Implications of Bio-modification on Moisture Damage Mechanisms in Asphalt Binder Matrix

by

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ABSTRACT

Bio-modification of asphalt binder brings significant benefits in terms of increasing sustainable and environmental practices, stabilizing prices, and decreasing costs. However, bio-modified asphalt binders have shown varying performance regarding susceptibility to moisture damage; some bio-oil modifiers significantly increase asphalt binder's susceptibility to moisture damage. This variability in performance is largely due to the large number of bio-masses available for use as sources of bio-oil, as well as the type of processing procedure followed in converting the bio-mass into a bio-oil for modifying asphalt binder. Therefore, there is a need for a method of properly evaluating the potential impact of a bio-oil modifier for asphalt binder on the overall performance of asphalt pavement, in order to properly distinguish whether a particular bio-oil modifier increases or decreases the moisture susceptibility of asphalt binder. Therefore, the goal of this study is a multi-scale investigation of bio-oils with known chemical compositions to determine if there is a correlation between a fundamental property of a bio-oil and the resulting increase or decrease in moisture susceptibility of a binder when it is modified with the bio-oil. For instance, it was found that polarizability of asphalt constituents can be a promising indicator of moisture susceptibility of bitumen. This study will also evaluate the linkage of the fundamental property to newly developed binder-level test methods. It was found that moisture-induced shear thinning of bitumen containing glass beads can differentiate moisture susceptible bitumen samples. Based on the knowledge determined, alternative methods of reducing the moisture susceptibility of asphalt pavement will also be evaluated. It was shown that accumulation of acidic compounds at the interface of bitumen and aggregate could promote moisture damage. It was further found that detracting acidic compounds from the interface could be done by either of neutralizing active site of stone aggregate to reduce affinity for acids or by arresting acidic compounds using active mineral filler. The study results showed there is a strong relation between composition of bitumen and its susceptibility to moisture. This in turn emphasize the importance of integrating knowledge of surface chemistry and bitumen composition into the pavement design and evaluation.

DEDICATION

I dedicate this dissertation to the One whom I have already dedicated my whole life to, my Lord and Savior Jesus the Christ. Here are the ABCD reasons why.

Admitted - I admitted that I was guilty of breaking God's law. Sinning once breaks God's law, and I have lied, stolen, and disobeyed my parents, which is already 3 of the 10 commandments. Romans 3:23 says "for all have sinned and fall short of the glory of God." I knew that I have to be punished for my sins just as any good and fair judge would have to do to someone who had broken the law. Rom 6:23b For the wages of sin is death.

Believed – I believed that no amount of good works would excuse me from the sentencing and punishment of my crimes against God's law. My only hope to be freed was if someone completely innocent could take my place and take the punishment I deserved. God knew that no one could accomplish this, so he himself became a man in the person of Jesus Christ. Laying aside His Divine attributes, Jesus lived a perfect life and committed no sin. This sinless life allowed Him to be my legal substitute, which means that He can take my place as guilty and was punished as a criminal through His death on the cross. 2 Cor. 5:21 says, "For our sake he (God) made him (Jesus Christ) to be sin who knew no sin, so that in him we might become the righteousness of God." This literally means that because Christ was perfect and had no sin, he was able to take my sin and punishment on Himself so I could be set free.

Confessed– I confessed/acknowledged my sins to God knowing that I am deserving of eternal punishment for breaking God's law. I have confessed/acknowledged that I cannot become right with God by doing good things but only through faith in Jesus Christ's substitutionary death for my sins and bodily resurrection from the dead as He foretold thus proving His authority and power over death. Ephesians 2:8-9 says, "For by grace you have been saved through faith. And this is not your own doing; it is the gift of God, not a result of works, so that no one may boast." This verse explains that salvation from my deserved punishment is an undeserved and unmerited gift obtained only by faith and was paid for by the sinless life Jesus lived. It is not anything I could have ever been able earn because even my good deeds are filthy rags (Isa. 64:6). Romans 10:10 says, For with the heart one believes and is justified and with the mouth one confesses and is saved.

Dedicated - Out of a heart of gratefulness, joy, and love now as a free man, in 2007, I dedicated my life to Jesus and asked Him to lead me according to His will. My life is not my own but is now lived in way, which would please Him. Now that I am free from the bondage of sin and secure in my standing with God, I am committed to growing my relationship with Him because He loves me more than anyone else ever has or ever will.

John 3:16-17 - "For God so loved the world, that he gave his only Son, that whoever believes in him should not perish but have eternal life. For God did not send his Son into the world to condemn the world, but in order that the world might be saved through him."

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CHAPTER 1. INTRODUCTION

1.1 Background

According to the Federal Highway Administration, the United States has over 8.77 million lane-miles for highway travel, and approximately 94% are made with asphalt pavement (FHWA, 2018; NAPA, 2019). Nearly $30 billion is spent each year in the US alone for asphalt construction and maintenance, and in England and Wales, the total cost is nearly $3.5 billion per year (Anderson, et al., 2000, Asphalt Industry Alliance [AIA], 2020).

The significant cost investment required for asphalt roads highlights the importance of research on asphalt pavement to extend performance and reduce degradation while minimizing cost. One of the primary causes of distress in asphalt pavement is moisture susceptibility, which leads to moisture damage. One survey found that 41 out of 50 US states report moisture damage as a major cause of premature pavement failure, with as much as $200 million spent each year in prevention (Hicks et al., 2003; Christensen et al., 2015; Williams et al., 2017).

Moisture damage occurs when water from rainfall, melting ice, seepage, or capillary effects diffuses into the pavement, causing chemical reactions that weaken the cohesion of the binder to itself and the adhesion of the binder to aggregates (Hossain and Tarefder, 2013, Airey and Choi, 2002). Moisture damage can also lead to increased cracking, potholes, and rutting in asphalt pavements (Grenfell et al., 2014). These distresses related to moisture damage are expected to become increasingly prevalent, since annual precipitation for the US in 2017 was above average for the fifth consecutive year (NOAA, 2018).

Additives are used in asphalt binder to help improve the performance of the asphalt binder against distresses such as moisture damage and to increase pavement sustainability through the use of renewable bio-resources. Nearly 1.6 billion dry tons of biomass could be used in the US alone from sources such as landfills, lagoons, crops, and from managing the dead trees that pose risks of forest fires (US Dept. of Energy, 2016; WH Exec. Ord. 2018). There are several benefits of modifying petroleum-based binders with bio-oils: up to 70% lower production cost; lower energy consumption and lower emissions during asphalt paving; and increased use of recycled asphalt materials (Anthony et al., 2017; Podolsky et al., 2017). Although other performance factors have been investigated for bio-modified asphalt binders, there is a lack of research on the moisture susceptibility of bio-oils; this lack of research is reported to be a direct factor in limiting the use of bio-oils in asphalt pavement (Gong et al., 2017) In addition, of the studies that do investigate the moisture susceptibility of bio-modified asphalt binders, the results can vary significantly and are not always consistent between studies. However, some asphalt mixtures using certain bio-oils blended with petroleum asphalt do show a consistent susceptibility to moisture damage (Su et al., 2018; Majidifard et al., 2019). Additionally, moisture damage tests and current methods used to determine moisture susceptibility can present results contrary to field results and may not reflect what is occurring on the molecular level in terms of moisture susceptibility (Cuadri et al., 2015). A fundamental understanding of bio-oil on the molecular level is crucial to understanding the relationship that a bio-oil modifier has to asphalt binder and how that relationship affects the bio-modified asphalt binder's performance regarding moisture susceptibility. In addition, having a mechanical test that can relate molecular-level interaction would allow for more dependable evaluations of the moisture susceptibility of asphalt binder.

1.2 Research Objectives

The goal of this research is to understand the varied impact of bio-oils on asphalt binder through a better understanding of the linkage between fundamental properties of the bio-oils and the bio-oils' moisture susceptibility. An additional goal of this research is to address the need for development of a method for testing the moisture susceptibility of an asphalt binder that can be easily adopted by industry using existing testing equipment.

1.3 Research Approach

In order to address the objectives of this study, the following milestones and research questions will be investigated. A summary of the research approach is given in Figure 1.

- Multiscale approach to study the moisture susceptibility of Bio-Modified Asphalt
    - Is there an effect of modifiers on moisture susceptibility at the binder and mixture level and how does it compare with commercial additives?

    - This will be tested by performing moisture level mixture testing and binder level cohesive and adhesive testing, and molecular dynamics on key molecules noted within the various bio-oils.
- Molecular Interactions Between Modifiers and Asphalt Matrix
    - Is there an identifiable parameter which can be utilized to help measure the level of moisture susceptibility of a bio-oil and can it be easily measured?
    - This will be performed by identifying chemical compositions and performing density functional theory analysis of the molecules. The results will then be compared to experimental results
- Develop Test Methods to Evaluate Moisture Susceptibility of Asphalt
    - Is there a test parameter which can capture the results of the molecular interactions in terms of moisture susceptibility?
    - This is will investigated by the development of the contact angle moisture susceptibility index (CAMSI) and the moisture induced shear thinning index (MISTI) and their respected correlation to the tensile strength ratio test (TSR).
- Develop Methods to Improve Resistance of Bio-modified Asphalt to Moisture Damage
    - What types of remediation techniques can be utilized to improve the moisture resistivity of asphalt?

    - This will include mixture and binder level testing of two different methods of remediation. The first involves passivating the aggregate/binder interface with molecules which ensure proper bonding. The second method involves preventing the troublesome molecules from reaching the aggregate/binder interface reducing the interaction.
- Study Economic Viability and Market Landscape
    - How is the proposed test and the use of bio-oils relevant to the asphalt market?

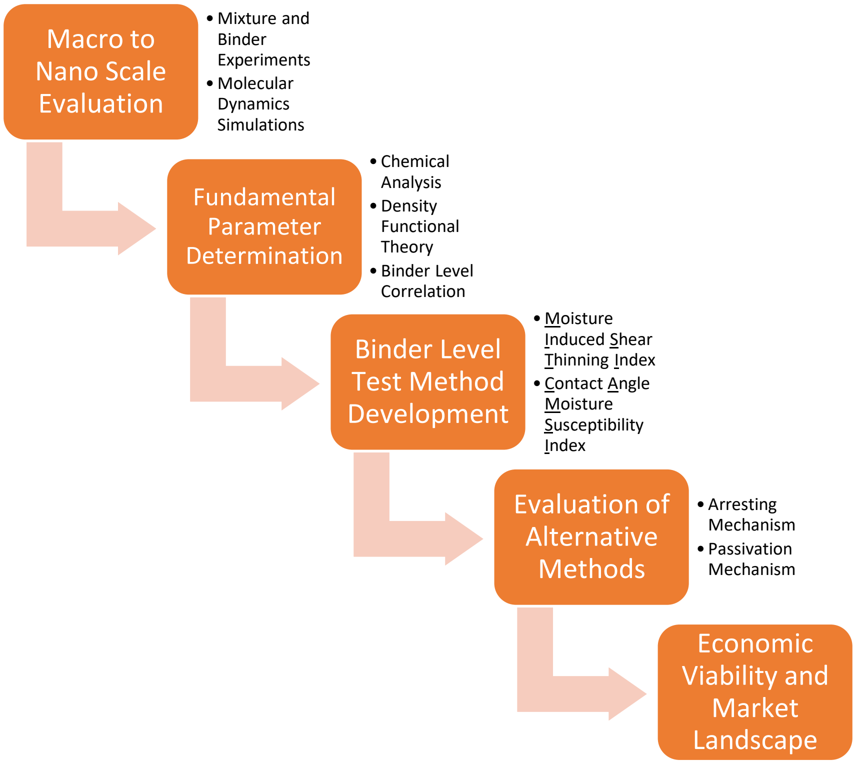

Figure 1- 1 Experimental Flow Diagram of Research Plan

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2. CURRENT STATE OF KNOWLEDGE

2.1 Moisture Damage

2.1.1 How Moisture Damage Occurs

Moisture damage occurs when water from underneath seepage, capillary effects, rainfall, or ice melting diffuses into the pavement, causing chemical reactions that weaken the cohesion of the binder to itself and the adhesion of the binder to aggregates (Hossain and Tarefder, 2013, Airey and Choi, 2002). However, the effects have been shown to vary depending on the type of aggregate used: limestone and marble aggregates are less susceptible to water damage, and granite is more susceptible (Airey, et al., 2008, Cui et al., 2014). Because of transportation costs, states are limited to whatever aggregate is locally available; therefore, the objective of this study is to investigate the use of binder modification to help reduce moisture susceptibility in asphalt mixtures.

Although moisture-related distresses can appear minuscule, the effect can be magnified by time and cause significant damage to asphalt pavement. There are several ways in which water can enter into the asphalt pavement structure. From Figure 2-1, the most obvious means of water infiltration is via the pavement surface through surface discontinuities such as pavement distresses and cracks, both intentional and unintentional. Water can also infiltrate through the sides of the pavement structure from rainwater seepage from ditches as well as by surface and higher-ground runoff from elevation differences. An unnoticed source of water infiltration is the water table underneath the structure; infiltration could become an issue due to a rising water table. However, the most common means of water movement into the pavement structure is through capillary movement under the pavement. This water then turns into vapor once it reaches above the capillary fringe. Without proper drainage, the area underneath the structure can become saturated with capillary water. If the subgrade becomes too saturated, the water can even travel on into the actual pavement through the air voids. This could become even more problematic if the pavement heats up, causing the water to vaporize; this could cause high pore pressures in the pavement that would increase with traffic loads, causing severe stress in the pavement and eventually debonding or stripping.

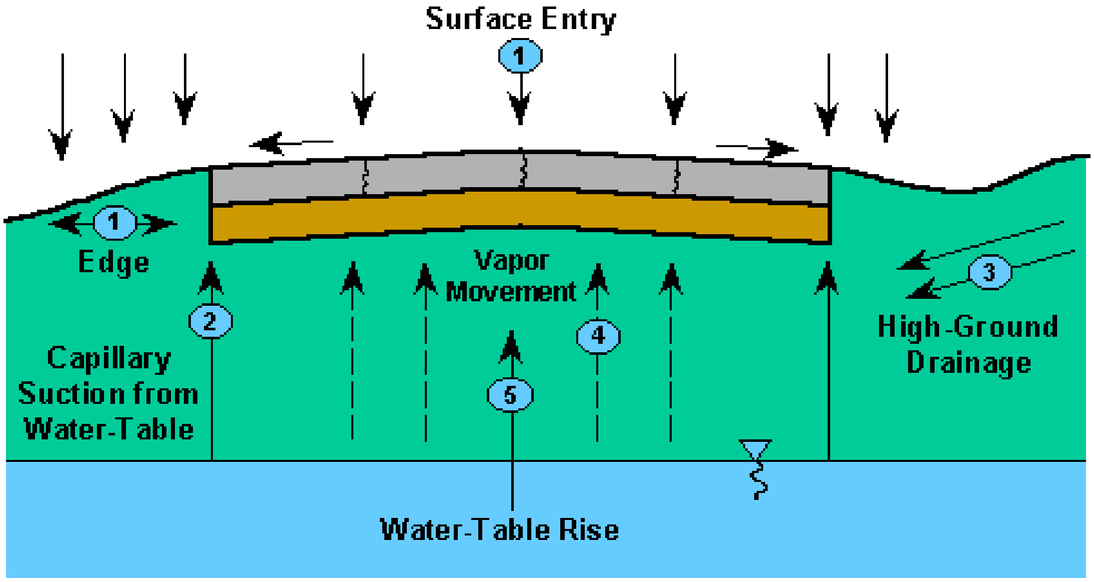

Figure 2- 1 Ways Water Infiltrates to the Pavement Structure (ACPA, 2013).

2.1.2 Pavement Distresses From Moisture Damage

Stripping is defined as the loss of adhesion between the asphalt binder and aggregate. It is very clearly identified when there is a mixture of coated and uncoated asphalt aggregates. In Figure 2-2, samples from a Hamburg wheel-tracking test show major stripping due to the test, as shown by the fine particles being more brown than black, both in the middle of the sample and also removed from the sample and sitting on top of the molds. Additional evidence of stripping is that the tops of aggregates in the middle of the sample are completely clean or stripped of asphalt binder.

Figure 2- 2 Asphalt Mixture with Major Moisture Stripping

Though stripping can be easily identified after it occurs, it usually starts at the bottom of the pavement layer and progresses to the surface. Therefore, it is difficult to identify until it has appeared on the surface via various pavement distresses. The first distress it can cause is bleeding, as shown in Figure 2-3a. Bleeding is defined as the presence of excessive asphalt binder on the asphalt pavement surface. Figure 2-3b shows an example of rutting, which is defined as longitudinal surface depression in the wheel path caused by a lack of adhesion between the aggregates and the asphalt binder (NC DOT, 2011). Bleeding and rutting can be a result of water being present inside the mixture due to a lack of proper compaction, unevaporated water in the aggregate, inadequate water drainage, or lack of aggregate-binder interaction (Hicks et al., 2003). The aforementioned issues can also be seen in fatigue cracking, as shown in Figure 2-4. Further accelerating these distresses on pavement are freeze-thaw water cycles that combine with the weight of traffic loads, which can lead to the dislodging of asphalt, as also shown in Figure 2-4. When stripping begins at the surface and progresses downward, it results in the pavement distress called raveling, as shown in Figure 2-5. Raveling is defined as the dislodging of aggregate particles or loss of asphalt binder coating, resulting in the progressive loss or wearing away of the surface of the asphalt pavement (NCDOT, 2011).

Figure 2- 3 Asphalt Pavement Distresses: (a) Bleeding, (b) rutting (LDOT, Pavement Interactive)

Figure 2- 4 Asphalt Pavement Distresses: Cracking

Figure 2- 5 Asphalt Pavement Distresses: Raveling (Pavement Interactive, Yellowstone Park)

2.2 Factors Influencing Moisture Damage

It is generally difficult to pinpoint a single cause for certain effects, due to the involvement of several interacting factors. This is especially the case when it comes to determining the cause of moisture-related damage in asphalt pavements, which has been extensively studied since the early 1900s. Solaimanian et al. (2003) compiled a list of factors that can contribute to moisture-related distresses, as shown in Figure 2-6. From Figure 2-6, there are factors related to the actual production and construction of pavements, such as segregation of the aggregates within the mix, the proficiency in producing the mix at the plant and compacting it in the field, and things such as miscommunications between contractors and plant operators. Another important factor in moisture-related distresses is the climate: the range of temperatures and the amount of rainfall in a particular area. Other issues include factors that are not directly related to the pavement itself, such as the surface and subsurface drainage of the surrounding area, as well as things like resurfacing jobs and most prominently, the amount of traffic load. However, the factor that can be most controlled and understood is the factors related to the mix design, particularly the use of additives and the chemistry of the binder and aggregate.

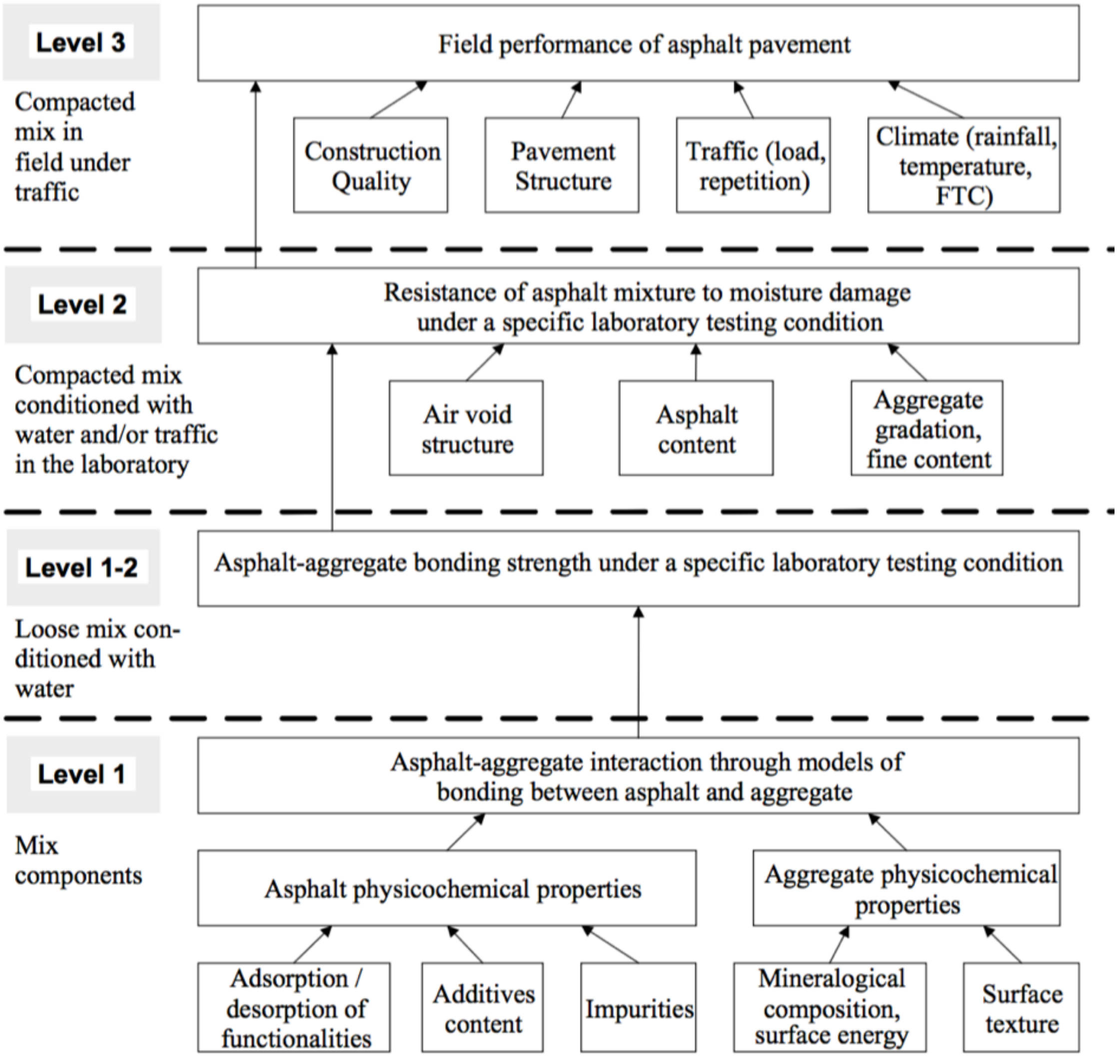

Figure 2- 6 Factors which Contribute to Moisture-Related Distresses (Solaimanian et al., 2003).

2.3 Moisture Susceptibility of Bio-Modified Asphalt

Table 2-1 contains some of the studies investigating the moisture susceptibility of bio-oil in asphalt pavement. As shown, some bio-oils such as waste vegetable oil or other plant based bio-oils consistently have an increased susceptibility to moisture damage. However, other plant based bio-oils other plant based oils such as wood chip blend show no difference while pine tree bio-oil was shown to improve in one study and decrease in another. Such discrepancies highlight the need for proper bio-oil screen but also a need for more accurate moisture susceptibility tests.

Table 2- 1 Studies Testing the Moisture Susceptibility Bio-Modified Asphalt

Bio-Oil Modifier	**Test Performed**	**Impact on Moisture Susceptibility**	**Authors**
Waste Vegetable Oil	Stripping Inflection Point (SIP) via Hamburg Wheel Tracking Test (HWTT)	Decrease	Zaumanis et al., 2014
Red Oak	Tensile Strength Ratio (TSR)	Decrease	Williams et al., 2015
Corn Extract	SIP via HWTT and TSR	Decrease	Buss et al., 2015
Wood Chip Blend	Tensile Strength Ratio (TSR)	No Change	You et al., 2012
Guayule Rubber	SIP via HWTT and TSR	Decrease/Increases	Lusher and Richardson, 2014
Pine Tree	SIP via HWTT and TSR	No Change	Mohammed et al., 2013
Pine Tree	SIP via HWTT	Increase	Zaumanis et al., 2014;
Plant Blend	TSR	Increase	Austroads, 2013
Waste Vegetable Grease	SIP via HWTT	Increase	Zaumanis et al., 2014

2.4 Methods for Testing Moisture Damage

Though the effects of moisture on asphalt pavement are universally accepted and observed, there has been much debate on how to design laboratory tests for moisture damage that accurately predict field performance. There are four main categories of tests for moisture damage: aggregate alone, loose mixtures, compacted mixtures, and binder alone.

2.4.1 Aggregate Methylene Blue Test

Though aggregate testing does not categorize as an asphalt mixture stripping test, testing the aggregate can provide indications as to whether stripping would occur when the aggregate is blended with asphalt binder. One such test that is being used is the French-developed Methylene-Blue Test, which identifies the amount of potentially harmful clay, organic, or other fine particles in the aggregate. The presence of such material could significantly prevent adequate binder coating. The test has been recommended by the International Slurry Seal Association and also has a supplemental testing procedure used by the Ohio Department of Transportation (ISSA, 1989; ODOT, 2002). To perform the test, aggregate passing the No. 200 sieve is washed, dried, and dispersed in distilled water. Once it has been blended consistently, a dilution of methylene blue is titrated into the solution of fine aggregate and distilled water. After additional stirring for 1 minute, a droplet of the aggregate/distilled water/MB solution is taken using a glass rod and placed onto a filter paper. A clear, well-defined circle of MB-stained dust will then form on the filter paper and will be surrounded by an outer ring of clear water. More MB is to be titrated into the solution until a permanent light-blue outer ring is observed in the ring of clear water. Once this is reached, the amount of MB added to the solution is recorded and the test ends. The correlations between the amount of methylene blue and the expected pavement performance is shown in Table 2. A concentration of methylene blue from 5-6 mg/g predicts excellent pavement performance (low moisture susceptibility), while a concentration greater than 20 mg/g predicts a failure in pavement performance (high moisture susceptibility).

Kandhal et al., investigated the use of the methylene blue test, the sand equivalent value, and a plasticity index to evaluate a wide variety of aggregates to determine which test would correlate best to two tests: the tensile strength ratio (TSR) test from AASHTO T282, and the stripping inflection point (SIP) through the Hamburg Wheel-Tracking Test (Kandhal et al., 1998). The results found the highest correlation to be with the methylene blue test, with an R value of 0.79 with the TSR and 0.82 with the SIP.

Table 2- 2 Correlation of Methylene Blue Concentration and Expected Pavement Performance (Kandhal and Parker, 1998)

Methylene Blue (mg/g)	**Expected Pavement Performance**
5-6	Excellent
10-12	Marginally Acceptable
16-18	Problems or Possible Failure
20+	Failure

2.4.2 Loose Mixture Testing

One of the methods for testing the moisture susceptibility of hot-mix asphalt is by testing it after it has been blended with the binder and aggregates, but before it is compacted. This is what the industry refers to as a “loose mix.” These are the four main types of loose-mixture testing for moisture susceptibility:

- immersion (static immersion, water immersion, ultrasonication)
- bottle spinning (film stripping, rolling bottle)
- boiling (boiling water)
- chemical blending (English chemical immersion, chemical blending, net absorption)

These tests are described below.

2.4.2.1 Static Immersion Test

This method to determine the moisture susceptibility of a loose mix simply immerses the sample in water. The static immersion test involves preparing 100 grams of aggregate between the sizes of 6.3 and 9.5 mm, then blending it with 5.5% binder by weight. The sample is then conditioned at 60°C for 2 hours before being cooled and separated. It is then immersed into 600 ml of distilled water at 25°C for 16 to 18 hours. The sample is then evaluated through the glass jar to determine the level of stripping with the passing criteria only being if the amount of aggregate coated with binder is at least 95%. Issues surrounding this test are the variability in the results and the subjectivity of determining that 95% of the aggregate is coated. Although the test is still an AASHTO test (AASHTO T182), these issues most likely contributed to its removal as an ASTM standard (formerly ASTM D1664). The test was altered some to include 4 hours of agitation and was denoted as the dynamic immersion test. However, this test addition has not been included in any standard.

2.4.2.2 Water Immersion Test

The static immersion test was further developed to improve it, resulting in the total water immersion test. This test requires 3 replicates; it assesses the amount of aggregate coverage by the binder after 3 hours of soaking in water at 40°C. Comparative testing found that the total water immersion test showed a significant improvement in distinguishing moisture-susceptible aggregates, but the test still needs some improvements (Liu et al., 2014).

2.4.2.3 Ultrasonic Method

Another means of water-conditioning the samples using the immersion method is by ultrasonication (Anderson & Goetz, 1956). For the test, 30 polished stones are taken, and each one is coated with 2 grams of binder at a thickness of approximately 0.12 mm. Three replicate samples are then submerged and subjected to ultra-sonic waves, then visually assessed for stripping after 5, 10, 15, and 20 minutes of conditioning. Research using this method found that it was not sensitive enough to distinguish between mixtures with good field performance and those with poor field performance in moisture susceptibility (Liu et al., 2014).

2.4.2.4 Film Stripping Test

Another test is the film stripping test, which is used by the California Department of Transportation (CalTrans, 2014). The samples are made by separating the coated aggregates and cooling them to room temperature. Afterwards, the loose mix is heated in the oven at 140°F for 15 to 18 hours before being placed in a glass jar. Once the sample and the jar are cooled, distilled water is added to the container and the entire contents are sealed. The jar is then placed into a spinning apparatus and rotated for 15 minutes; then a visual inspection of the amount of stripping observed under a fluorescent light based on the total surface of the blend is recorded. This test is not widely used outside of California.

2.4.1.5 Rolling Bottle Test

Another similar test is the rolling-bottle test, in which 170 grams of aggregates are heated to 105°C overnight and then blended with 5.7 grams of hot asphalt binder at 120°C. After breaking down the sample and allowing it to cool to room temperature, the sample is then stored between 12 and 64 hours, then tested. The bottles are half-filled with distilled water and 150 grams of the loose mix. The bottle is then placed in a bottle roller for 6 hours at 60 rpm. According to the standard, the degree of stripping is then visually determined by two technicians independently (BS, 2012). The process is then repeated for three more cycles at 12, 48, and 72 hours with the water being replaced at each interval. Each time this process is performed, a value to the nearest 5% is determined and an average degree of remaining coverage is then determined for the mixture.

2.4.2.6 Boiling Water Test

The boiling water test, also known as the Texas boiling test, is another loose-mixture test for determining moisture susceptibility. In this test, the loss of adhesion is determined visually through placing approximately 250 grams of the blended aggregate and binder material in boiling distilled water for 10 minutes +/- 15 seconds. After skimming any binder that was removed, the sample is cooled to room temperature and dried. According to the standard, any areas that look brown or translucent are considered fully coated

(ASTM, 2012). An example of a stripped sample from the Texas boiling test is shown in Figure 2-7.

Figure 2- 7 Sample with Major Moisture Stripping after the Texas Boiling Test (Liu et al., 2014)

2.4.2.7 English Chemical Immersion Test

Another test involving the method of boiling the mixture is the English Chemical Immersion Test in Standard Method TMH1 B11 (Road Research Library, 1986). This test is not widely used. In this test, the asphalt binder and aggregate mixture is separated and left to cool at room temperature. 50 mL of boiling distilled water is prepared and 10 grams of the mixture is placed into the water for 1 minute. Afterwards, the water is drained and the sample is placed on filter paper. After drying the sample, the stripping value is determined. If no stripping has occurred, the procedure is repeated with 9 incremental inclusions of sodium carbonate (Na_2CO_3), with the lowest being a molar concentration of 1/256 (0.41 g. per 1 L) and the highest being 1/1 (106 g. per 1 L). The sample is then given a Riedel and Weber (R&W) number depending on the concentration at which stripping is observed.

2.4.2.8 Chemical Blending Test

Chemical blending is another means of testing the moisture susceptibility of loose mixes. An early chemical-blending test that was developed involved the reaction of the exposed siliceous or calcareous aggregate to a suitable acid (Ford et al., 1974). The pressure generated from the chemical reaction can then be related to the amount of aggregate that was stripped of asphalt binder after the mix was initially conditioned with water. The duration of the test is less than 10 minutes and shows high reproducibility while, unlike other loose-mix tests, also providing a quantitative evaluation of stripping. However, the use of a highly toxic and corrosive acid discourages the test’s usage.

2.4.2.9 Net Absorption Test

The net absorption test is a loose-mixture moisture test developed under the Strategic Highway Research Program (Curtis et al., 1993). However, instead of blending the aggregate and binder together in the traditional way, the asphalt binder is blended with toluene and then introduced to the aggregate. The amount of binder left in the solution and the amount absorbed by the aggregate is then measured. Water is then added, thus removing some asphalt binder from the aggregate. The amount of binder is measured again, and the amount of binder remaining on the aggregate is denoted as the net absorption. Although the test can be performed quickly and has merit in comparing different aggregate types, it has been found that it offers inconclusive correlations to the modified Lottman test and no correlation with wheel-tracking results (Scholz et al., 1994). Overall, the use of some loose-mix testing methods does have merit and the capability to some extent to help distinguish between moisture-prone and moisture-resistant mixes. However, the test lacks being able to mimic traffic, pore pressure, and mixed mechanical properties (Solaimanian et al., 2003).

2.4.3 Compacted Mixture Testing

2.4.3.1 Modified Lottman Tensile Strength Ratio Test

Testing methods using compacted samples consist of indirect tensile tests, also known as the modified Lottman and Root-Tunnicliff tests, in which six samples are split into two sets: one is conditioned in water, and the other is not. The average tensile strength values of each set are then used to determine a ratio also known as the tensile strength ratio (TSR) or AASHTO T283. A survey conducted by the Colorado Department of Transportation on the methods used by state agencies in the US found that the most popular method (used by 60% of agencies) is AASHTO T283 (NCHRP 9-34). However, using this method, agencies have reported mixed success with issues such as repeatability, sample prep, and the lack of repeated loading to simulate the effects of traffic (Berger et al., 2003).

