# Asphalt Binder Rheological Characterization for Extreme Climate Events

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16. ABSTRACT

Seal coats, also known as chip seals, are a cost-effective preventive maintenance treatment used to extend the service life of flexible pavements. In addition to properties of seal coat materials, heavy vehicle loading and sustained extreme temperatures that appear to occur with increasing frequency, also contribute to premature pavement distresses. Asphalt, being a thermoplastic polymer, is significantly affected by fluctuations in ambient temperatures, and current test protocols have not been developed with extreme climate patterns we experience today, in mind. Conducting laboratory experiments for fluctuating extreme conditions is a highly resource- and time-intensive endeavor. Therefore, finding more effective ways to evaluate asphalt binder response under a different performance scenarios can be very helpful to pavement engineers. If such an approach is available, that can also help in the development of material systems such as novel asphalt modifiers that can help improve pavement performance under extreme temperatures. This research project focused on (1) assessing future climate trends, (2) relating climate patterns to pavement performance, and (3) assess molecular dynamics (MD) simulations as an effective way to establish relationships between asphalt chemical composition and rheological properties at extreme temperatures. Findings from this research can help build and maintain highways that are more resilient to extreme climate conditions. The outcomes of this research will enable highway agencies to develop new asphalt modification and testing protocols to better predict pavement performance.

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## SI* (MODERN METRIC) CONVERSION FACTORS

### APPROXIMATE CONVERSIONS TO SI UNITS

| SYMBOL | WHEN YOU KNOW | MULTIPLY BY | TO FIND | SYMBOL |
|---|---|---|---|---|
| | | **LENGTH** | | |
| in | inches | 25.4 | millimeters | mm |
| ft | feet | 0.305 | meters | m |
| yd | yards | 0.914 | meters | m |
| mi | miles | 1.61 | kilometers | km |
| | | **AREA** | | |
| $in^2$ | square inches | 645.2 | square millimeters | $mm^2$ |
| $ft^2$ | square feet | 0.093 | square meters | $m^2$ |
| $yd^2$ | square yard | 0.836 | square meters | $m^2$ |
| ac | acres | 0.405 | hectares | ha |
| $mi^2$ | square miles | 2.59 | square kilometers | $km^2$ |
| | | **VOLUME** | | |
| fl oz | fluid ounces | 29.57 | milliliters | mL |
| gal | gallons | 3.785 | liters | L |
| $ft^3$ | cubic feet | 0.028 | cubic meters | $m^3$ |
| $yd^3$ | cubic yards | 0.765 | cubic meters | $m^3$ |
| | | NOTE: volumes greater than 1000 L shall be shown in $m^3$ | | |
| | | **MASS** | | |
| oz | ounces | 28.35 | grams | g |
| lb | pounds | 0.454 | kilograms | kg |
| T | short tons (2000 lb) | 0.907 | megagrams (or "metric ton") | Mg (or "t") |
| | | **TEMPERATURE (exact degrees)** | | |
| °F | Fahrenheit | 5 (F-32)/9<br>or (F-32)/1.8 | Celsius | °C |
| | | **ILLUMINATION** | | |
| fc | foot-candles | 10.76 | lux | lx |
| fl | foot-Lamberts | 3.426 | candela/$m^2$ | cd/$m^2$ |
| | | **FORCE and PRESSURE or STRESS** | | |
| lbf | poundforce | 4.45 | newtons | N |
| lbf/$in^2$ | poundforce per square inch | 6.89 | kilopascals | kPa |

