Rheology and Surface Free Energy of Modified Asphalt Binder Containing Anti-stripping Additives

by

© Towhidul Islam

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Abstract

Since 2008, the number of roads in Canada has been going up due to rapid urbanization and economic growth, and by 2020, there is more than 1.08 million kilometres of roads across the country. Around 90% of roads managed in Canada are paved with asphalt materials. During the service life, asphalt pavement experiences various surface distresses due to aging, the effect of environmental factors, and traffic loading. A way to mitigate the early deterioration of asphalt pavement is to blend suitable modifiers and additives with asphalt binders during asphalt mixture production. The current study aims to understand the relative effect of different liquid anti-stripping additives on the rheological and fundamental properties of styrene butadiene styrene (SBS)- and Gilsonite-modified binders (4 and10% by the weight of base binder, respectively) containing various percentages of anti-stripping additives in short-term aging conditions. Four different anti-stripping additives: ZycoTherm SP2 (0.05%, 0.075%, and 0.1%), Kling Beta 2914 (0.5%, 0.75%, and 1%), Pave Bond Lite (0.5%, 0.75%, and 1%), and AD-Here (0.5%, 0.75%, and 1%) were selected for this study. To attain our research goal, anti-stripping additives were blended to SBS and Gilsonite modified PG 58-28 binder. Later, all binders were aged using Rolling Thin Film Oven (RTFO) protocol. This thesis summarizes the results of rheological behaviour by considering the rutting and cracking parameters, such as the Superpave rutting parameter, Shenoy's rutting parameter, non-recoverable creep compliance, and Glover-Rowe parameter. Additionally, this study considered using the Surface Free Energy (SFE) as a fundamental material property to evaluate the cohesive bond strength of the Gilsonite-modified asphalt binders. The results show that anti-stripping additives significantly affect the binders' rheological behavior and fundamental properties, which can influence the overall performance of the asphalt binder. Furthermore, the comparative analysis showed that Gilsonite-modified binders containing liquid

anti-stripping additives enhance the moisture damage, rutting and cracking resistance of asphalt binders.

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Dedication

Especially to the loving memory of my grandfather Dr. Abdus Salam, who has a significant contribution to my education and who always wanted to see me successful. I would also like to dedicate this thesis to my maternal grandparents Abbas Uddin Chowdhury and Rokeya Begum.

Disclaimer

This research was performed in cooperation with the City of St. John's. The contents of this report reflect the views of the authors who are responsible for the opinions, findings, and conclusions presented herein. The contents do not necessarily reflect the official views or policies of the City of St. John's and Memorial University. This thesis does not constitute a standard, specification, or regulation.

List of Acronyms

AASHTO: American Association of State Highway and Transportation Officials

AASHO: American Association of State Highway Officials

AC: Asphalt Concrete

ASTM: American Society for Testing and Materials

CA: Contact Angle

CAM: Christensen-Anderson Model

CRM: Crumb Rubber Modifier

CSCE: Conference of the Canadian Society for Civil Engineering

CTAA: Canadian Technical Asphalt Association

DOT: Department of Transportation

DSR: Dynamic Shear Rheometer

EVA: Ethylene-Vinyl Acetate

FHWA: Federal Highway Administration

FT: Freezing and Thawing

G-R: Glover-Rowe

HDPE: High-Density Polyethylene

HL: Hydrated Lime

HMA: Hot Mix Asphalt

LAS: Liquid Anti-stripping Additives

LCA: Life Cycle Analysis

LCCA: Life Cycle Cost Analysis

LDPE: Low-density polyethylene

LLDPE: Linear Low-Density Polyethylene

MD: Moisture Damage

MDR: Moisture Damage Ratio

MSCR: Multiple Stress Creep Recovery

MUN: Memorial University of Newfoundland

NCHRP: National Cooperative Highway Research Program

NL: Newfoundland and Labrador

PG: Performance Graded

PPA: Polyphosphoric Acid

RAP: Reclaimed Asphalt Pavement

RTFO: Rolling Thin Film Oven

R-value: Rheological Index

SBR: Styrene-Butadiene-Rubber

SBS: Styrene-Butadiene-Styrene

SFE: Surface Free Energy

SHRP: Strategic Highway Research Program

TAC: Transportation Association of Canada

TCH: Trans-Canada Highway

TTS: Time-Temperature Superposition

WLF: Williams-Landel-Ferry

Table of Contents

List of Figures

List of Tables

Chapter 1: Introduction

1.1 Background and Motivation

Flexible pavement is the most widely used pavement structure in Canada and other countries around the world. Since 2008, the number of roads in Canada has been going up due to rapid urbanization and economic growth, and by 2020, there was more than 1.08 million km of roads across the country. Out of those, 90% of roads are constructed with an asphalt mixture (Length of Canada's Public Road Network, 2003). For the construction of these asphalt roads, road agencies require an extensive amount of asphalt binder, where asphalt binder plays a significant role in the performance of asphalt pavement.

As a viscoelastic and thermoplastic material, stress-strain characteristics of asphalt are both time- and temperature-dependent. As a result, asphalt binder exhibits significant deformation with wheel load and temperature change. Asphalt binder becomes stiffer and more elastic when subjected to rapid load and low temperature. Similarly, it becomes softer and viscous when subjected to high temperatures and a longer loading duration (J.S. Chen et al., 2008; Zaniewski & Pumphrey, 2004). When pavement is subjected to wheel load, vertical compressive stress is induced along with the asphalt layer, and horizontal tensile stress is generated at the bottom of the asphalt layer. The Hot Mix Asphalt (HMA) must be resilient to endure these compressive stresses and prevent premature permanent deformation. Numerous studies have acknowledged that the use of asphalt additives and modifiers with asphalt binders can improve rutting resistance, stripping resistance (moisture damage), and mixture durability. Therefore, a wide variety of materials may be used to modify the behavior or properties of asphalt.

St. John’s region has an adverse climate condition that includes high amounts of rain (1191 mm annually) and snowfall (3220 mm annually), frequent freeze-thaw cycle (from late fall through early spring, a high frequency of temperature fluctuations above and below 0 °C), drastic temperature variation (-7 °C to 20 °C and rarely below -13 °C or above 26 °C), and extremely high winds (City of St. John’s, 2016). In addition, traffic loading and tire pressures on the roads have increased several folds over the last few decades. These factors can have very adverse effects on road pavements and cause various pavement distresses and failures. Deteriorated road conditions can impair the ability of drivers to operate the vehicles safely, significantly reduce roadway capacity, and increase travel times. Transportation performance and road safety can be improved by improving roadway conditions. The first step toward this is understanding how various road conditions and distresses evolve.

Highway agencies have acknowledged the benefits of using modified asphalt binders to reduce the amount and severity of pavement distress and to increase the service life of the pavement. The advantage of using these modified asphalts is improved rutting resistance, stripping resistance (moisture damage) and improved mixture durability. A wide variety of materials may be used to modify the behavior or properties of asphalt.

Asphalt modification has been in practice for over 150 years (Mund et al., 2009). Changes in traffic volumes and loading, new refining technology, copolymer chemistry, environmental pressure to recycle waste (rubber tires, shingles), and performance graded (PG) asphalt specifications have all contributed to spectacular wide-reaching growth in the use of modified asphalt binders over the last ten to fifteen years (Mund et al., 2009). Since there is usually some cost associated with modification, it is important to identify the specific performance parameters that might be improved with additives or process changes. Specific binder and mix properties can be designed by selecting the suitable binder and ensuring the additive used is well-suited to the asphalt.

With the incorporation of modifiers, the thermal susceptibility, rutting resistance, and fatigue cracking properties of the binder can be significantly improved (Yildirim, 2007). Using polymer modifiers is the most successful practice to resist excessive plastic deformations at high temperatures (Gordon D Airey, 2002). Among them, styrene butadiene styrene (SBS) block copolymers, styrene-butadiene-rubber (SBR), high-density polyethene (HDPE), and ethylene-vinyl-acetate (EVA) are the most commonly used modifiers. The use of SBS polymer enhances the resistance against moisture-induced damage of HMA (Alata & Ethem rg, 2013), resistance against rutting and cracking as well (R. Bin Ahmed et al., 2021), which may double the pavement's service life (Iskender et al., 2012a).

Asphalt binder and aggregate are the two main components in asphalt pavement. The bond between asphalt binder and aggregate is primarily liable for ensuring excellent performance. Stripping due to the break of this bond can further cause rutting, raveling, cracking, etc., leading to the complete failure of the asphalt pavement (G D Airey et al., 2007; Baldi-Sevilla et al., 2017; X. Chen & Huang, 2007). Various studies prove that the stripping of the asphalt pavement can be minimized by adding anti-stripping agents (J. Cheng et al., 2011; Xiao et al., 2010). Another study indicates that aliphatic amine-based liquid anti-stripping agents can increase the asphalt mixture's stripping and rutting resistance (Park et al., 2017). Asphalt pavement performance is largely dependent on asphalt binder properties to resist moisture-induced cracking, raveling and to reduce rutting. The emergence of different asphalt additives and modifiers has triggered attempts to obtain improved asphalt mixture to reduce life-cycle pavement maintenance costs.

1.2 Objectives

This thesis project aims to:

- Develop a quantitative understanding of the performance of different asphalt modifiers and liquid anti-stripping additives at different dosage rates
- Evaluate the rutting performance of modified binders containing anti-stripping additives at different dosages using Superpave, Shenoy's Superpave rutting parameter, and non-recovery creep compliance
- Compare the effects of cracking performance of modified binders using Glover-Rowe cracking parameter, crossover frequency, and rheological index value
- Understand the combined effect of modifiers and anti-stripping additives dosage on the rheological properties of asphalt binder
- Investigate the rutting performance and cracking susceptibility of Gilsonite as an alternative to SBS polymer
- Rank different modified binders based on their rheological performances after evaluating the Glover-Rowe parameter, Superpave rutting parameter, Shenoy parameter, crossover frequency, and rheological index from the frequency sweep testing and non-recoverable creep compliance parameter from the Multiple Stress Creep Recovery (MSCR) test to categorize the binder suitability for standardized traffic loading according to AASHTO M332
- Quantify the moisture-induced damage resistance of modified asphalt binder after evaluating cohesive bond energy from the surface free energy (SFE) method

1.3 Thesis Framework

This thesis is prepared in a manuscript format. Outcome of the study is presented in 6 chapters.

Chapter 1 presents the background, motivation, objectives and the contribution of the present study.

Chapter 2 summarizes the current practice on the usage of asphalt additives and modifiers in other provinces in Canada and the U.S. Again, this review focuses on compiling recent developments on rutting and moisture resistance additives, and this summary has been used for optimal experimental design for laboratory investigation. Also, the research gaps of the modified asphalt binders are presented and considered to complete the research objectives and the works for Chapters 3-4. This chapter was submitted as a technical report to the City of St. John's.

Chapter 3 presents the rheological characterization of modified asphalt binder. This chapter was presented at the 101st Annual Meeting of Transportation Research Board (TRB) held in Washington, DC, USA, on January 9-13, 2021. Also, part of this chapter has been accepted for the 67th Annual Conference of Canadian Technical Asphalt Association (CTAA). This chapter will be submitted to a journal as a technical paper in Construction and Building Materials.

Chapter 4 presents the multiple stress creep recovery analysis of modified asphalt binder. This chapter was submitted to the Transportation Association of Canada (TAC) Conference 2022.

Chapter 5 investigates the moisture damage resistance performance of modified asphalt binder containing liquid anti-stripping additives. This chapter will be submitted to a journal as a technical paper. A potion of this chapter and some analysis from chapter 3 will be submitted to the 102nd Annual Meeting of Transportation Research Board (TRB).

Chapter 6 summarizes the general conclusions of this study and recommendations and suggestions for future works.

1.4 Significant Contributions

1.4.1 Journal Articles

- **Islam, T.**, Hossain, K., Aurilio, M., Bazan, C., & Caul, G. (2022). Experimental Investigation on Rheological Properties of SBS and Gilsonite Modified Asphalt Binders Containing Liquid Anti-Strip Additives. Journal of Construction and Building Materials by Elsevier. (planning to submit)

1.4.2 Conference Papers

- **Islam, T.**, Aurilio, M., Hossain, K., Bazan, C., & Caul, G. (2022). Evaluation of Rheological Properties of SBS and Gilsonite Modified Asphalt Binders Containing Liquid Anti-Strip Additives. Presented at 101st Annual Meeting of the Transportation Research Board (TRB) of National Academies of Science and Engineering. Washington DC, USA, January 12-16. This is the most reputable conference in Transportation Engineering field in the world.

- **Islam, T.**, Hossain, K., Aurilio, M., Bazan, C., & Caul, G. (2022). Laboratory Investigation on Rheological Properties of Gilsonite Modified Binders with Different Anti-Stripping Agents. Transportation Association of Canada (TAC). Edmonton, AB, Canada. (Under Review)

- **Islam, T.**, Hossain, K., Aurilio, M., Bazan, C., & Caul, G. (2022). Investigation on Rheological and Fundamental Behaviour of Gilsonite Modified Binders. Annual

Conference of the Canadian Society for Civil Engineering (CSCE). Whistler, BC, Canada. (Abstract Accepted)

- Feroz, S. I., **Islam, T.**, Hossain, K., Aurilio, M., Bazan, C., & Caul, G. (2022). Effect of Rejuvenators and Anti-Stripping Agents on Creep Recovery Property of Modified Aged Binder. 67th Annual Conference of Canadian Technical Asphalt Association (CTAA). West Kelowna, BC, Canada. (Abstract Accepted)

1.4.3 Technical Report

- **Islam, T.,** Hossain, K., (2020). Development of Improved Asphalt Mixture for the City of St. John's: A Literature Review on Asphalt Binder Additives and Modifiers. City of St. John's, St. John's, Newfoundland and Labrador.

1.5 Co-Authorships

All the research presented in the technical reports, journals, and conference papers in chapters 2-4 has been conducted by the author of this thesis Towhidul Islam, under the supervision of Dr. Kamal Hossain and Dr. Carlos Bazan. Towhidul Islam also prepared the draft manuscript. The other co-authors supervised the research and reviewed the manuscript.

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Chapter 2: Literature Review

Co-Authorship: This chapter has been submitted to **City of St. John's** as a Technical report as: Islam, T., Hossain, K., (2020), "Development of Improved Asphalt Mixture for the City of St. John's: A Literature Review on Asphalt Binder Additives and Modifiers**."**

2.1 Abstract

Asphalt binder plays a significant role in the performance of asphalt pavement. It is well known that asphalt mixture is a complicated material, and it is difficult to fully understand its behavior. Various performance analysis techniques are used to understand the behavior of asphalt mixtures, particularly when small amounts of additives or modifiers are added to the asphalt mixtures. These additives or modifiers are used to develop more durable and stable asphalt mixtures. These new mixtures can increase the structural capacity of the pavements and can better resist extreme weather conditions and stress from the ever-increased traffic loading. The ultimate goal of this research is to develop an asphalt mixture through various performance analysis tests and techniques to enhance rutting and moisture-induced damage resistance in asphalt. An extensive review has been conducted and is presented in this chapter as an initial task of this study. This review summarizes the current practice on the usage of asphalt additives and modifiers in other provinces in Canada and the U.S.A. Again, this review focuses on compiling recent developments on rutting and moisture resistance additives, and this summary will be used for optimal experimental design for laboratory investigation.

2.2 Introduction

The City of St. John's is responsible for the construction, management, and maintenance of approximately 1,100 kilometers of paved roads. More than 90% of the roads managed by the city are paved with asphalt surfacing. An adverse climate is persistent almost year-round in the region, and it seriously impacts the performance of asphalt pavement.

When a wheel load is applied to a pavement, vertical compressive stress is induced along with the asphalt layer, and horizontal tensile stress is induced at the bottom of the asphalt layer. The hot mix asphalt (HMA) must be resilient to resist these compressive stresses, prevent premature permanent deformation, and withstand repeated load applications without premature fatigue cracking.

Highway agencies have acknowledged the benefits of using modified asphalt binders to reduce the amount and severity of pavement distresses and to increase the service life of pavement. The advantage of using these modified asphalts is improved rutting resistance, stripping resistance (moisture damage), and improved mixture durability. A wide variety of materials may be used to modify the behavior or properties of asphalt. Table 1 shows some of the typical categories of modifiers.

The main goal of this research is to reduce the rate of occurrence of these distresses by designing and developing improved asphalt binder and asphalt mixtures appropriate for St. John's environmental and loading conditions. This research will develop recommendations on specifications for asphalt binders, modifiers, and additives to enhance the rutting and moisture resistance of pavement. This chapter will focus on reviewing recent developments on rutting and moisture resistance additives and will be used for optimal experimental design for laboratory investigation. Table 2.1 represents the generic classification of asphalt modifiers and additives.

Table 2.1: Generic classification of asphalt modifiers and additives (Roberts et al., 1996)

Types of Modifier and Additives	Examples
1. Filler	• Mineral Filler: crusher fines, lime, portland cement, fly ash • Carbon black • Sulfur
2. Extender	• Sulfur • Lignin
3. Rubber • Natural latex • Synthetic latex • Black copolymer • Reclaimed rubber	• Natural rubber • Styrene-butadiene or SBR • Styrene-butadiene-styrene or SBS • Recycled tires
4. Plastic	• Polyethylene • Polypropylene • Ethyl-vinyl-acetate, EVA • Polyvinyl chloride, PVC
5. Combination	• Blends of polymers in 3 and 4
6. Fiber	• Natural: Asbestos, rock wool • Man-made: Polypropylene, polyester, fiberglass
7. Oxidant	• Manganese salts
8. Antioxidant	• Lead compounds • Carbon • Calcium salts
9. Hydrocarbon	• Recycling and rejuvenating oils • Hardening and natural asphalts
10. Antistrip	• Amines • Lime

2.3 Roadway Conditions of St. John's

St. John's region has an adverse climate condition that includes high amounts of rain (1191 mm annually) and snowfall (3220 mm annually), frequent freeze-thaw cycle (from late fall through early spring, a high frequency of temperature fluctuations above and below 0 °C), drastic temperature variation (-7 °C to 20 °C and rarely below -13 °C or above 26 °C), and extremely high winds (City of St. John's, 2016). In addition, traffic loading and tire pressures on the roads have increased several folds over the last few decades. These can have very adverse effects on road pavements and cause various pavement distresses and failures. Deteriorated road conditions can impair the ability of drivers to operate their vehicles safely, significantly reduce roadway capacity, and increase travel times. Transportation performance and road safety can be improved by improving roadway conditions. The first step toward this is understanding how various road conditions and distresses evolve. A field survey conducted by Memorial University in 2017 found that rutting and moisture induced damage (e.g., raveling and pothole) are the major distresses on city roads and Trans-Canada Highways.

2.4 Pavement Surface Distress

Pavement surface distress is the irregularity of the road surface, which affects the comfort and safety of the road user. Because of the negative effects of various factors, including traffic loading and environmental factors, pavement deteriorates, which can result in rutting, cracking, raveling, patching, potholes, polished slippery surfaces, and miscellaneous distress. The following presents an overview of these pavement distresses.

2.4.1 Rutting

Surface depression in the wheel path is known as rutting. Pavement uplift may occur along the sides of the rut. Ruts are particularly evident after rain when they are filled with water. There are two basic types of rutting: mix rutting and subgrade rutting. Rutting can occur as a result of pavement being plastic and depressed by heavy loads or by the grinding effect of studded tires. The significant effect of studded tires is observed in the transportation jurisdictions where studded tires are still allowed, specifically in northern states in the United States, Canada, and northern Europe. Moreover, inadequate compaction during construction will also result in rutting because once the pavement is opened to traffic, it will continue to compact in the wheel paths under traffic loading. Wheel paths with rutting can easily be filled with water from rain and snowmelt. Figure 2.1 and 2.2 show certain types of rutting that might have occurred primarily due to studded tires or poor asphalt mix design. Splashed water from the rutted strips by a vehicle in front of a vehicle in an adjacent lane can suddenly cover windshields with muddy water. Thus, it can impair a driver's vision for safe driving.

Figure 2.1: Asphalt design-related rutting (permanent deformation on wheel path) on Torbay and Stavanger (left) and Torbay and Gleneyre (right), St. John's

Figure 2.2: Abrasive loss related rutting on Kenmount and Columbus Rd, St. John’s

2.4.2 Potholes and Delamination

Potholes are small, bowl-shaped depressions in the pavement surface that penetrate all the way through the HMA layer down to the base course. Potholes often form in areas that have poor drainage, high traffic volumes, or frequent cracks from other pavement distresses such as fatigue or thermal cracking. Also, freeze-thaw cycles during the winter months are strongly associated with pothole creation. During freeze-thaw cycles, expansion and contraction occur in pavement materials. These expansions and contractions induce stresses in pavement and result in micro-cracking. These small cracks turn into a bigger hole with the stresses from traffic loading. Figure 2.3 shows some patterns of potholes in a service lane.

Figure 2.3: Moisture induced damage pothole and delamination in different streets of St. John’s

2.4.3 Raveling

Raveling is defined as the wearing away of the pavement surface because of the and loss of asphalt binder and dislocating of aggregate particles. It is one of the most common asphalt pavement distresses that occur on Canadian highways. Raveling will increase pavement roughness, which results in poor ride quality and road and tire noise. Loose stones that can break windshield glass and raveling that can cause hydroplaning and it shortens pavement longevity. Figure 2.4 shows some examples of raveling in different city streets.

2.4.4 Cracking and Roughness

Several different types of pavement cracking, such as fatigue, thermal, moisture and aging-related cracking, can be caused in the life of a road pavement which have been shown in Figure 2.5. The extremely cold temperatures, excessive precipitation, salting, and strain from winter tires can cause severe cracks in the pavement. Although it is impossible to prevent all cracks, addressing the causes behind them can help determine the best way to reduce cracks in the asphalt pavement.

As indicated before, if pavement cracks are not treated, they can lead to bigger holes, “potholes”, which can have severe consequences on traffic safety. Pavement roughness is generally defined as a form of unevenness in the pavement surface that affects safety.

Figure 2.4: Micro-cracking and raveling of new binder mix in different city streets in St. John’s.

Figure 2.5: Representative illustrations on cracking in different city streets in St. John’s.

2.4.5 Patching

All flexible pavements require patching sometimes during their service life. Generally, pavement patching is conducted temporarily to repair local distresses. A thin layer is removed from the faulty area of the pavement and replaced with a new paving material. Patching contributes to address road safety and ride quality issues. In general, less preparation and care are taken to conduct a patching project which leads to cracking and unevenness of the pavement presented in Figure 2.6.

Figure 2.6: Representative illustrations on patching in different city streets in St. John's.

2.4.6 Asphalt Additives and Modifiers

Asphalt modification has been in practice for over 150 years (Mund et al., 2009). Changes in traffic volumes and loading, new refining technology, copolymer chemistry, environmental pressure to recycle waste (rubber tires, shingles), and performance graded (PG) asphalt specifications have all contributed to spectacular wide-reaching growth in the use of modified asphalt binders over the last ten to fifteen years (Mund et al., 2009). Since there is usually some economic cost associated with modification, it is important to identify the specific performance parameters that might be improved with additives or process changes. Specific binder and mix properties can be designed by selecting the suitable binder and ensuring the additive used is well-suited to the asphalt.

This chapter presents a summary of physical properties, testing standards, and comparative field trials of different types of modifiers such as elastomeric and plastomeric polymers, crumb rubber, special relining processing methods, oxidation, chemical catalysts, and other chemical additives, gelling agents, oils and softening agents, bituminous extenders, fillers, and fibre.

2.5 Reasons to modify an asphalt binder

Depending on the asphalt source and the average climatic conditions, the main reasons for the use of asphalt modification are (Roberts et al., 1996):

- minimizing the rutting by making the binder stiff at high temperatures,
- minimizing the thermal cracking by making the binder soft and increasing the elasticity of the mixture at low temperatures,
- improving the resistance of the mixture due to fatigue,
- reduce moisture sensitivity by improving binder-aggregate bonding,
- improving the resistance due to abrasion by reducing raveling,
- reduce bleeding issues,
- improving aging or oxidation resistance,
- improving pavement durability results in the reduction of life cycle costs of pavement
- reducing the layer thickness of the pavement, and
- developing the overall performance of HMA pavement.

2.6 Polymer Additives

2.6.1 Elastomers

Polymers are macromolecules which are made of macromolecules. The physical properties of the resulting polymer are controlled by the chain and chemical structure of the monomers. The most common polymer additives are styrene-butadiene-styrene (SBS) copolymer, styrene-butadiene-rubber (SBR), and ethylene-vinyl acetate (EVA) (Yildirim, 2007; Rahi et al., 2014). It is necessary to use polymers in order to improve the performance grade (PG) high-temperature grade of the binder. The advantage of polymer modifiers will vary depending on the dosage, morphology, molecular weight, chemical properties, and molecular structure of the material. Each of these factors, as well as the crude source, refining method, and grade of neat asphalt binder, is critical. Among these additives, SBS is the most commonly used elastomeric type copolymer. Various studies found that SBS modified asphalt binder exhibits greater permanent deformation resistance at high temperatures, cracking at low temperatures and fatigue cracking as well (Gordon D. Airey, 2003; Iskender et al., 2012b; X. Lu & Isacsson, 1997; Xiaochun Lu et al., 1998). The SBR is usually crosslinked with sulfur, where the physical and chemical properties are determined by the level of crosslinking. SBR emulsions are utilized as modifiers since they are a lightly crosslinked rubber that does not totally melt during processing. Normal application of the SBR is by a latex emulsion, with the water content of the asphalt cement being flashed out of the asphalt cement mix. Figure 2.7 shows illustration of the physical look of some elastomeric polymers.

(a) **(b)** **(c)** **(d)**

Figure 2.7: Representative illustrations of (a) SBS (Adapted from “SBS block copolymer,” 2017) ; (b) SBR (Adapted from “SBR copolymer,” 2014) ; (c) EVA (Adapted from “EVA-resin,” n.d.) ; and (d) Elvaloy (Adapted from "Farooq," 2018)

2.6.2 Plastomers

Plastomers are also popularly called “polyethylene”. Low-density polyethylene LDPE, high-density polyethylene (HDPE), and linear low-density polyethylene (LLDPE) are the most common plastics (Daly, 2017). Other polyolefins employed include polypropylene and ethylene-propylene copolymer, and EVA copolymer. The most recent studies on using plastomers are mentioned here in Table 3. Figure 2.8 shows some of these plastomers. The addition of plastomer appears to result in the greatest potential benefit amongst the modified binders and least susceptible to moisture damage. EVA and LDPE exhibit the best performance in terms of Rut Depth and Wheel Tracking Slope, EVA-9% shows the best result (Toraldo & Mariani, 2014). HDPE content of 5% by weight of asphalt is recommended as it reduces the moisture susceptibility and temperature susceptibility (Attaelmanan, Feng, & Ai, 2011).

(a) **(b)** **(c)**

Figure 2.8: Representative illustrations of (a) LDPE (Adapted from "Low Density Polyethylene," n.d.); (b) HDPE (Adapted from "HDPE-granule," n.d.) ; (c) LLDPE (Adapted from "LLDPE granules," n.d.)

2.6.3 Crumb Rubber (GTR)

The formation of a significant network between the binder and the modifier in the SBS modified asphalt binder results in enhanced rutting resistance. Additionally, by accumulating micro-damage, it is demonstrated that the application of the SBS binder has a high cracking resistance. Since a long time GTR has been studied as an alternative material in terms of improving virgin asphalt performance from scrap tires. Currently, North America and Europe have started the use of GTR in the pavement industry. This crumb rubber material, also known as a crumb rubber modifier (CRM), can be blended with HMA mixtures by either a wet process or a dry process (Lo Presti & Airey, 2013). Previous studies found that the addition of crumb rubber into asphalt binder can produce asphalt pavements that exhibit increased pavement life, decreased traffic noise, reduced maintenance costs and resistance to rutting and cracking (Huang et al., 2002; H. H. Kim et al., 2017; H. H. Kim & Lee, 2015). Figure 2.9 represents different mesh sizes of rubber.

Figure 2.9: Representative illustrations of crumb rubber (Adapted from "Crumb Rubber (GTR)," 2013)

2.7 Other Nonbituminous Modifiers and Additives

The main reason for long-term aging in asphalt pavements is oxidation. This process causes pavement to become stiffer and more susceptible to cracking. It is possible to extend the life of asphalt pavements by using an antioxidant as a performance enhancer in the asphalt binder. Note that, the discussion on antioxidants is very limited on available literature. Lignin is an easily available antioxidant that is widely used. The lignin has an overall effect of widening the temperature range of the binders. According to the testing results, lignin included in the coproducts improves the binders' characteristics at intermediate and low temperatures. The impacts of oxidative aging products were analyzed, and some antioxidant properties were found (Christopher Williams & McCready, 2008). Another antioxidant, i.e., Bentonite, is used in an asphalt binder to delay aging and thus increase the life of an asphalt pavement. Due to the presence of Bentonite, a considerable improvement in asphalt mixture rutting resistance has been found during asphalt aging. (Apeagyei et al., 2008). Figure 2.10 represents the physical look of an antioxidant.

(a) **(b)**

Figure 2.10: Representative illustrations on (a) Bentonite (Adapted from "Bentonite Rheological Additive," n.d.), and (b) Lignin (Adapted from "Lignin Powder," n.d.)

2.7.1 Anti-stripping Agents

Anti-stripping agents are used to prevent the asphalt mix from moisture damage, which is also known as stripping. Both liquid anti-stripping agents and lime additives are used to resist stripping (Daly, 2017). Many anti-stripping agents have been used in asphalt mixtures in the past, including amido amines, imidazolines, polyamines, hydrated lime, organo-metallics, and acids (Daly, 2017). The majority of liquid anti-stripping agents currently in use are chemical compounds that contain amines. The surface free energy of the asphalt binder and aggregate is a significant material parameter that determines the adhesive bond strength between the asphalt binder and the aggregate as well as the cohesive bond strength of the asphalt binder. As a result of these bond energies, the asphalt mixture is more resistant to distress like fatigue cracking and moisture-induced damage. Nowadays, many different forms of chemical and natural modification are applied to asphalt binders, and these modifications have an impact on their chemical and mechanical characteristics. The addition of polymers, additives (e.g., anti-stripping agents), and oxidative agents to the asphalt binder are the three most common examples of modifications. Most of the liquid anti-stripping additives are referred to as "surface-active agents." Liquid anti-stripping additives in asphalt cement help to lower surface tension, which in turn helps to enhance adhesion between the binder and the aggregate. In all circumstances, the goal of using anti-stripping additives is to prevent the stripping of asphalt cement from the aggregate in HMA mixtures. In a research by Bhasin et al. (2007), for asphalt binders, the surface free decreased when liquid anti-stripping agents were added and consequently improved fracture resistance due to better adhesion between the aggregate and the binder. Figure 2.11 shows an illustration of the physical look of an anti-stripping agent.

