

Scientific Innovations in Microsurfacing and Slurry Seal Mixture Design

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16. Abstract <p>Pavement preservation treatments that utilize asphalt emulsions are growing in popularity due to the overwhelming need for infrastructure preservation and treatment cost effectiveness, as well as because of the versatility of asphalt emulsion applications. Emulsions are not well understood by many practitioners in the civil engineering community. The integration of new technologies into asphalt emulsion specifications and quality assurance programs has lagged compared to rheological specifications adopted in the hot-mix asphalt industry.</p> <p>Part of the challenge is due to the complexity of asphalt emulsion systems and the need to tailor asphalt emulsion formulation to each treatment and, sometimes, each project. Microsurfacing and slurry seal treatments use quick-setting emulsions. The emulsion formulations and mixture designs may be engineered to work together to maintain adequate consistency during mixing and then rapidly set and break once placed on the roadway surface. This rapid break allows for rapid curing of the new pavement surface, allowing the road to be opened to traffic in as little as one hour after treatment application. The formulation of microsurfacing and slurry seal emulsions is crucial to achieving this rapid break.</p> <p>The primary objective of this study was to investigate if zeta potential could be useful as a measure of emulsion stability and set time in slurry seal and microsurfacing emulsions and mixtures. An experimental design was developed to study zeta potential as a function of important asphalt emulsion formulation parameters: the pH of the emulsifier solution, emulsifier dosage in the continuous phase, and temperature of the asphalt emulsion while measuring zeta potential. Fine aggregates of various reactivity (limestone and bentonite) were suspended in the solution and titrated into the emulsion while changes in zeta potential were measured. The point of zero zeta potential, or the isoelectric point, at which the emulsion flocculates was also observed.</p> <p>Finally, an experiment was designed to observe cohesion measurements at various levels of water content and asphalt emulsion content, while using specially formulated emulsions for which pH and zeta potential were known. Findings demonstrate proof-of-concept for using zeta potential as a scientific measurement that could help engineer and measure the reactivity of asphalt emulsions and provide better understanding of aggregate-emulsion interactions. Study limitations and opportunities for future research are also presented.</p>			
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EXECUTIVE SUMMARY

Pavement preservation is increasingly needed as practitioners are required to maintain adequate service levels for more miles of roadways on fewer dollars. Asphalt emulsions are used in many pavement preservation treatments due to their versatility for many applications. Use of asphalt emulsions is growing, helping keep pavement preservation treatment costs relatively low compared to other major rehabilitation alternatives. However, despite increased use, asphalt emulsions are not well understood by many end users due to lack of experience and/or training. Limited understanding of emulsion materials may cause agencies to be hesitant about adopting cost-effective pavement preservation treatments while some agencies may adopt pavement preservation but avoid using asphalt emulsions by choosing materials more harmful to the environment, such as cutback asphalts.

Stability and breaking mechanisms are major factors impacting the performance of an asphalt emulsion and pavement preservation treatment. Asphalt emulsions are classified as rapid setting, medium setting, quick setting and slow setting in increasing order of their stability. Quick-setting emulsions are commonly used for treatments like microsurfacing and slurry seals. These emulsions are formulated to be highly stable while stored; however, they rapidly break on contact with aggregates, while allowing adequate mixing time. The quick set allows traffic to quickly return to the roadway surface. Proper mixing time and setting characteristics make slurry seal or microsurfacing emulsion formulation and mixture design critical to implementing successful pavement preservation treatments.

The setting process of the slurry seal or microsurfacing mixture is influenced by the mixture design and many other external factors (e.g., temperature and aggregate reactivity); however, this study explores a scientific way to quantify and measure set time. Asphalt emulsions, just like other colloidal systems, have a diffused double layer formed by the difference in electric potential between charges on the asphalt droplets in the dispersed phase and the continuous phase. The fundamental understanding of zeta potential within a colloidal system also applies to asphalt emulsions. This report investigates the feasibility of using zeta potential as a new parameter for measuring emulsion stability for asphalt emulsions used in slurry seals and microsurfacing mixtures.

Research Methodology

This study consisted of two phases, a study to determine the effects of emulsion formulation parameters on the zeta potential of asphalt emulsions and a study to determine the effect of emulsion stability on slurry seal mixture performance.

In order to determine the emulsion formulation parameters that affect the zeta potential of asphalt emulsions, a number of slurry seal emulsions were prepared with PG 64-22 binder and a quick-setting emulsifying agent. The dosage of the emulsifier was varied as well as the formulation for the pH of the emulsifier solution and the impact to the asphalt emulsion was measured by observing changes in zeta potential.

Nine emulsions were produced, each with three different levels of emulsifier dosage and pH. These emulsions were tested for zeta potential in a Malvern Zetasizer Nano NS at three different temperatures. A repeated measures surface response design was employed to statistically analyze the effect of the three levels of emulsifier dosage, pH, and temperature on zeta potential. Each level of emulsifier dosage, pH, and temperature was measured three times by the Zetasizer, which led to a total of 81 readings.

In the second part of the study, the setting properties and cohesion development of mixtures using quick-set asphalt emulsion were studied to determine if zeta potential measurements provided an indication of set time for slurry mixtures. Slurry seal mixtures were designed based on the dry weight of aggregates and prepared with different amounts of emulsion and water content. The emulsions used in the mixture designs were the same emulsion formulations developed in the first phase of the study. The slurry seal mixtures were tested for cohesive strength developed after both 60 and 90 minutes. A surface response experimental design was used to determine the factors that affect cohesive strength and therefore emulsion performance. The statistical analysis shows zeta potential was a significant factor in the study's model of cohesion development.

Key Findings

Key findings from both phases of the study are listed below. All findings are limited to the materials and dosages studied in the experiment.

Effect of Emulsion Formulation Parameters on Emulsion Zeta Potential

- The ranges of pH and temperature studied had a significant effect on the measured zeta potential of emulsions.
- A decrease in pH reduced zeta potential for high emulsifier dosages, especially at 25°C.
- Emulsifier dosage had a significant effect on emulsion zeta potential according to the statistical model, but not as significant as the effects of pH and temperature.
- A reduction in zeta potential was observed at a pH level of 1.5 for all emulsifier dosages in the study.

Effect of Emulsion Stability on Performance of Slurry Seal Mixes

- pH had a significant effect on the cohesive strength of slurry seal mixes after 60 minutes of curing, with less stable emulsions gaining strength faster and having higher cohesion values than more stable emulsions.

- The effect of pH ceased to be significant at 90 minutes, indicating that the more stable emulsions continued to gain strength until they were level with the less stable emulsions.
- Emulsion content had a significant effect on cohesive strength at both 60 and 90 minutes, as higher emulsion content meant more emulsion residue was available to form bonds between aggregates.
- The moisture content of aggregates did not have a significant effect on cohesive strength; however, higher water content did improve workability and mix timing, especially with higher emulsion contents.

INTRODUCTION

State of the Practice and Problem Statement

Microsurfacing and slurry seals are pavement preservation surface treatments used to slow pavement cracking/deterioration and correct minor rutting. These treatments also provide a new wearing surface for the roadway. Studies are showing these treatments cost-effective and their use has been increasing throughout Iowa.

A major advantage to microsurfacing and slurry seal mixtures is time-to-traffic can be engineered to resume traffic operations in as little as one hour after treatment application. This is made possible with the help of quick-setting asphalt emulsions, cement, and additives.

Emulsions used in these treatments are either modified, in the case of microsurfacing, or nonmodified, in the case of slurry seals. Quick-set emulsions are designed to break or set when they come in contact with aggregates, but the emulsion break is subject to many factors that include emulsion temperature, the nature of the aggregates, the wind and moisture conditions on the site and, most importantly, the emulsion formulation parameters like chemical dosage and emulsion pH.

In general, agencies would like to enhance QC/QA procedures for pavement preservation treatments and asphalt emulsions. Many agencies would also like specifications to emphasize the importance of quality workmanship.

This study focuses on important variables in asphalt emulsion manufacturing and on measuring how changes in these parameters influence the stability and setting characteristics of a slurry mixture. Many civil engineering practitioners are not familiar with the asphalt emulsion and slurry-mixture parameters that influence setting time. Therefore, this research project aims to use scientific measurements and controlled experimental design to show how parameters influence setting time for slurry seal and microsurfacing mixtures.

Critical Focus Areas

This paper seeks to answer two major questions:

- What are the important factors that govern the stability of a variety of emulsions?
- Can zeta potential measurements be used as an indicator of set time for quick-set emulsions in emulsion slurry mixes?

As explained in the problem statement, it is hard to determine how stable an emulsion is in the field without performing mix tests first. Often, contractors make field adjustments to the slurry mixture to balance the setting time with field conditions (e.g., high temperatures that can

accelerate set or vice versa). Making field adjustments requires contractors to have experienced crews and value high quality workmanship.

With this study, important emulsion-manufacturing parameters were studied, specifically including pH and emulsifier dosage. Measurements include zeta potential testing of the emulsion (a scientific measurement of stability) and cohesion testing of various slurry mixtures.

This report presents a controlled experiment to study the influence of important emulsion-manufacturing parameters on set time. Use of scientific measurements in the mixture design stages of a microsurfacing or slurry seal project have the potential to enhance the accuracy of mixture adjustments and develop emulsion formulations that can be more readily adapted to field conditions or aggregate reactivity.

LITERATURE REVIEW

Microsurfacing is a method of pavement preservation which involves laying down a thin layer of crushed aggregates, fillers, and polymer-modified asphalt to maintain the functional integrity of the pavement surface. The fillers commonly used in microsurfacing are portland cement and additives that control emulsion setting.

Like other pavement preservation treatments, microsurfacing is a preventative treatment and not a cure for pavement structural defects; however, it has been successfully used to correct rutting, seal cracks, and improve the pavement texture and ride quality (Bae and Stoffels 2008).

The popularity of modified asphalt emulsions has led to an increase in the use of pavement preservation treatments like microsurfacing, which make use of polymer-modified emulsions. However, because of the esoteric nature of asphalt emulsions, and because the breaking point of a microsurfacing/slurry seal mixture is extremely critical, there is a growing need to better understand the microsurfacing mix design process and strategies for engineering the breaking point of a microsurfacing mixture (Robati et al. 2015).

Studies have shown that, on average, microsurfacing adds about 3–5 years of life to existing pavements by reducing rutting and improving surface ride quality. Microsurfacing is also one of the more cost-effective pavement preservation strategies due to its fast application and completion time; microsurfaced roads can typically be opened to traffic in as early as one hour (Ilias et al. 2017, Bae and Stoffels 2008).

Many studies point to the cost-effectiveness of microsurfacing as a pavement preservation treatment. A study by Ilias et al. (2017) found that multiple applications of microsurfacing coats over the life of a pavement are one of the most effective pavement preservation strategies observed. Labi et al. (2007b) noted that microsurfacing, on average, accounted for an international roughness index (IRI) decrease of 0.442 m/km. This study also found microsurfacing increased the pavement condition index (PCI) by 6.2 based on a scale from 0–100.

The Indiana DOT has observed improvements in the structural number (SN), IRI and PCI of pavements after the application of microsurfacing (Ji et al. 2013a). This study determined microsurfacing would be a cost-effective strategy as long as it extends pavement service life more than 1.6 years, which previous studies have pointed out is a threshold that microsurfacing treatments regularly exceed.

This review summarizes microsurfacing literature related to mix design/applications, the science of polymer-modified asphalt emulsions, and means of working toward engineering the breaking point of emulsion mixtures for different aggregate types or application purposes to enhance design.

Polymer-Modified Asphalt Emulsions: Foundation of Microsurfacing Mixtures

Innovations in asphalt emulsions are fast opening the door to broader applications of low cost and energy-efficient pavement preservation strategies. However, increasing loads and the higher demands placed on roadway infrastructure have expanded the need for enhanced binder performance. One method for enhancing performance is to add polymers to the asphalt emulsions.

For preservation applications with nonheated aggregate, emulsions in general provide better performance than hot applied asphalt (e.g., a chip seal design), since emulsions provide better adhesion (Gransberg and Zaman 2005, Shafii et al. 2011). Studies have further shown that chip seals perform better with a polymer-modified emulsion than a regular nonmodified emulsion due to the polymer film aiding in chip retention and cohesion (Lubbers and Watson 2005).

The performance of a polymer-modified asphalt emulsion depends greatly on the manner of modification of the asphalt and/or emulsion. Polymers are usually added to asphalt binder before emulsification, and this leads to a different microstructure compared to when polymers are added to the binder during or after emulsification. This is especially true for latexes (King and Johnston, 2012).

Depending on the type of polymer and time of addition, either a monophasic or biphasic emulsion residue will be produced. Modification before milling usually leads to a monophasic asphalt and polymer, with the polymer-modified asphalt forming one phase dispersed in the liquid medium. Postmilling modification (i.e., adding the modifier after the emulsion has been milled) leads to the formation of a biphasic emulsion with both asphalt and polymer droplets being suspended in the emulsion (Forbes et al. 2001).

Phase separation can occur in asphalt emulsions as well as in the base asphalt if there is incompatibility between the polymer and asphalt or if there is insufficient blending of the polymer-modified asphalt (Becker et al. 2001).

A study by Kucharek et al. (2002) involved modifying an emulsion with 3% SBR latex but adding the latex at different stages. They directly modified the binder by adding 3% latex to the emulsifier solution and made another emulsion by adding half of the polymer to the binder (1.5%) and the other half (1.5%) to the emulsifier solution. They noted that the emulsions with polymer-modified asphalt performed better than the latexes and also reduced the curing time required for the polymer network to form.

Polymers used in the modification of asphalt are usually either latexes or solid polymers. Latexes like natural rubber latex (NRL) and styrene-butadiene rubber (SBR) latex are two common polymers that are emulsified in liquid form. Styrene-butadiene-styrene (SBS) is one of the most commonly used solid polymers added to asphalt due to its compatibility.

Asphalt Emulsion Stability: A Critical Parameter for Treatment Success

Asphalt emulsion stability is critical to the success of a slurry seal/microsurfacing design. A controlled set is important for two reasons: first, the emulsion must remain in a liquid state while aggregates are coated during the short mixing period. Second, the engineered mixture must set quickly so the road can be reopened to traffic in a short period of time. Emulsion stability depends on an emulsion's chemistry, its physical characteristics and manufacturing process. The next section addresses the importance of each of the above factors on emulsion stability.

Emulsion chemistry depends heavily on the emulsifier type, which influences its stability. Different emulsifiers will lead to different setting characteristics. Amines are commonly used for cationic rapid-set emulsifiers, ammonium chlorides for cationic slow-set emulsifiers, tall oils for anionic rapid sets and phenols for anionic slow-set emulsions (James 2006). A review of the literature reveals other emulsifiers like the reaction products of polyamines with polycarboxylic anhydrides (Schilling 1985). Other examples of emulsifiers are a cationic slow-set lignin-based amine emulsifier (Ludwig and Fiske 1977). In addition, Wang et al. (2013) studied the effect of early cement hydration on an asphalt-emulsion–cement-paste composite using an anionic lignin-amine-based emulsifier. Mercado et al. (2014) used a dodecyl-amine-based surfactant to study the breaking of cationic amine-based oil in a water emulsion and as a result of addition of an alkali.

The pH of the electrolyte solution also plays an important role in emulsion stability. Thus, the pH of the emulsion is tied closely with the zeta potential of the emulsion system. Cationic emulsions typically need low pH values to maintain stability, while anionic emulsions often need high pH values.

Firoozifar et al. (2010) noted that a pH of 1.5 was required for optimal stability in a cationic bituminous emulsion. Lesueur and Potti (2004) showed that a change in pH reduced the interparticle repulsive forces due to the cancellation of droplets' surface charges, leading to agglomeration. They noted that for a cationic emulsifier, an increase in pH causes the amine groups to lose their protons and hence their positive charge, decreasing their repulsive forces, thereby causing breaking. The opposite is true for an anionic emulsifier which breaks if the pH of the solution decreases.

The particle size of an emulsion is another important factor determining emulsion stability (James 2006). Asphalt emulsions are made up of small droplets of asphalt that are broken up by shearing. There is a change in surface energy when emulsions are broken up, with an increase in surface area from the smaller droplets that are formed from larger asphalt droplets. This change in energy leads to a positive change in entropy, which leads to instability.

In order to surmount this positive change in entropy, a stabilizer in the form of an emulsifier needs to be added to the solution. The concept of free energy can best be understood using the 2nd law of thermodynamics, which states that the entropy or state of randomness of an isolated system will always tend to increase over time or, in other words, it is the natural tendency of an isolated system to move toward a state of disorder.

The tendency of a system to move toward this state of disorder can be determined by calculating the change in the free energy of the system, also known as the change in Gibbs energy, ΔG . Isolated systems that move towards a higher state of disorder have a positive value of ΔG while systems that are not isolated, where energy can be transferred to and from the system, and that move towards a more organized state have a negative ΔG (Chang 2005). The change in Gibbs free energy for a system can be calculated using equations 1 and 2 given below:

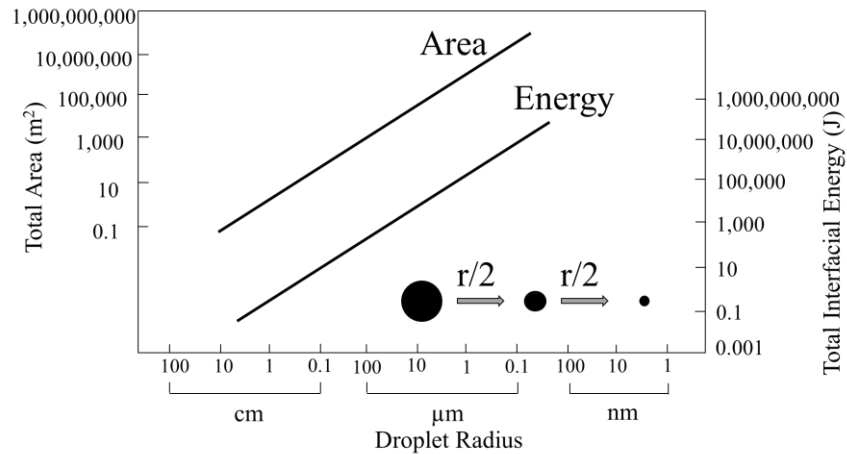
$$\Delta G = \Delta H_{system} - T\Delta S_{system} \quad (1)$$

$$\Delta H_{system} = \Delta A\gamma_{12} \quad (2)$$

where ΔH_{system} is the increase in the entropy of the system, ΔA is the change in total surface area when large emulsion droplets are sheared into smaller drops, γ_{12} is the energy of the system per unit area or surface tension in the case of an emulsion, and $T\Delta S_{system}$ is the configurational entropy of the system, which is usually positive since a large number of droplets creates more randomness.

