CHEMICAL, MORPHOLOGICAL, AND RHEOLOGICAL PROPERTIES OF VARIOUS REJUVENATED ASPHALT BINDERS

by

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Abstract

Reclaimed asphalt pavement (RAP) material is considered as an economical approach for sustainable pavement construction. However, usage of higher RAP binder content is more susceptible to pavement cracking. Using rejuvenators with RAP binder is a widely used approach to address the issues related to RAP binder. This study used thin film oven test (TFOT) aged binder with three types of rejuvenators including waste cooking oil (UT/R1), modified waste cooking oil (TR/R2), and Hydrolene (HL/R3). Also, in some cases, styrene butadiene styrene (SBS) polymer was added with UT/R1 and TR/R2 rejuvenated binders to compare the performances. To understand the behavior and the performance of these rejuvenators, three sets of characterization tests were conducted: chemical, morphological, and rheological. Gas Chromatography-Mass Spectroscopy (GC-MS) and Fourier Transformed Infrared Spectroscopy (FTIR) was employed for chemical characterization, while Atomic Force Microscopy (AFM) was used for morphological analysis. Later, a frequency sweep test and surface free energy (SFE) test was conducted to understand the rheological performances and moisture damage resistance of rejuvenated asphalt binders respectively. Based on the experimentation, the study reveals that UT/R1 softens the binders most, whereas TR/R2 rejuvenator eliminates these issues and showed better rheological performances of the binder. However, in case of moisture susceptibility, TR/R2 rejuvenated binder seems to have poor resistance and the highest resistance was recorded for UT/R1 rejuvenated binders. This study observes a good correlation between chemical, morphological and rheological performances of binders which are expected to contribute to the performance evaluation and characterization of rejuvenated asphalt mixes.

Acknowledgments

With an aspiration for a faster and better world and affinity for research and innovation in the field of Engineering and Technology, it was my unbound dream of studying in one of the top universities. Being a part of ARTEL pavement research group at the Memorial University of Newfoundland becomes my first step to achieve my dream. Throughout my journey to the master's program was excellent and I would like to acknowledge numerous individuals, without those contributions and support, my journey towards my goal might not be smooth.

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I would also like to acknowledge the financial support provided by the Leslie Harris Centre of Regional Policy and Developments and Multi-Material Stewardship Board of Government of Newfoundland and Labrador, and the School of Graduate Studies (SGS) for research funding. Their financial contribution to my research keeps me to stay focused on my research goal. I also wish to thank Dr. Lidan Tao and Dr. Helen Zhang from the Environment Engineering Lab, Dr. Luc Y. Beaulieu and Mr. Sajjad Salimi from the Department of Physics, Dr. Huck K. Grover and Nick Ryan from the Department of

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It was difficult for me to adapt to a new condition and environment of St. John’s, NL. Thanks go to all of my ARTEL research group members, especially Surya Swarna Teja for his continuous suggestions, advice, research ideas, and feedback. I am also expressing my gratitude to my friend Auchib Reza, Riju Saha, and Suborno Debnath for being a family member in St. John's and providing mental support during my stay in MUN. Besides that, I want to thank the Teaching Assistant Union of Memorial University of Newfoundland (TAUMUN), and Engineering Graduates’ Students Society (EGSS) to give me some opportunity to work for them and help me to improve my leadership skills.

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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. In Canada, we have more than 415.6 thousand km of paved road (Length of Canada's Public Road Network, 2003). Out of those, 90% of roads are constructed with an asphalt mixture. For the construction of these asphalt roads, road agencies require an extensive amount of binder which is an expensive item in asphalt pavement. The natural environment has been severely damaged by emissions from the production of this large amount of binder. Transportation agencies looking for alternative solutions to address these problems started using recycled materials for environmental sustainability. The most commonly recycled materials are reclaimed asphalt pavement (RAP). Using RAP in pavement construction helps reduce construction costs up to 34%, limits the amount of wastes going into landfilling projects, and reduces the emission of greenhouse gases from the new binder production process (Kandhal & Mallick, 1997; Zaumanis et al., 2013).

RAP has been successfully used in hot mix asphalt (HMA) since the 1970's. Many developed countries have already started using RAP materials as a pavement base or sub-base course. RAP binder has also been widely used for producing fresh asphalt. According to Transportation Research Record Circular E-C188 (Kazmierowski et al., 2014), the USA used 95%, the Netherlands 73%, France 61.9% and all of Europe 65% of total produced RAP materials in 2012. Japan is using almost 100% RAP, mainly due to the storage space limitations of these materials. This amount of RAP was utilized either in different layers of pavement or in the production of fresh HMA or warm mix asphalt (WMA) (Kazmierowski et al., 2014). However, in the USA and Canada, different jurisdictions limit the percentage of RAP that can be used. The Ministry of Transportation Ontario (MTO) allows up to 20% of RAP to be used in the surface course and 40% for the base course (Esenwa et al., 2013). In the USA, 27 states have been using almost 20% RAP, with the number increasing every year (Kazmierowski et al., 2014). In some areas of Canada and the Netherlands, road agencies are already using 100% RAP in the field and the results show promising performance using RAP not only in the underlying asphalt layers but also in the top layer (Esenwa et al., 2013; Hagos et al., 2016).

In the field of pavement construction, the usage of RAP materials can be a sustainable approach. In general, RAP materials can be divided into two components: 1) RAP aggregate and 2) RAP binder. RAP aggregates can be used as a base or sub-base materials (Hoppe et al., 2015) and RAP binders can be used as a binder or mixed with a fresh binder to produce a new type of binder. However, there is also strong documentation that RAP binder is highly oxidized due to its long-term exposure to the environment. This oxidation changes its physical and rheological properties (Al-Qadi et al., 2007). This phenomenon is known as ‘age-hardening’, and it alters the intermolecular structure, resulting in reduced ductility and increased fatigue cracking (Elkashef & Williams, 2017; Song et al., 2018). Also, it decreases the overall relaxation capacity of HMA, which leads to the formation of cracks in the pavement (Branthaver et al., 1993). To address these issues and restore the original rheological properties, rejuvenators are commonly blended with the RAP binders to make the binder soft and to improve fatigue performance. In general, rejuvenators are lighter oil components which are similar to asphalt and help to reduce the viscosity and the oxidation of the aged binder (Brown, 1988). Many studies have already been conducted to understand the effects of rejuvenation on RAP binder. The restoration behavior of rejuvenated asphalt binder, however, is not clear, and neither is the change of the rejuvenated binder's performance in terms of rheology at the fundamental level. This study aims to fill these gaps by evaluating different rejuvenator's impacts on RAP binder at different percentages to achieve the goal of sustainable pavement construction.

1.2 Objectives

Based on a comprehensive literature review as stated in Chapter 2, the following objectives have been considered for this thesis project:

- To develop a quantitative understanding of the performance of different rejuvenators at varying concentrations added with the aged binder
- To evaluate the chemical characteristics and molecular properties of different rejuvenators employed for the study using GC-MS technique
- To understand the mechanical and morphological features of rejuvenated asphalt binder at the micro level using FTIR and AFM technique
- To rank different rejuvenated 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 AASTHO M332

- To quantify the moisture-induced damage resistance of rejuvenated asphalt binder after evaluating cohesive bond energy from surface free energy (SFE) method.

1.3 Thesis Framework

This thesis is prepared in manuscript format. The outcome of the study is presented in six chapters.

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

Chapter 2 provides an extensive literature review on the rejuvenated asphalt binder, highlighting the effectiveness of using waste cooking oil as a rejuvenator. Also, the research gaps of the rejuvenated asphalt binders are shown and considered to finalize the research objectives and the works for Chapters 3-5. This chapter was published in the Journal of Construction and Building Materials as a review paper.

Chapter 3 presents the chemical and morphological characteristics of rejuvenated asphalt binder. A part of this chapter will be published as a technical paper in the proceeding of the RILEM International Symposium on Bituminous Materials that will be held at Lyon, France from June 08-10, 2020. Also, some new analysis has been conducted in chapter 5 and a new journal paper accepted for publication in ASCE Journal of Materials in Civil Engineering as a technical paper.

Chapter 4 presents the rheological characterization of rejuvenated asphalt binder. This chapter was presented at the 99th Annual Meeting of Transportation Research Board (TRB) held in Washington, DC, USA on January 14th, 2020. The chapter was also submitted for publication to the Journal of Construction and Building Materials as a technical paper.

Chapter 5 investigates the moisture damage resistance performance of rejuvenated asphalt binder. A part of this chapter and some analysis from chapter 3 has been accepted for publication in ASCE Journal of Materials in Civil Engineering as a technical paper.

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

At the end of all chapters, reference sections include the references cited in the chapters as parts of stand-alone papers.

1.4 Significant Contributions

1.4.1 Journal Articles

- Ahmed, R B., Hossain, K. (2019). Waste Cooking Oil as an Asphalt Rejuvenator: A State-of-the-Art Review. Journal of Construction and Building Materials. https://doi.org/10.1016/j.conbuildmat.2019.116985

- Ahmed, R B., Hossain, K., Hajj, R M. (2020). Chemical, Morphological, and Fundamental Behavior of Rejuvenated Asphalt Binders. ASCE Journal of Materials in Civil Engineering. http://doi.org/10.1061/(ASCE)MT.1943-5533.0003564

- Ahmed, R B., Hossain, K., Aurilio, M. (2020). Characterization of Asphalt Rheology Using Waste Cooking Oil as a Rejuvenator. Journal of Construction and Building Materials. Under Review. Submitted on February 06, 2020.

1.4.2 Conference Papers

- Ahmed, R B., Hossain, K. (2020). Characterizing Rejuvenated Asphalt Binders Using FTIR and AFM Techniques. RILEM International Symposium on Bituminous Materials. Lyon, France.

- Ahmed, R B., Hossain, K., Aurilio, M. (2020). Rheological Characterization of Rejuvenated Asphalt Binders. Presented at 99th 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.

- Ahmed, R B., Aurilio, V., Hossain, K. (2020). Using Rejuvenating Agents to Improve Hot Mix Asphalt Incorporating Reclaimed Asphalt Pavement (RAP). 65th Annual Conference on Canadian Technical Asphalt Association (CTAA). Kelowna, BC, Canada.

1.4.3 Technical Report

- Hossain, K., Ahmed, R B. (2019). Application of Waste Cooking Oil in Construction of Asphalt Pavement. Harris Centre – MMSB Waste Management Applied Research Fund, St. John’s, Newfoundland and Labrador. https://www.mun.ca/harriscentre/reports/MMSB_Waste/Final_Hossain.pdf

1.5 Co-Authorships

All the research presented in the journals and conference papers in chapters 2-5 has been conducted by the author of this thesis, Rayhan Bin Ahmed, under the supervision of Dr. Kamal Hossain. Mr. Ahmed also prepared the draft manuscript. The other co-authors supervised the research and reviewed the manuscript.

1.6 References

Al-Qadi, I. L., Elseifi, M., & Carpenter, S. H. (2007). *Reclaimed asphalt pavement - A literature review* (Issue FHWA-ICT-07-001). https://doi.org/http://hdl.handle.net/2142/46007

Branthaver, J., Petersen, J., Robertson, R., Duvall, J., Kim, S., Harnsberger, P., Mill, T., Ensley, E., Barbour, F., & Schabron, J. (1993). Binder characterization and evaluation. Volume2: Chemistry. In *Strategic Highway Research Program* (Vol. 2, Issue SHRP-A-368). http://trid.trb.org/view.aspx?id=386723

Brown, E. R. (1988). Preventive Maintenance of Asphalt Concrete Pavements. *Transportation Research Record: Journal of the Transportation Research Board*, 6–11.

Elkashef, M., & Williams, R. C. (2017). Improving fatigue and low temperature performance of 100 % RAP mixtures using a soybean-derived rejuvenator. *Construction and Building Materials*, *151*, 345–352. https://doi.org/10.1016/j.conbuildmat.2017.06.099

Esenwa, M., Davidson, J. K., Kucharek, A. S., & Moore, T. (2013). 100 % Recycled

Asphalt Paving , Our Experience. *Canadian Technical Asphalt Association (CTAA)*, 207–218.

Hagos, E., Shirazi, M., & Wall, A. van de. (2016). The development of 100% RAP asphalt mixture with the use of innovative rejuvenator. *6th Eurasphalt & Eurobitume Congress*, *June*. https://doi.org/10.14311/ee.2016.093

Hoppe, J. E., Lane, D. S., Fitch, G. M., & Shetty, S. (2015). Feasibility of Reclaimed Asphalt Pavement (RAP) Use As Road Base and Subbase Material. In *VCTIR 15-R6, Virginia Center for Transportation Innovation and Research*.

Kandhal, P. S., & Mallick, R. B. (1997). Pavement Recycling Guidelines for State and Local Governments: Participant's Reference Book. *Fhwa-Sa-98-042*, *December*, 301. https://www.fhwa.dot.gov/pavement/recycling/98042/

Kazmierowski, T. J., McGennis, R. B., Paul, H., Salomon, D. R., & Haddock, J. (2014). Application of Reclaimed Asphalt Pavement and Recycled Asphalt Shingles in Hot-Mix Asphalt: National and International Perspectives on Current Practice. *Transportation Research Circular E-C188*, *October*.

Length of Canada's public road network. (2003).

Song, W., Huang, B., & Shu, X. (2018). Influence of warm-mix asphalt technology and rejuvenator on performance of asphalt mixtures containing 50% reclaimed asphalt pavement. *Journal of Cleaner Production*, *192*, 191–198. https://doi.org/10.1016/j.jclepro.2018.04.269

Zaumanis, M., Mallick, R. B., & Frank, R. (2013). Use of Rejuvenators for Production of

Sustainable High Content Rap Hot Mix Asphalt. *XXVIII International Baltic Road Conference*, 1–10.

Chapter 2 Literature Review

Co-Authorship: This chapter has been published to Journal of Construction and Building Materials as a review paper as: Ahmed, R. B., Hossain, K. (2019), 'Waste Cooking Oil as an Asphalt Rejuvenator: A State-of-the-Art Review'. Most of the research in this chapter has been conducted by the first author. He also prepared the draft manuscript. The other author supervised the research and reviewed the manuscript.

2.1 Abstract

In Canada, over 90% of the paved roads are asphalt pavements. Most of these pavements were built decades ago, which are currently exhibiting a significant amount of surface distresses. These distresses includes potholes, rutting (deformation in the wheel path), and cracking. To repair these distressed pavements, the road agencies spend millions of dollars every year, of which a significant portion goes to acquiring new natural aggregates and asphalt. To reduce the rehabilitation cost, road agencies use up to 100% reclaimed asphalt pavements (RAP) in new construction. However, the asphalt available in recycled pavements is oxidized and stiffened due to various environmental processes which are susceptible to thermal and fatigue cracking. To soften and to decrease the viscosity of the RAP materials, various rejuvenators are being in practice. The rejuvenators are able to reactivate and restore the original properties of this long-term aged asphalt binder. Using Waste Cooking Oil (WCO) is one of the eco-friendly solutions which contains the similar lighter oil components of asphalt and can be used as an acceptable rejuvenator. Recent

studies showed that WCO has an excellent potential to be used as a good rejuvenator in the hot mix asphalt (HMA) industry. This review article summarizes the performance and adverse effects of WCO as a rejuvenator.

2.2 Introduction

In the pavement industry, using reclaimed asphalt pavement (RAP) material is a preferable method for enhancing environmental sustainability. Road agencies have been using RAP materials to reduce the burden on natural aggregate and to lower the disposal problems of reclaimed pavements. In addition, some new environmental regulations are contributing to making RAP materials more attractive to highway agencies. Whether, during the long-term service of asphalt binder, it is continuously exposed to hot air and temperature, resulting in a change in their physical and rheological properties (Al-Qadi et al., 2007). Several past studies show that the oxidized binder in RAP materials decreases the overall relaxation capacity of HMA and as a result, the binder exhibits more brittle nature that leads to the formation of cracks between the interface of aggregates and the binder (Branthaver et al., 1993). To address these problems, it is common to blend recycled asphalt with some recycling agents known as a rejuvenator to reactivate its original property and to improve its fatigue performance (Elkashef & Williams, 2017). Generally, RAP materials consist of 4-6% of asphalt binder by weight of aggregate (Song et al., 2018), which could reduce the cost of construction up to 34% for a range between 20-50% of the RAP content (Brown, 1988; Kandhal & Mallick, 1997).

Waste cooking oil (WCO) is generally produced after cooking and frying activities and can be used as a good rejuvenator due to having similar lighter oil components of asphalt. Every year, food markets are generating a massive amount of WCO: China generates 826 million gallons, the United States generates 3 million gallons, and other countries produce even more (Sun et al., 2016). Disposal of this waste cooking oil is a primary concern because it may lead to ecological, environmental and municipal problems. In addition, WCO might tax sewerage lines to coagulate and block sewers if it is not properly discharged (Lei et al., 2017). Moreover, it will increase the organic load on the sewer system and create operational problems (Sheinbaum et al., 2015). Therefore, recycling of WCO in asphalt binder materials can be a source of proper conversion of waste materials to sustainable materials.

A number of studies have been conducted worldwide in the reuse of WCO due to its consistent performance as a potential waste material to rejuvenate the asphalt binders (Datt et al., 2017; Dokandari et al., 2017; Sun et al., 2017). Zargar found that using 3-4% of WCO by weight of the binder can increase the penetration value, which resembles virgin asphalt (Zargar et al., 2012). Similarly, Asli studied the physical properties of WCO as a rejuvenator with RAP materials and suggests that upto 5% WCO be used without compromising the performance of pavement mixtures while using a rejuvenating agent in the mixture (Asli et al., 2012). Whereas, Ji (Ji et al., 2017) extend the WCO percentage upto 8% for recovering the rutting resistance of aged binder at high temperature. Another study was conducted in the USA by Wen (Wen et al., 2012) and found that the addition of WCO based binder increases the low-temperature resistance and the moisture susceptibility. However, the study noted that the resistance to fatigue cracking, rutting, and stiffness of the mixture, decreased as WCO based binder was added in the mixture. Contrary to a study conducted by Wen, significant fatigue cracking resistance was recorded by Maharaj (Maharaj et al., 2015) and concluded that the fatigue resistance of the mixture increased as WCO was added.

Most of the studies on this research topic conducted in the past comprised only basic and rheological tests such as penetration, softening point, dynamic shear rheometer (DSR), bending beam rheometer (BBR), and recommended that WCO can be utilized in asphalt pavement construction. While these tests only provide information on the overall performance of the asphaltic materials, they are not designed to provide information on their fundamental properties or to capture the interaction that occurs between WCO and aged or virgin asphalt.

During the blending of WCO with asphalt, the interaction occurs at an atomic/nanoscale level, and it is required to understand the behavior of WCO rejuvenated asphalt at the microscopic level. When this research was conducted, there was insufficient research to understand the performance of WCO at a fundamental level. Recently a new concept has been introduced on pavement construction in the Netherlands that uses a microcapsule containing WCO (microWCOs) as a rejuvenator. Schlangen (García et al., 2011) developed an encapsulation system (1.60mm medium size) to use in porous asphalt pavement. The test results show higher tensile resistance of capsules and better skid resistance after eliminating the use of direct oil in the pavement. Correspondingly in China, Su (Su et al., 2015) used microWCOs, fabricated by a shell membrane using a prepolymer of methanol melamine formaldehyde (MMF). The study reported that microWCOs could be penetrated in an aged binder and survive in melting bitumen, showing thermal stability and survival during repeated loading tests. So, from the evaluation of previous studies, it is noted that WCO may not be used as a full replacement of the binder, but maybe a satisfying rejuvenator to be used in flexible pavement construction.

The primary objective of this study is to review published articles and summarize how WCO is contributing as a rejuvenating agent for the aged binder and as a performance-enhancing agent in a neat binder. This article starts with summarizing the effect of WCO empirical test methods, such as penetration, softening point, and ductility that follows rheological properties such as kinematic viscosity, dynamic shear modulus, and elastic property of the binder. Besides, the performance of WCO in asphalt mixture level was also summarized. Furthermore, the summary was extended to include chemical and molecular properties of WCO.

2.3 Investigation of the Performance of WCO using Classical Testing

Asphalt binder is the main constituent of pavement construction, which affects the strength, durability, stiffness, rutting, fatigue life and moisture damage of HMA mixtures. The addition of WCO with neat or RAP materials largely affects the binder property. Penetration, softening point and ductility tests are used as an indicative test for fundamental properties of a binder. Besides, rheological tests including kinematic viscosity, complex modulus (G^*), and elastic property [i.e., phase angle (δ), creep stiffness (s) and creep rate (m value)] are also investigated to predict the performance of asphalt binder.

2.3.1 Basic Properties Tests

The fundamental properties of the rejuvenated asphalt binder include penetration, softening point, and ductility tests is illustrated in Figure 2.1-Figure 2.3 respectively. The penetration test is conducted to evaluate the consistency of an asphalt binder. Generally, RAP materials are hard and exhibit a brittle nature. To soften the aged binder, WCO was added as a rejuvenator at various concentrations. Asli, Zargar, and Azahar (Asli et al., 2012; Azahar et al., 2016; Zargar et al., 2012) conducted experiments on different penetration graded binders (30/40, 40/50, 50/60, 60/70), the aged and unaged binders with different percentages (1%-5%) of WCO by the weight of the binder. From Figure 2.1-Figure 2.2, it is observed that with the addition of WCO, the penetration value increases while the softening point value decreases. The aged binder of the bitumen group Pen50/60, Pen40/50, Pen30/40 needed 1%, 3% and 4% of WCO respectively to achieve the original penetration grade of 80/100. Whereas for the softening point value (Figure 2.2), it requires about 4%, 2% and 1% WCO for an unaged group of Pen30/40, Pen40/50, and Pen50/60 respectively to resemble 80/100 grade bitumen. Moreover, a higher penetration value was achieved for untreated samples, and a higher softening point temperature was achieved for treated WCO. For both treated and untreated WCO, the softening point value continuously decreased with the increase of WCO concentrations as expected, and the maximum temperature was recorded at 45ºC and 40ºC for 3% treated WCO and 3% untreated WCO respectively. This might be due to be the modification of WCO and better chemical bonding with asphalt. Therefore, modification of WCO (treated WCO) should exhibit higher temperature resistance of asphalt and might be good for hot climatic regions.

Similarly, Rolling Thin Film Oven (RTFO) test aged asphalt showed lesser penetration and higher temperature resistance compared to all unaged binder. This is the fact of aging, which makes the binder stiffer.

The flexibility and the tensile deformation of asphalt can be evaluated by ductility test. From the study of Sun (Sun et al., 2016), ductility increased sharply with the addition of WCO but reduced suddenly when the oil percentage is 6% or more, shown in Figure 2.3. The anomalous point was found when 8% of WCO was added. The reason might be due to non-homogeneity in the blending of WCO with control asphalt. It is also noted that, with the change of asphalt grade, ductility changes significantly like A_o (Pen 60/80), and B_o (Pen 40/60) grade. Moreover, a notable change is seen from the SBS modified asphalt C_o (Pen 40/60+SBS), where the ductility is approximately twice of the virgin asphalt of B_o (Pen 40/60) grade. The addition of SBS polymer makes the binder more ductile due to its more dispersion nature in asphalt binder. Sun (Sun et al., 2017) conducted their study on Pen 70, optimized bio-asphalt (OBA) and SBS modified asphalt (SBS-MA) binders to evaluate the feasibility of using waste cooking oil residue (WCOR). Results found that the ductility of OBA was close to SBS-MA and much lower than Pen70, which may cause due to the existence of polymer in bio-oil. In general, the addition of higher concentration of WCO increases the ductility, which can improve the plasticity of binder (Ji et al., 2017). In addition, higher ductility indicates the ability of the binders' good deformability, which shows good performance to resist thermal cracking of asphalt binder (Leung & Guo, 2006).

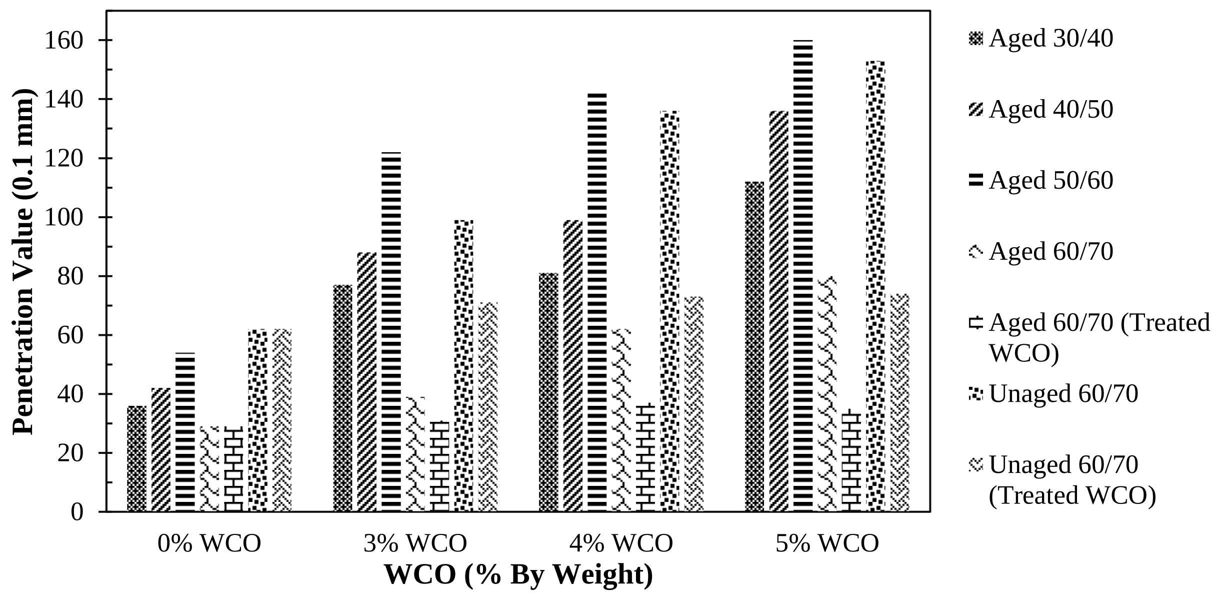


Figure 2.1 Relationship Of Penetration Value with Different Percentages of WCO (Adapted from (Asli et al., 2012; Azahar et al., 2016; Zargar et al., 2012))

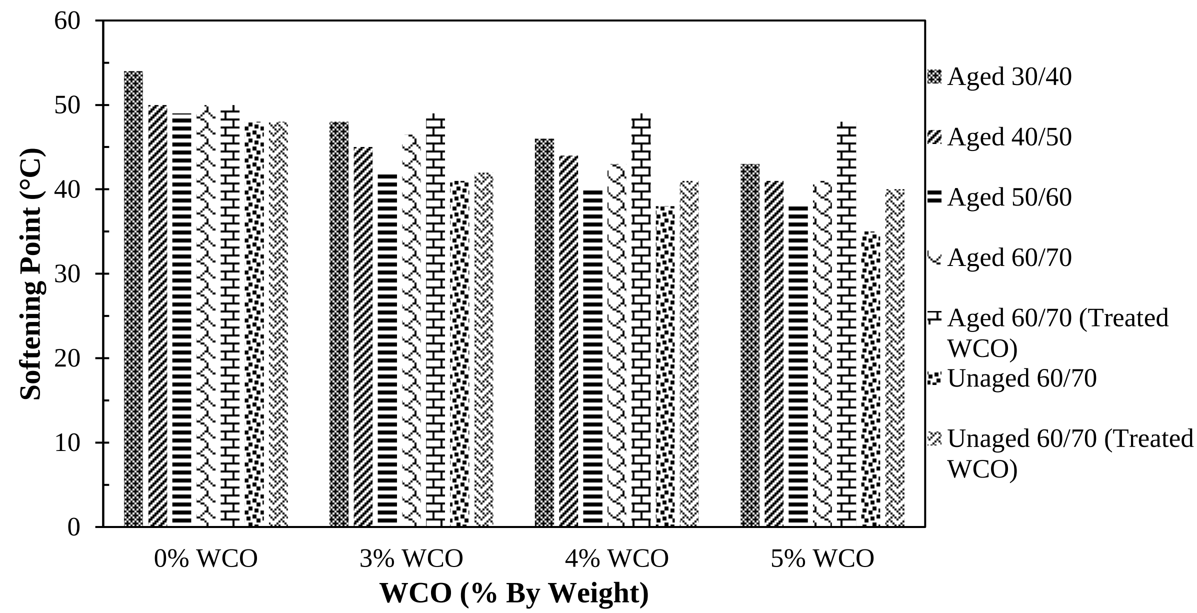


Figure 2.2 Relationship of Softening Point Value with Different Percentages of WCO (Adapted from (Asli et al., 2012; Azahar et al., 2016; Zargar et al., 2012))

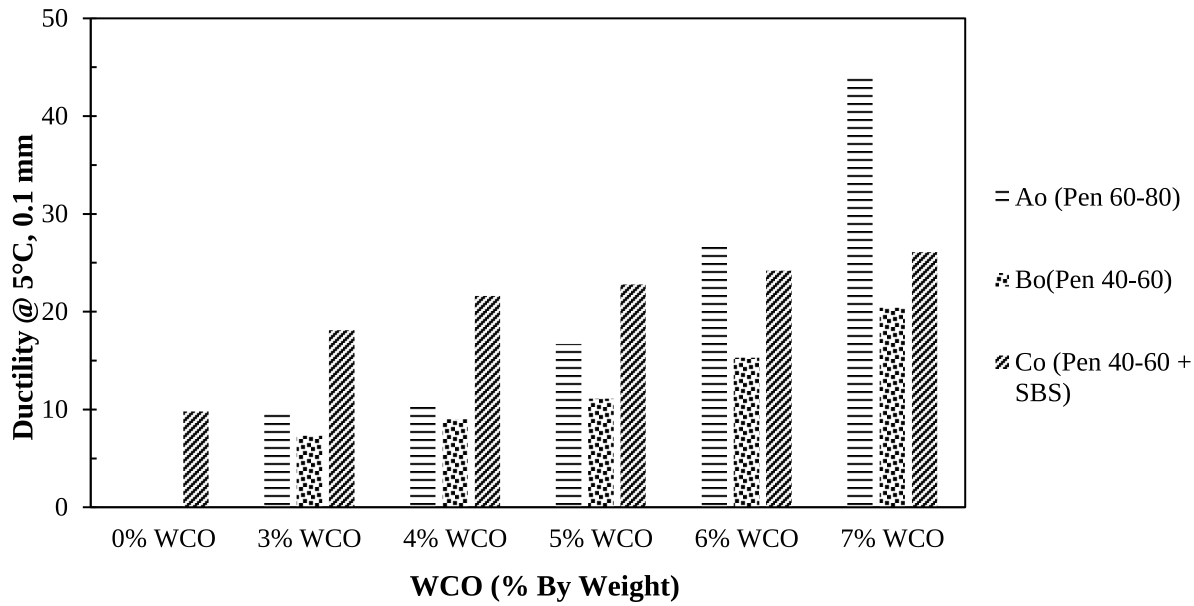


Figure 2.3 Relationship Of Ductility Value With Different Percentages of WCO (Adapted from (Chen et al., 2014))

2.3.2 Investigation of WCO Modified Binder using Rheological Testing

2.3.2.1 Effect of WCO on Viscosity and Mixing & Compaction Temperature

The rotational viscosity test result of WCO based binder at different temperature levels is illustrated in Figure 2.4. The data shows that the viscosity is constantly decreasing with the addition of WCO while temperature continuously increases. The maximum value was recorded at 1.074 Pa.s at 120°C while it had been gradually decreasing with the addition of WCO. A drastic change of viscosity was recorded at 150°C, where viscosity approximately dropped to 21.5% from the previous temperature and afterward steadily decreased. Similar to 150°C, a downward trend was perceived at 180°C but not similar to viscosity as 120°C. Zargar (Zargar et al., 2012) conducted a study on aged 40/50 grade bitumen at 135°C and found that the addition of 4% WCO can achieve almost the same viscosity of 80/100 grade bitumen. Huang (Sun et al., 2016) noted that the addition of WCO decreased the viscosity of the asphalt binder because of the dilution effect and reduced the construction temperatures of binder (AMB) mixtures. Generally, from an economic perspective, the lower viscosity can reduce the mixing and compaction temperature of the mix. The reduced mixing and compaction temperature is favorable in the construction site and also for saving cost. Although the lower viscosity can be achieved using an excessive percentage of rejuvenator, then it might be a matter of poor serviceability. The lower the serviceability, the material will be softer and susceptible to rutting. Azahar et al. (Azahar et al., 2016) observed a change of viscosity after the modification of WCO. Compare to untreated WCO, the treated WCO exhibits higher viscosity as well as the higher internal resistance. This could be the reason for chemical modification of WCO, which achieves better bonding with asphalt and makes the binder stiffer than untreated WCO modified binder. Also, the higher viscosity is related to the high adhesive performances of the mixtures. Thus, treated WCO might be better to be used as a rejuvenator based on its performance.

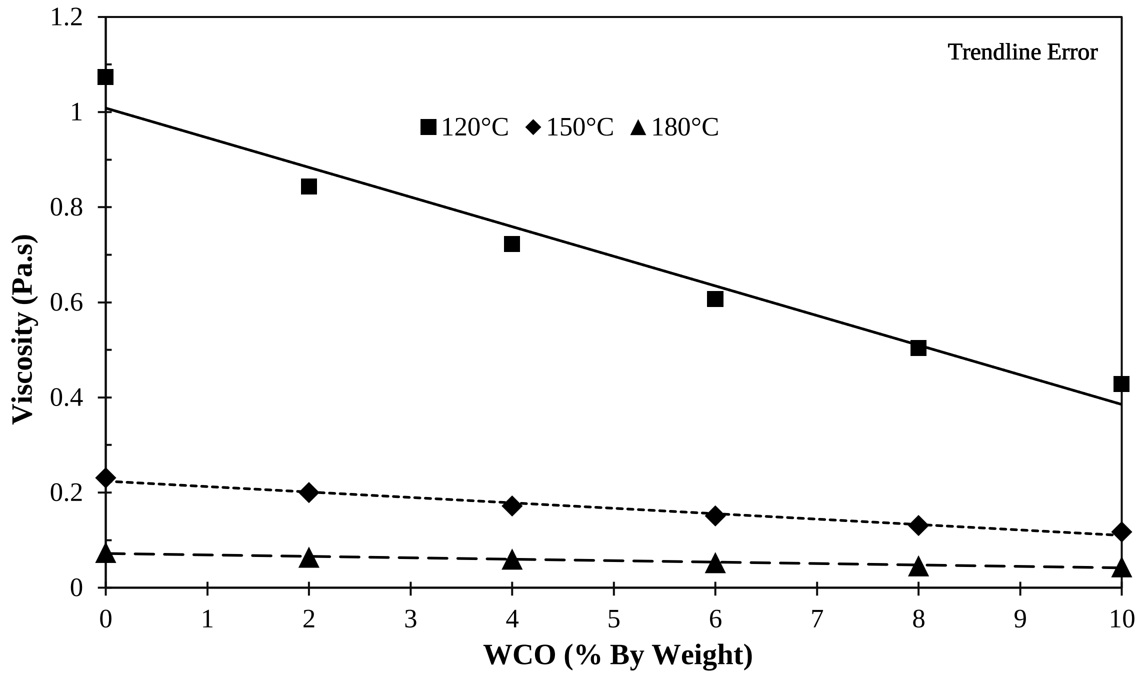


Figure 2.4 Relationship of Viscosity with Different Percentages of WCO at Different Temperature (Data Adapted from(Bailey & Philips, 2010))

2.3.2.2 Rutting & Fatigue Resistance

The rheological characteristic is prominently determined by the dynamic shear rheometer (DSR) test in order to verify any changes in the behavior of the binders or the shear resistance. DSR measures the complex shear modulus ($G*$) and phase angle (δ) of unaged binders, short-term aged (using the Roll Thin Film Oven (RTFO)) and long-term aged binder (using the Pressure Aging Vessel (PAV)) (Hidayah et al., 2012). Generally, asphalt with a higher $G^*/\mathrm{Sin}\delta$ value at high temperature shows higher rutting resistance (Chen et al., 2014). The addition of WCO based bio-oil results in a decrease of complex modulus and an increase of phase angle for asphalt binder at medium and high temperatures, which means adding bio-oil could decrease the deformation resistance and elastic recovery performance of control asphalt (Azahar et al., 2016; Chen, Xiao, et al., 2014; Sun et al., 2016). Sun. (Sun et al., 2017) experimented on OBA, Pen 70 and SBS-MA binders and found that the rutting factor decreased with the increase of temperature. Also, the performance grade temperatures of OBA, PEN 70 and SBS-MA were measured 70.3^{o}C, 66.9^{o}C, and 73.2^{o}C respectively, which represented that OBA has better high-temperature performances than virgin PEN 70 binder. For the WCO modified binder, the addition of oil concentrations decreases the $G*$ value and increases the δ value. As a result, there will be a reduction in $G^*/\mathrm{Sin}\delta$ value and therefore, the failure temperature as well. Similar results were also observed by Yu and Chen. (Chen et al., 2014; Yu et al., 2014). Azahar (Azahar et al., 2016) found that the improvement of WCO quality improves the rheological performances of the modified asphalt binder. The rutting resistance was recorded 0.799, 0.608, and 0.47 kPa for 3%, 4% and 5% untreated WCO respectively at 64^{o}C while for treated WCO it was recorded 0.699, 0.676, and 0.637 kPa at 70^{o}C. In addition, this study noticed that the maximum rut resistant temperature for untreated and treated WCO are 64^{o}C and 70^{o}C respectively. This indicates that the treated WCO can improve the rutting resistance (Azahar et al., 2016). Similar results of better rutting resistance were also observed by Zhang (Zhang et al., 2017) after improving the quality of WCO by chemical modification. Therefore, it can be concluded that WCO as a rejuvenator/modifier might have negative impacts on rutting performance of asphalt binder. The modification of WCO showed better rutting performance due to the better chemical bonding with asphalt could be a better alternative. In addition, using SBS polymer with WCO might show promising rutting performance and elastic recovery of binder based on the study of Yang. (Yang et al., 2019).

From the Strategic Highway Research Program (SHRP), a mathematical correlation was presented to determine the rutting and fatigue cracking performance of asphalt binder based on the rheological parameters G* and δ (Kennedy et al., 1994). A lower value of G* and higher value of δ is recommended to have better fatigue cracking resistance. Based on the analysis of rutting resistance, it was sound that using WCO as a rejuvenator decreases the G* and increases the δ, which is bad for rutting performance. Whereas, these parameters criteria are better for fatigue cracking resistance. An experimental study conducted by Maharaj (Maharaj et al., 2015) and found that the increasing concentration of WCO increase the fatigue cracking resistance of asphalt binder. Also, a similar study was conducted by Majidifard.(Majidifard et al., 2019), and found good cracking resistance using WCO. In addition, the use of SBS polymer to improve the rutting resistance of binder was also found the improvement in cracking resistance as well from different studies (Kim et al., 2009; Singh & Girimath, 2016). Therefore, the using of WCO as a rejuvenator might be a concern for rutting performance, which can be mitigated by modification of WCO or using SBS polymer. Whereas, superior fatigue cracking performance should be observed for using WCO rejuvenator.

