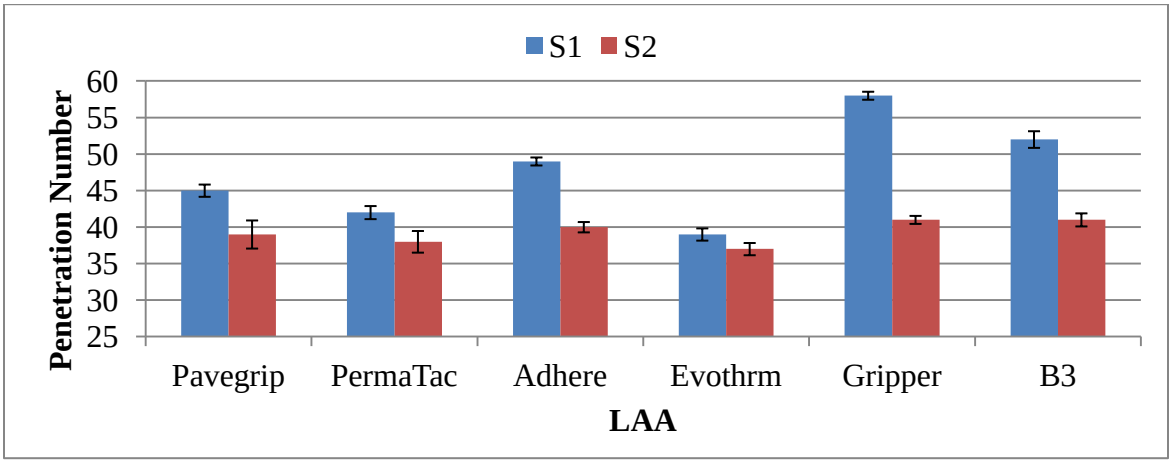

Figure 5.2: Penetration Test Results for PPA+LAA Modified Samples.

5.1.2 Rotational Viscosity (RV) Test Results

RV data, shown in Table 5.1, followed the same pattern as the penetration values for binders from both sources. As expected, PG 64-22 binder (e.g., B1S1 from Source 1) from any particular source showed the lowest viscosity. As mentioned earlier, penetration data showed that binders from Source 1 were softer than Source 2 at a room temperature. But, it was not the case for viscosity values at higher temperatures. Binders from Source 2 showed considerably lower viscosity values (softer) than the corresponding binders from Source 1. The viscosity of the binders decreased upon the addition of LAA (Kao Gripper®).

From RV test data, the mixing and compaction temperatures for all 16 asphalt binder samples were estimated as recommended by the Asphalt Institute (AI). As per AI, these temperatures

should be determined where the viscosity-temperature line crosses the viscosity ranges of 170 ± 20 mPa.s (mixing temperature range) and 280 ± 30 mPa.s (compaction temperature range). The viscosity temperature line was determined using the procedure described in ASTM D2493, "Standard Viscosity-Temperature Charts for Asphalts." Table 5.2 shows the mixing and compaction temperatures of PG 64-22 (S1B1 and S2B1), PPA-modified PG 70-22 (S1B3 and S2B3), SBS-modified PG 70-22 (S1B7 and S2B7) and PPA+SBS modified PG 76-22 (S1B8 and S2B8) binders. As seen from Table 5.2, the mixing and compaction temperatures of SBS-modified PG 70-22 binder (S1B7 or S2B7) are significantly higher than those of PPA-modified PG 70-22 binder (S1B3 or B2B3). Thus, from the energy consumption perspective, PPA-modified binders exhibit more favorable results than the SBS counterparts.

Table 5.1: Rotational Viscosity (mPa.s) Data of S1 and S2 samples

Binder Type	**Viscosity at Testing Temperature**			
	135°C	**150°C**	**165°C**	**180°C**
S1B1	504.17	254.17	145.83	75.00
S1B2	595.83	287.50	150.00	75.00
S1B3	704.17	345.83	183.33	100.00
S1B4	554.00	270.83	145.83	75.00
S1B5	733.33	312.5	154.17	75.00
S1B6	733.33	325.00	162.50	75.00
S1B7	1271.00	595.67	312.50	175.00
S1B8	1929.33	870.67	450.00	262.50
S2B1	445.83	208.33	112.50	62.50
S2B2	570.83	270.83	133.33	75.00
S2B3	645.83	295.83	145.83	75.00
S2B4	620.83	304.17	145.83	75.00
S2B5	745.33	340.83	162.50	75.00
S2B6	704.17	341.67	187.50	100.00
S2B7	1271.00	554.17	279.17	162.5
S2B8	1767.00	758.33	350.00	187.50

Table 5.2: Mixing and Compaction Temperatures of PPA and SBS Modified Binders

Source 1				
Binder Type	**Mixing Temperature (°C)**		**Compaction Temperature (°C)**	
	High	Low	High	Low
S1B1	165	158	150	145
S1B3	170	164	157	152
S1B7	183	177	171	165
S1B8	191	186	180	175
Source 2				
Binder Type	**Mixing Temperature (°C)**		**Compaction Temperature (°C)**	
	High	Low	High	Low
S2B1	158	152	146	142
S2B3	164	159	154	149
S2B7	182	176	168	162
S2B8	185	180	173	168

5.1.3 Dynamic Shear Rheometer (DSR) Test Results

DSR tests were done in three aging conditions, unaged, RTFO-aged and PAV-aged in order to characterize the viscoelastic behavior of asphalt binders at high and intermediate service temperatures. Figures 5.3 through 5.6 show DSR test results of unaged and RTFO-aged asphalt binders. As seen in these figures, all tested binders met the corresponding Superpave rutting factor ($G^*/\sin\delta$) criteria at their high PG temperatures ($G^*/\sin\delta$ should be at least 1.00 kPa for unaged binders and 2.20 kPa for RTFO-aged binders). The dark horizontal lines in these figures represent the Superpave acceptance criteria. It is clear that PPA-modified unaged and RTFO-aged binders showed increased rutting factor ($G^*/\sin\delta$) compared to the unmodified binders. Moreover, SBS-modified binders indicated higher rutting resistance than the corresponding PPA-modified PG 70-22 binders.

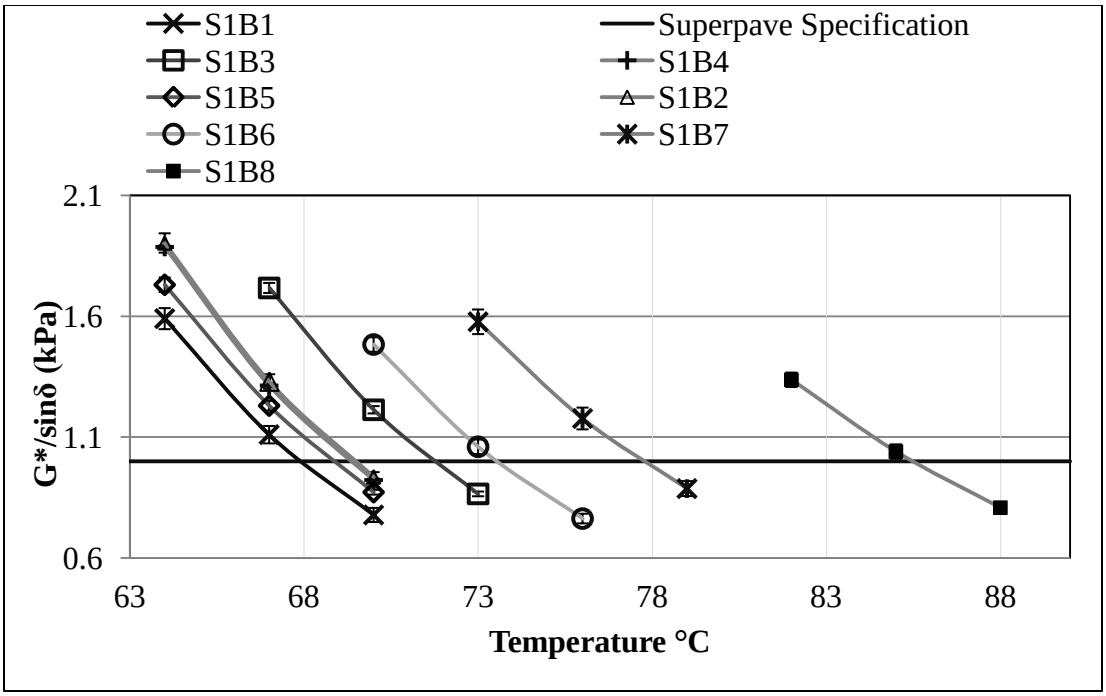

Figure 5.3: DSR Test Results of Unaged Binders from Source 1.

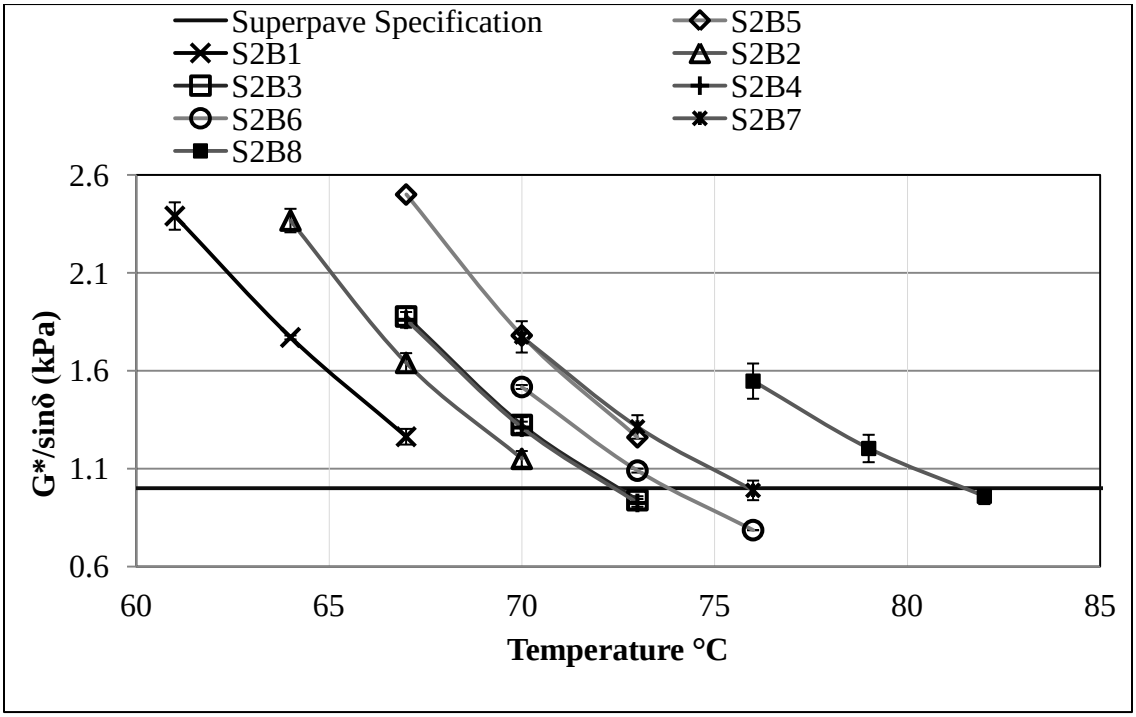

Figure 5.4: DSR Test Results of Unaged Binders from Source 2.

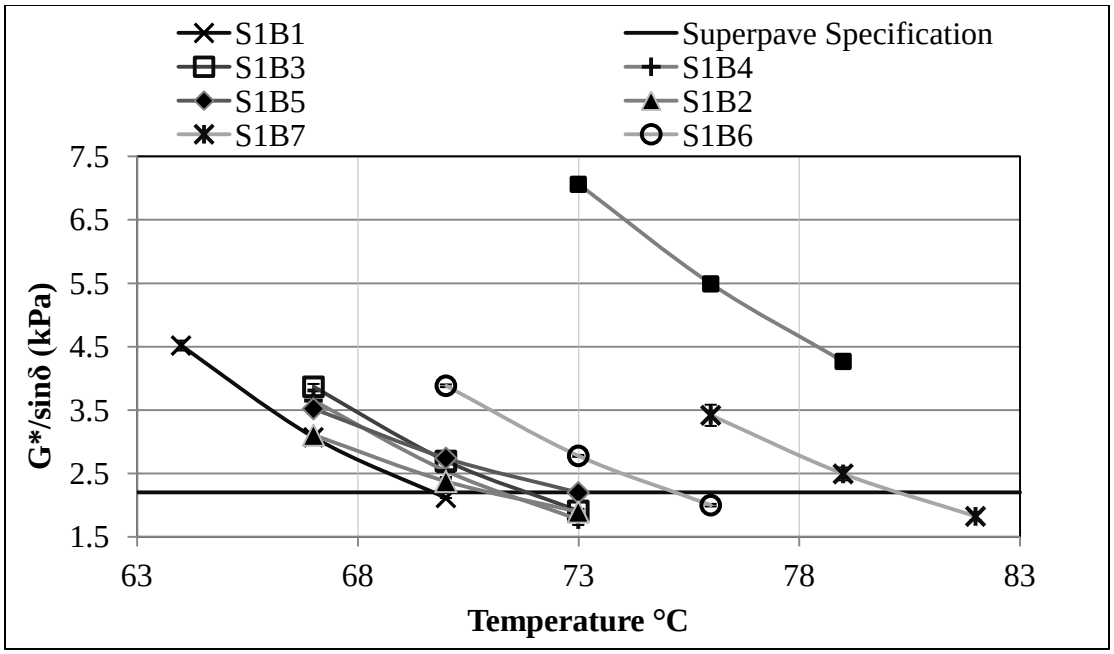

Figure 5.5: DSR Test Results of RTFO-aged Binders from Source 1.

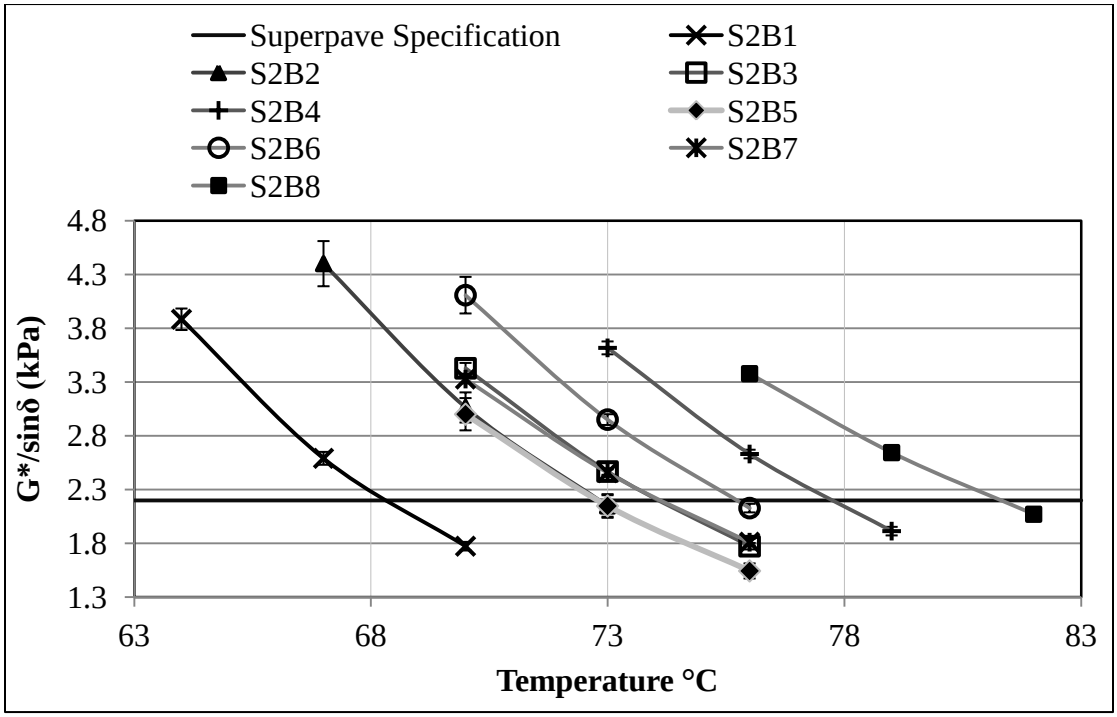

Figure 5.6: DSR Test Results of RTFO-aged Binders from Source 2.

As seen in Figures 5.7 through 5.10, the addition of LAA decreased the rutting resistance of PPA-modified binders in both aging conditions. Among the LAAs, Gripper (S1B4-Gripper)

was found to be the most compatible, whereas Adhere HP Plus was the least compatible. In the case of the unaged condition and for Source 1, Gripper plotted slightly below the minimum value of Superpave acceptance (Figure 5.7). But, for Source 2, the unaged Gripper-modified binder passed the Superpave specification limit for G*/sinδ, which should be at least 1.00 kPa. Under the RTFO-aging condition, the Gripper-modifies binders from both sources passed the Superpave specification limit for G*/sinδ, which should be at least 2.20 kPa. The other LAAs-modified binders from either source failed to meet the Superpave rutting criteria for both unaged and RTFO-aging conditions. Thus, it is recommended to use a compatible LAA such as Gripper when PPA is used as a modifier. This becomes an issue when contractors are given an option to use LAA in asphalt mixes. However, it may not be a problem when refineries blend a compatible LAA. Therefore, it is important for the ArDOT to know which LAA, if any, is used in the PPA-modified binder.

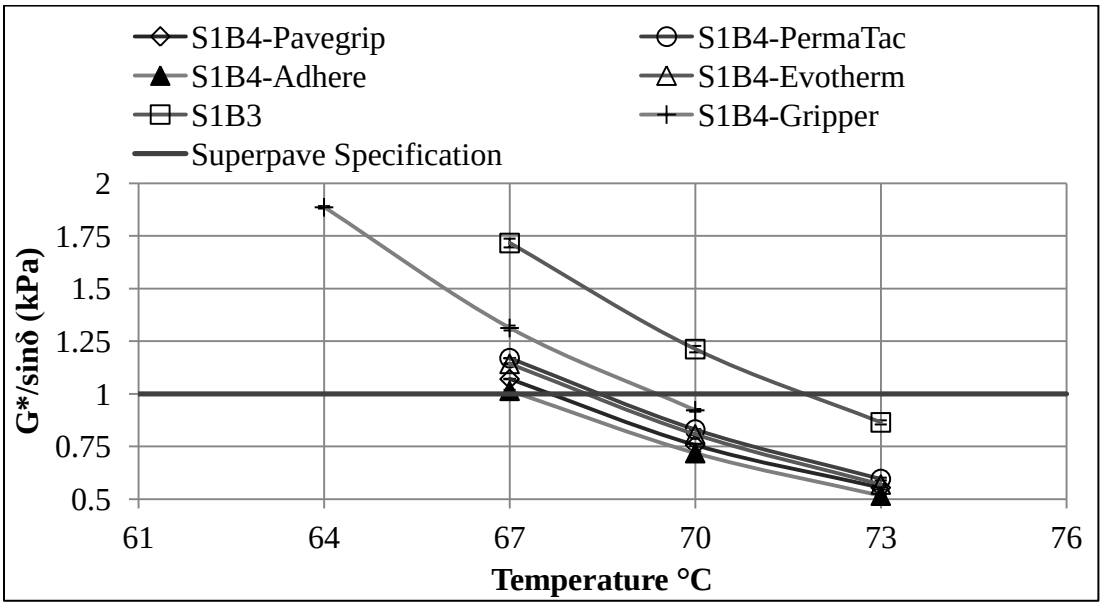

Figure 5.7: DSR Test Results of Unaged PPA+LAA Modified Binders from Source 1.