### APPROXIMATE CONVERSIONS FROM SI UNITS

| SYMBOL | WHEN YOU KNOW | MULTIPLY BY | TO FIND | SYMBOL |
|---|---|---|---|---|
| | | **LENGTH** | | |
| mm | millimeters | 0.039 | inches | in |
| m | meters | 3.28 | feet | ft |
| m | meters | 1.09 | yards | yd |
| km | kilometers | 0.621 | miles | mi |
| | | **AREA** | | |
| $mm^2$ | square millimeters | 0.0016 | square inches | $in^2$ |
| $m^2$ | square meters | 10.764 | square feet | $ft^2$ |
| $m^2$ | square meters | 1.195 | square yards | $yd^2$ |
| ha | hectares | 2.47 | acres | ac |
| $km^2$ | square kilometers | 0.386 | square miles | $mi^2$ |
| | | **VOLUME** | | |
| mL | milliliters | 0.034 | fluid ounces | fl oz |
| L | liters | 0.264 | gallons | gal |
| $m^3$ | cubic meters | 35.314 | cubic feet | $ft^3$ |
| $m^3$ | cubic meters | 1.307 | cubic yards | $yd^3$ |
| | | **MASS** | | |
| g | grams | 0.035 | ounces | oz |
| kg | kilograms | 2.202 | pounds | lb |
| Mg (or "t") | megagrams (or "metric ton") | 1.103 | short tons (2000 lb) | T |
| | | **TEMPERATURE (exact degrees)** | | |
| °C | Celsius | 1.8C+32 | Fahrenheit | °F |
| | | **ILLUMINATION** | | |
| lx | lux | 0.0929 | foot-candles | fc |
| cd/$m^2$ | candela/$m^2$ | 0.2919 | foot-Lamberts | fl |
| | | **FORCE and PRESSURE or STRESS** | | |
| N | newtons | 0.225 | pound-force | lbf |
| kPa | kilopascals<br>inc | 0.145 | pound-force per squareh | lbf/$in^2$ |

# LIST OF ABBREVIATIONS

| | |
|---|---|
| VRA | Vulnerability and Risk Assessment |
| TechMRT | Texas Tech Center for Multidisciplinary Research in Transportation |
| SPTC | Southern Plains Transportation Center |
| TTU | Texas Tech University |
| IPCC | Intergovernmental Panel on Climate Change |
| USDOT | United States, Department of Transportation |
| FHWA | Federal Highway Administration |
| AASHTO | American Society of State Highway and Transportation Officials |
| NCHRP | National Cooperative Highway Research Program |
| NASA | National Aeronautics and Space Administration |
| FEMA | Federal Emergency Management Agency |
| DHS | Department of Homeland Security |
| IH | Inter-State Highway |
| TxDOT | Texas, Department of Transportation |
| MnDOT | Minnesota, Department of Transportation |
| TSHA | Texas State Historical Association |
| GCMs | Global Climate Models |
| GFDL | Geophysical Fluid Dynamics Laboratory |
| NHC | National Hurricane Center |
| NCDC | National Climatic Data Center |
| EPA | United States Environmental Protection Agency |
| SRES | Special Report Emission Scenarios |
| NOAA | National Oceanic and Atmospheric Administration |

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# ASPHALT BINDER RHEOLOGICAL CHARACTERIZATION FOR EXTREME CLIMATE EVENTS

## Final Report

by

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## EXECUTIVE SUMMARY

This research project was conducted with two objectives; facilitate the development of new asphalt modification protocol(s) with the help of novel techniques to assess material quality, assess the feasibility of a molecular dynamics (MD) based protocol to evaluate modified asphalts for enhanced performance. The work was carried out with a particular focus on improving binder performance under extreme high-temperature conditions in flexible pavements containing preventive maintenance treatments such as seal coats in the FHWA Region 6 States. According to predictions by the Environmental Protection Agency (EPA), depending on emission scenarios the average temperature in the United States will rise by 4 to 11 °F over the next century. The number of days with temperature above 90 °F is projected to increase throughout the U.S, especially in the southeast and southwest areas where the number would rise to 150 or more days per year under high emission scenarios. Considering the extent of damage caused by the 2009 and 2011 droughts in FHWA Region 6, It is prudent for the highway agencies to find new ways that can aid in the development of novel material systems that can be resilient under forecasted high-temperature scenarios.