2.4.3.2 *Hamburg Wheel Tracking Test*

Another compacted asphalt mixture moisture test involves the use of wheel tracking on top of a submerged sample. The most notable of these wheel-tracking tests is that of the Hamburg wheel-tracking device (AASHTO T-324). As shown in Figure 2-8, the hamburg wheel tracking test (HWTT) been growing in popularity as a moisture susceptibility test due to its repeated loading and its capability to indicate susceptibility to moisture stripping (Solaimanian et al., 2007).

Figure 2- 8 Hamburg Wheel Tracking Device

2.4.3.3 *Moisture Induced Stress Tester (MiST)*

In addition to mixture testing, the use of conditioning machines to simulate field conditions have also been developed. In an attempt to simulate field conditions, various moisture conditioning approaches have been developed to water condition, asphalt mixture samples. One of these approaches is the moisture induced stress tester (MiST) in which the samples undergo repeated pressure and vacuum cycles to generates pore pressure within the compacted asphalt sample (Arepalli et al., 2019).

2.4.4 Binder Level Testing

Though not as widely recognized, binder-level testing has also been performed in order to help predict and determine the moisture susceptibility of an aggregate/binder combination. The most notable method of binder-level testing is that of measuring the surface free energy, which previous research has used to quantify aggregate/binder adhesion (National Academies of Sciences, Engineering, and Medicine, 2007; Hefer et al., 2006). Although comparing the surface energies of bitumen and aggregate is one approach to rationally designing pavement mixtures with better interfacial properties, the easiest method to calculate surface energies is by measuring the contact angle of liquid droplets on a flat bitumen surface. However, as easy as contact-angle measurement is in theory, there are a number of practical considerations that must be taken into account when measuring liquid contact angles on bitumen. At the root of many of these considerations is the fact that bitumen is not one homogenous material but is a complex mixture of hundreds if not thousands of different molecules that may act independently from one another. Thus, it is a questionable assumption that a measurement of the bitumen-air interface energy would be a representative indicator of the nature of the bitumen-aggregate interface. An undeniable benefit of contact-angle measurements is that they are quick, easy, and inexpensive, and they remain a useful characterization tool. However, they are also prone to artifacts that may not be representative of the sample, and sole reliance on such measurements without a sufficient appreciation of all of the potential pitfalls could yield misleading results.

2.5 Methods for Improving Moisture Damage

2.5.1 Liquid Antistripping Agents

The most commonly used method for improving the bond between the asphalt binder and the aggregate is to modify the asphalt binder with liquid antistripping agents (Caro, 2018). It has been reported that the majority of these antistripping agents are composed of molecules containing amine functional groups (Epps et al., 2003). In these organic compounds, it is suggested that the amine functional group interacts generally with the surface of the aggregate, while the hydrocarbon tail interacts with the asphalt binder (Harnish, 2010). This bridging effect was modeled and observed using molecular dynamics (Oldham et al., 2017). However, the use of liquid antistripping agents has been shown to be ineffective in variously modified asphalt binders (Buddhala et al., 2012). Therefore, the chemical composition of a modified binder and the surface chemistry of the aggregate could vary the effectiveness of antistripping agents in an asphalt mix.

2.5.2 Mineral Fillers

Though mineral fillers have primarily been used for reducing avoids voids in asphalt pavement mixtures, mineral fillers are also a common means of reducing the moisture susceptibility of asphalt pavement (Brown et al., 2009). Mineral fillers are defined by ASTM D242 as passing the No. 16, 30, 50, and 200 sieves at 100%. 97-100%, 95-100%, and 70-100%, respectively, and mineral fillers must compose no more than 6% of the mixture by mass (Speight, 2016). Though there are certain size specifications, mineral fillers can be derived from natural sources such as crushed aggregates as well as fillers from hydrated lime, fly ash, Portland cement, and steel slag (Roberts et al., 1996). It has been reported that the nature of a mineral filler strongly influences whether cohesive or adhesive moisture damage bond failure will occur, due to the mineral filler's physicochemical interaction with the asphalt binder (Kim et al., 2002; Lesueur and Little, 1999). The evaluation of eight field sections in Nevada indicated that the use of lime extended the service life of the pavement by an average of 3 years (Sebaaly et al., 2003). In general, hydrated lime has been consistently used to decrease moisture susceptibility, while the use of some clays has actually increased moisture susceptibility (Diab and Enieb, 2018).

Figure 2- 9 Hydrated Lime (left) and Cement (right)

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CHAPTER 3 A BOTTOM-UP APPROACH TO STUDY THE MOISTURE SUSCEPTIBILITY OF BIO-MODIFEID ASPHALT

3.1 Abstract

Causes and remedies for moisture damage at the interface of binder and siliceous stone aggregates is not fully understood and is considered as one of the most elusive and intractable pavement distresses. In recent years, increasing environmental awareness and decreasing availability of virgin materials have promoted the use of bio-materials to decrease adverse environmental impacts from petroleum-based products and support sustainable practices. Considering source dependency and composition variation in bio-materials, it is important to relate composition to fundamental materials properties in order to ensure adequate overall performance particularly in terms of resistance to moisture. Therefore, the current study uses a bottom-up approach to evaluate the performance of an asphalt binder additive from swine manure (Bio-modifier) as a means of not only improving but also understanding moisture resistance in asphalt pavement. Bio-modification was found to show improved moisture resistance at the binder level and the mixture level when compared to two other commercially available additives. Further analysis of the binder doped with representative molecules of the additives showed varying differences in adhesion and moisture susceptibility. To provide in-depth understanding of the underlying interaction mechanisms between water and binder, molecular dynamic simulations were performed on a blend of asphaltene and dopant molecules placed on a silica oxide substrate and exposed to water molecules. Study results revealed the passivation mechanism of bio-modifiers as a dominant factor contributing to enhanced resistance to moisture damage. It was found that bio-modifiers molecules occupy active sites of silica oxide preventing nucleation and growth of acidic compounds at the binder-silica interface. Such acidic compounds are water soluble and their presence at the interface can be detrimental leading to moisture damage. Study results showed anchored bio-modifiers molecules further interact with asphaltene molecules to provide bridging mechanism between binder and silica. This in turn leads to enhanced resistance to moisture damage in bio-modified binders adhered to siliceous surfaces such as quartz and granite stone aggregates.

Keywords: moisture susceptibility, passivation, crystallization, adhesion, bio-modifier, warm mix asphalt

3.2 Introduction

Asphalt mixtures are composed of two components: stone aggregates, which provide the skeleton and strength of the mixture; and asphalt binder, which binds the stones together, preventing any dislodging, and ensures a better load/stress dispersion across the entire pavement. Moisture damage occurs when the presence of water negatively impacts the stone aggregate or the asphalt binder individually or the interfacial bond between the two. A recent survey of 19 state departments of transportation in the US found that majority of them considered moisture damage as a major issue affecting the durability of flexible pavements in their respective states (Caro, 2018). Although the effects of moisture damage are widespread, there is still a lack of understanding of key factors causing moisture damage as well as test methods to measure propensity to moisture damage in pavements. The survey found that the top two solutions for improving moisture resistance were the use of hydrated lime (31%) and liquid antistripping agents (56%); each is summarized below.

The use of hydrated lime has been well researched and is based on modification of the structure of the aggregates. which are typically siliceous in origin and thus more prone to moisture susceptibility. In this method, the fine aggregates passing the No. 4 sieve are replaced with hydrated lime, which contains calcium ions that are much more resistant to the effects of water (Lessueur & Ritter, 2013). The use of hydrated lime has shown superior performance in mixtures conditioned in tap water as well as saltwater, even after 14 days (Ebrahim & Behiry, 2013). The values of the stripping inflection point and tensile strength ratios were significantly improved in terms of moisture resistance at 1.5% hydrated lime concentrations, even after blending hygroscopic additives with the asphalt binder (Hurley, 2006). Though the benefits of hydrated lime are well documented, the production process, via calcination from limestone, generates large amounts of harmful greenhouse gases such as CO, SO_2, NO_x, and CO_2 (Schlegel & Shtiza, 2014,Beach et al., 2003).

Liquid antistripping agents, also known as adhesion agents or promoters, are the most widely used option for improving the moisture resistance of asphalt mixtures. There is a wide variety of chemical additives sold as anti-stripping; the majority are based on the use of amide and amines (Hung et al., 2019). How they improve the adhesion between aggregate and asphalt binder is still a matter of debate. One recent theory which was recently illustrated using Atomic Force Microscopy, Transmission Electron

Microscopy as well as chemical mapping is that the polar functional groups such as those in amine and amides occupy active sites of stone aggregate preventing nucleation and growth of acidic compounds, which are highly moisture susceptible at the interface of bitumen and stones (Hung et al., 2019). Another theory is that polar function groups will interact with the aggregate, while the hydrocarbon tail of the amine will interact with the asphalt binder, thus creating a bridging effect (Logarai, 2002; Little et al., 2018). Another theory suggests that the amine improves adhesion by acting as a surfactant, reducing the surface tension of the asphalt binder and consequently increasing the binder's wettability (Banerjee et al., 2012; Sol- Sánchez et al., 2017). With either theory being plausible, the use of amines to improve asphalt binder seems to rely heavily on its functional group and hydrocarbon tail. Therefore, additives containing similarly performing molecules can be used, particularly in blends of aggregate and asphalt binder that are susceptible to moisture damage.

The increasing use of bio-derived additives for asphalt binder has shown promising benefits in terms of improving performance at the binder level and at the mixture level (Fini et al., 2011). However, additional research is needed to determine the moisture susceptibly of bio-modified binders. You et al. (2012) investigated the moisture susceptibility of traditional asphalt pavement modified with 5% or 10% bio-oil derived from waste wood; they found that although the moisture susceptibility was not negatively affected, a slight reduction in indirect tensile strength was observed (You et al., 2012). These findings are consistent with a comparative study on alternative binders conducted by Austroads in which the moisture susceptibility of several plant-based bio-oils such as

Floraphiate, Vegecol, and Pinechem was evaluated using tensile strength ratio and wheel-tracking tests (Austroads, 2013). The use of waste vegetable oil showed to increase mixture susceptibility to moisture damage and increased rut depth compared to conventional hot-mix asphalt as measured by Hamburg wheel-track testing (Bahadori et al., 2018). Generally, bio-based asphalt binder alternatives have shown differing results, with some showing improvements in reducing moisture susceptibility, some having no effect, and some adversely effecting moisture susceptibility (Xiao et al., 2013; Xiao and Amirkhanian, 2010; Buss et al., 2015; Lusher and Richardson, 2014; Cooper et al., 2013; Zhao et al., 2014). Bio-oils have also been used as softening or rejuvenating agents to improve properties such as creep compliance and fracture energy (Oldham et al., 2015; Hill et al., 2016). In one study, the evaluation of pine tree bio-mass and waste vegetable oil as rejuvenating agents found that although resistance to low-temperature cracking was improved, moisture susceptibility was increased with waste vegetable oil and decreased with pine tree oil (Zaumanis et al., 2014). Considering that such variation stems from differences in bio-oil composition, generalizing their performance characteristics is misleading. With such variation in results, there is an urgent need to not only evaluate the moisture susceptibility of each bio-modified asphalt, but also relate moisture susceptibility to bio-oil's chemical composition.

Therefore, the objective of this paper is to apply a bottom-up approach to study moisture susceptibility of a bio-modified binder derived from swine manure, using following steps:

- The binder’s adhesive performance will be evaluated using the direct adhesion test.
- Moisture susceptibility will be determined by observing the change in recoverable strain within the binder and the contact angle of the binder to a silica surface before and after water conditioning.
- The tensile strength ratio using the modified Lottman test and rutting profile using the Hamburg wheel-tracking test will be determined for bio-modified virgin mixes and bio-modified recycled asphalt pavement mixes, then compared to mixtures using commercially available additives.
- Afterwards, dopant compounds representative of the prevalent molecules of Bio-modifier and commercial additives will be blended into the base binder to study the role of the molecules on the adhesiveness and moisture susceptibility of the binder.
- Finally, the individual role of the molecules on unaged and aged asphaltenes will be evaluated, using molecular dynamics simulations for binder-silica interface exposed to water.

3.3 Experimental Procedure

3.3.1 Materials

The control asphalt binder selected for this study is Superpave PG 64-22, a binder grade that is commonly used in the United States. Bio-modifier was produced using a hydrothermal liquefaction process of raw swine manure reported elsewhere (Fini et al., 2011). Previous research has successfully used bio-modifiers at 5%-10% dosage based on binder weight (Hill et al., 2016; Hill et al., 2013). Therefore, for this study, 5% and 10% Bio-modifier was introduced to control binder at 135°C for 30 minutes at 1800 rpm. Bio-modified binder is denoted BMB, and the two concentrations are denoted 5% BMB and 10% BMB.

For comparison purposes, the 5% BMB mixtures were compared to mixtures containing two commercially available additives denoted AD1 and AD2 which are taken from a referenced study (26). AD1 refers to the mixtures containing an organic additive composed of a synthetic paraffin wax with carbon chain lengths ranging from C40 to C115. AD2 refers to the mixtures containing an additive derived from fatty amines.

Studying effects of additives in asphalt is complex; therefore, to properly study the role of additives, there is a need to study their compounds in isolation with the binder. This in turn provides insights to synthesize effective additives and modifiers. Therefore, we chose paraffin wax (C26H54) and hexadecylamine (C16NH35) as representative compounds for the AD1 and AD2 additives. The study performed by Fini et al. (2011) found that the amide functional groups are among major compounds in the Bio-modifier used to make BMB. Therefore, we chose to use the compound Hexadecylamide (C16NOH33) which has the same length carbon chain as that found in the Bio-modifier. The above three dopants (paraffin wax, hexadecylamine and Hexadecylamide) were blended into the binder at 1% concentration for binder testing only. For simplicity, the binder samples containing the above dopants are referred to as paraffin wax, amine, and amide in this study. It should be emphasized that to the best of our knowledge, the study of isolated compounds of these asphalt additives have not been performed before and this is the first attempt to do so.

The aggregate used for this study was obtained from Open Road Paving Co. LLC; it contains CM16 (9.5 mm nominal maximum aggregate size), FM 20 (manufactured) sand, FM02 (natural) sand, and limestone mineral filler. The CM16 and the FM20 aggregates were characterized as dolomitic limestones. Additional information about the aggregate can be found (Hill et al., 2013).

3.3.2 Mix Design

The mixtures were made using all virgin aggregate following the gradation shown in Figure 1. The control samples contained an effective asphalt content of 4.9%, resulting in an air void of 4.0%, which is shown in Table 1 along with the volumetric data. For the mixture level analysis we compared control asphalt with bio-modified asphalt containing 5% bio-modified binder (5% BMB). For the 5% BMB samples, no modifications were made to the aggregate gradation or the asphalt content. The number of gyrations selected for this study was 70, which relates to the requirements of a low- to medium-volume road. The control sample was mixed and compacted at hot-mix asphalt temperatures of 150°C and 135°C, respectively. The 5% BMB samples were mixed and compacted at warm-mix asphalt temperatures of 135°C and 120°C.

Table 3- 1. Asphalt Mixture Gradations for Virgin, 15%, 45% RAP Mixtures (Hill et al., 2013)

Sieve (mm)	Percent Passing (%)		
	Virgin	15% RAP	45% RAP
25.0	100.0	100.0	100.0
19.0	100.0	100.0	100.0
12.5	100.0	99.9	100.0
9.5	98.8	98.8	99.1
6.25	86.9	85.6	84.1
4.75	77.2	76.1	75.2
2.36	55.3	55.1	56.8
1.18	34.4	35.1	34.0
0.60	21.4	21.0	20.8
0.30	11.7	11.7	12.2
0.15	7.5	7.9	8.5
0.075	5.8	6.3	7.0

Table 3- 2. Mixture Volumetrics (Hill et al., 2013)

	Air Voids	**Total Asphalt Content**	**VMA**	**VFA**
Virgin	4.0%	6.7%	15.3%	73.7%
15% RAP	4.0%	6.7%	15.5%	74.4%
45% RAP	4.0%	6.3%	15.3%	73.3%

3.4 Testing Methods

3.4.1 Dynamic Modulus and Multiple Creep Stress Recovery Test

In order to determine the effect of water on room-temperature properties, the multiple stress creep recovery test (MSCR) was performed following the AASHTO T-350 procedure but not at standard temperatures. In the test, the samples are subjected to a constant load for a certain amount of time, followed by a relaxation period with the load removed for a specific amount of time. The test records two measures: the non-recoverable creep compliance (J_{nr}), which is related to the rutting performance of the material; and the percent recovery, which determines how much the sample returns to its original shape after loading. In order to determine the cohesive moisture susceptibility of the bitumen, samples were conditioned in water at 25°C for 120 hours. After conditioning, the tests were performed using a Malvern Kinexus Pro and were tested at 25°C in order to prevent any healing within the asphalt binder. The results consisted of the average of three different specimens.

3.4.2 Direct Adhesion Test

The direct adhesion test (DAT) was used to determine the effect of moisture on the adhesion of the control and the Bio-modified samples. The samples were prepared following AASHTO TP-89, which is used to test crack sealants. The binder was poured into a mold between two pieces of smooth aluminum and allowed to adhere to the surface of each. After trimming and demolding, the specimens were allowed to condition in a temperature-controlled water bath for 120 hours (Figure 1). Then they were tested to determine the amount of strain and load required to debond the binder from one of the surfaces. Due to the brittle behavior of the binder compared to sealants, the samples were tested at 6°C in order to ensure completely adhesive failure.

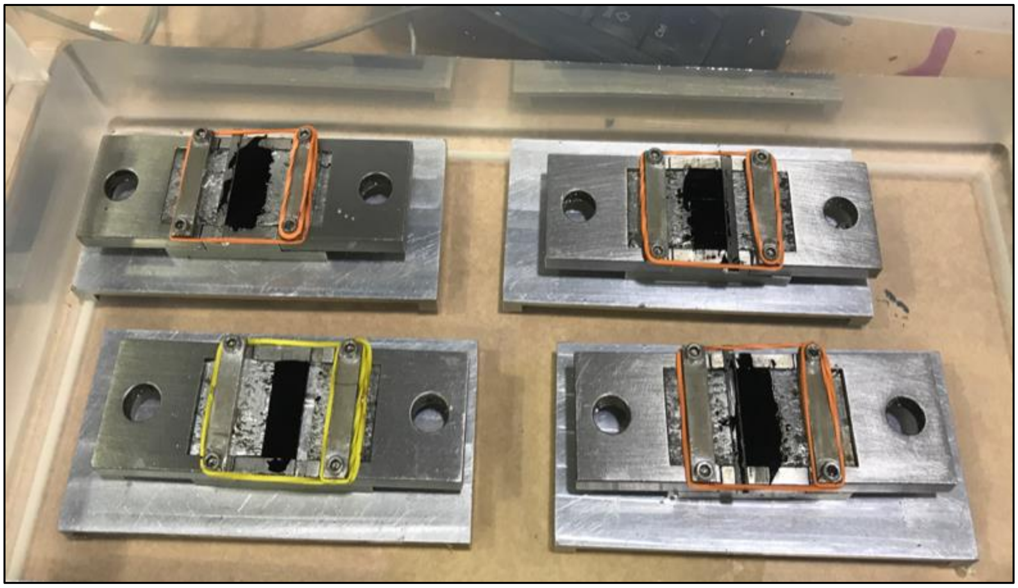

Figure 3- 1. Direct Adhesion Test Samples for Control, 5%, and 10% BMB in Water Conditioning Bath at Room Temperature

3.4.3 Contact Angle Measurement

The interfacial energy between the bitumen and a glass slide was used as a surrogate for the interaction between modified bitumen and siliceous aggregate. To cast specimens, the silica glass slides were sterilized in acetone, isopropanol, and water, then sonicated for 10 minutes each, followed by drying with nitrogen gas. To ensure the removal of any monolayers of materials, the slides were then placed into the UV ozone for 15 minutes. Within an hour of cleaning, 15 mg of each bitumen was placed on the glass slides and left in the oven for 30 minutes at 150°C to ensure proper coating, followed by annealing at room temperature for 1 hour following the method developed by Fini's group (Hung et al., 2017). Following that samples were placed into a vial of deionized water containing 5 mL of water at 80°C for 2 hours (Figure 2). Then the vial was placed into a bath of deionized water at room temperature for 5 minutes, followed by drying using nitrogen gas. Each specimen was then imaged at room temperature using a ramé-hart Model 260 standard contact angle goniometer. The contact angles were then determined using the DROPimage Advanced software package. Twelve readings were collected for both the dry, unconditioned sample and the wet, conditioned samples. From the resulting dry and wet-conditioned contact angle results, the contact-angle moisture-susceptibility index (CAMSI) was determined for each sample using Equation (1).

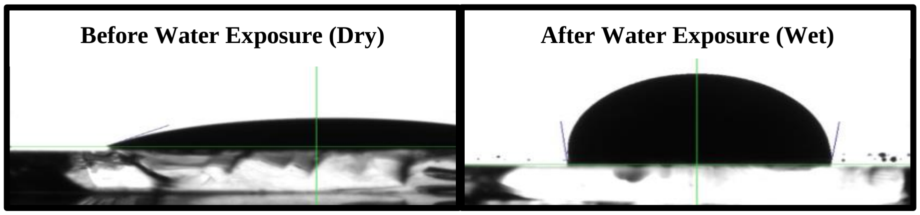

Figure 3- 2. Contact Angle of Bitumen on Glass Slide Before and After Water Exposure

$$Contact\ Angle\ Moisture\ Susceptiblty\ Index = \frac{(Contact\ Angle_{Wet} - Contact\ Angle_{Dry})}{Contact\ Angle_{Dry}} \quad (1)$$

3.4.4 Tensile Strength Ratio Test

In order to determine the moisture sensitivity of the modified specimens, the tensile strength ratio (TSR) test was performed according to AASHTO T-283. Three unconditioned samples and three conditioned samples for control and binders containing each of the three additives (bio-modifier, AD1, AD2) were compacted to 7.0% +/- 0.5% air voids. The conditioned samples were first saturated to a degree between 70% and 80%. After saturation, the samples were subjected to freezing at -18°C for 16 hours; they were then allowed to thaw for 24 hours at 60°C. The tensile strength of each sample was then measured at 25°C. The tensile strength ratio was calculated by dividing the tensile strength of a conditioned sample by that of an unconditioned sample.

3.4.5 Hamburg Wheel-Tracking Test

In order to determine the rutting and stripping performance of the asphalt, the Hamburg wheel-tracking test (HWTT) was performed following AASHTO T-324. Samples were compacted to 7% ± 0.5% air voids and cut using a masonry saw. They were then placed in molds inside the stainless steel tray mounting system. The test was performed by rolling a steel wheel across the surface of the specimen submerged in a temperature-controlled water bath at 50˚C. The number of wheel passes and the rut depth of the sample were recorded. Based on the Texas DOT and Iowa DOT, the allowable rut depth is 12.5 mm at 10,000 wheel passes. The rut depth results are used to determine the stripping inflection point (SIP), the point at which the rate of the rut depth begins to increase significantly. The SIP is directly related to the moisture susceptibility of the sample (Martin et al., 2014).

3.4.6 Molecular Dynamics

In order to understand the intermolecular interactions between a modifier and bitumen on one side and an aggregate surface on the other side, molecular dynamics (MD) simulations were performed. The molecules used are shown in Figure 3. It has been documented that there is a strong correlation between asphaltene content and interfacial adhesion properties. Therefore, among various compounds in asphalt, the unaged and aged asphaltene molecules (Figure 3-a,b) developed by Fini's group were used for the simulation (Martin-Martinez et al., 2015). The three compounds used for the binder dopant testing, paraffin wax ($C_{26}H_{54}$), hexadecylamine ($C_{16}NH_{35}$), and hexadecylamide ($C_{16}NOH_{33}$), were also used as part of the molecular dynamics simulations. The material selected to represent the aggregate was silica (SiO_2), which makes majority of typical granite stones. The specific silica molecule selected in this study is Pearson ID number 1250190. To build a more realistic silica surface representing stone aggregates, the silica was oxygen-terminated, replacing hydrogen atoms as shown in Figure 3-f.

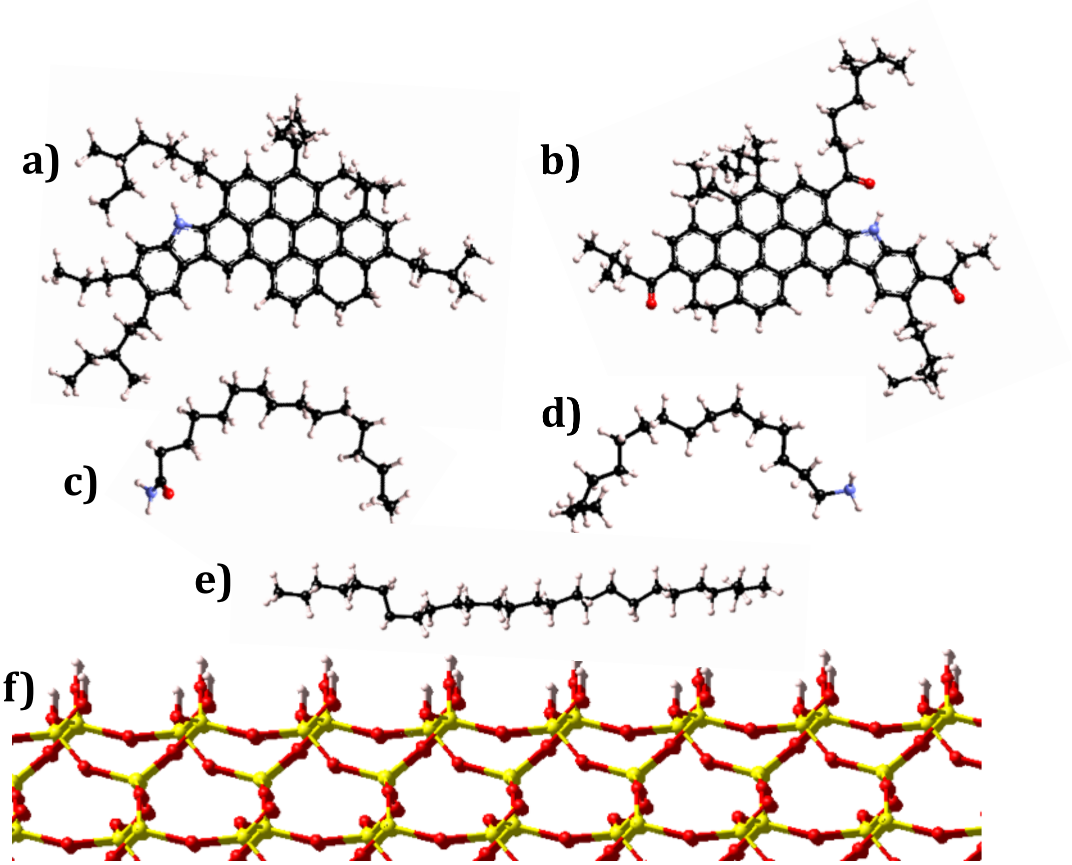

Figure 3- 3. a) Unaged Asphaltene, b) Aged Asphaltene, c) Amide, d) Amine, e) Wax, and f) Oxygen-Terminated Silica Slab

The molecular dynamics platform used was the Large-scale Atomic/Molecular Massively Parallel Simulator also known as LAAMPS. In order to make the results as realistic as possible, the system was first minimized to a potential energy of less than 1.0 KJ/mol/Ang using the conjugate gradient method, and two stages of simulations were performed. The first involved randomizing the placement of the molecules to eliminate any possible bias based on their initial positions. This was done by setting the initial temperature to 800 K followed by an NVT ensemble at 298 K for 100 ps, then an NPT ensemble starting at 800 K and 1000 atm and ending at 298 K and 1 atm for 30 ps. The final positions of this stage were then used as the initial positions for stage 2 as the system was subject to another NVT and NPT at 298 K and 1 atm for 10000 ps. The values used for analysis were taken from the final NPT ensemble. 1 fs was chosen as the global system time step and the Nose-Hoover thermostat-barostat was used to simulate the temperature and pressure respectively, with the non-bonded terms being cut off at 9.5 Å and tail corrections included using long-range Van der Waals interactions.

3.5 Results and Discussion

3.5.1 Multiple Creep Stress Recovery

The non-recoverable creep compliance (J_{nr}) results for the control, 5% BMB, and 10% BMB are shown in Figure 4 before and after conditioning at 25°C. The results show that increasing the percentage of Bio-modifier in BMB leads to higher J_{nr} values, which indicate samples with an increased susceptibility to rutting. Increased susceptibility to rutting is typically the case for more viscous binders compared to less viscous ones. In addition, it is interesting to note that the effect of moisture conditioning led to lower J_{nr} values, which indicates an increase in recoverable creep compliance within the asphalt binder material.

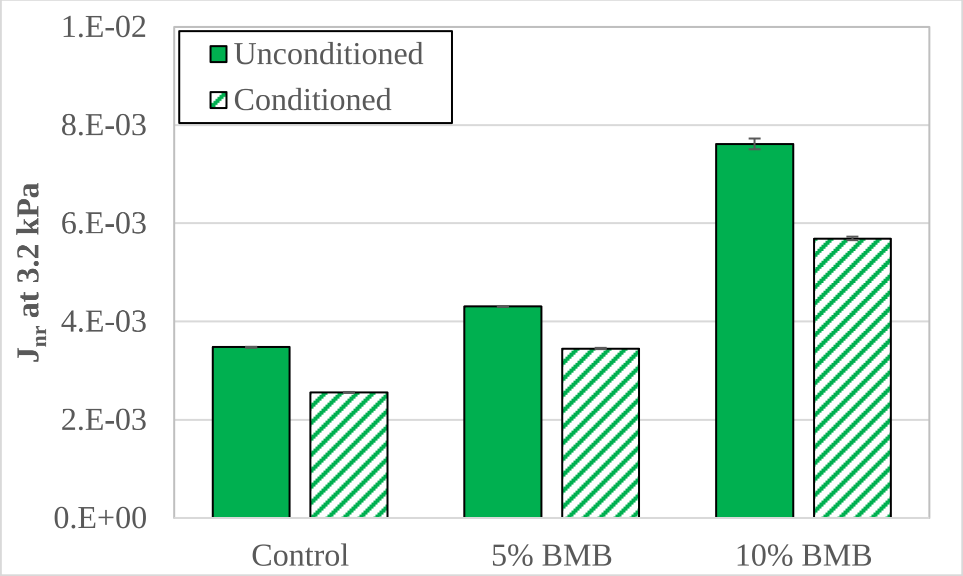

Figure 3- 4. Jnr Results for Control, 5% BMB, and 10% BMB Specimens at 25°C.

J_{nrdiff} is the difference between the J_{nr} values performed at a stress of 0.1 kPa and at a stress of 3.2 kPa, which represent slow-moving and fast-moving traffic, respectively (Federal Highway Adminstration [FHWA], 2011). In the traditional sense, the lower the difference in J_{nr} results (J_{nrdiff}), the better the quality of the polymer network within the binder (D’Angelo, 2010). Since the samples were not tested at standard temperatures, J_{nrdiff} cannot be assumed to have the traditional meaning. However, the authors checked if a trend of the impact of water on J_{nrdiff} could be seen. In Figure 5, the J_{nrdiff} was low (7%) for the unconditioned; however, after conditioning, the J_{nrdiff} increased to 23.50%, indicating an increasing difference in resistance to high and low shear due to the presence of moisture. The inclusion of 5% BMB led to a slightly improved overall performing J_{nrdiff}. However, for 10% BMB, though the unconditioned had a slightly higher J_{nrdiff}, the conditioned sample had a significantly lower J_{nrdiff} compared to both the control and the 5% BMB. In Figure 6, increasing the Bio-modifier percentage in BMB led to a decrease in elastic performance as the percent recoverable strain was reduced slightly, yet the presence of moisture had a notable increase on the percent recoverable strain at 3.2 kPa.

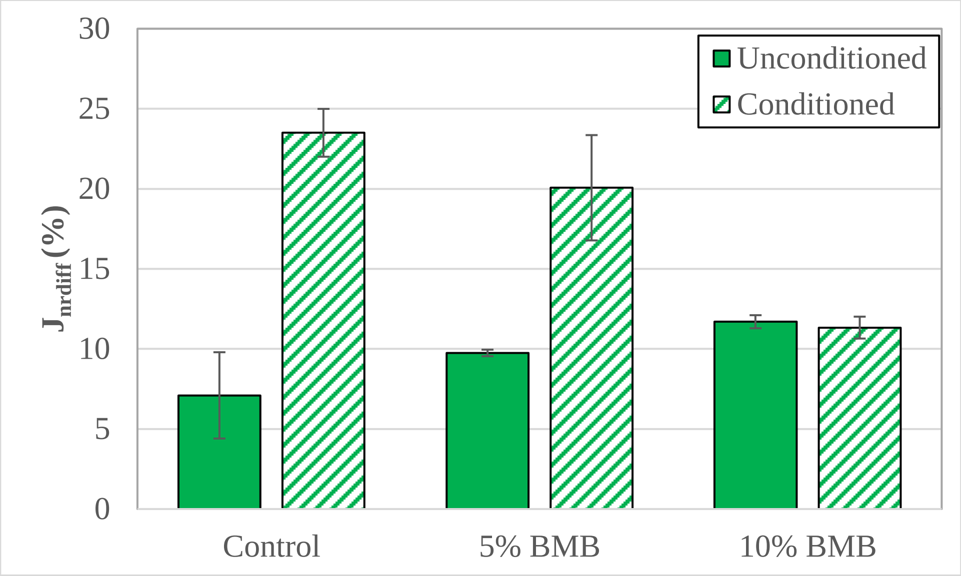

Figure 3- 5. Jnrdiff between 0.1 and 3.2 kPa for Control, 5% BMB, and 10% BMB Specimens at 25°C.