(a) **(b)** **(c)** **(d)** **(e)**

Figure 2.11: Representative illustrations of liquid anti-stripping agents (a) ZycoTherm SP2, (b) Pave Bond Lite, (c) Kling Beta 2914, (d) AD-Here, and (e) Hydrated Lime

2.7.2 Stiffening Agents

2.7.2.1 Polyphosphoric Acid

Polyphosphoric acid is known as PPA, which is a liquid mineral polymer additive used either by itself or with other polymers. The increasing popularity of PPA has led to its use as a partial replacement for polymer modification (Fee et al., 2010). Figure 2.12 shows an illustration of the physical appearance of polyphosphoric acid and Table 7 summarizes some major findings from the recent study on this additive.

Figure 2.12: Representative illustration of polyphosphoric acid (PPA) (Adapted from "Polyphosphoric-acid-ppa," n.d.)

2.7.2.2 Gilsonite

Gilsonite is a natural deposit of mineral bitumen, which is brittle in its raw form. However, this black mineral can be applied with bitumen because of its good affinity for asphalt (Liu & Li, 2008). In tropical countries, roads built with asphalt layers must be made with bituminous mixtures containing asphalt that is reasonably stiff, to increase resistance against rutting. Gilsonite modified HMAs were prepared using either wet or dry processes. Gilsonite increases stiffness and improves the performance grade of a virgin binder at high temperatures of service (Quintana et al., 2016). The research conducted by Mirzaiyan et al. (2019) demonstrates that Gilsonite and SBS exhibit an almost similar effect on the resistance to rutting of bitumen. It also shows that increasing the Gilsonite content improves high-temperature rutting performance. Nonetheless, thermal cracking due to the brittleness at low temperatures is a typical drawback of Gilsonite modification of binders (Rajbongshi & Das, 2009). In the near future, the shortage of butadiene supply could lead to a further increase in SBS costs. Thus, the use of Gilsonite can be considered as an alternative solution to using polymers. Figure 2.13 illustrates the physical appearance of the Gilsonite.

Figure 2.13: Representative illustrations of Gilsonite

2.7.3 Nanomaterials

Nanomaterials are those materials which are at least within 1–100 nm in one dimension. The advantage of using nanomaterials is their large surface area and small size, which promotes distinctive characteristics such as the tunnel effect of macroscopic quantum and surface effect. In some studies, it has been found that nanomaterials exhibit high-temperature sensitivity, high ductility, high stain resistance, and low electrical resistivity (Simon et al., 2008; Veytskin et al., 2015; Yang et al., 2010; Zheng & Wilkie, 2003; Zhou et al., 2014). Because of those unique phenomena, the application of nanomaterials is now accepted worldwide. Some commonly used nanomaterials are carbon nanotubes, nanowires, nanofibers and nanoceramics. Moreover, some autonomous properties of materials at the nanoscale include the ability to self-clean, self-heal, self-remember, and self-sense. As a result, the current needs for highway pavements are well met by these novel characteristics. Thus the application of nanotechnology in the sectors of pavement materials, such as asphalt modification with nanoparticles, was greatly promoted by researchers and engineers. Nanoparticles were first introduced into asphalts by Xiao and his collaborators in order to investigate the rheological properties of the materials. It has been confirmed that the addition of nanomaterials can significantly enhance asphalt's performance by improving visco-elasticity, high temperature properties, and resistances to aging, fatigue, and moisture damage (Abdelrahman et al., 2014; Ameri et al., 2013; Dong et al., 2008; B. Li et al., 2010). Nano-scale materials show good performances on low-temperature cracking resistance and high-temperature performance (Li et al., 2017).

2.7.4 Steel and Copper Slag

Steel slag is a byproduct of the process of making steel from iron. Adhesion, durability, and resistance to rutting are all well-known properties of the steel slag that is commonly used in asphalt pavement (Shafabakhsh & Ani, 2015). Copper slag is a byproduct of copper manufacturing mostly made up of heavy metals. The accumulation of a considerable volume of this material from natural source across the planet poses a significant environmental risk. Steel and copper slag can be used as a replacement of mineral aggregate in asphalt mixtures which shows significant durability and resistance to rutting (Abdelfattah et al., 2018). Figure 2.14 shows illustration of the physical look of steel and copper slag.

(a) **(b)**

Figure 2.14: Representative illustrations of (a) steel slag (Adapted from "Steel slag briquetting machine," n.d.); and (b) copper slag (Adapted from "Marco Abrasives-Copper Slag," n.d.)

2.8 Overall Highlights of Literature Review

Based on the review, detailed information of a wide range of asphalt additives and modifiers is summarized and presented in Table 2.2. This information includes name of the products and optimum dosage rate that can be implemented to study these products.

Table 2.2: Name and optimum dosage rate of the selected asphalt additives and modifiers

Additives and Modifiers	Optimum dosage (% of asphalt unless indicated otherwise)
Elasromer	
• SBS	4
• SBR (UP-5000)	0.67% by weight of aggregate
• EVA	7
• Elvaloy	3
Plastomer	
• HDPE	5
• LDPE	5
• LLDPE	6-9
• PET	5
Acrylic fibers	0.3
Crumb rubber	5 and 10
AD-Here	0.5-1
Redicote C-2914	0.5-1
Pave Bond	0.5-1
Hydrated lime	2
Gilsonite	10
ZycoTherm	0.05-0.125
Steel slag	50% by weight of aggregate
Copper slag	40% by weight of aggregate

2.9 Summary of Findings from the Literature Review

Asphalt pavement performance is largely dependent on asphalt binder properties to resist moisture-induced cracking, raveling and to reduce rutting. The emergence of different asphalt additives and modifiers has triggered attempts to obtain improved asphalt mixture to reduce life-cycle pavement maintenance costs. This chapter summarizes the positive and negative effects of different additives and modifiers. Based on the review, the following conclusions are drawn:

- Many studies in the literature show that asphalt additives and modifiers can improve the rutting and moisture-induced damage resistance of the mixtures.
- The performance of rut resistant modifiers, including Styrene–butadiene–styrene (SBS), ethylene-vinyl-acetate (EVA), acrylic fibre, and Gilsonite, has been evaluated; and they showed encouraging results. From our review, we were not able to identify if the City of St. John's has been using any of these modifiers. These may be considered for further study in the experimental program of this research project.
- For improving moisture resistance, the performance of Ad-here, SBS copolymer, and hydrated lime were studied before. These were also in the current specification of the City of St. John's. In our experimental program, we may include to a study of the current dose rate along with some new dose rates and new procedures to enhance the overall performance of the mixture.
- During this review, it was found that many studies have been trying some new additives, including different nanomaterials, ZychoTherm, Pave Bond, and Redicote. These are also potential to include in the experimental program.

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Chapter 3: Evaluation of Rheological Properties of SBS and Gilsonite Modified Asphalt Binders

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3.1 Abstract

Premature failure is a frequent phenomenon in the bituminous concrete pavement. One of the common approaches to mitigate early pavement deterioration is to incorporate a wide variety of modifiers or additives with asphalt binder. The goal of this research is to evaluate the relative effect of different modifiers and anti-stripping additives on the rheological properties of asphalt binders. To attain the research goal, four anti-stripping additives: ZycoTherm SP2, Kling Beta 2914, Pave Bond Lite, and AD-Here were used at different dosages for laboratory investigation. These anti-stripping additives were blended to a styrene-butadiene-styrene (SBS) polymer and Gilsonite modified PG 58-28 binder. Then all binders were aged using Rolling Thin Film Oven (RTFO) protocol. Note that, studies on the rheological parameters, especially for Gilsonite modified binders, have not been investigated in the available literature. Therefore, the rutting and cracking parameters, such as the Superpave rutting parameter, Shenoy's rutting parameter, crossover frequency, Rheological index and Glover-Rowe parameter were evaluated for SBS and Gilsonite modified binders. The rheological properties of the modified binder were investigated

using the dynamic shear rheometer (DSR) based on CA master curve parameters. Comparative rutting parameters analysis showed that both SBS and Gilsonite modified binders enhance the rutting performance of asphalt binder. However, cracking parameter analysis showed that the SBS with anti-stripping additives improves cracking resistance relative to the Gilsonite.

3.2 Introduction

According to the United Nations report in 2018, over 82% of the population in North America lives in urban areas. Predictions show that this could increase up to 90% by the middle of this century (United Nations Department of Economic and Social Affairs, 2018). Consequently, roads and highways play a significant role in meeting future demands in economic growth and development. Asphalt pavement has been extensively used in North America to construct roads and highways because of its sustainability and excellent performance. For example, about 90% of the roads managed in Canada are paved with asphalt surfacing. Similar reports show that over 94% of roads in the United States of America and 96% in Mexico are asphalt pavement (Virginia Asphalt Association, 2020).

As a viscoelastic and thermoplastic material, stress-strain characteristics of asphalt are both time and temperature-dependent. As a result, asphalt binder exhibits significant deformation with wheel load and temperature change. Asphalt binder becomes stiffer and more elastic when subjected to rapid load and low temperature. Similarly, it becomes softer and viscous when subjected to high temperatures and a longer loading duration (J.S. Chen et al., 2008; Zaniewski & Pumphrey, 2004). When pavement is subjected to wheel load, vertical compressive stress is induced along the asphalt layer, and horizontal tensile stress is generated at the bottom of the asphalt layer. The hot mix asphalt (HMA) must be resilient to endure these compressive stresses and prevent premature permanent deformation. Numerous studies have acknowledged that the use of asphalt additives and modifiers with asphalt binders can improve rutting resistance, stripping resistance (moisture damage), and mixture durability. Therefore, a wide variety of materials may be used to modify the behaviour or properties of asphalt.

With the incorporation of modifiers, the thermal susceptibility, rutting resistance, and fatigue cracking properties of the binder can be significantly improved (Yildirim, 2007). Using polymer modifiers is the most successful practice to resist excessive plastic deformations at high temperatures (Gordon D Airey, 2002). Among them, styrene butadiene styrene (SBS) block copolymers, styrene-butadiene-rubber (SBR), high-density polyethene (HDPE), and ethylene-vinyl-acetate (EVA) are the most commonly used modifiers. The use of SBS polymer enhances the resistance against moisture-induced damage of HMA (Alata & Ethem rg, 2013), resistance against rutting and cracking as well (Ahmed et al., 2021), which may double the pavement's service life (Iskender et al., 2012).

Gilsonite is a natural deposit of mineral bitumen, which is brittle in its raw form. However, this black mineral can be applied with bitumen because of its good affinity for asphalt (Liu & Li, 2008). The research conducted by Mirzaiyan et al. (Mirzaiyan et al., 2019) demonstrates that Gilsonite and SBS exhibit an almost similar effect on the resistance to rutting of bitumen. It also shows that increasing the Gilsonite content improves high-temperature rutting performance. Nonetheless, thermal cracking due to the brittleness at low temperatures is a typical drawback of Gilsonite modification of binders (Rajbongshi & Das, 2009). In the near future, the shortage of butadiene supply could lead to a further increase in SBS cost. Thus, the use of Gilsonite can be considered as an alternative solution to using polymers.

Asphalt binder and aggregate are the two main components in asphalt pavement. The bond between asphalt binder and aggregate is primarily liable for ensuring excellent performance.

Stripping due to the break of this bond can further cause rutting, raveling, cracking, etc., leading to the complete failure of the asphalt pavement (G D Airey et al., 2007; Baldi-Sevilla et al., 2017; X. Chen & Huang, 2007). Various studies prove that the stripping of the asphalt pavement can be minimized by adding anti-stripping agents (Cheng et al., 2011; Xiao et al., 2010). Another study indicates that aliphatic amine-based liquid anti-stripping agents can increase the asphalt mixture's stripping and rutting resistance (Park et al., 2017).

Notwithstanding, studies on these rheological parameters (especially for Gilsonite modified binders) have not been performed in the available literature. Thus, this paper evaluates the rheological characteristics, including Superpave rutting parameter, Shenoy's parameter, Glover-Rowe cracking parameter, Crossover frequency, and Rheological index of SBS (4% by the weight of base binder) and Gilsonite (10% by the weight of base binder) modified binders containing various percentages of anti-stripping additives in short-term aging conditions. Four different anti-stripping additives: ZycoTherm SP2 (0.05%, 0.075%, and 0.1%), Kling Beta 2914 (0.5%, 0.75%, and 1%), Pave Bond Lite (0.5%, 0.75%, and 1%), and AD-Here (0.5%, 0.75%, and 1%) were selected for this study.

3.3 Rheological Parameters

3.3.1 Superpave Rutting Parameter ($G^*/Sin\delta$)

Following the ever-increasing use of modifiers and additives in asphalt mixture, the research on the characterization of asphalt binders has increased significantly in the past few years. Previously, different traditional tests, i.e., viscosity, penetration, ductility, softening, and flashing point tests, have been extensively used to determine the rutting performance of asphalt binders (Domingos & Faxina, 2015; Loizos et al., 2009). Due to several limitations of these tests, such as loading condition, test temperature frequency, lack of interrelation with properties, and undesirable performance for modified binders, researchers have tried to develop rutting parameters for asphalt binders which can be used to evaluate rutting behaviour at high temperatures. The American Strategic Highway Research Program (SHRP) developed an approach to assess the rutting potential of asphalt binder by using Dynamic Shear Rheometer (DSR), known as the Superpave rutting parameter ($G^*/\mathrm{Sin}\delta$) (AASHTO T 315-12, 2012). According to the Superpave rutting factor criteria, ($G^*/\mathrm{Sin}\delta$) must be a minimum value of 2200 Pa for aged binders.

3.3.2 Shenoy's Rutting Parameter ($\mathbf{G^*/(1-(1/tan\delta sin\delta))}$)

Research on the Superpave rutting parameter was principally focused on unmodified asphalt binders. Due to the strain recovery property of modified binders, $G^*/Sin\delta$ lacks adequacy. In 2001, Shenoy suggested a new rutting parameter: $G^*/(1-(1/\tan\delta\sin\delta))$ (Shenoy, 2001), which can be adopted to evaluate the rutting potential more accurately (especially for modified binders) than the Superpave rutting parameter (Shenoy, 2004a, 2004b). A binder with a higher $G^*/\mathrm{Sin}\delta$ and $G^*/(1-(1/\tan\delta\sin\delta))$ value shows high rut resistance.

3.3.3 Glover-Rowe (G-R) parameter ($\mathbf{G^*(cos\delta)^\wedge 2/sin\delta}$)

The Glover-Rowe (G-R) parameter is also used to characterize the rheological properties of the asphalt binder. Earlier, Glover et al. (Glover et al., 2005) introduced a rheological parameter to evaluate the pavement cracking potential, known as the "Glover parameter" ($G'/(\eta'/G')$). Rowe et al. (G. M. Rowe et al., 2014) simplified Glover's parameter to $G^*(\cos\delta)^\wedge 2/\sin\delta$ at 15°C and 0.005 rad/s, termed as the "Glover-Rowe" parameter. Based on Rowe's criteria, a $G^*(\cos\delta)^\wedge 2/\sin\delta$ value of 180 kPa refers to the warning of damage. If the $G^*(\cos\delta)^\wedge 2/\sin\delta$ value exceeds 600 kPa, significant cracking is expected. The Glover-Rowe parameter was developed for nonelastomeric modified binders, and recent research has shown that the test has difficulty differentiating cracking performance in modified binders (Kluttz, 2019).

3.3.4 Crossover Frequency (W_c) and Rheological Index (R)

The crossover frequency is the frequency where the storage (G′) and loss (G″) modulus are equal at a specific temperature (D W Christensen & Anderson, 1992). In general, crossover frequency can be considered as the hardness indicator of the asphalt binder at the desired temperature. The rheological index is a log-based difference between the glass modulus and the dynamic modulus at the crossover frequency. The Rheological Index (R-value) is expected to increase with the aging of asphalt binder. The crossover frequency and Rheological Index Black Space Diagram is another widely accepted indicator to investigate the resistance against thermal cracking for asphalt binders (Mensching et al., 2015).

3.4 Objectives

The main objectives of this study include:

- Evaluating the rutting performance of SBS and Gilsonite modifiers containing anti-stripping additives at different dosages using Superpave and Shenoy's Superpave rutting parameter
- Comparing the effects of cracking performance of SBS and Gilsonite modified binders using Glover-Rowe cracking parameter, crossover frequency, and rheological index value
- Understanding the combined effect of modifiers and anti-stripping additives dosage on the rheological properties of asphalt binder
- Investigating the rutting performance and cracking susceptibility of Gilsonite as an alternative to SBS polymer

3.5 Materials And Experimental Design

3.5.1 Asphalt Binder

PG 58-28 as the control binder was used in this study. PG 58-28 is generally used in the province of Newfoundland and Labrador, Canada. Pyramid Construction Ltd. supplied the asphalt. A thorough investigation was conducted on a controlled PG 58-28 binder.

3.5.2 Modifiers and Anti-stripping Additives

Two different modifiers were used for laboratory evaluation to complete the goal of this research. The modifiers are presented in Figure 3.1. The modifiers used included:

- SBS modified PG 58-28, obtained from Yellowline Asphalt Products Limited
- Gilsonite, obtained from American Gilsonite Company

Four different anti-stripping additives were used in this research. The anti-stripping additives are presented in Figure 3.2. Table 3.1 presents the physical and chemical properties of three liquid anti-stripping additives. The additives used included:

- ZycoTherm SP2, obtained from Zydex Industries
- Pave Bond Lite, obtained from Yellowline Asphalt Products Limited
- Kling Beta 2914 (Redicote C-2914), obtained from Nouryon
- AD-Here, obtained from Valero Energy Inc.

Table 3.1: Physical And Chemical Properties Of Four Liquid Anti-stripping Additives

Properties	ZycoTherm SP2	Kling Beta 2914	Pave Bond Lite	AD-Here
Physical State	Liquid	Liquid	Liquid	Liquid
Odour	Sligh aromatic	Ammoniacal	Ammoniacal	Amine

Colour	Pale yellow	Brown (dark)	Brown (dark)	Brown (dark)
Relative density	1.03 g/cc (at 30 ℃)	1.01 g/cc (at 20 ℃)	-	0.97 g/cc (at 20 ℃)
Viscosity	150 CPS (at 30℃)	175 CPS (at 30℃)	-	1,000 - 2,000 CPS (at 5℃)
pH values	-	11.5	-	10.9
Boiling point	>200 ℃	-	>200 ℃	>216 ℃
Flash point (closed cup method)	>85 ℃ and >250 ℃	>200 ℃	154 ℃	>300 ℃
Solubility in water	dispersible	Soluble	-	-

Figure 3.1: Asphalt Modifiers (a) Gilsonite and (b) SBS

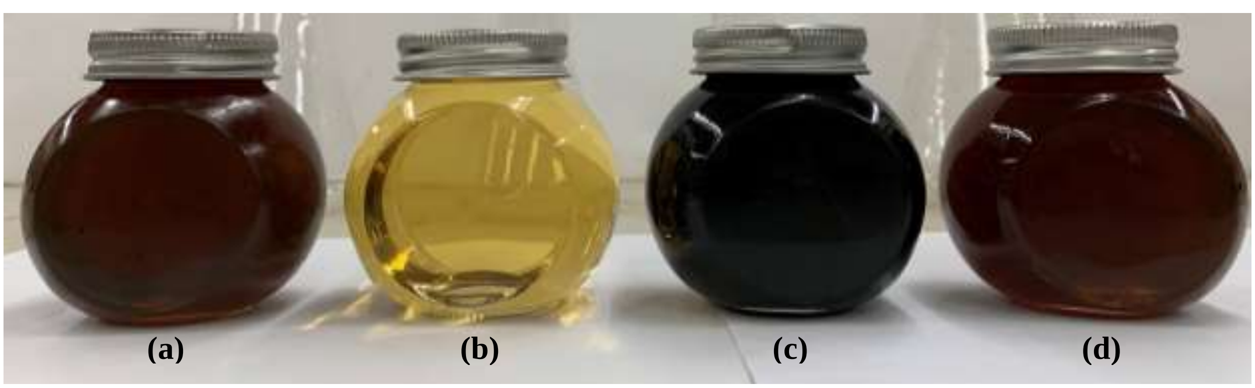


Figure 3.2: Anti-stripping Additives (a) ZycoTherm SP2, (b) Pave Bond Lite, (c) Kling Beta 2914 and (d) AD-Here

3.5.3 SBS and Gilsonite Modification with Asphalt Binders

In this research, SBS and Gilsonite modified binders were used to examine the improvement of rutting resistance. SBS modified binder was provided by Yellowline Asphalt Products Limited, where 4% linear SBS polymer (by the weight of binder) was used. For Gilsonite modification, the preheated pure bitumen and 10% Gilsonite powder were blended for 90 minutes at a temperature of 180°C with the help of a magnetic stirrer.

3.5.4 Blending Anti-stripping Additives with Modified Asphalt Binders

Asphalt binder PG 58-28 was blended with three types of liquid anti-stripping additives ZycoTherm SP2 (0.05%, 0.075%, and 0.1%), Kling Beta 2914 (0.5%, 0.75%, and 1%), Pave Bond Lite (0.5%, 0.75%, and 1%), and AD-Here (0.5%, 0.75%, and 1%). First, the modified asphalt binder was heated at 180ºC for 60 minutes to make it fluid enough for mixing. The modified binders were blended with the different application rates of additives. The blending process was conducted using a magnetic stirrer for 30 minutes at 180ºC.

Finally, The Rolling Thin Film Oven Test (AASHTO T 240) was used for short-term laboratory aging of the base binders and modified binders, and the standard aging procedures for the RTFOT are 163ºC and 75 mins.

3.5.5 Experimental Methodology

Several rheological tests were performed using a Dynamic Shear Rheometer (DSR). The frequency sweep test protocol was performed using the Malvern Panalytical Kinexus DSR-III rheometer. For DSR testing, a 25 mm diameter parallel plate with a 1 mm gap was chosen. The testing temperatures were 46ºC, 52ºC, 58ºC, 64ºC, and 70ºC. Test frequency ranged from 0.1-10Hz with a strain rate of 0.1%. The experimental plan of this study is illustrated in Figure 3.3.

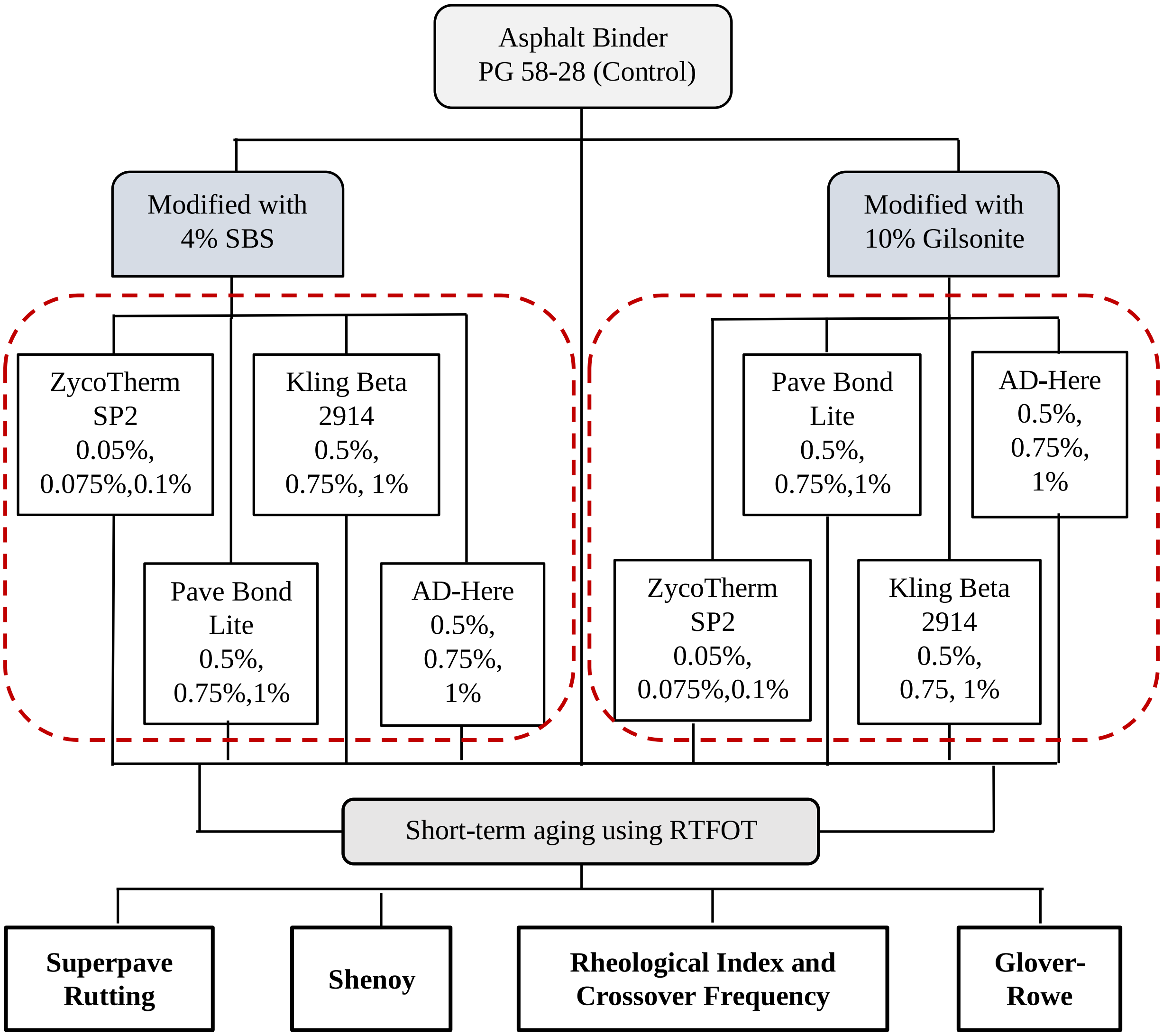


Figure 3.3: Experiment Design Matrix for Rheological Characterization

3.6 Results And Discussions

3.6.1 Complex Modulus Master Curves

One of the significant advantages of the master curve is that it can be used to investigate the rheological properties of viscoelastic asphalt binders. Frequency sweep tests were performed to depict different master curves using the time-temperature superposition (TTS) principle where complex modulus or the phase angle is plotted against reduced frequency on a log–log scale (Ferry, 1980). In this study, the master curves were developed using the Christensen-Anderson (CA) model (Donald W. Christensen et al., 2017) and shifted at the reference temperature of 58ºC. The shift factor was estimated by the Williams-Landel-Ferry (WLF) equation (Geoffrey M. Rowe & Sharrock, 2011). All the models used in this study are listed below.

Complex shear modulus: $G^* = Gg[1 + \left(\frac{Wc}{Wr}\right)^{\left(\frac{log2}{R}\right)}]^{-(\frac{R}{log2})}$ …….……………………………… (1)

Phase angle: $\delta = 90/(1 + \frac{Wr}{Wc})^{(\frac{log2}{R})}$……………………………………………………….... (2)

Shift factor: $loga(T) = -\frac{C1(T-Tr)}{C2+T-Tr}$……………………………………………………… (3)

Where,

G_g = glassy modulus (= 1 Gpa, assumed)

W_r = reduced frequency

W_c = crossover frequency

R = rheological index

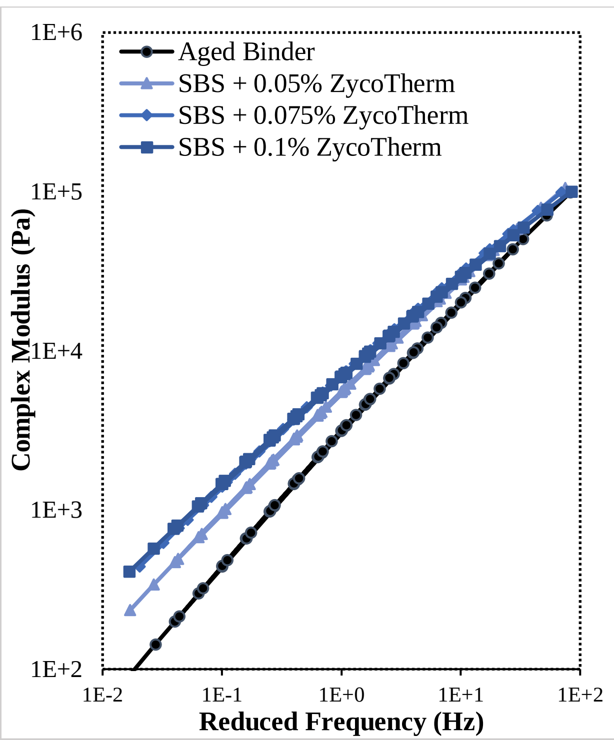
$C1, C2$ = empirically determined constants

T = test temperature; and

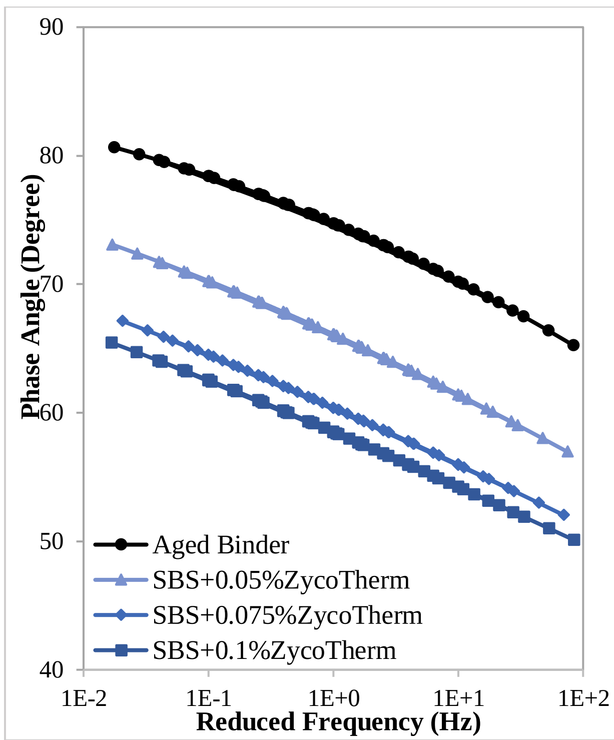
T_r = reference temperature

Figure 3.4 and 3.5 depict the master curve for SBS and Gilsonite modified binders with all three anti-stripping additives, respectively. The master curve of the RTFO aged binder is considered the control in this study. According to Christensen et al. (2017), the shape of the master curves mostly depends on the Rheological index. The increase of the R-value causes the master curve to be flat. Various studies have reported the flattening manner of binder (Wasiuddin et al., 2014). In this study, aged SBS modified binders with all three anti-stripping additives (Figure 3.4) show the expected flattening pattern. With the addition of additives, the binder becomes softer. As a result, the complex modulus decreases. The phase angle value against reduced frequency from the frequency sweep test for all SBS modified binders are illustrated in Figure 3.4. All binders exhibit improved elastic behaviour compared to the unmodified aged binder. It is also evident that with the increase of concentration, the elastic property improves.