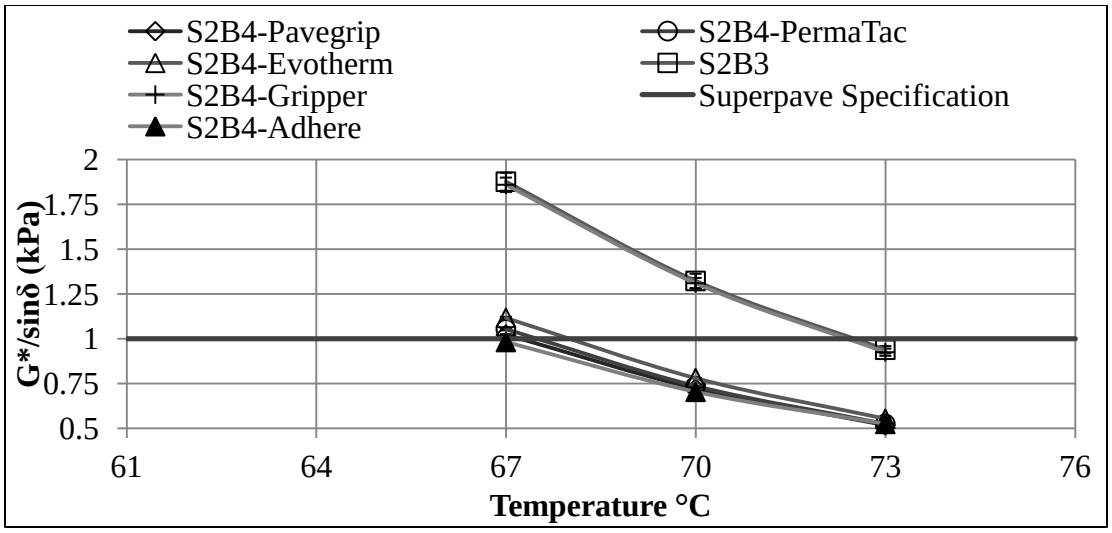

Figure 5.8: DSR Test Results for Unaged PPA+LAA Binders from Source 2.

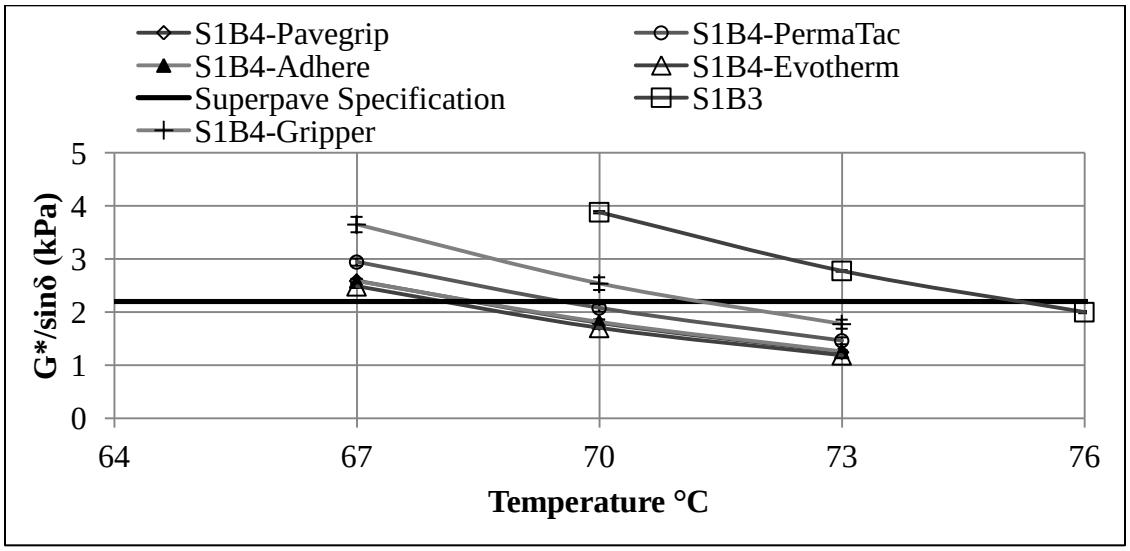

Figure 5.9: DSR Test Results of RTFO-Aged PPA+LAA Binders from Source 1.

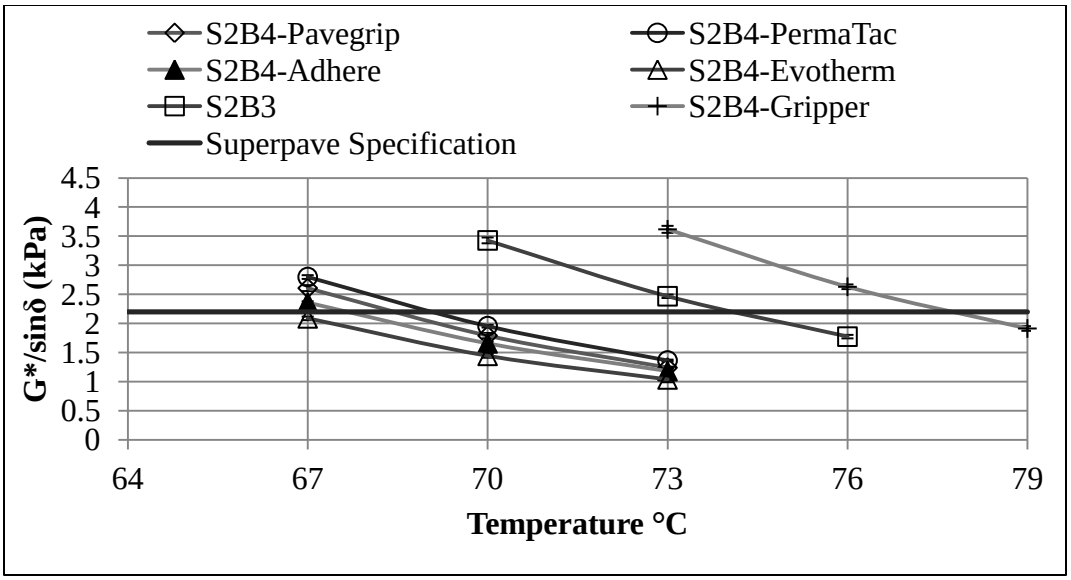

Figure 5.10: DSR Test Results of RTFO-Aged PPA+LAA Binders from Source 2.

DSR test results (Figures 5.11 and 5.12) on PAV-aged binders show fatigue characteristics of tested asphalt binders. As required by Superpave specifications, the G*•sinδ value of a PAV-aged binder at the intermediate temperature should not be more than 5000 kPa. The horizontal lines in these figures represent the Superpave maximum limit for fatigue resistance of binders. Test results reveal that all tested binder samples met the Superpave fatigue criterion. Test results also indicate that PPA-modified binders (S1B3 or S2B3) are more fatigue resistant than the corresponding SBS-modified binders (S1B7 or S2B7). No specific trend (increasing or decreasing) was observed in the case of foamed asphalt binders. In the case of Source 1, the fatigue resistance of the foamed binder (S1B5) slightly decreased, whereas it improved in the case of Source 2 binder. However, foamed binders (S1B5 and S2B5) from both sources met the Superpave specified fatigue criterion.

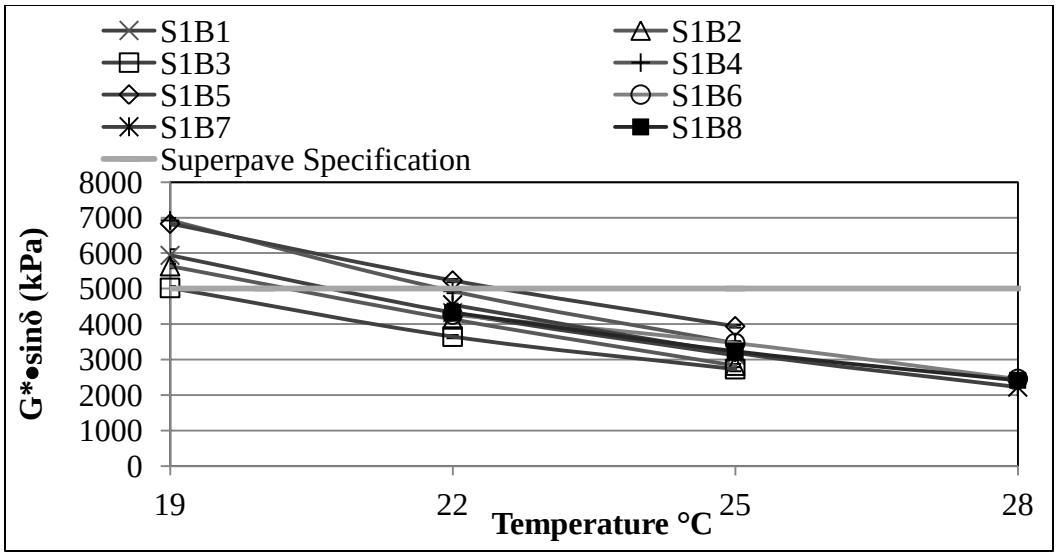

Figure 5.11: DSR Test Results of PAV-aged Binders from Source 1.

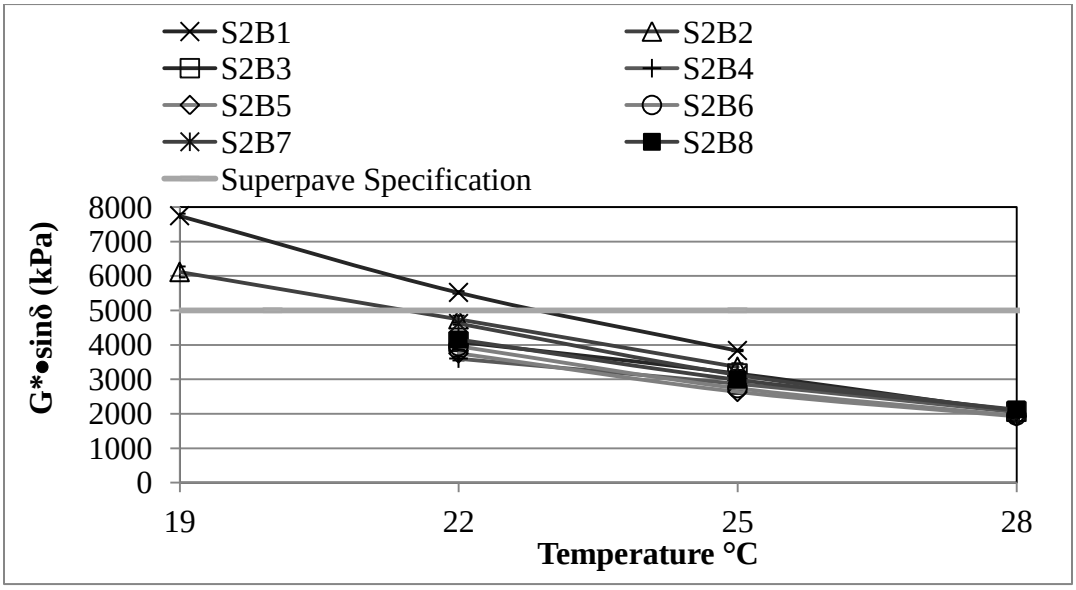

Figure 5.12: DSR Test Results of PAV-aged Binders from Source 2.

As seen from Figures 5.13 and 5.14, the addition of LAA in PPA-modified PG 70-22 binders did not cause them to fail the Superpave specification limit for fatigue even though G*•sinδ values increased in several cases. As a matter of fact, the fatigue resistance of the PPA-modified binder from Source 1 increased when Gripper was used as the LAA. These findings also indicate the need for a proper selection of a LAA for PPA-modified asphalts.

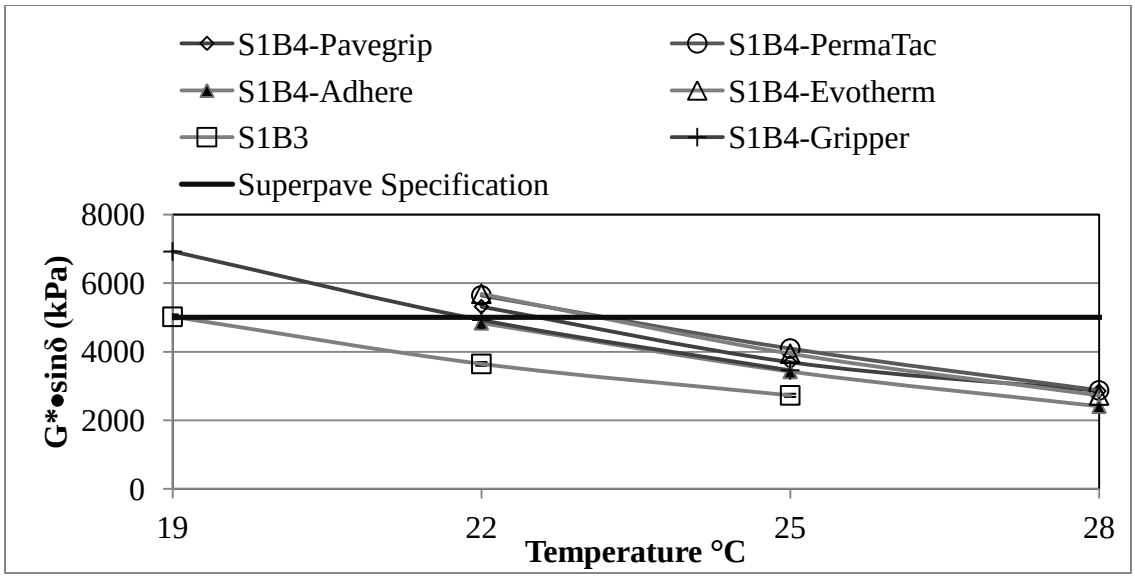

Figure 5.13: DSR Test Results of PAV-aged PPA+LAA Binders from S1.

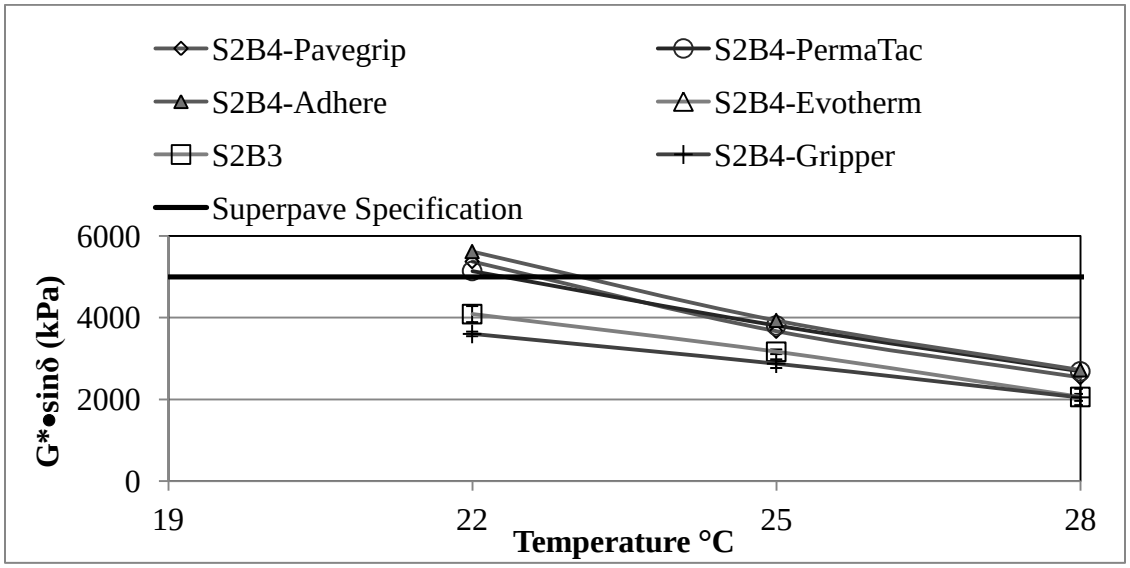

Figure 5.14: DSR Test Results of PAV-aged PPA+LAA Binders from S2.

5.1.4 Bending Beam Rheometer (BBR) Test Results

BBR tests were performed to measure low temperature stiffness and stress relaxation properties of asphalt binders. From the BBR test results, creep stiffness (S-value) and the slope of the stiffness curve (m-value) at 60s were measured. It could be noted that all BBR tests were conducted at 10^{o}C higher than the low PG temperatures of the binders, as recommended by the Superpave test specifications. For instance, in the case of PG 70-22 binders, BBR tests were

conducted at -12°C. Superpave specifications require binder's S-value should be not more than 300 MPa, and m-value should be at least 0.300.

S-values of tested binder samples are plotted in Figures 5.15 and 5.16. From these figures, it is seen that all tested binders comfortably met the Superpave S-value criterion. At a test temperature of -12°C, the lowest S-value for all tested binders from Source 1 is observed for S1B8, which is a PPA+SBS modified PG 76-22 binder. Between PPA- and SBS-modified PG 70-22 binders from Source 1, S1B7 (SBS-modified) showed lower creep stiffness at -12°C than the other. In the case of all binders from Source 2, the lowest creep stiffness was observed for S2B4 (LAA+PPA-modified PG 70-22 binder).