Findings from this research show that modified binders have a much higher likelihood of performing well in hot weather conditions in Region 6 states. A wide array of modifiers has been used with asphalt ranging from latex, copolymers such as SBR and Styrene-Butadiene-Styrene (SBS), phosphoric acid, waste crumb rubber and various combinations of them, just to name a few. The current industry specifications are developed to pre-screen asphalt modifiers that can be used with binders in seal coats and asphalt concrete. However, the assessment of the modifier impact over an extended period is a challenging task even if they are backed by results from extensive standardized tests. This research has focused on developing a more fundamental approach to better understand the binder modification process, its effectiveness, and reliability. One such method is the molecular dynamics simulation of the modified asphalt binder. Such an approach allows highway agencies such as State DOTs to more effectively screen asphalt binders, and also enable binder suppliers to develop better-performing asphalts by simulating the asphalt cement, the modifier and more importantly, their interactions. That way, the binder producer can evaluate asphalts obtained from different crude oil sources and plant types. Under Task 4 of this report, the methodologies and the results of research on molecular simulation are presented.

In this research, the MD simulation technique was evaluated for its feasibility as a tool to screen binder modifiers and to predict modified binder performance. It was found that addition of Styrene Butadiene Rubber (SBR) increases the degree of asphaltene aggregation in the system. The effect of the adding SBR on the rheological properties of asphalt was also studied. The shear viscosity of the SBR modified system at a high temperature (i.e., in the rubbery state) was significantly higher than that of the unmodified (neat) asphalt system. This observation agreed with the diffusivity results showing that adding SBR to asphalt reduced the translational mobility of the system constituents, thus improving the likelihood of better performance of the binder.  Based on results from laboratory tests presented under Task 2, Laboratory Testing of Binders), the strain sweep and multiple stress creep recovery (MSCR) tests are capable of effectively identifying seal coat binders that can perform well in extreme high-temperature conditions. Even though the material selection is only one of several factors considered in seal coat design, using the suitable binder appears to be a crucial element to ensure well-performing and resilient seal coats.

This study, though limited in scope, allowed the research team to assess the feasibility of using molecular dynamics simulation to achieve a more fundamental evaluation of modified asphalt binders. The results indicate that MD simulations can be effectively used to evaluate the interaction of asphalt binder modifiers with asphalt cement under a wide array of service conditions, more specifically extreme high temperatures. The technique is ready for implementation in a controlled setting where modified binders, both conventional and novel, can be used in actual projects where field performance during a two-year period can be monitored and correlated with results from MD simulations as well as rheological and standard quality control tests.

# INTRODUCTION

## PROBLEM STATEMENT

Sustained extreme (hot and cold) climate spells result in significant pavement distresses, and they appear to occur with increasing frequency. Asphalt is significantly affected by this problem, but existing test protocols have not been developed with such extreme conditions in mind. Conducting laboratory experiments for ever-changing extreme conditions is a highly resource and time intensive endeavor. Therefore, finding more efficient and effective ways to evaluate highway material response under a myriad of performance scenarios can be very helpful. If such a technique is feasible, that will also facilitate the development of novel material systems such as asphalt modifiers to withstand extreme climate scenarios. This research focused on, 1) analyzing climate data to predict future weather patterns, 2) relating climate to pavement condition, and 3) use techniques of molecular modeling to elucidate the relationship between asphalt chemical composition and rheological properties. The effect of modifiers on asphalt viscoelastic properties was also a particular focus. Research findings can help build and maintain highways that better adapt to more extreme climate conditions. The outcomes of this research will enable researchers to develop new asphalt modification and testing protocols to predict pavement performance.

## BACKGROUND

Chip seals, also known as seal coats, shown in Figure 1, are a highly cost-effective preventive maintenance treatment used to extend the life of flexible pavements *(1)*. However, as the traffic levels increase, particularly heavy traffic, seal coats never reach the intended service life they were designed for. There are three primary types of chip seal distresses; aggregate loss (i.e., raveling), flushing/bleeding and cracking (Figure 1).

The researchers leveraged previous research conducted on seal coats to identify mechanisms of common distresses and how they are related to asphalt binder properties and climate-related factors. Aggregate loss usually occurs due to the poor bond between aggregate and binder and can occur either at the very early stages or several years after construction. Aggregate-binder compatibility issues, combined with the conditions during construction, are usually the main reasons for aggregate loss *(2)*. Bahia et al. showed that the presence of moisture also affects the aggregate-binder bond strength and used the Bitumen Bond Strength Test to evaluate it *(3)*. Cracking is another long-term distress that can occur due to several reasons, including the presence of cracks in underlying layers, binder stiffness during cool weather, and temperature fluctuation. Two other forms of distress are flushing or bleeding, caused by the binder being too soft during the hot summer weather. The most common chip seal performance problem that occurs in this region is flushing which occurs when aggregate particles get pushed into the binder, resulting in the asphalt binder rising up and even flow over the top of the aggregate. This leads to a reduced skid resistance raising wet weather safety concerns.