The formation of an emulsion by shearing larger particles into a number of smaller droplets results in a large increase in the surface area of the new system and causes the term $\Delta A\gamma_{12}$ to be much larger than $T\Delta S_{system}$. This in turn leads to a positive value of ΔG and, as mentioned above, leads to an unstable system thermodynamically, which leads in turn to the coagulation of an emulsion in the absence of a surfactant. However, in the presence of a surfactant, the surface tension of the dispersed phase is greatly reduced and γ_{12} decreases significantly, causing $\Delta A\gamma_{12}$ to decrease enough for it to be adequately small that ΔG can become negative and stable emulsification can again take place.

The charges that attach themselves to emulsion droplets and cause interparticle repulsion reduce the total free energy of the emulsion and stabilize it (Tadros 2013). Smaller particles also lead to lower phase separation and sedimentation rates. The rate of sedimentation for an emulsion is directly proportional to the square of the radius of the emulsion particles, with smaller particles being significantly less prone to sedimentation (Zhang et al. 2012, Yang et al. 2013). This process is illustrated in Figure 1.



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Figure 1. Surface energy increase with increase in surface area

Emulsion breaking is of critical importance in pavement surface treatments since emulsion breaking either too early or too late can be detrimental to the success of the surface treatment. The breaking of emulsions was simulated by Lane and Ottewill (1976), who prepared emulsions using cationic surface active agents, and then used quartz particles to induce breaking. They also studied the mobility of emulsion particles in suspension.

The Derjaguin-Landau-Verwey-Overbeek (DLVO) theory has often been used to explain emulsion stability and breaking. The theory explains emulsion stability in terms of a balance between two interparticle forces, the electrostatic repulsion caused by like charges from the added emulsifier on the emulsion droplet surface and the van der Waals attractive forces that exist between two particles separated by a small distance. In order for the particles to remain in stable suspension, the electrostatic repulsive forces should be equal to or greater than the attractive or van der Waals forces.

Rodríguez-Valverde et al. (2003) determined through calculations of the zeta potential and Hamaker constant that the stability of asphalt emulsions conforms to the DLVO theory. Lesueur and Potti (2004) have used the DLVO theory to explain the breaking of emulsions as resulting from one of two possibilities: either the added aggregates attract the charged emulsifier particles from the asphalt particle surfaces, therefore reducing the interparticle repulsive forces, or water evaporation automatically brings the asphalt particles closer together so the interparticle repulsive forces are overcome by the attractive van der Waals forces.

Salou et al. (1998) has related the stability of asphalt emulsions to the chemical and interfacial properties of asphalt using the DLVO theory. This study took into account the zeta potential of asphalt droplets in an acidic medium and also the asphaltene-to-resin content. Its authors determined that the asphaltene-resin ratio plays a role in determining the stability of emulsions by controlling the polar components in asphalt.

Zeta Potential: A Potential Measurement of Asphalt Emulsion Stability

Zeta potential is defined as the potential difference between the surface charges on the emulsion droplets and the electrolyte charges in the emulsion solution. Zeta potential arises due to the diffused double layer that exists between the surface charges covering an asphalt droplet and the surrounding charged particles in the solution, which are equal in magnitude but oppositely charged than those on the surface. These oppositely charged particles act as a shield for other around-the-surface charges and form a layer known as the diffused layer.

The size of the diffused layer depends on the magnitude of surface charges on the asphalt droplets. The secondary extension of the diffused layer is known as the stern layer and together they form the diffused double layer.

The zeta potential is a measurement of the potential between the charges present in the diffused layer only. Experimentally, zeta potential is determined by identifying the electrophoretic mobility of emulsion particles by inducing an electric field across two opposite plates of a measuring cell containing the emulsion and measuring the flow of the particles between these plates. The electrophoretic mobility is then calculated using equation 3:

$$\mu_e = \frac{V_p}{E_x} \quad (3)$$

where μ_e is the electrophoretic mobility, V_p is the particle velocity and E_x is the electric field applied across the two plates of the measuring cell. The zeta potential is then calculated from the electrophoretic mobility using the Smoluchowski equation (equation 4). The Smoluchowski equation is expressed as follows:

$$\mu_E = \frac{\epsilon \zeta}{\eta} \quad (4)$$

where μ_E is the electrophoretic mobility, ϵ is the permittivity of the continuous phase of the emulsion, ζ is the zeta potential of the emulsion being measured, and η is the dynamic viscosity of the continuous phase. The zeta potential can be calculated using equations 3 and 4 if the properties of the continuous phase of the emulsion, which in most cases is water, are known and if the velocity of the particles are mobilized under a known electric field.

Zeta potential values are typically positive for cationic emulsions and negative for anionic emulsions and aggregates (Lee and Ahn 2016). As zeta potential values approach zero, emulsions get more and more unstable with breaking occurring at the point of zero zeta potential. This can be achieved by adding particles with zeta potential opposite to that of the zeta potential of the emulsion.

There has been an increased interest in measuring the zeta potential of asphalt emulsions in order to study coalescence and breaking. A study by Lee and Ahn (2016) studied four different

emulsions as well as different additives and determined that cationic emulsions cured rapidly when in contact with negatively charged aggregates. Its authors determined that pH has a significant role to play in determining the zeta potential of the emulsion-aggregate mix, with a lower pH showing positive zeta potential and a high pH showing negative zeta potential.

This connects well to what is known about cationic emulsions needing a lower pH to maintain stability while anionic emulsions need a higher pH to maintain stability. This was confirmed by Wang et al. (2013) who found, in addition, that water evaporation from an emulsion rapidly decreases the zeta potential irrespective of the charge.

Ziyani et al. (2014) examined the zeta potentials of three different aggregate types: limestone, dolomite, and gneiss. They noted that emulsion breaking occurs because of the high affinity of the aggregate surface for the emulsifier particles attached to asphalt droplets. They also found that the methylene blue test values of the aggregate did not affect the breaking value of emulsions. This breaking value is defined as the amount of material needed to break 100g of emulsion.

A similar study by the same authors determined the surface properties of mineral aggregates and analyzed adhesion using contact angle values and the Young-Dupree equation for pure liquids. The authors noted that quartzite has the highest surface energy while gneiss has the lowest (Ziyani et al. 2016).

Methylene blue values are typically used to “index” the reactivity of aggregates due to their fines content. The test is a measure of how much methylene blue dye is adsorbed onto the surface of an aggregate.

Clays are the most reactive portions of aggregate and can influence emulsion breaking. Liu et al. (2004) determined that montmorillonite was most attracted to bitumen droplets and noted that this could result in a coating of droplets which would prevent coagulation. Similar research has shown that kaolinite also forms films around asphalt droplets and prevents coagulation (Jiang et al. 2010).

Yukselen and Kaya (2008) have noted that the amount of material is not a significant factor in determining methylene blue values and they did not find a significant difference in the methylene blue values for soils passing the #40 and #200 sieves. They recommend the methylene blue test for determining the cation exchange capacity of aggregates as well as the swell potential of clays. Despite this research being geared toward soils, it could have potential applicability to aggregates.

Yool et al. (1998) noted that while the methylene blue test gives an accurate representation of the reactivity of aggregates, it does not determine which clay materials are present. They point out that the adsorption of methylene blue on the surface of clay particles is not in proportion to the detrimental effects of clay minerals on a concrete mix. Identification of the nature of any clay minerals present can be overcome by adding a glycol dye to the aggregates which reduces the

adsorption of methylene blue. Given that different clay materials adsorb differently on the surface of asphalt droplets, this could be a useful method in differentiating between different clay components.

It is interesting to note that asphalt droplets have their own polar charge. Asphaltenes and resins both contain acid and base functional groups and hence contribute to the polar nature of the asphalt droplet. This can affect the electrophoretic mobility of asphalt droplets in an electrolytic solution and influence breaking (Takamura and Chow 1985). Jada and Salou (2002), in another paper, also found that the properties of asphalt appear to affect the breaking of emulsions.

Microsurfacing Mix Design Methods

Microsurfacing, as explained in earlier sections, is used to extend pavement life. Microsurfacing mixture design is largely based on test standards available from the International Slurry Seal Association. These standards provide a logical framework for evaluating mixing time, set time, time-to-traffic, minimum allowable asphalt content and maximum allowable asphalt content. However, mix design methods could be greatly improved by incorporating scientific measurements into the process, especially measurements that can be used to make emulsion formulation adjustments to compensate for the varying reactivity of different aggregates.

Microsurfacing, in particular, is in need of a standard procedure to determine aggregate reactivity for locally sourced aggregates, since the same emulsion used in two different projects might yield different results due to different aggregate surface properties. This section outlines previous case studies on microsurfacing, highlighting their insights and shortcomings.

Microsurfacing mix designs typically consist of an engineered mixture of emulsified asphalt, water to manage mix consistency, mineral fillers, aggregate, and chemical additives. The job of the chemical additives and filler material is to control workability and breaking. If the mixture is not engineered properly, emulsions can break prematurely or breaking may be delayed, based on the aggregates they come in contact with as well as weather conditions (ISSA 2010).

Microsurfacing has been used in Georgia on I-75 to seal cracks and correct raveling (Watson and Jared 1998). Watson and Jared noted that no additional cracking or raveling occurred during the study. The authors concluded microsurfacing should provide between 5 and 7 years of added service life for moderate traffic corridors and 3-4 years of additional service life with heavier traffic.

Another study in Minnesota investigated the performance of microsurfacing using a softer PG 48-34 binder as base for an emulsion (Johnson et al. 2007). This surface was designed as a flexible overlay on a low-volume road. The study evaluated pre- and post-construction cracking, with an evaluation of the treatment six months after construction (after one winter of service) and noted that 71% of cracks had reflected up to the surface, while microsurfacing decreased the rutting 20% right after construction and the amount of rutting remained similar six months later. The study also noted an increase in the surface friction.

A study by Labi et al. (2007a) compared the cost-effectiveness of microsurfacing vs. a thin hot-mix overlay based on four factors, namely the treatment service life, the improvement in pavement condition, the area bounded by the performance curve, and two cost factors, namely the agency and total cost. They noted that microsurfacing was more cost-effective than a thin overlay when only agency costs were taken into account; however, in terms of overall costs, the thin overlay appears more cost-effective for heavier traffic while for low- or medium-traffic roads, microsurfacing still appears to be the more cost-effective option.

Researchers in Chennai, India, have used chrome shavings as a substitute for aggregate and have noted favorable results in terms of placing and finishing the microsurfacing mixture as well as that the mixture continued to meet performance expectations after a year (Kamaraj et al. 2016).

Microsurfacing has also been used to address reflection cracking and potholes in concrete pavements. Though reflective cracks occurred after microsurfacing, the cracking was much easier to contain and prevented recurrence of potholes (Berg et al. 2009). Similarly successful trials with microsurfacing have been observed in Indiana (Ji et al. 2013, Labi et al. 2006), where reductions in IRI and increases in the pavement condition rating (PCR) have been among the most noted benefits.

A survey in Texas revealed that project selection and contractor understanding of treatment implementation are important factors for project success (Broughton and Lee 2012). Case studies in Louisiana have also noted a benefit from microsurfacing with improvements to PCI and reduced cracking. Despite rut filling not being the primary objective of many microsurfacing projects, data have still shown an improvement in sections with rutting of approximately 0.5 inches (Temple et al. 2002). Table 1 summarizes the case studies of various microsurfacing projects and their effects on pavement service life.

Table 1. Experimental testing plan for determining the cohesive strength of slurry seal mixes

Location	Reference	Mix Design Details	Performance Measurements	Post-Construction Performance
Minnesota	(Johnson et al. 2007)	PG 48-34–modified binder. Aggregates sourced locally and met type II gradation requirements.	Rutting, reflection cracking, friction, and IRI	Rutting reduced by 20% post-construction. 71% of cracks were reflected to the surface. Friction was improved. IRI depended on the amount of aggregates.
Chennai, India	(Kamaraj et al. 2016)	Microsurfacing mixture with chrome shavings as a fine aggregate. The shavings were impregnated in a slow-set cationic polymer-modified emulsion.	Providing more flexibility on the road surface with the help of the chrome shavings as reinforcement.	Section was qualitatively monitored for two years, with the surface found adequate for urban roads as a pavement preservation layer or alternate routine maintenance treatment.
Louisiana	(Temple et al. 2002)	Polymer-modified asphalt emulsion. Well-graded 3/8 th -inch crushed aggregate, mineral filler, and water.	Data for multiple project locations were analyzed to determine the cost-effectiveness of microsurfacing and its effect on rutting, cracking, raveling, and other pavement distresses.	Median PCI was 85 after 60 months of service, and only 10% of pavements showed a PCI of less than 80. Significant improvement in relation to cracking. Rutting improvements were observed.
Utah	(Berg et al. 2009)	No mix design details available. Treatment was performed by a private contractor.	Severe cracking and potholes on I-70. Needed a cost-effective treatment to extend the life of the road. Microsurfacing was employed as a concrete pavement treatment.	Cracks did reflect after 2 years, but potholes remained filled and the cracks were tighter and more manageable. Was recommended as a means of extending the life of concrete pavements.
Minnesota	(Bae and Stoffels 2008)	No mix design details.	Study looked at microsurfacing to treat thermal cracking and evaluated cost-effectiveness.	Cracks with a 0.7 cm depth and 0.58 cm width were reduced by 80%.
Indiana	(Labi et al. 2006)	Mix designs used polymer-modified emulsions, mineral filler, water, and fine aggregate.	Measured effectiveness if microsurfacing in terms of the three parameters of IRI, rutting, and pavement condition rating.	Effectiveness of microsurfacing was measured and ranged 2–10 years for IRI, 15 years or more for rutting, and 4–15 years for pavement condition rating.
Texas	(Broughton and Lee 2012)	Mix designs according to TxDOT TTI 1289, but actual mix designs varied considerably across the state.	Mainly looked at factors important to the success or failure of microsurfacing projects.	Survey analysis determined that project selection was important to project success. Contractor experience also played an important role in project success.
Indiana	(Ji et al. 2013)	A separate study from the project mentioned above. This study involved a total of four test sites. A heavily polymer-modified emulsion was used with polymer content between 3–4% and a nominal aggregate size of 3/8 th in. The emulsion application rate was 0.017 to 0.025 lb/in ² .	Determined that in order for microsurfacing to be economically viable, it should provide an extension of 1.6 years of service life.	The service life extension as a result of microsurfacing met the required criteria; furthermore, only a 2-point increase was noted in surface roughness in the two sections that employed microsurfacing when compared to a 4-point increase in the control sections.

TEST PLAN AND PROCEDURE

Research Plan and Tasks

The research objective of this study was to determine the feasibility of zeta potential as a parameter to measure the stability and performance of asphalt emulsions.

This study consisted of two phases. Phase 1 was comprised of determining the formulation parameters that have a significant effect on the zeta potential of an emulsion and hence its stability. Results from Phase 1 were then used to determine the independent variables to be applied to Phase 2.

Phase 2 studies cohesion values for slurry/microsurfacing mixtures. Cohesion values were measured at different time intervals to estimate set time and time-to-traffic. The second phase investigated if differences in the zeta potential results impacted cohesion test results and consisted of conducting cohesion tests at intervals of 30 or 60 minutes. This was done using a cohesion tester in accordance with the International Slurry Seal Association's (ISSA's) TB-139 (ISSA 2017a) to determine the resulting cohesive force developed by the mix over time.

The research plan was broken down into several tasks, which are described below.

Task 1: Designing an experimental plan for testing

A suitable experimental plan is important to ensure that results are obtained efficiently within a reasonable time frame. Both Phase 1 and Phase 2 of this research project had more than two independent variables and multiple treatment levels. This would have made it extremely time-consuming to conduct a full factorial experimental design, in which the number of experiments is xn , where x is the number of independent variables and n is the number of treatments. Including replicates, of course, increases sample preparation and testing time even further.

The first phase of testing, therefore, involved measuring the zeta potential of emulsions with different formulation parameters. The experiment was designed with three independent variables measured at three levels: pH (1.5, 2.0, and 2.5), emulsifier dosage (1.2%, 1.5%, and 1.8% by weight of emulsifier solution) and temperature (25°C, 37.5°C, and 50°C). Testing was performed on a Malvern Zetasizer programmed to take three zeta potential measurements at each temperature for each sample. This resulted in a repeated measures design that provided 81 responses of zeta potential in total, with 9 samples needing to be prepared, each of which would be tested 3 times at 3 temperatures.

The second phase of testing included testing of slurry seal mixtures for the cohesive strength of slurry seal mix designs while changing three independent variables. The independent variables each included three levels: pH during the emulsifier formulation (1.5, 2.0 and 2.5), emulsion content of the mixture (14%, 16%, and 18% by weight of the mix), and water content of the

mixture (4%, 6%, and 8% percent by the dry weight of the aggregate). For cohesion testing, all samples would have had to be mixed, cast, and tested individually. Therefore, it was decided to use a surface response design. A surface response design is less accurate than a full factorial design but significantly reduces the number of tests to run, in this case from 27 to 15. For cohesion testing, it was decided to have two replicates for each trial, while the treatments were randomly assigned to each sample, as shown in Table 2.