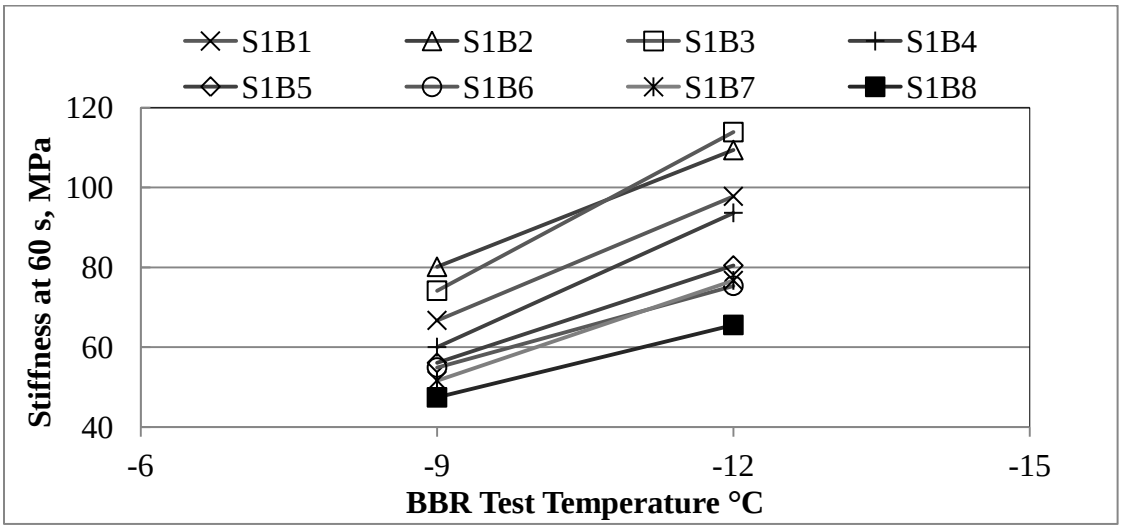

Figure 5.15: Creep Stiffness of Binders from Source 1.

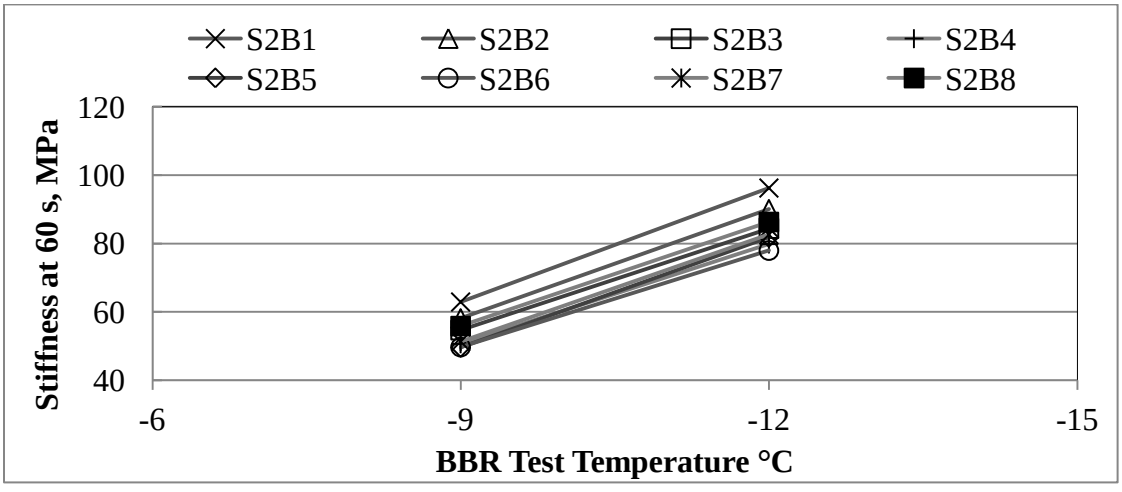

Figure 5.16: Creep Stiffness of Binders from Source 2.

As seen from Figures 5.17 and 5.18, all tested binder samples comfortably met the Superpave m-value criterion at their low PG temperature (-22^{o}C). At a testing temperature of -12°C, the highest m-value was achieved for both S1B7 and S1B8. Their m-values at any particular test temperature (-9°C or -12°C) are the same, and they overlap each other in the chart. At -12°C, among all binders from Source 2, the highest m-value was found to be 0.4, which was observed for S2B5 (PPA-modified foamed PG 70-22) and S2B6 (PG 64-22+1% PPA). For Source 2, at -12°C, the same m-value was observed S2B3 and S2B7.

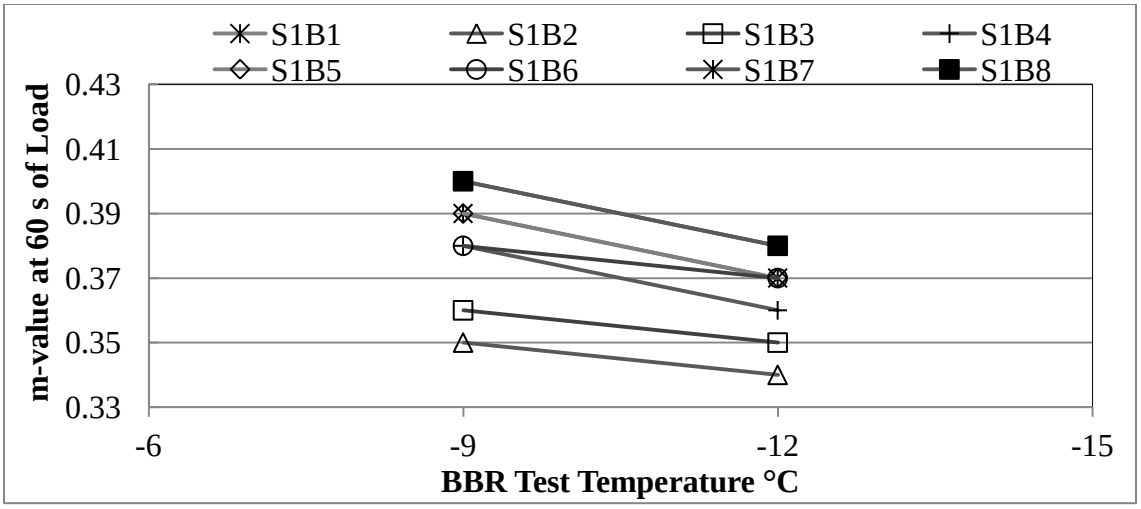

Figure 5.17: "m-values" of Binders from Source 1.

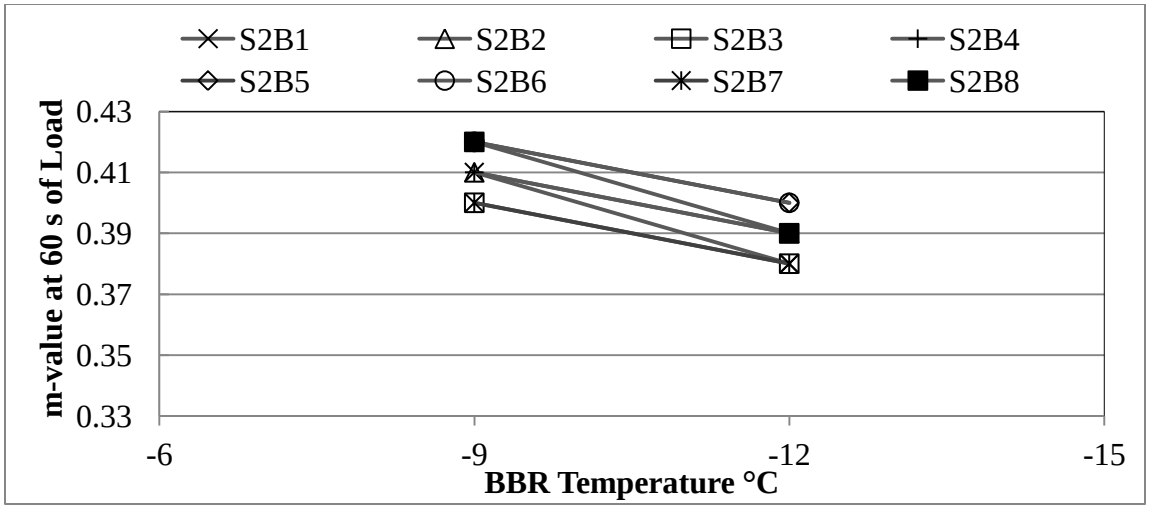

Figure 5.18: "m-values" of Binders from Source 2.

5.1.5 Moisture Susceptibility Analysis Using Surface Free Energy (SFE) Analysis

Moisture damage or stripping in asphalt mixtures is related to the adhesive bond energy and the magnitude of reduction in this energy when the asphalt binder debonds from the aggregate surface in the presence of water. It is believed that the affinity of the aggregates for water is greater than that of the asphalt binder. During the stripping process, water diffuses through the thin film of asphalt binder or mastic and collects on the surface of the aggregate. Therefore, the estimation of these adhesive energies has the potential to be used as a screening tool for material selection. Further, it is important to understand the effect of PPA modifications on moisture susceptibility of binder aggregate systems through a fundamental science approach, called the surface science.

Moisture susceptibility of asphalt binders was measured by conducting the SFE analysis. The SFE could be defined as the amount of energy produced by a new interface inside a vacuum. SFE tests were conducted on unaged binders at a room temperature. The first part of the SFE analysis was to measure the static contact angles of the asphalt binders and aggregate samples using three probe liquids (water, ethylene glycol, and formamide) of known SFE components. Four aggregates were chosen for the SFE analysis in this study. Two of these aggregates were sandstone (Preston Sandstone) and gravel (Preston Gravel) from Arkansas, and SFE values of two other aggregates (Snyder Granite and Martin Marietta Mill Creek [MMMC] Granite) were chosen from literature for comparison.

From the contact angles of asphalt binders and aggregate samples, the SFE components, namely, a mono-polar acidic component (Γ^{+}), a mono-polar basic component (Γ^{-}), and an apolar or Lifshitz-van der Waals component (Γ^{LW}) were calculated. Figures 5.19 and 5.20 show the contact angles of the asphalt binder samples coated on thin glass slides. In general, among three probe liquids, water made the highest contact angles with the asphalt binder samples. Between binders from Source 1 and Source 2, the samples from the former had higher contact angles than those from the latter, which was expected as binders from Source 2 binders were stiffer than those of Source 1 at a room temperature.

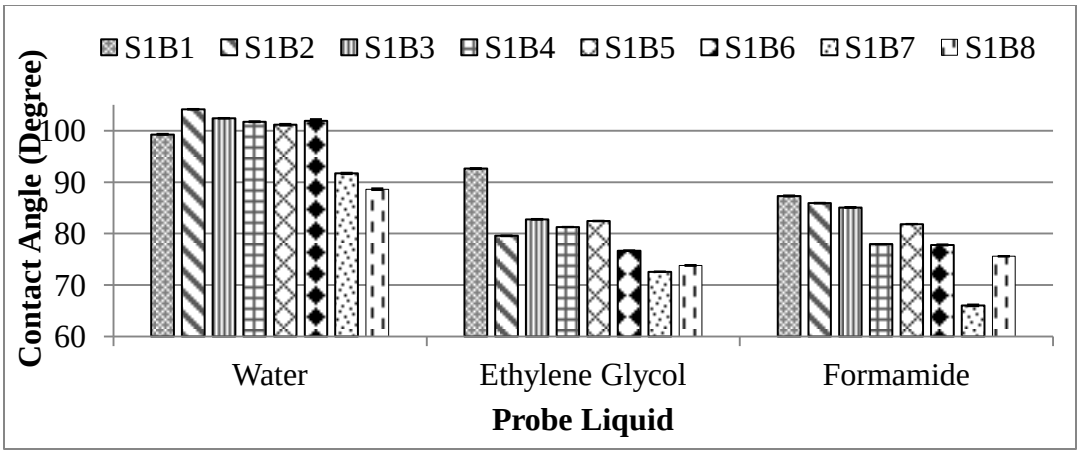

Figure 5.19: Contact Angles of Binders from Source 1.

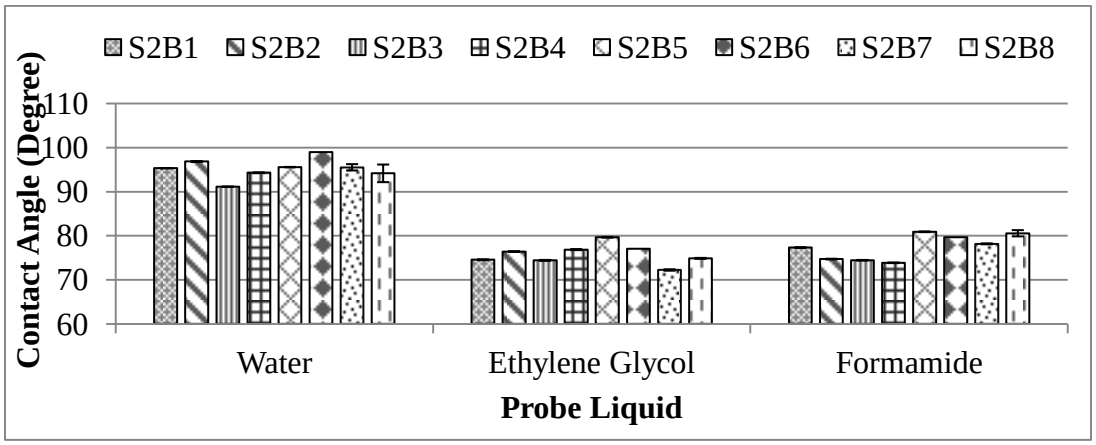

Figure 5.20: Contact Angles of Binders from Source 2.

Table 5.3 shows the SFE parameters along with work of cohesion (WOC) values for asphalt binders. In this table, Γ^{ab} is the acid-base component of the SFE, and it is the geometric average of Γ^{+} and Γ^{-}**.** It could be noted that the WOC is applicable for asphalt binders, and it is twice of Γ^{total}, which is the sum of Γ^{ab} and Γ^{LW}. The higher the WOC of an asphalt binder, the more energy is needed to break its cohesive bonds. The SFE values of aggregates are irrelevant while estimating asphalt binder's WOC. For Source 1 binders, the highest WOC was observed from S1B8, which was a combination of PPA- and SBS-modified binder. But, none of the binders modified solely by PPA had higher cohesion energy compared to their base binders (PG 64-22 aka S1B1). Rather, for Source 1, all binders modified by PPA alone showed less cohesion energy than S1B1. While comparing PPA-modified (S1B3) and SBS-modified (S1B7) binders, S1B7 had higher cohesion energy than S1B3. In Source 2, S2B3 possessed an increased WOC compared to S2B1 and S2B7. However, the WOC of S2B6 (1.0% PPA) decreased compared to

S2B3 (0.75% PPA), indicating a decreasing trend of bond energy beyond the optimum dosage of PPA. Another interesting observation was that the addition of LAA decreased the cohesion energy of S2B3, defeating the purpose of adding LAA. It could be noted that adhesion bonds between the aggregates and binder of an asphalt mixture are dominating parameters over the cohesive bonds for achieving favorable moisture resistance, and a LAA is added to improve the adhesive bonds. The adhesive bonds between aggregates and asphalt binders are discussed in the subsequent section.

Table 5.3: SFE Parameters (mJ/m^2) and Cohesion Energy (mJ/m^2) of asphalt binders

Probe Liquid/ Test Sample	Γ^+	Γ^-	Γ^{LW}	Γ^{ab}	Γ^{total}	W^{CL}
Water	25.50	25.50	21.80	-	72.80	N/A
Ethylene Glycol	1.92	47.00	29.00	-	48.00	N/A
Formamide	2.28	39.60	39.00	-	58.00	N/A
Snyder Granite	0.10	8.43	35.15	1.87	37.03	N/A
MMMC Granite	0.42	36.98	35.84	7.89	43.73	N/A
Preston Gravel	20.93	14.95	13.75	35.37	49.12	N/A
Preston Sandstone	20.76	14.76	13.56	35.00	48.56	N/A
S1B1	12.61	2.56	0.94	11.36	12.30	24.60
S1B2	12.50	2.30	0.18	10.72	10.90	21.80
S1B3	12.50	2.31	0.43	10.74	11.17	22.34
S1B4	12.52	2.35	0.53	10.84	11.37	22.74
S1B5	12.54	2.39	0.62	10.94	11.56	23.12
S1B6	12.51	2.33	0.50	10.79	11.29	22.58
S1B7	12.92	3.34	2.90	13.13	16.03	32.06
S1B8	13.23	4.00	3.55	14.54	18.09	36.18
S2B1	12.70	2.63	2.15	11.55	13.70	27.40
S2B2	12.59	2.36	1.87	10.90	12.77	25.54
S2B3	13.02	3.44	3.01	13.38	16.39	32.78
S2B4	12.72	2.81	2.38	11.95	14.33	28.66
S2B5	12.61	2.57	2.14	11.38	13.52	27.04
S2B6	12.37	2.00	1.54	9.94	11.48	22.96
S2B7	12.67	2.83	2.44	11.97	14.41	28.82
S2B8	12.67	2.83	2.44	11.97	14.41	28.82

The variation of adhesion energy under the dry condition (ΔG_{dry}) is shown in Table 5.4. The work of adhesion is defined as the amount of energy necessary to separate two materials at their interface. As seen from this table, MMMC granite showed higher ΔG_{dry} values than the others, irrespective of the binder types. Among all tested aggregates, under the dry condition, SBS- and PPA-modified PG 76-22 binder (S1B8) from Source 1 showed the highest ΔG_{dry} value. In the case of Source 2, PPA-modified PG 70-22 binder (S2B3) showed the highest ΔG_{dry}. The ΔG_{dry} values between Preston gravel and Preston sandstone did not have significant differences, but they were notably lower than those of MMMC granite. The SFE data also shows that an increase in the PPA amount did not increase the ΔG_{dry} value for Preston's gravel or sandstone. It can be noted that the higher the ΔG_{dry}, the better adhesive bonds exist between aggregates and binder under the dry condition. It is the opposite in the case of the adhesion energy under the wet condition (ΔG_{wet}) as values presented in Table 5.5 are negative.

Table 5.4: Work of Adhesion (mJ/m^2) for Asphalt-Aggregate System in Dry Condition

Binder Sample	Aggregates			
	Preston Gravel	Preston Sandstone	Snyder Granite	MMMC Granite
S1B1	34.7	34.4	32.1	54.8
S1B2	30.5	30.3	25.6	48.1
S1B3	32.2	32.0	28.3	50.9
S1B4	32.8	32.5	29.2	51.8
S1B5	33.2	33.0	29.9	51.8
S1B6	32.6	32.4	28.9	51.5
S1B7	40.4	40.2	41.1	64.1
S1B8	42.1	41.8	43.5	66.8
S2B1	38.4	38.2	38.1	60.9
S2B2	37.6	37.3	36.8	59.5
S2B3	40.8	40.5	41.5	64.7
S2B4	39.0	38.8	39.0	61.8
S2B5	38.3	38.1	38.0	60.7
S2B6	36.4	36.2	35.1	57.6
S2B7	39.1	38.9	39.2	62.0
S2B8	39.1	38.9	39.2	62.0

The ΔG_{wet} is a measure of adhesion energy under the wet condition and the negative values suggest the de-bonding potential of asphalt binders and aggregates in the presence of

water. From Table 5.5, it could be seen that the addition of PPA slightly decreased (as values are negative) the ΔG_{wet} of the binders from Source 1, which would make the binder more moisture susceptible. On the other hand, binders from Source 2 acted differently with the addition of PPA. For instance, the addition of 0.75% PPA (S2B3) slightly increased the ΔG_{wet} of the base binder (S2B1) from -12.9 mJ/m^2 to -12.1 mJ/m^2, indicating an increased resistance to stripping. Furthermore, LAA was found to be ineffective in reducing the negative bond energy under the wet condition. It could be noted that the combination of adhesion energy values under both dry and wet conditions rather than only dry or wet condition would have to be considered in determining the compatibility between aggregates and binders and a get a better understanding of their stripping resistance. The term "compatibility ratio," introduced by Texas Transportation Institute (TTI), is illustrated next.