State Departments of Transportation in the five States of USDOT Region 6 spend hundreds of millions of dollars annually to maintain and preserve its highway pavement infrastructure. In Texas alone, at any given time, over fifty percent of the State highway network lane miles is covered with seal coats, and over $250 million is spent annually on such applications. In addition, a comparable amount is spent on thin asphalt overlay construction; a common preventive maintenance measure adopted particularly in urban and suburban settings. Highway agencies are finding it increasingly challenging to maintain and preserve their highway networks in a satisfactory condition due to several factors including increased traffic levels (both ADT and heavy vehicles), increased construction costs, and reduced levels of available funding. More recently, highway agencies are facing roadway preservation challenges due to problems caused by extreme weather (4). One such notable event took place in 2011 when Region 6 States experienced a severe drought with ambient temperatures exceeding 100°F for unusually long period resulting in extensive pavement repairs and a record-setting wildfire season that year. Highway pavements with chip seal surface courses experienced unusually high levels of deterioration as a result of this one event.

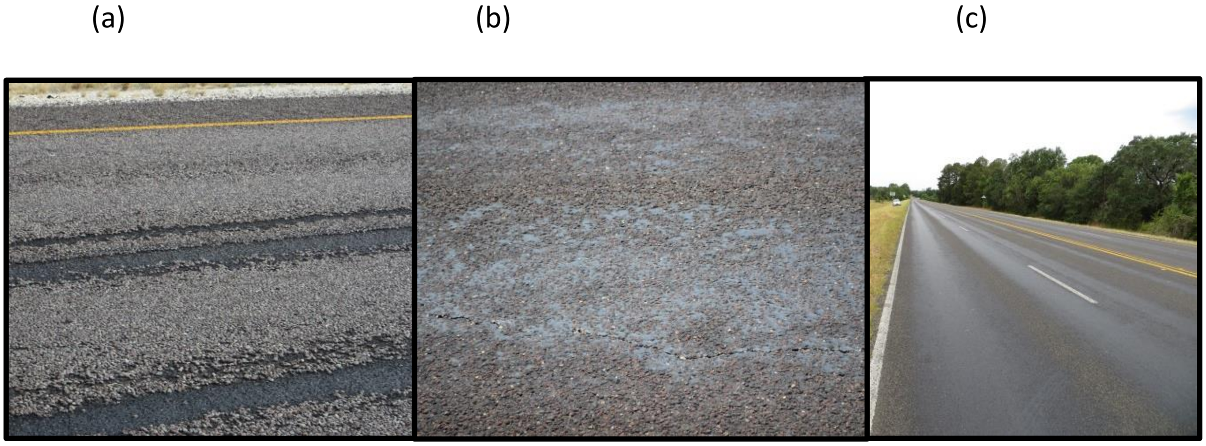

Figure 1. Common Chip Seal Distresses, (a) Aggregate Loss, (b) Cracking, and (c) Flushing.

This research project was aimed at supplementing research work that has been completed and currently being conducted by Texas Tech researchers under the sponsorship of Texas Department of Transportation (TxDOT). Research on preventive maintenance seal coats began at Texas Tech in 1997 with a comprehensive, statewide constructability review. This resulted in a near-complete overhaul of the TxDOT seal coat specification and contracting practices. Since that time, additional research work has been conducted on the material, and constructability-related aspects of the chip seal preventive maintenance process. Some of these studies include binder-aggregate compatibility, binder quality assurance, surface treatment constructability assessment, laboratory evaluation of emulsified asphalt chip seal constructability and more recently a research project on the performance assessment of chip seals constructed using different binders both modified and unmodified.