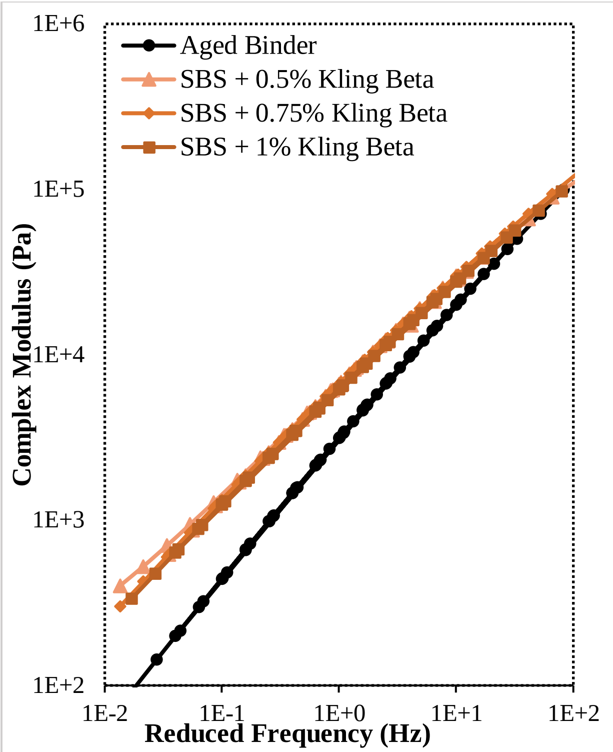
Gilsonite modified binders with ZycoTherm, Kling Beta, Pave Bond, and AD-Here (Figure 3.5) exhibit no significant changes in stiffness value when dosage rates were increased. Exceptionally, Gilsonite modified binders with 1% Kling Beta, 0.5% AD-Here and 0.1% ZycoTherm show slightly increased stiffness at higher loading frequencies compare to the aged binder, which indicates an increase in rutting resistance at higher temperatures. Phase angle versus reduced frequency in Figure 3.5 shows that all Gilsonite modified binders with anti-stripping additives exhibit viscous behaviour compared to the unmodified aged binder.



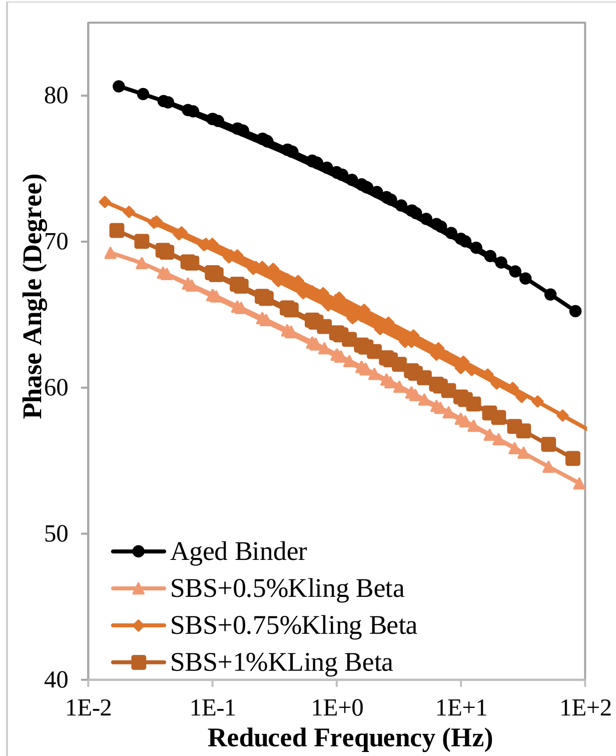
(a)



(b)

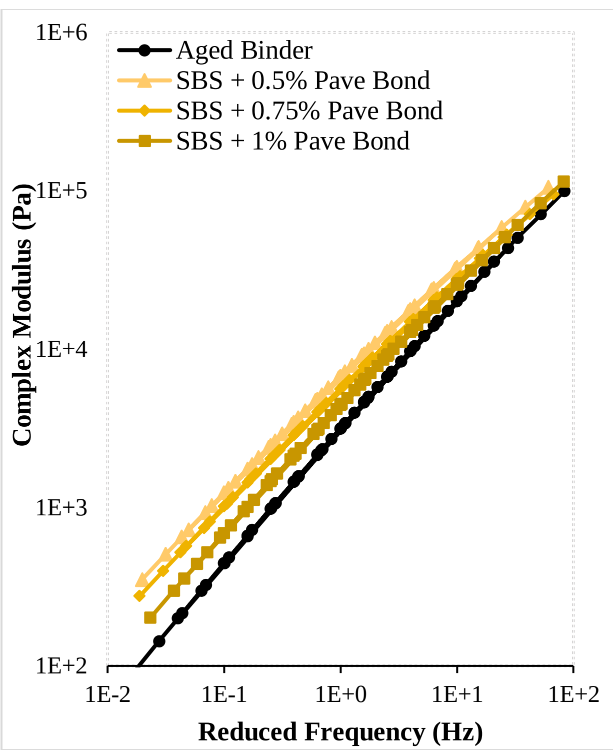


Aged Binder
SBS + 0.5% Kling Beta
SBS + 0.75% Kling Beta
SBS + 1% Kling Beta
Complex Modulus (Pa)
Reduced Frequency (Hz)
1E+6
1E+5
1E+4
1E+3
1E+2
1E-2
1E-1
1E+0
1E+1
1E+2

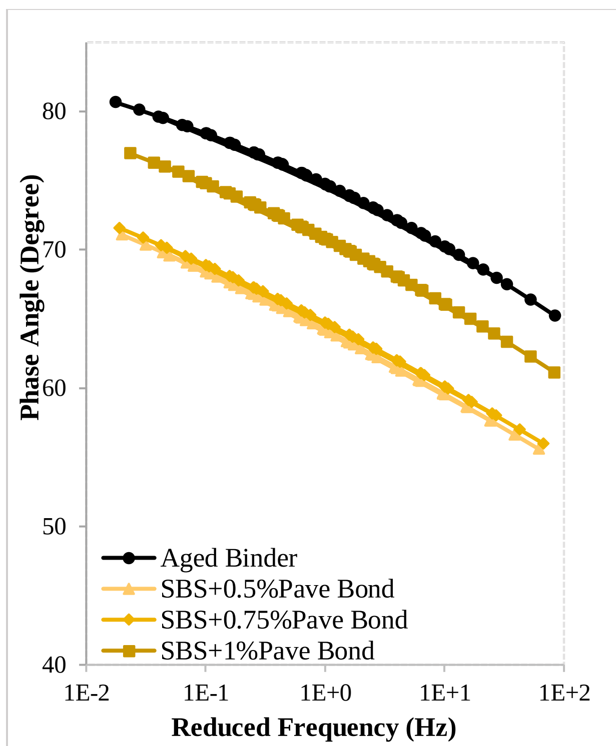


Aged Binder
SBS+0.5%Kling Beta
SBS+0.75%Kling Beta
SBS+1%KLing Beta
Phase Angle (Degree)
Reduced Frequency (Hz)
80
70
60
50
40
1E-2
1E-1
1E+0
1E+1
1E+2

(c) **(d)**

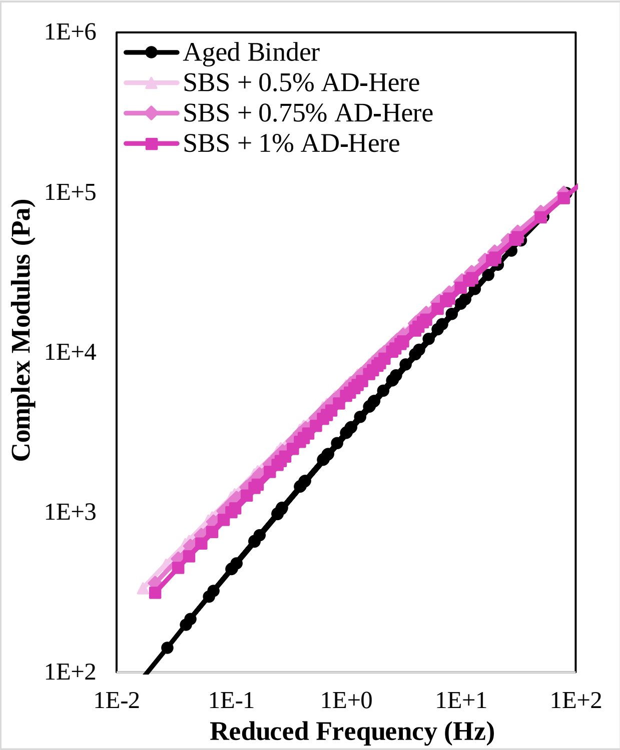


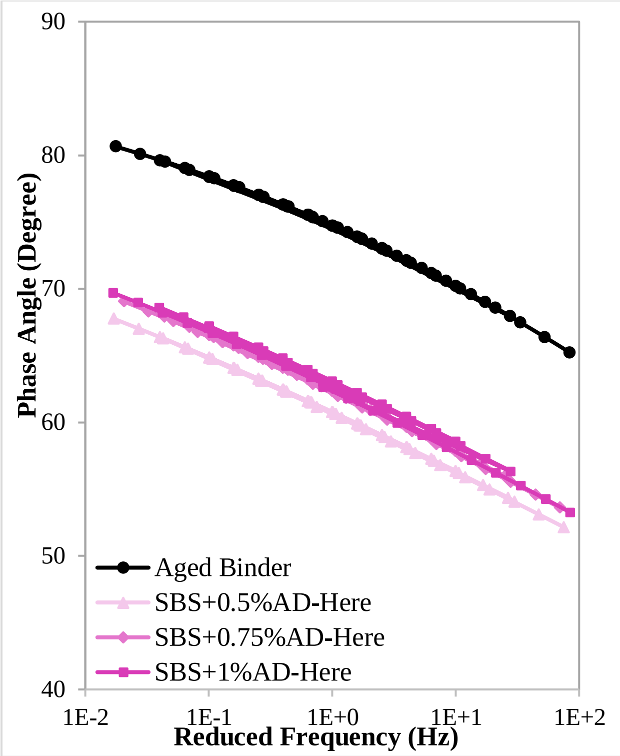
Aged Binder
SBS + 0.5% Pave Bond
SBS + 0.75% Pave Bond
SBS + 1% Pave Bond
Complex Modulus (Pa)
Reduced Frequency (Hz)
1E+6
1E+5
1E+4
1E+3
1E+2
1E-2
1E-1
1E+0
1E+1
1E+2



Aged Binder
SBS+0.5%Pave Bond
SBS+0.75%Pave Bond
SBS+1%Pave Bond
Phase Angle (Degree)
Reduced Frequency (Hz)
80
70
60
50
40
1E-2
1E-1
1E+0
1E+1
1E+2

(e) **(f)**





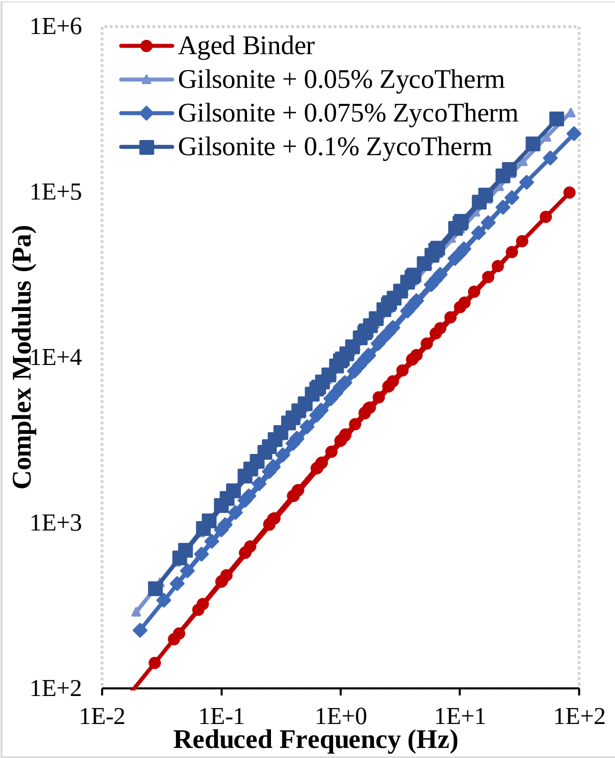
(g) **(h)**

Figure 3.4: (a) Complex modulus and (b) Phase angle master curve of SBS+ZycoTherm SP2

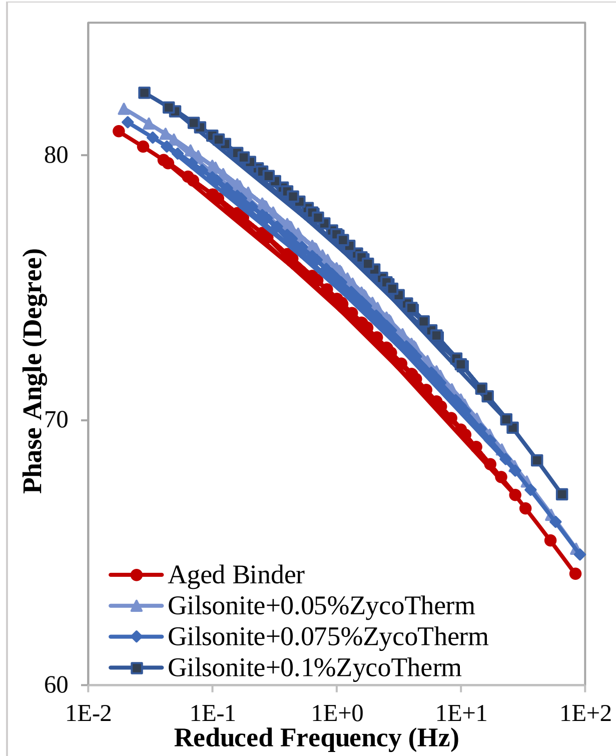
(c) Complex modulus and (d) Phase angle master curve of SBS+Kling Beta 2914

(e) Complex modulus and (f) Phase angle master curve of SBS+Pave Bond Lite

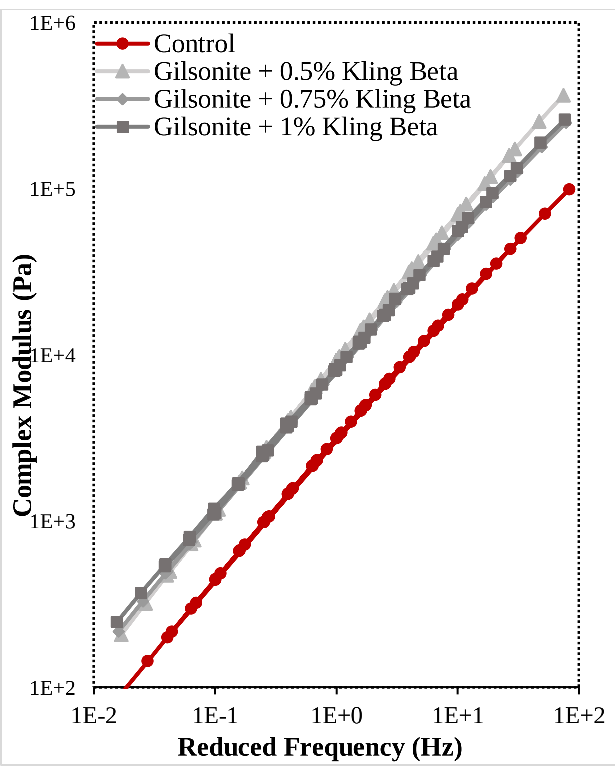
(g) Complex modulus and (h) Phase angle master curve of SBS+AD-Here


Aged Binder
Gilsonite + 0.05% ZycoTherm
Gilsonite + 0.075% ZycoTherm
Gilsonite + 0.1% ZycoTherm
1E+6
1E+5
1E+4
1E+3
1E+2
Complex Modulus (Pa)
1E-2
1E-1
1E+0
1E+1
1E+2
Reduced Frequency (Hz)

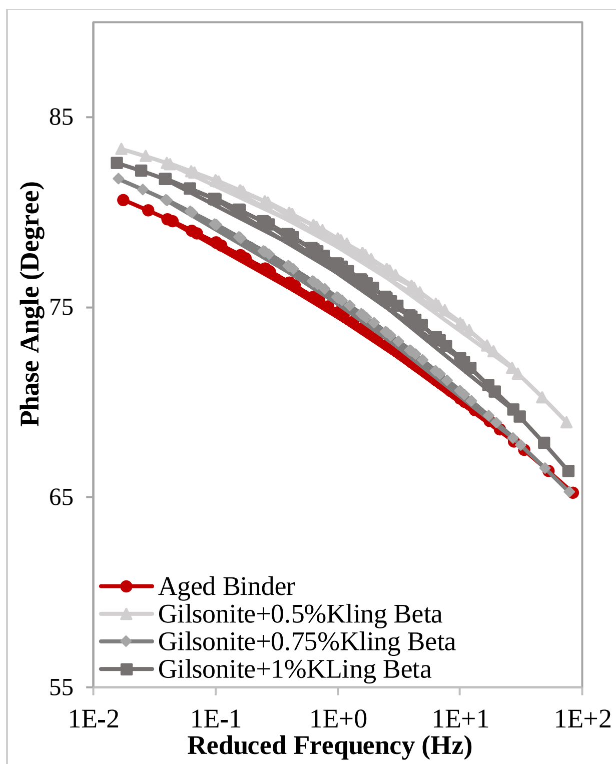
(a)


80
70
60
Phase Angle (Degree)
Aged Binder
Gilsonite+0.05%ZycoTherm
Gilsonite+0.075%ZycoTherm
Gilsonite+0.1%ZycoTherm
1E-2
1E-1
1E+0
1E+1
1E+2
Reduced Frequency (Hz)

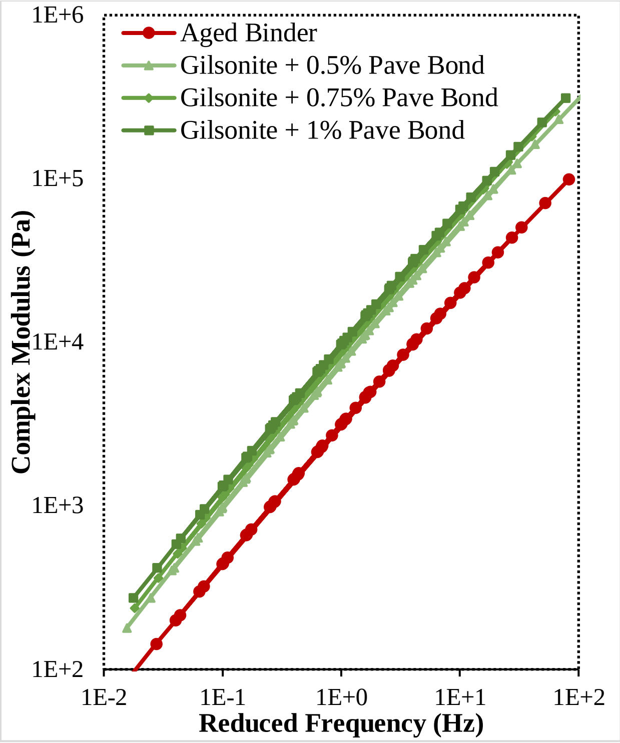
(b)

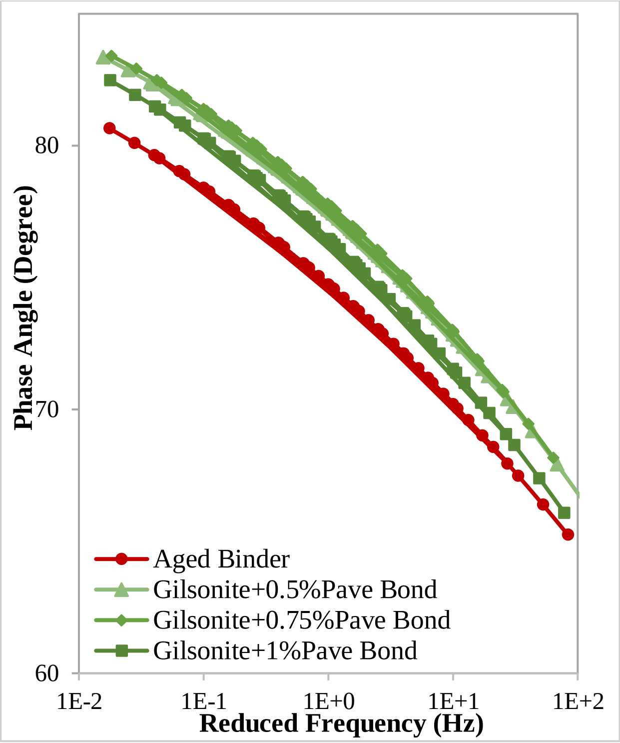

Control
Gilsonite + 0.5% Kling Beta
Gilsonite + 0.75% Kling Beta
Gilsonite + 1% Kling Beta
1E+6
1E+5
1E+4
1E+3
1E+2
Complex Modulus (Pa)
1E-2
1E-1
1E+0
1E+1
1E+2
Reduced Frequency (Hz)

(c)

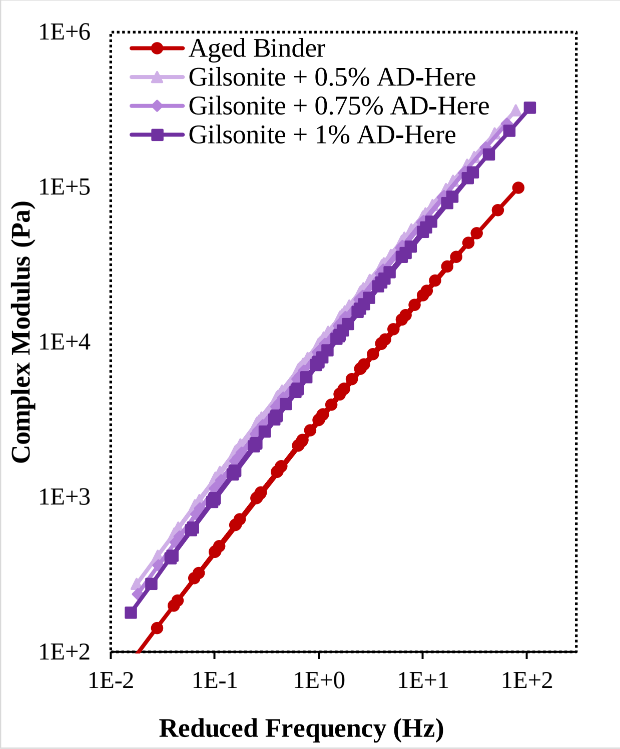

85
75
65
55
Phase Angle (Degree)
Aged Binder
Gilsonite+0.5%Kling Beta
Gilsonite+0.75%Kling Beta
Gilsonite+1%KLing Beta
1E-2
1E-1
1E+0
1E+1
1E+2
Reduced Frequency (Hz)

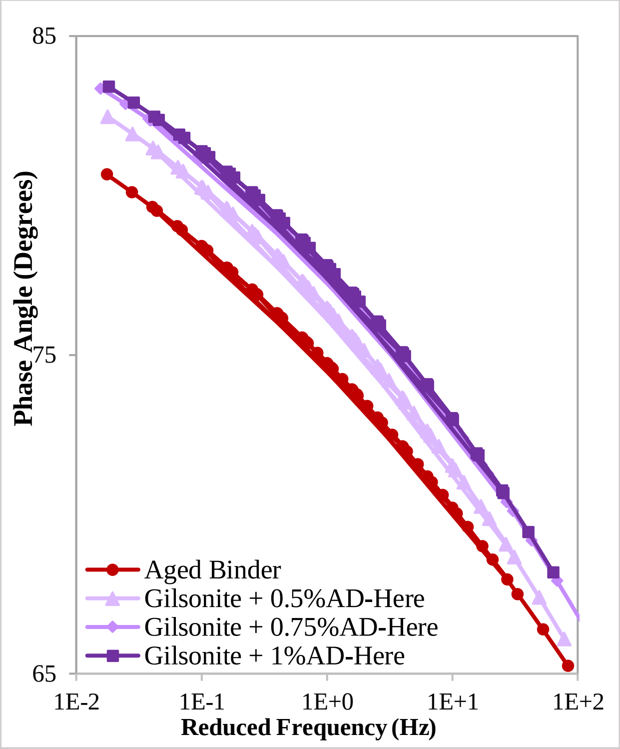
(d)


Aged Binder
Gilsonite + 0.5% Pave Bond
Gilsonite + 0.75% Pave Bond
Gilsonite + 1% Pave Bond
1E+6
1E+5
1E+4
1E+3
1E+2
Complex Modulus (Pa)
1E-2
1E-1
1E+0
1E+1
1E+2
Reduced Frequency (Hz)


Aged Binder
Gilsonite+0.5%Pave Bond
Gilsonite+0.75%Pave Bond
Gilsonite+1%Pave Bond
80
70
60
Phase Angle (Degree)
1E-2
1E-1
1E+0
1E+1
1E+2
Reduced Frequency (Hz)

(e) **(f)**


Aged Binder
Gilsonite + 0.5% AD-Here
Gilsonite + 0.75% AD-Here
Gilsonite + 1% AD-Here
1E+6
1E+5
1E+4
1E+3
1E+2
Complex Modulus (Pa)
1E-2
1E-1
1E+0
1E+1
1E+2
Reduced Frequency (Hz)


Aged Binder
Gilsonite + 0.5%AD-Here
Gilsonite + 0.75%AD-Here
Gilsonite + 1%AD-Here
85
75
65
Phase Angle (Degrees)
1E-2
1E-1
1E+0
1E+1
1E+2
Reduced Frequency (Hz)

(g) **(h)**

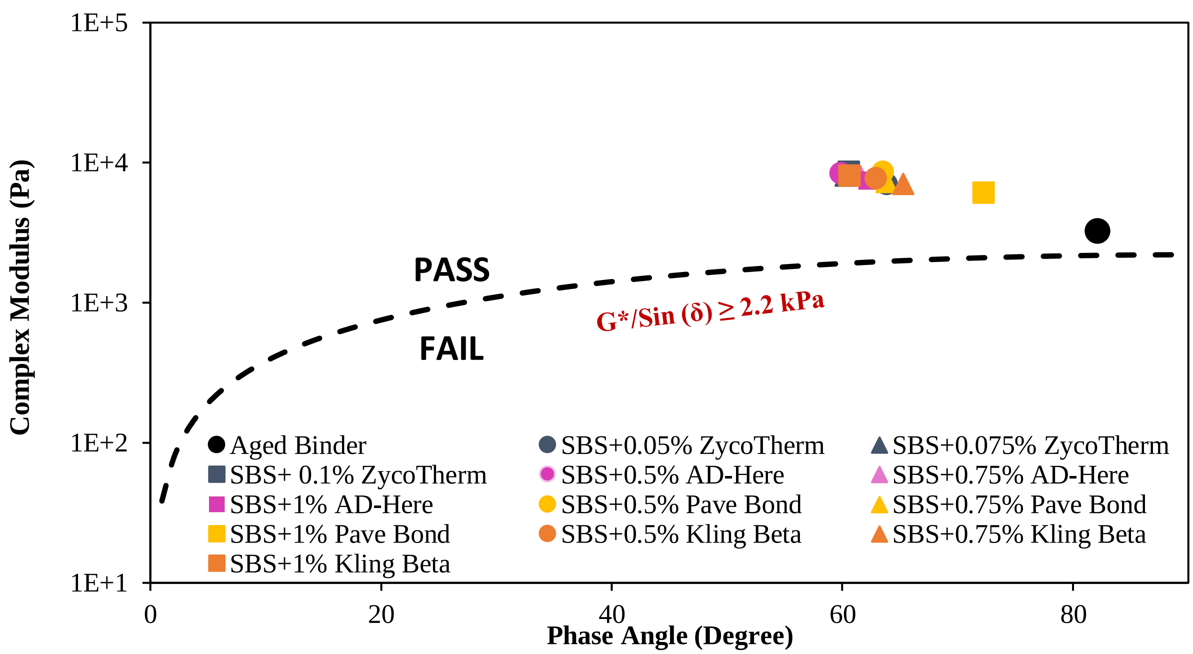
Figure 3.5: (a) Complex modulus and (b) Phase angle master curve of Gilsonite+ZycoTherm (c) Complex modulus and (d) Phase angle master curve of Gilsonite+Kling Beta 2914 (e) Complex modulus and (f) Phase angle master curve of Gilsonite+Pave Bond Lite (g) Complex modulus and (h) Phase angle master curve of Gilsonite+AD-Here

3.6.2 Superpave Rutting Parameter

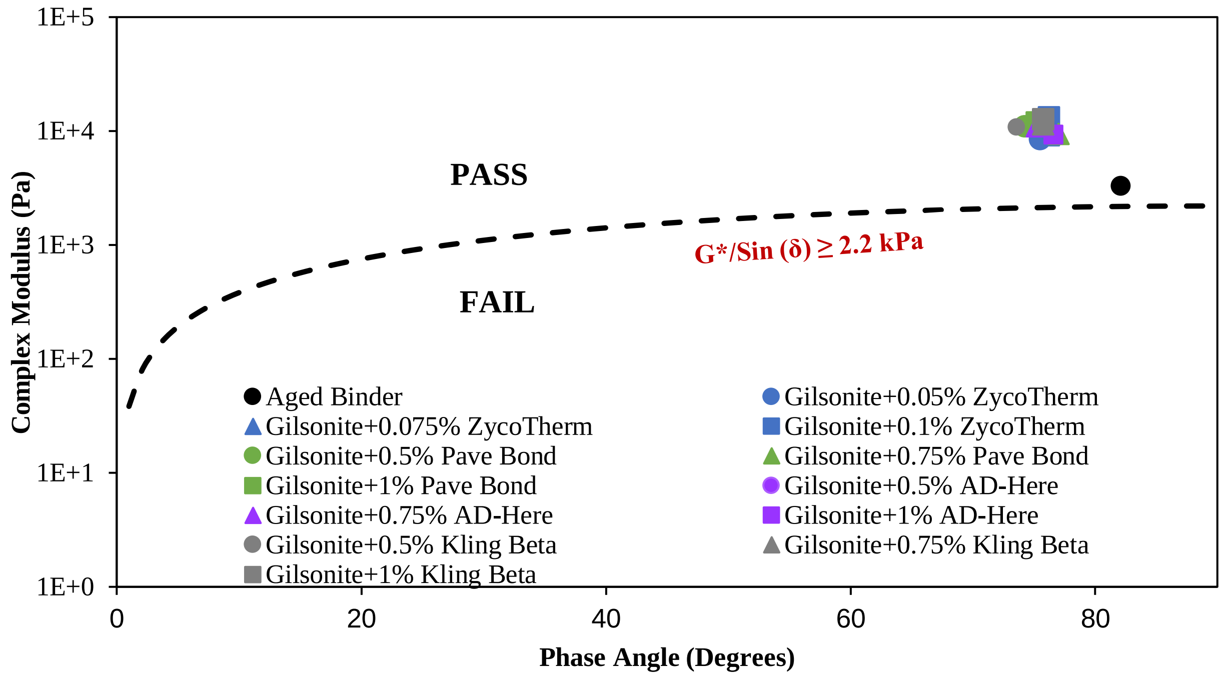
The Superpave rutting parameter value ($G^*/Sin\delta$) of SBS and Gilsonite modified binders containing anti-stripping additives are shown in Figure 3.6 and 3.7, along with their damage criteria, respectively. $G^*/Sin\delta$ is evaluated at high-temperature 58ºC, 10 rad/s. The higher $G^*/Sin\delta$ value is desirable in terms of rutting resistance. It is witnessed that the dosages of additives significantly influence the rutting behaviour of binders.