Table 5.5: Work of Adhesion (mJ/m^2) for Asphalt-Aggregate System in Wet Condition

Binder Sample	Aggregates			
	Preston Gravel	Preston Sandstone	Snyder Granite	MMNC Granite
S1B1	13.9	14.3	29.8	17.5
S1B2	15.1	15.5	29.3	16.8
S1B3	14.6	15.1	29.8	17.4
S1B4	14.5	14.9	29.9	17.5
S1B5	14.4	14.8	29.9	17.5
S1B6	14.5	14.9	29.9	17.5
S1B7	12.2	12.5	29.3	17.5
S1B8	11.6	11.9	27.9	16.6
S2B1	12.9	13.3	30.8	18.7
S2B2	13.2	13.6	31.4	19.1
S2B3	12.1	12.4	29.0	17.4
S2B4	12.7	13.1	30.4	18.4
S2B5	13.0	13.3	31.0	18.8
S2B6	13.7	14.1	32.4	19.8
S2B7	12.7	13.1	30.4	18.4
S2B8	12.7	13.1	30.4	18.4

The "compatibility ratio" of an asphalt binder and aggregate system indicates the potentiality of moisture resistance of the binder with the aggregate. A higher compatibility ratio (CR) means the binder and aggregate system is less vulnerable to moisture damage. It is the ratio

of ΔG_{dry} and $-\Delta G_{wet}$. Generally, the CR increases if the ΔG_{dry} increases and/or ΔG_{wet} decreases, and vice versa. In particular, a CR value of less than 0.5 is considered to be very poor, whereas CR values of more than 0.5 signify good compatibility between binder and aggregates. To be more precise if the CR value is greater than 1.5 the compatibility is rated "very good" and it is graded as an "A." The range of CR between 0.5 and 1.5 means "good" and graded as "B" whereas and CR values between 0.5 and 0.75 means "poor" and graded as "C." Furthermore, CR values less than 0.5 means "very poor" compatibility and graded as "D." As suggested by the TTI researchers, the qualitative description of compatibility is shown in Table 5.6**.**

Table 5.6: Qualitative Description of Compatibility

Compatibility Ratio Range	Grading
Greater Than 1.5	A (Good)
0.75 – 1.5	B
0.5 – 0.75	C
Less Than 0.5	D (Poor)

The compatibility analysis of tested asphalt binder samples from Source 1 and Source 2 are shown in Figures 5.21 and 5.22, respectively. From these figures, it is seen that the CR values of the binder aggregate systems ranged from "B" to "A." Further, it is see that the two aggregates (Preston's gravel and sandstone) collected from Arkhola, AR showed very close CR. With the addition of 0.5% PPA, which was the optimum amount of PPA for Source 1, yielded significantly higher CR values than other aggregates. From the CR values of binders from Source 2, it was clear that both gravel and sandstone had very similar CR values. On the other hand, MMMC granite showed the highest CR values and Snyder granite showed the lowest. Moreover, for Source 2, PPA-modified PG 70-22 (S2B3) showed higher CR values than either PPA+SBS modified PG 76-22 (S2B8) or SBS-modified PG 70-22 (S2B7).

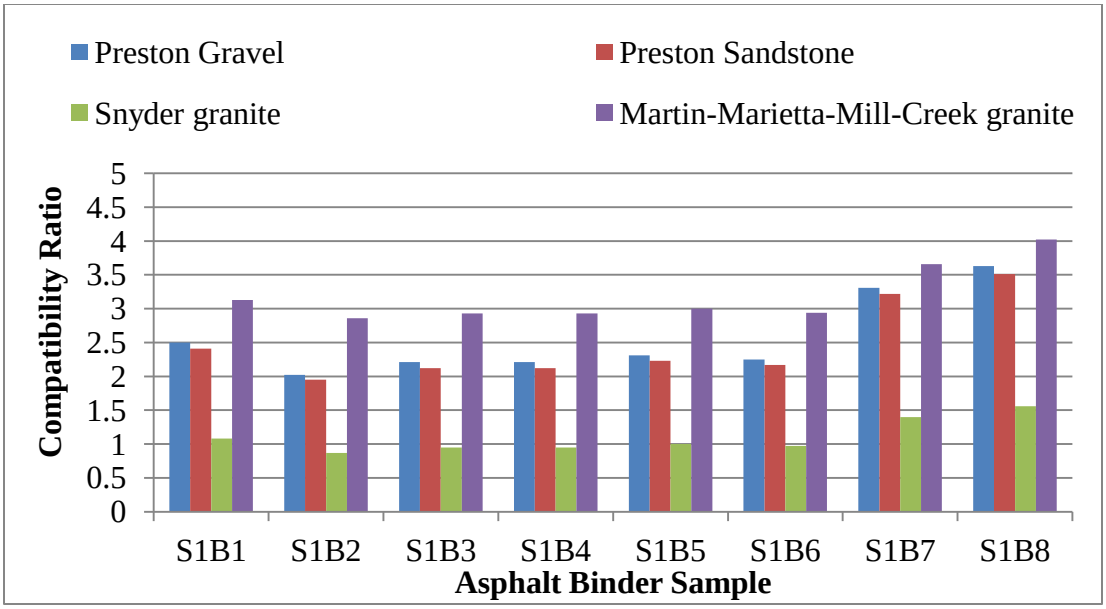

Figure 5.21: Compatibility Ratio of Binders from Source 1.

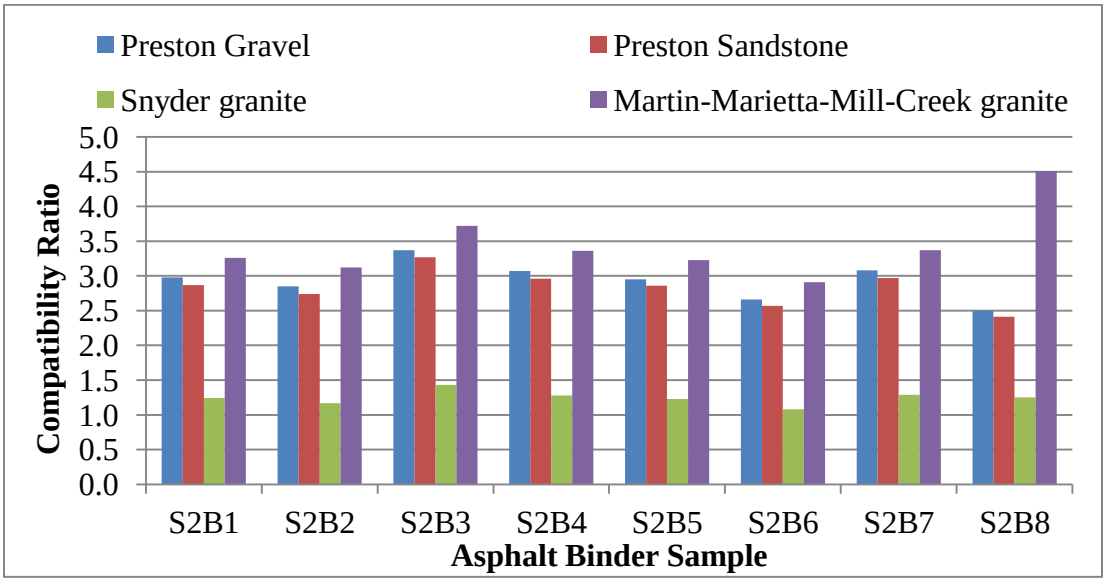

Figure 5.22: Compatibility Ratio of Binders from Source 2.

The variations of CR with varying PPA contents are shown in Figures 5.23 and 5.24. As seen from these figures, there is no significant change in CR values with the addition of PPA in Source 1 binders. However, for Source 2 binders, it is clear that the CR value is the highest at the optimum amount of PPA, but gradually decrease afterward. This indicates a reduction of the effectiveness of PPA in term of stripping resistance when higher than the optimum amount is used during the modification process.

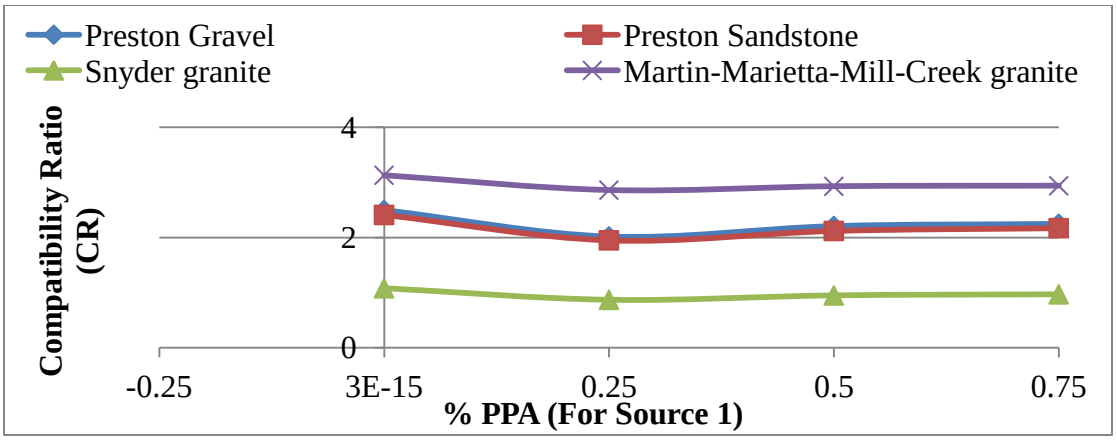

Figure 5.23: Variation of CR Values with Different Dosage of PPA for Source 1.

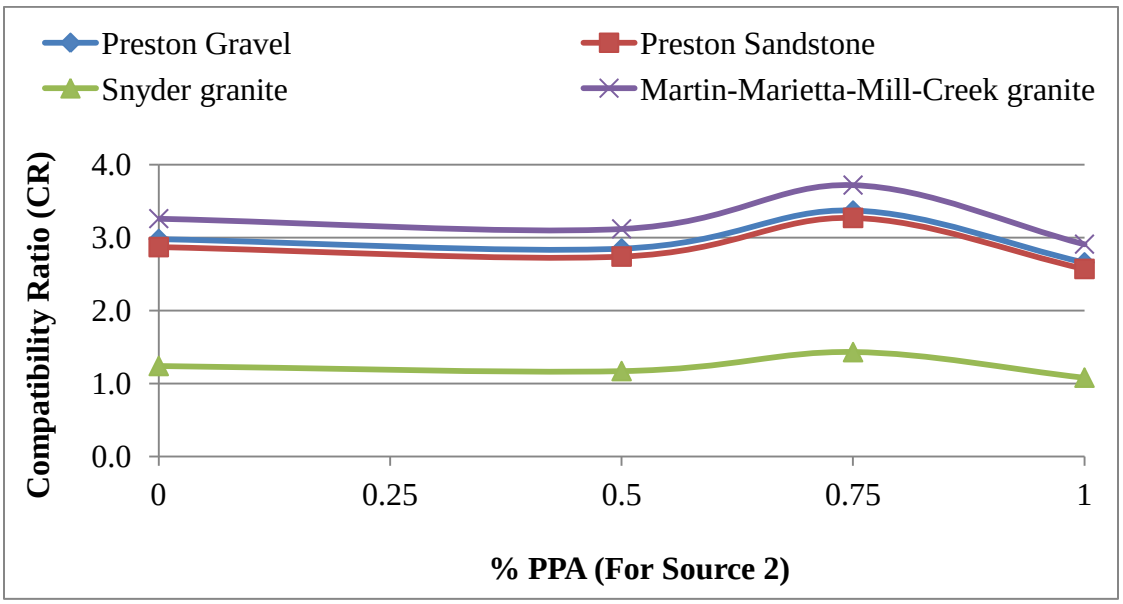

Figure 5.24: Variation of CR Value with Different Dosage of PPA for Source 2.

The CR values of PPA+LAA modified binders are shown in Table 5.7. From CR data presented in this table, it is evident that the CR values are in the compatibility category of "B" or "A." However, for Source 1, the CR value reduced significantly when AD-Here HP Plus was used as the LAA. This alluded to a hypothesis that if a "C" category of binder aggregate system was modified with AD-Here HP Plus, its CR would degrade to "D." However, MMMC granite was found have the same or increased CR values with all LAAs. In the case of Source 2 and any of the Preston aggregates (gravel and sandstone), the CR value decreases significantly for all LAAs except Kao Gripper® X2. However, MMMC granite was found have the increased CR

values with PermaTac Plus and AD-Here HP Plus. Such observations reiterate the need for a careful selection of LAA when PPA is used as a modifier.

Table 5.7: Compatibility Ratio of PPA+LAA Modified Binders

Source 1				
	Preston Gravel	**Preston Sandstone**	**Snyder Granite**	**MMMC Granite**
S1B4-Pavegrip	2.09	2.02	1.07	3.97
S1B4-Permatac	1.70	1.64	0.87	3.18
S1B4-Adhere	2.19	2.12	1.12	4.15
S1B4-Evotherm	2.18	2.11	1.11	4.10
S1B3	2.21	2.12	0.95	2.93
S1B4 (Gripper)	2.26	2.18	0.98	2.93
Source 2				
	Preston Gravel	**Preston Sandstone**	**Snyder Granite**	**MMMC Granite**
S2B4-Pavegrip	1.79	1.73	0.92	3.33
S2B4-Permatac	2.23	2.15	1.14	4.20
S2B4-Adhere	2.36	2.28	1.21	4.43
S2B4-Evotherm	1.67	1.61	0.85	3.05
S2B3	3.37	3.27	1.43	3.72
S2B4 (Gripper)	3.07	2.96	1.28	3.36

5.1.6 Elastic Recovery (ER) and Multiple Stress Creep Recovery (MSCR)

Elastic recovery (ER) tests of the unaged binder samples were performed at ArDOT Materials Division under the guidance of Ms. Dawn Richards. The ER tests were done in accordance with AASHTO T 301. As expected, very high ER values were observed for binders containing SBS or in a combination of SBS and PPA. The corresponding ER values for S1B7, S1B8, S2B7, and S2B8 were found to be 85%, 84%, 88.5%, and 84%, respectively. The base binder samples (S1B1 and S2B1) did not show any noticeable ER, which was also expected. However, very low ER values were observed for binders containing PPA (no SBS) or PPA along with LAA. The corresponding ER values of S1B2, S1B3, S1B4, S1B5, and S1B6 binder samples were found to be 5.5%, 6.5%, 7.0%, 7.5%, and 8.5%, respectively. Similarly, the ER values of S2B2, S2B3, S2B4, S2B5, and S2B6 binder samples were found to be 6.5%, 7.0%, 7.0%, 10.5%, and 10.0%.

The MSCR tests were conducted on RTFO-aged binder samples at A-State Asphalt Binders Laboratory. The MSCR tests were conducted in accordance with AASHTO T 350. Similar to ER, very low MSCR % Recovery values were observed for PPA-modified binders. The MSCR percent recovery values of S1B1, S1B2, S1B3, and S1B6 were found to be 1.91%, 4.26%, 2.46%, and 9.91%. Based on J_{nr} values, the MSCR grades of S1B1, S1B2, S1B3, and S1B6 were PG 64S-XX, PG 64H-XX, PG 64S-XX, and PG 64H-XX, respectively. Binders from Source 2 showed similar behavior. MSCR % Recovery values of S2B1, S2B2, S2B3, and S2B6 were found to be 1.38%, 3.35%, 4.03%, and 8.91%, respectively. Furthermore, the MSCR grade of any of these binders (S2B1, S2B2, S2B3, or S2B6) was estimated as PG 64H-XX. These test results suggest that neither ER nor MSCR test is capable of characterizing PPA-modified binders' creep and recovery behavior. It could be noted that both ER and MSCR tests were meant to be used for characterizing polymer-modified binders. The former is a PG Plus test, and the latter is meant to be a replacement of the ER test method. Thus, it is recommended that an alternate be explored for proper investigation of PPA-modified binders.

5.2 Chemical Test Results

5.2.1 Acidity Measurement Test

This test is useful in understanding the level of acidity of the binder, and thereby selecting compatible aggregates for the asphalt mixture. Asphalt binders were tested for the acid number to check the level of acidity after PPA- and/or SBS-modification. Figure 5.25 shows acid number data for binders from both sources. The test results revealed that the neat binder from Source 1 was inherently basic and that from Source 2 acidic. The acidity increases (pH decreases) with the addition of PPA, which is expected as PPA is an acid. It is also observed that the foaming (S1B3 or S2B3) of the PPA-modified binder (S1B5 or S2B5) reduces its acidity.

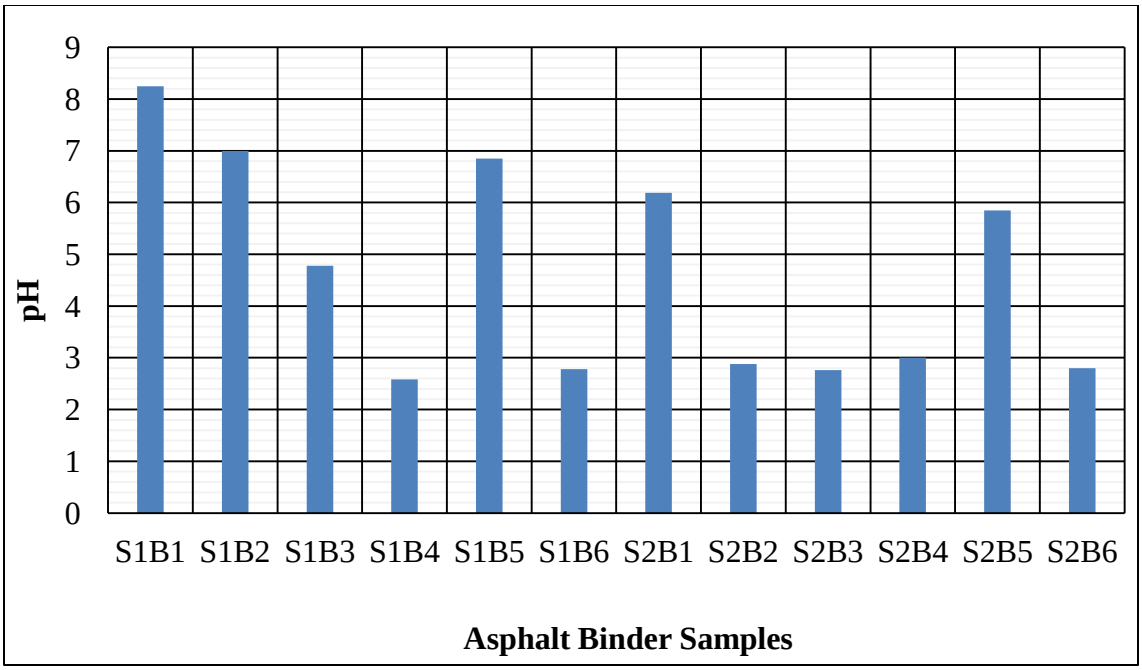

Figure 5.25: pH of Asphalt Binders.

