UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

CHARACTERIZATION OF RUTTING IN ASPHALT PAVEMENTS USING LABORATORY TESTING

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

Degree of

DOCTOR OF PHILOSOPHY

By

SHIVANI RANI
Norman, Oklahoma
2019

CHARACTERIZATION OF RUTTING IN ASPHALT PAVEMENTS USING LABORATORY TESTING

A DISSERTATION APPROVED FOR THE
SCHOOL OF CIVIL ENGINEERING AND ENVIRONMENTAL SCIENCE

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DEDICATION

“To my Parents and Family Members”

ACKNOWLEDGEMENTS

First of all, I would like to thank Almighty and my all-time believers, Shiva and Durga, for providing me with this opportunity and ability to pursue a doctoral degree in civil engineering.

I would like to express my deepest appreciations and gratitude to my mentor and the chair of my doctoral committee, Professor Musharraf Zaman. Dr. Zaman is a professor who believes in hard work and transmits the same to his students. He provides continuous guidance, support, inspiration, and encouragement to his students to achieve success in their lives. I was inspired by his enthusiasm, positive energy, and hardworking attitude to work harder. His endurance, hearing, comments, and suggestions at all stages of work helped me a lot in improving my research work. Dr. Zaman's high standard for research and professionalism have broadened my thinking and improved my professional communication skills. With his guidance and encouragement, I have been inspired to work rigorously on challenging areas of this arena of pavement materials and contribute to our asphalt industry. I am thankful to him for providing me with the opportunity to work with him. May God bless him with more success and happiness in his life.

Also, I am grateful to Dr. Rouzbeh Ghabchi for being on my doctoral committee. I appreciate his guidance and mentorship throughout the years. He was always my go-to person for discussing the problems and troubleshooting them. He always welcomes innovative ideas and process to achieve them, which helped me in broadening my thinking. His commitment to high-quality work has improved me professionally. During the Ph.D. program, I was privileged to work with him on several projects related to pavement distresses under Dr. Zaman's supervision. Currently, he is working as an "Assistant Professor" at the South Dakota State University, South Dakota, USA. I wish God Almighty would bless him with a lot of success and fulfill his dreams.

I would like to gratefully thank Dr. Edgar A. O'Rear for serving on my doctoral committee and always being supportive and helpful. The discussions I had with him improved my understanding of the effects of polymers. I am grateful to him for providing me with the opportunity to work with him and his student, Mr. Connor Dugan, on a research project jointly led by him and Dr. Zaman. The project broadened my knowledge and understanding of binders' performance.

I would like to offer my appreciations to Dr. Kianoosh Hatami for serving on my doctoral committee. I attended a class "Geosynthetics" during my first semester of the Ph.D. program at the University of Oklahoma (OU). I learned a lot from Dr. Hatami's class and was impressed by his practical knowledge and experience in the area of Geosynthetics and other related areas. I would like to thank Dr. Kanthasamy K. Muraleetharan for serving on my doctoral committee.

I would like to thank Dr. Amy Cerato for serving as a graduate liaison on my committee and sharing her thoughts with me. My first graduate class at OU was "Engineering Geology" offered Dr. Cerato. I enjoyed the field trips planned by her during that class. Those trips helped get real-time learning and experience.

I am grateful to many companies in Oklahoma for providing the materials, i.e., asphalt mix, asphalt binder, additives, and aggregates, required for this study. Specifically, I am thankful to Silver Star Construction Co., Haskell Lemon Construction

Co., Schwarz Paving, Calumet Refinery, Holly Frontier Refinery, Valero Refinery, Ingevity, ArrMarz, and Lion Refinery. Also, the financial support provided by the Southern Plain Transportation Center (SPTC), the Oklahoma Department of Transportation (ODOT), and the Federal Highway Administration (FHWA) is acknowledged highly. Without the support from these companies and the agencies, this study would have been difficult to complete.

Moreover, I wish to thank every member of the Pavement Materials and Systems Group at the University of Oklahoma for their contribution during this study. Special thanks to Mr. Syed Ashik Ali, Mr. Mohammad Ashiqur Rahman, Mr. Kenneth Hobson, Dr. Amir Arshadi, Dr. Manik Barman, Mr. Nayan Kumar Naidu Raguluri, Mr. Vijay Kanth Reddy Srilam, Mr. Sai Srikanth Kola, Dr. Moeen Nazari, Dr. Dominique Pittenger, and Dr. Nur Hossain. I attended a class “Asphalt Mix and Design” offered by Dr. Pittenger that assisted me in dealing with some difficulties during my work. I am thankful to Mr. Micheal Schmitz (Mike) for his technical support in laboratories.

I would like to express my sincere appreciation to the academic and administrative staff members of the School of Civil Engineering and Environmental Science (CEES), the Gallogly College of Engineering (GCoE) Dean’s Office, the Graduate College, the Mewbourne School of Petroleum and Geological Engineering (MPGE), and Southern Plains Transportation Center for their help and support. Special thanks to Mrs. Susan Williams and Mrs. Abby Young for tracking my records and keeping me organized. With their help, I have never missed any important deadline. I would like to thank Mrs. Audre Carter for handling my payroll and resolving any associated issues. I would like to acknowledge the help provided by Mrs. Marlene

Smith, Mrs. Trinia Pearson, Mrs. Karen Kelly, Mrs. Sara Vaughan, Mrs. Brenda Clouse, Mrs. Sonya Grant, Mrs. PJ Meek, and Mrs. Cerry Leffler.

Lastly, I would like to express my endless love and gratitude to my family members: Mrs. Anjna Rani (my mother), Mr. Anil Kumar (my father), Mrs. Akansha Agarwal (my sister), and Mr. Saurabh Agarwal (my brother) for their blessing, understanding, encouragement, and inspiration towards my work. Their blessings have given me strength to get through the problems and to fulfill my dreams of becoming a Doctor of Philosophy. Even though I had to stay in a far distance from them to fulfill my dream, they never stopped supporting me, and they have been a great source of positive energy throughout my years at OU. I also admire their immense efforts in raising me from a small town in India to a well-known University in the United States of America. I would like to mention some of my friends' names, namely Ms. Manami Roy, Ms. Varsha Jhawar, Ms. Shikha Srivastava, Ms. Shugofa Dastgeer, Ms. Rashmi Thapaliya, Mr. Rishabh Jain, and Mr. Akhil Srivastava, who have helped and encouraged me throughout the years to pursue my dream.

(SHIVANI RANI)

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ABSTRACT

In asphalt pavements, rutting is one of the main concerns at high in-service temperatures. Rutting in a Hot Mix Asphalt (HMA) pavement can occur either through plastic flow or shear in structural layers. Rutting in HMA layers depends on several factors, such as binder grade, binder content, aggregate gradation, percent air voids, binder viscosity, moisture level, traffic level, temperature, and soil conditions. Excessive rutting can result in structural failure, loss of control while driving, and hydroplaning during wet road conditions. When traffic volume rises, and especially during hot summer days, pavement failure due to rutting increases tremendously. These failures need to be addressed. The present study evaluates the rutting potential of asphalt mixes using conventional and non-conventional laboratory tests conducted on asphalt mixes and binders. Different additives, namely Polyphosphoric Acid (PPA), a Warm-Mix Asphalt (WMA) additive, and a liquid Anti-Stripping Agent (ASA) were selected and tested for this purpose.

During this study, 49 different binder blends were prepared by mixing asphalt binders (PG 58-28, PG 64-22, PG 70-28, and PG 76-28) with different amounts of PPA (0%, 0.5%, 1.0%, 1.5%, and 2.0%), WMA additive (0% and 0.5%), and ASA (0% and 0.5%). Laboratory tests, namely Dynamic Shear Rheometer (DSR) and Multiple Stress Creep and Recovery (MSCR), were conducted on the selected PG 58-28 binder to measure its rutting potential at different test temperatures and under different aging conditions. Other laboratory tests, namely Bending Beam Rheometer (BBR), and Rotational Viscometer (RV) were also performed to determine the Performance Grade (PG), viscosity, fatigue resistance, and oxidative aging of the neat and modified samples of PG 58-28 binders. It was found that the use of PPA enhances the rutting resistance

without adversely impacting the low-temperature cracking resistance. Adding 1.0% or a higher amount of PPA bumped the Superpave® high-temperature PG by one grade. This was likely attributed to an increase in the concentration of asphaltenes in the base binder due to the addition of PPA. However, blending the binders with the WMA additive and ASA did not impact their rutting resistance and PG grade. The MSCR test results indicated that the binder blends containing PPA can sustain a larger traffic level without undergoing significant rutting. The binder blends containing 1.5% to 2.0% PPA were found to sustain an extreme level of traffic loading at 58°C and were therefore designated as PG 58E-28. Additionally, it was observed that blending PG 58-28 binder with a combination of PPA and WMA additive or ASA improved its resistance to rutting. The higher the PPA amount, the higher the improvement in the rutting resistance. However, this improvement due to the WMA additive, ASA, and PPA in the blend was found to be less than that of the PPA modification alone. Therefore, the effectiveness of PPA in a PPA-modified binder is expected to decrease due to the addition of ASA and WMA additives. Based on these findings, using 0.5% ASA or 0.5% WMA additive was found to neutralize the effect of 1.0% to 1.5% PPA. This was due to fact that using an amine-based additive with an acid-based additive nullifies the effect of each other and creates an amine salt depending on the chemistry of the base binder. Therefore, one should exercise care in using PPA with the selected WMA additive and ASA.

The rutting resistances of PG 64-22, PG 70-28, and PG 76-28 asphalt binders were found to increase as a result of blending them with 0.5% WMA additive, 1.5% PPA, and 0.5% ASA. This improvement was more significant for polymer-modified

binders. This was possibly due to additional cross-linking effects of PPA with polymers enhancing the polymer network by developing polymer strands. Polymer strands enhance stability and stiffness of the modified binders. Therefore, an improvement in rutting resistance of associated asphalt mixes is expected due to the addition of WMA additive, PPA, and ASA in the mix.

A mechanistic approach, namely Surface Free Energy (SFE), was used to evaluate the moisture-induced damage potential of binder blends and mixes containing PPA and ASA. For this purpose, 10 different binder blends containing PPA and ASA were used to determine their SFE components. Then, different energy parameters, namely the wettability, the works of adhesion, cohesion, debonding, and the energy ratio were determined with five different aggregates, namely limestone, granite, gravel, quartzite, and basalt. The results indicated that PPA does not impact the cohesive bond of the neat PG 58-28 binder. However, depending on the aggregate type, PPA may improve the adhesive bond between the binder and the aggregate. Among the aggregates considered in this study, the maximum improvement in the adhesive bond was observed for the gravel aggregate. The binder blends containing PPA and ASA were found to have lower interfacial energy parameters than the binder blends containing ASA and, in some cases, those containing PPA. Based on these observations, using ASA would not reduce the moisture-induced damage potential of PPA-modified binders. Additionally, the use of 1.5% PPA, with or without ASA, was found to be an effective concentration, contributing to the improved adhesive bond and the wettability of the neat PG 58-28 binder.

Additionally, four different mixes with binder blends containing the PG 64-22 binder modified by using PPA, WMA additive, and ASA were prepared in the laboratory and tested using a Hamburg Wheel Tracking (HWT) device to evaluate their rutting and moisture-induced damage potential. It was found that the tested mixes have low rutting and moisture-induced damage potential. The Tensile Strength Ratio (TSR) test results, however, revealed the possibility of moisture-induced damage in some cases, which was not supported by the HWT test results. Lack of a strong mechanistic-basis of the TSR test in identifying moisture-induced damage could be responsible for this observation.

CHAPTER

1

INTRODUCTION

1.1 Rutting

More than 90% of roads in the United States are paved using asphalt mixes (USDOT, 2017). An asphalt mix is a composite material that consists of mineral aggregates and asphalt binder. While aggregates provide a load bearing structure for an asphalt mix, the binder holds the aggregates together and consequently, provides tensile strength to the mix. The common distresses in an asphalt pavement are rutting, fatigue cracks, reflective cracks, low-temperature cracks, and moisture-induced damage (Roberts et al., 1991; Bonnetti, 2002; NCHRP Report 468, 2002; Lu and Harvey; 2006; Gorkem and Sengoz, 2009; Jahromi, 2009; Wu and Chen, 2011; Abed and Al-Azzawi, 2012; Miller and Bellinger, 2014; Kargah-Ostadi, 2017). At high temperatures, however, rutting is the main concern.

Rutting is the permanent deformation in the asphalt pavement or underlying base or subgrade caused by repeated traffic loads. Rutting deformation can occur either through plastic flow in the Hot Mix Asphalt (HMA) layer or shear in one of the underlying layers (Brown et al., 2009). According to Krugler et al. (1985), three different mechanisms are responsible for rutting: (1) consolidation due to traffic; (2) plastic deformation due to instability of the mix; and (3) instability due to stripping of the binder underneath the surface course. A pavement usually experiences rutting in three different stages: (i) primary rutting or wear rutting due to environmental conditions and traffic loading; (ii) secondary rutting or structural rutting due to permanent deformation of structural layers; and (iii) tertiary rutting or instability rutting due to lateral movement of materials within an asphalt pavement (Dawley et al., 1990; Brown et al., 2009). A significant amount of rutting causes structural failure, loss of control while driving, and hydroplaning caused by the accumulation of water (Huang, 2004; Hoffman and Sargand, 2011). With increased traffic volume and tire pressure, heavy overloading, and bad weather conditions, rutting has become a major problem across the globe (Qing-lin, 2001).

In view of widespread impacts, rutting is one of the criteria for the design of asphalt pavements in the United States (AASHTO, 1993). Other Countries such as India, China, and Europe also incorporate rutting as a design criterion (Zu-Kang, 2003). The present study aims to evaluate performance of mixes and binders relative to rutting. Designing mixes that are significantly resistant to rutting would exhibit good performance at high temperatures but may experience other distresses at low or intermediate temperatures such as fatigue cracking and low-temperature cracking due to high stiffness. Therefore, the overall performance of asphalt binders and mixes should be evaluated at different temperatures (high, intermediate or low), aging conditions, and distresses. Although the primary focus of this dissertation is rutting, other distresses, namely low-temperature cracking, fatigue cracking, and oxidative aging are addressed. In addition, the moisture-induced damage potential of binders and mixes, also referred to as the asphalt binder-aggregate system, is addressed. In this dissertation, the words ‘asphalt binder’ and ‘asphalt mix’ are used interchangeably with words ‘binder’ and ‘mix’, respectively. Similarly, the words ‘rutting’, ‘rut depth’, and ‘permanent deformation’ are used interchangeably.

1.2 Factors Influencing Rutting

Rutting is affected by several factors such as air voids, mineral filler content, dynamic modulus of mix, complex modulus of binder, binder grade, temperature, axle load, tire pressure, traffic level, and compaction level. These factors have been studied over the years by many researchers (e.g., Barksdale and Itani, 1989; Lee et al., 1999; Chadbourn, et al., 1999; Park et al., 2001; Tarefder and Zaman, 2002; Tutumluer, 2005; Chen et al., 2005; Lee et al., 2007; Huang et al., 2008; Hossain, 2010; Nejad, 2011; Zhao, 2011; Archilla and Diaz; 2011; Larrain and Tarefder 2016; Hossain, 2017; Wang et al., 2017; Ghabchi et al., 2018, *Effectiveness of WMA additive on PPA-modified asphalt binders containing anti-stripping agent*, manuscript in review process; Rani et al., 2018, Evaluation of liquid anti-stripping agent on the performance of asphalt binders and mixes containing polyphosphoric acid, manuscript in review process). For instance, the Federal Highway Administration (FHWA, 1988) reported that high binder content is one of the main factors for increased rutting. Tarefder et al. (2003) ranked the binder grade at the top of the list of parameters contributing to rutting followed by temperature, aggregate gradation, moisture, and binder content. However, Hussan et al. (2017) ranked temperature as the most influential factor and binder content as the third influential factor. These researchers also observed that the flakiness index of aggregates affects the rutting potential; an increase in the flakiness index increases rutting. Zou (2017) reported mix type as the most influential factor when considering the rutting performance of asphalt pavements. Within an asphalt mix, binder grade is more influential than aggregate gradation (Zou, 2017). By contrast, Stakston and Bahia (2003) reported that the resistance to rutting primarily depends on the aggregate gradation. A mix with strong aggregates but bad gradation would likely fail in the field due to rutting. In a study conducted by Golalipour (2012), it was reported that rutting resistance increased when aggregate gradation was near the upper limit curve of the job mix formula. According to Kim and Souza (2009) and Leon and Charles (2015), an increase in angularity reduces rutting due to better interlocking between aggregates. Ramli et al. (2013) studied the effects of fine aggregate angularity on rutting and noted that mixes with more angular aggregates are less susceptible to rutting. In a recent study by Hossain (2017), it was observed that rutting is more sensitive to change in traffic intensity instead of variation in material or geometric properties. Effects of other factors to rutting are presented in Table 1.1.

1.3 Available Techniques for Determination of Rutting

1.3.1 Laboratory Tests

Several laboratory tests are available for measuring contributions of both binders and mixes to rutting. For example, Dynamic Shear Rheometer (DSR) tests can be used to determine the rutting potential of binders at different temperatures and under different aging conditions (AASHTO T 315, 2012). The DSR measures the complex modulus (G*) and phase angle (δ) of a binder at test temperatures. These properties are used to determine the rutting factor – an indicator of binder's contributions to rutting. According to Bahia (1995), mechanistically rutting is directly proportional to the work dissipated in each traffic loading cycle, which is inversely proportional to the factor

(G*/sinδ). Therefore, the factor (G*/sinδ) is widely used to evaluate rutting resistance. A higher G*/sinδ value, which may be achieved by increasing G* or decreasing δ, suggests lower potential of work dissipation in a loading cycle, higher recovery of the applied deformation, and lower rutting.

The rutting potential of mixes can be measured using static creep tests in which a mix specimen is subjected to static load and rutting is measured after unloading. Several previous studies have shown that Hamburg Wheel Tracking (HWT) tests, Asphalt Pavement Analyzer (APA), and Flow Number (FN) tests allow the measurement of rutting under repetitive loading of desired magnitude and cycle (NCHRP 508, 2003; Lu and Harvey, 2006; Bonaquist, 2012). Ideally, rutting performance of constructed pavements can be determined using a Full-Scale Accelerated Pavement Testing (APT) facility, where a heavy vehicle simulator runs over a full-scale pavement (Metcalf, 1996; Khan et al., 2013).

1.3.2 Field Measurement

In the field, rutting can be measured manually using a straight edge-rut gauge combination. It usually measures the difference in elevation between the center of the wheel path and a line connecting two points located at a distance of 2-feet from the center of the wheel path (ASTM E 1703, 2010). A better way of measuring rutting manually is to use a Face Dipstick®. A Face Dipstick® provides a much more precise rut profile than the straight edge-rut gauge combination (FHWA, 2013; Hossain, 2017). In recent years, several automated techniques (digital image-based) have been developed which allow the measurement of rutting in real-time. For example, the Texas Department of Transportation (TxDOT) developed a 5-point acoustic sensor system for rut data collection using Pavement Management Information System (PMIS) (AASHTO PP 38-00, 2005). In 2009, TxDOT designed a system, named VRUT, to measure rutting from continuous transverse profiles at highway speeds. The system utilizes a ‘high-power infrared laser line projector and a high-speed 3D digital camera with built-in laser line image processing capability’ (Huang et al., 2013). Similarly, a Laser Rut Measurement System (LRMS) characterizes rutting along the transverse direction using laser profilers (Hoffman and Sargand, 2011; Serigos et al., 2012).

1.3.3 Empirical Models

Several empirical models are available for predicting rutting in asphalt pavements. These models basically consider the number of load repetitions and limit the deformation in the top asphalt layer or the accumulation of deformation in each layer. However, these models do not include the fundamental properties of materials and the effect of mixed traffic levels. Some of those empirical models are listed in Table 1.2. Table 1.2 also presents the rut prediction model used in the Mechanistic Empirical Pavement Design Guide (MEPDG) software, also called AASHTOWare, for the design of asphalt pavements. The MEPDG rut model can be calibrated for local conditions to accommodate the effect of local traffic, material properties, and environmental conditions. For example, Hossain (2017) determined the local calibration parameters for prediction of rut depth in asphalt pavements based on the traffic and environmental conditions in Oklahoma. The material properties were calculated using laboratory testing.

1.3.4 Numerical Modelling

The permanent deformation (or rutting) can be predicted using Two-Dimensional (2-D) or Three-Dimensional (3-D) numerical models of pavements, as done by many researchers (e.g., Zhou and Scullion, 2002; Bakheet et al., 2001; Allou et al., 2007; Desai, 2007; Kim et al., 2007; Wu and Chen, 2011; Walubita et al., 2014). For instance, Wu et al. (2011) developed a Finite Element (FE) model using a commercially-available software, ABAQUS, to investigate the permanent deformation of flexible pavements including a cementitiously-stabilized base or subbase. Temperature dependency of the asphalt material was considered by adjusting the loading modulus at every 25,000 load repetitions. Abed and Al-Azzawi (2012) developed a 2-D plane strain FE model using ANSYS to estimate the permanent deformation of asphalt pavements. The estimated stress parameters from the FE model were used in the local empirical models to estimate rutting. Using a 3-D FE model, Hu (2017) found that inclined tires and decelerating vehicles generate the maximum shear stress, which results in an increased vertical strain in a pavement. Nahi et al. (2014) reported that creep models can be used to determine the rutting potential of mixes based on the FE simulation of a dynamic creep test. Zhou and Scullion (2011) proposed a rut prediction model based on the FE analysis of 49 different test sections capturing the three-stage permanent deformation of mixes.

1.4 Need for This Research

As noted earlier, an asphalt pavement may experience different types of distresses such as rutting, fatigue, raveling, moisture-induced damage, and fatigue cracking. At high in-service temperatures, however, rutting is the main concern (Brown et al., 2009). Rutting in HMA layers depends on several factors, such as binder grade, binder content, aggregate gradation, percent air voids, binder viscosity, moisture level, traffic level, temperature, and soil conditions (Nejad, 2011; Larrain and Tarefder 2016; Hossain, 2017; Wang et al., 2017). Excessive rutting can cause structural failure of pavement, loss of control while driving, and increased chances of hydroplaning. With increased traffic volume, axle loads, tire pressure, and temperature, rutting is expected continue to remain a major issue in asphalt pavements and an active area of research.

Several asphalt binder modifiers, namely, polymers (elastomers or rubbers and plastomers or plastics), fibers, and oxidants are available that can enhance the resistance of asphalt mixes to rutting. For example, Jamshidi et al. (2012) and Arshad et al. (2013) found that the addition of Sasobit® wax to a binder enhances its resistance to rutting by increasing stiffness and decreasing viscosity. Gandhi and Amirkhanian (2007) also reported that adding Sasobit® and Asphamin® to a binder leads to an increase in stiffness. However, the extent of stiffness improvement depends on the amount of WMA additives as well as its type. Zhang and Yu (2010) also reported an increase in stiffness when modifying a binder using Styrene–Butadiene Rubber (SBR).

In the past few years, several studies have been conducted on the use of Polyphosphoric Acid (PPA) to improve the mechanical properties of binders (e.g., Kodrat et al., 2007; Arnold et al., 2009; Baldino et al., 2013). The addition of PPA to an asphalt binder is found to increase its stiffness at high temperatures (Maldonaldo et al., 2006; Baldino et al., 2013; Edwards et al., 2006/2007). Subsequently, PPA decreases the sensitivity of binders to temperature variation and also increases their resistance to rutting. Yan et al. (2013) observed a higher softening point and viscosity (at 135˚C) in

PPA-modified binders, compared to their non-modified counterparts. The aforementioned studies have also reported that PPA-modified binders show a higher resistance to low-temperature cracking than those containing waxes.

Although the use of PPA showed a number of advantages, its use has been restricted or limited to 0.5% by several state Departments of Transportation (Maurer and D'Angelo, 2012). Preferring polymers over PPA for binder modification due to its possible adverse reactions with other additives such as hydrated lime and its unknown long-term performance, have limited its use in asphalt mixes. For example, the Oklahoma Department of Transportation (ODOT) has limited the use of PPA in asphalt binders due to the possibility that PPA can cause an increase in moisture-induced damage potential (FHWA, 2012). Al-Qadi et al. (2014) reported a mixed performance of PPA-modified binders against moisture-induced damage. It was reported that incorporation of PPA in a mix containing granite aggregates increased its resistance to moisture-induced damage. On the other hand, the use of PPA in a mix containing limestone aggregates decreased its potential for moisture-induced damage. Furthermore, using PPA is expected to reduce the workability of asphalt mixes due to increased viscosity and require a higher mixing temperature during production and a higher compaction temperature (Filippis et al., 1995; Maldonado et al., 2006). Thus, study of PPA in asphalt binders remains a topic of interest to researchers.

The present study evaluates the effects of different amounts of PPA on the rutting resistance of binders and mixes. The present study also examines their moisture-induced damage potential considering different types of aggregates. The moisture-induced damage potential of asphalt binders is estimated using the Surface Free Energy

(SFE) method (Hefer et al., 2006; Arabani and Hamedi, 2011; Ghabchi et al., 2013). Moreover, the effect of the PPA on the long-term performance (i.e., fatigue cracking, and mixing and compaction temperatures required during pavement construction) is investigated.

The widespread practice for reducing the moisture-induced damage potential is to use Anti-Stripping Agents (ASAs) such as hydrated lime and liquid ASA (Tarrer et al., 1989; Xiao and Amirkhanian, 2010). Similarly, WMA additives or foaming methods are generally used to lower the viscosity of asphalt binders and to reduce the production temperatures of mixes (Button et al., 2007; Prowell et al., 2007; Chowdhury and Button, 2008; Estakhri, 2012; Rubio et al., 2012). The effects of these additives when used separately on mechanical properties of asphalt binders and mixes have been evaluated in several studies (Button et al., 2007; Prowell et al., 2007; Chowdhury and Button, 2008; Huang et al., 2008; Xiao et al., 2010; Estakhri, 2012; Rubio et al., 2012; Abuawad et al., 2015). However, to the author’s knowledge, not many studies have been undertaken to evaluate the combined effects of the abovementioned additives on the properties of asphalt binders and mixes pertaining to pavement performance. Therefore, the current study is undertaken to evaluate the combined effects of asphalt binder source, aggregate type, WMA additives, PPA, and ASA on the rutting and moisture-induced damage potential of asphalt mixes. Specifically, efforts are made to characterize the rheological performance of various grades of binders (PG 58-28, PG 64-22, PG 70-28, and PG 76-28) containing PPA, amine-based WMA additives, and amine-based ASA in different amounts.

Apart from the rutting and moisture-induced damage potentials, performance of binder blends and mixes against other distresses such as low-temperature cracking and fatigue cracking, and oxidative aging is also studied. The objective is to evaluate the overall performance of the binder blends and mixes due to modifications by PPA, ASA, and WMA additive. Effects of different temperatures (high, intermediate or low) and aging conditions (unaged, RTFO-aged, and PAV-aged) are also examined. For this purpose, a wide range of laboratory tests, namely Dynamic Shear Rheometer (DSR), Bending Beam Rheometer (BBR), Surface Free Energy (SFE), and Rotational Viscometer (RV) were conducted at different temperatures on 49 different binder blends. Also, Hamburg Wheel Tracking (HWT) and Tensile Strength Ratio (TSR) tests were conducted on asphalt mixes to evaluate their rutting and moisture-induced damage potentials, respectively. Table 1.3 presents a summary of the laboratory tests conducted in this study.

1.5 Objectives

The specific objectives of this study are as follows:

- Evaluate the effects of PPA, in different amounts, on the rheological and mechanical properties of PG 58-28 binders and their resistance to different pavement distresses, namely rutting, low-temperature cracking, fatigue cracking, moisture-induced damage, and oxidative aging;
- Examine the interaction of an amine-based WMA additive and an amine-based ASA with an acid-based PPA and their combined impact on the rheological properties of base binders and rutting resistance of asphalt mixes;

- Determine the effects of using acid-based PPA, an amine-based WMA additive and an amine-based ASA on the traffic loading capacity of base binders and stress sensitivity induced in the base binders due to these additives;
- Determine the Superpave® PG and MSCR grade of binder blends containing PPA, ASA, and WMA additive;
- Evaluate the effect of PPA and ASA on the cohesive bond strength of a PG 58-28 binder and calculate the interfacial energy parameters, namely the work of adhesion, work of debonding, wettability, and energy ratio for the different combinations of binder-aggregate systems using their SFE components;
- Examine the effect of using one combination of a chemical WMA additive, PPA and ASA on the rutting, oxidative hardening, fatigue cracking, and Superpave® PG grade of PG 64-22, PG 70-28, and PG 76-28 asphalt binders and study the cross-linking of PPA with polymers when used in polymer-modified binders;
- Compare the rutting resistance and moisture-induced damage potential of mixes containing a chemical-based WMA additive, PPA, and ASA by conducting HWT and TSR tests.

1.6 Structure of This Dissertation

This dissertation focuses on the rutting characterization of asphalt pavements using laboratory testing. Also, the moisture-induced damage potential of binders and mixes are investigated using the SFE approach. The findings of this work are presented in four chapters (Chapter 2 to Chapter 5). These chapters are formatted as four journal papers. One of these papers has been accepted, while the other papers are currently under review. A brief description of each chapter is given below:

Chapter 1 presents background on rutting, its mechanisms, influencing factors, and the available techniques for evaluation of rutting. This chapter also identifies the research needs and objectives of this dissertation.

Chapter 2 includes a study conducted to evaluate the rutting, fatigue, Superpave® PG, dynamic viscosity, and moisture-induced damage potential of binders containing a chemical-based WMA additive. For this purpose, a PG 58-28 binder blended with different amounts of a chemical-based WMA additive was tested. A wide range of laboratory tests, namely DSR, BBR, RV, and SFE, were conducted on the prepared binder blends under different temperatures and aging conditions.

Chapter 3 presents the effects of PPA on the rutting, fatigue, and dynamic viscosity of a PG 58-28 binder when used alone and in combination with ASA. Also, the Superpave® PG and MSCR grades were determined and compared after binder modification using PPA and ASA. A total of 20 different binder blends were prepared using a PG 58-28 binder from two different sources. The binder blends were tested under different conditions using DSR, BBR, RV, and MSCR tests. The results were analyzed to examine the source dependency of the binder and effects of PPA and ASA on the resistance to oxidative aging.

Chapter 4 discusses the effects of PPA, ASA, and WMA additive on the rutting, fatigue, dynamic viscosity, and moisture-induced damage potential of binders and mixes. For this purpose, 16 different binder blends were prepared using four different grades of binder, namely PG 58-28, PG 64-22, PG 70-28, and PG 76-28. Three different laboratory tests, namely DSR, BBR, and RV, were conducted on the binder blends to determine their performance after modification. Also, four different mixes were prepared in the laboratory using a PG 64-22 binder blended with PPA, ASA, and WMA. The mixes were tested in the laboratory for rutting and moisture-induced damage potential using HWT and TSR tests.

Chapter 5 evaluates the moisture-induced damage potential of binders and mixes containing PPA and ASA using the SFE approach. The SFE components of binder blends were determined using the Dynamic Wilhelmy Plate method. The SFE components of five different aggregates, namely limestone, granite, gravel, quartzite, and basalt, were taken from the available literature. Based on the SFE components of binder and aggregates, different interfacial energy parameters were evaluated and used as an indicator of rutting.

Chapter 6 presents the overall summary and conclusions of this study. The recommendations for future works are also included in Chapter 6.

Table 1.1 Factors Influencing Rutting

Factor	Change in Factor	Effect on Rutting
Asphalt Binder		
Performance Grade	Increase	Decrease
Viscosity	Increase	Decrease
Complex Modulus	Increase	Decrease
Aggregate		
Gradation	Gap-Graded to Continuous	Increase
Flakiness Index	Increase	Increase
Surface Texture	Smooth to Rough	Decrease
Size	Increase in NMS	Increase
Shape	Angular to Regular	Decrease
Fine Aggregate Angularity	Higher	Decrease
Asphalt Mixture		
Binder Content	Low to Optimum	Decrease
	Optimum to High	Increase
Fine Content	Increase	Decrease
Dynamic Modulus	Softer to Stiffer	Decrease
Air Void Content	Optimum to Low/High	Increase
Voids in Mineral Aggregate	Increase	Decrease
Test Conditions		
Temperature	Increase	Increase
Moisture	Dry to wet	Increase
Load Repetitions	Increase	Increase
Tire Pressure	Increase	Increase
Tire Inclination	Increase (a certain limit)	Increase
Compaction Level	Increase	Decrease

Table 1.2 Available Rut Models

No.	Rut Model		Reference
1	$\varepsilon_p = a_1 + b_1 logN$ $\varepsilon_p = \frac{b_1}{N}$ (N>1)	a_1, b_1 = regression coefficient	Barksdale (1972)
2	$\varepsilon_p = aN^b$	a, b = regression coefficient	Monismith et al. (1975)
3	$\varepsilon_p^l = a(\frac{N}{1000}^{b})$	a = permanent strain after 1000 cycles b = permanent strain rate	Huurman (1977)
4	$RD = \alpha.N^{\beta}.T^{\theta}$	α, β, θ = coefficients of equation	SHRP (1993)
5	$log\frac{\varepsilon_P}{\varepsilon_r} = log\ C + 0.4262 \log N$ $C = \frac{T^{2.02755}}{5615.391}$ (AASHTO 2002 Model)	ε_r = resilient strain	Witczak (2001)
6	$\frac{\varepsilon_P\ (N)}{\Delta\varepsilon_r} = a_1.T^{a_2}.N^{a_3}$	$\Delta\varepsilon_r$ = resilient Strain a_1, a_2, a_3 = material parameters	ARA (2004), Salama et al. (2007), Hu et al. (2011)
7	$RD = \sum_{i=1}^{n} 10^{-5.72}.T_i^{2.512}.\{\frac{0.58}{V}.N\}^{0.743.(\frac{\tau_i}{\tau_{0i}}^{0.472})}$	τ = shear stress V = traffic speed	Su et al. (2008)
8	$RD = C\sum_{i=1}^{n} N_i^a.L_i^b.T_i^c.t_i^d$	C= adjustment factor for traffic wander effect L = load ratio t = loading duration a, b, c, d = coefficients of equation	Fwa et al. (2004)
9	$RD = \sum_{i=1}^{n} \varepsilon_i^p h_i$ (total rut depth) $\frac{\varepsilon_p}{\varepsilon_r} = K_z\beta_{r1}10^{K_{r1}}T^{\beta_{r2}k_{r2}}N^{\beta_{r3}k_{r3}}$ (MEPDG Model)	h = thickness of sublayer ε_r = resilienst strain β_{r1}, β_{r2}, β_{r3} = local calibration coefficients k_{r1}, k_{r2}, k_{r3} = national coefficients K_z = depth coefficient factor	MEPDG (2004)

RD (ε_P) = total rut depth (permanent strain),
N = number of load repetitions,
T = temperature,
n = number of layers

Table 1.3 List of Laboratory Tests Conducted in this Study

Test	Standard	Purpose	Test Time including Man Hours	Specifications/ Recommendations	Test Outcomes
Shear Mixing		Blend asphalt binder with PPA, WMA or ASA	1.5 hours for sample preparation; 45 minutes for blending; 15 minutes for cleaning		Modified asphalt binders
Rolling Thin-Film Oven (RTFO)	AASHTO R 240	Simulate aging condition of asphalt binders during plant mixing and compaction	1.5 hours for sample preparation; 85 minutes for RTFO-aging; 30 minutes for sample extraction		RTFO-aged asphalt binders
Pressure Aging Vessel (PAV)	AASHTO R 28	Simulate long-term aging condition of asphalt binders which occurs during the 5 to 10 years of service life of the pavement	1.5 hours for sample preparation; 20-22 hours for Aging; 30 minutes for sample extraction		PAV-aged asphalt binders
Rotational Viscometer (RV)	AASHTO T 316	Determine the temperature required for proper mixing of asphalt mixes and pumping of asphalt binders	1.5 hours for sample preparation; 2-2.5 hours for testing a binder sample at four different temperatures	*Mixing and Compaction Temperatures* Viscosity at mixing temperature = 285 mPa.s Viscosity at Compaction temperature = 175 mPa.s	• Dynamic viscosity of asphalt binders at different test temperatures • Test temperature required for mixing asphalt binder with aggregates and compacting asphalt mix samples

Dynamic Shear Rheometer (DSR)	AASHTO T 315	Determine rutting potential of asphalt binders at high temperatures through testing unaged and RTFO-aged asphalt binders	1.5 hours for sample preparation; 3.5 hours for testing three binder samples at three different temperatures	*<u>Rutting Potential</u>* $G^*/\sin\delta \geq 1.0$ kPa (unaged) $G^*/\sin\delta \geq 2.0$ kPa (RTFO-aged) *<u>Fatigue Potential</u>* $G^*.\sin\delta \leq 5000$ kPa (PAV-aged)	• Rutting factor ($G^*/\sin\delta$) at different temperatures • Continuous and high-temperature PG of asphalt binders • Optimum amount of PPA to prepare the asphalt mix samples
Multiple Stress Creep and Recovery Test (MSCR)	AASHTO TP 70 AASHTO M 332	to determine the rutting potential, stress sensitivity, and % recovery of asphalt binders at high temperatures through testing RTFO-aged asphalt binders	1.5 hours for sample preparation 2.5 hours for testing three binder samples at one temperature	*<u>Traffic Loading</u>* 'S' – Standard Traffic (<10 million ESAL and >70 km/h traffic speed), 'H' – Heavy Traffic (10-30 million ESAL or slow-moving traffic at 20-70 km/h), 'V' – Very Heavy Traffic (>30 million ESAL or standing traffic having speed <20 km/h), 'E' – Extremely Heavy Traffic (> 30 million ESAL and standing traffic having speed <20 km/h)	• Non-recoverable Creep Compliance (J_{nr}) and % Recovery of asphalt binders at different stress levels • Traffic level intensity a binder can sustain during its service life • MSCR grade of binder blends
Bending Beam Rheometer (BBR)	AASHTO T 313	Estimate low-temperature cracking resistance of asphalt binders	2.5 hours for sample preparation; 2.5 for sample conditioning; 30 minutes for testing two binder beam samples at one temperature	*<u>Low-Temperature Cracking</u>* $m_{60} \geq 0.3$ $S_{60} \leq 300$ MPa	• m_{60} and S_{60} values at different temperatures • Low-temperature cracking resistance and continuous low-temperature PG of binders
Surface free energy (SFE)		Estimate the moisture-induced	3.0 hours for sample preparation;		• Dynamic contact angles of asphalt binders with

		damage potential of asphalt binders	3.0 hours for testing 15-binder samples with three different probe liquids at room temperature		three different solvents, namely water (bipolar), formamide (mono-polar) and glycerin (apolar) • SFE components, namely total SFE, acidic component and basic component, of asphalt binders
Hamburg Wheel Tracking (HWT)	AASHTO T 324	Estimate rutting and moisture-induced damage potential of asphalt mixes	2.5 hours for mix preparation; 4.0 hours of mix conditioning; 2.5 hours for sample compaction using Superpave gyratory compactor*	*Rutting Potential* Rut depth < 12.5 mm *Moisture-Induced Damage Potential* SIP > 20,000 cycles	• Creep slope, stripping inflection point (SIP) and stripping slope of asphalt mixes • Rut depth of asphalt mixes containing PPA, WMA additive, and ASA
Tensile Strength Ratio (TSR)	AASHTO T283	Evaluate moisture-induced damage potential of asphalt Mixes	2.5 hours for mix preparation; 20.0 hours of mix conditioning; 3.0 hours for sample compaction using Superpave gyratory compactor*	*Moisture-Induced Damage Potential* TSR ≥ 0.8	• Indirect tensile strength of asphalt mixes in dry and wet conditions • TSR ratio of asphalt mixes containing PPA, WMA additive, and ASA

*first samples were compacted at different % air voids to determine the required amount of asphalt mix corresponding to 7±0.5% air voids

CHAPTER

2

LABORATORY CHARACTERIZATION OF ASPHALT BINDERS CONTAINING A CHEMICAL-BASED WARM MIX ASPHALT ADDITIVE[*]

ABSTRACT

Different technologies, namely foamed asphalt, synthetic waxes, zeolites and chemical additives, are used to produce Warm Mix Asphalt (WMA). The present study was undertaken to evaluate the effect of using different amounts of an amine-based chemical WMA additive on the rheology, Performance Grade (PG), and moisture-induced damage potential of an asphalt binder (PG 58-28). Superpave® specifications were used to evaluate the rheological properties and PG of the asphalt binder. Also, a mechanistic approach-based on the Surface Free Energy (SFE) method was used to evaluate the moisture-induced damage potential of the asphalt binder combined with commonly used aggregates in an asphalt mix. It was found that the dynamic viscosity of the asphalt binder is not significantly affected after blending it with the WMA additive.

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[*] *This chapter has been submitted to the ASTM Journal of Testing and Pavement Materials under the title "Laboratory Characterization of Asphalt Binders Containing a Chemical-Based Warm Mix Asphalt Additive" and accepted for publication. The current version has been formatted for this dissertation.*

It was also observed that the Superpave® high-temperature PG and the rutting factor ($G^*/sin\delta$) do not reduce by an increase in the WMA additive content. However, the continuous low-temperature PG of the asphalt binder decreases with an increase in the amount of WMA additive. Furthermore, it was found that the fatigue resistance ($G^*.sin\delta$) increases after blending the binder with the WMA additive. The SFE results of the asphalt binder revealed that the WMA additive used in this study reduces the moisture-induced damage potential of the asphalt mixes. However, the extent of this improvement was found to largely depend on the aggregate type. The outcomes of this study are expected to help better understand the influence of amine-based chemical WMA additives on rheological and long-term performance of asphalt mixes.

Keywords*:* Amine-based chemical WMA additive, performance grade, rheology, surface free energy, moisture-induced damage, rutting, fatigue

2.1 Introduction

Emission of greenhouse gases and harmful fumes, and over-consumption of non-renewable energy resources during the production and construction have always been a concern for the asphalt industry (Chowdhury and Button, 2008; Dorchies, 2008; Chehovits and Galehouse, 2010). In the mid-1990s, several Warm Mix Asphalt (WMA) technologies, namely, foamed asphalt, synthetic waxes, zeolites, and chemical additives, were developed which allow the reduction of mixing and compaction temperatures by 25° to 40°C (Chowdhury and Button, 2008; Zaumanis, 2010; Rubio et al., 2012; Brown, 2016). WMA technologies also reduce the energy consumption, emissions, fumes, and odors (Brown, 2016). Also, a number of WMA technologies are known to improve compaction of asphalt mixes (compaction aid) in the field (Hurley and Prowell, 2005; Button et al., 2007). There are other mechanisms that can enhance better workability of a WMA at low temperatures, such as chemical changes in binder, altered electric charge, reduced internal friction in the asphalt binder, improved wettability of the aggregate, and emulsification effects (Hanz et al., 2010; Hill et al., 2011; Fakhri et al., 2013). As a result, 72% companies in the United States used WMA technologies producing approximately 115 million tons of WMA mix, according to 7th annual survey conducted by National Asphalt Pavement Association (NAPA) in 2016 (Hansen and Copeland, 2017). The chemical WMA additives (CWMAs) were used for approximately 21.1% of the total WMA mix produced in 2016 (Hansen and Copeland, 2017).

The impact of using CWMA in the asphalt binders and asphalt mixes has consistently been studied using both laboratory experiments and field observations

(Button et al., 2007; Prowell et al., 2007; Estakhri, 2012). Bennert et al. (2010) studied the effects of different WMA additives on the performance of asphalt mixes containing polymer-modified binder. It was observed that the addition of CWMA slightly decreases the high-temperature Performance Grade (PG) of the asphalt binder but does not affect its dynamic viscosity. However, the resulting mixes were found to increase in the workability and compactability with an increase in the amount of WMA additive. Hurley and Prowell (2006) observed a reduction in air voids up to 1.5% as a result of using CWMA in the asphalt mixes, allowing a reduction in asphalt binder content. Also, an improvement in compaction effort was seen for the asphalt mixes containing CWMA at a temperature as low as 100˚C. Alvarez et al. (2012) used non-destructive X-ray CT scanning and subsequent image analysis techniques on the asphalt mixes containing CWMA. A lack of pore connectivity was observed in the central portion of the asphalt mixes containing CWMA, an indication of a denser packing and improved compaction over conventional HMA mixes. Additionally, laboratory tests conducted on the asphalt mixes containing CWMA exhibited less rutting compared to the HMA mixes (Hurley and Prowell, 2006). This effect was attributed to the improved compactability provided using CWMA. Similar results were also observed in the field test sections constructed using asphalt mixes containing CWMA (Hurley and Prowell, 2005; Davidson, 2006; Prowell et al., 2007). The field sections containing CWMA were constructed at lower temperatures than those for the HMA sections. However, in-place densities of WMA sections were equal to or higher than those of HMA sections showing an improved resistance to rutting as a result of using a WMA additive in the mix. The use of CWMA was also found to improve the adhesion at the asphalt binder and aggregate interface resulting in a reduction in the moisture-induced damage potential (Ghabchi et al., 2013). However, lowering the production and compaction temperatures may result in incomplete drying of aggregates and therefore, increase the moisture-induced damage potential (Hurley and Prowell, 2006; Howson et al., 2009; Arabani and Hamedi, 2011).

The moisture-induced damage potential of asphalt mixes can be determined by performing a Tensile Strength Ratio (TSR) test in the laboratory in accordance with the AASHTO T 283 test method (AASHTO, 2010). Based on the TSR test, Hurley and Prowell (2006) and Zhang (2010) reported an increased propensity of moisture-induced damage for asphalt mixes containing WMA additives. However, in other studies, it was reported that the TSR test in some cases does not accurately capture the moisture-induced damage potential of WMA mixes due to its empirical nature (Malladi et el., 2015; Ghabchi et al., 2014). For example, Kim et al. (2012) found a reduction in TSR value for laboratory-produced WMA mixes compared to their HMA counterparts. However, asphalt mixes containing WMA additives performed as well as HMA mixes in the field. After four years, no cracks or premature damage were observed in either HMA or WMA field sections. Malladi et al. (2015) also questioned the validity of TSR test for WMA mixes. In their study, satisfactory performance was reported for asphalt mixes containing WMA additives against moisture-induced damage using an Asphalt Pavement Analyzer (APA). Therefore, many researchers (e.g., Cheng et al., 2002; Kim et al., 2004; Hefer et al., 2006; Bhasin and Little, 2007; Bhasin and Little, 2007; Rani et al., 2018, *Evaluation of moisture-induced damage potential of asphalt mixes containing PPA and ASA using SFE approach*, manuscript in review process) have used the Surface Free Energy (SFE) method as a mechanistic tool to evaluate the moisture-induced damage potential of the asphalt mixes. The SFE approach quantifies the non-polar, acid and base SFE components of asphalt binders and aggregates in order to evaluate their adhesion and debonding potentials (Bhasin et al., 2007). Many studies have used the SFE approach to investigate the performance of asphalt mixes containing WMA additives (Arabani et al. 2012; Buddhala et al. (2011). However, to the authors' knowledge, only a few studies have applied the SFE approach to investigate the moisture-induced damage potential of asphalt mixes containing CWMA. Also, no previous studies have examined the effect of CWMA on the moisture-induced damage potential of the asphalt binder containing a softer grade binder, namely PG 58. Ghabchi et al. (2013) examined the effect of CWMA on the wettability and moisture-induced damage potential of asphalt mixes using the SFE approach. In that study, a PG 64 -22 asphalt binder was used. In the present study, the SFE method was used to evaluate the effects of an amine-based CWMA on the moisture-induced damage potential of asphalt mixes. For this purpose, a softer grade binder, i.e., PG 58-28, was used. Also, three commonly used aggregates in asphalt mixes, namely limestone, granite, and gravel, were used to examine the surficial interaction of the selected CWMA with different aggregates. The SFE components of asphalt binders were determined using the Dynamic Wilhelmy Plate (DWP) method, while the SFE components of aggregates were taken from the available literature. Adhesion and Debonding were determined to analyze the performance of the resulting mixes in the presence and absence of water. Finally, the energy ratio parameter was used to evaluate the effect of aggregate type and CWMA content on the moisture-induced damage potential of asphalt mixes.