The black space diagram in Figure 3.6(a) provides a clear image of rutting resistance for all SBS modified binders as a function of dosages for different anti-stripping additives. According to the Superpave criteria, all SBS modified binders passed the damage limit. Figure 3.7(a) shows $G^*/Sin\delta$ values for SBS modified binders containing anti-stripping additives. The results show that the addition of ZycoTherm SP2 and Kling Beta 2914 increases the $G^*/Sin\delta$ value, respectively. It indicates an increasing trend of rut resistance of binder with ZycoTherm and Kling Beta concentration increase. $G^*/Sin\delta$ value for RTFOT aged PG 58-28 is reported to be 3.28 kPa which is close to the damage limit. The maximum increase in rutting resistance can be observed up to 0.1% ZycoTherm compared to the rest of the binders. In comparison, 0.075% ZycoTherm, 0.5% AD-Here, and 1% Kling Beta show better rutting performance. However, Pave Bond Lite and AD-Here show a decreasing trend of rutting performance. Thus, it can be concluded that incorporating Pave Bond lite with SBS makes the binder soft at high temperatures. Generally, SBS polymer is a combination of polystyrene and polybutadiene materials. SBS becomes durable and stiff material because of the combination of polybutadiene and polystyrene. Nowadays SBS is very popular polymers for improving the binder stiffness and rutting resistance.

Black Space Diagram in Figure 3.6(b) shows that all Gilsonite modified binders passed the damage criterion line. Figure 3.7(b) illustrates the rutting performance of Gilsonite modified binders in terms of dosages for different anti-stripping additives. It is evident that almost all Gilsonite modified binders improve the rutting resistance in the same way SBS does, where it shows no significant difference in rutting resistance with the change of additives dosages. Still, Gilsonite with 0.1% ZycoTherm SP2 shows the highest rutting resistance due to the better chemical bonding with Gilsonite. For Pave Bond and AD-Here, the loss of rutting resistance is observed with the increase of dosage. Generally, Gilsonite makes bitumen stiffer and increases its viscosity, which consequently makes asphalt concrete stiffer.

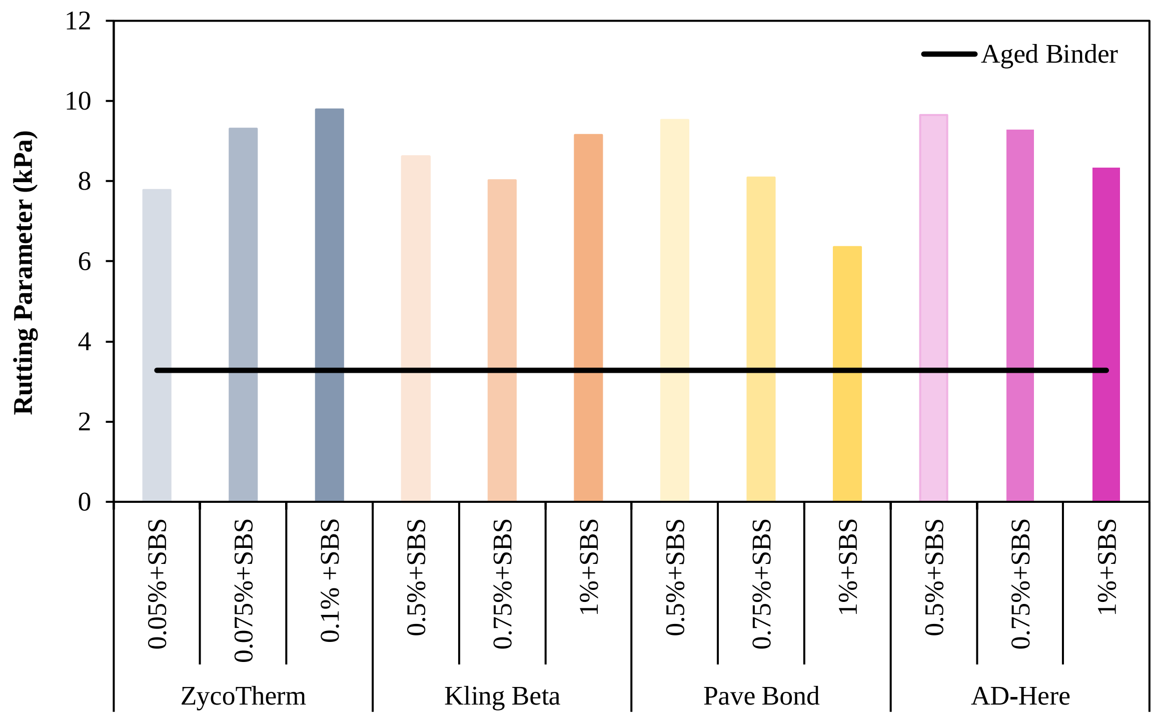


(a)

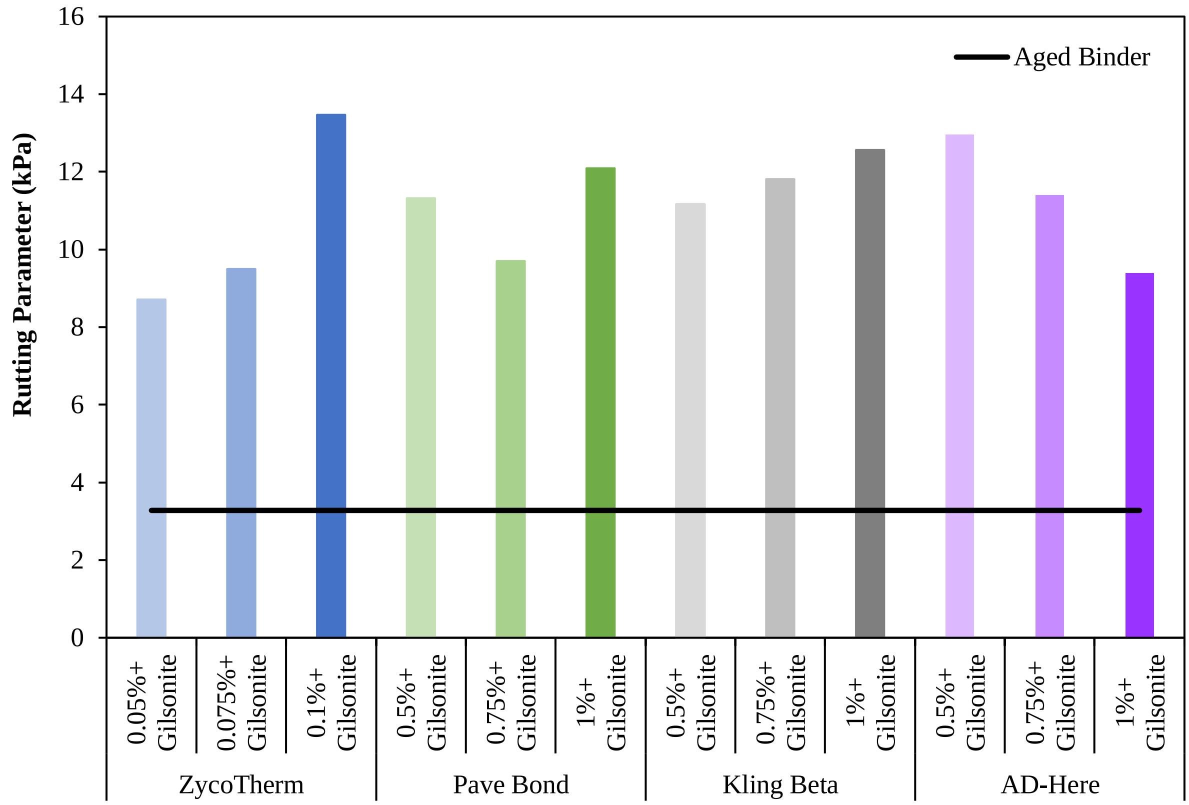


(b)

Figure 3.6: Black Space Diagram of Superpave parameter (a) SBS and (b) Gilsonite modified binders



(a)



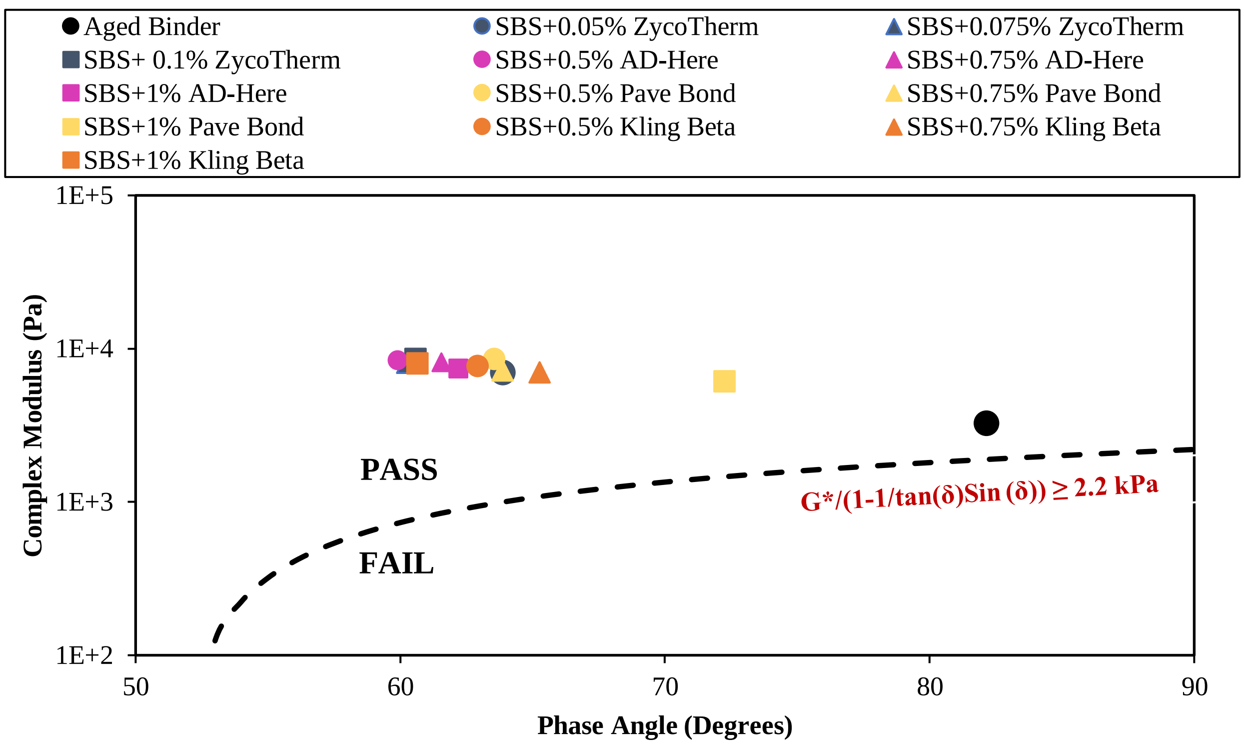
(b)

Figure 3.7: Evaluation Superpave Rutting parameter (a) SBS and (b) Gilsonite modified binders

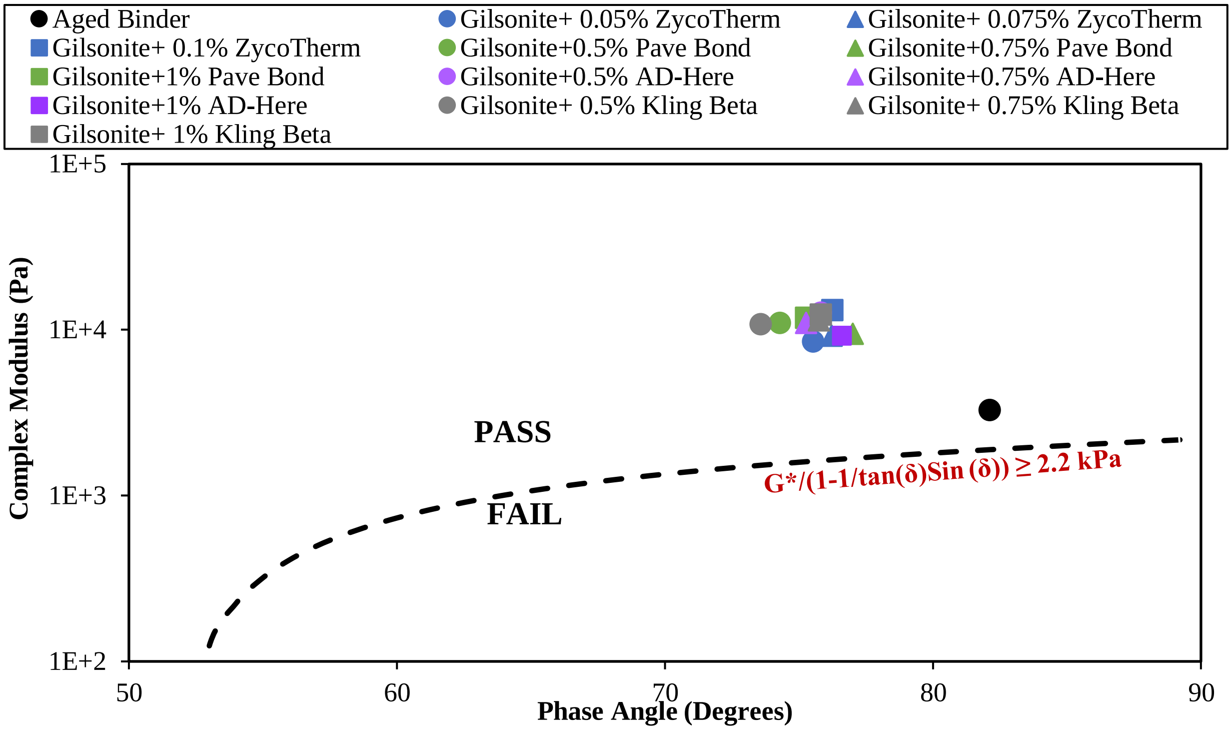
3.6.3 Shenoy Parameter

Shenoy's and Superpave rutting parameters are measured from G* and δ from the master curve. Shenoy's rutting parameter effectively measures the rutting performance of the modified binder, as it is more sensitive to phase angle δ. All the parameters were kept the same for this analysis to compare Shenoy's parameter with the Superpave rutting parameter. Figure 3.8(a) and (b) present the black space diagram of Shenoy's damage criteria for SBS and Gilsonite modified binders, respectively. All SBS and Gilsonite modified binder samples passed the damage criteria. Additionally, it can be observed that both Shenoy's and Superpave rutting parameters are similar in terms of increasing and decreasing trends of rutting performance for different additives.

The SBS modified binder with ZycoTherm and Kling Beta (in Figure 3.9(a)) show a significant increase of the Shenoy's rutting parameter. In contrast, the addition of Pave Bond and AD-Here show the loss in the Shenoy's rutting parameter similar to the Superpave rutting parameter (Figure 3.7(a)). Figure 3.9(b) shows no significant difference in rutting resistance with the change of additives dosages among all Gilsonite modified binders. However, Gilsonite with 0.1% ZycoTherm SP2 shows the highest rutting resistance. For Pave Bond and AD-Here, the loss of rutting resistance is observed with the increase of dosage. It can also be stated that Shenoy's parameter shows a higher value of rutting resistance compared to the Superpave rutting parameter.

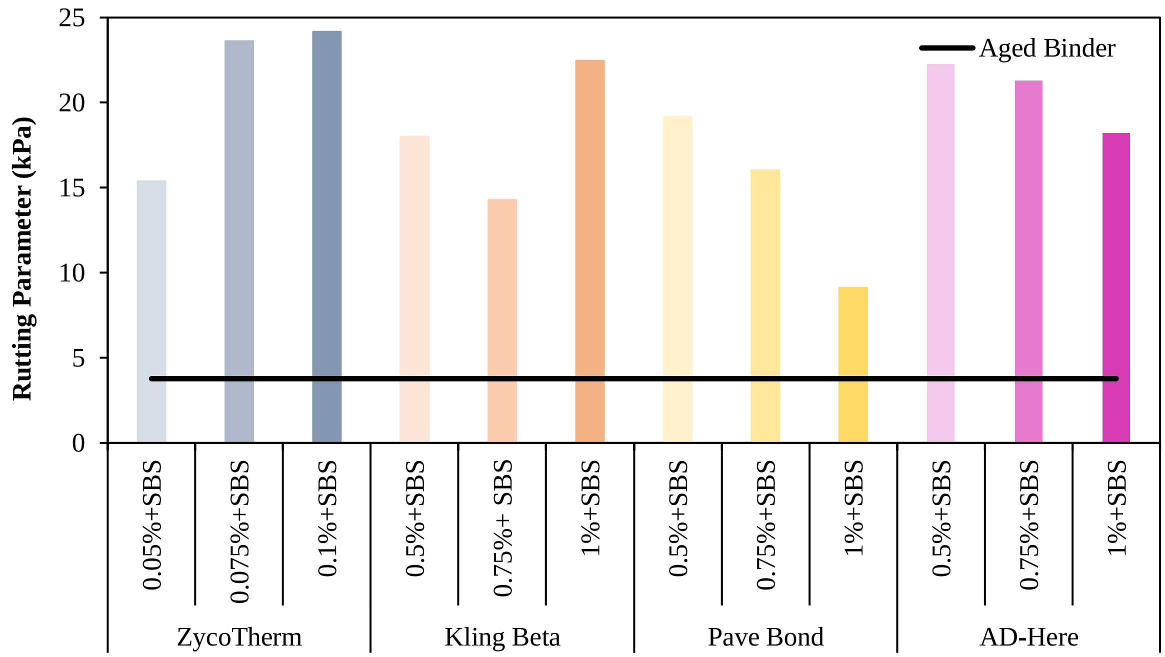


(a)

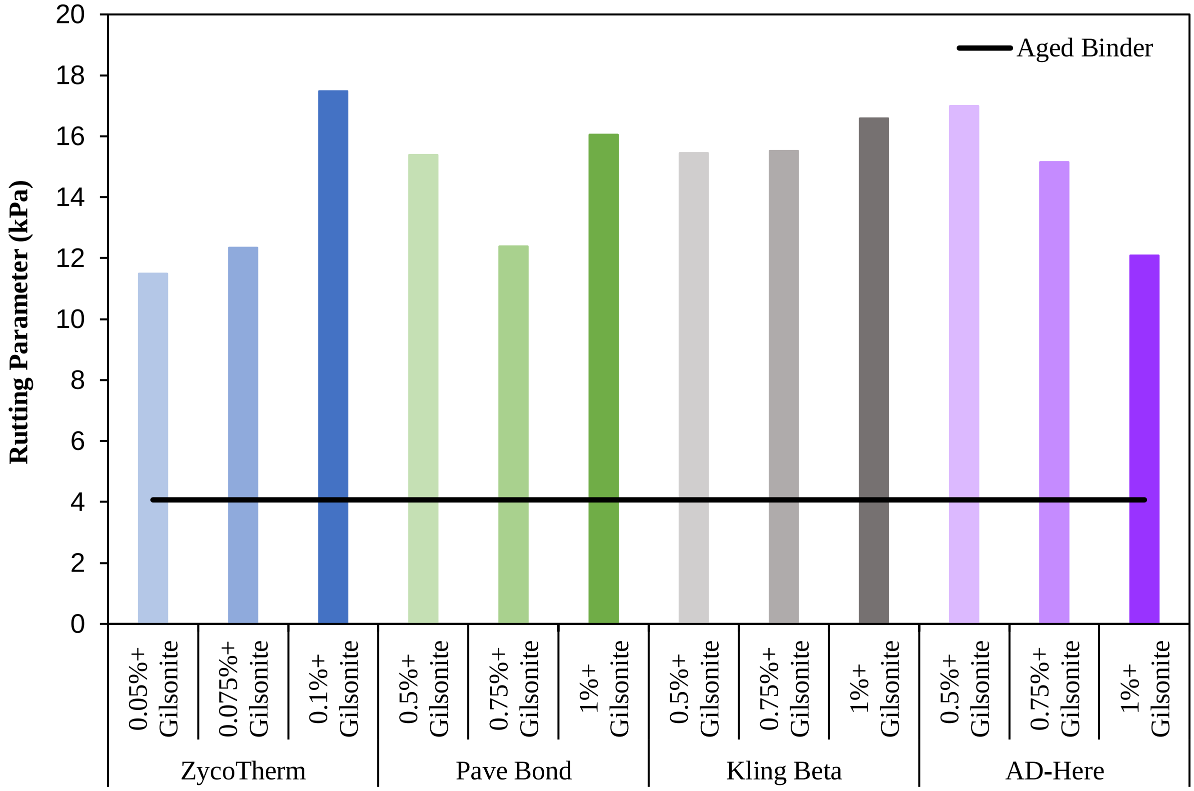


(b)

Figure 3.8: Black Space Diagram of Shenoy's Parameter (a) SBS and (b) Gilsonite modified binders



(a)



(b)

Figure 3.9: Evaluation of Shenoy's Parameter (a) SBS and (b) Gilsonite modified binders

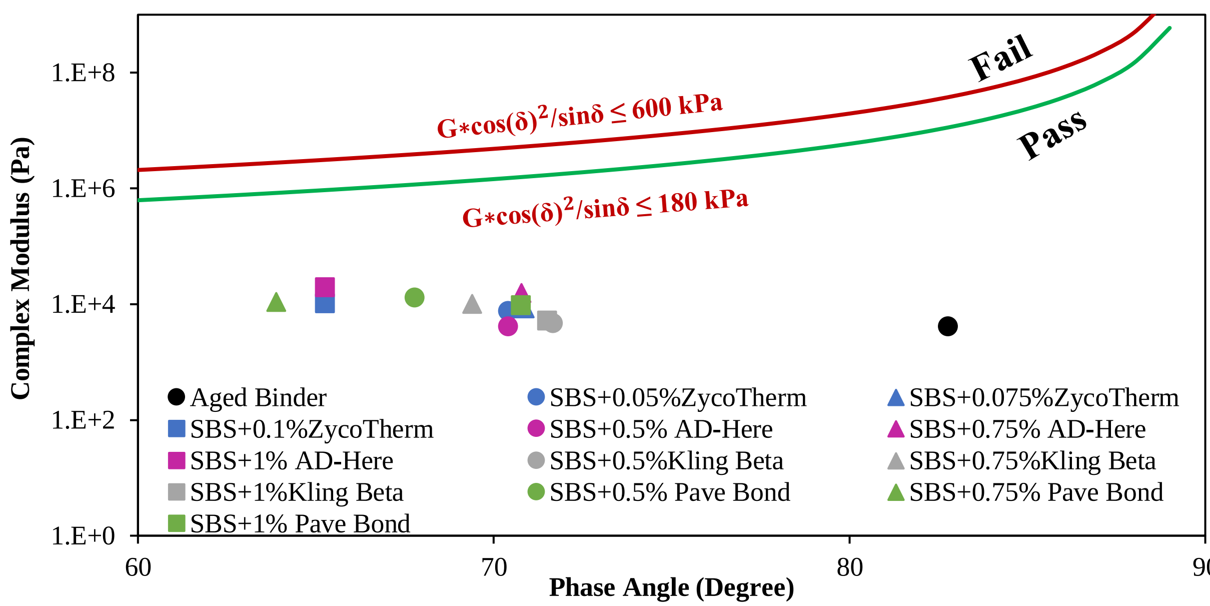
3.6.4 Glover-Rowe Parameter

The Glover-Rowe parameter was measured using the DSR frequency sweep test data. Using these data again, the CA model was applied to develop master curves. Finally, the complex shear modulus G* and phase angle δ were calculated at 15ºC and 0.005 rad/s reduced frequency. This low frequency is challenging to achieve with the DSR testing equipment. Therefore, the CA model was applied to develop master curves at a reference temperature of 15°C to obtain the G* and δ values at 0.005 rad/s.

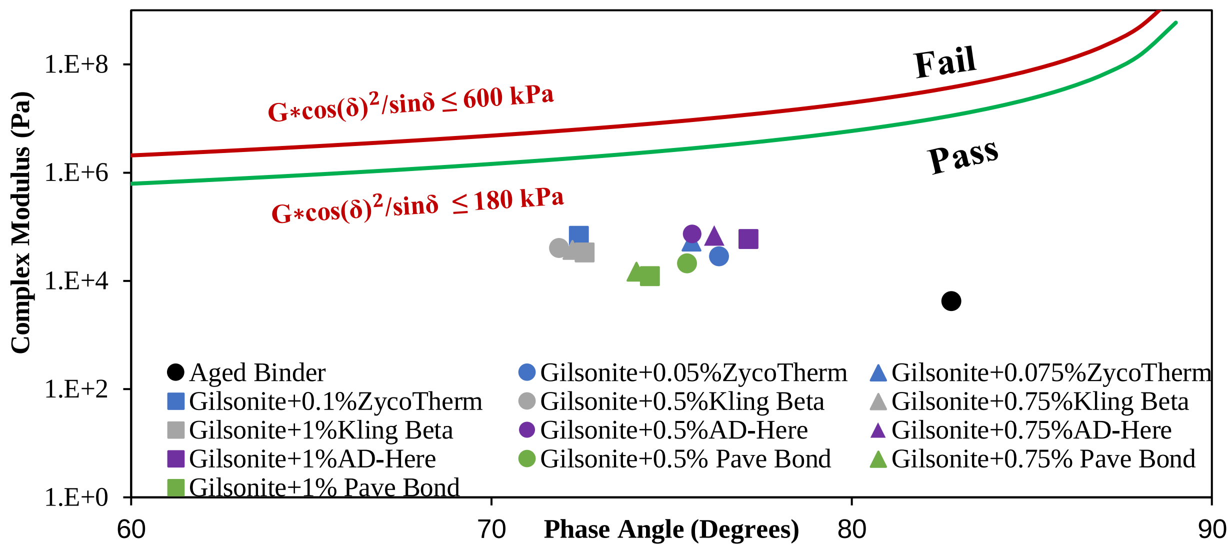
Damage warning: $G^*(\cos\delta)^\wedge 2/\sin\delta = 180$ kPa .... (4)

Damage limit: $G^*(\cos\delta)^\wedge 2/\sin\delta = 600$ kPa .... (5)

The G-R parameter of the SBS and Gilsonite modified binders in the Black Space Diagram are presented in Figure 3.10 (a) and (b), respectively. The G-R parameter location for each SBS and Gilsonite modified aged binders in Black Space Diagram passed the Glover-Rowe damage criteria. The result shows that cracking resistance increases with additives concentration in SBS and Gilsonite modified binders. Exceptionally, SBS and Gilsonite modified binders with ZycoTherm show decreased cracking performance with the increase of dosages. The only result the G-R parameter definitively shows is that the SBS improves cracking resistance relative to the Gilsonite. In SBS modified binders, the presence of polybutadiene components in SBS allows it to completely swell with the lighter parts of asphalt to form a network structure, which increases the flexibility of the binder and the cracking resistance of SBS modified binders.