5.2.2 Saturates Aromatics Resins and Asphaltenes (SARA) Analysis

The outcomes of the chromatographic separation of both sets of binders were analyzed. The results have been presented in Figures 5.26 and 5.27. Asphalt binder samples from the Canadian crude source, i.e. Source 1, had a high asphaltenes content (15%) compared to those (12.8%) from the Arabian crude source, i.e. Source 2. The asphaltenes content increases and resins content decreases with the addition of PPA, which makes the binder stiffer than its base binder. These observations are in agreement with the findings of rheological data presented earlier in this report.

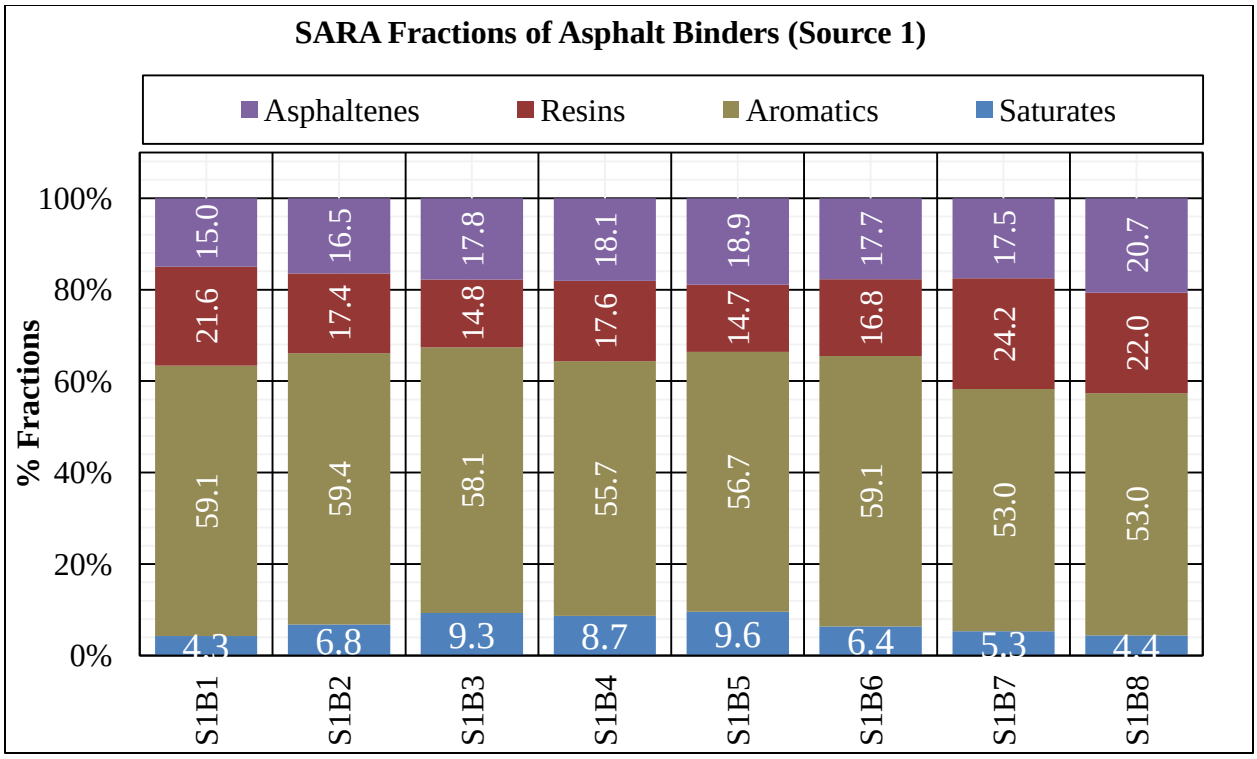

Figure 5.26: SARA Fractions of Source 1 Asphalt Binders.

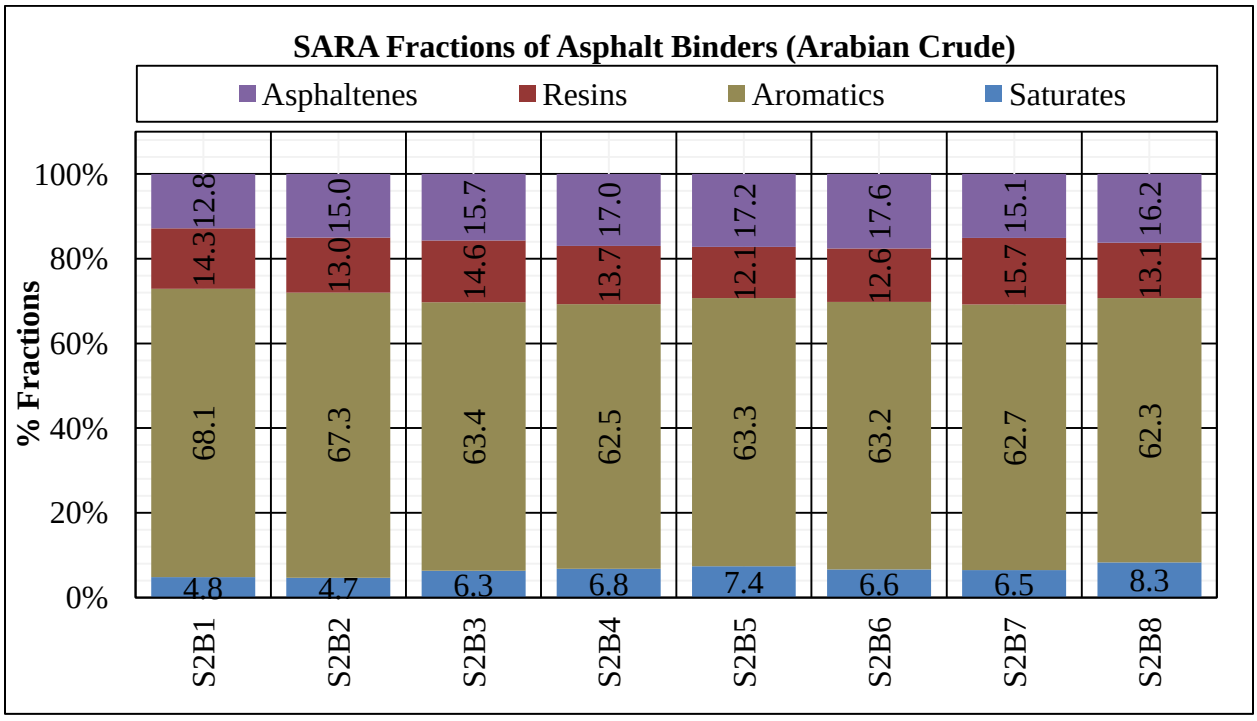

Figure 5.27: SARA Fractions of Source 2 Asphalt Binders.

5.2.3 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analysis is a common and quick technique to identify the functional groups present in asphalt binders. It is commonly used in the asphalt industry to identify the presence of any specific functional group in asphalt binders. The main purpose of performing the FTIR tests (the IR card method) was to observe any differences in the peaks due to the addition of PPA in asphalt binders. Figure 5.28 shows the FTIR spectra of S1B1 and S1B2, and Figure 5.29 shows the FTIR spectrum for PPA-modified binders from S1.

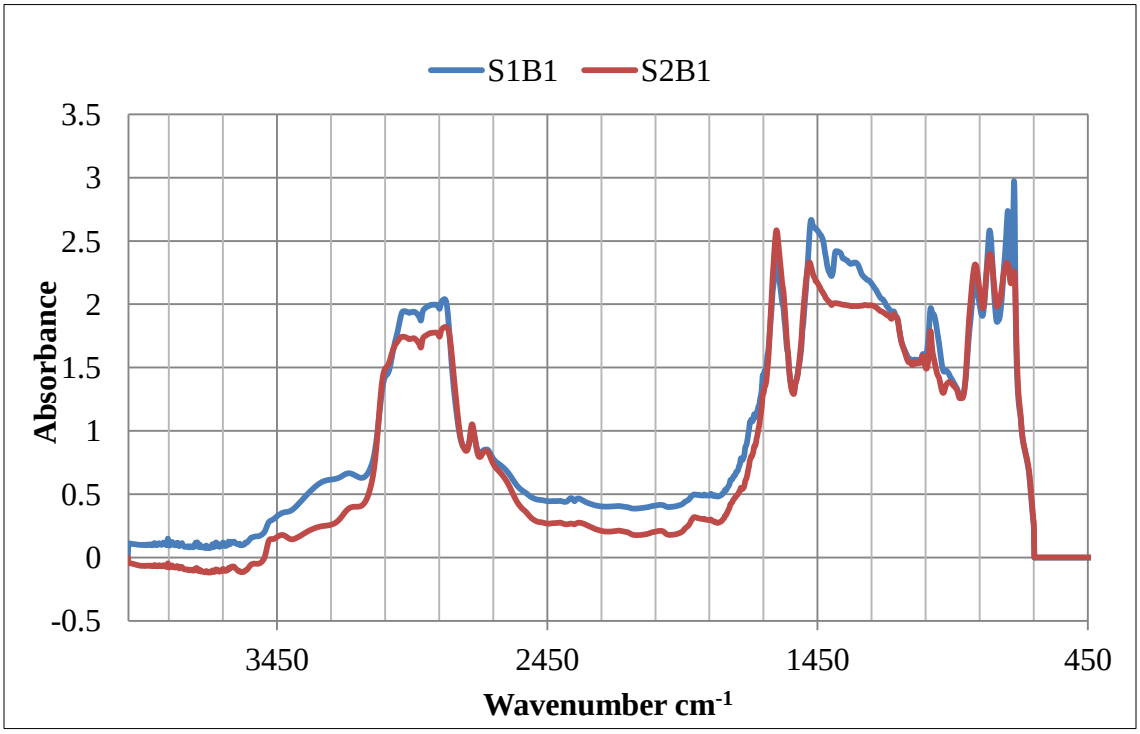

Figure 5.28: FTIR Spectrum of PG 64-22 Binders from S1 and S2.

At wavenumber between 800 and 810 cm^{-1}, a peak was located for all three binder samples. This marks the presence of alkyl halides. It could be noted that the absorbance of this peak for S1B2 increases with an increasing amount of PPA, but for more than the optimum amount, which was 0.5% for this source, the absorbance reduced. This peak could be described as the control functional group for unmodified binders. Moreover, the peak from 1740 -1600 cm^{-1} signifies a strong presence of –OH. On the other hand, the peak found in the region of 1380-1395 cm^{-1} strongly marks the presence of aromatics (= C-H). The second analyzed peak was

found at 1595 to 1600 cm^{-1}, which marks the presence of aromatics as well, prompting to call this as a predominant functional group for PPA-modified asphalt.

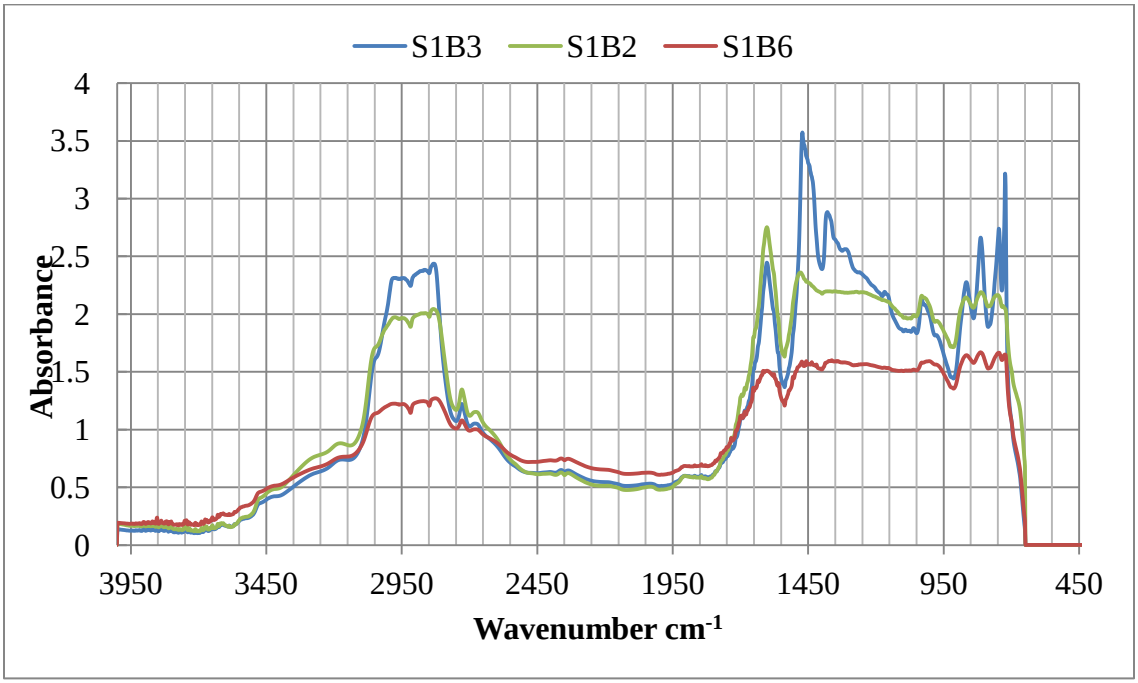

Figure 5.29: FTIR Spectra of PPA-modified Binders from Source 1.

Figure 5.30 shows the FTIR spectra of PPA-modified binders from Source 2. As seen in this figure, a peak was found at 800 to 810 cm^{-1} in Source 2 binders as well. However, unlike Source 1, S2B6 showed the highest absorbance in Source 2, whereas S2B2 showed the lowest. Furthermore, a similar dip was also found at 1540 cm^{-1} in this source. Similar to the mechanistic tests, FTIR tests were also performed on the LAA modified binders.

Figures 5.31 and 5.32 show the FTIR spectra of PPA+LAA modified binders from Sources 1 and 2, respectively. The peaks for these binders are in agreement with the data presented earlier. However, higher absorbance values are observed at 1595 to 1600 cm^{-1} cm^{-1}. At a wavenumber of 1380-1395 cm^{-1}, a reasonably lower peak than the PPA-modified binder is observed.

Figures 5.33 and 5.34 show the FTIR spectra for S2B7 and S2B8, respectively. FTIR analysis of polymer modified samples shows peaks at 965cm^{-1}, attributed to SB and SBS. The ratio of the SB and SBS peak versus the asphalt peak is then used to determine the polymer content of the asphalt.

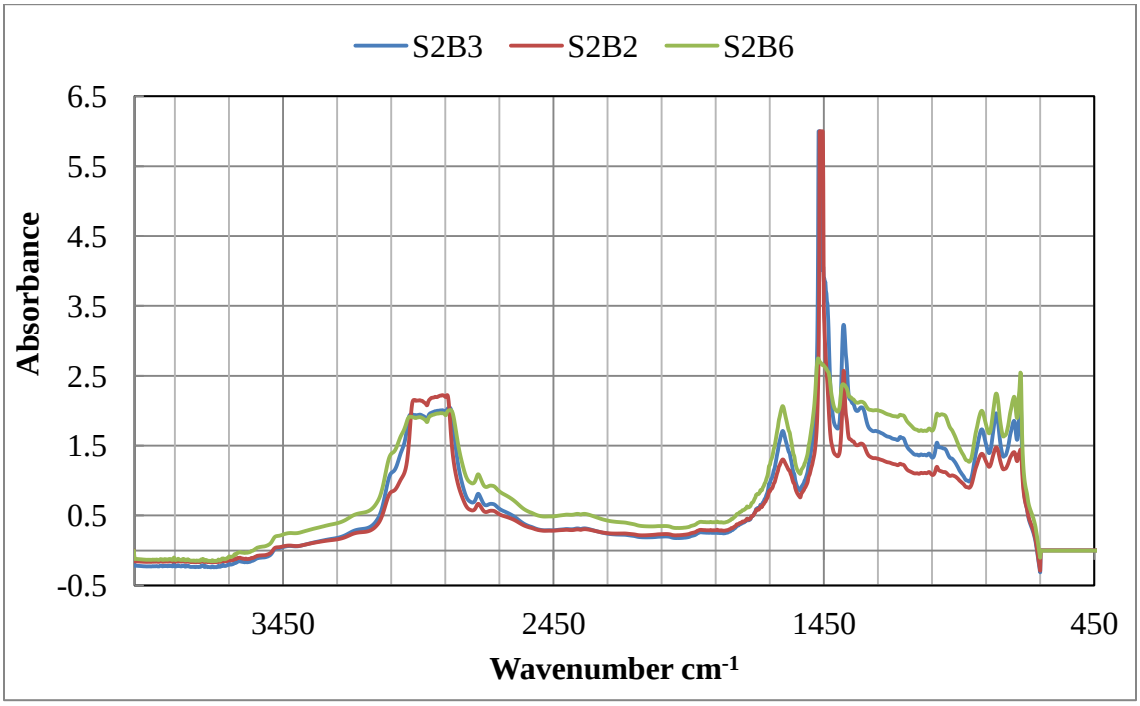

Figure 5.30: FTIR Spectra of PPA-modified Binders from Source 2.