2.2 Objectives

In the present study, the effect of an amine-based CWMA on the rheological properties, dynamic viscosity, and moisture-induced damage potential of a PG 58-28 asphalt binder was investigated. The SFE approach was used to evaluate the effect of the CWMA additive on the moisture-induced damage potential of the asphalt binder when used with limestone, gravel and granite aggregates. The specific objectives of this study are as follows.

1. Evaluate the effect of CWMA on the PG and dynamic viscosity of the asphalt binder;
2. Evaluate the rut and fatigue cracking resistance of both neat binder and the one containing WMA additive;
3. Determine the SFE components of neat binder and the one containing CWMA;
4. Evaluate the effect of CWMA on the adhesive bond strength at the aggregate-asphalt binder interface and the moisture-induced damage potential of the asphalt mix.

2.3 Materials and Testing

2.3.1 Sample Preparation

A PG 58-28 asphalt binder and a WMA additive (WM-1) were collected from an Oklahoma refinery and a local material supplier, respectively. WM-1 is an amine-based CWMA having low viscosity at room temperature. WM-1 is an amine-based WMA additive, with an amine value greater than 500 mg KOH/g. Physically, it is a dark amber liquid having a density of 8.1 lb/gal and a specific gravity of 0.97.

According to its manufacturer, WM-1 is expected to increase adhesion at the asphalt binder-aggregate interface and is suitable to be used in dense-graded mixes, mixes containing RAP, ultra-thin overlays, Stone Mastic Asphalt (SMA) mixes, and asphalt rubber mixes. The factory-recommended amounts of this additive to be used in mixes are 0.25% to 0.75% (by the weight of the asphalt binder). Therefore, in the present study, the asphalt binder was blended with four different amounts of WM-1, namely 0%, 0.25%, 0.5%, and 0.75% by weight of asphalt binder.

The additive and asphalt binder were blended by using high shear mixer at a rotational speed of 1000 rpm for 45 minutes at 145˚C (Huang et al., 2008; Zhang and Yu, 2010; Baldino et al., 2013). Before mixing, 120 g of asphalt binder was heated at 150˚C for two hours to liquefy. Then the additive was added and mixed with the binder. After mixing, the asphalt binders were kept in closed canisters at constant room temperature to minimize oxidation. Rolling Thin Film Oven (RTFO) and Pressure Aging Vessel (PAV) procedures were used for simulating the short- and the long-term aging of asphalt binders in accordance with AASHTO T 240 (AASHTO, 2013a) and AASHTO R 28 (AASHTO, 2012a), respectively.

2.3.2 Dynamic Shear Rheometer

The Dynamic Shear Rheometer (DSR) test was performed in accordance with AASHTO T 315 (AASHTO, 2012c) test standard on unaged and RTFO-aged asphalt binders. Both unaged and RTFO-aged asphalt binder samples were tested at three different temperatures, namely 55˚, 58˚ and 61˚C. Rutting factor (G*/sinδ) values were calculated at the test temperatures using measured complex modulus (G*) and phase angle (δ). Then, high-temperature continuous and the Superpave® PG of asphalt binders were determined in accordance with AASHTO M 320 (AASHTO, 2010b) standard specifications. The DSR tests were also performed at 16˚, 19˚ and 22˚C on PAV-aged asphalt binders to determine the fatigue factor (G*.sinδ) values.

2.3.3 Bending Beam Rheometer

The Bending Beam Rheometer (BBR) tests were conducted on PAV-aged asphalt binders in accordance with AASHTO T 313 (AASHTO, 2012b) test standard. The test was conducted at two different temperatures, namely -18˚ and -21˚C. The creep relaxation (m_{60}) and stiffness (S_{60}) values, measured after 60 seconds of load application were used to determine the low-temperature PG of the asphalt binders.

2.3.4 Rotational Viscometer

The Rotational Viscometer (RV) tests were performed at different temperatures, namely 135°, 150°, 165°, and 180°C, on unaged asphalt binders to determine their dynamic viscosity values, as an indication for workability of asphalt mix during mixing and compaction. The tests were conducted in accordance with AASHTO T 316 specifications (AASHTO, 2013b).

2.3.5 Surface Free Energy

The SFE components of the asphalt binders were determined through measuring the Dynamic Contact Angle (DCA) values using Dynamic Wilhelmy Plate (DWP) test (Wasiuddin et al., 2006; Ghabchi et al., 2014). For this purpose, three different probe liquids were used in this study, namely water (bipolar), glycerin (apolar) and formamide (mono-polar). To prepare the DCA samples, the asphalt binder was heated in an oven to liquefy at a temperature of 150˚C for two hours. Then, a 25 by 50 mm standard cover plate was dipped in the liquid asphalt binder to create a binder coating on it. Before dipping the plate, the plate was passed at least three times through the flame in order to dry and clean their surface. The coated plate was kept vertically in the oven at a temperature of 150˚C for 4 minutes to drip down excess asphalt binder. It helped to obtain a smooth and bubble-less coating of asphalt binder. Each sample was visually inspected for any defect or inconsistency. A total of 18 samples were selected for conducting a DWP test on each asphalt binder. Finally, the samples were kept in a desiccator overnight. Five out of eighteen samples were tested with water, five with glycerin and five with formamide. The probe liquids were selected based on the previous studies (Wasiuddin et al, 2007, 2007; Habal and Singh, 2016). After measuring the contact angles, the SFE components of the asphalt binders were calculated using the Equation 2.1 (Van Oss, 2002).

$$\Gamma_L(1 + cos\theta) = 2(\sqrt{\Gamma_A^{LW}\Gamma_L^{LW}} + \sqrt{\Gamma_A^{+}\Gamma_L^{-}} + \sqrt{\Gamma_A^{-}\Gamma_L^{+}}) \tag{2.1}$$

Subscripts *A* and *L* represent the energy parameters associated with asphalt binder and probe liquid, respectively. The total SFE component (Γ^{Total}) can be expressed as:

$$\Gamma^{Total} = \Gamma^{LW} + \Gamma^{AB} \tag{2.2}$$

$$\Gamma^{AB} = 2\sqrt{\Gamma^{+}\Gamma^{-}} \tag{2.3}$$

where,

Γ^{AB} = acid-base SFE component of total SFE, mJ/m^2,

Γ^{+}= monopolar acidic SFE component, mJ/m^2,

Γ^{-}= monopolar basic SFE component, mJ/m^2, and

$\Gamma^{\boldsymbol{LW}}$ = Lifshitz-van der Waals SFE component, mJ/m^2.

The variation in the acid, base, and Lifshitz- van der Waals SFE components of the asphalt binder as a result of blending it with different additives or modifiers might affect the bonding between the asphalt binder and aggregate (Arabani and Hamedi, 2010; Arabani et al., 2011; Buddhala et al., 2011). Therefore, as suggested by Bhasin et al. (2007), the determined SFE components were further processed to calculate interfacial energies, namely the work of adhesion and the work of debonding. The work of adhesion was calculated using Equation 2.4 and defined as the energy required to break one interface comprising two distinct materials into two interfaces. A high magnitude of the work of adhesion is beneficial as it indicates a stronger bond between the asphalt binder and aggregate. The work of debonding was calculated using Equation 2.5. The work of debonding is always negative in magnitude as it defines the reduction in free energy while separation of the asphalt binder and aggregate in presence of water. The lower the absolute value of work of debonding, the higher the resistance of asphalt binder-aggregate system to moisture-induced damage. In a study conducted by Bhasin et al. (2007), the work of adhesion and the work of debonding were combined into a single parameter, namely energy ratio as shown in Equation 2.6.

$$W_{AS} = 2(\sqrt{\Gamma_A^{LW}\Gamma_S^{LW}} + \sqrt{\Gamma_A^{+}\Gamma_S^{-}} + \sqrt{\Gamma_A^{-}\Gamma_S^{+}}) \tag{2.4}$$

$$W_{ASW}^{wet} = \Gamma_{AW} + \Gamma_{SW} - \Gamma_{AS} \tag{2.5}$$

$$ER_1 = |\frac{W_{AS}}{W_{ASW}^{wet}}| \tag{2.6}$$

where,

W_{AS} = work of adhesion, mJ/m^2,

W_{ASW}^{wet} = work of debonding, mJ/m^2,

ER_1 = energy ratio,

Γ_{AW} = interfacial energy between asphalt binder and water, mJ/m^2,

Γ_{SW} = interfacial energy between aggregate and water, mJ/m^2,

Γ_{AS} = interfacial energy between asphalt binder and aggregate, mJ/m^2, and

Subscripts A, S, and W define the energy parameters for the asphalt binder, aggregate or stone, and water, respectively.

2.4 Results and Discussions

2.4.1 Dynamic Shear Rheometer

Figures 2.1 and 2.2 present the rutting factor (G*/sinδ) determined at different temperatures for unaged and RTFO-aged asphalt binders, respectively. From Figure 2.1, it is evident that the addition of WM-1 to the neat binder increases the rutting factor by 10-19%, depending on the amount of WM-1. For instance, at 58˚C, using 0.25% and 0.75% WM-1 increase the rutting factor by 17% (from 1.15 kPa to 1.34 kPa) and by 10% (from 1.15 kPa to 1.27 kPa), respectively. Based on the DSR results and considering the Superpave® specifications (AASHTO M320, 2010b), the high-temperature PG of the asphalt binders was determined. The results are presented in Table 2.1. From Table 2.1, the high-temperature continuous PG of the neat binder increases from 59.4°C to 60.1°C with the addition of WM-1. But, the use of WM-1, irrespective of its amount, cannot change the Superpave® grade of the neat binder. As a result, an asphalt mix containing WM-1 is expected to exhibit similar rutting resistance than the one without any additive when used in the same traffic and environmental conditions. This effect is likely attributed to the surface chemistry of the selected CWMA which, according to manufacturer, works as a surfactant. Thereby, it impacts the polarity of the asphalt binder matrix, instead of asphalt binder’s grade. Xiao et al., (2012), Yu et al. (2016) and Rani et al. (2017a) also observed a slight increase in the rutting factor and high-temperature PG of the asphalt binder after blending it with a CWMA.

Furthermore, as shown in Figure 2.2, only RTFO-aged asphalt binder containing 0.25% WM-1 depicts an improved rutting factor compared to that of the neat binder. The RTFO-aged asphalt binders containing 0.5% or 0.75% WM-1 shows 8% lower rutting factor values than those measured for the neat binder. Based on these results, it can be noted that using a high amount of WM-1 helps reduce the oxidative aging of the neat binder. This may be attributed to the reduced production of carbonyl compounds during oxidative aging resulting in a lower conversion of maltenes to asphaltenes (Lau et al., 1992).

The fatigue factor ($G^{*}.sin\delta$) measured using the DSR test conducted on PAV-aged asphalt binders is presented in Figure 2.3. It is evident from Figure 2.3 that fatigue factor decreases with an increase in the temperature. Also, the blending of WM-1 with binder reduces its fatigue factor at all tested temperatures of 16°, 19°, and 22°C. The reduction in the fatigue factor is about the same for all the amounts of WM-1, see Figure 2.3. For instance, the fatigue factor of the neat binder is 4,500 kPa at 19°C which decreases by 12% (to 3,950 kPa) and 13% (to 3,900 kPa) after adding 0.25% and 0.50% WM-1, respectively. Based on the DSR test results and considering the Superpave® specifications (AASHTO, 2010b), the intermediate performance temperature of the asphalt binders was also determined using linear regression analysis. The results are presented in Table 2.1. According to Table 2.1, the intermediate performance temperature of the neat binder decreases by 1.1 ˚C, from 18.4˚C to 17.3˚C, after blending it with any amounts of WM-1 (0.25%, 0.50%, and 0.75%). A decrease in intermediate performance temperature is favorable as it signifies a relatively softer material which can sustain a larger number of load repetitions without experiencing significant cracking. These results agree with the ones observed on the RTFO-aged asphalt binders, which means that WM-1 lowers the oxidative aging rate of the neat binder. Therefore, after oxidation in the PAV, the asphalt binders containing WM-1 are less stiff than the neat binder. Based on these observations, the use of WM-1 is expected to increase the durability and the resistance to fatigue cracking of asphalt mixes.

2.4.2 Bending Beam Rheometer

The low-temperature PG of the asphalt binders measured using m_{60} and S_{60} values from BBR test are presented in Table 2.1. From Table 2.1, an increase of 1.4˚C can be observed in the low-temperature continuous PG of the neat binder after addition of 0.75% WM-1. However, adding WM-1 has no visible effect on the Superpave® low-temperature PG of the neat binder. These results indicate that the addition of WM-1 increases the low-temperature cracking potential of the neat binder. But the asphalt binder containing WM-1 performs as good as the neat binder till -28°C. Based on the results of the tests conducted on unaged and RTFO-aged asphalt binders, a reduction in the oxidative aging was observed (Table 2). Therefore, addition of WM-1 was expected to make a binder softer at low-temperatures, with improved resistance to low-temperature cracking. However, the results of the BBR tests conducted on the PAV-aged binders indicated that the asphalt binders containing WM-1 might be slightly stiffer than the neat binder at low-temperatures. Similar observations are also reported in a study conducted by Arega et al. (2011) on the asphalt binders containing CWMA. In a recent study conducted by Yu et al. (2016), it was also reported that the use of relatively high amount of a CWMA, approximately 5% by weight of the asphalt binder, is helpful in reducing the low-temperature PG of the asphalt binder. Therefore, additional research needs to be conducted to understand the effect of using high amounts of WM-1 on the PG and the rheology of asphalt binders.

2.4.3 Dynamic Viscosity

The dynamic viscosity values measured for the asphalt binders at selected temperatures are presented in Figure 2.4. From Figure 2.4, it can be observed that the dynamic viscosity of the asphalt binders, in general, decreases with an increase in temperature. No significant differences in the measured dynamic viscosity values of the asphalt binders are observed at the selected test temperatures. For example, the asphalt binder (with or without WM-1) exhibits the dynamic viscosity values approximately equal to 300 mpa.s at 135°C and 50 mpa.s at 180°C. As a result, the mixing temperature for the asphalt mixes with or without WM-1 is expected to be the same. This may be attributed to the fact that WM-1, according to the manufacturer, is a surfactant. Therefore, as noted before, WM-1 changes the polarity of the asphalt binder molecules, not the asphaltenes concentration which is a viscosity building component (Brown et al., 2009). Due to change in polarity, the asphalt binder containing WM-1 would provide an improved affinity with aggregates aiding in compaction and production of asphalt mixes at a lower temperature. Tao et al. (2009), Bennert et al. (2010), and You et al. (2011) also observed that asphalt binders containing a CWMA exhibited similar dynamic viscosity values with that measured for the neat asphalt binder at high temperatures such as 135°C. However, a reduction in the dynamic viscosity value has been observed after blending the asphalt binder with a CWMA at temperatures ranging from 90° to 130°C (Tao et al., 2009). From a production and construction point of view, one can say that the WMA mixes containing WM-1 additive can coat the aggregates and be compacted at low temperatures without forfeiting their aggregate coating quality and compactability.

2.4.4 Dynamic Contact Angle of Asphalt Binders

The measured DCAs and the Standard Deviation (SD) values of the asphalt binders with the probe liquids, namely water, glycerin, and formamide, are presented in Table 2.2. As shown in Table 2.2, the standard deviation values calculated for the measured DCA are relatively small (between 0° and 0.4°), indicating a good repeatability of the test results. A single-factor ANOVA analysis was also performed considering $\alpha = 0.05$ to examine the statistical variation in the DCA after binder modification. The null hypothesis for the analysis was that *WM-1 does not affect the binder interaction with the probe liquid and therefore the DCA angle*. For this purpose, the measured DCA data were divided into three groups based on the concentration of WM-1, namely 0 - 0.25%, 0 - 0.50%, and 0 - 0.75%. The calculated F-values, p-values, and $F_{critical}$ values are presented in Table 2.3. As shown in Table 2.3, the p-values for water and formamide probe liquids are less than 0.05 and the F-values are greater than the $F_{critical}$ value for all three groups. This indicates the rejection of null hypothesis and the significant effect of adding WM-1 on the DCA with water and formamide. However, for glycerin, the p-value is higher than 0.5 and the F-value is less than the $F_{critical}$ value only for the 0 - 0.5% group. For other groups (0 - 0.25% and 0 - 0.75%), the p-value is less than 0.05 and the F-value is greater than the $F_{critical}$, indicating an impact of WM-1 on the DCAs measured with glycerin. Considering the outcomes of the statistical analysis, it can be concluded that WM-1 affects the DCA of the neat binder with the selected probe liquids. This in turn affects the SFE components of the neat binder and its adhesion with aggregates after modification.

According to Table 2.2, the measured DCAs of the neat binder with water is 110.2˚ which decreases to 107.4˚ after the asphalt binder’s modification by using 0.75% WM-1. The measured DCA of neat binder with glycerin is 99.9˚. Addition of 0.25% WM-1 decreases the DCA to 98.6° which increases to 99.5° after adding 0.50% and 0.75% WM-1. It is evident from Table 2.2 that blending the asphalt binder with WM-1 does not considerably affect its DCA with glycerin. For the neat binder, from Table 2.2, the DCA with formamide is equal to 93.6° and the addition of WM-1 results in a decrease in the DCA, equal to 92.7°. According to Sharfrin and Zisman (1960), if the contact angle of a material with a probe liquid is less than 90˚, the wetting is favorable, or the probe liquid has a potential to wet the material surface. It indicates that the probe liquids were not able to wet the surface of any of the asphalt binders. However, the use of WM-1 decreases the resistance of the asphalt binder to wetting by different probe liquids. The reduced DCA values also suggest that the WM-1 may enhance the polarity of the neat PG 58-28 asphalt binder, attracting more bipolar molecules of water and mono-polar molecules of formamide. The drop in the DCA values is expected to affect the SFE of the asphalt binders and its interaction with aggregates, as discussed in the following section.

2.4.5 Surface Free Energy Components of Asphalt Binders and Aggregates

The measured DCA values, SFE components of the selected probe liquids (Table 2.4) (Hefer et al, 2006), and Equations 2.1, 2.2, and 2.3 were used to determine the SFE components of the asphalt binder blends. The SFE components of the PG 58-28 asphalt binder containing different amounts of WM-1 are summarized in Table 2.5. From Table 2.5, the total SFE (Γ^{total}) of the asphalt binder is 14.76 mJ/m^2 and decreases to 14.62 mJ/m^2 after adding 0.25% WM-1, and then increases to 16.10 mJ/m^2 and 16.31 mJ/m^2 with blending it with 0.50% and 0.75% WM-1, respectively. A similar trend was observed in a non-polar SFE component (Γ^{LW}) of the asphalt binder. An increase in the total SFE component is advantageous as it depicts an increased amount of energy required to debond the asphalt binder coated over the aggregate in the presence of water. On the other side, the acid-base SFE component (Γ^{AB}) first increases from 0.67 mJ/m^2 to 0.91 mJ/m^2 and then decreases to 0.42 mJ/m^2 and 0.32 mJ/m^2 with the addition of 0.25%, 0.50%, and 0.75% WM-1, respectively. A similar trend of variation can be observed for the acid SFE component (Γ^+), Table 2.5. Only base SFE component (Γ^-) showes a continuous increase with increasing the WM-1 content in the neat binder. One may expect that an asphalt binder containing WM-1 will have an improved adhesion bond with an acidic aggregate such as granite. However, it may be difficult to obtain a strong bond with a basic aggregate such as limestone. This is due to the surface chemistry of Lewis acid and base, which makes a highly acidic material less likely to form a strong adhesive bond with another highly acidic material. An increase or decrease in the SFE components of an asphalt binder helps in understanding their interaction with different acidic or basic aggregates but cannot quantify the moisture-induced damage potential of the asphalt mixes (Arabani and Hamedi, 2010; Arabani et al., 2011). Therefore, the work of adhesion, the work of debonding, and the energy ratio were determined, as suggested by Bhasin et al. (2007). For this purpose, three different aggregates, namely granite, gravel, and limestone were selected. The SFE components of the selected aggregates were adopted from the available literature and are presented in Table 2.6 (Ghabchi et al.,2014; Buddhala et al., 2011; Bhasin et al., 2007). Among the selected aggregates used in this study, the limestone aggregate was tested by the team using the Universal Adsorption Device (USD) for determination of the SFE components. The results are reported in another paper (Ghabchi et al., 2014). All three aggregates have high basic SFE component than acid SFE component and subsequently, should anticipate a strong bond with an acidic asphalt binder.

2.4.6 Work of Adhesion

The work of adhesion between asphalt binders and aggregates were determined using the SFE components of the materials and Equation 2.4. The work of adhesion values is presented in Figure 2.5. From Figure 2.5, it is evident that the work of adhesion of the neat PG 58-28 asphalt binder is the highest (105.8 mJ/m^2) with granite aggregate and the lowest (82.1 mJ/m^2) with limestone aggregate. It indicates that the neat PG 58-28 asphalt binder has a stronger adhesion bond with granite aggregate than that with limestone or gravel aggregates. Adding 0.25, 0.50%, and 0.75% WM-1 to the asphalt binder is found to increase its work of adhesion with granite aggregate from 102.7 mJ/m^2 to 104.2, 105.8 and 107.1 mJ/m^2, respectively. For limestone and gravel aggregates, the work of adhesion increases by adding 0.25% WM-1 and then decreases for a higher amount of WM-1 (0.5% and 0.75%). These observations indicate that the addition of WM-1 to asphalt strengthens its adhesive bond with granite aggregate. A higher adhesive bond means a higher energy required to separate the asphalt binder from aggregate. However, for limestone and gravel aggregates, the use of high amounts

(>0.25%) of WM-1 may not be as beneficial. This is probably due to the increased alkalinity of the neat binder after modification with WM-1 reducing the force of attraction of the binder with alkaline aggregates (having a base SFE component higher than acid SFE component) following the surface chemistry of Lewis acid and base (Good, 1992).

Although the work of adhesion is an important parameter required for characterization of moisture-induced potential of asphalt mixes, according to Bhasin et al. (2007), it cannot quantify the moisture-induced damage potential of the asphalt mix. This parameter and other energy parameters are required for calculation of the energy ratio, which is a better parameter to rank the moisture-induced damage potential of the asphalt mix. However, in arid areas having a little or no rainfall, work of adhesion would represent the performance of asphalt-binder and aggregate system. Based on the results, it can be concluded that adding a high amount of WM-1 (>0.25%) may reduce the adhesion bond between the asphalt binder and aggregate (limestone and gravel) resulting in a poor asphalt binder and aggregate system.

2.4.7 Work of Debonding

The work of debonding values for all twelve combinations of asphalt binders and aggregates were calculated using Equation 2.5 (Figure 2.6). From Figure 2.6, it is evident that the work of debonding of asphalt binder without any WM-1 is found to be 204.1, 55.7, and 247.0 mJ/m^2 with limestone, granite, and gravel aggregates. An increase in the amount of WM-1 in the asphalt binder results in a slight decrease in the work of debonding values for granite aggregate and an increase of the work of debonding for both limestone and gravel aggregates. Based on these observations, the use of WM-1 is expected to improve the asphalt binder's resistance to the moisture-induced damage when used with granite aggregate, slightly. Similar to the work of adhesion, the work of debonding alone cannot rank the mixes based on their moisture-induced damage potential (Bhasin et al., 2007). This parameter is required to determine the energy ratio, by which the moisture-induced damage potential is evaluated (Bhasin et al., 2007).

2.4.8 Energy Ratio

Based on the work of adhesion and the work of debonding, an energy ratio was determined for all twelve combinations of asphalt binder blends and aggregates using Equation 2.6 (Figure 2.7). A high energy ratio meant less moisture-induced damage potential for an asphalt mix. From Figure 2.7, it is evident that the energy ratio values for the neat PG 58-28 binder with granite, limestone, and gravel aggregates are 1.84, 0.40, and 0.38, respectively. The addition of 0.75% WM-1 to the asphalt binder results in an improvement in energy ratio from 1.84 to 1.96, approximately by 5%, for granite aggregate. However, adding 0.5% or 0.75% WM-1 to the asphalt binder moderately reduces its energy ratio from 0.40 to 0.35 for limestone aggregate and from 0.36 to 0.31 for gravel aggregate approximately a 10% reduction for both combinations. Bhasin et al. (2006) also observed low energy ratio values for the asphalt binders and aggregates having large base SFE component than acid SFE component following the surface chemistry of Lewis acid and base. Moreover, Buddhala et al. (2011) reported a decrease in the work of adhesion and work of debonding of the highly basic aggregates with the asphalt binder having a high base SFE component. Among the twelve tested asphalt binder-aggregate systems, the highest energy ratio (1.96) is observed for the asphalt binder containing 0.75% WM-1 with granite aggregate indicating lowest moisture-induced damage potential. Additionally, adding 0.25% WM-1 to the binder showed an increase in the energy ratio value for all aggregate types. However, the increase in the energy ratio was very small. For instance, from Figure 7, the energy ratio increased from 1.84 to 1.89 (2.7%) for granite aggregate, from 0.40 to 0.44 (10%) for limestone aggregate, and from 0.36 to 0.40 (11%) for gravel aggregate after modification of the neat binder by using 0.25% WM-1. It indicated that the use of WM-1 may improve the resistance of the asphalt binder-aggregate system to moisture-induced damage, but only slightly.

2.5 Conclusions

The present study evaluated the effects of different amounts (0%, 0.25%, 0.50% and 0.75%) of an amine-based chemical WMA additive (WM-1) on the rheological properties, Superpave® PG, rutting, fatigue, and moisture-induced damage potential of a PG 58-28 asphalt binder. The moisture-induced damage potential was evaluated for the asphalt-aggregate systems using the SFE technique. Based on the results and discussion presented in the preceding sections, the following conclusions are drawn:

1. The use of WM-1 reduced the oxidative aging of the asphalt binder. As a result, the asphalt binder was found to exhibit an increased resistance to fatigue cracking without impacting the rutting or low-temperature cracking performance with the addition of WM-1. Therefore, asphalt mixes containing WM-1 are expected to have a longer life than those without WM-1.

2. A high amount of WM-1, i.e., 0.75%, did not show any mechanistic advantage towards improving rutting or fatigue cracking performance of the asphalt binder. This was likely due to unchanged chemical composition of the asphalt binder after modification with WM-1. Conducting chemical tests such as SARA analysis can help understand the effect of WM-1 at different amounts.
3. The neat binder showed a stronger affinity for the granite aggregate than limestone or gravel aggregate. Therefore, an asphalt mix containing granite aggregate and the tested PG 58-28 asphalt binder is expected to have higher resistance to moisture-induced damage than the one containing limestone or gravel aggregate.
4. The use of 0.25% of WM-1 was found to improve the adhesion bond of the neat binder with the selected aggregates. However, the results indicated that adding any higher amount of WM-1 (>0.25%) to the neat binder may not be beneficial; a higher amount of WM-1 may result in a lower adhesion bond between the binder and aggregate, when used with limestone and gravel aggregates.
5. Based on the results, a slight improvement was observed in the moisture-induced damage resistance of the asphalt binder-aggregate system, irrespective of aggregate type, due to 0.25% WM-1. For instance, the use of 0.25% WM-1 increased the energy ratio only by 2.7%, 10%, and 11% for the asphalt binder-aggregate system containing granite, limestone, and gravel aggregates, respectively.

6. The use of a higher amount of WM-1 (>0.25%) was found to increase the moisture-induced damage potential of the asphalt mixes containing aggregates with a base SFE component higher than their acid component. This is due to the increased alkalinity of the neat binder after modification with WM-1.

It is important to note that this study focused on the impact of a chemical WMA additive (in different dosages) on the PG 58-28 asphalt binder. Effects of source and polymer-modification were not evaluated, which can be a potential area of future studies. Furthermore, master curves can be generated to investigate the rheological performance of the asphalt binder at different temperatures and frequencies, and to evaluate the effect of WM-1 on the rheological performance under those temperatures and frequencies.

Acknowledgements

The authors would like to acknowledge the Oklahoma Department of Transportation (ODOT) and Southern Plain Transportation Center (SPTC) for their financial support. Special thanks and appreciation to Dr. Edgar O’Rear at the University of Oklahoma for his support in conducting this study. Also, the contribution of materials by the Haskell Lemon Construction Co. and MeadWest Co., renamed Ingevity Co. is also acknowledged.

Table 2.1 Performance Grading of the Asphalt Binders under Unaged, RTFO-, and PAV-aged Conditions

Amount of WM-1	Aging Condition	G*/sinδ or [G*.sinδ], kPa	High-Temperature Continuous PG, ˚C	Intermediate Performance Temperature ˚C	Low-Temperature Continuous PG, ˚C	Superpave® PG
0%	Unaged	1	59.4	-		**PG 58-28**
	RTFO-Aged	2.2	59.7	-		
	PAV-Aged	[5000]	-	18.4	-32.3	
0.25%	Unaged	1	60.3	-		**PG 58-28**
	RTFO-Aged	2.2	59.9	-		
	PAV-Aged	[5000]	-	17.3	-31.9	
0.50%	Unaged	1	60.1	-		**PG 58-28**
	RTFO-Aged	2.2	59.0	-		
	PAV-Aged	[5000]	-	17.4	-30.3	
0.75%	Unaged	1	60.0	-		**PG 58-28**
	RTFO-Aged	2.2	59.3	-		
	PAV-Aged	[5000]	-	17.3	-30.9	

Table 2.2 Dynamic Contact Angles of Asphalt Binders Containing Different Amounts of WM-1

Binder Type	Amount of WM-1 (%)	Dynamic Contact Angle					
		Water		Glycerin		Formamide	
		Average	SD	Average	SD	Average	SD
PG 58-28	0	110.2˚	0.1˚	99.9˚	0.1˚	93.6˚	0.3˚
	0.25	109.3˚	0.0˚	98.6˚	0.1˚	92.6˚	0.2˚
	0.50	108.5˚	0.3˚	99.5˚	0.1˚	92.8˚	0.4˚
	0.75	107.4˚	0.2˚	99.5˚	0.2˚	92.7˚	0.3˚

Table 2.3 ANOVA Analysis of Measured DCAs with Different Solvents

Solvent Type	WM-1 (%)	F-value	P-value	F critical
Water	0-0.25%	9.54	1.49E-02	5.32
	0-0.50%	40.89	2.10E-04	5.32
	0-0.75%	211.20	4.92E-07	5.32
Glycerin	0-0.25%	68.60	3.40E-05	5.32
	0-0.50%	0.94	3.62E-01	5.32
	0-0.75%	6.85	3.08E-02	5.32
Formamide	0-0.25%	47.54	1.25E-04	5.32
	0-0.50%	14.67	5.02E-03	5.32
	0-0.75%	19.91	2.11E-03	5.32

Table 2.4 Surface Energy Components, mJ/m^2, of Probe Liquids at 20˚C (Van Oss et al., 2002)

Probe Liquid	Γ^{+}	Γ^{-}	Γ^{LW}	Γ^{Total}	SD
Water	25.5	25.5	21.8	72.8	0.2
Glycerin	3.92	57.4	34	64	0.3
Formamide	2.28	39.6	39	58	0.2

Table 2.5 Surface Free Energy Components of the Asphalt Binders

Binder Type	WM-1 (%)	Surface Free Energy Components, mJ/m^2				
		Γ^{+} (Acid)	Γ^{-} (Base)	Γ^{LW} (Non-Polar)	Γ^{AB} (Acid-Base)	Γ^{total} (Total)
PG 58-28	0	0.15	0.74	14.09	0.67	14.76
	0.25	0.26	0.79	13.71	0.91	14.62
	0.50	0.04	1.14	15.67	0.42	16.10
	0.75	0.02	1.49	15.99	0.32	16.31

Table 2.6 Surface Free Energy Components, mJ/m^2, of Limestone, Granite, and Gravel Aggregates

Aggregate	Literature Source	Γ^{+}	Γ^{-}	Γ^{LW}	Γ^{AB}	Γ^{total}
Limestone	Ghabchi et al. (2014)	17.50	741.40	51.40	227.80	279.20
Granite	Buddhala et al. (2011)	24.10	96.00	113.20	96.20	229.40
Gravel	Bhasin et al. (2007)	23.00	973.00	57.50	299.20	356.70

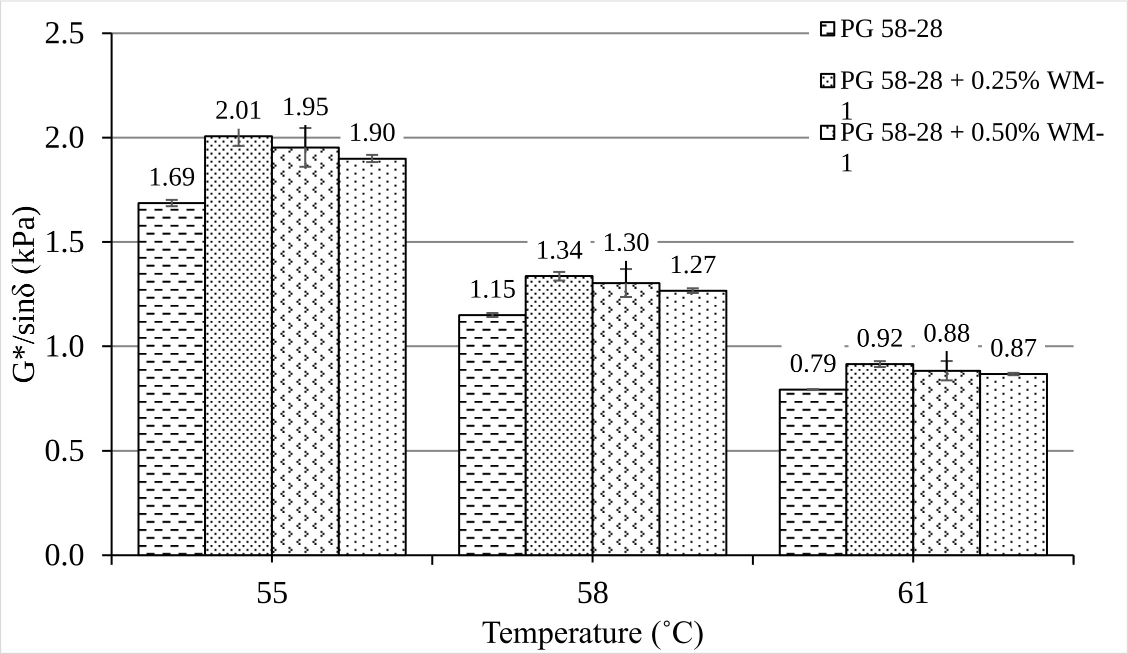

Figure 2.1 DSR Test Results Conducted on Unaged Asphalt Binders Containing Different Amounts of WM-1

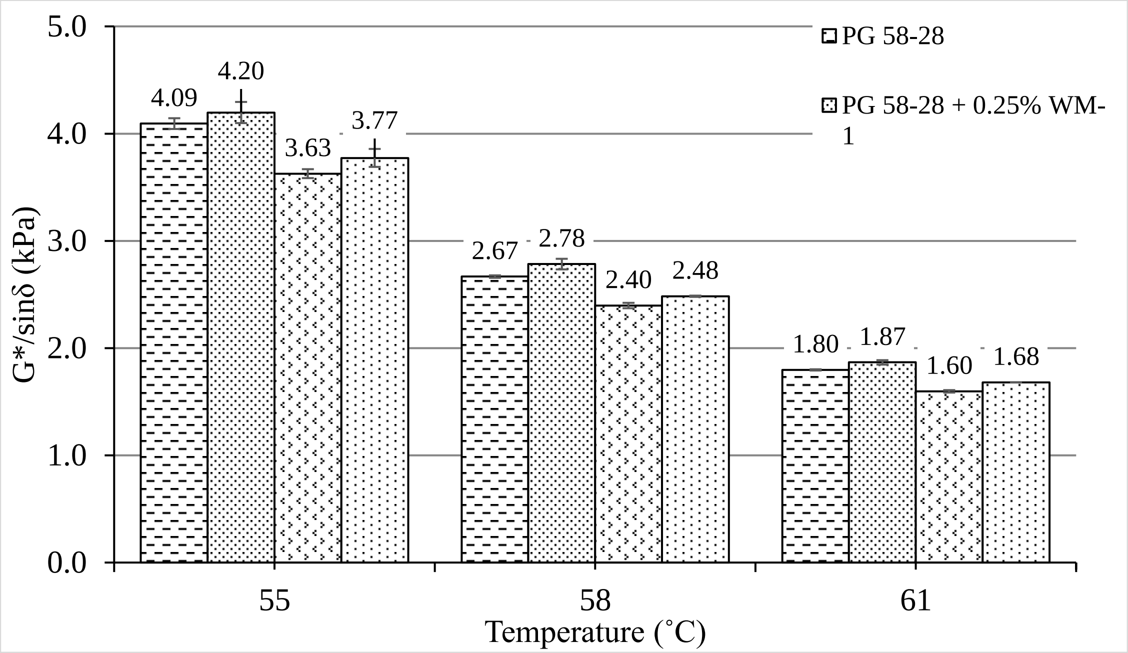

Figure 2.2 DSR Test Results Conducted on RTFO-Aged Asphalt Binders Containing Different Amounts of WM-1

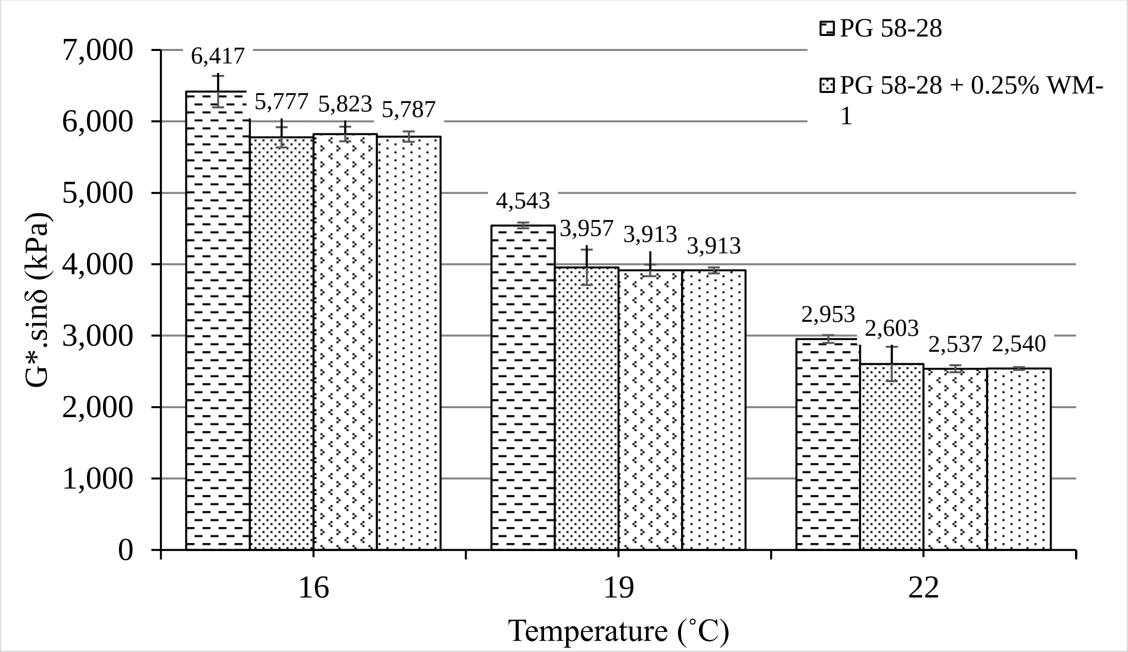

Figure 2.3 DSR Test Results Conducted on PAV-Aged Asphalt Binders Containing Different Amounts of WM-1

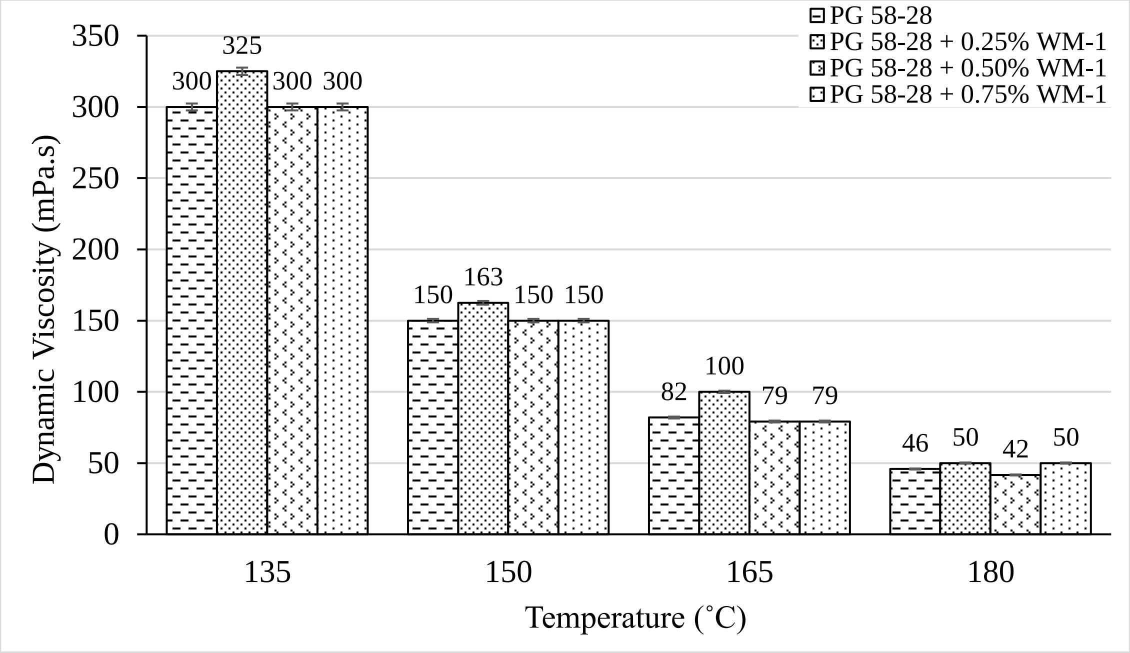

Figure 2.4 RV Test Results Conducted on Unaged Asphalt Binders Containing Different Amounts of WM-1

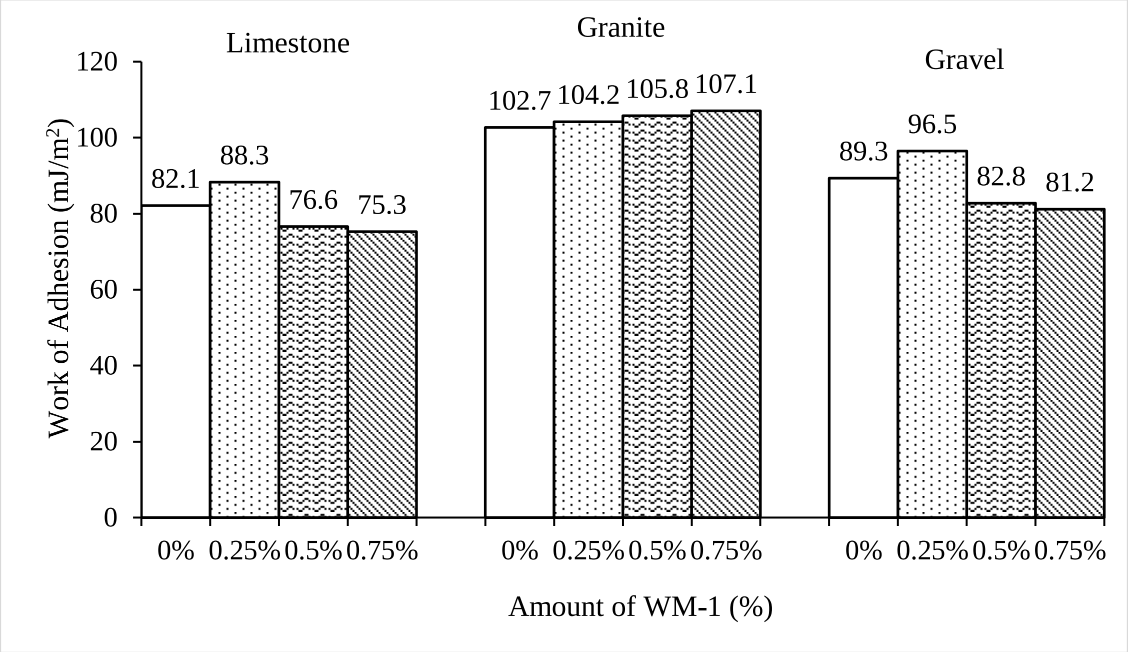

Figure 2.5 Work of Adhesion of PG 58-28 Asphalt Binder Blended with 0%, 0.25%, 0.50%, and 0.75% WM-1 with Limestone, Granite, and Gravel Aggregates

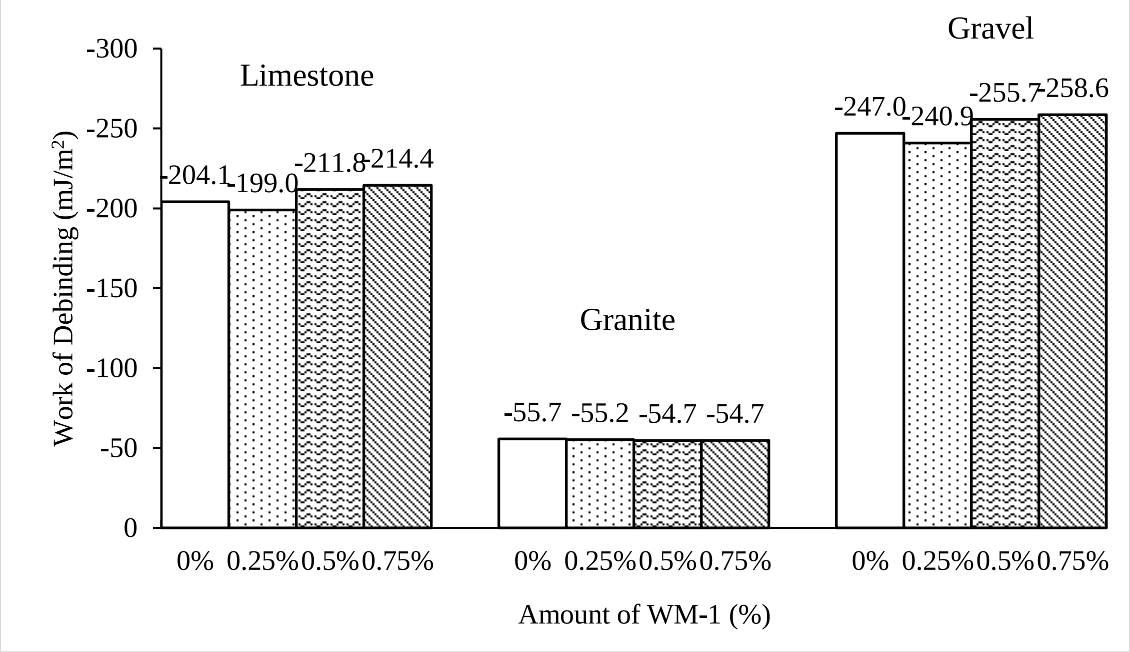

Figure 2.6 Work of Debonding of PG 58-28 Asphalt Binder Blended with 0%, 0.25%, 0.50%, and 0.75% WM-1 with Limestone, Granite, and Gravel Aggregates

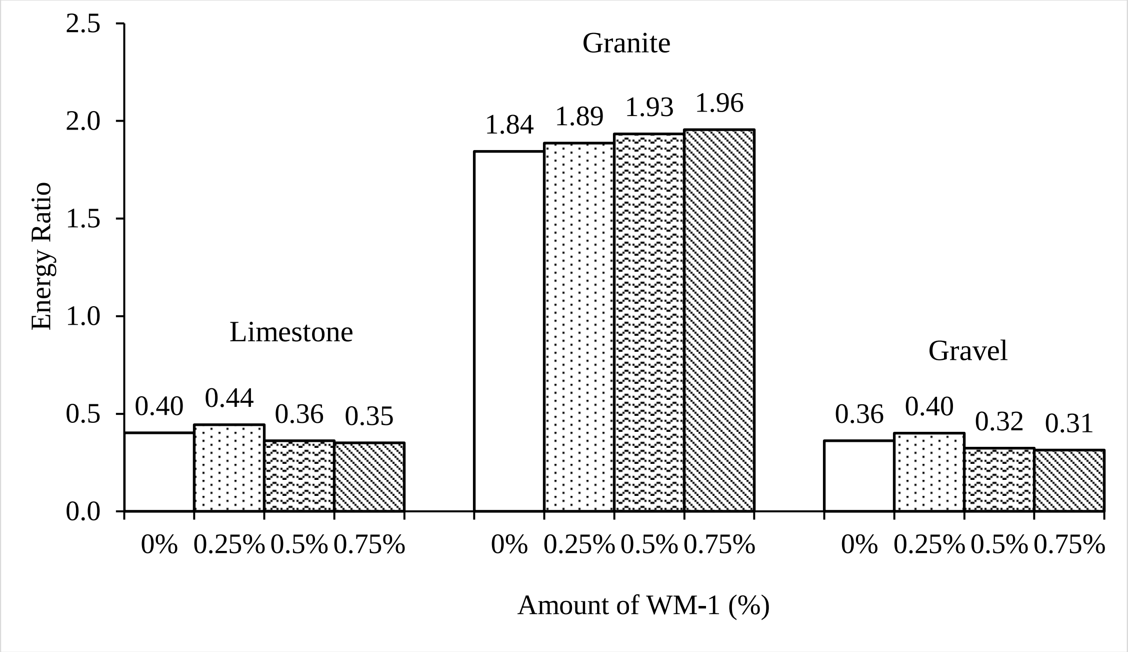

Figure 2.7 Energy Ratio of PG 58-28 Asphalt Binder Blended with 0%, 0.25%, 0.50%, and 0.75% WM-1 with Limestone, Granite, and Gravel Aggregates

CHAPTER

3

EVALUATION OF LIQUID ANTI-STRIPPING AGENT ON THE PERFORMANCE OF ASPHALT BINDERS AND MIXES CONTAINING POLYPHOSPHORIC ACID†

ABSTRACT

Polyphosphoric Acid (PPA) is used to enhance stiffness of a binder and help increase its resistance to rutting. However, due to the hydrophilic nature of PPA, increased propensity for moisture-induced damage could be a problem with using this additive. Use of an Anti-Stripping Agent (ASA) such as hydrated lime and liquid ASA is a common practice in the industry to minimize moisture-induced damage in asphalt pavements. Using an amine-based ASA along with PPA can negatively impact the resistance of a mix to moisture-induced damage. In the present study, the effects of an amine-based liquid ASA on the rheological performance of PPA-modified binders were evaluated. Also, the effects of PPA on the rheological performance of neat binders were evaluated. For this purpose, dynamic shear rheometer, bending beam rheometer,

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† *This chapter has been submitted to the International Journal of Pavements Research and Technology under the title "Evaluation of Liquid Anti-Stripping Agent on the Performance of Asphalt binders and Mixes containing Polyphosphoric Acid." The current version has been formatted for this dissertation.*

rotational viscometer, and Multiple Stress Creep Recovery (MSCR) tests were conducted on the PG 58-28 binder collected from two different sources. It was found that the use of PPA enhances the rutting resistance and dynamic viscosity of the binders without affecting its low-temperature cracking resistance, the amount of enhancement depending on the amount of PPA and source of the binder. The addition of liquid ASA to the PPA-modified binder nullifies the effect of PPA on the binder's rutting resistance and dynamic viscosity. Also, it was found that the use of 0.5% liquid ASA can neutralize the effect of 1.0% PPA. Furthermore, based on the MSCR test results, it was observed that although the PPA-modified binders can sustain higher traffic loads with an improved % Recovery, those binders are more stress-sensitive as compared to the neat binders and the ones containing PPA and ASA. Overall, the results from this study are expected to help understand the associated impacts of using PPA, alone and with amine-based ASA, on the characteristic performance of binders against pavement distresses, namely rutting and low-temperature cracking. It can be a critical factor in performing mix designs for pavements.