(a)

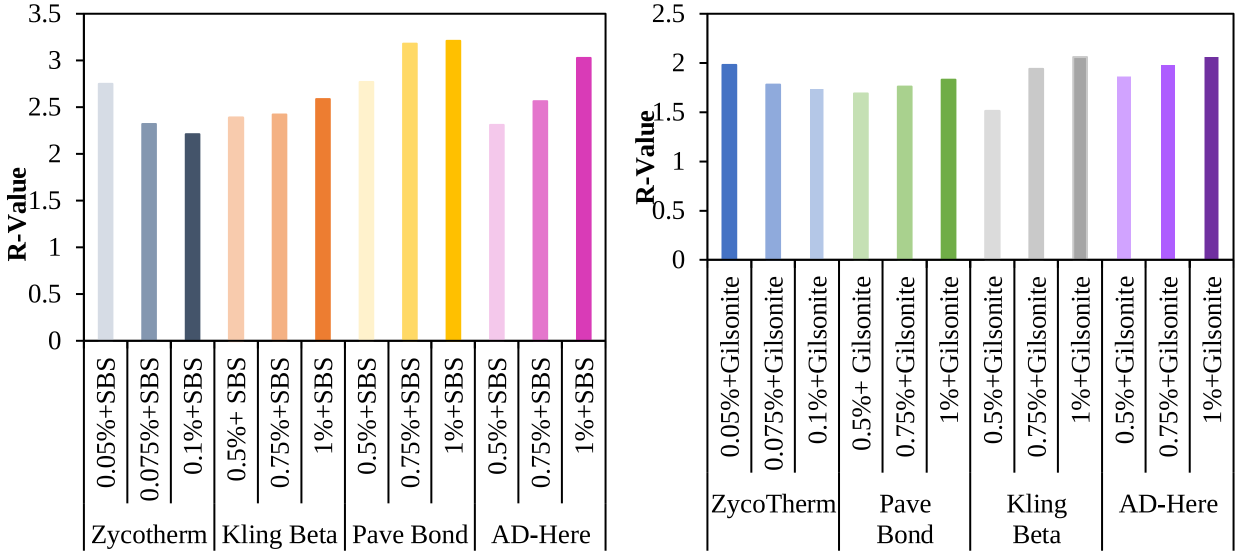


(b)

Figure 3.10: Black Space Diagram of G-R parameter (a) SBS and (b) Gilsonite modified binders

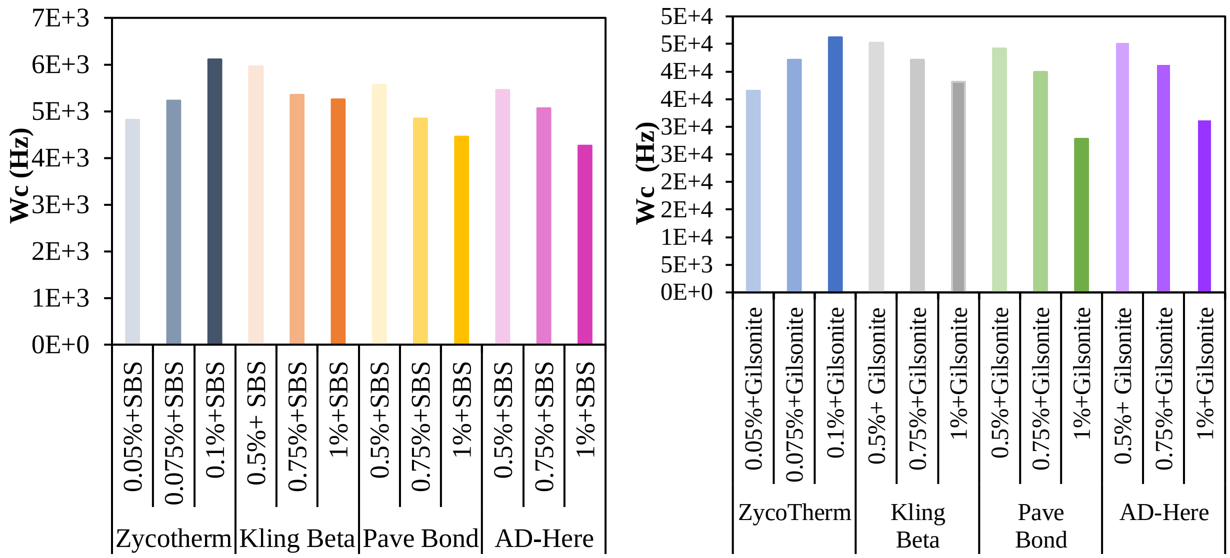
3.6.5 Rheological Index (R) and Crossover Frequency (W_c)

Typically, a lower R-value with a higher crossover frequency is the most desirable combination of a binder with good cracking resistance. The R and W_c are obtained from the CA-based master curve at the 15ºC reference temperature. Figure 3.11 (a) and (b) show the R-value of SBS and Gilsonite modified binders, respectively. The result shows that the addition of anti-stripping additives in SBS and Gilsonite modified binder causes the increase of the rheological index. Usually, a larger R follows with a flattening of the curve, i.e., more elastomeric behavior (Figure 3.4). The result shows that the SBS improves cracking resistance relative to the Gilsonite, almost similar to the G-R parameter analysis (Figure 3.10). From Figure 3.12, it can be seen that W_c decreases with the increase of additives' concentration in SBS and Gilsonite modified binders with the exception. However, the interactions between the SBS/Gilsonite and additives may be playing a role here. Still, there is no specific pattern of improving cracking resistance detected compared to the aged binder. Again, SBS is the most significant influencer on this parameter.



(a) **(b)**

Figure 3.11: Rheological Index (a) SBS and (b) Gilsonite modified binders



(a) **(b)**

Figure 3.12: Crossover Frequency (a) SBS and (b) Gilsonite modified binders

3.7 Conclusions

Based on the experimental results of the present study, the following conclusions can be drawn.

- The Master curve of the aged SBS modified binders with three anti-stripping additives under this study showed the flattening pattern. With the addition of additives, the binder becomes softer. As a result, the complex modulus decreases. On the contrary, Gilsonite modified binders displayed no significant change in stiffness value when dosage rates were increased. Exceptionally, Gilsonite modified binders with 1% Kling Beta, 0.5% AD-Here and 0.1% ZycoTherm showed slightly increased stiffness at higher loading frequencies than the aged binder.
- For the phase angle, all SBS modified aged binders exhibited improved elastic behaviour compared to the unmodified aged binder. In contrast, Gilsonite modified aged binders with anti-stripping additives exhibited viscous behaviour compared to SBS modified binders.
- Based on Shenoy's rut parameter analysis, all SBS and Gilsonite modified binders passed the rutting criterion line. Almost all SBS modified binders showed better rutting resistance compared to the Gilsonite modified binders. Among all binders, SBS + 0.1% ZycoTherm showed the highest rutting resistance. In comparison, Gilsonite + 0.1% ZycoTherm also exhibited the highest rutting resistance among all Gilsonite modified binders only.
- Analysis of Superpave and Shenoy's rutting parameters showed a similar increasing and decreasing trend in the rutting performance of binders. Between Shenoy's and Superpave rutting parameters, it was also observed that the Shenoy's parameter shows a higher value of rutting resistance than the Superpave rutting parameter.

- The G-R parameter to evaluate the fatigue cracking resistance showed that binders become softer with the increase of additives' concentration and exhibited higher cracking resistance. Exceptionally SBS and Gilsonite modified binders with ZycoTherm showed decreased cracking performance with the increase of dosages, respectively. The only result the G-R parameter definitively showed is that the SBS improves cracking resistance relative to the Gilsonite with the anti-stripping additives.
- R and W_c expressed similar characteristics to those of the G-R parameter. But there is no specific pattern of improving cracking resistance is detected based on the R and W_c analysis.

3.8 Acknowledgments

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3.9 Author Contributions

The authors confirm their contribution to the paper as follows: Towhidul Islam and Dr. Kamal Hossain designed the experiments, analyzed the data, prepared the manuscript, and reviewed the manuscript. Mike Aurilio contributed the materials and conducted laboratory tests. Dr. Carlos Bazan and Gary Caul carefully reviewed and improved the manuscript. All authors reviewed the results and approved the final findings of this study.

3.10 Declaration of Conflicting Interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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Chapter 4: MSCR Analysis of SBS and Gilsonite Modified Asphalt Binders

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4.1 Abstract

During the service life, asphalt pavement experiences various surface distresses due to aging, the effect of environmental factors, and traffic loading. Premature failure is a frequent phenomenon in the bituminous concrete pavement. With time, the demand and expenses of bituminous material are increasing and with the rapid increase of traffic, the life cycle of pavement is deteriorating and causing aging, rutting, and thermal cracking problems. A way to mitigate the early deterioration of asphalt pavement is to blend suitable modifiers and additives with asphalt binders during asphalt mixture production. However, the pavement is more susceptible to rutting when mixed with asphalt additives due to the softening effect of the additives. The current study focuses on evaluating the relative effect of different dosages of additives with SBS and Gilsonite modification on the rutting and elastic recovery properties of aged asphalt binders. Four different anti-stripping additives: ZycoTherm SP2 (0.05%, 0.075%, and 0.1%), Kling Beta 2914 (0.5%, 0.75%, and 1%), Pave Bond Lite (0.5%, 0.75%, and 1%), and AD-Here (0.5%, 0.75%, and 1%) were selected for this study. The multiple stress creep recovery (MSCR) test is a widely used method to evaluate the rutting resistance in the Superpave performance grading (PG) system. This study summarizes the results MSCR test by considering the rutting and elastic recovery parameters, such as non-recoverable creep compliance value at 3.2 KPa, stress sensitivity analysis, and percent recovery

analysis to evaluate the resistance against rutting of the SBS and Gilsonite-modified asphalt binders. Comparative rutting parameter analysis showed that SBS and Gilsonite modified binders enhance the rutting resistance of asphalt binders.

4.2 Introduction

In North America, over 82% of the population lives in metropolitan areas. According to the UN report, by the middle of this century, this could have risen up to 90% (United Nations Department of Economic and Social Affairs, 2018). As a result, roads and highways play a critical role in satisfying the needs of the future in terms of economic growth and development. Over the last few decades, the need to develop a more sustainable form of pavement construction has led to a surge in the usage of asphalt materials. In Canada, asphalt surfacing is used to pave around 90% of the roads (Virginia Asphalt Association, 2020). However, the presence of certain conditions, such as water penetration, traffic loading, and the poor characteristics of the asphalt binder and aggregate particles, may cause the bonding between binder and aggregate particles to break (Baldi-Sevilla et al., 2017; Kringos et al., 2008; Yan et al., 2015). This is also known as stripping. Asphalt binder and aggregate are the two main components in asphalt pavement. The bond between asphalt binder and aggregate is primarily liable for ensuring excellent performance. Further damage from stripping might include rutting, corrugations, cracking etc., leads to the eventual failure of the asphalt pavement. Therefore, preventing the stripping problem in asphalt pavement is critical (Canestrari et al., 2011; Mehrara & Khodaii, 2013).

The Hot Mix Asphalt (HMA) must be resilient to endure the pavement distress and prevent premature permanent deformations. Many researchers found that the use of anti-stripping agents (ASA) and modifiers with asphalt binders can improve rutting resistance, stripping resistance (moisture damage), and mixture durability. Therefore, a wide variety of materials may be used to modify the behaviour or properties of asphalt. Several researchers have suggested that applying anti-stripping agents to asphalt pavement can reduce the amount of stripping that occurs (Cheng et al., 2011; Xiao et al., 2010). Moreover, according to another study, the use of liquid anti-stripping agents containing aliphatic amines can improve the stripping and rutting resistance of asphalt mixtures (Park et al., 2017). The current study aims to evaluate the relative effect on the rheological properties of the Gilsonite modifier containing different anti-stripping agents.

With the incorporation of modifiers, the thermal susceptibility, rutting resistance, and fatigue cracking properties of the binder can be significantly improved (Yildirim, 2007). Using polymer modifiers is the most successful practice to resist excessive plastic deformations at high temperatures (Airey, 2002). Among them, styrene butadiene styrene (SBS) block copolymers, styrene-butadiene-rubber (SBR), high-density polyethene (HDPE), and ethylene-vinyl-acetate (EVA) are the most commonly used modifiers. The use of SBS polymer enhances the resistance against moisture-induced damage of HMA (Alata & Ethem, 2013), resistance against rutting and cracking as well (Ahmed et al., 2021), which may double the pavement's service life (Iskender et al., 2012). Gilsonite is a naturally occurring deposit of the black and brittle mineral bitumen. It is also known as asphaltite, the most widely used bitumen resource in the market. Another unique feature of Gilsonite is that it has a good affinity for asphalt (Liu & Li, 2008). In addition, Gilsonite has approximately 50 times higher rigidity than conventional bitumen, which is due to its higher softening point. Researchers found that Gilsonite and SBS had an essentially identical effect on the resistance against rutting. It also concludes that adding Gilsonite to the mix enhances high-temperature rutting performance (Mirzaiyan et al., 2019). However, A common drawback of Gilsonite-modified binders is the development of cracks due to their brittle behaviour at low temperatures, which has a negative effect on performance at low temperatures (Rajbongshi & Das, 2009).

Hence, this study covers the laboratory evaluation using MSCR parameters, such as the non-recoverable creep compliance, stress sensitivity analysis, and percent recovery analysis. These parameters were evaluated for short-term aged SBS and Gilsonite modified binders (4% and 10% by the weight of the base binder, respectively) containing anti-stripping agents. Four different anti-stripping agents: ZycoTherm SP2 (0.05%, 0.075%, and 0.1%), Kling Beta 2914 (0.5%, 0.75%, and 1%), and Pave Bond Lite (0.5%, 0.75%, and 1%) and AD-Here (0.5%, 0.75%, and 1%) were chosen for this study.

4.2.1 Multiple Stress Creep Recovery Test (MSCR)

The multiple stress creep recovery test, often known as the MSCR test, was recently approved for use in the Superpave performance grading (PG) system in order to improve the rutting evaluation. This test uses the creep-recovery concept to evaluate the binder's permanent deformation behaviour (Singh & Kataware, 2016). The percentage of recovery and the amount of non-recoverable creep compliance are two important criteria that derive from the MSCR test. The non-recoverable creep compliance (Jnr) is calculated to evaluate the deformation as per the AASHTO M 332. A non-recoverable creep compliance, which is measured at 3.2 kPa, can be used to estimate how resistant an asphalt binder is to permanent deformation when subjected to conditions of repetitive loading. A lower value of J_{nr} implies a lower rate of deformation that can lead to higher rutting resistance (Wasage et al., 2011). Previous research has shown that this J_{nr} is a better indicator for rutting potential when compared to the Superpave Rutting parameter. As such, some states within the United States of America have begun adopting AASHTO M 332 as their standard specification. This test uses the non-recoverable creep compliance (J_{nr}), stress sensitivity and the percentage of recovery obtained (Singh & Kataware, 2016). This test has been proven to correlate more precisely with the rutting performance of asphalt mixtures than the conventional Superpave criteria. In this study, the non-recoverable creep compliance (Jnr) and stress sensitivity were calculated to evaluate the deformation as per the AASHTO M 332 (AASHTO M 332, 2021). AASHTO M 332 specifications classify the binders as E, V, H or S, as shown in Table 4.1, based on the Jnr value at 3.2 kPa.

Table 4.1: AASHTO M 332 specification

AASHTO M 332 specification	Binder Classification	Meaning	Jnr value at 3.2 kPa (1/kPa)
Greater than 30 million ESALs and < 20 km/h	E	Extreme High	0.0–0.5
Greater than 30 million ESALs or < 20 km/h	V	Very High	0.5–1.0
Between 10 and 30 million ESALs or 20–70 km/h	H	High	1.0–2.0
<10 million ESALs and ＞70 km/h	S	Standard	2.0–4.5

4.3 Objectives

The main objectives of this study include:

- Investigating the rutting performance of SBS and Gilsonite modifiers containing anti-stripping agents at different dosages using MSCR analysis
- Evaluating the effects of rutting performance of SBS and Gilsonite modified binders using the non-recoverable creep compliance, stress sensitivity analysis, and percent recovery analysis.

- Evaluating the effect of asphalt additives and modifiers on the elastic recovery of the aged binder
- Finding the optimum dosage which will increase the elastic recovery and rutting resistance.

4.4 Materials and Methods

4.4.1 Asphalt Binder, Modifiers and Anti-stripping Additives

PG 58-28 as the control binder was used in this study, supplied by Pyramid Construction Ltd. PG 58-28 is used in the province of Newfoundland and Labrador, Canada. In this study, SBS and Gilsonite were used as a modifier, obtained from the Yelloline Asphalt Products Limited and American Gilsonite Company, respectively. Four different anti-stripping agents were used in this research. The anti-stripping agents used included: ZycoTherm SP2, Kling Beta 2914 (Redicote C-2914), Pave Bond Lite, and AD-Here were obtained from Zydex Industries, Nouryon, and Yellowline Asphalt Products Limited, respectively.

4.4.2 Blending Modifiers and Anti-stripping Additives with Asphalt Binder

In this study, SBS and Gilsonite modified binders were used to examine the improvement of rutting resistance. SBS modified binder was provided by Yellowline Asphalt Products Limited, where 4% linear SBS polymer (by the weight of binder) was used. For Gilsonite modification, pure bitumen was preheated at 180°C initially. After that, 10% Gilsonite powder (by the weight of the base binder) was blended into a neat binder at 180°C for 90 minutes with the help of a magnetic stirrer (illustrated in Figure 4.1(a)). Further, SBS and Gilsonite modified asphalt binder was mixed with four types of liquid anti-stripping agents: ZycoTherm SP2 (0.05%, 0.075%, and 0.1%), Pave Bond Lite (0.5%, 0.75%, and 1%), Kling Beta 2914 (0.5%, 0.75%, and 1%), and AD-Here (0.5%, 0.75%, and 1%). The blending process was conducted using a magnetic stirrer for 30 minutes at

180ºC. Finally, the Rolling Thin Film Oven Test (RTFOT) was employed to prepare the short-term aged binders as per AASHTO T240 protocol. Figure 4.1(b) presents the samples prepared to fulfill our research goal.

(a) **(b)**

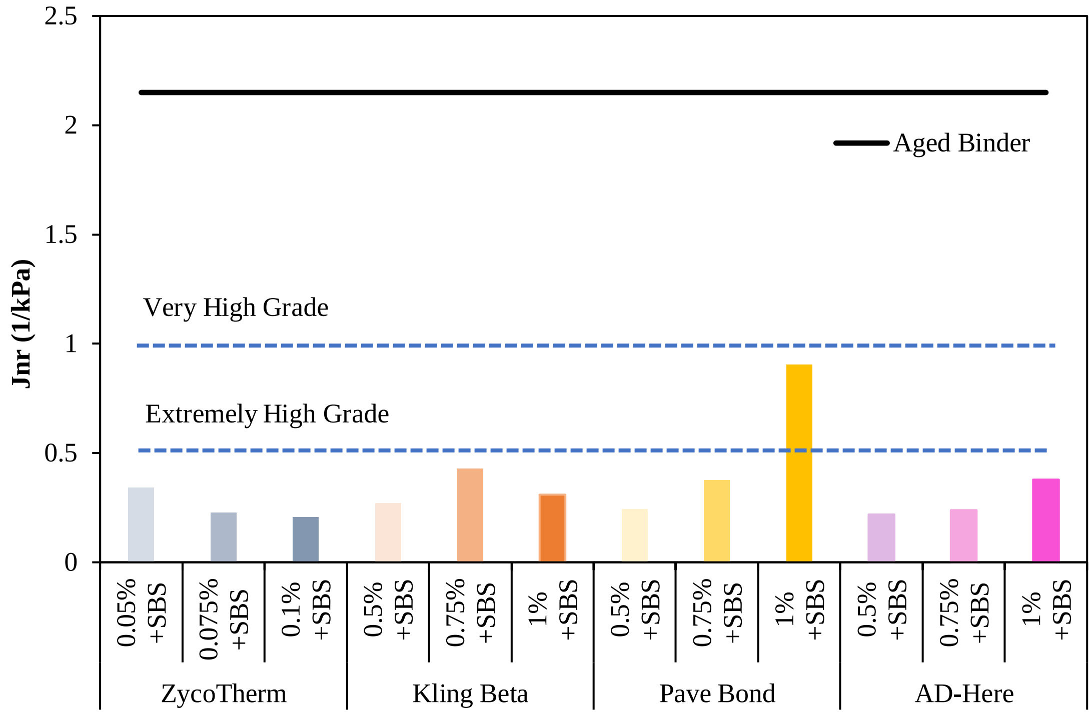
Figure 4.1: (a) Sample Preparation Using Magnetic Stirrer and (b) Samples Prepared for RTFOT and MSCR Test

4.5 Results and Discussion

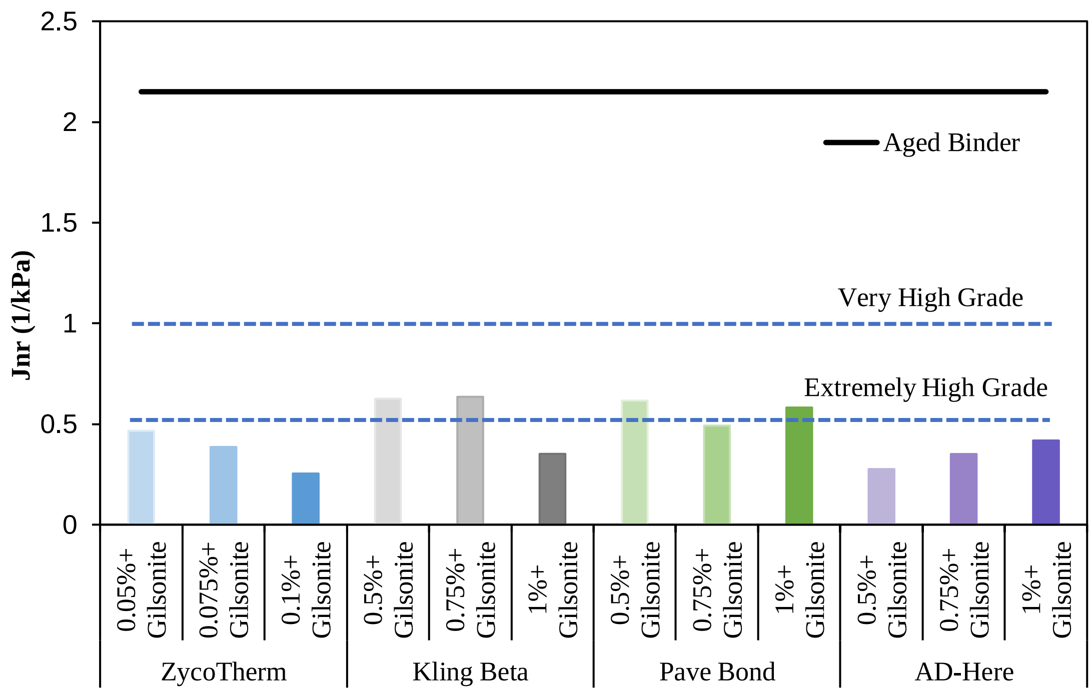
4.5.1 Non-recoverable Creep Compliance (Jnr) at 3.2 kPa

The non-recoverable creep compliance (Jnr) is calculated to evaluate the deformation as per the AASHTO M 332. In asphalt binder testing, the Jnr (measured at 3.2 kPa and 58ºC) was used to determine the resistance of an asphalt binder to permanent deformation when subjected to repeated loading conditions. A lower value of Jnr implies a lower rate of deformation that can lead to higher rutting resistance (Wasage et al., 2011). Figure 4.2 (a) and (b) show the Jnr values at 3.2 kPa for SBS and Gilsonite modified binders containing different anti-stripping additives, respectively. The Jnr value of the aged binder was found to be 2.15 kPa^{-1}. With the addition of varying doses of the anti-stripping agent, Jnr value also changed accordingly. The aged binders modified with anti-stripping agents show better rutting performance than the aged binder as the value of Jnr is less than 2.15 kPa^{-1}. With the modification of SBS, it is expected that there would be a reduction of the Jnr value of the aged SBS modified binder with the percentages of anti-stripping agents (Figure 4.2 (a)). For the Pave bond lite and AD-Here, the Jnr value increases with the increase of additives' concentration, which indicates the decrease of rut resistance. Among all SBS modified binders, the maximum Jnr value is found for 1% of Pave Bond Lite, which indicates the least rut performance. However, SBS with 0.1% ZycoTherm exhibits the best rutting performance as the value of Jnr is minimum.

From Figure 4.2 (b), it is evident that all Gilsonite modified binders show little significant difference in rutting resistance with the change of additive dosages. However, Gilsonite modified binders with ZycoTherm, and Kling Beta show a regular increasing pattern of rutting performance with the increase of concentration. Where Pave Bond lite and AD-Here show a decreasing pattern of rutting performance with the increase of concentration. Here, the best rutting performance can be observed for Gilsonite with 1% ZycoTherm and 0.5% AD-Here, respectively. According to AASHTO M 332, all SBS modified binders (except SBS+1% Pave Bond) can be graded for 'Extremely High Grade.' Similarly, Gilsonite with ZycoTherm (0.05%,0.075%,0.1%), AD-Here (0.5%,0.75%,1%), Kling Beta (1%) and Pave Bond (0.75%) can be graded for 'Extremely High Grade', respectively. The rest of the modified binders can be graded for 'Very High Grade.'



(a)



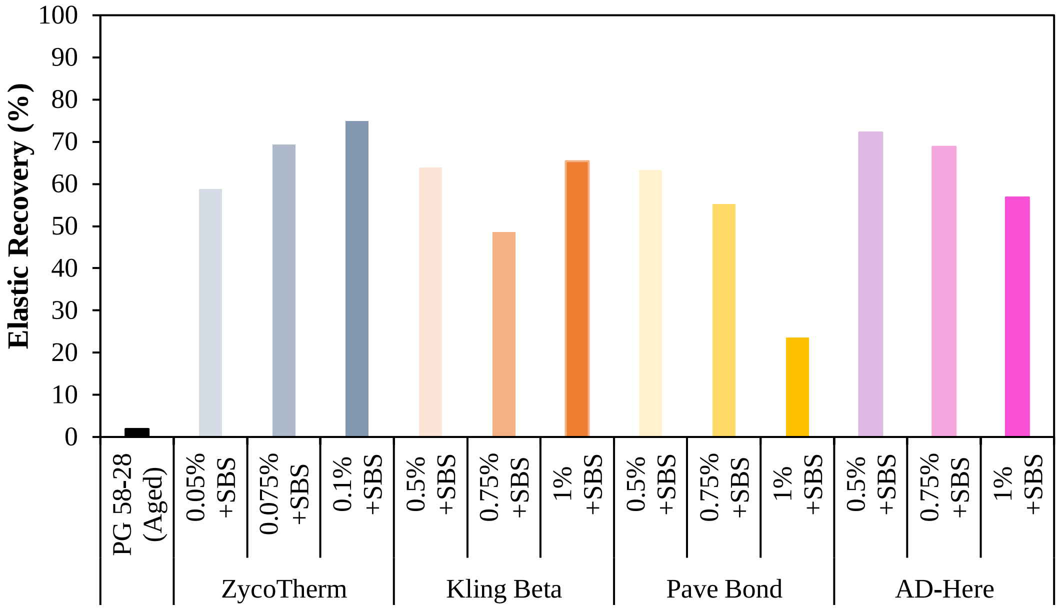
(b)

Figure 4.2: Jnr of (a) SBS and (b) Gilsonite modified binders

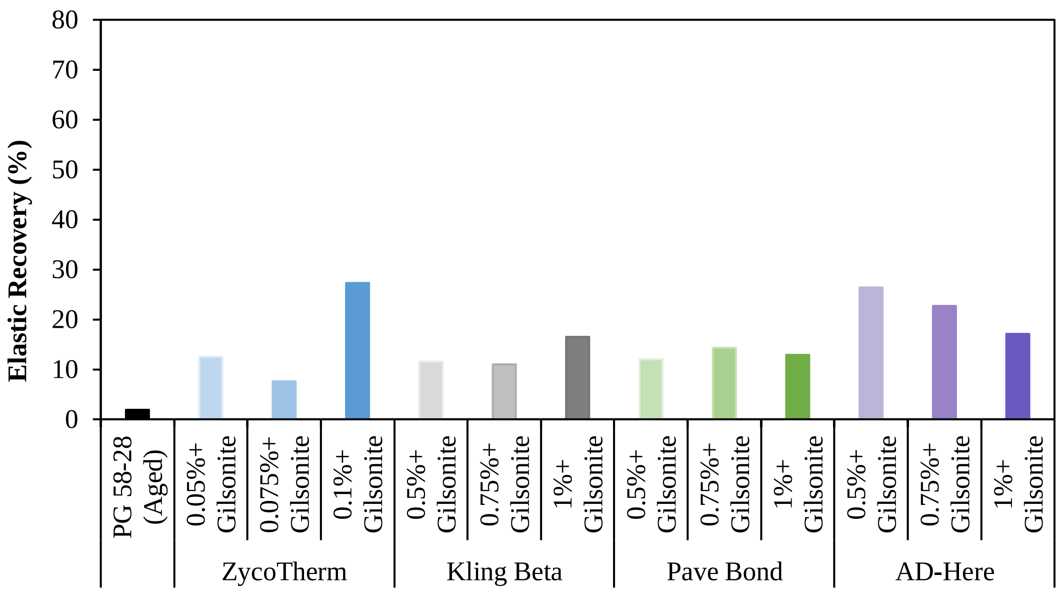
4.5.2 MSCR Percent Elastic Recovery (R%)

It is appropriate to measure the rutting resistance of the asphalt binder using the MSCR test because it can simulate field conditions of pavement in terms of loading. This test consists of creep loading for 1 second and recovery for 9 seconds over multiple stress levels ranging from 0.1 to 3.2 kPa. The nonrecoverable creep compliance is calculated by taking the average non-recovered strain from all 10 creep and recovery cycles and corresponding applied stress in each of those cycles. In addition, the average percent recovery (R%) can be another indicator of the elasticity of the asphalt binder. It can be measured from the average ratio of recovered strain to maximum strain in each cycle. The combination of a lower nonrecoverable creep compliance (Jnr) and a higher average percent recovery (R) implies that the asphalt binder has a higher level of rutting resistance.

In general, SBS is a thermoplastic elastomer polymer, which behaves like elastomeric rubbers to improve the elastic behaviour of the binders. This characteristic helps to reduce the permanent deformation of the SBS modified binders. Overall, SBS and Gilsonite modified binders with 1% ZycoTherm SP2 showed the best elastic recovery, respectively (illustrated in Figure 4.3). On the other hand, it is evident that all Gilsonite modified binders show little difference in elastic recovery with the change of additive dosages (illustrated in Figure 4.3 (b)). From analysis, among all modified binders, SBS modified binders with the anti-stripping agent showed better elastic recovery than the Gilsonite modified binders.