2.3.2.3 Thermal Cracking Resistance

The low-temperature performances of the binder were measured by BBR tests, characterized by creep stiffness and the m-value. The stiffness reflects the anti-cracking capacity of the binders at low temperature, and the low temperature makes the strain capacity of the binders to drop quickly. The m-value represents the creep rate of the binders, and a higher m-value meant higher relaxation capability (Sun et al., 2017). From the study of Sun (Sun et al., 2017), it can be observed that OBA shows better low temperature cracking resistance than Pen 70 binder as well as SBS-MA (SBS Modified Asphalt). The study also found that the OBA (optimized bio-asphalt) has better cracking resistance at -12°C and the grading temperature was noted at -18°C. At low temperatures, the rejuvenated asphalts exhibited higher δ values and lower G* values than virgin asphalt, which indicated that adding WCO was effective for restoring the low-temperature cracking resistance of an asphalt (Zhang et al., 2017). Zhang (Zhang et al., 2017) experimented on different WCO rejuvenated asphalt, aged and virgin asphalt to correlate the stiffness and the m value. The study demonstrates that for the temperature range from -12°C to -18°C, stiffness increases while m value decreases for all types of binder which increases the risk of thermal cracking. Whereas, some other studies have found improvement of thermal cracking resistance of using WCO rejuvenator (Bahadori et al., 2019; Zhu et al., 2019). As, the decreasing of lower temperature makes the binder stiffer, the addition of WCO rejuvenator might soften the binder and reduce the G* value. The reduction of G* parameter, helps the binder to achieve better cracking resistance. Therefore, it can be concluded that the effect of thermal cracking resistance and critical low temperature of rejuvenated asphalt depends on the type of WCO and also the qualities of WCO used for asphalt rejuvenation.

2.4 Investigation of WCO Modified HMA Mixtures

2.4.1 Permanent Deformation

Rutting is an unacceptable problem of pavements and is a significant cause of safety issue during wet weather conditions as well as for excessive fuel consumption (Leiva-Villacorta et al., 2017). With the addition of WCO, stiffness and the rutting resistance of the bio-asphalt constantly decreases (Wen et al., 2012). To predict rutting performances, a limited number of experiments has been conducted on WCO rejuvenated HMA mixtures. Only a few researchers had done some study on rutting performance. Sun (Sun et al., 2017) conducted a permanent deformation test named Dynamic Stability (DS) that exhibits the dynamic stability of different mixtures at high temperatures of 60°C and shows a similar result in Figure 2.5 for OBA & SBS-MA mixtures. Also, all the binder mixtures satisfy the critical value of high-temperature dynamic stability including 2400 times/mm for OBA and SBS-MA mixtures and 800 times/mm for the ordinary binder mixtures. This result is also consistent with the field performance as the OBA mixtures contain different polymer contents that make the binder stiffer than the normal WCO based mixes and exhibits better rutting resistance.

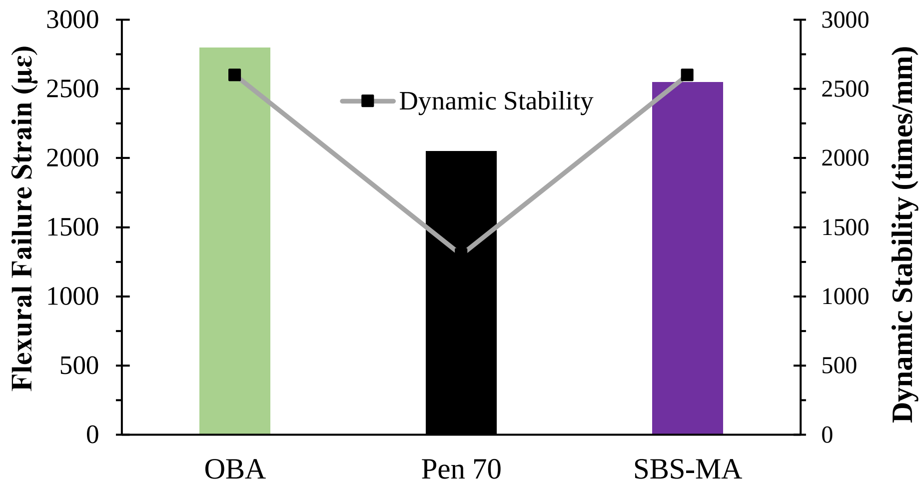


Figure 2.5 Performance of WCO Based HMA Mixture Related to High and Low Temperature (Adapted from (Sun et al., 2017))

2.4.2 Fatigue and Thermal Performance

Table 2.1 represents the comparison of the IDT fatigue test, thermal test, and moisture test results for several binders. From Table 2.1, results show that by adding WCO based bio-asphalt, the failure strength, critical strain energy density (CSED) and fracture work decreases, which indicates that it reduced the fatigue cracking resistance. Failure strength indicates the peak stress of the sample from the stress-strain curve. This peak stress was used to calculate the CSED of the sample to determine the fatigue cracking resistance. With the increment of WCO based bio-asphalt percentages, CSED also increases which represents the increase of low temperature thermal cracking resistance. Also from Figure 2.5, all mixtures satisfy the required specification of failure strain ≥ 2500 μƐ for modified asphalt and failure strain ≥ 2000 μƐ for conventional asphalt (Sun et al., 2017). As such, it might be a good mixture in case of low temperature cracking resistance.

Table 2.1 Comparison of IDT Fatigue, IDT Thermal & IDT Moisture Test Results with Different Percentages of Bio-Asphalt (Adapted from (Wen et al., 2012))

		IDT Fatigue Test			IDT Thermal		IDT Moisture
Asphalt Type	Bio-asphalt %	Failure Strength (Pa)	CSED (Pa)	Fracture Work (N-mm)	Failure Strength (Pa)	CSED (Pa)	TSR
PG 58-28	0	1,086,409	9,524	Not tested	6,501,831	5,992	0.87
PG 58-28	30	643,816	5,670	Not tested	4,961,625	12,437	0.89
PG 58-28	60	350,951	3,119	Not tested	4,503,408	16,280	0.80
PG 82-16	0	2,775,770	20,686	45,618	6,827,405	7,477	0.90
PG 82-16	10	2,227,055	16,688	37,117	6,235,349	7,797	0.83
PG 82-16	30	1,783,134	10,522	25,424	4,664,153	10,633	0.89
PG 76-22	0	2,778,322	13,693	35,390	6,069,766	7,614	0.97
PG 76-22	10	2,507,714	12,539	31,043	5,801,009	7,721	0.93
PG 76-22	30	2,033,478	9,068	26,523	5,156,961	8,927	0.91

2.4.3 Moisture Susceptibility Performance

Hot Mix Asphalt (HMA), which is made from certain materials can be very sensitive with the presence of water in the pavement. It may cause severe stripping between the aggregate and binder, creating potholes and affecting traffic safety. The tensile strength ratio (TSR) value denote the requirement of moisture susceptibility of the mixture. From Table 2.1, data from bio-oil rejuvenated binder shows that all the samples satisfy the AASTHO minimum criteria for the TSR ratio and the ratio is above 80% for all the binder mixes. Hence, the mixers should have better resistance to water damage. It is also to be noted that, the reduction of moisture susceptibility of HMA depends on the adhesion between asphalt binder and aggregate. Also, adhesion is correlated with the viscosity of binder and higher viscosity attributed to the higher adhesion. As the viscosity of untreated WCO is less than treated WCO, it is a concern for moisture susceptibility performance of HMA. In addition, the existence of FFA in WCO might increase the water affinity to the binder and leads to higher moisture susceptibility. Therefore, it required to have an in-depth analysis of the performance prediction of WCO rejuvenated HMA.

2.5 Chemical Characterization of WCO Modified Binder

2.5.1 Acid Content in WCO and Effect on Performance

The properties of WCO largely depend on the degradation process, operation temperature during frying activities, as well as the presence of impurities in WCO (Azahar et al., 2016; Hidayah et al., 2012). The quality of waste cooking oil is determined by the presence of acid contents like high free fatty acid (FFA). In general, all kinds of waste oil contain a higher amount of FFA contents. The FFA generates during frying activities as the oil is continuously heated to high temperatures with the presence of moisture and air content that creates several degradation processes. One of the major issues in the production of free fatty acid (FFA) by the hydrolysis process due to the presence of moisture (Sanli et al., 2011). The presence of FFA weakens the adhesion of WCO with bitumen. Besides, it reduces the binder’s rheological properties, which have an adverse effect on pavement mixture performance. GC-MS analysis is a widely used technique to identify the fatty acid content of waste cooking oil. Asli (Asli et al., 2012) studied the chemical compositions of WCO, which is presented in Figure 2.6. The data indicates that the Palmitic acid (38.35%) occupies the second-largest percentages of acid concentration in WCO, after Oleic acid (43.67%). Also, the existence of similar higher acid contents was also reported in different studies(Gong et al., 2016; Majidifard et al., 2019). These chemical contents in waste cooking oil are the fundamental characteristics to control the behavior of the rejuvenated asphalt (Asli et al., 2012). Also, the chemical structure of these two acids exhibits both polar and non-polar ends, which is saturated aliph and shows an indication of water affinity of WCO. Therefore, the rejuvenation with WCO might have higher moisture susceptibility, which will lead to premature pavement failure. To conclude, it is clear that the waste cooking oil may be harmful to the rejuvenated asphalt due to its affinity to water. Therefore, modification of WCO is required to reduce the FFA content and to achieve better performances.

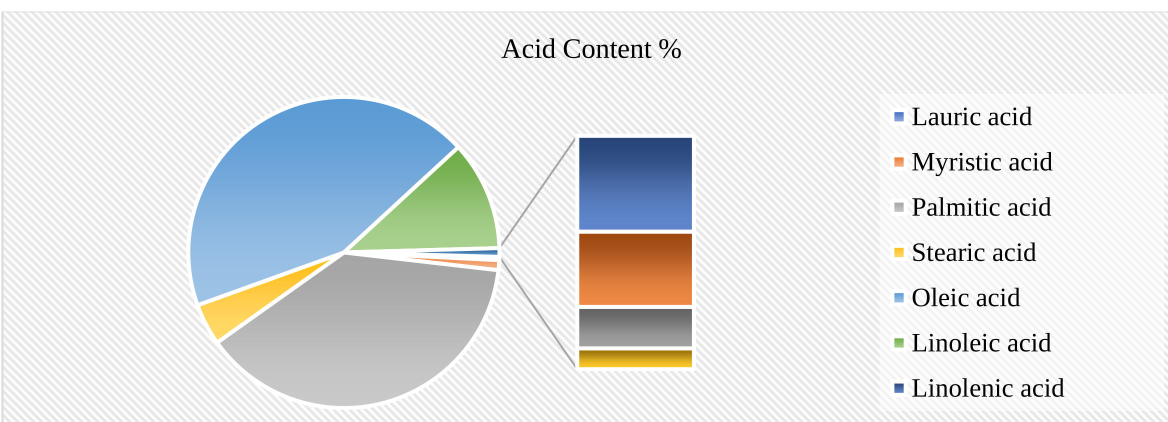


Figure 2.6 Chemical Properties of WCO (Adapted from (Asli et al., 2012))

2.5.2 Effect of WCO on Asphalt Molecular Compositions (SARA)

At the molecular level, asphalt is considered as a complex organic compound because it consists of different molecular groups. Depending on the polarity and size, they can be divided as saturate, aromatic, resin and asphaltene (SARA). Asphaltene is a relatively stiffer and disperse domain, and later three forms a liquid substance to hold the asphaltene which is known as maltene. To understand the better characteristics of these components, thin layer chromatography (TLC-FID) is a rapid and accurate method (Hossain & Hossain, 2018). With the change or modification of binder, not only the fraction content changes but also there is a change in their chemical property, which is responsible for oxidation reaction and volatilization. Due to this, the transformation within saturates, aromatics and resin may be responsible for the degradation or enhancement of the macro properties of asphalt during aging and rejuvenation, such as viscosity, rutting resistance at high temperature and cracking resistance at low temperature (Gong et al., 2016). The change of their SARA fraction contents can be easily understood from their peaks when the base binder is rejuvenated by WCO (Figure 2.7). From the figure, it was found that the virgin asphalt shows different peaks than the TFOT aged and oil-rejuvenated asphalt. Especially for aromatics peak, which indicates the change of chemical property of virgin asphalt due to oxidation and volatilization reaction to form aged asphalt. Whereas, it is also mentioned that the asphaltenes peaks are almost the same for all and they overlapped with each other; results in less influence of chromatograms on the change of the formulation of asphalt. Zhang (Zhang et al., 2017) also studied on the SARA fractions for virgin (A_0), aged asphalt (B_0) and WCO rejuvenated asphalt (A_1-A_8) and found that the aged asphalt B_0 shows better resin and asphaltenes content than virgin asphalt $A_{0.}$ However, with the addition of WCO (A_{1-} A_8), saturates and aromatics are decreasing linearly while the other two contents are increasing. This is due to the dilution of resins and asphaltenes for the various qualities of WCOs. The colloidal instability index (I_c) value for virgin asphalt is 0.305 which is similar to the binder A_{1-} A_4, but the other binder A_5- A_8 has a higher I_c value compared to the virgin asphalt and lower compared to the aged binder. The difference in mechanical properties among the virgin, aged, and rejuvenated asphalt binders are due to the change of their chemical fractions in SARA components. Rejuvenation of binder increases the saturates content, which reduces the binder stiffness (Allen et al., 2014), while it increases the aromatics content that helps to restore the original properties of aged binder (Yu et al., 2014). Therefore, rejuvenation with oil might reduce the binder rutting property, whereas it will exhibit overall better performances compared to the aged binder.

2.5.3 Effect of WCO on Asphalt Morphologies and Micro-Mechanical Properties

Asphalt binder is a complex mixture of different organic chemical substances, which is obtained from the fractional distillation process of petroleum oil production. The higher variability of the chemical contents might form micro structures and is responsible for the change of physical properties of asphalt that includes stiffness, modulus of elasticity, adhesion, and dissipation energy (Allen et al., 2012; Fischer et al., 2014). To observe the micro structures and morphological behavior of asphalt, Atomic Force Microscopy (AFM) is one of the most widely used tools. AFM is capable to map surface force (adhesion) and surface topography (roughness) of asphalt after extracting information from tip-sample interactions (Bellitto, 2012). The key reason for the widespread application of AFM is the simple sample preparation techniques and the ability to operate at any temperature (Das et al., 2016). Generally, two techniques are used to prepare the AFM sample: 1) spin casting, and 2) heat casting. Also, from the AFM images, three phases are observed: 1) catana phase; 2) peri-phase, which is peripheral to the catana phase; 3) perpetua phase, which is adjacent to the peri-phase (Hossain & Hossain, 2018; Jahangir et al., 2015). A number of studies has been conducted to understand the existence of micro structures and their related morphological behavior in the asphalt binder. The micro structures are looks like bumble bees and Loeber (Loeber et al., 1996) named it as "bee" structure. Also, some other studies found the existence of bee structures in asphalt and correlated with the rheological performances of asphalt binder (Nahar et al., 2013; Pauli et al., 2011; Rebelo et al., 2014). Majority of the studies reported the increase in number of bee structures due to aging of binder, which was decreasing after the rejuvenation effect (Nahar et al., 2014). Whereas, different observations were also reported by few other researchers and they concluded that the rejuvenation does not always alter the formation of microstructures for an aged/virgin binders and therefore, the performance evaluation of rejuvenated binder might not be based on the micro-structures of asphalt (Chen et al., 2018; Yu et al., 2014). Despite all of this research, a very limited number of studies has been conducted with WCO rejuvenated asphalt to understand the fundamental characteristics and micro-mechanical behavior. Gong (Gong et al., 2017) experimented on Pen50 and SBS modified asphalt of a virgin, aged and rejuvenated asphalt respectively. Figure 2.8 shows the different textures or bee structures of these asphalt grades. For virgin Pen50 grade asphalt, clear bees can be seen from Figure 2.8 while the size of bees reduced for both the cases of aged and rejuvenated

Pen50 asphalt. Both of these have a higher quantity of bee structures compare to virgin Pen50 binder, which is unexpected and might be due to the polar component aggregation. For SBS modified asphalt, diffusion plays a significant role in reducing the microstructure for rejuvenated asphalt grade, while it doesn't change much for aged and virgin asphalt. In terms of adhesive force, aging reduces the adhesion between asphalt and aggregate. Whereas, the addition of WCO based bio-oil increases the adhesion for both aged and SBS modified binder, which is an indication of restoring the performance of rejuvenated asphalt binder. Also in China, Ma (Ma et al., 2019) studied on the morphological characteristics of rejuvenated asphalt binder and found that addition of rejuvenator increases the adhesion and the bonding area of binder.

A similar experiment was conducted by Azahar (Azahar et al., 2016) after changing the quality and quantity of WCO (5% treated & 5% untreated). The experimental study illustrated that the virgin 60/70 asphalt showed more surface roughness (2.705 nm) than treated and untreated rejuvenated asphalt of 2.499 nm and 1.791nm respectively. The high surface roughness exhibits the increment of the ''bee" shaped structure that tended to reduce adhesive performance. Theoretically, the addition of rejuvenator fills up the intermolecular gap of the rough surface and that enhanced the contact surface area which helps to increase the adhesion of rejuvenated asphalt binder (Dong et al., 2017; Ma et al., 2019; Oliveira et al., 2012). Treated WCO shows moderate flat Catana phase because of having a good coating and adherence properties between asphalt and aggregates. In addition, this potential helps to have a good strength of HMA of treated WCO than untreated WCO. The low adhesive performance of the untreated WCO was the result of the fluidity property. The lubrication properties exhibited dominant effects that caused the sliding in the internal particle and thereby reduced the chemical bonding with the aggregates. The low chemical bonding characteristic and having different polarity groups affected the low strength performance of the untreated WCO mixture (Azahar et al., 2017). Therefore, the addition of rejuvenator reduces the bee structures of the binders and the stiffness of binders as well. Also, the fluidity and polarity factors play a vital role which is responsible for poor strength of untreated WCO HMA mixtures.

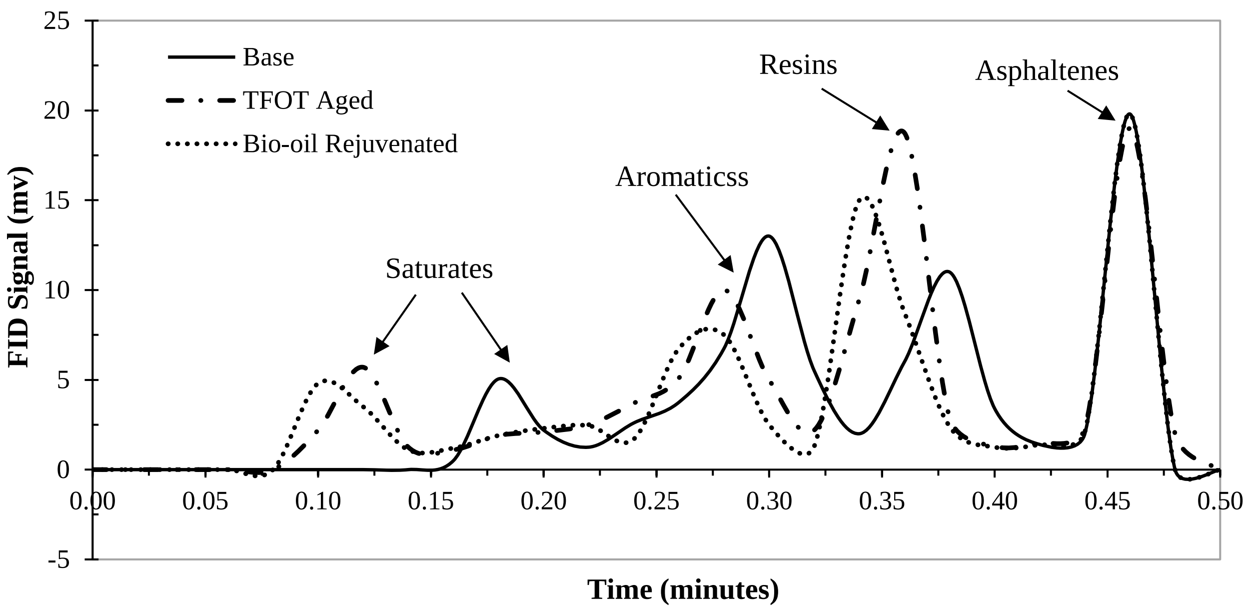


Figure 2.7 Chromatograms of Virgin, Aged And Rejuvenated Asphalts of Pen50 Grade (Adapted from (Gong et al., 2016))

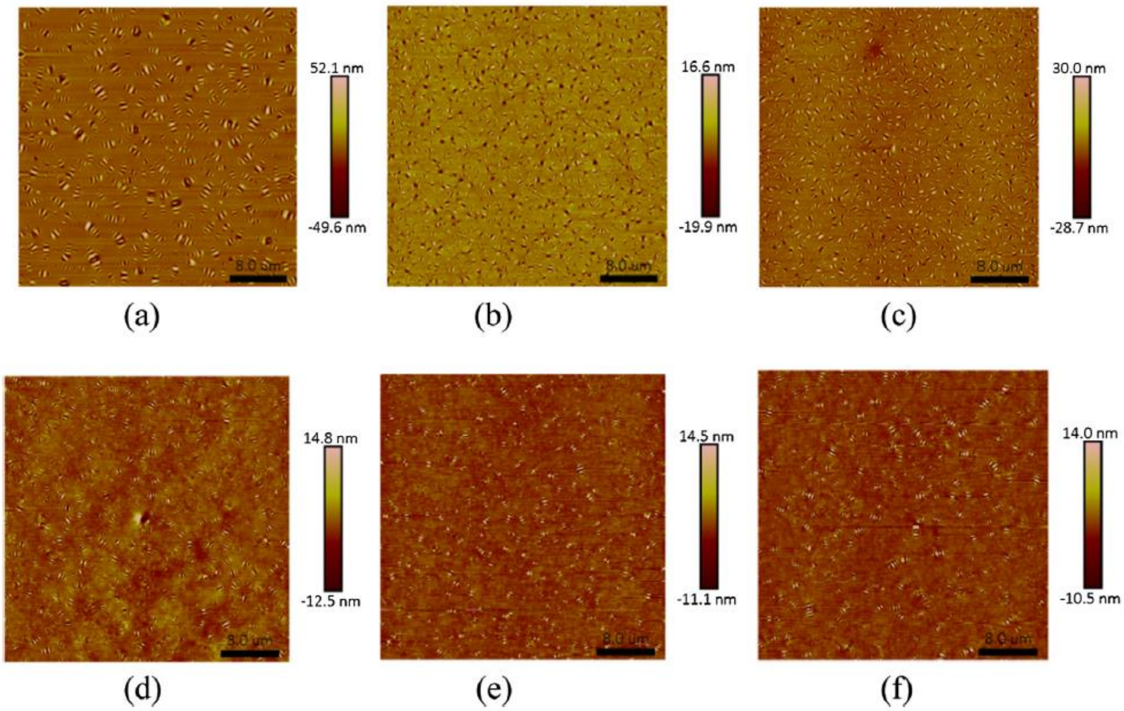


Figure 2.8 AFM Topographies of Asphalts: (a) Virgin Pen50 Asphalt; (b) Aged Pen50 Asphalt; (c) WCO Rejuvenated Pen50 Asphalt; (d) Virgin SBS Modified Asphalt; (e) Aged SBS Modified Asphalt; and (f) WCO Rejuvenated SBS Modified Asphalt (Adapted from (Gong et al., 2017) with permission)

2.5.4 Effect of WCO on Asphalt Oxidative Potential

The chemical functional groups were analyzed using different series of Fourier Transform Infrared Spectroscopy (FTIR). FTIR is the only analytical method which provides ambient temperature operation and to directly monitor the vibrations of the functional groups simultaneously which characterize the molecular structure and govern the course of chemical reactions. In principle, FTIR also provides continuous (near real-time) and low maintenance operation compared to gas chromatography and mass spectroscopy. Based on the previous experimental analysis, the region between 2.5 mm and 25 mm (4000 to 400 cm^{-1}) is the most attractive for chemical analysis (Doyle, 2017). Out of those bands, 1030 and 1700 cm^{-1} correspond to sulfoxide (S=O), and carbonyl (C=O) respectively that reflects the aging and rejuvenating degree of asphalt (Herrington & Ball, 1996). Table 2.2 illustrates the observation of different chemical groups using FTIR. From Table 2.2, it is clear that the WCO based bio-oil rejuvenated asphalt is different from the conventional asphalt as it contains alcohol O-H stretch peaks at 3500 cm^{-1}. It is also notable that the WCO based bio-oil is a complex organic mixture containing carbon, hydrogen, nitrogen and sulfur elements which resemble asphalt (Gong et al., 2017). For the rejuvenated asphalt, the quality of WCO influences the gradual increment of sulfoxide (S=O) and decrease of carbonyl (C=O) peaks (Zhang et al., 2017). Test results show that the existence of C=O stretch (1744 $cm^{-1)}$ was available in all rejuvenated asphalt while it's concentration was lower for treated binders and higher for untreated binders. This peak is responsible for making the binder softer which is most prone to rutting (Azahar et al., 2016). With the modification of the quality of WCO, the C-H bond, as well as C=C stretch aromatic bond, increased for all percentages of treated WCO. The exciting thing noticed in this study is, there is an increase in rutting resistance with treated WCO compared to untreated WCO from our previous evaluation, which is also noticed in FTIR test, as the C=O stretch (1744 cm^{-1}) was very negligible here.

Table 2.2 Observation of Different Virgin, Aged and Rejuvenated Asphalt using FTIR

Materials	Observation (yes/no)					
	Alcohol O-H stretch	C-H bond	C=O stretch	C=C stretch aromatic	Alkyl C-O	C-C alkane group
			Sun et al. (2017)			
Waste cooking oil residue (WCOR)	✗	✓	✓	✗	✓	✓
Hydrocarbon resin (HR_1)	✗	✓	✓	✓	✓	✓
Optimized bio-asphalt (OBA)	✗	✓	✓	✓	✓	✓
			Gong et al. (2015)			
Bio-oil	✓	✓	✓	✗	✓	✓
Pen50 (virgin + aged + WCO rejuvenated)	✗	✓	✗	✓	✗	✓
SBS Modified(virgin + aged + WCO rejuvenated)	✗	✓	✗	✓	✗	✓
			Zhang et al. (2017)			
WCO rejuvenated Asphalt	✗	✓	✓	✓	✓	✓
			Azahar et al. (2016)			
Untreated WCO (3%, 4% & 5%)	✗	✓	✓	✓	✓	✓
Treated WCO (3%, 4% & 5%)	✗	✓	✗	✓	✗	✓
			Zargar et al. (2012)			
Virgin Binder (80/100)	✗	✗	✗	✓	✓	✓
Aged Binder	✗	✗	✗	✓	✓	✓
WCO rejuvenated Binder	✗	✗	✗	✓	✓	✓
WCO	✗	✗	✓	✓	✓	✓

2.6 Summary

Asphalt binder is the main component in the flexible pavement construction. To reduce the dependency on petroleum-based asphalt and to make sustainable pavement, asphalt binder from RAP is considered during pavement construction. In recent years, a number of studies have been conducted or being conducted to examine if WCO can be used as a rejuvenator with RAP materials. Still, there are some issues related to using WCO in the pavement. The summary of the issues is presented below:

- The identification of optimal application rates of WCO rejuvenator is still on debate.
- The performance evaluation of rutting and cracking resistance is inadequate, especially for cold climate context.
- The chemical and fundamental interaction effect of WCO with different types of asphalt modifiers to improve pavement performance is needed.
- The existing research on the fundamental properties of WCO rejuvenated binder at the micro level is inadequate.
- The field performance evaluation of WCO rejuvenated HMA is not done.

In this work, we reviewed a number of published articles on performance and adverse effects of WCO on binder and HMA performances. From the literature review, the following conclusions can be drawn:

- The dosing rate of WCO can influence the properties of the rejuvenated asphalt binder significantly. The basic properties such as penetration, ductility increases with WCO addition while softening point and viscosity decreases gradually. This indicates that there is an increase in flexibility at low temperatures, which might lead the binder become more rutting susceptible.
- The DSR and BBR tests exhibits good rheological properties of WCO based asphalt. This indicates the decrease in the complex modulus G* and the increase of the m value, which might enhance the thermal cracking resistance. However, it might experience reduction in elastic recovery performance.
- The existence of free fatty acid (FFA) is found in GC-MS analysis of WCO which is responsible for the hydrophilic characteristic. A few studies reported that treatment of WCO could eliminate the acid content and shows excellent chemical and rheological performances.
- FTIR test result exhibited a higher rate of undesirable chemical components (e.g., C=O stretch) for untreated WCO, which is responsible for softening the binder and inducing rutting failure. Otherwise, similar chemical compositions were found for other binders.
- From HMA performance evaluation, the reduction of fracture energy and CSED leads to low fatigue resistance; however it shows better low-temperature thermal cracking with the increase in thermal CSED. Also, all the WCO based bio-asphalt fulfilled the TSR requirement.

This review focuses on the performances of the WCO based asphalt and its possibility for use in HMA mixes, primarily as a rejuvenating agent while using RAP in the mixes. While usage of WCO has been shown promising to enhance the performance of many binder properties (e.g., ductility, fatigue resistance), many studies also reported usage of WCO could negatively affect other properties (e.g., rutting resistance). Indeed, further investigation is needed to better understand the optimal dosing rate for different percentages of WCO with RAP in the fundamental level along with its field performance.

2.7 References

Al-Qadi, I. L., Elseifi, M., & Carpenter, S. H. (2007). *Reclaimed asphalt pavement - A literature review* (Issue FHWA-ICT-07-001). https://doi.org/http://hdl.handle.net/2142/46007

Allen, R. G., Little, D. N., Bhasin, A., & Glover, C. J. (2014). The effects of chemical composition on asphalt microstructure and their association to pavement performance. *International Journal of Pavement Engineering*, *15*(1), 9–22. https://doi.org/http://dx.doi.org/10.1080/10298436.2013.836192 The

Allen, R., Little, D., & Bhasin, A. (2012). Structural Characterization of Micromechanical Properties in Asphalt Using Atomic Force Microscopy. *Journal of Materials in Civil Engineering*, *24*(10), 1317–1327. https://doi.org/10.1061/(ASCE)MT.1943-5533.0000510

Asli, H., Ahmadinia, E., Zargar, M., & Karim, M. R. (2012). Investigation on physical properties of waste cooking oil - Rejuvenated bitumen binder. *Construction and*

Building Materials, *37*, 398–405. https://doi.org/10.1016/j.conbuildmat.2012.07.042

Azahar, W. N. A. W., Jaya, R. P., Hainin, M. R., Bujang, M., & Ngadi, N. (2016). Chemical modification of waste cooking oil to improve the physical and rheological properties of asphalt binder. *Construction and Building Materials*, *126*, 218–226. https://doi.org/10.1016/j.conbuildmat.2016.09.032

Azahar, W. N. A. W., Jaya, R. P., Hainin, M. R., Bujang, M., & Ngadi, N. (2017). Mechanical performance of asphaltic concrete incorporating untreated and treated waste cooking oil. *Construction and Building Materials*, *150*, 653–663. https://doi.org/10.1016/j.conbuildmat.2017.06.048

Bahadori, A., Li, R., Zhang, K., & Xin, J. (2019). Performance Evaluation of Hot Mix Biobinder. *International Airfield and Highway Pavements Conference*. https://doi.org/https://doi.org/10.1061/9780784482476.008

Bailey, H. K., & Philips, P. (2010). *Asphalt Rejuvenation* (Patent No. US Patent 0034586 A1).

Bellitto, V. (2012). *Atomic Force Microscopy- Imaging, Measuring and Manipulating Surfaces at the Atomic Scale*. InTech.

Branthaver, J., Petersen, J., Robertson, R., Duvall, J., Kim, S., Harnsberger, P., Mill, T., Ensley, E., Barbour, F., & Schabron, J. (1993). Binder characterization and evaluation. Volume2: Chemistry. In *Strategic Highway Research Program* (Vol. 2, Issue SHRP-A-368). http://trid.trb.org/view.aspx?id=386723

Brown, E. R. (1988). Preventive Maintenance of Asphalt Concrete Pavements.

Transportation Research Record: Journal of the Transportation Research Board, 6–11.

Chen, A., Liu, G., Zhao, Y., Li, J., Pan, Y., & Zhou, J. (2018). Research on the aging and rejuvenation mechanisms of asphalt using atomic force microscopy. *Construction and Building Materials*, *167*, 177–184. https://doi.org/10.1016/j.conbuildmat.2018.02.008

Chen, M., Leng, B., Wu, S., & Sang, Y. (2014). Physical, chemical and rheological properties of waste edible vegetable oil rejuvenated asphalt binders. *Construction and Building Materials*, *66*, 286–298. https://doi.org/10.1016/j.conbuildmat.2014.05.033

Chen, M., Xiao, F., Putman, B., Leng, B., & Wu, S. (2014). High temperature properties of rejuvenating recovered binder with rejuvenator, waste cooking and cotton seed oils. *Construction and Building Materials*, *59*, 10–16. https://doi.org/10.1016/j.conbuildmat.2014.02.032

Das, P. K., Baaj, H., Tighe, S., & Kringos, N. (2016). Atomic force microscopy to investigate asphalt binders : a state-of-the-art review. *Road Materials and Pavement Design*, *17*(3), 693–718. https://doi.org/https://doi.org/10.1080/14680629.2015.1114012

Datt, R., Kumar, Amit, & Kumar, Ashish. (2017). Waste Cooking Oil as a Rejuvenating Agent in Aged Bitumen. *International Journal of Control Theory and Applications*, *10*, 127–134.

Dokandari, P. A., Kaya, D., Sengoz, B., & Topal, A. (2017). Implementing Waste Oils with Reclaimed Asphalt Pavement. *Proceedings of the 2nd World Congress on Civil, Structural, and Environmental Engineering (CSEE 17)*, 1–12. https://doi.org/10.11159/icsenm17.142

Dong, Z., Liu, Z., Wang, P., & Gong, X. (2017). Nanostructure characterization of asphalt-aggregate interface through molecular dynamics simulation and atomic force microscopy. *Fuel*, *189*, 155–163. https://doi.org/10.1016/j.fuel.2016.10.077

Doyle, W. M. (2017). *Principles and Applications of Fourier Transform Infra- red (FTIR) Process Analysis*. http://www.hellma-axiom.com/pdf/technical_notes/AN-906.pdf

Elkashef, M., & Williams, R. C. (2017). Improving fatigue and low temperature performance of 100 % RAP mixtures using a soybean-derived rejuvenator. *Construction and Building Materials*, *151*, 345–352. https://doi.org/10.1016/j.conbuildmat.2017.06.099

Fischer, H. R., Dillingh, E. C., & Hermse, C. G. M. (2014). On the microstructure of bituminous binders. *Road Materials and Pavement Design*, *15*(1), 1–15. https://doi.org/http://dx.doi.org/10.1080/14680629.2013.837838

García, Á., Schlangen, E., & Van De Ven, M. (2011). Properties of capsules containing rejuvenators for their use in asphalt concrete. *Fuel*, *90*(2), 583–591. https://doi.org/10.1016/j.fuel.2010.09.033

Gong, M., Yang, J., Zhang, J., Zhu, H., & Tong, T. (2016). Physical-chemical properties of aged asphalt rejuvenated by bio-oil derived from biodiesel residue. *Construction and Building Materials*, *105*(15), 35–45. https://doi.org/10.1016/j.conbuildmat.2015.12.025

Gong, M., Zhu, H., Pauli, T., Yang, J., Wei, J., & Yao, Z. (2017). Evaluation of bio-binder modified asphalt ' s adhesion behavior using sessile drop device and atomic force microscopy. *Construction and Building Materials*, *145*, 42–51. https://doi.org/10.1016/j.conbuildmat.2017.03.114

Herrington, P. R., & Ball, G. F. A. (1996). Dependence Oxidation Mechanism of Asphalt. *Fuel*, *75*(9), 1129–1131. https://doi.org/https://doi.org/10.1016/0016-2361(96)00042-7

Hidayah, N., Rosli, M., & Ezree, M. (2012). *A Short Review of Waste Oil Application in Pavement Materials*. https://doi.org/10.13140/2.1.1379.7767

Hossain, K., & Hossain, Z. (2018). A Synthesis of Computational and Experimental Approaches of Evaluating Chemical, Physical and Mechanistic Properties of Asphalt Binders. *Advances in Civil Engineering*, *2019*, 20. https://doi.org/https://doi.org/10.1155/2019/1795958

Jahangir, R., Little, D., & Bhasin, A. (2015). Evolution of asphalt binder microstructure due to tensile loading determined using AFM and image analysis techniques. *International Journal of Pavement Engineering*, *16*(4), 337–349. https://doi.org/http://dx.doi.org/10.1080/10298436.2014.942863 Evolution

Ji, J., Yao, H., Suo, Z., You, Z., Li, H., Xu, S., & Sun, L. (2017). Effectiveness of

Vegetable Oils as Rejuvenators for Aged Asphalt Binders. *Journal of Materials in Civil Engineering*, *29*(3). https://doi.org/https://doi.org/10.1061/(ASCE)MT.1943-5533.0001769

Kandhal, P. S., & Mallick, R. B. (1997). Pavement Recycling Guidelines for State and Local Governments: Participant's Reference Book. *Fhwa-Sa-98-042*, *December*, 301. https://www.fhwa.dot.gov/pavement/recycling/98042/

Kennedy, T. W., Huber, G. A., Harrigan, E. T., Cominsky, R. J., Hughes, C. S., Von Quintus, H., & Moulthrop, J. S. (1994). *Superior performing asphalt pavements (Superpave): the product of the SHRP asphalt research program*. http://worldcat.org/isbn/030905821X

Kim, S., Sholar, G., Byron, T., & Kim, J. (2009). Performance of polymer-modified asphalt mixture with reclaimed asphalt pavement. *Transportation Research Record: Journal of the Transportation Research Board*, *2126*(1), 109–114.

Lei, Z., Bahia, H., Yi-qiu, T., & Ling, C. (2017). Effects of refined waste and bio-based oil modifiers on rheological properties of asphalt binders. *Construction and Building Materials, 148*, 504–511. https://doi.org/10.1016/j.conbuildmat.2017.05.101

Leiva-Villacorta, F., Vargas-Nordcbeck, A., & Aguiar-Moya, J. P. (2017). Permanent deformation and deflection relationship from pavement condition assessment. *International Journal of Pavement Research and Technology*, *10*(4), 352–359. https://doi.org/10.1016/j.ijprt.2017.03.005

Leung, D. Y. C., & Guo, Y. (2006). Transesterification of neat and used frying oil :

Optimization for biodiesel production. *Fuel Processing Technology*, *87*(10), 883–890. https://doi.org/https://doi.org/10.1016/j.fuproc.2006.06.003

Loeber, L., Sutton, O., Morel, J., Valleton, J., & Muller, G. (1996). New direct observations of asphalts and asphalt binders by scanning electron microscopy and atomic force microscopy. *Journal of Microscopy*, *182*(1), 32–39. https://doi.org/https://doi.org/10.1046/j.1365-2818.1996.134416

Ma, W., Huang, T., Guo, S., Yang, C., Ding, Y., & Hu, C. (2019). Atomic force microscope study of the aging / rejuvenating effect on asphalt morphology and adhesion performance. *Construction and Building Materials*, *205*, 642–655. https://doi.org/10.1016/j.conbuildmat.2019.01.151

Maharaj, R., Ramjattan-Harry, V., & Mohamed, N. (2015). Rutting and Fatigue Cracking Resistance of Waste Cooking Oil Modified Trinidad Asphaltic Materials. *Scientific World Journal*, *2015*. https://doi.org/10.1155/2015/385013

Majidifard, H., Tabatabaee, N., & Buttlar, W. (2019). ScienceDirect Investigating short-term and long-term binder performance of high-RAP mixtures containing waste cooking oil. *Journal of Traffic and Transportation Engineering (English Edition)*, *6*(4), 396–406. https://doi.org/10.1016/j.jtte.2018.11.002

Nahar, S. N., Dillingh, B., Erkens, S., Schmets, A. J. M., Fischer, H. R., Scarpas, A., & Schitter, G. (2013). Is Atomic Force Microscopy suited as Tool for fast Screening of Bituminous Materials? An Inter-laboratory Comparison Study. *92nd Annual Meeting, Transportation Research Board*, 1–16.