Keywords: Superpave® performance grading, rheology, viscosity, polyphosphoric acid (PPA), anti-stripping agent (ASA), rutting, fatigue, and moisture-induced damage

3.1 Introduction

Significant efforts have been made by researchers and industry in the past to minimize rutting in asphalt pavements. Several Warm-Mix Asphalt (WMA) additives and modifiers for binders namely, polymers (elastomers or rubbers and plastomers or plastics), fibers, and oxidants have been used in mixes to enhance their resistance to rutting (Gandhi and Amirkhanian, 2007; Zhang and Yu, 2010a; Jamshidi et al., 2012). For example, Jamshidi et al. (2012) and Arshad et al. (2013) reported that the addition of Sasobit® to the binder enhances its resistance to rutting by increasing the stiffness. Gandhi and Amirkhanian (2007) also reported that the use of Sasobit® and Asphamin® in the binder leads to an increase in the stiffness. The extent of stiffness enhancement was dependent upon the amount of WMA additive as well as its type. Zhang and Yu (2010a) observed a rise in stiffness due to modifying the binder by Styrene–Butadiene Rubber (SBR). In recent years, several studies have been conducted on the use of Polyphosphoric Acid (PPA) to improve the mechanical properties of binders (e.g., Bishara et al., 2001; Falkiewicz and Grzybowski, 2004; McGennis et al., 2004; Orange et al., 2004; Maldonado et al., 2006; Kodrat et al., 2007; Arnold et al., 2009; Baldino et al., 2013).

The use of PPA is known to be an effective way to increase the stiffness of binders. It has been found that the addition of PPA can significantly augment the stiffness of binders at high temperatures, and depending upon the source of the binder, may improve the low-temperature Performance Grade (PG) as well (Bishara et al., 2001; Falkiewicz and Grzybowski, 2004; McGennis et al., 2004; Orange et al., 2004; Maldonado et al., 2006; Kodrat et al., 2007; Baldino et al., 2013; Al-Qadi et al., 2014).

PPA modification has been found to decrease the sensitivity of binders to temperature variation and increase their resistance to rutting. Yan et al. (2013) observed higher softening point and viscosity (at 135˚C) of the PPA-modified binders. Edwards et al. (2006) reported that adding wax or PPA to binders makes them stiffer. PPA-modified binders exhibited higher resistance to low-temperature cracking than those containing waxes (Edwards et al., 2006). To understand the mechanisms of using PPA, several researchers have investigated the effects of the PPA on binders at a molecular level (Giavarini et al., 2000; Baumgardner, 2005; Jaroszek, 2012; Yan et al., 2013). It was reported that PPA increases the concentration of asphaltenes at the expense of saturates, resins, or cyclics present in the binder. Also, it was found that adding PPA decreases the size of asphaltenes and dispersed them into the asphalt matrix. Consequently, PPA increased the stiffness and viscosity of the binders (Jaroszek, 2012; Yan et al., 2013). However, the effect of PPA was found to be dependent on the composition of the base binder. A number of mechanisms such as cross-linking of PPA with asphalt segments, formation of ionic clusters, and cyclization of alkyl aromatics could explain the reason for an increase in stiffness of binder due to the addition of PPA (Baumgardner, 2005).

Despite the abovementioned advantages associated with using PPA, moisture-induced damage potential of mixes may increase due to the hydrophilic nature of PPA. Several recent studies have reported the effect of PPA modification on the moisture-induced damage potential of mixes (Reinke et al. 2012; D’Angelo, 2012; Shulga et al., 2012). In a field and laboratory study conducted in MnROAD, D’Angelo (2012) reported no increase in moisture-induced damage due to using PPA-modified binders. Shulga et al. (2012) observed a decrease in Tensile Strength Ratio (TSR) when PPA-modified binder was used in the production of a foamed WMA mix. Similarly, King et al. (2002) reported an increased moisture-induced damage potential due to PPA-modification of binders. Other studies have shown that the aggregates are prone to moisture-induced damage, might exhibit an increase propensity to stripping because of PPA-modification of binder (e.g., Arnold et al., 2009; Reinke et al. 2012). Usually, an Anti-Stripping Agent (ASA) is used for mixes having a potential for moisture-induced damage.

One should exercise care when using a PPA-modified binder with an amine-based ASA. According to King et al. (2002), when basic compounds are added to mixes containing a PPA-modified binder, the acid modifier and the basic ASA may react with each other to form an amine salt. As a result, the ASA might not resist the moisture-induced damage, and instead contribute to moisture-induced damage either by making the asphalt film more permeable to water or by emulsifying the asphalt in the presence of heat, moisture, and traffic (King et al., 2002). Also, a partial neutralization between the PPA and the ASA might lead to a partial loss of the increased binder stiffness ($G^*/\sin\delta$) achieved from the PPA modification (Buchner, 2005).

In the present study, efforts were made to examine the effects of an amine-based ASA and PPA on the rheological and mechanical properties (PG, Dynamic Viscosity (DV), rutting, and fatigue) of the binders through laboratory testing. For this purpose, 18 different binder blends were prepared in the laboratory using the PG 58-28 binder from two dissimilar sources. In addition to the DSR test, Multiple Stress Creep Recovery (MSCR) tests were performed to determine the stress sensitivity and elastic recovery before and after binder modification. To study the stress-sensitivity of binders due to modification, a stress level of 10 kPa was added to the conventional 0.1 and 3.2 kPa stress levels of the MSCR test method.

3.2 Objectives

The specific objectives of this study are listed below:

1. Examine the effect of PPA on the performance of neat PG 58-28 binders with respect to rutting resistance, fatigue cracking, and low-temperature cracking;
2. Evaluate the effect of an amine-based liquid ASA on the performance of PPA-modified binders;
3. Determine the PG and MSCR grades of the binders containing PPA or PPA and ASA;
4. Evaluate the effect of PPA or PPA and ASA on the stress sensitivity of neat PG 58-28 binders;
5. Investigate the source dependency of the binder.

3.3 Materials

Two PG 58-28 and two PG 64-22 binders from different sources were used in this study. Also, a 105% grade PPA, an amine-based WMA additive, and an amine-based liquid ASA were used. These materials were collected from their suppliers. In addition, limestone and granite aggregates of different sieve sizes were collected for the preparation of mixes.

3.3.1 Polyphosphoric Acid

The PPA is an oligomer produced either by heating a dispersed solution of phosphorus pentoxide (P_2O_5) and phosphoric acid (H_3PO_4) or by dehydration of H_3PO_4

at elevated temperatures (Masson, 2008). PPA is generally available in different grades such as 100%, 105%, 115%, and 123% depending on the amount of P_2O_5 present in the product with respect to H_3PO_4. For example, 100% PPA contains 72.4% P_2O_5. For this study, 105% PPA was selected; the amount of P_2O_5 for this PPA was 79.5%. According to Platonov (2002), the lower the grade, the lower the viscosity of PPA. The 105% PPA used in this study is of relatively low viscosity consisting of short chains of mono- and di- meric segments (ortho- and pyro- phosphoric acids). Therefore, it was easier to use 105% PPA at room temperature compared to high grades of PPA. To evaluate the effect of PPA on the mechanistic properties of binders, the binders were modified with four different amounts of PPA, namely 0.5%, 1.0%, 1.5%, and 2.0% by the weight of the binder.

3.3.2 Anti-Stripping Agent

As noted previously, the ASA used in this study was an amine-based liquid ASA having a specific gravity close to 1.0. It has a low-viscosity which makes it easier to use at low temperature. It is expected to reduce moisture-induced damage potential of mixes by enhancing adhesion between binder and aggregate. According to manufacturer’s recommendation, the amount of ASA ranges from 0.25% to 1.0% by weight of the binder. In this study, the amount of ASA was kept constant at 0.5% by weight of the binder.

3.4 Preparation of Binders for Testing

Neat binders were blended with the required amount of PPA and ASA using a High Shear Mixer (HSM). Different blending methods have been used by researchers previously for mixing binder and additives or modifiers. For example, Singh and

Sawant (2016), Zhang and Yu (2010), and Baldino et al. (2013) have used HSM at a rotational speed varying between 500 rpm and 5000 rpm. In the present study, the binder and additive were blended in the HSM for 45 minutes using a rotational speed of 1,000 rpm. The blending temperature varied between 145° and 155°C depending on the type of the binder and the amount of additive. For example, a temperature of 145°C was used for blending PG 58-28 with up to 1.0% PPA, whereas a temperature of 155°C was used for blending PG 58-28 with a higher amount (1.5% and 2.0%) of PPA. As listed in Table 3.1, in total, 18 different binder blends were prepared for testing. The short-term aging and long-term aging were simulated using a Rolling-Thin Film Oven (RTFO) and a Pressure Aging Vessel (PAV) in accordance with AASHTO T 240 (AASHTO, 2013a) and AASHTO R 28 (AASHTO, 2012a) methods, respectively.

3.5 Laboratory Test Methods

3.5.1 Dynamic Shear Rheometer

The DSR tests were conducted on unaged, RTFO-aged, PAV-aged binders following AASHTO T 315 (AASHTO, 2012) specifications at both high and intermediate in-service temperatures. The high in-service test temperatures were selected as 55°, 58°, and 61°C and the intermediate in-service test temperatures were selected as 16°, 19°, and 22°C, respectively. The DSR test was used to measure the rheological properties of the binder blends, namely complex modulus (G*, ratio of measured stress to the applied strain) and phase angle (δ, phase angle between stress and strain). The measured values of G* and δ were used to determine the rutting resistance, fatigue resistance, and high-temperature PG of the binder blends.

3.5.2 Bending Beam Rheometer

The BBR tests were conducted in accordance with AASHTO T 313 (AAHSTO, 2013) on PAV-aged binders at low in-service temperatures namely, -18° and -21°C. For this test, beam samples of 127 x 12.7 x 6.35 mm dimensions were prepared using aluminum molds. The samples were subjected to a constant load of 980 ± 50 mN, applied at the mid-point of beam. The flexural stiffness (S) and stress creep relaxation (m) values measured at 60 seconds after load application (m_{60} and S_{60}) were used to calculate the low-temperature PG of the binder blends.

3.5.3 Rotational Viscometer

The rotational viscometer tests were conducted on both unaged and RTFO-aged binders at four different temperatures of 135°, 150°, 165°, and 180°C following AASHTO T 316 (AASHTO, 2013) test protocol. This test was used to measure the DV of the binder blends at the selected temperatures, based on the torque required to maintain 20 rpm rotating speed. The DV values were further used to determine the temperatures required for proper mixing and production of the mixes. As per Superpave® specifications (AASHTO M 320, 2010), a binder should have a DV of 170 mpa.s for mixing the binder with aggregate and a DV of 280 mpa.s for compacting the mix samples.

In addition to mixing and compaction temperatures, the RV results were used to determine Aging Index (AI) from Equation 3.1. According to Gandhi et al. (2009), Yu et al. (2009), and Kim et al. (2013), AI is an indicator of aging resistance or extent of hardening of the binder blends.

$$Aging\ Index\ (AI) = \frac{Viscosity\ (RTFO{-}aged) - Viscosity\ (unaged)}{Viscosity\ (unaged)} \tag{3.1}$$

3.5.4 Multiple Stress Creep Recovery

The MSCR tests were conducted on the RTFO-aged binder blends in accordance with AASHTO TP 70 (AASHTO, 2009) to determine their elastic response and stress sensitivity at high in-service temperatures. According to the standard, a binder sample was subjected to 10 loading cycles at 0.1 kPa shear stress, followed by 10 loading cycles at 3.2 kPa shear stress. One loading cycle consisted of 1 second of creep loading and 9 seconds of recovery, as shown in Figure 3.1. The results were analyzed to determine the non-recoverable creep compliance (J_{nr}) and % Recovery using Equation 3.2 and Equation 3.3, respectively. The J_{nr} value at 3.2 kPa stress level was used to determine the MSCR grade of the binder blend in accordance with AASHTO M 332 (AASHTO, 2014). To examine the stress sensitivity due to modification of the binder, a stress level of 10 kPa consisting of 10 loading cycles at 10 kPa shear stress level was added to the test procedure. Then, the measured J_{nr} and % Recovery values at 10 kPa stress level were compared with those at 0.1 kPa and 3.2 kPa stress levels.

$$J_{nr} = \frac{Non-Recoverable\ Shear\ Strain}{Applied\ Shear\ Stress}\ (\text{kPa}^{-1}) \tag{3.2}$$

$$\%\ Recovery = \%\ of\ Recoverable\ Shear\ Strain \tag{3.3}$$

3.6 Results and Discussions

3.6.1 Rutting Performance of Asphalt Binders

3.6.1.1 Rutting Factor (G/sinδ) Using Dynamic Shear Rheometer Test*

Figure 3.2 presents the measured rutting factor at different temperatures for unaged and RTFO-aged PPA-modified binders from Source 1 and Source 2. It can be observed from Figure 3.2 that adding PPA to the binder increases the rutting factor irrespective of the binder source, aging condition, and temperature. For instance, at

58˚C the rutting factor of the S1 PG 58-28 binder under unaged condition is increased from 1.15 kPa to 2.02, 3.65, 5.14, and 7.62 kPa due to the addition of 0.5%, 1.0%, 1.5%, and 2.0% PPA, respectively. For the S2 PG 58-28 binder under unaged condition, using 0.5%, 1.0%, 1.5%, and 2.0% PPA increases the rutting factor from 1.27 kPa to 2.20, 3.86, 6.92, and 13.07 kPa, respectively, at 58˚C. Therefore, mixes containing PPA-modified binder are expected to exhibit improved resistance to rutting at elevated temperatures. Similar observations were made by other researchers (e.g., King et al., 2002; Orange et al., 2004; Edwards et al., 2006; Maldonaldo et al., 2006; Arnold et al., 2009; Baldino et al., 2012). The increase in rutting factor due to PPA modification can be explained through the findings of Baumgardner (2005), Jaroszek (2012), and Yan et al. (2013). Based on these researchers, PPA increases the concentration of asphaltenes at the expense of saturates, resins, or cyclics present in the binder. Consequently, PPA helps increase the stiffness of the binder and improve the rutting performance of asphalt mixes.

The measured rutting factor of unaged S1 and S2 PG 58-28 binders is plotted against the selected amount of PPA in Figure 3.3. It is evident from Figure 3.3 that the rutting factor increases linearly with the added amount of PPA, similar to the observations made by Fee et al. (2010). However, it is important to note that the binder source and temperature play an important role in defining the rate of increase in the rutting factor. For example, from Figure 3.3, the slope of the linear trendline of S1 PG 58-28 binder is 3.2 at 58˚C; however, it is 2.32 at 61˚C. These results indicate that the higher the temperature the lower the effect of PPA. This might be due to enhanced dispersion of asphaltenes into maltenes and breakage of polar bonds between the asphaltenes molecules at high temperatures (Manolis, 2014). Similarly, the slope of the trendline of S2 PG 58-28 binder is 5.66 at 58˚C, which is approximately 76% higher than the slope of the trendline of S1 PG 58-28 binder at 58˚C. This might be due to high stiffness of the neat S2 PG 58-28 binder.

Furthermore, the results presented in Figure 3.2 indicate that the effect of PPA is dependent on the source of the binder. The increase in the rutting factor due to PPA is higher for the S2 PG 58-28 binder than that for the S1 PG 58-28 binder. From Figure 3.2, at 58°C, using 2.0% PPA increases the rutting factor by 562% (from 1.15 kPa to 7.62 kPa) for the S1 PG 58-28 binder, while the corresponding increase is 929% (from 1.27 kPa to 13.07 kPa) for the S2 58-28 binder. Based on these results, a binder with a high base stiffness can be used for maximizing the benefit of PPA. These results are consistent with the observations of Baumgardner (2005) and Huang et al. (2011). According to Baumgardner (2005), the effect of PPA is dependent upon the chemical composition of the base binder which can result in different stiffening mechanisms such as formation of PPA adduct, cross-linking of neighboring asphalt molecules, and formation of ionic clusters or cyclization of alkyl aromatics. One theory suggests that the response of binder to PPA modification depends on the level of asphaltenes in the binder (Martin, 2004; Orange et al., 2004). A binder with high amount of asphaltenes results in a more consolidated long-range network of asphaltenes after PPA modification.

The rutting factor of binders containing PPA and ASA is presented in Figure 3.4. From Figure 3.4, the addition of PPA and ASA increases the rutting factor of the neat PG 58-28 binder from both S1 and S2 sources. An increase in the dosage of PPA further improves the rutting factor. However, it can be seen from Figure 3.4 that the source of binder is an important factor. For the S2 PG 58-28 binder, a sudden increase is observed in the rutting factor after increasing the PPA content from 1.5% to 2.0%. For other PPA contents (0.5%, 1.0%, and 1.5%), the rutting factor is approximately the same (Figure 3.4). However, for the S1 PG 58-28 binder, rutting factor increases continuously with an increase in PPA content. Therefore, mixes containing PPA and ASA are expected to exhibit a higher resistance to rutting compared to mixes containing the neat binder, without these additives. Istiaque (2016) also reported that the binder containing PPA and ASA has a higher rutting factor than the neat binder.

Furthermore, comparing Figure 3.4 with Figure 3.2, the use of ASA in combination with PPA provides a lower rutting factor or rutting resistance as compared to using PPA alone. Consequently, the binder containing PPA and ASA is expected to behave softer than the binder containing PPA alone. King et al. (2002), Chin and Oliver (2007), Huang et al. (2011), and Mahmud (2016) reported similar results due to adding ASA in the PPA-modified binder. According to King et al. (2002), when strong basic compounds like ASA are added to a mix containing a PPA-modified binder, the acid modifier and the basic ASA may react with each other to form an amine salt. Miknis and Schuster (2009) also reported the formation of calcium phosphates and calcium dihydrogen phosphate due to the combined use of PPA and hydrated lime and therefore, does not provide any added benefit of using PPA.

3.6.1.2 Non-Recoverable Creep Compliance (J_{nr}) Using Multiple Stress Creep Recovery Test

The measured J_{nr} values of the RTFO-aged PPA-modified binders at 0.1 kPa, 3.2 kPa, and 10 kPa stress levels are presented in Figure 3.5. From Figure 3.5, the J_{nr} values is the highest for the neat S1 and S2 PG 58-28 binders at all selected stress levels. The addition of PPA decreases the J_{nr} value; the higher the PPA content, the lower the J_{nr} value. For instance, from Figure 3.5a, at 0.1 kPa stress level and at 58°C, the neat S1 PG 58-28 binder has the J_{nr} equal to 3.05 kPa^{-1} which reduces to 1.5, 0.7, 0.25, and 0.07 kPa^{-1} after adding 0.5%, 1.0%, 1.5%, and 2.0% PPA to the binder, respectively. At 3.2 kPa, the J_{nr} value is found to be as low as 0.09 kPa^{-1} for the binder containing 2.0% PPA. As suggested by D’Angelo (2010), a reduction in the J_{nr} value represents an increase in rutting resistance when used in a mix. Accordingly, the use of PPA increases the rutting resistance of the neat S1 and S2 PG 58-28 binders, supporting the DSR test results. A similar trend can be observed for the neat and PPA-modified binders at a higher test temperature of 64˚C (Figure 3.5b). The only difference is that the J_{nr} values at 64˚C are higher than the corresponding values at 58˚C. As shown in Figure 3.5, the binder containing 1.0% PPA has the J_{nr} values of 0.7 kPa^{-1} and 2.7 kPa^{-1} at 58°C and 64°C, respectively. These results signify that the binder becomes softer at high temperatures (as one expects) and more PPA is required to improve the resistance against rutting.

As mentioned earlier, the binder blends were also subjected to an additional stress level of 10 kPa to evaluate their stress sensitivity. As shown in Figure 3.5, the J_{nr} value of each binder increases when subjected to 10 kPa stress level. From Figure 3.5, the increase in the J_{nr} value for the neat PG S1 58-28 binder at 58˚C is only 18.7%, i.e. 3.04 kPa^{-1} at 0.1 kPa to 3.6 kPa^{-1} at 10 kPa. However, for the PPA-modified binders, the J_{nr} values at 0.1 kPa and 10 kPa differs by a much larger amount. The binder containing 1.0% and 2.0% PPA have 94.6% and 316% difference in the J_{nr} values at 0.1 kPa and 10 kPa stress levels, respectively, at 58°C. At 64°C, the % difference in the J_{nr} values increases to 111% and 476% for binders containing 1.0% and 2.0% PPA, respectively. These results clearly indicate that PPA enhances the stress sensitivity of the neat binders, although it decreases the J_{nr} value. Therefore, it is expected that PPA-modified mixes may experience increased permanent deformation or rutting when subjected to increased traffic loading and temperature. One should exercise care in using a high amount of PPA in mixes and accommodate the stress sensitivity of binders in the mix design process.

The measured J_{nr} values of the S1 and S2 PG 58-28 binders containing PPA and ASA are presented in Figure 3.6 at 58˚C. As shown in Figure 3.6, the addition of 0.5% PPA and 0.5% ASA to the S1 PG 58-28 binder increases the J_{nr} value by 8%. An increased amount of PPA to 1.0% or higher decreases the J_{nr} value. For instance, the binder containing 2.0% PPA and 0.5% ASA has a J_{nr} value of 1.4 kPa^{-1} at 3.2 kPa stress level. These results indicate that the use of 1.0% or higher PPA is required to help increase the rutting resistance of the neat binders when used with ASA. It is because using PPA and ASA together nullifies the effect of PPA, as noted previously. As a result, the binder containing ASA and PPA is relatively softer than the binder containing PPA alone, as demonstrated in Figure 3.6 and Figure 3.5a. Therefore, asphalt mixes containing PPA and ASA are expected to undergo higher rutting compared to mixes containing PPA only. The DSR test shows similar results, as discussed in the previous section.

3.6.1.3 % Recovery Using Multiple Stress Creep Recovery Test

The measured % Recovery of the S1 and S2 PG 58-28 binders containing PPA is shown in Figure 3.7. As expected, the % Recovery is highest at the 0.1 kPa stress level and reduces with an increase in the stress level. Also, the neat S1 and S2 PG 58-28 binders have no significant recovery at any selected stress levels. The addition of PPA increases the % Recovery; the higher the PPA concentration, the higher the % Recovery. For instance, from Figure 3.7, using 2.0% PPA increases the % recovery from 0% to 65% for the S1 PG 58-28 binder and from 0.5% to 81% for the S2 PG 58-28 binder at the 3.2 kPa stress level. D'Angelo (2010) suggested that % Recovery can be used to evaluate the rutting resistance of binders and their interaction with polymers. Accordingly, it can be noted that adding PPA enhances the rutting resistance of the neat PG 58-28 binders obtained from both sources. This may be attributed to the increased concentration of the asphaltenes, which results in a more consolidated long-range network of asphaltenes (Martin, 2004; Baumgardner, 2002) and therefore, enables the binder to undergo higher permanent deformation. Additionally, Figure 3.6b shows that the PG 58-28 binders (from both S1 and S2) containing PPA would have higher rutting potential at 64 °C due to lower % Recovery at that temperature. This might be attributed to enhanced dispersion of asphaltenes into maltenes and breakage of polar bonds between asphaltenes molecules at high temperatures (Manolis, 2014).

Furthermore, Figure 3.8 presents the % Recovery of the S1 and S2 PG 58-28 binders containing PPA and ASA at 58°C. From Figure 3.8, the binders containing PPA and ASA have none or very low % Recovery. For instance, the binder containing 2.0% PPA and 0.5% ASA exhibit % Recovery of 19%, 6%, and 0.5% at 0.1, 3.2, and 10 kPa stress levels, respectively. These results indicate that unlike mixes containing PPA alone, the mixes containing ASA and PPA together may not be able to recover deformation under traffic loading and experience more rutting. As mentioned previously, it may be due to using PPA and ASA together, which counteracts the effect of each other and creates amine-salt (King et al., 2002). Therefore, one should exercise care when using PPA and ASA together and consider their possible impact on rutting performance.

3.6.1.4 Relationship Between MSCR and DSR Test Results

In the past, it has been reported that the G*/sinδ cannot be related to J_{nr} for modified binders (Golalipour, 2011). However, since both the DSR and the MSCR tests are used to evaluate rutting performance, their test results were correlated in this study. The rutting factor (G*/sinδ) was related to non-recoverable creep compliance (J_{nr}), as shown in Figure 3.9. Figure 3.9 also demonstrates that a power function exists between G*/sinδ and J_{nr} values for the modified binders, irrespective of stress levels. At 3.2 kPa, the equation of power function is given below:

$$G^*/sin\delta = 6.0996{J_{nr}}^{-0.488} \tag{3.4}$$

Using this equation and the DSR data, one can predict the intensity of traffic loading a binder can sustain due to modification.

3.6.2 Fatigue Performance of Asphalt Binders

Figure 3.10 and Figure 3.11 present the measured fatigue factor of the binders at the tested temperatures. As expected, the fatigue factor decreases with an increase in the temperature. The addition of PPA alone or in combination with ASA reduces the fatigue factor. For example, from Figure 3.10, the fatigue factor of the S1 PG 58-28 binder is 4,540 kPa at 19°C, which decreases by 10 to 14% due to the addition of PPA. Similarly, the use of PPA in the S2 PG 58-28 binder reduces the fatigue factor by 4 to 20%, depending upon the PPA content (Figure 3.10). As a result, the temperatures at which fatigue cracking is expected for the neat S1 and S2 PG 58-28 binders are 18.4°C and 18.1°C, respectively. The addition of 2.0% PPA to the neat binders decreases the fatigue cracking temperature to 16.9°C (1.5°C reduction) for the S1 PG 58-28 binder and to 15.9°C (2.3°C reduction) for the S2 PG 58-28 binder. These results indicate that PAV-aged PPA-modified binders are softer than the PAV-aged neat binders. Therefore, it is expected that the mixes containing PPA-modified binder would be more durable (cracking-wise) than conventional mixes. This may be due to reduced oxidative aging of the binders after PPA modification. It is also evident from Figures 3.10 and 3.11 that the binders containing PPA and ASA perform similar to those containing PPA only. Therefore, it can be noted that the addition of ASA does not provide any added benefits towards improving the fatigue cracking performance of the binder. Unlike rutting performance, the use of ASA does not exhibit any adverse effects on the fatigue cracking performance of the PPA-modified binder.

3.6.3 Performance Grading of Asphalt Binders

The PG grades of binders were determined based on the DSR and BBR results and are shown in Figure 3.12. As expected, from Figure 3.12, both S1 and S2 PG 58-28 binders meet the Superpave® requirements (AASHTO M 320, 2010) to be graded as PG 58-28. The addition of PPA to these binders increases their high-temperature PG for both sources. For instance, from Figure 3.12, addition of 1.0% PPA bumps the high-temperature PG grade of the neat PG 58 binders by one grade to PG 64. Adding 1.5% and 2.0% PPA increases the high-temperature PG by 5°and 7°C to PG 65 and PG 67, respectively. Contrarily, Figure 3.12 shows the low-temperature PG decreases after modification using PPA. Using 2.0% PPA in the S2 PG 58-28 asphalt binder decreases the low-temperature PG from PG -28 to PG -34. This may be attributed to the lower oxidative aging of PPA-modified binder resulting in a relatively softer binder (Huang et al., 2008). These results indicate that the use of PPA enhances the binder’s performance against high-temperature distresses such as rutting and low-temperature cracking performance. In previous studies, it was found that the addition of PPA significantly increases the stiffness of binders at high temperatures, and depending upon the binder source, it may or may not improve the low-temperature PG grade as well (Bishara et al., 2001; Falkiewicz and Grzybowski, 2004; Martin et al., 2004; Orange et al., 2004; Kodrat et al., 2007; Maldonado, 2007; Maldonado et al., 2006; McGennis, 2009; Baldino et al., 2013; Al-Qadi et al., 2014). Consequently, it can be noted that PPA can reduce a binder’s sensitivity to temperature variation with enhanced resistance to rutting.

Furthermore, from Figure 3.12, 0.5% and 1.0% PPA have no influence on the high- and low- temperature PGs of the neat binders, when used with 0.5% ASA. Similarly, the S1 and S2 PG 58-28 binders containing 2.0% PPA and ASA have lower PG (high and low) as compared to the ones containing 2.0% PPA only. However, in case of the S2 PG 58-28 binder, adding 2.0% PPA and 0.5% ASA bumps the PG to PG 64-28 without impacting the low-temperature cracking performance. This is probably due to high percentage of PPA. These results indicate that the use of ASA (amine) along with PPA (acid) neutralizes the effect of PPA following the surface chemistry of acids and amines (King et al., 2002; Fee et al., 2010). According to King et al. (2002), adding acid-based and amine-based additives or modifiers together in the binder creates amine salt and, therefore, nullifies each other's effects. Also, adding two different additives would increase the mix production cost. These results are supported by the observations made by King et al. (2002), Chin and Oliver (2007), Chin and Oliver (2007), Huang et al. (2011), Liu et al. (2016), and Mahmud (2016).

3.6.4 Multiple Stress Creep Recovery (MSCR) Grading

The MSCR test data at 3.2 kPa stress level were used to determine the MSCR grade of the binder in accordance with AASHTO MP 19 (AASHTO, 2010) specifications and results are presented in Table 3.2. As shown in Table 3.2, the MSCR grade of the neat S1 and S2 PG 58-28 binders is PG 58S-XX, where 'S' defines the intensity of traffic loading. The binder blends with grading 'S' can be subjected to a traffic loading less than 10 million ESAL and standard traffic moving speed (more than 70 KM/hour). The addition of 0.5%, 1.0%, 1.5%, 2.0% PPA to the neat S1 and S2 PG 58-28 binders improve their performance grade to PG 58H-XX, PG 58V-XX, PG 58E-XX, and PG 58E-XX, respectively. These results show that the neat S1 and S2 PG 58-28 binder can sustain a higher traffic loading at 58°C after PPA-modification. The binders containing 1.0% or higher amount of PPA can sustain extreme traffic loading (> 30 million ESAL) at 58°C, without undergoing significant permanent deformation. The basic difference between the binder blends containing 1.0% PPA and the binder blends containing 1.5% or 2.0% PPA is that the binder blends containing 1.5% or 2.0% PPA can be subjected to slow moving traffic (less than 20 KM/hour), in addition to 30 million ESAL traffic loading, whereas the binder blend containing 1.0% PPA would not. Furthermore, as expected, an increase in test temperature from 58°C to 64°C results in a lower MSCR grade. Only the binder containing 2.0% PPA maintains its grade of PG 58E-xx at 64°C for both sources, possibly due to a higher amount of PPA. These results suggest that using 1.5% or 2.0% PPA in the areas of very heavy to extremely heavy traffic loading and at high temperature situation is beneficial. Similar results are reported in a study conducted by Rani et al. (2019a, b).

Table 3.2 also presents the MSCR grade of the binders containing PPA and ASA. Accordingly, the binders containing 0.5% or 1.0% PPA with 0.5% ASA has an MSCR grade of PG 58S-XX, which shows that the binder can be used in the standard loading (< 10 million ESAL) situation. The use of a higher amount of PPA, i.e., 1.5% or 2.0%, increases the MSCR grade by one level to PG 58H-XX (10-30 million ESAL). These results signify that the binder containing PPA and ASA cannot sustain traffic loading more than 30 million ESAL although PPA is used in large amounts. It is important to note that the MSCR grade of the binder containing 2.0% PPA and 0.5% ASA is equivalent to the binder containing 0.5% or 1.0% PPA. It suggests that using 0.5% ASA could neutralize the effect of 1.0%-1.5% PPA.

3.6.4.1 Polymer Method

In this study, the polymer method was also used to analyze the MSCR test results. For this purpose, the J_{nr} values at 3.2 kPa stress level were plotted against % Recovery values at the 3.2 kPa stress level and then compared with the polymer curve, as shown in Figure 3.13. The polymer curve signifies the presence of elastomeric polymers in the binder. The binders falling above the curve are modified by using a proper amount of elastomeric polymers with a good recovery of applied strain under traffic loading and vice-versa. As shown in the Figure 3.13, all the binders, irrespective of the source and temperature, fall below the curve. Only the binders containing 2.0% PPA touch the curve at the bottom. It indicates that although PPA enhances the stiffness of the neat PG 58-28 binders, it cannot improve their strain recovery capability significantly, as compared to the elastomeric polymers. Similar results are reported in a study conducted by Rani et al. (2019b). A high amount of PPA can be used to have a good % recovery, but it might make the binder too stiff with a high potential of premature cracking.

3.6.5 Dynamic Viscosity of Asphalt Binders

Figure 3.14 shows the DV values of the S1 and S2 PG 58-28 binders blended with different dosages of PPA. It is seen that the addition of PPA increases the DV of the neat S1 and S2 PG 58-28 binders. As shown in Figure 3.14, the DV of the S1 PG 58-28 binder is 300 mPa.s at 135°C, which increases to 387, 533, 687, and 962 mPa.s due to 0.5%, 1.0%, 1.5%, and 2.0% PPA, respectively. Similarly, the DV of the S2 PG 58-28 binder increases from 312 mPa.s to 412, 687, 833, and 1341 mPa.s as a result of adding 0.5%, 1.0%, 1.5%, and 2.0% PPA. Orange et al. (2004) and Maldonaldo et al. (2006) also found similar effects of adding PPA. The increase in DV due to the addition of PPA can be explained from the findings of Baumgardner (2005) and Yan et al. (2013). According to these researchers, the addition of PPA enhances the asphaltenes content of the binder. Since asphaltenes are the viscosity building component of the binder (Brown et al., 2009), an increase in its concentration results in an enhanced viscosity of the neat binder.

Furthermore, for the S1 PG 58-28 binder, the addition of 1.0% and 2.0% PPA increases the DV approximately by 1.8 and 3.2 times, respectively, compared to that for the neat binder (Figure 3.14). However, for the S2 PG 58-28 binder, the DV increases by 2.2 and 4.3 times due to addition of 1.0% and 2.0% PPA, respectively. Based on these results, the source of the binder seems to play an important role in understanding the effects of PPA use. Similar observations were made by other researchers (see e.g., King et al., 2002; Orange et al., 2004; Edwards et al., 2006; Maldonaldo et al., 2006; Arnold et al., 2009; Baldino et al., 2012). At elevated temperatures such as 180°C, the effect of PPA is insignificant as indicated by approximately the same DV of the binders containing different amounts of PPA (Figure 3.14).

The measured DV of binders at different temperatures was further processed to determine the mixing and compaction temperatures. The results are summarized in Table 3.3. From Table 3.3, the compaction temperature increases by 6°, 12°, 15°, and 25°C for the S1 PG 58-28 binder and by 6°, 15°, 17°, and 25°C for the S2 PG58-28 binder due to the addition of PPA by 0.5%, 1.0%, 1.5%, and 2.0%, respectively. Similarly, the mixing temperature increases by 3^{o}C to 24°C for the S1 PG 58-28 binder and by 6 to 26°C for the S2 PG 58-28 binder, depending upon the dosage of PPA. These results clearly indicate that the addition of a high amount of PPA (2.0%) raises the mixing and compaction temperatures significantly (by 24°C to 26°C). Increased mixing and compaction temperatures are detrimental to cost due to increased fuel consumption.

As presented in Figure 3.15, the addition of ASA and PPA increases the DV of the neat PG 58-28 binders from both sources. From Figure 3.15, the S1 and S2 PG 58-28 binders containing 0.5%, 1.0%, and 1.5% PPA with ASA have approximately the same DV values, moderately higher than that for the neat binders. For instance, the S1 PG 58-28 binder containing 0.5%, 1.0%, or 1.5% PPA has 10% higher DV (350 mPa.s) compared to the neat binder. Only the binders containing 2.0% PPA and ASA exhibits an increase in the DV by 1.4 times for the S1 PG 58-28 binder and 1.8 times for the S2 PG 58-28 binder. Comparing these results with those containing PPA only (Figures 3.14 and 3.15), it is evident that using ASA in the PPA-modified binder reduces the DV. As mentioned earlier, it could be attributed to the development of amine salt because of reaction of the amine component of ASA with the acidic component of PPA (King et al., 2002). Based on these results, it was found that using 0.5% ASA can neutralize the effect of 1.0% to 1.5% PPA depending upon the chemical composition of the base binder. Therefore, when 2.0% PPA was used with 0.5% ASA, the increase in the DV was equivalent to the increase in the DV on adding just 0.5% or 1.0% PPA.

The mixing and compaction temperatures for the binders containing PPA and ASA are presented in Table 3.3. From Table 3.3, the addition of PPA (up to 1.5%) and ASA does not considerably change the mixing and compaction temperatures of the neat S1 and S2 PG 58-28 binders. The use of 2.0% PPA with ASA shows an increase of 8° to 11°C in temperature. These results indicate that the use of ASA helps reduce the mixing and compaction temperatures of the PPA-modified binders. This is attributed to the decrease in DV of the PPA-modified binder after modifying with ASA. However, one should be careful in using ASA with PPA because they can neutralize the effect of each other, as mentioned earlier, and impact the rutting performance adversely.

3.6.6 Aging Index of Asphalt Binders

The AI values obtained from Equation 3.1 at 135˚, 150˚, and 165˚C are presented in Figure 3.16 for the S1 and S2 PG 58-28 binders modified by PPA and ASA. The addition of PPA increases the AI at all temperatures for both sources. However, at a high temperature (165 ˚C), the increase in AI after PPA modification is relatively small, depending upon the source of the binder. For example, 2.0% PPA increases the AI of the neat S1 PG 58-28 binder from 0.48 to 2.30 (480%) at 135˚C and from 0.42 to 0.95 (250%) at 165˚C. Similarly, for the S2 PG 58-28 binder, 2.0% PPA enhances the AI by 750% at 165˚C, which is half of the increase at 135˚C. These results suggest that PPA hardens the binder significantly. Consequently, elevated temperatures are required to liquefy the binder containing PPA in the mix production process. It is anticipated that an increase in temperature would help melt the remaining resins present in the modified binder and allow dispersion of the asphaltenes clusters in the matrix. Furthermore, from Figure 3.16b, it is evident that the use of ASA with PPA nullifies the hardening effect of PPA. The binders containing PPA and ASA have similar AI values irrespective of their sources and test temperatures. These results suggest that the binders containing ASA and PPA are more durable than the binder containing PPA alone. The binders containing PPA, however, exhibit fatigue factors similar to binders containing both ASA and PPA, suggesting similar level of durability of binders. This may be attributed to high initial oxidative aging of the PPA-modified binders, which slows down with time due to formation of carbonyl and sulfoxide compounds in the initial stage of aging (Huang et al., 2008).

3.7 Conclusions and Recommendations

In this study, the effect of using an amine-based liquid ASA on the laboratory performance of the PPA-modified binders was evaluated along with the effect of PPA modification on the performance of neat binders obtained from different sources. For this purpose, rutting, fatigue cracking, low-temperature cracking, Superpave® PG, and DV of the binders were used as indicators of performance. Also, HWT and TSR tests were conducted to determine the rutting and moisture-induced damage potential of the associated mixes containing modified binders. Based on the results presented in the preceding sections, the following observations are made:

1. The use of PPA was found to be an effective way of improving the rutting binders without adversely impacting the low-temperature cracking resistance. The study indicated a linear effect of PPA on the rutting resistance of binders. Adding 1.0% or a higher amount of PPA bumped the Superpave® high-temperature PG by one grade. Therefore, mixes containing PPA are expected to exhibit lower rutting in the field in comparison to conventional mixes.
2. Based on the MSCR test data, the non-recoverable creep compliance of the binder decreased and % Recovery increased due to PPA modification. It indicated that the binder can sustain a larger traffic level without undergoing significant permanent deformation (rutting). It was seen that the binders

containing 1.5% or 2.0% PPA can sustain an extreme level of traffic loading at 58°C and therefore designated as PG 58E-28.

3. It was observed that change in the source of same grade binders can result in different effects of PPA modification with respect to rutting performance. The results indicated that the stiffer the base binder, the higher the effect of PPA modification on the rutting resistance of the binder. For instance, using 2.0% PPA increased the rutting factor by 562% for the S1 PG 58-28 binder having a rutting factor of 1.15 kPa. However, the corresponding increase in the rutting factor for the S2 PG 58-28 binder was much higher (929%). The rutting factor of this binder was 1.27 kPa.
4. Similar to the rutting resistance, the dynamic viscosity of the binder increased due to PPA modification. A high amount of PPA increased the DV of the binder substantially. As a result, elevated temperatures are required for the production of mixes. For instance, adding 2.0% PPA, increased the mixing temperature by 28˚C. Elevated temperatures are detrimental to cost due to increased consumption of fuels and reduced hauling distance. Therefore, one should be exercise care in using high amount of PPA.
5. The results indicate that the use of PPA can improve the fatigue resistance of binders. As a result, mixes containing PPA are expected to exhibit longer durability and less sensitivity to temperature variation with enhanced resistance to rutting. Also, a binder containing both ASA and PPA may exhibit similar fatigue resistance as that for a binder containing PPA alone.

6. The use of ASA and PPA increased the rutting, fatigue, and DV of the neat binders. Therefore, mixes containing ASA and PPA are expected to perform better than conventional mixes. However, the results indicated that using ASA with PPA decreased the performance of binders against rutting and low-temperature cracking as compared to the performance of the PPA-modified binder. Also, none of the binders containing ASA and different amounts of PPA exhibited an increase in the PG of the base binder. It was observed that using 0.5% ASA can nullify the effect of 1.0% to 1.5% PPA.
7. Although PPA-modified binders showed a good resistance against rutting, they are expected to exhibit less % Recovery of deformations in the field as compared to polymer-modified binders. Therefore, it is recommended that PPA be used in conjunction with polymer to improve the % Recovery of the neat binder, as suggested by Orange et al. (2004).