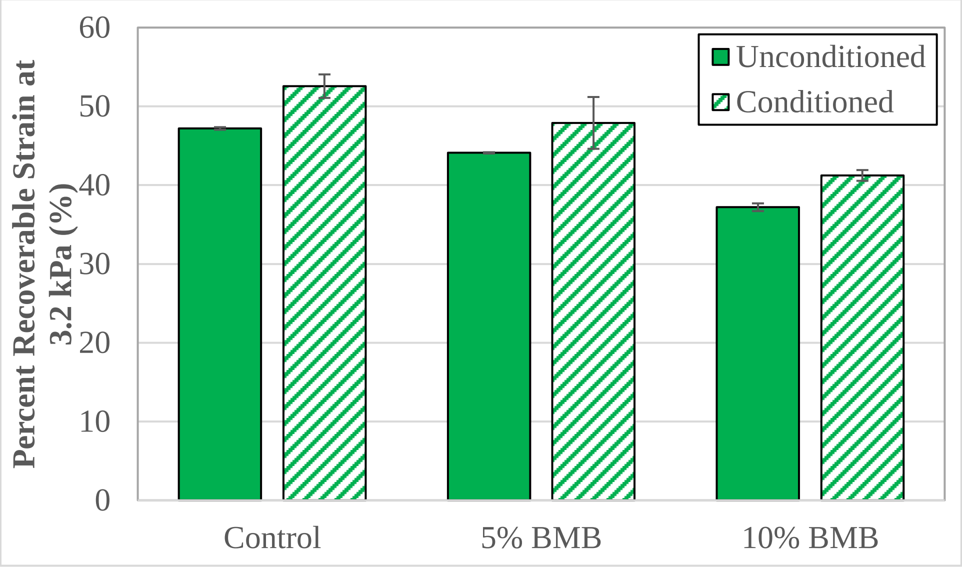

Figure 3- 6. Percent Recoverable Strain at 3.2 kPA for Control, 5% BMB, and 10% BMB Specimens at 25°C.

Figure 7 shows the moisture susceptibility of all three of the MSCR results: control, 5% BMB, and 10% BMB. The inclusion of 5% BMB led to a 25% reduction in J_{nr} moisture susceptibility, a 54% reduction in J_{nrdiff}, and a 24% reduction in percent recoverable strain. At 10% BMB, there was a 5% reduction in J_{nr} moisture susceptibility, a 95% reduction in J_{nrdiff} moisture susceptibility, and a 5% reduction in percent recoverable strain. Overall, the MSCR results from moisture conditioning indicate that the presence of Bio-modifier can significantly improve the control binder's resistance to cohesive moisture damage.

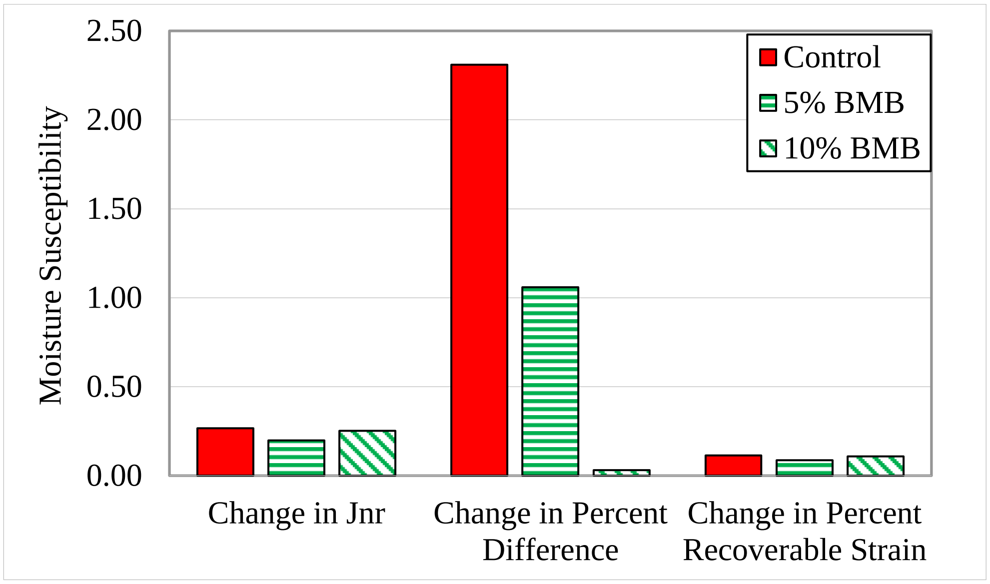

Figure 3- 7. Moisture Susceptibilities of MSCR results for Control, 5% BMB, and 10% BMB Specimens at 25°C.

3.5.2 Direct Adhesion Test

In Figures 8 and 9, the direct adhesion test results are shown for the control, 5%, and 10% BMB samples. The inclusion of BMB resulted in unconditioned failure strokes 27% and 179% higher than that of the control binder. After conditioning, the differences between the samples became even more evident; the failure strokes for BMB were 260% and 446% higher than that of the control binder, meaning that the BMB was able to increase the compliance and strain at failure in binder. In addition to strain value, the failure loads were recorded and are shown in Figure 10. The presence of 5% BMB was not shown to significantly alter the unconditioned control sample's failure load, while 10% BMB increased the failure load by 17%. After water conditioning, the failure load of 5% BMB and 10% BMB found to be similar and nearly 38% higher than that of the control binder. The combination of the cohesive performance from MSCR and both higher failure strokes and loads indicates that the BMB was able to improve the overall adhesion of the binder to the aluminum pieces even after 120 hours of isothermal water conditioning.

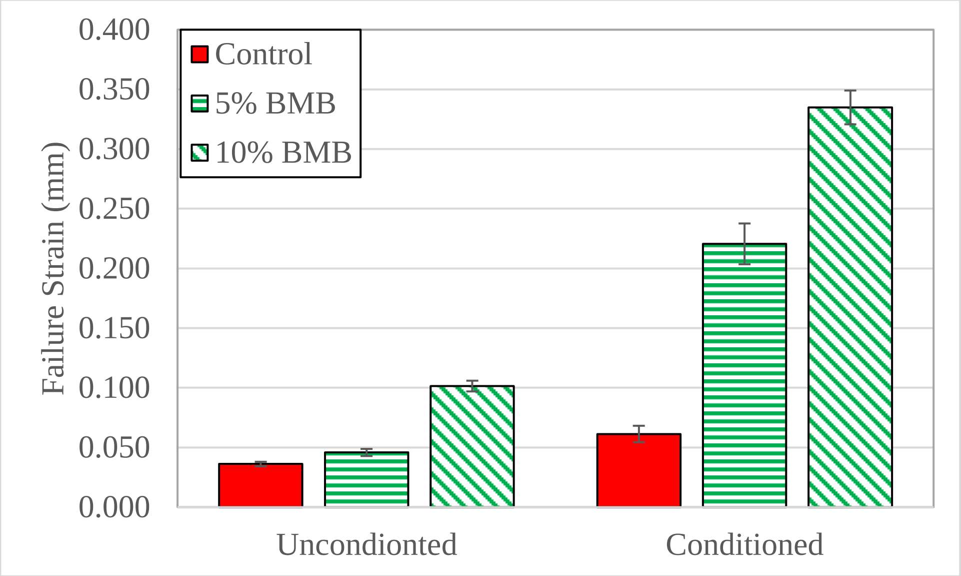

Figure 3- 8. Failure Strain Results for Control, 5% BMB, and 10% BMB at 6°C.

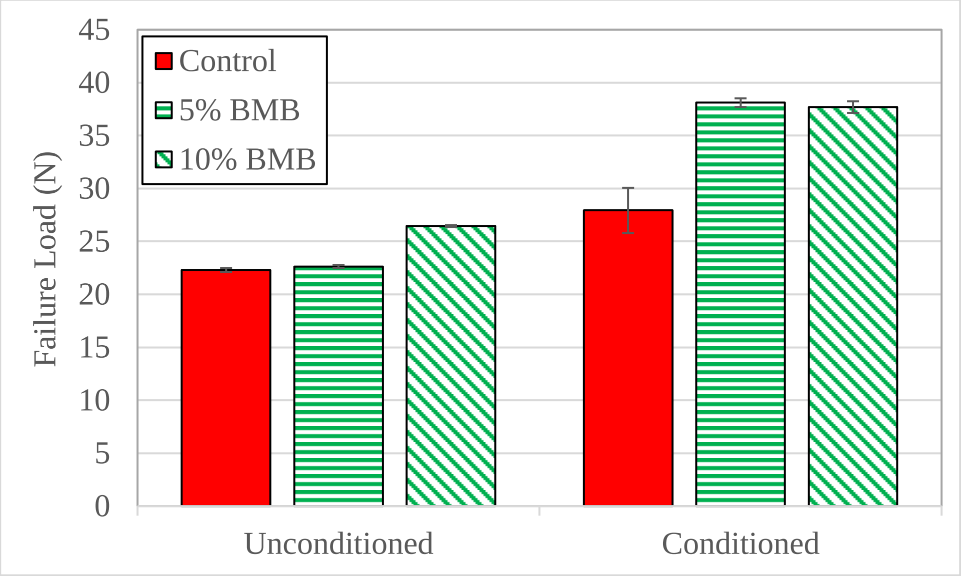

Figure 3- 9. Failure Load Results for Control, 5% BMB, and 10% BMB at 6°C.

3.5.3 Contact Angle Results

In Figure 10, the contact angle images for control, 5% BMB, and 10% BMB samples are shown. The unconditioned dry samples do not appear to show a significant difference between control and either BMB sample. Figure 11 shows that the bio-modified samples had a slightly higher contact angle at dry than the control, with 5% BMB and 10% BMB having similar angle values. After 2 hour water conditioning at 80°C, the performance of each sample significantly changed. The control sample was beaded to approximately 133°, indicating that the sample was noticeably affected by the presence of the water. However, the inclusion of 5% BMB and 10% BMB led to respective contact angles 48 and 92 degrees lower than the control. The contact angle moisture susceptibility index (CAMSI) values reflect the improved moisture resistance of the bio-modified samples: the calculated index is 6.38 for 5% BMB and 2.26 for 10% BMB, compared to 21.86 for the control.

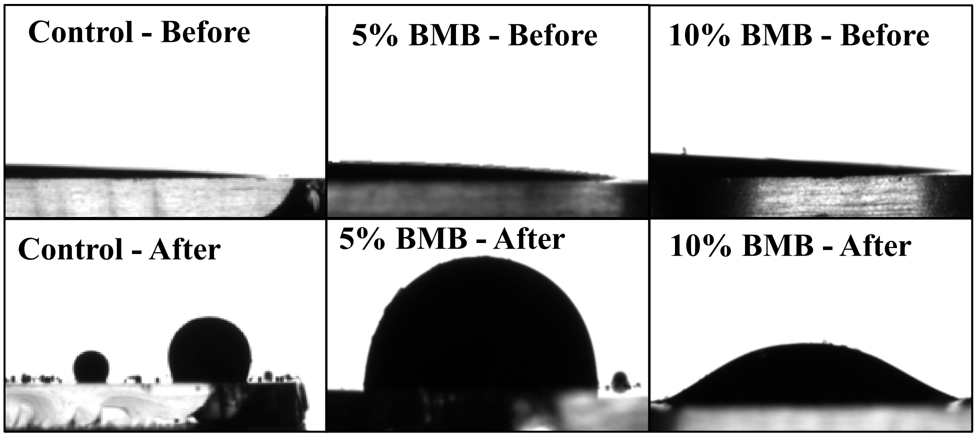

Figure 3- 10. Failure Load Results for Control, 5% BMB, and 10% BMB at 6°C.

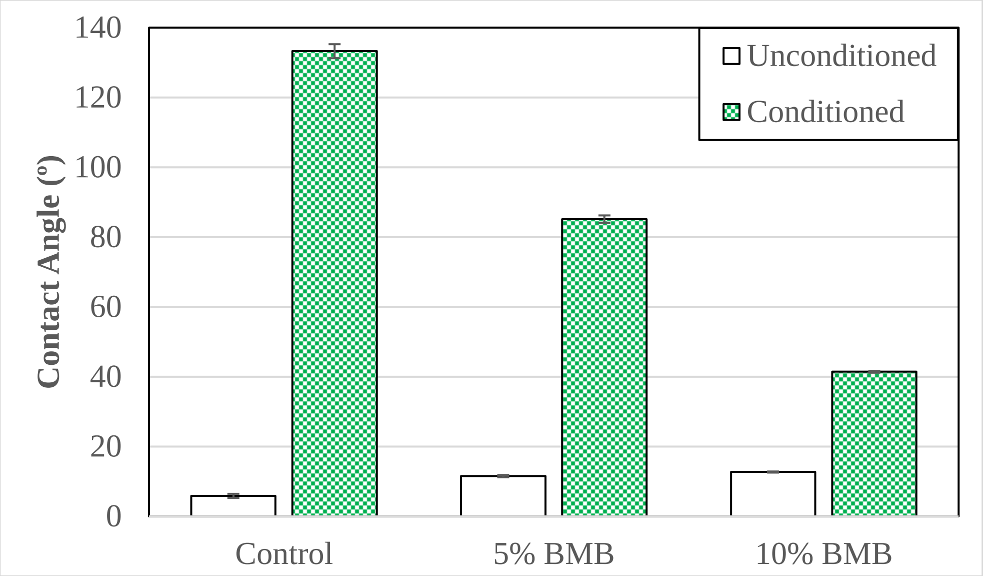

Figure 3- 11. Contact Angles of Specimens Before and After Water Exposure.

3.5.4 Tensile Strength Ratio

The average tensile strength ratio values for Control mixture, BMB, AD1, and AD2 mixtures with 0%, 15%, and 45% RAP are shown in Figure 14. The results show an improvement in TSR results with the inclusion of RAP. When observing the general effect of BMB, the TSR is shown to be higher than the control and AD1 while being comparable to AD2 at 45% RAP, with all cases having a TSR higher than 75% (Wisconsin DOT, 2014). The improved resistance to moisture in case of BMB at the mixture level is consistent with the improvements observed at the binder level as mentioned in the previous section.

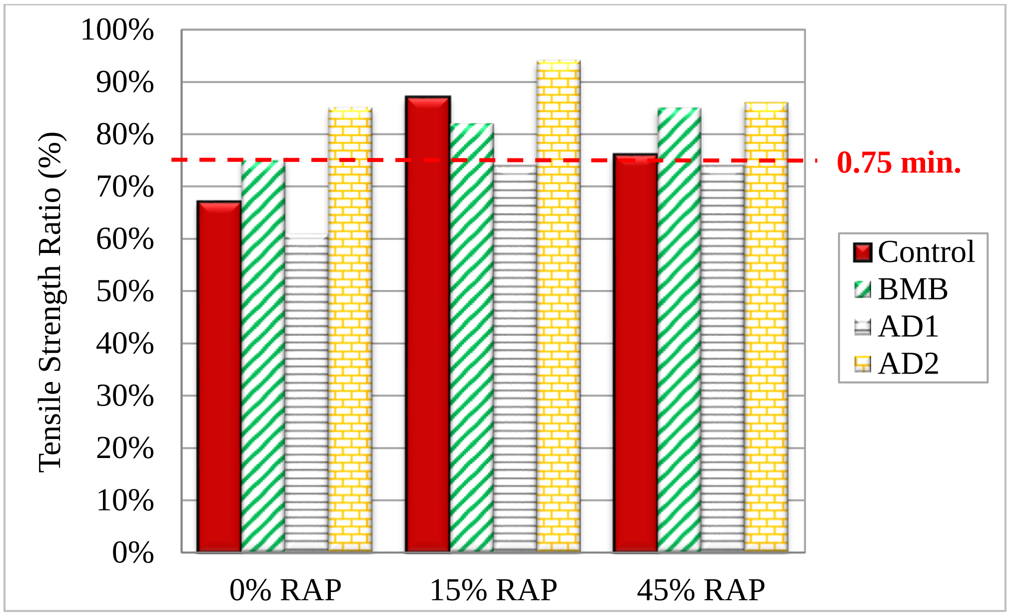

Figure 3- 12. Tensile Strength Ratio Test Results for Control Binder, BMB, AD1, and AD2 with 0%, 15%, and 45% RAP.

3.5.5 Hamburg Wheel-Tracking Test Results

In order to further compare the BMB, Figures 13-15 plot the HWTT results for control, BMB, AD1, and AD2 with 0%, 15%, and 45% RAP. The results highlight the ability of the RAP to improve the rutting performance of all four sets of samples. However, the differing rutting plots indicate characteristics of each of the additives. The control and AD1 show a heightened resistance to rutting. In terms of moisture susceptibility as measured by SIP, the BMB has higher resistance to moisture damage than AD2 (Table 3).

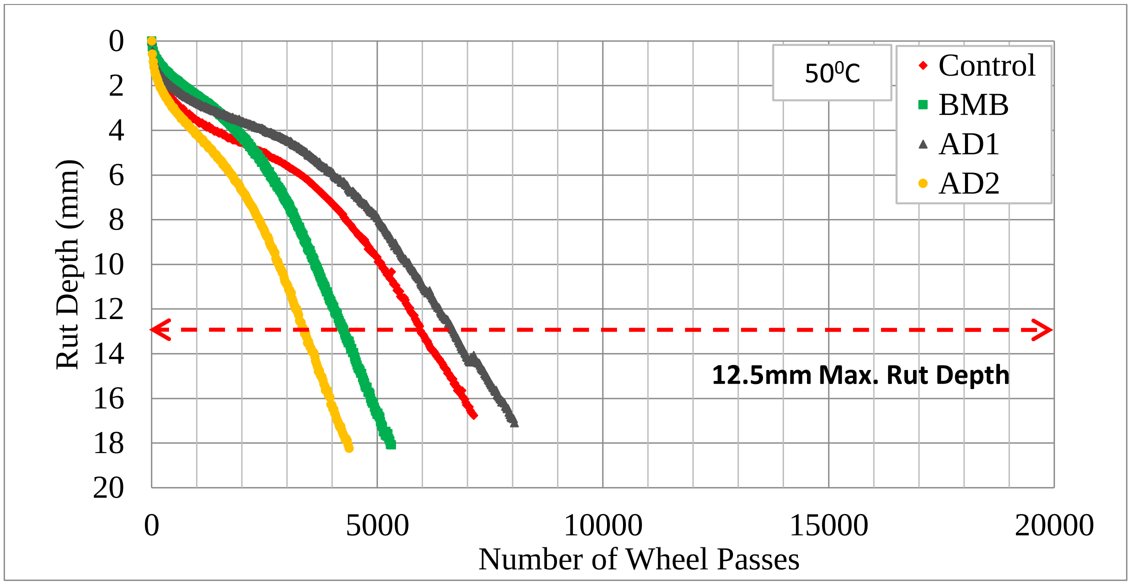

Figure 3- 13. Hamburg Wheel-Tracking Test for Specimens with 0% RAP.

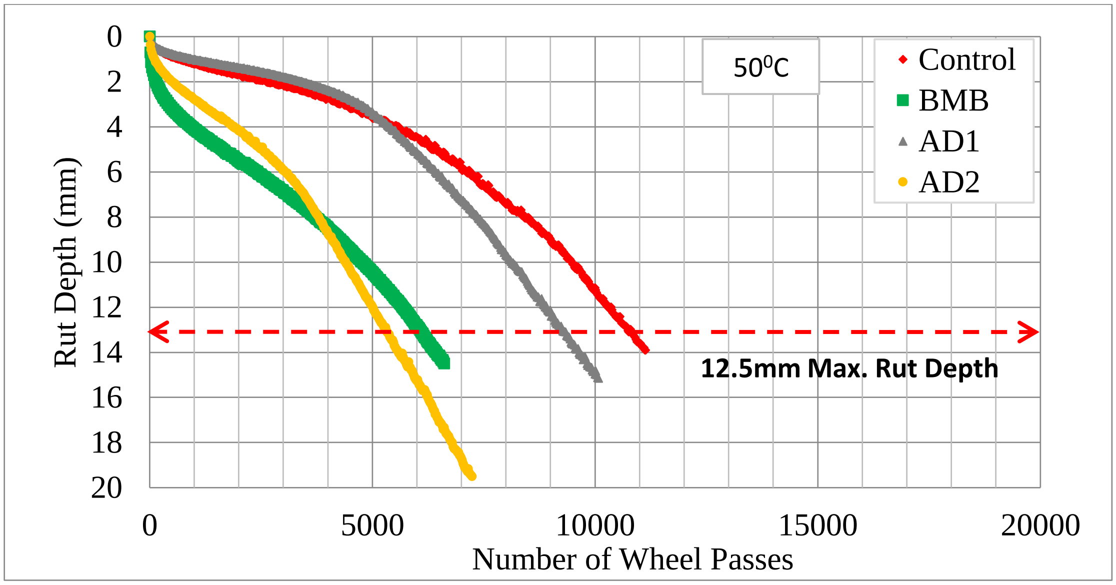

Figure 3- 14. Hamburg Wheel-Tracking Test for Specimens with 15% RAP.

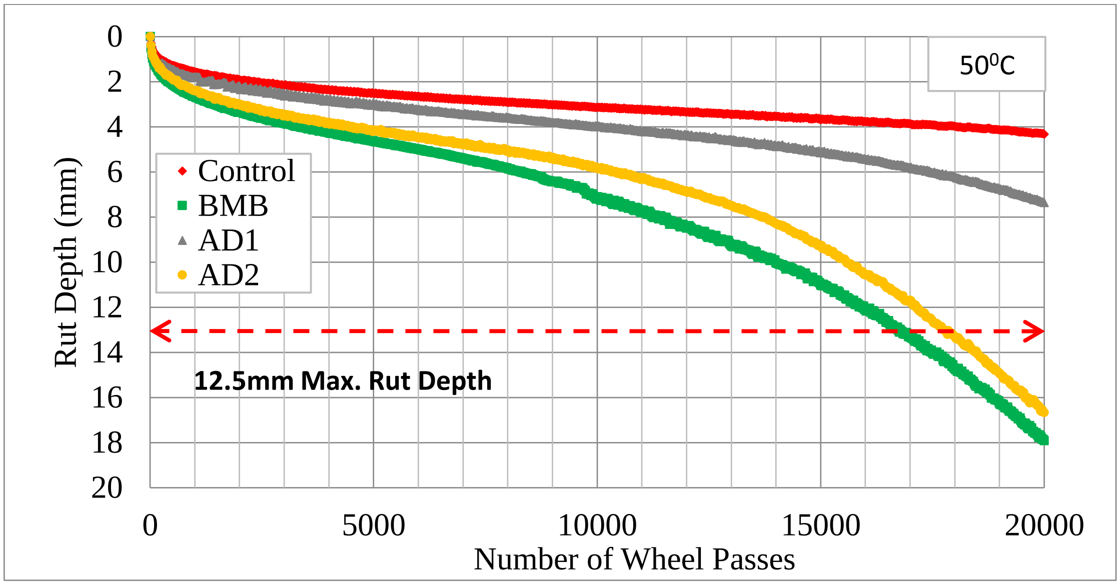

Figure 3- 15. Hamburg Wheel-Tracking Test for Specimens with 45% RAP.

Table 3- 3. Hamburg Wheel-Tracking Test Moisture Results (Hill, 2011)

	Stripping Inflection Point (Wheel Passes)		
	0% RAP	**15% RAP**	**45% RAP**
Control	3,320	6,500	-
BMB	2,200	4,500	12,000
AD1	4,040	5,100	-
AD2	1,800	3,000	10,340

3.5.6 Study Effect of Dopant on Binder Rheology

To determine how the rheology of the control bitumen was affected by the addition of dopants, the dynamic shear rheometer (DSR) was used to measure modulus and phase angle at frequencies ranging from 0.1 to 100 rad/s at temperatures ranging from 76°C to 46°C. As shown by the master curves in Figure 16, the addition of the dopants had a marginal softening effect on the control bitumen.

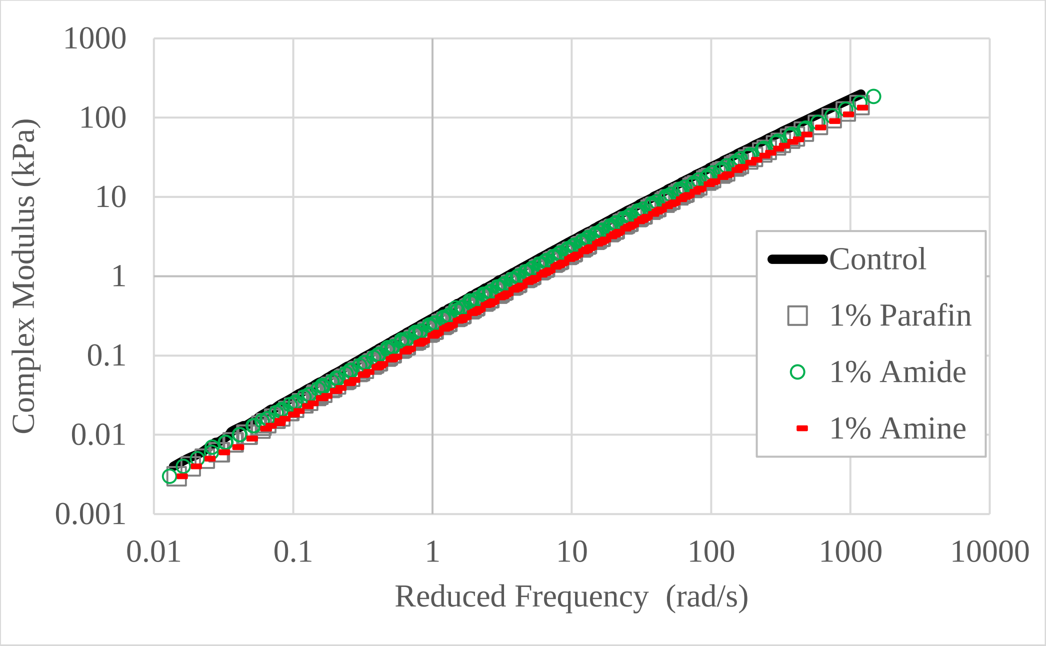

Figure 3- 16. Complex Modulus Master Curves for Control, 1% Paraffin Wax, 1% Amide, and 1% Amine Specimens.

The bonding energy was measured by calculating the area under the load-versus-displacement curve of the direct adhesion test results. Figure 17 shows that the bond energy increased with the inclusion of the amide and amine, while the paraffin was found to decrease the bond energy of the binder. The stark difference in results highlights the differing mechanisms of each of the dopants and their respective impacts on adhesion, despite using such small percentages and having similar complex moduli values.

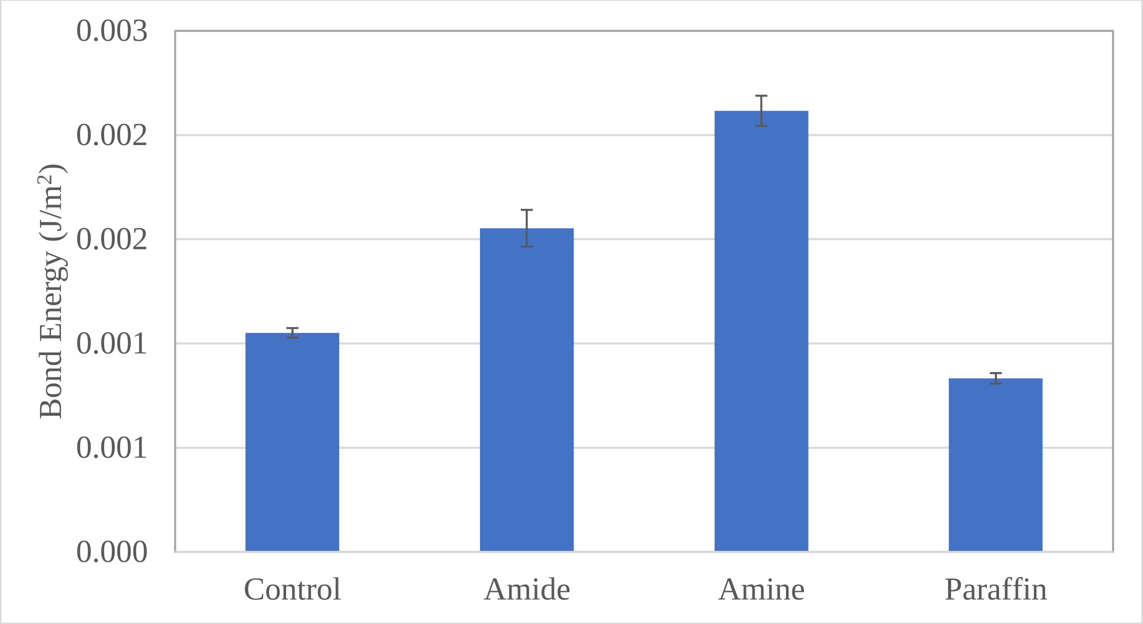

Figure 3- 17. Bond Energy Results for Control, 1% Paraffin Wax, 1% Amide, and 1% Amine Specimens.

From the results in Figure 18, the control, paraffin, and amide show only a slight difference in dry contact angle results; however, the 1% amine-doped bitumen showed a significantly higher dry contact angle. After water conditioning, the contact angle of all the bitumen samples increased significantly. It was shown that the amine-modified sample had a significantly lower contact angle compared to the rest of the specimens. To determine the effect of moisture on the bitumen's contact angle, Equation 1 was used to determine the contact-angle moisture-susceptibility index (CAMSI) for each sample.

The calculated values show that the paraffin-modified bitumen had the highest index of 32.9, followed by 21.8 for control, 13.4 for amide-modified bitumen, and 2.6 for amine-modified bitumen. From the data, it appears that the presence of the amine led to a 88%

reduction in the CAMSI index compared to control bitumen, indicating that amine-modified bitumen's adhesion to silica was least affected by the presence of water. This is consistent with previous studies showing that amines can significantly improve moisture resistance (Wasliddin et al., 2007).

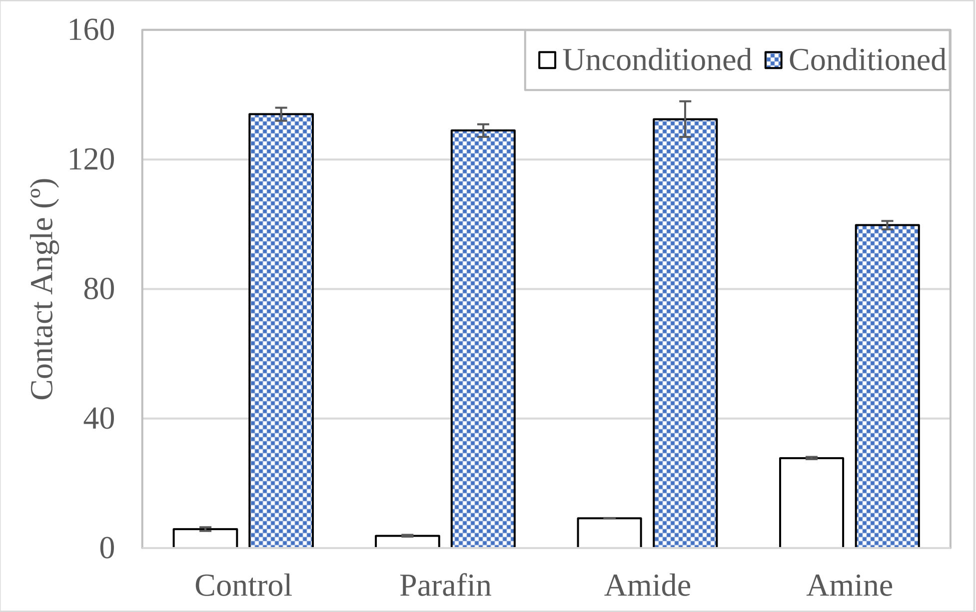

Figure 3- 18. Contact Angle Results for Dry and Water-Conditioned (Wet) Specimens.

3.5.7 Molecular Dynamics

Using molecular dynamics, dopant/asphaltene systems were created and simulated in order to determine the resulting adhesion energy of the blend to the surrogate silica surface in the presence of water. With negative values denoting attraction and positive being repulsive, the inclusion of dopants was shown in general to improve the attraction of both asphaltenes to the silica surface, as shown in Table 4. The samples that showed the strongest adhesion to the silica surface was the unaged asphaltene blends without water, with the amide blend being the strongest. However, once water is introduced, the adhesion of the amide/unaged asphaltene to the silica significantly decreases, but it is still comparable to the other molecules. The amine/unaged asphaltene blend had the highest adhesion to silica even in the presence of water. With the aged asphaltenes, the adhesion was generally lower but the change in adhesion between wet and dry with the dopants is less, thus showing more moisture resistance than the unaged asphaltenes. This trend is generally observed in the mixture results, as the mixtures with RAP were more moisture resistant. The paraffin blend was observed to be the least affected by the use of the unaged and aged asphaltenes, due to paraffin's non-polar nature.