Nahar, S., Qiu, J., Schmets, A., Schlangen, E., Shirazi, M., Schitter, G., Scarpas, A., Nahar, S. N., Qiu, J., Schlangen, E., Shirazi, M., Schitter, G., & Scarpas, A. (2014). Turning Back Time : Rheological and Microstructural Assessment of Rejuvenated Bitumen. *93rd Annual Meeting, Transportation Research Board*, *January*, 1–17.

Oliveira, R. R. L. De, Albuquerque, D. a. C., Cruz, T. G. S., & Leite, F. M. Y. and F. L. (2012). Measurement of the Nanoscale Roughness by Atomic Force Microscopy: Basic Principles and Applications. *Atomic Force Microscopy - Imaging, Measuring and Manipulating Surfaces at the Atomic Scale*, 256. https://doi.org/DOI: 10.5772/37583

Pauli, A. T., Grimes, R. W., Beemer, A. G., Turner, T. F., & Branthaver, J. F. (2011). Morphology of asphalts , asphalt fractions and model wax-doped asphalts studied by atomic force microscopy. *International Journal of Pavement Engineering*, *12*(4), 291–309. https://doi.org/10.1080/10298436.2011.575942

Rebelo, L. M., Cavalcante, P. N., Sousa, J. S. De, Filho, J. M., Soares, S. A., & Soares, J. B. (2014). Micromorphology and microrheology of modified bitumen by atomic force microscopy. *Road Materials and Pavement Design*, *15*(2), 300–311.

Sanli, H., Canakci, M., & Alptekin, E. (2011). Characterization of Waste Frying Oils Obtained from Different Facilities. *World Renewable Energy Congress*, 479–485. https://doi.org/10.3384/ecp11057479

Sheinbaum, C., Balam, M. V., Robles, G., Lelo De Larrea, S., & Mendoza, R. (2015). Biodiesel from waste cooking oil in Mexico City. *Waste Management and Research*, *33*(8), 730–739. https://doi.org/10.1177/0734242X15590471

Singh, D., & Girimath, S. (2016). Investigation of rheological properties and Superpave PG of PMB mixed with reclaimed asphalt pavement binders. *Construction and Building Materials*, *126*, 834–842. https://doi.org/10.1016/j.conbuildmat.2016.09.084

Song, W., Huang, B., & Shu, X. (2018). Influence of warm-mix asphalt technology and rejuvenator on performance of asphalt mixtures containing 50% reclaimed asphalt pavement. *Journal of Cleaner Production*, *192*, 191–198. https://doi.org/10.1016/j.jclepro.2018.04.269

Su, J. F., Qiu, J., Schlangen, E., & Wang, Y. Y. (2015). Investigation the possibility of a new approach of using microcapsules containing waste cooking oil: In situ rejuvenation for aged bitumen. *Construction and Building Materials*, *74,* 83–92. https://doi.org/10.1016/j.conbuildmat.2014.10.018

Sun, D., Du, Y., Zhu, X., Lu, T., Pang, Q., Shi, S., & Dai, Z. (2017). Evaluation of optimized bio-asphalt containing high content waste cooking oil residues. *Fuel*, *202*, 529–540. https://doi.org/10.1016/j.fuel.2017.04.069

Sun, D., Lu, T., Xiao, F., Zhu, X., & Sun, G. (2017). Formulation and aging resistance of modified bio-asphalt containing high percentage of waste cooking oil residues. *Journal of Cleaner Production*, *161*, 1203–1214. https://doi.org/10.1016/j.jclepro.2017.06.155

Sun, Z., Yi, J., Huang, Y., Feng, D., & Guo, C. (2016). Properties of asphalt binder modified by bio-oil derived from waste cooking oil. *Construction and Building Materials, 102*, 496–504. https://doi.org/10.1016/j.conbuildmat.2015.10.173

Wen, H., Bhusal, S., & Wen, B. (2012). Laboratory evaluation of waste cooking oil–based bioasphalt as sustainable binder for hot-mix asphalt. *Alternative Binders for Sustainable Asphalt Pavements, Transportation Research Circular, No. E-C165, Transportation Research Board, National Academies, Washington, DC, 25*(10), 49–60. https://doi.org/10.1061/(ASCE)MT.1943-5533.0000713.

Yang, Z., Zhang, X., Yu, J., & Xu, W. (2019). Effects of Aging on the Multiscale Properties of SBS-Modified Asphalt. *Arabian Journal of Science and Engineering*, *44*(5), 4349–4358. https://doi.org/https://doi.org/10.1007/s13369-018-3399-4

Yu, X., Zaumanis, M., Dos Santos, S., & Poulikakos, L. D. (2014). Rheological, microscopic, and chemical characterization of the rejuvenating effect on asphalt binders. *Fuel*, *135*(1), 162–171. https://doi.org/https://doi.org/10.1016/j.fuel.2014.06.038

Zargar, M., Ahmadinia, E., Asli, H., & Karim, M. R. (2012). Investigation of the possibility of using waste cooking oil as a rejuvenating agent for aged bitumen. *Journal of Hazardous Materials*, *233–234*, 254–258. https://doi.org/10.1016/j.jhazmat.2012.06.021

Zhang, D., Chen, M., Wu, S., Liu, J., & Amirkhanian, S. (2017). Analysis of the relationships between waste cooking oil qualities and rejuvenated asphalt properties. *Journal of Materials*, *10*(5). https://doi.org/10.3390/ma10050508

Zhu, J., Zhang, K., Liu, K., & Shi, X. (2019). Performance of hot and warm mix asphalt mixtures enhanced by nano-sized graphene oxide. *Construction and Building Materials*, *217*, 273–282. https://doi.org/10.1016/j.conbuildmat.2019.05.054

Chapter 3 Chemical Characteristics and Morphological Properties of Rejuvenated Asphalt Binders

Co-Authorship: A part of this chapter has been accepted for the RILEM International Symposium of Bituminous Materials Conference and the proceedings will be published by Springer. Also, additional tests have been conducted and results are being analyzed; they have been reported to ASCE Journal of Materials in Civil Engineering and published as a technical paper as: Ahmed, R. B., Hossain, K., Hajj, M. Ramez. (2020), 'Chemical, Morphological, and Fundamental Behavior of Rejuvenated Asphalt Binders'. The first author has conducted most of the research in this chapter. He also prepared the draft manuscript. The other authors supervised the research and reviewed the manuscript.

3.1 Abstract

Usage of RAP in pavement construction is very economic when the first cost is considered. However, the asphalts available in RAP are already oxidized, which can induce premature pavement distresses. The use of a rejuvenator is a common practice to reduce the issues of using RAP. Three different types of oils that include raw used oil, modified used oil, and Hydrolene are studied as rejuvenators. A number of basic and advanced testing were conducted to investigate the effectiveness of rejuvenators with the aged binder. A TFOT aged PG 58-28 binder was used as an aged binder, followed by mixing three rejuvenators at 3%, 6% and 9% by the weight of the total binder. To understand the characteristics and performance of these rejuvenators, three sets of characterization tests were conducted:

rheological, chemical, and morphological. This paper presents a summary of results from our chemical and morphological studies. Gas Chromatography-Mass Spectroscopy (GC-MS) was conducted to identify the chemical composition of rejuvenators, while Fourier Transformed Infrared Spectroscopy (FTIR) was conducted for obtaining chemical functional group information. Furthermore, an Atomic Force Microscopy (AFM) was conducted for obtaining the micro-morphological properties of rejuvenated asphalt binders. The collected data showed that rejuvenation changes the chemical composition and alters the micro-structures of binders significantly, which impacts the overall performances of binder. In fact, from this experimental study, a good correlation was found between the chemical compositional and morphological features and the rheological performance of binder. The research findings are expected to contribute to the performance evaluation and characterization of rejuvenated asphalt mixes.

3.2 Introduction

Over the last few decades, the necessity for developing a sustainable method of pavement construction led to the increase use of recycled materials. In general, reclaimed asphalt pavement (RAP) is the major source of recycled materials that can be used for pavement construction. However, the main concern of using RAP materials is the age hardening. Aging of the binder is one of the main reasons for pavement distresses (Zhang et al., 2012), which negatively affects the rheological properties of asphalt binder. This causes asphalt to become stiffer and more brittle. Therefore, RAP can induce early cracking in the pavement. When RAP is employed in pavement construction, it is recommended to use rejuvenators. A rejuvenator is basically an asphaltic material that contains lighter oil fragments similar to that of asphalt. Based on past studies, the inclusion of rejuvenator improves the performance of the aged binder after reducing its viscosity (Brown, 1988).

Asphalt is a very complex chemical substance having a wide variety of organic molecules of varying size and polarity (Guern et al., 2010). Based on the source and chemical extraction process, the chemistry and rheology of asphalt is also highly varied. All these factors are associated with the formation of microstructure in asphalt binder at the micro-level (Petersen et al., 1994). Past studies reported that these microstructures have an influence on creep, deformation and stiffness behavior of asphalt binder, which are vital properties for the overall pavement performance (Allen et al., 2012, 2014).

When asphalt binder ages, the fundamental chemical property, and microstructure also changes significantly (Hossain et al., 2019). As a consequence, asphalt loses its vital engineering properties including adhesion, binding capacity, and flexibility. These changes eventually lead to pavement failure (Masson et al., 2006). When we do rejuvenation during recycling, one of the underlying questions is how rejuvenation helps to retrieve these properties, which is still not clear. Therefore, this effort is designed to obtain an understanding of how the chemistry and microstructure of asphalt binder changes as rejuvenator is added with the aged binder.

3.3 Summary of Review

To obtain an understanding of chemical properties and the functional groups of asphalt binders, various spectroscopy techniques have been employed, that includes FTIR, NMR, and XPS. Out of these techniques, FTIR is the most widely used.

Recently, in the USA, Hossain et al. (Hossain et al., 2013) investigated the effect of different additives on the performance of asphalt binders using FTIR. This study reports that a good correlation exists between the chemical compositions of asphalt binder with its rheological properties. Furthermore, the effect of modifiers on the aged binder was investigated by Yao et al. (Yao et al., 2013), which found that the oxidation rate reduced in the binder through a functional group analysis from FTIR spectra. Moreover, the effect of different chemical functional groups on the performances of asphalt rheology is also investigated by many research groups and the interested readers can consult these articles for detailed information (Glover et al., 2005; Greenfield & Zhang, 2009; Domke et al., 1999; Nasrazadani et al., 2010).

For asphalt microstructure analysis, the researchers across the world have increasingly been using Atomic Force Microscopy (AFM) and these studies reported that an AFM is very dependable for this purpose (Golubev et al., 2008; Jahangir et al., 2015; Nahar et al., 2013; Soenen et al., 2014; Wang & Liu, 2017). Loeber et al. was the first group to conduct comprehensive research on asphalt binder microstructure topic and they reported on the existence of a “bee” like structure in asphalt in micro-scale (Loeber et al., 1996). A similar observation was then made by some other studies which noted that these microstructures are associated with asphalt morphology and rheological performance

(Allen et al., 2014; Fischer et al., 2014; Pauli et al., 2011; Rebelo et al., 2014). With this AFM system, Fisher et al. evaluated the micromechanical property of asphalt, including adhesion, hardness, elasticity, and dissipation energy (Fischer et al., 2013). Zhang (Zhang et al., 2012) studied the effects of aging on the binder morphology and found that the binder morphology changes significantly with the extent of aging. The effects of using modifiers and rejuvenators on aged binders were also studied using AFM techniques. Hossain et al. investigated the effect of different waste modifiers with RAP and RAS materials using the AFM-PFQNM technique (Hossain et al., 2017). This research found that a significant change in morphology occurred after the modification of RAP. Furthermore, the study reported a notable change in the micromechanical properties. Most of the studies in this area found a good correlation between the formations of microstructure (bee structure) and modification/rejuvenation of binders. Some studies also reported differing observations (Yu et al., 2014). They noticed that the addition of rejuvenator does not always form a new microstructure or influence the existing microstructures. In spite of these researches, still, there is a knowledge gap on how rejuvenation affects the asphalt morphology and microstructure. Also, the compatibility among different binders and rejuvenators, as well as polymer modification, is still not clear at the atomic level. This research will provide an insight of the interaction of the material that occurs at an atomic/nanoscale level to quantify the performance of the binder.

3.4 Objectives

The primary objective of this study is to obtain a better understanding of the effects of different rejuvenators on asphalt chemical properties and morphological features. To realize these objectives, scientific laboratory tests were conducted on standard asphalt binder (age conditioned and rejuvenated specimens) used in Newfoundland and Labrador, Canada. As a rejuvenator, an off the shelf product and alternative materials were tested. Chemical characteristics and the molecular properties of rejuvenators and the rejuvenated binders were evaluated by employing advanced techniques such as GC-MS to identify the chemical composition of rejuvenator, FTIR for obtaining the chemical function groups information, and AFM for obtaining micrographs of the specimens for micro-morphological analysis.

3.5 Material Collection

3.5.1 Asphalt Binder

The PG 58-28 binder is used in the Southern region of Newfoundland and Labrador, Canada. Therefore, this binder was selected for this study, which was supplied by Bitumar Inc., USA. The Thin Film Oven (TFO) test was employed to prepare the laboratory simulated aged binder as per the guideline of ASTM D1754 (ASTM, 2018). In this process, a constant heat of 163ºC was applied to the neat binder for 5 hours to prepare the aged sample.

3.5.2 Rejuvenators

Rejuvenators studied in this research are used cooking oil and Hydrolene. Used cooking oil has been studied in two forms- one form is collected raw oil (denoted as UT) and another form that is chemically processed oil (denoted as TR). UT was collected from two different sources (NJs Kitchen and Eco Oil Limited). The used oil samples consisted of many fried fragments which were then removed by a screener. Based on the purity and appearance of both samples after filtration, the samples provided from Eco Oil Limited were used for total experimental study. Hydrolene (denoted as HL) was provided by HollyFrontier Corporation for this study.

3.6 Chemical Characterization of Rejuvenators

The chemical properties of rejuvenators are the fundamental characteristics that dominate the behavior of asphalt. Rejuvenator HL is a commercially available material and its fundamental properties are well-known. However, UT is a used oil and its fundamental properties are still unknown. Also, there is a high possibility of change of UT's properties based on its source and use.

One of the major properties for the used oil is the existence of free fatty acid (FFA) and the quality of such used oil material is determined by the quantity of FFA (Azahar et al., 2016). FFA is produced during frying activities by the hydrolysis process as the oil is continuously heated to high temperatures with the presence of moisture and air content that creates several degradation processes (Sanli et al., 2011). The quantity of FFA depends on the degradation process, operation temperature during frying activities, as well as the presence of impurities in UT (Nur et al., 2016). The presence of FFA weakens the adhesion with bitumen. Additionally, it reduces the binder adhesive properties which have an adverse effect on pavement mixture performance (Azahar et al., 2016; Gong et al., 2016).

There are several analytical methods to identify the components in oil and fats, like high-performance liquid chromatography-mass spectrometry (HPLC-MS), nuclear magnetic resonance (NMR), high-performance size exclusion chromatography (HPSEC), and gas chromatography-mass spectrometry (GC-MS)(Abidin et al., 2013). Among them, GC-MS is a simple, fast, reliable and widely used technique to quantify the compositions of fats and oil. To execute GC-MS analysis, the direct injection of the sample into the equipment system is not possible. Therefore, it requires proper sample preparation and GC-MS operation method.

3.6.1 GC-MS Analysis

3.6.1.1 Sample Preparation

This experiment was performed to identify and quantify the fatty acids and fatty acid methyl esters (FAME) in UT rejuvenator. This study used the methylation procedure for GC-MS analysis, shown in Figure 3.1. The sample was methyl esterified by potassium hydroxide/methanol (KOH/MeOH) method as per ISO 12966-2:2017 (ISO 12966-2: Animal and Vegetable Fats and Oils — Preparation of Methyl Esters of Fatty Acids, 2017). In the derivatization process, 0.03g sample was mixed with 1mL 0.5 mol L^{-1} KOH/MeOH solution along with 1 mL n-hexane. The combined solution was vortexed for 30 mins and then centrifuged. To make the solution acidic and neutralized, hydrochloric acid (HCl) was added and tested with a pH kit. After that, the upper n-hexane layer was collected from the separated two layers of solution for further injection in the GC-MS system. The sample preparation approach has been presented in Figure 3.1(a-d).

3.6.1.2 Operational Technique

An Agilent DB-5 MS (Agilent Technology, USA) was employed to analyze the FAME in UT rejuvenator. A capillary column of 30m in length having an internal diameter of 0.250mm and film thickness of 0.25μm were used. Table 3.1 lists the conditions of GC-MS operation.

3.6.1.3 Analysis of Chromatograms

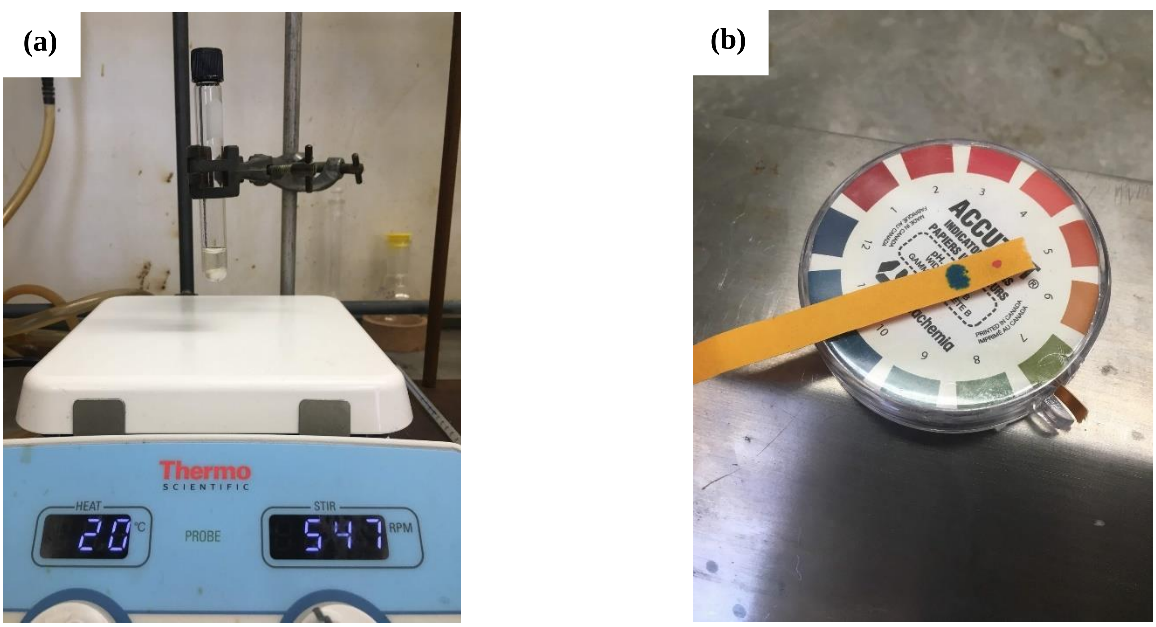
The GC-MS chromatograms were analyzed using the NIST 08 spectral library. The retention time and the area percentages are recorded in Table 3.2. As UT oil is a complex mixture, there were over 30 peaks in the results. Only eight peaks were selected based on the minimum area of 5% of the largest peak.

Figure 3.2(a) shows the chromatograms of the UT sample. All the main components were identified in the chromatograms and also separated from each other. For clarity, the solvent n-hexane has not shown in chromatograms. From the chromatograms, it is clear that all the peaks belong to the long-chained C16-C18 fatty acid methyl esters (FAME) (Zhang et al., 2015). The molecular weight of all the FAME ranges from 260-360 g/mol, which is much lower than asphalt (700 g/mol). Oleic acid and Linoleic acid appear at the retention time of 29.86 min and 29.37 min having the highest area concentration of 68.5% and 19.54% respectively. As fatty acid has been converted into FAME by the methylation process, the three main components were found in UT rejuvenator: Oleic acid (68.51%), Linoleic acid (19.54%), and Palmitic acid (5.42%). The mass spectrums of these three major components along with their molecular structures have been represented in Figure 3.2(b-d).

3.6.1.4 Results from GC-MS

Molecular structure from Figure 3.2 exhibits that all molecules have both polar (-CH_2-) and non-polar (-COO-) ends, which denotes that molecules are hydrophilic and have a strong affinity to water. This affinity has a harmful effect on the overall moisture susceptibility of asphalt when mixed with UT rejuvenator. Furthermore, this FAME might have negative effects on asphalt's rheological properties (Azahar et al., 2016). It can be concluded that the reduction of the FFA content is required for better performance of UT rejuvenated asphalt.

(a) **(b)**



(c)

(d)

Figure 3.1 Sample Preparation for GC-MS Analysis (a) Vortexed Solution (b) pH Test, (c) Prepared Solution and Solvent, and (d) An Agilent DB-5 MS System

3.6.2 Chemical Modification of UT Rejuvenator

UT rejuvenator generally contains high FFA contents, and the percentages of FFA might vary over sources. The generation of FFA depends upon the duration of frying activities. The acid value test is an indicator to determine the FFA content in fats and oil. With the difference in the source of the collected sample, the acid value also differs. Typically, the acid value varies from 2%-7% (Azahar et al., 2016). The lower the acid value, the higher the performance of rheological properties. Based on the literature review, the Transesterification process has been selected to modify the UT rejuvenator.

3.6.2.1 Transesterification Process

Transesterification is a common method used to produce bio-diesel using alkali catalysts. This process includes some chemical reactions of UT rejuvenator with methanol and NaOH. Prior to executing the transesterification process, several parameters should be selected (i.e., total reaction time, the volume of methanol to oil, and the concentration of

NaOH). These parameters have significant impacts on the final products and the proper conversion of UT rejuvenator.

Table 3.1 GC-MS Operation Parameters Used for UT Sample

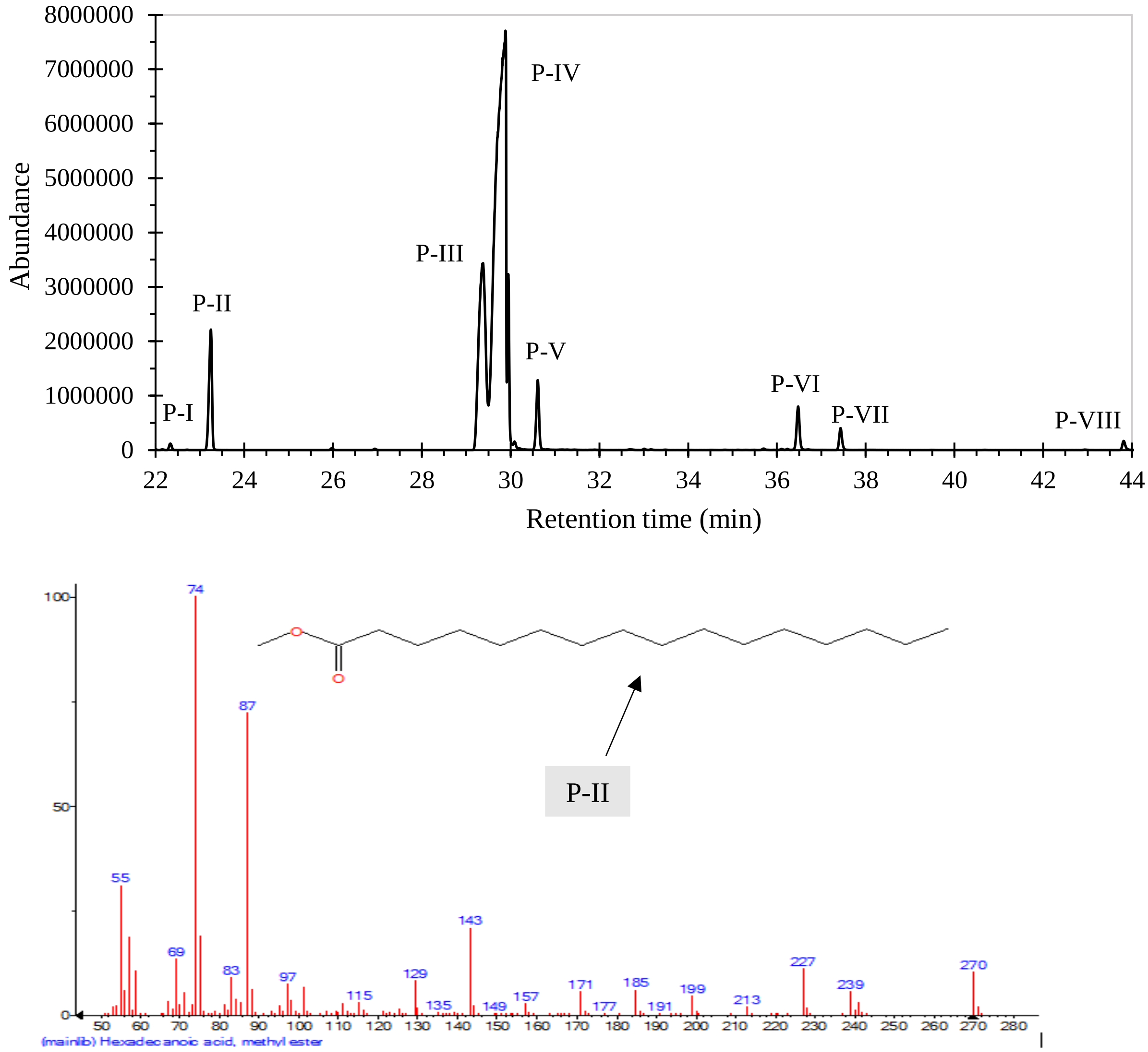
Instrument	Agilent DB-5 MS			
Inlet				
Injection type	Split mode			
Injection temperature	250 ºC			
Injection volume	$1\mu L$			
Split ratio	50:1			
Carrier gas	Helium			
Flow rate	1 mL/min			
Column head pressure	12.77 psi			
Oven				
Oven Program	ºC/min	Next ºC	Hold time (min)	Runtime (min)
	-	140	5	5
	2.50	240	10	55
Mass Spectrometer (MS)				
Auxiliary temperature	230 ºC			
Solvent delay	3 mins			
Mode	Scan			
Quadrupole temperature	150 ºC			
Scan mode range m/z	50-550 u			

Table 3.2 Chemical Composition of UT Sample from GC-MS Analysis

Peak #	Retention time (min)	Molecule	Synonym	Concentrations (%)	Molecular weight (g/mol)
P-I	22.334	9-Hexadecenoic acid, methyl ester, (Z)	Palmitoleic acid	00.27	268
P-II	23.243	Hexadecanoic acid, methyl ester	Palmitic acid	05.42	270
P-III	29.37	9,12- Octadecadienoic acid (Z,Z)-,methyl ester	Linoleic acid	19.54	294
P-IV	29.867	9-Octadecenoic acid (Z), methyl ester	Oleic acid	68.51	296
P-V	30.616	Octadecanoic acid, methyl ester	Stearic Acid	02.91	298
P-VI	36.48	Cis-11-Eicosenoic acid, methyl ester	-	01.97	324
P-VII	37.434	Eicosanoic acid, methyl ester	Eicosanoic acid	00.95	326
P-VIII	43.818	Docosanoic acid, methyl ester	Myristic acid	00.43	354

(a)

(b)



Abundance
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
22
24
26
28
30
32
34
36
38
40
42
44
Retention time (min)
P-I
P-II
P-III
P-IV
P-V
P-VI
P-VII
P-VIII
100
50
0
74
87
55
69
83
97
115
129
135
143
149
157
171
177
185
191
199
213
227
239
270
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
230
240
250
260
270
280
(mainlib) Hexadecanoic acid, methyl ester
P-II

(c)

(d)

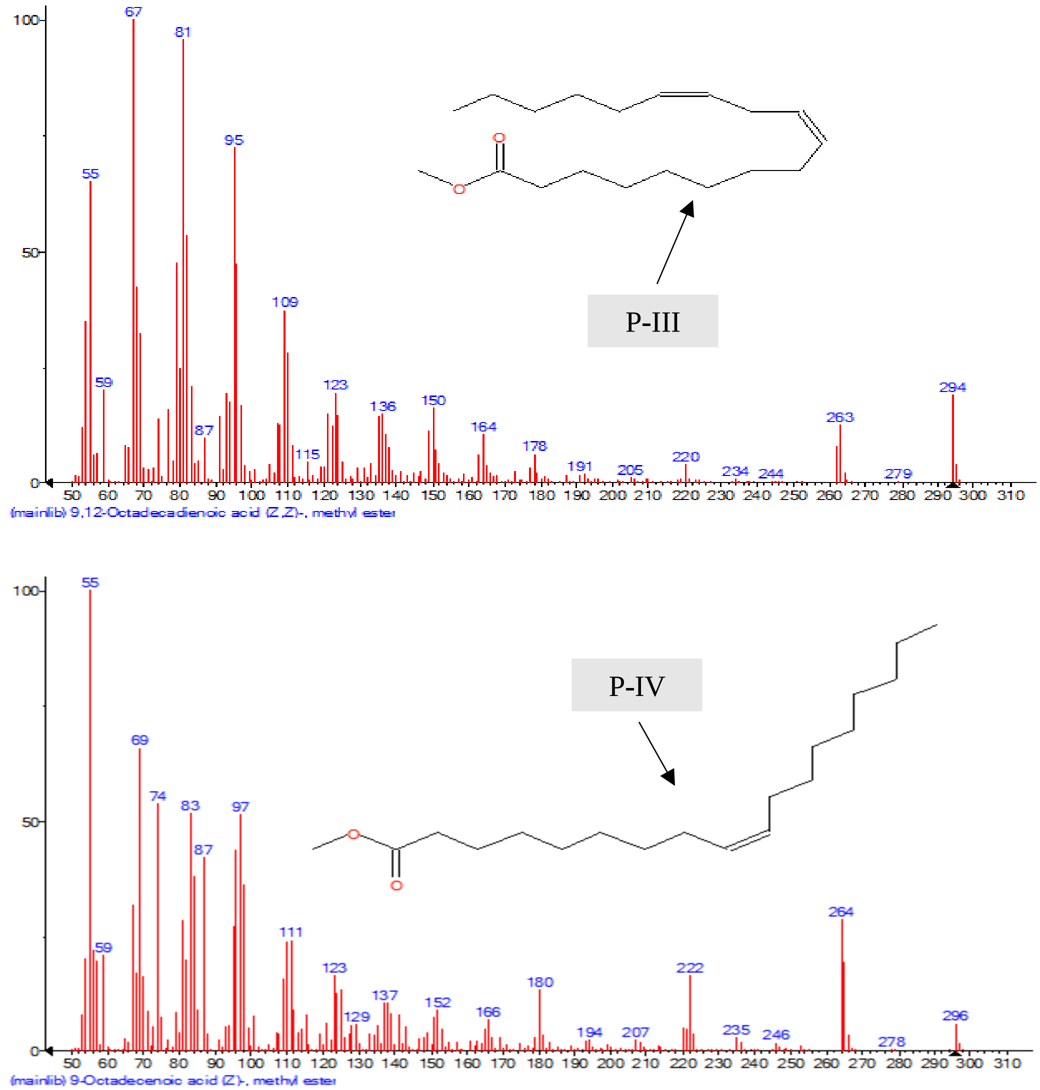


Figure 3.2 (a) Derived Chromatograms for UT Sample; Images of the Acid Components from the Mass Spectrometer: (b) Palmitic Acid, (c) Linoleic Acid, and (d) Oleic Acid

Based on the study of Leung (Leung & Guo, 2006) the optimum ratio of methanol to oil was selected 7:1. The concentration of NaOH was taken 1.1% of the volume of oil. In a simplified procedure, a total of 100 mL oil, 700 mL methanol and 1.1 mL NaOH were being mixed properly. Later, this solution was placed on the heater and a magnetic stirring bar was inserted into the solution to make a homogeneous mix. When the temperature reached to 60 ºC, the reaction started, and the solution was heated for the next 20 min. The solution was kept overnight to allow the two phases to become separated. The upper phase is modified (esters) and the concentrated lower phase was glycerol. The upper phase was light yellow in color, whereas the lower phase was dark brown in color as shown in Figure 3.3(d). After the transesterification process, the upper modified sample phase is collected and denoted as TR.

3.6.2.2 Result from the Transesterification Process

Please recall that the main aim of modification was to reduce the FFA content. The acid value test was conducted according to ASTM D5555 (ASTM, 2018) to observe the change of acid value before and after transesterification process. The test found acid value of 5.45 mL/g for UT sample, whereas it reduces to 1.95 mL/g for the TR sample. This reduction of acid value might play a significant role to improve the property of rejuvenator and rejuvenated asphalt binder. After modification, now we have one new types of rejuvenator which is named as TR and all types of rejuvenators UT, TR, and HL are shown in Figure 3.3(e).

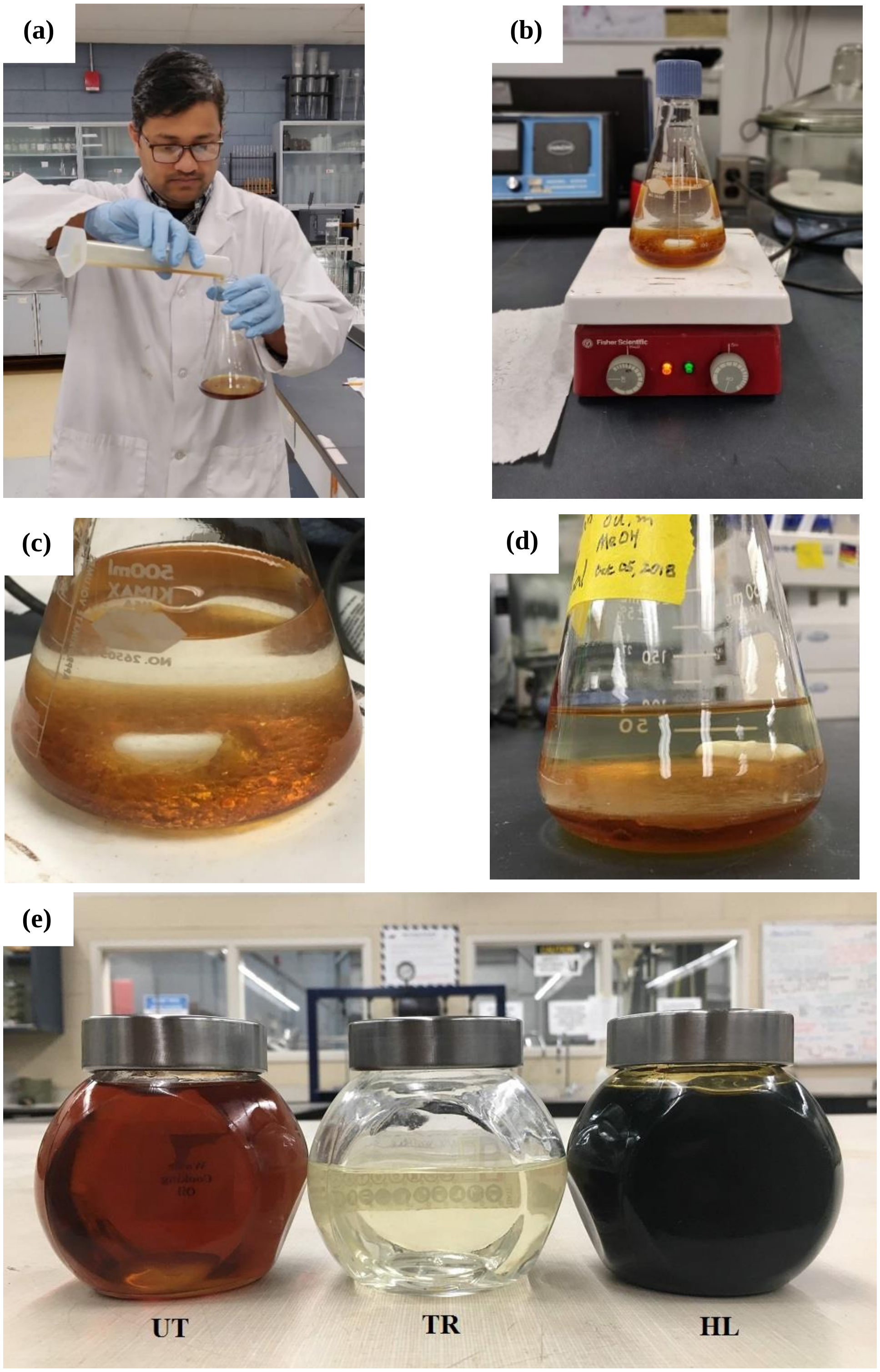


Figure 3.3 Transesterification Process (a) Mixed Solution of Oil, Methanol, and NaOH, (b) Prepared Solution on Hot Plate, (c) Beaker Equipped with Magnetic Stirrer and the

Chemical Reaction, (d) Separated Two Distinct Phases After 24 Hours, and (e) Types of Rejuvenator

3.7 Experimental Design of Rejuvenated Asphalt Binder

3.7.1 Blending Rejuvenators and Asphalt Binders

Rejuvenated asphalt binder was prepared by mixing aged asphalt binder with three types of rejuvenators UT, TR, and HL. First, the aged asphalt was heated to make it fluid enough to mix it with oil. Later, a different application rate of rejuvenators like 3%, 6%, and 9% by the weight of base asphalt was mixed. The blending process was conducted manually with a glass stirrer for 30 minutes at 100ºC. All the rejuvenators were liquid and had low viscosity, that why this blending time was selected to achieve a homogeneous mix. Therefore, the prepared samples were used for further experimental analysis.

3.7.2 Fourier Transform Infrared Spectroscopy (FTIR) Test

FTIR was used to analyze the chemical functional groups of asphalt. FTIR is the only analytical method that provides ambient temperature operational capability that directly monitors the vibrations of the functional groups. These vibration footprints are then used to characterize the molecular structure which governs the course of chemical reactions (Doyle, 2017). Furthermore, FTIR also provides continuous (near real-time) and low maintenance operation compared to gas chromatography and mass spectroscopy.