Overall, this study showed that PPA can be successfully used to improve rutting, fatigue, and low-temperature cracking performance of binders. However, using an amine-based ASA with PPA can neutralize the effect of PPA. One needs to be careful in using PPA in combination with ASA in mixes, as it may lead to premature failure of pavement such as rutting when subjected to traffic loading.

Acknowledgements

The authors are greatly thankful to the Southern Plain Transportation Center (SPTC) and the Oklahoma Department of Transportation (ODOT) for providing financial assistance for this study. The authors gratefully acknowledge the contributions of Haskell Lemon Construction Co. of Norman for providing the required materials.

Table 3.1 List of Prepared Binder Blends for Testing

No.	Type of Neat Binder and Source	Binder Modification (% by the weight of binder)		Nomenclature for Binder Blend	No.	Type of Neat Binder and Source	Binder Modification (% by the weight of binder)		Nomenclature for Binder Blend
		PPA (P)	ASA (A)				PPA (P)	ASA (A)	
1	PG 58-28 OK, Source 1 (S1)	-	-	S1	10	PG 58-28 OK, Source 2 (S2)	-	-	S2
2		0.5	-	S1P0.5	11		0.5	-	S2P0.5
3		1	-	S1P1.0	12		1	-	S2P1.0
4		1.5	-	S1P1.5	13		1.5	-	S2P1.5
5		2	-	S1P2.0	14		2	-	S2P2.0
6		0.5	0.5	S1P0.5A	15		0.5	0.5	S2P0.5A
7		1	0.5	S1P1.0A	16		1	0.5	S2P1.0A
8		1.5	0.5	S1P1.5A	17		1.5	0.5	S2P1.5A
9		2	0.5	S1P2.0A	18		2	0.5	S2P2.0A

Table 3.2 MSCR Grade of the S1 and S2 PG 58-28 Binders Containing PPA and ASA

Binder Type	Test Temp. (°C)	MSCR Grade	Binder Type	Test Temp. (°C)	MSCR Grade	Binder Type	Test Temp. (°C)	MSCR Grade
S1	58	PG58S-XX	S1	64	PG64S-XX			
S1P0.5	58	PG58H-XX	S1P0.5	64	PG64S-XX	S1P0.5A	58	PG58S-XX
S1P1.0	58	PG58V-XX	S1P1.0	64	PG64S-XX	S1P1.0A	58	PG58S-XX
S1P1.5	58	PG58E-XX	S1P1.5	64	PG64V-XX	S1P1.5A	58	PG58H-XX
S1P2.0	58	PG58E-XX	S1P2.0	64	PG64E-XX	S1P2.0A	58	PG58H-XX
S2	58	PG58S-XX	S2	64	PG64S-XX			
S2P0.5	58	PG58H-XX	S2P0.5	64	PG64S-XX	S2P0.5A	58	PG58S-XX
S2P1.0	58	PG58V-XX	S2P1.0	64	PG64H-XX	S2P1.0A	58	PG58S-XX
S2P1.5	58	PG58E-XX	S2P1.5	64	PG64E-XX	S2P1.5A	58	PG58H-XX
S2P2.0	58	PG58E-XX	S2P2.0	64	PG64E-XX	S2P2.0A	58	PG58V-XX

‘S’ – Standard Traffic Loading (<10 million ESAL and standard traffic at >70 KM/hour),
‘H’ – Heavy Traffic Loading (10-30 million ESAL or slow-moving traffic at 20-70 KM/hour),
‘V’ – Very Heavy Traffic Loading (>30 million ESAL or standing traffic at <20 KM/hour),
‘E’ – Extremely Heavy Traffic Loading (> 30 million ESAL and standing traffic at <20 KM/hour)

Table 3.3 Mixing and Compaction Temperatures of S1 and S2 PG 58-28 Binders

Binder Type	Mixing Temperature (°C)	Change in Mixing Temperature (°C)	Compaction Temperature (°C)	Change in Compaction Temperature (°C)
S1	149	-	137	-
S1P0.5	152	3	143	6
S1P1.0	160	11	149	12
S1P1.5	163	14	152	15
S1P2.0	173	24	162	25
S1P0.5A	150	1	140	3
S1P1.0A	150	1	141	4
S1P1.5A	152	3	142	5
S1P2.0A	157	8	146	9
S2	150	-	139	-
S2P0.5	156	6	145	6
S2P1.0	163	13	154	15
S2P1.5	165	15	156	17
S2P2.0	176	26	164	25
S2P0.5A	151	1	141	2
S2P1.0A	152	2	142	3
S2P1.5A	152	2	142	3
S2P2.0A	161	11	149	10

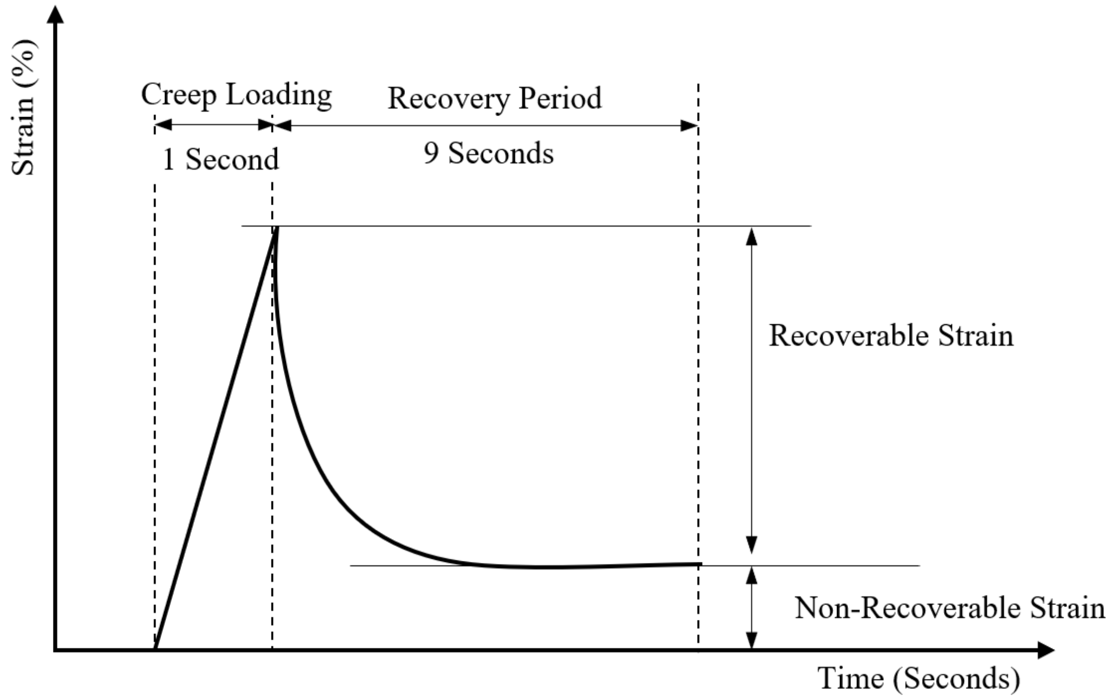
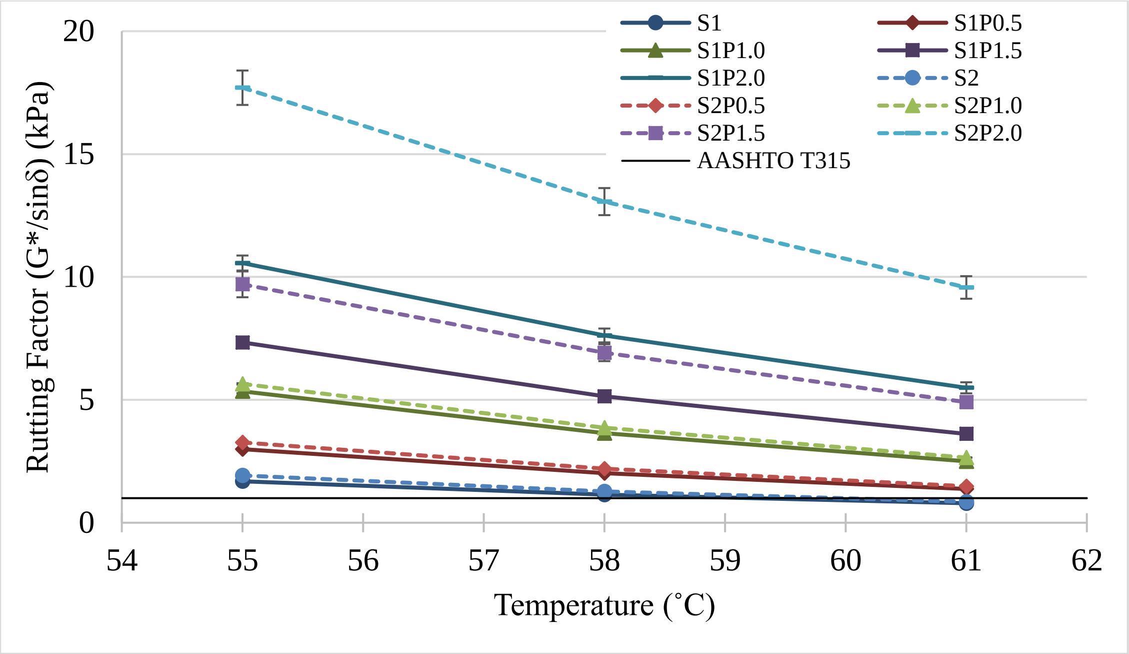
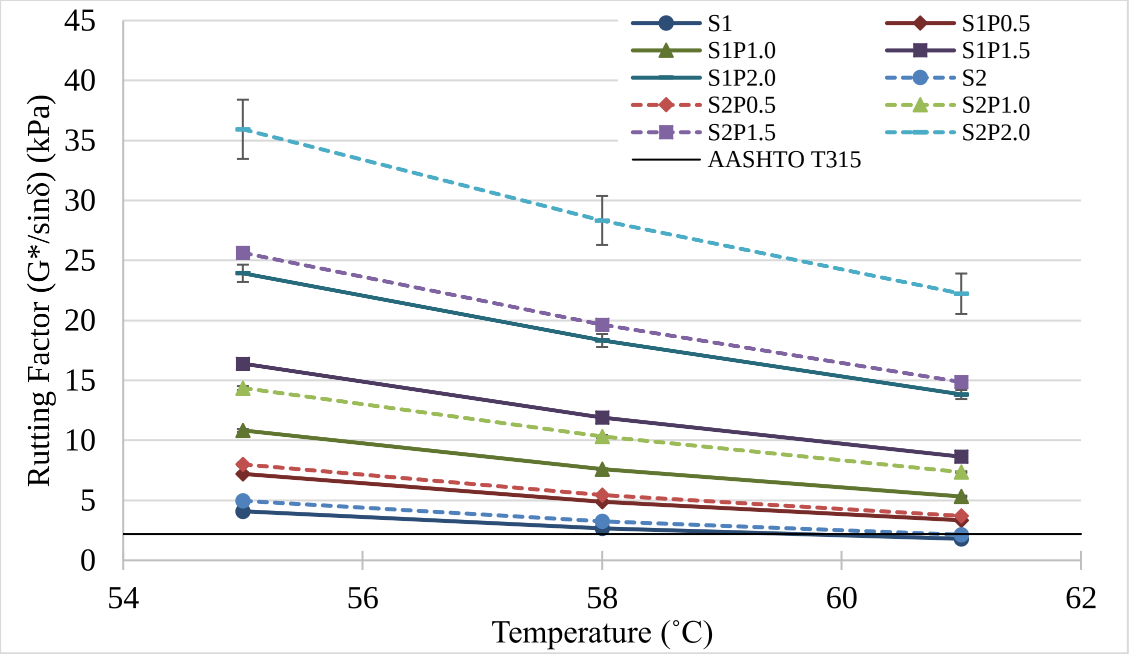


Figure 3.1 Typical 10-Seconds Loading Cycle in the Multiple Stress Creep Recovery (MSCR) Test



(a)



(b)

Figure 3.2 Rutting Factor of Unaged (a) and RTFO-Aged (b) S1 and S2 PG 58-28 Binders Blended with PPA

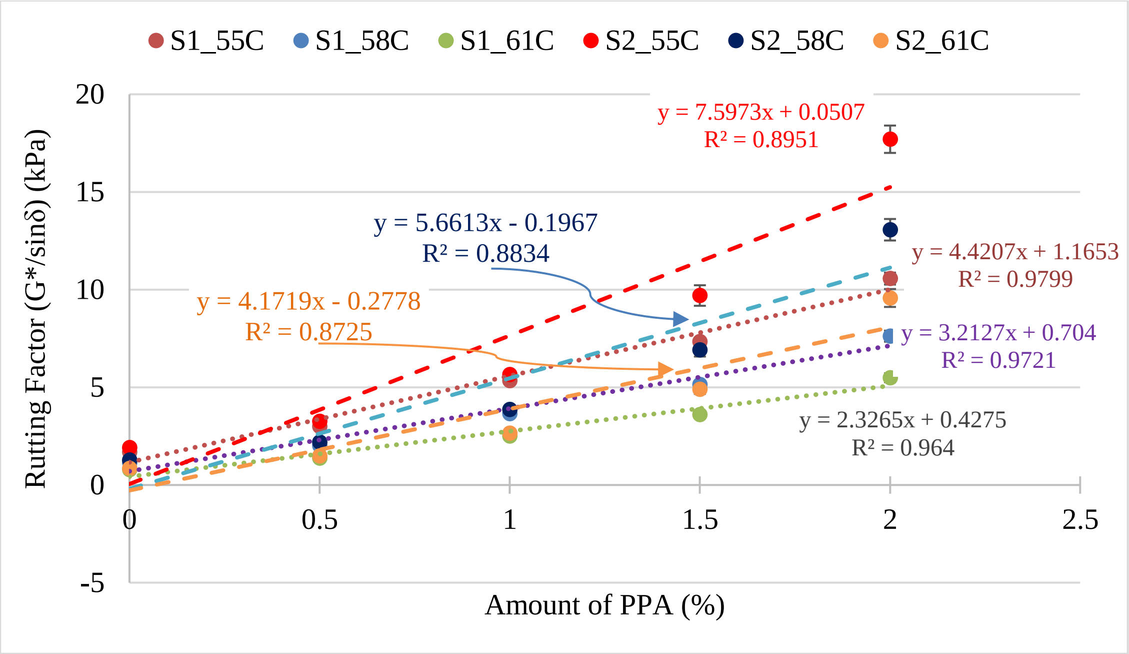
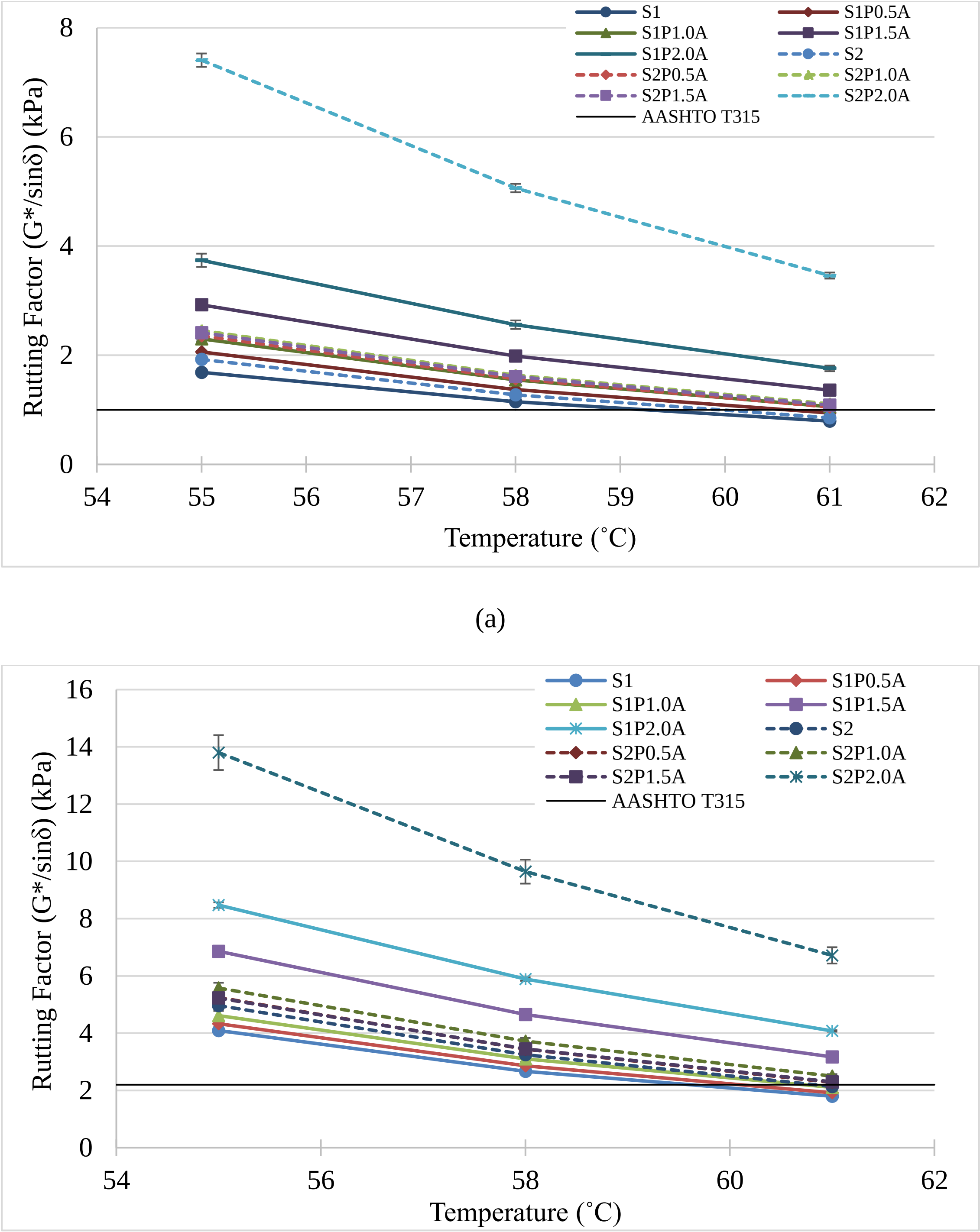


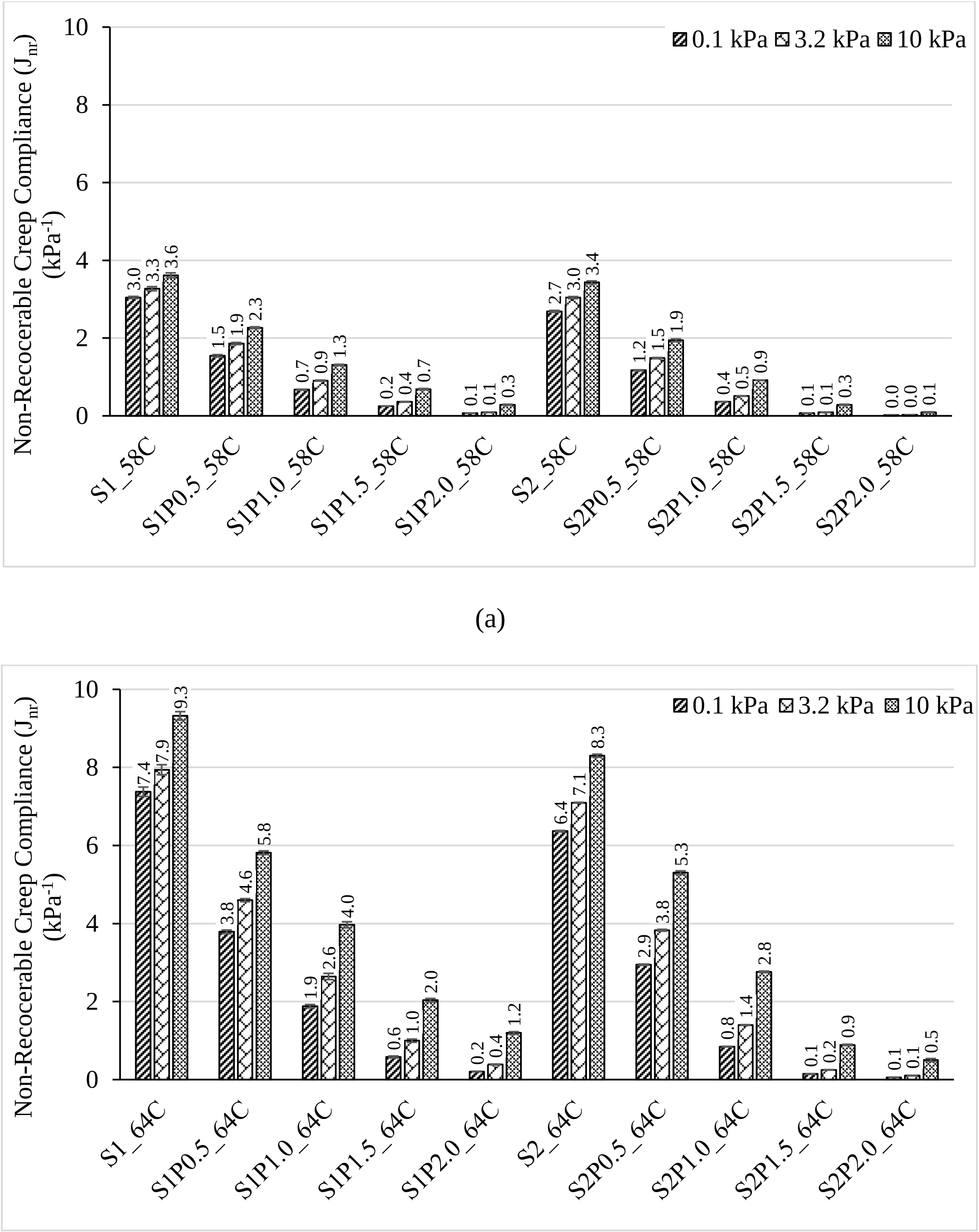
Figure 3.3 Rutting Factor of Unaged S1 and S2 PG 58-28 Binders at Different Amounts of PPA



(a)

(b)

Figure 3.4 Rutting Factor of Unaged (a) and RTFO-Aged (b) S1 and S2 PG 58-28 Binders Blended with PPA and ASA



(a)

(b)

Figure 3.5 Non-Recoverable Creep Compliance of RTFO-Aged S1 and S2 PG 58-28 Binders Containing PPA at (a) 58°C and (b) 64°C

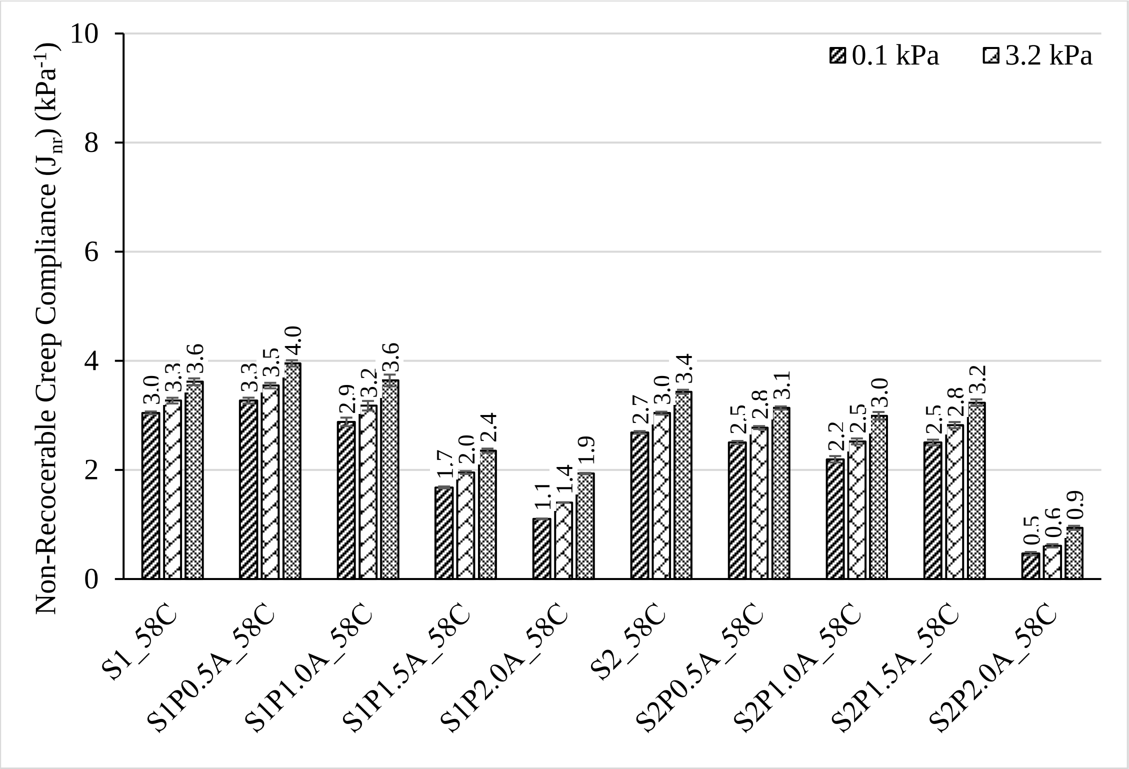


Figure 3.6 Non-Recoverable Creep Compliance of RTFO-Aged S1 and S2 PG 58-28 Binders Containing PPA and ASA at 58°C

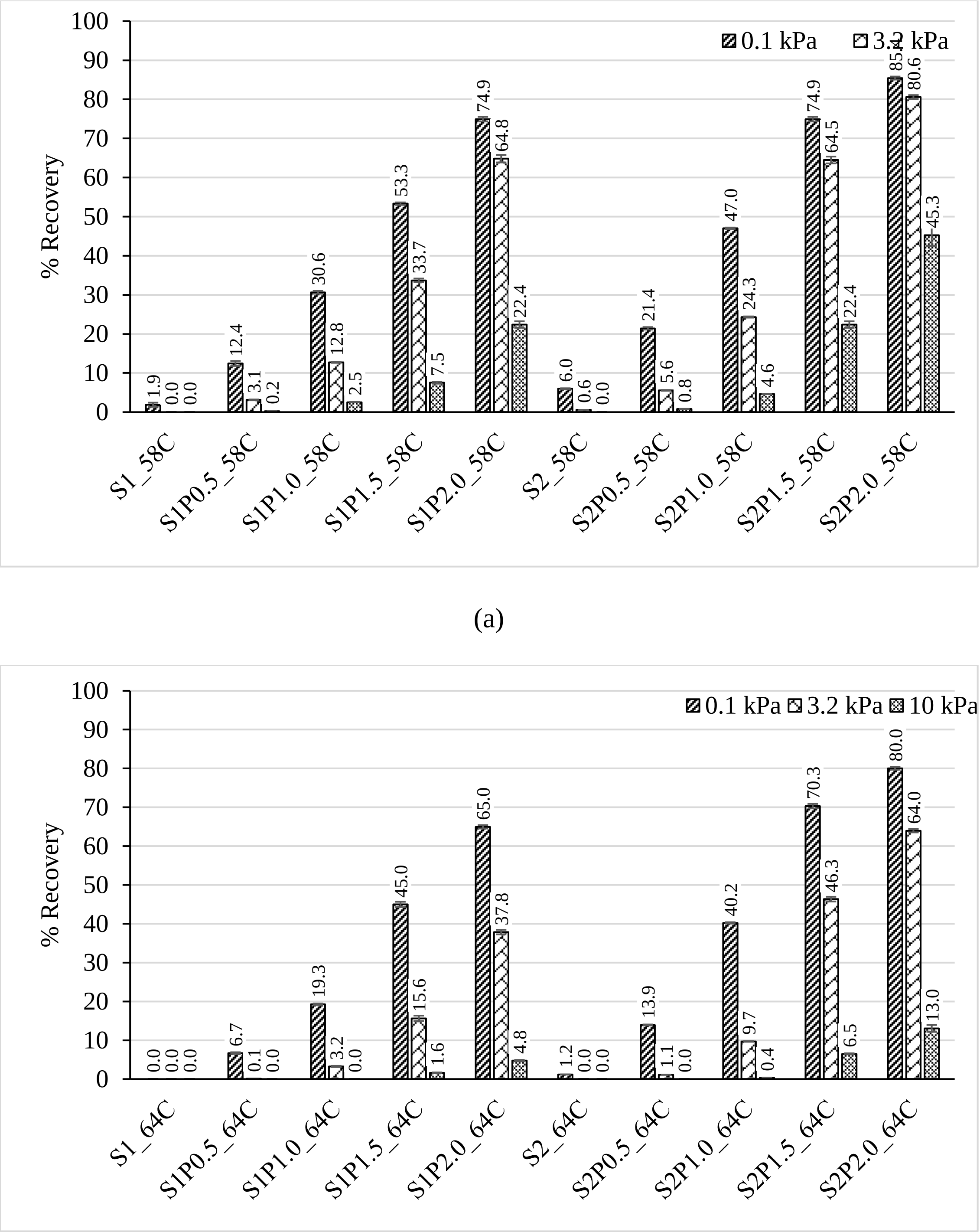


Figure 3.7 % Recovery of RTFO-Aged S1 and S2 PG 58-28 Binders Containing PPA at (a) 58° C and (b) 64°C

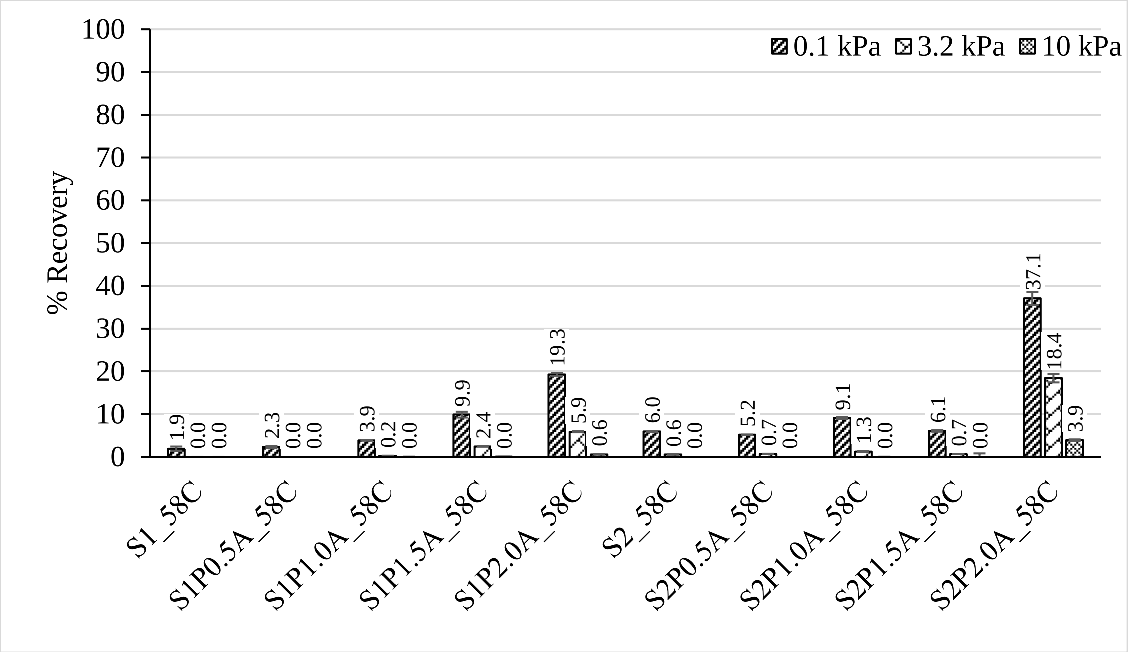


Figure 3.8 % Recovery of RTFO-Aged S1 and S2 PG 58-28 Binders Containing PPA and ASA at 58°C

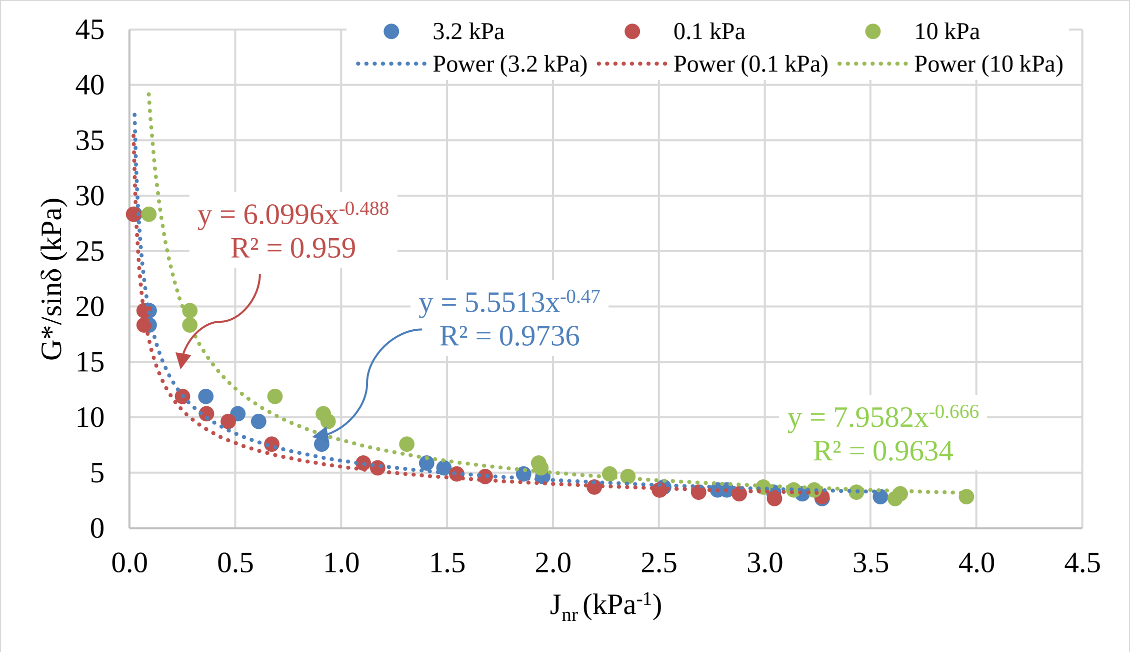


Figure 3.9 Rutting Factor vs Non-Recoverable Creep Compliance for the Modified Binder Blends at 58°C

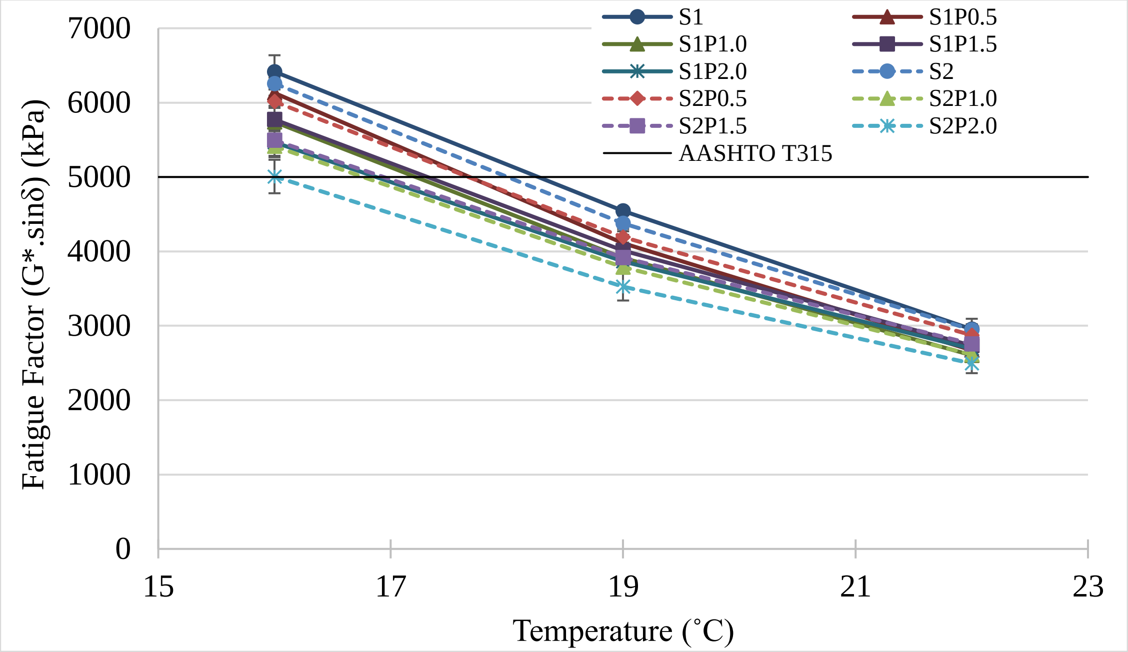


Figure 3.10 Fatigue Factors of PAV-Aged S1 and S2 PG 58-28 Binders Blended with PPA

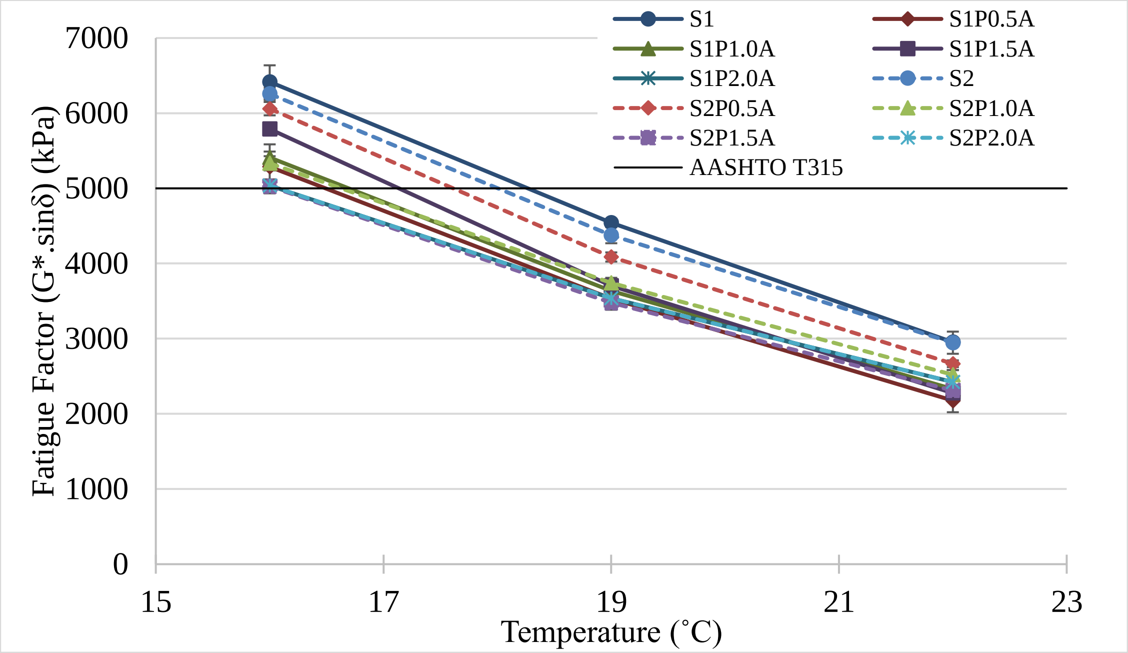


Figure 3.11 Fatigue Factors of PAV-Aged S1 and S2 PG 58-28 Binders Blended with PPA and ASA

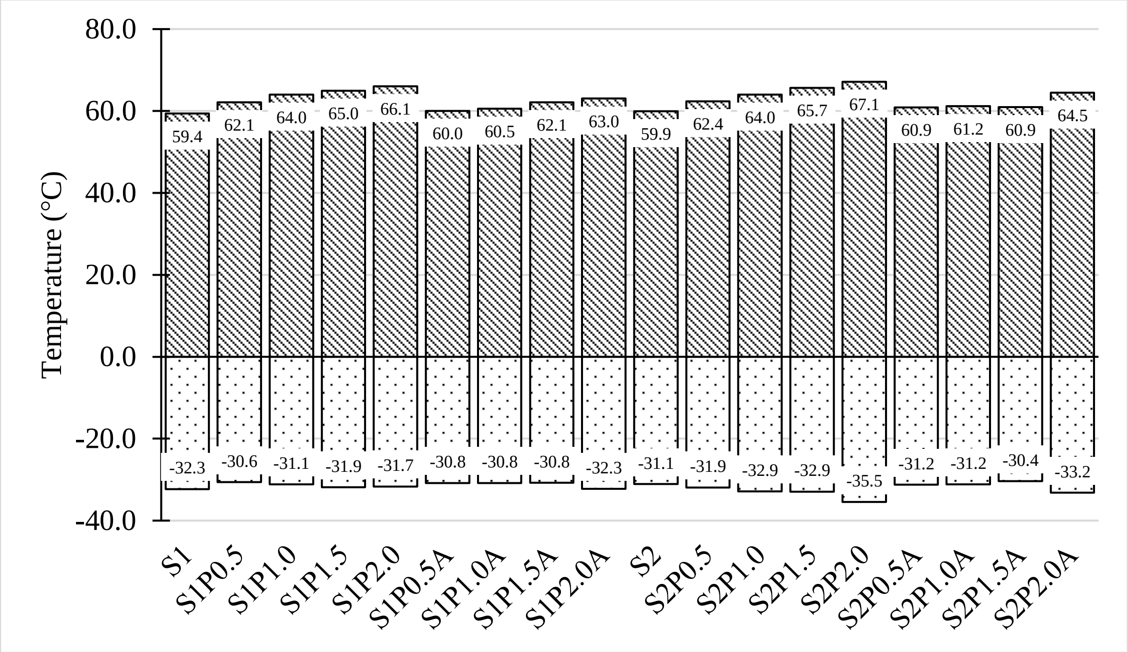


Figure 3.12 Performance Grading of Binders

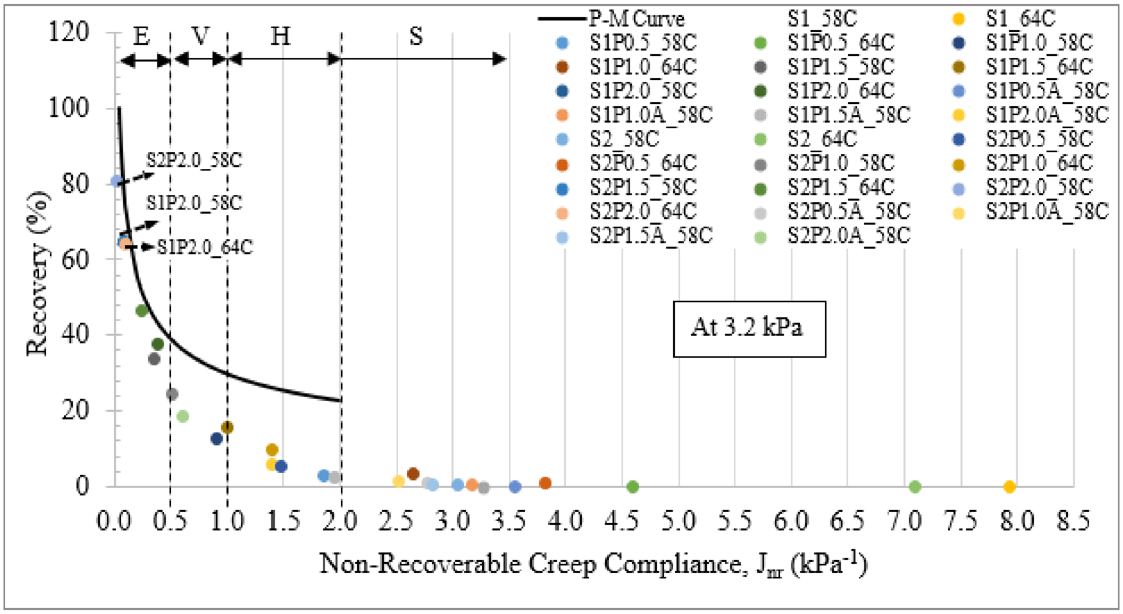


Figure 3.13 Non-Recoverable Creep Compliance versus % Recovery at 3.2 kPa

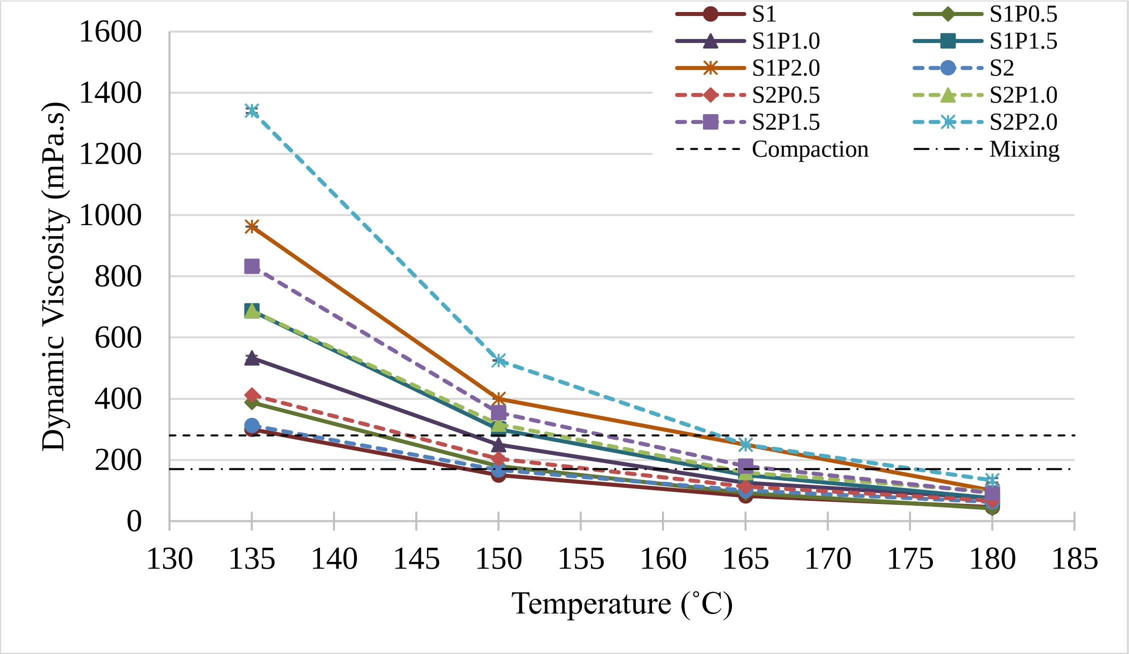


Figure 3.14 Dynamic Viscosity of S1 and S2 PG 58-28 Binders Blended with PPA

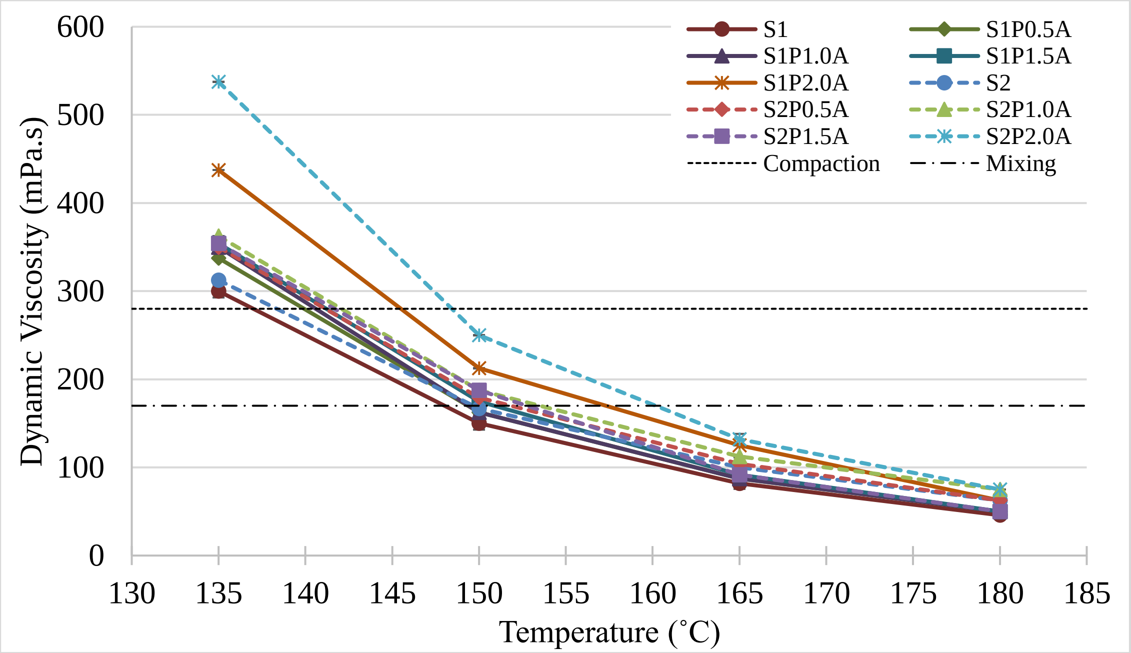
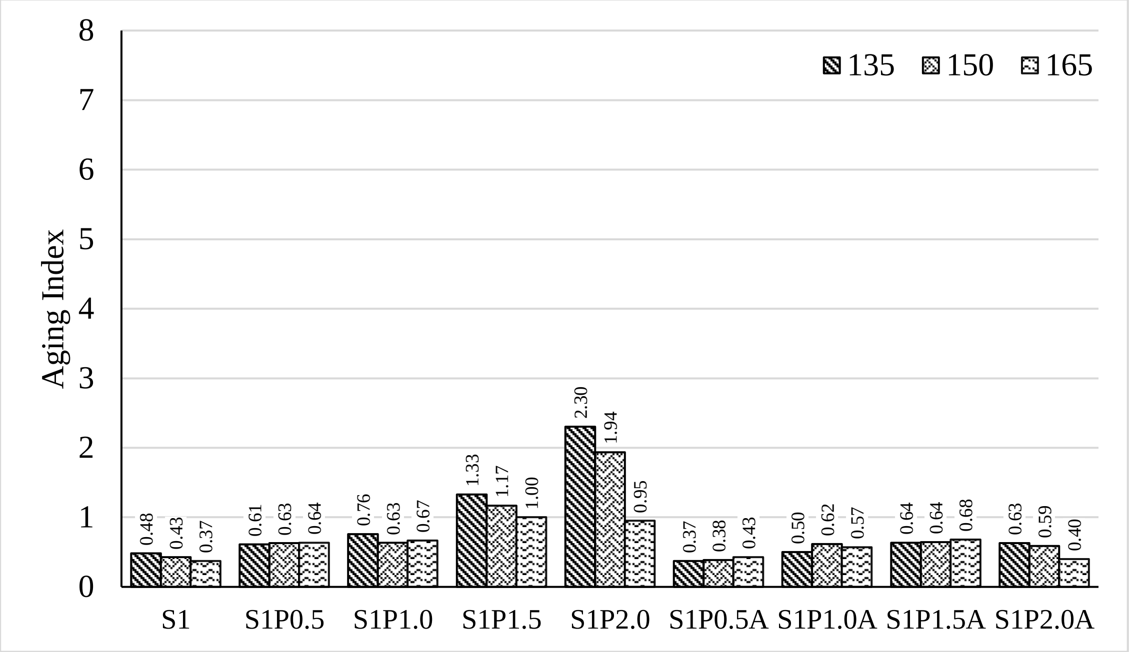
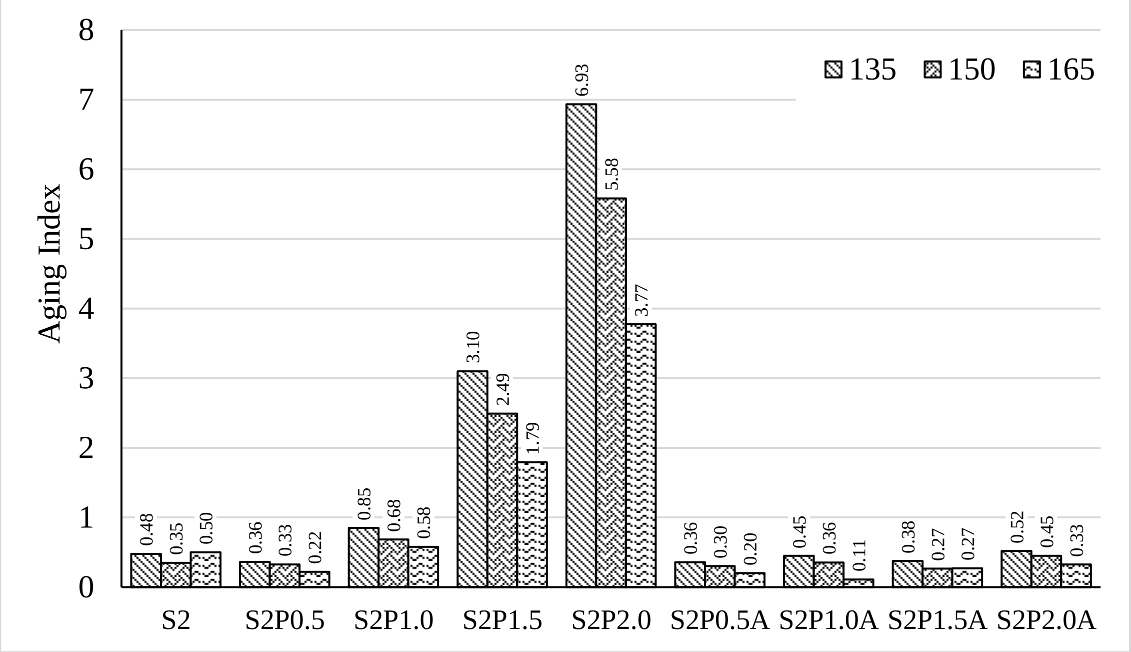