Table 2. Experimental testing plan for determining the cohesive strength of slurry seal mixes

Experiment #	Emulsion content (by weight of mix) Low = 14%, Medium = 16%, High = 18%	pH of the emulsifier solution during formulation Low = 1.5 Medium = 2.0 High = 2.5	Moisture content (by weight of dry aggregate) Low = 4% Medium = 6% High = 8%	Cohesive strength
1	Medium	Low	Low	XX
2	Medium	Low	High	XX
3	Medium	High	Low	XX
4	Low	Medium	High	XX
5	Medium	Medium	Medium	XX
6	High	Low	Medium	XX
7	Low	Medium	Low	XX
8	Low	High	Medium	XX
9	High	Medium	High	XX
10	Medium	Medium	Medium	XX
11	Medium	Medium	Medium	XX
12	Medium	High	High	XX
13	Low	Low	Medium	XX
14	High	Medium	Low	XX
15	High	High	Medium	XX

A surface response design model assumes a three-dimensional (3D) experimental space with one axis (Y) being the response and the two other axes being the two independent variables. The response is then modeled based on the two independent variables by keeping the third independent variable constant, producing a two-dimensional (2D) surface. Then additional measurements are taken to create multiple surfaces by changing the third independent variable.

One example of surface response design is the Box-Behnken design, which places the independent variables and levels at the edges of a 3D box, while one iteration at one level of one of the independent variables is placed at the center to reduce the error (Figure 2).

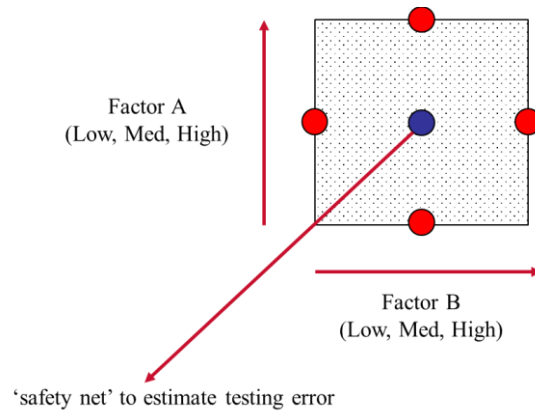


Figure 2. The Box-Behnken design

For this study, a Box-Behnken design was generated using the statistical software JMP for the three independent variables with three levels each.

Task 2: Preparing emulsions of varying formulations according to the experimental plans

The next task of the project was to formulate and manufacture the asphalt emulsions that would be used in both experimental phases. The emulsions were prepared using the same PG 64-22 binder from the same asphalt terminal. (Asphalt binder chemistry and emulsifiability can be asphalt-source-dependent, so controlling experiments by using the same base asphalt is important.) To focus the study specifically on engineering the set time of emulsions, only nonmodified emulsions were included in the zeta potential and cohesion measurements. Percent residue was measured for each prepared emulsion to ensure flow rates into the mill accurately reflected the set points of the pumps.

Task 3: Studying the rheological properties of microsurfacing and slurry seal emulsions and residues

This task involved examining the rheological properties of microsurfacing emulsions and their residues and included tests to determine the complex modulus of the emulsion and the emulsion residue, creep recovery in the case of modified emulsions and how they compare with modified binders, as well as particle size analysis. Particle size analysis plays an important role in emulsion stability, and the rheological properties of the emulsion affect its ability to be pumped and applied as a treatment while remaining stable. The creep recovery test determines which modification method produces the most creep recovery and how a polymer-modified emulsion performs in creep recovery when compared to its base binder.

Task 4: Measuring the zeta potential of the different asphalt emulsion formulations

The objective of the first phase of the project was to observe how emulsion formulation parameters (specifically, pH and emulsifier dosage) influenced zeta potential and how these measurements changed with temperature.

Zeta potential is defined as the potential difference between the charges on the surface of the asphalt droplets and the oppositely charged ions in the dispersion phase of the emulsion. Zeta potential depends on the ionic concentration of the solution, specifically the concentration of ions in the continuous phase that are opposite in charge to those attached to the surface of the dispersed particles. Hence, the pH of the solution plays an important role in emulsion stability. Cationic emulsions have positive charges on the surface of the dispersed phase and, as a result, need a continuous phase with a very low concentration of negative charges to remain stable. This indicates that a low pH is crucial to the stability of cationic emulsions. The opposite is true for anionic emulsions, which need an alkaline continuous phase to remain stable.

For the total change in the free energy of the emulsion system to remain negative, enough emulsifier molecules must be present in order to coat the asphalt particles and increase surface tension. Temperature also plays a major role because it represents energy being transferred into the system which affects emulsion stability. Therefore, the three independent variables chosen were emulsifier dosage, emulsion pH, and temperature.

In order to obtain satisfactory and repeatable data, the emulsions had to be diluted down to very low concentrations of 1:250 (1-part emulsion in 250-parts pH solution). This is because zeta potential measurements on the Malvern Zetasizer are achieved by measuring the electrophoretic mobility of the emulsion droplets and relating this value to the zeta potential using the Smoluchowski equation. Light scattering is involved in this process and the dilution is necessary to achieve stable readings.

Task 5: Determining the effect of aggregate reactivity on emulsions' zeta potential and the isoelectric point of the emulsion

The isoelectric point of an emulsion is defined by the point at which the zeta potential of the emulsion is zero and irreversible flocculation occurs. The isoelectric point can be achieved both by the addition of aggregates and by changing the solution's pH, although the two may occur simultaneously.

Determining the isoelectric point of an emulsion with different aggregates can help gauge both emulsion and aggregate reactivity and may be a useful test in determining the right emulsion formulation to use in a particular field application.

Task 6: Determining the effect of zeta potential on emulsion performance

Phase 2 of the project involved determining if emulsion formulation parameters had any effect on slurry seal set time. This was achieved by measuring the cohesive force developed once slurry seal mixtures set according to the ISSA test method (ISSA 2017a).

When a slurry seal mixture sets, the water in the system is pushed out due to the flocculation of asphalt particles around the aggregates, which forms adhesive bonds. The residual asphalt

content of the emulsion and the percent of emulsion used in the mix design determine the amount of asphalt that will be present in the mix.

In order to determine the effect of the stability of the emulsion, emulsions of different pH levels were used in the experimental design. pH was chosen as a factor since it drives the protonation of the emulsifier and hence determines stability in an emulsion formulation.

Using a Box-Behnken experimental design, 15 permutations of the 3 independent variables—pH, emulsion content, and water content—were created. The distribution of these samples was shown in Table 2.

Task 7: Analysis of results

Results obtained from Phases 1 and 2 were statistically analyzed and are discussed in terms of their scientific merit based on the theory presented in the literature review. While a full factorial design for the zeta potential experimental plan would have ensured a statistical model with higher statistical power compared to the Box-Behnken design, significant effects and logical trends were still observed via this study's Box-Behnken surface response design model.

Materials and Methodology

Asphalt Emulsion Preparation

A 64-22 base asphalt binder was used to prepare the different emulsions used for the experimental plan testing zeta potential and cohesive strength. To avoid introducing other complexities into the experiment, only one nonmodified base asphalt was used and one emulsifier type. An amine-based quick-set emulsifying agent was used to make the emulsion soap solution. The manufacturer recommended the emulsifier solution be prepared with an emulsifier dosage of 1.5% at a solution pH of 1.5–2.5. Both emulsifier dosage and pH were varied as part of the experimental design. Deionized water was used for preparation of the emulsifier solution, along with hydrochloric acid with a concentration of 33.3%. The methodology for preparing the emulsion was as follows:

1. **Testing the base asphalt viscosity:** Temperature vs. viscosity curves were measured for the asphalt binder to be used in the emulsion production. The purpose of the testing was to determine the proper milling temperature for the emulsion. This is an important step in emulsion manufacturing since heating the binder to a high temperature could cause the emulsion to exit the mill at a temperature above the boiling point of water, causing the water to evaporate and therefore the emulsion to set. An optimal asphalt temperature allows the asphalt to have enough viscosity to be pumped and milled easily and avoid high pressures, ensuring correct flow rates (Figure 3).

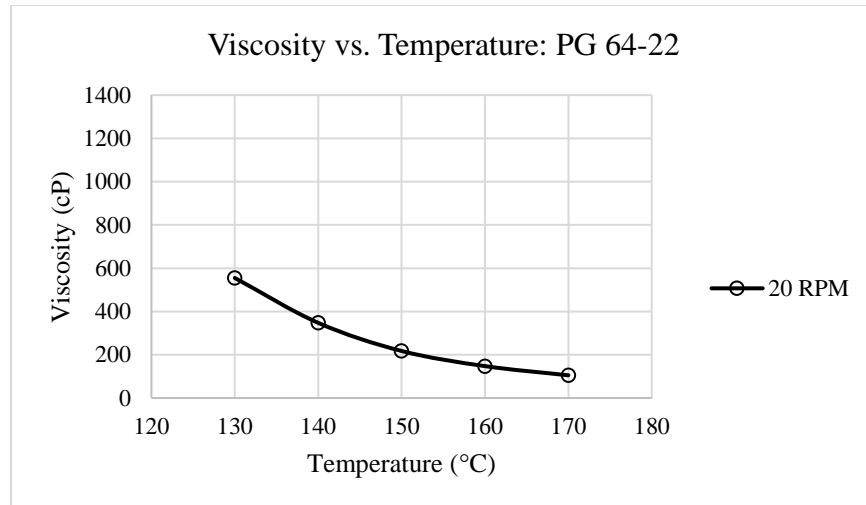


Figure 3. Viscosity vs. temperature for nonmodified PG 64-22 binder

2. **Preparing the emulsifier or ‘soap’ solution that will be the continuous phase of the emulsion:** This step involved determining a target batch volume based on which the quantities of emulsifier, water, and acid could be calculated. The amount of water was added to a beaker with a magnetic stirrer and was heated on a hot plate to 35°C before the emulsifier was added. Once all the emulsifier had been added to the beaker, hydrochloric acid was added slowly while the solution’s pH was monitored. The pH was thus decreased to the desired level according to the experimental plan and the amount of acid used was noted. The emulsifier solution was maintained at 40°C to eliminate the effects of temperature on pH during the solution’s transfer to the emulsion mill (Figure 4).



Figure 4. Asphalt emulsion mill

3. **Emulsion manufacturing:** Asphalt was added to the bitumen tank of the emulsion mill at a temperature close to the temperature required to be maintained during milling. The four

heated components—the bitumen tank, bitumen pipelines, shear mill, and soap tank—were all maintained at the required temperatures before milling commenced. In addition, the emulsion exit temperature was monitored and the initial flow of emulsion was discarded till the flow rates had stabilized. The asphalt emulsion was then collected and stored in high-density polyethylene jars at room temperature until use. A measured weight of emulsion was allowed to dry overnight on a plate of known weight in order to calculate the amount of residue to ensure that the target residue quantity had been met.

Rheological Testing of Emulsions and Residue

As part of a side study, a PG 58-28 binder was used to prepare polymer-modified emulsions for testing emulsion rheology. This side experiment did not compare between the polymer modifiers but addressed questions the research team had for manufacturing polymer-modified emulsions for future work. These observations will be useful for future investigations studying the performance of microsurfacing mixtures where polymer modification is required.

For this study, four emulsions were produced and tested: a nonmodified slurry seal emulsion, a latex-modified microsurfacing emulsion with 3.5% latex by total weight of the emulsion with latex added premilling, a latex-modified microsurfacing emulsion with 3.5% latex by total weight of the emulsion with latex added postmilling, and an emulsion with asphalt binder premodified with 6% SBS polymer manufactured for high compatibility with asphalt.

The first latex emulsion produced had the latex added to the emulsifier solution before milling and the second latex emulsion produced had the latex emulsion added after milling. Rheological comparisons were made to observe changes between the premilling and postmilling addition of the SBR latex polymer. For the SBS-modified emulsion, the research team wanted to observe differences between the base asphalt and emulsion residue characteristics.

The experimental setup involved a dynamic shear rheometer with a cup-and-bob attachment for measuring viscosity and complex modulus as a function of temperature and applied strain. During testing, each emulsion was stored at room temperature prior to testing and was allowed to condition in the rheometer for 10 minutes at the start temperature before testing began. Tests were carried out in the following sequence:

1. Strain sweeps at 1 Hz and 50°C to determine the linear viscoelastic range of each emulsion
2. Temperature sweeps from 30°C to 70°C to determine the rheological behavior of each emulsion
3. Viscosity vs. time profiles with two shear rates to determine recovery for storage and pumping purposes

The first step involved carrying out strain sweeps using a frequency of 1 Hz across a strain range of 0.01% to 10% in order to obtain the linear viscoelastic range of the emulsions. The temperature was kept constant at 50°C. Once the linear viscoelastic range was determined, temperature sweeps were performed on the emulsions for the range of 30°C to 70°C. The

emulsions were kept stable at 30°C for 10 minutes in the rheometer to allow their temperatures to equilibrate and then were heated at a uniform rate of 0.7°C/min. The values of storage modulus (G'), loss modulus (G''), complex modulus (G^*) and $\tan \delta$ were determined.

Finally, three emulsions (the control slurry seal emulsion, the SBS-modified emulsion, and the latex emulsion modified postmilling) were tested for change in rheological behavior related to change in shear rate, with the two shear rates of 0.1 s⁻¹ and 100 s⁻¹ being applied. The emulsions were heated at the two temperatures of 30°C and 50°C. A shear rate of 0.1 s⁻¹ was applied for 200 seconds before the shear was increased to 100 s⁻¹ for another 200 seconds, followed by the rate being dropped back to 0.1 s⁻¹ for a final 200 seconds. The percent change in viscosity was observed as a function of time over the entire test period.

Particle size analysis was performed to ensure proper milling was being achieved, and rheological testing of emulsion residues was performed on a dynamic shear rheometer using a 24 mm plate at 58°C to perform multiple-stress creep recovery (MSCR) testing. The temperature of 58°C was chosen with respect to the high temperature grade of the base asphalt binder used.

In order to determine the amount of SBS polymer to be added to the binder, a 400 g batch of base binder was modified with 7% SBS polymer and then diluted to 6%, 5%, and 4% using unmodified binder. Samples were run through the MSCR test procedure to determine their elastic recoveries, which were plotted against their concentration per volume of binder as shown in Figure 5.

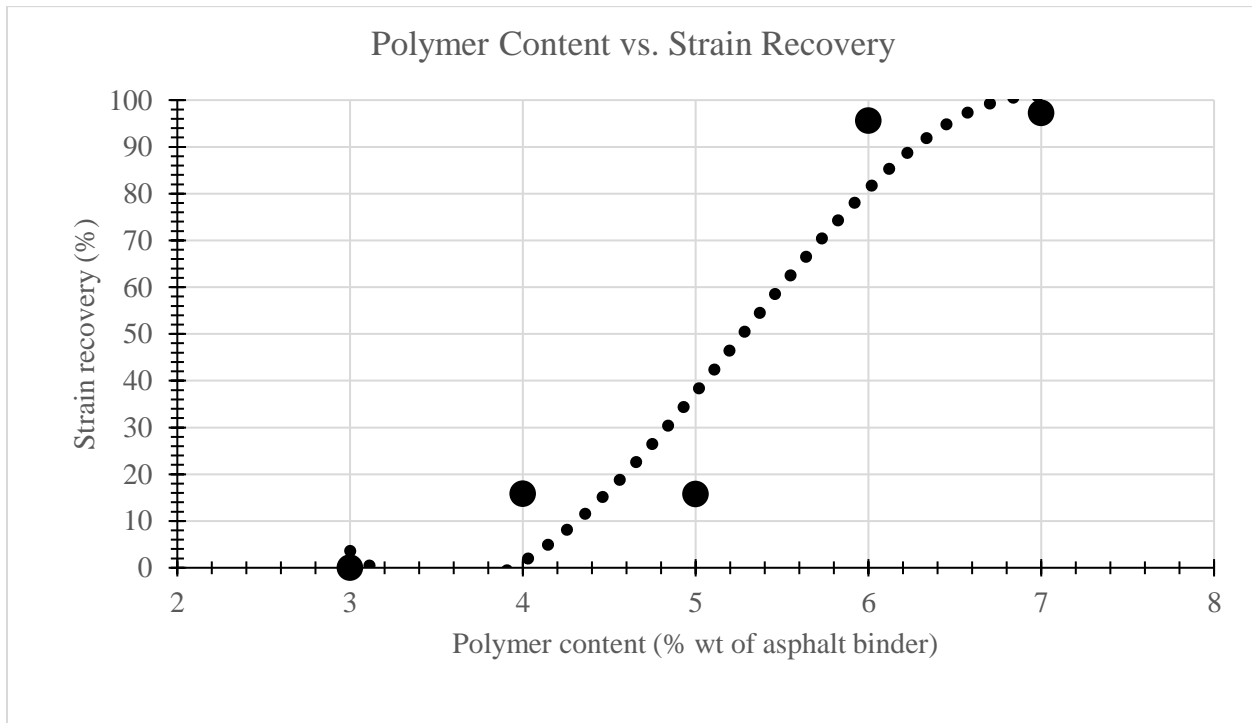


Figure 5. Polymer content (SBS) vs. strain recovery

As seen in Figure 5, the results took the form of an ‘S’ curve, with the optimum amount of polymer being at the crest of the S curve before 7%. Higher dosages than the optimum would not have added to the elastic recovery of the binder. Hence, 6% SBS was chosen as the optimum dosage to create a base asphalt with high recovery for potential future use in microsurfacing mixtures.

Zeta Potential Measurements

Measurements were made on a Malvern Zetasizer using a standard operating procedure (SOP) created specifically for asphalt emulsions. This SOP was created to test each sample at three different temperatures and take three readings at each temperature.

Dilution was achieved using a holding solution of distilled water and 33.3% w/w hydrochloric acid. These solutions were used to disperse the asphalt emulsions having a corresponding pH, so that the pH of the emulsion dilution remained constant. A pipette was used to disperse 1 ml of emulsion in 250 ml of holding solution that was then dispersed evenly with a magnetic stirrer. The diluted emulsions were placed in a Malvern folded capillary cell before being inserted into the Zetasizer. Results were then compiled into a repeated measures design and analyzed in JMP.

Determining the Isoelectric Point of an Emulsion and Measuring Aggregate Reactivity

The titrant used to find the point of zero zeta potential was prepared by adding 1.5 g of aggregate fines passing the #200 sieve to 20 ml of water in a scintillation valve. Following this, 0.1 g of sodium hexametaphosphate was added to the fines to allow for even dispersion and to prevent settlement. Two suspensions were created, one containing limestone fines and the other containing bentonite, a highly reactive clay. The emulsion used for this part of the study was a nonmodified emulsion with an emulsifier dosage of 1.5% emulsifier by weight and a pH of 1.5.