A Bruker series FTIR was used to analyze the functional groups of asphalt. This machine is equipped with a diamond ATR (Attenuated Total Reflection) that allows the measuring of the changes that occur in the IR beam. ATR technique helps to examine the sample directly either in a solid or liquid state without any special sample preparation techniques. Based on the previous experimental analysis, the scan range was selected from $400cm^{-1}$ to $4000cm^{-1}$ (Doyle, 2017). The final detection of functional groups in the sample was detected after completing 36 scans to reduce any error. The sample preparation technique is straightforward compared to other methods. The sample which has been prepared after blending with rejuvenators can be used for this test. Firstly, the spatula was heated at a high temperature to melt the asphalt sample when it can come in contact with the asphalt. The spatula was inserted at a required depth of the sample container to take the sample. To avoid any errors, the sample was not taken from the top surface because this layer might be contaminated with dust or other unwanted particles. After collecting a drop of the sample, it was scratched smoothly on the ATR surface, and then the automated computed system started detecting the functional groups of the sample. Then, the scratched sample was removed using n-hexane which is highly soluble in asphalt.

3.7.3 Atomic Force Microscopy (AFM) Test

AFM is one of the most widely used microstructures and morphology observation tools. AFM is non-destructive and is capable of providing insight on surface topography, stiffness, adhesion, elasticity, and the molecular interaction through imaging or force-curve analysis (Bellitto, 2012). The reason behind its widespread application is its easy sample preparation technique and operation at any temperature (Das et al., 2016). For the sample preparation, there are two methods: 1) spin casting and 2) heat casting. This study used a heat casting approach for sample preparation. In this process, a bead of the mixed sample was poured on the glass slide and then kept at 150ºC for 15 minutes to have a smooth surface. Later, the sample was cooled at room temperature and tested after 48 hours.

A Multimode SPM (Scanning Prove Microscope) was used for imaging the sample. The operation was conducted at room temperature (26ºC) in tapping mode (topography and phase) using the rectangular silicon tip. The cantilever was 4 µm thick, 125 µm long, and 30 µm wide and having a nominal spring constant of 40N/m. The scan size of 10 µm × 10 µm was selected for all the samples. For data analysis and image processing, Nanoscope 5.31 software was used.

3.8 Results and Discussions

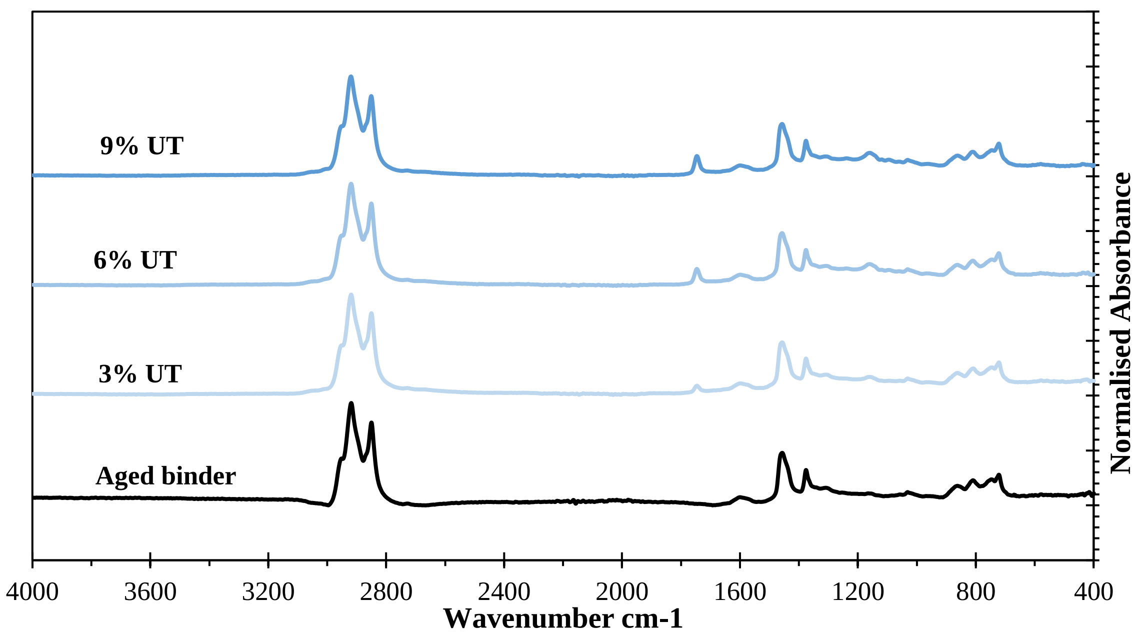
3.8.1 Effect of Rejuvenators on Asphalt Oxidative Potential

The functional groups of rejuvenated asphalt binder were analyzed by IR spectrum table (Infrared Spectroscopy Absorption Table, 2014; IR Spectrum Table & Chart) and represented in Figure 3.4(a-c) respectively. Also, the typical spectrums of aged asphalt have been shown. Based on the previous studies (36), the analysis was conducted in the region from 400 $cm^{-1}$to 4000 cm^{-1} to identify the corresponding peaks of the binder. Out of those bands, 1032 cm^{-1} and 1744 cm^{-1}correspond to sulfoxide (S=O) and carbonyl (C=O) respectively, which reflects the aging and rejuvenating degree of asphalt (Herrington & Ball, 1996). The carbonyl peak at 1744 cm^{-1} belongs to the ester carbonyl functional group which exhibit the existence of used oil content (UT) in rejuvenated asphalt which is found in a very negligible amount for aged asphalt, TR and HL rejuvenated samples. The intensity of C=O bond is 0.053, 0.091, and 0.108 respectively for 3%, 6%

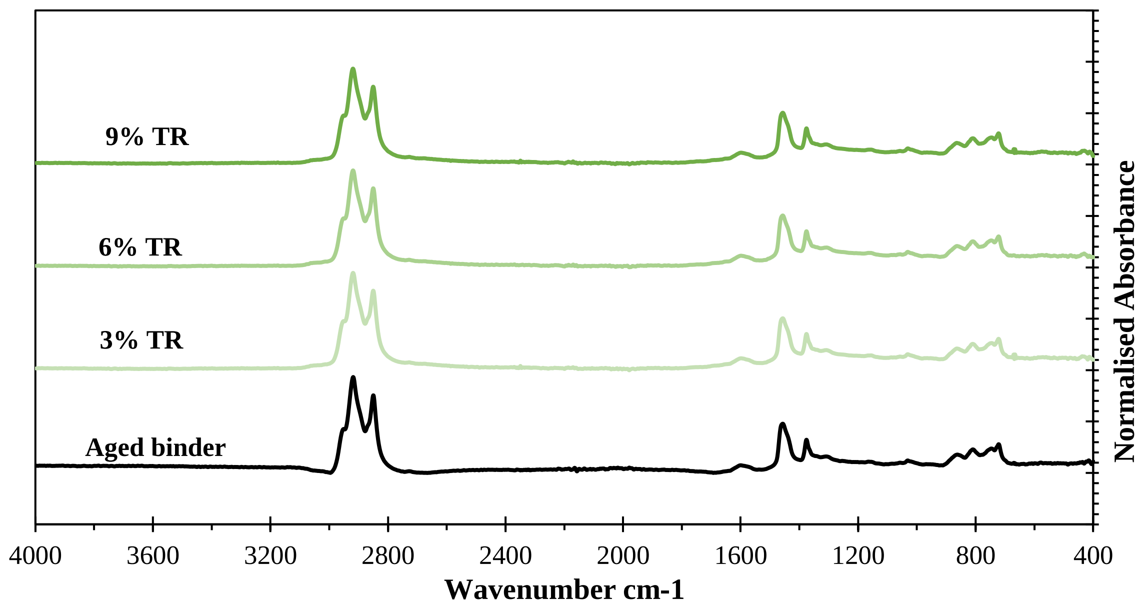
and 9% of UT sample. However, this peak intensity decreased gradually for increasing dosage of HL rejuvenator and 9% HL shows the lowest peak. According to the literature review, this C=O bond is a saturated aliph and it is responsible for making the binder softer which is more prone to rutting (Azahar et al., 2016). Therefore, 9%HL should give more stiffness, but the experimental rheological result exhibited lower stiffness for this (reported in Chapter 4). Also, this peak intensity was recorded 0.0176, 0.0171, and 0.0189 for 3%, 6%, and 9% TR rejuvenated sample. This result is consistent with our previous analysis, as 6%TR sample shows higher stiffness and therefore higher viscosity.

For all types of samples, the highest peak was detected at 2921 $cm^{-1}$and 2851.91 cm^{-1} that belongs to the Sp^3 C-H methyl group. Except for HL rejuvenated sample, there was no significant difference found for aged, UT, and TR samples. The lower intensity was recorded for only HL rejuvenated sample. Another Sp^3 C-H and C=C (alkane) bond was detected at 1374 $cm^{-1}$and 725 cm^{-1}respectively. Similar to the previous peak, these peak intensities also do not have any influence. The presence of C=C aromatic bond was detected at 1452 $cm^{-1}$for all the samples which exhibit a strong bonding of the constituents. For aged asphalt, the intensity was 0.279, whereas for UT and H sample, the intensity increases with the decrease of oil percentages. All TR rejuvenated samples show the better intensity and the highest was recorded for 6%TR sample like before.

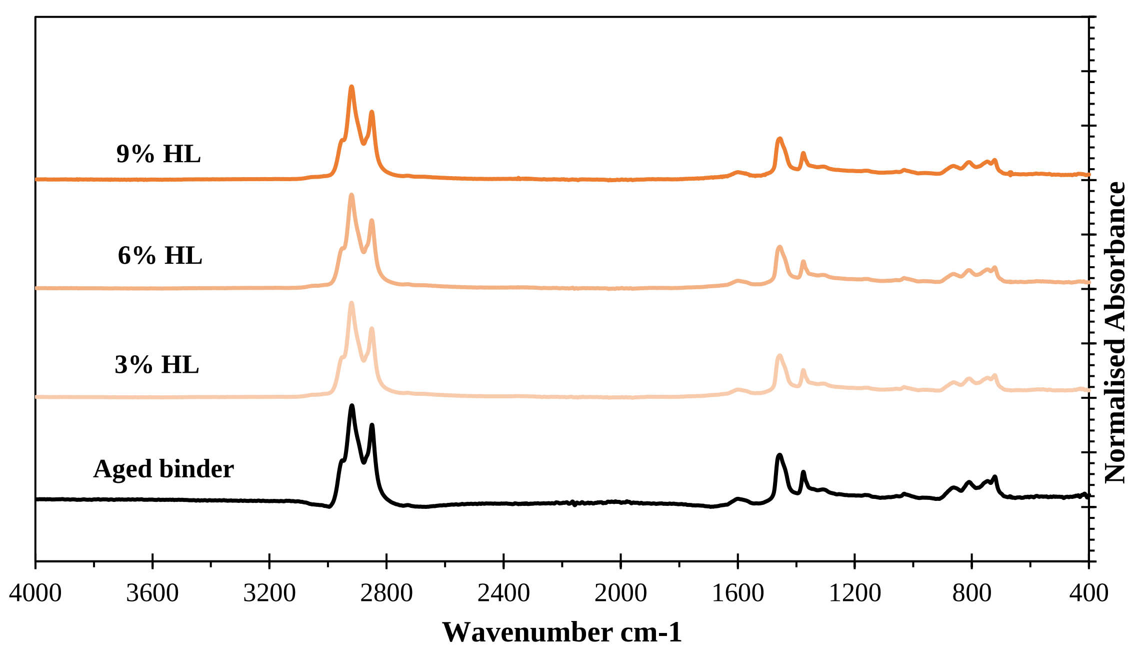
Another identical peak was found at 1161.15 cm^{-1}wavelength, which belongs to C-O alcohol peak. This peak was only observed for UT rejuvenated sample with an intensity of 3% = 0.102, 6% = 0.119, and 9% = 0.127. However, this group was not present in TR and HL rejuvenated sample. This might be the reason for the modification of rejuvenator and reduction of free fatty acid after transesterification process. There was another distinct peak of Sulfoxide (S=O) found at 1032 cm^{-1} which is only an identification of the aged sample, and not present in the unaged sample. This characteristics also match with other previous studies done with aged asphalt (Gong et al., 2016; Zhang et al., 2017). The intensity of S=O peaks varies with the quality of rejuvenator and it is higher for TR rejuvenated samples. Therefore, the conclusion can be drawn from the FTIR spectrum analysis that the chemical constituents of binder can be changed with the change of rejuvenator type and also the quality of rejuvenator. Quality improvement has a notable influence on the rejuvenation property and that might dominate the overall performance of the binder.



(a) FTIR Spectrum for UT Sample



(b) FTIR Spectrum for TR Sample



(c) FTIR Spectrum for HL Sample

Figure 3.4 Normalized FTIR Spectra of Aged, UT, TR, and HL Rejuvenated Binder

3.8.2 Effect of Rejuvenators on Asphalt Morphologies

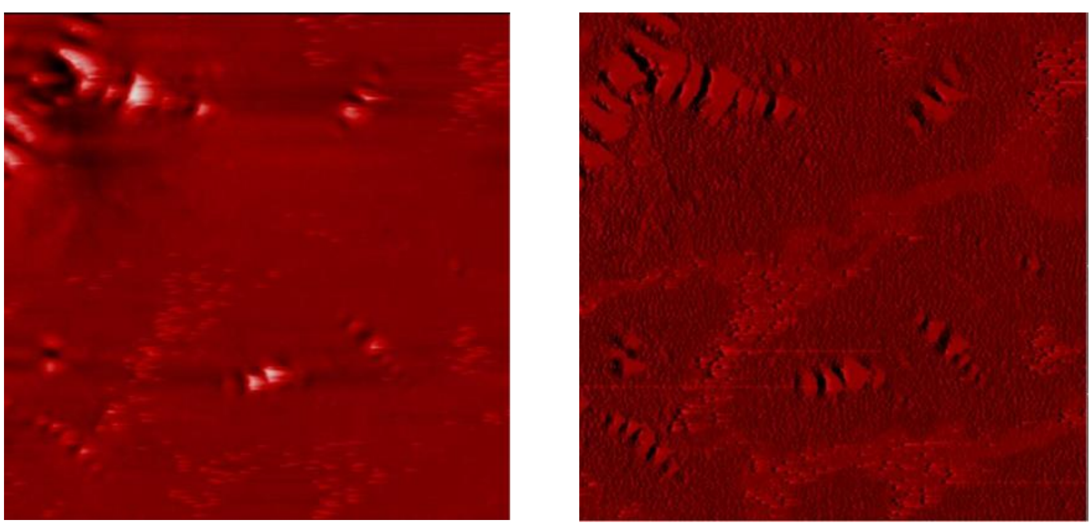
Generally, asphalt has three distinct morphological phases: a disperse phase, a surrounding larger phase of disperse phase, and a continuous phase (Fischer et al., 2014; Jahangir et al., 2015). These three phases are also named differently in asphalt literature. The central part (disperse) within each highlighted area is called the catana phase (so-called, bee), immediately around the catana phase is called the interstitial/periphase and both of these phases are suspended from another phase called the perpetua phase or matrix. Micrographs of sample topography for various experimental scenarios are shown in Figure 3.5. Besides the topographic micrographs, corresponding phase images are shown in Figure 3.5. Figure 3.5 shows that all specimens exhibited a bee like structure, which is also reported in many past studies (Hossain & Hossain, 2018). However, in general, this bee like structures was less present in phase image than topographs.

For the aged sample, a combination of different sized bee structure (small and large bees) was observed in the topographic image. Furthermore, one can also easily notice that the aged specimen had exhibited a fewer number of bees than specimens with rejuvenators, in general. Also, some white spots are present in the topographic image, which is also clearly visible in the Perpetua domain of phase image. These morphological features might be due to the aging of binder, which perhaps has created some irregularities on the surface. Also, the aged sample exhibits two distinct phases of asphalt (disperse phase and matrix phase) in the phase image. For 3% UT sample (Figure 3.5(b)), the size of the bee structures decreased compared to the aged binder. When the UT rejuvenator concentrations increased from 3% to 6%, the quantity of bee structure decreased but the larger sized bee structure was observed. In this case (6%UT), the two phases were very difficult to differentiate and the phase contrast between the two phases changed significantly compared to 3%UT sample. According to Rebelo et al. (Rebelo et al., 2014), the brighter the phase represents the higher phase lag which will enhance the viscous behavior of the binder. This phenomenon is also consistent with the result we got from the rheological tests as mentioned in chapter 4. Also, a dark region was observed for 6%UT around the periphrases in Figure 3.5(c), which might be "sal" phase mentioned by Masson et al. (Masson et al., 2006).

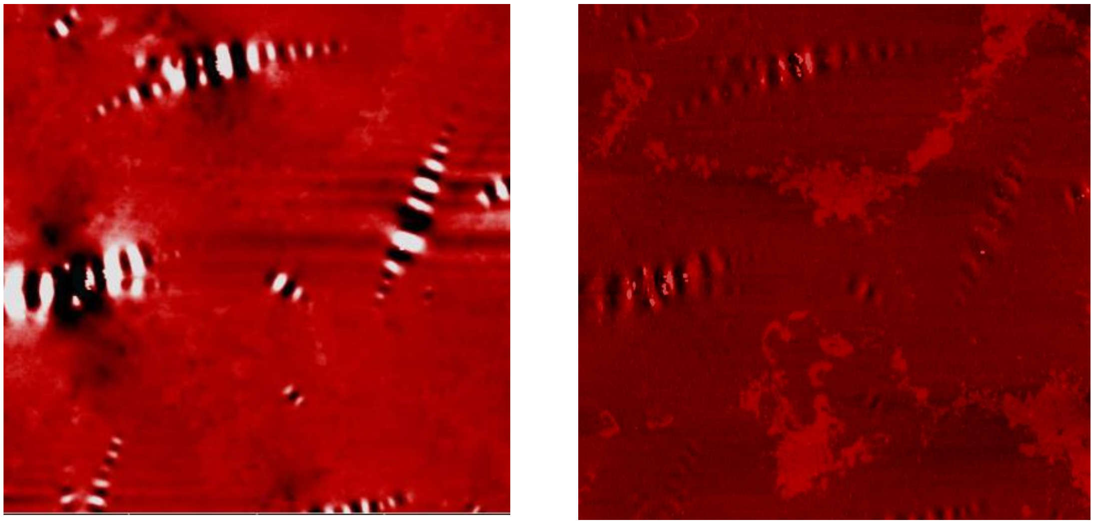
For the 3%TR rejuvenated sample in Figure 3.5(d), a significant increase of bee structures was observed compared to aged and UT samples. A higher amount of bee structures was associated with the higher stiffness of the binder. In the case of 6%TR sample, a reduced quantity of bee structures with reduced size was noticed. Relatively, a high stiffness value was observed for TR rejuvenated sample among the binders tested through a frequency sweep test reported in chapter 4. It was also noticed in Figure 3.5(e) that, the bee structures are densely located with each other. However, a clear disperse phase and matrix phase was available for 3%TR samples. In addition, some black dark spots are visible for 6%TR in the topographic image which might be the so-called "sal" phase in asphalt.

Figure 3.5(f-g) exhibited the micrographs of HL rejuvenated asphalt binder. For the HL rejuvenated samples, it can be seen that these micrographs have the lowest bee structures among the binders. Similar to 3%UT and 3%TR samples, 3%HL also exhibits a clear identification of disperse and matrix phase. For this sample, a high Perpetua phase is observed. Based on the colloidal model of Yen (Yen, 1991) most of the binder shows “sol” configuration, whereas, a higher elevated region is observed which might be due to “gel” configuration having larger clusters. In addition to that, 6%HL rejuvenated asphalt shows higher brighter phase which is responsible for having enhanced loss moduli and higher viscous property of asphalt.

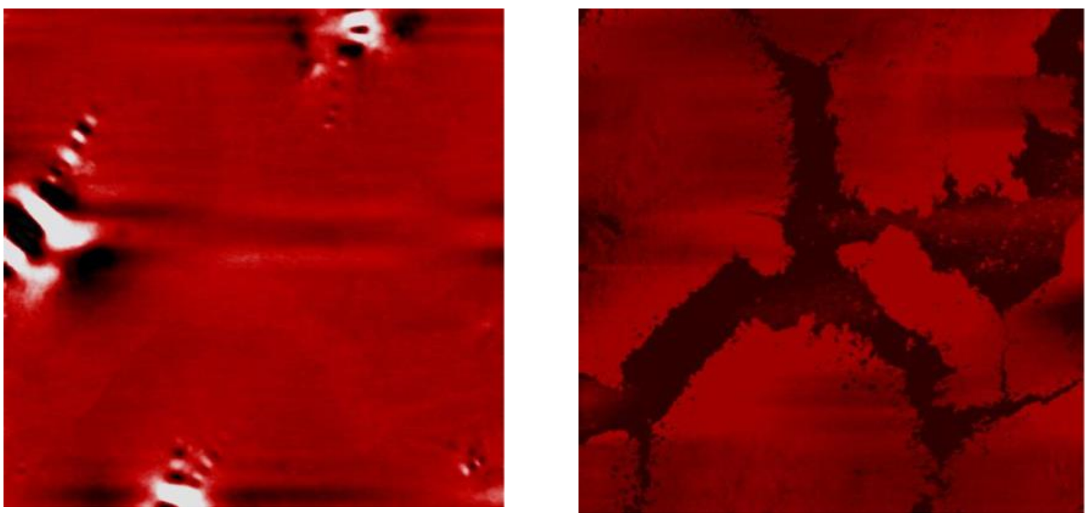
Based on the topographic and phase image analysis of different samples, it can be observed that the increase of rejuvenation dosage reduces the number of bee structures. This phenomenon implies that the rejuvenation of aged binder tends to achieve the properties of the virgin binder, where the quantity of bee structure is less than aged binder. Also, a difference in phase-contrast was observed between the samples, although the phase angle was the same for all binders. This indicates a change of morphology with rejuvenation. In addition, with the use of different types of rejuvenators and different dosing, the significant changes in the morphological features were observed.



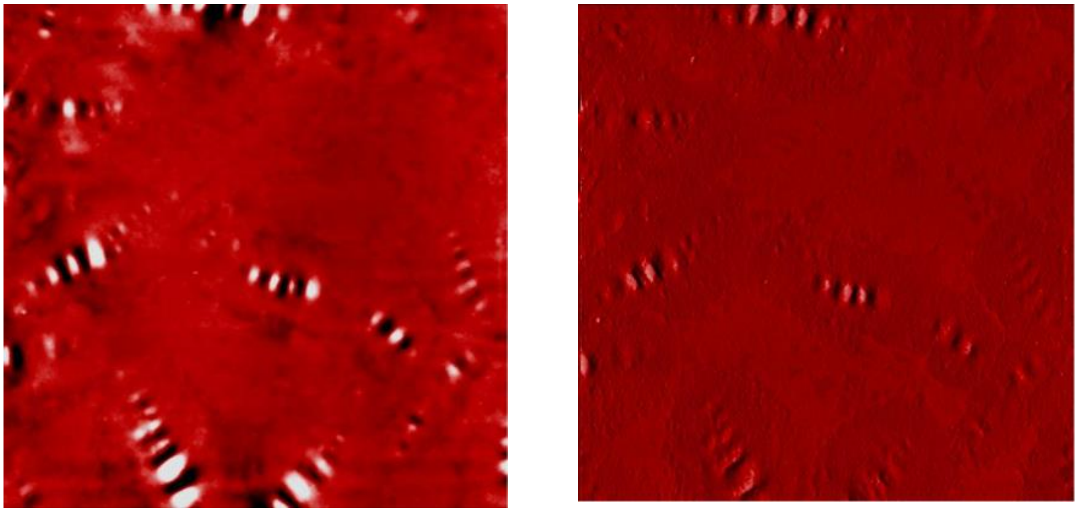
(a) Micrograph of Aged Sample



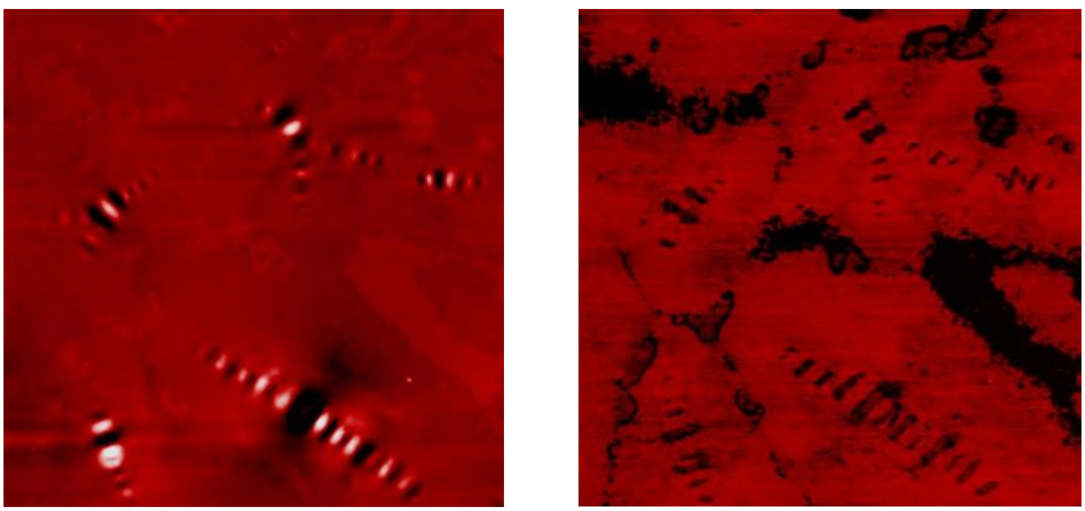
(b) Micrograph of 3% UT Sample



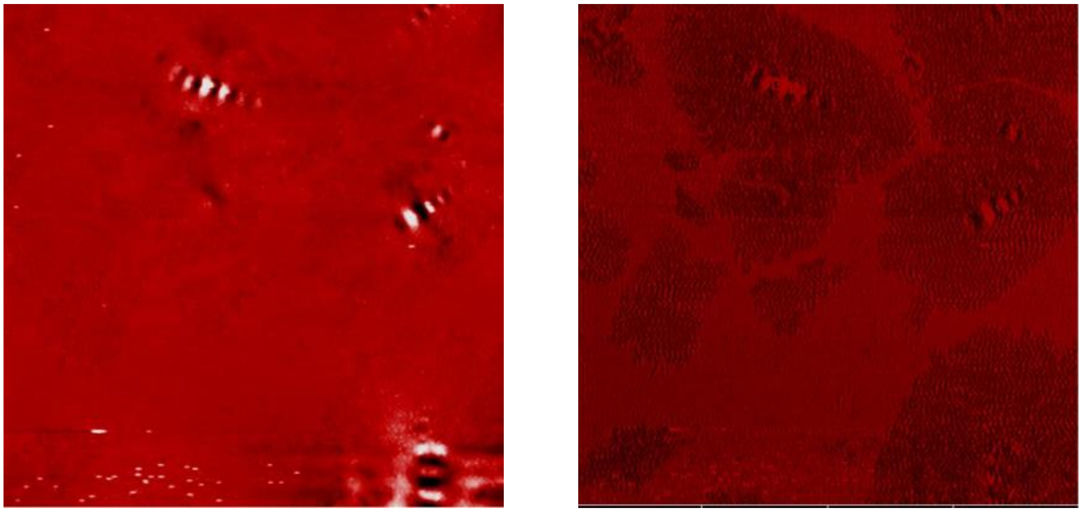
(c) Micrograph of 6% UT Sample



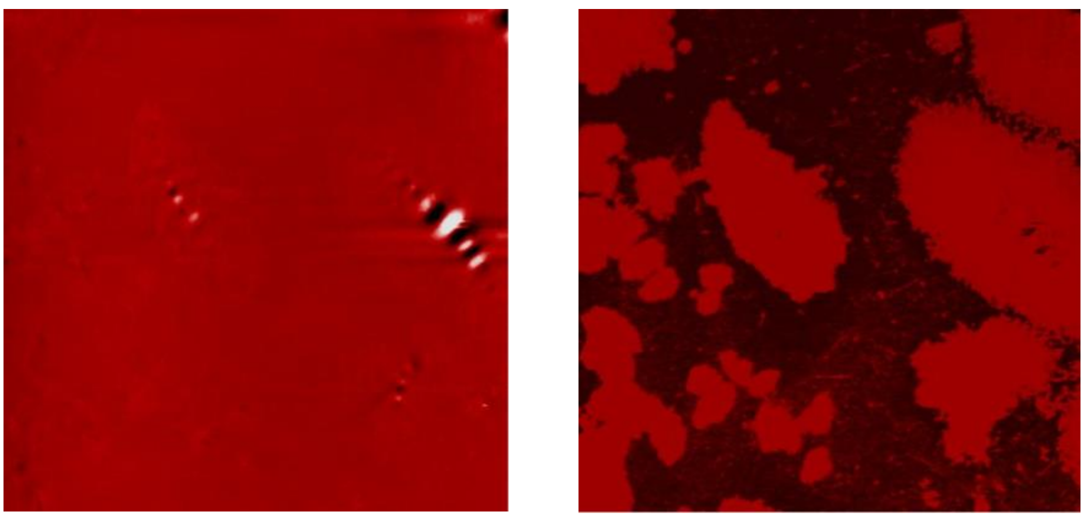
(d) Micrograph of 3% TR Sample



(e) Micrograph of 6% TR Sample



(f) Micrograph of 3% HL Sample



(g) Micrograph of 6% HL Sample

Figure 3.5 Topography (left) and Phase (right) Images of Different Rejuvenated Binder. Image Dimension 10µm ×10µm; Topography Image Scale 155.6 nm; Phase Image Scale 34°

3.9 Summary

This research used three different types of rejuvenators that include raw waste cooking oil (UT), modified waste cooking oil (TR) and Hydrolene (HL) to understand the rejuvenating behavior in laboratory prepared aged binder. Also, this study aimed to evaluate the chemical composition and morphological behaviors of rejuvenated asphalt binder. From this experimental work, the following conclusions can be drawn:

- Free fatty acid (FFA) was observed in UT rejuvenator by GC-MS analysis, which enhances hydrophilic characteristics of asphalt binder and it is harmful to moisture susceptibility. Therefore, it is required to reduce the FFA content to improve the quality of the rejuvenator.
- The improved quality of UT rejuvenator after the transesterification process influenced the rejuvenation behavior with aged asphalt, and higher quality of UT (lower acid value) can lead to better performance with aged asphalt including higher stiffness of binder.
- FTIR test results exhibited a higher rate of C=O stretch at 1744 cm^{-1} for UT, which is responsible for softening the binder and inducing rutting failure. From GC-MS analysis, it was noticed that all the FFA's have (-COO-) ends which might results in higher C=O stretch for the UT rejuvenated binders as well. Whereas, this stretch was very negligible for TR and HL rejuvenated binders, shows better stiffness. Due to the modification of TR rejuvenator, FFA decreased and also the decrease of C=O stretch in the TR rejuvenated binders. Also, the HL/R3 is a commercially

manufactured oil which might have lower FFA, because the generation of FFA mostly occurs during the hydrolysis process at the presence of high temperature and moisture contents. The presence of lower C=O stretch for TR and HL rejuvenated binders attributed to the higher stiffness of the binder. This result was also consistent with the stiffness trend found at the rheological test as mentioned in chapter 4.

- From the topography and phase images of AFM, a change in terms of quantity and size of the bee structure has been observed. The decreased number of bees, with the increase of bee size, was observed for the increased dosage of rejuvenation. The decrease number of bee structures generally indicates the softening behavior of binders. For the UT rejuvenated binders, a lower quantity of bee structures was found, which might be due to the existence of FFA in the UT rejuvenators and accelerate the softening process of the binder. The higher bee structure was found for TR rejuvenated samples. A higher number of bees reflects the higher stiffness of the binder which was also consistent with the rheological tests as mentioned in chapter 4.
- Based on the phase-contrast analysis of different samples, a significant change of morphological features was observed for the binders. The higher percentages of rejuvenation (6%) show the brighter phase image, which indicates the higher loss modulus of the binders. This variation in phase-contrast might be due to the higher rejuvenator dosage which changes the dissipation of energies between the AFM tip and the sample. Also, the change of viscoelasticity, adhesion, and the topographic features of the samples. For this experimental analysis, the binder surface was oily

at higher rejuvenation dosage, which might also result in different phase contrasts of the binder.

3.10 References

Abidin, S. Z., Patel, D., & Saha, B. (2013). Quantitative Analysis of Fatty Acids Composition in the Used Cooking Oil (Uco) by Gas Chromatography À Mass Spectrometry (gc – ms). *Canadian Journal of Chemical Engineering*, *91*(12), 1896–1903. https://doi.org/10.1002/cjce.21848

Allen, R. G., Little, D. N., Bhasin, A., & Glover, C. J. (2014). The effects of chemical composition on asphalt microstructure and their association to pavement performance. *International Journal of Pavement Engineering*, *15*(1), 9–22. https://doi.org/http://dx.doi.org/10.1080/10298436.2013.836192 The

Allen, R., Little, D., Bhasin, A., & Lytton, R. (2012). Identification of the Composite Relaxation Modulus of Asphalt Binder Using AFM Nanoindentation. *Journal of Materials in Civil Engineering*, *25*(4), 530–539. https://doi.org/10.1061/(ASCE)MT.1943-5533.0000615

ASTM. (2018). *Standard Test Method for Effects of Heat and Air on Asphaltic Materials (Thin-Film Oven Test)* (Vol. 09, Issue Reapproved 2014). https://doi.org/10.1520/D1754

Azahar, W. N. A. W., Jaya, R. P., Hainin, M. R., Bujang, M., & Ngadi, N. (2016). Chemical modification of waste cooking oil to improve the physical and rheological properties of asphalt binder. *Construction and Building Materials*, *126*, 218–226.

https://doi.org/10.1016/j.conbuildmat.2016.09.032

Bellitto, V. (2012). *Atomic Force Microscopy- Imaging, Measuring and Manipulating Surfaces at the Atomic Scale*. InTech.

Brown, E. R. (1988). Preventive Maintenance of Asphalt Concrete Pavements. *Transportation Research Record: Journal of the Transportation Research Board*, 6–11.

Das, P. K., Baaj, H., Tighe, S., & Kringos, N. (2016). Atomic force microscopy to investigate asphalt binders : a state-of-the-art review. *Road Materials and Pavement Design*, *17*(3), 693–718. https://doi.org/https://doi.org/10.1080/14680629.2015.1114012

Doyle, W. M. (2017). *Principles and Applications of Fourier Transform Infra- red (FTIR) Process Analysis*. http://www.hellma-axiom.com/pdf/technical_notes/AN-906.pdf

Fischer, H. R., Dillingh, E. C., & Hermse, C. G. M. (2014). On the microstructure of bituminous binders. *Road Materials and Pavement Design*, *15*(1), 1–15. https://doi.org/http://dx.doi.org/10.1080/14680629.2013.837838

Fischer, H., Stadler, H., & Erina, N. (2013). Quantitative temperature-depending mapping of mechanical properties of bitumen at the nanoscale using the AFM operated with PeakForce Tapping TM mode. *Journal of Microscopy*, *250*(3), 210–217. https://doi.org/10.1111/jmi.12036

Glover, C. J., Davison, R. R., Domke, C. H., Ruan, Y., Juristyarini, P., Knorr, D. B., &

Jung, S. H. (2005). Development of a New Method for Assessing Asphalt Binder Durability with Field Validation. In *Research Report: FHWA/TX-05/1872-2 2*. (Vol. 7, Issue 2).

Golubev, Y. A., Kovaleva, O. V, & Yushkin, N. P. (2008). Observations and morphological analysis of supermolecular structure of natural bitumens by atomic force microscopy. *Fuel*, *87*(1), 32–38. https://doi.org/https://doi.org/10.1016/j.fuel.2007.04.005

Gong, M., Yang, J., Zhang, J., Zhu, H., & Tong, T. (2016). Physical-chemical properties of aged asphalt rejuvenated by bio-oil derived from biodiesel residue. *Construction and Building Materials*, *105*(15), 35–45. https://doi.org/10.1016/j.conbuildmat.2015.12.025

Greenfield, M. L., & Zhang, L. (2009). Developing Model Asphalt Systems Using Molecular Simulations. In *Final Report: URITC PROJECT NO. 000216*.

Guern, M. Le, Chailleux, E., Farcas, F., Dreessen, S., & Mabille, I. (2010). Physico-chemical analysis of five hard bitumens : Identification of chemical species and molecular organization before and after artificial aging. *Fuel*, *89*(11), 3330–3339. https://doi.org/10.1016/j.fuel.2010.04.035

H.Domke, C., Davison, R. R., & Glover, C. J. (1999). Effect of Asphaltenes on SHRP Superpave Specifications. *Journal of Energy Fuels*, *13*(2), 340–345. https://doi.org/https://doi.org/10.1021/ef980194s

Herrington, P. R., & Ball, G. F. A. (1996). Dependence Oxidation Mechanism of

Asphalt. *Fuel*, *75*(9), 1129–1131. https://doi.org/https://doi.org/10.1016/0016-2361(96)00042-7

Hossain, K., & Hossain, Z. (2018). A Synthesis of Computational and Experimental Approaches of Evaluating Chemical, Physical and Mechanistic Properties of Asphalt Binders. *Advances in Civil Engineering*, *2019*, 20. https://doi.org/https://doi.org/10.1155/2019/1795958

Hossain, K., Karakas, A., & Hossain, Z. (2019). Effects of Aging and Rejuvenation on Surface Free Energy Measurements and Adhesion of Asphalt Mixtures. *Journal of Materials in Civil Engineering*, *31*(7). https://doi.org/10.1061/(ASCE)MT.1943-5533.0002780

Hossain, Z., Asce, A. M., Lewis, S., Zaman, M., Asce, F., Buddhala, A., & Rear, E. O. (2013). Evaluation for Warm-Mix Additive-Modified Asphalt Binders Using Spectroscopy Techniques. *Journal OfMaterials in Civil Engineering*, *25*(2), 149–159. https://doi.org/10.1061/(ASCE)MT.1943-5533.0000562.

Hossain, Z., Rashid, F., Mahmud, I., & Rahaman, M. Z. (2017). Morphological and Nanomechanical Characterization of Industrial and Agricultural Waste – Modified Asphalt Binders. *International Journal of Geomechanics*, *17*(3), 1–12. https://doi.org/10.1061/(ASCE)GM.1943-5622.0000767.

Infrared Spectroscopy Absorption Table. (2014). Chemistry LibreTexts. https://chem.libretexts.org/Ancillary_Materials/Reference/Reference_Tables/Spectroscopic_Parameters/Infrared_Spectroscopy_Absorption_Table

IR Spectrum Table & Chart. (n.d.). SIGMA - ALDRICH. https://www.sigmaaldrich.com/technical-documents/articles/biology/ir-spectrum-table.html

ISO 12966-2: Animal and vegetable fats and oils — Preparation of methyl esters of fatty acids. (2017).

Jahangir, R., Little, D., & Bhasin, A. (2015). Evolution of asphalt binder microstructure due to tensile loading determined using AFM and image analysis techniques. *International Journal of Pavement Engineering*, *16*(4), 337–349. https://doi.org/http://dx.doi.org/10.1080/10298436.2014.942863 Evolution

Leung, D. Y. C., & Guo, Y. (2006). Transesterification of neat and used frying oil : Optimization for biodiesel production. *Fuel Processing Technology*, *87*(10), 883–890. https://doi.org/https://doi.org/10.1016/j.fuproc.2006.06.003

Loeber, L., Sutton, O., Morel, J., Valleton, J., & Muller, G. (1996). New direct observations of asphalts and asphalt binders by scanning electron microscopy and atomic force microscopy. *Journal of Microscopy*, *182*(1), 32–39. https://doi.org/https://doi.org/10.1046/j.1365-2818.1996.134416

Masson, J.-F., Leblond, V., & Margeson, J. (2006). Bitumen morphologies by phase-detection atomic force. *Journal of Microscopy*, *221*(1), 17–29.