Table 3- 4. Simulated Adhesion Energy of Asphaltene Blends using Molecular Dynamics

	Adhesion Energy with Unaged Asphaltenes ($KJ/Å^2$)			**Adhesion Energy with Aged Asphaltenes ($KJ/Å^2$)**		
	Dry	**Wet**	**Change**	**Dry**	**Wet**	**Change**
Asphaltene	**0.03**	**1.42**	**1.39**	**0.09**	**3.25**	**3.15**
Amide Blend	**-45.8**	**-0.80**	**45.0**	**-2.63**	**-0.61**	**2.02**
Amine Blend	**-7.41**	**-1.54**	**5.87**	**-2.85**	**-0.80**	**2.04**
Paraffin Blend	**-4.78**	**-0.69**	**4.09**	**-4.76**	**-0.60**	**4.16**

3.6 Summary and Conclusions

This paper investigated the merits of using Bio-modifier derived from swine manure to improve the moisture resistance of binder. At the binder level, the MSCR, the DAT, and the contact angle measurements were performed on the Bio-modified binder before and after water conditioning. Mixture-level testing with and without RAP via the modified Lottman test and the Hamburg wheel-tracking test was then performed using Bio-modified mix and compared to mixtures containing commercially available additives. To further examine the effects of the additives, representative molecules of each additive were blended with the binder to determine their specific effects on adhesion and moisture susceptibility. Finally, molecular dynamics simulations were performed for asphalts doped with each additive and placed on silica oxide substrate and exposed to water. Study results revealed the passivation mechanism of bio-modifiers is a dominant factor contributing to enhanced resistance to moisture damage. From the above investigations, the following specific conclusions were drawn:

1. It was found that bio-modifiers molecules occupy active sites of silica oxide; this in turn prevents nucleation and growth of acidic compounds at the binder-silica interface. Anchored bio-modifiers molecules further interact with asphaltene molecules to provide bridging mechanism between binder and silica which is resistance to water molecules.

2. The inclusion of 5% BMB and 10% BMB leads to a more moisture-resistant binder when bonded to a silica surface. Additionally, the direct adhesion test results showed that 10% BMB had significantly improved failure strain compared to the control binder. The differences between Bio-modified binder and non-Bio-modified binder were notable after extended moisture conditioning.

3. TSR results for the Bio-modified samples were improved compared to those of the control and AD1 but were nearly the same as AD2. The Hamburg wheel-tracking test showed better improved rutting results for the control and AD1 and decreased for BMB and AD2. However, in terms of moisture susceptibility, BMB showed improved SIP values despite in some cases having a higher rut depth. Binders doped with amide and amine functional groups showed improved adhesion and moisture-susceptibility index.

4. Molecular dynamic simulations of unaged and aged asphaltenes blended with the dopants and placed on a silica-oxide substrate showed that aged asphaltenes had lower adhesion energies to the silica surface but were more resistant to the displacement caused by water. The paraffin molecule was indifferent to the use of unaged or aged asphaltenes. The amide doped asphalt had the highest adhesion to the siliceous surface without the presence of water molecules, while the amine had the overall highest adhesion to asphalt with water molecules present.

It should be noted that this study focused on the moisture susceptibility of bio-modified asphalt from swine manure and highlighted the crucial role of the bio-modifier's composition on moisture damage; however, the composition of bio-modifiers can change after aging (Hosseinnezhad et al., 2019; Fini et al., 2016). Therefore, there is a need to study how the moisture susceptibility of various other bio-modified asphalts would change after aging. In addition, it was found that conditioning the bio-modified asphalt in water for an extended time led to a stiffening effect and could cause softening with other bio-modified asphalts. Further study is needed to decouple the effect of oxidation, water diffusion and other plausible mechanisms on stiffness and moisture damage of bio-modified asphalt.

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CHAPTER 4 MOLECULAR INTERACTIONS BETWEEN MODIFIERS AND ASPHALT MATRIX

4.1 Abstract

Many bio-modifiers have recently been introduced to the asphalt industry to improve the performance of asphalt mixtures, rejuvenate aged asphalt, and/or partially replace asphalt binder. It is critical to screen these bio-modifiers for their susceptibility to moisture damage before they are used in construction. This study develops a computational approach and a laboratory technique to predict the moisture susceptibility of modifiers used in asphalt binder mixtures. The computational approach uses the “polarizability” factor, which is one of the conceptual descriptors in density functional theory. Polarizability is indicative of the formation of instantaneous dipoles that are oriented in the applied field. A lower polarizability indicates a lower propensity of the chemical species to interact with other species in their chemical environment. The laboratory method defines a moisture-induced shear-thinning index. Moisture-induced shear thinning measures the loss of interfacial bonds between asphalt binder and siliceous surfaces due to water exposure. Both proposed indicators are used to evaluate and compare bio-modifiers from four sources: waste vegetable oil, swine manure, algae, and a co-liquefied blend of swine-manure and algae. In a comparative study, waste vegetable oil with a high content of long-chain alkanes and fatty acids showed the highest polarizability and the highest moisture-induced shear-thinning index, indicating the highest susceptibility to moisture damage. In contrast, the chemical composition of the bio-modifier produced from the co-liquefaction of swine manure and algae showed the lowest polarizability and the lowest moisture-induced shear-thinning index, indicating the highest resistance to moisture damage.

4.2 Introduction

Moisture damage is a common distress in asphalt pavements that leads to rapid deterioration in pavement quality. Asphalt pavements are mixtures of stone aggregates, asphalt binder, and additives. A reduction in pavement integrity due to moisture damage can manifest in several ways, including adhesive failure and cohesive failure. Adhesive failure (stripping) occurs in the interfacial bonds between the binder and the stone aggregates; cohesive failure occurs within the asphalt binder due to the weakening of intermolecular forces and breaking of the bonds (Canestrari et al., 2010; Terrel & Al-Swailmi, 1994; Chaturabong & Bahia, 2018; Kakar et al., 2015). Adhesive forces in the binder-aggregate interface are strongly affected by the chemistry and physico-mechanical properties of the individual components: the binder and the aggregates. The chemical compositions and molecular structures of the binder constituents are key factors in the strength and nature of the bonds formed within or between components. Though adhesive failure is known as the major contributing factor, moisture damage is basically attributed to a combination of mechanisms leading to premature failure in asphalt concrete pavement (Kakar et al., 2015).

Although some key aspects of moisture damage are not fully understood, a variety of modifiers, polymers, anti-strip additives, and new technologies such as warm-mix asphalt have been introduced to improve the resistance of asphalt concrete to moisture damage. In recent years, new bio-additives derived from biomass have become promising candidates to function as partial replacements (a modifier replaces less than 10% of the asphalt binder) or direct alternatives for asphalt binder (Raouf & Williams, 2010) The primary source (biomass) of the bio-based materials encompasses a range of biodegradable substances with animal or vegetal origin, such as wood-based materials (Yang et al., 2013; Yang et al., 2014), microalgae (Chailleux et al., 2012), waste cooking oil (Sun et al., 2016; Chen et al., 2014; Wen et al., 2012), corn stover (Raouf & Williams, 2010), and swine waste (Fini et al., 2011; You et al., 2011; Xiu et al., 2011). Based on laboratory evaluations using the Hamburg wheel-tracking test, the modified Lottman test, the semi-circular bending test, and the thermal stress restrained specimen test, bio-modified asphalt binders have shown improved mechanical properties compared to conventional mixtures. (Tayh et al., 2014; Mohammad et al., 2013). With respect to moisture susceptibility, the tests conducted give different results for bio-binders modified with bio-oils derived from different primary sources.

Studies show that binders containing bio-modifiers made from swine manure are less susceptible to both moisture and oxidative aging (Fini et al., 2015). The effect of 5% % bio-oil from swine manure (by weight of binder) on a mix containing 40% recycled asphalt pavement (Mogawer et al., 2012). The results indicated that while the cracking resistance of the mixture was improved, no difference was found for rutting and moisture damage. The Hamburg wheel-tracking test, as an indication of susceptibility to stripping, was performed on five modifiers: waste vegetable oil, waste vegetable grease, organic oil, distilled tall oil, and aromatic extract. The test results indicated that waste vegetable oil could not pass the criterion required for moisture susceptibility (Zaumanis et al., 2014). In another laboratory evaluation performed on a series of bio-binders modified by pine oil, not all the bio-modified samples passed the stripping inflection point, indicating their moisture susceptibility. Compatibility of a bio-oil with virgin binder and the quantity required for optimum blending are two additional concerns that should be addressed through mixture testing. Use of incompatible bio-oils or too high a percentage of bio-oil could be associated with loss of cohesion and adhesion, leading to raveling and moisture damage (Zaumanis et al., 2014).

Currently, moisture damage susceptibility is assessed through field investigations (Chaturabong et al., 2018), laboratory experiments (Solaimanian et al., 2003), and analytical studies (Kakar et al., 2015However, with the introduction of new materials and modern technologies to enhance asphalt binder's properties, there is an increased need for indicators that can predict the moisture susceptibility of a modified binder. This study describes two indicators to identify the bio-based materials that have lower moisture susceptibility. The first estimation relies on the appropriateness of a particular descriptor in conceptual density functional theory (DFT) in predicting the moisture susceptibility of a modified binder. The basic idea in conceptual DFT (Parr & Yang, 1995; Geerlings et al., 2003; De Proft & Geerlings, 2001; Ayers et al., 2005; Geerlings et al., 2014) (also known as chemical or chemical reactivity DFT) is that every reaction of a system is associated with a perturbation in the number of electrons, external potential, or both: $E(N, v), (\partial E/\partial N)_v$ and $(\partial E/\partial v)_N$. The extent of perturbation determines the response of the system to the external agent and offers an answer to the question of how strongly the system is perturbed during the reaction (Geerlings et al., 2014). In the context of conceptual DFT, several reactivity descriptors have been introduced to analyze chemical reactivity and site selectivity, such as global hardness and softness (Cárdenas et al., 2011; De Proft et al., 2007), the Fukui function (Sablon et al., 2007), electronegativity, and polarizability. This study focuses on the feasibility of using polarizability as a potential indicator to predict susceptibility to moisture damage.

In a comparative study, the DFT-based polarizabilities are calculated and compared for four bio-oils with animal or vegetal origin: waste vegetable oil, swine-manure oil, *C. merolae* algae oil, and a mixture of swine-manure oil and algae oil. Our theoretical findings at the micro level are verified by experiment data obtained from rheology-based descriptors of moisture susceptibility, contact-angle moisture-susceptibility test results, and moisture-induced shear-thinning ratios.

4.3 Materials and Methods

4.3.1 Computational Details

In the theoretical section, molecular-level calculations were performed through a density functional approach embedded in the Gaussian 09 package (Frisch et al., 2009). Becke's three-parameter hybrid exchange functional and the Lee-Yang-Parr correlation functional (B3LYP) (Becke, 1993; Lee et al., 1988) were used as the functional**.**

Polarizability (α) was calculated here at the B3LYP/6-311G* level to evaluate the reactivity of compounds in four different bio-oils. The α quantity is computed in terms of its *x*, *y*, *z* components using Equation 1:

$$\langle\alpha\rangle = \frac{1}{3}\left[\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right] \tag{1}$$

4.3.2 Bio-Oil Production

For this study, bio-oil production started with three feedstocks of biomass: algae, pretreated swine manure, and crude waste vegetable oil. These were converted into four bio-oils: algae oil, swine-manure oil, oil from a co-liquified mixture of algae oil and swine-manure oil, and waste vegetable oil. The algae is a unicellular species of red algae called Galdieria sulphuraria. (Hirooka and Miyagishima, 2016). Due to its acidophilic and thermophilic nature, the algae was maintained in a solution of cyanidium sulfate and ammonium sulfate with a vitamin component at 40°C for growth at the Center for Algae Technology and Innovation (AzCATI) at the Arizona State University Polytechnic Campus in Mesa, AZ. (Dandamudi et al., 2017). The second biomass was pretreated swine manure that was obtained from the Mt. Olive, NC, facility of Bio-Adhesive Alliance Inc. The conversion of the biomasses into bio-oils used a hydrothermal liquefaction process. The algae sample and the swine-manure sample were weighed respectively to obtain a 20% concentration by dry weight to distilled water. For the co-liquefied sample, the amount of algae and the amount of swine manure were each exactly half of the total dry mass. The slurry was then poured into a stainless steel cylindrical chamber and continually stirred while being heated to 330°C using a Parr 4843 bench-top reactor. After the reaction was completed and the reactor was brought to standard temperature and pressure, the solution was removed and blended with dichloromethane; this was followed by solvent extraction using a rotation viscometer. The resulting bio-oil was then sealed and stored at 4°C until testing. The third biomass was crude waste vegetable oil obtained from Mahoney Environmental Inc., Phoenix, AZ, a processing facility for waste cooking oil. The process consists of initially filtering out remaining large food debris, followed by heat separation at 180°C. The typical yield of waste vegetable oil (WVO) from the filtered solution is 80%, with the additional 20% being waste vegetable grease. The final separated WVO has a moisture, impurities, unsaponifiables (MIU) of 2% or less and an average free fatty acid (FFA) content of 4.5%.

4.3.3 Gas Chromatography Mass Spectrometry

The chemical composition of each bio-oil was determined using gas chromatography / mass spectrometry. Samples were diluted with dichloromethane before being injected into an Agilent 6890N GC 5973N Single Quadrupole mass spectrometer for vaporization and ionization detection.

4.3.4 Asphalt Binder Samples

The asphalt binder selected for the experiments was obtained from Associated Asphalt in Greensboro, NC, and has an unaged performance grade of PG64-22. This asphalt binder grade is commonly used across the United States. Two types of binder sample were extracted from the original binder, denoted as Binder A and Binder B. Binder A was the base binder used for the contact-angle measurements and the bitumen bond-strength test. Binder B was the base binder for the shear-rate test. Samples of algae oil, swine-manure oil, the co-liquefied blend of algae and swine manure, and waste vegetable oil were added to bitumen at 5% and 10% concentrations by weight of the base binder, then blended at 135°C for 5 minutes.

4.3.5 Contact Angle Moisture Susceptibility

Contact-angle measurements of asphalt binder on a chemically sterilized glass substrate were performed in order to determine the corresponding interfacial energy. The glass substrates were first prepared by sonication for 10 minutes first in acetone, followed by isopropanol, then water. The substrates were dried using nitrogen gas and placed in UV ozone for 15 minutes. Within an hour of the glass substrate being cleaned, a 15-mg droplet of a modified asphalt binder was placed in the middle of the glass. Both the droplet and glass substrate were cured in an oven at 150°C for

30 minutes. The corresponding contact angle was measured after annealing for 1 hour at room temperature. For moisture conditioning, samples were placed into a vial of 5 mL deionized water for 2 hours at 80°C. The vial was then carefully placed into a water bath at room temperature for 5 minutes. The sample was then removed and lightly dried using nitrogen gas before contact-angle measurement. Measurements were taken using a ramé-hart Model 260 standard contact-angle goniometer at room temperature. A total of 12 readings were taken of each asphalt binder before and after exposure to water. The contact-angle moisture-susceptibility index was then determined for each specimen using Equation 2.

$$Contact\ Angle\ Moisture\ Susceptiblty\ Index = \frac{(Contact\ Angle_{Wet} - Contact\ Angle_{Dry})}{Contact\ Angle_{Dry}} \quad (2)$$

4.3.6 Moisture-Induced Shear Thinning Index (MISTI)

In order to determine the moisture susceptibility of the intermolecular interaction between asphalt binder and aggregates, the moisture-induced shear-thinning index was determined using an Anton-Parr MCR 302. Samples were made by blending the asphalt binder with 50% glass beads by weight of binder; the glass beads had a selected diameter of 100 microns. The samples were mixed for 5 minutes at 145°C, then 10 samples weighing 0.3 grams each were poured into 8-mm molds and annealed for 30 minutes. Five were tested immediately in the dry state; the other five were demolded and placed into distilled water at 60°C for 24 hours, then removed from the water bath and lightly dried before testing. A ramping shear rate of 0.1 to 420 1/s was selected for the test, with the testing temperature being adjusted in order to obtain an initial viscosity of approximately 1000 Pa.s. Once the graph of viscosity versus shear rate was obtained, a power-law equation was fitted to the steepest portion of the shear-thinning curve to calculate the slope. An example of this is shown in Figure 1. The Moisture-Induced Shear-Thinning Index was then determined using Equation 4.

$$\text{Moisture Induced Shear Susceptibilty Ratio} = \frac{\text{Power Law Fitted Slope of Conditioned Sample}}{\textit{Power Law Fitted Slope of Unconditioned Sample}} \quad (4)$$

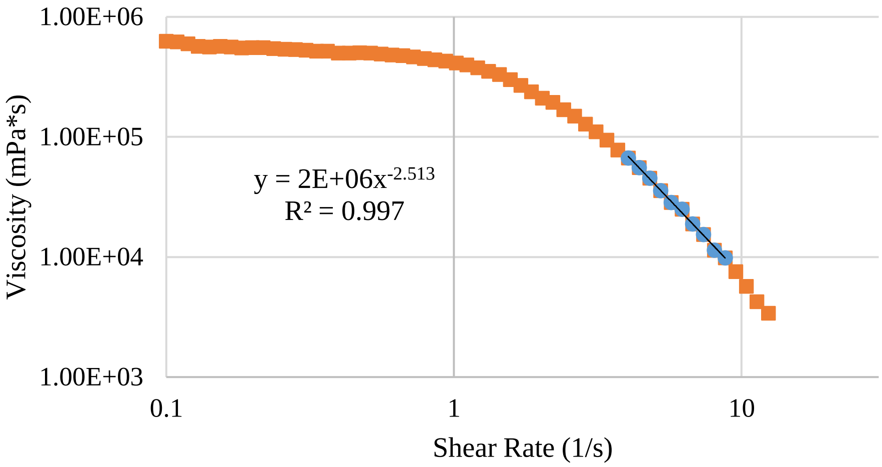

Figure 4- 1 Shear Thinning Curve Determination Example

4.4 Results and Discussion

4.4.1 Polarizability of Waste Vegetable Oil Compounds

The use of waste vegetable oil in asphalt binder has been previously studied. At 12% dosage by weight of binder, waste vegetable oil with a composition of sunflower and canola oils, having large concentrations of oleic and linoleic acids, can rejuvenate aged asphalt, increasing its fatigue (service) life; however, the waste vegetable oil negatively impacted the asphalt binder's resistance to moisture (Zaumanis et al., 2014).

Based on the GC/MS area of the individual compounds detected by mass spectrometry, accounting for 87% of the total area, 10 molecules of waste vegetable oil and their corresponding DFT-based polarizability values are shown in Table 4-1; molecular structures of the species listed are shown in the supporting information (SI) file, Table S1. As shown in this table, the fatty acid composition of the waste vegetable oil used in this study consists of a high percentage of cis-vaccenic (44%), dihomolinoleic (14%), and octadecanoic (12%) acids. As evidenced by the high polarizability values, the electron densities of saturated and unsaturated long-chain fatty acids in this waste vegetable oil are easily affected by the external electric field; this could be due to the proximity of other ions or dipoles such as water molecules. The high polarizability values of waste vegetable bio-oil compounds facilitate the formation of instantaneous dipoles that are oriented in the applied field. Such electron-cloud deformation is an indicator of chemical softness of these compounds in waste vegetable oil and their greater propensity for interaction with highly polar active species present in the environment, such as water molecules or oxygen-carrying chemical agents; a greater propensity for interaction with water molecules increases the moisture susceptibility of asphalt binder modified by this waste vegetable oil.

Table 4- 1 DFT-based Polarizability Values for Molecular Species Identified in Waste Vegetable Oil. The Corresponding Molecular Structures are shown in SI as Table S1.

	Waste Vegetable Oil	Formula	Area %	α (Bohr^3)
1	cis-Vaccenic acid	C18H34O2	44	216.09
2	Dihomolinoleic acid	C18H32O2	14	225.09
3	Octadecanoic acid	C18H36O2	12	216.40
4	Glyceryl monooleate	C21H40O4	5	260.42
5	2-Undecen-1-ol, (E)-	C11H22O	3	134.16
6	2-Linoleoylglycerol	C21H38O4	2	260.76
7	Palmitic acid vinyl ester	C18H34O2	2	217.92
8	Glycidyl oleate	C21H38O3	2	217.92
9	10-Undecynoic acid	C11H18O2	2	126.57
10	Glycidyl palmitate	C19H36O3	1	228.91
			87%	

4.4.2 Polarizability of Algal-Oil Compounds

The target algal bio-oil in this study is produced through hydrothermal liquefaction of a low-lipid microalgae named *Cyanidioschyzon merolae* (*C. merolae*). The primitive red algae *C. merolae* is a small organism (1.5 μm in diameter) living in thermal acidic environments (pH 1.5, 45°C) such as hot springs and geysers in volcanic areas such as Yellowstone National Park in the U.S. and Java in Indonesia (De Luca et al., 1978) The yield and chemical composition of the liquefied bio-oil depend on the composition of the origin biomass. Based on biochemical analysis of the microalgal feedstock, *C. merolae* is rich in carbohydrates and proteins. As shown in Table 4-2, taken from reference,[34] the lipid content of the *C. merolae* feedstock is low: 4.35% ± 0.91. The high content of protein in *C. merolae* , 47.8% ± 1.6, leads to a high nitrogen content in the liquefied bio-oil.

Table 4- 2 Biochemical and Elemental Analysis of C. merolae.

Biochemical (wt.%)	
Lipids	4.35 ± 0.91
Proteins	47.8 ± 1.6
Carbohydrates	37.85
Elemental (wt.%)	
C	48.13
H	5.14
N	9.99
S	1.24
O[a]	35.5
High heating value (MJ.kg $^{-1}$)	18.11

[a] Calculated by difference

Based on studies performed on hydrothermally liquefied *C. merolae* bio-oil using Gas Chromatography / Mass Spectroscopy (GC/MS), the bio-oil produced from *C. merolae* is a complex mixture of various compounds including fatty acids, saturated and unsaturated alkenes, phenols, and aromatic and polar compounds such as oxygen- and nitrogen-containing compounds (Dandamudi et al., 2017). The molecular structures of the first ten compounds identified in *C. merolae* algae oil are shown in SI file Table S2. As shown in Table 4-3, the long-chain fatty acid of hexadecanoic acid, with a peak area percentage of 9.7%, is one of the main compounds detected in *C. merolae* bio-oil; it is followed by a series of saturated and unsaturated alkenes. Long-chain alkanes of the algae oil, such as undecane derivatives in Table 4-3, are mostly attributed to the decarboxylation of the fatty acids in temperatures higher than 310ºC (Watanabe et al., 2006). The high polarizability values for long-chain fatty acids (Table 1 for WVO, and Table 3 for algae oil) compared to other compounds make them more vulnerable to organic acids and indicate their propensity to physically/chemically interact with water molecules.

As shown in Table 4-1, long-chain fatty acids in WVO such as cis-vaccenic acid, dihomolinoleic acid, and octadecanoic acid contribute to at least 70% of the total peak area, whereas the contribution of long-chain fatty acids in algae oil slightly exceeds 10%, indicating the presence of more moisture-susceptible compounds in WVO compared to algae oil. In parallel, the polarizability values for the first 10 compounds available in WVO and *C. merolae* oil have been plotted in Figure 4-2 to provide insight into the trend ruling the moisture susceptibility of the compounds in the two bio-oils. As clearly shown, *C. merolae* molecules are considerably less polarizable than WVO molecules. This means that algae molecules will be less affected by the presence of polar groups such as water molecules.

Table 4- 3 DFT-based Polarizability Values for Molecular Species Identified in *C. merolae* Algae Oil. The Corresponding Molecular Structures are shown in SI as Table S2.

	Algae Oil	**Formula**	**Area%**	**α (Bohr^3)**
1	n-Hexadecanoic acid	C16H32O2	9.7	191.90
2	Heptane, 2,4-dimethyl-	C9H20	6.7	103.60
3	Undecane, 3,7-dimethyl-	C13H28	6.3	152.06
4	Octane, 4-methyl-	C9H20	6.1	105.38
5	1-Undecene	C11H22	5.3	131.26
6	Phenol	C6H6O	5.2	63.25
7	2-Pentanol, 4-methyl-	C6H14O	4.6	73.31
8	Undecane, 4,7-dimethyl-	C13H28	4.5	152.00
9	Undecane, 5-methyl-	C12H26	3.4	141.03
10	p-Cresol	C7H8O	3.4	76.52
			55.2%	
	Algae Oil (Nitrogen-containing Compounds)			
11	Pyrazine, 2,5-dimethyl-	C6H8N2	3.3	76.83
12	Indole	C8H7N	3.3	87.79
13	Pyrazine, methyl-	C5H6N2	3.2	62.97
14	Cyclo(L-prolyl-L-valine)	C10H16N2O2	2.6	123.51
15	N,3-Diethyl-3-octanamine	C12H27N	2.5	146.30
16	N-Butylnonan-1-amine	C13H29N	2.5	162.39
17	Pentanamide	C5H11NO	2.0	66.16
15	Pyrazine, trimethyl-	C7H10N2	1.9	89.64
19	Pyrazine, ethyl-	C6H8N2	1.7	74.62
20	N,N-Diethyloctadecanamide	C22H45NO	1.7	268.72
			24.7%	

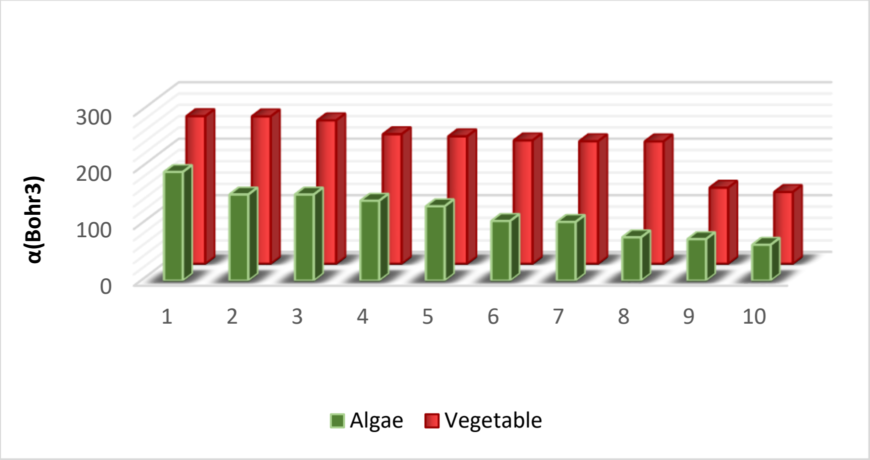

Figure 4- 2 Comparison of the Polarizability Values of the first 10 Compounds of WVO and *C. merolae* Algae Oil. The Values are taken from Tables 4-1 and 3 and sorted from Maximum to Minimum.

It is worth mentioning that the first 10 molecules of WVO, with the highest contribution percentage, cover 87% of the total compounds detected by the mass spectrophotometer; the first 10 molecules of *C. merolae* algae cover 55.2% of the total compounds detected. Liquefaction of a microalgae with high protein content usually results in an oil with high nitrogen content (Minowa et al., 1995; Yang et al., 2004), so a notable percentage of nitrogen-containing compounds is expected for liquefaction of the *C. merolae* feedstock containing a high content of protein (47.8% ± 1.6). As shown in Table 4-3, about 25% of algae compounds are in the form of small cyclic and acyclic molecules such as indole, amine, amide, and pyrazine derivatives, which are produced through conversion of amino acids (H_2N-CHR-COOH) during hydrothermal liquefaction processes. From the polarizability standpoint, these small organic molecules are mostly less polarizable than long-chain alkanes or fatty acids, reinforcing the idea that algae compounds are mainly less moisture susceptible compared to those in WVO.

4.4.3 Polarizability of Swine Manure Oil

Aside from the contribution of swine manure in fertilizers, storing excess manure is a significant challenge in manure-management practices. Traditional storage systems such as lagoons and high stacks cannot control the environmental factors impacting the microbial survival in these areas. Animal manure is an important source of emissions of trace gases such as CO_2 and methane (CH_4) into the atmosphere. Manure deposition can potentially be dispersed across large drainage areas. Converting swine manure into bio-adhesive or asphalt bio-binder could be a solution not only for aged asphalt but also for the challenge of manure management.

In the present study, the swine-waste oil is provided through thermochemical liquefaction processing of swine manure under relatively high temperature (T=305 ºC) and pressure (P=10.3 MPa) in a batch isothermal reactor. The chemical characterization of the material using GC/MS and NMR[12] indicates a molecular weight distribution of 250-450 g/mol, which is notably lower than that of petroleum-asphalt binder with an average molecular weight of approximately 700 g/mol.

Vardon et al.'s studies show that swine manure has a moderate lipid and high carbohydrate content, with a distribution of 25% protein, 22% lipid, and 37% carbohydrate including lignin, cellulose, and hemicellulose (Vardon et al., 2011). An abbreviated listing of the molecules detected in swine manure bio-oil is shown in Table 4-4 (Xiu et al., 2010); the corresponding molecular structures are shown in SI file, Table S3. As shown in this table, hexadecanoic, oleic, and pentadecanoic fatty acids make a notable contribution to the total peak percentage (52.6%). The protein content in swine manure (25%) is considerably lower than that in *C. merolae* algae (~48%), and consequently the nitrogen percentage in swine manure oil (~4%) (Vardon et al., 2011; Xiu et al., 2010; Fini et al., 2011) is lower than that in *C. merolae* algae (~10%) (Dandamudi et al., 2017). However, after fatty acids, nitrogen-containing compounds, particularly amides, are notably present in the chemical composition of swine manure: amide derivatives such as dodecanamide, octadecenamide, and heptanamide are among the main compounds found in swine-manure oil (Table 4-4). Phenols in this table (in addition to ketones) are the result of carbohydrate conversion.

The molecular species detected in swine-manure oil are not as light as algae-based molecules and comparatively have higher polarizability values. However, the lower polarizability values of the main compounds of swine-manure oil (Table 4-4) compared to those of WVO show better moisture resistance for the bio-binders modified by swine-manure bio-oil. In Figure 4-3, the polarizability values are compared for the first 10 compounds of swine-manure oil, which cover 71% of the total peak area, and those for WVO, which cover 87% of the total peak area. The slightly lower polarizability of swine-manure compounds compared to WVO may be explained by swine manure's higher content of carbohydrate, which has a lower conversion efficiency in comparison with lipids. Biller and Ross have shown that both proteins and lipids are converted to oil most efficiently without the use of catalysts, while carbohydrates need catalysts, such as Na_2CO_3, to be well processed. (Biller & Ross, 2011).

Table 4- 4 DFT-based Polarizability Values for Molecular Species Identified in Swine-Manure Oil (Xiu et al., 2010). The Corresponding Molecular Structures are shown in SI as Table S3.

	Swine Manure Oil	Formula	Area %	α (Bohr^3)
1	Hexadecanoic acid	$C_{16}H_{32}O_2$	28.2	191.90
2	Oleic Acid	$C_{18}H_{34}O_2$	24.4	216.69
3	Dodecanamide	$C_{12}H_{25}NO$	5.5	148.91
4	9-Octadecenamide, (Z)-	$C_{18}H_{35}NO$	2.6	220.65
5	Heptanamide, 4-ethyl-5-methyl-	$C_{10}H_{21}NO$	2.4	122.47
6	Hexanal,O-methyloxime	$C_7H_{15}NO$	2.3	96.87
7	Phenol	C_6H_6O	1.5	63.25
8	Limonene dioxide	$C_{10}H_{16}O_2$	1.5	109.61
9	Phenol, 4-ethyl-	$C_8H_{10}O$	1.3	88.44
10	Pentadecanoic acid	$C_{15}H_{30}O_2$	1.3	179.95
			71%	

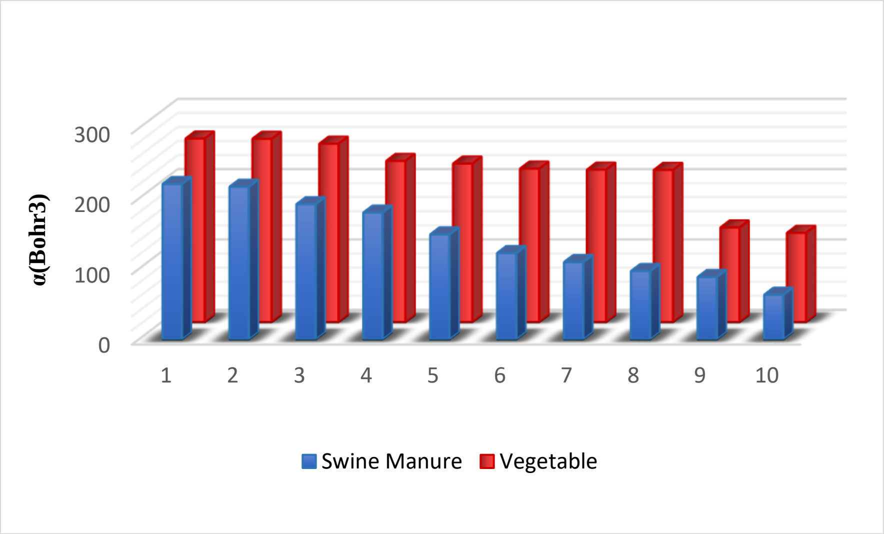

Figure 4- 3 Comparing the Polarizability Values for the first 10 compounds of Waste Vegetable and Swine Manure Oil. The Values are taken from Tables 2 and 5 and sorted from Maximum to Minimum.