Figure 3.15 Dynamic Viscosity of S1 and S2 PG 58-28 Binders Blended with PPA and ASA



(a)



(b)

Figure 3.16 Aging Index of (a) S1 PG 58-28 and (b) S2 PG 58-28 Binders

CHAPTER

4

EFFECTIVENESS OF WMA ADDITIVE ON PPA-MODIFIED ASPHALT BINDERS CONTAINING ANTI-STRIPPING AGENT[‡]

ABSTRACT

Chemical Warm Mix Asphalt (WMA) additives are widely used by the asphalt pavement industry to reduce mixing and compaction temperatures, save energy, preserve the environment and obtain better field densities. Although the effects of chemical WMA additives on asphalt binder and mix properties have been studied before, their interactions with other chemical additives such as Polyphosphoic Acid (PPA) and liquid Anti-Stripping Agents (ASA) have not been thoroughly examined. The current study was undertaken to evaluate the effect of different amounts of PPA on rheological properties of different grades of asphalt binders containing a chemical WMA additive in presence and absence of ASA. Also, the effect of using chemical WMA additive, PPA, and ASA on rutting and moisture-induced damage potential of asphalt mixes was evaluated. Four different asphalt binders, namely PG 58-28, PG 64-

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[‡] *This chapter has been submitted to the International Journal of Pavements Engineering under the title "Effectiveness of WMA Additive on PPA-Modified Asphalt Binders Containing Anti-Stripping Agent" and accepted for publication. The current version has been formatted for this dissertation.*

22, PG 70-28, and PG 76-28, were blended with different amounts of PPA, WMA additive, and ASA and tested in a Dynamic Shear Rheometer and a Bending Beam Rheometer. The results indicated that blending WMA additive and PPA with all tested binders increases the rutting and fatigue resistance. While blending PPA with asphalt binders in presence of the WMA additive and ASA increases the rutting resistance of the blends, it reduces their resistance to fatigue cracking. Also, it was observed that the use of WMA additive, ASA and PPA can reduce the effectiveness of the PPA in bumping the high-temperature Performance Grade (PG) of asphalt binder with an insignificant effect on low-temperature PG. In addition to rheological tests, Hamburg Wheel Tracking (HWT) and Tensile Strength Ratio (TSR) tests were conducted on mixes containing WMA additive, PPA and ASA. The HWT results exhibited low rut depths with no indication of moisture-induced damage, while the TSR test results suggested some indications of moisture-induced damage. The outcomes of this study are expected to help improve the durability of asphalt pavements containing PPA, WMA additive, and ASA through gaining a better understanding of the effects of those additives on mechanical properties of binders and mixes.

Keywords: Warm-Mix Asphalt (WMA), Polyphosphoric Acid (PPA), Liquid Anti-Stripping Agent (ASA), Rutting; Fatigue, Rheology, Superpave® PG.

4.1 Introduction

Chemical Warm Mix Asphalt (WMA) additives are widely used by the asphalt industry for production of WMA mixes due to their environmental, economic, and technical benefits. Also, unlike the process-driven WMA technologies, such as water injection and foaming, production of WMA using chemical additives does not require making significant modifications to asphalt plants. Chemical WMA additives are generally used to increase the workability of asphalt mixes at lower mixing and placement temperatures (Button et al., 2007; Prowell et al., 2007; Chowdhury and Button, 2008; Estakhri, 2012; Rubio et al., 2012; Singh et al., 2017). Different mechanisms or a combination of mechanisms may contribute to improved workability of WMA mixes at low temperatures, such as reducing asphalt binder's internal friction, chemical changes, lubricating effect, emulsification, and reducing asphalt binder's viscosity (Hanz et al., 2010; Hill et al., 2011).

With introduction of several new additives and mix performance enhancers, the WMA additives are not the only chemicals added to asphalt mixes. Many other chemicals, such as Polyphosphoric Acid (PPA), liquid Anti-Stripping Agents (ASA), hydrated lime, rejuvenators, polymers and other modifiers are also being added to the asphalt binders to improve their performance and enhance their mechanical properties. The effects of WMA additives, PPA, ASA, polymers and other chemicals, when they are used separately, on mechanical properties of asphalt binders and mixes have been evaluated in several studies (e.g., Button et al., 2007; Prowell et al., 2007; Chowdhury and Button, 2008; Huang et al., 2008; Xiao et al., 2010; Estakhri, 2012; Rubio et al., 2012; Abuawad et al., 2015). However, not many studies have been undertaken to evaluate the combined effect of the abovementioned chemicals on properties of asphalt binders and mixes. Therefore, the current study was undertaken to evaluate the effect of a chemical WMA additive on the rheological properties of different grades of asphalt binders containing different amounts of PPA in presence and absence of ASA. Also, the combined effect of asphalt binder source, aggregate type, chemical WMA additive, PPA and ASA on rutting and moisture-induced damage potential of asphalt mixes was examined.

4.1.1 Chemical WMA Additives

Chemical WMA additives are usually produced as a combination of different chemical compounds such as surfactants, emulsifiers, aggregate coating enhancers and ASA (Capitão et al., 2012). Therefore, depending on the type of additive used for production of a WMA mix, its chemical and mechanical properties may vary. Some studies have concluded that the WMA and HMA mixes can have almost equal in-service performances (Kim et al., 2012a,b). The WMA mixes, as a result of low mixing and compaction temperatures, experience less plant aging. Less aging leads to asphalt pavements having a lower stiffness, higher ductility (Sanchez et al., 2011; Bennert et al., 2011) and therefore, a better resistance to fatigue and low-temperature cracking (Jenkins, 2000; Diefenderfer and Hearon, 2009; David et al., 2011). In addition, better workability of WMA mixes at low temperature results in higher field densities which in turn contributes to a more durable pavement structure. However, a number of concerns are associated with WMA mixes in general, and those prepared using chemical additives, in particular. These concerns can be summarized under two major categories (1) moisture-induced damage potential (e.g. Xiao et al., 2009, 2010; Garcia et al., 2017;

Amelian et al., 2018) and (2) susceptibility to rutting (Zhao et al., 2012; Xiao et al., 2012; Hamzah et al., 2013).

4.1.2 PPA in Asphalt Binders and Mixes

The effect of using PPA on mechanical, chemical, and rheological properties of asphalt binders has been evaluated in several studies previously (Filippis et al., 1992; Bonemazzi and Giavarini, 1999; King et al., 2002; Orange et al., 2004a, b; Huang et al., 2008; Al-Qadi et al., 2014; Abuawad et al., 2015). It was reported that adding PPA to asphalt binders results in a reduction in penetration and an increase in softening point, stiffness, viscosity, elastic modulus, high-temperature Performance Grade (PG), and resistance of the asphalt binder to rutting and low-temperature cracking (Filippis et al., 1995; Bonemazzi and Giavarini, 1999; and Giavarini et al., 2000; King et al., 2002; Edwards et al., 2007; Huang et al., 2008). Increase in stiffness and viscosity of the asphalt binders after blending them with PPA is a result of a concentration of asphaltenes and formation of insoluble materials due to using orthophosphoric acid and anhydrous phosphoric anhydride and increase in the amount of asphaltenes of high-molecular weight by converting the aromatics to resins and resins to asphaltenes (e.g., Filippis et al., 1992, 1995; Giavarini et al., 1996; Bonemazzi and Giavarini, 1999; Giavarini et al., 2000; Baumgardner, 2005; Yan et al., 2013). Despite its numerous benefits, a number of concerns are associated with the use of PPA in asphalt binders. For example, it has been reported that the use of PPA may result in a disturbance in the linear relationship between carbonyl absorbance and the aging shift factor of the asphalt binder (Huang et al., 2008). Also, it has been observed that using 2.0% PPA bumps the PG of the base binder by two grades but reduces the resistance of asphalt mix to moisture-induced damage (King et al., 2002; Arnold et al., 2009; Shulga et al., 2012). The use of PPA in asphalt binders has been found to establish cross-links between the asphalt binder and polymer and reduce the required amount of polymer in binder (Li et al., 2011; Orange et al., 2004a, b). However, using a high amount of phosphorous compounds was found to reduce the concentration of the asphaltenes because part of asphaltenes was converted to insoluble materials (Filippis et al., 1992). In another study, it was observed that using an amine-based ASA in an asphalt mix containing PPA-modified binder resulted in severe moisture-induced damage and a reduction in binder's stiffness as a result of acid-base interaction (King et al., 2002). In summary, the main concerns associated with using PPA in asphalt mixes include the following: (1) increased risk of moisture-induced damage (King et al., 2002; Arnold et al., 2009; Shulga et al., 2012); (2) over interaction of PPA with other chemicals in the binders; and (3) risk of reduced workability of the mix as a result of increased viscosity of the binder (Filippis et al., 1995; Maldonado et al., 2006).

4.1.3 ASA in Asphalt Binders and Mixes

Anti-stripping agents, such as hydrated lime and liquid ASA are widely used to enhance asphalt-aggregate adhesion and reduce the moisture-induced damage potential of associated mixes (Xiao et al., 2010; Kim et al., 2012; Park et al., 2017; Zhu et al., 2018). Although the ASAs generally work well with a wide range of asphalt binders and aggregates, they should be used with precautions. A number of chemicals in asphalt mixes, such as PPA, may react and interfere with amine-based ASAs and result in adverse effects on the durability and performance of the asphalt mix (Bishara et al., 2001; King et al., 2002). In a study conducted by the Federal Highway Administration

(FHWA), the use of hydrated lime was found to be an effective way to reduce the moisture-induced damage potential of asphalt mixes containing PPA-modified binders and those without any PPA (Arnold, 2014). Therefore, the benefit of using an amine-based WMA additive or amine-based ASA might be questionable when used with PPA due to their chemical interference.

Despite the abovementioned concerns, the literature on the implications of using PPA with chemical WMA additives and ASAs on the performance of binders against pavement distresses, such as rutting, fatigue, and low-temperature cracking is limited. Therefore, the current study was undertaken to characterize the rheological properties of different grades of asphalt binders, namely PG 58-28, PG 64-22, PG 70-28, and PG 76-28 containing a chemical WMA additive, with different amounts of PPA, in the presence and absence of a liquid ASA. For this purpose, laboratory tests on asphalt binders, namely Dynamic Shear Rheometer (DSR) and Bending Beam Rheometer (BBR) were conducted under different temperatures on 16 different binder blends. The test results were analyzed to determine the rutting, oxidative hardening, fatigue, low-temperature cracking, and Superpave® PG of the binder blends. Also, asphalt mixes were produced using a PG 64-22 asphalt binder from two different sources containing chemical WMA additive, PPA, and ASA, and two different types of aggregates (limestone and granite) and tested to characterize their rutting and moisture-induced damage potential by conducting Hamburg Wheel Tracking (HWT) and Tensile Strength Ratio (TSR) tests.

4.2 Objectives

The specific objectives of this study were as follows:

1. Evaluate the effect of blending a chemical WMA additive and different amounts of PPA in presence and absence of ASA on the rutting, oxidative hardening, fatigue cracking, and Superpave® PG grade of a PG 58-28 binder;
2. Evaluate the effect of using one combination of a chemical WMA additive, PPA and ASA on the rutting, oxidative hardening, fatigue cracking, and Superpave® PG grade of PG 64-22, PG 70-28, and PG 76-28 asphalt binders;
3. Determine the rutting resistance and moisture-induced damage potential of the asphalt mixes containing a chemical WMA additive, PPA and ASA by conducting HWT and TSR tests.

4.3 Materials and Sample Preparation

4.3.1 Materials for Binder Study

Two Styrene Butadiene Styrene (SBS) polymer-modified (PG 70-28 and PG 76-28) and two unmodified asphalt binders (PG 58-28 and PG 64-22), a chemical WMA additive and an ASA were collected from local material suppliers. According to its manufacturer, the WMA additive was an amine-based dark amber liquid with viscosity values varying from 280 to 560 centipoises at 27°C and 80 to 160 centipoises at 49°C. The amine value of the WMA additive (>500 mg KOH/g) meets the requirements set by DOTs for the minimum amine value of an adhesion promoter. The selected WMA additive is reported to improve aggregate coating. It contains surfactants which enhance the adhesion of aggregates to the asphalt binder while promoting workability. The selected WMA additive is known to help produce asphalt mixes at temperatures 35 to 50°C lower than those used for production of conventional HMA. The collected WMA additive provides minimum mixing and compaction temperatures of 104 and 66°C, respectively. The recommended rate of this additive varies from 0.25 to 0.75% by the weight of the asphalt binder. The ASA was an amine-based liquid having a low viscosity at room temperature. Also, a PPA of 105% grade (75.9% of P_2O_5) was collected. Table 4.1 presents different combinations of the asphalt binders and additives evaluated in this study. According to Table 4.1, 16 different binder blends containing different amounts of PPA, ASA, and WMA additive were mixed using a High Shear Mixer (HSM). The HSM was operated at a rotational speed of 1,000 rpm for 45 minutes, as recommended by the literature (Arnold et al., 2009; Zhang and Yu, 2010; Baldino et al., 2012, 2013; Yan et al., 2013). The blending temperatures varied from 145˚ to 175˚C, depending on the PG grade of the binder.

4.3.2 Materials for Mix Study

In addition to collection of asphalt binders and additives described in the previous section, a PG 64-22 asphalt binder from two sources and aggregates from 10 cold bins were collected from two local asphalt plants. The collected aggregates consisted of limestone, granite and sandstone. The collected materials were used for conducting Superpave® mix designs of four different asphalt mixes and production of mixes in the laboratory. Table 4.2 presents the gradations of the cold bins and the mineralogy of the aggregates used for mix designs.

4.3.3 Volumetric Mix Designs

Four mixes having a Nominal Maximum Aggregate Size (NMAS) of 12.5 mm were designed in accordance with AASHTO M 323 (AASHTO, 2017) standard specification and AASHTO R 35 (AASHTO, 2017) standard practice for volumetric mix design. Two of the asphalt mixes contained mostly granite (G) and two others contained mostly limestone (L) aggregates. Also, PG 64-22 asphalt binders collected from two different sources were used in the mix designs. Different aggregate types and binder sources were used to better understand the combined effect of asphalt binder source, aggregate mineralogy and additives (0.5% WMA additive, 1.5% PPA, and 0.5% ASA) on rutting and moisture-induced damage characteristics of WMA mixes. For convenience, these mixes will be referred to as L-1, G-1, L-2, and G-2, hereafter. The letters and numbers in the name of each mix indicate the aggregate type and the source of PG 64-22 asphalt binder, respectively. For example, L-1 represents a mix containing mostly limestone (L) aggregate and a PG 64-22 collected from source 1. The volumetric properties namely, asphalt binder content (AC%), Voids in Mineral Aggregates (VMA), Voids Filled with Asphalt (VFA), Dust Proportion (DP), and aggregate structure of each mix are presented in Table 4.3. Also, the combined aggregate gradation curves for each mix are presented in Figure 4.1.

4.4 Laboratory Tests

4.4.1 Tests on Asphalt Binders

Laboratory tests, namely Rolling-Thin Film Oven (RTFO), Pressure Aging Vessel (PAV), DSR, and BBR were conducted on asphalt binder blends prepared for this study. The results were processed to determine the rutting resistance, oxidative hardening, resistance to fatigue cracking, and Superpave® PG grade of binder blends. The workflow and test matrix followed for the evaluation of the asphalt binder blends are shown in Figure 4.2.

4.4.1.1 Rolling-Thin Film Oven

The asphalt binder blends were short-term-aged using a RTFO, in accordance with AASHTO T 240 standard method (AASHTO, 2013) to simulate the binder aging during plant production, transportation, and compaction. Approximately 35 ± 0.5 grams of unaged asphalt binder were heated and poured into four to five RTFO bottles. Asphalt binder was aged in the rotating carriage at a temperature of 163˚C and hot air flow of 4 liters/minute for 85 minutes. The collected RTFO-aged asphalt binders were later used to perform the DSR and PAV tests.

4.4.1.2 Pressure Aging Vessel

The asphalt binder blends were long-term-aged using a PAV, in accordance with AASHTO R 28 standard practice (AASHTO, 2012) to simulate the in-service aging of asphalt binders, 5 to 10 years after construction of the pavement (Brown et al., 2009). Approximately, 50 ± 0.5 grams of RTFO-aged asphalt binder were poured in two PAV plates. The plates were placed in the PAV and aged at 100˚C under an air pressure of 2.07 MPa for 20 hours. The collected PAV-aged asphalt binders were used to conduct DSR and BBR tests.

4.4.1.3 Dynamic Shear Rheometer

The DSR tests were conducted on asphalt binder blends in accordance with AASHTO T 315 standard method (AASHTO, 2012). The complex modulus (G*) and phase angle (δ) of the tested asphalt binder blends at different temperatures were obtained from the DSR tests. Table 4.4 shows the binder types, aging conditions and testing temperatures for each binder blend. As seen in Table 4.4, depending on the high PG temperature of the base binder used in each blend, the DSR tests were conducted on unaged and RTFO-aged specimens at temperatures ranging from 55˚ to 79˚C. Also, the PAV-aged binder blends, depending on the intermediate PG temperature of their base binders were tested at temperatures ranging from 16˚ to 31˚C. The measured G* and δ values were used to determine the high Superpave® PG, rutting factor (G*/sinδ) at high temperature, and fatigue factor (G*sinδ) at intermediate temperature. The DSR tests were conducted on three replicates of each asphalt binder blend.

4.4.1.4 Bending Beam Rheometer

The BBR tests were conducted on PAV-aged asphalt binder blends in accordance with AASHTO T 313 standard method (AASHTO, 2013). The flexural stiffness (S) and creep compliance (m) of the asphalt binder blends at different times of load application were obtained from these tests. The measured values after 60 seconds of load application (S_{60} and m_{60}) were used to determine the low-temperature PG of the asphalt binder blends. Table 4.4 shows the binder types, aging conditions and testing temperatures for each binder blend. As seen from Table 4.4, depending on the low PG temperature of the base binder used in each blend, the BBR tests were conducted on PAV-aged specimens at temperatures ranging from -9˚ to -18˚C. The BBR tests were conducted on two replicates of each asphalt binder blend.

4.4.2 Tests on Asphalt Mixes

Laboratory tests, namely the Hamburg Wheel Tracking (HWT) and the Tensile Strength Ratio (TSR) were conducted on asphalt mixes designed and produced in the laboratory. Tests were conducted on asphalt mixes with a PG 64-22 binder (from two different sources) containing 0.5% WMA additive, 1.5% PPA and 0.5% ASA and two types of aggregates (granite and limestone). A workflow and test matrix followed for evaluation of asphalt mixes are shown in Figure 4.3.

4.4.2.1 Hamburg Wheel Tracking Test

The HWT tests were conducted on all four types of asphalt mixes (L-1, L-2, G-1 and G-2) in accordance with AASHTO T 324 standard method (AASHTO, 2017). At least four specimens of each mix having a diameter of 150 mm and a height of 60 mm were compacted using a Superpave® Gyratory Compactor (SGC) with target air voids of 7.0% ± 0.5%. The HWT tests were conducted on specimens submerged in water at 50˚C. The loading cycle consisted of up to 20,000 wheel passes. The wheel passes and deformation data were used to determine rut depth, creep slope (rate), Stripping Inflection Point (SIP), and stripping slope, if applicable.

4.4.2.2 Tensile Strength Ratio Test

The TSR tests were conducted on asphalt mixes according to AASHTO T 283 standard method (AASHTO, 2014) to determine the moisture-induced damage potentials of all four mixes (L-1, L-2, G-1, and G-2). Six cylindrical specimens of each mix having a diameter of 150 mm and a height of 95 mm were compacted using a SGC with target air voids of 7.0% ± 0.5%. The specimens were divided into two subsets with similar average air voids. One subset was moisture-conditioned (wet subset), while the other subset was not (dry subset). Then, the average Indirect Tensile Strengths (ITS) of dry (ITS_{dry}) and moisture-conditioned (ITS_{wet}) samples were measured by testing them in a Mechanical Testing System (MTS) loading frame. The TSR value of each mix was determined as a ratio of ITS_{wet} to ITS_{dry}. A TSR value of greater than 80% indicates adequate resistance to moisture-induced damage.

4.5 Results and Discussions

4.5.1 Asphalt Binder Test Results

4.5.1.1 Rutting Resistance of PG 58-28 Binder Blends

Rutting factors (G*/sinδ) of the unaged and RTFO-aged PG 58-28 binders blended with WMA additive, PPA, and ASA measured at 55˚, 58˚, and 61˚C are presented in Figure 4.4. From Figure 4.4 it is evident that the rutting factor of unaged and RTFO-aged PG 58-28 binder increases after adding 0.5% WMA additive and by increasing the amount of PPA (0.5, 1.0, 1.5, and 2.0%) in the blend. For example, at 58˚C, the rutting factor of unaged neat PG 58-28 binder (1.15 kPa) after addition of 0.5% WMA additive and increasing the amount of PPA to 0.5, 1.0, 1.5, and 2.0% increases by 12.8, 42.6, 95.7, and 156.2%, respectively. Similarly, the rutting factor of RTFO-aged neat PG 58-28 binder (2.67 kPa) after adding 0.5% WMA additive and increasing the amount of PPA to 0.5, 1.0, 1.5, and 2.0% increases by 12.4, 35.5, 68.9, and, 152.4%, respectively. A similar trend of increasing rutting factor of PG 58-28 asphalt binder containing WMA additive due to an increase in the amount of PPA can also be observed at other testing temperatures (55˚ and 61˚C). In other words, an amine-based WMA additive and PPA when used together with a PG 58-28 binder are able to effectively increase the rutting factor of the binder blend. These results support the use of WMA additive and PPA to enhance the resistance of a PG 58-28 binder to rutting. Although an acidic (PPA) and a basic (an amine-based WMA additive) agent are present in the blends, the addition of PPA is still capable of modifying the binder matrix and improving its stiffness by increasing the concentration of asphaltenes at the expense of saturates (Baumgardner, 2005). Consequently, it is anticipated that mixes containing

PPA and WMA additive would exhibit a higher rutting resistance compared to the mixes without any additives.

However, a different trend of variation in the rutting factor of the PG 58-28 asphalt binder with the amount of PPA is observed, after the addition of an amine-based ASA to the blends. From Figure 4.4, it is evident that the rutting factor of unaged PG 58-28 binder containing 0.5% WMA additive and 0.5% ASA increases with an increase in the amount of PPA (0.5, 1.0, 1.5, and 2.0%). For example, at 58˚C, the rutting factor of unaged PG 58-28 binder containing WMA and ASA (1.84 kPa) exhibits 10.4, 11.2, 26.7, and 55.3% increase, after increasing the amounts of PPA in the blends to 0.5, 1.0, 1.5, and 2.0%, respectively. These amounts of increase in rutting factors with the PPA amount are approximately one-third of those observed in binder blends without ASA. Therefore, the PPA's effectiveness in increasing the rutting factors of WMA mixes containing PPA, in the presence of ASA, is about one-third of the PPA's effectiveness in the absence of ASA. The adverse effect of using ASA on the rutting factor is even more pronounced for RTFO-aged asphalt binder blends. For example, at 58˚C, the rutting factor of the RTFO-aged PG 58-28 binder containing WMA and ASA (2.78 kPa) exhibits a 1.6% decrease and then 2.8, 14.4, and 46.5% increase, after increasing the amount of PPA in the blends to 0.5, 1.0, 1.5, and 2.0%, respectively. Therefore, the PPA's effectiveness in improving the rutting resistance of the WMA mixes containing PPA, in the presence of ASA, is about one-fourth of that in the absence of ASA. A similar trend of variation in rutting factor of PG 58-28 asphalt binder containing WMA and ASA with an increase in the amount of PPA is also observed at other testing temperatures (55˚, and 61˚C). Therefore, it can be concluded that using PPA and WMA additive, in the presence of ASA, may not provide any considerable advantage towards improving the rutting performance of mixes. It is supported by the fact that an amine-based ASA counteracts with the acid (PPA) resulting in an amine-salt (King et al., 2002), making less PPA available for increasing the concentration of asphaltenes and improving the binder matrix (stiffness).

4.5.1.2 Comparing Rutting Resistance of PG 58-28, PG 64-22, PG 70-28 and PG 76-28 Blends

Figure 4.5 presents the rutting factors of unaged and RTFO-aged binders of various grades, namely PG 58-28, PG 64-22, PG 70-28, and PG 76-28 without any additives and those containing 0.5% WMA additive, 1.5% PPA, and 0.5% ASA. The selection of 1.5% PPA is based on findings of Liu et al. (2016) and Ge et al. (2017) that suggested limiting the amount of PPA to 1.5% to minimize the aggregation of PPA particles. Also, selection of 0.5% WMA additive and 0.5% ASA was based on their manufacturers' recommendations. As shown in Figure 4.5, using a combination of WMA additive, PPA, and ASA improve the rutting factor of the binder blends compared to those of the neat binders, at the testing temperatures. However, the extent of improvement depends on the grade of the neat binder. For example, the rutting factors of the unaged PG 58-28, PG 64-22, PG 70-28, and PG 76-28 asphalt binders at their testing temperatures on average increased by 26.6, 35.8, 37.1, and 50.3%, respectively as a result of blending them with 0.5% WMA additive, 1.5% PPA, and 0.5% ASA. Similarly, the rutting factors of the RTFO-aged PG 58-28, PG 64-22, PG 70-28, and PG 76-28 asphalt binders at their testing temperatures on average increased by 14.4, 25.0, 30.3, and 35.4%, respectively as a result of blending them with 0.5%

WMA additive, 1.5% PPA and 0.5% ASA. These observations indicate that the effectiveness of the PPA modification for WMA mixes becomes more significant with increased PG grade of the base binder or by using Polymer-modified Binders (PMB). This is due to additional cross-linking effect of PPA with polymers, which provides stronger stability and higher stiffness to the modified binders (Orange et al., 2004a, b).

4.5.1.3 Sensitivity of Binder Blends to Oxidative Aging

From Figures 4.4 and 4.5, it is evident that the increase in the rutting factors of asphalt binders containing WMA additives, PPA and ASA after RTFO aging are comparatively lower than those before aging. A summary of the rutting factors of all of the asphalt binders tested in this study, before and after RTFO-aging, is presented in Figure 4.6. From Figure 4.6 it is evident that the rutting factors of the asphalt binders after RTFO aging are between 1.65 and 2.35 times higher than those in unaged condition. Also, it was observed that the rutting factors of the RTFO-aged polymer-modified binders (PMBs) are 1.65 to 2.00 times higher than those of the unaged binders. However, RTFO-aged non-PMB binders exhibits rutting factors which are 2.35 to 2.00 times higher than those of the unaged binders. In other words, the PMB binders are less sensitive to aging.

In order to quantify the sensitivity of each asphalt binder to oxidative aging a parameter, namely Oxidative Hardening Index (OHI) was used, as shown in Equation 4.1.

$$OHI = \frac{\sum_{i=1}^{n}(G_i{}^* \sin\delta_i)_{RTFO}}{\sum_{i=1}^{n}(G_i{}^* \sin\delta_i)_{Unaged}} \tag{4.1}$$

where, *n* is the number of temperatures at which a binder was tested in a DSR. These temperatures were selected based on the high temperature PG of a binder. The

$G_i^*$and δ_i are the shear moduli and phase angles of the asphalt binder blends measured at i th testing temperature, respectively. The higher the OHI value, the more sensitive an asphalt binder is to oxidative aging. The OHI values of asphalt binder blends are calculated and shown in Figure 4.7.

From Figure 4.7 it can be observed that the neat non-PMB binders exhibit the highest OHI values. For example, the neat PG 58-28 and neat PG 64-22 binders exhibit the OHI values of 2.36 and 2.30, respectively. However, the polymer-modified binders exhibit comparatively lower OHI values. For example, the neat PG 70-28and neat PG 76-28 PMB binders have OHI values of 2.03 and 1.87, respectively. In other words, the oxidative hardening reduces with an increase in polymer modification. Also, it is found that addition of WMA additive and PPA to asphalt binder reduces the oxidative hardening. However, this reduction varies with the amount of PPA. For example, the OHI of the neat PG 58-28 containing 0.5% WMA additive reduces from 2.36 to 2.11, 2.20, 2.00, and 2.27 with addition of 0.5, 1.0, 1.5, and 2.0% PPA, respectively. A similar trend in the variation in OHI values with the amount of PPA can be observed in presence of WMA additive and ASA, see Figure 4.7. For example, the OHI of the PG 58-28 containing 0.5% ASA and 0.5% WMA additive reduces from 2.28 to 2.04, 2.11, 2.05, and 2.15 with the addition of 0.5, 1.0, 1.5, and 2.0% PPA to asphalt binder blends, respectively. Also, the OHI values of the PG 64-22, PG 70-28, and PG 76-28 asphalt binders reduce from 2.30, 2.03, and 1.87 to 2.11, 1.89, and 1.68, respectively, as a result of the addition of 0.5% WMA, 1.5% PPA, and 0.5% ASA to asphalt binder blends. The observed reduction in oxidative aging of the asphalt binders is explained by the fact that the WMA and ASA additives reduce the production of carbonyl compounds during aging. Also, PPA lowered the aging reaction rate by absorbing higher activation energy (Zhang and Yu, 2010). As a result, WMA additive, ASA, and PPA help lower the oxidative aging of the binder. A reduction in the oxidative aging is considered beneficial as it can enhance the fatigue life of asphalt mixes in their service lives.

4.5.1.4 Fatigue Cracking Resistance of PG 58-28 Binder Blends

Figure 4.8 presents the values of the fatigue factors (G* sinδ) measured by conducting the DSR tests at 16˚, 19˚, and 22˚C on PAV-aged PG 58-28 binder blends containing WMA additive, ASA, and different amounts of PPA. From Figure 4.8, it is evident that blending WMA additive and PPA with asphalt binder results in a decrease in the fatigue factor with increasing the amount of PPA. For instance, the fatigue factor of neat PG 58-28 binder at 16˚C (6416.7 kPa) reduces by 11.0, 15.9, 16.6, and 19.7% as a result of mixing 0.5, 1.0, 1.5, and 2.0% PPA, respectively, in presence of 0.5% WMA additive. Reductions of up to 20.7 and 22.5% in fatigue factors of neat PG 58-28 asphalt binder, as a result of addition of PPA to binder blends, are also observed at 19˚ and 22˚C, respectively. According to Zhang et al. (2016), a reduction in fatigue factor indicates that binder blend becomes softer than the neat binder after long-term PAV aging with improved resistance to oxidation. For an asphalt pavement subjected to repeated loading of different magnitudes and frequencies, using an asphalt binder with improved oxidative resistance is expected to enhance the fatigue life of the pavement under different climatic conditions (Mashaan et al., 2014). This is due to the presence of PPA in the mixes which reduced the rate of oxidative aging with time by forming the carbonyl and sulfoxide compounds in the initial stage of aging (Huang et al., 2008). A reduction in OHI values, reported earlier in this study, confirms the reduction in oxidative aging as a result of using PPA in binder blends.

Additionally, From Figure 4.8, it can be observed that adding different amounts of PPA to asphalt binder blends containing WMA additive, and ASA, in general, results in an increase in fatigue factor with increased amount of PPA. In other words, using an amine-based ASA, WMA additive, and PPA in a binder blend reduces its resistance to fatigue cracking. For example, the fatigue factor of PG 58-28 binder containing 0.5% WMA additive and 0.5% ASA at 16˚C (5613.3 kPa) experiences +2.7, -7.8, -3.3, and +16.3% change, as a result of blending it with 0.5, 1.0, 1.5, and 2.0% PPA, respectively. A similar trend of variation in fatigue factor of the binder blends with PPA amount is also observed at 19˚ and 22˚C.

These findings, in general, suggest that the use of ASA with PPA and WMA additives can reduce the resistance of an asphalt mix to fatigue cracking. This is possibly due to the dispersion characteristic of the selected ASA which reacts with acid groups of PPA, asphaltenes, and resins and disperses their clusters in the binder matrix (Harnish, 2010). As a result, the modified binder undergoes a faster oxidation due to the increased available surface area during aging. However, it is important to note that ASA, according to the manufacturer, is an adhesion promoter between the binder and aggregate. ASA liberates the electron-rich polar components, which can be easily absorbed by the aggregate at the surface (Harnish, 2010). Consequently, ASA is expected to create a strong adhesion bond at the binder-aggregate interface. Since this study had a focus on the properties of the binder blends, the interaction of the ASA with aggregates and its implications on fatigue life of asphalt mix was not investigated. The

ASA, therefore, may help improve the long-term performance and durability of mixes in the field by improving the binder-aggregate bond.

4.5.1.5 Comparing Fatigue Resistance of PG 58-28, PG 64-22, PG 70-28 and PG 76-28 Blends

Figure 4.9 presents the fatigue factors measured for the neat PG 58-28, PG 64-22, PG 70-28, and PG 76-28 asphalt binders and those containing a blend of 1.5% PPA, 0.5% WMA additive, and 0.5% ASA. As shown in Figure 4.9, the addition of 1.5% PPA, 0.5% WMA additive, and 0.5% ASA to PG 58-28 asphalt binder results in a reduction in its fatigue factor by 16.6, 19.0, and 17.9% at 16˚, 19˚, and 22˚C testing temperatures, respectively. However, the fatigue factors of other asphalt binders, namely PG 64-22, PG 70-28, and PG 76-28, do not significantly change after addition of PPA, WMA additive, and ASA. As a result, it is expected that mixes containing binders blended with 1.5% PPA, WMA additive, and ASA would have the resistance to fatigue cracking similar to or slightly better than those produced by neat asphalt binders.

4.5.1.6 Performance Grade of Binder Blends

Figure 4.10 presents the continuous high- and low-temperature PGs of neat binders and binder blends containing WMA additive, ASA, and different amounts of PPA based on the DSR and BBR test results (AASHTO M 320, 2010). From Figure 4.10, the high-temperature continuous grade of the neat PG 58-28 binder increases as a result of blending it with PPA and WMA additives. For instance, the high-temperature performance grade of the PG 58-28 binder (59.4˚C) increases by 0.4˚, 1.8˚, 2.8˚, and 4.0˚C after blending it with 0.5, 1.0, 1.5, and 2.0% PPA, respectively, in presence of 0.5% WMA additive. Although an improvement in continuous high-temperature grade of the binder blends with an increase in the amount of the PPA is observed, no bump in PG grade is achieved through using PPA and WMA additive. However, as reported in the literature, one to two grade bumps in the high-temperature PG is expected when 0.5 to 1.5% PPA is blended with a similar type of asphalt binder. This is due to the fact that using an amine-based WMA additive reacts with the PPA and neutralizes its cross-linking effect in polymer chains, making it less effective. This effect is more pronounced when another amine-based additive, namely ASA, is added to the binder blends. From Figure 4.10 it can be observed that the high-temperature performance grade of the PG 58-28 binder (59.4˚C) increases by 0.1˚, 0.4˚, 0.9˚, and 2.0˚C after blending it with 0.5, 1.0, 1.5, and 2.0% PPA, respectively, in presence of 0.5% ASA and 0.5% WMA additive. It is, thus, evident that addition of the PPA in presence of an amine-based WMA additive and an ASA is significantly (>50%) less effective in raising the high-temperature grade than when added to asphalt binder blends containing WMA additive only. It can be explained by the fact that presence of more alkali compounds (0.5% WMA additive and 0.5% ASA) neutralizes more PPA and therefore, reduces its effectiveness in improving the high-temperature PG grade through cross-linking and enhancing the polymer network by developing polymer strands (Orange et al., 2004a, b).

The effect of blending neat PG 64-22, PG 70-28, and PG 76-28 asphalt binders with a combination of 0.5% WMA additive, 0.5% ASA, and 1.5% PPA on their continuous high temperature grade is presented in Figure 4.10. From Figure 4.10, it is evident that blending neat PG 64-22, PG 70-28, and PG 76-28 asphalt binders with a combination of 0.5% WMA additive, 0.5% ASA, and 1.5% PPA raise their high-temperature grades of the binders by 1.5˚, 2.4˚, and 3.1˚C, respectively. As observed earlier, the effectiveness of using PPA increases when polymer-modified asphalt binders are used. However, no bump in the PG of the binders is observed as a result of blending them with PPA, in presence of WMA additive and ASA.

Unlike the high-temperature grade, the addition of PPA, WMA additive, and ASA, in general, results in an insignificant increase in the low-temperature continuous PG of the binder blends. Therefore, the Superpave® low-temperature PG of the binder blends remains unchanged. From Figure 4.10, it is evident that the low-temperature grade of PG 58-28 (-32.3˚C) after blending it with 0.5, 1.0, 1.5, and 2.0% PPA, including 0.5% WMA additive in all blends, increases by 1.3˚, 1.2˚, 0.6˚, and 0.4˚C, respectively. The increase in the low-temperature grade is found to be even less significant when blending PPA, WMA additive, and ASA with the PG 58-28 asphalt binder. From Figure 4.10, it is evident that the low-temperature PG of the PG 58-28 asphalt binder containing 0.5% ASA and 0.5% WMA additive (-31.5) increases by 0.7˚, 0.6˚, 0.6˚, and 0˚C, as a result of blending it with 0.5, 1.0, 1.5, and 2.0% PPA, respectively. Also, from Figure 4.10, it is evident that blending neat PG 64-22, PG 70-28, and PG 76-28 asphalt binders with a combination of 0.5% WMA additive, 0.5% ASA, and 1.5% PPA change their high-temperature grades by +0.8˚, -0.9˚ and -0.1˚C, respectively. These results indicate that the use of a moderate amount of PPA with WMA additive and ASA is not expected to have any significantly effect on the low-temperature cracking resistance of the binder blends.

4.5.2 Asphalt Mix Test Results

4.5.2.1 Hamburg Wheel Tracking Test

As noted previously, four mixes (L-1, L-2, G-1 and G-2) were designed and produced using a PG 64-22 asphalt binder from two different sources (1 and 2) and 0.5% WMA additive, 1.5% PPA and 0.5% ASA containing two different types of aggregates, namely limestone (L) and granite (G) with an NMAS of 12.5 mm. The HWT tests were conducted on the aforementioned mixes and measured rut depths with the number of wheel passes are presented in Figure 4.11. From Figure 4.11, it can be observed that none of the tested mixes exhibits substantial rutting. Mixes L-1, G-1, L-2 and G-2 exhibit average rut depths of 2.9, 3.0, 2.9, and 3.7 mm, respectively. All of the tested mixes have similar rut depths after 20,000 wheel passes, while G-2 exhibits a slightly higher average rut depth. Also, no Stripping Inflection Point (SIP) is observed for any of the tested mixes, as shown in Figure 4.11. This suggests that none of the tested mixes are susceptible to moisture-induced damage. Therefore, it is expected that all of the mixes containing different types of aggregates, PG 64-22 binder from different sources, and a blend of 0.5% WMA, 1.5% PPA and 0.5% ASA show a very good resistance to rutting and moisture-induced damage.

While not many studies have been conducted on the combined effect of PPA, ASA, and WMA additive on rutting and moisture-induced damage, a mixed rutting performance has been reported for asphalt mixes containing PPA-modified asphalt binders. For example, Bonemazzi and Giavarini (1999), King et al. (2002), Orange et al. (2004a, b), Maldonaldo et al. (2006), Reinke et al. (2009), and Al-Qadi et al. (2014) reported a reduction in rut depths due to the use of a PPA-modified binder in mixes.

However, the results reported by Abuawad et al. (2015) showed that the use of PPA may increases the rut depths. Based on the findings presented herein, the mixes containing PPA, ASA, and WMA additive are expected to exhibit a good resistance to rutting and moisture-induced damage.

4.5.2.2 Tensile Strength Ratio Test

The average tensile strength values measured for the moisture-conditioned (ITS_{wet}) and dry-conditioned (ITS_{dry}) samples and the TSR values calculated for each mix are presented in Figure 4.12. From Figure 4.12, the highest ITS_{dry} and ITS_{wet} values are found for Mix L-2, followed by G-2, L-1, and G-1. Therefore, one can say that the PG 64-22 asphalt binder collected from Source 2 blended with 0.5% WMA additive, 1.5% PPA, and 0.5% ASA establishs a better bond between aggregates than that collected from Source 1 and blended with the same additives. Also, it is evident that binder blends from both sources make a better bond with limestone aggregate than with granite aggregate. This type of difference between the bond strengths in binder-aggregate systems is known to be due to differences in surface chemistry and free energy components of phases present in an asphalt mix (Bhasin and Little, 2007; Ghabchi et al., 2013).