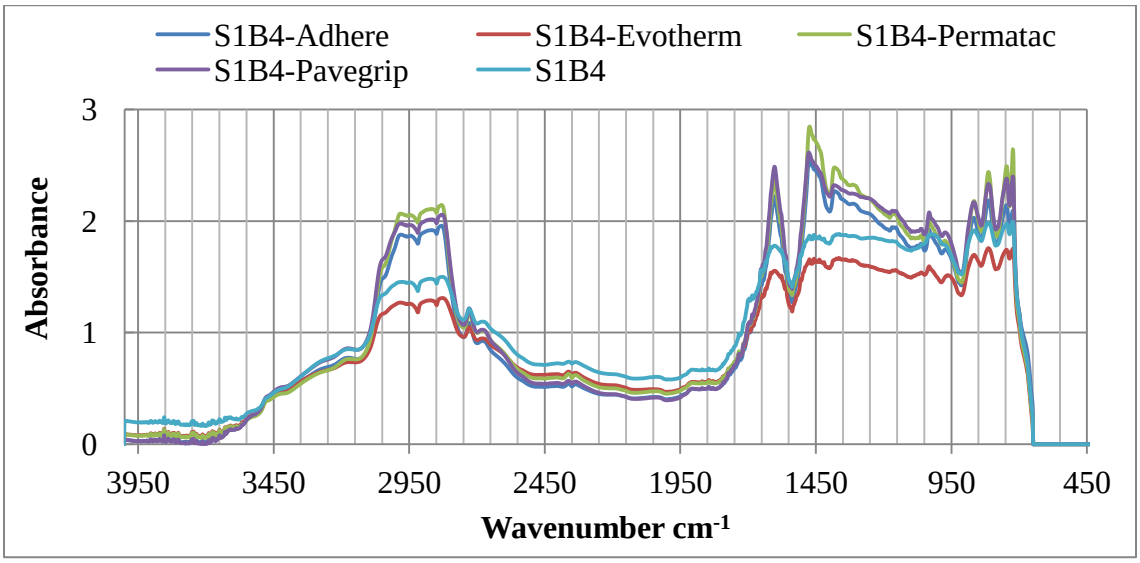

Figure 5.31: FTIR Spectrum for PPA+LAA binders from Source 1.

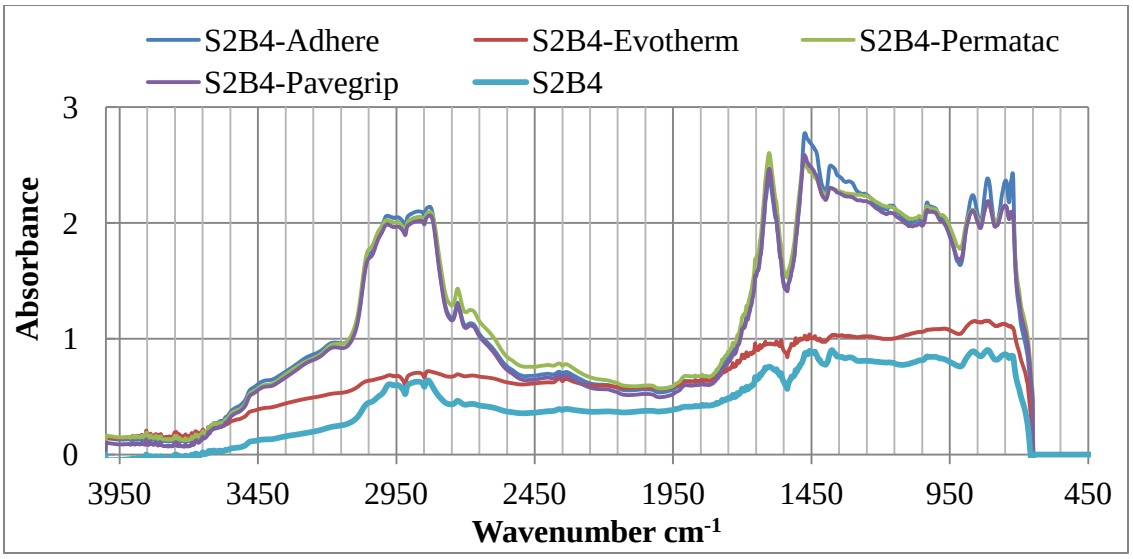

Figure 5.32: FTIR Spectrum for PPA+LAA Modified Binders from Source 2.

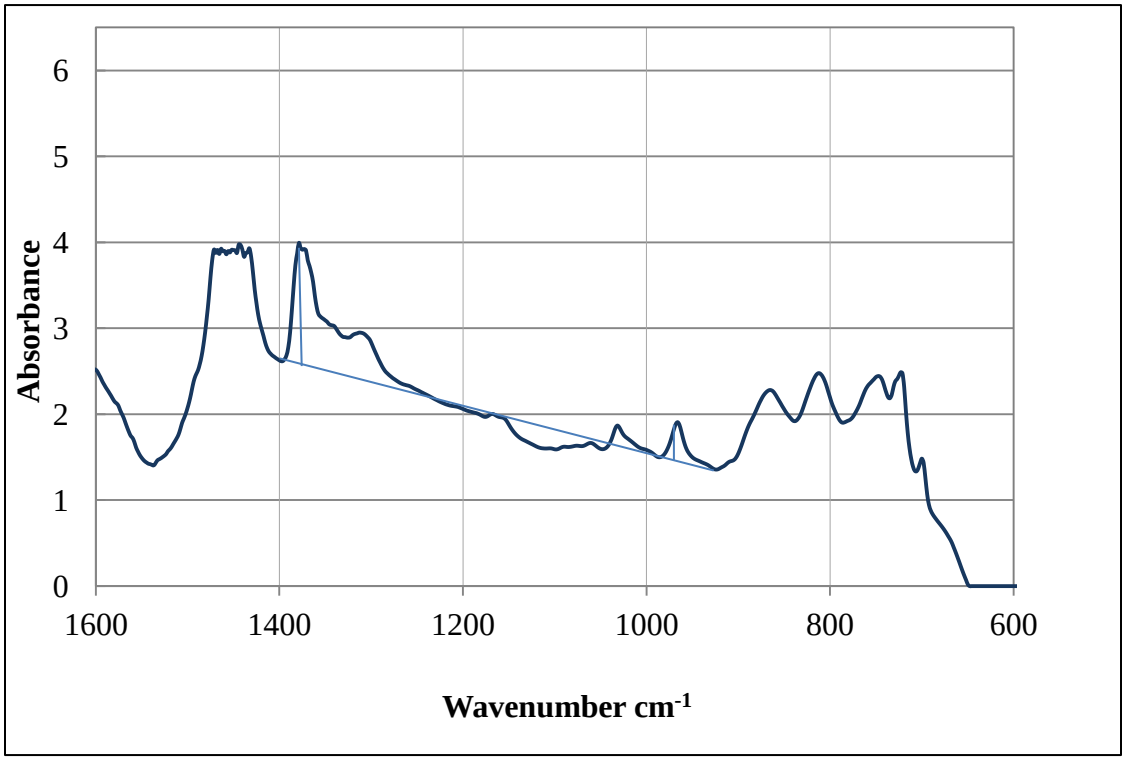

Figure 5.33: Polymer Content Analysis of S2B7.

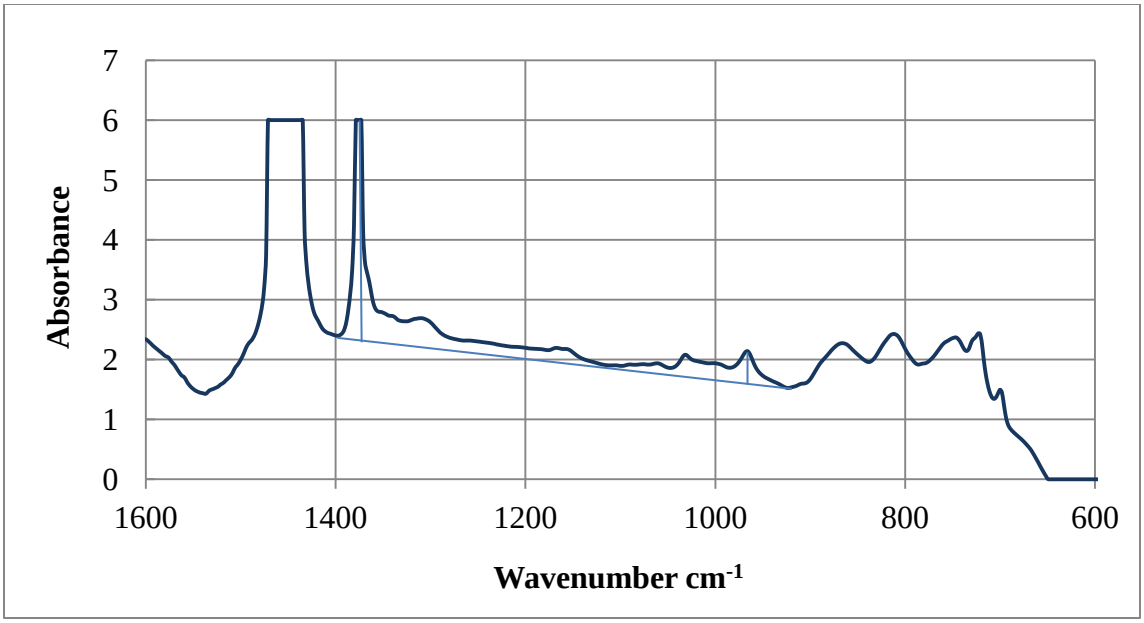

Figure 5.34: Polymer Content Analysis of S2B8.

The absorbance and area analysis for S2B7 (2% SBS) and S2B8 (2% SBS and 0.75% PPA) is shown in Table 5.8. As seen in this table the absorbance ratios of S1B7 and S1B8 are 0.35 and 0.10, respectively, which correspond to a corresponding polymer content of 5%, and 1.85%. However, the SBS content in these binders was 2%. According to the area analysis, the area rations of S1B7 and S1B8 are 0.25 and 0.13, respectively, indicating the corresponding polymer contents of 3.5% and 2%. Thus, the area analysis appears to be a better approach than the absorbance analysis to predict the polymer content.

Table 5.8: Absorbance and Area Analysis of S2B7 and S2B8

Sample	Absorbance	Area	Absorbance	Area	Absorbance Ratio	Area Ratio
	Peak 966		Peak 1375			
S1B7	0.428	8.463	1.237	34.432	0.35	0.25
S1B8	0.382	6.552	3.526	51.334	0.10	0.13

Under the supervision of Ms. Dawn Richards, the ArDOT Materials Division personnel also ran quantitative testing for the polymer content by FTIR on the samples that were indicated as having 2% SBS. This testing was done in accordance with AASHTO T 302. The SBS contents in S1B7, S1B8, S2B7, and S2B8 samples were found to be 1.97%, 2.07%, 1.96%, and 2.19%, respectively. Interestingly, after heating some of the cans and mixing them thoroughly,

consistent and expected results were observed. The repeatability of the test method was supposed to be +/- 0.2%, which also found in this study.

5.3 Mixture Performance Tests

5.3.1 Evaluation of Rutting and Stripping of Asphalt (ERSA) Test

The ERSA test determines the susceptibility of premature failure of HMA caused by weakness in the aggregate structure, inadequate binder stiffness, or moisture damage. The ERSA test is essentially identical to the Hamburg Wheel Test. The wheel has a load of 158 lbs, and it should make 52 passes across the specimen per minute with a maximum speed of 0.305 m/s. The machine is limited to running 20,000 cycles. Arkansas specifications for surface courses require a maximum rut depth of 8.000 mm at 8,000 cycles for an APA style wheel tracking tests. For ERSA test, the maximum cycle value of 8,000 cycles and a maximum rut depth of 8.0 mm are utilized.

The ERSA test was done for five mixtures, namely, S1B1, S1B3, S1B4, S1B5, and S1B7. The aggregates were from Van Buren and are known to be moisture susceptible. The summary of ERSA test results is shown in Figure 5.35. For S1B1, the numbers of passes required for 8.0 mm rut depth were 13,372 (6,686 cycles). After 16,000 passes (8,000 cycles), the rut depth was 10.26 mm. In the case of the foamed PPA-modified PG 70-22 mixture (S1B5), the passes at to 8.0 mm were 10,494 (5,247 cycles). The PPA-modified PG 70-22 mixture (S1B3) reached a rut depth of 1.48 mm at 8000 cycles. The rut depths for S1B4 and S1B7 mixtures were 1.18 and 2.7 mm, respectively. On the other hand, for the PPA-modified PG 70-22 mixture (S1B3), PPA+LAA modified mixture (S1B4), and SBS-modified PG 70-22 (S1B7), after 16,000 passes (8,000 cycles), the rut depth of 8.0 mm was not reached (Table 5.9). In another way, the number of passes to reach a rut depth of 8 mm for these mixes (S1B3, S1B4, and S1B7) were more than 16,000. Therefore, it is demonstrated that adding either PPA or PPA+LAA to the binder helps to improve the rutting resistance of the mixture by more than a 100%.

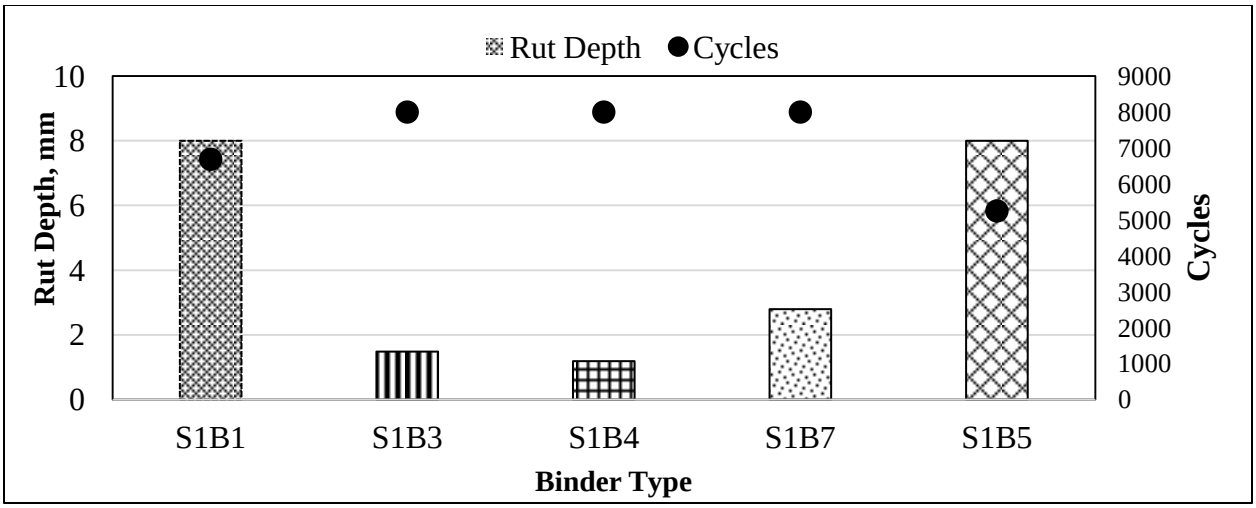

Figure 5.35: Summary of ERSA Test Results.

Table 5.9: Evaluation of Rutting and Stripping of Asphalt Mixtures

Mixture with Binder Sample	No. of Passes to 8.000 mm			No. of Cycles to 8.000 mm		
	Left	Right	Average	Left	Right	Average
PG 64-22 (S1B1)	11,682	15,060	13,371	5,841	7,530	6,686
PG 64-22 + 0.5% PPA (S1B3)	>16,000	>16,000	>16,000	>8,000	>8,000	>8,000
PG 64-22 + 0.5% PPA + 0.5% LAA (S1B4)	>16,000	>16,000	>16,000	>8,000	>8,000	>8,000
PG 64-22 + 2% SBS (S1B5)	>16,000	>16,000	>16,000	>8,000	>8,000	>8,000

5.3.2 Uniaxial Dynamic Modulus

Dynamic modulus is often used to rank rutting and cracking characteristics of asphalt concrete. In order to measure the Dynamic Modulus of an asphalt concrete sample, a dynamic load is applied at different frequencies: 0.1 Hz, 0.5 Hz, 1.0 Hz, 5 Hz, 10 Hz, and 25 Hz. Samples are tested at five different temperatures: -10°C, 4°C, 21°C, 37°C, and 54℃. The amplitude of the

load as well as the vertical deformation of the specimen using three extensometers is recorded. The ratio of the amplitudes of vertical stress to vertical strains is then computed in order to obtain the value of dynamic modulus for each combination of frequency and temperature by following AASHTO T62-07. Specimens of 100 mm diameter and 150 mm height were used. Figure 5.36 shows master curves for five mixtures, and Figure 5.37 shows the shift factors. While the three master curves had a relatively similar dynamic modulus, PG 64-22 (S1B1), PPA-modified PG 70-22 (S1B3), PPA+LAA modified (S1B4), PPA-modified foamed (S1B5) and SBS-modified (S1B7) mixtures literally lie on top of each other, while the S1B5 shows a slightly higher stiffness at intermediate reduced frequencies. Additionally, the SBS-modified PG 70-22 (S1B7) mixture shows higher stiffness in the low frequencies and lower stiffness in the higher frequencies. Lower stiffness at low frequencies indicates a lower level of cracking susceptibility while lower stiffness at high frequencies indicates a higher level of rutting susceptibility.

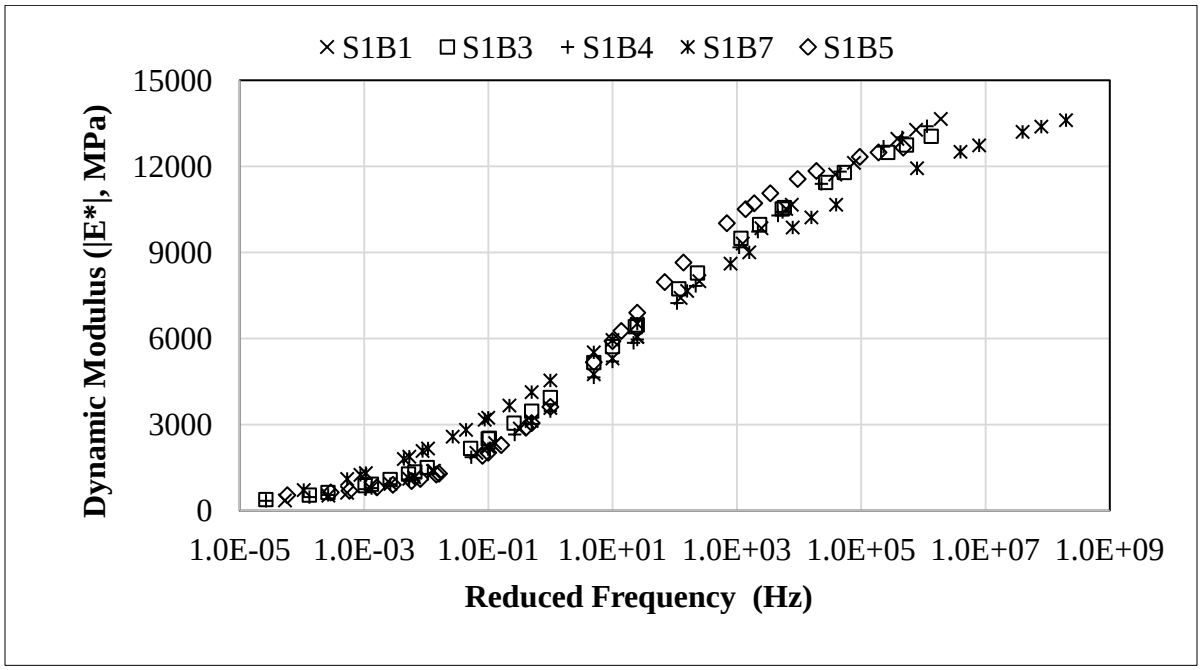

Figure 5.36: Uniaxial Dynamic Modulus Master Curves Summary.