4.4.4 Polarizability of Co-liquefied Swine Waste-Algae Oil (Co-liquefied Oil)

So far, it has been shown that the individual liquefaction of *C. merolae* is a high-protein (~48%) low-lipid (~5%) source, and swine manure is a moderate-lipid (~22%) high-carbohydrate (~37%) source. The molecular species of a co-liquefaction mix of *C. merolae* and swine manure are shown in Table 4-5; the corresponding molecular structures are shown in SI file, Table S4. It should be noted that the chemical composition shown in the GC/MS spectrum for the co-liquefaction product is largely affected by the feedstock combination ratios; the chemical compounds shown in Table 4-5 are for a mix with a 1:1 ratio of swine manure and algae. Comparison of the GC/MS results for the main chemical compounds detected in co-liquefied mixed bio-oil with those of each individual bio-oil shows that nitrogen-containing compounds in cyclic structures have increased notably among the main compounds in co-liquefied mixed bio-oil. A notable reduction is also observed for the long-chain alkane and fatty acid molecules in the mixed bio-oil, suggesting that degradation of carbohydrates and lipids is increased. Interestingly, the size of the main compounds in the mixed bio-oil is notably decreased compared to that in each individual bio-oil. The reduction in polarizability values (Table 4-5, Figure 4-4) of the compounds detected in the co-liquefied mixed bio-oil compared to swine-manure oil and *C. merolae* oil predicts a lower moisture susceptibility for the co-liquefied mixed bio-oil.

Table 4- 5. DFT-based Polarizability Values for Molecular Species Identified in a Bio-Oil resulting from the Co-Liquefaction of Swine Manure and *C. merolae* Algae. The Corresponding Molecular Structures are shown in SI as Table S4.

	Co-liquefied Oil	Formula	Area %	α (Bohr^3)
1	p-Cresol	C_7H_8O	6	76.52
2	Phenol	C_6H_6O	3	63.25
3	2-Pyrrolidinone, 1-methyl-	C_5H_9NO	3	62.85
4	1-Ethyl-2-pyrrolidinone	$C_6H_{11}NO$	3	74.42
5	Piperidine, 1-pentyl-	$C_{10}H_{21}N$	3	122.27
6	9H-Pyrido[3,4-b]indole, 1-methyl-	$C_{12}H_{10}N_2$	3	144.94
7	Myristamide, N-methyl-	$C_{15}H_{31}NO$	3	186
8	Phenol, 4-ethyl-	$C_8H_{10}O$	2	88.44
9	Piperidine, 1-butyl-	$C_9H_{19}N$	2	110.35
10	Benzonitrile, 2,4,6-trimethyl-	$C_{10}H_{11}N$	1	113.94
			29%	

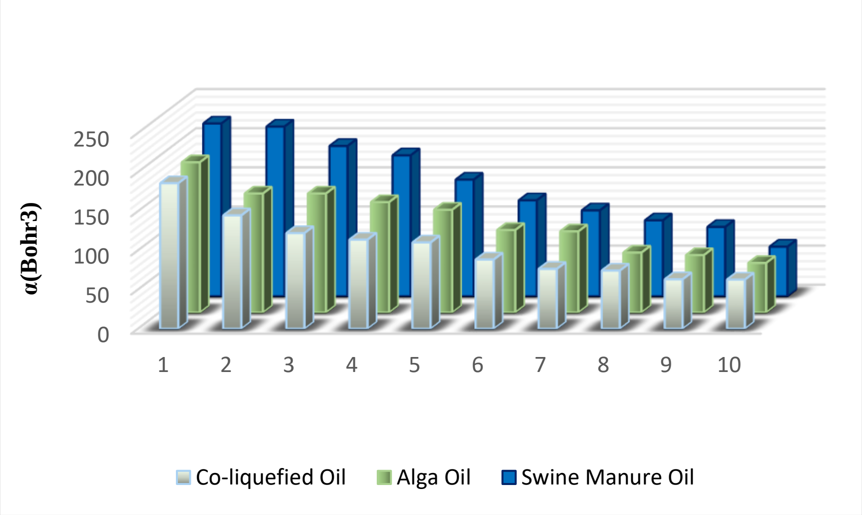

Figure 4- 4 Comparing the Polarizability Values for the first 10 compounds of Swine-Manure Oil, *C. merolae* Algae Oil, and a Co-Liquefied Mixture of Swine-Manure and *C. merolae* Algae.

4.4.5 Contact Angle Moisture Susceptibility

The contact-angle values for the four bio-modified asphalt binders clearly show the differential effect of bio-modifiers on the binder's surface energy and wettability (Hung et al., 2017; Fini et al., 2017). In the presence of water, the contact angle of binder modified with algae oil showed little to no change. This was in-line with study performed by Hosseinnezhad et al. The samples with co-liquefied oil and swine-manure oil performed similarly, while the change in contact angle for conditioned WVO was significantly higher than all other scenarios (Figure 4-5).

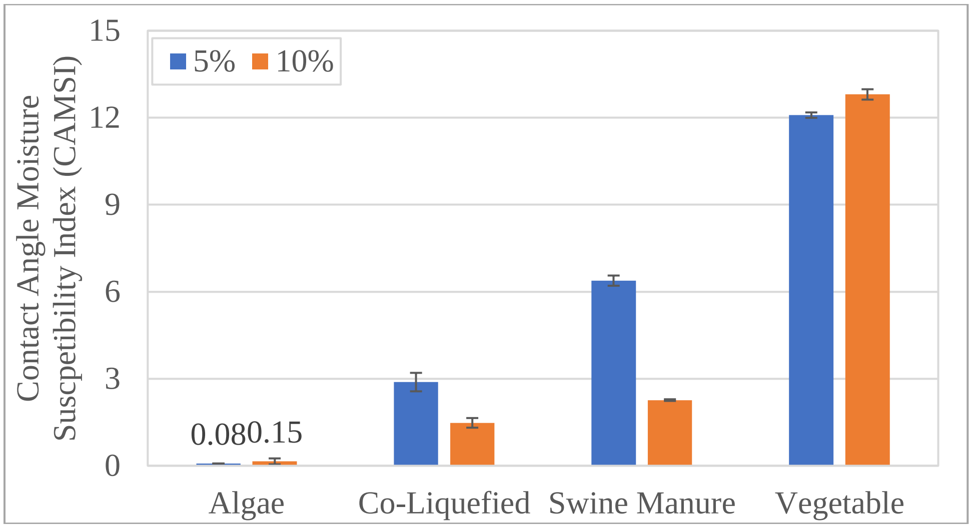

Figure 4- 5 Contact Angle Moisture Susceptibility Index for the 5% and 10% Bio-Modified Binder Samples.

4.4.6 Moisture-Induced Shear Thinning Index (MISTI).

The rate of shear thinning was calculated using a power-law model fitted to viscosity verse shear rate data beyond the onset of thinning. The ratio of the power-law slopes for dry samples and wet samples (MISTI – see Equation 4) was used as an indicator of the loss of intermolecular interactions between asphalt and glass beads; glass beads were used as inclusions in binder as a proxy for siliceous stone interfaces. The results show the co-liquefied oil had the lowest MISTI (the least susceptible to moisture damage), followed by algae oil and swine-manure oil. The binder modified with WVO had the highest MISTI (the most susceptible to moisture damage), due to WVO's large amounts of polarizable molecules (Figure 4-6).

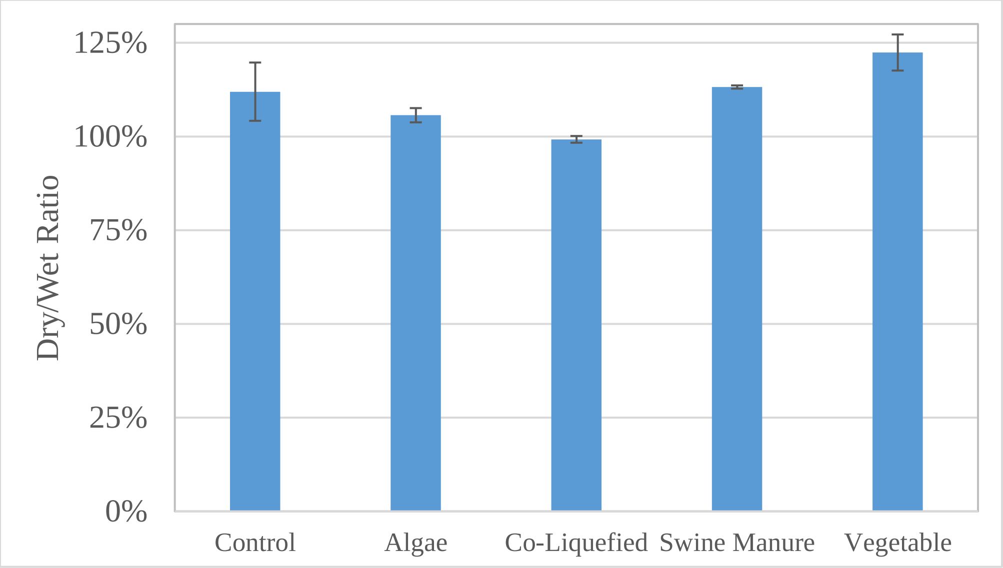

Figure 4- 6 Moisture-Induced Susceptibility Index for Bio-Modified Binder

4.5 Conclusion

The reduction in pavement integrity due to exposure to moisture manifests itself in stripping of the binder from the stone aggregate or in cohesive failure within the binder. However, current test methods are not adequate to detect binders that are susceptible to moisture damage before they are used in construction. This study introduced two indicators to evaluate the moisture susceptibility of bitumen based on fundamental material properties: polarizability at the molecular level; and a Moisture-Induced Shear Thinning Index (MISTI) at the macro level. Since some bio-modifiers used in the asphalt industry are implicated in moisture damage, the applicability of the proposed indicators was verified in the context of four bio-modifiers with known chemical compositions: waste vegetable oil, swine-manure oil, *C. merolae* algae oil, and a co-liquefied blend of swine-manure and algae.

A lower polarizability and a lower MISTI value indicate a lower susceptibility to moisture damage. Based on the study results, waste vegetable oil had the highest polarizability and MISTI values compared to the other bio-oils, suggesting that the waste vegetable oil, with a high content of long-chain alkanes and fatty acids, has the highest propensity for interaction with surrounding polar groups such as water molecules. This result is in accordance with the field observations and laboratory results from the Hamburg wheel-tracking test that show high moisture susceptibility for binder modified with waste vegetable oil (Zaumanis et al., 2014). For manufacturers, the insights provided in this study, in terms of the relationship between composition of modifiers and moisture resistance of bitumen, can allow for the design of highly effective modifiers. Based on this study's newly developed indicators, polarizability and MISTI, for the four bio-oils tested, the co-liquefied 1:1 mix of swine manure and *C. merolae* algae is predicted to have the lowest susceptibility to moisture damage, followed by *C. merolae* algae oil, then swine-manure oil; the highest susceptibility to moisture damage is predicted for waste vegetable oil.

4.6 References

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4.7 Supporting Information

Molecular structures of the compounds identified in waste vegetable oil, swine-manure oil, *C. merolae* algae oil, and a co-liquefied 1:1 mixture of swine manure and algae are shown below in Table 4-6, 4-7, 4-8, and 4-9.

Table 4- 6 Supporting Table Waste Vegetable Oil.

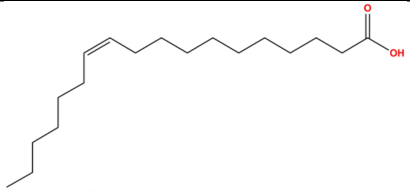
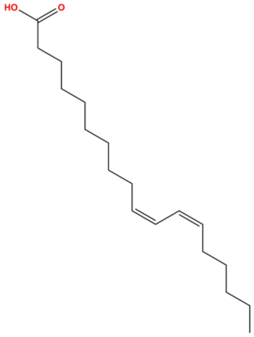
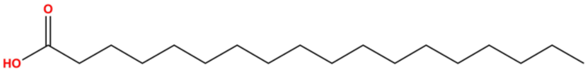
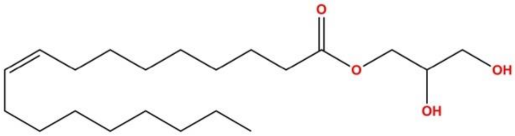
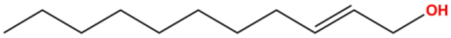
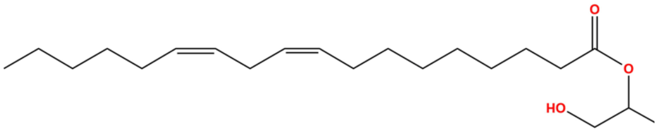
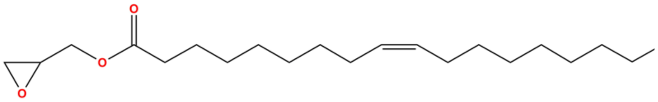
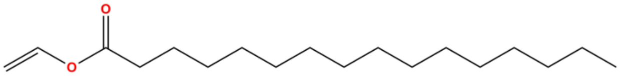
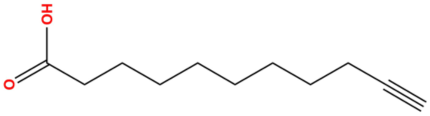
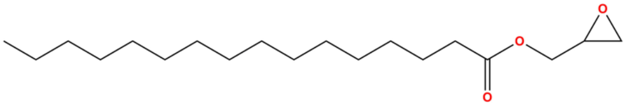
Waste Vegetable Oil	**%**	**polarizability (α)**	**Molecular Structure**
cis-Vaccenic acid	44	216.09	
Dihomolinoleic acid	14	225.09	
Octadecanoic acid	12	216.40	
Glyceryl monooleate	5	260.42	
2-Undecen-1-ol, (E)-	3	134.16	
2-Linoleoylglycerol	2	260.76	
Glycidyl oleate	2	253.39	
Palmitic acid vinyl ester	2	217.92	
10-Undecynoic acid	2	126.57	
Glycidyl palmitate	1	228.91	

Table 4- 7. Supporting Table Swine-Manure Oil

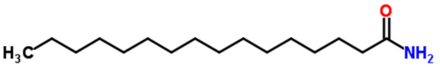
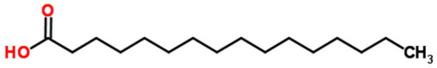
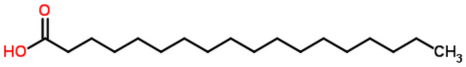
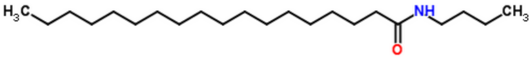
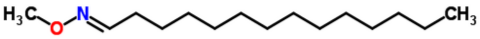
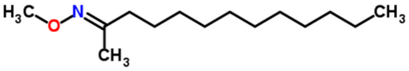
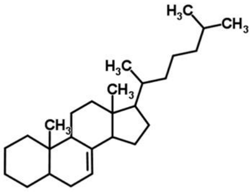
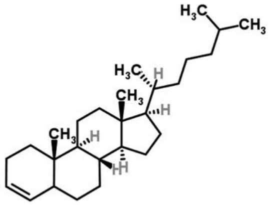
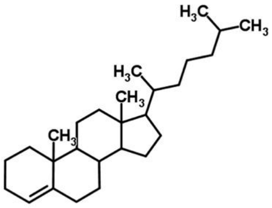
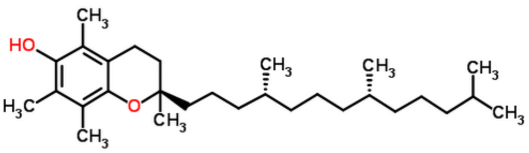
Swine-Manure Oil	**%**	**polarizability (α)**	**Molecular Structure**
Hexadecanamide (bb1)		196.68	
Hexadecanoic acid (bb6)		192.49	
Octadecanoic acid (bb7)		216.40	
n-Butyl octadecanamide (bb2)		269.65	
Tetradecanal o-methyloxime (bb8)		192.38	
2-Tridecanone o-methyloxime (bb9)		178.92	
Cholest-7-ene (bb3)		290.88	
Cholest-3-ene (bb4)		293.71	
Cholest-4-ene (bb5)		292.49	
α-Tocopherol (bb10)		337.40	

Table 4- 8 Supporting Table Co-Liquefied Oil

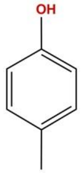
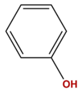
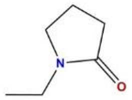
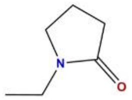
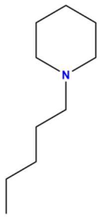
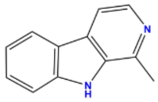
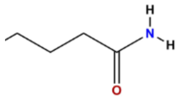
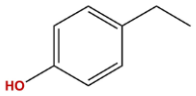
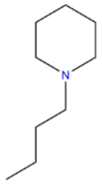
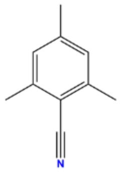
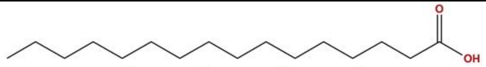
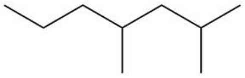
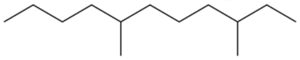
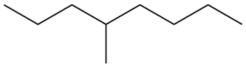
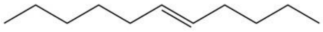
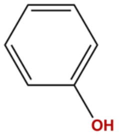
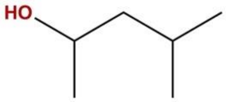
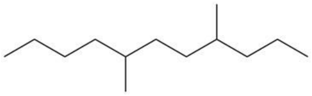
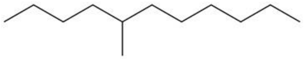
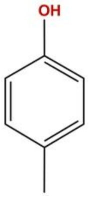
Swine-Manure Oil + Algae Oil	%	polarizability (α)	Molecular Structure
p-Cresol	6	76.52	
Phenol	3	63.25	
2-Pyrrolidinone, 1-methyl-	3	62.85	
1-Ethyl-2-pyrrolidinone	3	74.42	
Piperidine, 1-pentyl-	3	122.27	
9H-Pyrido[3,4-b]indole, 1-methyl-	3	144.94	
N-Methyl tetradecanamide	3	186.00	
Phenol, 4-ethyl-	2	88.44	
Piperidine, 1-butyl-	2	110.35	
Benzonitrile, 2,4,6-trimethyl-	1	113.94	

Table 4- 9 Supporting Table Algae Oil

Algae Oil	**%**	**polarizability (α)**	**Molecular Structure**
n-Hexadecanoic acid	9.7	191.90	
Heptane, 2,4-dimethyl-	6.7	103.60	
Undecane, 3,7-dimethyl-	6.3	152.06	
Octane, 4-methyl-	6.1	105.38	
1-Undecene	5.3	131.26	
Phenol	5.2	63.25	
2-Pentanol, 4-methyl-	4.6	73.31	
Undecane, 4,7-dimethyl-	4.5	152.00	
Undecane, 5-methyl-	3.4	141.03	
p-Cresol	3.4	76.52	

CHAPTER 5 DEVELOP TEST METHODS TO EVALUATE MOISTURE SUSCEPTIBILITY OF ASPHALT

5.1 Abstract

Moisture damage in asphalt pavement is a costly distress which often occurs at the bottom of the asphalt layer and is not detectable until major pavement damage has already occurred. Therefore, understanding the effect of moisture on asphalt is necessary to improve pavement durability and enhance service life. Although moisture damage is mainly associated with the bonding behavior of bitumen and aggregate, factors such as the composition of the water to which the pavement is being exposed should also be considered. Therefore, this paper studies how the properties of bitumen and asphalt mixture can change due to exposure to either acidic or salt water. The Tensile Strength Ratio (TSR) test was utilized for mixture testing while binder testing consisted of the Binder Bond Strength (BBS), Shear Rate Test (SRT), and Contact Angle (CA) measurements before and after water conditioning in distilled, acid, and salt water. It was shown that acidic water could accelerate damage both in mixture and binder level while specimens conditioned in salt water did not show a significant increase in moisture susceptibility compared to distilled water conditioning.

Keywords: Moisture damage, water composition, acid, salt, pH, bitumen

5.2 Introduction

It has been clearly shown in the lab as well as in the field that the effect of moisture on asphalt pavements has a significant impact on the overall pavement's performance (Don et al., 2008). Detrimental pavement performance can lead to large economic, social, and environmental costs.

The effect of oxygen present in the atmosphere is commonly known to cause aging and hardening of bitumen. In addition, studies have also found that the presence of moisture not only accelerates pavement aging and hardening (Huang, et al., 2012) but also affects the bitumen–aggregate interface (Fini, et al., 2019). The amount of oxidation in asphalt due to moisture is increased when it is combined with the traffic load, especially when the pavement contains cracks (Obando, 2017). The goal of pavement maintenance is to prevent water from entering cracks in the asphalt and thus causing further damage (Cox, et al., 2018).

Additionally, many studies have shown that certain chemicals and contaminants in water could accelerate pavement damage (Xue, et al., 2016) (Hossain, et al., 2016). The exposure of pavements to salt is common in coastal areas because of the tidal inundations (Setiadji, et al., 2017) and in colder regions due to the use of de-icing agents on highway pavements (Hassan, et al., 2002). The impact of different de-icing materials, based on salt concentration, has attracted the attention of many researchers (Wang, et al., 2017). Some studies suggest that the level of damage on asphalt depends on the concentration of salt (Setiadji, et al., 2017) while other research has reported that the combined effects of salt under freeze-thaw conditions and water flow intensity cause deterioration of asphalt pavements (Amini & Tehrani, 2014).

The rapid increase of gases such as Carbon Dioxide (CO_2), Nitrogen Oxide (NO), and Sulfur Dioxide (SO_2) has caused the atmosphere to become increasingly acidic. The occurrence of acid rain has been found to be prevalent and consistent in various areas within industrial cities (Hong Kong Meteorological Society, 2003). Therefore, it has been noted that acid rain could accelerate the deterioration of the pavements (Obando, 2017) (Xue, et al., 2016). Chemical studies have shown that the accumulation of alkane acids at the bitumen-silica interface increased the chance of hydrolysis when exposed to water thus causing the acceleration of moisture damage (Fini, et al., 2019). It is hypothesized that the presence of acid and other contaminants in water could increase moisture damage. Therefore, this paper studies the effect of acidic and salt water on the mixture and bitumen level via a comprehensive laboratory testing.

5.3 Materials

5.3.1 Mixtures

This study utilizes two field mixtures one containing 0% RAP and the other 15% RAP. The samples were manufactured by Southwest Asphalt and were placed by the City of Phoenix, Arizona. Sampling occurred in-situ from three different trucks before leaving the asphalt plant (Zalghout, 2019). **Table 1** shows the gradation for both the Control and 15% RAP mixtures which contain 1.1% of hydrated lime and no antistripping agents.

Table 5- 1 Gradation of Aggregate within the Asphalt Mixtures

Sieve US - mm	Passing (%)	
	City of Phoenix Mix Design Target	Production Limits
1" - 25.0	100	
3/4" - 19.0	95	88 - 100
1/2" - 12.50	85	78 - 92
3/8" - 9.50	75	68 - 82
#4 - 4.75	58	51 - 65
#8 - 2.36	44	39 - 49
#30 - 0.600	24	19 - 29
#200 - 0.075	4.0	2.0 - 6.0

Before compacting the samples, equal portions of each truck mix were taken and thoroughly blended to ensure a representative mix was achieved. Afterwards, the blended samples were placed in the oven for 1 hour at 150ºC before compaction.

5.3.2 Asphalt Binders

The control binder for this study was a PG 70-10 and was provided by Western Refining located in Phoenix, Arizona. The 15% RAP binder was acquired by means of solvent extraction from the field produced mixtures following ASTM D5404. The 15% RAP mixtures had approximately 88.4% virgin PG 70-10 by weight when blended at the asphalt plant. The specific gravities of control and 15% RAP binders were 1.021 and 1.050 at 25ºC respectively. Additional analysis on the rheological properties of the control and RAP properties can be found elsewhere (Zalghout, 2019).

5.3.3 Preparation of Conditioning Water (Salt and Acidic Water)

Rock salt is one of the most common types of salt used to melt snow on the pavements in the US (Howard, 2014). To simulate field salt water conditions from the use of road salt, tap water was blended with 24% rock salt. This percentage of rock salt was selected according to the procedure of melting ice used by some contractors in the US (CSX Corporation, 2016). To dissolve the rock salt in the water, the mix was hand-blended for 10 minutes. The resulting pH was measured to be 7.6.

The three main components of acid rain are carbon dioxide (CO_2), nitrogen oxide (NO), and sulfur dioxide (SO_2) (National Atmospheric Deposition Program, 2019). Among these three, CO_2 contributes the most to the acidity of rainwater (Casiday & Frey, 1998). Therefore, to accurately produce acid rain, compressed CO_2 was pumped into a container filled with distilled water (pH of 6.8) until the pH of the water decreased to 3.5. It should be noted that due to the initial loss of some CO_2 due to its phase separation from water, all tests with acidic water were performed with a final pH of 3.6 (instead of the intended 3.5).

5.3.4 Asphalt Mastic Preparation

To understand the interaction of the asphalt binder with siliceous aggregates, fine glass beads (100 micron) were blended with the asphalt binder at a concentration of 50% by weight of the binder. To prepare the mastic, the glass beads were hand-blended with the bitumen at 155°C for 5 minutes.

5.4 Methods

5.4.1 Tensile Strength Ratio (TSR)

Testing specimens were obtained after coring and cutting mixtures to a height of 180 mm and a diameter of 100 mm. The samples were subjected to moisture damage following AASHTO T283 using the freeze-thaw procedure. After vacuum saturation was performed to obtain the required saturation level, samples were placed in a freezer at 18°C for 16h, followed by being placed in a water bath at 60°C for 24h. Finally samples were placed in another water bath at 25°C for 2 hours. This procedure was performed using tap, acidic, and salt water. To prevent contamination, water conditioning was performed in glass jars and placed in the water bath as shown in Figure 1. The indirect tensile strength was measured using an IPC T-100 Universal Testing Machine (UTM). The tensile strength ratio (TSR) was calculated using Equation 1.

$$\text{Tensile Strength Ratio (TSR)} = \frac{\text{Average tensile strength of the conditioned subset } (\mathrm{S_{tw}})}{\text{Average tensile strength of the unconditioned subset } (\mathrm{S_{td}})} \qquad (1)$$

Figure 5- 1 Containers for Conditioning Samples in Salt and Acidic Water

5.4.2 Binder Bond Strength (BBS) test

The pull-off tensile strength of asphalt binder from a siliceous surface was measured and determined via the bitumen bond strength test according to AASHTO TP 91. In order to have a consistent surface for testing and one composed of a SiO_2, glass was selected as the surface substrate. The testing apparatus was the PATTI Quantum Gold Model which was calibrated before each testing set to a loading rate of 100 psi/second. The pull-off strength moisture susceptibility ratio is defined simply as the ratio of dry to wet pull-off strength.

5.4.3 Shear Rate Test (SRT)

The change in viscosity was observed under a ramping shear rate from 0.1 to 420 1/s to observe the transition from zero shear viscosity to shear-thinning behavior. This has been reported to relate to the molecular interaction within the asphalt binder material (Choi, et al., 2017). The testing temperature was adjusted to accommodate an initial viscosity of approximately 1000 Pa.s which has been noted as an optimal viscosity range for observing shear thinning behavior. The instrument utilized was an Anton Parr MCR 302 dynamic shear rheometer; the test was performed using an 8 mm parallel plates. five replicates were tested and the average of three was reported.

5.4.4 Contact Angle (CA)

The asphalt binder’s susceptibility to stripping was observed by measuring the contact angle of asphalt binder on a glass slide before and after water conditioning. The substrate used as a surrogate for siliceous stone aggregates was glass, which were first chemically cleaned using acetone, isopropanol, and water followed by 15 minutes in the UV-Ozone cleaner. Moisture conditioning occurred at 80°C for 2 hours followed by drying with nitrogen gas. Measurements were taken using a ramé-hart Model 260 standard contact angle goniometer. Six readings were collected in different areas of the dry (unconditioned) and the wet (conditioned) samples.

5.5 Results and Discussion

5.5.1 Tensile Strength Ratio

Results of the tensile strength ratio test showed higher strength values of the unconditioned specimen compared to conditioned ones, which is in-line with previous field studies (Kim & Hwangb, 2003). The strength of 15% RAP mixtures were higher than control which is also in agreement with prior work (Maaty & Ibrahim Elmohr, 2015). Based on the average peak tensile strength results, the Tensile Strength Ratio (TSR) was estimated. Table 2 shows a summary of the results.

Table 5- 2 Peak Tensile Stresses and TSR Results for Control and 15% RAP samples.

Type of Sample	Aspect	Unconditioned	Tap Water Conditioned	Salt Water Conditioned	Acidic Water Conditioned
Control	Average Indirect Tensile Strength (kPa)	1312.6	1077.3	1161.2	936.7
	COV (3 samples)	2.6%	2.1%	7.2%	8.6%
	TSR		**82.1%**	**88.5%**	**71.4%**
15%RAP	Average Indirect Tensile Strength (kPa)	1540.4	1235.8	1352.3	1062.4
	COV (3 samples)	3.4%	6.0%	3.6%	8.1%
	TSR		**80.2%**	**87.8%**	**69.0%**

As can be seen, the strength of the conditioned samples after 24 hours in salt water slightly increased compared to those conditioned in tap water. However, the difference was not statistically significant. According to (Moore & Mitchell, 1974) the small increase in the tensile strength could be related to the aggregate composition-pore water chemical interactions.

On the other hand, samples conditioned in acidic water showed 10.7% and 11.2% decrease in tensile strength for Control and 15%RAP, respectively. In addition, it was noticed that after acid water conditioning, some fine aggregates were separated from the samples and precipitated to the bottom of the conditioning bath. The effect of acid water on the pavements is classified as a chemical erosion which starts with the loss of properties in the asphalt matrix (Xue, et al., 2016).

Regarding to the TSR results, both control and 15%RAP samples had values over 80% when the conditioning was in tap water while salt water conditioned samples showed a 6% increase in TSR compared to tap water conditioned specimens. It has been documented that the effect of salt on pavements is due to the cation exchange between the clay part of the pavement material and the salt water, or interface between feldspars in the aggregates and salt (de Carteret, et al., 2014). The negative effect of natural salt water such as tidal water, can be explained by the presence of additional chemicals like chloride and sulfate with varying concentrations, however, detailed information on the exact influence of each chemical compound on the pavement performance has been difficult to determine (Setiadji, et al., 2017).

The lowest TSR values were found to be the ones conditioned in acidic water. Acidic water conditioned specimens had a decrease in the TSR of around 11% compared to the ones conditioned in tap water. Therefore, moisture damage in pavements was considerably increased by exposure to acidic water. The acidic water effect causes the loss of mass in the asphalt mixture and leaves the aggregates exposed (Xue, et al., 2016). This in turn leads to a loss of bonding between aggregates and binder thus accelerating the moisture damage.

Figure 5- 2 a) Salt Water Conditioned Sample, b) Acidic Water Control Conditioned

5.5.2 Bitumen Bond Strength (BBS) test

Table 3 presents a summary of the BBS test results after different conditioning scenarios for both control PG 70-10 and the extracted binder from the 15% RAP mixtures. The 15% RAP samples showed consistently higher pull-off tensile strength values compared to the control binder. The type of failure was mostly adhesive and did not alter significantly from dry to acid and distilled conditioned samples. However, the samples conditioned in salt water failed via cohesive failure for both samples. Results for both Control and 15% showed an increase in peak tensile force required to pull-off the binder adhered to glass after water conditioning than in dry conditions. This non-intuitive behavior is because the effect of the water is limited only to the boundary edge of the binder and the glass and not through the pores of the aggregate surface as with typical aggregate substrates. This then allows us to focus solely on the impact of water on the asphalt binder's properties and ability to adhere to the surface. An increasing tensile strength after water conditioning while using glass surfaces was also observed in previous research. Through the use of LVDTs, the authors found that the higher values were actually due to the binder stiffening from the water conditioning. (Lachance-Tremblay, et al., 2019).

With that being said, the sample conditioned in acid water had the lowest pull off tensile strength compared to the distilled and salt water and the lowest. The significant differences in tensile strengths and in index values for both samples denote the impact of differing water compositions on the pull-off tensile strength of the asphalt binder from the glass surface.