In addition, from Figure 4.12 it can be observed that all mixes have TSR values less than 0.8, expect for Mix G-2 with a TSR value of 0.94. Based on these results, it is expected that Mix G-1 exhibits the highest resistance to moisture-induced damage in the field. Mixes L-1, G-1, and L-2 exhibit a reduction in their tensile strengths after moisture-conditioning and therefore, have TSR values of 0.72, 0.77, and 0.78, respectively, lower than that measured for G-2. Although, they do not pass the minimum TSR requirement of 0.8 as per AASHTO T 283 (AASHTO, 2014), their TSR values are not substantially lower than 0.8. It should be noted that the HWT test does not exhibit any indication of moisture-induced damage for the tested mixes (Figure 4.11). Also, it can be observed that mix L-2, which has ITS_{dry} and ITS_{wet} values higher than those of G-2, has a TSR value (0.78) lower than that of the G-2 (0.94). This is one of the shortcomings of the TSR test as it lacks a strong mechanistic basis (Ghabchi, 2013). While, King et al. (2002), Reinke et al. (2009), D'Angelo (2012), and Shulga et al. (2012) observed either a slight or no increase in the TSR value of mixes due to PPA modification, adding ASA to blend is known to either improve or reduce the resistance of an asphalt mix to moisture-induced damage, depending on the aggregate, binder, and ASA type (King et al, 2002; Arnold et al., 2009; Fee et al., 2010; Abuawad et al., 2015). The anti-stripping behavior of an amine additive is typically attributed to the nitrogen lone pair of electrons, which shows strong affinity of the aggregate surface in the presence of water (King et al., 2002). When such basic compounds are added to a mix containing PPA-modified binder, the acid modifier and the basic ASA may react with each other to form an amine salt. However, the extent of this reaction highly depends on the chemistry of the asphalt binder. Overall, the results presented in this study indicate that using ASA and PPA additives together in an asphalt mix containing a chemical WMA additive do not result in a significant moisture-induced damage.

4.6 Conclusions

Rheological properties of PG 58-28, PG 64-22, PG 70-28, and PG 76-28 asphalt binders were evaluated before and after blending them with a chemical WMA additive, a PPA, and an amine-based ASA, through testing them in the laboratory using a DSR and a BBR. Also, TSR and HWT tests were conducted on four different mixes designed using PG 64-22 asphalt binders from two sources and blended with a chemical WMA additive, a PPA, and an amine-based ASA containing limestone and granite aggregates. Based on the findings of this study, the following conclusions are drawn:

1. The addition of PPA and WMA additive to a PG 58-28 binder improved its resistance to rutting. The higher the PPA amount, the higher the improvement in the rutting factor (an indicator of rutting resistance). The highest increase in rutting factor was observed when 2.0% PPA was added to PG 58-28 binder containing 0.5% WMA additive. Thus, mixes containing PPA and WMA additive are expected to exhibit a higher rutting resistance compared with those without any additive.
2. The rutting resistance of PG 58-28 binder increased due to the addition of PPA, WMA additive, and ASA to the blend. However, the improvement in rutting factor due to WMA additive, ASA, and PPA in the blend was less effective than that of binder blends containing only PPA and WMA additive. Therefore, effectiveness of PPA in a PPA-modified binder is expected to reduce due to the addition of ASA and WMA additive.
3. The rutting resistance of PG 64-22, PG 70-28 and PG 76-28 asphalt binders was found to increase due to the addition of 0.5% WMA additive, 1.5% PPA, and 0.5% ASA. This improvement was more significant for polymer-modified binders. Therefore, an improvement in rutting resistance of the asphalt mixes is expected due to the addition of WMA additive, PPA, and ASA in the mix.

4. Blending PPA with PG 58-28 asphalt binder containing chemical WMA additive was found to enhance its resistance to fatigue cracking with an increase in the amount of blended PPA.
5. Blending PPA with PG 58-28 asphalt binder containing chemical WMA additive and ASA, in general, reduced its resistance to fatigue cracking.
6. No significant differences in the fatigue cracking resistance of the neat PG 64-22, PG 70-28, and PG 76-28 binders and those containing 0.5% WMA additive, 1.5% PPA, and 0.5% ASA were observed.
7. Use of WMA additive, ASA, and PPA is expected to help lower the oxidative aging of the asphalt binders. This effect was more pronounced for binder blends containing low amounts of PPA. A reduction in the oxidative aging is beneficial as it can enhance the fatigue life of asphalt mixes in their service lives.
8. The use of PPA and WMA additive or PPA, WMA additive, and ASA, in any combinations, cannot bump the high-temperature Superpave® PG grade of any asphalt binders used in this study. Blending of WMA additive and/or ASA significantly reduced the effectiveness of PPA in bumping the high-temperature Superpave® PG grade of the asphalt binders.
9. Overall, it was found that a combination of using 0.5% amine-based WMA additive and 2% PPA or a combination of 0.5% amine-based WMA additive, 1% PPA, and 0.5% ASA resulted in the highest resistance to rutting and fatigue cracking.

10. Testing of asphalt mixes containing PPA, WMA, and ASA using a Hamburg Wheel Tracking device revealed their significant resistance to rutting, with no indication of susceptibility to moisture-induced damage.
11. The TSR test results from mixes containing PPA, WMA, and ASA, however, revealed possibility of moisture-induced damage in some cases, which was not supported by the HWT test results. Lack of a strong mechanistic-basis of TSR in identifying moisture-induced damage can be responsible for such incoherencies.

Based on the findings, scope and limitations of this study, the following recommendations are made for future studies:

1. It is recommended that a study be undertaken on the moisture-induced damage potential of the asphalt binder blends containing PPA, WMA additive and ASA using a mechanistic approach such as Surface Free Energy (SFE) method.
2. In order to gain a better understanding of the effect of the asphalt binder chemistry on the rheological properties of the asphalt binders, it is recommended that elemental analyses of asphalt binder blends, containing different amounts of WMA additive, PPA and ASA be conducted in a future study.

Acknowledgements

The authors would like to thank the Oklahoma Department of Transportation (ODOT) and the Southern Plain Transportation Center (SPTC) for financial support of this study. Special thanks are due to Silver Star Construction Company and Haskell

Lemon Construction Company for providing materials for this study. The authors would also like to extend their sincere appreciation to Dr. Amir Arshadi, Dr. Manik Barman, and Mr. Md Ashiqur Rahman for their help with this study.

Table 4.1 Binder Blends Prepared for this Study

No.	Type of Neat Binder	Additive Type and Amount (% by the weight of binder)			Binder Blend's Code
		WMA (W)	PPA (P)	ASA (A)	
1	PG 58-28	-	-	-	H58
2		0.5	0.5	-	W58-P0.5
3		0.5	1.0	-	W58-P1.0
4		0.5	1.5	-	W58-P1.5
5		0.5	2.0	-	W58-P2.0
6		0.5	-	0.5	W58-A
7		0.5	0.5	0.5	W58-P0.5-A
8		0.5	1.0	0.5	W58-P1.0-A
9		0.5	1.5	0.5	W58-P1.5-A
10		0.5	2.0	0.5	W58-P2.0-A
11	PG 64-22	-	-	-	H64
12		0.5	1.5	0.5	W64-P1.5-A
13	PG 70-28	-	-	-	H70
14		0.5	1.5	0.5	W70-P1.5-A
15	PG 76-28	-	-	-	H76
16		0.5	1.5	0.5	W76-P1.5-A

Table 4.2 Gradations and Types of Aggregate Stockpiles

Sieve Size (mm)	Percentage Passing (%)									
	Bin No. 1	Bin No. 2	Bin No. 3	Bin No. 4	Bin No. 5	Bin No. 6	Bin No. 7	Bin No. 8	Bin No. 9	Bin No. 10
Mineralogy*	L	L	G	L	S	G	L	G	G	S
19.0	100	100	100	100	100	100	100	100	100	100
12.5	97	44	100	99	100	88	100	100	100	100
9.5	65	7	100	97	100	62	100	100	100	100
4.75	8	2	95	72	100	5	94	90	62	99
2.36	4	2	70	41	99	1	56	65	69	95
1.18	3	2	47	24	99	1	30	43	47	84
0.60	2	2	29	16	94	1	18	26	33	65
0.30	2	2	15	12	66	1	10	13	22	40
0.15	2	1	7	9	10	1	6	6	14	14
0.075	1.2	1.2	4.1	7.9	1.2	0.5	3.5	3.5	9.4	1.6

** Mineralogy of Aggregates – L: Limestone; G: Granite; S: Sandstone.*

Table 4.3 Volumetric Properties and Aggregate Structure of Designed Mixes

Mix Type (Aggregate-Binder Source)	Asphalt Binder Grade	AC[†] (%)	Additive Type			%VMA[‡] Required[+] >14	%VFA[§] Required[+] 70 – 80	DP[¤] Required[+] 0.6 – 1.2
			WMA (%)	PPA (%)	ASA (%)			
L-1	PG 64-22	6.2	0.5	1.5	0.5	16.8	76.3	0.8
G-1	PG 64-22	5.5	0.5	1.5	0.5	16.2	74.6	0.6
L-2	PG 64-22	6.4	0.5	1.5	0.5	17.0	76.0	0.7
G-2	PG 64-22	5.6	0.5	1.5	0.5	16.0	74.5	0.6

Mix Type	Percentage of Each Bin (%)									
	Bin No. 1	Bin No. 2	Bin No. 3	Bin No. 4	Bin No. 5	Bin No. 6	Bin No. 7	Bin No. 8	Bin No. 9	Bin No. 10
Mineralogy[*]	L	L	G	L	S	G	L	G	G	S
L-1	10	10	43	27	10	-	-	-	-	-
G-1	-	-	-	-	-	37	17	11	20	15
L-2	10	10	43	27	10	-	-	-	-	-
G-2	-	-	-	-	-	37	17	11	20	15

[+] *AASHTO M 323 volumetric mix design requirement.*

[*] *Mineralogy of aggregates – L: Limestone; G: Granite; S: Sandstone.*

[†] *Asphalt Content*

[‡] *Voids in Mineral Aggregates*

[§] *Voids Filled with Asphalt*

[¤] *Dust Proportion*

Table 4.4 Selected Temperatures for Conducting DSR and BBR Tests

No.	Binder Blend	Test Temperature (˚C)		
		DSR (AASHTO T 315)		BBR (AASHTO T 313)
		Unaged and RTFO-aged	PAV-Aged	PAV-Aged
1	H58	55˚; 58˚; 61˚C	16˚; 19˚; 22˚C	-18˚; -21˚C
2	W58-P0.5			
3	W58-P1.0			
4	W58-P1.5			
5	W58-P2.0			
6	W58-A			
7	W58-P0.5-A			
8	W58-P1.0-A			
9	W58-P1.5-A			
10	W58-P2.0-A			
11	H64	61 ˚; 64˚; 67˚C	22˚; 25˚; 28˚C	-12˚; -15˚C
12	W64-P1.5-A			
13	H70	67˚; 70˚; 73˚C	22 ˚, 25 ˚; 28˚C	-18˚; -21˚C
14	W70-P1.5-A			
15	H76	73˚; 76˚; 79˚C	25˚; 28˚; 31˚C	-18˚; -21˚C
16	W76-P1.5-A			

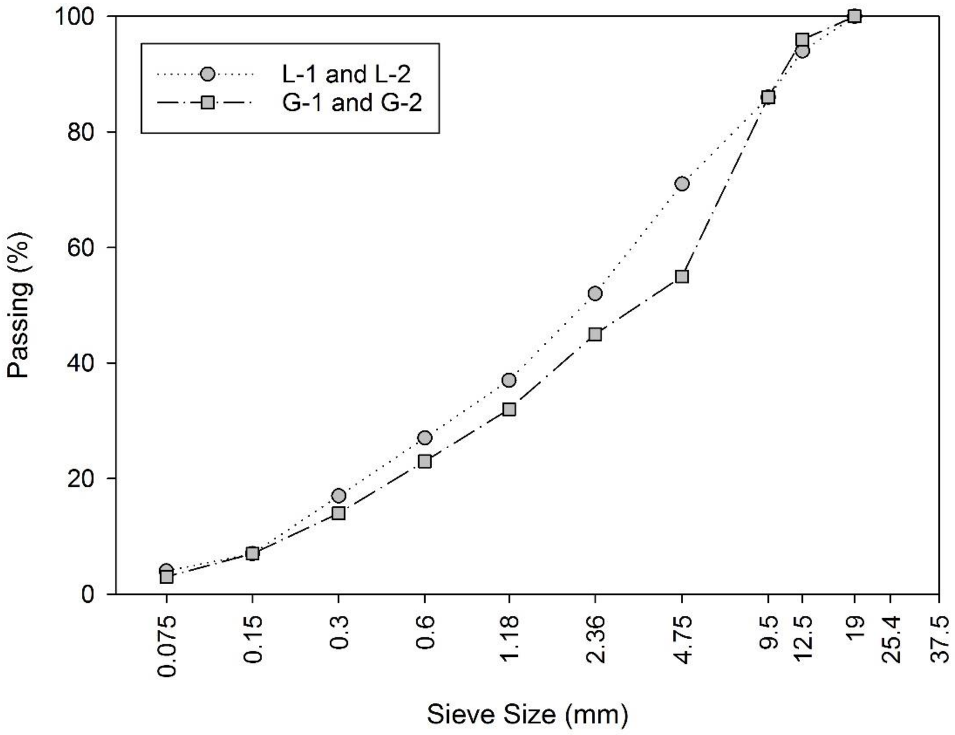
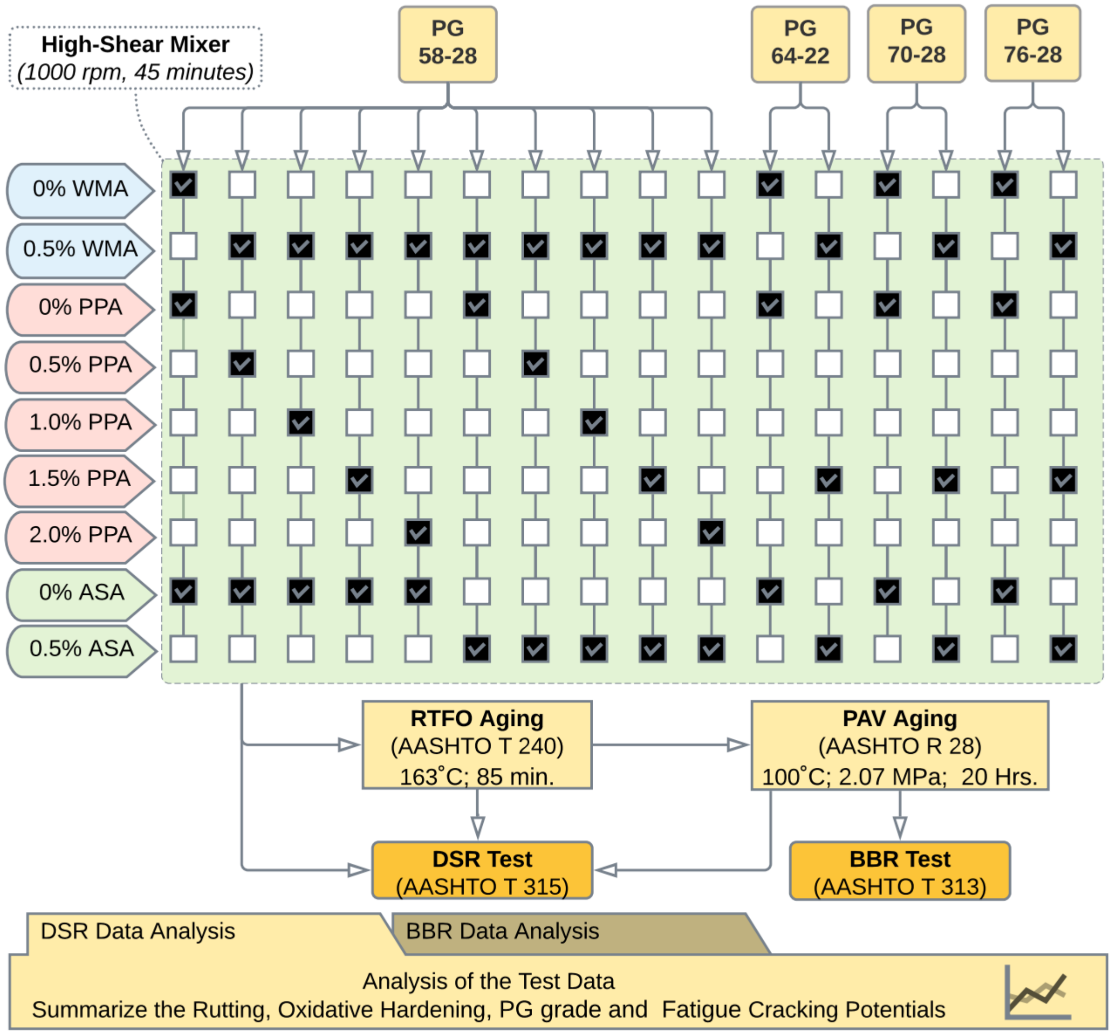


Figure 4.1 Aggregate Gradation Curves for Asphalt Mixes



	PG 58-28										PG 64-22		PG 70-28		PG 76-28	
0% WMA	☑	☐	☐	☐	☐	☐	☐	☐	☐	☐	☑	☐	☑	☐	☑	☐
0.5% WMA	☐	☑	☑	☑	☑	☑	☑	☑	☑	☑	☐	☑	☐	☑	☐	☑
0% PPA	☑	☐	☐	☐	☐	☑	☐	☐	☐	☐	☑	☐	☑	☐	☑	☐
0.5% PPA	☐	☑	☐	☐	☐	☐	☑	☐	☐	☐	☐	☐	☐	☐	☐	☐
1.0% PPA	☐	☐	☑	☐	☐	☐	☐	☑	☐	☐	☐	☐	☐	☐	☐	☐
1.5% PPA	☐	☐	☐	☑	☐	☐	☐	☐	☑	☐	☐	☑	☐	☑	☐	☑
2.0% PPA	☐	☐	☐	☐	☑	☐	☐	☐	☐	☑	☐	☐	☐	☐	☐	☐
0% ASA	☑	☑	☑	☑	☑	☐	☐	☐	☐	☐	☑	☐	☑	☐	☑	☐
0.5% ASA	☐	☐	☐	☐	☐	☑	☑	☑	☑	☑	☐	☑	☐	☑	☐	☑

Figure 4.2 Workflow and Test Matrix for Binder Blends

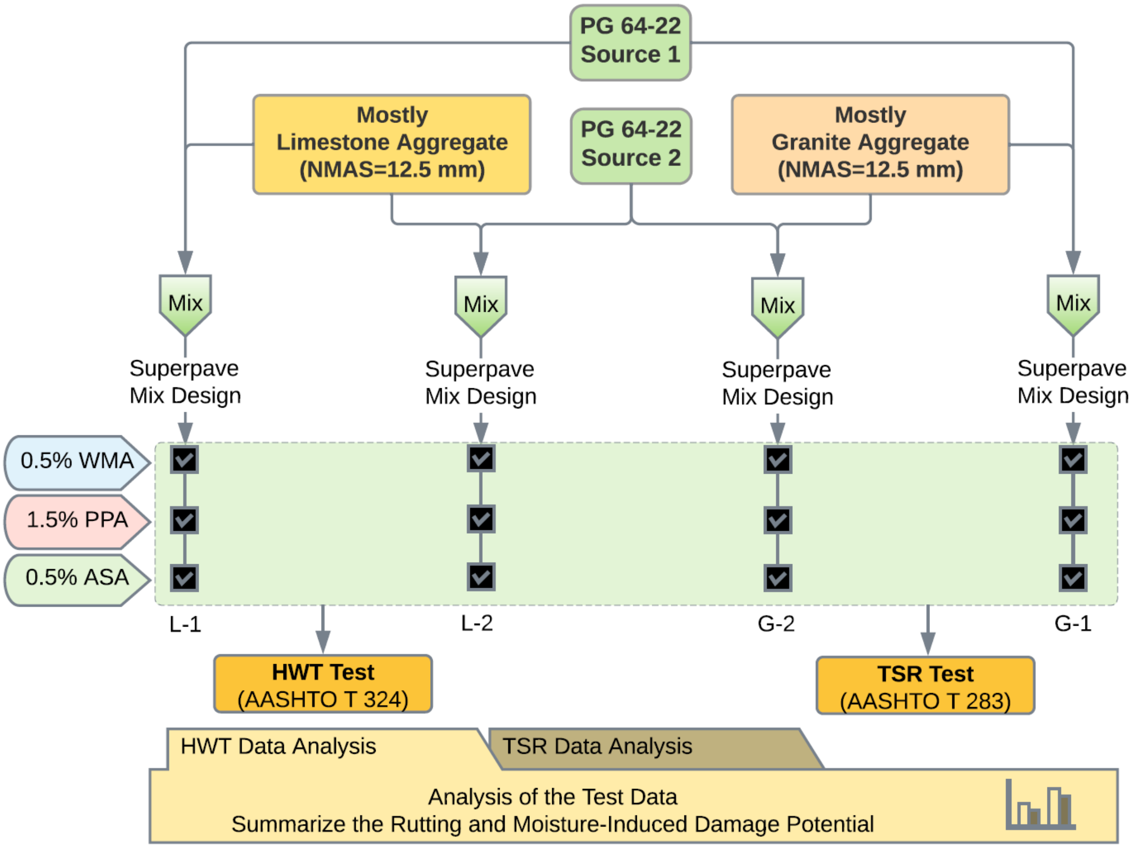


Figure 4.3 Workflow and Test Matrix for Asphalt Mixes

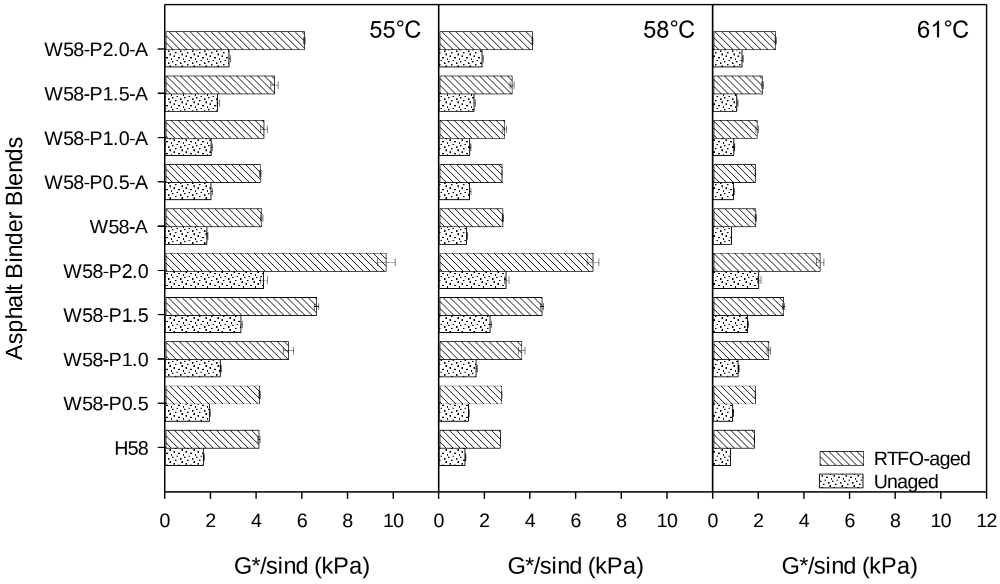


Figure 4.4 Rutting Factors (G*/sinδ) of Unaged and RTFO-aged PG 58-28 Binder Blends Containing Different Amounts of WMA Additive, PPA and ASA at 55˚, 58˚, and 61˚C

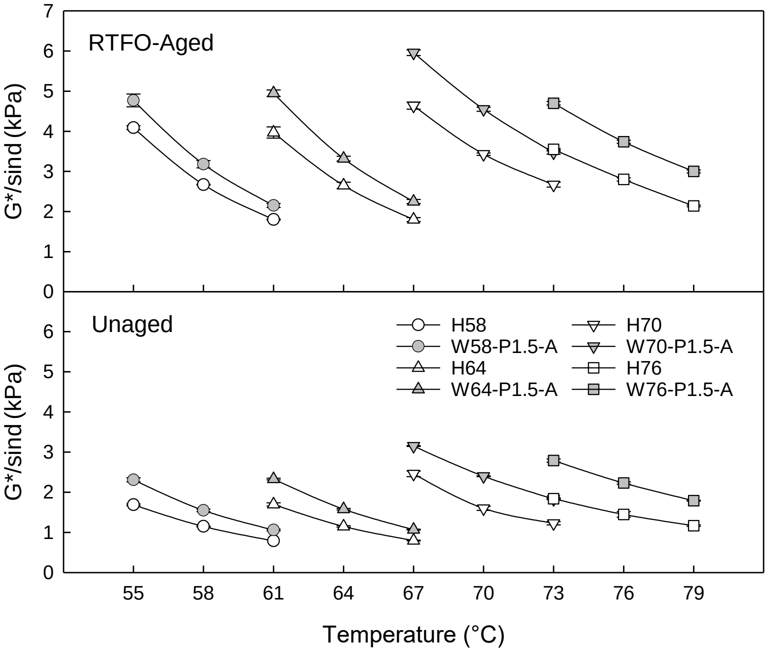


Figure 4.5 Rutting Factors (G*/sinδ) of Unaged and RTFO-aged Neat Binders and Binder Blends Containing 0.5% WMA Additive, 0.5% ASA, and 1.5% PPA at Different Test Temperatures

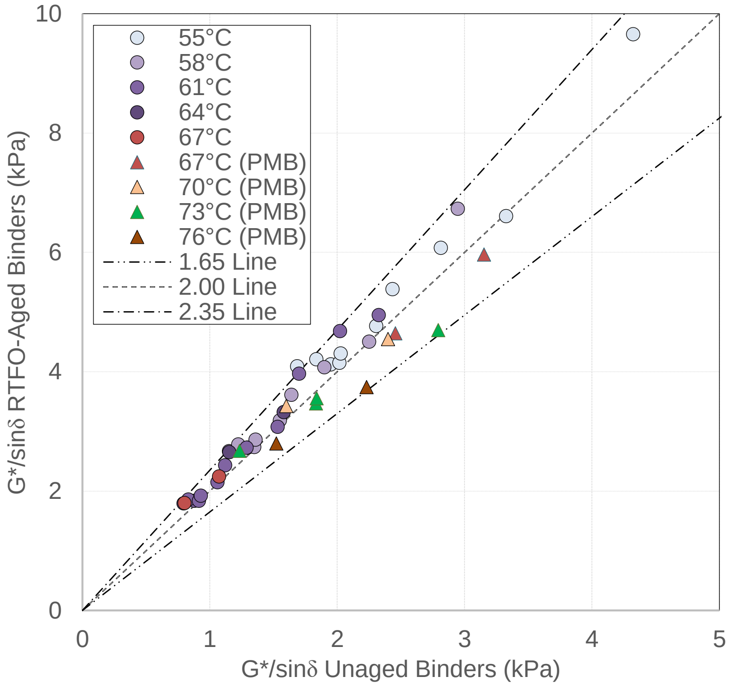


Figure 4.6 Comparison of Rutting Factors (G*/sinδ) of Unaged and RTFO-aged Binder Blends at Different Temperatures

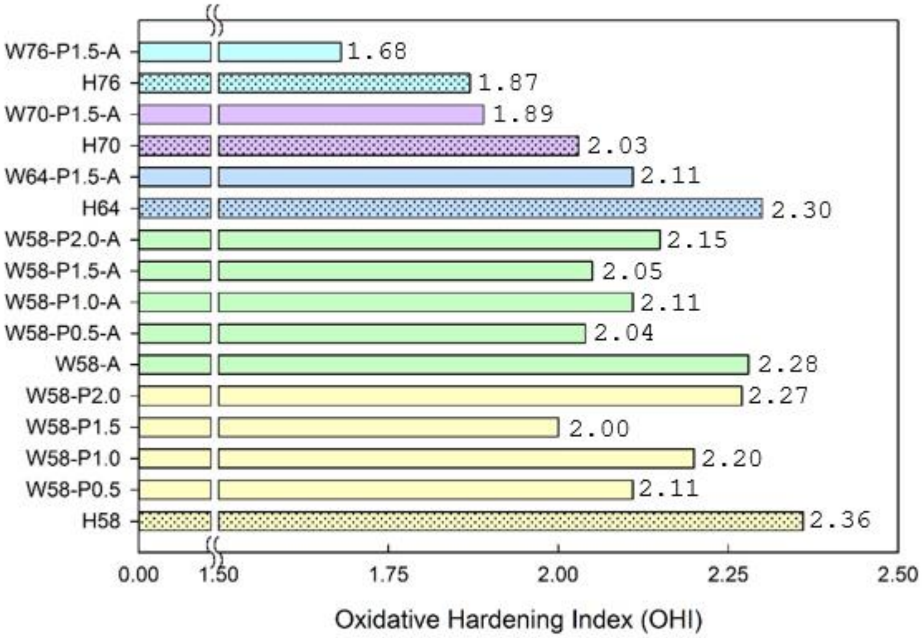


Figure 4.7 Oxidative Hardening Indices of Binder Blends

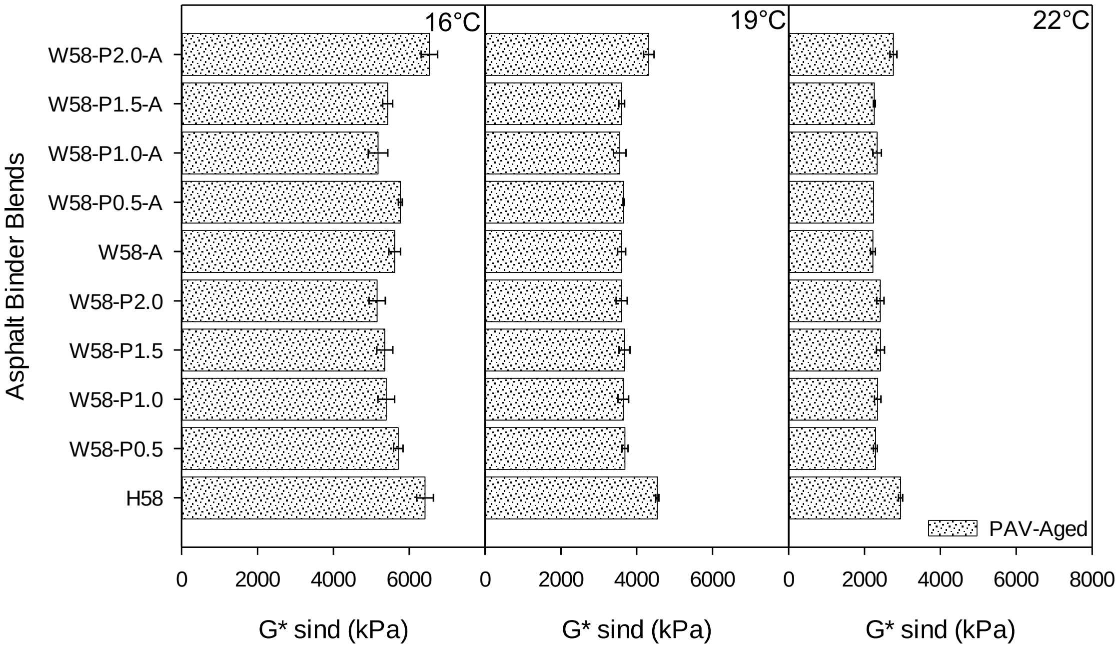


Figure 4.8 Fatigue Factors of PAV-Aged PG 58-28 Binder Blends

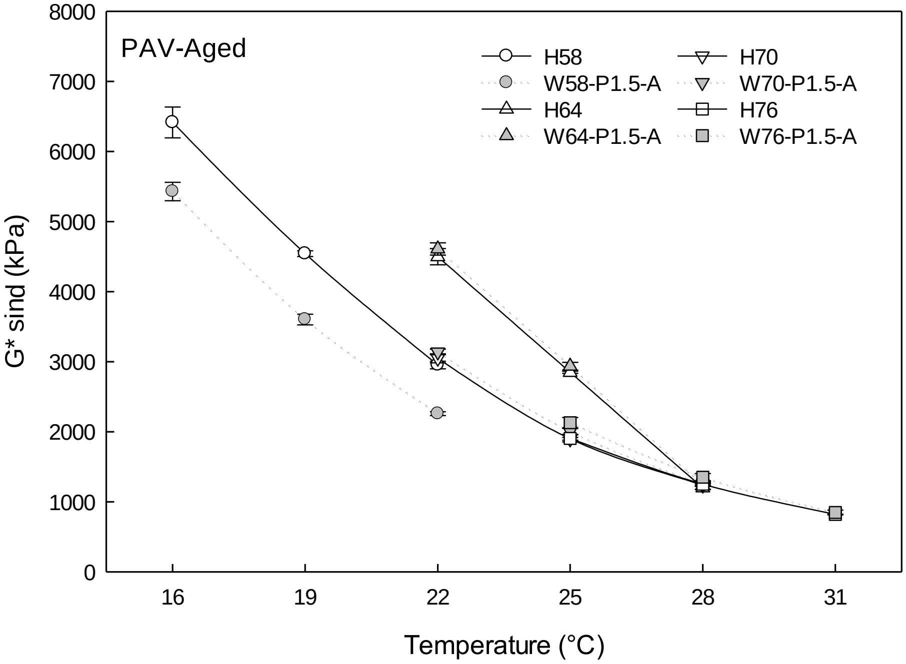


Figure 4.9 Fatigue Factors of Binders of Various Grade with and without PPA, WMA Additive, and ASA

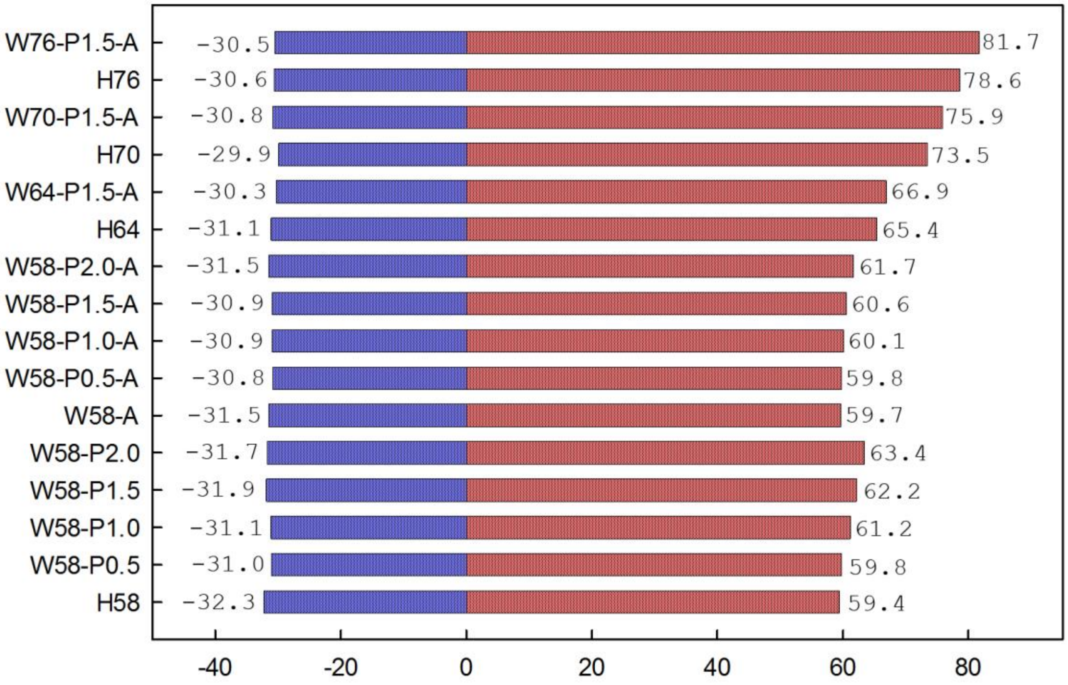


Figure 4.10 Continuous Performance Grades of Binder Blends

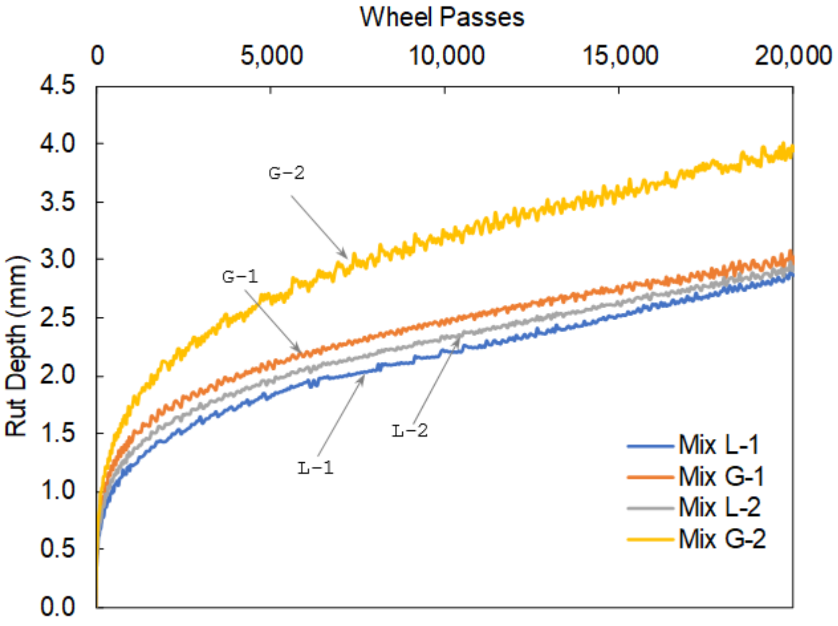


Figure 4.11 Rut Depths and Wheel Passes from Hamburg Wheel Tracking Test

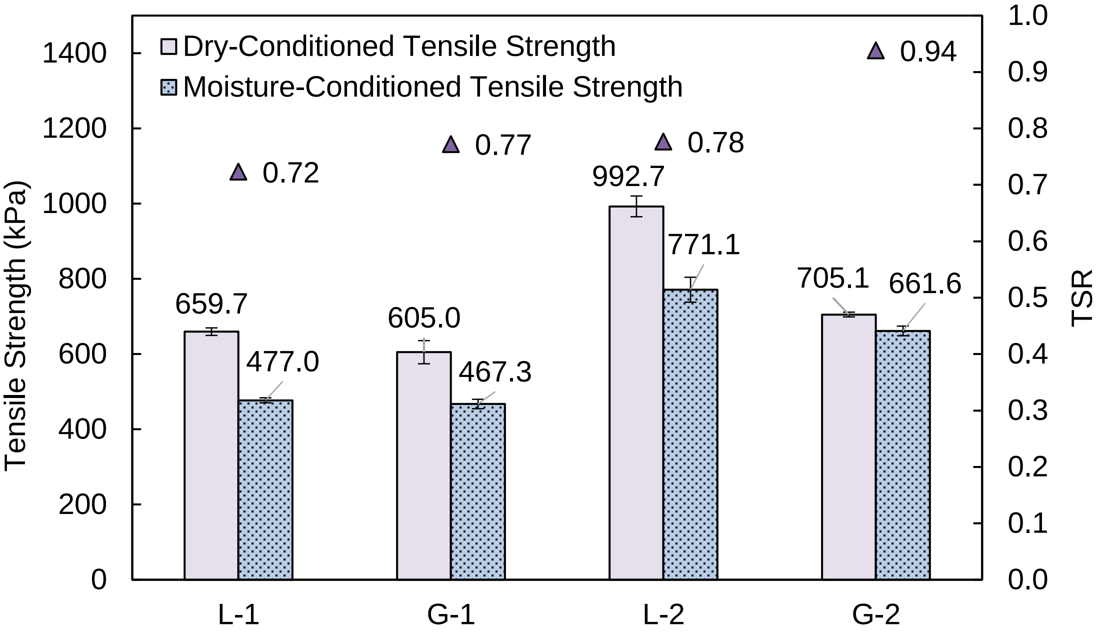


Figure 4.12 Indirect Tensile Strengths and TSR Values of Asphalt Mixes

CHAPTER

5

EVALUATION OF MOISTURE-INDUCED DAMAGE POTENTIAL OF ASPHALT MIXES CONTAINING PPA AND ASA USING SFE APPROACH[§]

ABSTRACT

Polyphosphoric Acid (PPA) is generally used to stiffen the base binder. However, due to its hydrophilic nature, it sometimes is added with an Anti-Stripping Agent (ASA) to minimize the moisture-induced damage potential. But, adding an amine-based ASA may or may not help the PPA-modified binder considering the surface chemistry of both the PPA and ASA, which needs to be examined. This study evaluates the moisture-induced damage potential of binders and mixes containing PPA and ASA using a mechanistic-based Surface Free Energy (SFE) approach. For this purpose, a PG 58-28 binder was blended with different amounts of PPA and ASA using a high shear mixer. The SFE components of the binder blends were determined using dynamic contact angles measured with three different probe liquids, namely water,

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[§] *This chapter has been submitted to the Road Materials and Pavement Design under the title "Evaluation of Moisture-Induced Damage Potential of Asphalt Mixes Containing PPA and ASA Using SFE Approach." The current version has been formatted for this dissertation.*

glycerin, and formamide. Also, five different types of aggregates were selected, namely limestone, gravel, quartzite, granite, and basalt. Based on the SFE components of the binder blends and aggregates, different energy parameters (work of cohesion, wettability, work of adhesion, work of debonding, and energy ratio) were determined. The results indicated that the use of PPA does not affect the cohesive bond of the neat binder. However, depending on the aggregate type, it may improve the adhesive bond between the binder and aggregate. Additionally, it was observed that using a high amount of PPA can increase the debonding of the binder from the aggregate surface. As a result, there was no significant effect on the moisture-induced damage potential of mixes as a result of using PPA-modified binder in the mix. This study also showed that ASA is not recommended to be used with the PPA-modified binder as it does not improve the resistance of binders and mixes containing PPA to moisture-induced damage. Among all the concentrations, the use of 1.5% PPA with and without ASA is found to be the most effective in improving the adhesive bond and wettability of the binder with aggregates. The results from this study are expected to help engineers and others to improve the practice of using PPA in asphalt mixes.

Keywords: Surface Free Energy, Cohesion, Adhesion, Wettability, Debonding, Energy Ratio, Polyphosphoric Acid, Anti-Stripping Agent, and Moisture-Induced Damage

5.1 Introduction

Moisture-induced damage is one of the major causes of poor pavement performance both in rural and urban roadways. The common examples of the moisture-induced damage are localized bleeding, potholes, particle segregation, and degradation (McGennis et al., 1984; Cross and Brown, 1993; Fwa and Ang, 1993; Wasiuddin et al., 2006; Liddle and Choi, 2007; Khosravi et al., 2013; Dong et al., 2014). Most of the moisture-induced damage cases are attributed to poor mechanical interlocking, loss of physical adhesion at binder-aggregate interface, loss of cohesion at the binder-binder interface, and chemical interactions between minerals and binders in the presence of moisture (McGennis et al., 1984; Cheng et al., 2003; Bhasin et al., 2006; Caro et al., 2008; Mehrara and Khodaii, 2013; Dong et al., 2017).

The current state of practice for evaluating moisture-induced damage potential of asphalt mixes is based on the Tensile Strength Ratio (TSR) test (ODOT, 2009), where the mechanical properties of unconditioned specimens are compared with those of moisture-conditioned specimens (AASHTO T 283, 2007). Although the TSR test helps determine the moisture-induced damage potential of mixes, many researchers have reported that the TSR results may not correlate with field observations, especially for mixes containing additives (Kim et al., 2012; Ghabchi et al., 2014; Malladi et el., 2015). It may be due to the empirical nature of the test that lacks a mechanistic base to address the failure (Bhasin et al., 2007; Ghabchi et al., 2014). Another widespread practice is to determine the stripping inflection point using the Hamburg Wheel Tracking (HWT) test in accordance with AASHTO T 324 (AASHTO, 2014). However, the stripping inflection point does not address the basic failure mechanisms, as mentioned above, related to moisture-induced damage (Ghabchi et al., 2014). Therefore, it is important to consider a mechanistic approach which can correlate the fundamental properties affecting the binder-aggregate interaction with the moisture-induced damage (Bhasin et al., 2007). The Surface Free Energy (SFE) has been used successfully as a mechanistic tool to evaluate the moisture-induced damage in mixes (Cheng et al., 2002; Kim et al., 2004; Hefer et al., 2006; Bhasin and Little, 2007; Bhasin et al., 2007; Rani et al., 2018, *Laboratory characterization of asphalt binders containing a chemical-based warm mix asphalt additive*, manuscript accepted for publication).

According to Majidzadra and Brovold (1968), the free energy of the overall system (aggregate-water-binder) reduces due to stripping of binder at the interface. However, the amount of reduction in the free energy depends on the surface characteristics of both the binder and aggregates. The SFE approach uses the SFE of binder, aggregates, and water to quantify the potentials of adhesion and debonding between aggregates and binder in the presence of moisture (Van Oss et al., 1988; Adamson and Gast, 1997; Della Volpe and Siboni, 2000). Cheng et al. (2002) and Kim and Little (2003) suggested correlations between the SFE components of binder and aggregates with the moisture-induced damage of mixes. Wasiuddin et al. (2006, 2007) applied the SFE approach to examine the effect of Anti-Stripping Agents (ASA) and found that the ASA increased the wettability of binders over aggregates by reducing their acid component and increasing their base component. Wasiuddin et al. (2007) also used the SFE results to differentiate the influence of the ASA on the performance of neat and polymer-modified binders. Similarly, Little and Bhasin (2006) and Bhasin et al. (2004) utilized SFE approach to successfully predict the impact of additives on the adhesion bond between the binder and aggregate at the interface. Bhasin et al. (2007) estimated different interfacial energy parameters, namely work of adhesion, work of debonding, work of cohesion, and energy ratio using the SFE components of binders and aggregates. The parameters were compared with the results of mechanical tests (creep and dynamic modulus) performed in the direct tensile mode of loading. The results indicated that the interfacial energy parameters relate better with the ratio of fatigue life in dry and wet conditions than the dynamic modulus in tension.

Arabani and Hamedi (2011) found that Polyethylene (PE) improves the wettability of binder on aggregate and adhesion bond between binder and aggregate by significantly reducing the overall SFE of the system. Also, the results correlated well with the dynamic modulus ratio of mixes. Many other studies have considered the SFE approach to investigate the different additives or modifiers on the moisture-induced damage potential of binders, aggregates, and mixes (Buddhala et al., 2011; Howson, 2011; Arabani et al., 2012; Sarsam and Al–Azawee, 2012; Ghabchi et al., 2013; Tan and Guo, 2013; Hesami et al., 2013; Khodaii et al., 2014; Nejad et al., 2014; Kakar et al., 2016). However, to the authors' knowledge, no study has been reported evaluating the effect of Polyphosphoric Acid (PPA) in conjunction with an ASA on the moisture-induced damage potential of binders and mixes, using the SFE approach. Although the primary purpose of using PPA is to increase the stiffness of binders, it also impacts the basic chemical composition, molecular structure, and the asphaltenes concentration of binders (Baumgardner et al., 2005; Jaroszek, 2012; Yan et al., 2013). This may, in turn, affect the SFE components of the neat binder, interaction of the binder with aggregates, and the moisture-induced damage potential of mixes. On the other hand, an ASA is generally used to decrease the moisture-induced damage potential of a mix (Buddhala et al., 2011; Hesami et al., 2013; Park et al., 2017). However, using an amine-based ASA with an acid-based PPA may not work as expected. This study analyzes a total of 50 different binder-aggregate combinations containing PPA and ASA for the moisture-induced damage potential.

5.2 Objectives

The specific objectives of this study are to:

1. Determine the SFE components of a PG 58-28 binder before and after modification by using different combinations of PPA and ASA;
2. Examine the effect of PPA and ASA on the cohesive bond of the binder;
3. Calculate the interfacial energy parameters, namely work of adhesion, work of debonding, wettability, and energy ratio, for the different combinations of binder-aggregate using their SFE components;
4. Evaluate the moisture-induced damage potential of mixes when PPA is used alone and in combination with ASA.