Nahar, S. N., Dillingh, B., Erkens, S., Schmets, A. J. M., Fischer, H. R., Scarpas, A., & Schitter, G. (2013). Is Atomic Force Microscopy suited as Tool for fast Screening of Bituminous Materials? An Inter-laboratory Comparison Study. *92nd Annual*

Meeting, Transportation Research Board, 1–16.

Nasrazadani, S., Mielke, D., Springfield, T., & Ramasamy, N. (2010). Practical Applications of FTIR to Characterize Paving Materials. In *Technical Report: FHWA/TX-11/0-5608-1*.

Nur, W., Azahar, A. W., Bujang, M., Jaya, R. P., Hainin, M. R., Ngadi, N., & Mohamad, M. (2016). Chemical Identification of Waste Cooking Oil as additive in Bitumen. *Key Engineering Materials Submitted*, *700207*(May), 2016–3. https://doi.org/10.4028/www.scientific.net/KEM.700.207

Pauli, A. T., Grimes, R. W., Beemer, A. G., Turner, T. F., & Branthaver, J. F. (2011). Morphology of asphalts , asphalt fractions and model wax-doped asphalts studied by atomic force microscopy. *International Journal of Pavement Engineering*, *12*(4), 291–309. https://doi.org/10.1080/10298436.2011.575942

Petersen, J. C., Robertson, R. E., Branthaver, J. F., Harnsberger, P. M., Duvall, J. J., Kim, S. S., Bahia, H. U., Dongre, R., Antle, C. E., & Sharma, M. G. (1994). Binder Characterization and Evaluation Volume 4 : Test Methods. In *Strategic Highway Research Program, National Research Council* (Vol. 4).

Rebelo, L. M., Sousa, J. S. De, Abreu, A. S., Baroni, M. P. M. A., Alencar, A. E. V, Soares, S. A., Filho, J. M., & Soares, J. B. (2014). Aging of asphaltic binders investigated with atomic force microscopy. *Fuel*, *117*, 15–25. https://doi.org/10.1016/j.fuel.2013.09.018

Sanli, H., Canakci, M., & Alptekin, E. (2011). Characterization of Waste Frying Oils

Obtained from Different Facilities. *World Renewable Energy Congress*, 479–485. https://doi.org/10.3384/ecp11057479

Soenen, H., Besamusca, J., Fischer, H. R., & Chailleux, E. (2014). Laboratory investigation of bitumen based on round robin DSC and AFM tests. *Journal of Materials and Structures*, *47*(7), 1205–1220. https://doi.org/https://doi.org/10.1617/s11527-013-0123-4

Standard Test Method for Determination of Free Fatty Acids Contained in Animal , Marine , and Vegetable Fats and Oils Used in Fat Liquors and Stuffing Compounds 1 (Vol. 95, Issue Reapproved 2017). (2018). https://doi.org/10.1520/D5555-95R17.3.4

Wang, M., & Liu, L. (2017). Investigation of microscale aging behavior of asphalt binders using atomic force microscopy. *Construction and Building Materials*, *135*, 411–419. https://doi.org/10.1016/j.conbuildmat.2016.12.180

Yao, H., You, Z., Li, L., Wei, S., Huei, C., & Khin, Y. (2013). Rheological properties and chemical analysis of nanoclay and carbon microfiber modified asphalt with Fourier transform infrared spectroscopy. *Construction and Building Materials*, *38*, 327–337. https://doi.org/10.1016/j.conbuildmat.2012.08.004

Yen, T. (1991). Asphaltene/resin plus oil interconvention: an investigation into colloidal model of asphaltene. *Workshop on the Chemical Components and Structure of Asphalt Materials*, 10.

Yu, X., Zaumanis, M., Dos Santos, S., & Poulikakos, L. D. (2014). Rheological, microscopic, and chemical characterization of the rejuvenating effect on asphalt binders. *Fuel*, *135*(1), 162–171. https://doi.org/https://doi.org/10.1016/j.fuel.2014.06.038

Zhang, D., Chen, M., Wu, S., Liu, J., & Amirkhanian, S. (2017). Analysis of the relationships between waste cooking oil qualities and rejuvenated asphalt properties. *Journal of Materials*, *10*(5). https://doi.org/10.3390/ma10050508

Zhang, H. L., Yu, J. Y., Feng, Z. G., Xue, L. H., & Wu, S. P. (2012). Effect of aging on the morphology of bitumen by atomic force. *Journal of Microscopy*, *246*(1), 11–19. https://doi.org/10.1111/j.1365-2818.2011.03578

Zhang, M., Yang, X., Zhao, H. T., Dong, A. J., Wang, J., Liu, G. Y., Wang, P., Cheng, C. L., & Zhang, H. (2015). A quick method for routine analysis of C18 trans fatty acids in non- hydrogenated edible vegetable oils by gas chromatography e mass spectrometry. *Food Control*, *57*, 293–301. https://doi.org/https://doi.org/10.1016/j.foodcont.2015.04.027

Chapter 4 Rheological Characterization of Rejuvenated Asphalt Binder

Co-Authorship: This chapter has been presented in the 99th Annual Meeting of Transportation Research Board (TRB) and also submitted to a journal as a technical paper as: Ahmed, R. B., Hossain, K., Aurilio, M. (2020), ‘Characterization of Asphalt Rheology Using Waste Cooking Oil as a Rejuvenator’. Most of the research in this chapter has been conducted by the first author. He also prepared the draft manuscript. The other authors supervised the research and reviewed the manuscript.

4.1 Abstract

Using reclaimed asphalt pavement (RAP) material in pavement construction is an environmentally friendly practice. However, the asphalt available in recycled pavements is already oxidized and stiffened due to various environmental processes. As a result, using RAP binder in cold regions like Canada can have a significant negative effect on pavement performance and may accelerate the pavement distresses especially thermal cracking along with the alteration of rheological properties. Rejuvenators are used with aged binder for reactivating and restoring the original properties of the asphalt binder. This study investigates the rheological performance of aged binders rejuvenated with waste cooking oil (WCO). WCO was used in two forms: raw/untreated WCO (R1) and chemically modified/treated WCO (R2). Also, a commercially available rejuvenator, Hydrolene H90T (R3) was used to compare the performance of the binder. The thin film oven test (TFOT) aged PG 58-28 binder was mixed with R1, R2, and R3 rejuvenator at the concentrations of 3%, 6%, and 9% respectively determined by the weight of the total binder. To enhance the

rutting resistance, styrene-butadiene-styrene (SBS) was also blended with rejuvenated binders and tested. A frequency sweep test was conducted at a wide range of temperatures and frequencies to determine the rutting and cracking parameters such as Glover-Rowe, Superpave rutting, Shenoy, Crossover frequency, and Rheological index. In addition to that, the MSCR test was performed to gain an in-depth understanding of the rutting criteria of binders. Based on the comparative study of different rejuvenated binders, the binder rejuvenated with R2 seems to be effective in improving the overall performance of the binder. Also, a significant correlation was found between the different rutting and cracking parameters with different dosage of asphalt rejuvenation.

4.2 Introduction

Using recycled asphalt pavement (RAP) materials in pavement construction helps to reduce construction costs up to 34%, limits the amount of waste in landfills and the emission of greenhouse gases (Kandhal & Mallick, 1997; Zaumanis et al., 2015). RAP materials might help road agencies to achieve their goals of sustainable pavement construction, however, there is also strong evidence that the RAP binder is highly oxidized due to its long-term exposure to environments that changes the binder’s chemical and rheological properties (Al-Qadi et al., 2007). Oxidation also decreases the overall relaxation capacity of hot mix asphalt (HMA) which can lead to cracks in the pavement (Branthaver et al., 1993). To address these issues and to restore the original rheological properties and pavement performances, rejuvenators are commonly blended with RAP materials to make the binder softer.

Rejuvenators have lighter oil components which are similar to asphalt. Oil type rejuvenators help to reduce the viscosity of aged binder (Brown, 1988). Many studies have already been conducted to understand the effect of rejuvenation on RAP binder. However, a limited amount of research has been performed on the different rheological properties of rejuvenated binders. This study aims to fill that gap by examining the rheological properties of different rejuvenated binders.

In general, asphalt molecules can be divided into two groups based on polarity: a) asphaltenes, and b) maltenes (García et al., 2010). The maltenes are a liquid phase which includes saturates, aromatics, and resins. During the aging of asphalt, the molecular composition of the asphalt changes resulting in a change in the rheological properties. The change of the molecular composition causes, an alteration of the asphaltene-maltene ratio is also observed in aged asphalt. To balance the asphaltene-maltene content in aged asphalt, and to restore the molecular composition of asphalt we can use oil type rejuvenators (Mogawer et al., 2013).

Many studies reported a significant change in asphalt rheological properties after rejuvenation. Changes included a decrease in rutting resistance and an increase in cracking resistance. With the addition of rejuvenators, a significant increase in fatigue resistance was also observed, but the rutting resistance also dropped as the rejuvenators make binders softer. Some positive results are also reported in terms of rutting after rejuvenation. Yang and You (Yang & You, 2015) found that rejuvenation decreased the non-recoverable creep compliance (J_{nr} value) and increased the elasticity of the binder which is a good indication of rutting resistance.

In recent years, numerous researchers have investigated the use of waste oil for rejuvenation to improve the environmental sustainability of asphalt pavements (Aflaki et al., 2014; Al-Omari et al., 2018; Chen et al., 2014; Fini et al., 2011; Gong et al., 2017). In Spain, work completed by Romera et al., indicated that the application of recycled motor oil can postpone the permanent deformation and reduce mixing and the compaction temperature of an aged binder (Romera et al., 2006). Following Romera, in Malaysia Asli (Asli et al., 2012) incorporated waste cooking oil to asphalt rejuvenation. The study used raw waste oil to observe the change of rheological properties of the binder. This research suggests using up to 5% of rejuvenator oil with the aged binder to achieve better pavement performance. Another study was conducted by Azahar (Azahar et al., 2016) who concluded that the chemical modification of rejuvenator improves the rutting resistance and reduces the temperature susceptibility of the rejuvenated binder. A new approach has been developed in the Netherlands (García et al., 2011) that uses encapsulated rejuvenators rather than mixing them directly with the aged binder. These encapsulated rejuvenators will act as an injector after cracking in the aged binder. These test results also show better skid resistance on pavement. Similarly, in China, oil-based capsulation was applied to the pavement which showed improved thermal resistance (Su et al., 2015).

Research typically indicates that oil type rejuvenators reduce the rutting resistance of binders. The effect of styrene-butadiene-styrene (SBS) polymer to improve the performance of hot mix asphalt (HMA) has also been widely studied (Xu et al., 2014). In the USA, Xu et al. studied the effect of SBS on oil rejuvenated asphalt and found it to be very promising in terms of rutting resistance and elastic recovery (Yang et al., 2019). Some studies have also seen an improvement in cracking resistance after the SBS modification (Kim et al., 2009; Singh & Girimath, 2016; Singh & Kataware, 2016).

During this research project, the authors conducted a comprehensive review to better understand the topic and summarize the existing research gaps (Ahmed & Hossain, 2019). A brief summary of these gaps is presented here.

- The optimal dosing rates for rejuvenators are still not identified.
- Performance evaluation of different rejuvenators in terms of rutting and cracking resistance are inadequate
- The effect of polymer modification on rejuvenated asphalt binder has not been considered in depth

After taking these research gaps into consideration, this study has the following objectives:

- To develop a quantitative understanding of the performance of waste cooking oil (WCO) as a rejuvenator
- To understand the effect of varying concentrations of rejuvenators added to the aged binder
- To evaluate the rutting and cracking parameters of different rejuvenated blends by calculating Glover-Rowe parameter, Superpave Rutting parameter, Shenoy Parameter, Crossover Frequency, and Rheological Index from the frequency sweep testing

- To determine the non-recoverable creep compliance parameter from the Multiple Stress Creep Recovery (MSCR) test to categorize binder suitability for standardized traffic loading according to AASTHO M332
- To rank the different rejuvenators based on their rheological performance

4.3 Material Collection and Experimental Design

4.3.1 Asphalt Binder

The base binder used in this study is PG 58-28, which is generally used in the Southern region of Newfoundland and Labrador, Canada. The asphalt was supplied by Bitumar USA, Inc. and a thorough investigation was conducted on the controlled PG 58-28 binder. Furthermore, an aged binder was obtained through simulating short term aging (Thin-Film Oven Test) following the protocol prescribed in ASTM D1754 (ASTM, 2018). Using this method, the neat liquid asphalt (PG58-28) undergoes constant thermal aging at 163ºC for 5 hours in a convection oven. For convenience, the short-term aged binder has been represented as the aged binder throughout this paper. Due to limitations with access to equipment at that time, this study was performed using of TFOT aging protocol rather than using rolling thin film oven (RTFOT) and pressure aging vessel (PAV) system. However, this should not limit our ability to understand and compare the performance of various rejuvenated materials as they interact with the controlled aged binders.

4.3.2 Rejuvenators

Three different rejuvenators were used in this study. The rejuvenators are waste cooking oil (WCO), chemically modified WCO and Hydrolene, which are denoted as R1, R2, and R3 respectively. R1 was collected from two different sources (NJs Kitchen and Eco Oil Limited). R1 samples contained many fried fragments, which were later removed by a screener. Based on the purity and appearance of both samples after filtration, the samples provided from Eco Oil Limited were used for the duration of the experiment. R2 was obtained after the transesterification of R1(Leung & Guo, 2006), which contained a high amount of free fatty acid (FFA). The presence of FFA weakens the adhesion properties of binder which affects binder performance (Azahar et al., 2016; Gong et al., 2016). Transesterification was completed by the Environment Engineering Lab at Memorial University to reduce the FFA contents. R3 was provided by HollyFrontier Corporation. An acid value test was also conducted on R1 and R2 rejuvenator, since the acid value is higher in natural waste materials compared to the commercially manufactured materials. The measured acid values before and after modification of R1 are shown in Table 4.1 and the rejuvenators are presented in Figure 4.1.

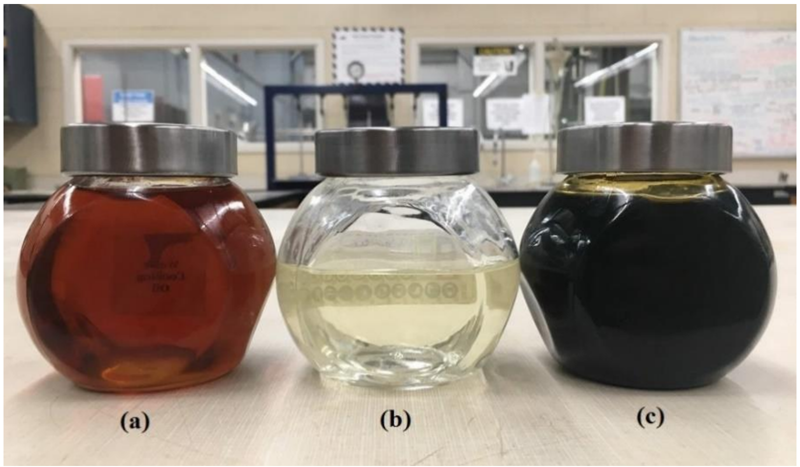


Figure 4.1 Types of Rejuvenators a) R1, b) R2, and c) R3

Table 4.1 Acid Value of R1 and R2 Rejuvenator

Sample	**Volume of KOH (mL)**	**% Free Fatty Acid (based on Oleic acid %)**	**Acid Value (mL/g)**
R1	0.70	2.74	5.45
R2	0.25	0.97	1.95

4.3.3 Blending Rejuvenators and Asphalt Binders

Rejuvenated asphalt binders were prepared by mixing aged asphalt binder with three different types of rejuvenators: R1, R2, and R3. In every case, the first step was to heat the aged asphalt at 100ºC for 30 minutes, which made it fluid enough to mix with the rejuvenators. We then blended aged asphalt with the different application rates of rejuvenators, including 3%, 6%, and 9% based on the weight of the aged asphalt. The blending process was conducted manually with a glass stirrer for 30 minutes at 100ºC. All the rejuvenators were liquid and had low viscosity which allowed us to produce a homogeneous mix.

4.3.4 SBS Modified Rejuvenated Binder

To examine the improvement of rutting resistance, this research prepared some SBS modified rejuvenated binder specimens. Linear SBS was provided by Yellowline Asphalt Products Limited. A proprietary cross-linking agent was also used at 10% weight of the polymer to stabilize the SBS. It should be noted that SBS was only used with the R1 and R2 rejuvenators at 4% weight of the binder. For the blending, the R1 and R2 rejuvenated binders were preheated until they became fluid. Once the temperature reached 180ºC, then the SBS was mixed and stirred with a mechanical stirrer for 45 minutes. Later, the cross-linking agent was added and mixed for another 30 minutes to produce the modified sample.

4.3.5 Testing

After preparing all types of rejuvenated asphalt binder, rheological tests were conducted using a Dynamic Shear Rheometer (DSR) as per AASHTO T 315 with the help of Yellowline Asphalt Products Ltd at their Hamilton asphalt terminal. The Malvern Panalytical Kinexus DSR-III rheometer was used, and frequency sweep test protocol was followed. Furthermore, rSpace software was used for data acquisition. A 25 mm diameter parallel plate with 1mm gap was selected. The temperature range was selected from 40ºC-70ºC with an interval of 6ºC. Also, test frequency varied from 0.1-10 Hz with a strain rate of 0.1% for each temperature.

4.4 Results and Discussions

4.4.1 Complex Modulus Master Curves

The frequency sweep test data using the DSR equipment allowed for the completion of the complex modulus master curve which was plotted using the Christensen-Anderson (CA) model (Christensen et al., 2017; Christensen & Anderson, 1992). The master curves were shifted using a reference temperature of 58ºC and the shift factor was determined by the Williams-Landel-Ferry (WLF) equation. All the models used in the data analysis are presented below.

$$G^*(w) = Gg[1 + \left(\frac{Wc}{Wr}\right)^{\left(\frac{log2}{R}\right)}]^{-(\frac{R}{log2})} \qquad \ldots (1)$$

$$\delta(w) = 90/(1 + \frac{Wr}{Wc})^{(\frac{log2}{R})} \qquad \ldots (2)$$

$$loga(T) = -C1(T - Tr)/(C2 + T - Tr) \qquad \ldots (3)$$

Where, $G^*(w)$ = complex shear modulus; $\delta(w)$ = phase angle; Gg = glass modulus assumed equal to 1 Gpa; Wr = reduced frequency; Wc = crossover frequency; R = rheological index; $loga(T)$= shift factor; $C1, C2$ = empirically determined constants; T = test temperature; and Tr = reference temperature.

4.4.1.1 Effects of Rejuvenators on Aged Binder

Figure 4.2 represents the complex modulus master curves of aged binders rejuvenated with three rejuvenators. Additionally, the figure also includes the master curve of the aged binder for comparison. According to Anderson et al., as asphalt ages, the shape of master curves typically flattens and cause the R-value (Rheological index) to increase. This flattening pattern of master curves was also observed in some previous studies (Wasiuddin et al., 2014; Yu et al., 2014). As expressed in Figure 4.2(a) (Master Curve for R1), the complex modulus is relatively higher at higher frequencies and lower at lower frequencies. As the dosing increases, the binder becomes softer and complex modulus values decrease. However, the difference in modulus values is more prominent at higher frequencies. For R2 (Figure 4.2(b)), no significant change in stiffness value was noticed when dosing rates were increased. Interestingly, with the R2 rejuvenator, the stiffness value at higher loading frequencies outperformed the aged binder indicating an increase in rutting resistance at higher temperatures. This may be due to the rejuvenator which increased the stiffness of binder after the transesterification process. The transesterification process may reduce the capacity of R2 to rejuvenate the aged asphalt.

Modulus behavior for R3 was observed in Figure 4.2(c). A similar pattern was observed when compared to R1, however, at higher frequencies, 3% and 6% of this rejuvenator showed relatively higher complex modulus than that of the aged binder. Whereas, 9% R3 exhibited lower stiffness among the R3 binders. Similar to R1 and R2 rejuvenator, R3 also showed almost a similar pattern at lower frequencies.

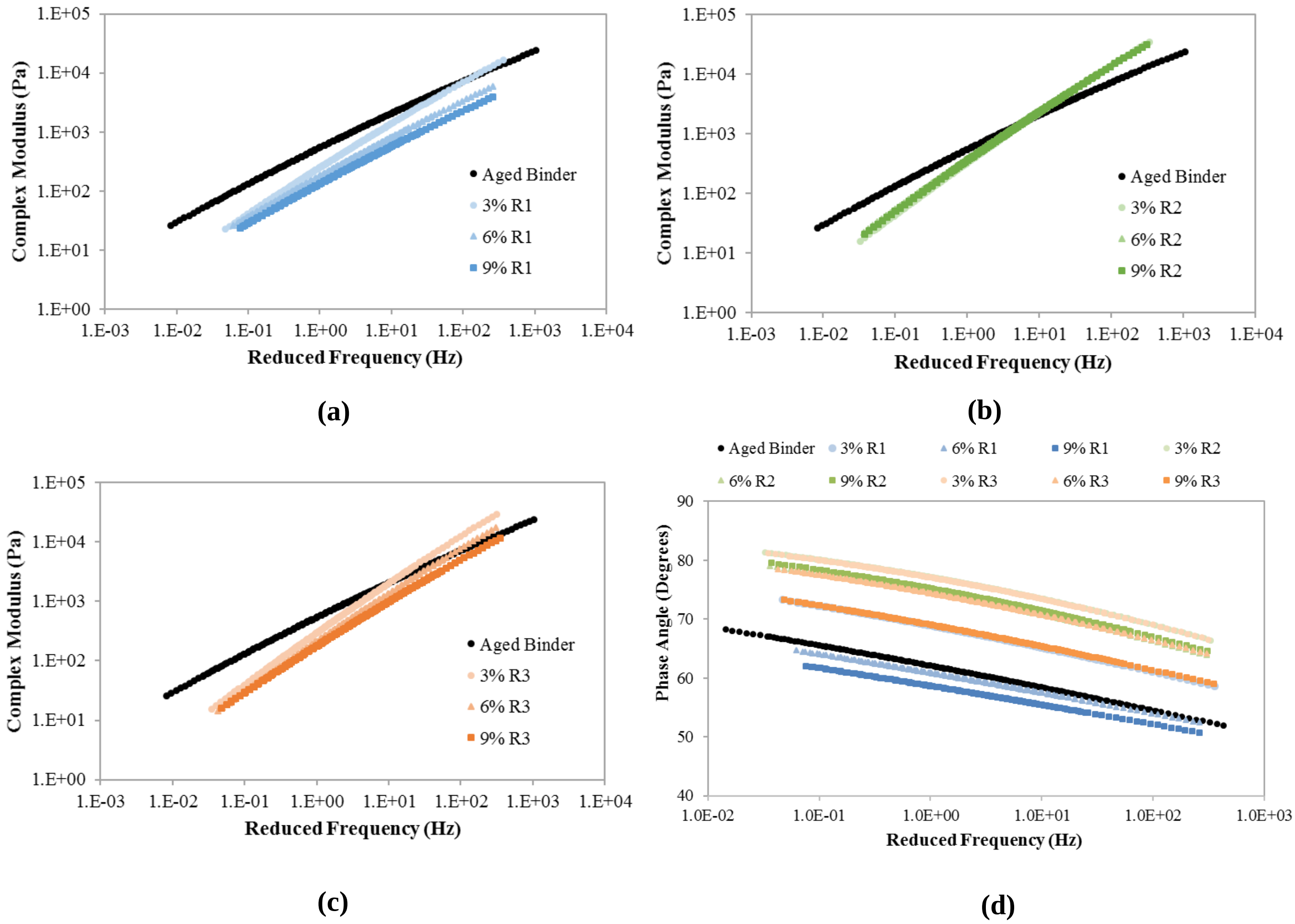


Figure 4.2 Complex Modulus Master Curves of (a) R1, (b) R2, and (c) R3 Rejuvenated Binders; Combined Phase Angle Master Curves (d) for R1, R2, and R3 Rejuvenated Binders

Figure 4.2(d) reports the phase angle value from the DSR test for all the rejuvenated and aged binders. In general, the R2 and R3 rejuvenated binders exhibited more viscous behavior than R1 rejuvenated binder. When the performance of application rates within a rejuvenator are compared, it can be seen that generally a high application rates result in improved elastic properties. Among all the binders, an equivalent phase angle master curve was noticed for 6% of R2 and R3, 3% R1 and 9% R3 rejuvenator.

4.4.1.2 Effect of Rejuvenators with SBS Polymer

SBS polymer was added to R1 and R2, and this was used to examine the effect of SBS on rejuvenated asphalt. From the experimental data, it was found that all the SBS modified binders follow the same trends. To improve figure clarity, only 6% R1 and R2 SBS modified binders master curves were presented for comparison. Figure 4.3(a) compares the binder stiffness with the impact of polymer on rejuvenated asphalt. Figure 4.3(a) shows that the SBS modified R1 shows higher stiffness compared to the unmodified R1. This is due to the increased elastomeric properties of SBS. Compare to the R1 and R2 SBS modified binders, the R2 modified binders are the stiffest. At high frequencies, all the concentrations of R2 modified binders were fairly similar in master curves, whereas 3% R2 SBS modified binders give a lower stiffness followed by 6% and 9% addition. Among all the rejuvenated modified binders, SBS modified R2 is the stiffest binder and this result matches with the unmodified binder when mixed with R2.

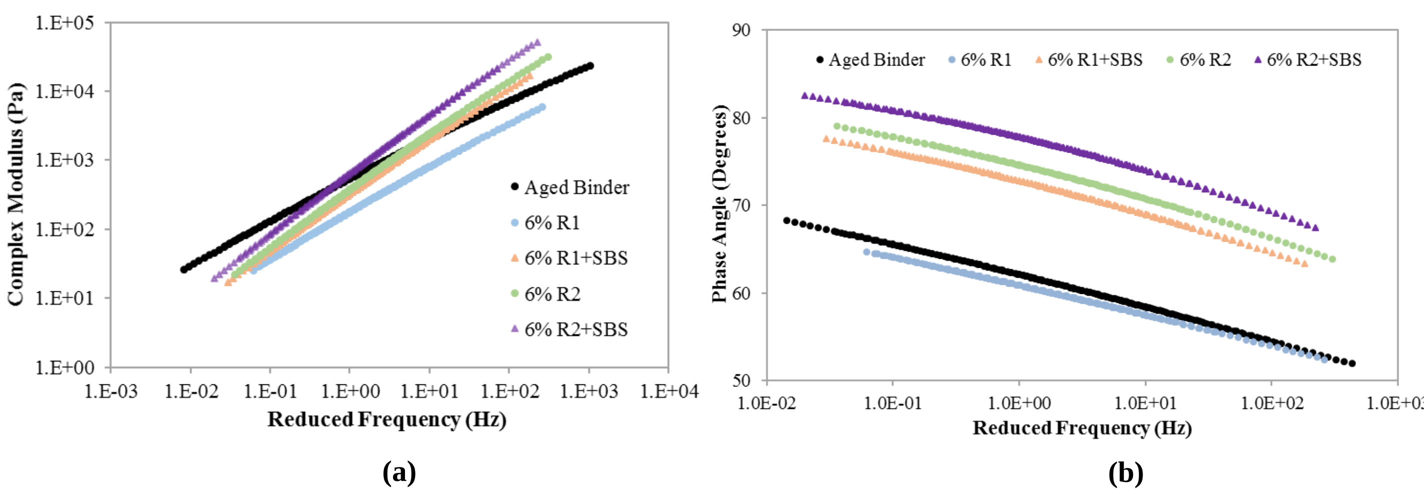


Figure 4.3 Complex Modulus (a) and Phase Angle (b) Master Curves of SBS Modified Binder

Figure 4.3(b) shows the phase angle master curves of the SBS modified R1 and R2 rejuvenated binders. Both R1 and R2 modified binders show unexpectedly more viscous behavior with the addition of higher concentrations of rejuvenators. Compared to both modified and unmodified R1 binders, modified R1 shows a higher viscous behavior than an unmodified binder and also provides a higher phase angle than the control binder. This might be attributed to the poor compatibility of SBS with the rejuvenators because SBS typically lowers the phase angles. In the case of the SBS modified R2, a higher phase angle and a higher stiffness are observed than the unmodified R2 binder. At 6% and 9% of SBS modified R2 rejuvenation, an equivalency of phase angle master curve is noticed.

4.4.2 Glover-Rowe Parameter

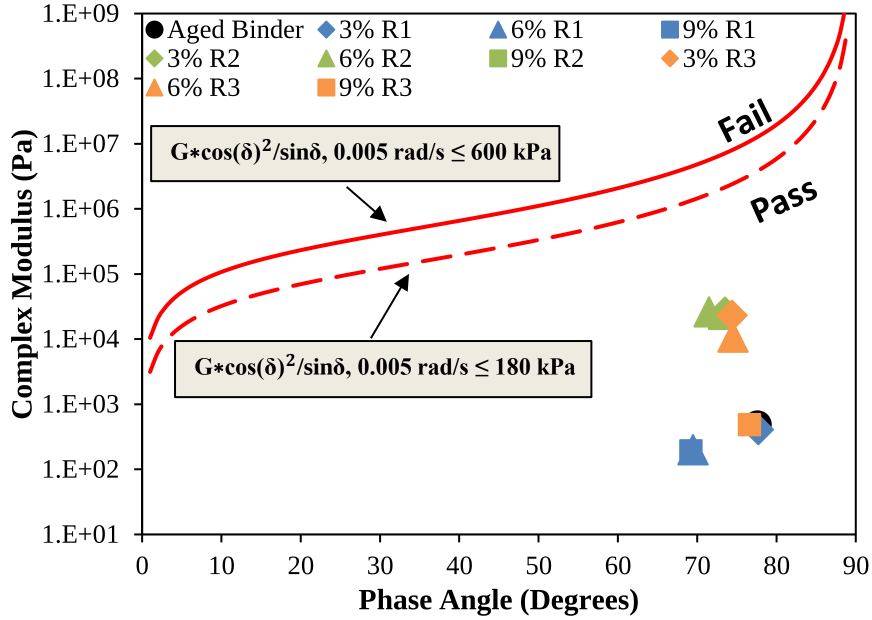
The Glover-Rowe (G-R) parameter is used to indicate the cracking susceptibility of the asphalt binder. The G-R parameter is calculated from the DSR frequency sweep test data. To capture the complex shear modulus G* and phase angle δ at the temperature frequency combination of 15ºC and 0.005 rad/s, the master curves were constructed using the CA model. According to Rowe, a G-R value of 180 kPa corresponds to the onset of damage, while a value greater than 600 kPa are prone to block cracking issue of the asphalt binder (Anderson et al., 2011; Pournoman et al., 2018). The location relative to this damage zone is used as a relative indicator of cracking resistance.

Damage onset: $G^{*}\ (cos\delta)^\wedge 2/sin\delta = 180\ kPa$ … (4)

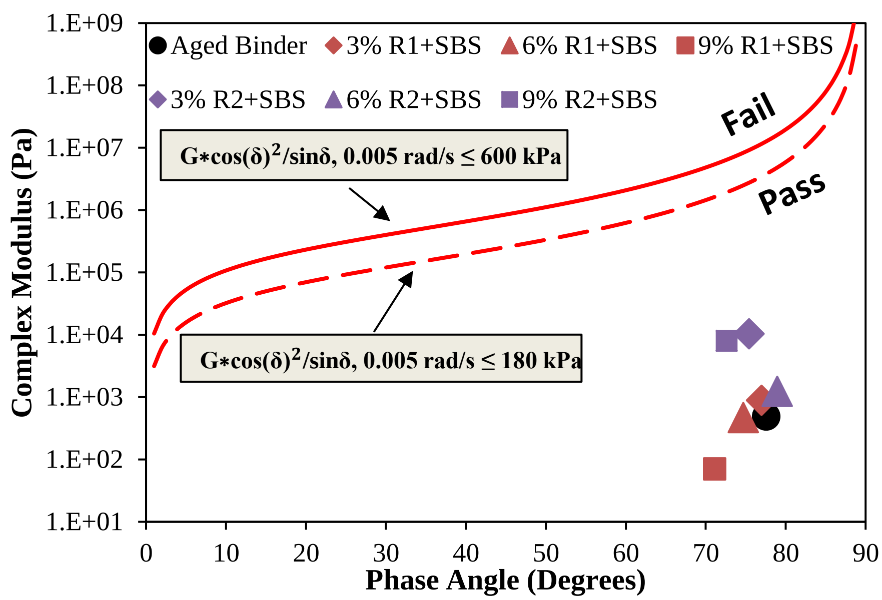
Significant cracking: $G^{*}\ (cos\delta)^\wedge 2/sin\delta = 600\ kPa$ … (5)

Figure 4.4(a) represents the black space diagram of different rejuvenated asphalt binder. This black space diagram gives a clear explanation of rejuvenation impact with aged binder, where time-temperature superposition (TTS) calculative effort is no longer required (Rowe, 2014; Rowe & Sharrock, 2011). As the aging increases, the binder becomes brittle which makes it more prone to cracking. With the addition of rejuvenation, the binder softens and exhibits higher resistance to cracking.

For the R1 rejuvenated binder shown in Figure 4.4(a), all the concentrations show similar cracking susceptibility to the aged binder. Whereas for R2 rejuvenator, higher cracking susceptibility has been observed for all concentrations due to its binder stiffening and the change to load response. Similar patterns are also observed for R3 rejuvenated binder, where the 9%R3 binder shows lower G-R parameter value compare to others. For all samples described above, the extent of rejuvenation dosage makes the binder softer due to their molecular change. Softer binders can make it less susceptible to cracking when compared to the stiffer binder, but the response of loading is also important. When comparing each concentration of R1, R2, and R3, 6%R1 and 9%R1 seems to be more effective to improve the cracking resistance.



(a) G-R Parameter of R1, R2, and R3 Rejuvenated Binders



(b) G-R Parameter of SBS Modified Binders

Figure 4.4 Black Space Diagram of G-R Parameter for Different Rejuvenated Binders

4.4.2.1 Effect of SBS on G-R Parameter

The G-R parameter value of rejuvenated binders with the SBS polymer has been shown in Figure 4.4(b). In the case of R1, 3%R1+SBS and 6%R1+SBS show a higher G-R value than an unmodified binder. Whereas, 9%R1+SBS binder exhibit lower G-R value which may mean higher cracking resistance. For R2 rejuvenator, 3%, 6%, and 9% SBS modified binder shows lower G-R value compared with unmodified rejuvenated concentrations, which demonstrated that SBS modified binder might improve the cracking susceptibility of the aged binder. Compare to SBS modified R1 and R2 binder, R1 shows better performances compare to R2. In general, the aged binders are more prone to cracking. To address the cracking issue in the pavement, usage of rejuvenators and SBS polymers are recommended based on our experimental analysis. It should be noted that evaluating SBS modified binders with the G-R parameter may not be as effective as evaluating binders that do not contain SBS due to the change in elastomeric properties (Kluttz, 2019)

4.4.3 Superpave Rutting Parameter

The Superpave rutting parameter value of different types of rejuvenated asphalt binders have been shown in Figure 4.5 along with their damage criteria. Based on the high temperature of all rejuvenated binder, the rutting performance was evaluated at 46ºC. The higher $G^{*}/Sin\delta$ value is considered to be a desirable characteristic in terms of rutting resistance. It was observed that the rutting performance is highly influenced by different dosage of rejuvenators. Generally, the higher the rejuvenation concentrations result in lower rutting resistance.

The black space diagram in Figure 4.5(a) provides a clear visualization of rutting resistance due to the impact of rejuvenation. It was observed that all the R1 rejuvenated binders fall below the damage criteria line and failed to achieve the rutting criteria. A similar trend was observed for R3; however, the sample with the 3% R3 rejuvenation and the aged binder had similar performance. Both the binders are on the line of damage criteria and are in the critical stage of rutting. In the case of R2, all the samples passed the damage criterion and they show very good rutting performance.

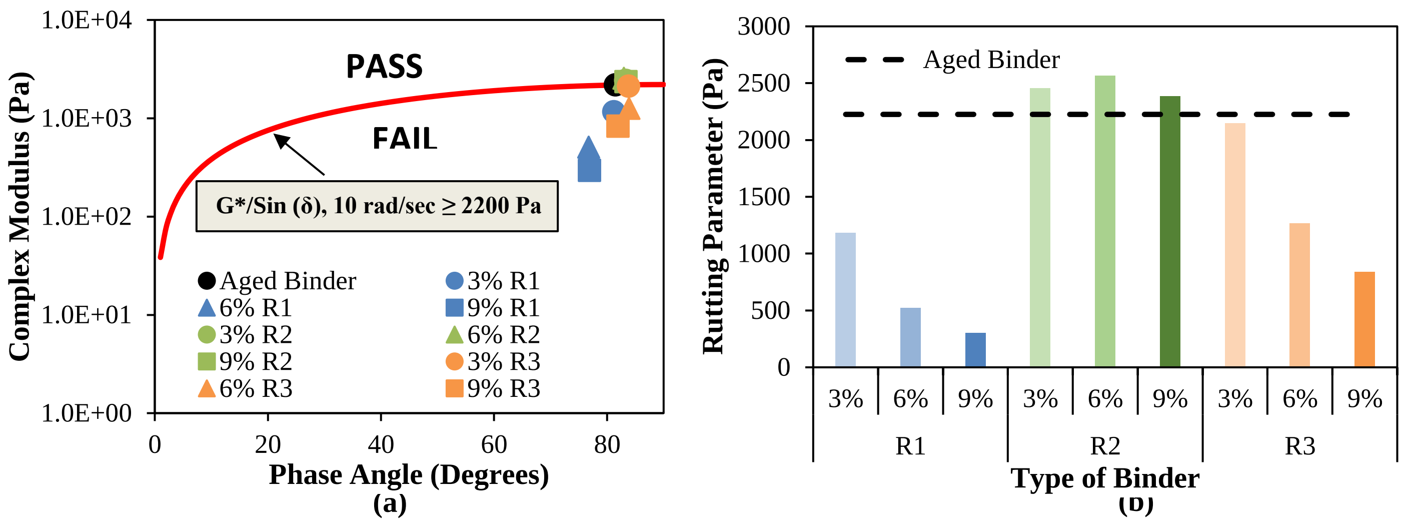


Figure 4.5 Superpave Rutting Parameter for (a) R1, R2, and R3 Rejuvenated Binders; (b) Comparison of Superpave Rutting Parameter

To understand the relative performance of different dosage of rejuvenators, rutting parameters are also shown in Figure 4.5(b). For R1 and R3 rejuvenated binders, a decreasing trend of rutting resistance is observed with the increase of rejuvenator dosage. Based on the data, comparatively a better rutting resistance is noticed for R3. The rutting resistance of 3%R3 was recorded as 2.1 kPa which is comparable with the aged binder (2.2 kPa). Also, significant changes are observed between R1 and R3 rejuvenated binder when dosing rate increase from 3% to 9%. The 3%R1 and 6%R3 rejuvenated binder shows similar rutting performance, whereas 9%R1 shows the least resistance to rutting which can also be observed from the master curves in Figure 4.2(a).