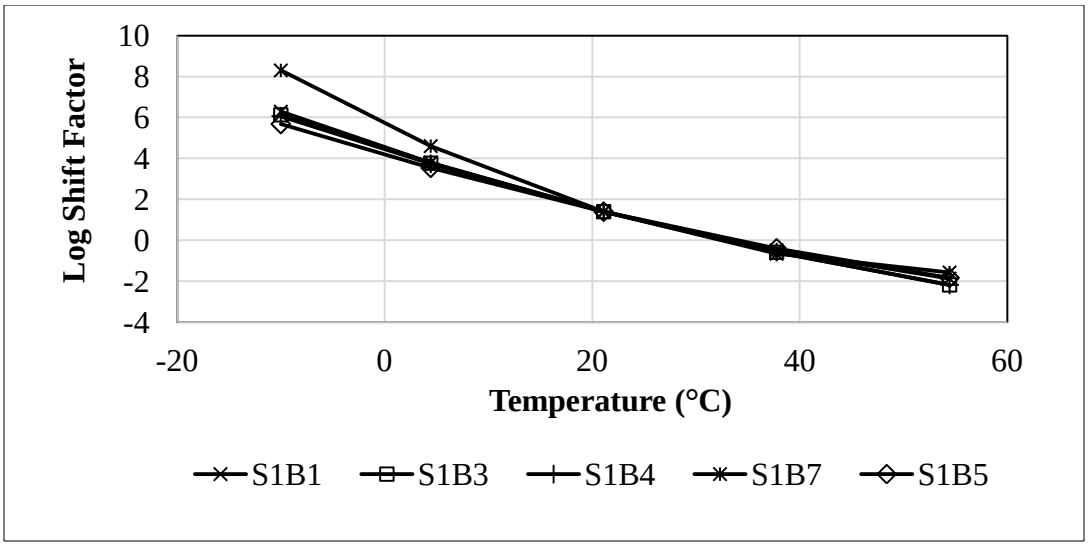

Figure 5.37: Shift Factor – Uniaxial Dynamic Modulus.

5.3.3. Semi-Circular Bend (SCB) Fracture Test

Semi-Circular Bend (SCB) Test determines the fracture energy and fracture toughness at low temperatures of asphalt mixtures by its semi-circular geometry. Figures 5.38 and 5.39 show the fracture energy in J/m^2 of each material at -10°C and -24°C, respectively. In Figure 5.38, S1B3 shows greater fracture energy than the other materials at -10°C, indicating the 0.5% PPA increased cracking resistance at low temperatures greater than the low temperature binder grade. However, in Figure 5.39, S1B7 shows greater fracture energy than the other materials at -24°C, indicating the SBS modification increased cracking resistance at low temperatures lower than the low temperature binder grade.

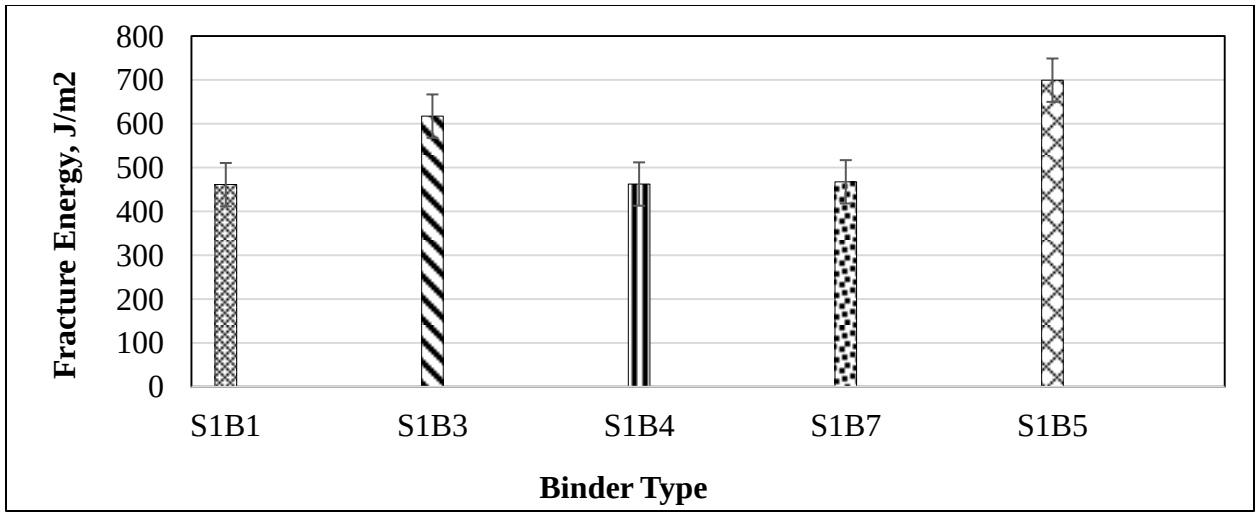

Figure 5.38: Summary of SCB Test Fracture Energy at -10°C.

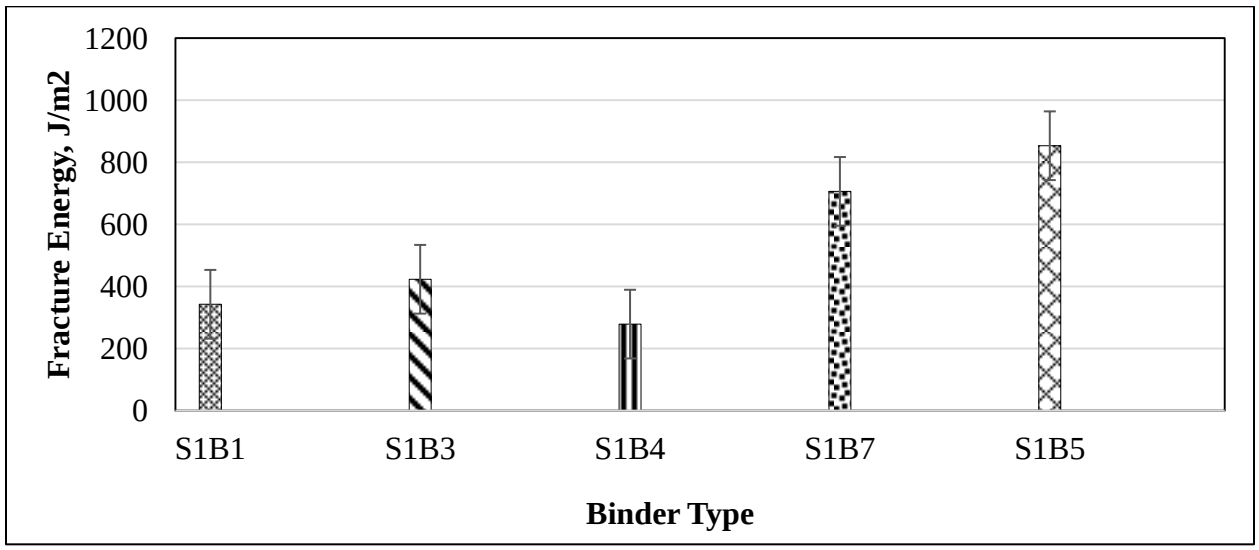

Figure 5.39: Summary of SCB Test Fracture Energy at -24°C.

5.3.4 IDT Creep Compliance and Indirect Tensile Strength

Creep compliance is defined as the time-dependent strain divided by the applied stress and indirect tensile strength is the strength shown by a specimen that is subject to tension. The purpose of the test was to determine the tensile creep by the application of a static load of fixed magnitude along the diametrical axis of the specimen for the duration of 100 seconds. During the creep test, loads were selected to remain horizontal strain in the linear viscoelastic range, which

was typically below of 500 x 10^{-6} mm/mm. When the creep tests were finished at each temperature, the tensile strength was determined by applying a load to the specimen at a rate of 12.5mm of ram movement per minute. The IDT tensile strengths at -10°C for all four samples are shown in Figure 5.40. The PPA-modified foamed PG 70-22 binder S1B5 showed the highest tensile strength among the five tested mixtures, indicating the highest cracking resistance. Furthermore, between the two PG 70-22 binders, the PPA-modified (S1B3) mixture showed higher tensile strength than the SBS-modified (S1B7) mixture.

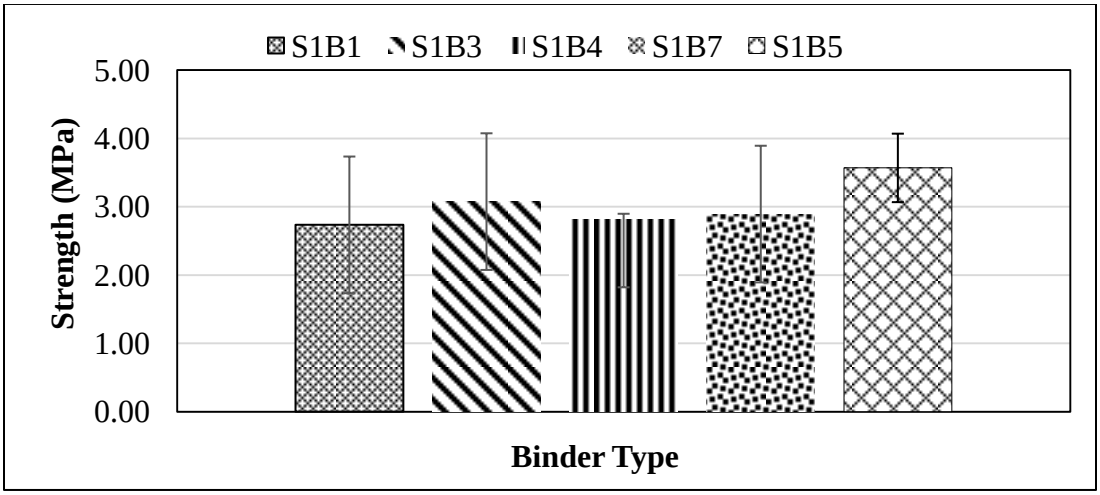

Figure 5.40: Summary of IDT Tensile Strength at -10°C.

5.3.5 Tensile Strength Ratio

The purpose of tensile strength ratio (TSR) (AASHTO T 283) test was to assess the effects of saturation and accelerated water conditioning with a freeze-thaw cycle, of compacted asphalt mixtures. The tensile strength ratios of five tested mixture samples are shown in Figure 5.41. Between the two PG 70-22 mixtures, the SBS-modified (S1B7) mixture showed higher tensile strength under both wet and dry conditions. Moreover, the tensile strength results of LAA-modified mixtures did not show any improvement from the results of PPA-modified mixtures, which correlates with the data obtained from the SFE analysis of the corresponding asphalt binders.

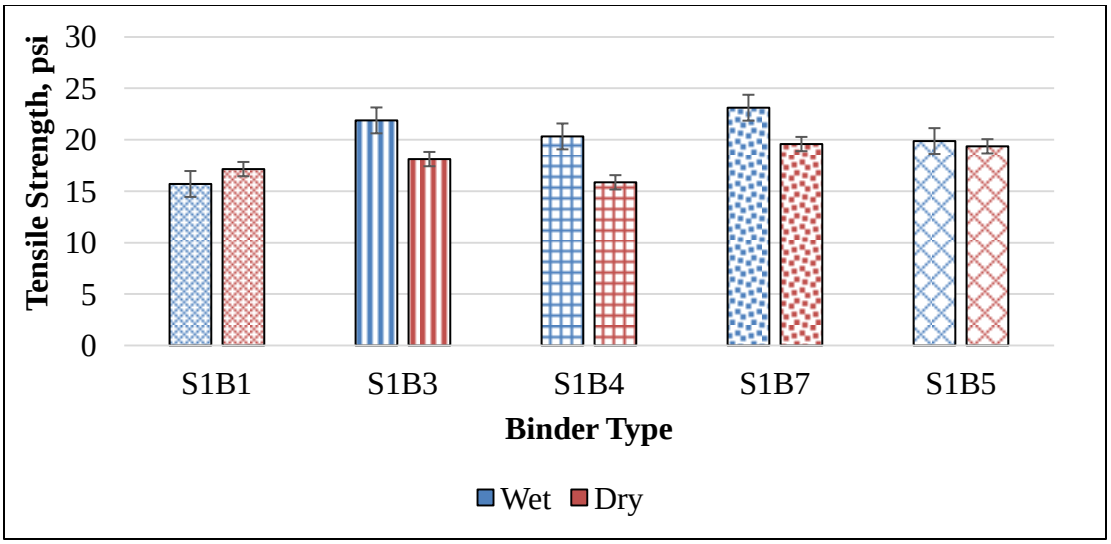

Figure 5.41: Summary of Tensile Strength Ratio.

5.4 Field Performance Data Collection

RAP samples containing PG 76-22 binder were collected from I-30 and I-40 to check the presence of PPA along with any possible detrimental effects on the mixture performance. These RAP samples were collected as part of a related project (ArDOT sponsored TRC 1404). In addition, field performance data of these pavement sections were collected from the ArDOT databases. The ArDOT-supplied MMHIS software was used to analyze the necessary data retrieved from the database. Two types of pavement performance data (IRI and rutting) were analyzed.

5.4.1 Acid Detection Test

At first, the recovered binders from RAPs of ten pavement sections were tested to detect the presence of PPA. The binder was separated from aggregates of the RAP by following the centrifuge method, in which nPB was used as the solvent. The binder from the solution (binder+nPB) was then recovered by using a rotavapor. A total of 42 recovered binder samples were tested for PPA detection. The details of these binder samples are shown in Table 5.10. Among the 42 samples tested for acid detection test, only five of them were tested positive for PPA. All five of those PPA-modified binders were recovered from one particular section. The ArDOT job number for this section is B60115 (Section No. 10), which is located on I-30 near Arkadelphia, AR. The cylindrical core samples were collected from the I-30 Westbound near Mile Markers 242.8, 246.0, and 248.0. For these locations, the IRI and rutting data were also

analyzed by using the MMHIS software.

Table 5.10: Acid Detection Test Sample Details for Field Performance Data Collection

Section No.	Section Performance	Job number	Number of Samples Tested	Number of PPA Detected Samples
1	Good	B10102	9	0
2	Medium	B10103	8	0
3	Poor	B40102	7	0
4	Medium	BX0103	5	0
5	Good	BX0102	1	0
6	Poor	BB0803	4	0
7	Poor	BB0805	1	0
8	Poor	BB0105	1	0
9	Good	B70102	1	0
10	Good	B60115	5	5

5.4.2 MMHIS Results

A higher roughness index indicates a severely deteriorated pavement, as roughness index is the measure of the vertical stress received by the pavement surface. Moreover, a higher roughness index indicates a pavement with more surface deformation than a pavement with a lower roughness index. So, it is imperative that a pavement with good performance to have a lower roughness index. Figure 5.42 shows the IRI data for Section 10, which is a “good” performing section. The average IRI values indicate that the roughness of this section was well below the threshold values for Arkansas.

The rutting data for this section is showed in Figure 5.43. Rutting is the permanent surface depression, which is formed along the wheel paths. Similar to the IRI values, rutting values for this section also met the ArDOT cutoff value for a good performing section. The threshold value of rutting in Arkansas for a fair pavement is 0.35 in/mile. As Figure 5.43 shows the rutting values stayed within this value for most of the times.

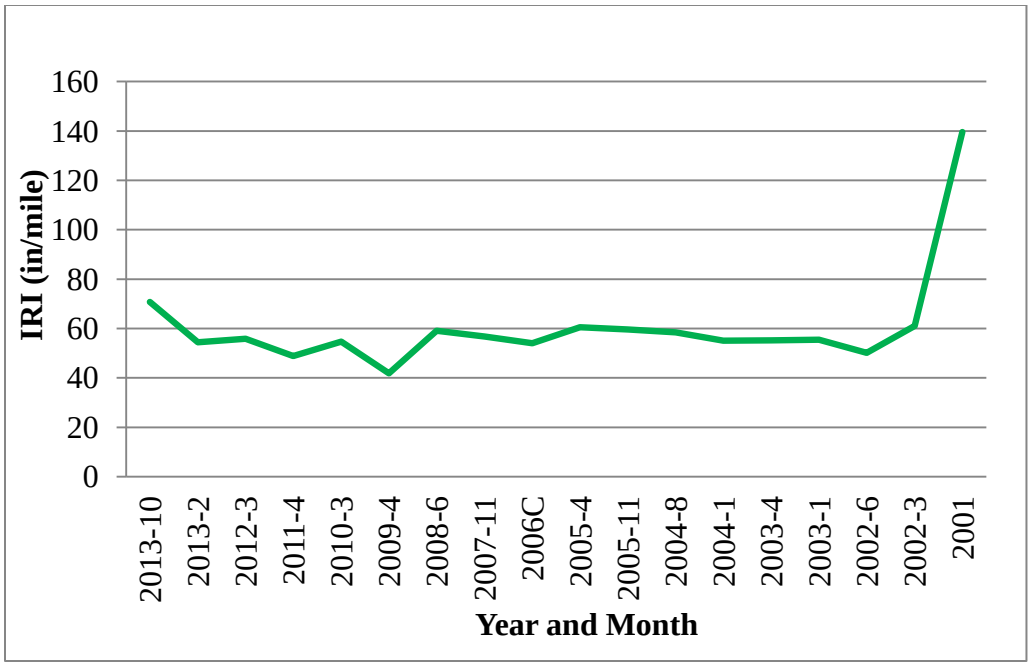

Figure 5.42: Average IRI Values for Mixture Containing PPA-modified Binder.