5.3 Materials

5.3.1 Binder and Aggregates

An asphalt binder with a Superpave® Performance Grade (PG) of PG 58-28 was collected from a local refinery in Oklahoma. In this study, the collected binder is referred to as “S1.” Also, five different aggregates were selected for evaluation, namely limestone, quartzite, gravel, granite, and basalt.

5.3.2 Polyphosphoric Acid

The primary purpose of using PPA is to increase the stiffness of the neat binders and to enhance the rutting performance of mixes in the field. The main compounds required to produce PPA are phosphoric acid (H_3PO_4) and phosphorous pentoxide (P_2O_5). Either H_3PO_4 or dispersed solution of P_2O_5 and H_3PO_4 can be heated at a high temperature to prepare the PPA (Masson, 2008). However, depending upon the process used and the concentration of P_2O_5 with respect to H_3PO_4, PPA can be of different grades, such as 100%, 105%, 110%, 114%, and 123%. For example, 100% PPA is known as ortho polyphosphoric acid and contains 72.4% P_2O_5 (Masson, 2008). To evaluate the effect of PPA on the SFE components of the collected binder, 105% grade PPA was used in different amounts, specifically 0%, 0.5%, 1.0%, 1.5%, and 2.0% (by weight of the binder). The primary reason for the selection of the 105% grade PPA was its lower viscosity at room temperature in comparison to higher grades which makes to easier to work with. As reported by Platonov (2002), 105% PPA consists of short chains of mono- and di- meric segments (ortho- and pyro- phosphoric acids) that make it less viscous and easier to use compared to high grades of PPA.

5.3.3 Anti-Stripping Agent

As noted previously, an ASA, such as hydrated lime, phosphate esters, and aminoamides is primarily used to enhance the resistance of binders and mixes against moisture-induced damage. In this study, an amine-based ASA having a specific gravity close to 1.0 was collected from a local material supplier. According to the manufacturer, the agent has the capability of increasing the adhesion bond between the binder and aggregates and therefore, improves the resistance of mixes against moisture-induced damage. Also, for the best performance, the manufacturer recommends using ASA in an amount ranging from 0.25% to 1.0% by weight of the binder. For this study, 0.5% (by weight of the binder) was selected and used.

5.3.4 Preparation of Binder Blends

Consistent with the objectives of this study, a total of 10 binder blends were prepared using different amounts of PPA and ASA (Table 5.1). To prepare a binder blend, the neat binder was first heated at 145°C for 2 hours to liquefy. Then, the required amounts of additive were added to the neat binder. A high shear mixer was used at 1,000 rpm for 45 minutes to blend the neat binder with the additives. The blending protocol was selected based on the recommendations from other studies (e.g., Singh and Sawant, 2016; Zhang and Yu, 2010; and Baldino et al., 2013). The mixing temperature varied from 145˚ to 165˚C, depending upon the PPA concentration and its combination with ASA. For instance, the neat binder and 0.5% ASA were blended at 145˚C. While, the neat binder and 2.0% PPA were mixed at 165˚C.

5.4 Methodology

Figure 5.1 shows the work flow and the procedure used in this study for the evaluation of moisture-induced damage potential of binders and mixes containing PPA and ASA.

5.4.1 Surface Free Energy Components of Binders

The SFE is defined as the amount of external energy required to create a surface area by a unit area under vacuum (Van Oss et al., 1988). According to the Good-Van Oss-Chaudhary theory, the total SFE of a material can be divided into three components, namely acid SFE, base SFE, and Lifshitz-van der Waals SFE components, based on the molecular interaction between the particles (Van Oss et al., 1988). The acid SFE and base SFE components are combined to calculate the acid-base SFE components Γ^{AB}, as shown in Equation 5.1. Then, the total SFE can be calculated by using Equation 5.2.

$$\Gamma^{AB} = 2\sqrt{\Gamma^{+}\Gamma^{-}} \tag{5.1}$$

$$\Gamma^{Total} = \Gamma^{LW} + \Gamma^{AB} \tag{5.2}$$

where,

Γ^{Total} = total SFE of the asphalt binder,

Γ^{AB} = acid-base component of total SFE,

Γ^{+} = acid SFE component,

Γ^{-} = base SFE component,

Γ^{LW} = Lifshitz-van der Waals SFE component.

When a material of low SFE, such as a binder, comes in contact with the probe liquids, it forms a contact angle at the interface of the material and probe liquid (Bhasin et al., 2006). This contact angle can be calculated experimentally and related to the SFE components of the material using the Young-Dupre postulate (Good, 1992). In this study, Equation 5.3 was used to calculate the SFE components of the binder (A) with different probe liquids (L).

$$\Gamma_L(1 + cos\theta) = 2(\sqrt{\Gamma_A^{LW}\Gamma_L^{LW}} + \sqrt{\Gamma_A^{+}\Gamma_L^{-}} + \sqrt{\Gamma_A^{-}\Gamma_L^{+}}) \tag{5.3}$$

where,

θ = contact angle between the binder and probe liquid, It is noted that there are four unknowns, i.e, Γ^{+}, Γ^{-}, Γ^{LW}, and θ in Equation 5.3. To evaluate these unknowns, first θ was measured with three different probe liquids, i.e. water (bi-polar), glycerin (apolar), and formamide (monopolar), using the Dynamic Wilhelmy Plate (DWP) method. The probe liquids were selected based on the earlier studies available in the literature (Wasiuddin et al., 2006, 2007; Habal and Singh, 2016; Ji et al., 2017). Then, the remaining three unknowns, i.e. SFE components of binder, were determined by solving three simultaneous equations. The SFE components of selected probe liquids, namely water, glycerin, and formamide, were taken from the available literature (Van Oss et al., 2002) and are given in Table 5.2.

In the DWP method, the kinetic force equilibrium during immersion and withdrawal of a binder sample from a probe liquid (Figure 5.2) is measured to determine the contact angle. In the present study, a DCA analyzer was used to conduct the DWP tests in accordance with the procedure reported by Wasiuddin et al. (2006). Accordingly, a sample (a glass plate coated with binder) was carefully hung on the balance using a plier. Then, the probe liquid was placed underneath the sample on the DCA analyzer plate. The plate was moved upward sufficient enough not to touch the sample from bottom or side. After that, the test was started with a constant rate of immersion and withdrawal and force values were recorded using computer software (winDCA). The correction for buoyancy was applied using the software. The contact angle measured during the immersion is called advancing contact angle, while the angle determined during the withdrawal is called receding contact angle (Wasiuddin et al., 2006), as shown in Figure 5.2. At least five samples of each binder blend were tested with each probe liquid to ensure repeatability of results.

5.4.1.1 Sample Preparation for the DCA Measurement

The procedure reported by Wasiuddin et al. (2006) was used herein to prepare the binder samples for the DCA measurement. Accordingly, approximate 120 g of a binder blend was liquified in an oven at the required temperature. Table 5.3 presents the temperature used for liquification of binder blends. The binder blend was stirred at a regular interval to maintain consistency. After ensuring liquefaction, a glass plate of 25 x 50 x 0.5 mm dimensions was passed 10 times in less than 10 seconds through the flame of the Bunsen burner to evaporate any moisture present on the surface of the plate. Then, the lower 5-6 mm of the plate was dipped in the binder to coat the plate surface with the binder. The coated plate was kept vertical in the oven for 3 minutes to allow excess binder to drip off and to have a thin and uniform coating. The prepared sample was checked visually for smoothness (without any bubble). The other side of the sample, which does not interact with the probe liquid during testing, was covered with a small piece of masking tape. Finally, the sample was kept overnight in a desiccator for curing. A set of 18 samples were prepared for each binder blend. Figure 5.3 shows a photographic view of the DCA samples. With 10 different binder blends, a total of 180 samples were prepared and used for the DCA measurement.

5.4.2 Surface Free Energy Components of Aggregates

When a material of high SFE, such as an aggregate, comes in contact with a probe liquid, it absorbs the probe liquid resulting in a reduced SFE. This reduction in SFE is known as the spreading pressure and can be calculated experimentally using a Universal Adsorption Device (USD). In general, the USD device works on the vapor sorption isotherm phenomenon, which indicates the amount of vapor absorbed by the aggregate surface at a constant temperature and pressure (Bhasin, 2007). Similar to binders, three probe vapors of known SFE components and different polarity are required to determine the SFE components of an aggregate. For example, water (bi-polar vapor), n-Hexane (apolar vapor), and Methyl Propyl Ketone (MPK, mono-polar vapor) can be used, as considered by several other researchers in the past (Ghabchi et al., 2014). In the present study, the SFE components of the selected aggregates, namely limestone, granite, quartzite, gravel, and basalt were adapted from the available literature and are summarized in Table 5.4. The selection of these aggregates helped evaluate 50-different binder-aggregate systems and understand the effect of PPA and ASA on the moisture-induced damage potential.

5.5 Experimental Results

5.5.1 Dynamic Contact Angles of Binder Blends

Figure 5.4 presents the measured DCAs of the binder blends with the selected probe liquids, namely, water, glycerin, and formamide. The corresponding standard deviations are also presented in this figure. As shown in Figure 5.4, the error bars for the measured DCAs with water, glycerin, and formamide are very small, indicating a good repeatability of the test results.

5.5.1.1 Water

From Figure 5.4, the average DCA of the neat binder with water is 110.2°. The addition of PPA, ASA, or both in general reduces the DCA value, depending on the type and concentration of the additive. For example, adding 0.5%, 1.0%, 1.5% and 2.0%PPA to the neat binder reduces the DCA of the neat PG 58-28 binder by 1.7° and 0.6°, respectively. Further increasing the PPA amount does not significantly affect the

DCA with water. For example, adding 1.5% and 2.0% PPA to binder is found to keep the DCA unchanged and reduce it by 0.7°, respectively, see Figure 5.4. These observations suggest that adding a small or large amount of PPA may affect the neat binder in two ways: first, it increases the water absorbance capacity due to hydrophilic nature of PPA (Arnold et al., 2012; FHWA, 2014), and second, improve its wettability due to reduced contact angle between the binder and water (Figure 5.4). These behaviors can be differentiated by studying the interfacial energy parameters of the binder blends with different aggregates, as discussed in the following sections.

Furthermore, it is evident from Figure 5.4 that the addition of ASA results in a DCA of 103.1°, which is 7.1° lower than that of the neat binder. It suggests that using ASA increases the wettability of the binder and provides an improved coating of the binder on aggregates, similar to the findings reported by Wasiuddin et al. (2006 and 2007). On the other hand, the use of ASA in combination with PPA was found to increase the DCA with water. It is evident from Figure 5.4 that the binder blends containing 0.5% and 1.0% PPA with 0.5% ASA have the DCA of 109.5° and 109.9°, respectively. The binder blends containing 1.5% and 2.0% PPA with 0.5% ASA have the DCA of 108.5°, which is significantly higher than the DCA for the binder containing 0.5% ASA. While comparing the results of the binder blends containing PPA with the results of the binder blends containing PPA and ASA, it can be observed that the DCA of the binder blend containing 1.5% or 2.0% PPA and 0.5% ASA is equivalent to the DCA of the binder blend containing 0.5% PPA. The DCA of the binder blend containing 0.5% PPA and 0.5% ASA is equivalent to the DCA of the binder blend containing 2.0% PPA. Therefore, it is anticipated that the binder blends containing 0.5%

PPA would exhibit a similar behavior as the binder blend containing 1.5% or 2.0% PPA and 0.5% ASA. This may be due to the neutralization of PPA when added with an amine-based ASA, as reported by King et al. (2002).

5.5.1.2 Glycerin

As shown in Figure 5.4, the DCA of the neat binder with glycerin is 99.8°. The addition of PPA does not significantly affect the DCA of the neat binder with glycerin, unlike the effect observed in case of water. From Figure 5.4, the DCA of the binder blends containing 0.5% to 2.0% PPA have the DCA values ranging from 99.0° to 99.6°, which is close to the DCA of the neat binder. By contrast, the binder blends containing PPA and ASA show larger variations in their DCA values. The highest and lowest DCA values with glycerin are obtained for the binder blend containing 1.0% PPA and 0.5% ASA and the binder blend containing 0.5% ASA, respectively. The binder blends containing 0.5%, 1.5% or 2.0% PPA with 0.5% ASA have a similar DCA values of approximately 99.4°. These results indicate that the use of ASA can improve the wettability of the binder with an apolar probe liquid by reducing the contact angle between the binder and probe liquid. On the other hand, using PPA may reduce the wettability of the binder by the apolar probe liquid. Additionally, it can be seen from Figure 5.4 that the binder blend containing 2.0% PPA and 0.5% PPA has the same DCA as that of the binder blend containing 0.5% PPA. Similarly, the binder blend containing 0.5% PPA and 0.5% ASA has approximately the same DCA as that for the binder blend containing 2.0% PPA only. Therefore, it is expected to have a similar bonding of these binders with an apolar solvent.

5.5.1.3 Formamide

The DCA of the neat binder with formamide is 93.6° (Figure 5.4). The effect of adding PPA with or without ASA on the DCA with formamide was found similar to that observed with glycerin. It is evident form Figure 5.4 that the DCA varies only by ± 0.5˚ due to PPA modification. The binder blends containing 1.0% PPA or higher have the same DCAs. Additionally, a maximum reduction of 5.7˚ is observed for the binder blended with 0.5% ASA. As a result, the binder blend containing 0.5% ASA has a lower DCA than 90˚. According to Sharfrin and Zisman (1960), these results indicate that formamide is able to wet the binder surface for the binder blend containing 0.5% ASA. Also, the addition of PPA reduces the wettability of the neat binder by the mono-polar probe liquids.

Based on the measured DCA of the binder blends, it can be concluded that the addition of PPA, with or without ASA, affects the DCA of the neat binder with the selected probe liquids. An increase or a reduction in the DCA value can significantly influence the SFE components and the resulting interaction between the binder and aggregates (Arabani and Hamedi, 2011; Bhasin et al., 2007; Arabani et al., 2012). Consequently, the moisture-induced damage potential can vary depending on the type and amount of additives, as discussed in the proceeding sections.

5.5.2 Surface Free Energy Components

The SFE components, namely acid, base, non-polar, acid-base, and total SFE components, of the binder blends play an important role in the moisture-induced damage potential of mixes as they define the binder’s ability to adhere with the aggregate (Bhasin et al., 2007). As noted previously, the SFE components were calculated using Equations 5.1 to 5.3 and results are presented in Figure 5.5a for the binder blends containing PPA. The corresponding results for the binder blends containing PPA and ASA are presented in Figure 5.5b.

5.5.2.1 Non-Polar Component (Γ^{LW})

It can be seen from Figure 5.5 that the non-polar SFE component (Γ^{LW}) of all binder blends is higher than the acid SFE, the base SFE, or the acid-base SFE components and is approximately the same as the total SFE component. Adding PPA, in general, decreases the Γ^{LW} of the neat binder, except when using 0.5% PPA. As shown in Figure 5.5a, the Γ^{LW} of the neat binder is 14.03 mJ/m^2. Adding 0.5% PPA results in a slightly higher Γ^{LW} (i.e., 0.15 mJ/m^2) than the neat binder. However, the binder blends containing 1.0%, 1.5%, and 2.0% PPA have the Γ^{LW} values of 12.93, 11.78, and 12.65 mJ/m^2, respectively, which are lower than the Γ^{LW} of the neat binder. Similarly, the binder blends containing 0.5%, 1.5%, and 2.0% PPA with 0.5% ASA have lower Γ^{LW} values than that of the neat binder (Figure 5.5b). Among all binder blends, the one containing ASA (no PPA) has the highest Γ^{LW}. The binder blend containing 1.5% PPA with or without ASA have relatively the same Γ^{LW}. According to Jones and Kennedy (1991), the Γ^{LW} represents the non-polar molecules present in a binder, which work as a matrix for polar components. Therefore, an increase in the Γ^{LW} may result in an enhanced work of adhesion and improved adhesion bond at the interface of the binder and aggregate (Jones and Kennedy, 1991). Therefore, adding ASA is expected to improve the adhesion property of the neat binder. By contrast, using a high amount of PPA may adversely affect the adhesion between the binder and aggregate. This may be due to reduced resins' concentration after PPA modification leading to less sticky binder, as reported by Baumgardner (2005) and Yan et al. (2013).

5.5.2.2 Acid SFE and Base SFE Components

It is evident from Figure 5.5a that adding PPA increases the base SFE Component (Γ^-) of the neat binder. For instance, the use of 0.5, 1.0%, 1.5%, and 2.0% PPA enhances the Γ^- by 0.38, 0.26, 0.03, 0.23 mJ/m^2, respectively. It means that PPA would improve the adhesion bond of binder with aggregates having a high acid SFE component. The improvement would be the maximum if the quantity of PPA is limited to 0.5%. Similarly, the acid SFE Component (Γ^+) increases after PPA modification, expect when using 0.5% PPA. From Figure 5.5, the binder containing 0.5% has the same Γ^+ as that for the neat binder. The use of 1.0%, 1.5%, and 2.0% PPA increases the Γ^+ by 0.06, 0.29, and 0.12 mJ/m^2, respectively. These results indicate that the binder blends containing 1.0% or higher PPA would adhere better with aggregates having a high base SFE component than the neat binder. The use of 1.5% PPA would provide the maximum increase in the adhesion bond. As evident from Table 5.3, most of the aggregates have a high base SFE component in comparison to the acid SFE component. Therefore, it is anticipated that PPA would improve the adhesion bond with these aggregates.

Furthermore, as expected, the use of 0.5% ASA improves both acid SFE and base SFE components, similar to the findings reported by (Wasiuddin et al., 2006 and 2007). It indicates that ASA would enhance the adhesion bond between the binder and aggregates, irrespective of aggregate type. However, it also shows a decrease in both acid SFE and base SFE components when PPA is used with ASA. According to Figure 5.5, the binder blend containing 0.5% PPA and 0.5% ASA has 0.91 mJ/m^2 Γ^- and 0.36 mJ/m^2 Γ^+, which are 1.01 and 0.14 mJ/m^2 lower than the binder blend containing 0.5%

ASA. However, an increase in the PPA content to 1.5% increases the Γ^- to 1.34 mJ/m^2 (also the highest among all the binder blends) and Γ^+ to 0.31 mJ/m^2. The Γ^- and Γ^+ again reduce with a further increase in the PPA content to 2.0%. Therefore, it can be concluded that the use of 1.5% PPA is expected to provide the best adherence with the both acidic and basic aggregates if used with 0.5% ASA. This is likely due to the effect of ASA on the PPA-modified binders causing dispersion of asphaltenes agglomeration (Harnish, 2010). According to Harnish (2010), amine groups of ASA react with the acid groups of the asphaltenes-resins cluster of the binder and disperse the cluster. With this dispersion, more e -rich (electron-rich) and polar components are available in the matrix to be absorbed by the aggregates, which may result in an improved adhesion bond between the binder and the aggregate.

5.5.3 Cohesive Failure within the Binder

Cheng et al. (2002) defines the work of cohesion as the amount of energy required to create a unit surface within the same materials under vacuum pressure. Figure 5.6 shows the mechanism of cohesive failure in the mix. In case of properly coated and dried aggregates, water first surfaces the binder layer and punches the layer to cause a cohesive failure.

The work of cohesion can be calculated based on the SFE components of a binder and equals to two times of the total SFE of the binder, see Equation 5.4. In this study, the interfacial energy between the binder and aggregate was also calculated using Equation 5.5. It was assumed that this interfacial energy represents the cohesion failure within the binder in the presence of moisture, and therefore, termed as cohesive failure energy. Also, the ratio of the work of cohesion and cohesive failure energy was calculated and defined as the cohesive energy ratio of the binder, see Equation 5.6.

$$Work\ of\ Cohesion, W_{AA} = 2\Gamma^{Total} \tag{5.4}$$

$$Cohesion\ Failure\ Energy,$$

$$W_{AW} = \Gamma_{AW} = \Gamma_A + \Gamma_W - 2\sqrt{\Gamma_A^{LW}\Gamma_W^{LW}} - 2\sqrt{\Gamma_A^{+}\Gamma_W^{-}} - 2\sqrt{\Gamma_A^{-}\Gamma_W^{+}} \tag{5.5}$$

$$Cohesive\ Energy\ Ratio, ERc = \frac{W_{AA}}{\Gamma_{AW}} \tag{5.6}$$

The measured W_{AA}, W_{AW}, and ERc for the binder blends are presented in Figure 5.7. It is evident form Figure 5.7 that the addition of PPA, in general, reduces the W_{AA} of the neat binder, except when adding 0.5% PPA. The binder blend containing 0.5% PPA has a slightly (0.58 mJ/m^2) higher W_{AA} than that of the neat binder. Other binder blends containing 1.0%, 1.5%, and 2.0% PPA have W_{AA} values that are 1.68, 3.50, and 2.05 mJ/m^2 lower than the W_{AA} of the neat binder, respectively. A reduction in the W_{AA} indicates a higher potential of water punching through the binder layer (Tan and Guo, 2013). Accordingly, the PPA-modified binders are expected to exhibit less resistance to cohesive failure than the neat binder. This is attributed to the reduced SFE of the binder after PPA modification, as depicted in Figure 5.5. Consequently, a lower amount of energy is required to create a new surface. Additionally, the W_{AW} reduces due to PPA. The reduction in the cohesive failure energy is relatively the same irrespective of the PPA concentration. For instance, adding 0.5%, 1.0%, 1.5%, and 2.0% PPA reduces the interfacial energy between the binder and water by 1.82, 1.61, 1.81, and 1.86, respectively. Based on the W_{AA} and W_{AW} results, the ERc of binder blends was calculated and the results are presented in Figure 5.7. It can be seen that the ERc is 0.74 for the neat binder and it does not experience any significantly change after PPA modification. These results indicate that the addition of PPA did not affect the cohesive failure resistance of the neat binder. Therefore, the PPA-modified binder is expected to exhibit a similar resistance against cohesive failure in the field. However, in some studies such as FHWA (2014), a high amount of PPA was found to increase the moisture-induced damage potential of the mix. Considering the observations of this study and of the previous studies, it can be said that the interaction of PPA-modified binder with the selected aggregate becomes important when quantifying the moisture-induced damage potential of mix containing PPA.

Furthermore, the addition of ASA increases the W_{AA} by 3.96 mJ/m^2 and decreases the W_{AW} by 6.66 mJ/m^2. As a result, the ERc of the binder blend containing ASA is equal to 1.0, which is significantly higher than that for the neat binder. It indicates that the addition of ASA would increase the cohesive failure resistance of the binder. By contrast, no improvement in the resistance to cohesive failure was observed when ASA was added with PPA. From Figure 5.7, the ERc for the binder blend containing PPA and ASA is the same as that for the neat binder. Therefore, it is expected that binders containing PPA and ASA would exhibit a similar cohesive failure resistance compared to the binders containing PPA or the neat binder. Additionally, the binder blends containing 1.0% PPA and 0.5% ASA has the same $W_{AA,}$ W_{AW}, and ERc as that for the neat binder, suggesting comparable performance. This may be due to the neutralization of PPA by amine-based ASA (King et al., 2002). King et al. (2002) reported that the amine groups of ASA may react with the acid groups of PPA and neutralize the effect of PPA by forming an amine salt in the mix. As a result, the ASA may not help increase the resistance of PPA-modified binders and mixes against moisture-induced damage.

5.5.4 Work of Adhesion

The work of adhesion (W_{AS}) is defined as the amount of free energy required to separate two interfaces from one interface consisting of two distinct materials (asphalt binder and aggregate in this case) under vacuum (Bhasin et al., 2007). The W_{AS} can be calculated using Equation 5.7 based on the SFE components of binder (subscript *A*) and aggregate (subscript *S*). A high value of W_{AS} is favorable as it indicates a strong adhesion bond between binder and aggregate and thereby, less risk of moisture-induced damage.

$$W_{AS} = 2(\sqrt{\Gamma_A^{LW}\Gamma_S^{LW}} + \sqrt{\Gamma_A^{+}\Gamma_S^{-}} + \sqrt{\Gamma_A^{-}\Gamma_S^{+}}) \tag{5.7}$$

Figure 5.8a presents the calculated W_{AS} of different aggregates with the binder blends containing PPA. In general, it can be seen from Figure 5.8a that the W_{AS} increases for the limestone, gravel, and quartzite aggregates due to PPA modification. However, the increase in the W_{AS} is not significant for the quartzite aggregate. For example, the W_{AS} is 82.46 mJ/m^2 between the neat binder and limestone aggregate. Addition of PPA (up to 2.0%) increases the W_{AS} to 93.13 mJ/m^2. The W_{AS} between the neat binder and quartzite aggregate is 73.47 mJ/m^2, which increases to 76.80 mJ/m^2 due to the addition of 1.5% PPA. Additionally, the W_{AS} of the limestone, gravel, and quartzite aggregates decreases when adding a high amount of PPA (i.e., 2.0%). From these results, the use of 1.5% PPA would provide the maximum improvement in the adhesion bond between the binder and aggregate. For granite and basalt, a fluctuating pattern is observed in the W_{AS}, with a small variation due to PPA. Therefore, it can be concluded that the adhesion bond between the binder and aggregate (granite and basalt) would likely be not impacted due to PPA modification. Furthermore, among all aggregates, only gravel shows the maximum benefits of PPA addition. Adding 1.5% PPA increases the W_{AS} by 12.61 mJ/m^2.

Figure 5.8b presents the W_{AS} of different aggregates with the binder blends containing PPA and ASA. As expected, the use of ASA enhances the W_{AS}, regardless of the aggregate type. However, a decrease in the W_{AS} is seen as a result of using PPA and ASA together. It can be seen from Figure 5.8b that the binder blends containing PPA and ASA have lower W_{AS} than that of the neat binder or the binder blend containing 0.5% ASA. For instance, adding 1.0% PPA with 0.5% ASA results in a reduction of 21.63, 24.64, 12.09, 12.60, and 15.47 mJ/m^2 in W_{AS} for the limestone, gravel, quartzite, granite, and basalt, respectively, in comparison to the W_{AS} of the binder blend containing ASA. An increase in the PPA content to 1.5% helps increase the W_{AS}, but only slightly, which again decreases when adding 2.0% PPA and 0.5% ASA together. Therefore, it is anticipated that a binder containing PPA (up to 1.0%) with 0.5% ASA would exhibit lower adhesion bond with aggregates than the binder containing PPA or ASA alone. And, the use of 1.5% PPA would provide the maximum W_{AS} when used with 0.5% ASA. While comparing the results of the PPA-modified binder with the binder blends containing ASA, it is seen that the binder blends containing PPA and ASA have relatively the same W_{AA} as that for the binder blends containing PPA. It means that the addition of ASA is not expected to improve the adhesion bond when used with PPA. This is essentially the neutralizing effect of ASA on the PPA-modified binder. A similar effect of ASA was reported by King et al. (2002).

5.5.5 Work of Debonding

The work of debonding (W_{ASW}^{wet}) is defined as a reduction in the free energy due to separation of the asphalt binder from the aggregate in the presence of waster (Bhasin et al., 2007). The work of debonding, also known as the work of adhesion in the presence of water, is a measure of the separation of the binder from the aggregate at the interface in the presence of moisture (or water) and can be calculated using Equation 5.8. According to Bhasin et al. (2007), a high magnitude of the W_{ASW}^{wet} is not beneficial as it indicates a higher potential of moisture-induced damage to occur under wet condition. Therefore, a reduction in the work of debonding implies a more durable asphalt binder-aggregate system, with less propensity for moisture-induced damage.

$$W_{ASW}^{wet} = \Gamma_{AW} + \Gamma_{SW} - \Gamma_{AS} \tag{5.8}$$

where,

Γ_{AW} = the interfacial energy between asphalt binder and water,

Γ_{SW} = the interfacial energy between aggregate and water,

Γ_{AS} = the interfacial energy between asphalt binder and aggregate.

Figures 5.9a and 5.9b present the W_{ASW}^{wet} values of different aggregates with the binder blends containing PPA and with the binder blend containing PPA and ASA, respectively. From Figure 5.9a, the addition of PPA alone or in combination with ASA, in general, does not significantly affect the W_{ASW}^{wet} for the quartzite, granite, and basalt aggregates. It indicates that PPA would not impact the moisture-induced damage potential of mixes containing quartzite, granite, and basalt aggregates. For the limestone and gravel aggregates, however, the W_{ASW}^{wet} values are higher for the PPA-modified binder than the neat binder, being the highest for the binder blend containing 1.5% PPA.

This indicates that PPA would help reduce the moisture-induced damage potential of mixes containing limestone and gravel aggregates. Additionally, among all the binder blends containing PPA and ASA, only the binder blend containing 1.5% PPA and 0.5% ASA exhibits the W_{ASW}^{wet} comparable to the binder blend containing 0.5% ASA. Therefore, it can be concluded that using 1.5% PPA, with or without ASA, would provide the maximum debonding resistance to the mix. Furthermore, among all the aggregates, the W_{ASW}^{wet} values are found to be the highest and the lowest for gravel and granite aggregates, respectively. Therefore, it is expected that the resistance to moisture-induced damage will be the lowest and highest with the gravel and granite aggregates, respectively.

5.5.6 Wettability

It is well known that the binder is a hydrophobic material and aggregates are hydrophilic materials (Tarrer and Wagh, 1991). Therefore, it is not easy for all binders to wet aggregate surface and there is need to analyze a binder's ability to coat a given aggregate. The ability of a binder to wet the aggregate surface can be evaluated through wettability. The wettability is defined as energy released during coating of aggregate by the binder (Wassiuddin et al., 2005). The higher the wettability of a binder, the easier it is to coat the aggregate. Wettability ($S_{A/S}$) of a binder can be calculated using Equation 5.9, also known as the spreading coefficient of the binder over aggregate.

$$S_{A/S} = \Gamma_S - \Gamma_{AS} - \Gamma_A \tag{5.9}$$

where,

Γ_S = total SFE of aggregate,

Γ_{AS} = interfacial energy between aggregate and binder,

Γ_A = total SFE of binder.

Figure 5.10 presents the wettability of the binder blends containing PPA and ASA over different types of aggregates (limestone, gravel, quartzite, granite, and basalt). It can be seen from Figure 5.10 that the use of 0.5% PPA does not significantly change the wettability of the binder. Increasing the PPA concentration to 1.5% enhances the wettability of the neat binder, except for granite aggregate. However, further increasing the PPA to 2.0% decreases the wettability. These results indicate that the binder blend containing PPA would better coat the aggregate than the neat binder when 1.5% PPA is used in the blend. Additionally, among all the aggregates, gravel depicted the maximum benefit of PPA. For gravel, the wettability increases from 60.33 to 76.44 mJ/m^2 due to the addition of 1.5% PPA to the neat binder. By contrast, a reduction in the wettability is observed when PPA was used with ASA, irrespective of the aggregate type. It can be seen from Figure 5.10b that the binder blends containing 0.5% ASA have $S_{A/S}$ values of 66.52, 76.19, 49.77, 81.48, and 70.45 mJ/m^2 with limestone, gravel, quartzite, granite, and basalt aggregates, respectively. Adding 1.0% PPA to the binder decreases the $S_{A/S}$ by 17.68, 20.68, 8.14, 8.64, and 11.51 mJ/m^2 over the limestone, gravel, quartzite, granite, and basalt aggregates, respectively. However, the binder blends containing 1.5% PPA or 2.0% PPA exhibited better wettability than the binders containing 0.5% and 1.0% PPA when used with 0.5% ASA. It means that a higher amount of PPA is required to coat the aggregates when used with 0.5% ASA. Also, it can be concluded that using 1.5% PPA, with or without ASA, would provide the maximum wettability of the binder for all the aggregates selected in this study. These results are consistent with the W_{AS} results, discussed in the previous section.

5.5.7 Energy Ratio

Although the work of adhesion, work of debonding, or wettability, could define the bonding or stripping potential of binders and aggregates, but they alone cannot rank the moisture-induced damage potential of mix (Bhasin et al., 2007). For that purpose, Bhasin et al. (2007) suggested an energy ratio parameter, namely ER1. The ratio ER1 combines the effect of both W_{AS} and W_{ASW}^{wet} to mechanistically evaluate the moisture-induced damage potential of the mixes and can be calculated using Equation 5.10. In this study, ER1 was determined for all 50 different binder-aggregate systems containing PPA and ASA to evaluate their moisture-induced damage potential.

$$ER1 = \frac{W_{AS}}{W_{ASW}^{wet}} \tag{5.10}$$

The ER1 of the binder blends containing PPA and ASA with different aggregates are shown in Figure 5.11. It is evident from Figure 5.11a that the addition of PPA up to 1.0% does not significantly affect the ER1, except for granite aggregate showing an increase in the ER1 at the 0.5% PPA modification level. An increase in the PPA content to 1.5% improves the ER1. However, a further increase in the PPA content decreases the ER1. Therefore, it can be concluded that 1.5% PPA is expected to provide the maximum reduction in the moisture-induced damage potential. Additionally, it is evident from Figure 5.11a that among all the aggregates, the highest improvement in ER1 is found for quartzite aggregate. For instance, the ER1 for the neat binder and quartzite aggregate is 1.09, which increased to 1.20 due to the addition of 1.5% PPA. Also, the highest ER1 is 1.84 observed for the granite aggregate. It means that the granite aggregate would exhibit the lowest moisture-induced damage potential, followed by the quartzite.

This study also shows that the moisture-induced damage potential reduces if PPA is used with ASA, as indicated by a lower ER1 for the binder blends containing PPA and ASA compared to the binder blend containing ASA (Figure 5.11b). For instance, the use of PPA up to 1.0% with 0.5% ASA reduces the ER1 by 0.14-0.40 depending upon the aggregate type, resulting in the ER1 lower than that for the neat binder. The binder blends containing 0.5%, 1.5%, or 2.0% PPA and 0.5% ASA have approximately the same ER1. Therefore, it is anticipated that mixes containing 0.5%, 1.5%, or 2.0% PPA and 0.5% ASA would exhibit a similar resistance to moisture-induced damage. While comparing the binders containing PPA with the blends containing PPA and ASA, no significant variations were observed in the ER1 values. The ER1 was found to vary by 0.3-0.8, depending on the aggregate type and PPA content. Therefore, it can be concluded that the ASA may not affect the moisture-induced damage potential of the mixes if used with PPA.

Furthermore, according to Bhasin et al. (2006), the resistance of the asphalt binder-aggregate system can be ranked in four different categories, namely A, B, C, and D. The asphalt binder-aggregate system having ER1 value greater than 1.5 falls in A category and is the least susceptible to moisture-induced damage. The categories B and C represent good to fair resistance to moisture-induced damage having ER1 values ranging from 0.75 to 1.5 and 0.5 to 0.75, respectively. The asphalt binder-aggregate system having ER1 value less than 0.5 falls in D category with the highest risk of moisture-induced damage. Ranking of the all the considered 50 different asphalt binder-aggregate systems is presented in Table 5.5. It is evident from Table 5.5 that the asphalt binder-aggregate systems containing limestone or gravel aggregate, with or without additives, falls in the D category. Therefore, it is expected to exhibit a low resistance to moisture-induced damage in the field. On the other hand, the asphalt binder-aggregate systems containing quartzite or basalt aggregate, which fall in Category B, represent fair to good resistance to moisture-induced damage. As mentioned above, the addition of PPA alone or PPA with ASA does not make any significant effect on the moisture-induced damage potential of asphalt binder-aggregate systems containing quartzite or basalt aggregate. The least risk of moisture-induced damage is expected when using granite aggregate as the asphalt binder-aggregate systems containing granite aggregates falls in Category A. In previous studies, mix performance of asphalt binder-aggregate systems containing granite aggregates are observed. In a study conducted by Bhasin et al. (2006), Bhasin et al. (2007), Buddahala et al. (2011), it was reported that asphalt binder-aggregate systems containing granite aggregates have more propensity for moisture-induced damage in comparison to those systems containing limestone or gravel aggregates. By contrast, Arabani and Hamedi (2011), Rani et al. (2017b), and Rani et al. (2018) reported that using granite aggregates provide better adhesion bond in dry conditions with asphalt binder than limestone aggregates and therefore, expect to provide higher resistance to moisture-induced damage.

5.6 Conclusions

In this study, the effects of using PPA in conjunction with ASA on the SFE components of a PG 58-28 binder were evaluated. For this purpose, 10 different binder blends were prepared and the DCA measurements were performed with three different probe liquids (water, glycerin, and formamide). Based on the DCA values, the SFE components were determined. Then, different energy parameters, namely the wettability, the work of adhesion, the work of cohesion, the work of debonding, and the energy ratio, were calculated. Finally, the results were analyzed to quantify the effect of using PPA with and without ASA on the moisture-induced damage potential of binders and mixes. Based on the results presented herein, the following conclusions can be drawn:

1. PPA did not impact the cohesive strength of the neat binder. However, depending on the aggregate type, it may improve the adhesion bond between the binder and the aggregate. Among all the selected aggregates, the maximum improvement in the adhesion bond was observed for the gravel aggregate. On the other hand, the adhesion bond of the binder with granite or basalt aggregate was found unaffected after PPA modification.
2. The results of the wettability were consistent with the work of adhesion. Therefore, it is anticipated that the PPA would enhance coating of the neat binder on limestone, gravel and quartzite aggregates, contributing to a better adhesion bond.
3. The addition of PPA did not have any significant effect on the energy ratio and therefore, it is anticipated not to impact the moisture-induced damage potential significantly. The results showed that PPA improved the adhesion bond, but also increased the work of debonding in magnitude. This was attributed to the hydrophilic nature of PPA. As a result, adding PPA may not exhibit a huge impact on the moisture-induced damage potential of mixes.
4. One of the objectives of this study was to evaluate the moisture-induced damage potential when using PPA and ASA together. The results indicated

that the binder blend containing ASA improved interfacial parameters than the neat binder. However, the binder blends containing PPA and ASA lowered interfacial energy parameters than the binder blend containing ASA and, in some cases, the binder blend containing PPA. Based on these observations, it can be concluded that the using ASA does not affect the moisture-induced damage potential of the PPA-modified binders.

5. The use of 1.5% PPA, with or without ASA, was found to be an effective concentration, contributing to the improved adhesion bond and the wettability of the neat binder. Therefore, it is expected to have an improved adhesion bond and reduced moisture-induced damage potential in the field.

Overall, this study showed that PPA improves the wettability of the binder and its adhesion bond with aggregates. However, the selection of aggregates is very important to have that improvement. The addition of ASA in the PPA-modified binder did not provide any added benefit pertaining to the resistance for the moisture-induced damage.

5.7 Limitations of this Study

It the present study, the SFE components of aggregates were taken from the literature. Since the same aggregate type can have different SFE components depending upon its source, the effect of adding PPA and ASA may impact the binder-aggregate system differently. Also, this study does not consider the rheological properties of the binder blends containing PPA and ASA which may impact the overall dosage selection of PPA, with and without ASA, having a balanced design.

5.8 Recommendations for Future Studies

This study did not consider the effect of void ratio, aggregate surface area, binder content, asphalt binder film thickness, and temperature. This can directly or indirectly impact the moisture-induced damage potential of mixes. Considering the limited scope of this study, these parameters can be considered as potential topics for future study.

Acknowledgements

The authors offer their gratitude to the Southern Plain Technical Center and the Oklahoma Department of Transportation for providing the financial support to conduct this study. The authors are thankful to Haskell Lemon Construction Company, Valero Refinery, and ArrMaz for providing materials for this study. The authors would like to acknowledge the contribution of Mr. Kenneth Hopson, Dr. Amir Arshadi, and Mr. Micheal Schmitz in this study.

Table 5.1 List of the Binder Blends Used in this Study

Neat Binder Type	PPA* (P, %)	ASA* (A, %)	Name of Binder Blend	PPA* (P, %)	ASA* (A, %)	Name of Binder Blend
PG 58-28	-	-	S1	-	0.5	S1A
	0.5	-	S1P0.5	0.5	0.5	S1P0.5A
	1	-	S1P1.0	1	0.5	S1P1.0A
	1.5	-	S1P1.5	1.5	0.5	S1P1.5A
	2	-	S1P2.0	2	0.5	S1P2.0A

* Added by the weight of the neat binder

Table 5.2 Surface Free Energy Components of the Probe Liquids at 20˚C (Van Oss et al., 2002)

Probe Liquid	Γ^{+}	Γ^{-}	Γ^{LW}	Γ^{Total}	SD
Water	25.5	25.5	21.8	72.8	0.2
Glycerin	3.92	57.4	34	64	0.3
Formamide	2.28	39.6	39	58	0.2

Table 5.3 Oven Temperature Used for Liquification of Binder Blends

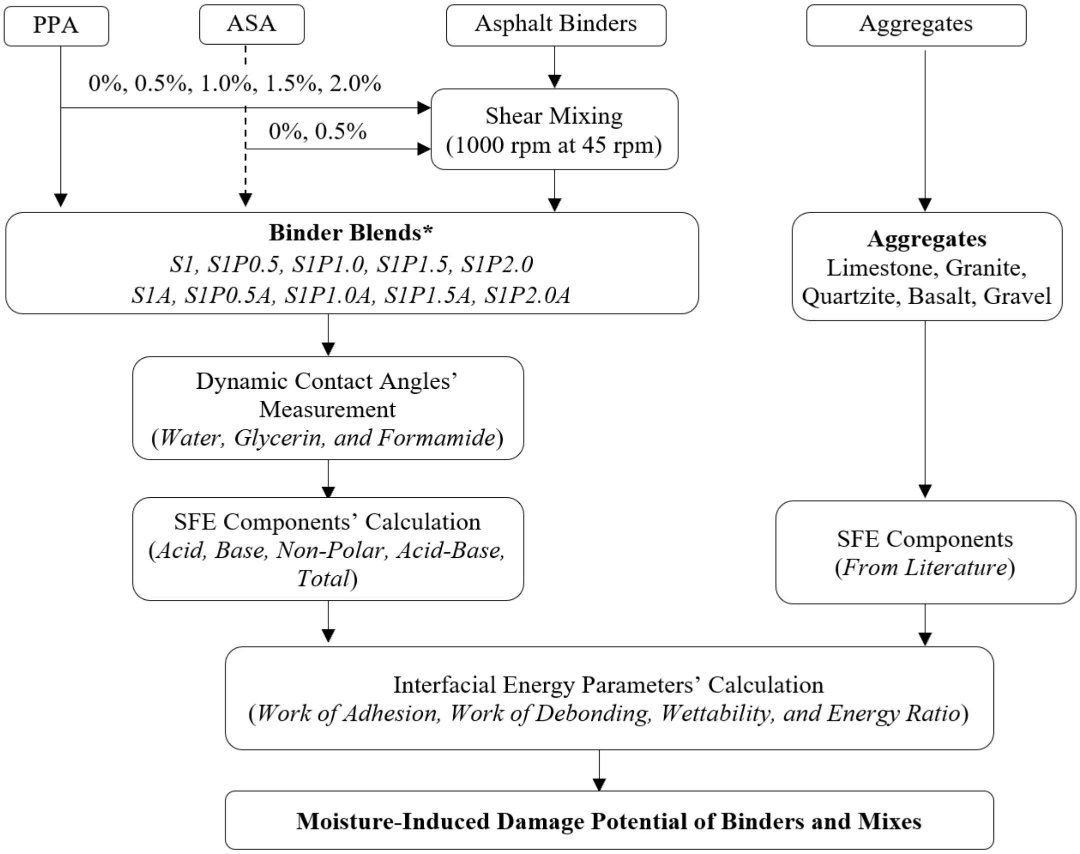
Binder Type	S1	S1P0.5	S1P1.0	S1P1.5	S1P2.0	S1A	S1P0.5A	S1P1.0A	S1P1.5A	S1P2.0A
Temperature (°C)	145	145	150	155	160	145	145	145	145	150

Table 5.4 Surface Free Energy Components of Selected Aggregates

Aggregate Type	Literature Source	Γ^+ (Acid)	Γ^- (Base)	Γ^{LW} (Non-Polar)	Γ^{AB} (Acid-base)	Γ^{total} (Total)
Limestone	Ghabchi et al. (2014)	17.5	741.4	51.4	227.8	279.2
Granite	Arabani and Hamedi (2011)	46.37	678.98	44.3	354.88	399.18
Quartzite	Arabani and Hamedi (2011)	19.67	583.53	54.91	214.27	269.18
Gravel	Bhasin and Little (2007)	23	973	57.5	299.2	356.8
Basalt	Cong et al. (2016)	58.31	143.85	77.48	183.17	206.65

Table 5.5 Ranking of Asphalt Binder-Aggregate System based on Energy Ratio

Binder Type	**Limestone**		**Gravel**		**Quartzite**		**Granite**		**Basalt**	
	ER1	**Category**	**ER1**	**Category**	**ER1**	**Category**	**ER1**	**Category**	**ER1**	**Category**
S1	0.40	D	0.36	D	1.09	B	1.84	A	0.94	B
S1P0.5	0.41	D	0.37	D	1.08	B	1.89	A	0.99	B
S1P1.0	0.42	D	0.38	D	1.08	B	1.79	A	0.96	B
S1P1.5	0.48	D	0.44	D	1.20	B	1.76	A	0.97	B
S1P2.0	0.44	D	0.40	D	1.12	B	1.79	A	0.97	B
S1A	0.51	C	0.47	D	1.25	B	2.20	A	1.19	B
S1P0.5A	0.43	D	0.38	D	1.11	B	1.83	A	0.97	B
S1P1.0A	0.38	D	0.34	D	1.01	B	1.81	A	0.93	B
S1P1.5A	0.45	D	0.41	D	1.10	B	1.76	A	1.00	B
S1P2.0A	0.43	D	0.39	D	1.10	B	1.84	A	0.99	B



** P = PPA, A = ASA, number = concentration of PPA (Table 1)*

Figure 5.1 Work Flow for the Evaluation of Moisture-Induced Damage Potential of Binders and Mixes

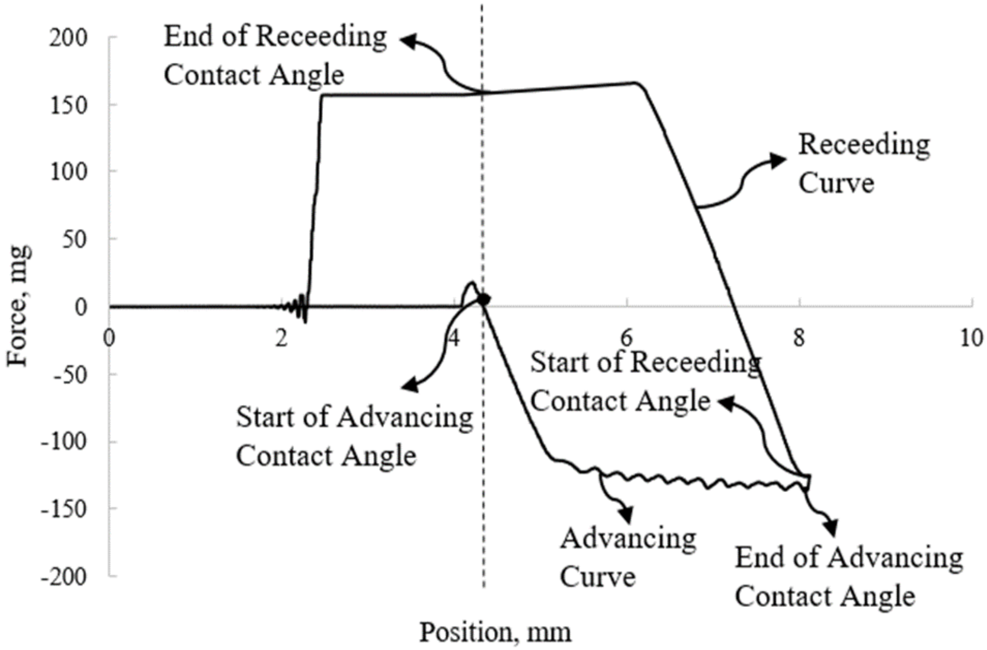


Figure 5.2 Typical Dynamic Wilhelmy Plate Test Results Obtained Using Dynamic Contact Analyzer

