

Enhancing the Fundamental Knowledge and Use of Asphalt Emulsions Using Systematic Scientific and Engineering Approaches

**Final Report
August 2018**



Sponsored by

Iowa Highway Research Board
(IHRB Project TR-708C)
Midwest Transportation Center
U.S. DOT Office of the Assistant
Secretary for Research and Technology



**IOWA STATE
UNIVERSITY**
**Institute for
Transportation**

About MTC

The Midwest Transportation Center (MTC) is a regional University Transportation Center (UTC) sponsored by the U.S. Department of Transportation Office of the Assistant Secretary for Research and Technology (USDOT/OST-R). The mission of the UTC program is to advance U.S. technology and expertise in the many disciplines comprising transportation through the mechanisms of education, research, and technology transfer at university-based centers of excellence. Iowa State University, through its Institute for Transportation (InTrans), is the MTC lead institution.

About InTrans

The mission of the Institute for Transportation (InTrans) at Iowa State University is to develop and implement innovative methods, materials, and technologies for improving transportation efficiency, safety, reliability, and sustainability while improving the learning environment of students, faculty, and staff in transportation-related fields.

ISU Non-Discrimination Statement

Iowa State University does not discriminate on the basis of race, color, age, ethnicity, religion, national origin, pregnancy, sexual orientation, gender identity, genetic information, sex, marital status, disability, or status as a U.S. veteran. Inquiries regarding non-discrimination policies may be directed to Office of Equal Opportunity, 3410 Beardshear Hall, 515 Morrill Road, Ames, Iowa 50011, Tel. 515-294-7612, Hotline: 515-294-1222, email eooffice@iastate.edu.

Notice

The contents of this report reflect the views of the authors, who are responsible for the facts and the accuracy of the information presented herein. The opinions, findings and conclusions expressed in this publication are those of the authors and not necessarily those of the sponsors.

This document is disseminated under the sponsorship of the U.S. DOT UTC program in the interest of information exchange. The U.S. Government assumes no liability for the use of the information contained in this document. This report does not constitute a standard, specification, or regulation.

The U.S. Government does not endorse products or manufacturers. If trademarks or manufacturers' names appear in this report, it is only because they are considered essential to the objective of the document.

Quality Assurance Statement

The Federal Highway Administration (FHWA) provides high-quality information to serve Government, industry, and the public in a manner that promotes public understanding. Standards and policies are used to ensure and maximize the quality, objectivity, utility, and integrity of its information. The FHWA periodically reviews quality issues and adjusts its programs and processes to ensure continuous quality improvement.

Iowa DOT Statements

Federal and state laws prohibit employment and/or public accommodation discrimination on the basis of age, color, creed, disability, gender identity, national origin, pregnancy, race, religion, sex, sexual orientation or veteran's status. If you believe you have been discriminated against, please contact the Iowa Civil Rights Commission at 800-457-4416 or the Iowa Department of Transportation affirmative action officer. If you need accommodations because of a disability to access the Iowa Department of Transportation's services, contact the agency's affirmative action officer at 800-262-0003.

Technical Report Documentation Page

1. Report No. IHRB Project TR-708C	2. Government Accession No.	3. Recipient's Catalog No.			
4. Title and Subtitle Enhancing the Fundamental Knowledge and Use of Asphalt Emulsions Using Systematic Scientific and Engineering Approaches		5. Report Date August 2018			
		6. Performing Organization Code			
7. Author(s) Ashley Buss (orcid.org/0000-0002-8563-9553), Irvin Pinto (orcid.org/0000-0003-0311-4049), Minas Guirguis (orcid.org/0000-0002-6555-2266), Eric Cochran (orcid.org/0000-0003-3931-9169), and Matthew Panthani (orcid.org/0000-0002-3795-2051)		8. Performing Organization Report No.			
9. Performing Organization Name and Address Institute for Transportation Iowa State University 2711 South Loop Drive, Suite 4700 Ames, IA 50010-8664		10. Work Unit No. (TR AIS)			
		11. Contract or Grant No. Part of DTRT13-G-UTC37			
12. Sponsoring Organization Name and Address <table style="width: 100%; border: none;"> <tr> <td style="width: 50%;">Midwest Transportation Center 2711 S. Loop Drive, Suite 4700 Ames, IA 50010-8664</td> <td style="width: 50%;">U.S. Department of Transportation Office of the Assistant Secretary for Research and Technology 1200 New Jersey Avenue, SE Washington, DC 20590</td> </tr> </table> Iowa Highway Research Board Iowa Department of Transportation 800 Lincoln Way Ames, IA 50010		Midwest Transportation Center 2711 S. Loop Drive, Suite 4700 Ames, IA 50010-8664	U.S. Department of Transportation Office of the Assistant Secretary for Research and Technology 1200 New Jersey Avenue, SE Washington, DC 20590	13. Type of Report and Period Covered Final Report	
		Midwest Transportation Center 2711 S. Loop Drive, Suite 4700 Ames, IA 50010-8664	U.S. Department of Transportation Office of the Assistant Secretary for Research and Technology 1200 New Jersey Avenue, SE Washington, DC 20590		
14. Sponsoring Agency Code					
15. Supplementary Notes Visit www.intrans.iastate.edu for color pdfs of this and other research reports.					
16. Abstract <p>Due to their lower application temperature, lower energy consumption, and lower viscosity, asphalt emulsions are gaining popularity in the United States and worldwide. About 3 million tons of asphalt emulsion are produced in the US, which accounts for 5% to 10% of the total asphalt consumption. However, there is still a lack of understanding of the mechanisms by which asphalt emulsions are produced and how they work.</p> <p>This report reviews current literature available on asphalt emulsions to determine the present state of the practice, documents the development of an asphalt laboratory at Iowa State University, reports asphalt emulsion results, and creates an action plan for future work.</p> <p>Two standard emulsions, one non-modified and one polymer-modified, were produced in the laboratory using a state-of-the-art laboratory-scale asphalt emulsion mill, emulsion properties were compared and experience was gained. To determine standards by which to compare emulsions to the performance grade (PG) system of binder classification, master curves of elastic modulus (G^*) were plotted between emulsion residue and their base binders. The elastic recovery of polymer-modified asphalt emulsion residue was also tested to compare its performance with polymer-modified binders. Finally, sweep tests were conducted on laboratory-prepared chip seal samples to compare the aggregate mass lost between samples prepared with asphalt emulsion and hot applied asphalt.</p>					
17. Key Words asphalt emulsions—pavement preservation—polymer-modified emulsion		18. Distribution Statement No restrictions.			
19. Security Classification (of this report) Unclassified.	20. Security Classification (of this page) Unclassified.	21. No. of Pages 44	22. Price NA		

ENHANCING THE FUNDAMENTAL KNOWLEDGE AND USE OF ASPHALT EMULSIONS USING SYSTEMATIC SCIENTIFIC AND ENGINEERING APPROACHES

Final Report
August 2018

Principal Investigator

Ashley Buss, Assistant Professor
Civil, Construction, and Environmental Engineering, Iowa State University

Co-Principal Investigators

Eric Cochran, Associate Professor
Matthew Panthani, Associate Professor
Chemical and Biological Engineering, Iowa State University

Research Assistants

Irvin Pinto
Minas Guirguis

Sponsored by

Midwest Transportation Center,
U.S. Department of Transportation
Office of the Assistant Secretary for Research and Technology,
Iowa Highway Research Board, and
Iowa Department of Transportation
(IHRB Project TR-708C)

Preparation of this report was financed in part
through funds provided by the Iowa Department of Transportation
through its Research Management Agreement with the
Institute for Transportation

A report from

Institute for Transportation
Iowa State University

2711 South Loop Drive, Suite 4700

Ames, IA 50010-8664

Phone: 515-294-8103 / Fax: 515-294-0467

www.intrans.iastate.edu

TABLE OF CONTENTS

ACKNOWLEDGMENTS	vii
EXECUTIVE SUMMARY	ix
Background	ix
Research Methodology	ix
Key Findings	x
Implementation Readiness and Benefits	x
INTRODUCTION	1
Problem Statement	1
Current State of Practice	1
Critical Focus Areas	2
Objective	2
Emulsion Formulation	2
Important Factors to Consider for Emulsion Formation	3
LITERATURE REVIEW	4
The Significance of Particle Size	4
Factors Influencing Emulsion Stability	6
Engineering Asphalt Emulsions to the Aggregates	8
Polymer-Modified Emulsions	8
Emulsion Testing	11
Applications of Asphalt Emulsions to Pavement Preservation and Rehabilitation	11
TEST PLAN AND PROCEDURE	13
Research Plan	13
Specific Tasks	13
Polymer Modification of Asphalt Binder	16
Asphalt Emulsion Manufacturing Process	16
Testing for Emulsion Residue	20
RESULTS AND DISCUSSION	22
Particle Size Analysis	22
Saybolt Viscometer Flow Timings	23
Residue and Neat Binder Master Curve Analysis	23
MSCR Test Comparison	24
Sweep Tests	27
CONCLUSIONS AND FUTURE WORK	29
REFERENCES	31

LIST OF FIGURES

Figure 1. Dynamic shear rheometer used to run frequency sweeps and construct master curves	14
Figure 2. Shear mill for mixing polymers into asphalt binder (left) and SBS polymer (right)	16
Figure 3. Soap making process	17
Figure 4. Asphalt emulsion mill.....	18
Figure 5. Viscosity versus temperature sweep of non-modified PG 64-22 binder.....	19
Figure 6. Viscosity versus temperature sweep of polymer-modified PG 64-22 binder with 3% SBS by weight	19
Figure 7. Pouring emulsion samples for residue testing (left) and weighing the residue retained after 24 hours (right)	21
Figure 8. CRS-2 particle size distribution.....	22
Figure 9. CRS-2P particle size distribution	23
Figure 10. Complex shear modulus versus angular frequency (master curves) for neat binder and emulsion residue.....	24
Figure 11. PG 64-22 polymer-modified binder tested at 25°C, and at stress levels 0.1 KPa (left) and 3.2 KPa (right).....	25
Figure 12. PG 64-22 polymer-modified binder tested at 52°C, and at stress levels 0.1 KPa (left) and 3.2 KPa (right).....	25
Figure 13. CRS-2P residue tested at 25°C, and at stress levels 0.1KPa (left) and 3.2Kpa (right).....	26
Figure 14. CRS-2P residue tested at 52°C, and at stress levels 0.1KPa (left) and 3.2KPa (right).....	26
Figure 15. Percent mass loss versus application type	27

LIST OF TABLES

Table 1. List of tests performed with corresponding standard and expected values	15
Table 2. Saybolt viscometer flow timings	23
Table 3. MSCR results.....	27
Table 4. P-value calculated from student t test.....	27
Table 5. Mean and standard deviation for sweep tests	28

ACKNOWLEDGMENTS

The authors would like to thank the Iowa Department of Transportation (DOT), Iowa Highway Research Board (IHRB), Midwest Transportation Center, and U.S. Department of Transportation Office of the Assistant Secretary for Research and Technology for sponsoring this project. This was one of four pilot projects for novel or innovative ideas and fundamental advances that were sponsored.

The authors would like to thank Paul Kremer at Iowa State University for his help developing the asphalt emulsion laboratory. The authors would also like to acknowledge the assistance and materials provided by Ingevity, especially Tim O'Connell and Dave Welborn. Thank you to Bill Kubacki at Bituminous Materials for his assistance and providing asphalt, Vince Vopat at Bergkamp, Inc. for assistance with the laboratory mill, and Chris Lubbers with Kraton Polymers. Finally, we would also like to recognize the helpful conversations we have had over the past several years with many individuals who have spent their careers in industry improving asphalt emulsions.

EXECUTIVE SUMMARY

Background

Due to their lower application temperature, lower energy consumption, and lower viscosity, asphalt emulsions are gaining in popularity in the United States and worldwide. About 3 million tons of emulsion is produced in the US, which accounts for 5% to 10% of the total asphalt consumption. However, there is still a lack of understanding of the mechanisms by which asphalt emulsions are produced and how they work. A review of the literature identified the following shortcomings in current practice:

- Much of the available information is contained in patented literature. There is a lack of information on asphalt emulsion technology in peer-reviewed journals that are easily accessible to the local agencies and research institutions.
- Due to a lack of information available, there is a lack of understanding of asphalt emulsion applications, i.e., which type of emulsion to use in a particular situation.
- There is a need to develop scientific standards to compare different emulsions to replace antiquated methods.

The above shortcomings prevent researchers from developing asphalt emulsion formulations to better enhance roadway sustainability.

This research initiative will help disseminate knowledge on asphalt emulsions and help fuel a better understanding of emulsion components to improve standards and test methods for emulsions.