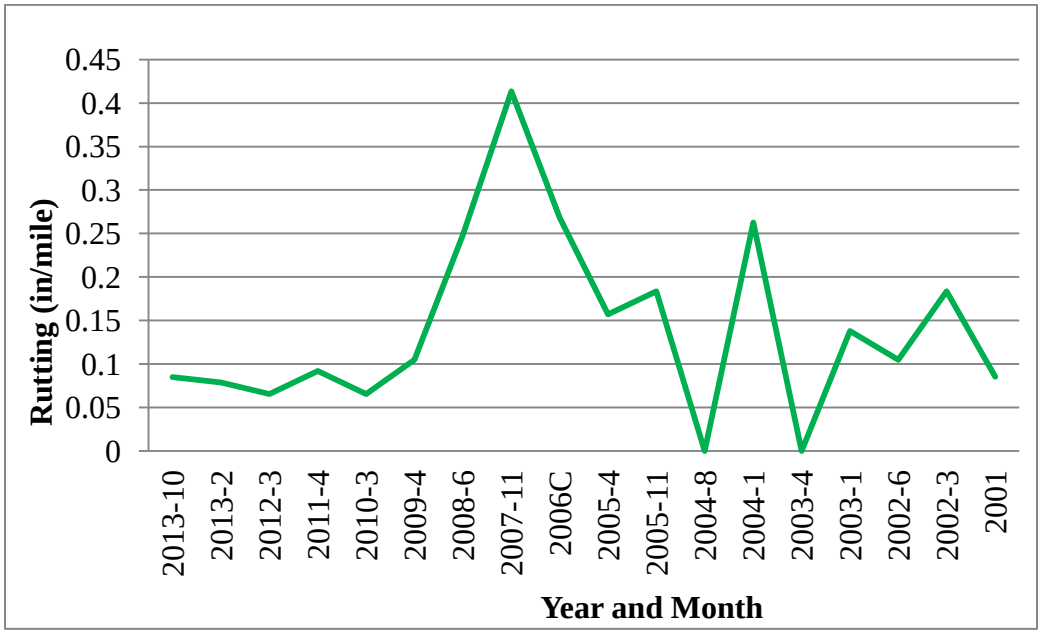

Figure 5.43: Average Rutting Data for Mixture Containing PPA.

5.4.3 Summary of Field Performance Data

The field performance of PPA-modified asphalt mixtures showed no causes of concerns, as the section from which the PPA-modified binder was found was a good pavement section, categorized by the ArDOT engineers.

6. Conclusions and Recommendations

6.1 Conclusions

- Penetration test results showed that PPA reduces the penetration value of asphalt binders, which indicates that PPA hardens the binder. However, SBS-modified binders showed even lower penetration values than the PPA-modified binders. Overall, the binders from Source 2 (S2) were considerably harder than the binders from Source 1 (S1).
- The rotational viscosity (RV) test results showed an increasing trend in viscosity of asphalt binders after PPA modification. However, the SBS-modified binders showed higher viscosities than the PPA-modified binders. The use of LAA decreased the viscosity of PPA-modified PG 70-22 binder.
- DSR test results showed an increase in G*/sinδ values in PPA-modified binders from both sources under both unaged and RTFO aging conditions. However, in the case of Source 1, all LAAs reduced the rutting factor of the PPA-modified binders. In the case of Source 2, only Kao gripper X2 was able to maintain the rutting factor of PPA-modified PG 70-22 binder.
- The fatigue factor (G*•sinδ) values from the DSR tests of PPA-modified binders were less than the corresponding SBS-modified binders, which signifies the possibility of better fatigue resistance of PPA-modified binder than the SBS-modified binder.
- BBR test results showed that PPA modified binders showed lower m-values than corresponding SBS-modified binders. Moreover, the PPA-modified binders showed higher stiffness (S) values at a lower temperature than SBS-modified binder of the same grade. This result could mean that PPA-modified binders could be susceptible to low temperature cracking. Among the sixteen tested binder samples, 0.5% PPA modified binder from Source 2 showed the lowest PG grade.
- The SFE analysis showed PPA-modified asphalts had different cohesive energy for binders from two different crude sources. And, the compatibility analysis of asphalt binders with four different aggregates showed that PPA-modified asphalt binders from Source 1 had lower adhesion energy in the dry condition and higher adhesion energy in the wet condition. The compatibility analysis also showed higher CR values for PPA-modified binders with the optimum dosage rates.

- FTIR analysis of PPA-modified binders with or without LAA showed functional groups such as alkyl halides, alkanes, hydroxyle and carboxylic acids. Throughout the spectrum, various peaks were found which showed the presence of aromatics, which seem to be the controlling functional group for the PPA-modified binders. Moreover, the spectrum of the LAA binders did not show any changes functional groups, but they changed the absorption values of the peaks.
- Mixture test results revealed superior dynamic modulus, creep compliance and indirect tensile strength, fracture energy, and tensile strength ratio of PPA-modified binders compared to the SBS-modified binder of the same PG grade.
- It is recommended that the dosage rate of PPA to be set upon the identification of the crude source of the asphalt binder. If the source is unknown, a dosage rate between 0.5% and 0.75% to be used.

6.2 Recommendations

- In this study, only foamed based WMA technology was tested with PPA-modified binders. However, the effects of different WMA additives needs to be tested on the performance of PPA-modified asphalt binders to ensure the performance of PPA-modified binders with WMA.
- Several LAAs (mostly ArDOT certified ones) were tested for determining the effect with PPA-modified binders. However, as the ArDOT allows many refineries outside Arkansas to supply asphalt binders that might use different LAAs, which could have negative results with PPA-modified binders. So further investigation of other LAAs in PPA-modified asphalts would be helpful.
- No RAP or RAS was used to modify asphalt binders in this study. So, the performance of PPA-modified binders with RAP was unknown. The effects of PPA on RAP and RAS need to be tested.
- Multiple Stress Creep Recover (MSCR) testing is considered as the best approach for evaluation of the rutting potential of the binder in place of the Elastic Recovery (ER). Thus, it is recommended to conduct a thorough MSCR study to establish necessary guidelines.

- Since the ER (a PG Plus test) or MSCR test method is not capable of characterizing PPA-modified binders, a new mechanistic or chemical based test method is recommended to be explored to substitute them.

6.3 Implementation

As mentioned in Section 6.2, additional laboratory tests and field performance of PPA-modified binders are recommended toward implementing the findings of this study. The following implementation strategies can be explored while ArDOT undertakes further studies and/or decisions on PPA-modified binders:

- PPA can be considered as a potential modifier of asphalt binders.
- It is suggested that ArDOT begins building a database about the combination of different modifiers and crude sources of asphalt binders so that necessary directives can be provided to the contractor in selecting compatible LAA and/or WMA additives. It would be the contractor's responsibility to obtain the information of the modifier used in the binder and report it to the ArDOT to ensure compliance.
- AASHTO TP 78 can be used to detect the presence of PPA in asphalt binder. Moreover, Acidity measurement test should be used to determine the extent of acidity in asphalt binders. The details of this test method would be available in the final report.

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The statements contained in this report are the sole responsibility of the authors, and do not necessarily reflect the official views of the Arkansas Department of Transportation. The use of specific product names in this paper does not constitute or imply an endorsement of those products. This document does not constitute a standard, specification, or regulation.

8 References

Walker, D. (2014). The Benefits of Modified Asphalts. Asphalt, *29*(1).

Bahia, H. U., Hanson, D. I., Zeng, M., Zhai, H., Khatri, M. A., & Anderson, R. M. (2001). Characterization of modified asphalt binders in superpave mix design (No. Project 9-10 FY'96).

D'Angelo, J., Kluttz, R., Dongre, R. N., Stephens, K., & Zanzotto, L. (2007). Revision of the Superpave high temperature binder specification: The multiple stress creep recovery test (With Discussion). Journal of the Association of Asphalt Paving Technologists, 76.

McDaniel, R., Soleymani, H., & Shah, A. (2002). Use of reclaimed asphalt pavement (RAP) under Superpave specifications: A regional pooled fund project.

Yildirim, Y. (2007). Polymer modified asphalt binders. Construction and Building Materials, 21(1), 66-72.

Pederson, N. J. (2007). Pavement Lessons Learned from the AASHO Road Test and Performance of the Interstate Highway System. Transport Research Board.

Monismith, C. L., Hudson, W. R., Finn, F. N., Skok Jr, E. L., & Shook, J. F. (2007). What Pavement Research Was Done Following the AASHO Road Test and What Else Could Have Been Done But Was Not. Interstate Highway System, 31.

Hallin, J. P. (2004). Development of the 2002 guide for the design of new and rehabilitated pavement structures: Phase II. Report for National Cooperative Highway Research Program, Transportation Research Board, National Research Council.

Terrel, R.L., and J.A. Epps. (1993). Using Additives and Modifiers in Hot Mixed Asphalt (Part A), National Asphalt Pavement Association, Report No. Q1P114A.

Lewandowski, L. H. (1994). Polymer modification of paving asphalt binders. Rubber Chemistry and Technology, 67(3), 447-480.

Orange, G., Martin, J. V., Menapace, A., Hemsley, M., & Baumgardner, G. L. (2004). Rutting and moisture resistance of asphalt mixtures containing polymer and polyphosphoric acid modified bitumen. Road materials and pavement design, 5(3), 323-354.

PATENT. (1997). WO 98/44047 (Ergon Inc.).

Orange, G., Dupuis, D., Martin, J. V., Farcas, F., Such, C., & Marcant, B. (2004). Chemical modification of bitumen through polyphosphoric acid: properties-micro-structure relationship. In PROCEEDINGS OF THE 3RD EURASPHALT AND EUROBITUME CONGRESS HELD VIENNA, MAY 2004 (Vol. 1).

Martin, J. V., Orange, G., & Marcant, B. (2004, June). Effect of Polyphosphoric Acid on Aging Behavior of Bituminous Binder. In the 41st Petersen Asphalt Research Conference, Laramie, WY.

Bennert, T., & Martin, J. V. (2012). Polyphosphoric Acid in Combination with Styrene-Butadiene-Styrene Block Copolymer. Polyphosphoric Acid Modification of Asphalt Binders, 70.

Tam, K. (2009). Polyphosphoric Acid–Modified Asphalt Cement. Polyphosphoric Acid Modification of Asphalt Binders, 109.

McGennis, R. B. (2009). Implementation of Polyphosphoric Acid Modification of Asphalt Binders and Related Experience. Polyphosphoric Acid Modification of Asphalt Binders, 136.

Ryan, J., & D'Angelo, J. A. (2012). Wisconsin Approach to Binder Modification. Transportation Research E-Circular, (E-C160).

Baumgardner, G. L. (2009). Why and How of Polyphosphoric Acid Modification? Polyphosphoric Acid Modification of Asphalt Binders, 14.

Masson, J. F. (2008). Brief review of the chemistry of polyphosphoric acid (PPA) and bitumen. Energy & Fuels, 22(4), 2637-2640.

Pamplona, T.F., Faxina, A.L. (2015). Effect of Polyphosphoric Acid on Asphalt binders with different chemical composition. 94th Annual Transportation Research Board Meeting Compendium Papers, Washington, D.C.

Li, X., Clyne, T., Reinke, G., Johnson, E. N., Gibson, N, Kutay, M. E. (2011). Laboratory Evaluation of Asphalt Binders and Mixtures Containing Polyphosphoric Acid. 90th Annual Transportation Research Board Meeting Compendium Papers, Washington, D.C.

Kodrat, I., Sohn, D., Hesp, S. (2007). Comparison of Polyphosphoric Acid-Modified Asphalt Binders with Straight and Polymer Modified Materials. J. Transportation Research Board, No. 1998, pp. 47-55.

Huang, S., Turner, T., Miknis, F., Thomas, K. (2008). Long Term Aging Characteristics of Polyphosphoric Acid-Modified Asphalts. J. Transportation Research Board, No. 2051, pp. 1-7.

Jafari, M., Babazadeh, A., Aflaki, S., (2015). Effects of Stress Levels on the Creep and Recovery Behavior of Modified Asphalt Binders with the Same Continuous Performance Grades. 94th Annual Transportation Research Board Meeting Compendium Papers, Washington, D.C.

Huang, S., Miknis, F., Schuster, W., Salmans, S., Farrar, M., Boysen, R. (2011). Rheological and chemical properties of hydrated lime and polyphosphoric acid- modified asphalts with long term aging. Journal of Materials in Civil Engineering. 23(5).

Baumgardner, G. L., Masson, J. F., Hardee, J. R., Menapace, A. M., & Williams, A. G. (2005). Polyphosphoric acid modified asphalt: proposed mechanisms. Journal of the Association of Asphalt Paving Technologists, 74, 283-305.

Daranga, C., Clopotel, C., Mofolasayo, A., & Bahia, H. U. (2009). Storage Stability and Effect of Mineral Surface on Polyphosphoric Acid-Modified Asphalt Binders. In Transportation Research Board 88th Annual Meeting (No. 09-2973).

Shulga, O., Maldonado, R., Romagosa, H., (2012). Effect of Foaming on Performance of Asphalt Modified with Polyphosphoric Acid. Retrieved from: http://www.icl-pp.com/SiteCollectionDocuments/Industrial/PPA%20in%20Asphalt/Application%20of%20PPA%20in%20WMA.pdf . Last accessed 10/11/16.

Maine Department of Transportation (2013). Field Test of a Polyphosphoric Acid (PPA) Modified Asphalt Binder on Rt. 1 in Perry. Technical Report 13-03. Retrieved from: http://ntl.bts.gov/lib/52000/52500/52557/report1303f.pdf. Last accessed 7/28/15.

Federal Highway Administration (FHWA). (2012). The Use and Performance of Asphalt Binder Modified with Polyphosphoric Acid (PPA). FHWA-HIF-012-030.

D'Angelo., J. A. (2009). Effect of polyphosphoric acid on asphalt binder properties. Transportation Research Circular E-C160, Polyphosphoric Acid Modification of Asphalt Binders, PP. 27-39.

Al-Qadi, I. L., Abauwad, I. M., Dhasmana, H., & Coenen, A. R. (2014). Effects of Various Asphalt Binder Additives/Modifiers on Moisture-Susceptible Asphaltic Mixtures. Illinois Center for Transportation.

Yan, K., Zhang, H., & Xu, H. (2013). Effect of polyphosphoric acid on physical properties, chemical composition and morphology of bitumen. Construction and Building Materials, 47, 92-98.

Baldino, N., Gabriele, D., Rossi, C. O., Seta, L., Lupi, F. R., & Caputo, P. (2012). Low temperature rheology of polyphosphoric acid (PPA) added bitumen. Construction and Building Materials, 36, 592-596.

Xiao, F., Amirkhanian, S., Wang, H., & Hao, P. (2014). Rheological property investigations for polymer and polyphosphoric acid modified asphalt binders at high temperatures. Construction and Building Materials, 64, 316-323.

Zhang, F., & Yu, J. (2009). The research for high-performance SBR compound modified asphalt. Construction and Building Materials, 24(3), 410-418.

Ryan, J., & Braham, A. (2015). The characterisation of foamed asphalt cement using a rotational viscometer. International Journal of Pavement Engineering, 1-9.

Scribd (2016). Table of Characteristic IR Absorptions. Online Article. Retrieved from the internet. https://www.scribd.com/doc/129244226/Table-of-Characteristic-IR-Absorptions. Last Access 10/23/2016.

Jia, X., Huang, B., Bowers, B. F., & Zhao, S. (2014). Infrared spectra and rheological properties of asphalt cement containing waste engine oil residues. Construction and Building Materials, 50, 683-691.

Retrieved from the Internet. Characteristic IR Absorption Frequencies of Organic Functional Groups. http://www2.ups.edu/faculty/hanson/Spectroscopy/IR/IRfrequencies.html. Last Access 10/23/2016.

Bagampadde, U., & Isacsson, U. (2006). Characterization of chemical reactivity of liquid antistripping additives using potentiometric titration and FTIR spectroscopy. Energy & fuels, 20(5), 2174-2180.

Ghebremeskel, G. N., & Shield, S. R. (2003). Characterization of binary/tertiary blends of SBR, NBR and PVC by IR spectroscopy. Rubber world, 227(4).

Cheng, D., Little, D., Lytton, R., & Holste, J. (2001). Surface energy measurement of asphalt and its application to predicting fatigue and healing in asphalt mixtures. Transportation Research Record: Journal of the Transportation Research Board, (1810), 44-53.

Van Oss, C. J., Chaudhury, M. K., and Good, R. J. (1998). Interfacial Lifshitz-van der Waals and Polar Interactions in Macroscopic Systems. Chemical Reviews, 88(6), pp. 941-972.

Bahramian, A. (2012). Evaluating surface energy components of asphalt binders using Wilhelmy Plate and Sessile Drop Techniques. Degree Project in Highway and Railway Engineering, Stockholm, Sweden, 2002.

Buddhala, A., Edgar, A. O., Zaman, M., Wasiuddin, N. M., & Hossain, Z. (2011). Effects of an amine anti-stripping agent on moisture susceptibility of sasobit and aspha-min mixes by surface free energy analysis. Journal of Testing and Evaluation, 40(1), 1-9.

Wasiuddin, N. M., & Zaman, M. M. (2010). Polymeric aggregate treatment using styrene-butadiene rubber (SBR) for moisture-induced damage potential. International Journal of Pavement Research and Technology, 3(1), 1-9.

Kittu, A. T., Bulut, R., & Harimkar, S. (2013). Comparison of Contact Angle Measurements on Granite with Respect to Surface Roughness.

Kittu, A. T., Bulut, R., & Harimkar, S. (2014, May). Comparison of Surface Energy Values of Limestone with Respect to Different 3D Surface Roughness Measurements. In Pavement Materials, Structures, and Performance (pp. 39-47). ASCE.

Koc, M., & Bulut, R. (2013). Evaluation of a warm mix asphalt additive using direct contact angle measurements. In Int. J. Pavements Conf. 2013.

Koc, M., & Bulut, R. (2013). Assessment of a sessile drop device and a new testing approach measuring contact angles on aggregates and asphalt binders. Journal of Materials in Civil Engineering, 26(3), 391-398.

Little, D. N., Bhasin, A., & Hefer, A. W. (2006). Using surface energy measurements to select materials for asphalt pavement. Texas Transportation Institute, Draft Final Report, Project 9-37, National Cooperative Highway Research Program, Washington D.C., 2006

Wasiuddin, N. M., Fogle, C. M., Zaman, M. M., & O'Rear, E. A. (2007). Effect of antistrip additives on surface free energy characteristics of asphalt binders for moisture-induced damage potential. Journal of testing and evaluation, 35(1), 36-44.

Arabani, M., Roshani, H., & Hamedi, G. H. (2011). Estimating moisture sensitivity of warm mix asphalt modified with zycosoil as an antistrip agent using surface free energy method. Journal of Materials in Civil Engineering, 24(7), 889-897.

Hefer, A. W., Bhasin, A., & Little, D. N. (2005). Bitumen surface energy characterization using a contact angle approach. Journal of Materials in Civil Engineering, 18(6), 759-767.

Yang, S., Braham, A., Chowdhury, N., & Hossain, Z. (2015, July). Linking the Field and Lab Performance of Interstate Pavements. In International Symposium on Systematic Approaches to Environmental Sustainability in Transportation.

Chowdhury, N., Hossain, Z., Yang, S., & Braham, A. (2015, March). A Framework for Premature Pavement Distress Evaluation. In IFCEE 2015.