The emulsion samples for titration were prepared similarly to those used for measuring zeta potential. The emulsion sample and titrant were placed in vials and attached to their respective tubing on the MPT-2 titrator, and the SOP for running the titration was initialized. The SOP involved titrating the emulsion with the solutions of limestone and bentonite fines and monitoring the change in zeta potential.

The pH at which the zeta potential first became negative (i.e., irreversible emulsion destabilization) was noted by the machine, along with the corresponding zeta potential. (The slope of the line connecting the two points, one before and one after the isoelectric point, gives insight into the reactivity of the material.)

Cohesion Testing

The cohesion test was performed using two ISSA standards, ISSA TB-113 (ISSA 2017b), which contains specifications for the preparation of slurry seal mixes, and ISSA TB-139 (ISSA 2017a), which contains directions on running the cohesion test. The cohesion tester is shown in Figure 6.

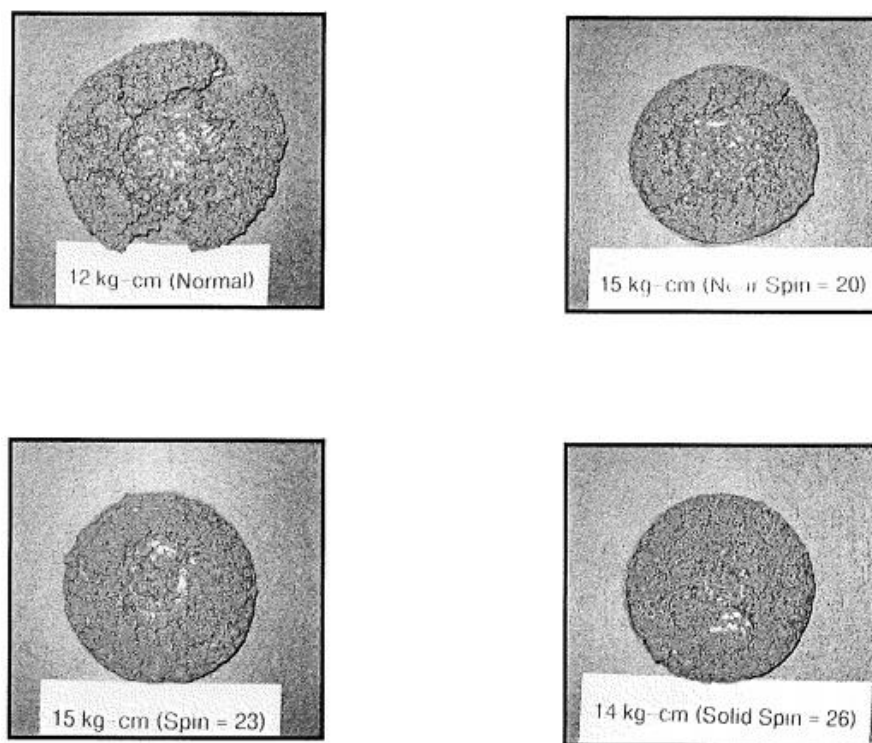


Figure 6. Cohesion Tester at Iowa State University

The procedure for cohesion testing is summarized as follows:

1. A known weight of oven-dried aggregate was chosen for the mix designs. This weight formed the basis of all calculations for water content, mineral filler, and emulsion content. The amount of aggregate chosen for all mix designs was 200 g.
2. Based on the weight of dried aggregate, mineral filler was added to the aggregate and was mixed thoroughly. ISSA TB-113 recommends 1–3% of mineral filler. The amount of mineral filler to be added to all mix designs was chosen to be 1.5%.
3. Water was then added to the aggregate-mineral mixture and was mixed together for 30 seconds. Three water content levels of 4%, 6%, and 8% had been chosen for testing based on the typical water content range for slurry seals.
4. The emulsion content was then added to the mix based on the weight of the dry aggregate, and the mix was stirred for 60 seconds before casting into ring-shaped molds.
5. The samples were trimmed using a straightedge and the molds were removed when the mix appeared visibly stable enough. The samples were then allowed to cure at room temperature in the laboratory.

6. Before the samples were tested, the cohesion tester was brought up to the desired pressure of 200 kPa and the neoprene rubber foot was cleaned.
7. The samples were placed one at a time under the rubber foot and the piston was allowed to drop on the sample. The piston was then twisted to an angle of 90° – 120° after six seconds of contact with the sample surface, and the reading on the torque wrench was noted.
8. Occasionally, the samples did not fail due to insufficient friction on the surface and the values of maximum torque not exceeding 20 Kg/cm, in which case predetermined values of cohesion according to the nature of the sample were used to determine the cohesive force (Figure 7 and Figure 8).



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Figure 7. Modes of rupture that determine cohesion if maximum values do not exceed 20Kg/cm



Figure 8. Modes of emulsified asphalt rupture: “solid spin” (left) and “normal” (right)

RESULTS AND DISCUSSION

Understanding the Rheological Properties of the Emulsions and Their Residues

Results of Tests Performed on the Emulsions

Particle Size Analysis

Particle size analysis was performed on latex-modified emulsions and a nonmodified emulsion. The latex was added at 3.5% by weight of total emulsion based on manufacturer recommendations. The results showed that the emulsions had a size distribution between 1–10 microns and particle sizes in the range of 2.8–3.14 microns (Figure 9).

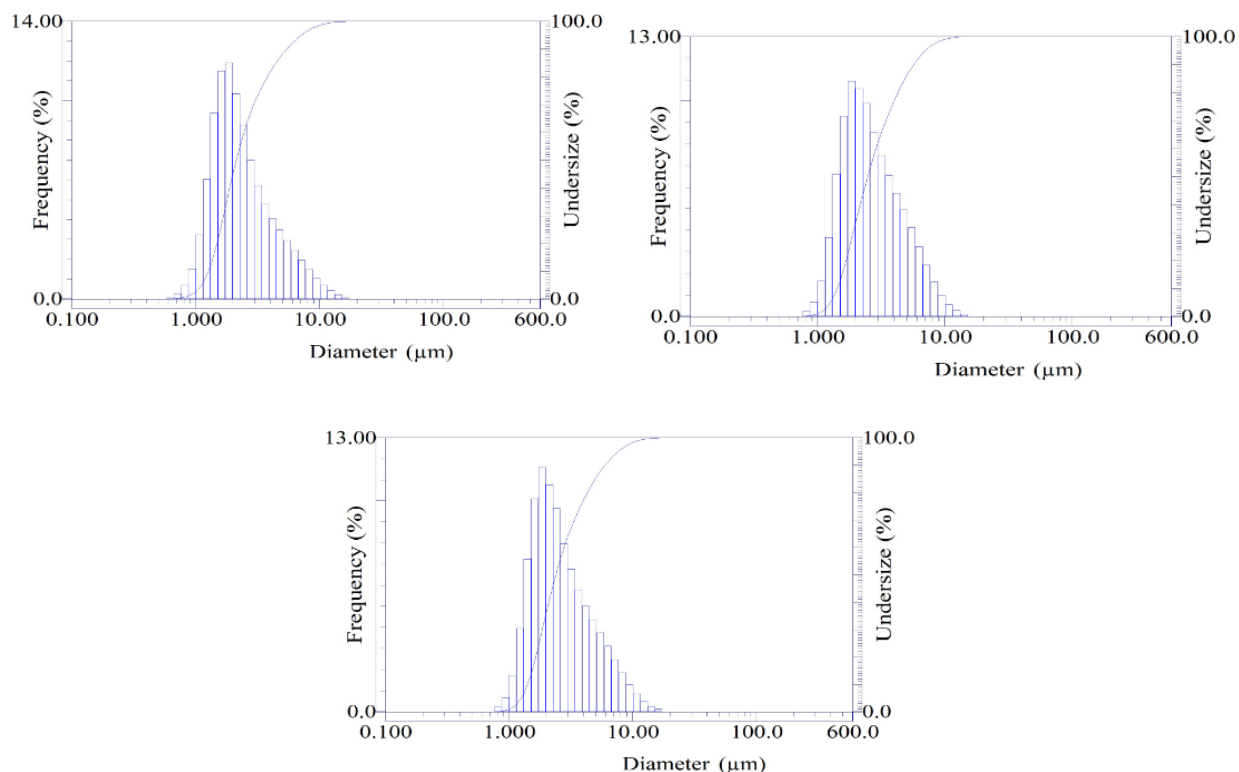


Figure 9. Particle size distributions of a latex-modified emulsion with latex added *after* emulsification (top left), a latex-modified emulsion with latex added to soap solution *before* emulsification (top right), and a nonmodified emulsion (bottom)

The largest particles were observed for the nonmodified emulsion, while the smallest particle sizes were seen in the emulsion with the latex added postemulsification.

Table 3 illustrates the particle size analysis according to the type of the emulsion and its mean particle size.

Table 3. Summary of emulsion particle size analysis

Emulsion Type	Mean Size	SD	Variance
Nonmodified	3.145 μm	2.145 μm	4.60 μm^2
Latex-modified (postemulsification)	2.840 μm	2.051 μm	4.21 μm^2
Latex-modified (latex added to soap solution)	3.014 μm	1.909 μm	3.65 μm^2

Strain Sweeps to Determine Linear Viscoelastic Limits of the Emulsions

The linear viscoelastic range is defined as the range where strain values deviate no more than 10% from the original strain. As seen in Figure 10, strain sweeps to determine the emulsions'

linear viscoelastic limits show that their linear viscoelastic range was small (i.e., 0.05% strain), undoubtedly due to the low viscosity of the emulsions.

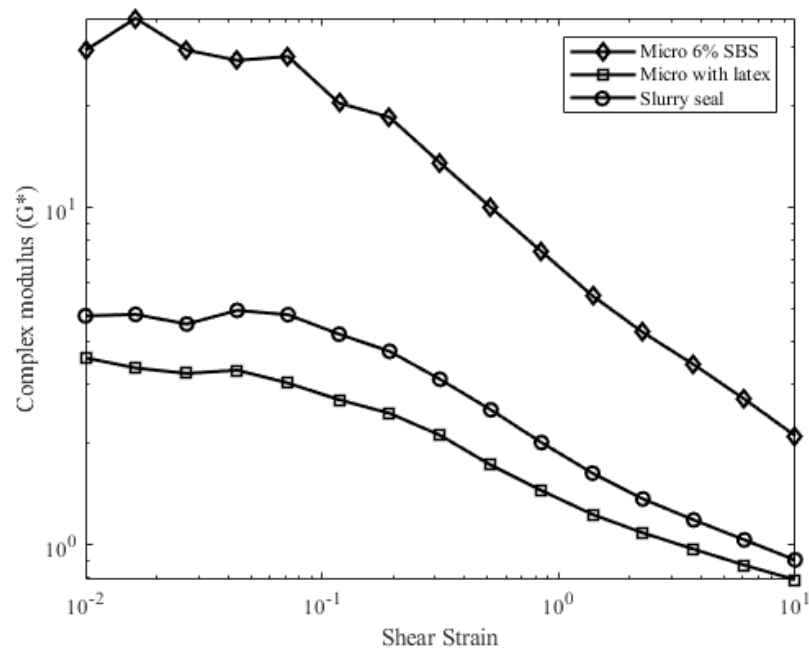


Figure 10. Complex modulus vs. shear strain

Temperature Sweeps

Temperature sweeps were carried out from 30°C to 70°C and the changes in storage, loss, and complex modulus were observed (Figure 10). Crossover points between loss and storage moduli mark a change of nature from viscous to elastic. A more stable G^* value also indicates better stability.

Figure 11 shows the two microsurfacing emulsions tested: one containing 6% SBS by weight of asphalt binder and one containing 3.5% latex by weight of emulsion.

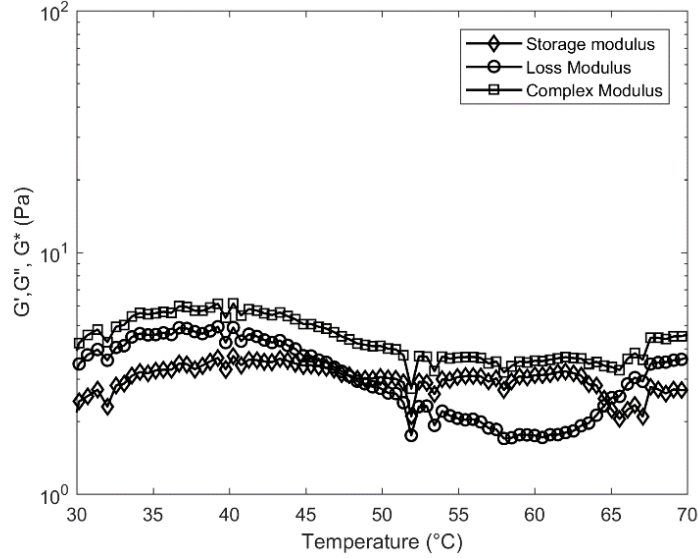


Figure 11. Slurry seal emulsion temperature sweeps

As seen in Figure 12, the microsurfacing emulsion containing the SBS mixed with the binder shows two crossover points between G' and G'' , indicating that the emulsion's behavior goes from viscous to more elastic and then back to viscous.

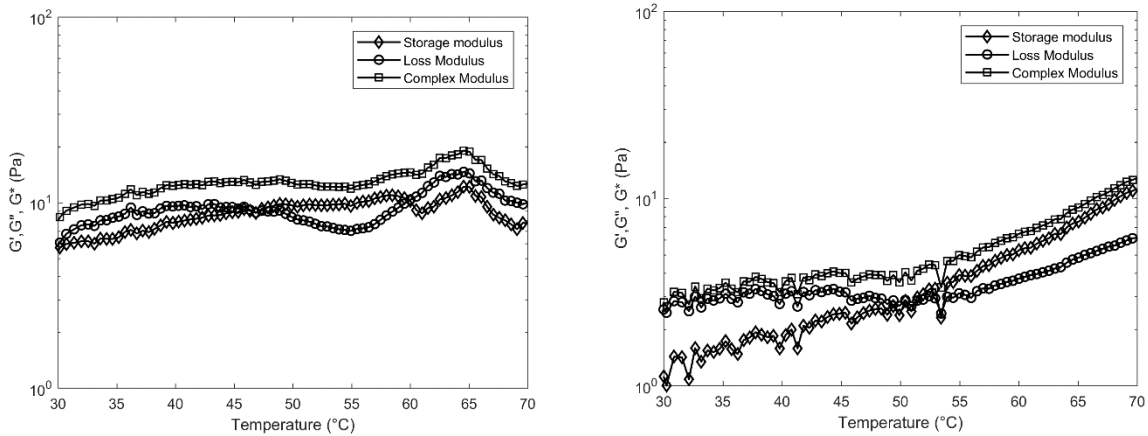


Figure 12. Microsurfacing emulsion temperature sweeps: Microsurfacing emulsion with 6% SBS microsurfacing emulsion (left) and microsurfacing emulsion with latex (right)

For the microsurfacing emulsion with SBS, the crossover point from viscous to elastic behavior is just under 50°C. The microsurfacing emulsion with latex has one crossover point, which occurs around 53°C. The transition from a viscous to elastic nature is more apparent in the emulsion containing latex, as both G' and G'' converge and diverge before and after the crossover point, respectively. This can be explained on the basis of free latex particles that are present in the continuous phase of the emulsion.

Effect of Varying Shear Strain on Emulsion Viscosity

The effect of varying shear strain on viscosity was also observed with the emulsion samples exposed to changing shear strains and the resulting percent change in viscosity plotted. The latex-modified emulsion tested for this part of the study was only the postmodified emulsion. The objective was not to make direct comparisons between the binders but to lay the groundwork for future studies.

Figure 13 summarizes the effect of varying shear on emulsions, which is important when considering the changes in shear that emulsions undergo when being pumped into trucks and sprayed onto pavements.

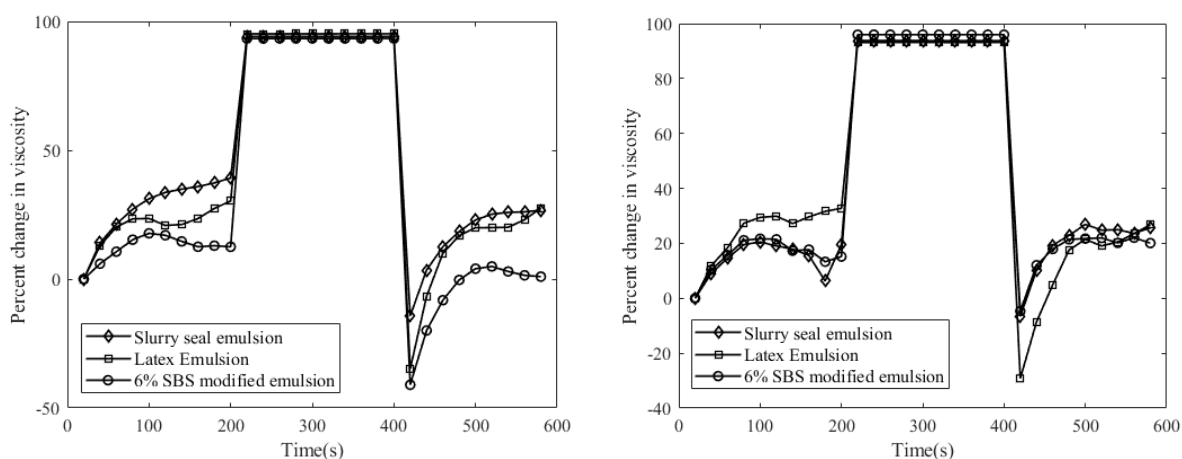


Figure 13. Change in viscosity over time for emulsions at 30°C (left) and 50°C (right)

Both the figures depict change in viscosity over time when the emulsions are subject to changing shears—from 0.1 s⁻¹ for 20 seconds, then a ramp up to 100 s⁻¹ for the next 20 seconds and finally dropping down to 0.1 s⁻¹ again for 20 seconds. At 30°C (Figure 13 left), a clear distinction can be made between modified and nonmodified emulsions, with the modified emulsions showing a greater change in viscosity with constant shear due to the presence of polymer/latex in their microstructure. This distinction is less obvious at 50°C (Figure 13 right). All the emulsions underwent the same percent change in viscosity when the shear rate was ramped up and the differences between emulsions were indistinguishable, which means that a nonmodified emulsion will show the same change in viscosity as a modified emulsion. When the shear rate was ramped down, all emulsions gradually regained their viscosities to a certain degree.