Research Methodology

Two emulsions were produced in an emulsion mill for purpose of comparison. One emulsion was a standard non-modified emulsion and the other emulsion was a polymer-modified emulsion made from a binder modified with a styrene-butadiene-styrene (SBS) polymer. Particle size analysis of both the emulsions was performed in order to get an idea of their individual microstructures. Viscosity tests were performed on both polymer-modified emulsion and non-modified emulsion to determine differences in rheology as a result of polymer modification. Residues were then obtained from both these emulsions to be compared with neat asphalt binder and polymer-modified asphalt binder. The asphalt binder grades were the same as those used in making emulsion and the same polymer that was used in the preparation of the polymer-modified binder was used to modify the binder to be emulsified. These residues were tested in the dynamic shear rheometer, and master curves of complex shear modulus versus frequency were plotted. Multiple stress creep recovery (MSCR) tests were performed on both the polymer-modified binder and the residue of the polymer-modified emulsion to determine how their elastic recoveries compared.

In order to determine their application potential, sweep tests were performed with aggregate and hot applied binder as well as asphalt emulsions to determine how emulsions and neat binder would compare when it came to field performance for chip seal applications.

Key Findings

Some of the main findings from preliminary emulsion formulation and testing indicate that the residues obtained from emulsions compare similarly to the neat binders and have slightly higher G^* values than their respective neat binders. Viscosity tests show that 66% and 68% residue non-modified emulsions have almost identical flow times and that the small increase, at the 66% to 68% residue range, does not significantly increase viscosity.

Particle size testing revealed that while the non-modified emulsion showed a narrower particle size distribution with a relatively larger mean particle size of 6 microns, the polymer-modified emulsion showed a wider particle size distribution with two distinct particle sizes, one that was assumed to be binder particles and the other assumed to be polymer particles. In future work, the amount of polymer can be optimized to milling temperature/speed, which would help narrow the particle size distribution.

Implementation Readiness and Benefits

Asphalt emulsions have the advantage of low viscosity at lower temperatures compared to hot applied asphalts. Now, properties of standard emulsions, both polymer-modified and non-modified, can be produced in the laboratory and their properties can be studied more in detail in a university setting.

Laboratory testing of emulsion residue showed that it performs similar to the base binder. The emulsion residue had slightly higher $|G^*|$ values than the base binder, especially at lower loading frequencies. This was also true for the polymer-modified emulsion residue, despite failing the Saybolt flow test and having a slightly lower elastic recovery than the polymer-modified base binder. More optimization in the lab is needed for production of polymer-modified asphalts. Further investigation and optimization studies for developing and manufacturing polymer-modified emulsions will yield better viscosity results and possibly higher elastic recovery.

INTRODUCTION

Problem Statement

The rising popularity of pavement preservation treatments has seen an increased interest in asphalt emulsions, which are often used in pavement preservation treatments like slurry seals, chip seals, tack coats, and microsurfacing. Asphalt emulsions have the advantage of being lower in viscosity and have lower application temperatures than normal bitumen, which helps reduce emissions and energy consumption and eliminates oxidation of asphalt. Lower operating temperatures also mean that asphalt emulsions are less hazardous to handle. However, the manufacturing of bituminous emulsions is a complicated process. Asphalt emulsions are formulated to suspend small asphalt droplets (oil) in water and stabilized with a suitable emulsifier. The formulation of these emulsions is a complex task since the type and amount of emulsifier and shearing force used in dispersion greatly affects the particle size and the stability of the emulsion and influences its properties (Ronald and Luis 2016). Asphalt emulsions are designed to be in a stable suspension when stored; however, when they come into contact with aggregate surfaces, the emulsions are formulated to break and form a layer of asphalt around aggregate particles. The rate at which the asphalt emulsion breaks depends on the chemical design and emulsifier used and on the nature of the aggregates the emulsion comes in contact with. Polymer modification of emulsions is also becoming increasingly common in order to achieve better performance parameters, with studies focusing on the stabilization of polymer-modified emulsions for better performance (Hesp and Woodhams 1992, Alade et al. 2016).

The particle size of asphalt emulsions plays an important role in stability. Smaller particle sizes are favorable for higher stability. The larger the particle size, the easier it is for particles to coalesce and cause the emulsion to break.

Current State of Practice

Due to their lower application temperature, lower energy consumption, lower viscosity, and the need for preservation and sustainable methods, asphalt emulsions are gaining in popularity in the United States and worldwide. About 3 million tons of emulsion is produced in the US, which accounts for 5% to 10% of the total asphalt consumption; however, there is still a lack of understanding of the mechanisms by which asphalt emulsions are produced and how they work. Some of the shortcomings in current practice are as follows:

- Much of the available information is contained in patented literature. There is a lack of information on asphalt emulsion technology in peer-reviewed journals that are easily accessible to the local agencies and research institutions.
- Due to a lack of information available, there is a lack of understanding of asphalt emulsion applications, i.e., which type of emulsion to use in a particular situation.
- There is an urgent need to develop scientific standards to compare different emulsions to replace antiquated methods.

The above shortcomings prevent researchers from developing asphalt emulsion formulations to better enhance roadway sustainability.

Critical Focus Areas

This project focused on better understanding of the underlying mechanisms that drive emulsion formation, stability, and setting. The project aimed to do the following:

- Disseminate available literature to gain a thorough knowledge of current practices in bituminous emulsion technology.
- Use the knowledge gained to formulate two standard emulsions, one non-modified and one polymer-modified.
- Compare the modified and non-modified emulsions with the help of standard emulsion tests like the Saybolt viscometer test, penetration test, and residue testing. In addition, perform rheological testing.
- In the comparison, focus on how polymer-modified emulsions compare to non-modified emulsions and how emulsion residue compares to the base binders used to create the emulsion.

Objective

As explained, there is an urgent need to improve the current understanding of how asphalt emulsions are formulated, produced and optimized for sustainable pavement construction, preservation, and rehabilitation.

Emulsion Formulation

Two standard emulsions were formulated with help from industry partners. One of the emulsions was non-modified while the other was modified with a polymer. A standard styrene-butadiene-styrene (SBS) polymer was used in bitumen modification; however, further optimization is needed in the laboratory's production of polymer-modified bitumen. The procedure for emulsion formulation is given below:

- Determine the amount of total solids (% residue) needed. The total amount of solids in a recipe determines the flow rates of the emulsifier-water soap solution and bitumen. Different emulsifiers were used to produce different types of emulsions based on their charge and setting time. The pH of the emulsion was controlled by titrating the soap solution with an acid (HCL).
- Produce a standard cationic rapid-set, non-modified emulsion with a target percent residue.
- Produce a standard polymer-modified emulsion using the same base asphalt grade and source to minimize error, with the same emulsifier.
- Compare the properties of both emulsions, polymer-modified and non-modified.
- Compare the residue of the emulsions to that of their base binders.

- Compare the strain recovery of the polymer-modified emulsion residue and the polymer-modified binder.
- Conduct sweep tests to determine the aggregate chip retention potential of emulsion residue compared with hot applied binder on laboratory-prepared chip seal samples.

Important Factors to Consider for Emulsion Formation

The formation, stability, and applicability of an emulsion depend on a number of factors namely:

- Particle size: smaller particle sizes typically mean more stable emulsions, since larger droplets can more easily coalesce.
- Mixing time: higher mixing times tend to produce smaller sized droplets due to longer application of shear.
- Mixing speed: assuming a mean droplet diameter of 2 μm at 2,000 rpm, increasing the mixing speed will decrease the droplet diameter further, while decreasing the mixing speed will correspondingly increase the droplet diameter.
- Asphalt content (volume fraction).

LITERATURE REVIEW

The rising popularity of pavement preservation treatments has seen an increased interest in asphalt emulsions, which are often used in pavement preservation treatments like slurry seals, chip seals, microsurfacing, fog seals, and tack coats. Asphalt emulsions are carefully produced and formulated blends of asphalt droplets suspended in water and stabilized with a suitable emulsifier. Other additives used in their formulation include latex and other various polymers, viscosity modifiers, solvents, and stabilizers. The formulation of these emulsions is a complex task since the type of emulsifier and shearing force used in dispersion greatly affect the particle size and the stability of the emulsion and, hence, influence its properties (Ronald and Luis 2016). Asphalt emulsions are designed to be in a stable suspension when stored; however, when they come into contact with aggregate surfaces, the emulsions are formulated to break and form a layer of asphalt around aggregate particles. The rate at which the asphalt emulsion breaks depends on the chemical design and emulsifier used.

Bituminous emulsions are typically oil-in-water emulsions (Alade et al. 2016, Arenas-Calderon et al. 2014, Banerjee et al. 2013). This means that globules of asphalt are dispersed in an aqueous phase. There have been cases where water-in-oil-in-water emulsions have been prepared based on cutback bitumen.

Bituminous emulsions typically contain 40% to 80% bitumen and are brown in appearance with varying consistency. Asphalt droplet particle sizes usually range from 0.5 to 20 microns (Ingevity). The lower the bitumen content, the lower the viscosity of the emulsion will be (Gingras et al. 2005). The concentration of bitumen has been increased to higher fractions as seen in a study by Arenas-Calderon et al. (2014), who prepared emulsions with bitumen percentages as high as 95% by catastrophic phase inversion. More details on catastrophic phase inversion will be discussed later.

The Significance of Particle Size

The viscosity of asphalt emulsions typically depends on the bitumen droplet size and distribution. Smaller droplet sizes lead to a higher viscosity. However, a smaller particle size distribution will decrease the viscosity of an emulsion (Barnes 1994). This is because particle deformity decreases with particle size and there are subtle effects due to Brownian or osmotic pressure where smaller particles have increased resistance to shear. Also, smaller particles have larger surface area, and if insufficient stabilizer is available, flocculation can occur. Particle size plays a larger effect on flocculated systems and flocculation plays a major role in determining viscosity.

Stokes' law can also be used to explain the relationship between particle size and phase separation (F. Wang et al. 2012, Yang et al. 2013). Particle size would play a role in the sedimentation of the emulsion according to the equation $\vartheta_0 = \frac{2r^2(\Delta\rho)}{9n}$, where ϑ_0 is the sedimentation rate of a single droplet, $\Delta\rho$ is the density difference between the external and internal phases, r is the radius of the droplet, and n is the shear viscosity. If the particle size

increases, so will the sedimentation rate. Also, since temperature affects the shear viscosity, a higher temperature would lower the shear viscosity and increase the sedimentation rate. Also noteworthy is the effect of the difference in densities between water and asphalt. The Stokes' equation shows that the sedimentation rate is directly proportional to the difference between the densities of the immiscible liquids. A positive difference, which would occur when the dispersed phase has a higher density, leads to sedimentation, while a negative difference, occurring when the dispersed phase is lighter, leads to creaming.

Emulsion particle size is mainly controlled in the production stage. Milling speed, milling time, amount of stabilizer, and the asphalt fraction all affect the particle size of an emulsion (Barnes 1994, Arenas-Calderon et al. 2014, Tadros 2013). In general, an increase in shear rate leads to smaller particles due to a large amount of energy in dispersion. Similarly, a longer milling time also leads to a reduction in particle size. Higher percentages of bitumen tend to increase particle size since there is an increase in the amount of solids, which makes coalescence more difficult to prevent (James 2006). The nature of the emulsifier also affects particle size. Emulsifiers, when diffused in solution, release ions that vary in chemical nature. They consist of a lipophilic tail and a hydrophilic head. The head of these ions can play a role in determining particle size. A larger head group leads to larger size particles formed while a smaller head group leads to smaller particles being formed. Protonation and deprotonation play an important role in the stability of emulsions. Protonation is the chemical process of a molecule receiving a hydrogen ion and taking on a positive charge, while deprotonation implies the opposite, where a molecule loses a hydrogen ion, which occurs especially in an aqueous solution. This concept can be applied to asphalt emulsions by observing the size of the polar segments of emulsifiers. Polar segments, which are highly stearic and bulky, cannot deprotonate easily if it approaches a negatively charged surface or a hydroxyl ion, which leads to higher stability but a slower set. Hence, from the above argument, fatty amines with large polar heads are more stable and find use in the manufacture of slow set emulsions (Schilling and Schreuders 1988). From a thermodynamic standpoint, smaller particles are more likely to flocculate and coagulate due to their large surface area. An increase in surface area as asphalt is broken up leads to an increase in surface energy. Mathematically, surface energy is given by the following: $\Delta A\gamma_{\text{tension}}$, where ΔA represents the positive change in area when a large asphalt droplet is broken up and γ_{tension} is the interfacial tension between asphalt and water. From the second law of thermodynamics, the free energy of formation of the emulsion $\Delta G_{\text{formation}}$ is as follows:

$$\Delta G_{\text{formation}} = \Delta A\gamma_{\text{tension}} - T\Delta S \quad (1)$$

where $T\Delta S$ is the increase in entropy. In order for the emulsion system that is being formed to be stable, there should be a reduction in the total free energy of the system, i.e., the total free energy $\Delta G_{\text{formation}}$ should be negative. Because of the large surface area of the droplets, $\Delta A\gamma_{\text{tension}}$ is greater than $T\Delta S$. Therefore, $\Delta G_{\text{formation}}$ is positive and the emulsion is unstable. The second law of thermodynamics reiterates the need for a large amount of energy that is needed for the emulsification process of two immiscible phases, in this case, water and asphalt. The second law of thermodynamics also points out that this energy gap needs to be maintained; the emulsified state is unstable, i.e., $\Delta G_{\text{formation}}$ is positive. Hence, in the absence of the required amount of emulsifier, the smaller particles will eventually coagulate. The emulsifier decreases the surface energy of the particles and reduces $\Delta G_{\text{formation}}$, thereby stabilizing the emulsion. Smaller particles

will need more emulsifier to coat their surfaces and cause interparticle repulsion due to their larger surface area.