A quick review of the literature on the impact of climate change on the transportation infrastructure, paint a rather bleak picture and predicts an increasing likelihood of extreme climate events the timing of which cannot be predicted with much accuracy. This applies to extremes at both the high and low-temperature levels. Asphalt binder will significantly influence pavement deterioration at both temperature extremes, and it is important for highway agencies to re-evaluate the applicability and relevance of their testing methods and material specifications in light of these new climate realities, and to explore more efficient and effective ways to evaluate such influences. This research project focused on studying the feasibility of advanced molecular simulation methods to supplement laboratory experiments to conduct more comprehensive evaluation of binder properties to ensure satisfactory performance under extreme climate scenarios.

Asphalt, a commonly used material for pavement, is a highly heterogeneous multicomponent mixture that is mainly composed of hydrocarbon molecules. Change in the temperature of the road surface can lead to the rutting and cracking issues at high and low temperatures, respectively. A potential approach for increasing the end-use properties of asphalt is the addition of polymeric modifiers such styrene butadiene rubber (SBR), molecular simulations were used in this work to study the effect of the addition of SBR on physical properties of asphalt. The primary goal of the molecular modeling work was to decipher the molecular mechanisms underlying the dependence of viscoelastic properties of asphalt on its composition. We used atomistically-detailed models for this purpose. These models enable prediction of the properties of the systems based on the knowledge of the chemical structure of the components, thus reducing the need for experimentation.

## OBJECTIVES

This research project was conducted with two primary objectives.

- Facilitate the development of new asphalt modification protocol(s)
- A molecular simulation-based protocol that can evaluate modified asphalts for extreme climate scenarios.

Criteria were developed to include the two research objectives indicated above, and they are presented under the *Conclusions and Recommendations* section of this report. These criteria include more effective guidance to select asphalt binders for preventive maintenance treatments resulting in longer lasting pavements and safer driving experience for the traveling public particularly pavements exposed to extreme climate scenarios.

## SCOPE

There are several accepted tests that have been developed to asses seal coat performance. However, these test methods do not seem to be effectively predicting the performance of seal coats under extreme climate scenarios. This research was aimed at supplementing and building upon the knowledge base developed from seal coat research conducted at Texas Tech over the past fifteen years by taking the important step of assessing standard test methods in the context of extreme climate scenarios that are becoming more and more common. The project included the following research tasks.

1. Review of literature on climate pattern predictions and how climate change will impact highway transportation infrastructure
2. Laboratory testing of asphalt binders to assess properties with regard to extreme climate events
3. Determine desired threshold binder property values to withstand possible extreme climate events
4. Molecular modeling to elucidate the relationship between asphalt chemical composition, modifier type/dosage/blending procedure and the rheological properties of the binder.
5. Reporting

The laboratory testing of asphalt binders under TASK 2 was conducted in two phases. Phase 1 involved the TxDOT SPR project *0-6747: Seal Coat Quality* that provided matching funds for this SPTC research *(4)*. In this phase, asphalt binders commonly used in State DOT work were tested to establish threshold material property values to calibrate the molecular modeling simulations.

## RESEARCH ACTIVITIES

### TASK 1. REVIEW OF LITERATURE

### Extreme Climate Events

#### Background

The global climate historically followed a predictable pattern of yearly and seasonal fluctuations with a consistent warming trend. The recent gradually increasing rate of change is often attributed to anthropogenic causes. Current data show patterns of extremes, ranging from extreme heat waves to floods. There is a need to have an effective protocol for Vulnerability Risk Assessment (VRA) of transportation infrastructures to better adapt to extreme weather and climate patterns. Events such as Hurricane Katrina and Super Storm Sandy caused large-scale damage to transportation infrastructure in the United States and created a heightened sense of awareness not only among professionals but the public in general. *(5)* VRA will help plan, design and operate resilient transportation infrastructures, and recent publications by the

FHWA *(5)*, NCHRP *(6)*, and the UK Highway Agency *(7)* provided important guidelines to improve infrastructure resiliency.

Different transportation infrastructures will have different degrees of risk from different climate events. Therefore, sound approaches for design for resilience and vulnerability risk assessment (VRA) are needed to evaluate the risks, rank vulnerabilities and repair priorities so authorities can respond to extreme climate events more effectively and in a timely manner. The damage caused to transportation infrastructure due to extreme climate events that occurred over the past few decades has highlighted the importance of effective VRA in the United States. This has triggered many governmental and private authorities to come up with solutions in addressing these climate events and be ready for them, and agencies such as FHWA and NCHRP have developed frameworks.