In the case of R2, an increase of rutting resistance is observed with the increase of rejuvenation dosage. This increasing $G^*/Sin\delta$ value is observed up to 6%R2 rejuvenation, whereas it decreases for 9%R2. For all the percentages of the R2 rejuvenated sample, it shows higher rutting resistance compare to the aged binder shown in Figure 4.5(b). The addition of R2 rejuvenator changes the chemical composition of aged binder, which makes the binder stiffer to achieve better rutting resistance. Compared with R1 and R3 rejuvenators, 3% addition of R2 improves the rutting resistance of 10.7% and 1.45% from 3%R1 and 3%R3 respectively. Based on the analysis above, it was determined that the increased concentrations do not always make the binder softer but depend on the quality and the type of rejuvenators used.

4.4.3.1 Effect of SBS on Superpave Rutting Parameter

The SBS polymer is widely used to improve the rutting resistance and the elastic response of the binder. This study uses SBS with only R1 and R2 rejuvenator to understand the extent of its improvement in rutting resistance. Figure 4.6(a) shows the black space diagram of the SBS modified R1 and R2 rejuvenated binder. From Figure 4.6(a), it was observed that all the concentrations of the SBS modified R2 rejuvenated binder passed the Superpave rutting resistance criteria. For R1 rejuvenated binder, the 3%R1+SBS clearly pass the rutting criteria and 9%R1+SBS fails to pass, whereas 6%R2+SBS is on the damage criterion line like the aged binder.

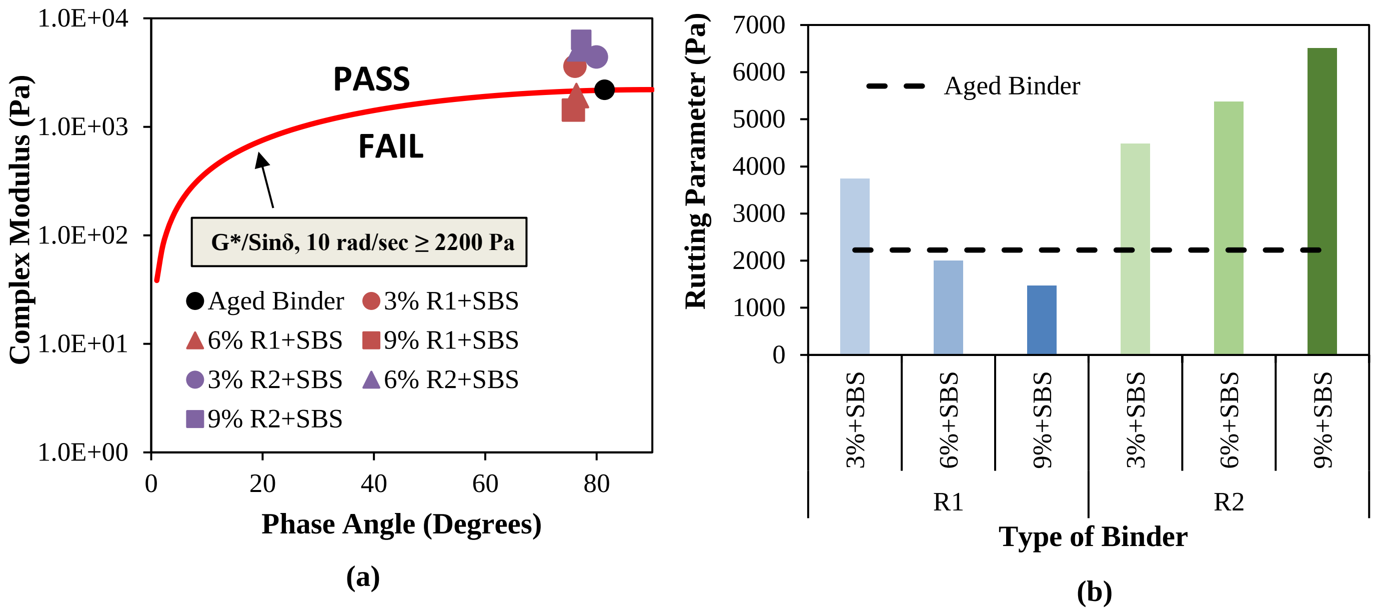


Figure 4.6 Superpave Rutting Parameter for (a) SBS Modified Binders; (b) Comparison of Superpave Rutting Parameter

For clarity, the comparative performance of the SBS modified R1 and R2 rejuvenated binder is shown in Figure 4.6(b). Like the previous analysis in Figure 4.3, SBS modified R2 rejuvenated binders show the highest stiffness. An improvement of stiffness has been observed for all the dosing rates of the SBS+R1 rejuvenators but not significantly. Here, 3%R1+SBS shows better rutting resistance than the aged binder, whereas 6% and 9% SBS modification still fails to exceed the rutting resistance of the aged binder. In the case of the R2+SBS, higher dosage of rejuvenators show the higher rutting resistance which is similar to the performance observed in Figure 4.3. This might be due to the better chemical bonding of SBS with the higher percentages of R2 rejuvenator and shows higher rutting resistance. It is also possible that R2 converts more asphaltenes to maltenes which are absorbed by the SBS causing further swelling. This increase in the swelling results in an increase in the rutting resistance (Dong et al., 2014). In the case of R1, it is evident that the addition of SBS mitigates some of the loss in rutting resistance that is introduced through the rejuvenation process.

4.4.4 Shenoy Parameter

The Superpave rutting parameter $G^*/Sin\delta$ is inadequate to rate the polymer modified binder at high temperature (Shenoy, 2004). To refine the existing parameter, Shenoy proposed the term $G^*/(1-(1/tan\delta sin\delta))$ through theoretical and experimental derivation (Shenoy, 2001). This parameter is more sensitive to phase angle δ and is very useful to measure the rutting resistance of the polymer-modified binder. To compare the Shenoy parameter with the existing rutting parameter, all the parameters were kept the same for this analysis.

Figure 4.7(a) shows the black space diagram of the Shenoy parameter for different types of rejuvenators at varying percentages. As the Shenoy parameter is dependent on complex modulus and phase angle, it is similar to the Superpave rutting parameter and their trends are also somewhat similar. Shenoy parameter provides a significant increase in some values compared to the Superpave rutting parameter. This is because Shenoy parameter is very sensitive to phase angle. Like Superpave rutting parameter, all the R2 rejuvenated binder passes the damage criteria whereas, all R1 rejuvenated binder fails significantly. The 3%R3 and the aged binder which was on the damage criteria line in Superpave black space diagram, pass this time because of the increased value of Shenoy parameter. Also, other dosing rates of R3 rejuvenated binder fails to achieve Shenoy parameter damage criteria and the least rutting resistance was noticed for R1 binders.

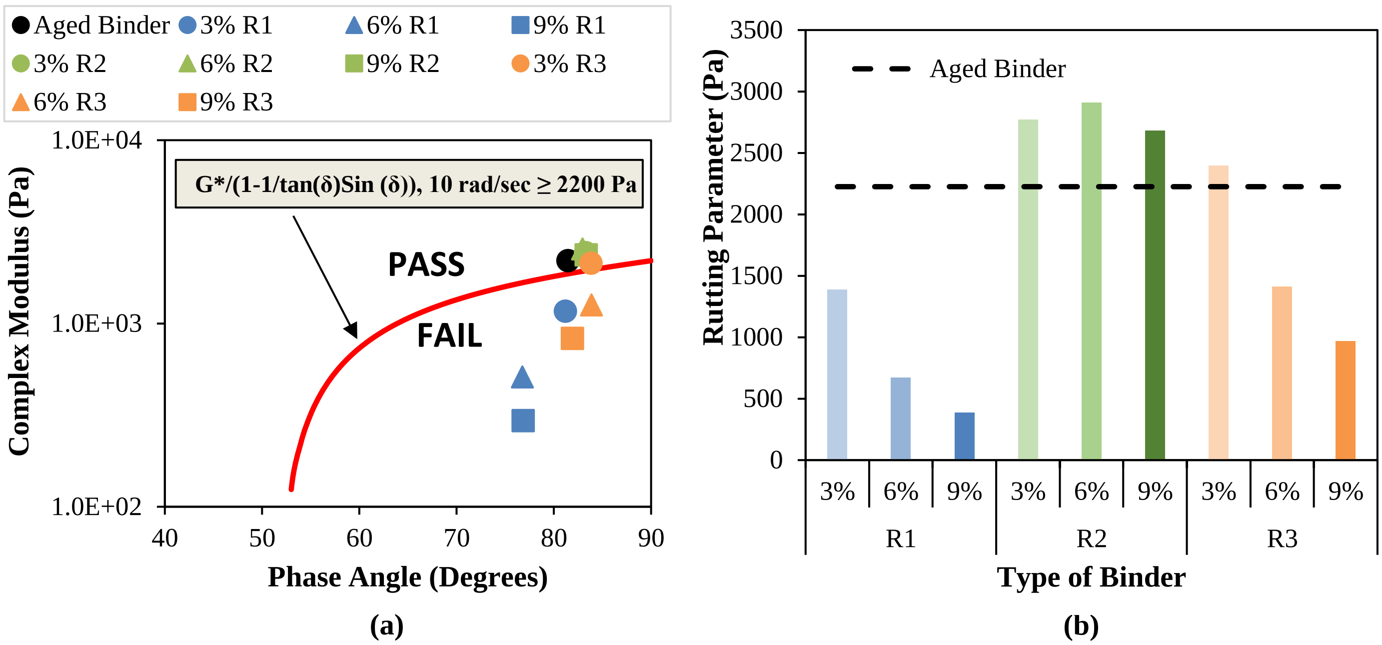


Figure 4.7 Shenoy Parameter for (a) R1, R2, and R3 Rejuvenated Binders; (b) Comparison of Shenoy Parameter

The relative performance of each concentration of the rejuvenators is shown in Figure 4.7(b). Like the Superpave rutting parameter, Shenoy parameter follows the same trend. The R2 rejuvenated binder shows the highest rutting resistance followed by R3 and R1 rejuvenated binder. The decreasing trend of rutting parameter with the increase of rejuvenator concentrations also contradicts here for the R2 rejuvenated binder like the Superpave rutting parameter. The 6%R2 rejuvenator shows the highest stiffness and decreased for the 9%R2 rejuvenation. From the observed data, it can be concluded that Shenoy parameter follows the consistent trend of the Superpave rutting parameter, no difference is figured out except some increased value. This may also indicate that the Shenoy parameter did not show significant improvement compared to the Superpave parameter, thus the use of MSCR analysis will be introduced later in this chapter.

4.4.4.1 Effect of SBS on Shenoy Parameter

The effect of SBS polymer with different rejuvenators on Shenoy parameter has been represented in Figure 4.8(a). From the black space diagram, it is observed that except the 9%R1+SBS, all the SBS modified binder passes the Shenoy parameter damage criteria. The highest complex modulus was achieved by 9%R2+SBS followed by 6%R2+SBS and 3%R2+SBS. Figure 4.8(b) represents the comparative performance of SBS modified with different dosage of rejuvenated binder. Once again, a similar trend was observed for all SBS modified binders like the Superpave rutting parameter. A higher bond was achieved for 9%R2+SBS rejuvenation and decreased with 6%R2+SBS and 3%R2+SBS. Whereas, an opposite trend was noticed for R1 rejuvenator with SBS and increased dosage. The increasing and the decreasing trend is similar to Superpave rutting parameters and no significant difference was recorded.

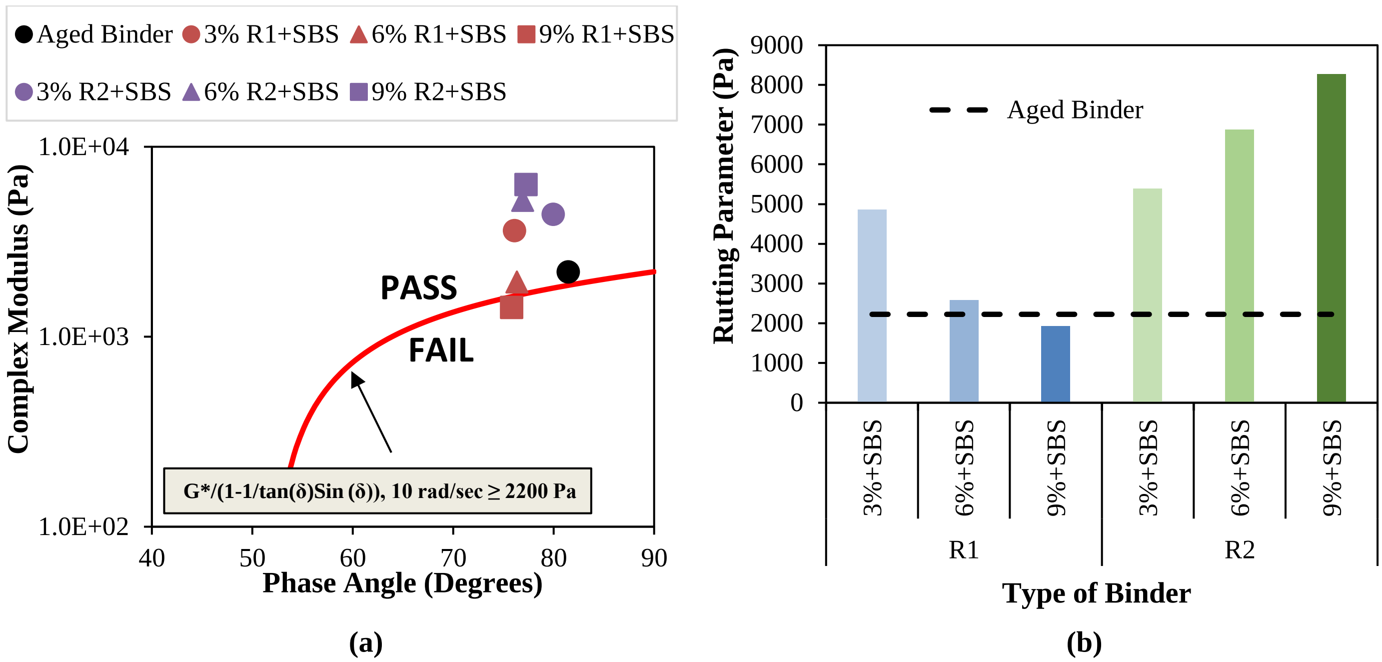


Figure 4.8 Shenoy Parameter for (a) SBS Modified Binders; (b) Comparison of Shenoy Parameter

4.4.5 R-Value and Crossover Frequency

Rowe (Rowe, 2014) proposed to understand the restoration behavior of rejuvenated asphalt binder using R value (rheological index) and w_c (crossover frequency). Generally, a lower R value with higher w_c shows less cracking susceptibility. For all rejuvenators tested in this project, the restoration of rheological behavior is desired and evaluated by determining the R value and w_c. Typically, binder oxidation and hardening leads to an increase in R value and the decrease in w_c value but this is also possible through the introduction of elastomers (Aurilio et al., 2017). A higher R value results in a flattened master curve and having a wide range of relaxation spectra which is consistent with master curves shown in

Figure 4.2. With the addition of a rejuvenator, an opposite trend was observed in previous studies (Mensching et al., 2016).

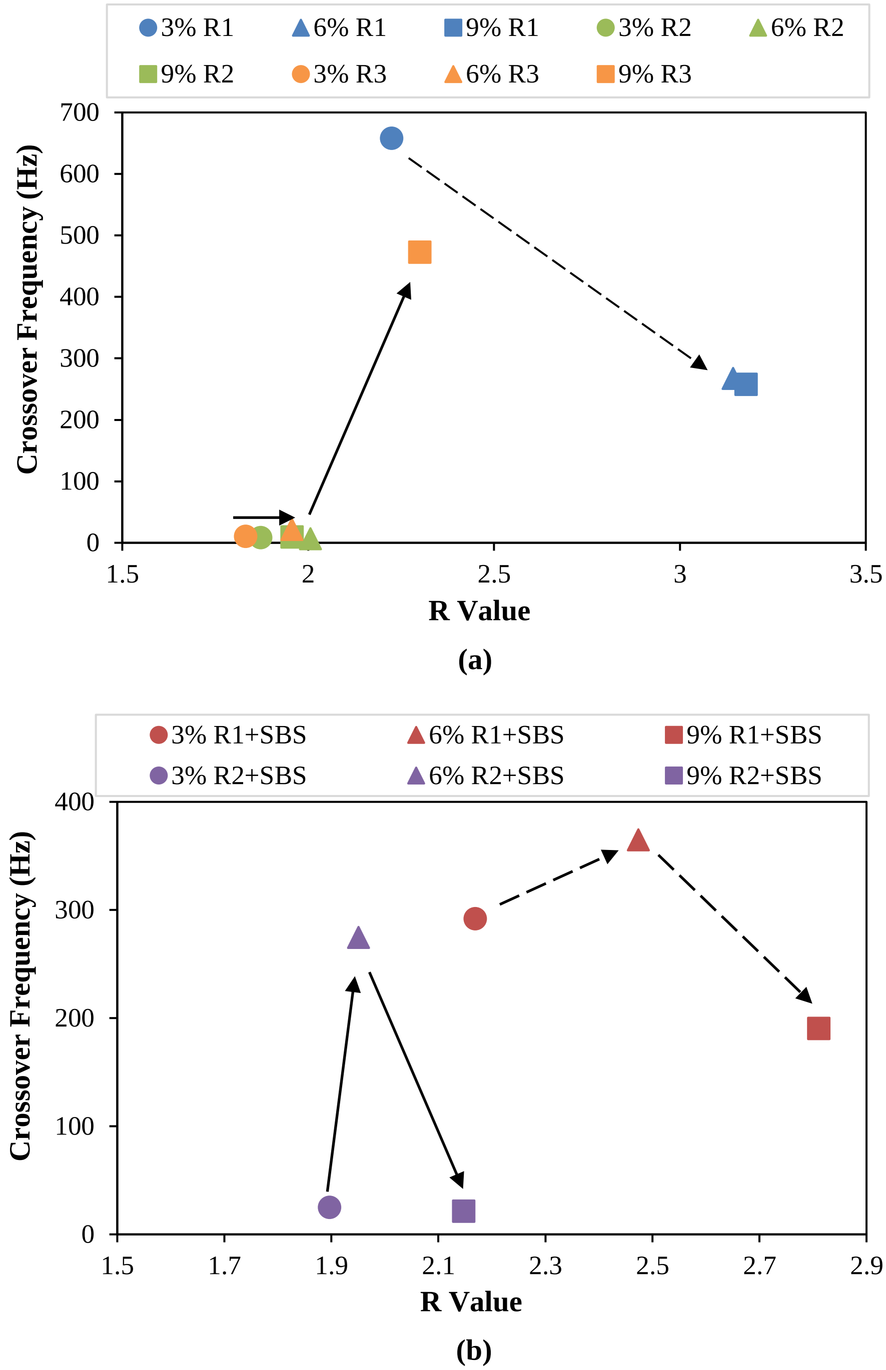


Figure 4.9 Crossover Frequency and R-index Parameter for Different Binders

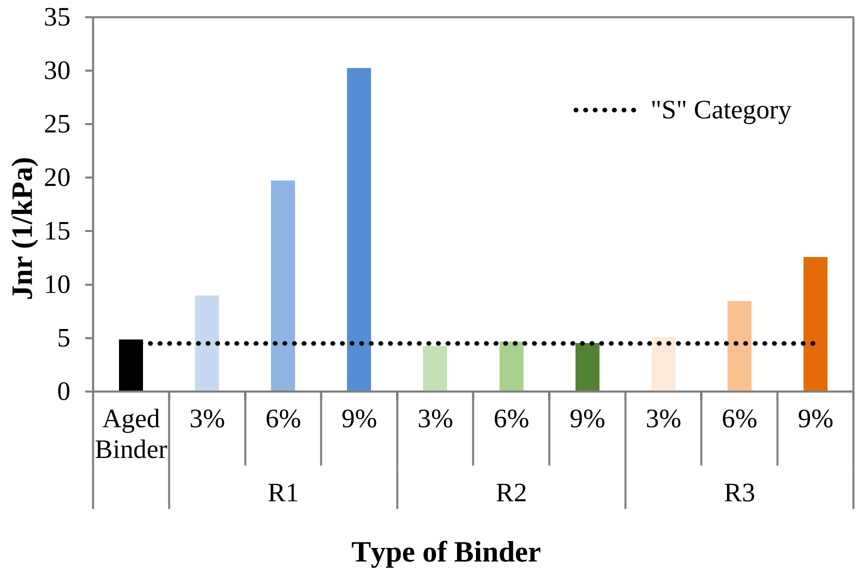
Figure 4.9(a) shows a change in R and w_c with the change of rejuvenator types and concentrations. The plotted R and w_c is obtained from the master curve at the reference temperature of 15ºC. Based on the data obtained, the performance of different concentrated rejuvenators can be grouped: high R + low w_c(type 1), low R + high w_c(type 2), and low R + low w_c(type 3). From the plot, 3%R1 and 9%R3 belongs to type 2 combination, whereas 6% and 9%R1 exhibit type 1. Similar to the analysis from the G-R parameter in Figure 4.4, type 1 is the most desirable and type 2 is similar to aged binder which also shows good performance. The other remaining binders belonged to type 3 and shows the worst performance.

The effect of SBS modification on the performance analysis of R-value and w_c are shown in Figure 4.9 (b). The SBS modified 6%R2, 3% and 6%R1 rejuvenation exhibited higher w_c value compared to others and were grouped as type 2. Consequently, the 9%R1+SBS rejuvenation is in type 1 and the remaining samples are in type 3 combination. Similar characteristics were also found like G-R parameter analysis and the type 1 combination contributed to the better cracking performance of binder compare to type 2.

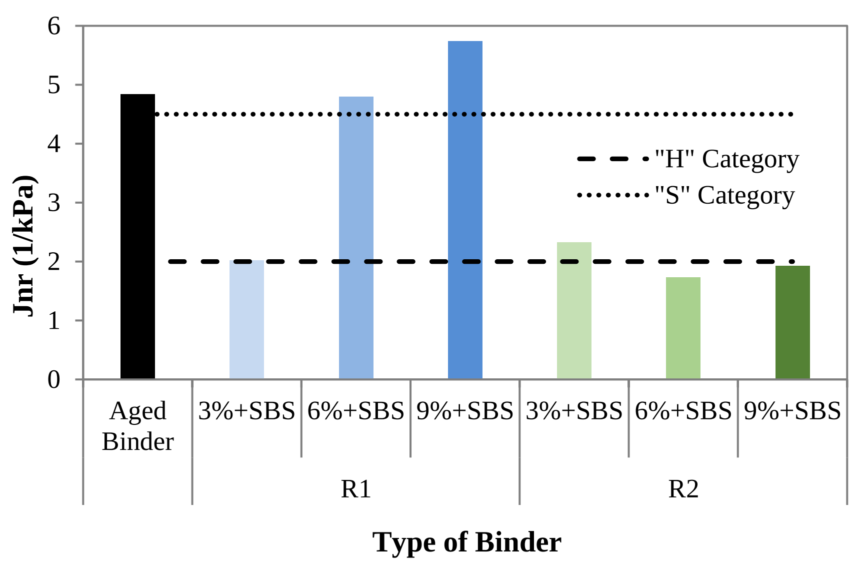
4.4.6 Multi Stress Creep Recovery Test (MSCR)

The MSCR test is well established creep-recovery concept to evaluate the binder's permanent deformation behavior (Singh & Kataware, 2016; Yang & You, 2015). As per the guideline from AASTHO M322, the non-recoverable creep compliance J_{nr} is calculated to evaluate the deformation. A higher value of J_{nr} indicates a higher deformation in binder, which can lead to higher rutting susceptibility. The MSCR test parameter determines the non-recoverable creep compliance (J_{nr}). Based on the result of J_{nr} at 3.2 kPa^{-1}, a binder can be selected for the different traffic categories, with 'S' having the lowest traffic and 'E' having the highest traffic according to the specification AASTHO M 332. Some studies found that there is a good correlation between J_{nr} and $G^*/sin\delta$ as both are for rutting parameters (Singh & Kataware, 2016). Whereas, other studies did not find any correlation between these properties which is why MSCR was developed to improve the evaluation of rutting resistance (Aurilio et al., 2017). For this study, the MSCR test was conducted with the DSR equipment and the sample, which was used for the frequency sweep test, was also tested here. Based on the binder used in this study (PG 58-28), the test temperature was selected at 58ºC for this analysis. Figure 4.10(a) shows the J_{nr} values at 3.2 kPa for different rejuvenated binders.

The J_{nr} value of aged binder was found to be 4.8 kPa^{-1}. With the addition of different dosing of rejuvenators, J_{nr} value also changed dramatically. For the R1 rejuvenated binder, J_{nr} value doubled with each increasing concentration, which indicates poor rut resistance. For the 9%R1, it reached 30 kPa^{-1}, which is considerably higher. Similarly, a higher J_{nr} value of R3 rejuvenation is found to be 5.08, 8.4, and 12.5 kPa^{-1} for 3%, 6%, and 9% respectively. Whereas for R2, J_{nr} value also started to increase but suddenly decreased for the 9%R2 and all the concentrations of R2 exhibit lower J_{nr}value compared to R1 and R3. The lower J_{nr} value was recorded for 3% addition and this result shows consistency with the previous analysis of the Superpave rutting parameters with the Shenoy parameters shown in Figure 4.7. Thus, it can be concluded that only R2 rejuvenator shows slightly better performance compared to others. Based on the data observed, it is clear that most of the binders fail to achieve the criteria for standard traffic loading “S” condition having J_{nr} of maximum 4.5 kPa^{-1}. Only the 3%R2 binder was suitable for “S” category traffic loading.



(a)



(b)

Figure 4.10 Jnr Comparison at 3.2 kPa of (a) R1, R2, and R3; (b) SBS Modified Binder

4.4.6.1 Effect of SBS on $\boldsymbol{J_{nr}}$

For the modification of R1 and R2 rejuvenated asphalt with SBS, it was expected that there would be a reduction of the J_{nr} value considering past analysis (Figure 4.10(b)). This is because the SBS shows excellent rutting performance, so J_{nr} value should decrease. For R1 rejuvenation, 3%+SBS shows very good rut resistance ("H" Category), whereas 6% and 9% gives a higher J_{nr} value and fails to achieve "S" grade criteria. For the R2 rejuvenator, the result shows expected excellent performance after the analysis from unmodified R2 rejuvenation. With the addition of R2 dosage, a sudden decrease was shown for 6%R2. For 9%, there was a slight increase in J_{nr} value which is also consistent with the rutting parameters. Still, all the concentrations of R2 achieve better rutting resistance. For 3%, 6%, and 9% SBS modified binder, ranking can be categorized in "S", "H", and "H" respectively. The higher rutting resistance was observed for 6%R2+SBS binder, similar to Superpave rutting and Shenoy parameter.

4.5 Summary

To reduce the dependency on neat asphalt and to make the sustainable pavement, asphalt binder from RAP has been considered as an economical pavement construction material. Rejuvenators are commonly used to enhance the rheological performance of RAP to prolong its service life. This research aimed to understand the effect of different types of rejuvenation with the laboratory simulated aged binder. Also, the performance of polymer modification on the rejuvenated asphalt binder has been accessed through the rheological tests. From this experimental study, the following conclusions can be drawn:

- Free fatty acid (FFA) was observed in R1 rejuvenator by GC-MS analysis. This acid enhances hydrophilic characteristics of asphalt binder. The existence of FFA was assumed to be harmful to moisture susceptibility. However, this assumption did not agree after the experimental result and UT rejuvenated binder shows better moisture susceptibility in chapter 5.
- Rejuvenation of the aged binder reduced the stiffness of the binder except for the modified rejuvenator R2. As the percentage of the R1 and R3 rejuvenators increased, the stiffness values consistently decreased. In general, aged binders have higher asphaltene + resin contents and lower saturates contents that make the binder stiffer. When a rejuvenator has been mixed with aged binder, a change of their molecular composition occurred which alters the asphaltene-maltene ratio of the binder. This consequence results in having lower viscosity and a softening point of the rejuvenated asphalt binder. Furthermore, if the dosing of rejuvenation increases, the binder becomes softer due to the fluidity effect of rejuvenators. The highest stiffness was observed for the R2 rejuvenator due to the chemical modification from R1 rejuvenator. The chemical modification by the transesterification process reduces the FFA contents and makes the binder stiffer. However, R1 rejuvenated binders exhibited the lowest stiffness among the alternatives, which was also observed from FTIR analysis as mentioned in chapter 3. Overall, the stiffness of the rejuvenated binder can be ranked as R2> R3> R1.
- The addition of SBS increased the stiffness of both the R1 and R2 rejuvenated binders. No data is available on the SBS plus R3 modified binder. SBS polymer is

a combination of polystyrene and polybutadiene materials. When this polystyrene and polybutadiene chains combines with each other, that makes SBS durable and stiff material. This bonding mechanism might eliminate some of the potential drawbacks of using rejuvenators with the addition of SBS.

- For the phase angle, the master curve increased for all concentrations of R2 and R3 rejuvenators, whereas it decreased for both 6% and 9%R1 rejuvenators. The lower phase angle attributed to the improved elastic properties of the binder, which might be due to the less stiffness behavior of the binders. SBS modification also increased the phase angle for both R1 and R2 rejuvenated binders. The higher phase angle was recorded for R2 rejuvenation. The higher phase angle of R2 rejuvenated binder shows more viscous nature of the binder, which was expected due to its higher stiffness as mentioned in the previous statement.
- The G-R parameter was calculated for evaluating the fatigue cracking susceptibility. For all percentages of R1, R2 and R3 rejuvenation, higher fatigue cracking resistance were observed. This is due to the softening behavior of rejuvenated binders that addresses the fatigue cracking resistance of the aged binder. A similar result was observed for SBS modification. SBS modified R1 rejuvenated binders showed good cracking resistance compare to R2. The existence of polybutadiene components of SBS fully swells with the lighter components of asphalt to form a network structure which improves the binder flexibility and cracking resistance of SBS modified binders.

- For rutting susceptibility, the Superpave rutting parameter was determined. With increasing percentages of rejuvenation, rutting resistance decreased. All the percentages of R2 passed the rutting criteria. The worst rutting resistance was noticed for the 9%R1 binder. In the case of SBS modification, with the exception of the 6%R1+SBS and 9%R1+SBS, all other binders passed the rutting criteria. Among the binders, the highest rut resistance was observed for the 9%R2+SBS. This might be due to the better compatibility of SBS with the R2 rejuvenated binders.
- In addition to the Superpave rutting parameter, the Shenoy parameter was also determined. In this case, only the 3%R3 passes the Shenoy criteria followed by others in Superpave rutting criteria and the higher rut resistance remained the same for R2 rejuvenated binders. Modification with SBS increased the resistance of all the binders and passed the rutting criteria, except the 9%R1+SBS binder. It is to note that, the complex bonding mechanism of polystyrene and polybutadiene makes the SBS modified binder a durable and more restrained from external pressure or load. These consequences help to improve the stiffness and the rutting resistance of SBS modified binders.
- The Rheological index and crossover frequency showed similar characteristics with the G-R parameter. 6%R1 and 9%R1 showed the most desirable characteristics. This result is consistent with the G-R parameter due to the softening behavior of the binder. Whereas for the SBS modification, 9%R1 exhibited better resistance to cracking. After SBS modification, R1 rejuvenated binder shows better flexibility

due to its swelling effect and that results in higher cracking resistance similar to G-R parameter.

- From the MSCR analysis, the R2 rejuvenator showed good performance compared to others sue to its higher stiffness. The binder with 3%R2 can be grouped in the 'S' category of traffic loading, whereas other binders fail to achieve any place in traffic loading criteria.
- Modification of SBS improved the performance of binders and decrease the J_{nr} value. Both 3%R1+SBS and 3%R2+SBS showed similar performance and can be grouped in the 'S' category. Whereas 6%R2+SBS and 9%R2+SBS showed excellent performance to be placed in the 'H' category of traffic loading. In general, SBS is a thermoplastic elastomer polymer, which behaves like elastomeric rubbers to improve the elastic behavior of the binders. This characteristics of SBS helps to reduce the permanent deformation of the binder.

Based on the results analyzed above, it can be concluded that R1 rejuvenator is very promising for improving the cracking resistance, whereas the opposite behavior was observed for rutting resistance. Using R1 rejuvenator alone for rejuvenation might not be beneficial for pavement performance, whereas SBS modification with R1 might be an alternative to improve the rutting resistance of the binder. Also, the usage of R2 (modified R1) could be a better solution in terms of improving the rutting and cracking resistance of binder. Certainly, further investigation is required at the mixture level to predict the behavior of rejuvenators and the performances in the field.

4.6 References

Aflaki, S., Hajikarimi, P., Fini, E. H., & Zada, B. (2014). Comparing Effects of Biobinder with Other Asphalt Modifiers on Low-Temperature Characteristics of Asphalt. *Journal of Materials in Civil Engineering*, *26*(3), 429–439. https://doi.org/10.1061/(ASCE)MT.1943-5533.0000835

Ahmed, R. B., & Hossain, K. (2019). Waste cooking oil as an asphalt rejuvenator : A state-of-the-art review. *Construction and Building Materials*, *230*, 116985. https://doi.org/10.1016/j.conbuildmat.2019.116985

Al-Omari, A. A., Khedaywi, T. S., & Khasawneh, M. A. (2018). Laboratory characterization of asphalt binders modified with waste vegetable oil using SuperPave specifications. *International Journal of Pavement Research and Technology*, *11*(1), 68–76. https://doi.org/10.1016/j.ijprt.2017.09.004

Al-Qadi, I. L., Elseifi, M., & Carpenter, S. H. (2007). *Reclaimed asphalt pavement - A literature review* (Issue FHWA-ICT-07-001). https://doi.org/http://hdl.handle.net/2142/46007

Anderson, R. M., King, G. N., Hanson, D. I., & Blankenship, P. B. (2011). Evaluation of the Relationship between Asphalt Binder Properties and Non-Load Related Cracking. *Journal of the Association of Asphalt Paving Technologists*, *80*, 615–664. https://trid.trb.org/view/1135500

Asli, H., Ahmadinia, E., Zargar, M., & Karim, M. R. (2012). Investigation on physical properties of waste cooking oil - Rejuvenated bitumen binder. *Construction and*

Building Materials, *37*, 398–405. https://doi.org/10.1016/j.conbuildmat.2012.07.042

ASTM. (2018). *Standard Test Method for Effects of Heat and Air on Asphaltic Materials (Thin-Film Oven Test)* (Vol. 09, Issue Reapproved 2014). https://doi.org/10.1520/D1754

Aurilio, M., Mikhailenko, P., & Baaj, H. (2017). Predicting HMA Fatigue Using the Double Edge Notched Tension Test and Multiple Stress Creep Recovery Test. *Proceedings of the Sixth-Second Annual Conference of the Canadian Technical Asphalt Association (CTAA)*, 267–290.

Azahar, W. N. A. W., Jaya, R. P., Hainin, M. R., Bujang, M., & Ngadi, N. (2016). Chemical modification of waste cooking oil to improve the physical and rheological properties of asphalt binder. *Construction and Building Materials*, *126*, 218–226. https://doi.org/10.1016/j.conbuildmat.2016.09.032

Branthaver, J., Petersen, J., Robertson, R., Duvall, J., Kim, S., Harnsberger, P., Mill, T., Ensley, E., Barbour, F., & Schabron, J. (1993). Binder characterization and evaluation. Volume2: Chemistry. In *Strategic Highway Research Program* (Vol. 2, Issue SHRP-A-368). http://trid.trb.org/view.aspx?id=386723

Brown, E. R. (1988). Preventive Maintenance of Asphalt Concrete Pavements. *Transportation Research Record: Journal of the Transportation Research Board*, 6–11.

Chen, M., Xiao, F., Putman, B., Leng, B., & Wu, S. (2014). High temperature properties of rejuvenating recovered binder with rejuvenator, waste cooking and cotton seed oils. *Construction and Building Materials*, *59*, 10–16. https://doi.org/10.1016/j.conbuildmat.2014.02.032

Christensen, D. W., & Anderson, D. A. (1992). Interpretation of Dynamic Mechanical Test Data for Paving Grade Asphalt Cements. *Journal of the Association of Asphalt Paving Technologists*, *61*, 67–116.

Christensen, D. W., Anderson, D. A., Rowe, G. M., Christensen, D. W., Anderson, D. A., & Rowe, G. M. (2017). Relaxation spectra of asphalt binders and the Christensen – Anderson rheological model. *Road Materials and Pavement Design*, *18*(1), 382–403. https://doi.org/10.1080/14680629.2016.1267448

Dong, F., Zhao, W., Zhang, Y., Wei, J., Fan, W., Yu, Y., & Wang, Z. (2014). Influence of SBS and asphalt on SBS dispersion and the performance of modified asphalt. *Construction and Building Materials*, *62*, 1–7. https://doi.org/10.1016/j.conbuildmat.2014.03.018

Fini, E. H., Kalberer, E. W., Shahbazi, A., Basti, M., You, Z., Ozer, H., & Aurangzeb, Q. (2011). Chemical Characterization of Biobinder from Swine Manure: Sustainable Modifier for Asphalt Binder. *Journal of Materials in Civil Engineering*, *23*(11), 1506–1513. https://doi.org/10.1061/(ASCE)MT.1943-5533.0000237

García, Á., Schlangen, E., & Van De Ven, M. (2011). Properties of capsules containing rejuvenators for their use in asphalt concrete. *Fuel*, *90*(2), 583–591. https://doi.org/10.1016/j.fuel.2010.09.033

García, Á., Schlangen, E., Ven, M. Van De, & Sierra-beltrán, G. (2010). Preparation of capsules containing rejuvenators for their use in asphalt concrete. *Journal of Hazardous Materials, 184*(1–3), 603–611. https://doi.org/10.1016/j.jhazmat.2010.08.078

Gong, M., Yang, J., Zhang, J., Zhu, H., & Tong, T. (2016). Physical-chemical properties of aged asphalt rejuvenated by bio-oil derived from biodiesel residue. *Construction and Building Materials*, *105*(15), 35–45. https://doi.org/10.1016/j.conbuildmat.2015.12.025

Gong, M., Zhu, H., Pauli, T., Yang, J., Wei, J., & Yao, Z. (2017). Evaluation of bio-binder modified asphalt ' s adhesion behavior using sessile drop device and atomic force microscopy. *Construction and Building Materials*, *145*, 42–51. https://doi.org/10.1016/j.conbuildmat.2017.03.114

Kandhal, P. S., & Mallick, R. B. (1997). Pavement Recycling Guidelines for State and Local Governments: Participant's Reference Book. *Fhwa-Sa-98-042*, *December*, 301. https://www.fhwa.dot.gov/pavement/recycling/98042/

Kim, S., Sholar, G., Byron, T., & Kim, J. (2009). Performance of polymer-modified asphalt mixture with reclaimed asphalt pavement. *Transportation Research Record: Journal of the Transportation Research Board*, *2126*(1), 109–114.

Kluttz, R. Q. (2019). Prepared Discussion on Relationships between Mixture Fatigue Performance and Asphalt Binder Properties. *Association of Asphalt Paving Technology*, 1–4.