Factors Influencing Emulsion Stability

The type of stabilizer used greatly affects the final emulsion properties. As explained in the previous section, emulsifiers surround bitumen droplets and create an energy barrier that prevents coagulation and negates the large positive surface energy and is, hence, key to the stability of an emulsion. Emulsifiers can be classified on the basis of their charge, namely anionic, cationic, (Rodríguez-Valverde et al. 2008) or nonionic. The key to keeping bitumen droplets in suspension and preventing coalescing is for the emulsifier to be adsorbed on the droplet surface. Since the emulsifiers carry a surface charge, the droplets coated with emulsifier repel one another and stay in suspension. Tadros (2013) explains that the mechanisms for emulsion breakdown are creaming and sedimentation, flocculation, Ostwald ripening (Kabalnov and Shchukin 1992, Tadros 2013), coalescence, and phase inversion (Arenas-Calderon et al. 2014, Tadros 2013). Creaming and sedimentation both occur due to density differences between the two liquids in an emulsion. If the dispersed phase is lighter, creaming occurs, which involves the lighter dispersed material to coagulate at the top of the primary phase. Sedimentation is the opposite, where an emulsion breaks down when the heavier dispersed phase settles to the bottom and coagulates. Ostwald ripening occurs when the average radii of emulsion particles grow over time due to the addition of smaller droplets on their surface. Phase inversion occurs when the dispersed phase now becomes the primary phase, usually due to the increase in the fraction of the dispersed phase beyond a certain amount (Kralchevsky et al. 2005, Bouchama et al. 2003). The concepts governing these individual mechanisms will be discussed later. By themselves, bituminous emulsions are unstable in nature. The particles have insufficient surface energy to counter flocculation and coalescence. Asphalt particles need an energy barrier in order to stay in suspension. This energy barrier is provided by surfactants and emulsifiers (Tadros 2013). When emulsifiers are adsorbed on the surfaces of the asphalt particles, they form double diffused layers, which repel other particles due to their similar surface charge (Acevedo et al. 2001, Ottewill 1977).

As explained above, adding a stabilizer to an emulsion of two immiscible liquids, in this case, asphalt and water, is critical to achieving a stable end product. The stability of an emulsion depends often on the electrolyte concentration in the emulsion, with lower electrolyte concentration often offering higher stability and favoring stronger double diffused layers between surfactant micelles and the interfaces of the two immiscible phases (Banerjee et al. 2013) and can be quantified by passing an electric current through an emulsion and measuring the voltage drop across the electrodes. A study by (Alade et al. 2016) confirmed that the concentration of salt in the continuous phase of an emulsion has an effect on the stability of the emulsion, with a low concentration of NaCl in aqueous phase to the order of 0.5% weight for weight (w/w) increasing emulsion stability as compared to a control sample; however, higher concentrations of NaCl above 1% w/w led to a decrease in emulsion stability. A similar study done using sodium carbonate as a surfactant showed a similar trend, with decreasing interfacial tension for low concentrations of Na₂CO₃ followed by a gradual increase in both surface tension and viscosity (Acevedo et al. 2001), showing that the percentage of stabilizer in emulsion formation is crucial. Rheology of emulsions can also be a factor used to determine emulsion

stability. Research has shown that a change in viscosity of an emulsion can point to coalescence. Since a stable emulsion would have a stable droplet size and constant droplet spacing, an increase in viscosity over time would point to increasing particle size and, hence, coalescence (Ronald and Luis 2016, Gutierrez et al. 2002). Hence emulsion stability can be determined by following the change in the rheology of the emulsion over time. A simple experiment to determine how rheology affected stability was proposed by Zhai et al. (2004), who tracked the changes in complex storage and loss modulus to determine the phase changes in asphalt emulsion. The differences in the rheological properties were related to the type of interactions in emulsified asphalts, i.e., electrostatic, steric, cationic, and anionic. The evolution of viscosity with time on the application of a constant shear rate was studied by Legrand et al. (2005), who used silica particles to cause emulsions to coalesce. They noted the change in viscosity η with a constant shear and found that η remains constant for a finite amount of time before rapidly increasing in the presence of silica particles. The authors noted that asphalt droplet particle size, amount of silica and its particle size, and shear rate were some of the factors that influenced the time at which viscosity sharply increased and the emulsion began to coalesce. Rheology is directly linked to temperature, and an increase in temperature will also increase the stability of emulsions according to Al-Sabagh et al. (1997), who proposed that the decrease in viscosity allows the surfactant to be more effectively transported to the oil-water interface, where they can stabilize the emulsion

Other research has shown similar trends in droplet diameter with mixing time, shear speed, and bitumen content (Gingras et al. 2005, Gutierrez et al. 2002). For a stable emulsion, it is desired that the drop sizes are as small as possible, with as high of a bitumen content as possible. However, as seen from trends shown in the above research, an increase in bitumen content leads to large drop sizes with a higher probability of phase separation. However, by using catastrophic phase inversions, stable emulsions with smaller droplet sizes at higher asphalt contents can be prepared (Arenas-Calderon et al. 2014). As explained earlier in this section, catastrophic phase inversion is a mechanism of emulsion breakdown. It is primarily employed to create emulsions of smaller size of opposite type, i.e., from water-in-oil to oil-in-water, merely by increasing the concentration of water in the emulsion. Since the two emulsions will have different conductivity due to the phase change, conductivity of the emulsion can be used to determine the point at which phase inversion occurs.

Asphalt emulsions are either cationic or anionic in nature depending on the charge of the head groups of the emulsifiers. Therefore, the pH of the soap solution has an important role to play in emulsion stability. A study of the effects of cement curing on the stability of asphalt emulsions shed light on the effects of Ca^{2+} ions on the zeta potential, and thus, the stability of the asphalt emulsions. Zeta potential is defined as the potential difference between a surface of a fluid particle and its surrounding media. The higher the zeta potential, the higher the stability of the emulsion. When cement cured, the release of Ca^{+2} ions caused an increase in pH and a sharp decrease in the zeta potential of cationic emulsions causing a loss in stability of the emulsion. On the other hand, curing aided the stability of anionic emulsions, causing them to be stable at pH values above 12. This information is particularly useful for a cement-emulsion stabilizer for cold-in-place and full-depth reclamation mixes, since a combination of the two stabilizers negates the negative effects of a single stabilizer system. Particle size was only slightly affected

by a drop in zeta potential. Due to coalescence, the particle size of cationic emulsions in the presence of Ca^{+2} ions was larger.

Engineering Asphalt Emulsions to the Aggregates

Asphalt emulsions generally break when brought in contact with aggregates. This is because aggregate particles contain cations, which raise the number of OH^- ions in the emulsion and lead to setting. Research has shown that the type of aggregate has an important role in determining when an emulsion will set (Ziyani et al. 2016). The surface energy of mineral aggregates has a major role in deciding the wetting potential of emulsions with the aggregate surface. Gneiss has the lowest surface energy when compared to quartzite, which has the highest surface energy and, hence, is more suited for emulsions since it shows a higher affinity for low-energy surfaces.

The chemistry of the asphalt emulsion also plays an important role in determining the nature of its setting. Emulsions can be manufactured to set at different rates based on the type of surfactants, their concentration, and additives used. The setting speed of emulsions is relative to its destabilizing effect. A rapid-set emulsion will set rapidly when brought in contact with aggregate, while a slow set emulsion would take hours to break when brought in contact with aggregate. The breaking time of emulsions has an important role to play in deciding its application. Slow-setting emulsions are commonly used in tack coats and fog seals, while rapid-setting emulsions are used in chip seals and microsurfacing. Pavement rehabilitation techniques like cold-in-place recycling and full-depth reclamation usually employ slow- and medium-setting emulsions. Apart from giving stability to emulsions, as mentioned in previous subsections, emulsifiers also give the emulsion a particular charge. This charge is responsible for determining the abovementioned setting characteristics (James 2006). Aggregates also take on certain surface charges in water. Acidic aggregates, which are high in silica, have a negative charge, while aggregates like limestone take up a positive charge; therefore, it is important to engineer the emulsion according to the aggregate properties. If emulsion and aggregate are not compatible, the emulsion will not set properly.

Cationic emulsions are favored over anionic emulsions for cold recycling due to the ability of cationic surfactants to react with both alkaline and acidic aggregates and form salts that are adsorbed on the interface of the aggregate surface and the emulsion, hence increasing the aggregate-asphalt bond (Oruc et al. 2007).

Polymer-Modified Emulsions

Just like in normal asphalt, polymers are also used to modify asphalt emulsions to enhance their physical properties, performance, and durability. Common polymers used to modify asphalt emulsions include SBS (Johnston and King 2012), acrylonitrile butadiene rubber (NBR) (H. Abedini et al. 2017), styrene-butadiene rubber (SBR) (M. Abedini et al. 2017, Takamura 2003), and natural rubber latex (NRL). Polymers that are added to asphalt may either be thermoplastic elastomers, thermoset elastomers or thermoplastic plastomers. Elastomeric polymers can be stretched up to 10 times their length without breaking and quickly return to their original state. SBS and crumb rubber are two of the common elastomers used to modify asphalt. Plastomeric

polymers, on the other hand, gain strength extremely quickly but are rather brittle in nature. Low-density polyethylene (LDPE) and ethyl vinyl acetate (EVA) are two examples of elastomers. Polymers can also be thermoplastic or thermoset. Polymers typically form a cross-linking system when mixed with asphalt. While this cross-linking system is permanent in thermoset polymers, this cross linking can be reversed and reformed in the case of thermoplastic polymers.

NRL is mixed with cationic surfactants and emulsified with asphalt in an emulsion mill. The produced emulsion is cationic and reacts with the anionic surface of the latex, which increases wettability (Johnston and King 2012). The corresponding system formed consists of latex particles dispersed around asphalt stabilized with surfactant molecules. When this system comes into contact with aggregates, the latex helps to form better bonding between the aggregate and the asphalt during curing due to the positively charged ions that surround its surface. Like NRL, SBR latex is another polymer that is added to an emulsion in liquid form along with the surfactant during emulsification. SBR latex forms a honeycombed polymer network through the emulsion. This helps form a strong bond between the aggregate and emulsion during curing. When the water evaporates, this honeycomb structure acts as welds, allowing the aggregate and emulsion to bond better, helping increase chip retention in chip seals. Most solid polymers are added to asphalt binder prior to emulsification. In contrast, water-soluble latex can be added to the emulsion after milling. This includes block polymers like SBS. SBS is a block copolymer that consists of chains of styrene and butadiene. These block polymers are lightweight and highly elastic. Reclaimed rubber is another modifier that can be used as a modifier in emulsified asphalts; however, due to its high molecular weight and extensive cross-linking, it is not highly compatible with asphalt binder and would cause phase separation on emulsification. In contrast, vulcanizing crumb rubber and shearing at a high speed improves compatibility and emulsifiability (Johnston and King 2012). SBS is perhaps the most compatible polymer that is used for asphalt modification and is also highly elastic (Shafii et al. 2011). It has a strong cross-linked structure that contributes to its strength and elasticity. Studies have shown that emulsified asphalts that contain SBS polymers show good adhesion to surfaces when compared to the unmodified binder (Serfass et al. 1992). EVA is another polymer that is used in asphalt modification for increased workability, but there have not been many records of it used in emulsions. Polyvinyl acetate (PVA) is another resin-based polymer that is available in emulsion form and therefore can readily be mixed with emulsified asphalt and that contains no flammable solvents (Toxqui-López et al. 2006). As explained above, polymers may either be post-blended or pre-blended with asphalt, either prior to, or during emulsification. There are four methods of including polymers in an emulsion formulation:

- Pre-blending, where the polymer is added to the asphalt binder prior to emulsification
- Co-milling, where binder, emulsifier and polymer are added to the mill in different streams and milled together
- Pre-batching with soap, where the polymer is incorporated into the soap solution
- Post-modification, where the polymer is added to the emulsion either at the plant or in the field

Literature reveals that most polymers, with the exception of latexes like NRL, SBR, and crumb rubber modifiers (CRMs), are added to the asphalt binder prior to emulsification (Johnston and King 2012). It is interesting to note that while some polymers display a widely uneven particle size, often characteristic of poor compatibility, the same modified binder when emulsified showed an even particle size distribution (Johnston and King 2012, Forbes et al. 2001). Phase separation and stability are the two problems that occur due to mixing an emulsion with solid polymers according to Becker et al. (2001). Therefore, post-mixing of solid polymers with an asphalt emulsion at a plant is discouraged. Some latexes in liquid form can be pre-batched with soap solution and then combined with the binder in a mill, like NRL and SBR latex. Depending on when polymers are added, either mono-phase or bi-phase emulsions are produced. Here, mono-phase emulsions mean a single phase of polymer-modified asphalt droplets, while a bi-phase emulsion implies an emulsion of both polymer and asphalt droplets. Pre-blending of asphalt with polymer leads to a mono-phase emulsion that is stable at high temperatures. However, in the case of bi-phase emulsions, they are most commonly produced at lower temperatures while mixing asphalt, and emulsifiers tend to separate out at higher temperatures (Forbes et al. 2001). In the case of a mono-phase emulsion, asphalt and polymer particles interact during modification of the binder, whereas for a bi-phase emulsion, these two phases only interact on curing, when the water evaporates and the polymers form a continuous film around the asphalt particles. Depending on the method of addition of polymer, the microstructure of the cured emulsion will vary. Pre-blending polymer with asphalt creates an uneven distribution of polymer particles, which forms an even distribution on emulsification and includes aggregation of polymer-maltene particles and aggregated asphaltenes. This can be contrasted with post-addition methods, which very clearly display asphalt particles distributed within a latex network.