Over the past ten years, the FHWA Region 6 that includes States of Texas, Oklahoma, Arkansas, Louisiana, and New Mexico, experienced extreme climate events that resulted in significant loss and disruption of transportation infrastructure. The heat waves in 2009 and 2011, hurricanes along the Texas and Louisiana gulf coats, and the floods in 2014 in Texas clearly indicate the unexpected nature of extreme climate and their effects on transportation infrastructure.

### Historical Patterns

When considering climate events in the future, having a good idea about the past events that happened and their patterns, is important. Although the patterns may seem to vary rapidly with changing frequency and intensity, the historical patterns hold the key to forecasting future patterns accurately and in showing what damages they will do. Over half a million years the atmospheric earth maintained its carbon dioxide level below 300 ppm. However, after 1950, this level increased at a rapid rate, and today the carbon dioxide level passes around 400 ppm *(8)*. Since 1880, the average global temperature increased by 1.4 °F, causing the reduction of land ice at a rate of 258 billion tons per year. In the past century, the global sea level rose about 17 centimeters (6.7 inches), but the rate of the sea level in the past decade- almost doubled than that of the last century. Records indicate that the Earth started warming in 1880, but this process increased rapidly after 1970. Out of the 20 warmest years after 1981, 10 of them occurred in the last 12 years. Records indicate these as the 10 warmest years in the history. Oceans absorb most of this heat, and since 1969 the top 700 meters (roughly 2300 feet) of the ocean showed warming of 0.302 °F. Due to this warming between 2002 and 2006, Greenland lost 150 to 250 cubic kilometers (36 to 60 cubic miles) of ice per year. Over the last several decades, Arctic sea ice seems to decrease rapidly in both its extent and thickness. Glaciers like the Alps, the Himalayas, the Andes, the Rockies, Alaska, and Africa experienced the same. Since, 1950 these high-temperature events increased gradually with increasing rainfall, while the number of low-temperature events decreased *(8)*. In recent decades the climate patterns have become highly variable and difficult to predict. Human behavior influenced these changes in different ways, as indicated in greenhouse gas emissions *(9)*. These events have heightened the need for adaptive measures to maintain the resilience of transportation infrastructure at a desirable level.

Extreme climate events affect transportation infrastructures in many ways including hurricanes, heat waves, droughts, extended cold spells, and floods. In this research, the focus is on temperature extremes. Extreme heat events occur when temperature spikes to very high levels or remains high over a long period of time. Such events occurred in Illinois (1995), Europe (2003), UK (2006), Illinois (2012), Wisconsin (2012) and Utah (2013). Such extreme heat events cause damage to highway pavements, bridges, and other transportation infrastructure. Impacts from extreme heat in the FHWA Region 6 is particularly strong. According to the Texas Department of Transportation (TxDOT), extreme heat waves in 2011 caused severe damage to the Texas roadway network. In 2011 and 2013, extreme heat caused older bridges in Oklahoma to buckle, including one in Guthrie, Texas near Highway 33. A portion of Interstate Highway 55 in Memphis, closer to Arkansas buckled due to an extreme heat wave that lasted more than a week. Due to heat waves occurring more and more frequently, the financial strain on transportation agencies due to frequent repair needs is becoming higher. The impact of cold spells on transportation infrastructure is related to transportation safety, infrastructure damage and economic output. In spite of the progress made in responding to such events, transportation agencies find it difficult to effectively respond to them. Historically, the impact of extreme cold spells in Region 6 States has not been strong. However, this could pose a problem in the future when it is least expected, causing significant problems in the region.