Table 5- 3 Pull off Tensile Strength Summary before and after Water Conditioning

Type of Sample	Aspect	Unconditioned	Distilled Water Conditioned	Salt Water Conditioned	Acidic Water Conditioned
Control	Average Pull-off tensile Strength (kPa)	2346.0	2914.6	3085.9*	2459.4
	COV (3 samples)	7.6%	4.3%	1.9%	4.1%
	Pull-off Strength Moisture Ratio		**80%**	**95%**	**76%**
15%RAP	Average Pull-off tensile Strength (kPa)	2909.9	3236.9*	3277.6	3128.4
	COV (3 samples)	6.7%	2.0%	2.6%	5.6%
	Pull-off Strength Moisture Ratio		**90%**	**93%**	**89%**

*Actual value beyond measurable tensile force limit of the machine

5.5.3 Moisture Induced Shear Thinning Index (MISTI)

The shear rate test results for the control and 15% RAP binder blended with 50% glass beads conditioned in distilled, acid, and salt water are given in Table 4. Due to the differing viscosities, the samples were tested at 64 and 70 ºC, respectively. Despite similar viscosities and shear thinning onsets, the power law slope shows a consistently steeper slope for the control binder indicating higher intermolecular interaction between glass and unaged (control binder) than that of glass to aged binder (extracted from the 15% RAP Mixture). Exposure to acidic water significantly altered the interaction of glass and binder for both unaged and aged binder as evidenced by the shear rate moisture susceptibility index values. It is also interesting to note that the increase in zero shear viscosity was lowest for acid water conditioned samples. The increased susceptibility to the acid water could be due to the increased interaction of ions to the more polar asphaltenes components of asphalt.

Table 5- 4 Moisture Induced Shear Thinning Index Results

	Dry		Distilled Water		Acidic Water		Salt Water	
	Unaged	Aged	Unaged	Aged	Unaged	Aged	Unaged	Aged
Power Law Slope	-2.72	-2.57	-3.15	-2.54	-3.59	-2.12	-2.81	-2.22
Zero Shear Viscosity	1015	931	1150	1080	1163	999	1280	1085
Onset of Shear Thinning (1/s)	1.57	1.87	1.18	1.00	1.28	1.14	1.21	1.31
Moisture Induced Shear Thinning Index			99%	102%	96%	106%	98%	109%

5.5.4 Contact Angle (CA)

The contact angle of the asphalt binder on the glass slide before and after water conditioning was measured and are given in the Table 5. The 15% RAP sample showed a high susceptibility to change in contact angle in both the distilled and the acid water. However, the salt water showed very little change meaning the asphalt binder sample did not bead up. The control binder was also tested but the beading was not uniform and could not be accurately measured. Therefore, the mass of the samples before and after moisture conditioning were recorded and compared to determine if samples absorbed water. From the results in Table 5, the control sample mass did not change with the salt water and the change in distilled water was only 0.0001 mg. However, the mass change in acidic water was 0.0036 mg.

Table 5- 5 Contact Angle and Mass Change Results for Control and 15% RAP Specimens

Change in Contact Angle			
	Distilled	Acid	Salt
Control (Unaged)	N/a	N/a	N/a
15% RAP (Aged)	94.72°	89.12°	3.56°
Change in Mass			
	Distilled	Acid	Salt
Control (Unaged)	0.0001 mg	0.0036 mg	0 mg
15% RAP (Aged)	N/a	N/a	N/a

5.7 Authors Contributions

In this article, Carlos Obando and Daniel Oldham performed all laboratory experiments, experimental plan, analysis of the results, and participated in the definition of the research topic, Elham H. Fini provided funding, the research topic and guidance for the conduct of the research and interpretation of the data, and Kamil E. Kaloush provided funding and guidance helping for the conduct of the research and interpretation of the date.

5.6 Conclusions

Moisture damage is one of the costliest and hard to detect pavement distresses and warrants a thorough investigation of factors affecting moisture susceptibility of pavements. This study examines whether water composition and its contamination with salt and acid can accelerate moisture damage in pavement. It was found that conditioning asphalt mixture samples with acidic water significantly lower the tensile strength ratio compared to conditioning in tap and salt water. Acid water conditioning showed significantly different results compared to distilled water on the mastic and binder level as well. BBS results showed an increase in the peak tensile force required to pull the samples of binder off of the glass slides after water conditioning. However, the acid conditioned peak tensile force samples were as much as 28% lower than samples after distilled and salt water conditioning. This is also shown through the 16% increase in slope of thinning and the lower increase in binder stiffness. In addition, the change in mass of the asphalt binder was over 30 times higher in acid water than compared to distilled. Overall, acid water showed significant damage at the binder, mastic, and mixture level. The effects of salt and tap water were not shown to be significant.

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CHAPTER 6 DEVELOP METHODS TO IMPROVE RESISTANCE OF BIO-MODIFIED ASPHALT TO MOISTURE DAMAGE

6.1 Introduction

According to the Federal Highway Administration, the United States has over 8.77 million lane-miles for highway travel, with approximately 94% being made with asphalt pavement (Federal Highway Adminstration [FHWA], 2018; National Asphalt Pavement Association [NAPA], 2019). This large percentage highlights the importance of asphalt pavement research to extend performance and reduce degradation while minimizing cost. One of the primary causes of distress in asphalt pavement is moisture susceptibility. This occurs when moisture penetrates the pavement; this moisture weakens the bond between the asphalt binder and the aggregate, causing what is known as stripping. This pavement distress is expected to become increasingly important, since the US annual precipitation in 2017 was above average for the fifth consecutive year (National Centers for Environmental Information, 2018).

The most commonly used method for improving the bond between the asphalt binder and the aggregate is to modify the asphalt binder with liquid antistripping agents (Caro, 2018). It has been reported that the majority of these antistripping agents are composed of molecules containing amine functional groups (Epps et al., 2003; Logaraj, 2002). In these organic compounds, it is suggested that the amine functional group interacts generally with the surface of the aggregate, while the hydrocarbon tail interacts with the asphalt binder (Harnish, 2010). This bridging effect was modeled and observed using molecular dynamics (Oldham et al., 2017). However, this mechanism has been shown to be ineffective in variously modified asphalt binders, thus indicating a dependency on the modified binder's chemical composition as well as on the surface chemistry of the aggregate (Buddhala et al., 2012).

Mineral fillers have primarily been used for filling voids between aggregates, but mineral fillers are also a common means of reducing the moisture susceptibility of asphalt pavement (Brown et al., 2009). Mineral fillers are defined by ASTM D242 as passing the No. 16, 30, 50, and 200 sieves at 100%. 97-100%, 95-100%, and 70-100%, respectively, and being no more than 6% of a mixture by mass (Speight, 2016). Though there are certain size specifications, mineral fillers can be derived from hydrated lime, fly ash, Portland cement, steel slag, or natural sources such as crushed aggregates (Roberts et al., 1996). It has been reported that the nature of the mineral filler strongly influences whether cohesive or adhesive bond failure will occur, due to the physicochemical interaction between the mineral filler and the asphalt (Kim et al., 2002; Lesueur & Little, 1999). The evaluation of eight field sections in Nevada indicated that the use of hydrated lime extended pavement life by an average of 3 years (Sebaaly et al., 2003). Hydrated lime has been consistently used to decrease moisture susceptibility, while the use of some clays has actually increased moisture susceptibility (Diab & Enieb, 2018).

Although field evaluation of moisture damage is the most common way of determining moisture susceptibility, the replacement and repair of damaged sections of road is costly, and the field evaluation is not always accurate. In a recent study, 18 different field mixtures classified in the field for moisture performance were retested in the lab for moisture damage; it was found that 8 out of the 14 samples that were field-classified as having “poor” moisture performance showed good moisture performance in the lab. In addition, lab tests found 1 of the 4 samples that were field-classified as having “good” moisture performance showed poor performance in the lab (Crawford, 2019). Current test methods are not always able to properly detect paving mixtures that are susceptible to moisture damage.

The two main categories of asphalt mixture testing are loose-mix testing and compacted-mix testing. Loose-mix testing involves the immersion of uncompacted aggregate and binder mixtures into water at certain temperatures and durations. Examples of the tests include the static immersion test, the rolling bottle test (RBT), the boiling water test (BWT), the total water immersion test, and the ultrasonic method. Although previous research has found that the RBT and BWT showed increased sensitivity in determining moisture susceptibility, those in the industry see loose-mix testing in general as more of a quick screening method rather than predicting actual field performance (Liu et al., 2013; -Berger et al., 2003).

The most common means of testing the moisture susceptibility of mixtures uses compacted specimens. Testing methods using compacted samples consist of indirect tensile tests, also known as the modified Lottman and Root-Tunnicliff tests; in these tests, six samples are split into two subsets for testing before and after conditioning in water. The average tensile strength values of each subset are then used to calculate a ratio known as the tensile strength ratio (TSR), following AASHTO T283. This TSR test is used by more than 60% of road agencies (National Academies of Science, Engineering, and Medicine, 2007). Despite its popularity, road agencies have reported mixed success with issues such as repeatability, sample preparation, and the lack of repeated loading to simulate the effects of traffic (Berger et al., 2003). Another moisture test performed on compacted asphalt specimens is a wheel-tracking test. The most notable such test uses the Hamburg wheel-tracking device, which has been growing in popularity as a moisture susceptibly test due to its repeating loading cycle and ability to detect susceptibility to moisture (Solaimanian et al., 2007).

Though not as widely recognized, binder-level testing has also been performed in order to help predict and determine the moisture susceptibility of an aggregate/binder combination. The most notable such test measures the surface free energy by quantifying the adhesion strength at the aggregate-binder interface (Hefer et al., 2006). Although comparing surface energies of asphalt binder and aggregate is one possible way to rationally design pavement mixtures with better interfacial properties, the easiest way to calculate surface energies is by measuring the contact angle of liquid droplets on a flat binder surface. However, as easy as contact angle measurement is in theory, there are a number of practical considerations that must be taken into account when measuring liquid contact angles on asphalt binder. At the root of many of these considerations is the fact that asphalt binder is not one homogenous material, but a complex mixture of hundreds if not thousands of different molecules that may act independently of each other. Thus, it is a questionable assumption that a measurement of the binder-air interface energy would be a representative indicator of the nature of the binder-aggregate interface. An undeniable benefit of contact angle measurements is that they are quick, easy, and inexpensive, and they remain a useful characterization tool. However, they are also prone to artifacts, and sole reliance on such measurements without proper appreciation of all of the potential pitfalls could yield misleading results.

To properly evaluate the premise of the two remedial methods used to address moisture damage in this study, in addition to conventional tests, we use a newly developed test method measuring the extent of emulsification at the interface of bitumen and stone aggregates when exposed to water (Obando et al., 2020). The new test, referred to as the moisture-induced shear thinning index (MISTI) test, applies a shear rate sweep test on bitumen samples containing glass beads. The change in shear thinning rate before and after the sample is exposed to water is used as an indicator of interface degradation. Once the test is completed, the shear-thinning slope is fitted to a power-law equation to determine the intermolecular interactions between the matrix and inclusions, following the method used by Leng and coworkers in petroleum research (Choi et al., 2017). A description of the fundamental science behind the MISTI test and how it is established based on a combination of energetics at the interface and the polarizability of bitumen molecules has been published elsewhere (Mousavi et al., 2019).

It has been shown that the MISTI test can adequately detect changes in the interface properties as related to the binding interaction between the inclusion and the matrix (Obando et al., 2020). The presence of acid compounds at the interface of bitumen and siliceous stones is implicated in moisture damage to asphalt pavement (Fini et al., 2019). Nucleation and growth of alkane acids occur at the interface of bitumen and siliceous surfaces, and neutralizing silica's active sites is an effective way to prevent such nucleation (Hung et al., 2019). It has been reported that the migration of acid to silica occurs due to the attractive forces between active sites on the silica surface and acid; this migration was successfully prevented by doping the binder with hexadecylamine, which passivated the active sites on the silica surface (Hung et al., 2019).

Another means of preventing acids from binding to the silica surface is by using an arresting mechanism, which holds back the acids from migrating to the silica surface (Fini et al., 2019). This phenomenon was observed when active mineral fillers with high surface area were shown to create internal competition sites to adsorb acids, superseding the stone aggregate. This in turn distributes acids among the fillers' high surface area, reducing the share of acid for the stone aggregate surface. The latter mechanism explains how hydrated lime and Portland cement with high surface area (about 21 and 35 m^2/g, respectively) are successful at preventing moisture damage in asphalt (Mississippi Lime Company, 2020; Odler et al., 2003). Since the MISTI test has been shown to be capable of detecting changes at the interface of bitumen and siliceous inclusions, here, we use the MISTI test to evaluate the efficacy of the abovementioned remedial methods to protect the interface against water. The remedial technologies are intended to provide built-in resistance mechanisms against moisture damage by doping bitumen with active filler and additives such as sodium-montmorillonite clay (MMT) and a polyethylene terephthalate based additive (PET).

6.2 Background

PET is a widely used polyester that can be found in items such as clothing, biomedical devices, and packaging (Farah et al., 2015). The reason for PET's wide usage is its unique capability to undergo strain hardening after being stretched within the rubbery region

(Ansari et al., 2011; Wang et al., 2015). In 2014, 45.8 million tons of PET was produced; this number is expected to increase to 80.9 million tons in 2020. (Statisitica, 2016). This includes but is not limited to 485 billion PET bottles, with an expected 20% increase by 2021. There have been several studies on the recycling of PET, including a recent evaluation of the use of PET in asphalt. Use of 1% shredded PET bottles (passing sieve No. 8) in asphalt mixtures as an aggregate replacement was shown to improve fatigue performance and reduce crack propagation (Moghaddam et al., 2012). Use of PET as an aggregate replacement for stone mastic asphalt showed improvement in rutting resistance until 4% PET concentration, but resistance to moisture was compromised (Ahmadinia et al., 2012). The use of shredded and extruded PET in asphalt reduced the rutting susceptibility and fatigue parameter, but the cigar tube test indicated a significant loss of storage stability (Ameri & Nasr, 2016). Asphalt mixtures using extruded PET were reported to have improved moisture resistance, with optimal percentages being about 7.5-10% by weight of asphalt binder (Ameri & Nasr, 2016b). PET treated with polyamines through a non-catalytic means was developed and researched as an anti-stripping agent for asphalt (Padhan et al., 2013). FTIR analysis showed the formation of amide peaks, and the boiling water test showed improved coating when asphalt binder was blended with 0.3 to 1.0% PET concentration by binder weight (Leng et al., 2018). The modified PET was researched further in combination with recycled asphalt pavement (RAP), which also was found to have improved coating after the boiling water test (Sreeram et al., 2018).

The use of nano-particles has been shown to be effective in being able to reduce the aging susceptibility of asphalt binder (Yao et al., 2013; Ashish et al. 2017). The use of montmorillonite clay (MMT) has been shown to improve barrier properties when blended in a matrix at 2-5% concentration (Fukushima et al., 2008). The use of sodium montmorillonite clay (Na-MMT) with SBS-modified asphalt binder was shown to increase the asphalt binder's elastic properties and resistance to aging (Yu et al., 2007). The use of Na-MMT in plywood has been shown to exfoliate when mixed in an acid-curing environment and increase the plywood's resistance to water damage (Lei et al., 2008). The resistance to moisture damage of bitumen doped with Na-MMT was investigated by evaluating the efficacy of Na-MMT to adsorb acids, diverting them from the interface of bitumen and stones in the aggregate (Mousavi et al., 2019). It was shown that acid molecules adsorb to Na-MMT due to significant interactions of the interlayer cation of Na-MMT and the oxygen of the carbonyl functional group of acids. Therefore, here we choose two additives (PET to demonstrate passivation, Na-MMT to demonstrate an arresting mechanism) to improve asphalt's resistance to moisture damage. In two separate experiments, we introduced 2% PET or 4% Na-MMT to an asphalt binder that showed evidence of moisture damage in the field, and we evaluated each scenario. The binder-level tests were performed using the contact angle moisture-susceptibility index, bitumen bond-strength test, and the moisture-induced shear rate index; the mixture-level tests were done using the boiling water test and the Hamburg wheel-tracking test.

6.3 Materials and Methods

6.3.1 Binder Preparation

The asphalt binder used in this study was a PG 58-28 produced by Parco in Athens, New York. The Performance Grade properties of the binder are provided by VTrans shown in

Table 1. The polyethylene terephthalate based additive (denoted as PET) was obtained from the chemical synthesis of waste PET water bottles into benzamide derivatives through an aminolysis process (Leng et al., 2018). Through this treatment process using the benzamide, the PET was made compatible with the asphalt binder thus reducing the possibility of severe phase separation. The sodium montmorillonite clay (MMT) was Cloisite-Na+, with an average dry particle size of less than 25 μm, obtained from BYK USA Inc. in Gonzales, Texas. Different methods were used to account for the addition of MMT to bitumen (Table 2). In one method, MMT was simply added to bitumen by weight. In the second method, MMT replaced a portion of natural fines added to the mix by weight. In the third method, the replacement of natural fines was done based on equivalent surface area of MMT (rather than weight). Using the Brunauer, Emmett and Teller (BET) instrument, the surface area of the MMT and the natural fines were determined to be 59.78 and 7.91 m^2/g, respectively. Therefore, the total surface area of the MMT-natural fines blend was set to be equivalent to the surface area of the natural fines alone. To produce modified binder specimens, 4% MMT or 2% PET (by the weight of binder) was added to the control binder at 135°C and blended for 30 minutes at 2,500 rpm. The resulting samples are referred as MMT-doped and PET-doped binder in this study.

Table 6- 1 General Properties of the Asphalt Binder Used in This Study

Original			
Flash Point	294℃	PG Specification Limit	≥ 230℃
Rotational Viscosity	0.270 Pa*s @ 135℃		≤ 3 Pa*s @ 135℃
DSR G*/sin(δ)	1.30 kPa		≥ 1.00 kPa
Rolling Thin Film Oven (RTFO)			
Mass Change	-0.501%	PG Specification Limit	≤ 1.00%
DSR G*/sin(δ)	3.34 kPa		≥ 2.20 kPa
Pressure Aging Vessel (PAV)			
DSR G*sin(δ)	3,382 kPa	PG Specification Limit	≤ 5000 kPa
BBR Stiffness	221 MPa		≤ 300 MPa
BBR m-value	0.347		≥ 0.300

Table 6- 2 Mass and Surface Area Values for Control, PET-doped, and MMT-doped Samples.

	Mass (g)			Surface Area (m^2)		
	Natural Fines Passing No. 200	MMT	Total	Natural Fines Passing No. 200	MMT	Total
Control	47.2	0	47.2	373.4	0	373.4
PET-doped	47.2	0	47.2	373.4	0	373.4
MMT$_a$ - doped	47.2	4	51.2	373.4	239.1	612.5
MMT$_b$ - doped	43.2	4	47.2	341.7	239.1	580.8
MMT$_c$ - doped	16.7	4	20.7	132.1	239.1	371.2

6.3.2 Mixture Preparation

The aggregates for this study were obtained from the Whitcomb Quarry in Colchester, Vermont. The aggregates consist of two 3/8 stockpiles, two types of screened sand, and RAP. The gradations of each are given in Table 3. This particular mix has been reported to exhibit poor moisture resistance in the field (Mallick et al., 2019). The total asphalt binder content for the mix was 6.0%, including 5.0% virgin binder and 1.0% RAP binder contribution. The mix contained 0.5% of the WMA additive Rediset, which was blended with the base binder for 15 minutes at 1200 rpm at 120°C. The binder and the aggregate were blended and compacted at 140°C and 120°C, respectively. The only asphalt samples made for this study were for Hamburg testing; therefore, the target air void was set to 7.0%. The specific gravity results for each specimen are shown in Table 4.

Table 6- 3 Individual Stockpiles and Final Combined Gradation of Mixtures.

	3/8-B	3/8- R	WSS	DSS	RAP	
Percent Used	12%	19%	37%	12%	20%	
Sieve Size						Final Combined
1/2" (12.5 mm)	100	100	100	100	100	100
3/8" (9.5 mm)	96	97	100	100	99	99
1/4" (4.75 mm)	12	28	89	99	81	68
No. 8 (2.36 mm)	3.0	3.0	53	77	60	42
No. 16 (1.18 mm)	3.0	2.0	35	54	44	29
No. 30 (0.6 mm)	2.0	2.0	24	38	33	21
No. 50 (0.3 mm)	2.0	1.0	15	26	23	14
No. 100 (0.15 mm)	2.0	1.0	8.0	16	16	8.5
No. 200 (0.075 mm)	1.0	0.7	3.6	8.8	11.7	5.0

Table 6- 4 Average Specific Gravity and Gyration Values for Mixtures compacted to 7% Air Void for Hamburg Wheel-Tracking Test (AASHTO T-324).

	Gmm	Gmb
Control	2.482	2.309
MMT_a – doped	2.472	2.296
MMT_b – doped	2.477	2.295
MMT_c - doped	2.484	2.300
PET – doped	2.477	2.302

6.4 Experimental Procedure for the Study of Bitumen's Cohesive Properties

The rheological properties of the asphalt binder were measured by an Anton Parr MCR 302 dynamic shear rheometer using an 8-mm parallel plate setup. In particular, the crossover modulus and crossover frequency, which are corresponding values at the point at which the viscoelastic modulus and elastic modulus are equal, were determined for each specimen, using a frequency range of 0.1 to 100 rad/s and temperatures of 16, 10, and 4°C. In addition, we used an 8-mm parallel plate setup and applied shear rate sweep test to measure both the zero-shear viscosity and the shear thinning behavior of each specimen.

6.5 Experimental Procedure for the Study of Bitumen's Adhesive Properties

The following sections describe the test methods used to study bitumen's adhesion properties in both the unconditioned state and the moisture-conditioned state.

6.5.1 Contact Angle Moisture-Susceptibility Test

The evolution of the interfacial bond between bitumen and siliceous stones (glass substrates were used as a surrogate for siliceous stones) was examined using contact angle measurements. To cast specimens, the silica glass slides were sterilized in acetone, isopropanol, and water, then sonicated for 10 minutes each, followed by drying with nitrogen gas. To ensure the removal of any monolayers of materials, slides were placed into UV ozone for 15 minutes. Within an hour of cleaning, 15 mg of each binder was placed on the glass slides and left in the oven for 30 minutes at 150°C to ensure proper coating, followed by annealing at room temperature for 1 hour. For water conditioning, the samples were placed into a vial of deionized water containing 5 mL of water at 80°C for 2 hours. The vial was placed into a bath of deionized water at room temperature for 5 minutes, followed by drying using nitrogen gas. Each specimen was then imaged at room temperature using a ramé-hart Model 260 standard contact angle goniometer. The contact angles were then determined using the DROPimage Advanced software package. Twelve readings were collected for both the unconditioned (dry) and the conditioned (wet) samples. From the contact angles measured for unconditioned and moisture-conditioned samples, the contact angle moisture-susceptibility index (CAMSI) was calculated using Equation 1.

$$Contact\ Angle\ Moisture\ Susceptiblty\ Index = \frac{(Contact\ Angle_{Conditioned} - Contact\ Angle_{Unconditioned})}{Contact\ Angle_{Unconditioned}} \quad [1]$$

6.5.2 Moisture-Induced Shear Thinning Index (MISTI)

For the moisture-induced shear thinning index, the samples were tested using the dynamic shear rheometer at a ramping shear rate from 0.1 to 420 1/s using the 8-mm spindle, in order to observe the change in viscosity of the material and in particular the shear thinning slope. It was observed that the optimal initial viscosity for observing the shear thinning slope is approximately 1Pa.s. Therefore, the testing temperature of 58°C was used to maintain 1Pa.s viscosity. In order to observe the effect of moisture damage between aggregate and binder, the asphalt binder was blended with 50% (by weight of the binder) glass beads with diameter of 100 microns. The glass bead size was selected to be several orders of magnitude smaller than the sample thickness.

Ten samples all measured to 0.30 grams were prepared; five of the samples were tested without water conditioning, and the other five were conditioned in distilled water at 60°C for 24 hours. After removing samples from the water, they were surface-dried before placing and trimming in the DSR at 25°C. The average of three replicates was used to determine the MISTI, which is defined as the ratio of shear thinning slopes of the unconditioned to moisture-conditioned samples.

6.5.3 Bitumen Bond-Strength Test (BBS)

The bitumen bond-strength test was performed according to AASHTO TP 91. Two substrates were selected for this study. The first was a solid glass substrate, in order to test the samples with a consistent and uniform roughness. The second substrate was cored and cut from a single large sedimentary rock obtained from the Glendale Quarry of Fisher Sand & Gravel; this is used widely in pavements in the area of Phoenix, Arizona. The moisture absorption of the stone was found to be 1.17%. Before testing, the aggregate surface was cleaned using an ultrasonic cleaner at 60°C for 1 hour in distilled water, followed by oven heating for 30 minutes at 60°C to remove the water. For the glass substrate, the samples were first submerged in acetone for 10 minutes before being cleaned using the ultrasonic cleaner. The pullout stubs were also placed in the oven at 60°C for 30 minutes for preheating purposes. Approximately 0.4 grams of asphalt binder was poured into an 8-mm DSR mold and allowed to cool to room temperature for 30 minutes. After preheating, the asphalt binder was placed on pullout stubs for 10 seconds, then immediately placed onto the preheated aggregate and allowed to sit for 24 hours before testing. For water conditioned samples, after 1 hour of sitting, the samples were placed into a water bath at 40°C for 24 hours. Afterwards, the samples were taken out and allowed to sit at room temperature for 1 hour before testing. Before testing, the pullout apparatus was calibrated to apply approximately 100 psi/second of load, to ensure a consistent loading rate on the samples. The pull-off strength moisture-susceptibility index was calculated using Equation [2] (Lachance-Tremblay et al., 2019).

$$\frac{Wet_{pull-off\ Strength} - Dry_{pull-off\ strength}}{Dry_{pull-off\ strength}}\ X\ 100\% \qquad [2]$$

6.5.4 Boiling Water Test (BWT)

The boiling water test was used in order to visually observe the stripping effects of the binder from the stone aggregates. To do so, 250 grams of uncompacted asphalt was separated and spread across a pan before being placed into the oven; once the samples reached 97°C, they were taken out of the oven and placed into 1800 mL of boiling distilled water. which was at a temperature of 99.2°C. After 10 minutes, the sample was cooled to room temperature. The stripped binder was skimmed off the top in order to prevent any recoating of aggregates. Once the water reached room temperature, the water was removed, and the sample was placed on a paper towel to dry for 24 hours before being evaluated (ASTM D3625).

6.5.5 Attenuated Total Reflectance Fourier-Transform Infrared Spectroscopy (ATR-FTIR)

The chemical analysis of the samples before and after the BWT was determined by attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR). The unit used is a Bruker FT-IR Spectrometer using a diamond ATR. The scanning range was set to 4000 cm-1 to 400 cm-1.

6.5.6 Hamburg Wheel-Tracking Test

The Hamburg wheel-tracking test was performed following AASHTO T-324. In this test, a steel wheel (158 lb) is tracked across the surface of a submerged asphalt mixture specimen for a selected number of cycles while the rut depth is continuously measured. The test duration was set to 20,000 passes or if the rut depth goes higher than 12.5 mm. The water-bath temperature was 45°C based on the binder grade used in the mixture. From the graph of rut depth versus number of wheel passes, the creep and moisture stripping slopes are obtained. The stripping inflection point has been shown to be an indicator of the moisture susceptibility of mixtures.

6.6 Results and Discussion

6*.6.1 Cohesive Properties Via the DSR*

Each specimen was characterized based on the elastic modulus and loss modulus as well as the crossover modulus and crossover frequency, which are corresponding values at the point where the elastic modulus is equal to the loss modulus. The crossover modulus for bitumen samples containing MMT decreased by 10% and those containing PET decreased by 27% compared to control bitumen (Figure 1). The effect of the MMT and PET was even more evident in case of crossover frequency (Figure 2). The crossover frequency of MMT-doped bitumen decreased by 71%, while that for bitumen containing PET decreased by 85%. The combination of both values denotes that the control binder becomes stiffer with both modifications. The stiffening effect from the MMT can be explained by the presence of the active filler increasing intermolecular interactions, while the PET stiffness can be attributed to polymerization within the binder.

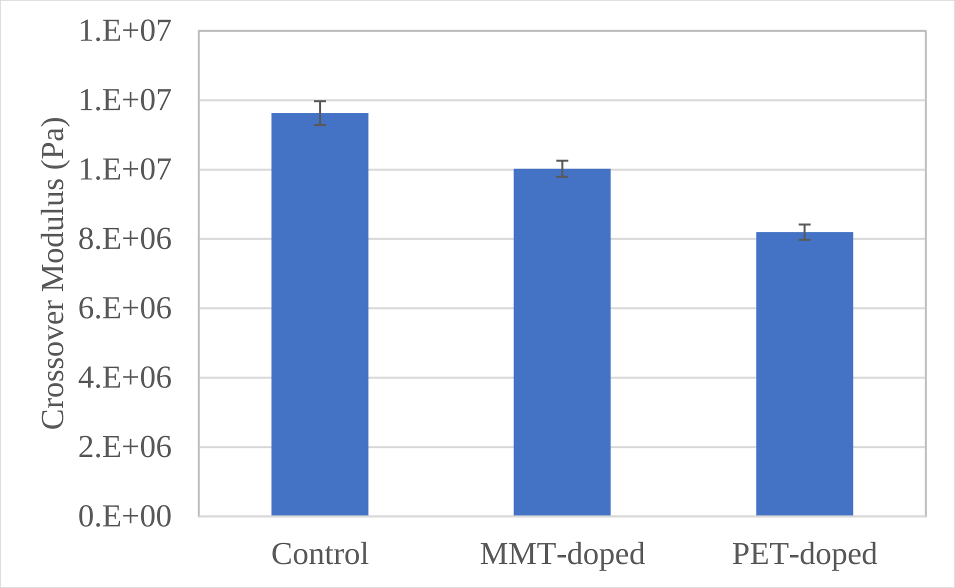

Figure 6- 1 Crossover Modulus of Control, MMT-doped, and PET-doped Samples at 10°C.

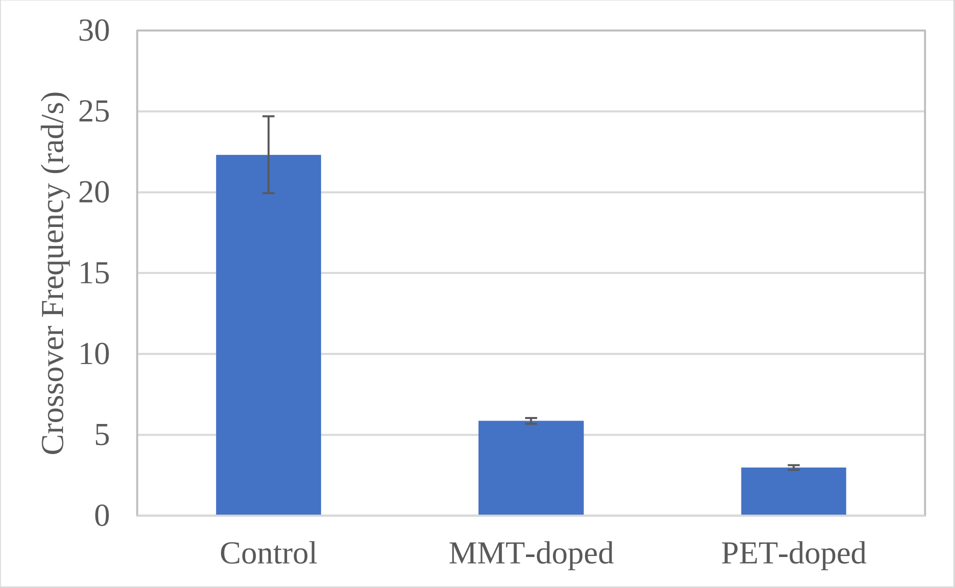

Figure 6- 2 Crossover Frequency of Control, MMT-doped, and PET-doped Samples at 10°C.

To further examine the cohesive properties of bitumen, the zero-shear viscosity and shear thinning behavior were examined. As shown in Figure 3, the zero-shear viscosities of both modified binders are nearly the same, with the viscosity value being significantly higher than that of the control binder. However, the control binder shear thinning occurs at a higher shear rate (delayed shear thinning), indicating higher cohesive energy in the bulk compared to modified scenarios. This was reflected in the onset of shear thinning of neat binder, which occurred at a significantly higher shear rate. In addition, the slope of the power-law curve of viscosity versus shear rate was found to be 13% higher for both PET-doped and MMT-doped binders (2.84), compared to the control binder (2.51). A higher slope may indicate higher intermolecular interactions owing to the presence of amine groups in PET as well as the high affinity of MMT platelets with select molecules in the asphalt binder. The higher slope of shear thinning leads to lower viscosity at shear rates above 1/s. For instance, at a shear rate of 3, the viscosity of the PET-doped specimen is 69 Pa*s, followed by the MMT-doped (150 Pa*s) and control (269 Pa*s) specimens. The lower viscosity indicates lower resistance to shear, which in turn facilitates relative movement of stone aggregates in the mixture. It should be noted that the shear rate during compaction is much higher than what is typically applied in the lab. A study by Yildirim and Kennedy showed the shear rate inside the Superpave Gyratory Compactor was approximately 490 1/s. (Yildirim and Kennedy, 2003). Considering the small film thickness around stone aggregate where the localized shear occurs, the shear rate can be far beyond the onset shear rate of thinning behavior. This further explains how bitumen with a high thinning behavior showed low compaction energy.

Furthermore, comparing the PET-doped and MMT-doped specimens, the MMT-doped specimen showed even lower compaction, which may be attributed to its weak interparticle interactions. The mechanical energy applied during compaction, as well as the presence of the amines within the amine-based additive used as a warm mix additive (Fini et al., 2017), may facilitate exfoliation of silica platelets, which may in turn reduce the energy required for compaction.

The latter was evidenced in a significantly lower number of gyratory for PET-doped and MMT-doped specimens compared to control. While the control mixture required 43 gyratory to reach 7% air void, PET-doped and MMT-doped scenarios needed 38 and 34 gyratory, respectively (Table 5).