Just like regular non-modified emulsions, particle size plays an important role in the stability of polymer-modified emulsions. In this case, the particle size and morphology of the polymer is equally important. A study by Sabbagh and Lesser (1998) has shown that the shape of polymer particles play an important role in determining the stability of an emulsion. They noted that low-stability emulsions had polymer particles that were teardrop shaped, while stable emulsions had mainly cylindrical- and spherical-shaped polymer particles.

Polymer-modified emulsions have several advantages when compared to polymer-modified binder, according to Shafii et al. (2011). The advantages include a more homogeneous dry film with better polymer distribution when compared to that of polymer-modified binder. This allows for better stone retention in chip seals due to better cohesion strength. The compatibility of the polymer network distribution in residue from emulsions is also better than that of polymer-modified binders, due to the fact that polymer-modified binders often have local agglomerations of polymers and polymer incompatibility (Forbes et al. 2001). Unlike modified asphalt binder, addition of polymers do not significantly affect the low temperature performance, leading to less thermal cracking.

Polymer-modified emulsions tend to perform better than regular emulsions in cases of pavement preservation treatments. Studies have shown that in the case of chip seals, chip retention is markedly better in polymer-modified emulsions than regular emulsions (Lubbers and Watson 2005).

Emulsion Testing

Emulsion testing includes both tests for emulsion properties and tests of the residue properties. In order to fully understand the properties of an emulsion, testing should be done on both the emulsion and its residue. Some of the methods used to measure emulsified asphalt properties found in literature are the direct shear rheometer, Brookfield viscometer, Canon marine fuel viscometer, and a Bohlin viscometer (Salomón et al. 2018). Emulsion stability can be tested using electrokinetic methods (Banerjee et al. 2013). Similar tests are also run on asphalt emulsion residue. This includes the dynamic shear rheometer (DSR) and the bending beam rheometer (BBR). Since asphalt emulsion residue is essentially binder, conventional binder tests can be run on the emulsion residue in order to compare them to that of non-emulsified asphalts of the same performance grade (PG) to determine their correlation.

Viscosity tests can help better understand the emulsion being tested. Using a Brookfield viscometer, thixotropic behavior can be observed on asphalt emulsions, possibly due to breaking of the emulsion microstructure, according to Salomón and Palasch (2002). Testing was run on both anionic and cationic emulsions. It was observed that cationic emulsions attained equilibrium viscosity faster than anionic emulsions, and this could be attributed to the difference in interaction of droplets and emulsion microstructure. The Saybolt viscometer test is also a common test method to determine emulsion viscosity, along with the paddle viscometer. However, of more critical importance is the performance of an emulsion after it has “broken” or has set. Hence, it is important to test the emulsion residue in order to determine how the emulsion will behave in the field under traffic and also to correlate emulsion residue to a non-emulsified PG binder.

A highly debated topic in emulsion testing is determining a suitable method to recover emulsion residue. The current residue recovery methods are distillation and oven drying. While distillation is a more scientific method of residue collection and is more widely used to test emulsion residue, there is some argument that distillation does not mirror the in-field residue properties due to its high temperatures, so the residue obtained in the field will not have the same properties as that obtained through distillation (Farrar et al. 2013, Marasteanu and Clyne 2006, Hanz et al. 2012). Residue recovery methods like the thin film evaporative method were used by Hanz et al. (2012) in order to extract residue for effectiveness of emulsions on chip seals. Salomón et al. (2018) used a moisture analyzer test method (ASTM D7040-07) to obtain emulsion residue and determined that residue contents correlated well with residue obtained by evaporation (ASTM D244). Farrar et al. (2013) developed a new residue recovery technique, which includes a thin film oxidative aging test called the simple aging test. They also developed a new test procedure to evaluate the recovered residue using a 4 mm DSR plate, which requires only 25 mg of sample, as compared to the 50 to 100 g of sample needed for the BBR in order to test residue at low temperatures.

Applications of Asphalt Emulsions to Pavement Preservation and Rehabilitation

Asphalt emulsions have gained popularity in their use in pavement preservation and rehabilitation. Emulsions are commonly used with other stabilizers like cement, or by

themselves, to stabilize cold-in-place or full-depth reclaimed layers. They are popular in pavement preservation strategies like fog seals, tack coats, cape seals, chip seals, and microsurfacing. Their ability to be used at considerably lower temperatures is a huge benefit. One of the strongest cases that can be made for asphalt emulsions is its environmental impact compared to more conventional treatments (Ergon Asphalt & Emulsions Inc. 2015). Treatments like microsurfacing are cheaper than hot mix or modified hot mix treatments and have a lower environmental impact factor. A similar comparison of chip seal projects in Texas shows considerable savings when comparing treatments with a CRS-2P emulsion and conventional AC15-5TR binder, with the emulsions scoring a significantly lower skid number cost. Asphalt emulsions are not always used as standalone stabilizers but are commonly mixed with cementitious materials for better stabilization performance (Pouliot et al. 2003, Tan et al. 2014, Niazi and Jalili 2009, Z. Wang et al. 2015). This is due to the fact that cement mortar is more resistant to permanent deformation while emulsion performs better with cracking (Oruc et al. 2007). The influence of Ca^{+2} ions on the stability of cationic and anionic emulsions has been discussed above; however, there are other considerations to be made for emulsion-cement mixes. One particular study by Hu et al. (2009) examined the adsorption of asphalt emulsions on cement grains and their effect on the flowability and viscosity of the mix. They noted that the cement-to-asphalt emulsion ratio and the type of emulsions both had a major role to play in the final cement-asphalt particle size. A larger cement-asphalt emulsion ratio led to a larger particle size with mixing time. Also, cationic emulsions created larger cement-asphalt particles than anionic emulsions.

TEST PLAN AND PROCEDURE

Research Plan

The research objectives for this project revolved around producing and quantifying the performance of the emulsion. A standard non-modified cationic rapid-set emulsion and a cationic rapid-set standard polymer-modified emulsion were formulated and compared with each other and with their respective neat binders, one modified and one non-modified. The testing compared the rheological properties of the emulsion and the emulsion residues with the neat binders. The following comparisons were made:

- Comparing the Saybolt viscosity properties of a non-modified emulsion (CRS) and a polymer-modified emulsion (CRS-2P) where the polymer is added to the binder prior to emulsification.
- The results of this test helped compare the rheological properties of a polymer-modified and non-modified emulsion. Emulsion microstructure, stability, and particle size all contribute toward viscosity.
- Comparing the rheological properties of base binders to the emulsion residue using a dynamic shear rheometer.
- Comparing the complex modulus $|G^*|$ of the base binders, both neat and polymer-modified, with those of the emulsion residue, both modified and non-modified to help understand how emulsions compare to their base binders. This test was performed in accordance with ASTM D7552.
- Comparing the properties of polymer-modified binder to that of a polymer-modified emulsion using the same base binder. In order to understand the role of polymers in emulsions and how they compare to polymer-modified hot applied asphalts, multiple stress creep recovery (MSCR) tests were run on both polymer-modified binder as well as the residue from polymer-modified emulsions.

Specific Tasks

The specifics of each test are explained below.

Task 1: Comparing the Rheological Properties of Emulsions

Task 1 involved comparing a non-modified emulsion with that of a polymer-modified emulsion. The two parameters to be examined were particle size and viscosity. For asphalt emulsions, both particle size and rheology are closely related. Emulsions with smaller particle sizes tend to be much less viscous when compared to emulsions with larger particle sizes. The effect of polymerization can also be examined with both particle size analysis and viscosity testing. Particle size testing was done on a Malvern Mastersizer 2000. The asphalt emulsion was added drop by drop to water in a beaker as it circulated through a lens with a laser beam to measure the scattering of light due to the particles. The amount of light scattered was then related to the

particle size. A light obscuration of greater than 50% was required to be achieved before particle size analysis could be performed.

Viscosity measurements on asphalt emulsions are largely done with a Saybolt Furol viscometer and a paddle viscometer. In the case of a Saybolt viscometer, the viscosity of the emulsion is measured as a function of the flow time through an orifice. A water bath controls the temperature of the liquid inside the Saybolt tube. The flow time for the Saybolt viscometer is defined as the time in seconds taken for 60 ml of liquid to flow through the Saybolt orifice at a specific temperature. The Saybolt tube is filled with emulsion and the temperature of the emulsion in the tube is carefully observed with a mercury thermometer accurate to 0.1°C. When the temperature comes to within $50 \pm 0.1^\circ\text{C}$, the stopper holding the emulsion in the tube is removed and the emulsion is allowed to flow into a beaker marked with a level indicator for 60 ml, and a timer is simultaneously started. The timer is stopped when the 60 ml mark is reached.

Task 2: Comparing the Rheological Properties of Base Binder to Those of Emulsion Residue

Task 2 mainly involved characterizing emulsion residue and comparing it to base binder. Since there is no PG grading system for emulsions, one of the primary challenges of emulsion applications is comparing its performance with that of hot applied asphalt. Comparing emulsion residue to base binder will bring about a comparison of performance of asphalt emulsions in similar conditions. A dynamic shear rheometer (Figure 1) is used to obtain the complex shear modulus of the binder and residue; master curves can then be constructed at a reference temperature over a wide range of frequencies.

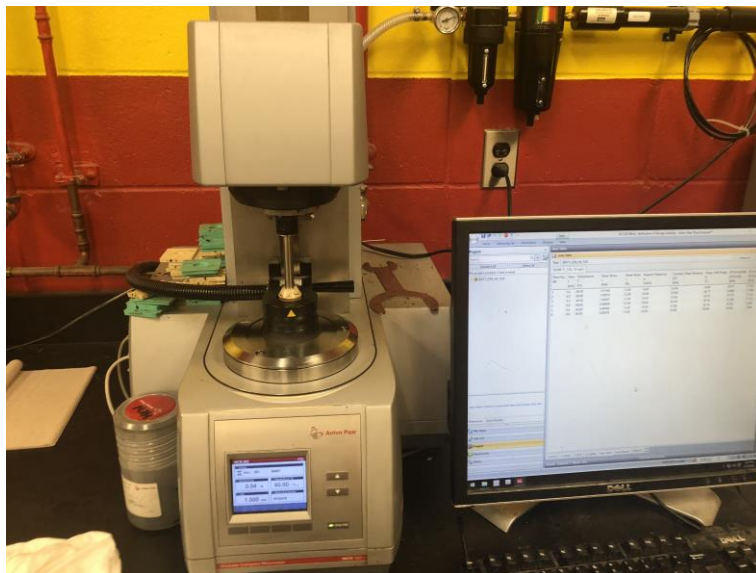


Figure 1. Dynamic shear rheometer used to run frequency sweeps and construct master curves

For this testing phase, 10 arbitrary frequencies were chosen between 0.1 rad/sec and 100 rad/sec, and testing was performed at 5 test temperatures of 22°C, 34°C, 46°C, 58°C, and 70°C. Master

curves were then created using the time-temperature superposition principle at a reference temperature of 25°C.

Task 3: Comparing Polymer-Modified Binder to Polymer-Modified Emulsion

Task 3 involved comparing the effectiveness of polymer modification on an emulsion by comparing its creep recovery to that of a polymer-modified binder. Binder with 3% w/w of SBS polymer was emulsified with Indulin AA-86 as an emulsifier. The resulting emulsion was a CRS-2P emulsion with a designed residue content of 66%. Higher residue contents were not designed for due to the high viscosity of the binder after polymer modification.

Task 4: Compare Chip Retention Capabilities of Asphalt Emulsion and Asphalt Binder

Task 4 involved the practical applications of asphalt emulsions as viable alternatives for hot applied asphalt in chip seal applications. Using ASTM D7000-11, which tests the curing performance characteristics of bituminous materials, the effectiveness of the film formed by emulsion or hot applied binder in preventing aggregate loss by the sweeping action of a brush over the sample surface was determined. In this test, asphalt emulsion or hot binder of a known quantity is first applied in an even layer over an asphalt felt disk before aggregate chips are added and embedded into the binder/emulsion by kneading action. The discs containing aggregate are then conditioned at a prescribed temperature of 35°C for one hour before being tested on a wet track abrasion tester, which consists of a brush mechanism mounted onto a Hobart mixer. The weight of the disc prior to testing (post conditioning) and the weight after testing is noted. The weight loss is determined to be the difference in weight of the sample disc before and after testing.