Rheological Properties of Emulsion Residue and Base Binder

One of the tests used to characterize the rheological properties of the emulsion residue and base binder was the multiple stress creep recovery (MSCR) test. This test plots stress recovery vs. nonrecoverable creep compliance (J_{nr}), with a minimum standard criterion required for binders and residue to be deemed sufficiently modified and pass the test. The minimum criteria is

depicted as a line in Figure 14, by which it can be seen that the level of polymer modification was insufficient due to a lack of elastic response from the binder.

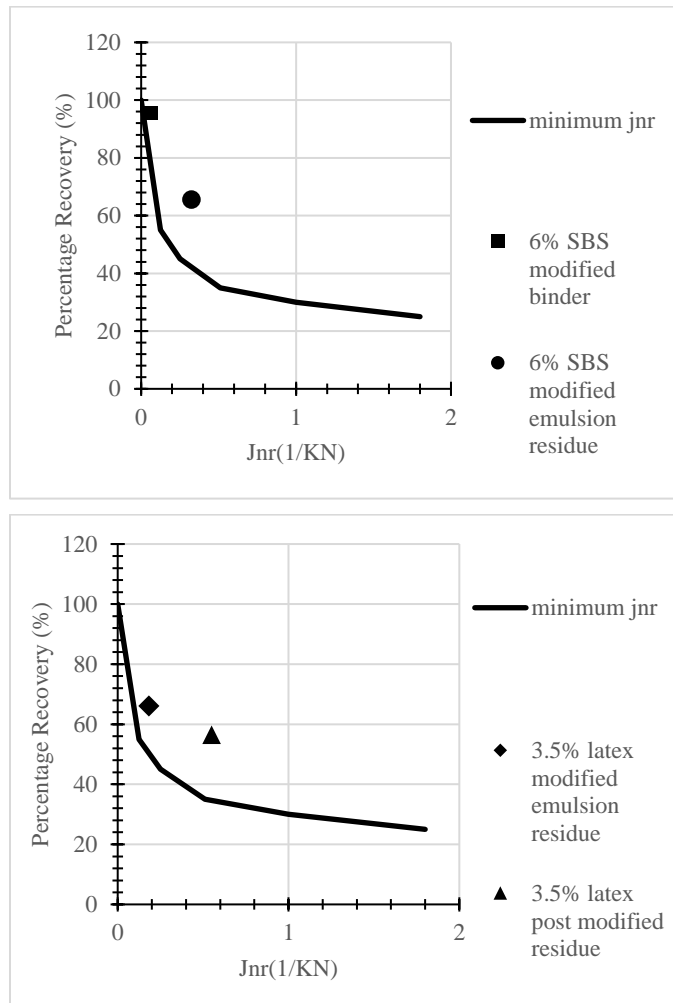


Figure 14. MSCR results: Percent recovery and J_{nr} (nonrecoverable creep compliance) tested at 58°C for SBS 6% modified binder and emulsion residue (top) and 3.5% latex-modified emulsion residue and 3.5% postmodified residue (bottom)

The 6% SBS was designed to have a very high elastic recovery at almost 98% and the process of emulsion manufacturing (for this emulsion) reduced the percent recovery as seen in the SBS emulsion residue (Figure 14 top). The 3.5% latex added premilling had higher elastic recovery compared to the latex added postemulsification (Figure 14 bottom). The base asphalt was assumed to fail MSCR testing, so MSCR tests on the nonmodified base asphalt were not performed.

Master curves, Figure 15, were performed at 58°C to observe the base asphalt and modified emulsion residue properties over a wide range of frequencies.

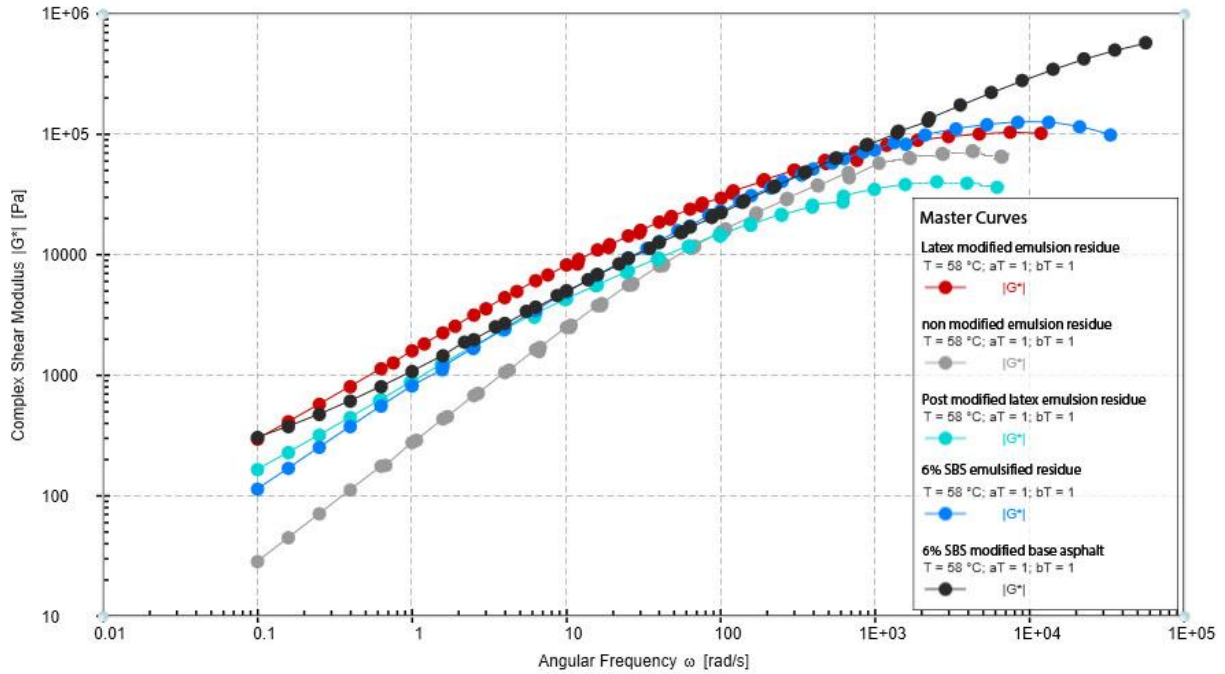


Figure 15. Complex shear modulus vs. angular frequency (master curve) of binders and base residue at 58°C

Phase 1: Effect of Emulsion Formulation Parameters on Zeta Potential

Model Summary and Significant Effects

The results from zeta potential measurements for the different emulsion formulations were statistically analyzed in JMP to determine influential factors and develop a model that best fits the experimental measurements. The significant model effects are shown in Table 4.

Table 4. Significant model effects

Source	Degrees of Freedom (DF)	Sum of Squares	F Ratio	p-Value
Emulsifier Dosage	2	106.109	5.5091	0.0066
pH	2	12,349.436	641.1796	<.0001
Emulsifier Dosage×pH	4	367.357	9.5365	<.0001
Temperature	2	6,877.592	357.0828	<.0001
Emulsifier Dosage×Temperature	4	144.748	3.7576	0.0091
pH×Temperature	4	71.759	1.8628	0.1303
Emulsifier Dosage×pH×Temperature	8	389.526	5.056	0.0001

The level of significance for an effect, be it an independent variable or an interaction, can be gauged from the p -statistic. The threshold of statistical significance is often set at a confidence level of 95% (i.e., an α value of 0.05). Any p -statistic that falls below this level can have its

corresponding effect deemed significant. Thus, low p -values, like most of those in Table 4, indicate a high level of statistical significance.

Figure 16 shows the model fit for predicted zeta potential values with the measured values.

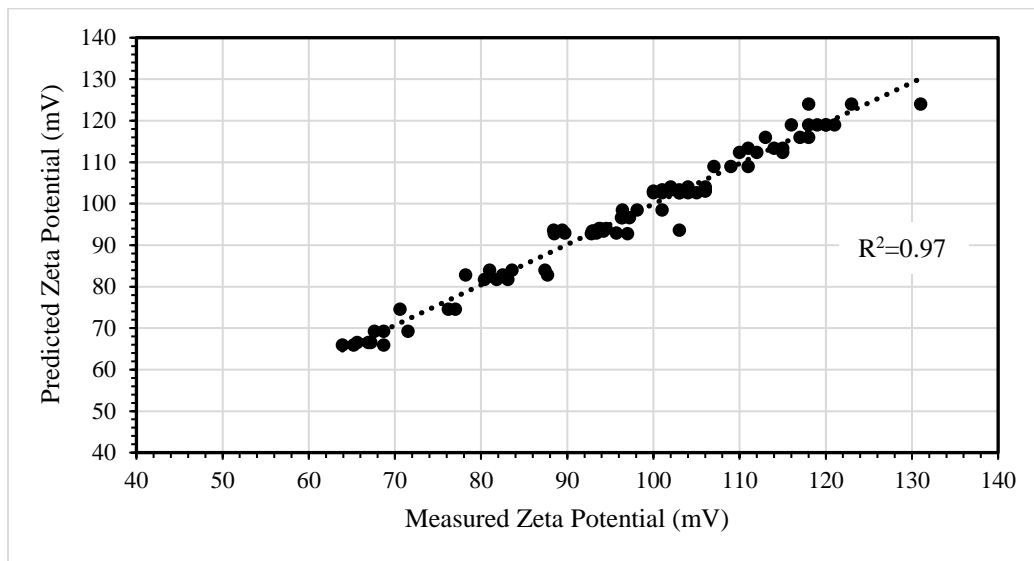


Figure 16. Measured vs. predicted zeta potential

The repeated measures surface model had an R^2 value of 0.97 and indicated that emulsion pH and temperature were the two significant independent variables, along with a significant interaction occurring between emulsifier dosage and the pH of the emulsifier solution used for emulsification. Emulsifier dosage also appears to have a significant effect on emulsion zeta potential; however, the emulsifier dosage's p -value is higher than that of the other independent variables. Figure 17 (left) illustrates how pH and temperature mask the influence of emulsifier dosage, and differences are not easily observed when comparing values for other variable permutations like temperature and pH. In contrast, trends for pH are observed in Figure 17 (right).

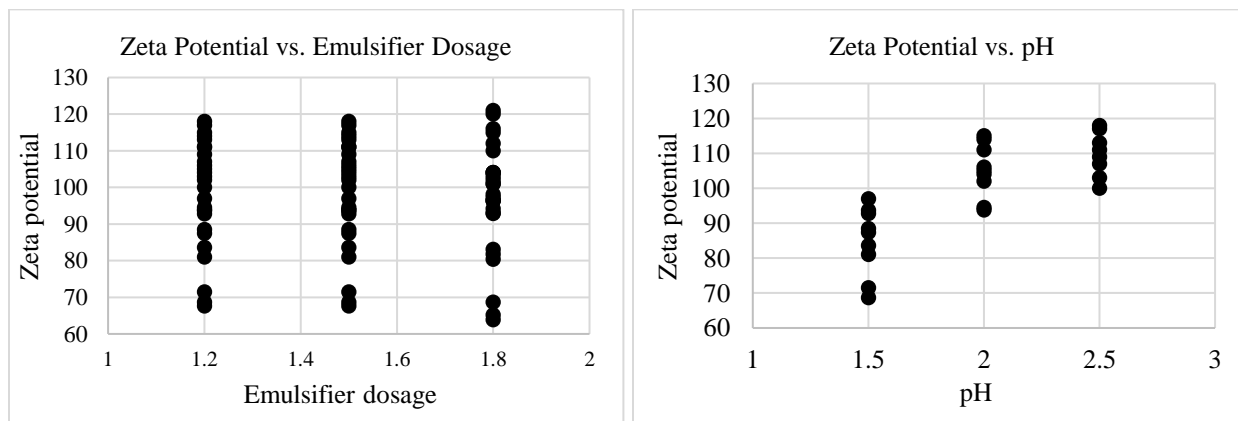


Figure 17. Zeta potential vs. emulsifier dosage (left) and pH (right)

Explanation of Significant Model Effects

Temperature had a significant effect on zeta potential, in that zeta potential decreased with increasing temperature, pointing to faster rates of reaction causing lower stability as the temperature rose. This helps explain why a contractor may need to decelerate set time for a micro/slurry seal mixture on a warm day.

Interestingly, zeta potential appeared to decrease with decreasing pH. Since the pH window studied was relatively narrow, the current trend could change at pH values that are higher; however, stability problems would likely result.

The decreasing zeta potential due to decreasing pH may be explained by understanding the process of droplet stabilization due to protonation. Protonation is defined as the chemical reaction by which H^+ ions present in a solution attach themselves to emulsifier molecules, creating a positively charged head group. When emulsifier molecules are first added to a solution, they do not bear a charge until they receive an H^+ ion, which becomes available upon the addition of an acid that decreases the pH solution.

This leads to the emulsifier head groups getting protonated, which gives them a positive charge. The positively charged head groups orient themselves away from the asphalt droplet surface, while their tail groups orient toward the asphalt. This leads to a positively charged droplet and a cationic emulsion.

Emulsifier head groups will continue to attach themselves to the asphalt droplet till its surface is completely covered with emulsifier molecules, which causes any excess emulsifier molecules to go into the solution and form micelles. The concentration of emulsifier at which emulsion droplets are fully covered, eventually leading to charged micelles being formed in the continuous phase, is called the critical micelle concentration. The pH of the emulsion controls how many emulsifier molecules are protonated, while the emulsifier dosage controls the number of molecules available for protonation.

The observations in Figure 18, Figure 19, and Figure 20 are summarized in Table 5, which is a table of Tukey's Honest Significant Differences between the means for levels of pH and emulsifier dosage at different temperatures. All means not connected by the same letter are significantly different.