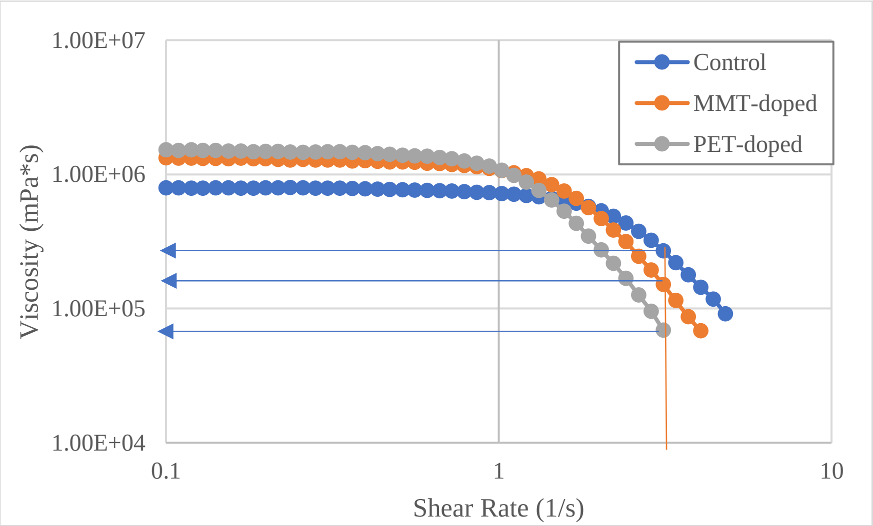

Figure 6- 3 Viscosity Versus Shear Rate of Control, MMT-doped, and PET-doped Samples at 58°C.

Table 6- 5 Average Gyration Values for Mixtures Compacted to 7% Air Void for Hamburg Wheel-Tracking Test (AASHTO T-324).

	Number of Gyrations
Control	43
MMT-doped	34
PET-doped	38

6.6.2 Contact Angle Moisture-Susceptibly Test

The behavior of each specimen before and after water conditioning is shown in Figure 4. After 2 hours at 80°C, it is shown that the control asphalt binder completely beaded up and de-wetted from the glass slide substrate. This indicates a decreased affinity of the SiO2 surface and an increased affinity to the water. The PET-doped samples are shown to have beaded up much lower than that of the control, indicating an increased affinity for the glass slide. The MMT doped binder samples behaved non-uniformly. The fact that the unconditioned MMT-doped binder sample shows a normal-looking droplet while the conditioned one loses its shape indicates some large expansion of the binder due to the exposure to water. This is consistent with the nature of MMT, which has been reported to swell in the presence of water due to the expansion of the spacing between silica platelets within the material, due to the hydration of the sodium ions (Peng et al., 2019). Considering that MMT can play as an active filler to arrest acidic compounds in bitumen (Mousavi et al., 2019), should the swelling be prevented via chemical treatment, MMT could be a promising low-cost additive for use in pavements.

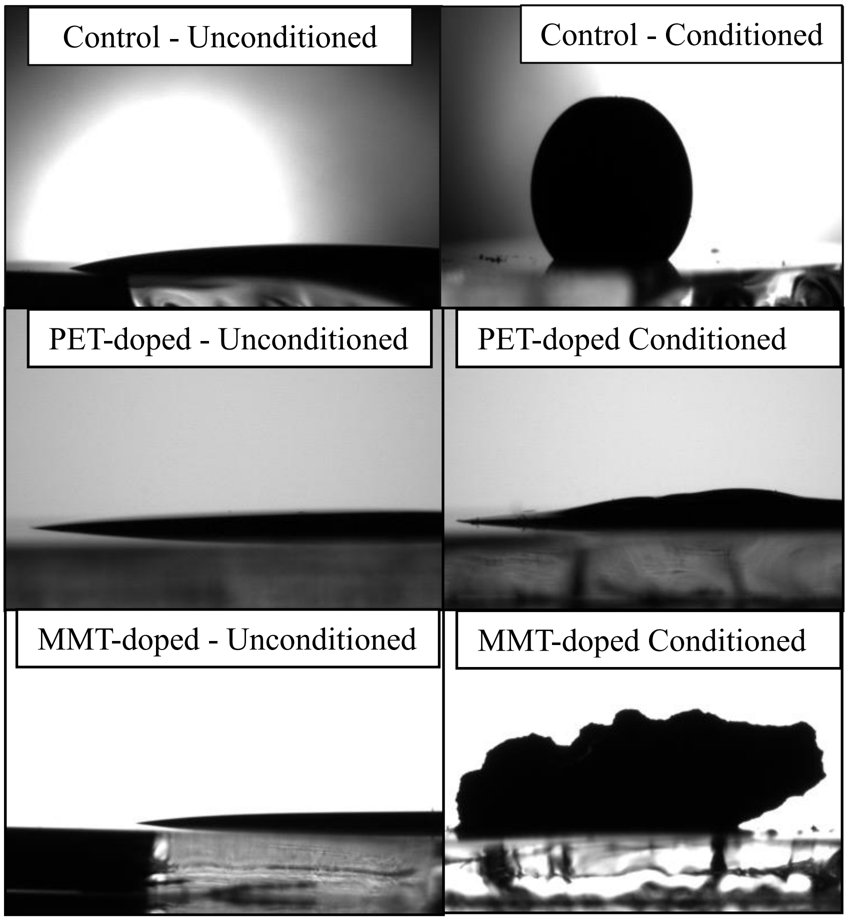

Figure 6- 4 Control, PET-doped, and MMT-doped Binder before and after Water Conditioning.

6.6.3 Bitumen Bond-Strength Test (BBS)

In Figure 5, the pull-off strength values of the modified and unmodified binders at dry conditions show that the inclusion of MMT did not significantly alter the pull-off strength of the control binder, unlike the inclusion of PET. This could be due to the filler nature of MMT in combination with the smooth nature of the glass slide surface and not being able to interlock with the surface. After water conditioning, the pull-off strength values were shown to increase, which appears counter-intuitive. However, previous research has observed this phenomenon after testing on glass surfaces (Lachance-Tremblay et al., 2019). The study noted that since water does not absorb through pores like typical stone aggregates, the water is limited only to the binder/aggregate interface on the surface, thus revealing a stiffening of the binder due to water conditioning. Therefore, in comparing the strength values before and after water conditioning, the pull-off strength moisture-susceptibility index was calculated. For the MMT-doped and PET-doped samples, the values were 42.4% and 52.3%, respectively, which are 21.7% and 31.6% more resistant to change due to water compared to the control samples. Lower index values have also been found to correlate to binders with increased polymer modification (Lachance-Tremblay et al., 2019).

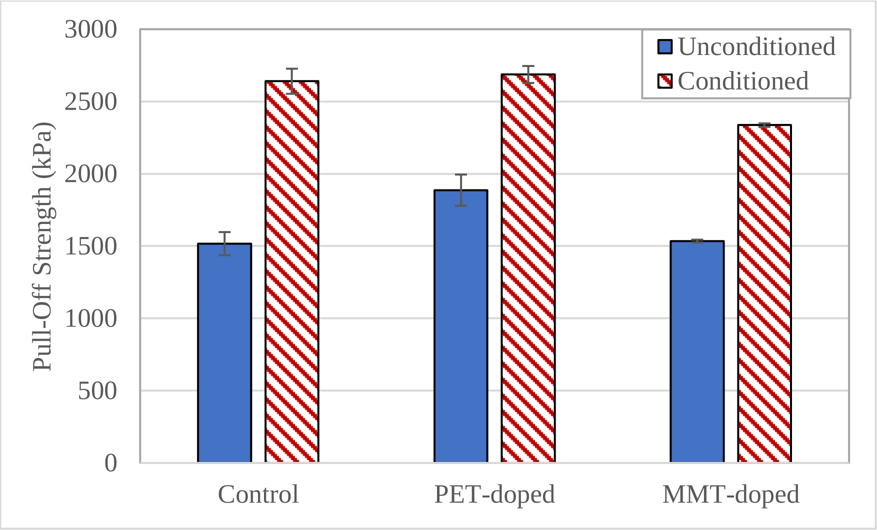

Figure 6- 5 Pull-off Strength Values for Control binder, PET-doped binder, and MMT-doped Binder before and after Moisture Conditioning on Glass Surface at Room Temperature.

For the pull-off strength values on the sedimentary rock, the behavior was different from that on the glass surface, as both the PET-doped and MMT-doped samples showed significantly higher (46% and 35%) strength values than the control, as shown in Figure 6 and Figure 7. After water conditioning, a decrease in strength value is also observed for all samples. In determining the pull-off strength moisture-susceptibility index, the PET-doped samples showed a 2% increase, while the MMT-doped samples increased the ratio by nearly 14%. The results could be attributed to the high water absorption of the stone (1.17%) as well as the roughness of the surface. In addition, the composition of sedimentary stones can be quite varied; therefore, additional analysis should be performed to further explain the binder/aggregate interaction. However, the MMT-doped samples appear to be more effective at decreasing the moisture susceptibility compared to PET-doped (Figure 7); this can be attributed to MMT's ability to arrest acidic compounds of bitumen, and prevent their migration to the surface of the stone (Mousavi et al. 2019). Images of the failure surfaces show the MMT-doped and PET-doped samples were able to show a decrease in the percentage of adhesive surface failure to the stone surface compared to the control binder.

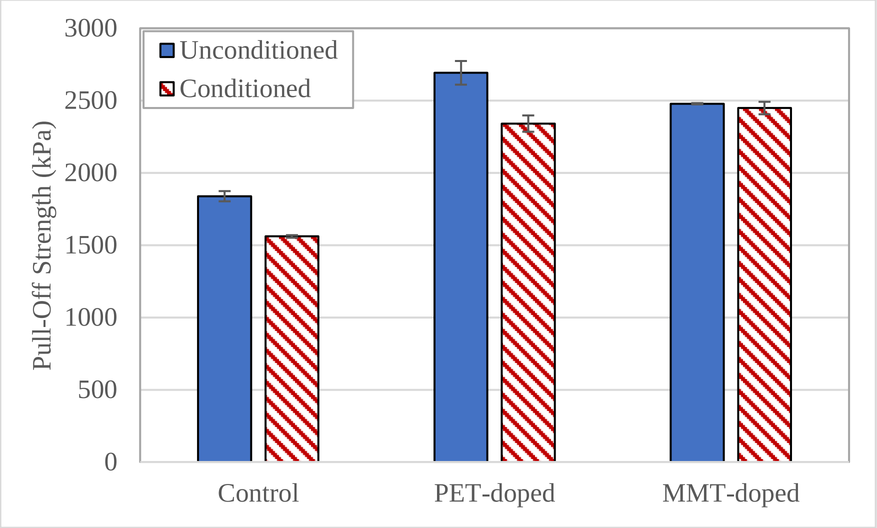

Figure 6- 6 Pull-off Strength Values for Control Binder, PET-doped Binder, and MMT-doped Binder before and after Moisture Conditioning on Stone Surface at Room Temperature.

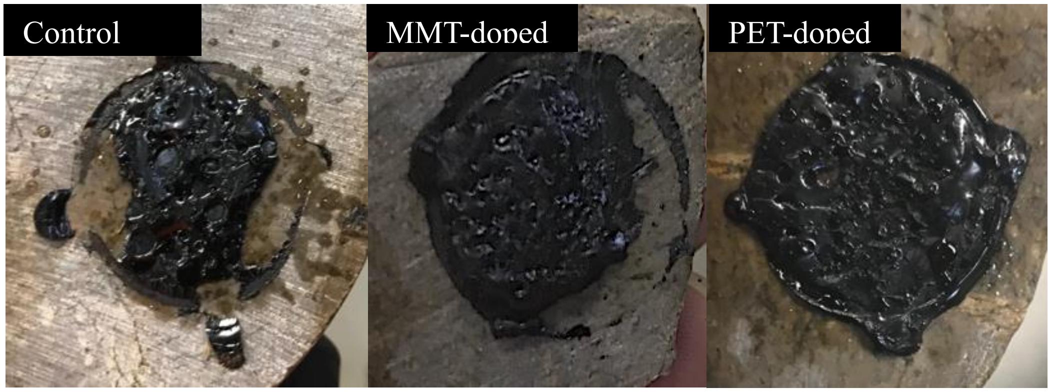

Figure 6- 7 Failure Surface for Control Binder, PET-doped Binder, and MMT-doped Binder after Moisture Conditioning and Testing on Stone Surface at Room Temperature.

6.6.4 Moisture-Induced Shear Thinning Index (MISTI)

In order to investigate the effect of water on binder-aggregate interactions, each bitumen sample was blended with glass beads (50% by weight) to perform the MISTI test. The results are shown in Table 6. All three samples show a steeper slope (higher value) after moisture conditioning, with the changes being the most evident in the PET-doped samples. The inclusion of MMT did not appear to influence the interaction between the binder and the glass beads significantly. The PET though showed increased interparticle interaction.

Table 6- 6 Power-Law Slope and MISTI for Control, PET-doped, and MMT-doped Samples.

		Unconditioned	Conditioned
Control	Power-Law Slope	2.252	2.281
	COV (3 samples)	2.1%	5.9%
	MISTI (Unconditioned/Conditioned)		**99%**
PET-doped	Power-Law Slope	2.444	2.793
	COV (3 samples)	3.4%	6.3%
	MISTI (Unconditioned/Conditioned)		**88%**
MMT-doped	Power Law Slope	2.179	2.332
	COV (3 samples)	5.5%	3.1%
	MISTI (Unconditioned/Conditioned)		**93%**

6.6.5 Boiling Water Test

For each scenario, the strength of binding to aggregates was evaluated after being subjected to boiling water. Though all the samples displayed some stripping of the stones from the aggregate, overall, the samples maintained a good coating of the aggregates, as shown in Figure 8. Overall, the PET-doped samples showed a dull color, and the control and MMT-doped samples were a little glossy.

Figure 6- 8 Control, MMT-doped, and PET-doped (left to right) Samples after Boiling Water Test

6.6.6 Attenuated Total Reflectance Fourier-Transform Infrared Spectroscopy

The FTIR analyses of the MMT-doped and PET-doped mixtures before and after the BWT are shown in Figures 9 and 10. The results show similar spectra for both conditioned states, with varying intensities. Results are consistent with that of previous research, which shows increased intensity in certain peaks after moisture conditioning (Crawford, 2019). As shown in Table 7, analysis of the FTIR spectra show signature peaks for both the MMT-doped and PET-doped mixtures. The FTIR spectra of MMT-doped mixtures, particularly after water conditioning, shows increased SiO2 and Fe-OH. This could be indicative of some exfoliation of the MMT (Madejova and Komadel, 2011; Katti et al., 2018; Fini et al., 2017). For the PET-doped mixtures, the region between

1693 to 1540 cm-1 is characteristic to amide peaks (Leng et al., 2018). The increased intensity of these peaks after water conditioning indicates a possible phase separation of the polymeric matrix, with polar molecules migrating to the bitumen surface, which may also explain the observed discoloration of PET-doped samples after water exposure.

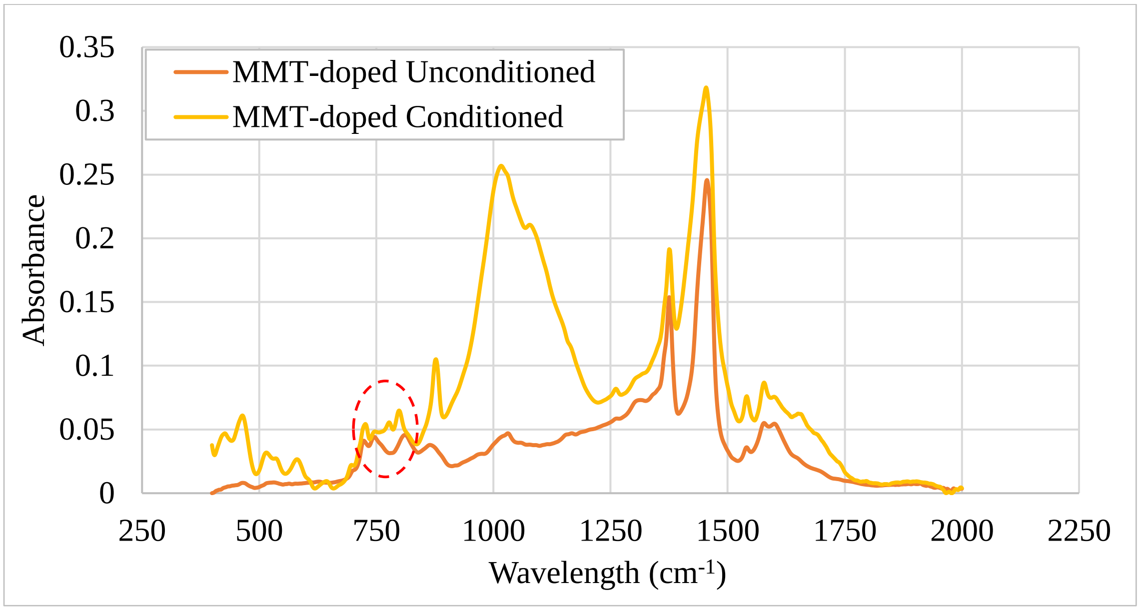

Figure 6- 9 FTIR Spectra of MMT-doped Mixture before and after Water Conditioning.

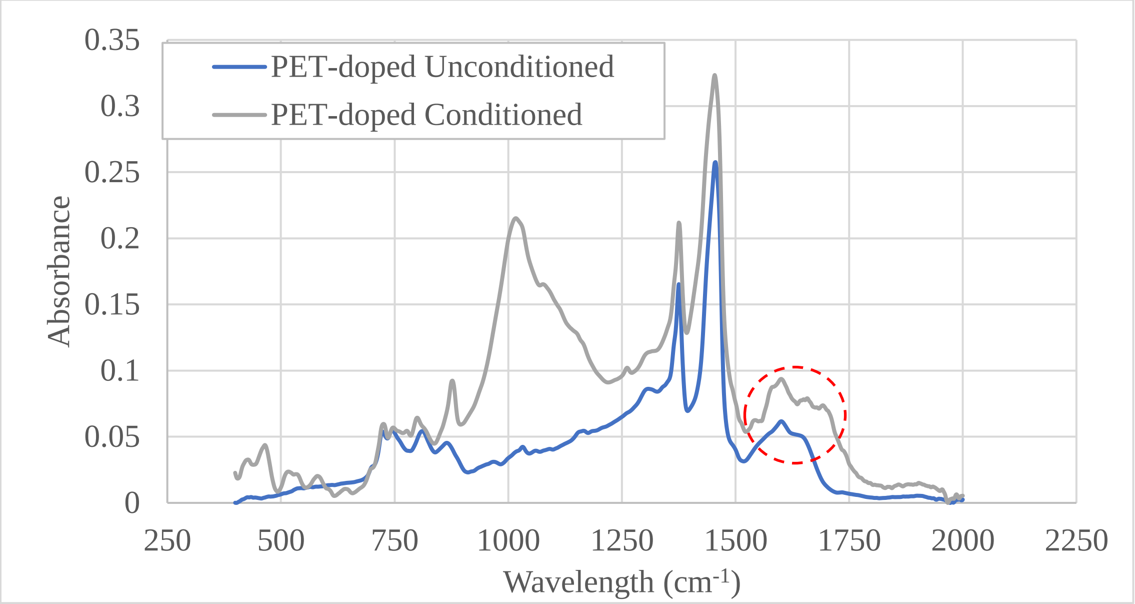

Figure 6- 10 FTIR Spectra of PET-doped Mixture before and after Water Conditioning.

Table 6- 7 MMT-doped and PET-doped Mixtures Functional Groups

MMT-doped Mixtures	
Wavelength	Functional Groups
778	SI-O Stretching of Quartz (Madejova and Komadel, 2001)
798	SI-O Stretching of Quartz and Silica (Madejova and Komadel, 2001; Katti et al., 2018)
878	Fe-OH Deformation (Katti et al., 2018)
1078	SI-O Stretching (Fini et al., 2017)
PET-doped Mixture	
Wavelength	Functional Groups
1544	N-H Bending Amide II Band (Parker, 1971; Leng et al., 2018)
1600	N-H Bending Amide II Band (Parker, 1971; Leng et al., 2018)
1643	C=O Stretching Secondary Amide (Parker, 1971; Leng et al., 2018)
1656	C=O, Amide I (Parker, 1971)
1693	C=O, Amide I (Parker 1971)

6.6.7 Hamburg Wheel-Tracking Test

The stripping inflection point (SIP) was determined for each scenario (Table 8). The SIP for the MMT scenario was found to be higher than that of the control sample, indicating adsorption of acids with MMT was helpful in diverting acids from the interface. However, it was not enough to eliminate the stripping phenomenon. The observed stripping and additional surface pores can be attributed to plausible ion exchange and formation of salts leading to significant expansion around MMT, as observed in the conditioned MMT-doped FTIR spectra; this was also confirmed by images taken from MMT-doped samples in the contact angle test. On the other hand, the PET-doped sample did not show any SIP, which showed the effectiveness of PET to passivate silica active sites to avoid moisture nucleation and growth (Figure 11).

With a nearly eight times higher surface area of MMT compared to the natural fines, the method of replacing a portion of fines with MMT is expected to have a significant effect on the overall properties of asphalt. So, we further examined the effect of the replacing method relative to other asphalt constituents, as shown in Table 9. The samples in which we accounted for the surface areas difference (MMTc) were shown to have the best results, as evidenced by the highest SIP value. In the cases in which we did not account for surface area, we simply included the MMT without adjusting the aggregate structure with MMTa or performed a simple weight replacement of natural fines with MMTb. The latter cases both showed worse stripping than MMTc, as shown in Figure 12.

Table 6- 8 Hamburg Wheel-Tracking Test Results for Control, MMTc, and PET-doped Samples

Specimen	Stripping Inflection Point
Control	16,800
MMT_c-doped	17,800
PET-doped	n/a

Figure 6- 11 Control, MMTc-doped, and PET-doped Mixtures (left to right) after the Hamburg Wheel Tracking Test

Table 6- 9 Stripping Inflection Point for MMT Inclusion Methods

Specimen	Stripping Inflection Point
MMT_a-doped	14,800
$MMT_{b\text{-}}$doped	14,100
MMT_c-doped	17,800

Figure 6- 12 MMTa-doped, MMTc-doped, and MMTb-doped Mixtures (left to right) after the Hamburg Wheel Tracking Test

6.7 Conclusion

This study examined the feasibility of developing built-in resistance against moisture damage using either passivation or an arresting mechanism. Starting with a specific moisture-susceptible paving mixture with proven moisture-damage issues in the field, two remedial methods were tested. The first method introduced polyethylene terephthalate (PET) to bitumen to neutralize active sites of siliceous stones, suppressing nucleation and growth of acids at the interface. The second method introduced sodium montmorillonite clay (MMT) to adsorb acids and prevent their migration to the interface of stone and bitumen. The efficacy of each method was measured at both binder and mixture levels. The change in contact angle after water conditioning was significantly reduced for PET-doped samples, proving the passivation power of PET. The contact angle index was not applicable to MMT-doped samples due to excessive swelling upon water exposure.

The moisture resistance based on the binder's pull-off strength for both MMT and PET showed a slight improvement when glass substrates were used, and a significant improvement when stone substrates were used. The moisture-induced shear thinning index of MMT-doped samples were found to be similar to that of the control binder, while the PET-doped samples showed an increased interparticle interaction indicating improved binder-aggregate binding. Testing the mixture using the boiling water test showed a high coating for all samples, with the PET-doped samples showing a dull black color while the control and the MMT-doped samples showed a shiny black color. Based on FTIR data, this could be a result of phase separation due to the enhanced PET-related peaks in the water-conditioned samples. Hamburg wheel-tracking test results showed PET-doped samples fully eliminated the stripping point, indicating strong resistance to moisture damage was achieved by adding PET. Although the MMT-doped samples had delayed stripping phenomenon as evidenced by a higher SIP point, they did not eliminate the chance of moisture damage. The FTIR peaks of the MMT-doped conditioned binder could be indicative of the expansive nature of the MMT and could be the reason for the formation of the large pores in the Hamburg test samples. It was found that there is a significant difference in the efficacy of active fillers depending on the replacement method used to introduce them into an asphalt mixture: accurately accounting for the surface area of the MMT compared to that of the natural fines it replaces in the asphalt mixture is critical to enable an effective arresting mechanism. Overall, both the arresting mechanism (by MMT) and the passivation mechanism (by PET) were shown to be effective in diverting acids from the interface of bitumen and stones. However, PET was found to be more effective at the mixture level. MMT's excessive swelling as well as its ion exchange may diminish its effect on asphalt's resistance to moisture. The newly developed MISTI tests were shown to be promising to detect moisture damage in asphalt samples, which are prone to moisture damage.

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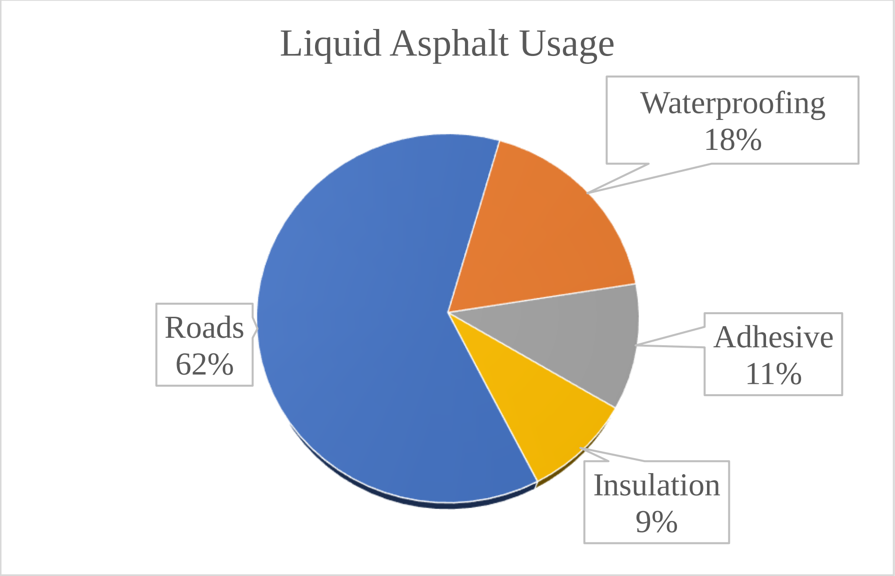
CHAPTER 7 STUDYING ECONOMIC VIABILITY AND MARKET LANDSCAPE

This chapter considers the economic viability and market landscape for the use of bio-oils as an alternative resource in the asphalt market.

7.1 Asphalt Market Overview

The use of asphalt as a material goes back to the times of Noah in the Old Testament of the Bible in Genesis 6:14, where God told him to make the ark of gopher wood and to cover the wood on the inside and the outside with pitch. The same word (pitch) was also used in the instructions to seal the basket of the infant Moses before his mother placed the basket in the river to save him from the Egyptians in Exodus 2:3. The word "asphalt" comes from the Greek word *asphaltos* and the Roman adaptation of the word *asphaltus* (Merriam-Webster, 2020). The Mesopotamians, Phoenicians, Greeks, and Romans all knew of its water-proofing properties and used it for sealing reservoirs, aqueducts, and their baths, but the Babylonians have the first recorded use of asphalt as a road-building material, dated at about 625 BC (APANM, 2020). Today, the current usage of liquid asphalt is approximately 62% for roadways, 18% for waterproofing, 11% for adhesive, and 9% as an insulation (GrandView Research, 2016). As shown in Figure 7-1, the global liquid asphalt market is expected to increase from 80.61 billion dollars to approximately 112.01 billion dollars in 2026, with a compound annual growth rate of 4.81% (Intrado, 2019).



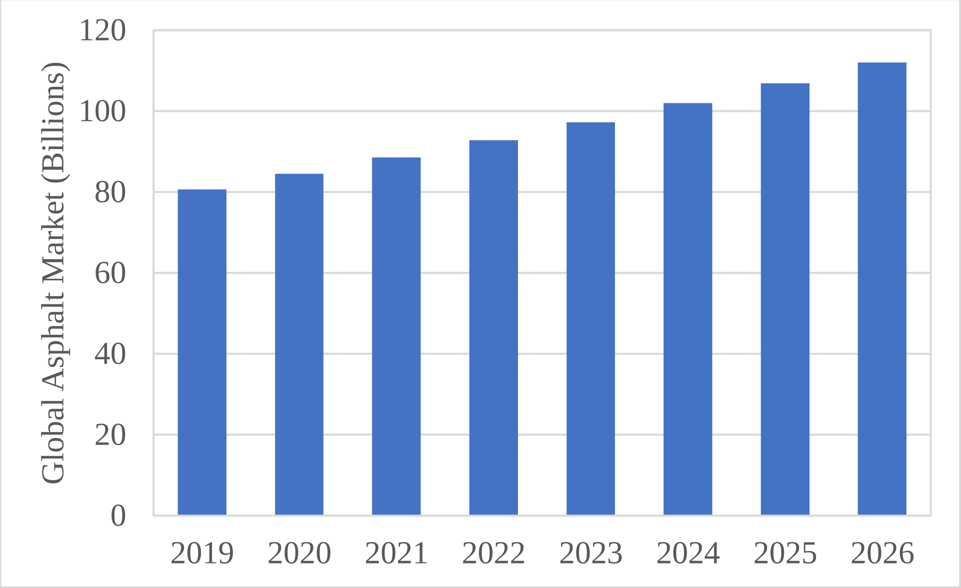


Figure 7- 1 Global Market Size for Liquid Asphalt Binder from 2020 to 2026 (Intrado, 2019).

7.2 Market Drivers and Restraints

The main drivers for the increased demand for asphalt are increasing infrastructure activities and increasing applications of polymer-modified bitumen. According to Grand View Research, there has been increased demand for road connectivity in emerging economies such as China, India, and Brazil as their standard of living and populations have increased (Grandview Research, 2017). Though the major market drivers for asphalt are in North America, Europe, Asia Pacific, Latin America, and Middle East and Africa, Asia Pacific is expected to experience the highest growth in asphalt demand.

There are two primary sources of asphalt: natural and refined. As suggested, naturally obtained asphalt can be found in either a solid state such as with gilsonite (found in locations in Utah) or in a soft/semi-solid state (found in locations such as Trindad Lake in Trinidad and the Bermudez Lake in Venezuela) (Swan, 2007). These natural asphalts account for approximately 5% to 10% of the total asphalt content in the market and were the primary source of asphalt until it was eclipsed by petroleum-based asphalt in 1907 (APANM, 2020). Petroleum-based asphalt is a residual co-product from the refining of crude oil after products such as diesel fuel, heating oil, and jet fuel have been removed (EIA, 2019). Asphalt was initially relatively abundant, but with the advent and increased implementation of coking technology that can further break down the asphalt residual material to other products, the amount of asphalt being produced has been decreasing. As shown in Figure 7-2, the yield of asphalt and road oil from crude oil has been consistently decreasing, from as high as 3.4% in 2000 to 1.8% in 2018 (EIA, 2020). The decrease in supply and the instability in oil prices have led to large fluctuations in asphalt binder prices, as shown in Figure 7-3. Between March 2017 and March 2020, the average monthly price of asphalt per ton increased as much as 78%, with some months showing as much as a 15% increase from the previous month (Asphalt Oil Market, 2020). This instability has prompted contractors to store large quantities of asphalt binder to help better control the costs of future projects (Grandview Research, 2017).

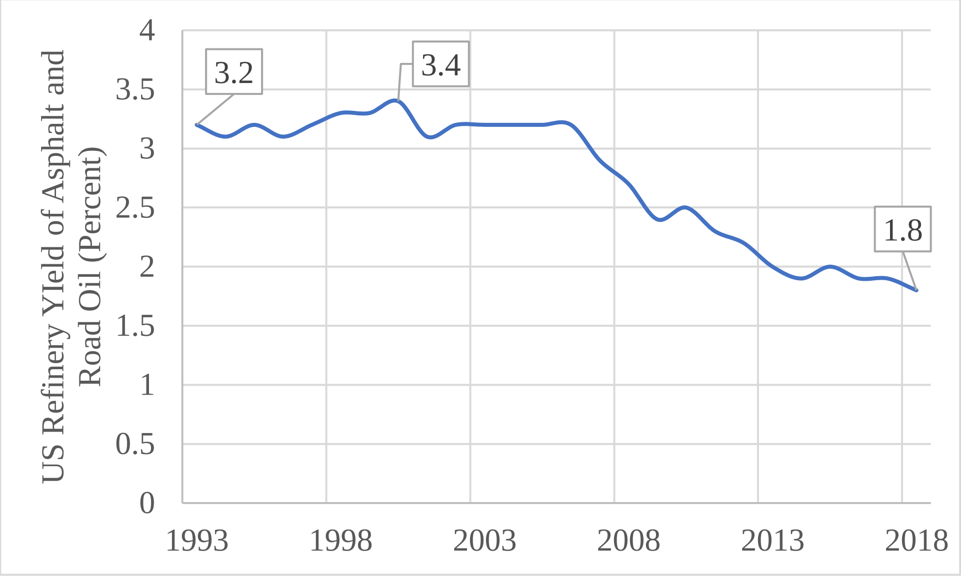


Figure 7- 2 US Refinery Yield of Asphalt and Road Oil (EIA, 2018).

Figure 7- 3 Average Asphalt Price Index (Asphalt Oil Market, 2020).