Table 1 sums up the tests that were performed to compare the different emulsion and binder types.

Table 1. List of tests performed with corresponding standard and expected values

Test name	Standard used	Measured parameter	Parameter range/ Expected values
Particle size analysis	n/a	Particle size Particle size distribution	Narrow particle size distribution. Particles <100 microns
Saybolt viscometer flow time	ASTM D7496-17	Flow time	100–400s
Dynamic shear rheometer test	ASTM D7175-15	G* (Elastic modulus)	n/a
MSCR (Multiple stress creep recovery)	AASHTO TP 70	% strain recovered Jnr (creep compliance)	Higher % recovery and low Jnr
Sweep test	ASTM D7000-11	% mass loss	n/a

Polymer Modification of Asphalt Binder

In order to manufacture a CRS-2P emulsion, SBS polymer was added at an amount of 3% w/w of total asphalt binder. Since this SBS polymer is manufactured in solid form, the polymer is added to the binder before emulsification. This is achieved by adding the polymer slowly to heated binder at high shear. A shearing speed of 3,000 rpm is typically used for polymer modification. Neat 64-22 binder was heated to 180°C before the polymer was added slowly to the binder at high shear. Care was taken that the polymer was added in small batches to ensure that all the polymer was allowed to melt in a timely manner before the next batch of polymer was added. Once all the polymer was added, the modified binder was allowed to cure for an hour under a lower shear speed of about 1,000 rpm. Figure 2 shows the machine used to mix in the polymer (left) and the SBS polymer (right).



Figure 2. Shear mill for mixing polymers into asphalt binder (left) and SBS polymer (right)

Asphalt Emulsion Manufacturing Process

The asphalt emulsion manufacturing process begins with the formulation of an emulsifying soap solution to ensure that the asphalt gets emulsified. The manufacture of this soap solution is critical to the production of the emulsion, and care must be taken so that sensitive parameters such as pH, emulsifier content, and temperature are maintained according to the design. The amount of soap solution is designed in batches of 2,000 g of water. The amount of emulsifier is added as per the directions from the manufacturer. A typical dosage for Indulin AA-86 is 0.3% w/w of water. In order for the emulsifier to properly disperse in water, the temperature of the water should be close to 40°C. Maintaining a consistent temperature also ensures that the pH of the soap batches can remain consistent since temperature has an effect on the pH of a solution.

The measurement of pH was done with an Oakton pH meter. The pH meter was calibrated on startup before the production of the first batch of soap. A constant pH of 2.0 is required to ensure the effectiveness of the soap solution. A picture of the soap making process is shown in Figure 3.



Figure 3. Soap making process

Once the water comes up to temperature, the desired amount of Indulin AA-86 is pipetted into the water, and the pH rise is observed. Since Indulin AA-86 is an amine-based emulsifier, adding it to water raises the pH due to the presence of the amine head group. In order to make the emulsifier workable, the amine groups need to be protonated with H^+ ions, which can be sourced from an acid. Enough muriatic acid (34% HCl) is added to the water-Indulin solution so that the pH is 2.0. As HCl is added to the solution, the nature of the solution turns from cloudy to clear dark yellow, as the amine head groups are protonated. The soap solution is then added to the water phase line of the emulsion mill. The asphalt emulsion mill is shown in Figure 4.

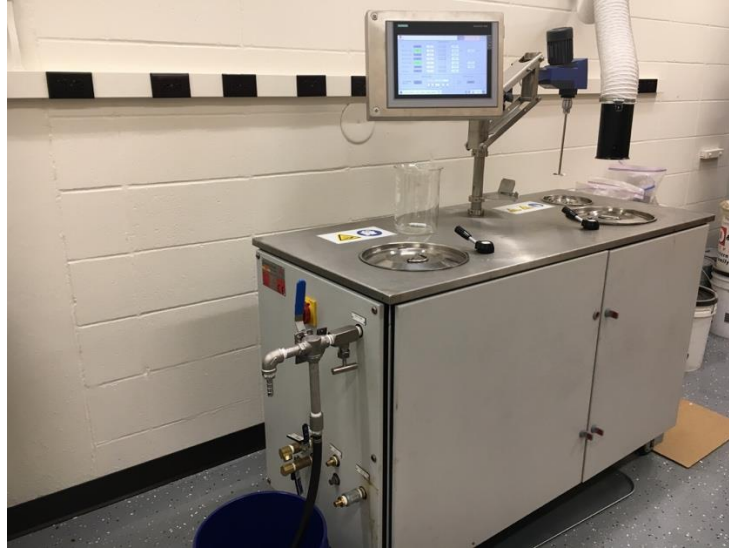


Figure 4. Asphalt emulsion mill

The soap tank is temperature controlled to maintain a temperature of 40°C. The temperature of the asphalt tank is maintained at 140°C to 160°C depending on the viscosity of the asphalt. The temperature of the water and the asphalt mill are important since both the soap and the asphalt binders have different viscosities. The difference in viscosity can lead to uneven particle sizes and unstable emulsions. The ideal viscosity of asphalt for emulsification is 200 cP, and the temperature at which this viscosity is obtained is known as the equiviscous temperature. One must also ensure that the temperature of the emulsion at the exit is lower than 100°C since higher temperatures will cause the water in the emulsion to boil upon exiting the mill. Exit temperatures can be controlled using the heat-exchanging element in the mill, which consists of a water-cooled set of pipes, which remove heat from the emulsion after it leaves the mill. This allows a higher asphalt temperature to ensure that the equiviscous temperature condition is met as well as preventing the resulting emulsion from boiling. This is especially true for polymer-modified asphalts, which have higher equiviscous temperatures. Figure 5 and Figure 6 show the temperature sweeps for non-modified and polymer-modified PG 64-22. It can be seen that the polymer-modified binder reaches 200 cP at a temperature of 25°C higher than the non-modified asphalt binder.

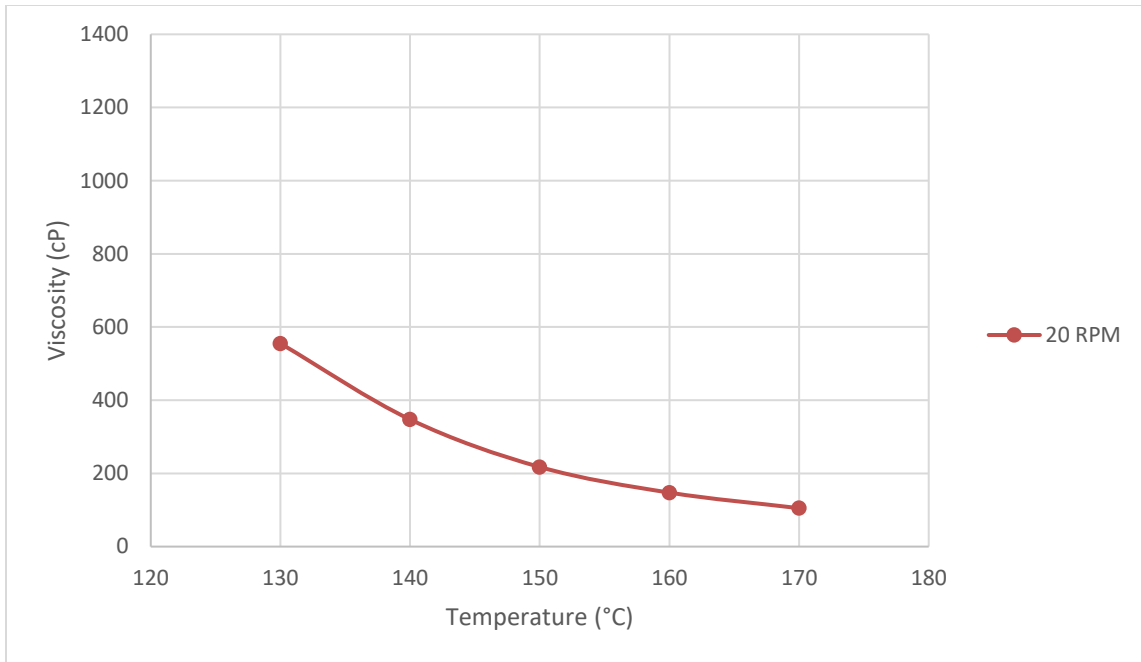


Figure 5. Viscosity versus temperature sweep of non-modified PG 64-22 binder

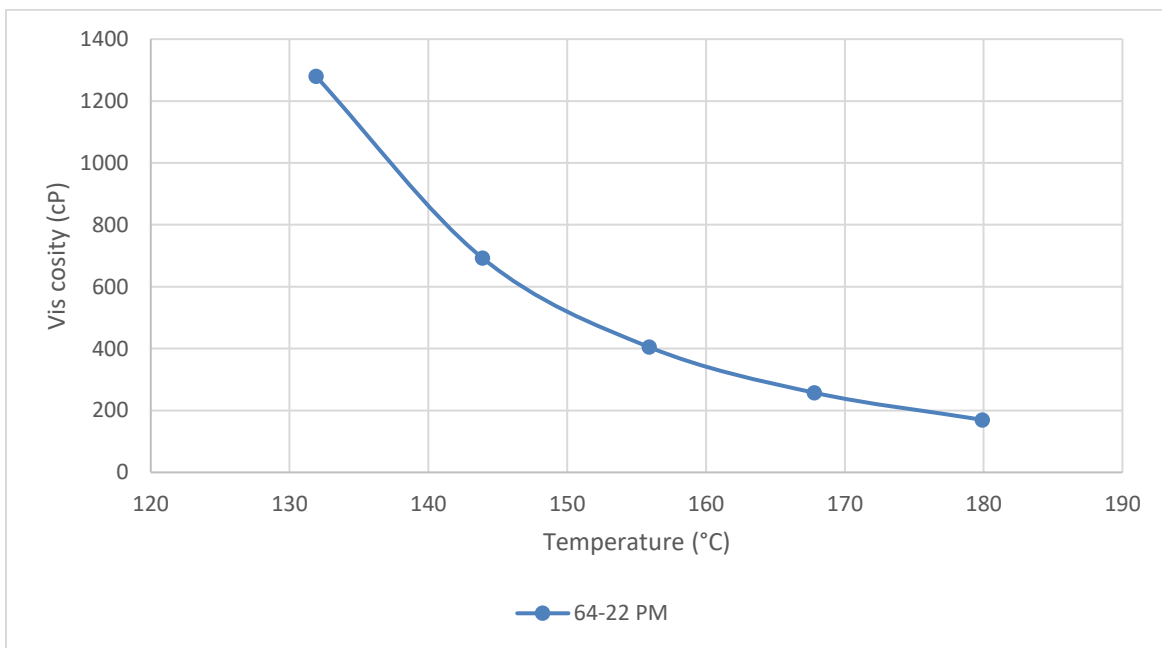


Figure 6. Viscosity versus temperature sweep of polymer-modified PG 64-22 binder with 3% SBS by weight

The equiviscous temperature can be used to determine the exit temperature of asphalt emulsion using the following equation:

$$\frac{(P_{asphalt} \times T_{asphalt} \times 0.5) + (P_{soap} \times T_{soap} \times 1)}{(P_{asphalt} \times 0.5) + P_{soap}} = T_{emulsion} \quad (2)$$

where:

$P_{asphalt}$ = weight % of asphalt

P_{soap} = weight % of soap

$T_{asphalt}$ = equiviscous temperature

T_{soap} = weight of soap

The asphalt emulsion is designed by minimum percent residue. For this study, 66% was chosen as the minimum percentage of residue. The residue can be controlled by varying the flow rates of the water phase and asphalt phase. Keeping the total flow into the mill constant, the water and asphalt rates are varied to get their desired ratio to equal the required residue fraction. Hence, 66% asphalt would be equal to 66 parts asphalt and 34 parts water, with the flow rates maintaining this ratio. Asphalt emulsion, once produced, is collected in bottles and tested immediately for compliance with the required residue percent. Asphalt emulsions with residues of 68% and 70% were also produced in the emulsion mill for comparison purposes.

Testing for Emulsion Residue

Every batch of asphalt emulsion produced was tested for minimum residue compliance. Asphalt emulsion was poured on paper plates of known weight, and the weight of the emulsion known was measured (Figure 7[left]). The emulsion was allowed to set for 24 hours at room temperature for all the water to evaporate before weighing the plate and the emulsion residue (Figure 7[right]).



Figure 7. Pouring emulsion samples for residue testing (left) and weighing the residue retained after 24 hours (right)

Knowing the weight of the plate, the final weight of the residue was measured, and hence the ratio of emulsion to residue was calculated as follows:

$$\text{Emulsion Residue } \% = \frac{\text{Weight of emulsion residue after drying}}{\text{Weight of emulsion poured}} \quad (3)$$

A similar process was used to obtain residue for testing. High temperature evaporation methods like distillation were not used since curing at high temperatures was not likely to occur in the field, and hence the ideal representation of a field sample would be obtained by simple evaporation at a constant room temperature.