*High Temperatures:* The surface temperature in the United States increased from 1901 at an average rate of 1.41 °F per century, and this rate increased rapidly from 1970. A similar pattern has been observed to the global rate of ricing temperature up to 1970, and after that, the United States got warmer at a rapid rate than the world's average rate *(10)*. High temperature or heat waves take number one as the fatal event in the United States. In the history, from 1930 to 1940, known as the *Dust Bowl*, gave the hottest years. Heat waves do not own a universal definition and normally measured using the Heat Wave Index. The United States defines the index as, a four-day period with an average temperature that would only occur once every 10 years, based on the historical records. After the Dust Bowl, the things cooled down around 1970, and the visible pattern suggests an increase of heat towards 2020, with hotter summers than the past years. The data indicate the percent land area within the contiguous 48 states, that had daily summer temperatures above the 95th percentile in the year with two separate curves, one for the summer daytime high and the other for summer night time *(10)*.

*Low Temperatures:* The coldest winter in the history observed in 1980, had more than 40 percent of the United States colder than the fifth percentile. The pattern indicates colder winters in the future with covering more areas in the States *(10)*.

## Prediction of Extreme Climate Events

In the field of climate science, forecasting of climate behavior significantly influences many other disciplines for applications such as planning, design and operations, in both the long- and short-term activities. As a result, climate science has grown significantly as a discipline, and they are often challenged to forecast medium-to-long-range climate behaviors as accurately as possible. The climate forecasting technique uses historical weather data and climate patterns to predict future climate behavior. Since climate change is attributed to anthropogenic factors, a variety of scenarios needs consideration to project climate patterns into the future. The effect of climate change on transportation infrastructure can be predicted by integrating climate prediction models with transportation infrastructure performance prediction models *(11)*, and this requires a multi-disciplinary approach.

General Circulation Models (GCM) serve as the foundation of climate prediction modeling. GCM uses the basic laws of physics, chemistry and fluid flow. In this model, the earth is divided into a three-dimensional grid onto which the models are applied. The two primary GCM types, Atmospheric General Circulation Model (AGCM) and Oceanic General Circulation Model (OGCM) are modeled using the Navier-Stokes equation on a rotating sphere (IPCC, 2013b). By using AGCMs' and OGCMs' as a foundation and adding sea-ice and land-surface components to them, the Global Climate Models (GCMs) are created. GCMs are primarily used for weather forecasting, understanding the climate and projecting climate into the future. The first GCM was created by Manbe and Bryan at the Geophysical Fluids Laboratory in Princeton, New Jersey. *(12)*.

Quantitative climate models include uncertainty models for magnitude, timing, and spatial distribution of future change, and therefore needs careful attention to provide the most accurate projections. These uncertainties are divide into three areas *(11)*;

- Natural Variability – exchange of heat, moisture and energy varies the shorter period aspects like temperature and precipitation, either periodic or chaotic. These small variations add up to make short-term future projections and averaging those short scale projections make long scale future projections. So, the variability of exchange of heat, moisture, and energy will have a significant effect on the projections.
- Scientific or Model Uncertainty – the challenge of modeling how much the earth's climate will change due to human behaviors or mainly the emissions to the atmosphere. Use of multiple GCMs will solve this problem.
- Scenario or Human Uncertainty – considers inputs to GCMs, like our idea about future population, technology, and energy supply. At least two scenarios of projections, representing the worst case and the more desirable case ensures the full range of events.

A range of GCMs created by different organizations is available for climate modeling and projections. These models differ primarily on the area of emphasis, and therefore, the selection of a GCM for a particular application must be done carefully in consultation with a climate science expert.

Future Projections

Climate change projections for the future use of past data and a large number of uncertainties make them less accurate. Normally forecasting more cases using different scenarios will give a range of possible values.

*High Temperatures: According to the EPA,* Depending on emission scenarios the global average temperature will rise by 2 to 11.5 °F, and the U.S average temperature will rise by 4 to 11 °F. The number of days above 90 °F will increase throughout the U.S, especially the southeast and southwest areas will get 150 or more days with temperatures 90 °F or above, under high emission scenarios. Also, under high emission scenarios, such high temperatures will occur more frequently, and projects about 10 °F hotter than current levels by the end of this century *(10)*. With these projections, in almost every scenario, the temperatures of FHWA region 6 states are projected to rise considerably than that of today, with respect to other states.

*Low Temperatures:* Even with the less concern regarding future low-temperature events, the pattern indicates colder winters in the future that covers more areas in the States *(10)*.