Leung, D. Y. C., & Guo, Y. (2006). Transesterification of neat and used frying oil :

Optimization for biodiesel production. *Fuel Processing Technology*, *87*(10), 883–890. https://doi.org/https://doi.org/10.1016/j.fuproc.2006.06.003

Mensching, D., Jacques, C., & Daniel, J. (2016). Applying the Glover-Rowe Parameter to Evaluate Low-Temperature Performance of Hot Mix Asphalt LTPP Sections. *Journal of Materials in Civil Engineering*, *28*(10). https://doi.org/10.1061/(ASCE)MT.1943-5533.0001606

Mogawer, W. S., Booshehrian, A., Vahidi, S., & Austerman, A. J. (2013). Evaluating the Effect of Rejuvenators on the Degree of Blending and Performance of High RAP , RAS , RAP / RAS Mixtures. *Road Materials and Pavement Design*, *14*(2), 193–213. https://doi.org/10.1080/14680629.2013.812836

Pournoman, S., Hajj, E. Y., Morian, N., & Martin, A. E. (2018). Impact of recycled materials and recycling agents on asphalt binder oxidative aging predictions. *Transportation Research Record*, *2672*(28), 277–289. https://doi.org/10.1177/0361198118797205

Romera, R., Santamaría, A., Peña, J. J., Muñoz, M. E., Barral, M., García, E., & Jañez, V. (2006). Rheological aspects of the rejuvenation of aged bitumen. *Journal of Rheologica Acta*, *45*(4), 474–478. https://doi.org/https://doi.org/10.1007/s00397-005-0078-7

Rowe, G. M. (2014). Interrelationships in Rheology for Asphalt Binder Specifications. *Canadian Technical Asphalt Association (CTAA)*, 457–483.

Rowe, G. M., & Sharrock, M. J. (2011). Alternate shift factor for describing the viscoelastic behaviour of asphalt materials. *Transportation Research Record: Journal of the Transportation Research Board*, *2207*(1), 125–135. https://doi.org/https://doi.org/10.3141/2207-16

Shenoy, A. (2001). Refinement of the Superpave Specification Parameter for Performance Grading Of Asphalt. *Journal of Transportation Engineering*, *127*(5), 357–362. https://doi.org/https://doi.org/10.1061/(ASCE)0733-947X(2001)127:5(357)

Shenoy, A. (2004). High Temperature Performance Grading of Asphalts through a Specification Criterion that Could Capture Field Performance. *Journal of Transportation Engineering*, *130*(1), 132–138. https://doi.org/https://doi.org/10.1061/(ASCE)0733-947X(2004)130:1(132)

Singh, D., & Girimath, S. (2016). Investigation of rheological properties and Superpave PG of PMB mixed with reclaimed asphalt pavement binders. *Construction and Building Materials*, *126*, 834–842. https://doi.org/10.1016/j.conbuildmat.2016.09.084

Singh, D., & Kataware, A. V. (2016). Comparison of different rheological parameters for rutting susceptibility of SBS + WMA modified binders. *Journal of Innovative Infrastructure Solutions*, *1*(1), 1–10. https://doi.org/https://doi.org/10.1007/s41062-016-0026-7

Su, J. F., Qiu, J., Schlangen, E., & Wang, Y. Y. (2015). Investigation the possibility of a new approach of using microcapsules containing waste cooking oil: In situ rejuvenation for aged bitumen. *Construction and Building Materials*, *74*, 83–92. https://doi.org/10.1016/j.conbuildmat.2014.10.018

Wasiuddin, N., Ashani, S. S., & Islam, M. R. (2014). *Evaluation of Dynamic Shear Rheometer Tests for Emulsions*. *2*.

Xu, J., Huang, S., & Qin, Y. (2014). Asphalt Pavement Recycling in Mainland China. *Application of Reclaimed Asphalt Pavement and Recycled Asphalt Shingles in Hot-Mix Asphalt: National and International Perspectives on Current Practice*, 51–59.

Yang, X., & You, Z. (2015). High temperature performance evaluation of bio-oil modified asphalt binders using the DSR and MSCR tests. *Construction and Building Materials*, *76*, 380–387. https://doi.org/10.1016/j.conbuildmat.2014.11.063

Yang, Z., Zhang, X., Yu, J., & Xu, W. (2019). Effects of Aging on the Multiscale Properties of SBS-Modified Asphalt. *Arabian Journal of Science and Engineering*, *44*(5), 4349–4358. https://doi.org/https://doi.org/10.1007/s13369-018-3399-4

Yu, X., Zaumanis, M., & Poulikakos, L. D. (2014). Rheological , microscopic , and chemical characterization of the rejuvenating effect on asphalt binders. *Fuel*, *135*, 162–171. https://doi.org/10.1016/j.fuel.2014.06.038

Zaumanis, M., Mallick, R. B., & Frank, R. (2015). Evaluation of different recycling agents for restoring aged asphalt binder and performance of 100 % recycled asphalt. *Journal of Materials and Structures*, *48*(8), 2475–2488. https://doi.org/https://doi.org/10.1617/s11527-014-0332-5

Chapter 5 Evaluation of Fundamental Behavior of Rejuvenated Asphalt Binders Using Surface Free Energy Method

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5.1 Abstract

Surface free energy (SFE) measurement is widely used to understand the moisture damage resistance of asphalt binder. This study investigates the effect of different rejuvenators on the cohesive bond energy of rejuvenated asphalt binders using SFE measurements. Three different types of rejuvenators, including waste cooking oil (UT), chemically modified/treated waste cooking oil (TR), and a commercially available rejuvenator Hydrolene H90T (HL) were used for this experimental study. The thin film oven test (TFOT) aged PG 58-28 binder was mixed with UT, TR, and HL rejuvenator at concentrations of 3%, 6%, and 9%, respectively, determined by the weight of the total binder. To compare the performance, styrene-butadiene-styrene (SBS) was also blended with rejuvenated binders and tested. An optical contact angle analyzer was used to obtain the contact angle of all rejuvenated binders. Later, SFE components and the cohesive bond energy was calculated as per Good-van-Oss-Chaudhury's postulation. The results showed that aging reduces the SFE components and rejuvenation improves the SFE components

significantly. Out of three SFE components, the Lifshitz Waals component contributed more compare to basic and acidic components of all binders, excluding TR+SBS modified binders. Also, rejuvenation improves the moisture damage resistance of binders significantly. After SBS modification, UT+SBS binders seem to improve the moisture resistance, whereas TR+SBS binders dropped the cohesive bond energy compared to unmodified rejuvenated binders. The results summarized in this study is expected to help quantify the moisture damage resistance of rejuvenated asphalt binders.

Keywords: Surface free energy (SFE), Reclaimed Asphalt Pavement (RAP), Rejuvenating Agent, Cohesive Bond Energy, Moisture Damage

5.2 Introduction

Reclaimed Asphalt Pavement (RAP) continues to be one of the key sustainable materials used for pavement construction. However, there is strong evidence that RAP binders are aged due to its long-term exposure to oxygen, moisture, UV radiation, and heat radiation (Al-Qadi et al., 2007). Aged RAP binder leads to increased binder stiffness and hampers the durability of the pavement. One of the critical factors that affect the durability of pavement is moisture damage (Grenfell et al., 2014). Moisture damage leads to premature pavement deterioration and reduces the bond strength of the asphalt aggregate matrix system. The underlying parameter that influences the moisture damage is the surface free energy (SFE) of the asphalt binder and aggregates. The SFE of asphalt binder and aggregate is used to measure the cohesion (asphalt-asphalt) and adhesion (asphalt-aggregate). A combination of these energy parameters is related to quantify the resistance against moisture-induced damage (Bhasin et al., 2007).

SFE is a promising technique for understanding cohesive and adhesive bonding of binders. Many studies have also reported the suitability of measuring SFE to correlate the adhesive and cohesive performance of binders and aggregates (Bhasin et al., 2007; Little & Bhasin, 2007; Lytton et al., 2005). Wasiuddin et al. studied on the RTFO and PAV aged binder produced from PG 64-22 and PG 70-28 binders (Wasiuddin et al., 2007). The study found a decrease in the Lewis acid component and an increase in Lewis base components with the extent of aging. Also, an increase in total SFE was also observed in this study. However, the opposite observation was also reported by Li et al. (Li et al., 2015). Ghabchi et al. (Ghabchi et al., 2014) studied the PG 64-22 and PG 76-28 binders blended with different proportions of RAP binder (0%, 10%, 25%, and 40%). The study observed an increase in SFE components and bond strength with an increase in RAP percentages. A similar study was also conducted by the collaboration of the University of Idaho and Texas A & M University with RTFO and PAV aged binder of PG 64-22 and PG 76-22. A decrease and a slight increase in total SFE was observed for PG 64-22 and PG 76-22 binder, respectively. Also, another study by Aguiar-Moya et al. (Aguiar-Moya et al., 2015) and the study reported an increase of adhesive bond strength for RTFO aged binder and a significant decrease after PAV aging.

In general, RAP binder is blended with rejuvenators to address different issues related to RAP materials. Rejuvenators are low viscous asphaltic materials that contain lighter oil fragments to reduce stiffness of the RAP binder (Ahmed & Hossain, 2019). Past studies have shown that rejuvenators are effective in improving the SFE and the cohesive bond strength of binders as well. Hossain et al. (Hossain et al., 2019) investigated the performance of two different types of rejuvenators to evaluate the moisture induce damage resistance of aged binders. The experimental study found an improved SFE and cohesive bond energy after rejuvenation. A similar improved observation was also obtained by Carrion et al. (Carrión et al., 2019) using bio-binder with RAP binder. However, a decrease of total SFE was recorded when Cecabase® chemical surfactant additive was mixed with TRFO and PAV aged PG-64 and PG-76 binder (Kakar et al., 2016). The fundamental compatibility among different binders and rejuvenators, as well as polymer modification, is still not clear. This study aims to characterize the binder based on their SFE and cohesive bond energy using different types of rejuvenators. The objectives of this study are as follows:

- To determine the effect on contact angles with different types of rejuvenated binders at varying dosing rates (3%, 6%, and 9%) using an optical contact angle analyzer.
- To determine the SFE components of different rejuvenated binders.
- To evaluate the binder's cohesive bond energy and to rank them based on their moisture-induced damage resistance.

5.3 Surface Free Energy Method

Surface free energy (SFE) of a material can be defined as the amount of the work required to create a new surface unit area of the materials in a vacuum. Several theories exist to explain the SFE of the solid or liquid. Out of those, Good-van-Oss-Chaudhury's (GVOC) (Oss et al., 1988) three-component theory is mostly used by researchers. These three components mainly comprise two polar components (a Lewis acid component and a Lewis base component) and a non-polar component, also known as the Lifshitz-van der Waals component. The total SFE of a material can be expressed as shown in equation (1)

$$\Gamma^{Total} = \Gamma^{LW} + 2\sqrt{\Gamma^{+}\Gamma^{-}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where,

Γ^{Total} = Total SFE of the materials,

Γ^{LW} = Lifshitz van der waals component,

Γ^{+} = Lewis acid component, and

Γ^{-} = Lewis base component

Based on the Young-Dupre's postulation and the Good's postulation, the work of adhesion or adhesive bond energy between a solid and a liquid can be expressed as follows in equation (2)

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

Where,

$\Gamma_L{}^{LW}, \Gamma_L{}^{+}, \Gamma_L{}^{-}$ = SFE component 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 (2), the SFE component of all probe liquids is known and the unknowns are three SFE components of solid. To evaluate three unknown components, three equations are required to solve this. The three equations are based on three probe liquids, whose SFE components are known and the contact angle between the individual liquid and solid materials needs to be measured.

In addition, 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 (3)

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

5.4 Material Collection and Experimental Matrix

5.4.1 Asphalt Binder

In this study, PG 58-28 binder was selected for base binder, which is generally used in the southern region of Newfoundland and Labrador. Later, a laboratory simulated aged binder was prepared using the standard TFOT aging procedure mentioned in ASTM D1754. For this aging, a neat asphalt undergoes a constant temperature of 163ºC for 5 hours in a convection oven.

5.4.2 Rejuvenators

Three types of rejuvenators were used for this study: Waste cooking oil, Modified waste cooking oil, and Hydrolene H90T denoted as UT, TR, and HL, respectively. Rejuvenator UT was collected from Eco oil limited and TR rejuvenator was modified from UT rejuvenator using the Transesterification method. HL is a commercially manufactured rejuvenator, which was supplied by HollyFrontier Corporation.

5.4.3 Preparation of Rejuvenated Asphalt Binder

The rejuvenated asphalt binder was prepared after mixing the aged binder with three types of rejuvenators. Rejuvenators were mixed at three selected percentages 3%, 6%, and 9% of the weight of the binder. All the rejuvenators were liquid and had low viscosity. The blending was conducted manually with a glass stirrer for 30 minutes at 100ºC to prepare a homogeneous mix. In addition to that, SBS was used with the UT and TR rejuvenators at 4% weight of the binder, provided by Yellowline Asphalt Products Ltd. A proprietary cross-linking agent was also used at 10% weight of the polymer to stabilize the SBS. For the blending, the UT and TR rejuvenated binders were preheated until they became fluid. Once the temperature reached 180ºC, then the SBS was mixed and stirred with a mechanical stirrer for 45 minutes. Later, the cross-linking agent was added and mixed for another 30 minutes to produce the modified sample.

5.4.4 Preparation of Test Specimens for Contact Angle Measurement

A smooth and dust-free surface is required to measure the contact angle of the liquid and solid. To obtain this type of surface, specially modified steel cans were used. The cans were 70 mm in diameter and 4 mm in height to prevent the overflow of asphalt binder as presented in Figure 5.1. To prepare the sample, asphalt binders were first heated at 100ºC for 2 hours so that they flowed similarly to a liquid, and the liquid asphalt was then poured into the cans. To reduce bias, all types of samples were poured from their respective sample containers. After pouring the asphalt into the cans, it was heated for another 30 mins at 100ºC to create a smooth, horizontal, and homogeneous surface. Later, the sample was allowed to cool down to room temperature and tested, after 36 hours of sample preparation, for all types of probe liquids.

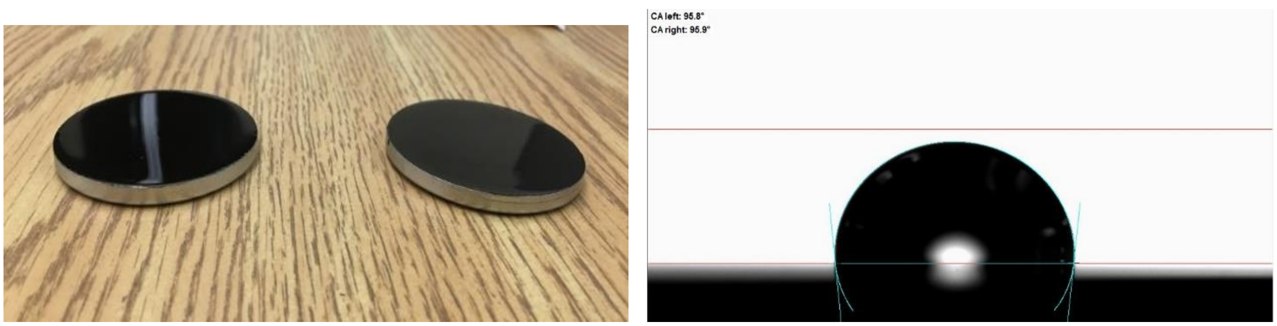

Figure 5.1 Prepared Specimen (left) and Measured Contact Angle of a Liquid Drop (right)

5.4.5 Contact Angle Measurement of Asphalt Binders

The sessile drop method was used to measure the contact angle, using an optical contact angle (OCA 15EC, DataPhysics Instruments, Germany) measurement device. To obtain the contact angle, this device is compatible with SCA 20 software, which can automatically detect the droplet shape and baseline, as shown in Figure 5.1. Also, this software can control the drop volume of liquids. A drop volume of 5µL was used for all the samples. For the syringe, a 1mL disposable syringe with an outer needle diameter of 0.9 mm was used.

To calculate the SFE of asphalt binder, this study used GVOC's three-component theory and it is required three probe liquids to three unknowns as mentioned in equation (2). However, the selection of three probe liquids is an important factor in measuring SFE. As mentioned by Bhasin (Bhasin et al., 2007), there are five probe liquids (distilled water, ethylene glycol, formamide, glycerol, and methyl iodide) used to obtain contact angles. Out of those, distilled water, formamide, and glycerol are the most used by researchers (Hossain et al., 2019; Wasiuddin et al., 2008) based on their condition number stated by Hefer (Hefer & Little, 2005). This study also used these three probe liquids to calculate SFE of asphalt binders based on their contact angles. The SFE components of the probe liquids are given in Table 5.1.

Table 5.1 Surface Free Energy Components of Probe Liquids (mJ/m^2) at 20ºC (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

5.5 Results and Discussion

5.5.1 Effect on Contact Angle (CA)

Table 5.2 shows the measured contact angles of all types of binders, including the base binder, TFOT aged, SBS modified, and unmodified rejuvenated binders. This table was prepared after 15 observations were taken for each sample and later tabulated to calculate the mean value, standard deviation (SD), and coefficient of variation (COV). Note that for the calculation of mean value, only the contact angle data having a difference of 1^o between CA(L) and CA(R) of the droplet shape have been considered.

Table 5.2 Contact Angle Summary of Different Binders

Materials	Distilled Water			Glycerol			Formamide		
	Mean	SD	COV %	Mean	SD	COV %	Mean	SD	COV %
PG 58-28	98.17	1.30	1.33	94.46	0.83	0.88	82.20	2.02	2.46
TFOT Aged	100.66	1.54	1.53	96.21	0.91	0.94	87.04	3.22	3.70
UT Rejuvenated Binder									
3% UT	98.47	1.04	1.05	95.90	0.89	0.93	81.96	2.50	3.05
6% UT	98.16	1.47	1.50	96.93	1.25	1.29	82.19	3.47	4.22
9% UT	97.47	1.20	1.23	114.20	1.54	1.34	82.43	4.62	5.60
TR Rejuvenated Binder									
3% TR	98.79	0.86	0.88	95.52	0.35	0.37	81.74	3.90	4.77
6% TR	98.39	0.83	0.85	95.28	0.67	0.71	80.90	1.16	1.43
9% TR	101.40	1.85	1.82	92.41	1.02	1.11	79.78	1.39	1.74
HL Rejuvenated Binder									

3% HL	98.34	0.87	0.88	95.71	0.88	0.92	83.55	4.00	4.79
6% HL	99.58	1.00	1.00	95.89	0.88	0.92	79.70	1.73	2.17
9% HL	98.77	0.76	0.77	97.05	0.60	0.62	81.64	3.51	4.30
SBS Modified UT Rejuvenated Binder									
3%UT+SBS	99.90	0.55	0.55	94.42	1.69	1.79	79.72	1.52	1.91
6%UT+SBS	99.63	1.40	1.41	94.96	0.64	0.67	79.75	1.42	1.77
9%UT+SBS	97.94	0.80	0.82	95.75	0.61	0.63	80.94	1.68	2.07
SBS Modified TR Rejuvenated Binder									
3%TR+SBS	99.37	0.84	0.85	93.41	0.73	0.78	83.27	1.97	2.36
6%TR+SBS	99.83	0.74	0.74	91.60	1.20	1.30	83.52	2.65	3.17
9%TR+SBS	100.10	1.25	1.25	90.33	0.92	1.02	81.16	1.61	1.99

Theoretically, when a binder ages, it becomes stiff, and the wettability of the binder decreases, which increases the contact angles of the aged binder. The result of this experimental study supports the same trend of increasing contact angles with all types of probe liquids.

5.5.1.1 Effect on Contact Angle (CA) of Rejuvenation

In general, when the contact angle of water is less than 90º, the solid is considered hydrophilic. This hydrophilic characteristic has a negative effect on moisture susceptibility and rheological performance. From Table 5.2, the UT rejuvenator had the lowest contact angle of water among the binders and the contact angle is continuously decreasing with the increase of UT dosage, which denotes the water affinity of UT rejuvenated binder. According to the chemical constituents of UT rejuvenator from GC-MS analysis as mentioned in chapter 3, UT rejuvenator contains free fatty acids (FFA) which have a strong affinity to water and hydrophilic. This statement is compatible with this experimental study. For the other contact angles with glycerol and formamide, increasing the dosing of UT increased the contact angles. The highest contact angle of 114.2º was recorded for 9% UT with glycerol, which might be due to the molecular force difference between glycerol and 9% UT.

For the TR rejuvenated binders, the contact angle with water did not follow any particular trend. However, for glycerol and formamide, it followed the trend of decreasing contact angles with the increase of TR dosage. In general, an increasing trend similar to UT was expected; however, the characteristics might change due to the modification of UT, which results in an increased stiffness, as mentioned in our rheological study (Ahmed et al., 2020). In the case of HL rejuvenated binder, the contact angle with glycerol increased, whereas others fluctuated widely with increasing HL dosage. This fluctuation might be a function of poor compatibility between this specific binder and this specific rejuvenator when using the blending process employed in this study.

5.5.1.2 Effect on CA of SBS modified Rejuvenated Binders

The SBS modified UT and TR rejuvenated binders followed exactly the same trend of increasing or decreasing contact angles with the change of liquid type. In the case of the UT+SBS modified binder, the contact angle increased slightly for all probe liquids compared to unmodified UT rejuvenators. Also, the contact angles were in between 80º-99º, and no unexpected increase of contact angles was observed with glycerin. SBS modification of TR rejuvenated binder also showed a slight difference in contact angles from unmodified TR rejuvenators. Contact angles increased slightly with water and formamide after SBS modification, whereas it decreased with glycerol.

Overall, there was not any particular trend of increasing or decreasing contact angles with the increase or decrease of rejuvenation dosage or SBS modification, 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 rejuvenated asphalt binders). This may also be a function of incompatibility among the various components of the blend, which included binder, rejuvenator, SBS polymer, and a cross-linking agent. Given that even different types of virgin and recycled asphalt materials can be less compatible with each other than others (Sreeram et al., 2019), the fundamental compatibility between a specific binder and different types of rejuvenators, along with polymer modification, is an important subject of future study which should not be ignored, but is beyond the scope of the present study.

5.5.2 Effect on SFE Components

The SFE components of asphalt binders play a significant role in quantifying the cohesion of the binder molecules and the ability to adhere between the binder and aggregate. Equation (1) is used to obtain the SFE components of asphalt binder, followed by the total SFE of the binder using equation (2). The SFE components of all the binders have been presented in Table 5.3.

Table 5.3 SFE Component Summary of Different Binders

Materials	Lifshitz-Waals Component (mJ/m^2)	Basic Component (mJ/m^2)	Acidic Component (mJ/m^2)
	Γ^{LW}	Γ^{-}	Γ^{+}
PG 58-28	38.22494517	3.24227893	1.778669653
TFOT Aged	25.19217536	3.240970164	0.320916612
UT Rejuvenated Binder			
3% UT	45.4542808	3.154694074	3.473811348
6% UT	49.092252	3.520128166	4.704495394
9% UT	155.3935446	6.251023348	60.14378751
TR Rejuvenated Binder			
3% TR	44.69008262	2.875673365	3.135306861
6% TR	47.69780296	2.870889014	3.699002145
9% TR	39.62936401	1.063212438	1.141410205
HL Rejuvenated Binder			
3% HL	37.45064734	3.648366917	1.975129097
6% HL	56.38474505	2.039725043	5.580665262
9% HL	52.24567508	3.019307833	5.345460947
SBS Modified UT Rejuvenated Binder			
3%UT+SBS	49.11072468	1.774902452	3.397877105
6%UT+SBS	51.54447789	1.948952748	4.127764424
9%UT+SBS	49.75933251	3.187708213	4.388936219
SBS Modified TR Rejuvenated Binder			
3%TR+SBS	29.57214797	2.727336476	0.415195387
6%TR+SBS	22.45395708	2.3703382	0.003181996
9%TR+SBS	26.40686109	1.6480908	0.008236255

5.5.2.1 Effect on SFE Components of Rejuvenated Binders

Table 5.3 represents the SFE components of all types of binders. For the PG 58-28 and TFOT aged binder, a decreasing trend of all SFE components was observed for TFOT aged binders. Comparatively, the Lifshitz-Waals component occupied the higher portion, followed by the base and acidic components. Similar observations of decreasing SFE components were also observed in other studies (Hossain et al., 2019; Kassem et al., 2018).

With the addition of rejuvenators, the Lifshitz-Waals components increased and regained the lost portion caused by TFOT aging. Notably, in most cases it crossed beyond the Lifshitz-Waals portion of PG 58-28 binder, indicating a better property than the original binder. The highest Lifshitz-Waals portion was found to be 155.5 mJ/m^2 for the 9% UT binder. This highest value was expected due to its high variability of contact angles with different liquids. However, it was not necessarily expected to be so much higher than other binders. Also, the other two polar components increased with the increase of UT dosage, which resulted in the highest SFE of the binder, as shown in Fig. 7. In the case of the TR rejuvenated binders, the Lifshitz-Waals portion increased up to 6%TR rejuvenation, whereas suddenly it decreased for 9%TR. A similar fluctuating trend was also observed for acidic components and an increasing trend of the basic component for the TR rejuvenated binders was observed with increased dosing. As a result, a lower SFE was recorded for the TR rejuvenated binder compared to UT. HL rejuvenated binder also followed a similar pattern and showed a higher portion of all SFE components compared to the TR rejuvenated binders, as shown in Figure 5.2.

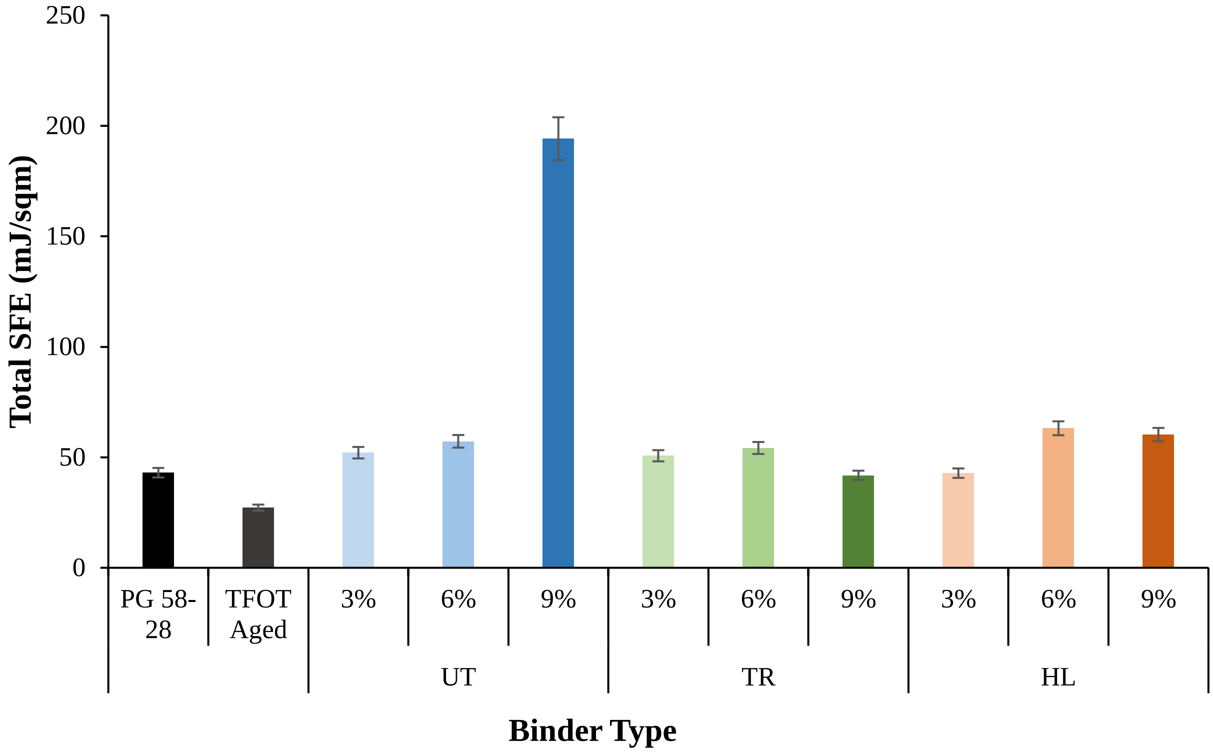

Figure 5.2 Total SFE of Different Binders

In summary, the non-polar component (Lifshitz-Waals) was higher for all binders except for the TFOT aged binder. After rejuvenation, the non-polar component increased gradually and regained the lost components of the PG 58-28 binder, in many cases making them more effective than the original binder properties. This indicates that rejuvenation can be effective in improving the SFE components of aged asphalt binder, but that the improved performance is not explicitly dependent on the initial binder properties, meaning that a binder can be "rejuvenated" to perform differently and better than the unaged binder with regard to moisture damage resistance. For the polar components (basic and acidic), a higher basic component was observed for both PG 58-28 and TFOT binder. After rejuvenation with UT, TR, and HL, this finding changed, and acidic component was the highest after the Lifshitz-Waals component. Out of the three rejuvenated binders, UT exhibited the highest acidic portion, followed by HL and TR. This might be due to the existence of FFA in the UT rejuvenator, as observed in the GC-MS analysis in chapter 3. However, acidic components were lowest for the TR rejuvenated binder, and this might be due to the reduction of FFA by the transesterification of UT rejuvenator.

5.5.2.2 Effect on SFE Components of SBS Modified Rejuvenated Binders

Table 5.3 summarizes the SFE components of SBS modified binders and their respective total SFE has been presented in Figure 5.3. After modification of UT rejuvenated binder with SBS, there was a slight increase of Lifshitz-Waals components up to 6%UT+SBS and then a reduction for 9%UT+SBS. The difference in the Lifshitz-Waals components before and after modification with SBS was large. For the other two polar components, both increased with the increase of UT dosage, whereas the polar component values dropped after SBS modification. As a result, the total SFE value remained the same except for 9%UT+SBS, which showed a dramatic decrease, indicating that perhaps the 9% UT measurements without SBS was off for some reason. For SBS modified TR rejuvenated binders, all of the SFE components dropped significantly, and in some cases, the SFE components were lower than for TFOT aged binders without SBS. This happened especially for basic and acidic portions of the TR+SBS modified binders, resulting in a drastic decrease in the total SFE, and the value dropped to about 50% of unmodified TR rejuvenated binders.

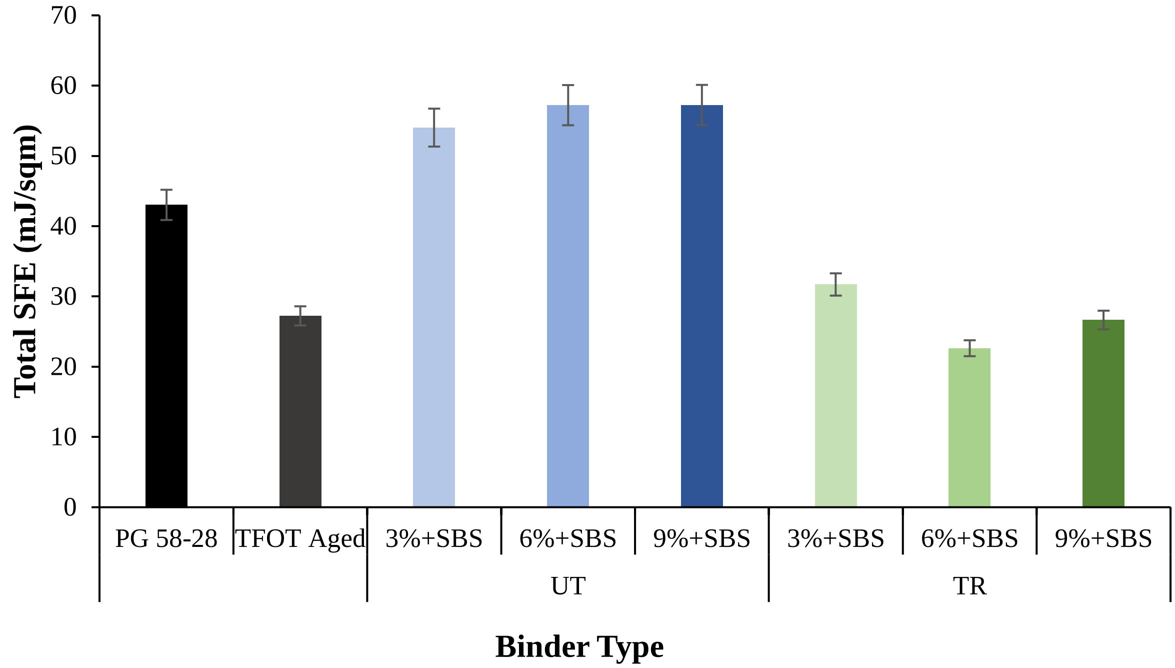

Figure 5.3 Total SFE of Different SBS Modified Binders

In general, the SBS is useful to improve the binder's elastic properties (Ahmed et al., 2020) and also to increase the Lifshitz-Waals components. Therefore, there should be an increase in total SFE as observed in some other studies (Ghabchi et al., 2014; Kakar et al., 2016). This study observed the increase of total SFE after UT+SBS modification. However, it dropped dramatically for TR+SBS modified binders. It is possible that the SBS has poor compatibility with TR rejuvenated binder, which is likely a cause of decreased adhesion and poor bonding within binder aggregate mixtures.

5.5.3 Effect on Cohesive Bond Energies

The cohesive bond energy of a binder can be defined as the amount of energy required to initiate 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.

Equation (3) is used to calculate the cohesive bond energy of respective binders and is represented in Figure 5.4 and Figure 5.5.

5.5.3.1 Effect on Cohesive Bond Energies of Rejuvenated Binders

The cohesive bond energy of PG 58-28 binder was recorded 86.05 mJ/m^2, whereas after TFOT aging it reduced to 54.46 mJ/m^2 as expected. This is because aged binder loses some of its basic molecular constituents that reduced the cohesive energy, initiating an early crack in the pavement. When the TFOT aged binder was rejuvenated with UT, the cohesive bond energy increased significantly with the increase of UT dosage. The highest value recorded was 388.34 mJ/m^2 for 9%UT rejuvenated binder. For TR rejuvenated binder, bond energies jumped up to 108.4 mJ/m^2 for 6%TR and then suddenly dropped to 83.66 mJ/m^2 for 9%TR. Although the bond energies were higher than the TFOT binder, they were less comparable with UT rejuvenated binders. In the case of HL rejuvenated binders, higher cohesive bond energies were recorded compared to TR rejuvenated binders. From Figure 5.4 it is clear that rejuvenation improved the cohesive bond energies of aged binder and UT rejuvenator was the most effective. Based on the experimental results, the binder with higher cohesive bond energies can be ranked as 9%UT > 6%HL > 9%HL, although the 9% UT results again seemed to show more issues.

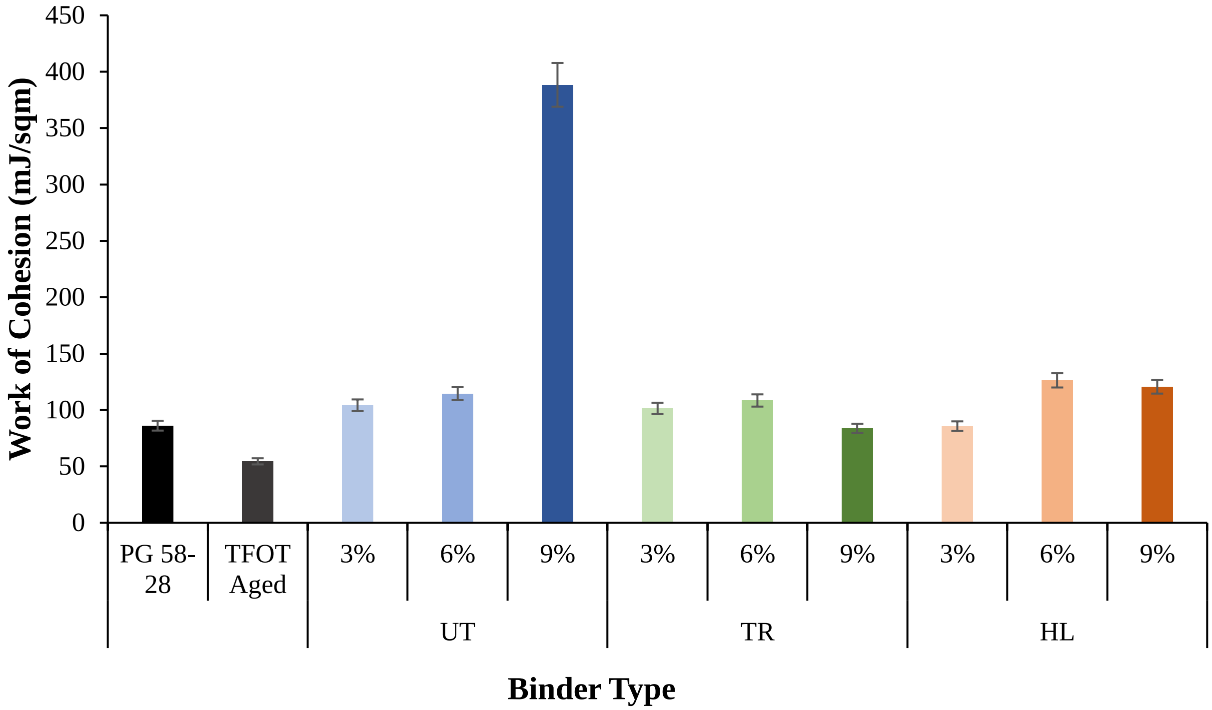

Figure 5.4 Cohesive Bond Energies of Different Binders

5.5.3.2 Effect on Cohesive Bond Energies of SBS Modified Rejuvenated Binders

Figure 5.5 shows the cohesive bond energies of the SBS modified rejuvenated binders. From the figure, all UT+SBS rejuvenated binders exhibited higher cohesive bond energy and seemed to be effective in improving the moisture damage resistance. Of all UT+SBS modified binders, the highest bond energy recorded was 114.48 mJ/m^2 for 9%UT+SBS. For TR+SBS modified binders, the bond energy decreased significantly, and in some cases, the bond energy was lower than both PG 58-28 and TFOT aged binder. The lowest bond energy recorded was 45.25 mJ/m^2 for 6%TR+SBS among all the binders. 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 unmodified binders, UT+SBS is effective in improving the damage resistance, which is consistent with previous studies showing SBS improves moisture damage resistance (Shirini & Imaninasab, 2016). However, using SBS in conjunction with TR may be less effective, considering they seem to be fundamentally incompatible, based on the reduction in cohesive bond energy when SBS is added to the TR rejuvenated binder. Note that it is generally desirable to use SBS since it improves the high-temperature properties of the binder.