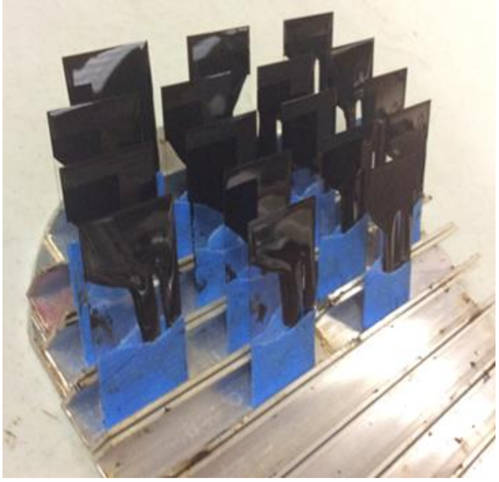


Figure 5.3 Photographic View of Dynamic Contact Angle Samples

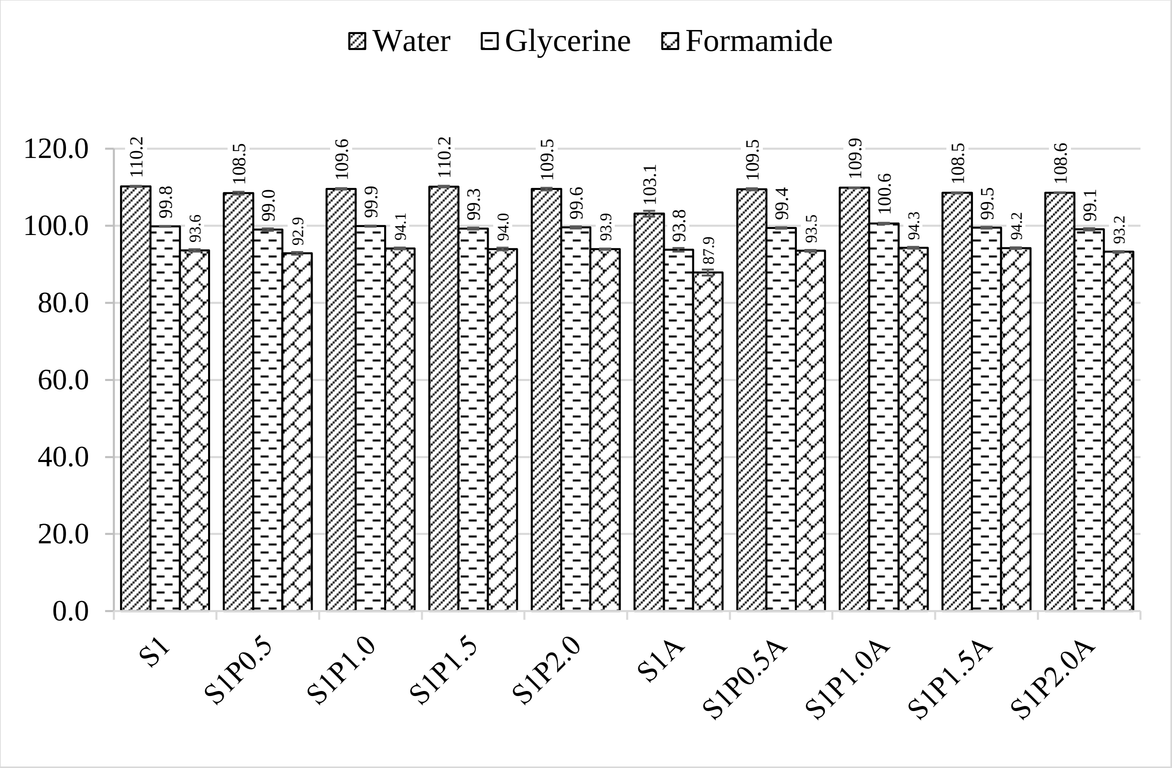
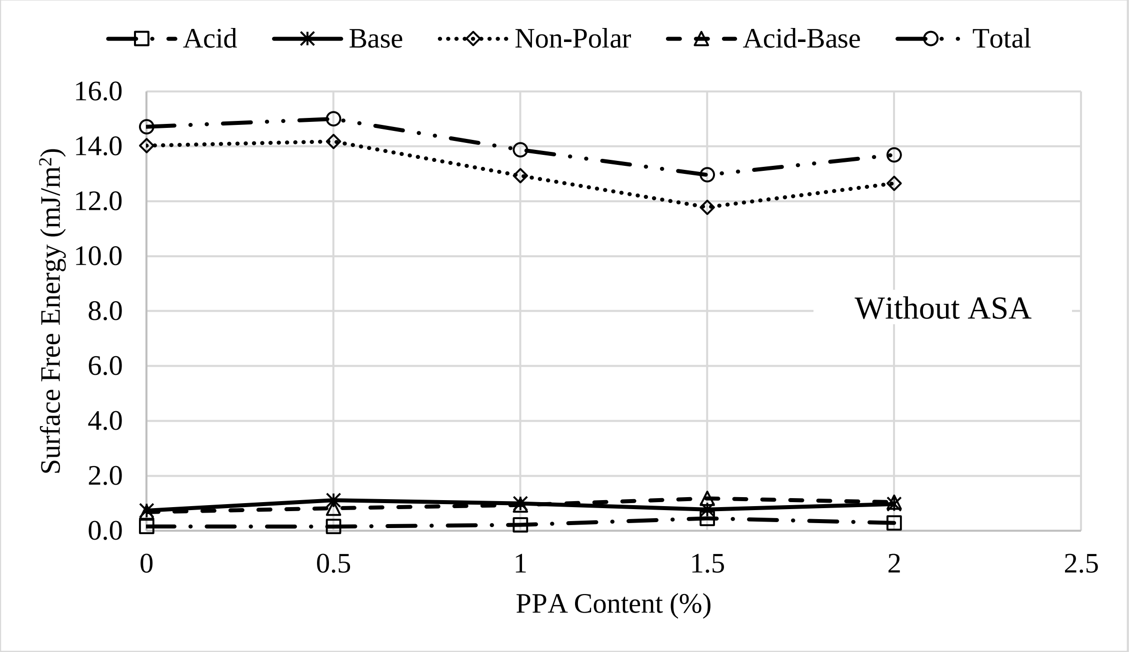
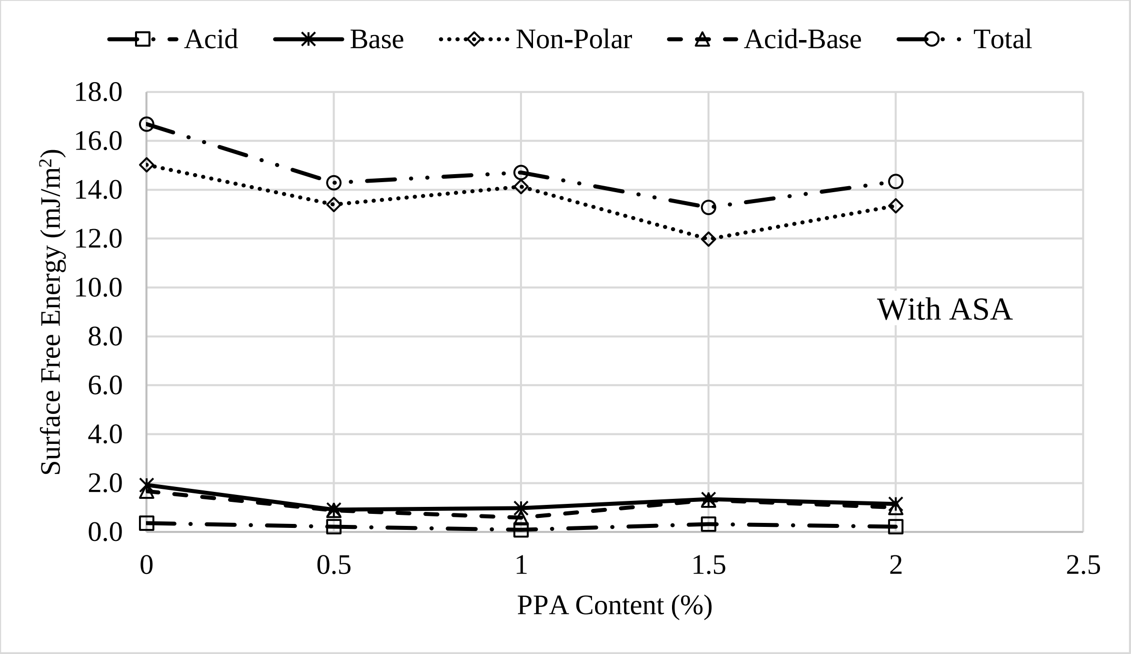


Figure 5.4 Dynamic Contact Angles of Binder Blends with Water, Glycerin, and Formamide Probe Liquids



(a)



(b)

Figure 5.5 Surface Free Energy Components of PG 58-28 Binder Containing (a) PPA, and (b) PPA and ASA

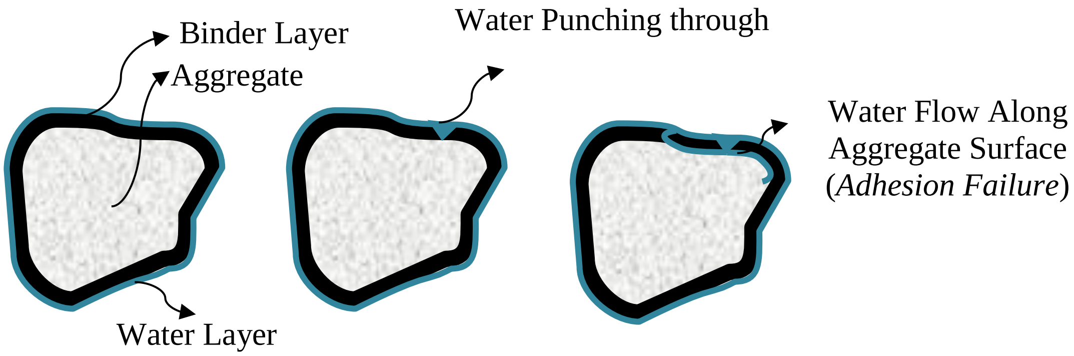


Figure 5.6 Cohesion and Adhesion Failure in a Mix

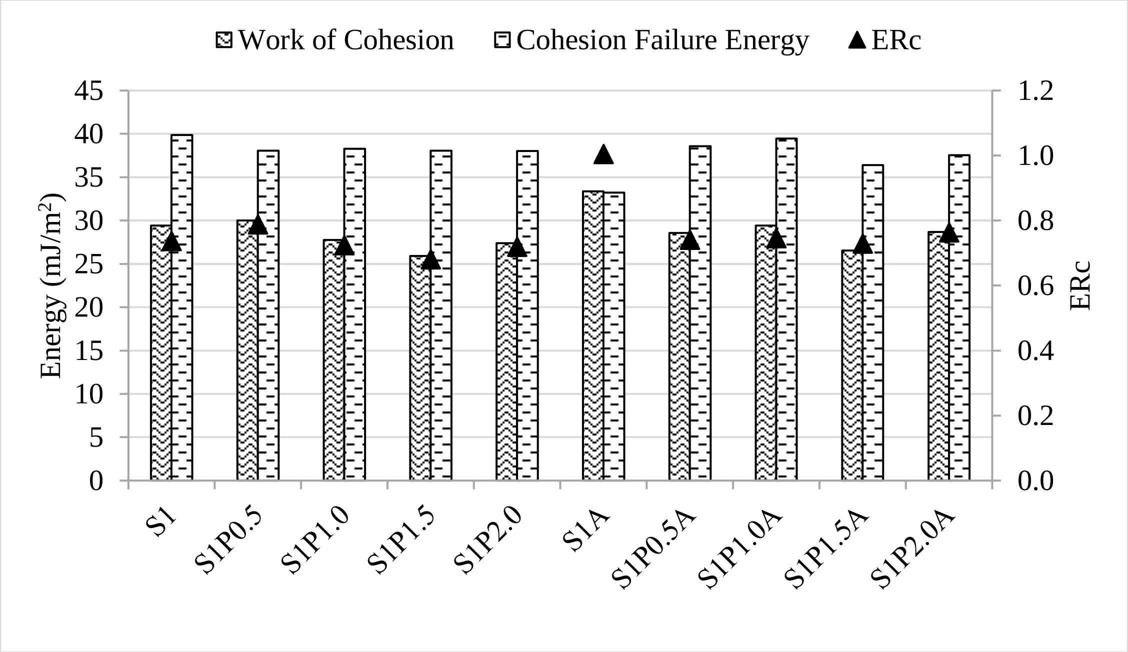
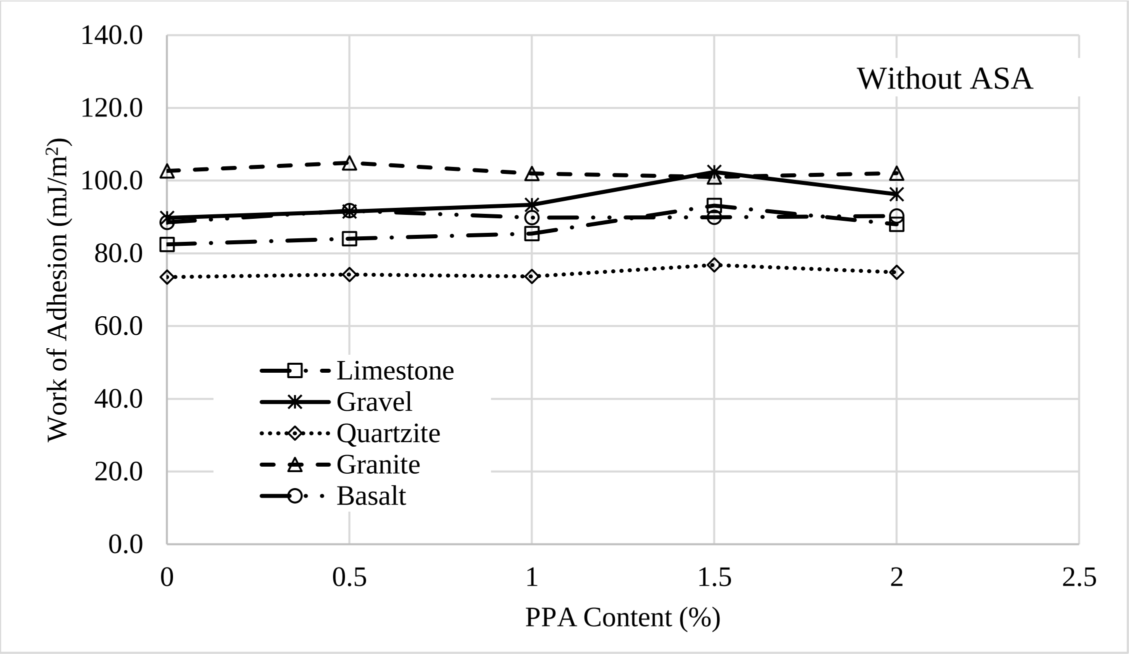
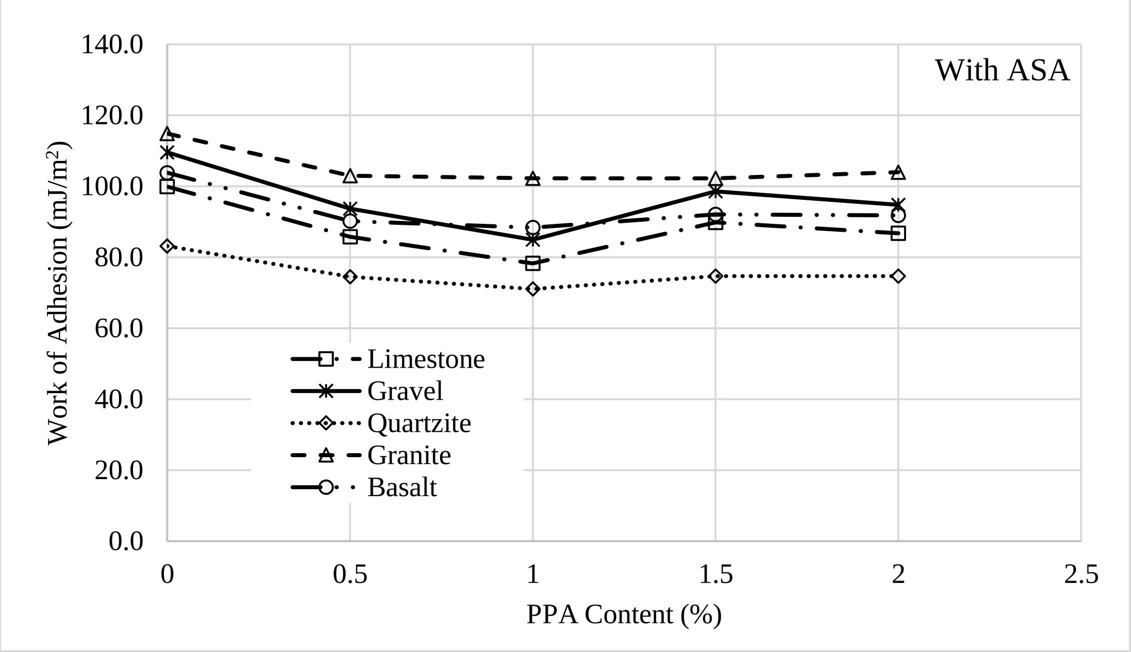


Figure 5.7 Work of Cohesion, Cohesion Failure Energy, and Cohesive Energy Ratio of Binder Blends Containing PPA and ASA

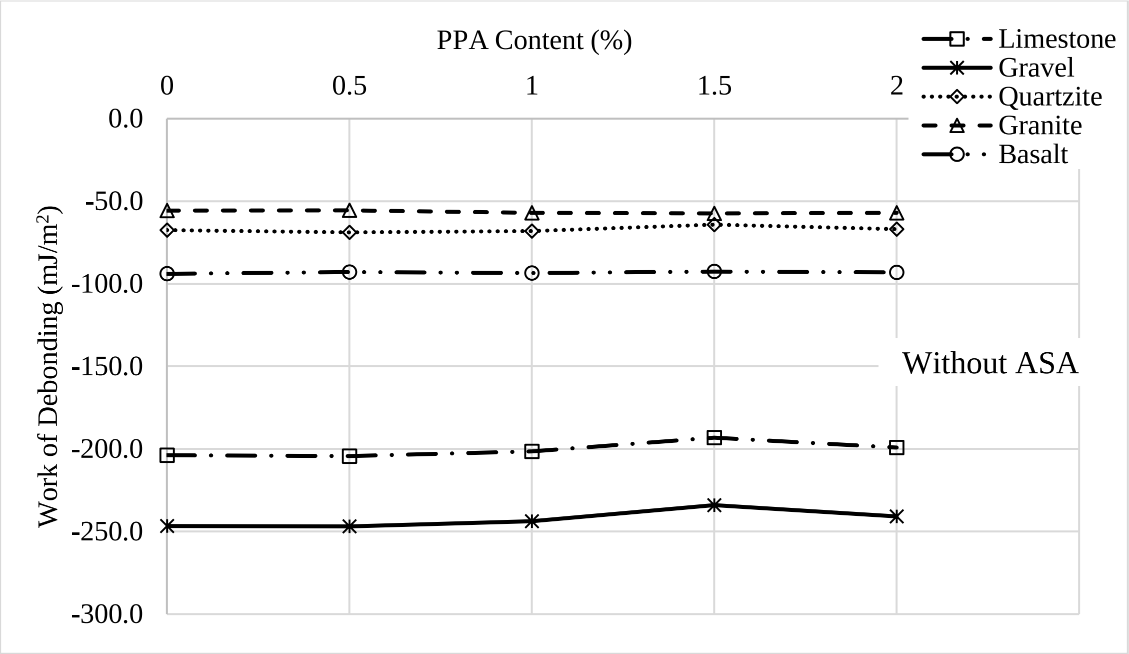


(a)

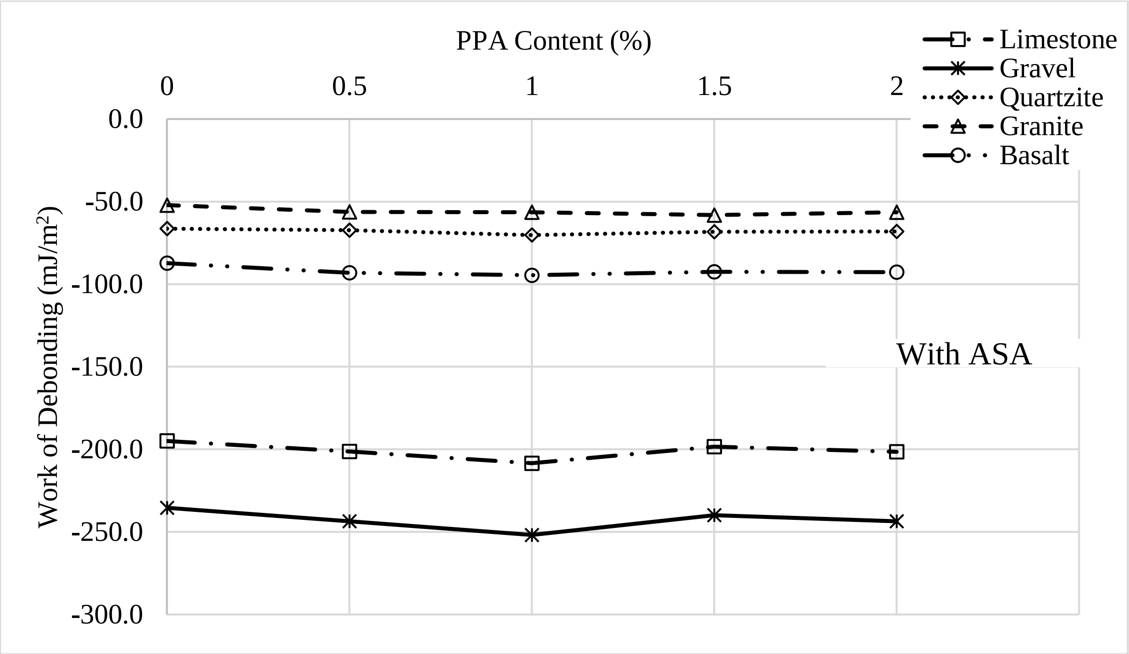


(b)

Figure 5.8 Work of Adhesion of Binder Blends Containing (a) PPA and (b) PPA and ASA with the Different Aggregates

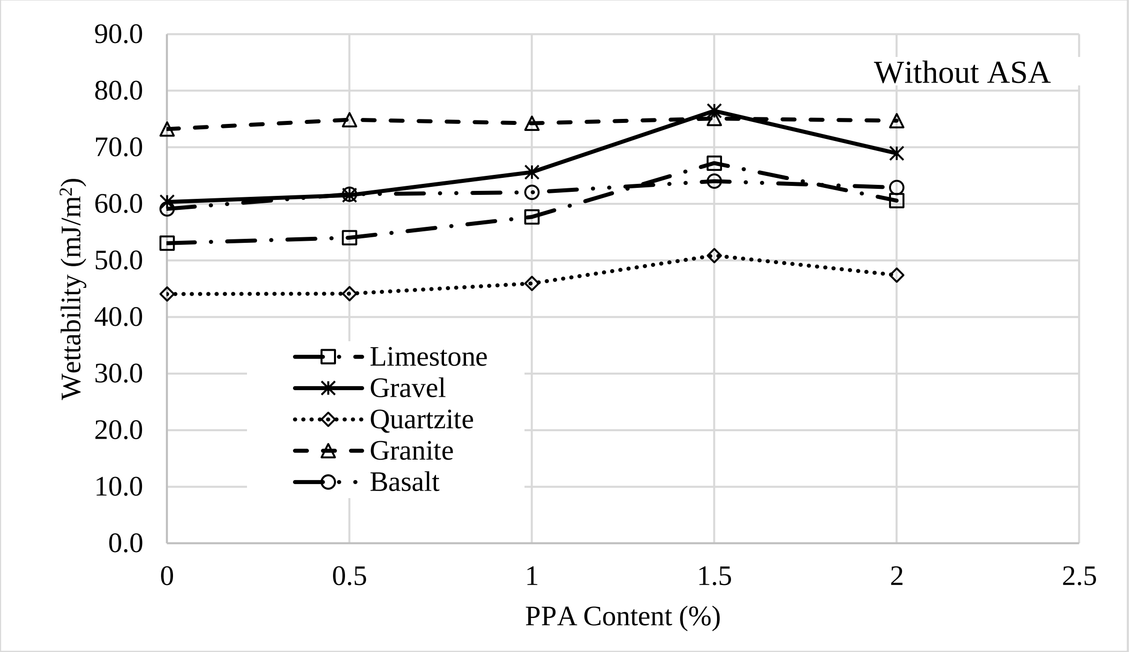


(a)

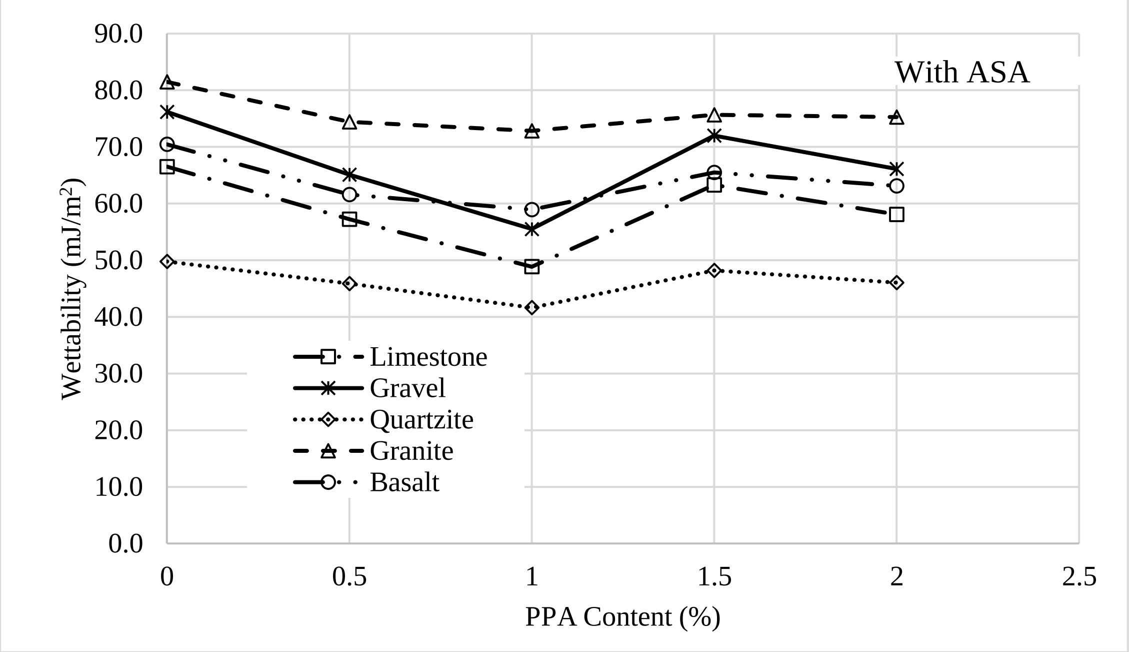


(b)

Figure 5.9 Work of Debonding of Binders Containing PPA and ASA with the Selected Aggregates, (a) without ASA and (b) with ASA

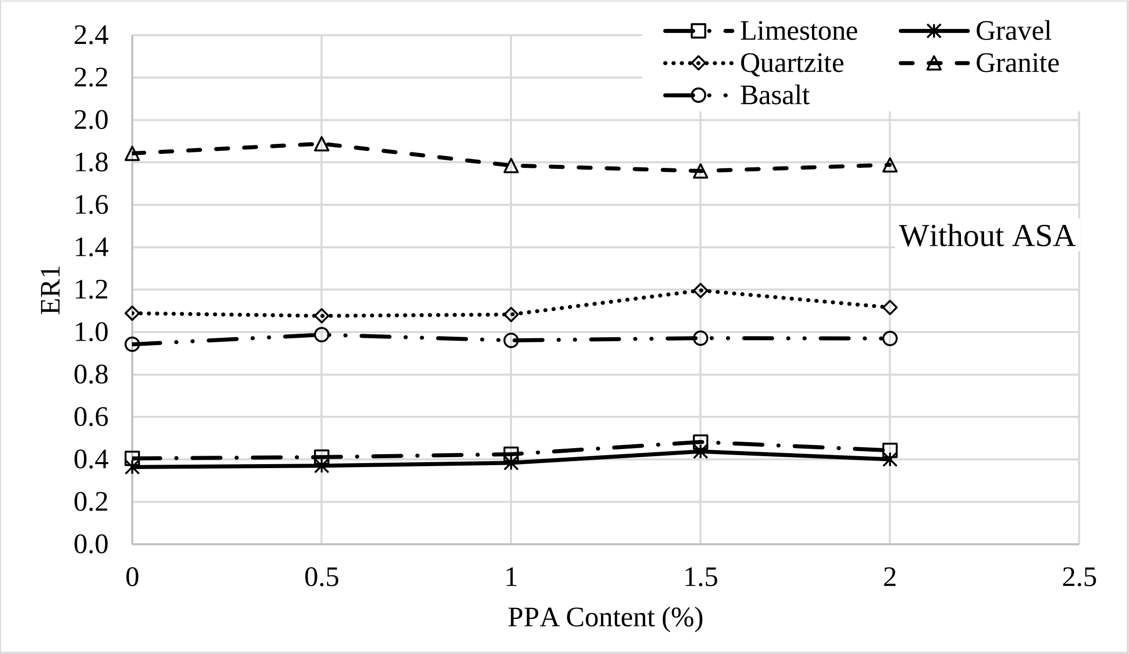


(a)

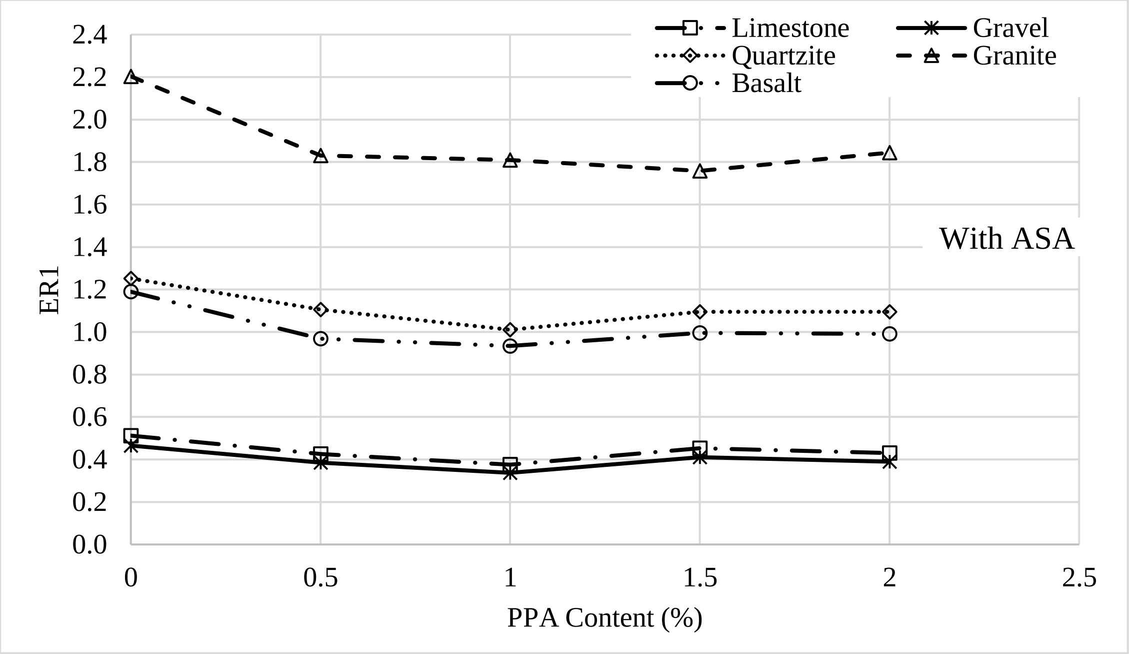


(b)

Figure 5.10 Wettability of Binder Blends Containing PPA (a) and PPA and ASA (b) with Different Aggregates



(a)



(b)

Figure 5.11 Energy Ratio (ER1) of Binders Containing PPA and ASA with the Selected Aggregates, (a) without ASA and (b) with ASA

CHAPTER

6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

This study focused on evaluating the effects of Polyphosphoric Acid (PPA) on the performance of asphalt binders relative to pavement distresses (rutting, low-temperature cracking and fatigue cracking), dynamic viscosity, oxidative aging, and traffic loading intensity that a binder can sustain. Also, the interaction of using an acid-based PPA with an amine-based Warm-Mix Asphalt (WMA) additive, an amine-based Anti-Stripping Agent (ASA), or polymers, in different combinations, and their possible effects on the performance of base binders, as mentioned above, were studied. The study was further extended to examine the influence of these additives, specifically PPA and ASA, on the cohesive bond of the base binders and the adhesion bonds between the binders and different types of aggregates. The results were analyzed to evaluate the moisture-induced damage potentials of binders and mixes containing those additives.

For this purpose, four different Superpave® grade asphalt binders, namely PG 58-25, PG 64-22, PG 70-28, and PG 76-28, were collected from six different sources. Two of these binders (PG 70-28 and PG 76-28) were the polymer-modified binders. Different additives, namely PPA, ASA, and WMA additive, were collected from local suppliers in Oklahoma. The collected additives were blended with the asphalt binder in different combinations using a High Shear Mixer (HSM) operating at 1,000 rpm for 45 minutes. PPA was used in four different amounts, i.e., 0.5%, 1.0%, 1.5%, and 2.0%. The amount of WMA additive varied from 0% to 0.75% at an interval of 0.25%. The concentration of ASA was kept constant at 0.5%. A total of 49 different binder blends were prepared in this study. The binder blends were also aged using Rolling Thin-Film Oven (RTFO) and Pressure Aging Vessel (PAV) to simulate short-term aging and long-term aging, respectively. The binder blends were tested using a wide range of laboratory tests, namely Dynamic Shear Rheometer (DSR), Bending Beam Rheometer (BBR), Rotational Viscometer (RV), Multiple Stress Creep and Recovery (MSCR), and Surface Free Energy (SFE) to fulfill the objectives of this study listed in Chapter 1. Topic-wise conclusions are presented below.

6.1.1 Effect of PPA, ASA, and WMA Additive on Rutting Resistance of Asphalt Binders

To evaluate the rutting potential of asphalt binders, laboratory tests, namely DSR and MSCR, were conducted at high test temperatures under different aging conditions. In the MSCR test, the binder blends were subjected to different stress levels of 0.1 kPa, 3.2 kPa, and 10 kPa to evaluate the traffic level a binder blend can sustain, and the stress sensitivity induced in the base binder due to modification. The test results were also analyzed to determine the Superpave® PG and MSCR grade of the binder blends. The following conclusions are drawn based on the results presented in previous chapters:

1. The use of PPA was found to be an effective way of improving the resistance of binders to rutting. A linear effect of PPA on the rutting

resistance of binders was evident from the results. Adding 1.0% or more PPA bumps the Superpave® high-temperature PG by one grade. Therefore, mixes containing PPA are expected to exhibit lower rutting in the field compared to conventional mixes. This was likely attributed to an increase in the concentration of asphaltenes in the base binder due to the addition of PPA. SARA analysis can be conducted in future to determine the concentration of asphaltenes before and after PPA modification.

2. For binders of the same grade, change in the source can result in different effects of PPA modification with respect to rutting performance. The results indicated that the stiffer the base binder, the higher the effect of PPA modification on the rutting resistance of the binder. For instance, using 2.0% PPA increased the rutting factor by 562% for the S1 PG 58-28 binder having a rutting factor of 1.15 kPa. However, the corresponding increase in the rutting factor for the S2 PG 58-28 binder was much higher (929%). The rutting factor of this binder was 1.27 kPa.
3. Based on the MSCR test data, the non-recoverable creep compliance of the binder decreased and % Recovery increased due to PPA modification. It indicated that adding PPA increased the stiffness of the base binder allowing the binder to sustain a larger traffic level without undergoing significant rutting. These results supported the DSR results. It was seen that the binder blends containing 1.5% or 2.0% PPA could sustain an extreme level of traffic loading at 58°C. Therefore, the binder was designated as PG 58E-28.

4. The use of WMA additive or ASA alone did not influence the rutting resistance of PG 58-28 binders significantly, irrespective of binder source. This was likely due to similar chemical compositions of the asphalt binder following modification by WMA additive or ASA. According to product specifications, these additives help increase workability and resistance to moisture-induced damage by changing the polarity of the base binders, but not their chemical compositions. Conducting chemical tests such as SARA can help understand the effect of these additives at different amounts.
5. The rutting resistance of the base binder was found to increase when using ASA and PPA or using the WMA additive and PPA together. Therefore, mixes containing ASA and PPA or WMA additive and PPA are expected to exhibit better performance than conventional mixes. However, the results indicated that the effectiveness of PPA in a PPA-modified binder reduced due to the addition of ASA and WMA additive. It was observed that using 0.5% ASA or 0.5% WMA additive could nullify the effect of 1.0% to 1.5% PPA. This was due to fact that using an amine-based additive with an acid-based additive nullifies the effect of each other and creates an amine salt depending on the chemistry of the base binder. Therefore, one should exercise care in using PPA with the selected WMA additive and ASA. Also, using three different additives in an asphalt mix would likely increase the production cost significantly without improving the rutting performance accordingly.

6. The rutting resistance of PG 64-22, PG 70-28, and PG 76-28 asphalt binders was found to increase due to the addition of 0.5% WMA additive, 1.5% PPA, and 0.5% ASA. Therefore, an improvement in rutting resistance of the asphalt mixes is expected due to the addition of WMA additive, PPA, and ASA in the mix. This improvement was more significant for polymer-modified binders. This was possibly due to additional cross-linking effects of PPA with polymers enhancing the polymer network by developing polymer strands. Polymer strands enhances stability and stiffness of the modified binders.
7. While comparing the PPA-modified binders with polymer-modified binders, the % Recovery of deformations of PPA-modified binders was lower than that of polymer-modified binders or binders containing PPA and polymers. Therefore, use of PPA in conjunction with polymer is expected to improve the % Recovery of the neat binder, as suggested by Orange et al. (2004).

6.1.2 Effect of PPA, ASA, and WMA Additive on Fatigue and Low-Temperature Cracking Resistance of Asphalt Binders

To examine the overall performance of asphalt binders, this study also evaluated the performance of binder blends pertaining to other distresses, namely low-temperature cracking and fatigue cracking. For this purpose, BBR and DSR tests were conducted on PAV-aged binder blends. The BBR tests were performed at low temperatures ranging from -12° to -21°C depending on the low-temperature grade of the base binder. The DSR tests were conducted at intermediate temperatures to evaluate the fatigue cracking potential of binder blends. Based on the results, the following conclusions are drawn:

1. The addition of PPA did not impact the low-temperature cracking resistance of the base binder. However, using ASA or WMA additive with PPA was found to decrease the performance of binder relative to low-temperature cracking, slightly, as compared to the performance of PPA-modified binders. None of the binder blends containing ASA or WMA additive and different amounts of PPA exhibited any change in the low-temperature PG of the base binder. Therefore, it is expected that asphalt mixes containing these additives in any combinations would exhibit similar resistance to low-temperature cracking;
2. Use of PPA was found to improve the fatigue resistance of base binder. Therefore, asphalt mixes containing PPA are expected to exhibit increased durability, less sensitivity to temperature variation, and enhanced resistance to rutting. This is attributed to the reduced oxidative aging of the base binder due to PPA modification through formation of carbonyl and sulfoxide compounds in the initial stage of aging (Huang et al., 2008).
3. Unlike rutting performance, using ASA did not exhibit any adverse effects on the fatigue cracking performance of the PPA-modified binder. Therefore, asphalt mixes containing ASA and PPA are expected to exhibit similar fatigue resistance as that of asphalt mixes containing PPA alone. By contrast, blending WMA additive and ASA with PPA-modified binder was found to reduce its resistance to fatigue cracking. This might be due to the dispersion characteristic of the selected ASA and WMA additives, which reacts with acid groups of PPA, asphaltenes, and resins and disperses their

clusters in the binder matrix (Harnish, 2010). As a result, the modified binder undergoes a faster oxidation due to the increased available surface area during aging;

4. No significant differences were observed in the fatigue cracking resistance of the neat PG 64-22, PG 70-28, and PG 76-28 binders and those containing 0.5% WMA additive, 1.5% PPA, and 0.5% ASA.

6.1.3 Effect of PPA, ASA, and WMA Additive on Dynamic Viscosity and Oxidative Aging of Asphalt Binders

RV and DSR tests were used to evaluate the effect of PPA, ASA, and WMA additive on the dynamic viscosity and oxidative aging of asphalt binders. The RV tests were conducted at 135°, 150°, 165°, and 180°C on unaged binder blends. The oxidative aging was calculated based on the DSR results on unaged and RTFO-aged binder blends. The following observations are made based on the test results:

1. Similar to the rutting resistance, the dynamic viscosity of PG 58-28 binder increased due to PPA modification. A high amount of PPA increased the DV of the binder substantially. As a result, elevated temperatures would be required for the production of mixes. For instance, adding 2.0% PPA increased the mixing temperature by 28˚C. Elevated temperatures are detrimental to cost due to increased consumption of fuels and reduced hauling distance. Therefore, one should exercise care in using a high amount of PPA;
2. The addition of WMA additive, ASA, and PPA did not substantially affect the dynamic viscosity of the base binders. Therefore, the mixing and

compaction temperatures for the asphalt mixes containing ASA, PPA, and WMA additive would be similar to those without any additive.

3. The use of WMA additive, ASA, and PPA lowered the oxidative aging of the asphalt binders. This effect was more pronounced for binder blends containing low amounts of PPA. A reduction in the oxidative aging is beneficial as it can enhance the fatigue life of asphalt mixes.

6.1.4 Moisture-Induced Damage Potential of Asphalt Binders Containing PPA, ASA, and WMA Additive

The moisture-induced damage potential of binders and mixes containing PPA and ASA was evaluated using the SFE approach. The SFE components of binder blends were determined using the Dynamic Wilhelmy Plate method. The SFE components of five different aggregates, namely limestone, granite, gravel, quartzite, and basalt, were taken from the available literature. Based on the SFE components of binder and aggregates, different interfacial energy parameters were calculated, and the following conclusions are drawn.

1. PPA did not impact the cohesive strength of the neat binder. However, depending on the aggregate type, it might improve the adhesion bond between the binder and the aggregate. Among all the selected aggregates, the maximum improvement in the adhesion bond was observed for the gravel aggregate. On the other hand, the adhesion bond of the binder with granite or basalt aggregate was found unaffected due to PPA modification.

2. The results of the wettability were consistent with the work of adhesion. Therefore, it is anticipated that the PPA would enhance the coating of the neat binder on limestone, gravel and quartzite aggregates, contributing to a better adhesion bond.
3. The addition of PPA did not have any significant effect on the energy ratio and therefore, it is anticipated not to impact the moisture-induced damage potential significantly. The results showed that PPA not only improved the adhesion bond but also increased the work of debonding in magnitude. This was attributed to the hydrophilic nature of PPA. As a result, adding PPA may not have any major impact on the moisture-induced damage potential of mixes.
4. One of the objectives of this study was to evaluate the moisture-induced damage potential when using PPA and ASA together. Based on the test results, the binder blend containing ASA improved interfacial parameters than the neat binder. However, the binder blends containing PPA and ASA lowered interfacial energy parameters than the binder blend containing ASA and, in some cases, the binder blend containing PPA. Based on these observations, it can be concluded that using ASA would not affect the moisture-induced damage potential of the PPA-modified binders.
5. The use of 1.5% PPA, with or without ASA, was found to be an effective concentration, contributing to the improved adhesion bond and the wettability of the neat binder. Therefore, it is expected to have an

improved adhesion bond and reduced moisture-induced damage potential in the field.

6.1.5 Performance of Asphalt Mixes Containing PPA, ASA, and WMA Additive Against Rutting and Moisture-Induced Damage

Four different mixes were prepared in the laboratory using PG 64-22 binder blends containing 1.5% PPA, 0.5% ASA, and 0.5% WMA additive. The concentration of PPA was selected based on the test results on binder blends. These mixes were tested in the laboratory for rutting and moisture-induced damage potential using Hamburg Wheel Tracking (HWT) and Tensile Strength Ratio (TSR) tests, respectively. The following conclusions are drawn based on the test results:

1. Testing of asphalt mixes containing PPA, WMA, and ASA using a Hamburg Wheel Tracking device revealed significant resistance to rutting, with no indication of susceptibility to moisture-induced damage.
2. The TSR test results from mixes containing PPA, WMA, and ASA, however, revealed possibility of moisture-induced damage in some cases, which was not supported by the HWT test results. Lack of a strong mechanistic-basis of TSR test in identifying moisture-induced damage can be responsible for such incoherencies.

6.2 Recommendations

Based on the findings, scope, and limitations of this study, the following recommendations are made for future studies:

1. In order to gain a better understanding of the effect of the asphalt binder chemistry on the rheological properties of asphalt binders, it is

recommended that elemental analyses of binder blends containing different amounts of WMA additive, PPA and ASA be conducted in a future study.

2. The selected amine-based WMA additive and amine-based ASA were found incompatible with PPA, nullifying the effect of PPA. A future study can be conducted using a different ASA and WMA additive that are compatible with PPA.
3. Effects of air voids, aggregate surface area, binder content, asphalt binder film thickness, and temperature on the moisture-induced damage potential of mixes were not included in the present study. It is recommended that these effects be studied in the future.
4. The current study shows potential of reducing the concentration of polymers in a mix when used with PPA. A future study may be undertaken to evaluate the effect of different concentrations and types of polymers to examine the compatibility between polymer and PPA and to determine the amount of reduction in the polymer content.
5. The present study can be extended to determine the required input parameters for the analysis and the design of asphalt pavements containing PPA (with or without WMA additive and ASA) using MEPDG.
6. It may be possible to develop correlations between SFE-based energy parameters of binder blends and TSR of asphalt mixes containing those binder blends. A future study may consider developing such correlations.
7. The Surface Free Energy (SFE) components of binder blends in this study were obtained from laboratory tests involving selected probe liquids, namely

water, glycerin, and formamide. A future study can be conducted to determine the SFE components using other probe liquids such as methylene iodide (diiodomethane, non-polar) and ethylene glycol (polar), as used by other researchers (Hollander, 1995; NCHRP 316, 2006). The results from different probe liquids may be compared with the results from the present study.

8. This study did not address the effect of aggregate texture and mineralogy on the performance of asphalt mixes. A future study may be conducted to addresses these aspects.
9. A field study may be undertaken to verify the findings of this laboratory-based study.

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