(a)



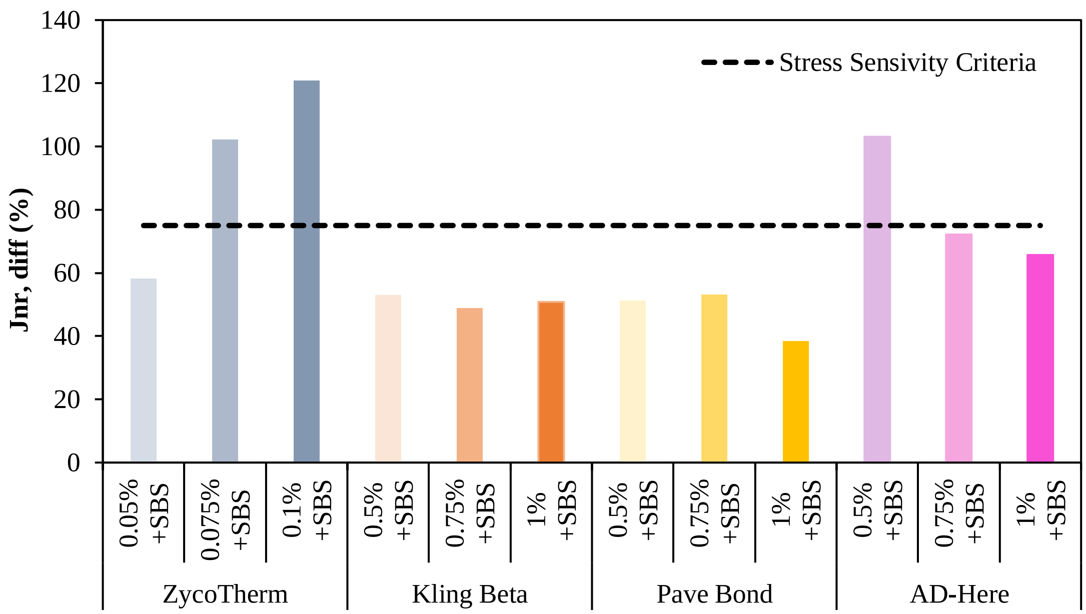
(b)

Figure 4.3: Percent Elastic Recovery of (a) SBS and (b) Gilsonite modified binders

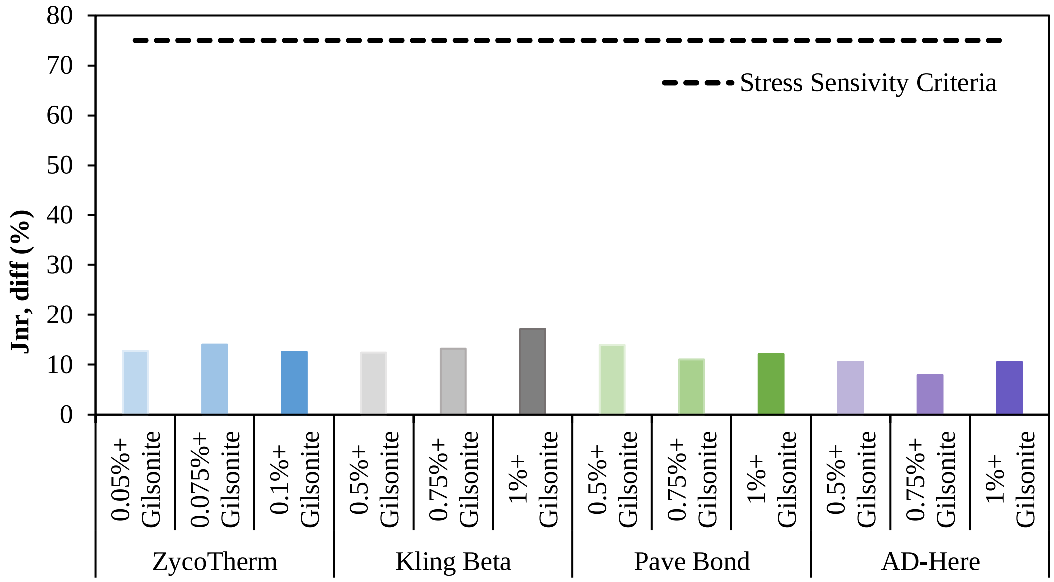
4.5.3 Jnr Difference

MSCR test not only allows the assessment of the nonlinearity of asphalt binder response but also identifies the excessive stress sensitivity of asphalt binders in the nonlinear range. The stress sensitivity, Jnr -diff, is the difference between the Jnr value at stress levels of 3.2 kPa and 0.1 kPa, as defined in Equation 1 (Wasage et al., 2011), is utilized as an indicator of stress-sensitivity of asphalt binders. According to AASHTO M 322, Jnr -diff should not exceed 75%. If it crosses this limit then, the asphalt binder may fail when experiencing higher stress or higher temperature in real-world which is different from the consideration in the laboratory (AASHTO M 332, 2021). From Figure 4.4, it is evident that the Jnr -diff value of all Gilsonite modified binders is less than 75% where some of the SBS modified binders show Jnr -diff value more than 75%.

$$J_{nr,diff} = \frac{J_{nr,3.2kPa} - J_{nr,0.1kPa}}{J_{nr,0.1kPa}} \times 100\% \quad (1)$$



(a)



(b)

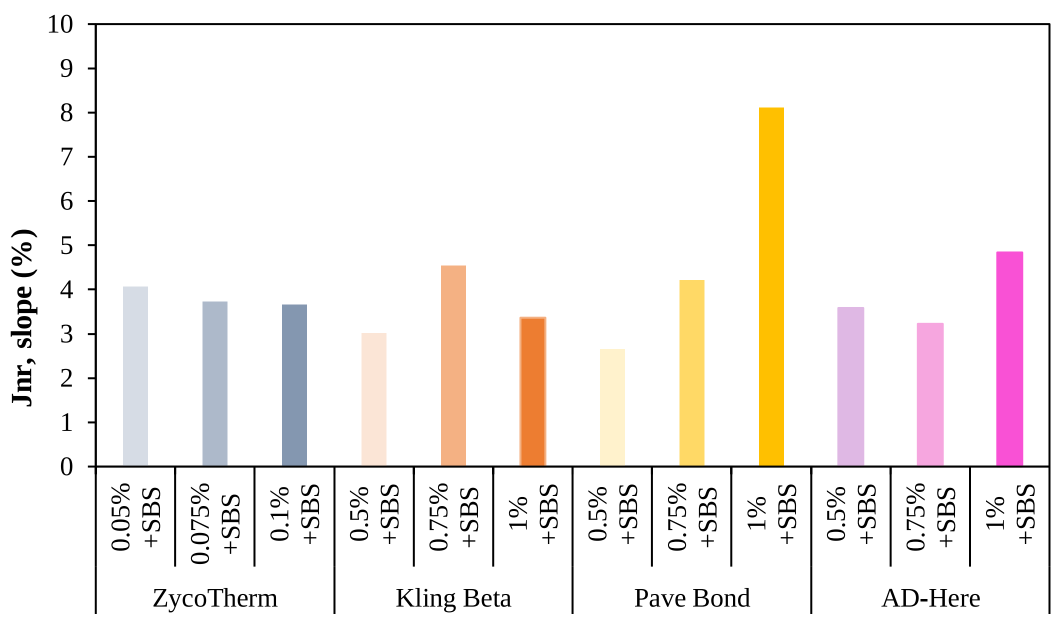
Figure 4.4: Jnr, diff of (a) SBS and (b) Gilsonite modified binders

4.5.4 Jnr Slope

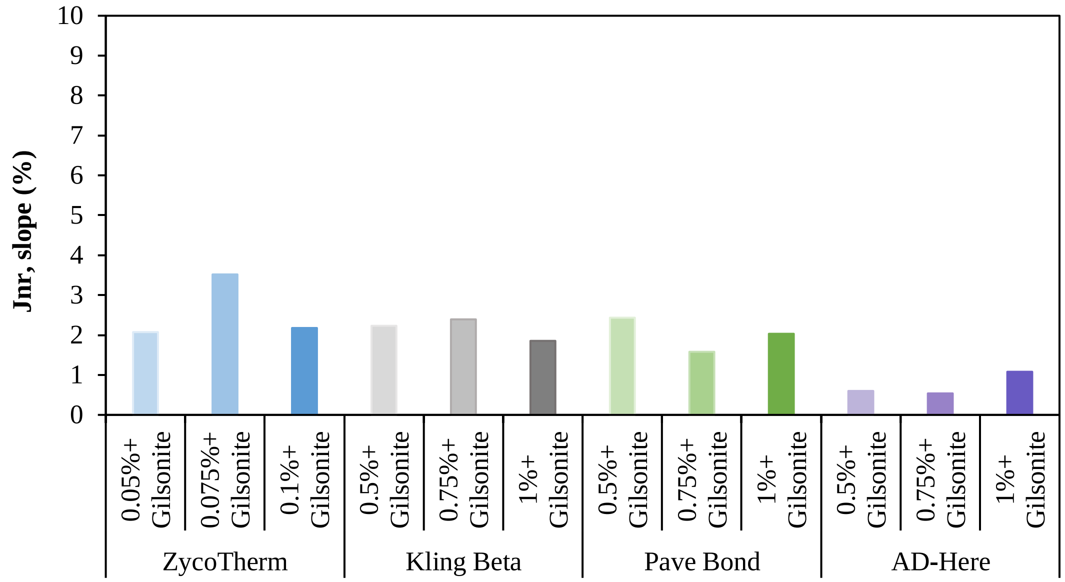
Initially, as an indicator of the stress sensitivity of asphalt binders, the percent difference in non-recoverable creep compliance obtained from the MSCR test was used. However, it is a matter of concern that there is no correlation between the percent difference and the field performance (Gaspar et al., 2019). MSCR test is widely used, and many researchers are concerned about the applicability of this 75% limit (Behnood & Olek, 2017; Laukkanen et al., 2015). A wax-modified asphalt binder has a Jnr difference value of more than 75% (Laukkanen et al., 2015). According to the previous method of stress sensitivity analysis, this binder should be eliminated from road construction as it was considered highly stress-sensitive. However, from the analysis, it was found that the Jnr value at 3.2 kPa was very small, which implies this binder was very rut resistant. Therefore, a contradiction arises between non-recoverable creep compliance and the percent difference. As a result, some researchers suggested that the percent difference criterion was not universally applicable (Behnood & Olek, 2017). Moreover, asphalt binders are highly dependent on the modifier type and the testing conditions.

Stemphihar et al. (2018) provided a promising approach for the analysis of stress sensitivity. This proposed parameter is denoted as the Jnr-slope. Then Equation 2 is used to calculate the stress sensitivity. This new approach does not unfairly penalize modified asphalt binders with low Jnr at 3.2 kPa and provides an equivalent assessment of stress sensitivity. In this study, all SBS and Gilsonite modified binders show that the Jnr-slope is also less than 75% as shown in Figure 4.5.

$$J_{nr,slope} = \frac{J_{nr,3.2kPa} - J_{nr,0.1kPa}}{3.1} \times 100\% \quad (2)$$



(a)



(b)

Figure 4.5: Jnr, slope of (a) SBS and (b) Gilsonite modified binders

4.6 Conclusions

Based on the experimental results of the present study, the following conclusions can be drawn.

- Based on MSCR analysis, it is evident that all SBS modified binders with the anti-stripping agent showed better performance than the Gilsonite modified binders.
- For Gilsonite modified binders, Gilsonite + ZycoTherm indicated better rutting resistance than other Gilsonite modified binders. However, the SBS modified binder with 0.1% ZycoTherm SP2 showed the best rutting performance compared to all binders.
- The complex bonding mechanism of polystyrene and polybutadiene made the SBS durable and more restrained from external pressure or load. These outcomes help to enhance the stiffness and the rutting resistance of SBS modified binders.

- Finally, it can be concluded that the MSCR results show a similar rutting resistance trend along with Superpave and Shenoy's rutting parameters. The rutting parameter analysis indicated that Jnr, %R, Jnr-diff, Jnr-slope are more reliable rutting parameters because of its credible test condition.

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Chapter 5: Investigation on Surface Free Energy of Modified Asphalt Binders

Co-Authorship: The abstract based on the partial result of this chapter has been accepted to the Annual Conference of the Canadian Society for Civil Engineering (CSCE): Islam, T., Hossain, K., Aurilio, M., Bazan, C., & Caul, G. (2022), "Investigation on Rheological and Fundamental Behaviour of Gilsonite Modified Binders."

5.1 Abstract

Moisture damage is the most common phenomenon of bituminous concrete pavement. During the past few decades, massive research has been done to reduce the moisture susceptibility of asphalt pavements. A way to mitigate the early deterioration of asphalt pavement is to blend suitable modifiers and additives with asphalt binders during asphalt mixture production. The current study aims to understand the relative effect of different liquid anti-stripping additives and modifiers on the fundamental behaviors of modified asphalt binders. Four liquid anti-stripping additives: ZycoTherm SP2, Kling Beta 2914, Pave Bond Lite, and AD-Here, were used at different dosage rates. SBS and Gilsonite modified PG 58-28 binders were blended with these anti-stripping additives. Later, all binders were aged using Rolling Thin Film Oven (RTFO) protocol. Current study considers using the Surface Free Energy (SFE) as a fundamental material property to evaluate the cohesive bond strength of the SBS and Gilsonite modified asphalt binders. An optical contact angle analyzer was used to obtain the contact angle of all modified binders. Later, SFE components and the cohesive bond energy were calculated as per Good-van-Oss-Chaudhury's postulation. The results showed that aging reduces the SFE components and SBS/Gilsonite with anti-stripping additives improves the SFE components significantly. The results show that anti-stripping additives significantly affect the binders' fundamental properties, which can influence

the overall performance of the asphalt binder. Furthermore, our comparative analysis shows that SBS and Gilsonite modified binders containing liquid anti-stripping additives enhance the moisture damage resistance of asphalt binders.

5.2 Introduction

Flexible pavement is the most widely used pavement structure in Canada and other countries around the world. Since 2008, the number of roads in Canada has been going up due to rapid urbanization and economic growth, and by 2020, there is more than 1.08 million km of roads across the country (Road Transportation, n.d.). Out of those, 90% of roads are constructed with an asphalt mixture. Asphalt is a thermoplastic substance that exhibits viscoelastic properties under most pavement operating circumstances, making it a vital component of pavement performance. Bitumen is a mixture of several hydrocarbons with a high melting point. Several types of high-boiling point hydrocarbons are found in bitumen, including straight or branched chains, saturated and unsaturated ring hydrocarbons as well as aromatic hydrocarbons, which include sulphur, nitrogen, and oxygen. Internal interactions between molecules and ions in this complicated chemical structure lead to bitumen binder having low-energy surfaces to adhere to aggregate (Arno W. Hefer et al., 2006). As a viscoelastic and thermoplastic material, stress-strain characteristics of asphalt are both time and temperature-dependent. As a result, asphalt binder exhibits significant deformation with wheel load and temperature change. The Hot Mix Asphalt (HMA) must be resilient to endure these and prevent premature permanent deformations. Numerous studies have acknowledged that the use of asphalt additives and modifiers with asphalt binders can improve rutting resistance, stripping resistance (moisture damage), and mixture durability.

Moisture damage can be defined as 'the progressive functional deterioration of a pavement mixture by loss of the adhesive bond between the asphalt binder and the aggregate surface and/or loss of the cohesive resistance within the asphalt binder principally from the action of water' (Kiggundu & Roberts, 1988). Moisture damage significantly reduces the strength of the asphalt mixture, ultimately resulting in a significant reduction in pavement performance. There are several ways in which moisture damage can occur, including adhesive failure between bitumen (bitumen-filler mastic) and aggregates, cohesive failure within bitumen (bitumen-filler mastic), and cohesive failure within aggregates (S. Kim & Coree, 2005). In most cases, moisture in asphalt pavements causes the asphalt film to separate from the aggregate particles, resulting in what the pavement community refers to as stripping. In the case of asphalt pavement, stripping causes various distresses, such as thermal and fatigue cracking, rutting, raveling, and bleeding. Moisture transport is the first step in the process of moisture damage, which eventually results in a decrease of cohesion and adhesion in asphalt concrete. This moisture can be transported in asphalt concrete by three ways: infiltration of water from the surface (permeability), capillary rise, and/or vapor diffusion (Masad et al., 2007).

Since 1932, researchers have been examining the aggregate-binder contact when it is exposed to moisture (Caro et al., 2008a). The presence of moisture in flexible pavements is one of the most significant causes of premature deterioration. Damage induced by moisture in asphalt pavement is defined as moisture-induced loss of the mechanical characteristics of asphalt concrete (Lytton et al., 2005b). It was not until the 1960s that moisture damage was first noticed as a serious problem for flexible pavement (Sebaaly et al., 2003). However, In the early 1980s, highway agencies began to pay attention to the damage caused by moisture (Caro et al., 2008b). Initially, visual inspection was employed to detect how much asphalt binder coating was lost from the aggregates' surface due to the action of water in an asphalt mixture. Following that, empirical methods were developed to evaluate moisture damage in loose or compacted samples, which used a quantifiable performance parameter to assess moisture damage. Despite the improvements and developments of asphalt mixture design procedures and a better understanding of the mechanisms of moisture damage, it is still considered one of the most common and complex problems facing the pavement community (N. M. Wasiuddin et al., 2007).

In order to overcome this issue, anti-stripping additives have been specified by several agencies in an effort to promote adhesion at the aggregate–asphalt interface. The additives and modifiers consist of liquid anti-stripping additives (LAS), hydrated lime (HL), styrene-butadiene-styrene (SBS), SBS with LAS, and polyphosphoric acid with HL are some previously studied materials, which showed good resistance against moisture damage. Liquid anti-stripping additives act as a chemical surfactant, which reduces the surface tension of aggregate and provides better surface coverage. The asphalt binder plays an important role as a carrier of these liquid additives (Sebaaly, 2007). The majority of the chemical additives used in asphalt mixtures are composed of amines, which are basic elements obtained from ammonia. Because of their significant affinity for the silica compounds present in the aggregates, amines are composed of long hydrocarbon chains that are capable of efficiently wetting the aggregate surface (Mercado, 2007).

The mechanisms that cause moisture damage must be understood in order to select suitable materials in an asphalt mixture that are resistant to moisture damage (Howson et al., 2009). Surface free energy properties of the materials can be used to assess these characteristics. Surface free energy (SFE) is defined as the energy needed to create a new unit surface area of material in vacuum conditions. As a result, SFE can be considered to describe the physico-chemical surface characteristics of bitumen and aggregates accurately, and it has been successfully applied as a tool for the selection of moisture-resistant materials (D. Cheng, 2002). The physico-chemical characteristics of bitumen and aggregates can be assessed using surface energy principles. A large number of studies have reported the usefulness of measuring SFE to correlate the adhesive and cohesive performance of binders and aggregates in a variety of applications (Bhasin et al., 2007; Lytton et al., 2005a). In general, Reclaimed asphalt pavement (RAP) binder is used to blend with rejuvenators, where rejuvenators act as low viscous asphaltic materials that contain lighter oil fragments to reduce the stiffness of the RAP binder (R. B. Ahmed & Hossain, 2020). A study by Hossain et al. (Hossain et al., 2019b), on the two different types of rejuvenators to evaluate the moisture induce damage resistance in the aged condition found an improved SFE and cohesive bond energy after rejuvenation. This study aims to characterize the binder based on their SFE and cohesive bond energy using different types of liquid anti-stripping additives on SBS and Gilsonite modified binders.

5.3 Surface Free Energy Method

Surface free energy (SFE) is defined as the energy needed to create a new unit surface area of material in vacuum conditions. There are several theories to explain the SFE of the solid or liquid. The measurement of contact angle using the Goniometer is the most common and simple approach used to determine the SFE characteristics of bitumen. Young described the contact angle approach first to determine the SFE properties (Ahmad, 2011). According to Young, the contact angle was defined by the surface tensions of solid, liquid, and air/vapour. Figure 5.1 illustrates the contact angle of probe liquid on a solid surface. Young's equation can be written as Equation 1:

$$\Gamma_{LA} Cos\theta + \Gamma_{SL} = \Gamma_{SA} \quad (1)$$

where L, S, A, and θ denote liquid, solid, air, and contact angle, respectively.

Van Oss et al. determined Lifshitze-Van der Waals interactions and Acid-Base interactions as two main interactions of surface energy components for a solid. Polar components are divided into Lewis acid and Lewis base components (Van Oss et al., 1988). The total SFE of a material can be written as Equation 2.

$$\Gamma^{Total} = \Gamma^{LW} + \Gamma^{AB} \quad \text{……………………………………………………………………………(2)}$$

Where,

Γ^{LW} = Lifshitze-Van der Waals component

Γ^{AB} = Acid-Base component

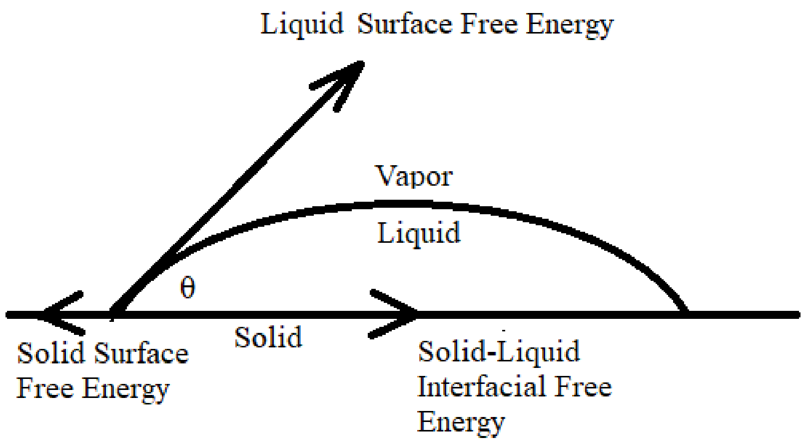


Figure 5.1: Contact angle of probe liquid on a solid surface

Lifshitz-Van der Waals forces are assumed to be the nonpolar force. The polar component is composed of Acid-Base interactions, which include electron acceptor-electron donor interactions and hydrogen bonding. Equation 3 represents Good, Van Oss and Chaudhury's acid-base theory.

$$\Gamma^{AB} = 2\sqrt{\Gamma^{+}\Gamma^{-}} \quad \text{……………………………………………………………………………...(3)}$$

Where,

Γ^{+}= Lewis acid component

Γ^{-}= Lewis base component

According to surface physical chemistry theory, SFE is the energy separating solid or liquid to produce a new interface in a vacuum. If the separated material is homogenous, the energy is described as cohesion. If the separated material is not homogenous and two different surfaces are produced, the energy would be described as the work of adhesion (W) (Tan & Guo, 2013). Based on Young-Dupre's postulation and Good's postulation, the work of adhesion or adhesive bond energy between a solid and a liquid can be expressed as follows in Equation 4.

$$W_{SL} = \Gamma_L(1 + cos\theta) = 2\sqrt{\Gamma_L{}^{LW}\Gamma_S{}^{LW}} + 2\sqrt{\Gamma_L{}^{+}\Gamma_S{}^{-}} + 2\sqrt{\Gamma_L{}^{-}\Gamma_S{}^{+}} \ldots\ldots\ldots\ldots \quad (4)$$

Where,

$\Gamma_L{}^{LW}, \Gamma_L{}^{+}, \Gamma_L{}^{-}$ = SFE components of liquid,

$\Gamma_S{}^{LW}, \Gamma_S{}^{+}, \Gamma_S{}^{-}$ = SFE component of solid (asphalt binder), and

θ = Contact angle between liquid and solid surface

In equation (4), the SFE components of solid ($\Gamma_S{}^{LW}$, $\Gamma_S{}^{+}, \Gamma_S{}^{-}$) are unknown, where SFE components of all probe liquids ($\Gamma_L{}^{LW}, \Gamma_L{}^{+}, \Gamma_L{}^{-}$) are known. The cohesive bond energy can also be measured after evaluating the three SFE components of solid (asphalt binder). The cohesive bond energy (Wc) is the function of intermolecular forces between the materials and can be expressed as Equation 5.

$$W_C = 2(\Gamma^{LW} + 2\sqrt{\Gamma^{+}\Gamma^{-}}) \ldots\ldots\ldots\ldots \quad (5)$$

5.4 Objectives

The main objectives of this study include:

- Determining the effect on contact angles with different types liquid anti-stripping additives (ZycoTherm, Pave Bond, Kling Beta and AD-Here) and modifiers (SBS and Gilsonite) using an optical contact angle analyzer
- Measuring the surface free energy components of SBS and Gilsonite modified bonders containing liquid anti-stripping additives
- Investigating the cohesive bond energy of SBS and Gilsonite modified bonders containing liquid anti-stripping additives
- Understanding the combined effect of modifiers and liquid anti-stripping additives dosage on the fundamental properties of asphalt binder
- Ranking the binders based on their moisture-induced damage resistance

5.5 Materials And Experimental Design

5.5.1 Asphalt Binder

PG 58-28 as the control binder was used in this study. PG 58-28 is generally used in the province of Newfoundland and Labrador, Canada. Pyramid Construction Ltd. supplied the asphalt. A thorough investigation was conducted on a controlled PG 58-28 binder.

5.5.2 Modifiers and Anti-stripping Additives

Two different modifiers were used for laboratory evaluation to complete the goal of this research. The modifiers used included:

- SBS modified PG 58-28, obtained from Yellowline Asphalt Products Limited
- Gilsonite, obtained from American Gilsonite Company

Four different anti-stripping additives were used in this research. The additives used included:

- ZycoTherm SP2, obtained from Zydex Industries
- Pave Bond Lite, obtained from Yellowline Asphalt Products Limited
- Kling Beta 2914 (Redicote C-2914), obtained from Nouryon
- AD-Here, obtained from Valero Energy Inc.

5.5.3 SBS and Gilsonite Modification with Asphalt Binders

In this research, SBS and Gilsonite modified binders were used to examine the improvement of rutting resistance. SBS modified binder was provided by Yellowline Asphalt Products Limited, where 4% linear SBS polymer (by the weight of binder) was used. For Gilsonite modification, the preheated pure bitumen and 10% Gilsonite powder were blended for 90 minutes at a temperature of 180°C with the help of a magnetic stirrer.

5.5.4 Blending Anti-stripping Additives with Modified Asphalt Binders

Asphalt binder PG 58-28 was blended with four types of liquid anti-stripping additives ZycoTherm SP2 (0.05%, 0.075%, and 0.1%), Kling Beta 2914 (0.5%, 0.75%, and 1%), Pave Bond Lite (0.5%, 0.75%, and 1%), and AD-Here (0.5%, 0.75%, and 1%), as shown in Figure 5.3 (a). First, the modified asphalt binder was heated at 180ºC for 60 min to make it fluid enough for mixing. The modified binders were blended with the different application rates of additives. The blending process was conducted using a magnetic stirrer for 30 min at 180ºC.

Finally, The Rolling Thin Film Oven Test (AASHTO T 240) was used for short-term laboratory aging of the base binders and modified binders, and the standard aging procedures for the RTFOT are 163ºC and 75 mins. Figure 5.2 illustrates the experimental plan of this study.