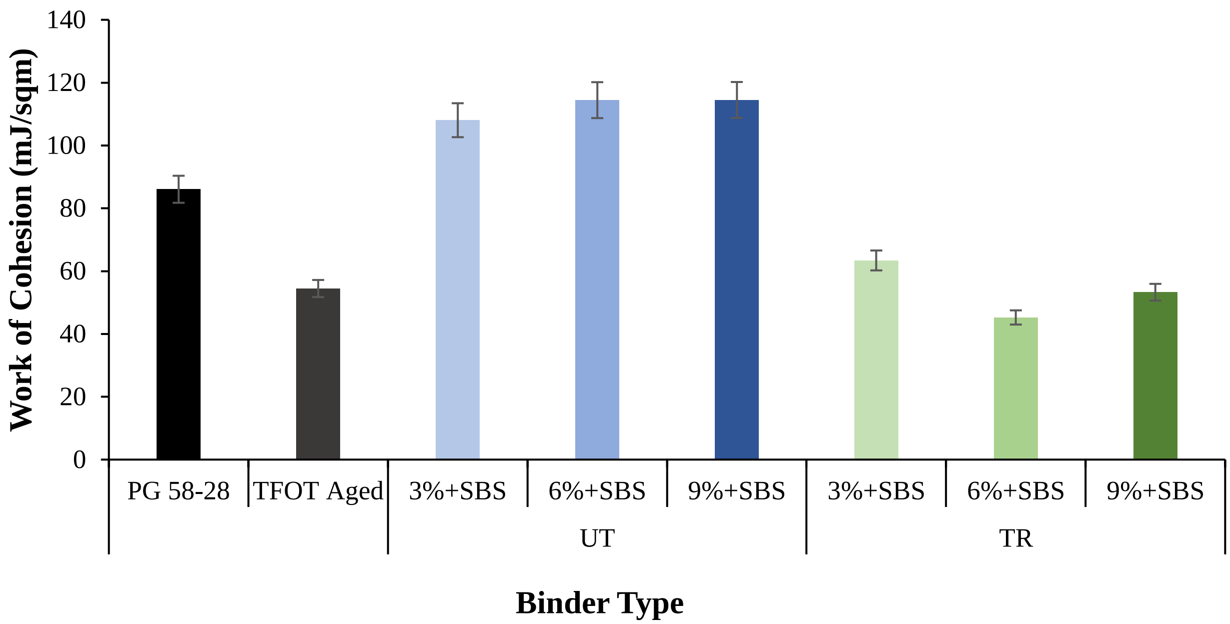

Figure 5.5 Cohesive Bond Energies of Different SBS Modified Binders

5.6 Summary

The present study aims to understand the effect of different types of rejuvenated binders in terms of their cohesive bond energy. To do so, a laboratory-simulated TFOT aged binder was rejuvenated with three types of rejuvenators including waste cooking oil (UT), modified waste cooking oil (TR), and Hydrolene H90T (HL) at the percentages of 3%, 6%, and 9% by the weight of the binder. In addition to that, SBS was used with UT and TR rejuvenated binders to understand the performance in terms of moisture damage resistance. The experimental study incorporates the measurement of contact angles with three different probe liquids to measure SFE components and to quantify the cohesive bond energy of respective binders. Based on the experimental evaluation, the following conclusion can be drawn.

- Free fatty acid (FFA) was observed in UT rejuvenator by GC-MS analysis. This acid enhances hydrophilic characteristics of asphalt binder. The existence of FFA was assumed to be harmful to moisture susceptibility. However, this assumption did not agree after the experimental result and UT rejuvenated binder shows better moisture susceptibility.
- Aging of binder increased the contact angle compared to the base PG 58-28 binder. However, the inclusion of rejuvenators improved the contact angles and is similar to or better than the base binder. This might be due to the rejuvenators changing the molecular properties and wettability of the base binder. A slightly higher contact angle was noticed with water and the highest contact angle was recorded with glycerol for 9% UT binder, which was unexpected. This variation of contact angles might be a result of the change in the molecular forces and the interactions between the probe liquid glycerol and solid surface.

- SBS modification slightly increased the contact angles with water. The contact angles with the other two probe liquids showed increasing and decreasing trends, when used with UT and TR rejuvenated binders, respectively. Modification with SBS makes the binder stiffer compared to the unmodified binder. Therefore, it changed the wettability of the binder which exhibited lower contact angles. As observed from the chapter 4, TR+SBS exhibited the highest stiffness and as a result, it changed the wettability of the binder and the contact angles reduced for these binders. For UT+SBS modified binders, contact angles increased slightly due to their softer nature. However, the fact that TR+SBS in some cases showed worse moisture resistance than the original binder may be an indicator that TR is not fundamentally compatible with SBS modification.

- The contribution of the Lifshitz-Waals component was much higher for all types of binders. Aging of the binder changed the molecular properties of the binder; as a result, the total SFE components of the binder also decreased. Within the polar components, basic components were more prevalent than acidic components. This finding was opposed to existing literature.

- Rejuvenation improved the Lifshitz-Waals component of the aged binder and altered the contribution of the polar components in the binder. This is an example of the fundamental mechanism of “rejuvenation” which occurs in the binder when using a rejuvenator. For rejuvenated binders, the acidic portion was more prevalent than basic components and 9% UT rejuvenated binder exhibited the highest total SFE among the binders.

- SBS modification with UT rejuvenated binder seemed to be effective in improving the total surface free energy (SFE), whereas lower SFE was recorded for TR+SBS modified binders; in some cases, the SFE was even lower than for the TFOT aged binder. In general, TR increased the binder stiffness and TR+SBS made the binder the stiffest among the binders, as is also mentioned in chapter 4. This results in higher contact angles and the total SFE of the binders could be an indicator of moisture resistance issues.

- Aging of binder decreased the cohesive bond energy of the base binder. Rejuvenation seemed 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. Binders with the highest cohesive bond energies were ranked as 9% UT > 6% HL > 9% HL. From chapter 4, it was noticed that 9% UT rejuvenated binder exhibited the highest fatigue cracking resistance among the binders, which was also consistent with the cohesive bond energies of the binder. The intermolecular forces between the UT rejuvenated binders and the rejuvenator's softening behavior might help to mitigate cohesive fracture within the binder and improve the cohesive bond energies. A similar relationship was also observed for 6% HL and 9% HL rejuvenated binders. However, it is notable that the UT rejuvenator did have a very high cohesive bond energy, which might be a function of the high amount of non-binder components changing the fundamental behavior of the material.

- UT+SBS modified binders improved the cohesive bond energies with increasing dosing rates of rejuvenator. However, TR+SBS modified binder showed the lowest cohesive bond energy and seemed to have poor moisture damage resistance. This is thought to be related to decreased fatigue cracking resistance, which was corroborated by the poorer cohesive bond energy and fatigue cracking resistance of TR+SBS in the chapter 4. It is postulated that there might be a fundamental incompatibility between this modified rejuvenator and the SBS polymer within the binder.

Future work in this area should consider the fundamental compatibility among different binders and rejuvenators, as well as polymer modification when used with rejuvenators. In addition, future researchers should focus on mortar and mixture-level testing to understand the true compatibility of the binder, rejuvenator, and different aggregates.

5.7 References

Aguiar-Moya, J. P., Salazar-Delgado, J., Baldi-Sevilla, A., Leiva-Villacorta, F., & Loria-Salazar, L. (2015). Effect of aging on adhesion properties of asphalt mixtures with the use of bitumen bond strength and surface energy measurement tests. *Transportation Research Record*, *2505*, 57–65. https://doi.org/10.3141/2505-08

Ahmed, R. B., & Hossain, K. (2019). Waste cooking oil as an asphalt rejuvenator : A state-of-the-art review. *Construction and Building Materials*, *230*, 116985. https://doi.org/10.1016/j.conbuildmat.2019.116985

Ahmed, R. B., Hossain, K., & Aurilio, M. (2020). Characterization of Asphalt Rheology

Using Waste Cooking Oil as a Rejuvenator. In *Construction and Building Materials*.

Al-Qadi, I. L., Elseifi, M., & Carpenter, S. H. (2007). *Reclaimed asphalt pavement - A literature review* (Issue FHWA-ICT-07-001). https://doi.org/http://hdl.handle.net/2142/46007

Bhasin, A., Howson, J., Masad, E., Little, D. N., & Lytton, R. L. (2007). Effect of modification processes on bond energy of asphalt binders. *Transportation Research Record*, *1998*, 29–37. https://doi.org/10.3141/1998-04

Bhasin, A., Little, D. N., Vasconcelos, K. L., & Masad, E. (2007). Surface free energy to identify moisture sensitivity of materials for asphalt mixes. *Transportation Research Record*, *2001*, 37–45. https://doi.org/10.3141/2001-05

Ghabchi, R., Singh, D., & Zaman, M. (2014). Evaluation of moisture susceptibility of asphalt mixes containing RAP and different types of aggregates and asphalt binders using the surface free energy method. *Construction and Building Materials*, *73*, 479–489. https://doi.org/10.1016/j.conbuildmat.2014.09.042

Grenfell, J., Ahmad, N., Liu, Y., Apeagyei, A., Large, D., & Airey, G. (2014). Assessing asphalt mixture moisture susceptibility through intrinsic adhesion, bitumen stripping and mechanical damage. *Road Materials and Pavement Design*, *15*(1), 131–152. https://doi.org/10.1080/14680629.2013.863162

Hefer, A., & Little, D. N. (2005). *Bitumen-Aggregate Systems and Quantification of the Effects of Water on the Adhesive Bond* (Issue December).

Hossain, K., Karakas, A., & Hossain, Z. (2019). Effects of Aging and Rejuvenation on

Surface-Free Energy Measurements and Adhesion of Asphalt Mixtures. *Journal of Materials in Civil Engineering*, *31*(7). https://doi.org/10.1061/(ASCE)MT.1943-5533.0002780

Jiménez del Barco Carrión, A., Carvajal-Muñoz, J. S., Lo Presti, D., & Airey, G. (2019). Intrinsic adhesive and cohesive assessment of the moisture sensitivity of bio-rejuvenated recycled asphalt binders. *Road Materials and Pavement Design*, *20*(sup1), S347–S364. https://doi.org/10.1080/14680629.2019.1588778

Kakar, M. R., Hamzah, M. O., Akhtar, M. N., & Woodward, D. (2016). Surface free energy and moisture susceptibility evaluation of asphalt binders modified with surfactant-based chemical additive. *Journal of Cleaner Production*, *112*, 2342–2353. https://doi.org/10.1016/j.jclepro.2015.10.101

Kassem, E., Garcia Cucalon, L., Masad, E., & Little, D. (2018). Effect of warm mix additives on the interfacial bonding characteristics of asphalt binders. *International Journal of Pavement Engineering*, *19*(12), 1111–1124. https://doi.org/10.1080/10298436.2016.1240563

Li, B., Yang, J., Li, X., Liu, X., Han, F., & Li, L. (2015). Effect of Short-Term Aging Process on the Moisture Susceptibility of Asphalt Mixtures and Binders Containing Sasobit Warm Mix Additive. *Advances in Materials Science and Engineering*, *2015*. https://doi.org/10.1155/2015/425827

Little, D. N., & Bhasin, A. (2007). Using Surface Energy Measurements to Select Materials for Asphalt Pavements. In *National Cooperative Highway Research*

Program (NCHRP) RRD 316. https://doi.org/10.17226/23182

Lytton, R. L., Masad, E., Zollinger, C., Bulut, R., & Little, D. (2005). Measurements of Surface Energy and Its Relationship to Moisture Damage. In *Fedaral Highway Administration (FHWA/TX-05/0-4524-2)* (Issue Project 0-4524).

Oss, C. J. Van, Chaudhury, M. K., & J., R. G. (1988). Interfacial Lifshitz-van der Waals and polar interactions in macroscopic systems. *Chemical Reviews*, *88*(6), 927–941. https://doi.org/https://doi.org/10.1021/cr00088a006

Shirini, B., & Imaninasab, R. (2016). Performance evaluation of rubberized and SBS modified porous asphalt mixtures. *Construction and Building Materials*, *107*, 165–171. https://doi.org/10.1016/j.conbuildmat.2016.01.006

Sreeram, A., Leng, Z., Hajj, R., & Bhasin, A. (2019). Characterization of compatibility between aged and unaged binders in bituminous mixtures through an extended HSP model of solubility. *Fuel*, *254*. https://doi.org/10.1016/j.fuel.2019.05.161

Wasiuddin, N., Fogle, C., Zaman, M., & O'Rear, E. (2007). Characterization of Thermal Degradation ofqa Liquid Amine Anti-Strip Additives in Asphaltqa Binders Due to RTFO and PAV-Aging. *Journal of Testing and Evaluation*, *35*(4), 387–394. https://doi.org/https://doi.org/10.1520/JTE100660

Wasiuddin, N. M., Zaman, M. M., & O'Rear, E. A. (2008). Effect of sasobit and Aspha-Min on wettability and adhesion between asphalt binders and aggregates. *Transportation Research Record*, *2051*, 80–89. https://doi.org/10.3141/2051-10

Chapter 6 Conclusions and Recommendations

6.1 Overview

Environmental sustainability has become a major issue throughout the world. The main goal of environmental sustainability is to reuse the used materials to reduce the production of new materials and the emission of greenhouse gas. Using asphalt binder from RAP material has been considered as an economical and sustainable approach for pavement construction. However, the RAP binder has some limitations regarding the fatigue cracking resistance of binders. This problem is more severe in cold regions like Canada. Using rejuvenators with RAP binder is a widely used approach to address the issues related to RAP binder. This research used three types of oil-based rejuvenators that includes waste cooking oil (UT/R1), modified waste cooking oil (TR/R2), and Hydrolene (HL/R3) with laboratory simulated aged binder to understand the performance of rejuvenated asphalt binder. Also, in some cases, the polymer was added with UT/R1 and TR/R2 rejuvenated binders to compare the performances. To understand the characteristics and the performance of these rejuvenators, three sets of characterization tests were conducted: chemical, morphological, and rheological. 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 3, 4, and 5. This chapter will only focus on general conclusions, limitations of this research, and the recommendations for future research.

6.2 Major Findings from Chemical and Morphological Analysis

- Free fatty acids (FFA) were observed in the UT/R1 rejuvenator by GC-MS analysis, which was assumed to increase the hydrophilic characteristics and moisture susceptibility of hot mix asphalt (HMA). FFA consists of carboxyl group (-COOH) end and this -COOH groups releases H^+ ions to contact with OH^- ions of water. Therefore, it is required to reduce the FFA contents from UT/R1 rejuvenator.

- FTIR test results exhibited a higher rate of C=O stretch at 1744 cm^{-1} for UT/R1, which is responsible for softening the binder. From the molecular structures of major FFA's obtained through GC-MS analysis of UT/R1 rejuvenator, it was noticed that all the molecules have (-COO-) ends, which might results in higher C=O stretch for the UT/R1 rejuvenated binders as well. The softening phenomenon of UT/R1 rejuvenated binder leads to poor rutting resistance which was also observed from rheological tests as described in Chapter 4. In contrast, C=O stretch was found very negligible for TR/R2 and HL/R3 rejuvenated binders and therefore shows better stiffness compared to UT/R1 rejuvenated binder. The reason for the lower C=O stretch in TR/R2 rejuvenator is due to the modification of the UT/R1 rejuvenator by the transesterification process. The transesterification process reduces the FFA contents of UT/R1 rejuvenator which forms a lower C=O stretch for TR/R2 rejuvenated binder. Also, HL/R3 is a commercially manufactured oil which might have lower FFA, because the generation of FFA mostly occurs during the hydrolysis process at high temperature and moisture contents. The presence of lower C=O stretch for TR/R2 and HL/R3 rejuvenated binders attributed to the higher stiffness of the binders. Also, a similar stiffness trend was found from the rheological characterization of binders as mentioned in chapter 4.

- From the AFM analysis, a decreasing number of bee structures was observed in aged binder with the increasing dosing rates of rejuvenation. The decreased number of bee structures generally indicates the softening behavior of binders. And the softening characteristics of a binder predominantly increase with the higher rejuvenation dosage. The reason is the use of lower viscous rejuvenator which alters the chemical composition and asphaltene-maltene ratio of the aged binder. Besides, the existence of FFA contents in the rejuvenator might accelerate the softening process. For the UT/R1 rejuvenated binders, a lower quantity of bee structures was noticed due to its softening characteristics as mentioned in the previous statement. Surprisingly, the lowest number of bee structures was observed for HL/R3 rejuvenated binders. However, this appears to contradict the rheological properties as mentioned in chapter 4. From the origin of bee structures, the extensive experimental study found that paraffin wax crystallization is responsible for the formation of bee structures in the binder. This bee structures formed due to the interaction of crystallising paraffin wax content and the remaining other contents in asphalt. As HL/R3 is a commercially manufactured rejuvenator, there might have less amount of wax contents in the chemical composition of the rejuvenator. This lower wax content might be responsible for the formation of lower number of bee structures in HL/R3 rejuvenated binder.

- The larger quantity of bee structures was found for TR/R2 rejuvenated sample. This larger quantity reflects the higher stiffness of the binder, which also supports the rheological test results mentioned in chapter 4. The higher binder stiffness is due to the transesterification of UT/R1 rejuvenator, which reduces the FFA contents.
- Based on the phase-contrast analysis, a significant change of morphological features was observed for the binders with higher concentrations (6%) of rejuvenation. This change of phase-contrast might be due to the use of higher rejuvenator dosing which changes the dissipation of energies between the AFM tip and the sample. Also, this change can be dependent on the viscoelasticity, adhesion, and the topographic features of the samples. For this experimental analysis, the binder surface was oily at higher rejuvenation dosing, which might also result in the variation of dissipation energy and topographic features of the binder.

6.3 Major Findings from Rheological Characterization

- Increasing dosage of rejuvenation with the aged binder reduced the stiffness of the binder except for the modified rejuvenator TR/R2. In general, aged binders have higher asphaltene + resin contents and lower saturates contents that make the binder stiffer. When a rejuvenator is mixed with an aged binder, a change of their molecular composition occurred, which alters the asphaltene-maltene ratio of the binder. This results in lower viscosity and softening point of the rejuvenated asphalt binder. Furthermore, if the dosing of rejuvenation continues to increase, the binder becomes softer due to the fluidity effect of rejuvenators. For the UT/R1 and HL/R3 rejuvenators, the stiffness values consistently decreased with the increase of rejuvenation dosage. This is because of softening characteristics of rejuvenators as mentioned in chapter 3 and the higher dosage of it make the aged binder softer. Contrary to UT/R1 and HL/R3 rejuvenators, TR/R2 rejuvenator did not always make the aged binder softer, sometimes improved the stiffness. This behavior might be due to the chemical modification of TR/R2 rejuvenator by the transesterification process, which reduces the FFA contents and improves stiffness. The highest stiffness was observed for the TR/R2 rejuvenator and UT/R1 exhibited the lowest stiffness among the alternatives which was also observed from FTIR analysis as discussed in Chapter 3. It can also be noted that the increased concentrations do not always make the binder softer, but it depends on the quality and the type of rejuvenators used. Overall, the stiffness of the rejuvenated binder can be ranked as TR/R2> HL/R3> UT/R1.

- Polymer modification with SBS increased the stiffness of both R1 and R2 rejuvenated binders. Generally, SBS polymer is a combination of polystyrene and polybutadiene materials. When this polystyrene and polybutadiene chains combine with each other, that makes SBS a durable and stiff material. Also, SBS is one of the widely used polymers to improve the binder stiffness and also to improve the rutting resistance of binder as well. Therefore, the drawbacks of UT/R1 rejuvenated binder of being soft could be addressed using SBS polymer.

- All the percentages of rejuvenated binders exhibited a significant increase in fatigue cracking resistance as observed from the G-R parameter. The inclusion of UT/R1 and HL/R3 rejuvenators made the binder softer and softer material improved the fatigue cracking resistance of the aged binder. TR/R2 rejuvenated binder did not always make the binder softer, however, it was enough to pass the fatigue cracking criteria of the G-R parameter. A similar observation was recorded after SBS modification. Although SBS polymer makes the binder stiffer, it also improved the low-temperature fatigue cracking resistance of the binder. The existence of polybutadiene components of SBS fully swells with the lighter elements of asphalt to form a network structure, which improved the binder flexibility and cracking resistance of SBS modified binders.
- For rutting susceptibility, the Superpave rutting parameter and Shenoy parameter was determined. The result shows that the increasing percentages of rejuvenation decrease the rutting resistance of the binders. From the experimental data, all the percentages of TR/R2 rejuvenated binders passed the rutting criteria which was expected through chemical and rheological characterization. This is because of the chemical modification of TR/R2 rejuvenator, which makes the binder stiffer. However, UT/R1 rejuvenated binders are softer which showed lower rutting resistance and also failed the rutting criteria. Similar to chemical characterization in chapter 3, HL/R3 rejuvenated binder showed higher stiffness and higher rutting resistance compared to UT/R1 rejuvenated binders. After SBS modification, the rutting resistance improved significantly. The complex bonding mechanism of

polystyrene and polybutadiene made the SBS a durable and more restrained from external pressure or load. These outcomes help to enhance the stiffness and the rutting resistance of SBS modified binders. For the SBS modified UT/R1 rejuvenated binders, a little improvement of rutting resistance occurred, whereas a reasonably higher improvement was observed for SBS+TR/R2 rejuvenated binders. This might be due to the better compatibility of SBS with the TR/R2 rejuvenated binders.

- Based on MSCR analysis, the TR/R2 rejuvenated binders showed good performance compared to others. The binder with 3%TR/R2 can only be grouped in the 'S' category of traffic loading, whereas other binders rejuvenated with UT/R1 and HL/R3 fail to achieve any place in traffic loading criteria due to the softening characteristics of the binders. Modification with SBS improved the performance of all binders and higher loading criteria was achieved with those binders. In general, SBS is a thermoplastic elastomer polymer, which behaves like elastomeric rubbers to improve the elastic behavior of the binders. This characteristic helps to reduce the permanent deformation of the SBS modified binders.

6.4 Major Findings from Surface Free Energy Analysis

- Aging of binder increased the contact angle compared to the base binder PG 58-28. However, after the inclusion of rejuvenators, it improved the contact angles and was similar to the base binder. This might be the reason for using rejuvenators that regained the molecular properties and improved the wettability of the aged binder.

In comparison, a slightly higher contact angle was noticed with water and the highest contact angle was recorded with glycerol. The variability of contact angles might be the effect of intermolecular forces between liquid and solid; also, the type of liquids been used for the measurement. After SBS modification, a slight decrease of contact angles was observed with glycerol and formamide. As SBS modification increases the binder stiffness, it changes the wettability of the binder which exhibits lower contact angles.

- Aging of binder reduced the surface free energy (SFE) components of all binders. Among the three SFE components, the contribution of the Lifshitz-Waals components was much higher for all types of binders. Rejuvenation regained the Lifshitz-Waals component of all the binders and as a result higher total SFE was achieved. This is the characteristic of a rejuvenator, which regained the original properties of aged binder. Among the binders, higher SFE was recorded for UT/R1 rejuvenated binders due to its lower contact angles. SBS modification with UT/R1 rejuvenated binder also seemed to be effective in improving the total SFE. In contrast, the lowest SFE was recorded for SBS+TR/R2 modified binders and sometimes even lower SFE compared to the aged binder. Based on the rheological results in chapter 4, TR rejuvenated binders are stiff and SBS+TR modification made the binder stiffer among the binders. As a result, a lower wettability of SBS+TR rejuvenated binder resulted in higher contact angles and therefore, lower SFE among the binders.

- All types of rejuvenated binders seemed to be effective in enhancing the cohesive bond energy and improving the moisture damage resistance as well. Cohesive bond energy is one of the energy parameters that is correlated with the fatigue cracking resistance of the binder. Among the binders, the higher cohesive bond energies were recorded for UT rejuvenated binders. From the rheological characterization in chapter 4, it was noticed that UT rejuvenated binder exhibit the highest fatigue cracking resistance among the binders which is also similar to the cohesive bond energies of UT rejuvenated binders. The intermolecular forces between the UT rejuvenated binders and the softening behavior might help to reduce the cohesive fractures within the binder to improve the cohesive bond energies. A similar correlation was also noticed between the cohesive bond energy and the fatigue cracking resistance for TR/R2 and HL/R3 rejuvenated binders.
- SBS modification also improved the cohesive bond energies of UT/R1 rejuvenated binder. The improvement in bond energies could be due to the swelling effect between SBS+UT/R1 rejuvenated binder. However, SBS+TR/R2 rejuvenated binders showed the lowest cohesive bond energy and seemed to have poor moisture damage resistance. Among the binder, SBS+TR/R2 rejuvenated binders are the stiffest, and therefore there might be a good possibility to propagate cohesive cracks within the binders which could be attributed to the lower cohesive bond energies of the binders. The results were also consistent with the fatigue cracking resistance of SBS modified TR rejuvenated binders as mentioned in chapter 4.

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 TFOT aging of the binder due to the limitations with access to equipment. Therefore, it could be better to examine the short-term and long-term performance of binder using rolling thin film oven test (RTFOT) and pressurized aging vessel (PAV) test respectively.
- During the mixing of the rejuvenator with the aged binder, the manual hand mixing process was used. As a result, there might not have a homogeneous mix of the binder. Therefore, it is recommended to use a magnetic stirring machine to achieve a homogeneous mix.
- Due to a lack of access to the instrument, AFM analysis was limited to only topography and phase-contrast analysis. It would be better to study the force-curve analysis of all binders to achieve better micro-morphological features.
- 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 mixture level to understand the actual mechanism between rejuvenated binders and aggregates.

Appendix A Published Articles

1. Waste Cooking Oil as an Asphalt Rejuvenator: A state-of-the-Art Review

This article has been published to Journal of Construction and Building Materials as a review paper as: Ahmed, R. B., Hossain, K. (2019), 'Waste Cooking Oil as an Asphalt Rejuvenator: A state-of-the-Art Review'. Most of the research in this paper has been conducted by the first author. He also prepared the draft manuscript. The other author supervised the research and reviewed the manuscript.

The overview of this journal is available in the following link.

Link to Journal Article:

https://www.sciencedirect.com/science/article/pii/S0950061819324274

2. Chemical, Morphological, and Fundamental Behavior of Rejuvenated Asphalt Binders

This article has been published to ASCE Journal of Materials in Civil Engineering as a technical paper as: Ahmed, R. B., Hossain, K., Hajj, R. M. (2020), ‘Chemical, Morphological, and Fundamental Behavior of Rejuvenated Asphalt Binders’. Most of the research in this paper has been conducted by the first author. He also prepared the draft manuscript. The other author supervised the research and reviewed the manuscript.

The journal article is now in production department of ASCE Journal of Materials in Civil Engineering.

3. Application of Waste Cooking Oil in Construction of Asphalt Pavement

This report has been submitted to the Harris Center - MMSB Waste Management Applied Research Fund (2017-18) project of Government of Newfoundland and Labrador and has been published online as: Ahmed, R. B., Hossain, K. (2019), 'Application of Waste Cooking Oil in Construction of Asphalt Pavement'. Most of the research in this report has been conducted by the first author. He also prepared the draft manuscript. The other author supervised the research and reviewed the manuscript.

The overview of this project report is available in the following link.

Link to Project Report:

https://www.mun.ca/harriscentre/reports/MMSB_Waste/Final_Hossain.pdf

Appendix B Laboratory Tests

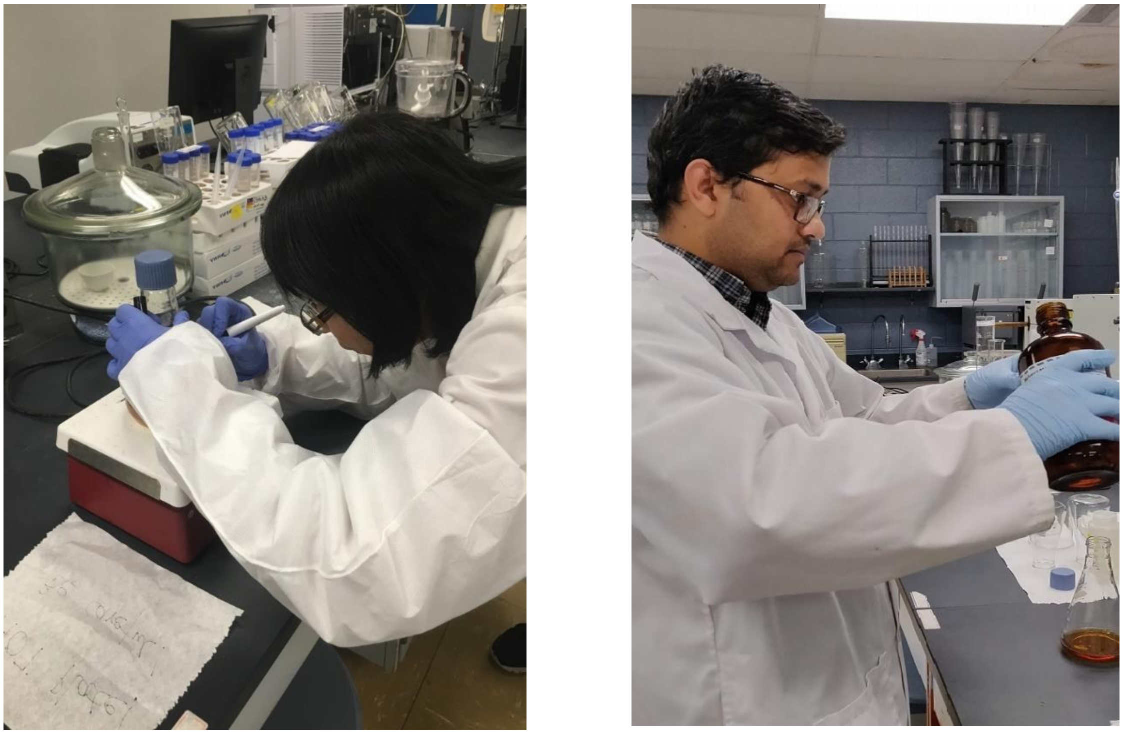

Figure B.1 Modification of WCO at Environment Engineering Lab, MUN

Figure B.2 Experimental Work on Rotational Viscometer at Asphalt Lab in MUN

Figure B.3 An Agilent DB-5 MS System for GC-MS Analysis at MUN

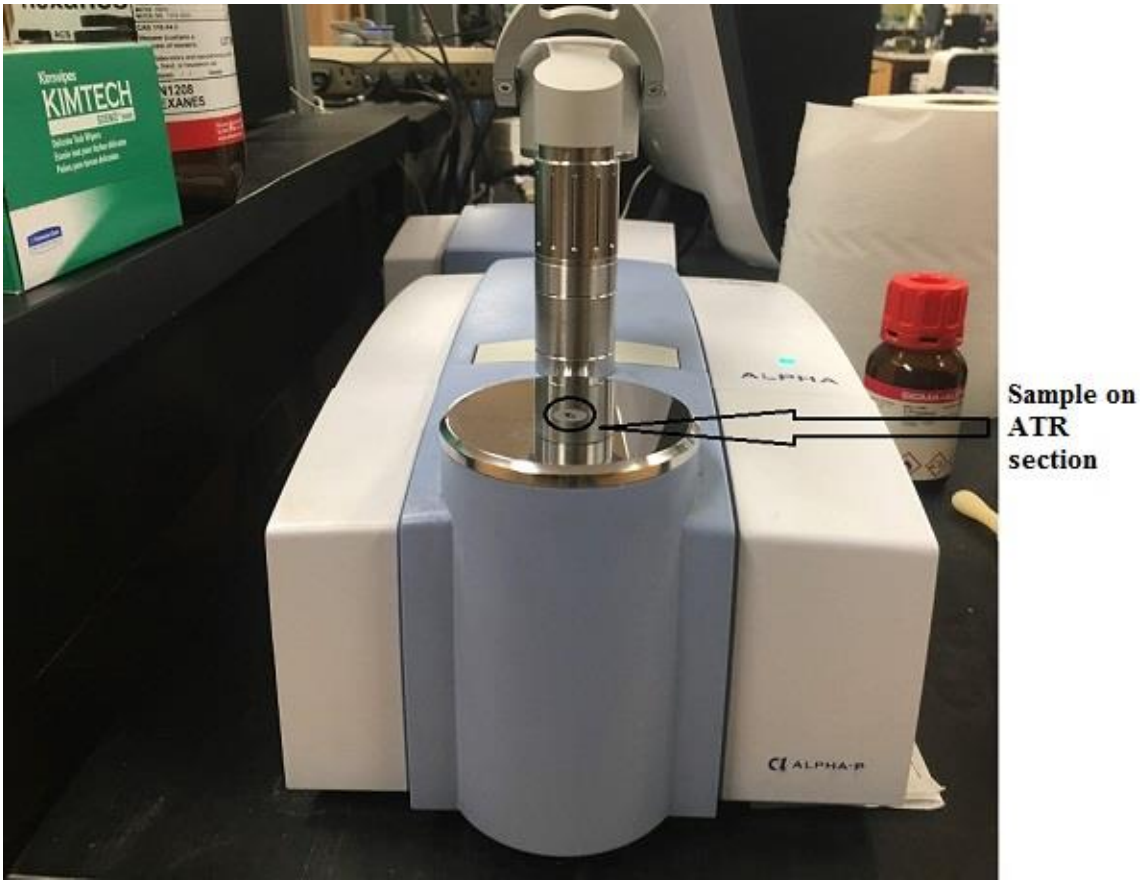

Figure B.4 A Bruker FTIR Test Equipment at MUN

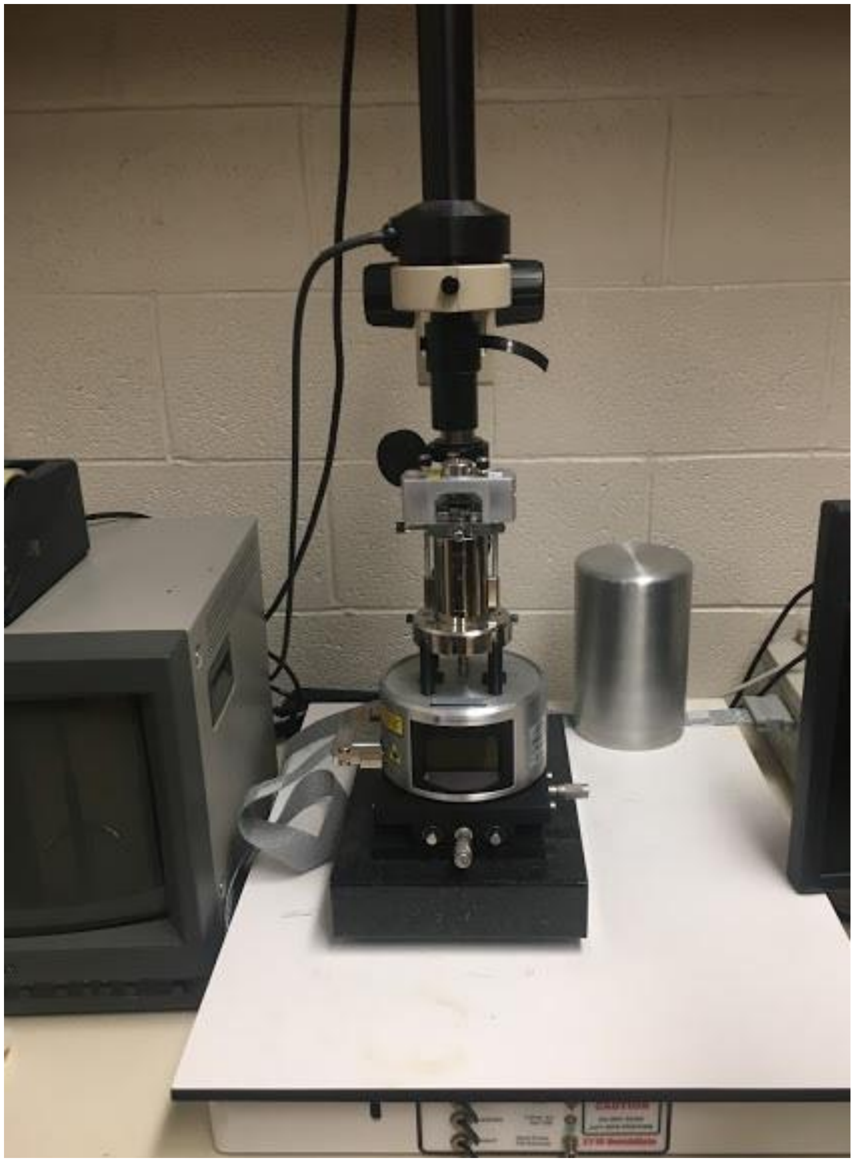

Figure B.5 Micromechanical Test with Atomic Force Microscope at MUN

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

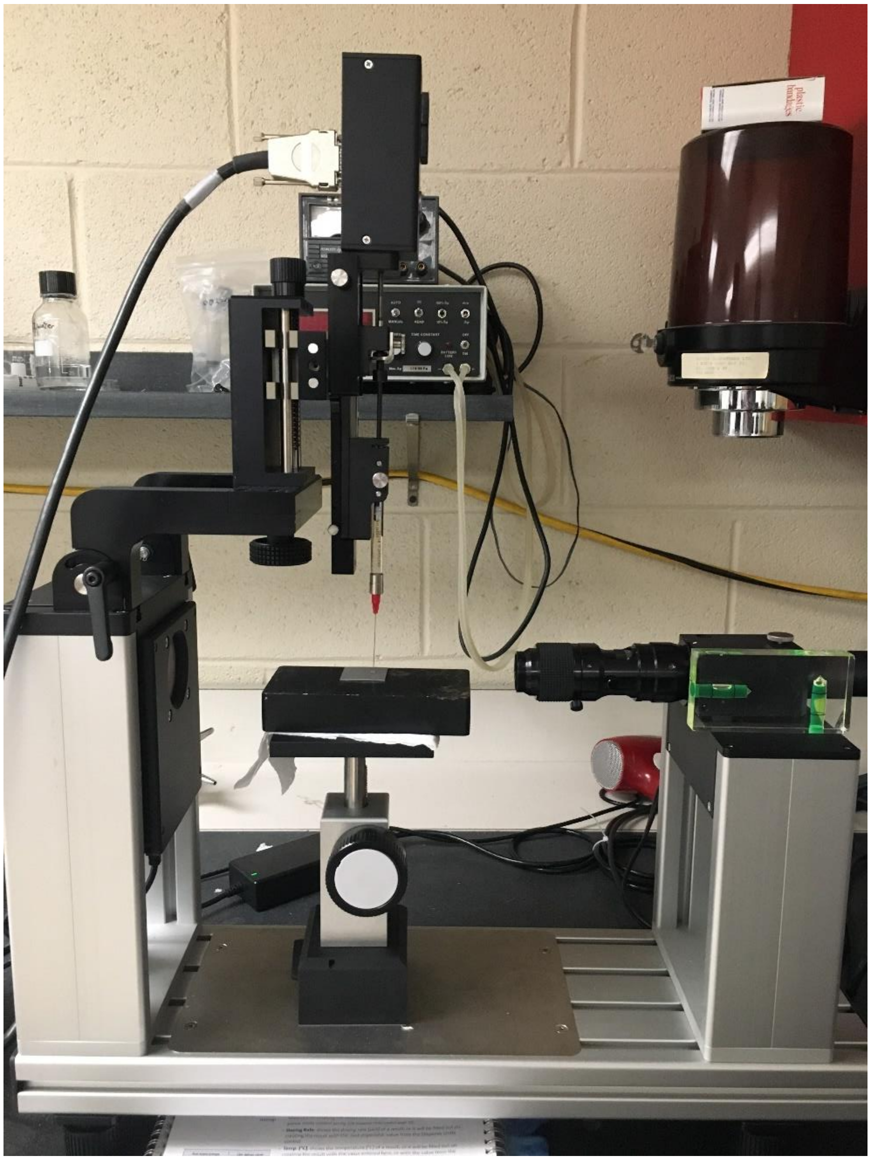

Figure B.7 Contact Angle Measurement Using OCA 15EC Equipment at MUN