RESULTS AND DISCUSSION

Particle Size Analysis

Particle size analysis of the emulsion particles gave an average particle size of 11 μm for the CRS-2 emulsion and two particle sizes of 3 μm and 10 μm for the CRS-2P. The CRS-2 emulsion in Figure 8 has a narrower particle size distribution when compared to the CRS-2P.

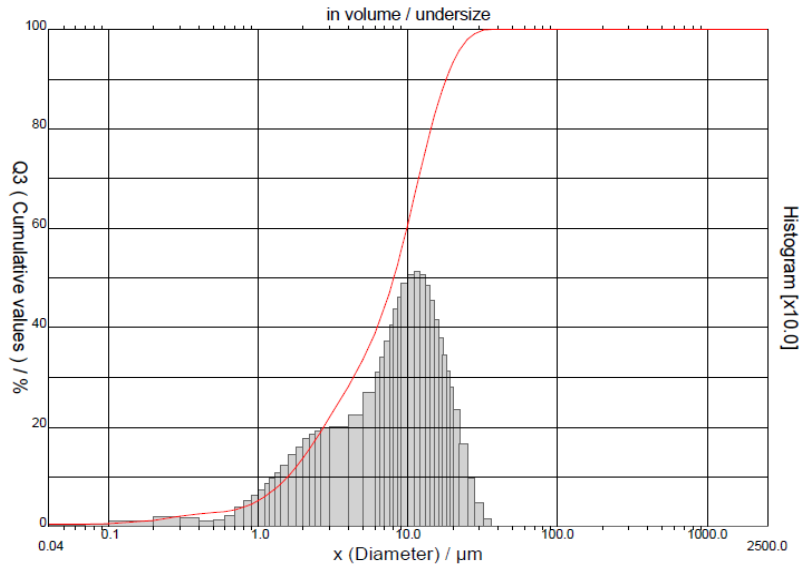


Figure 8. CRS-2 particle size distribution

The two different peaks observed in the particle size histogram for the CRS-2P distribution are shown in Figure 9. Further optimization of the polymer-modified bitumen is needed in future studies.

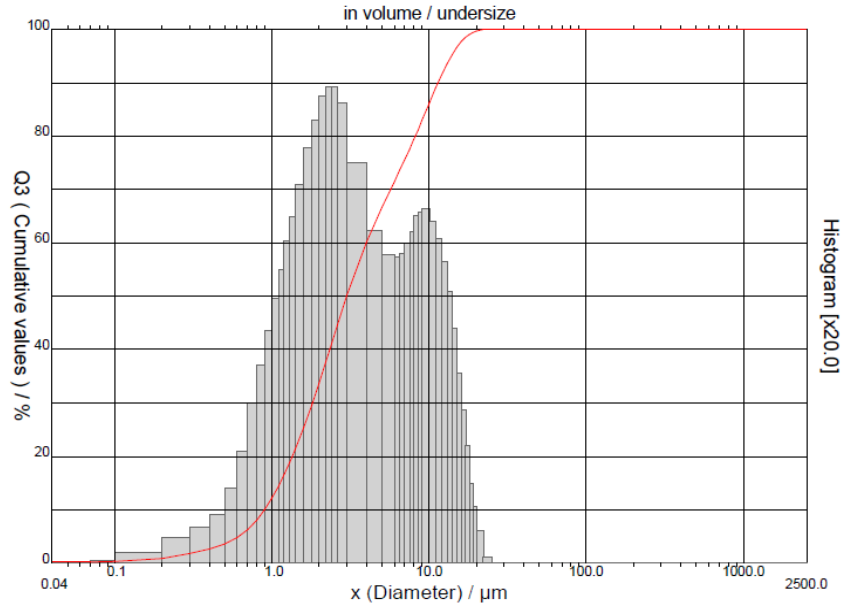


Figure 9. CRS-2P particle size distribution

Saybolt Viscometer Flow Timings

The Saybolt viscometer is commonly used to measure the viscosity of emulsified asphalts in terms of flow times according to ASTM D7496-17. The asphalt emulsion is heated up to 50°C in a water bath and allowed to run through the Saybolt orifice, and the flow times are recorded. Specifications for asphalt emulsions require the flow time to be between 100 and 400 seconds. Asphalt samples of two residue contents were tested in the Saybolt viscometer. Table 2 provides flow times of 201 seconds for the 66% residue and 197 seconds for the 68% residue for CRS-2. It was noted that the 68% residue showed a slightly lower viscosity than the 66% residue. However, the CRS-2P emulsion displayed extremely low viscosity and had a flow time under 100 seconds; therefore, it did not pass the Saybolt flow test. The low viscosity could be attributed to the wider particle size distribution of the CRS-2P emulsion.

Table 2. Saybolt viscometer flow timings

	CRS-2 (66% residue)	CRS-2 (68% residue)	CRS-2P (66% residue)
Saybolt flow time (s)	201	197	<100 (Did not pass)

Residue and Neat Binder Master Curve Analysis

Figure 10 shows a combined plot of master curves for the neat binder, polymer-modified binder, and the residue from the non-modified and polymer-modified emulsion.

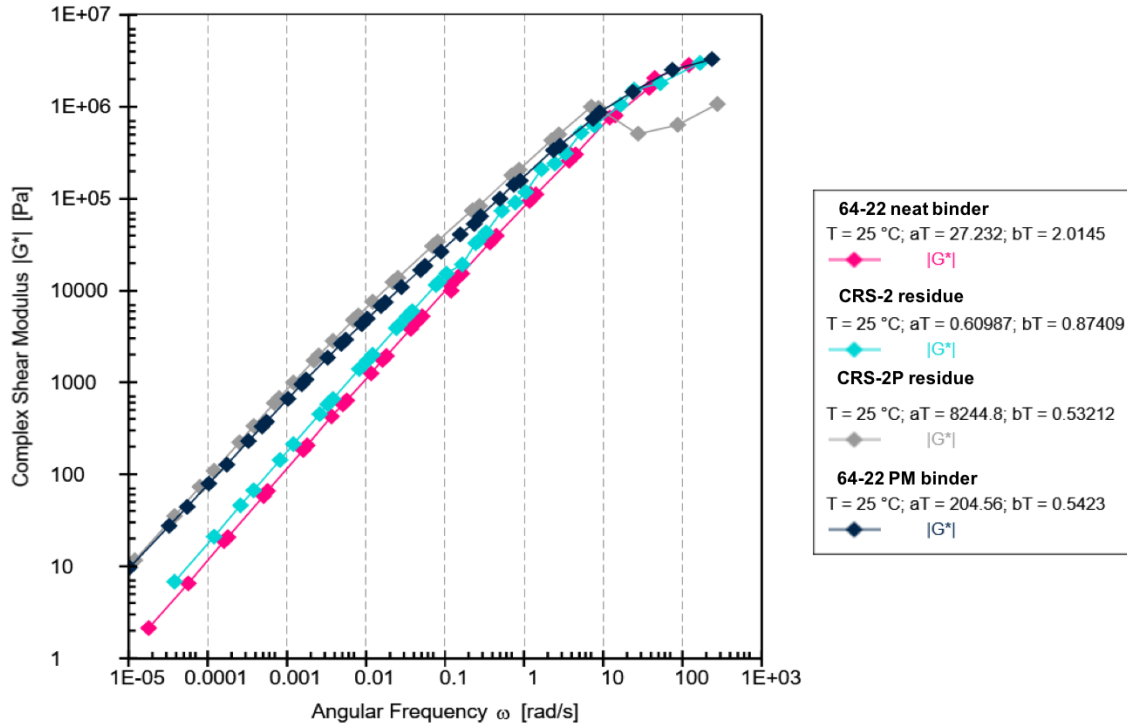


Figure 10. Complex shear modulus versus angular frequency (master curves) for neat binder and emulsion residue

The master curves show that the polymer-modified emulsion residue has the highest stiffness but is comparable to the stiffness of the polymer-modified binder. Similarly, the stiffness of the non-modified emulsion residue is lower than those of the modified binder and residue but comparable to the neat binder. The slight increase in stiffness shows that standard non-modified and polymer-modified emulsion residues are at least comparable, if not stiffer than their respective base binders. Since the scale used above is a logarithmic scale, the actual difference in stiffness between the individual binders and residues would be significantly higher than what can be visualized in a log-log plot.

It was also observed that the polymer-modified emulsion residue master curve shows a decrease in stiffness at 10 Hz, which could most probably be caused by slippage between the DSR plate and the binder. A 25 mm plate was used for all the test runs to maintain a uniform test procedure, and slippage between the plate and the binder could have occurred due to the binder's high stiffness.

MSCR Test Comparison

The MSCR test was used to compare the elastic strain recovering ability of the CRS-2P residue and the polymer-modified PG 64-22 binder. As mentioned in the previous section, the polymer used to modify the base binder at a concentration of 3% w/w. The polymer-modified binder and emulsion residue were tested at two temperatures, 52°C and 25°C. Plots of strain versus time and the percentage recovery and Jnr, or non-recoverable creep compliance. Figures 11 through 14

show results from the MSCR test to compare elastic recovery of the CRS-2P residue and the polymer-modified binder.

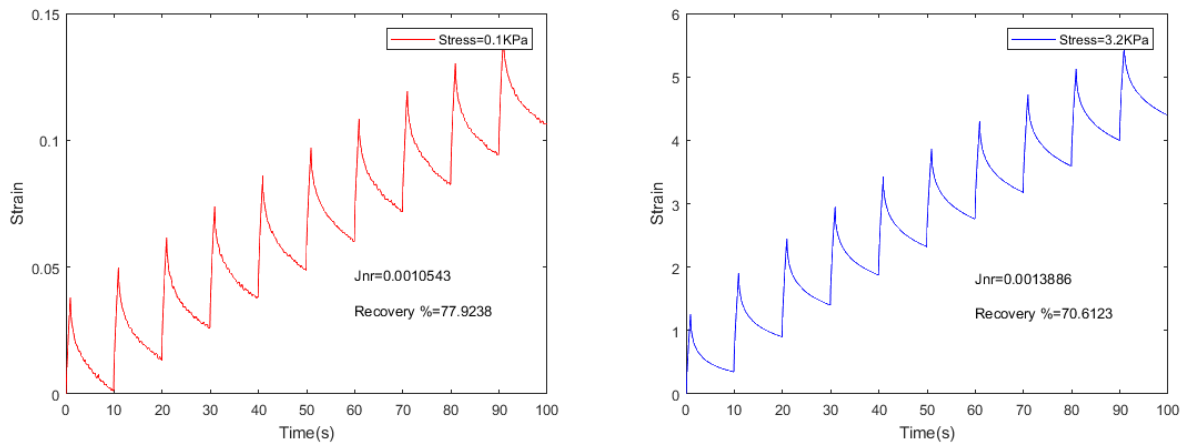


Figure 11. PG 64-22 polymer-modified binder tested at 25°C, and at stress levels 0.1 KPa (left) and 3.2 KPa (right)

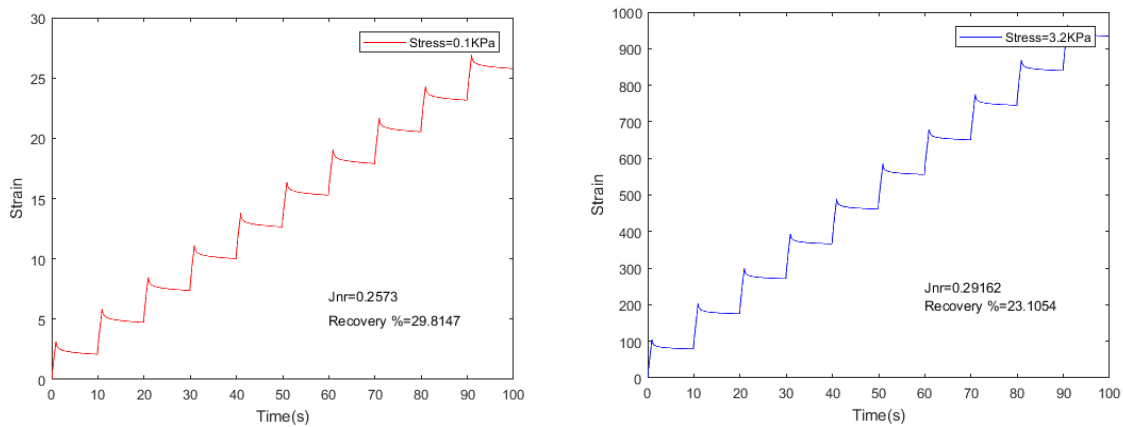


Figure 12. PG 64-22 polymer-modified binder tested at 52°C, and at stress levels 0.1 KPa (left) and 3.2 KPa (right)