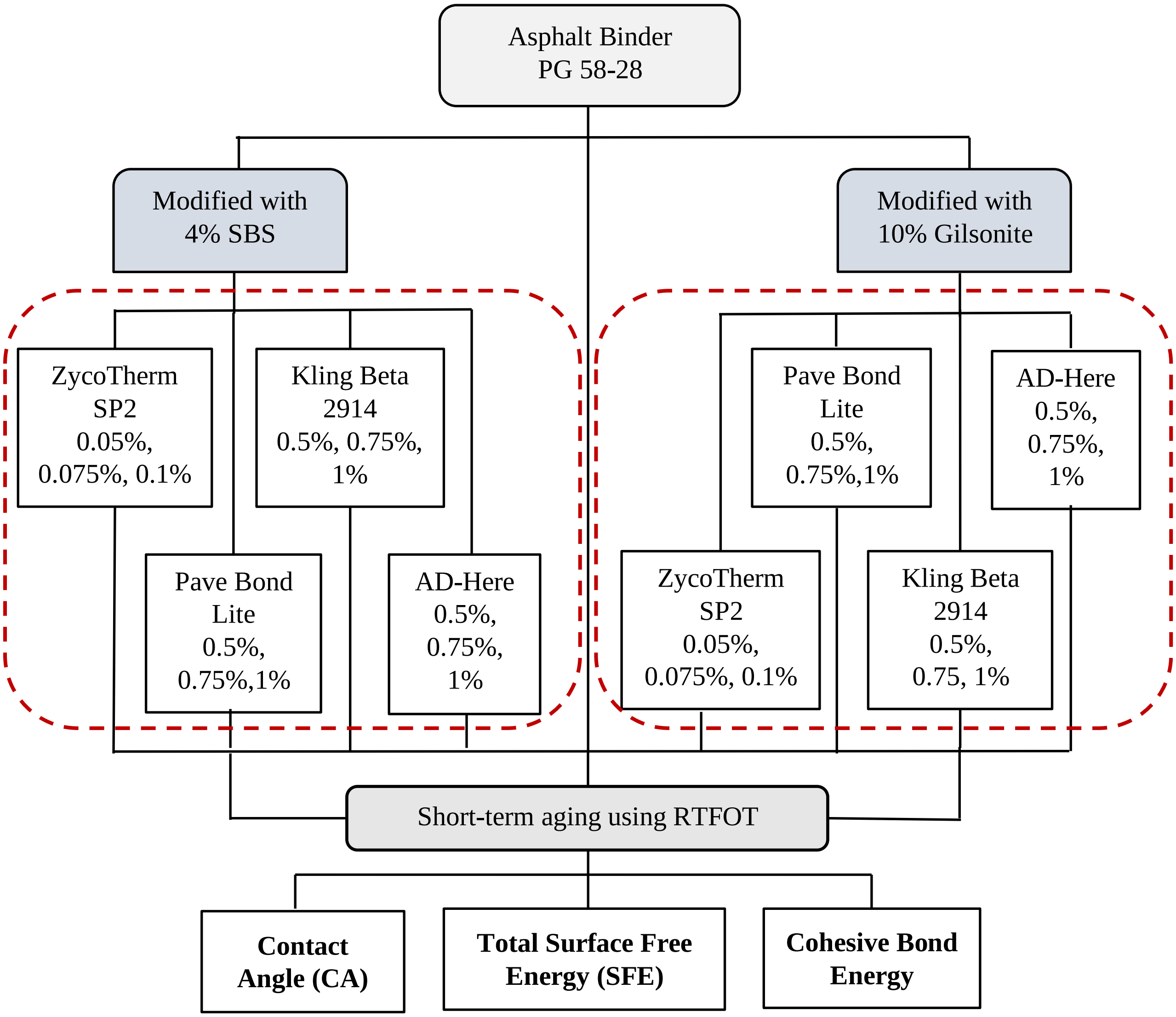
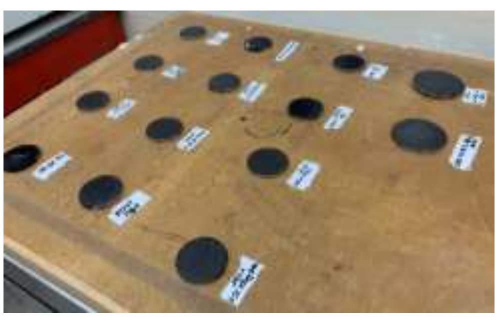


Figure 5.2: Experiment Design Matrix for Fundamental Characterization

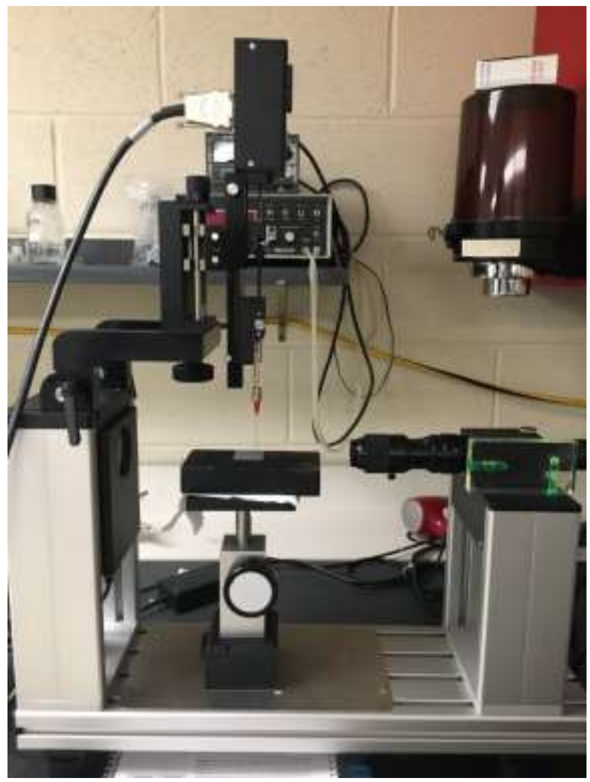
5.5.5 Preparation of Test Specimens for Contact Angle (CA) Measurement

To compute the contact angle of the liquid and solid, a dust-free and smooth surface is necessary. To make a dust-free and smooth surface, specially modified steel cans were used. The dimensions of can used for CA measurement were 75 mm in diameter and 5 mm in height to prevent the overflow of asphalt binder, as presented in Figure 5.3 (b). Initially, asphalt binders were first heated at 180ºC for 90 so that they flowed like a liquid, and the liquid asphalt was then poured into the cans. All samples were poured from their respective sample containers to reduce bias. Later, the asphalt in the cans was heated for another 30 mins at 180ºC to create a smooth, horizontal, and homogeneous surface. Finally, the sample was allowed to cool down to room temperature and tested after 24 hours of sample preparation for all types of probe liquids.

(a)



(b)



(c)

Figure 5.3: (a) Modified Binders with Anti-stripping Additives, (b) Samples Prepared for Contact Angle Measurement, and (c) Contact Angle Measurement Using OCA 15EC Device

5.5.6 Contact Angle Measurement of Asphalt Binders

The contact angle is an angle formed by a liquid at the 3-phase boundary where a liquid, vapor and solid intersect. The sessile drop method was used to measure the contact angle using an optical contact angle (OCA 15EC, Data Physics Instruments, Germany) measurement device, as presented in Figure 4.3 (c). This method is basically designed for characterizing the solid surface energy. With the advantage of precision pumps, sessile drop equipment can measure the contact angle of the droplet with high accuracy. It also gives the possibility of regulating the volume of a drop to maximize the sensitivity of the measurement. To measure the contact angle, this device is also connected with powerful operator software (SCA 20 software) to automatically monitor and analyse**.** Also, this software can automatically detect the droplet shape and baseline and control the drop volume of liquids. A volume of 5µL for a drop was used for all the samples. In this process, a 1mL disposable syringe with an outer needle diameter of 0.9 mm was used.

In this study, to compute the SFE components of asphalt binders, the GVOC's three-component theory was used, which requires three probe liquids. Equation 2 was used to solve the three unknowns for solid. However, the selection of three probe liquids is an essential factor in measuring SFE. As Bhasin (Bhasin et al., 2007) mentioned, five probe liquids (distilled water, glycerol, ethylene glycol, formamide, and methyl iodide) are used to compute contact angles. This study used these three probe liquids (distilled water, glycerol, and formamide) out of these five to calculate the SFE of asphalt binders based on their contact angles. These three are the most used probe liquids by researchers (R. Bin Ahmed et al., 2020; Hossain et al., 2019a) based on their condition number stated by Hefer (A. Hefer & Little, 2005). The SFE components of the mentioned three probe liquids are given in Table 5.1.

Table 5.1: Surface Free Energy Components of Probe Liquids (mJ/m^2) at 20ºC (Van Oss et al., 1988)

Liquid	Γ^{LW}	Γ^{+}	Γ^{-}	Γ^{Total}
Distilled Water	21.8	25.5	25.5	72.8
Formamide	39.0	2.28	39.6	58.0

Glycerol	34.0	3.92	57.4	64.0

5.6 Results and Discussion

5.6.1 Effect on Contact Angle (CA)

Tables 5.2 and 5.3 show the measured contact angles of all types of binders, including the base binder, RTFOT aged, SBS and Gilsonite modified binders containing anti-stripping additives. These tables show the mean values, standard deviations (SD), and coefficients of variation (COV) of the average of 10 observations. Note that for the calculation of the mean value, only the contact angle data having a difference of 1° between CA(L) and CA(R) of the droplet shape have been considered.

Table 5.2: Contact Angle Summary of SBS Modified Binders

Materials	**Distilled Water**			**Glycerol**			**Formamide**		
	Mean	**SD**	**COV %**	**Mean**	**SD**	**COV %**	**Mean**	**SD**	**COV %**
PG 58-28 (Unaged)	97.85	1.29	1.35	93.89	1.41	1.22	85.11	1.79	1.75
RTFOT Aged	99.78	1.34	1.42	95.35	1.23	1.37	84.24	2.39	2.71
SBS Modified (with 4% SBS)									
0.05% ZycoTherm	99.55	1.52	1.91	96.28	1.69	1.79	85.95	0.86	0.88
0.075% ZycoTherm	98.29	1.42	1.77	95.79	0.64	0.67	83.52	0.83	0.85
0.1% ZycoTherm	98.11	1.68	2.07	94.95	0.61	0.63	81.27	1.85	1.82
0.5% Kling Beta	97.05	1.04	1.05	95.21	4.00	4.79	83.12	0.89	0.93
0.75% Kling Beta	97.33	1.47	1.50	94.37	1.73	2.17	84.44	1.25	1.29
1% Kling Beta	95.28	1.20	1.23	96.21	3.51	4.30	82.07	1.54	1.34
0.5% Pave Bond	95.77	2.50	3.05	93.28	0.35	0.37	81.57	3.90	4.77
0.75% Pave Bond	93.28	3.47	4.22	95.29	0.67	0.71	84.99	1.16	1.43

1% Pave Bond	94.36	4.62	5.60	94.15	1.02	1.11	84.28	1.39	1.74
0.5% AD-Here	98.08	0.55	0.55	94.35	0.88	0.92	81.28	0.87	0.88
0.75% AD-Here	98.45	1.40	1.41	95.12	0.88	0.92	84.45	1.00	1.00
1% AD-Here	99.22	0.80	0.82	95.95	0.60	0.62	85.77	0.76	0.77

Table 5.3: Contact Angle Summary of Gilsonite Modified Binders

Materials	Distilled Water			Glycerol			Formamide		
	Mean	**SD**	**COV %**	**Mean**	**SD**	**COV %**	**Mean**	**SD**	**COV %**
PG 58-28 (Unaged)	97.85	1.29	1.35	93.89	1.41	1.22	85.11	1.79	1.75
RTFOT Aged	99.78	1.34	1.42	95.35	1.23	1.37	84.24	2.39	2.71
Gilsonite Modified (with 10% Gilsonite)									
0.05% ZycoTherm	99.24	1.33	1.85	95.15	1.43	1.79	85.95	0.35	0.85
0.075% ZycoTherm	98.15	1.95	1.09	94.33	1.98	0.67	83.27	0.63	1.42
0.1% ZycoTherm	98.05	1.32	1.55	93.91	1.21	0.63	83.92	1.05	0.88
0.5% Kling Beta	96.25	1.09	2.05	94.37	1.58	2.19	83.12	2.11	0.93
0.75% Kling Beta	96.92	1.98	1.97	93.22	1.35	3.45	84.44	3.95	1.85
1% Kling Beta	94.35	2.20	4.25	94.95	5.51	4.66	82.07	2.95	3.95
0.5% Pave Bond	94.77	1.45	1.98	94.25	1.41	2.58	84.28	3.11	4.77
0.75% Pave Bond	95.40	3.10	4.22	93.29	1.72	1.51	84.99	2.91	1.43
1% Pave Bond	93.25	4.62	4.95	95.30	2.75	1.59	81.57	1.45	1.74
0.5% AD-Here	98.05	0.95	1.09	93.92	1.85	1.05	81.28	0.87	1.76
0.75% AD-Here	98.18	1.88	1.75	94.11	1.75	1.50	84.45	1.45	1.85
1% AD-Here	98.39	1.45	0.95	95.07	1.95	1.23	85.77	1.36	1.15

In general, the wettability of the binder is defined as its ability to coat an aggregate easily. When a binder ages, it becomes viscous and stiff, and the wettability of the binder decreases. Due to a decrease in its spreading capability, which results in an increase in the contact angles of the binder. This experimental study supports the same trend of increasing contact angles with RTFOT aging, based on all types of probe liquids.

5.6.1.1 Effect on CA of SBS Modified Binders

Theoretically, a droplet with a lower contact angle indicates a hydrophilic surface. This condition reflects lower viscous properties, better wettability, better adhesion, and higher surface energy (Guy & Walker, 2016). Table 5.2 represents the contact angles of SBS modified binders with liquid anti-stripping additives in terms of additives' dosages rates. The results show that the addition of anti-stripping additives with SBS modified binders decreases the contact angle value for all probe liquids compared to RTFOT aged binders. It also indicates a decreasing pattern of contact angle for all probe liquids with the increase of ZycoTherm's concentration. Also, the contact angle difference among three probe liquids was observed, which might be due to the molecular force difference among liquids.

For the SBS modified binders with Kling Beta and Pave bond, the contact angle for each probe liquids doesn't follow any particular pattern with the increase of additives dosage. This fluctuation might be a function of the poor compatibility of this specific binder with these specific modifiers and additives when using the blending process employed in this study. However, the SBS modified binders with AD-Here follow the trend of increasing contact angles with increasing additives dosage.

5.6.1.2 Effect on CA of Gilsonite modified Binders

Table 5.3 represents the contact angles of Gilsonite modified binders with liquid anti-stripping additives in terms of additives' dosages rates. The results show that the addition of anti-stripping additives with Gilsonite modified binders decreases the contact angle value for all probe liquids compared to RTFOT aged binders. The Gilsonite modified binders with ZycoTherm shows a similar decreasing contact angle pattern for water and glycerol. Whereas the contact angle slightly increases in the case of the formamide. Also, AD-Here displays a similar decreasing contact angle pattern. From results, it is evident that the contact angles stay between 81º-99º, and no sudden increase or decrease in contact angles was observed with the probe liquids. Gilsonite modification of Pave Bond also exhibits a slight decrease in contact angles with the increase of additive concentration. Contact angles increased slightly with water and formamide after the addition of Kling Beta with SBS, whereas it decreased with glycerol.

Overall, it is evident there is no particular pattern of increasing or decreasing trend of contact angles observed with the increase or decrease of additives' dosage in Gilsonite modified binders, but variability was observed with the change of probe liquids. This denotes a variability of asphalt fundamental properties due to the complex interaction of molecular forces between the liquids and the solid surfaces (respective modified asphalt binders).

5.6.2 Effect on SFE Components

Surface free energy (SFE) is defined as the energy needed to create a new unit surface area of material in vacuum conditions. The SFE components (Lifshitz–van der Waals, Lewis acid, and Lewis base) of asphalt binders play a significant role in quantifying the cohesion of the binder molecules and the adhesion between the binder and aggregate. Equation 4 is used to obtain the SFE components of all binders using the probe liquids. Finally, Equation 2 and 3 are used to obtain the SFE components of the asphalt binders, which have been presented in Table 5.4 and 5.5.

Table 5.4: SFE Component Summary of SBS Modified Binders

Materials	Lifshitz-Waals Component (mJ/m2)	Basic Component (mJ/m2)	Acidic Component (mJ/m2)
PG 58-28	35.4615411	4.362422789	1.937866965
RTFO Aged	26.2742065	3.180970164	0.760916612
SBS Modified (with 4% SBS)			
0.05% ZycoTherm	51.7979618	3.43361207	1.5619971
0.075% ZycoTherm	53.092252	3.69603664	1.6362904
0.1% ZycoTherm	59.3938587	4.2242422	1.9813666
0.5% Kling Beta	43.6932051	3.1557993	1.26598933
0.75% Kling Beta	38.6902397	3.0141802	1.34942221
1% Kling Beta	52.62109977	3.56321096	1.73241682
0.5% Pave Bond	43.45367416	2.7773185	3.2213833
0.75% Pave Bond	41.38543641	2.4465236	2.9465624
1% Pave Bond	40.2495697	2.26968894	2.65402751
0.5% AD-Here	54.11050869	3.78218631	4.37702969
0.75% AD-Here	52.54439402	3.40769433	4.0371617
1% AD-Here	47.7592388	2.95716553	3.7981312

Table 5.5: SFE Component Summary of Gilsonite Modified Binders

Materials	Lifshitz-Waals Component (mJ/m2)	Basic Component (mJ/m2)	Acidic Component (mJ/m2)
PG 58-28	35.4615411	4.362422789	1.93786697
RTFO Aged	26.2742065	3.180970164	0.76091661
Gilsonite Modified (with 10% Gilsonite)			
0.05% ZycoTherm SP2	47.3192577	2.9578549	0.9155697
0.075% ZycoTherm SP2	49.1544768	3.0774831	1.0936477
0.1% ZycoTherm SP2	53.9774856	3.2315222	1.2799641
0.5% Kling Beta 2914	35.9356854	2.4255619	0.7258549
0.75% Kling Beta 2914	38.2885137	2.2578164	0.9339175
1% Kling Beta 2914	47.5432571	2.0345724	0.8574473
0.5% Pave Bond Lite	41.3798285	2.0711467	2.4293447
0.75% Pave Bond Lite	38.2864972	2.2114975	2.3314954
1% Pave Bond Lite	36.9282269	1.9572688	2.0712871
0.5% AD-Here	49.3956812	3.11289457	3.7985712
0.75% AD-Here	47.5298563	2.87512224	3.5332615
1% AD-Here	42.5417112	2.63147568	3.1325987

5.6.2.1 Effect on SFE Components of SBS Modified Binders

Table 5.4 represents the SFE components of all unaged, RTFOT aged, and SBS modified binders. Based on the aging condition, for the PG 58-28 and RTFOT aged binder, all SFE components show a decreasing pattern for RTFOT aged binders compared to unaged binders. Test results show that the Lifshitz–van der Waals portion varied from 38.69 - 59.39 mJ/sqm, the acidic component from 1.26 - 4.37 mJ/sqm, and the basic component varied from 2.26 - 4.22 mJ/sqm. Comparatively, the Lifshitz-Waals component occupied the higher portion, followed by the base and acidic components because of additional forces such as Keesom dipole-dipole, Debye dipole-induced dipole force and London dispersion (Arno Wilhelm Hefer, 2004). Similar observations of decreasing SFE components were also observed in other studies (Hossain et al., 2019a; Kassem et al., 2018).

For SBS modified binders containing anti-stripping additives, the addition of SBS and anti-stripping additives shows an increase in Lifshitz-Waals components and regained the lost portion caused by RTFOT aging. Remarkably, all SBS modified binders crossed beyond the Lifshitz-Waals portion of PG 58-28 binder, indicating a better property than the original binder, as shown in Figure 4.4. The ZoycoTherm in SBS modified binders shows an increasing trend in all SFE components with the increase of additives dosage. The highest total SFE was reported to be 65.18 mJ/m2 for the 0.1% ZycoTherm+SBS among all SBS modified binders. This highest value was expected due to its high variability of contact angles with different liquids. The other two polar components increased with the increase of the additive’s dosage, which resulted in the highest SFE of the binder. Pave bond and AD-Here in SBS modified binders exhibit a decreasing trend of total SFE with increasing additives' concentration. In the case of the Kling Beta, the Lifshitz-Waals portion decreased up to 0.5% dosage, whereas it suddenly increased for 1% Kling Beta. As a result, the lowest SFE was recorded for the 0.75% Kling Beta+SBS among all SBS modified binders.

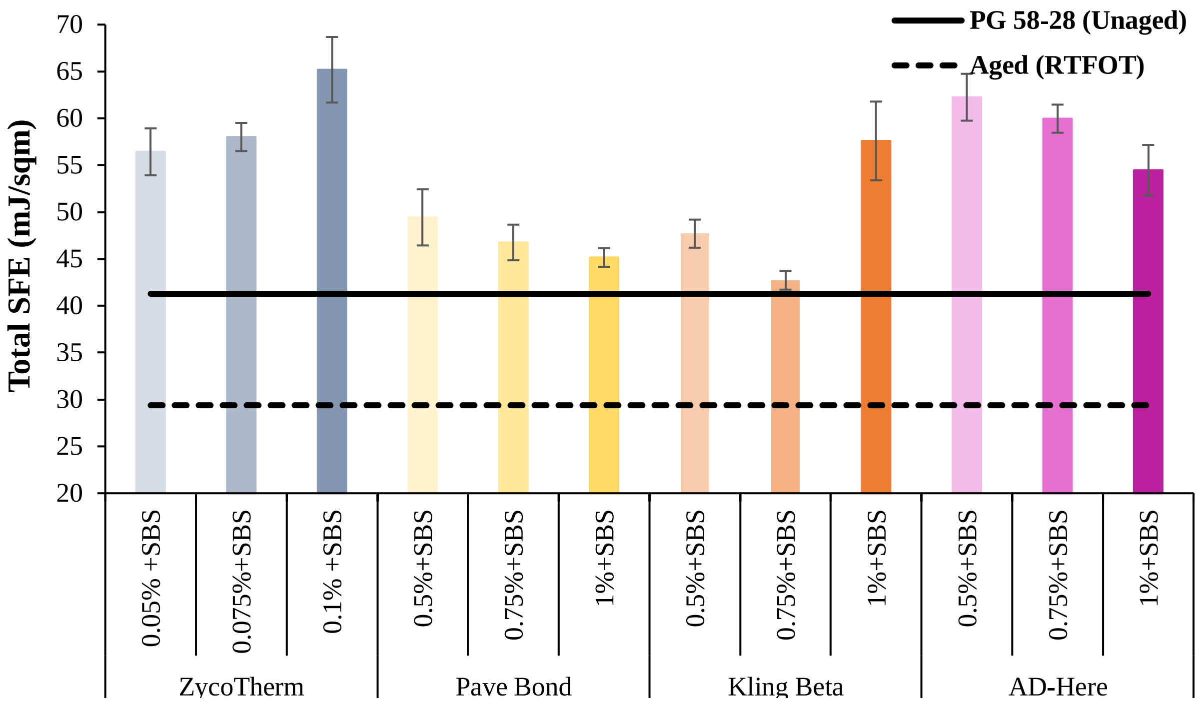


Figure 5.4: Total SFE of SBS Modified Binders

In summary, the non-polar component (Lifshitz-Waals) was higher for all SBS modified binders containing anti-stripping additives. Test results indicate that the modification with SBS and anti-stripping additives effectively improves the SFE components of the asphalt binder.

5.6.2.2 Effect on SFE Components of Gilsonite Modified Binders

Table 5.5 represents the SFE components of Gilsonite binders containing different anti-stripping additives. Test results show that the Lifshitz–van der Waals portion varied from 35.29 - 53.97 mJ/sqm, the acidic component from 0.72 – 3.79 mJ/sqm, and the basic component varied from 1.95 - 3.23 mJ/sqm. From the SFE components summary of SBS and Gilsonite modified binders, the loss of total SFE was observed for Gilsonite modified binders compared to SBS modified binders.

For Gilsonite modified binders containing anti-stripping additives, the addition of Gilsonite powder and anti-stripping additives shows an increase in total SFE components and regained the lost portion caused by RTFOT aging. However, Few Gilsonite modified binders couldn't cross beyond the Lifshitz-Waals portion of PG 58-28 binder, indicating a poor property than the original binder, as shown in Figure 4.5. The ZoycoTherm in Gilsonite modified binders shows a similar increasing trend in all SFE components like SBS modified binders with the increase of additives dosage. The other two polar components increase as well with the increase of the additive's dosage, which resulted in the highest SFE of the binder. The highest total SFE was reported to be 53.97 mJ/sqm for the 0.1% ZycoTherm+SBS among all SBS modified binders. In the case of the Pave bond and AD-Here in Gilsonite modified binders, exhibit a decreasing trend of total SFE with increasing additives' concentration. For Kling Beta, the Lifshitz-Waals portion also increases with the addition of Kling Beta. However, kling Beta shows Lowest total SFE among all anti-stripping additives.

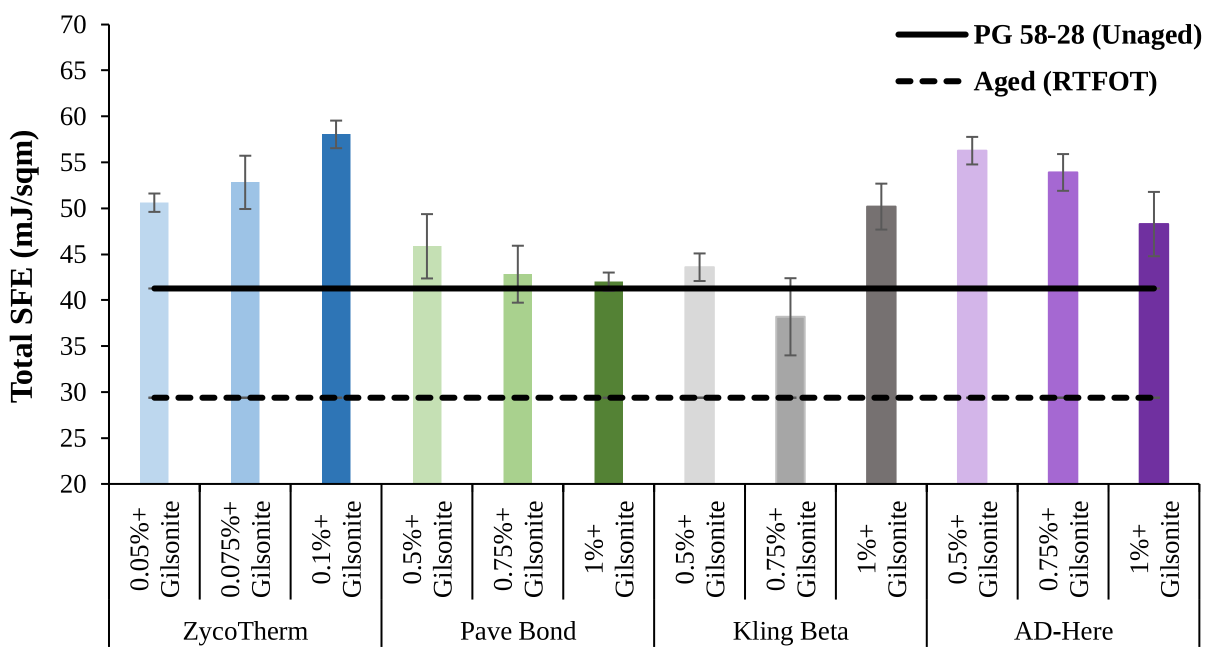


Figure 5.5: Total SFE of Gilsonite Modified Binders

5.6.3 Effect on Cohesive Bond Energies

The cohesive bond energy of a binder can be defined as the amount of energy required to initiate a crack or the cohesive failure of the binder. Therefore, it is desirable to have higher cohesive bond energies of the binder in order to achieve better moisture resistance. Cohesive bond energy is one of the energy parameters correlated with the fatigue cracking resistance of the binder. Equation 5 is used to calculate the cohesive bond energy of respective binders and is represented in Figure 5.6 and 5.7.

5.6.3.1 Effect on Cohesive Bond Energies of SBS and Gilsonite Modified Binders

The cohesive bond energy of PG 58-28 binder was recorded 82.55 mJ/m^2, whereas after TFOT aging it reduced to 58.77 mJ/m^2 as expected. This is because aged binder loses some of its basic molecular constituents that reduce the cohesive energy, initiating an early crack in the pavement. The cohesive bond energy increased significantly when the aged binder was modified by SBS/Gilsonite and anti-stripping additives. Among all SBS modified binders, the highest value recorded was 130.36 mJ/m^2 for 0.1% ZycoTherm+SBS, which indicates the highest resistance against the moisture damage. Since cohesive bond energies are measured from the total SFE, the increasing or decreasing trend of the cohesive bond energies of modified binders will follow the similar trend of total SFE in terms of the additives dosage rates. From Figure 5.6, It is also evident that all SBS modified binders exhibit good performance against moisture damage. Based on the experimental results, the binder with higher cohesive bond energies can be ranked as 0.1% ZycoThem+SBS > 0.5% AD-Here+SBS> 0.75% AD-Here+SBS > 0.075% ZycoThem+SBS.

Among all Gilsonite modified binders, the highest value recorded was 116.09 mJ/m^2 for 0.1% ZycoTherm+Gilsonite, which indicates the highest resistance against the moisture damage.

On the other hand, the lowest value recorded was 76.38 mJ/m^2 for 0.5% Kling Beta+Gilsonite. From Figure 5.7, the Gilsonite modified binders with higher cohesive bond energies can be ranked as 0.1% ZycoThem+Gilsonite > 0.5% AD-Here+Gilsonite > 0.075% ZycoThem+Gilsonite > 0.75% AD-Here+Gilsonite. The lower cohesive bond energy is related to early cracking and cohesive failure of binders in a mix and ultimately premature pavement failure. Therefore, in comparison with Gilsonite modified binders, anti-stripping additives + SBS is effective in improving the damage resistance, which is consistent with previous studies showing SBS improves moisture damage resistance.

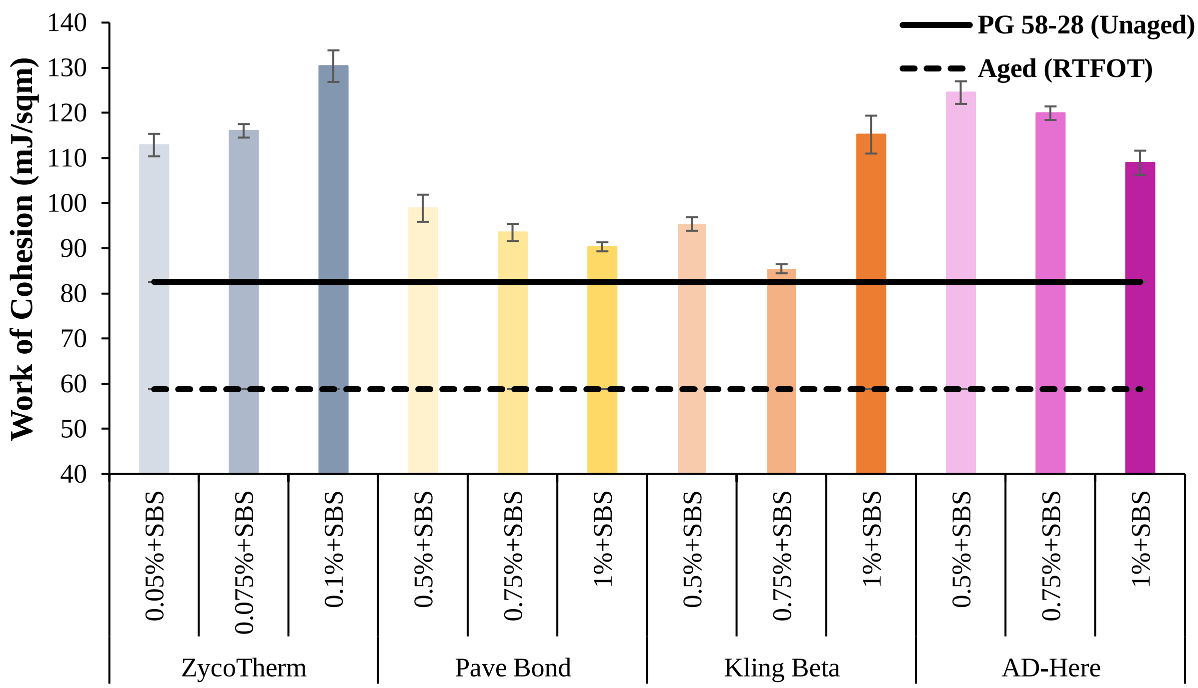


Figure 5.6: Cohesive Bond Energies of SBS Modified Binders

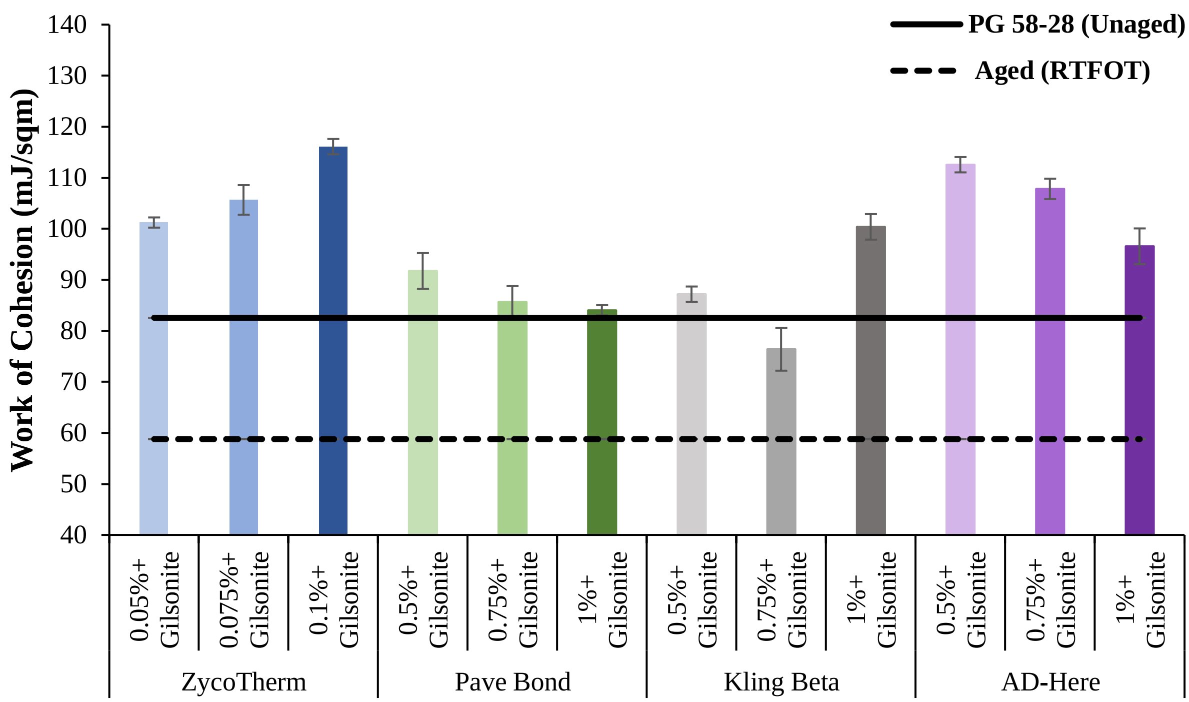


Figure 5.7: Cohesive Bond Energies of Gilsonite Modified Binders

5.7 Conclusion

The present study aims to understand the effect of different types of liquid anti-stripping additives and modifiers in terms of their cohesive bond energy. To obtain the research goal, four types of liquid anti-stripping additives: ZycoTherm SP2, Pave Bond Lite, Kling Beta 2914, and AD-Here at different percentages by the weight of the binder were employed in SBS and Gilsonite modified binders. To simulate the real field condition, all modified binders with anti-stripping additives were aged using RTFOT aging protocol. The experimental study incorporates the measurement of contact angles with three different probe liquids to measure SFE components and quantify the cohesive bond energy of respective binders. Based on the experimental evaluation, the following conclusions are drawn.