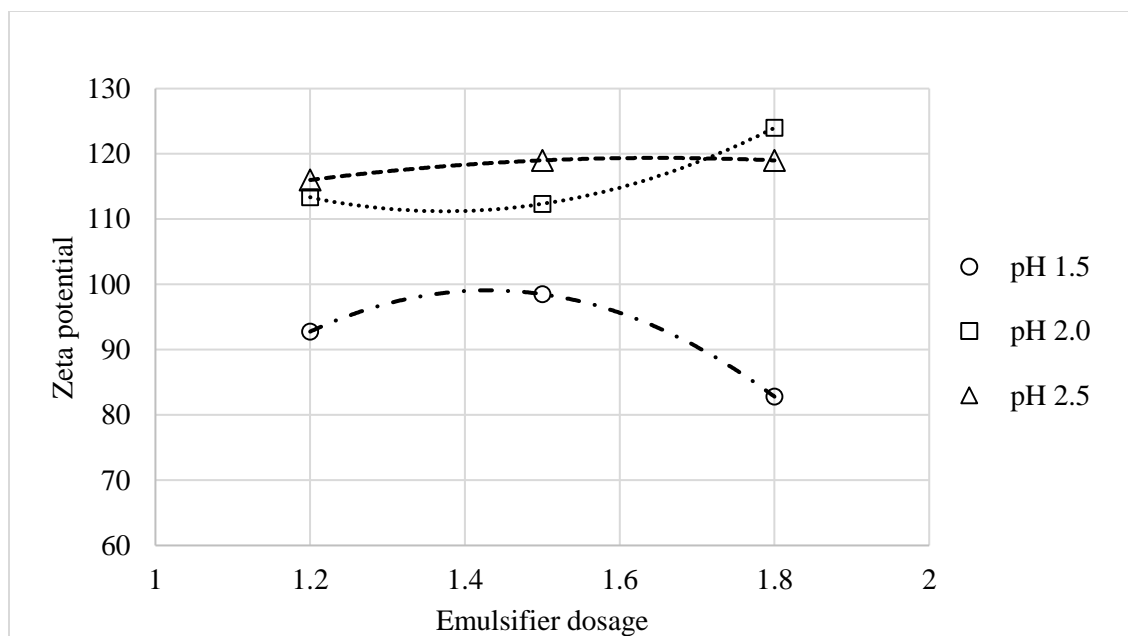


Figure 18. Zeta potential vs. emulsifier dosage at 25°C

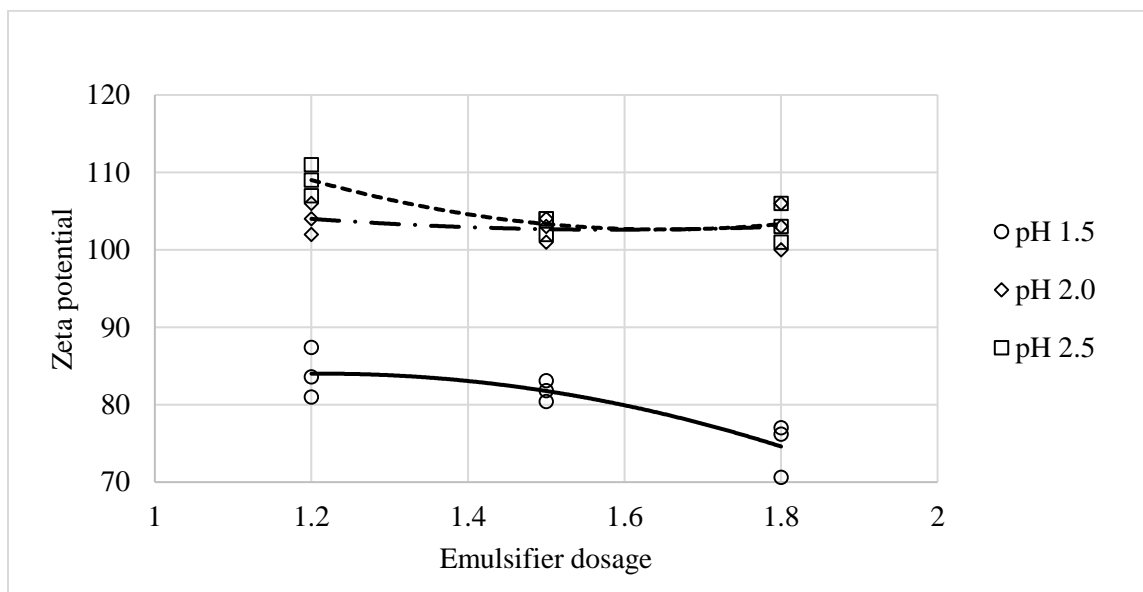


Figure 19. Zeta potential vs. emulsifier dosage at 37.5°C

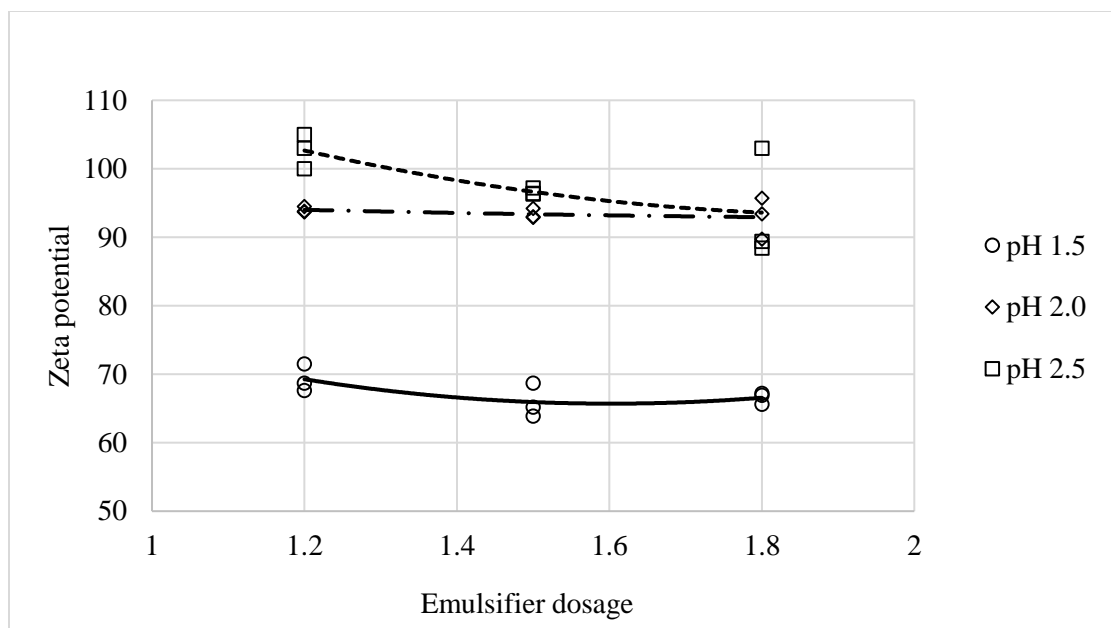


Figure 20. Zeta potential vs. emulsifier dosage at 50°C

Table 5. Tukey's HSD means with levels of significance

Temperature	Emulsifier dosage			pH		
	Level		Least Sq Mean	Level		Least Sq Mean
T=25°C	1.2	A	107.37	2.5	A	118.00
	1.5	A	109.94	2	A	116.56
	1.8	A	108.6	1.5	B	91.36
T=37.5°C	1.2	A	99.00	2.5	A	105.22
	1.5	B	95.92	2	A	103.22
	1.8	B	93.64	1.5	B	80.12
T=50°C	1.2	A	88.64	2.5	A	97.63
	1.5	AB	85.31	2	B	93.43
	1.8	B	84.37	1.5	C	67.26

When looking at how pH influences zeta potential values, Table 5 shows that emulsions formulated at pH 1.5 were significantly different from zeta potential values at other pH levels. A significant difference in zeta potential can also be seen for emulsifier dosages of 1.2% and 1.8% at temperatures of 37.5° and 50°C. These results point to a decrease in zeta potential at lower pH values for all temperatures tested. Decreasing pH led to more H⁺ ions being available to protonate excess emulsifier molecules, especially at higher dosages, and led to the critical micelle concentration being reached. The critical micelle concentration, as stated above, leads to charged micelles being formed in a solution, which causes a decrease in the stability of an emulsion (Jódar-Reyes et al. 2006). The authors hypothesize that the occurrence of this phenomenon caused the zeta potential to decrease for dosages of emulsifier above 1.5% and pH levels at 1.5.

Surface Response Plots

Based on the surface plots in Figure 21, it is clear that pH is an important formulation parameter.

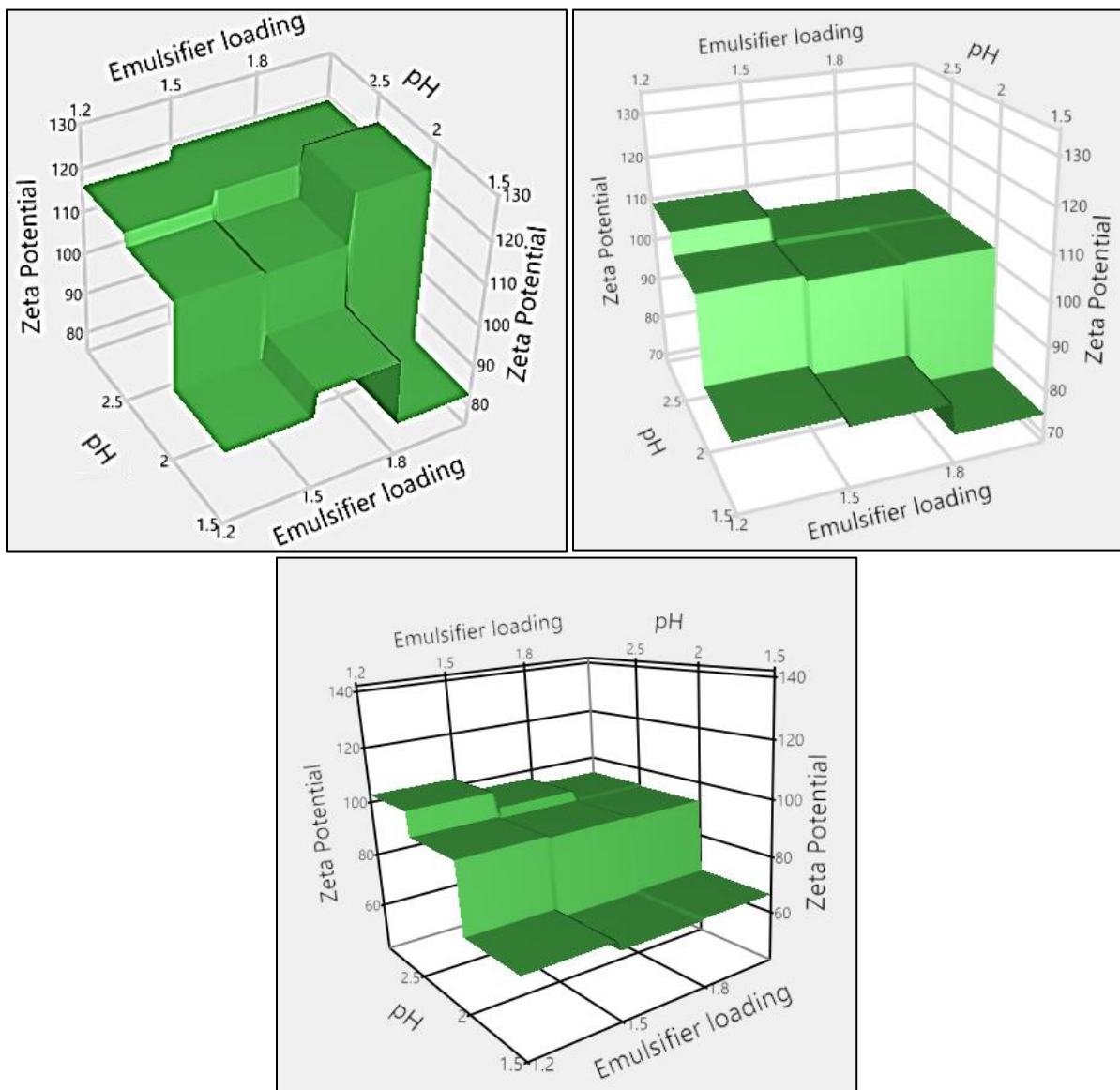


Figure 21. Surface plots of zeta potential vs. emulsifier dosage for 3 temperatures: 25°C (top left), 37.5°C (top right), and 50°C (bottom)

It must be noted though, that these results apply only to the emulsifier type used in this research, as the critical micelle concentration could vary, depending on the nature of the emulsifier. A limitation of this study is the difficulty of understanding the influence of the significant dilution of the emulsion needed in order to achieve stable zeta potential readings.

Determining the Isoelectric Point of an Emulsion with Two Types of Aggregate

In order to compare the effect of aggregates on the zeta potential of an emulsion, an emulsion with a known pH and emulsifier dosage was titrated with fines from limestone and bentonite. Figure 22 shows the result of this emulsion titration with these two types of fines.

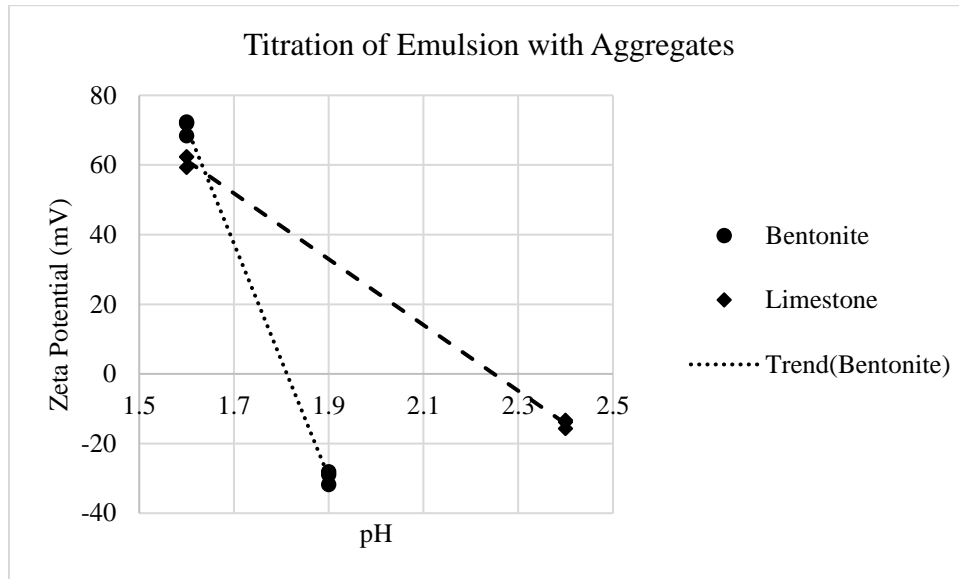


Figure 22. Isoelectric points for limestone and bentonite

Unlike the gradual change in zeta potential associated with varying the pH of different emulsions, the addition of aggregates led to a much more dramatic change in zeta potential. This points to a different mechanism of destabilization than simply changing the ionic strength of the emulsion solution, as was the case with the emulsions of different pH.

When aggregate particles are added to an emulsion, they do cause a change in the pH of the system. Being basic in nature, however, it is their surface charges that have more of an impact on flocculation. Fine aggregates have a large total surface area coated with charges corresponding to the aggregate's chemical nature.

Both limestone and bentonite have negatively charged surfaces, which in turn attract the positively charged head groups from the surfaces of asphalt particles. The charged head groups detach from the molecules, which makes them susceptible to flocculation, since they can no longer repel each other. Therefore, despite only slightly changing the pH, aggregate particles play a major role in emulsion destabilization.

The degree of reactivity for each of the aggregates can be determined from the slope of the plots determining the isoelectric point. The plot for bentonite is much steeper than for limestone, indicating that bentonite showed flocculation in the emulsion occurring much faster than did limestone and hence was more reactive. Bentonite has a much smaller mean particle size than limestone and thus more surface area. This results in bentonite having a larger negatively

charged surface available to remove the charged emulsifier molecules from the asphalt droplet surfaces when compared to limestone. Thus, bentonite exhibited greater reactivity based on changes in zeta potential when added to the emulsion.

Phase 2: Effect of Zeta Potential on Slurry Seal Performance

Summary of Model Developed

After establishing a relationship between zeta potential and the emulsion formulation parameters, the next phase of the study investigated the relationship between emulsion performance and slurry seal mix design. Also included in the experimental design as an independent variable was pH, which Phase 1 had demonstrated had a significant relationship with zeta potential.

The experimental plan for Phase 2 consisted of 15 samples with two replicates each, as determined by the Box-Behnken experimental design. Emulsion pH, emulsion content, and water content were the three independent variables. Two separate models were developed using the same Box-Behnken surface response experimental design for cohesion at 60 minutes and cohesion at 90 minutes.

The surface response model returned R^2 values of 0.79 for both the 60- and 90-minute cohesion models (Figure 23).

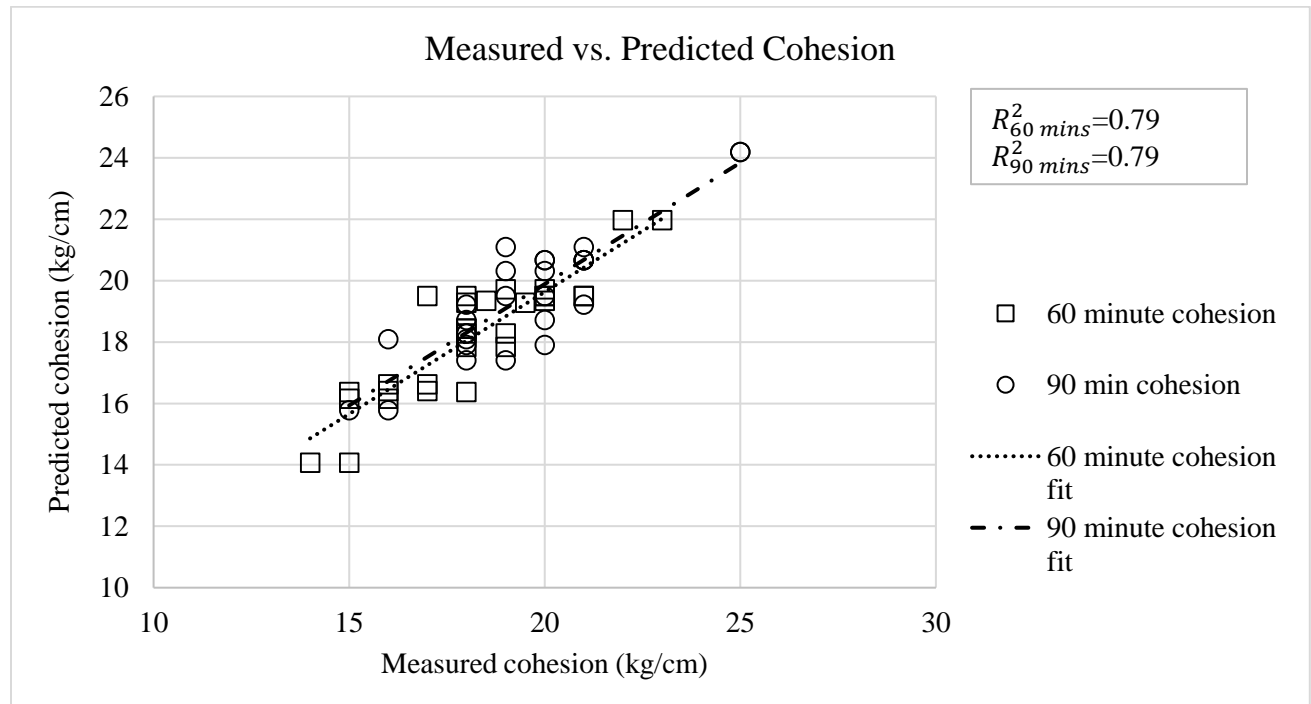


Figure 23. Predicted vs. measured cohesion

Summary of Significant Effects

The summary of the statistical significance of effects and interactions for the 60- and 90-minute cohesion models is given in Table 6.

Table 6. Summary of significant model terms for 60-minute and 90-minute cohesion models

Source	Model <i>P</i> -Value	
	60 min	90 min
pH×pH	0*	0.00004*
pH (1.5, 2.5)	0.00089*	0.84521
Emulsion Content (14, 18)	0.00238*	0.00045*
Emulsion Content×Water Content	0.06702	0.29037
Water Content×Water Content	0.13104	0.61943
Water Content (4, 8)	0.30467	0.47613
pH×Water Content	0.30943	0.41175
Emulsion Content×Emulsion Content	0.40059	0.2334
pH×Emulsion Content	0.76879	0.03788*

**P*-values less than 0.05 shown in red to represent statistical significance at $\alpha=0.05$

The summary of significant effects with both the 60- and 90-minute models shows that emulsion content in the mixture played an important role in cohesive strength formation. This can be seen to have had more of an effect after 90 minutes from the lower *p*-value for the 90-minute model.

The pH can be seen to have had a significant effect on cohesion development initially during curing at 60 minutes but to have had less of an effect at 90 minutes. The water content of the mixture for the percentages included in the study did not have a significant effect on cohesion.

There was a significant interaction between pH and emulsion content after 90 minutes of curing. It will also be noted that the Box-Behnken model includes terms of the form pH*pH and emulsifier content*emulsifier content, which signify the effect of the independent variable across all other independent variables in the model. This ensures that the variable significance across the range of the other independent variables is not ignored.

Effect of pH on Cohesive Strength

Figure 24 and Figure 25 show the effect of pH on the cohesive strength of the slurry seal mix.