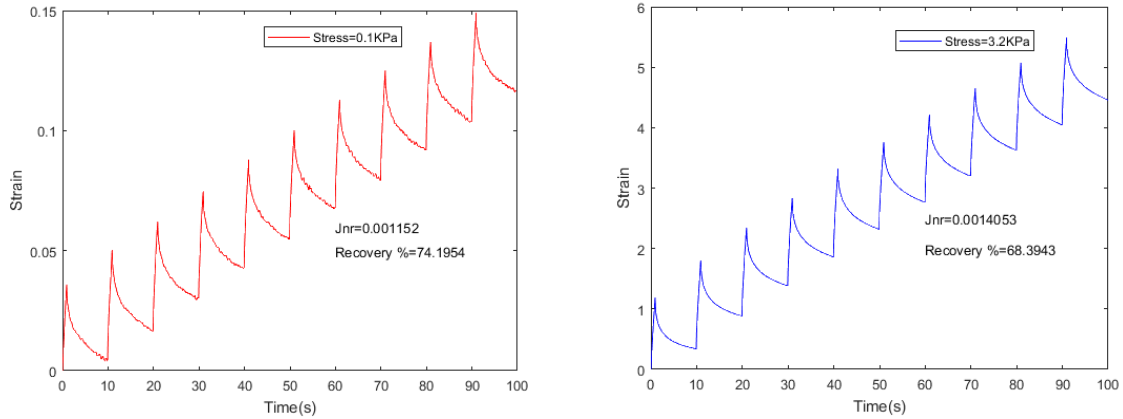


Figure 13. CRS-2P residue tested at 25°C, and at stress levels 0.1KPa (left) and 3.2Kpa (right)

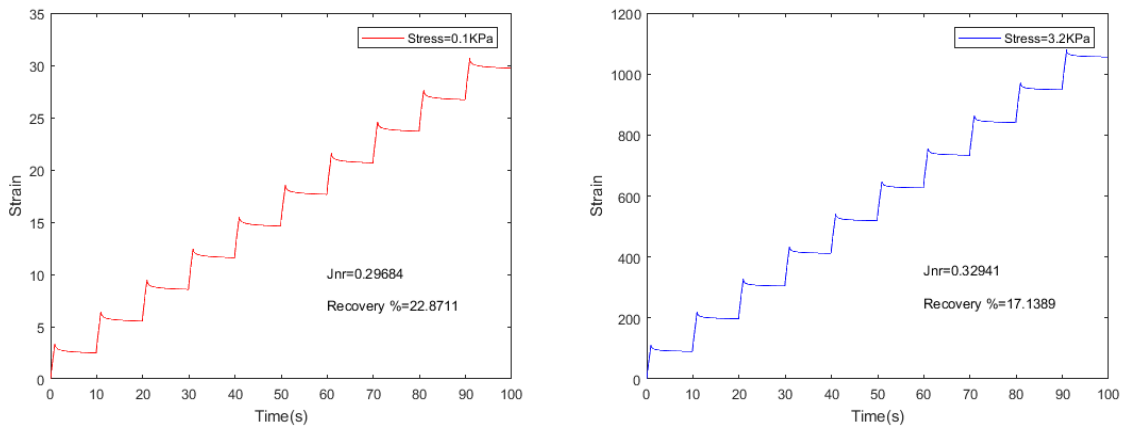


Figure 14. CRS-2P residue tested at 52°C, and at stress levels 0.1KPa (left) and 3.2KPa (right)

Results at 25°C show both the modified binder and the residue with a high recovery percentage, passing American Association of State Highway and Transportation Officials (AASHTO) standards for modified binders in heavy traffic. However, at 52°C, both the modified binder and emulsion residue showed poor strain recovery with high Jnr values. In all the results, the polymer-modified binder performed slightly better than the CRS-2P residue, but not by much. This points to the polymer-modified binder being extremely stiff but not highly elastic, leading to poor strain recovery. The binder stiffness can be deduced from viscosity versus temperature plots in Figure 5 and Figure 6. Since only one polymer content of 3% was used in this study, it is possible that the chosen polymer content was not in the region of the ideal polymer content for this particular binder and polymer. In order to determine the optimal amount of polymer to be added to a 64-22 binder, MSCR tests would have to be performed at different polymer contents to determine the ideal amount of polymer needed to make the binder sufficiently elastic. Table 3 summarizes the results for the MSCR test.

Table 3. MSCR results

Binder/Residue type	Temperature (°C)	Stress level (KPa)	Jnr (1/KPa)	% Recovery
64-22 PM (3% D1192)	25	0.1	0.00105	77.92%
64-22 PM (3% D1192)	25	3.2	0.00138	70.61%
64-22 PM (3% D1192)	52	0.1	0.2573	29.81%
64-22 PM (3% D1192)	52	3.2	0.2916	23.10%
CRS-2P	25	0.1	0.00115	74.19%
CRS-2P	25	3.2	0.00141	68.39%
CRS-2P	52	0.1	0.2968	22.87%
CRS-2P	52	3.2	0.3241	17.14%

Sweep Tests

Sweep test results show no significant difference in the mass loss between the hot applied binders and the emulsions. The p-values for each comparison were less than 0.05, as shown in Table 4, which supports the above statement.

Table 4. P-value calculated from student t test

Level	Level	Difference	p-Value
HA 64-22	HA 72-28	1.478531	0.3125
CRS-2	HA 72-28	1.084276	0.4132
HA 64-22	CRS-2	0.394255	0.7629

Note: t value: 2.20, $\alpha=0.05$

Figure 15 illustrates the mass loss for different application types.

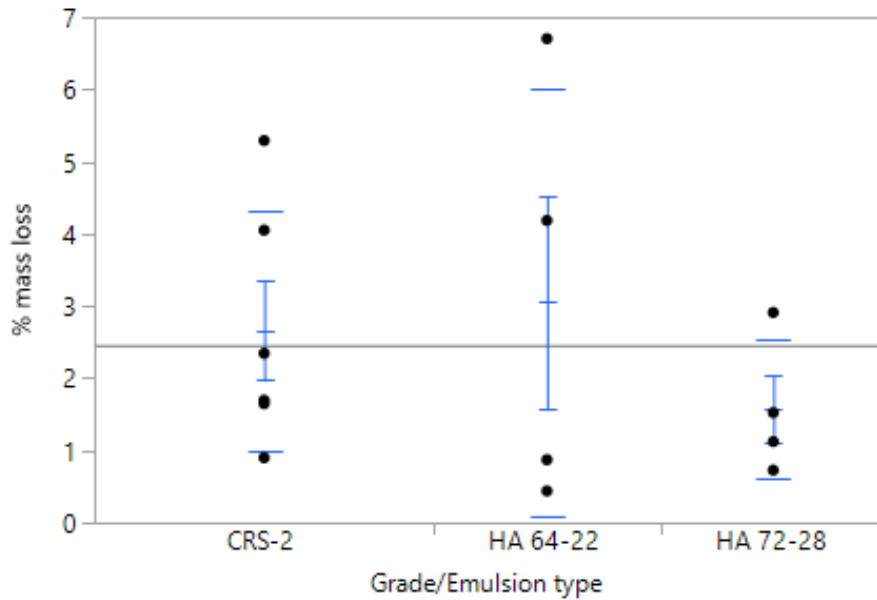


Figure 15. Percent mass loss versus application type

The CRS-2 showed marginally better chip retention than the hot applied PG 64-22 base binder but a lower retention than the PG 72-28 polymer-modified binder. Results from the CRS-2P emulsion could not be obtained due to extremely low viscosity of the emulsion, which resulted in poor chip retention. The results once again mirror the data obtained from residue versus base binder master curves, showing comparable performance between the emulsion and the base binder.

Another point worth noting is that the results from the application of the emulsion were a lot more consistent and had a lower standard deviation when compared to the base PG 64-22 binder, as seen in Table 5. However, the polymer-modified binder showed the smallest standard deviation. Producing a CRS-2P emulsion of higher viscosity would allow for interesting results when compared to the polymer-modified PG 72-28 binder.

Table 5. Mean and standard deviation for sweep tests

Application type	Number	Mean	Std. dev	Std. err mean
CRS-2	6	2.65653	1.67432	0.6835
HA 64-22	4	3.05078	2.95456	1.4773
HA 72-28	4	1.57225	0.95085	0.4754

CONCLUSIONS AND FUTURE WORK

With the increasing demand for pavement preservation strategies, the need to better understand the fundamentals of asphalt emulsions is of growing importance. Asphalt emulsions find use in several pavement preservation and rehabilitation strategies from microsurfacing to full-depth reclamation. The esoteric nature of asphalt emulsions means that only the manufacturing companies fully understand the end product and not much knowledge gets passed on to agencies, students or pavement practitioners. Emulsions are designed as delicately balanced systems of asphalt droplets suspended in water and are kept stabilized by emulsifiers. The stability, breaking, and curing process of emulsions all need to be better understood so they can be better implemented in practice.

This ongoing research seeks to demystify many of the mechanisms governing emulsified asphalt so that local agencies can make smarter decisions as to the type, quantity, and the manner in which these emulsions are used. The ability to formulate and manufacture emulsions by varying different parameters will help benchmark and evaluate current practices and drive further innovation in the field of pavement preservation and rehabilitation. Iowa State University has also been developing biopolymers for use with asphalt binder, which can also be incorporated into emulsions.

Preliminary formulations were used to manufacture two types of emulsion: a non-modified and a polymer-modified emulsion, both of the cationic rapid-setting type. Initial results showed that both emulsions met the minimum of 65% residue requirements. For viscosity, the non-modified emulsion had higher viscosity and met current specifications for Saybolt viscometer (flow time between 100 and 400 seconds) as compared to the low viscosity polymer-modified emulsion, which failed to meet Saybolt requirements. Additional optimization for the polymer-modified asphalt emulsion formulation will help to improve the blend. Particle size distributions indicated that the wider distribution of particle size for the polymer-modified binder was the likely cause for low viscosity. Emulsion residue was compared to that of its base binder, both polymer-modified and non-modified. Master curves were plotted to compare the elastic modulus of the material (G^*). Results showed that the emulsion residue was comparable to that of the base binder, with the emulsion residue showing higher values of G^* than each of their base binders. MSCR tests showed that the SBS polymer used imparted a high stiffness but low elasticity to the base PG 64-22 binder, resulting in poor strain recovery performance at 52°C but good recovery at a low temperature of 25°C. This could be the result of the amount of polymer added being assumed and not determined as being in the optimum range. Sweep test results also showed promise, since the CRS-2 non-modified emulsion performed comparably with a hot applied PG 64-22 base binder but fell behind in performance to a hot applied polymer-modified PG 72-28 binder. However, statistically, results did not show a significant difference between the mean weight losses for either application type.

This study has highlighted the potential of emulsified asphalts in the field of pavement engineering. Asphalt emulsions are a low-temperature alternative and provide opportunity for energy savings. Sweep tests also showed that emulsions could perform as well as, if not better than, a hot applied base binder. Further research could improve the understanding of polymer-

modified emulsions and lead to better emulsion formulation. With the newly purchased laboratory emulsion mill, a wide range of emulsions can be formulated to optimize performance in specific scenarios and environments. Experimentation with different emulsifier types and contents could help engineer a broader spectrum of emulsions that could be optimized for the aggregates that they would come in contact with. Experiments with locally available aggregates in an aggregate-emulsion system would go a long way toward ensuring that the right emulsion is used for better performance. Thus, the presented results serve as a starting snapshot on the multiple tests and trials that could be run on specially engineered emulsions manufactured to help improve the state of practice and current knowledge of emulsified asphalt.