- Aging of the binder using RTFOT increased the contact angle compared to the base PG 58-28 binder when water and glycerol were used as a probe liquid, but it decreased when formamide was used as a probe liquid. However, the inclusion of modifiers and anti-stripping additives improved the contact angles and resulted in better performance than the base binder. This might be due to the additives and modifiers changing the molecular properties and wettability of the base binder.
- Contact angle results of SBS modified binders with liquid anti-stripping additives show that the addition of anti-stripping additives with SBS modified binders decreases the contact angle value for all probe liquids compared to RTFOT aged binders with few exceptions. Modification with SBS makes the binder stiffer compared to the unmodified binder. However, the addition of liquid anti-stripping additives changes the wettability of the binder, which exhibited lower contact angles, resulting in good adhesion. In the case of Gilsonite modified binders with liquid anti-stripping additives, it also decreases the contact angle values. However, variability was observed with the change of probe liquids. This denotes a variability of asphalt fundamental properties due to the complex interaction of molecular forces between the liquids and the solid surfaces (respective modified asphalt binders).
- Among different anti-stripping additives, ZycoTherm with SBS follows a decreasing trend of contact angle, whereas AD-Here with SBS follows a decreasing trend in most cases with the increase of additives' concentration. However, there is no particular pattern of increasing or decreasing trend of contact angles was observed with the increase or decrease of additives' dosage in Gilsonite modified binders

- The contribution of the Lifshitz-Waals component is much higher for all types of binders. Aging of the binder changes the molecular properties of the binder; as a result, the total SFE components of the binder also decreased. Within the polar components, for some binders, basic components are more prevalent than acidic components. On the other hand, for the rest of the binders, acidic components are more prevalent than basic components, which is opposite to available exististing study results.
- The SFE components of asphalt binders play a significant role in quantifying the cohesion of the binder molecules and the adhesion between the binder and aggregate. For SBS modified binders containing anti-stripping additives, the addition of SBS and anti-stripping additives shows an increase in Lifshitz-Waals components and regained the lost portion caused by RTFOT aging. Remarkably, all SBS modified binders crossed beyond the Lifshitz-Waals portion of PG 58-28 binder, indicating a better property than the original binder. Again, the addition of Gilsonite and anti-stripping additives increases Lifshitz-Waals components. However, the loss of total SFE was observed for Gilsonite modified binders compared to SBS modified binders.
- Aging of the binder decreased the cohesive bond energy of the base binder. Modifiers and anti-stripping additives seem to be effective in enhancing the cohesive bond energy to improve cracking resistance. Cohesive bond energy is one of the energy parameters correlated with the fatigue cracking resistance of the binder. Between SBS and Gilsonite modified binders containing anti-stripping additives, SBS modified binders show higher cohesive bond energies compared to Gilsonite modified binders for each type of anti-stripping additives.

- Among all SBS modified binders, the highest cohesive bond energy was recorded for 0.1% ZycoTherm + SBS, which indicates the highest resistance against the moisture damage. In the case of Gilsonite modified binders, the highest value was recorded for 0.1% ZycoTherm+Gilsonite. From chapter 3, it is noticed that 0.1% ZycoTherm + SBS/Gilsonite modified binder exhibits the highest fatigue cracking resistance among the respective modified binders, which is also consistent with the cohesive bond energies of the binder. Additionally, ZycoTherm in both SBS and Gilsonite modified binders shows an increasing trend in cohesive bond energy with the increase of additives dosage. In contrast, AD-Here shows an increasing trend in cohesive bond energy with the increase of additives dosage.
- SBS modified binders with the highest cohesive bond energies are ranked as 0.1% ZycoThem + SBS > 0.5% AD-Here + SBS > 0.75% AD-Here + SBS > 0.075% ZycoThem + SBS. Again, for Gilsonite modified binders, the highest cohesive bond energies are ranked as 0.1% ZycoThem + Gilsonite > 0.5% AD-Here + Gilsonite > 0.075% ZycoThem + Gilsonite > 0.75% AD-Here + Gilsonite. From chapter 3, it was noticed that 0.1% ZycoTherm + SBS/Gilsonite modified binder exhibited the highest fatigue cracking resistance among the respective modified binders, which was also consistent with the cohesive bond energies of the binder.

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Chapter 6: Conclusions and Application of Research

6.1 Overview

According to the United Nations report in 2018, over 82% of the population in Canada lives in urban areas. Predictions show that this could increase up to 90% by the middle of this century. Consequently, roads and highways play a significant role in meeting future demands in economic growth and development. Asphalt pavement has been extensively used in North America to construct roads and highways because of its sustainability and excellent performance. In 2020, there is more than 1.08 million kilometres of roads across the country. Out of those, 90% of roads are constructed with an asphalt mixture. Asphalt is a thermoplastic substance that exhibits viscoelastic properties under most pavement operating circumstances, making it a vital component of pavement performance. Premature failure is a frequent phenomenon in the bituminous concrete pavement. Highway agencies have acknowledged the benefits of using modified asphalt binders to reduce the amount and severity of pavement distresses and to increase the service life of pavement. The goal of this research is to evaluate the relative effect of different modifiers and anti-stripping additives on the rheological properties of asphalt binders. To attain the research goal, four anti-stripping additives: ZycoTherm SP2, Kling Beta 2914, Pave Bond Lite, and AD-Here were used at different dosage rates for laboratory investigation. These anti-stripping additives were blended to SBS and Gilsonite modified PG 58-28 binder. To understand the characteristics and the performance of these modifiers and additives, an extensive review has been conducted on the usage of asphalt additives and modifiers in other provinces in Canada and the U.S. Based on the experimental study, this chapter presents a summary of the main finding. As the thesis has been organized in manuscript format, the specific findings are summarized in chapters 2, 3, 4and 5. This chapter will only focus on general conclusions, limitations of this research, and the recommendations for future research.

6.2 Major Findings from Literature Review

An extensive review has been conducted and is presented in this chapter 2 as an initial task of this study. This review summarizes the current practice on the usage of asphalt additives and modifiers in other provinces in Canada and the U.S. Again, this review focuses on compiling recent developments on rutting and moisture resistance additives, and the major findings from the review, was used for optimal experimental design for laboratory investigation.

- During this review, many studies show that asphalt additives and modifiers can improve the rutting and moisture-induced damage resistance of the mixtures.
- The performance of rutting resistant modifiers, including Styrene–butadiene–styrene (SBS), ethylene-vinyl-acetate (EVA), acrylic fiber, and Gilsonite, showed encouraging results.
- For improving moisture resistance, Ad-here, SBS copolymer, and hydrated lime and some new additives, including different nanomaterials, ZychoTherm, Pave Bond, and Redicote showed overall good performance.

6.3 Major Findings from Rheological Characterization and Its Application

- In this study, the rutting performance of SBS and Gilsonite modified binders containing anti-stripping additives at different dosages has been evaluated using Superpave, Shenoy's Superpave rutting parameter, and non-recovery creep compliance. Our limited study indicates that all SBS and Gilsonite modifiers improve the rutting resistance. Between SBS and Gilsonite modified binders, SBS modified binders show better rutting resistance compared to Gilsonite modified binders. The complex bonding mechanism of polystyrene and polybutadiene made the SBS durable and more restrained from external pressure or load. These outcomes help to enhance the stiffness and the rutting resistance of SBS modified binders. However, Gilsonite modified binders pass the damage limit indicated by Superpave and Shanoy's rutting parameter.

- Additionally, the MSCR result indicates that SBS provides better resistance to high-temperature rutting. Since SBS is a thermoplastic elastomer polymer, SBS behaves like elastomeric rubbers, improving the binders' elastic behaviour. Thus, SBS helps to reduce the permanent deformation of the asphalt binders. MSCRS result also supports that Gilsonite can be used as an alternative to SBS. Generally, Gilsonite makes bitumen stiffer and increases its viscosity, which consequently makes asphalt concrete stiffer. These results would be more accurate if PAV-aged binders could be used for laboratory investigations.
- Again, in this study, the effects of cracking performance of ZycoTherm, Kling Beta, Pave Bond and AD-Here in SBS and Gilsonite modified binder using Glover-Rowe cracking parameter, crossover frequency, and rheological index value has been compared. The results from the limited investigation for the resistance against thermal cracking show ZycoTherm and AD-Here enhance cracking resistance performance compared to the rest anti-stripping additives.
- Finally, among all SBS modified binders, 0.1% ZycoTherm + SBS and 0.5% AD-Here + SBS show the best resistance against rutting and cracking susceptibility accordingly. On the other hand, among all Gilsonite modified binders, 0.1% ZycoTherm + Gilsonite and

0.5% AD-Here + Gilsonite show the best resistance against rutting and cracking susceptibility accordingly.

6.4 Major Findings from Surface Free Energy Analysis and Its Application

- The present study aims to understand the effect of different types of liquid anti-stripping additives and modifiers in terms of their cohesive bond energy. To simulate the real field condition, all modified binders with anti-stripping additives were aged using RTFOT aging protocol. The experimental study incorporates the measurement of contact angles with three different probe liquids. Contact angle results of SBS modified binders with liquid anti-stripping additives show that the addition of anti-stripping additives with SBS modified binders decreases the contact angle value for all probe liquids. Modification with SBS makes the binder stiffer compared to the unmodified binder. However, the addition of liquid anti-stripping additives changes the wettability of the binder, which exhibited lower contact angles, resulting in good adhesion. In the case of Gilsonite modified binders with liquid anti-stripping additives, it also decreases the contact angle values.
- Aging of the binder using RTFOT increased the contact angle compared to the base PG 58-28 binder when water and glycerol were used as a probe liquid, but it decreased when formamide was used as a probe liquid. However, the inclusion of modifiers and anti-stripping additives improved the contact angles and resulted in better performance than the base binder. This might be due to the additives and modifiers changing the molecular properties and wettability of the base binder.
- The SFE components of asphalt binders play a significant role in quantifying the cohesion of the binder molecules and the adhesion between the binder and aggregate. For SBS modified binders containing anti-stripping additives, the addition of SBS and anti-stripping

additives shows an increase in Lifshitz-Waals components and regained the lost portion caused by RTFOT aging. Remarkably, all SBS modified binders crossed beyond the Lifshitz-Waals portion of PG 58-28 binder, indicating a better property than the original binder. Again, the addition of Gilsonite and anti-stripping additives increases Lifshitz-Waals components. However, the loss of total SFE was observed for Gilsonite modified binders compared to SBS modified binders.

- Aging of the binder decreased the cohesive bond energy of the base binder. Modifiers and anti-stripping additives seem to be effective in enhancing the cohesive bond energy to improve cracking resistance. Cohesive bond energy is one of the energy parameters correlated with the fatigue cracking resistance of the binder. Between SBS and Gilsonite modified binders containing anti-stripping additives, SBS modified binders show higher cohesive bond energies compared to Gilsonite modified binders for each type of anti-stripping additives.
- Among all SBS modified binders, the highest cohesive bond energy was recorded for 0.1% ZycoTherm + SBS, which indicates the highest resistance against the moisture damage. In the case of Gilsonite modified binders, the highest value was recorded for 0.1% ZycoTherm+Gilsonite. Additionally, ZycoTherm in both SBS and Gilsonite modified binders shows an increasing trend in cohesive bond energy with the increase of additives dosage. In contrast, AD-Here shows an increasing trend in cohesive bond energy with the increase of additives dosage.
- SBS modified binders with the highest cohesive bond energies are ranked as 0.1% ZycoThem + SBS > 0.5% AD-Here + SBS > 0.75% AD-Here + SBS > 0.075% ZycoThem + SBS. Again, for Gilsonite modified binders, the highest cohesive bond energies are

ranked as 0.1% ZycoThem + Gilsonite > 0.5% AD-Here + Gilsonite > 0.075% ZycoThem + Gilsonite > 0.75% AD-Here + Gilsonite. From chapter 3, it was noticed that 0.1% ZycoTherm + SBS/Gilsonite modified binder exhibited the highest fatigue cracking resistance among the respective modified binders, which was also consistent with the cohesive bond energies of the binder.

6.5 Limitations and Recommendations

Despite having a lot of experimental studies to satisfy the objectives of this thesis, there were some limitations during this study. Based on the limitations, the following recommendations are made for further study in the future.

- This study was limited to only RTFOT aging of the binder due to the limitations with access to equipment. Therefore, it could be better to evaluate long-term performance of binder using pressurized aging vessel (PAV) protocol.
- During the mixing of the modifiers and additives with binder, the magnetic stirrer was used. As a result, there might not have a homogeneous mix of the binder. Therefore, it is recommended to use high-speed sheer mixer to achieve a homogeneous mix.
- SFE test was only limited to the binder to quantify the cohesive bond energy. It would be better to go through the mixture to understand the adhesion performance between binder and aggregate.
- This study was only limited to laboratory, whereas the field application of rejuvenated asphalt binder might be very effective to access the real scenario of the pavement performances.

- Due to lack of time, this study only evaluates the performances of the binder. In the future, the study should be extended to the mastic and mixture level to understand the actual mechanism between modified binders and aggregates.

Appendix A: Laboratory Tests

Figure A.1: Samples Prepared for Rheological Characterization

Figure A.2: Sample Preparation Using Magnetic Stirrer

Figure A.3: Magnetic Bars Used in Magnetic Stirrer

Figure A.4: Convection Oven at MUN

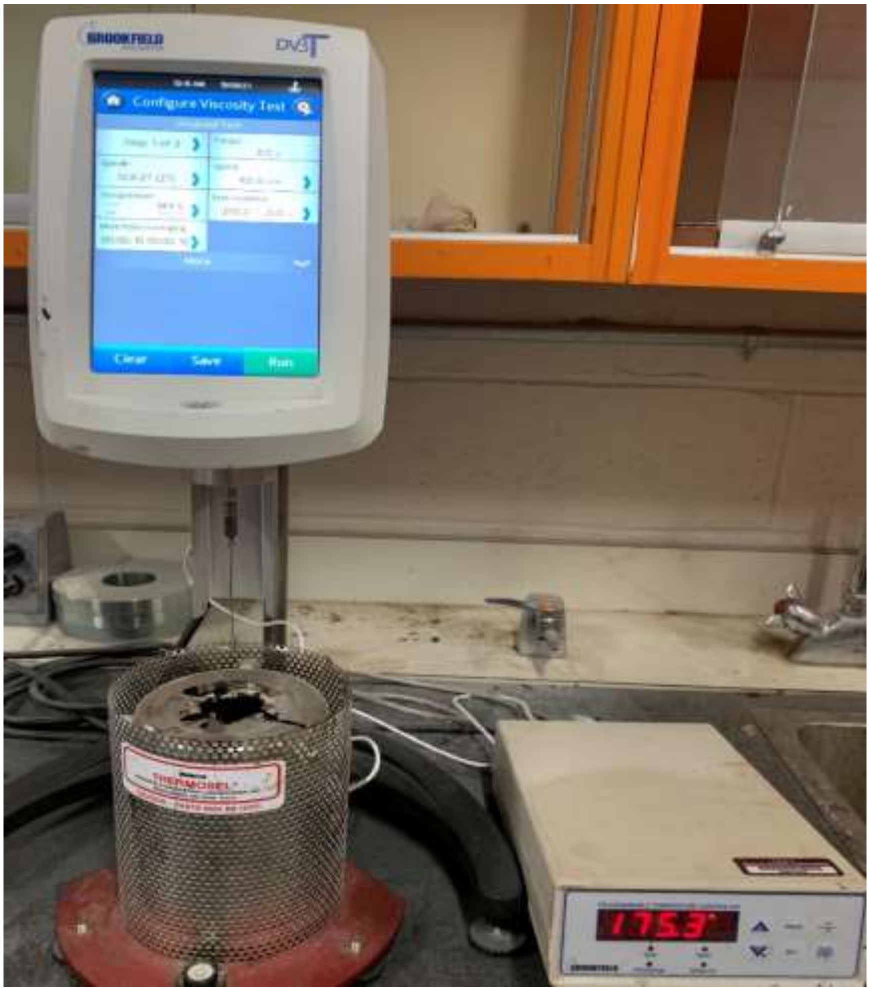

Figure A.5: Rotational Viscometer Facility at MUN

Figure A.6: A Malvern Panalytical Kinexus DSR-III Rheometer at Yellowline Asphalt Products Ltd.

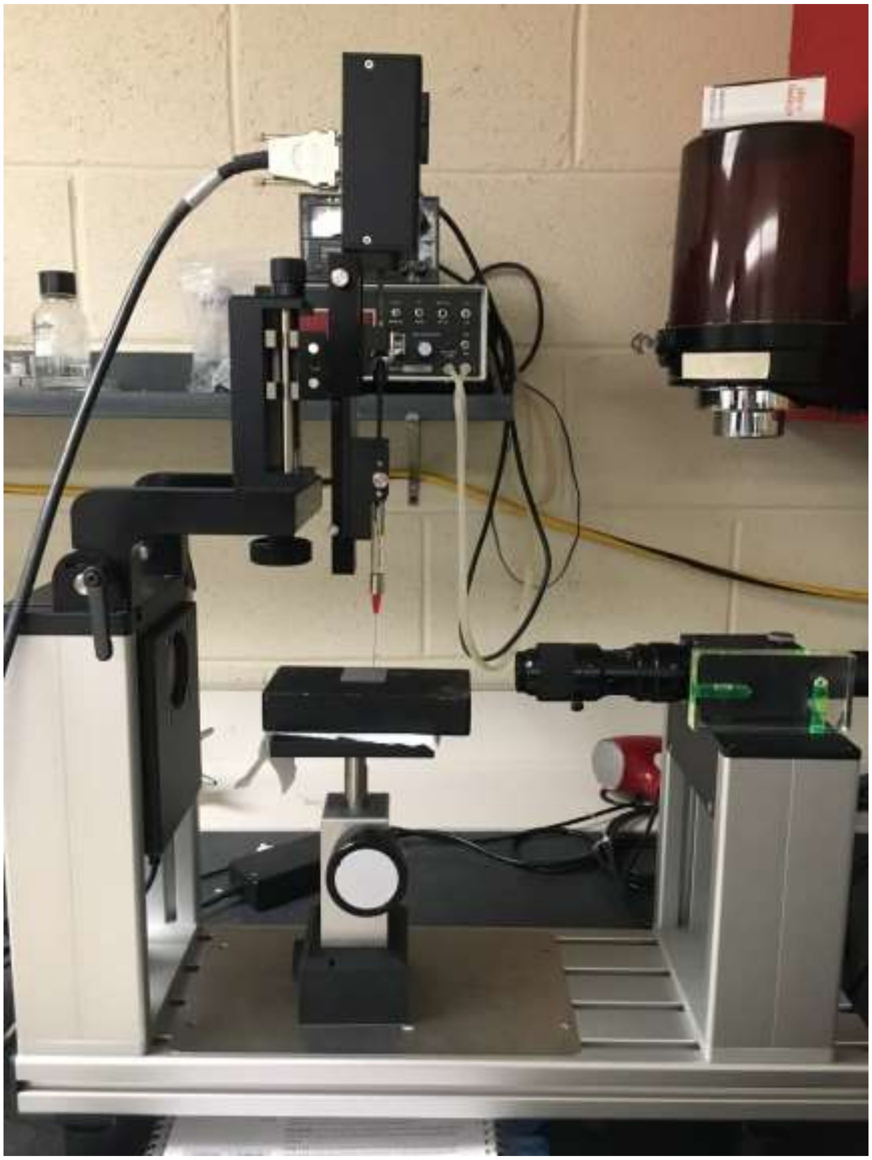

Figure A.7: Contact Angle Measurement Using OCA 15EC Equipment at MUN

Appendix B: Laboratory Test Data

Table B.1: Superpave and Shanoy Parameter of SBS Modified Binders

Binders	G*	Superpave (Pa)	Shanoy (Pa)
SBS+0.05% ZycoTherm	6.985	7778.812873	15378.91363
SBS+0.075% ZycoTherm	8.083	9308.209948	23609.95853
SBS+ 0.1% ZycoTherm	8.527	9788.443201	24161.8633
SBS+0.5% AD-Here	8.35	9649.524042	25253.56487
SBS+0.75% AD-Here	8.16	9281.679716	21280.99556
SBS+1% AD-Here	7.37	8329.319016	18202.42585
SBS+0.5% Pave Bond	8.531	9526.734458	19173.79272
SBS+0.75% Pave Bond	7.262	8089.716693	16024.34909
SBS+1% Pave Bond	6.054	6355.885109	9112.764891
SBS+0.5% Kling Beta	7.671	8613.186362	17979.13574
SBS+0.75% Kling Beta	7.035	7745.320452	14272.22097
SBS+1% Kling Beta	7.978	9151.930796	22460.46231

Table B.2: Glover-Rowe Parameter of SBS Modified Binders

Binders	G*	G-R (Pa)
SBS+0.05%ZycoTherm	7504	894.4617
SBS+0.075%ZycoTherm	9589.8051	1100.9
SBS+0.1%ZycoTherm	10039.2299	1932.729
SBS+0.5% AD-Here	4000	476.7919
SBS+0.75% AD-Here	15589.8051	1789.694
SBS+1% AD-Here	19039.2299	3665.388
SBS+0.5%Kling Beta	4607.9639	479.8766
SBS+0.75%Kling Beta	10057.9133	1330.201
SBS+1%Kling Beta	5082.8095	538.1551
SBS+0.5% Pave Bond	12670.3441	1954.225
SBS+0.75% Pave Bond	10790.5800	2327.341
SBS+1% Pave Bond	9368.1193	1074.591

Table B.3: Superpave and Shanoy Parameter of Gilsonite Modified Binders

Binders	G*	Superpave (Pa)	Shanoy (Pa)
Gilsonite+0.05% ZycoTherm	8.437	8712.218	3776.240677
Gilsonite+0.075% ZycoTherm	9.225	9498.695	11492.93807
Gilsonite+0.1% ZycoTherm	13.084	13468.74	12344.00565
Gilsonite+0.5% Pave Bond	10.9	11321.67	15388.86158
Gilsonite+0.75% Pave Bond	9.454	9702.672	12389.54713
Gilsonite+1% Pave Bond	11.696	12092.34	16053.24374
Gilsonite+0.5% AD-Here	12.57	12964.32	16994.60682
Gilsonite+0.75% AD-Here	11.03	11405.6	15154.12677
Gilsonite+1% AD-Here	9.135	9389.514	12088.41866
Gilsonite+0.5% Kling Beta	10.71	11164.29	15450.5236
Gilsonite+0.75% Kling Beta	11.45	11814	15519.73764
Gilsonite+1% Kling Beta	12.57	12964.32	16589.00762

Table B.4: Glover-Rowe Parameter of Gilsonite Modified Binders

Binders	G* Pa	G-R (Pa)
Gilsonite+0.05%ZycoTherm	27643.9435	1587.628
Gilsonite+0.075%ZycoTherm	53083.4109	3409.109
Gilsonite+0.1%ZycoTherm	65430.9358	6239.629
Gilsonite+0.5%Kling Beta	39805.0000	4044.413
Gilsonite+0.75%Kling Beta	36954.1226	3603.684
Gilsonite+1%Kling Beta	32694.2477	3064.646
Gilsonite+0.5%AD-Here	72694.2477	4649.884
Gilsonite+0.75%AD-Here	69405.2473	4078.301
Gilsonite+1%AD-Here	57275.8576	2902.173
Gilsonite+0.5% Pave Bond	20560.9414	1339.587
Gilsonite+0.75% Pave Bond	14742.7831	1161.403
Gilsonite+1% Pave Bond	11857.3776	888.1633

Table B.5: R and Wc value of SBS Modified Binders

Anit-Strip Additives	Percentages	R-Value	Wc (Hz)
	0.05%+SBS	2.75	4815.11
Zycotherm	0.075%+SBS	2.32	5226.38
	0.1%+SBS	2.211	6109.04
	0.5%+ SBS	2.387	5954.68
Kling Beta	0.75%+SBS	2.4217	5349.63
	1%+SBS	2.5867	5252.87
	0.5%+SBS	2.77	5565.35
Pave Bond	0.75%+SBS	3.18	4842.62
	1%+SBS	3.21	4454.46
	0.5%+SBS	2.311	5454.45
AD-Here	0.75%+SBS	2.5684	5063.21
	1%+SBS	3.068	4261.37

Table B.6: R and Wc value of Gilsonite Modified Binders

Anit-Strip Additives	Percentages	R-Value	Wc (Hz)
	0.05%+Gilsonite	1.98	36511.14
Zycotherm	0.075%+ Gilsonite	1.78	42137.75
	0.1%+ Gilsonite	1.73	46204.61
	0.5%+ Gilsonite	1.69	45160.48
Kling Beta	0.75%+ Gilsonite	1.76	42139.71
	1%+ Gilsonite	1.83	38144.52
	0.5%+ Gilsonite	1.51	44185.59
Pave Bond	0.75%+ Gilsonite	1.94	39932.29
	1%+ Gilsonite	2.06	27810.12
	0.5%+ Gilsonite	1.86	45144.52
AD-Here	0.75%+ Gilsonite	1.98	41192.2
	1%+ Gilsonite	2.06	31126.95

Table B.7: Jnr, Jnr-diff and Jnr-slope of SBS Modified Binders

Anit-Strip Additives	Percentages	Jnr (3.2) (1/kPa)	Jnr, diff (%)	Jnr, slope (%)
	0.05% +SBS	0.3424	58.15242494	4.061290323
ZycoTherm	0.075% +SBS	0.2287	102.1746818	3.728387097
	0.1% +SBS	0.207	120.8471141	3.653870968
	0.5% +SBS	0.2703	52.88461538	3.016129032
Kling Beta	0.75%+SBS	0.4293	48.80415945	4.541935484
	1%+SBS	0.3095	50.82846004	3.364516129
	0.5% +SBS	0.2428	51.18306351	2.651612903
Pave Bond	0.75% +SBS	0.3763	53.15425315	4.212903226
	1% +SBS	0.9057	38.42274186	8.109677419
	0.5% +SBS	0.2189	103.0819471	3.584225806
AD-Here	0.75% +SBS	0.2386	72.15007215	3.225806452
	1% +SBS	0.3784	65.67425569	4.838709677

Table B.8: Jnr, Jnr-diff and Jnr-slope of Gilsonite Modified Binders

Anit-Strip Additives	Percentages	Jnr (3.2) (1/kPa)	Jnr, diff (%)	Jnr, slope (%)
	0.05%+Gilsonite	0.4664	12.8062139	2.074193548
ZycoTherm	0.075%+Gilsonite	0.386	14.04299138	3.519354839
	0.1%+Gilsonite	0.2542	12.57685858	2.177419355
	0.5% +Gilsonite	0.6256	12.43709561	2.232258065
Kling Beta	0.75%+Gilsonite	0.6351	13.22873953	2.393548387
	1%+Gilsonite	0.3517	17.15393795	1.854783871
	0.5% +Gilsonite	0.6162	13.9633808	2.435483871
Pave Bond	0.75%+Gilsonite	0.492	11.06094808	1.580645161
	1%+Gilsonite	0.5819	12.14106764	2.032258065
	0.5% +Gilsonite	0.2761	10.56218058	0.643879514
AD-Here	0.75%+Gilsonite	0.351	7.952380952	0.538709677
	1%+Gilsonite	0.4182	10.52796983	1.080645161