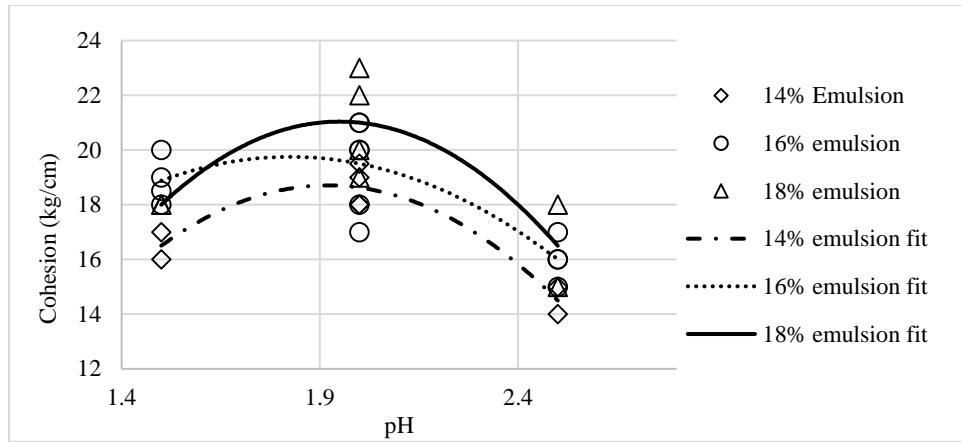


Figure 24. Cohesion vs. pH at 60 minutes

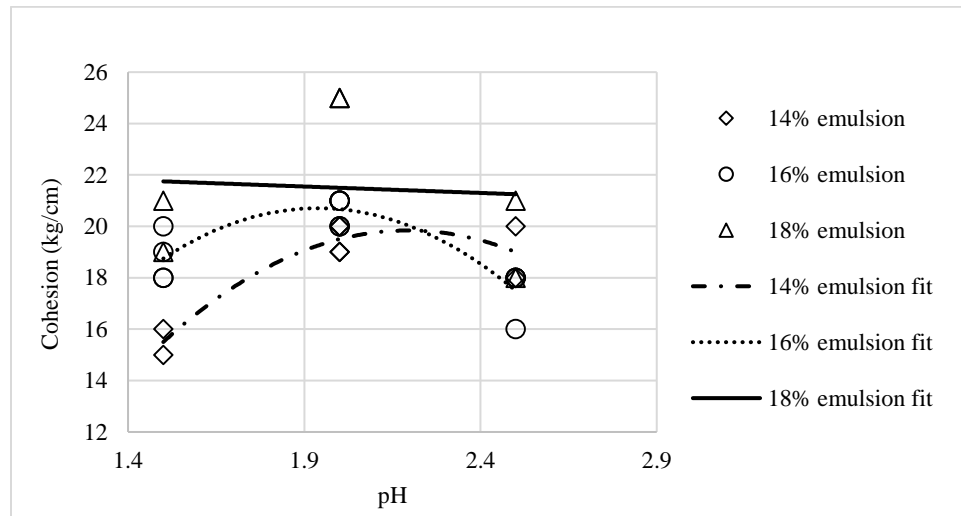


Figure 25. Cohesion vs. pH at 90 minutes

While pH played a significant role in strength formation for the first 60 minutes, cohesive strength at 90 minutes was statistically similar for all pH levels. Hence, the stability and zeta potential of the emulsion apparently affect cohesive strength during initial curing but may become less significant as time passes.

Specifically, the cohesive strength of emulsions with a pH of 1.5 and 2.0 had mostly developed their maximum strength by 60 minutes, while mixes with emulsions having a pH of 2.5 were significantly different at 60 and 90 minutes (Figure 26).

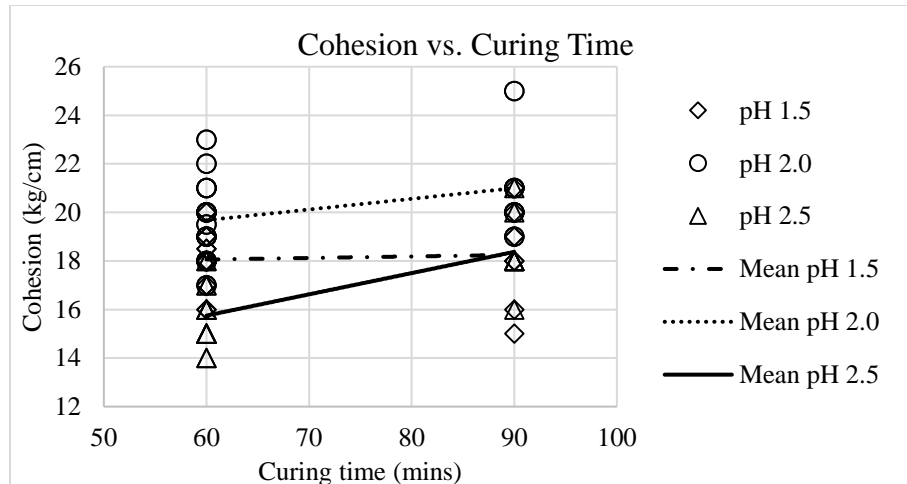


Figure 26. Cohesion vs. curing time for different pH levels

In other words, emulsions with a pH of 2.5 tended to gain strength more slowly than emulsions with a pH of 1.5. This finding interestingly parallels the zeta potential measurements where 2.5 was the most stable emulsion and had higher zeta potential measurements, whereas a pH of 1.5 was less stable and had lower zeta potential values.

Effect of Emulsion Content and Water Content on Cohesive Strength

Figure 27 shows the relationship between cohesive strength and emulsion content, the other significant factor in the performance of slurry seals.

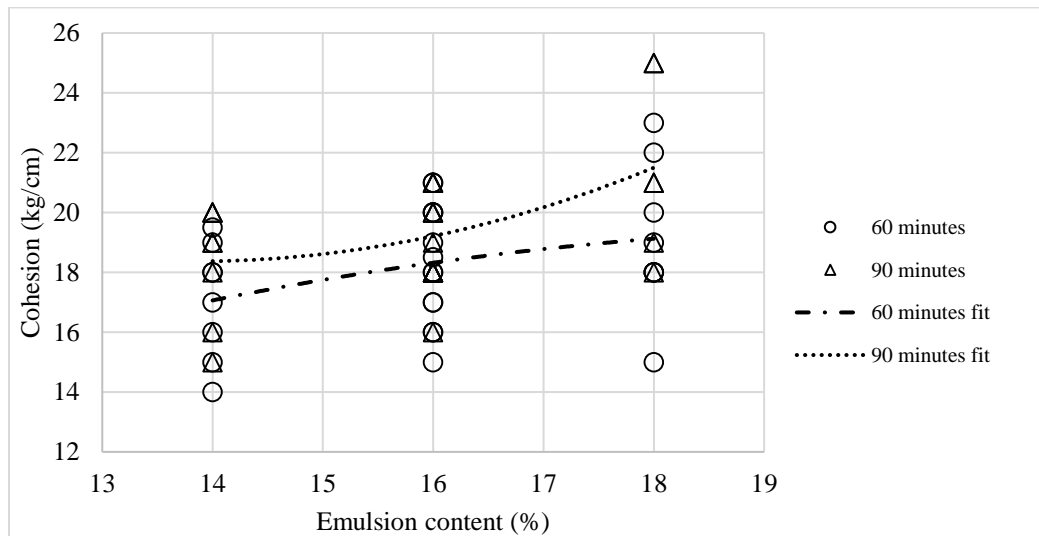


Figure 27. Cohesion vs. emulsion content

Cohesion increased for the increasing emulsion content in this study and higher cohesion values were observed at 90 minutes, showing that the mix continued to gain strength. A higher emulsion

content meant more asphalt residue was available to bond together the aggregates; however, the addition of more emulsion also meant more surfactant relative to the amount of aggregate in the system and this may have changed setting characteristics.

The cohesion values in Figure 28 compare mixtures with varied water content.

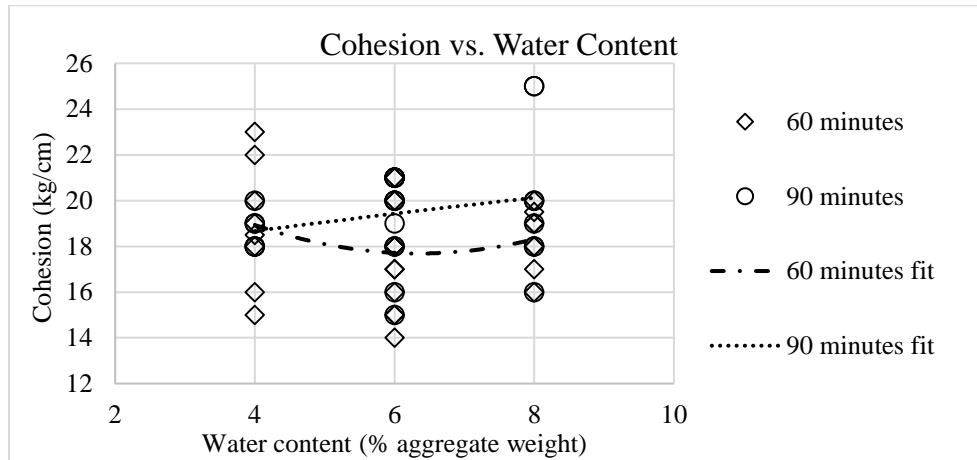
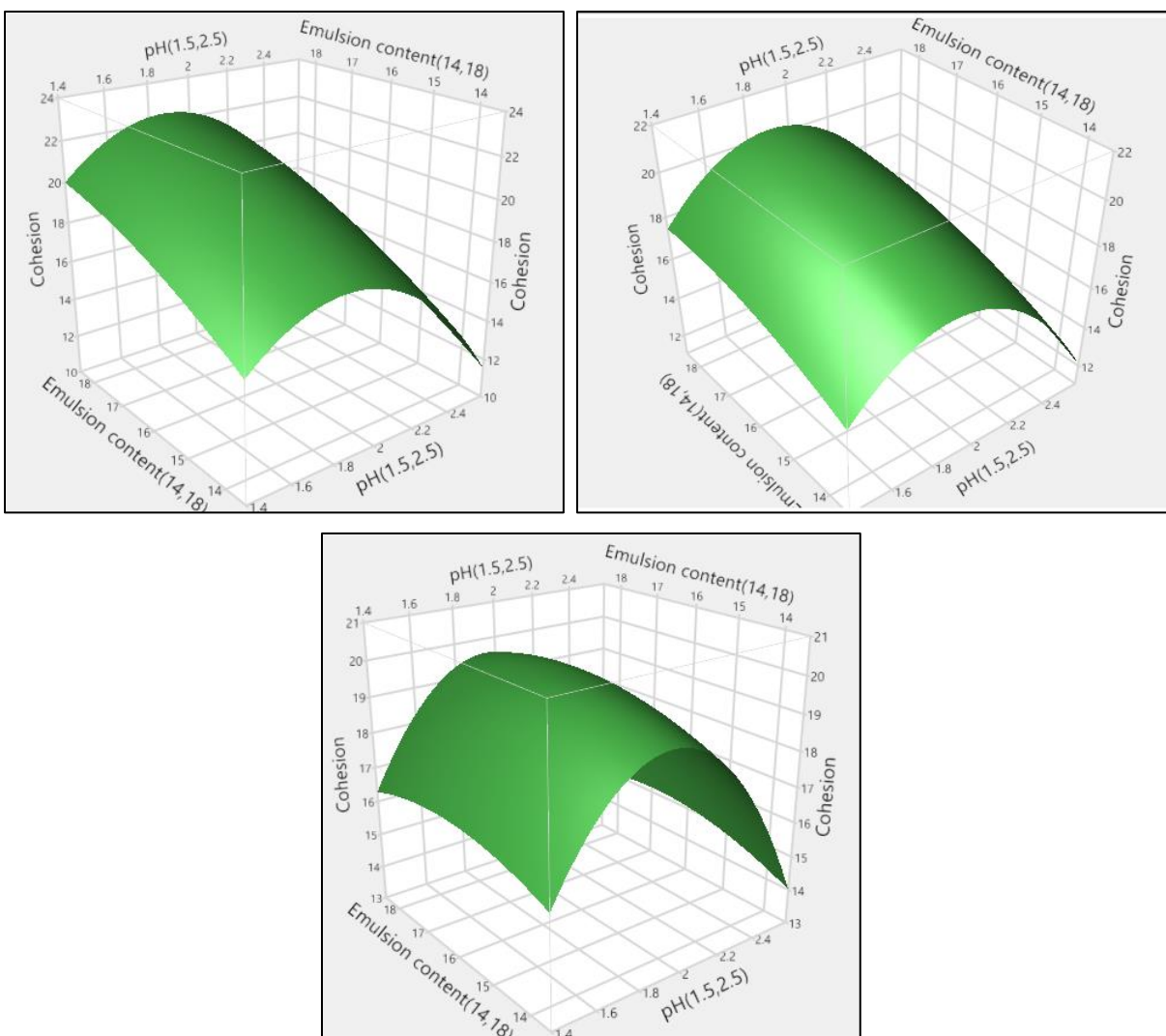


Figure 28. Cohesion vs. water content

The water did not play a significant role in observed cohesion development. The addition of water can therefore apparently aid in adjusting consistency, workability, and mixing time of slurry seal mixtures.

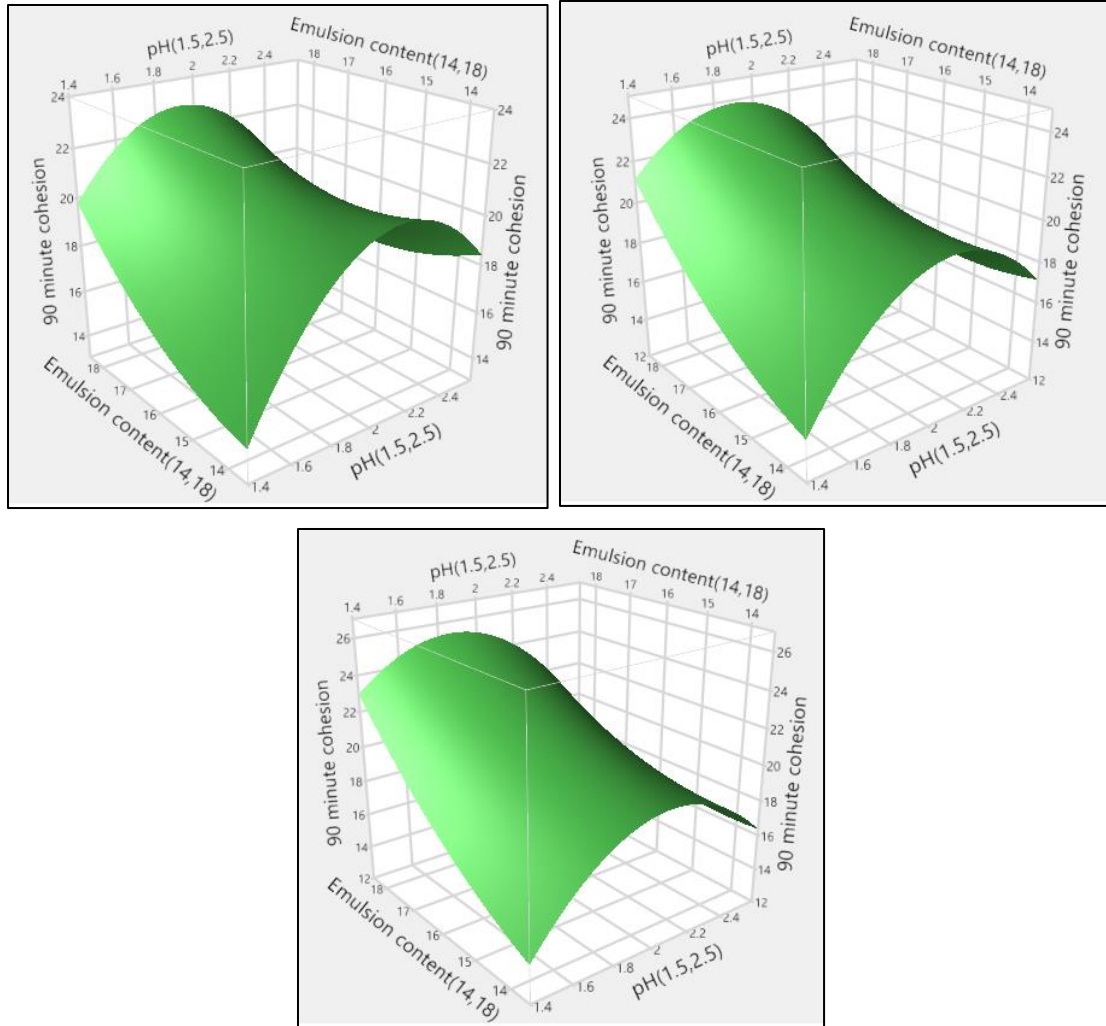
Surface Response Plots for 60- and 90-Minute Cohesion Times

The surface plots of cohesion in relation to pH and emulsion content are shown at 60 minutes in Figure 29 and at 90 minutes in Figure 30 for three percentages of water content. These surface plots provide a better understanding of how cohesion values may change for different pH values and emulsion content.



Values in parentheses along the X- and Y-axes represent the independent variable ranges of the experiment

Figure 29. Surface response plots for cohesion development at 60 minutes at 4% water content (top left), 6% water content (top right) and 8% water content (bottom)



Values in parentheses along the X- and Y-axes represent the independent variable ranges of the experiment

Figure 30. Surface response plots for cohesion development at 90 minutes at 4% water content (top left), 6% water content (top right) and 8% water content (bottom)

Zeta Potential as an Independent Variable

The ultimate goal of this research was to determine if the zeta potential of an emulsion can be used as a predictor for its cohesive performance in the field. Since pH was the common significant effect in both the zeta potential as well as the cohesion predictive models, it was decided to rerun the cohesion Box-Behnken model using zeta potential as an independent variable instead of pH for both the 60- and 90-minute cohesion times. The outcome of this statistical analysis is shown in Table 7.

Table 7. Summary of model effects with zeta potential as an independent variable

Source	Model <i>P</i> -Values	
	60 min	90 min
Zeta Potential×Zeta Potential	<0.00001*	0.00012*
Zeta Potential	<0.00001*	0.05145
Emulsion Content (14, 18)	0.00267*	0.00092*
Emulsion Content×Water Content	0.07017	0.25267
Water Content×Water Content	0.13557	0.71022
Water Content (4, 8)	0.30551	0.41639
Emulsion Content×Emulsion Content	0.4063	0.30087
Zeta Potential×Water Content	0.49158	0.66805
Zeta Potential×Emulsion Content	0.68582	0.09087

**P*-values less than 0.05 shown in red to represent statistical significance at $\alpha=0.05$

The outcome of the statistical analysis in Table 7 shows that using zeta potential as an independent variable had a significant effect on the 60-minute cohesion model and almost shows significance for the 90-minute cohesion model. In addition, the interaction term zeta potential*zeta potential is significant, which indicates that there are certain combinations of independent variables for which the zeta potential statistically influenced the cohesion value.