7.3 Proposed Solution's Current and Expected Impact

There has been increased interest in the use of bio-oils in asphalt binder because of rising asphalt binder prices, depleting crude oil reserves, and an increasing societal emphasis on sustainability and environmental awareness.

Bio-oils are defined as liquids that are derived from a recently living organism; examples range from plants or plant residuals to animal extracts (Basu, 2010). One benefit of using bio-based sources compared to petroleum-based sources is that bio-based sources are usually carbon-neutral or even carbon-negative, meaning that the release of carbon dioxide is less than or equal to the amount absorbed. Carbon-neutral products are becoming increasingly important due to the implementation of carbon taxes by some legislative government bodies. In addition, unlike petroleum-based sources, bio-based sources are renewable: bio-based sources can be replenished and restored. According to the Department of Energy, the number of dry tons of bio-masses available is increasing and can be as high as 1.6 Billion tons per year in 2040, which would be enough to replace the consumption of 2.2 billion barrels of petroleum products annually (US Dept. of Energy, 2016; US EIA, 2020). The different areas of bio-mass harvesting are shown in Figure 7-4. The addition of this amount of bio-masses to the market would help reduce the expected increase in asphalt demand and increase sustainable and environmentally practices within the asphalt industry. In addition, unlike petroleum-based products, which are gathered from specific areas, the accessibility of bio-mass is fairly high for most regions of the United States (Figure 7-5) (UCS, 2012).

The cost analysis of producing bio-oils from bio-masses has also been extensively investigated. The profitability of these facilities are largely based on the cost of raw materials, current price of petroleum crude, and the type of process procedure utilized. One study performed by the National Renewable Energy Laboratory found that when the cost of wood bio-mass per ton is less than $75 per ton, the process it profitable (Wright et al., 2010). The profit point for the processing of wood based bio-mass using fast pyrolysis would be when crude prices are above $54 per barrel (Asmaa et al., 2018). The conversion of sugar beet pulp using high temperature liquidfaction (HTL) has been calculated to be $0.54/gal which is comparable to the processing of crude (Goudriaan et al., 2000).

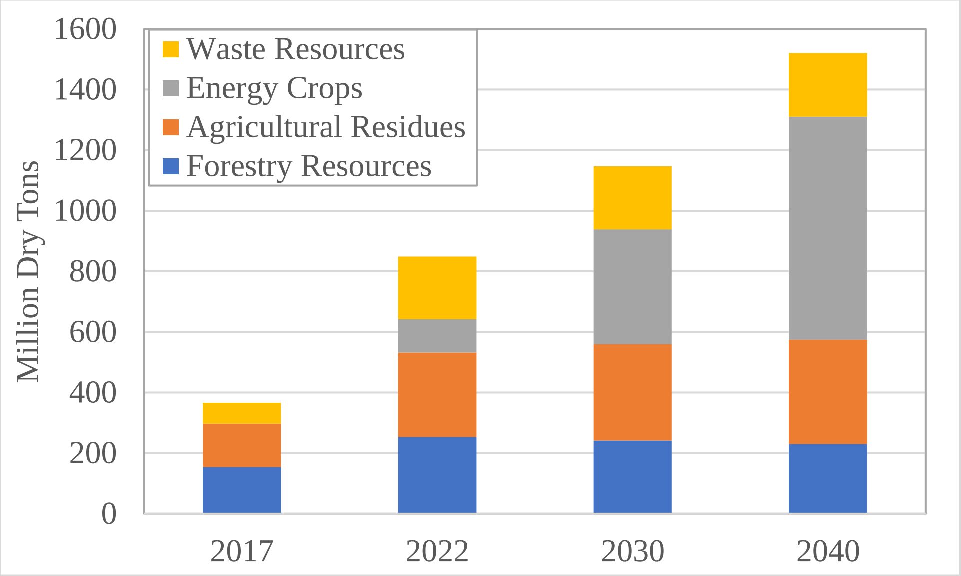


Figure 7- 4 Summary of Bio-Mass Production in the US (US DOE, 2016).

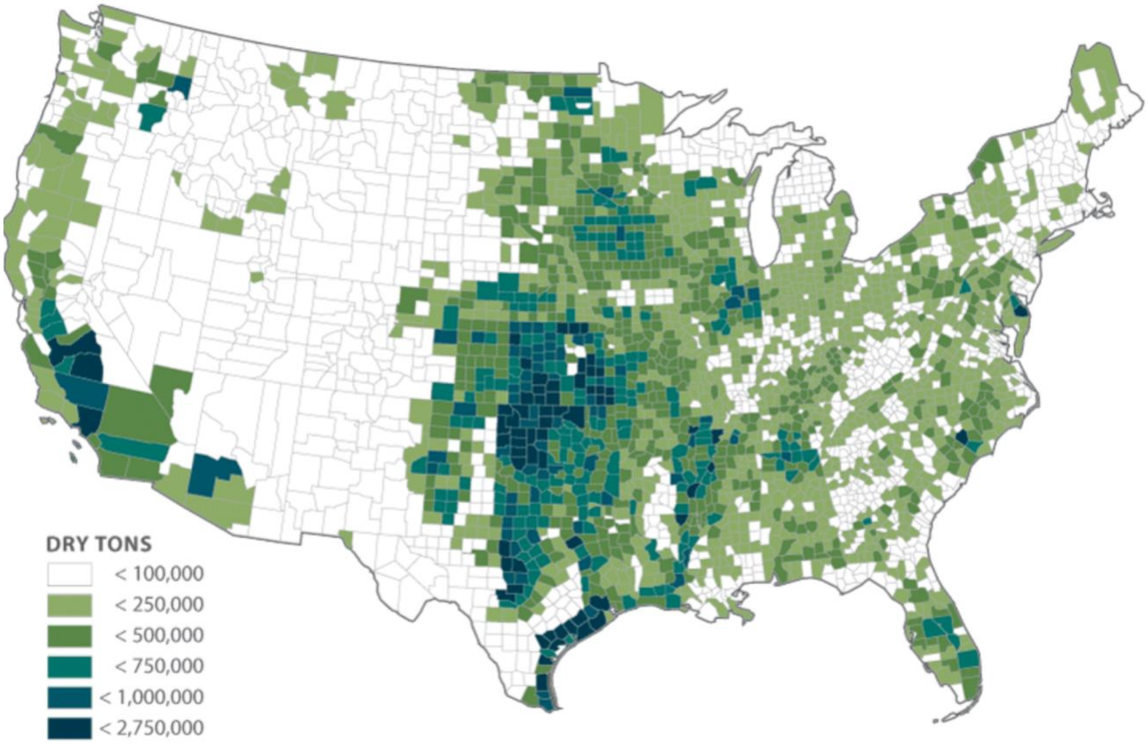


Figure 7- 5 Biomass Availability across the Continental United States (UCS, 2012).

7.4 Competitive Landscape

The competitive landscape for the use bio-oils in asphalt binder would be concrete pavements. Increasing the use of cementous materials for roads would replace the use of asphalt pavement, and it could be financially viable at times when the prices for asphalt binder are significantly high. However, in general, concrete is significantly higher in terms of costs to place and replace, compared to asphalt pavement. Also, asphalt pavement can be more rapidly replaced and reopened for traffic compared to concrete pavement, and unlike concrete pavement, asphalt pavement is 100% recyclable. In addition, in terms of environmental awareness, one study identified global warming, abiotic depletion, acidification, and marine ecotoxicity as the main impacts of cement production (Chen et al., 2010).

7.5 Application Trends and the Mindset of Impacted Industry

Despite possible resistance from the asphalt industry in terms of viewing bio-oils as a viable means of modifying asphalt binder, the industry is open to an alternative. This is evident from the increasing number of research projects involving the investigation of bio-oils in asphalt binder; the number has increased from zero in 2009 to 37 in 2017 (Figure 7-6) (Al-Sabaeei et al., 2020).

The barriers that prevent the use of bio-oils in asphalt binder involve decreased adhesion and increased susceptibility to aging, rutting, and moisture (Al-Sabaeei et al., 2020). If asphalt binder modified with bio-oils can perform similarly to 100% virgin petroleum and pass all required specifications, the industry will slowly move toward increased use of bio-oils in asphalt binder. This is especially true of government agencies, who are being influenced by the public to reduce costs and implement more sustainable and environmentally friendly policies.

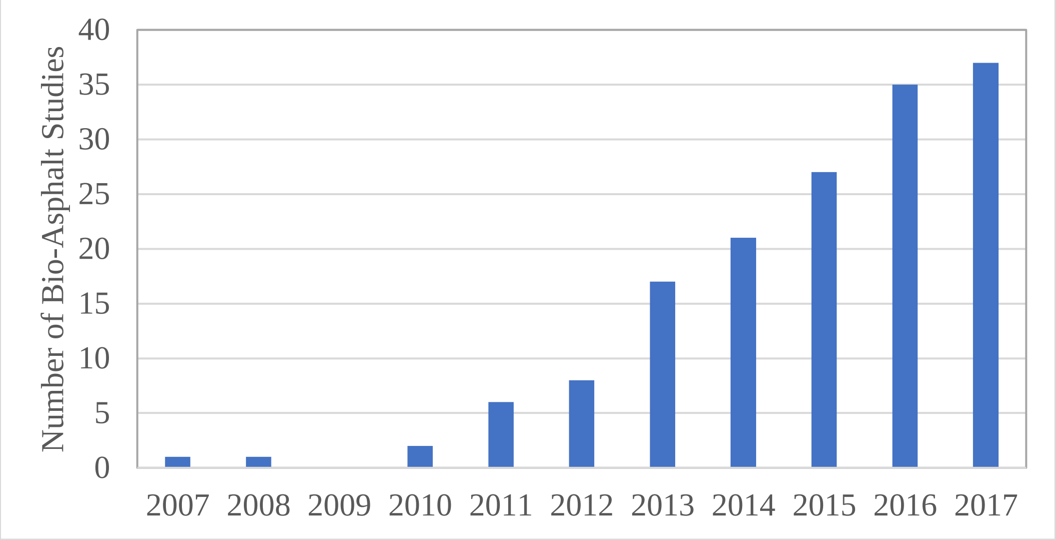


Figure 7- 6 Number of Studies Investigating the Use of Bio-modified Asphalts (Al-Sabeei et al., 2020).

7.5 Moisture Susceptibility Testing and Evaluation Methods of Bio-Modified Asphalt

With concerns being high for the performance of bio-oils in asphalt pavement, the industry looks to the aforementioned investigations to determine which bio-oils could be promising. Therefore, being able to accurately determine properties such as moisture susceptibility is very important for the utilization of that particular bio-oil. In Table 1, the moisture susceptibility of various bio-oils is given. However, as can be noted, some of the results for similar bio-oils can appear as contradictory. This could be a result of different testing methods. However, this also highlights the lack of consistent and representative moisture testing methods.

In Table 2, numerous moisture susceptibility testing methods are discussed. Many of the tests are performed on the loose or uncompacted asphalt specimens and do not represent field moisture conditioning with the evaluation of moisture susceptibility being largely subjective rather than quantitative. This unfortunately could lead to inconsistent evaluations and user bias. Other methods utilizing loose mixes which are quantitative unfortunately utilize hazardous chemicals and thus are not deemed feasible.

The most utilized method of moisture testing in the industry today is on compacted asphalt samples. The most popular tests is the tensile strength ratio (TSR) which compares the strength of moisture conditioned samples to samples which are not moisture conditioned. However, as reported earlier, this test has been shown to provide mixed success in actually determining moisture susceptibility (Berger et al., 2003). Another popular compacted moisture mixture test is the hamburg wheel tracking test (HWTT). In this test, a steel wheel is oscillating on the sample while it is fully submerged in water. The device then records the depth of the wheel into the sample while tracking the number of passes the wheel has made. From the rutting data, the stripping inflection point can be determined. Though this test has shown merit in determining moisture susceptibility, the testing sensitivity can be high and the device can be quite costly thus not easily attainable for wide spread moisture testing. In an attempt to simulate field conditions, various moisture conditioning approaches have been developed to water condition, asphalt mixture samples. One of these approaches is the moisture induced stress tester (MiST) in which the samples undergo repeated pressure and vacuum cycles to generates pore pressure within the compacted asphalt sample (Arepalli et al., 2019).

Aside from loose and compacted asphalt mixture testing, the use of binder testing for moisture testing has also been investigated. The bitumen bond strength test determines the change in pull off strength with and without moisture conditioning. However, high variance in results as well as inconsistencies such as substrate roughness make the test not widely performed. The contact angle moisture susceptibility index measures the difference in contact angle after moisture conditioning and simulates the stripping phenomenon of the binder from the aggregate. The test though needs additional evaluation. However, it has already shown an inability to test some samples and the contact angle measurement is not always consistent around the bead of asphalt binder. One binder test which is increasing in popularity utilizes measuring the surface free energy of the aggregate and the asphalt binder. By knowing these two values, one can determine how compatible the two materials are. This method though requires the use of a special device and the results can be prone to artifacts which would not be truly representative of the compatibility of the two materials.

The moisture induced shear thinning index (MISTI) is a newly developed test which measures the viscosity as a function of shear rate. The results are then used to calculate the shear thinning slope for each sample. The sample in this test consists of a 1:2 ratio of glass beads to asphalt binder. The glass beads are uniformly sized to be 0.1 mm or 100 microns. The ratio of the shear thinning slope before and after water exposure is correlated to the change at the interface of glass and asphalt binder. The test was inspired by our prior work with the contact angle based moisture damage evaluation (Hung et al.) and was motivated by the need for evaluating the chemistry-driven moisture damage phenomenon in order to decouple properties of the asphalt binder-stone interface from that of the asphalt bulk properties. The results of MISTI has been shown to correlate to the moisture susceptibility of bio-oils. It is also shown to be sensitive to any changes at the glass bead and asphalt binder interface. Therefore, it is considered to be a promising test to detect water-induced changes at the interface of the asphalt binder and glass beads (surrogates for siliceous aggregates). The test is also unique in that it utilizes a standard asphalt binder testing equipment (dynamic shear rheometer) which is commonly available in most asphalt labs using the Superpave PG testing system such as those of the Departments of Transportation and Quality control (QC) labs.

Table 7.1 Review of Moisture Susceptibility Studies of Bio-modified Asphalt

Bio-Oil Modifier	**Dosage**	**Application**	**Test Performed**	**Impact on Moisture Susceptibility**	**Authors**
Waste Vegetable Oil	12% by binder mass	Rejuvenator to Recycled Asphalt Pavement	Stripping Inflection Point (SIP) via Hamburg Wheel Tracking Test (HWTT)	Decrease	Zaumanis et al., 2014
Red Oak	~17% by binder mass	Blend with crumb rubber	Tensile Strength Ratio (TSR)	Decrease	Williams et al., 2015
Corn Extract	1.0% by binder mass	Additive to Neat Binder	Tensile Strength Ratio (TSR)	Decrease	Buss et al., 2015
Wood Chip Blend	5 and 10% by binder mass	Additive to Neat Binder	Tensile Strength Ratio (TSR)	No Change	You et al., 2012
Guayule Rubber	4.5 and 13% by binder mass	Rejuvenator and added to neat binder	SIP via HWTT and TSR	Decrease/Increases	Lusher and Richardson, 2014
Pine Tree	20 to 50% by mass of binder	Added to neat binder	SIP via HWTT and TSR	No Change	Mohammed et al., 2013
Pine Tree	12% by binder mass	Rejuvenator	SIP via HWTT	Increase	Zaumanis et al., 2014;
Plant Blend	100%	Alternative Binder	TSR	Increase	Austroads, 2013
Waste Vegetable Grease	12% by binder mass	Rejuvenator	SIP via HWTT	Increase	Zaumanis et al., 2014

Table 7.2 Review of Moisture Susceptibility Test Methods

Test Name	Reference	Test Material	Moisture Damage Indicator	Procedure	Concerns
Static Immersion Test	ASTM D1664	Uncompacted mix	Visual Stripping	25°C for 16 to 18 hours	Subjectivity of Determining Level of Coating
Water Immersion Test	Liu et al., 2014	Uncompacted mix	Visual Stripping	40°C for 3 hours	Subjectivity of Determining Level of Coating
Ultrasonic Method	Anderson & Goetz, 1956	Uncompacted mix	Visual Stripping	Sonicator for 5-20 mins	Poor Correlation to field results
Film Stripping Test	CalTrans, 2014	Uncompacted Mix	Visual Stripping	140°F for 15 to 18 hours then 15 minutes in water	Subjectivity of Determining Level of Coating
Rolling Bottle Test	BS, 2012	Uncompacted Mix	Visual Stripping	Sample placed in bottle roller for 12-72 hours	Length and Subjectivity of Determining Level of Coating
Boiling Water Test	ASTM, 2012	Uncompacted Mix	Visual Stripping	Sample placed in boiling water for 10 minutes	Subjectivity of Determining Level of Coating
English Chemical Immersion Test	Road Research Library, 1986	Uncompacted Mix	Visual Stripping	Blend with increasing amount of NaCO	Uses of Chemical blending and subjectivity of determining level of coating
Chemical Blending Test	Ford et al., 1974	Uncompacted Mix	Quantitative Measurements of Released Pressure from Chem Rxn	Blend mix with acid for 10 minutes	Use of highly toxic and corrosive acids
Net Absorption Test	Curtis et al., 1993	Uncompacted Mix	Weight of binder in solution and amount absorbed by aggregate	Binder/Toulene Blend mixed with aggregate	Inconclusive correlation to mixture testing
Tensile Strength Ratio	AASHTO T283	Compacted Mix	Conditioned and Unconditioned Strength Ratio	Freeze Thaw moisture conditioning and strength test	Mixed success in correlating to field conditions and results
Hamburg Wheel Tracking Test	AASHTO T324	Compacted Mix	Rutting Profile of Submerged Samples	Oscillating Steel wheel on submerged sample	Device large and costly and not easily accessible
Moisture Induced Stress Tester	ASTM D7870	Compacted Mix	Not a Test	Sample undergoes repeated pressure/vacuum cycles	Only a water conditioning device, not a test method for moisture damage
Surface Free Energy	Wasiuddin et al., 2007	Binder and Aggregate Components	Surface energy values	Use of cannon liquids or sessile drop method	Biased toward binder-air interface properties rather of binder-stone interface, May be prone to artifacts
Bitumen Bond Strength Test	AASHTO TP 91	Binder with Aggregate substrate	Change in Pull-off strength	Samples submerged for 24 hours at 40°C	Biased towards binder bulk properties, not sensitive to changes at the interface, high variability in pull-off values
Contact Angle Moisture Susceptibility Index	Hung et al., 2017	Binder with Glass Substrate	Change in Contact Angle after water conditioning	Sample is submerged in 80°C for 2 hours	Contact angles are not always measurable specially for modified binders
Moisture Induced Shear Thinning Index	This Dissertation	Glass Beads blended with asphalt binder	Change in shear thinning value after water conditioning	Conditioned samples are submerged for 24 hours at 60°C	Need more validation and round robin tests

7.6 Utilization of Moisture Induced Shear Thinning Index

Though the MISTI test has only been new developed, efforts to establish guidelines to distinguish poor performing asphalt binders in terms of moisture damage has been made. Considering that the MISTI value is a ratio of the shear thinning slope measured at both the dry and wet condition, an ideal scenario would be value of 100% thus representing no change due to the presence of water. The MISTI values of the various bio-oils give indication that +/-10% is acceptable; bio-oils having a MISTI value of 110% and showed adequate moisture resistance. However, values above 120% could have issues with moisture susceptibility as denoted by the sample containing waste vegetable oil, which has been reported to be highly prone to moisture damage. Further tests including performance evaluation, and round robin testing is needed to establish a threshold which is expected to be somewhere between MISTI of 115 to 120%.

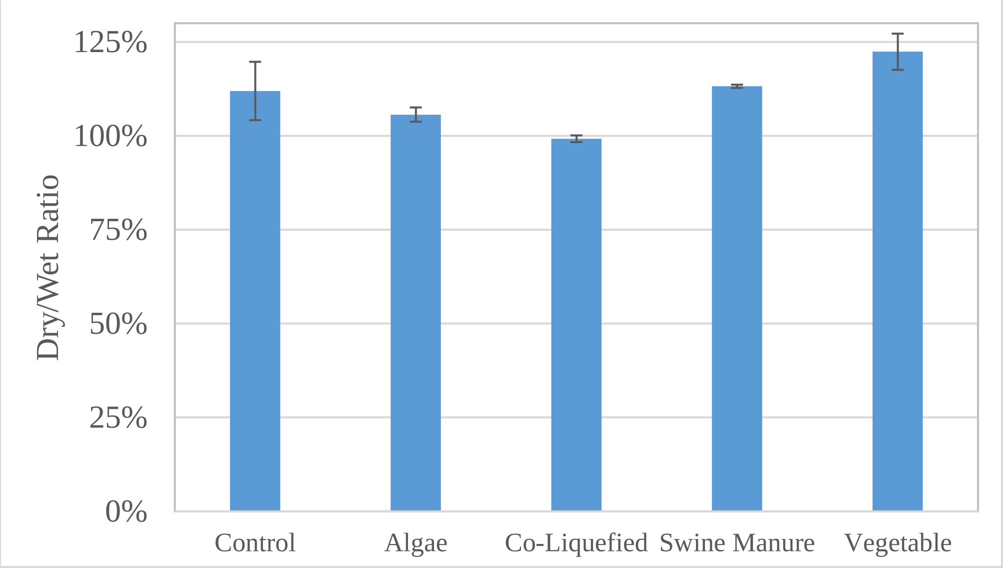


Figure 7- 7 Moisture-Induced Susceptibility Index for Bio-Modified Binder

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CHAPTER 8 CONCLUSIONS AND RECOMMENDATIONS

Conflicting results on the moisture susceptibility of various bio-oils have led to an increased hesitancy in their application and adaptation. Therefore, it is important to find one or more fundamental parameters that correlate to the moisture susceptibility of bio-modified asphalt. Identifying such parameters would allow for more-accurate screening of bio-oils, not only to prevent the use of moisture-susceptible bio-oils in asphalt pavement, but also to provide insights and instruction to bio-oil manufacturers and developers. Such insight can highlight molecular compounds that could cause moisture susceptibility and provide guidance on ways to mitigate the impact of such molecules on increasing the moisture susceptibility of asphalt pavement. The following sections summarize the findings of this study toward that goal.

8.1 Multiscale Approach to Study the Moisture Susceptibility of Bio-Modified Asphalt

The objective of this study was to use a multi-scale approach to track and evaluate the performance of an asphalt binder additive from swine manure (Bio-modifier) with known chemical composition, as a means of not only reducing, but also understanding moisture susceptibility in asphalt pavement. Bio-modification was found to show reduced moisture susceptibility at the binder level and the mixture level when compared to two other commercially available additives. Further analysis of the binder doped with representative molecules of the additives showed varying differences in adhesion and moisture susceptibility. To provide in-depth understanding of the underlying interaction mechanisms between water and binder, molecular dynamic simulations were performed on a blend of asphaltene and dopant molecules placed on a silica oxide substrate and exposed to water molecules. Study results revealed the passivation mechanism of bio-modifiers as a dominant factor contributing to reduced susceptibility to moisture damage. It was found that the bio-modifier's molecules occupy active sites of silica oxide, preventing the nucleation and growth of acidic compounds at the bitumen-silica interface. Such acidic compounds are water soluble, and their presence at the interface can be detrimental, leading to moisture damage. Study results showed that anchored bio-modifier molecules further interact with asphaltene molecules to provide a bridging mechanism between bitumen and silica. This in turn leads to reduced susceptibility to moisture damage in bio-modified binders that have adhered to siliceous surfaces such as quartz and granite stone aggregates.

8.2 Determination of a Fundamental Parameter to Correlate to Moisture Susceptibility

This study develops a computational and laboratory approach to evaluate the moisture susceptibility of additives and modifiers used in asphalt mixtures. From the evaluation, a fundamental parameter was determined to correlate to moisture susceptibility. The computational approach uses the “polarizability” factor, which is one of the conceptual density functional theory descriptors; the laboratory method uses a moisture-induced shear-thinning phenomenon. Polarizability is indicative of the formation of instantaneous dipoles that are oriented in the applied field. A lower polarizability indicates a lower propensity of the chemical species to interact with other species in their chemical environment. Moisture-induced shear thinning measures the loss of interfacial bonds between bitumen and siliceous surfaces due to water exposure. The above parameters are used in this study to evaluate and compare bio-modifiers made from four sources: waste vegetable oil, swine manure, algae, and a co-liquefied blend of swine manure and algae. In a comparative study, waste vegetable oil, which has a high content of long-chain alkane and fatty acids, showed the highest polarizability and moisture-induced shear thinning, indicating the greatest susceptibility to moisture damage. On the other hand, the chemical composition of the bio-modifier produced from the co-liquefaction of swine manure and algae showed the least polarizability and least moisture-induced shear thinning, indicating the least susceptibility to moisture damage.

8.3 Development of a Test Method to Evaluate The Moisture Susceptibility of Asphalt

The development of a binder moisture-susceptibility test involved correlating the tensile strength ratio (TSR) values of field-produced mixes to various binder-level moisture tests. In a comparative study, the binder moisture tests compared were the bitumen bond-strength (BBS) test, the contact-angle moisture-susceptibility index (CAMSI), and the moisture-induced shear-thinning index (MISTI). The type of water was also varied between distilled, acidic, and salt water, to determine its impact on moisture damage in the samples. The BBS test showed conflicting results, and the CAMSI could not be obtained. The MISTI results showed the closest correlation to the TSR results. The results showed that the control samples were less susceptible to moisture damage than the mixes modified with 15% RAP, and acidic water conditioning is the most damaging in terms of moisture damage, while distilled water is the least damaging.

8.4 Develop Methods to Improve Resistance of Asphalt To Moisture Damage

This study examines the feasibility of developing built-in resistance to moisture damage using either passivation or an arresting mechanism. A specific moisture-susceptible paving mixture with proven moisture-damage issues in the field was selected for this study. The damage was attributed to failure at the interface of bitumen and stone aggregate due to the accumulation of acidic compounds at the interface and subsequent dissolution in the presence of water. Here, we examine two remedial methods. The first method introduces an additive based on polyethylene terephthalate (PET) to asphalt binder to neutralize the active sites of siliceous stones, suppressing nucleation and the growth of acids at the interface. The second method introduces sodium montmorillonite clay (MMT) as an additive to asphalt binder, to adsorb acids and prevent their migration to the interface of stone and bitumen. Measurement of shear binding between siliceous substrates and asphalt binder using a shear rate sweep test showed increases of 21% and 43% due to the inclusion of MMT and PET, respectively. This improvement was also observed in the results of the bitumen bond-strength tests performed on glass and on stone substrates. Results of the evaluation at the mixture level using a Hamburg wheel-tracking test showed that the addition of MMT and PET reduced the susceptibility to moisture damage, as evidenced by the increasing number of cycles before moisture stripping occurred. For the PET-modified mixture, no stripping inflection was observed until 20,000 cycles. It was also observed that MMT's adsorption of acidic compounds from bitumen led to the appearance of surface dents after water conditioning. The PET-modified specimen showed some signs of color change after water exposure, without any signs of stripping. The study results help formulators design materials with built-in resistance mechanisms against moisture damage.

8.5 Recommendations

Based on the study findings, the following recommendations are made:

5. Considering that our study showed significant role of bitumen composition on its moisture susceptibility, as well as the frequent appearance of new bio-modifiers, additional multi-scale testing with linkage to chemical composition of new bio-modifiers with varying fabrication processes is needed to expand the database to accurately address the moisture susceptibility of a bio-modified asphalt.
6. Effects of aging on the moisture susceptibility of bio-modified asphalts was not in the scope of this study and should be investigated further as it would be highly dependent on the compositional changes which would occur in the bio-oils
7. Considering that our newly developed moisture-induced shear thinning index (MISTI) found to be promising to differentiate moisture susceptible bitumen, further evaluation is needed to properly correlate results to mixture testing and field performance.
8. The study results showed two recommended remedial methods to combat moisture damage in a pre-selected bitumen with known moisture damage problem. Further examination of the remedial methods with other known bitumen is recommended to determine efficacy of proposed remedies.

9. Montmorillonite clay showed to be effective as an active filler to detract acidic compounds from interface of bitumen and stone aggregates and work as a remedy against moisture damage, however, it is known that clay type structures have swelling issue causing expansion. It is recommended to examine feasibility of inducing full exfoliation of clay priori and/or modifying the clay not to expand before its application as active filler.
10. Considering that active filler mechanism found to be an effective remedy against moisture, its recommended that other abundant active fillers be examined and compared with those of montmorillonite clay.
11. Considering that treated Polyethylene Terephthalate found to be effective additive to reduce moisture damage, as well as the fact that it was made from waste plastics, it is recommended that other source of waste plastics be examined as possible asphalt modifier to enhance both pavement durability and sustainability.
12. Considering the significant positive environment and economic merits of selected bio-modification and remedial actions against moisture damage, a complete life cycle assessment for pavements deploying such mechanisms is recommended.

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APPENDIX A

PREVIOUSLY PUBLISHED WORK

Chapters 3, 4, and 6 are all studies that have been submitted for peer review and are not published. The references are given below:

> Mousavi, M., Oldham, D., & Fini, E. (2020) Polarizability and Moisture-Induced Shear Thinning Index: Fundamental Material Properties to Evaluate Moisture Susceptibility of Bitumen. Construction and Building Materials. Under Review.
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> Oldham, D. and Fini, E. (2020). A Bottom-up Approach to Study the Moisture Susceptibility of Bio-Modified Asphalt. Construction and Building Materials. Under Review
>
> Oldham, D., Fini, E., & Mallick, R. (2020). Reducing Susceptibility to Moisture Damage in Asphalt Pavements Using Polyethylene Terephthalate and Sodium Montmorillonite Clay. Construction & Building Materials. Under Review.

The only material, which has been published prior to the submission of this dissertation, is Chapter 5, which was in a conference proceeding for the Transportation Research Board. It is cited below:

> Obando, C., Oldham, D., Kaloush, E., & Fini, E. (2020) Effect of Composition of Water on Accelerating Moisture Damage in Pavement, Transportation Research Board Conference, Paper #20-06022, January 12-15, 2020, Washington D.C.

In this conference proceed; Daniel Oldham prepared all of the samples used for binder testing which includes weighing and blending the binder. Daniel also prepared all of the bitumen bond strength, contact angle moisture susceptibility, and moisture induced shear susceptibility index samples as well as performed the actual tests and the analysis. In addition, Daniel also helped with water conditioning the asphalt mixture samples for the Tensile Strength Ratio test.

APPENDIX B

COAUTHOR PERMISSION FOR PREVIOUSLY PUBSLISHED WORK

Co-Authors:

Carlos Obanado

Dr. Elham H. Fini

Dr. Kamil E. Kaloush

Have granted their permission for the use of the following conference proceeding to be used for the dissertation of Daniel Oldham.

> Obando, C., Oldham, D., Kaloush, E., & Fini, E. (2020) Effect of Composition of Water on Accelerating Moisture Damage in Pavement, Transportation Research Board Conference, Paper #20-06022, January 12-15, 2020, Washington D.C.

BIOGRAPHICAL SKETCH

Daniel Oldham grew up in rural North Carolina with two younger brothers. His mother is from the Philippines and his father from Bear Creek, NC. He received his elementary education from Coleridge Elementary School in Coleridge, NC. His secondary education was completed from Faith Christian School in Ramseur, NC where he graduated salutatorian. In 2008, he started an associate's degree Pre-engineering at Guilford Technical Community College (GTCC). In 2010, he enrolled also at North Carolina A&T State University (NC A&T) in the Bachelor's in Civil Engineering program. Upon graduating from both from both GTCC and NC A&T, with Summa Cum Laude honors for the later, in May 2013, Daniel started his Master's in Civil Engineering at NC A&T. His PhD work began in the Nanoengineering program in 2015 before he transferred to Civil, Environmental, and Sustainable Engineering Program at Arizona State University in 2019. He has a relatively long exposure to the transportation industry through working in his father's house moving business. With moving such large structures, he has worked closely with DOTs in terms of determining clearance issues as well as optimizing route selection. His asphalt pavement research started in 2010 focusing on the use of bio-rejuvenators for aged asphalt as a means of improving low temperature cracking. This research was performed at the Sustainable Infrastructure Lab in Greensboro, NC as well as the Illinois Center for Transportation in Rantoul, IL. Currently, Daniel's research is using a bottom-up approach to understand and aid the improvement of moisture resistance in asphalt pavement. He recently got married to a lovely woman in May of 2019 who grew up in a missionary family from Yap, Micronesia. He is very active in his church and loves the Lord dearly. He served as the Intern and Children's Church Director at Beulah Baptist Church under the direction of Dr. Neal Jackson in Bennett, NC. He is serving currently as the Pastoral Intern under the direction of Pastor Nathan Mestler at Tri-City Baptist Church in Chandler, AZ. He has also been able to travel on mission and humanitarian trips to every continent except Australia. He has received the prestigious Dwight D. Eisenhower Transportation Fellowship in 2012-2013 as well as in 2014-2015. In 2014, he was also selected as an ENO Transportation fellow. His work on advancing transportation materials led him to be a 2015 recipient of the 4 year NSF Graduate Research Fellowship. He was also featured on the White House Office of Science and Technology Policy blog for his work with bio-oils in asphalt. In 2016 , Daniel was selected to be the Southeastern Transportation Center Outstanding Student of the Year. To date, Daniel has been blessed to have over 20 journal publications, 11 conference papers, 260 citations, and over 3,800 reads.