REFERENCES

- Abedini, H., S. Naimi, and M. Abedini. 2017. Rheological Properties of Bitumen Emulsion Modified with NBR Latex. *Petroleum Science and Technology*, Vol. 35, No. 15, pp.1576–1582. doi:10.1080/10916466.2017.1319386.
- Abedini, M., A. Hassani, M. R. Kaymanesh, and A. A. Yousefi. 2017. Low-Temperature Adhesion Performance of Polymer-Modified Bitumen Emulsion in Chip Seals Using Different SBR Latexes. *Petroleum Science and Technology*, Vol 35, No. 1, pp. 59–65. doi:10.1080/10916466.2016.1238932.
- Acevedo, S., X. Gutierrez, and H. Rivas. 2001. Bitumen-in-Water Emulsions Stabilized with Natural Surfactants. *Journal of Colloid and Interface Science*, Vol 242, No. 1, pp. 230–238. doi:10.1006/jcis.2001.7728.
- Alade, O. S., K. Sasaki, Y. Sugai, B. Ademodi, and M. Nakano. 2016. Bitumen Emulsification Using a Hydrophilic Polymeric Surfactant: Performance Evaluation in the Presence of Salinity. *Journal of Petroleum Science and Engineering*, Vol. 138, pp. 66–76. doi:10.1016/j.petrol.2015.11.031.
- Al-Sabagh, A. M., N. N. Zaki, and A. M. Badawi. 1997. Effect of Binary Surfactant Mixtures on the Stability of Asphalt Emulsions. *Journal of Chemical Technology and Biotechnology*, Vol. 69, No. 3, pp. 350–356. [https://doi.org/10.1002/\(SICI\)1097-4660\(199707\)69:3<350::AID-JCTB699>3.0.CO;2-7](https://doi.org/10.1002/(SICI)1097-4660(199707)69:3<350::AID-JCTB699>3.0.CO;2-7).
- Arenas-Calderon, E., V. Sadtler, P. Marchal, L. Choplin, F. Delfosse, and M. Maze. 2014. Preparation of Highly Concentrated Bitumen Emulsions by Catastrophic Phase Inversion: Follow-Up of the Emulsification Process. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Vol. 458, pp. 25–31. doi:10.1016/j.colsurfa.2014.02.030.
- Banerjee, A., A. Bhasin, and J. Prozzi. 2013. Characterizing Stability of Asphalt Emulsions Using Electrokinetic Techniques. *Journal of Materials in Civil Engineering*, Vol. 25, No. 1, pp. 78–85. doi:10.1061/(ASCE)MT.1943-5533.0000552.
- Barnes, H. A. 1994. Rheology of Emulsions—a Review. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Vol. 91, pp. 89–95. doi:10.1016/0927-7757(93)02719-U.
- Becker, Y., M. P. Méndez, and Y. Rodríguez. 2001. Polymer Modified Asphalt. *Vision Tecnologica*, Vol. 9, No. 1, pp. 39–50. <http://citeseerx.ist.psu.edu/viewdoc/summary?doi=10.1.1.523.9807>.
- Bouchama, F., G. A. van Aken, A. J. E. Autin, and G. J. M. Koper. 2003. On the Mechanism of Catastrophic Phase Inversion in Emulsions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Vol. 231, Nos. 1–3, pp. 11–17. doi:10.1016/J.COLSURFA.2003.08.011.
- Ergon Asphalt & Emulsions, Inc. 2015. *Field Guide to Emulsions*. <http://ergonasphalt.com/docs/field-guide-2015.pdf>.
- Farrar, M. J., S. L. Salmans, and J.-P. Planche. 2013. Recovery and Laboratory Testing of Asphalt Emulsion Residue: Application of the Simple Aging Test (SAT) and 4-mm Dynamic Shear Rheometer Test. *Transportation Research Record: Journal of the Transportation Research Board*, No. 2370, pp. 69–75. <https://trrjournalonline.trb.org/doi/pdf/10.3141/2370-09>.

- Forbes, A., R. G. Haverkamp, T. Robertson, J. Bryant, and S. Bearsley. 2001. Studies of the Microstructure of Polymer-Modified Bitumen Emulsions Using Confocal Laser Scanning Microscopy. *Journal of Microscopy*, Vol. 204, No. 3, pp. 252–257. doi:10.1046/j.1365-2818.2001.00955.x.
- Gingras, J.-P., P. A. Tanguy, S. Mariotti, and P. Chaverot. 2005. Effect of Process Parameters on Bitumen Emulsions. *Chemical Engineering and Processing: Process Intensification*, Vol. 44, No. 9, pp. 979–986. doi:10.1016/j.cep.2005.01.003.
- Gutierrez, X., F. Silva, M. Chirinos, J. Leiva, and H. Rivas. 2002. Bitumen-in-Water Emulsions: An Overview on Formation, Stability, and Rheological Properties. *Journal of Dispersion Science and Technology*, Vol. 23, Nos. 1–3, pp. 405–418. doi:10.1080/01932690208984213.
- Hanz, A. J., P. Johannes, and H. U Bahia. 2012. Development of an Emulsion Residue Testing Framework for Improved Chip Seal Performance. *Transportation Research Record: Journal of the Transportation Research Board*, Vol. 2293, No. 1, pp. 106–113. doi:10.3141/2293-13.
- Hesp, S. A. and R. T. Woodhams. 1992. Stabilization Mechanisms in Polyolefin-Asphalt Emulsions. *Polymer Modified Asphalt Binders*, Eds. K. Wardlaw and S. Shuler. ASTM International, West Conshohocken, PA, pp. 1–19. doi.org/10.1520/STP17823S.
- Hu, S.-G., T. Wang, F.-Z. Wang, and Z.-C. Liu. 2009. Adsorption Behaviour between Cement and Asphalt Emulsion in Cement–Asphalt Mortar. *Advances in Cement Research*, Vol. 21, No. 1, pp. 11–14. doi:10.1680/adcr.2007.00034.
- Ingevity. *Asphalt Innovations Technical Manual*. Tulsa Pavement Technology Lab, Research and Development, Tulsa, OK.
- James, A. 2006. Asphalt Emulsions (Chemistry and Concepts). Asphalt Applications Technical Papers and Presentations by Akzo Nobel Chemicals Inc. http://www.e-asphalt.com/ingles/akzo/technical_paper/AEMA99-chemistry.pdf.
- Johnston, J. and G. King. 2012. *Polymer Modified Asphalt Emulsions: Composition, Uses, and Specifications for Surface Treatments*. FHWA-CFL/TD-12-004. Federal Highway Administration, Central Federal Lands Highway Division, Lakewood, CO. doi: 10.13140/RG.2.2.34586.03520.
- Kabalnov, A. S. and E. D. Shchukin. 1992. Ostwald Ripening Theory: Applications to Fluorocarbon Emulsion Stability. *Advances in Colloid and Interface Science*, Vol. 38, pp. 69–97.
- Kralchevsky, P. A., I. B. Ivanov, K. P. Ananthapadmanabhan, and A. Lips. 2005. On the Thermodynamics of Particle-Stabilized Emulsions: Curvature Effects and Catastrophic Phase Inversion. *Langmuir*, Vol. 21, No. 1, pp. 50–63. doi:10.1021/la047793d.
- Legrand, J., M. Chamerois, F. Placin, J. E. Poirier, J. Bibette, and F. Leal-Calderon. 2005. Solid Colloidal Particles Inducing Coalescence in Bitumen-in-Water Emulsions. *Langmuir*, Vol. 21, No. 1, pp. 64–70. doi:10.1021/LA047649S.
- Lubbers, C. and S. Watson. 2005. Basics of Polymers in Asphalt Emulsions. In *BASF Corporation Web Seminar*.
- Marasteanu, M. O. and T. R. Clyne. 2006. Rheological Characterization of Asphalt Emulsions Residues. *Journal of Materials in Civil Engineering*, Vol. 18, No. 3, pp. 398–407. doi:10.1061/(ASCE)0899-1561(2006)18:3(398).

- Niazi, Y. and M. Jalili. 2009. Effect of Portland Cement and Lime Additives on Properties on Cold in-Place Recycled Mixtures with Asphalt Emulsion. *Construction and Building Materials*, Vol. 23, No. 3, pp. 1338–1343. doi:10.1016/j.conbuildmat.2008.07.020.
- Oruc, S., F. Celik, and M. V. Akpinar. 2007. Effect of Cement on Emulsified Asphalt Mixtures. *Journal of Materials Engineering and Performance*, Vol. 16, No. 5, pp. 578–583. doi:10.1007/s11665-007-9095-2.
- Ottewill, R. H. 1977. Stability and Instability in Disperse Systems. *Journal of Colloid and Interface Science*, Vol. 58, No. 2, pp. 357–373. doi:10.1016/0021-9797(77)90148-5.
- Pouliot, N., J. Marchand, and M. Pigeon. 2003. Hydration Mechanisms, Microstructure, and Mechanical Properties of Mortars Prepared with Mixed Binder Cement Slurry-Asphalt Emulsion. *Journal of Materials in Civil Engineering*, Vol. 15, No. 1, pp. 54–59. doi:10.1061/(ASCE)0899-1561(2003)15:1(54).
- Rodríguez-Valverde, M. A., P. Ramón-Torregrosa, A. Páez-Dueñas, M. A. Cabrerizo-Vílchez, and R. Hidalgo-Álvarez. 2008. Imaging Techniques Applied to Characterize Bitumen and Bituminous Emulsions. *Advances in Colloid and Interface Science*, Vol. 136, Nos. 1–2, pp. 93–108. doi:10.1016/j.cis.2007.07.008.
- Ronald, M. and F. P. Luis. 2016. Asphalt Emulsions Formulation: State-of-the-Art and Dependency of Formulation on Emulsions Properties. *Construction and Building Materials*, Vol. 123, pp. 162–173. doi:10.1016/j.conbuildmat.2016.06.129.
- Sabbagh, A. B. and A. J. Lesser. 1998. Effect of Particle Morphology on the Emulsion Stability and Mechanical Performance of Polyolefin Modified Asphalts. *Polymer Engineering and Science*, Vol. 38, No. 5, pp. 707–715. doi:10.1002/pen.10236.
- Salomón, D. and M. Palasch. 2002. Kinetic Properties of Emulsified Asphalts. International Symposium on Asphalt Emulsion Technology. <http://pavementpreservationsystems.com/publications/Kinetic-Properties-of-Emulsified-Asphalts-May-2002.pdf>.
- Salomón, D., H. Zhai, J. Corona, and F. Castellanos. 2018. New Tools to Measure Emulsified Asphalt Properties. https://www.researchgate.net/profile/Delmar_Salomon/publication/266371045_New_Tools_to_Measure_Emulsified_Asphalt_Properties/links/581033af08ae009606bb9112/New-Tools-to-Measure-Emulsified-Asphalt-Properties.pdf.
- Schilling, P. and H. G. Schreuders. 1998. Improved Quick-Set Slurry Seal Emulsifiers with Tall Oil Derivatives. *Transportation Research Record: Journal of the Transportation Research Board*, No. 1171, pp. 98–107. <http://onlinepubs.trb.org/Onlinepubs/trr/1988/1171/1171-012.pdf>.
- Serfass, J. P., A. Joly, and J. Samanos. 1992. SBS-Modified Asphalts for Surface Dressing in Polymer Modified Asphalt Binders. *Polymer Modified Asphalt Binders*, Eds. K. Wardlaw and S. Shuler. ASTM International, West Conshohocken, PA, pp. 281–308. <https://doi.org/10.1520/STP17839S>.
- Shafii, M. A., M. Y. Abdul Rahman, and J. Ahmad. 2011. Polymer Modified Asphalt Emulsion. *International Journal of Civil & Environmental Engineering*, Vol. 11, No. 6, pp. 43–49. <http://citeseerx.ist.psu.edu/viewdoc/summary?doi=10.1.1.652.6498>.
- Tadros, T. F. 2013. Chapter 1. Emulsion Formation, Stability, and Rheology. In *Emulsion Formation and Stability*, 1–75. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA. doi:10.1002/9783527647941.ch1.

- Takamura, K. 2003. Polymer modified asphalt emulsions for treatment of road surfaces. US Patent 20030215286A1, filed May 14, 2002, and issued November 20, 2003. <https://www.google.com/patents/US20030215286>.
- Tan, Y., J. Ouyang, and Y. Li. 2014. Factors Influencing Rheological Properties of Fresh Cement Asphalt Emulsion Paste. *Construction and Building Materials*, Vol. 68, pp. 611–617. doi:10.1016/j.conbuildmat.2014.07.020.
- Toxqui-López, S., A. Olivares-Pérez, and I. Fuentes-Tapia. 2006. Polyvinyl Acetate with Cellulose Dinitrate Holograms. *Optical Materials*, Vol. 28, No. 4, pp. 342–349. doi:10.1016/J.OPTMAT.2005.01.022.
- Wang, F., Y. Liu, Y. Zhang, and S. Hu. 2012. Experimental Study on the Stability of Asphalt Emulsion for CA Mortar by Laser Diffraction Technique. *Construction and Building Materials* Vol. 28, No.1, pp. 117–121. doi:10.1016/J.CONBUILDMAT.2011.07.059.
- Wang, Z., X. Shu, T. Rutherford, B. Huang, and D. Clarke. 2015. Effects of Asphalt Emulsion on Properties of Fresh Cement Emulsified Asphalt Mortar. *Construction and Building Materials*, Vol. 75, pp. 25–30. doi:10.1016/j.conbuildmat.2014.11.013.
- Yang, Q., D. Ke, M. Yang, J. Hong, Q. Ran, and X. Wang. 2013. Effect of Salt Concentration on the Phase Separation of Bitumen Emulsions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Vol. 425, pp. 1–5. doi:10.1016/J.COLSURFA.2013.02.041.
- Zhai, H., D. Salomón, and E. Milliron. 2004. Using Rheological Properties to Evaluate Storage Stability and Setting Behaviors of Emulsified Asphalts. International Symposium on Asphalt Emulsion Technology. <http://pavementpreservationsystems.com/publications/Using-Rheological-Properties-to-Evaluate-Emulsified-Asphalts-ISAET-Nov-2004.pdf>.
- Ziyani, L., V. Gaudefroy, V. Ferber, and F. Hammoum. 2016. A Predictive and Experimental Method to Assess Bitumen Emulsion Wetting on Mineral Substrates. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Vol. 489, pp. 322–335. doi:10.1016/j.colsurfa.2015.11.002.

**THE INSTITUTE FOR TRANSPORTATION IS THE FOCAL POINT FOR TRANSPORTATION
AT IOWA STATE UNIVERSITY.**

InTrans centers and programs perform transportation research and provide technology transfer services for government agencies and private companies;

InTrans manages its own education program for transportation students and provides K-12 resources; and

InTrans conducts local, regional, and national transportation services and continuing education programs.



IOWA STATE
UNIVERSITY

Visit www.InTrans.iastate.edu for color pdfs of this and other research reports.