Figure 31 shows a fitted model of both the 60- and 90-minute cohesions using zeta potential as an independent variable, with R^2 values of 0.79 and 0.77 for the 60-minute and 90-minute models respectively.

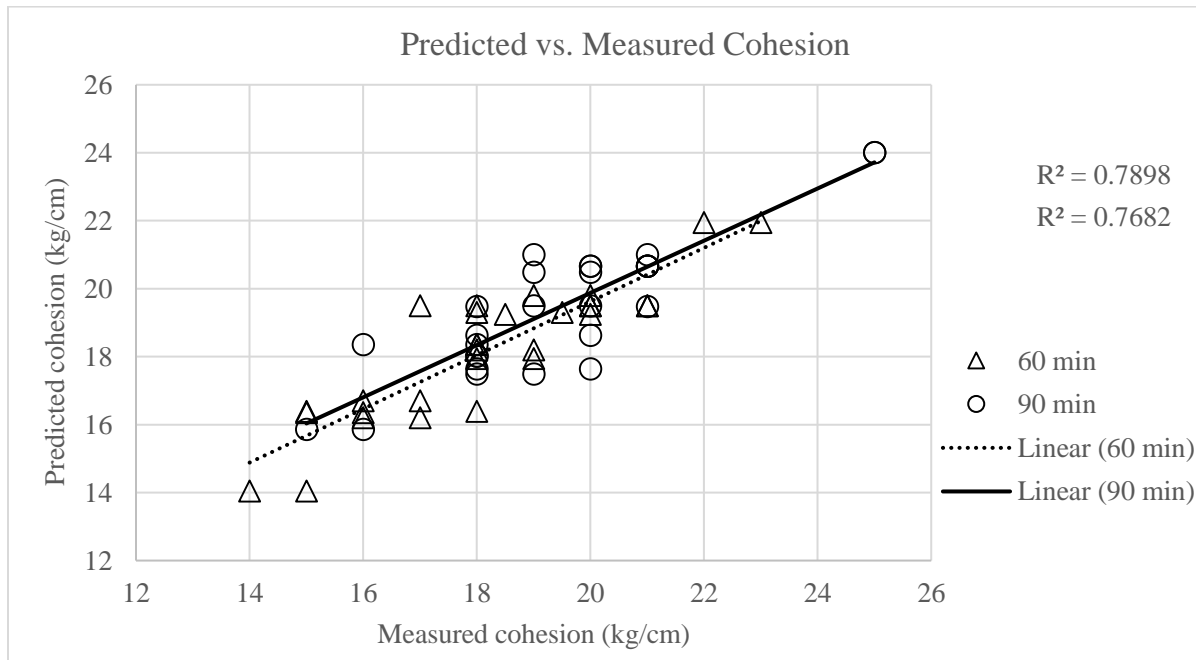


Figure 31. Predicted vs. measured cohesion with zeta potential as an independent variable

Plotting the zeta potential values against cohesion at 60 and 90 minutes shows that emulsions with high zeta potential values may develop cohesion more slowly due to their stability, while low zeta potential emulsions have slightly lower cohesion values than those with intermediate zeta potential (Figure 32). This could be due to insufficient time for the emulsion to cure.

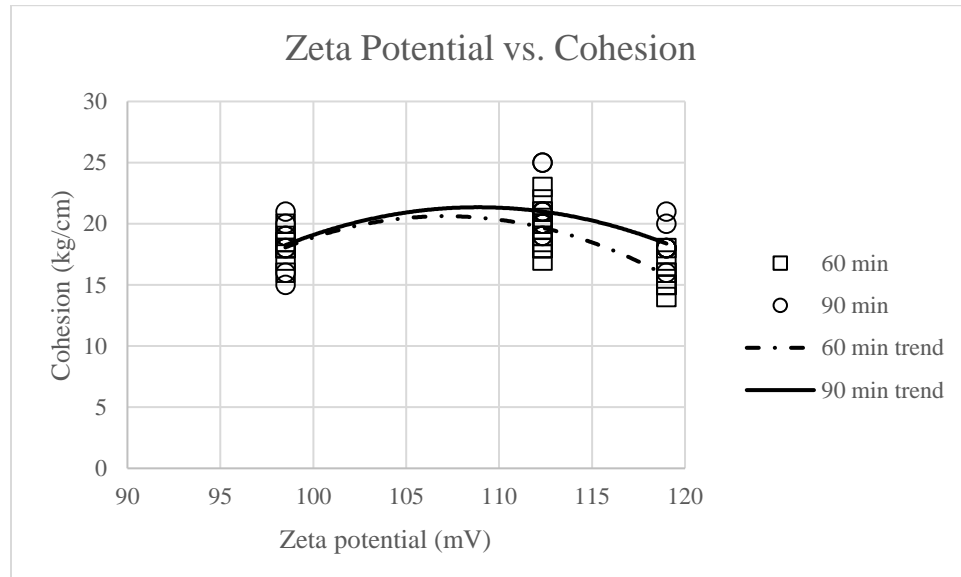


Figure 32. Zeta potential vs. cohesion for 60-minute and 90-minute cohesion times

These trends can be better seen via the surface plots in Figure 33 and Figure 34.

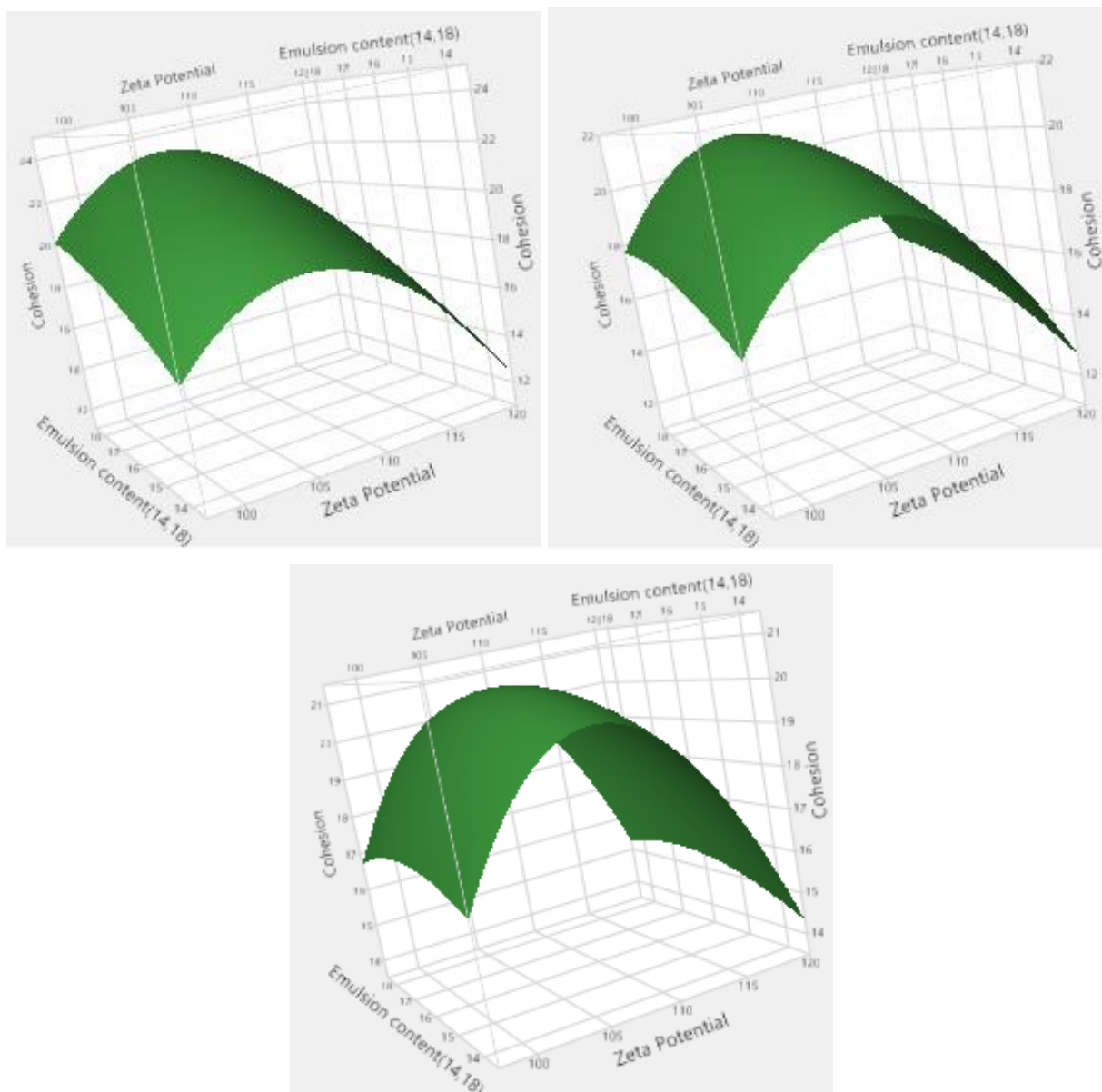


Figure 33. Surface plots for zeta potential and emulsion content vs. cohesion at 60 minutes for water content: 4% (top left), 6% (top right), and 8% (bottom)

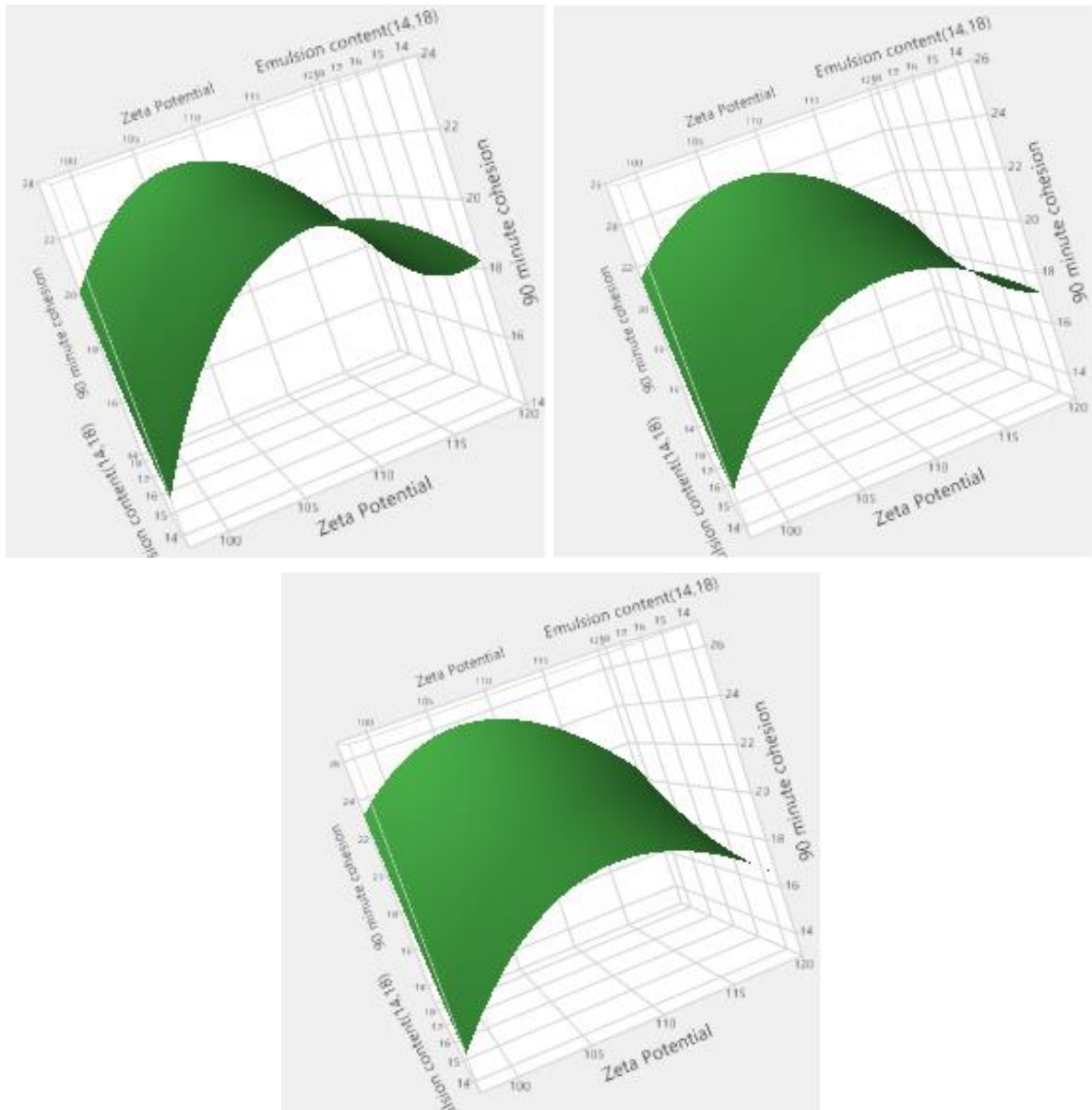


Figure 34. Surface plots for zeta potential and emulsion content vs. cohesion at 90 minutes for water content: 4% (top left), 6% (top right), and 8% (bottom)

CONCLUSIONS AND FUTURE WORK

Concluding Remarks

Microsurfacing and slurry seal treatments are increasingly being used for extending the life of pavements with mild-to-moderate cracking and minor rutting as well as to improve surface friction. Implemented successfully, they can be a cost-effective treatment for increasing pavement life; however, the complexity of the emulsion materials used can be daunting for civil engineering practitioners who are not familiar with pavement preservation applications that use asphalt emulsion materials.

Quick-setting emulsions are sensitive to the nature of aggregates as well as environmental factors and, as seen in this study, formulation can affect zeta potential. The study results presented in Table 8 indicate that zeta potential may play a role in better understanding the setting characteristics of slurry seal mixtures, provide an understanding of emulsion-fine aggregate interactions, and may help mixture designers better fine-tune emulsion formulations.

Table 8. Summary of results and observations for important study factors

Experimental Variable	Zeta Potential	Cohesion
pH	Emulsion formulations with a pH of 1.5 showed significantly lower zeta potential values than those with a pH of 2.0 and 2.5	pH had more of an effect at 60 minutes than 90 minutes
Temperature	<ul style="list-style-type: none">• Lower zeta potential was observed at higher temperatures, indicating faster setting• As temperature increased, fewer differences in zeta potential appeared relative to other variables	(Cohesion testing used an unvaried ambient laboratory temperature of 23°C)
Emulsifier dosage	<ul style="list-style-type: none">• Significant differences in zeta potential were observed for 1.2% and 1.8% emulsifier dosage at 37.5°C and 50°C• A potential interaction was identified between low pH and increased emulsifier dosage	(Emulsifier dosage during cohesion testing was held constant based on zeta potential findings)
Emulsion content	—	Cohesion increased with emulsion content

This study investigating the effect of emulsion formulation parameters on the stability and performance of slurry seal mixtures indicates that the pH of an emulsion is an important factor in its stability. Results show that pH governs the protonation of emulsifier molecules, and a sufficiently low pH can lead to the formation of free micelles in emulsion solutions, which are counterproductive to emulsion stability.

In order to determine if zeta potential—and, consequently, emulsion stability—have a role to play in emulsion performance, cohesion tests were run in this study on mix designs using emulsions of different pH, emulsion content, and water content. Study results indicate that the pH of an emulsion significantly affects cohesive strength for the first hour of curing; however, for all mixes with the same emulsion and water content at the percentages used in this study, samples cured for a longer period of time ultimately gained the same strength irrespective of emulsion pH. This may indicate that more stable emulsions gain strength more slowly than less stable emulsions.

This study's focus in Phase 1 on emulsion pH provided means of relating performance in terms of cohesion strength gain to zeta potential in Phase 2. However, it must be kept in mind that these results have been demonstrated to hold true only for the narrow window of pH and emulsifier dosage actually examined in this study.

pH levels higher than those used in this study may well lead to poor emulsion stability even when sufficient emulsifier has been added, due to the resulting low number of H⁺ ions available to protonate emulsifier molecules—and conversely, a low emulsifier dosage is unlikely to provide enough emulsifier molecules to be protonated at even low pH levels due to the high number of H⁺ ions available. However, most emulsions used during production in the field do not exceed the manufacturer's recommendation. Hence, this study's surface response models will likely prove to be a useful tool for local agencies' slurry seal design.

Limitations of the Current State of the Research

The results presented show it is possible to use zeta potential as an indicator of emulsion stability. However, certain limitations of the work need to be understood due to the many differences between laboratory formulation/testing and actual field behavior of an asphalt slurry seal mixture. Some of the possible shortcomings of this research are discussed below.

- The asphalt emulsions had to be diluted in order to be tested in the Zetasizer. The influence of dilution rates on the results is not entirely known.
- The aggregates used in producing the slurry seal mixes tested in this report contained 0% moisture. Oftentimes, aggregates used in the field have some level of moisture (3-4%). Future studies will investigate broader ranges of moisture levels.

- The humidity and temperature conditions in the laboratory were constant and are unlikely to be similar to those in the field, which could in turn affect the set time and strength development of slurry seal mixtures.

The above limitations highlight the challenges of adapting more scientific methods to the formulation and mixture design of slurry seal mixtures. However, the authors feel that the research presented provides a good starting point and foundation on which further research to narrow the gap between laboratory results and prediction of behavior in the field can build. This will lead to more intentional methods of adjusting mixture designs to meet unforeseen challenges in the field.

Possible Future Work

Since laboratory and field conditions vary greatly, future studies should verify if the differences in zeta potential demonstrated in this laboratory study are reflected under field conditions.

For example, the difference in temperature and humidity between field and laboratory conditions could contribute to a difference in strength gain. In addition, exposing samples to different environments could prove useful in determining important environmental factors that control the development of cohesive strength.

More research could also be done with various types of emulsions in order to study if zeta potential can help predict set time for emulsions having different chemistries such as tack coats and cold-in-place mixtures.

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