## Vulnerability Risk Assessment (VRA)

With the increase in the frequency of extreme climate events, many authorities identified the need to know their current trends and future trends, in order to prepare for those events. This chapter will look at the historical patterns and how they will behave in the future using some of the projections already made by researchers. Vulnerability Risk Assessment (VRA) is a tool that can be used to assess vulnerabilities by assessing and ranking these risks. The four primary criteria used in VRA to assess vulnerability include uncertainty, extent, and severity of disruption and rate of change in influence (i.e., climate change). Based on these criteria, VRA recommends candidate remedial action based on criticality and confidence, with each option accompanied by expected outcomes and estimated costs and benefits to help make the most optimal decision *(8)*. This study also identified that in order to make the VRA methodology more accurate, it needs high confidence levels in the climate projections and their intensities. Therefore, the climate change projection must contain the knowledge and experience of a climate change expert.

In the field of transportation, the traditional trend of using historical data in planning, designing, and operations, gave questions for the past few years. Many countries in Europe adopted ways of using forecasted climate data in their planning, design, and operations, with the aim of establishing a good solid framework for future events before they happen. As shown by UK Highway Agency *(8)*, a way of adaptation and mitigation shows a more feasible way of pro-acting to future climate-related situations, rather than the traditional way of reacting.

## Relevance of VRA

Almost all of the risk registers in highway agencies identify climate change as a priority risk. , Losing the transportation network integrity, will overlook the risk of not adjusting to the pre-defined climate risks in time and in magnitude. Unanswered risks will increase the maintenance, the impacts of climate events, the risk to road users and operational staff, and the risk of not reaching the destination safely and on time. Therefore, adaptation plans will give the confidence to face these events without any consequences. VRA will assess asset vulnerabilities against different criteria's and will prioritize them according to the threats posted by climate change. Clear ideas on making decisions about such events also support the adaptation work and will help to plan the future investments in transportation in an unpredictable climate.

Vulnerabilities identify the assets, services, uses or the operations of transportation infrastructures that are influenced by extreme climate events. Some of major climate-related risks, relating to transportation infrastructures identified by the UK highway agency *(8)* are;

- Reducing the asset condition and safety
- Reducing the network availability and/or functionality
- Increasing the costs to maintain a safe, serviceable network
- Increasing the safety risk to road workers
- Increasing the program and quality risks due to required changes in construction activities
- Making the current internal operational procedures of the authorities not appropriate
- Increasing the business management costs

Vulnerability assessment should cover the total life-span of the transportation infrastructure and the UK Highway Agency recommends the four vulnerabilities; uncertainty, extent of disruption, severity of disruption, rate of climate change.

## VRA of Transportation Infrastructure in FHWA Region 6

For the FHWA region 6, conducting the VRA using key transportation infrastructures such as bridges, roads, railways and airport, ports and waterways, and pipelines, will identify the key vulnerabilities so that the agencies could act accordingly in a proactive manner. By considering a climate event and relating the vulnerabilities of each asset to that climate event, will give more meaning and convenience to the VRA. This will help to prioritize the assets, in a foreseen climate event. It is reasonable to suggest that the assets ranked from highest to lowest priority are;

1. Marine Ports, Terminals, and Waterways
2. Roads and Highways
3. Bridges and Railroads and Airport/Helicopters
4. Natural Oil and Gas Pipelines

Calculated in relative with the climate events, these highly disruptive and time-critical assets and their vulnerabilities got the priority, depending on the extension and severity of the damages which will occur. The extent and Severity of disruption criteria played a major role in ranking the highly disruptive and time-critical assets/vulnerabilities.

With recent rapidly occurring climate events impacting the state transportation infrastructures, authorities have focused on coming up with solutions to make these structures more competence to climate events. The Gulf Coast Study carried out by FHWA has developed several methods in focusing climate events and transportation infrastructures. Such as;

- Assessing infrastructure Criticality in Mobile, AL
- Assessing the Sensitivity of Transportation Assets to Climate Change
- Climate Variability and Change in Mobile, AL
- Screening for Vulnerability
- Engineering Assessments of Climate Change Impacts and Adaptation Measures

As a result of the Golf Coast Study, FHWA has developed a framework which can be used in any location to assess the impact of different climate events on different transportation infrastructure. To use that framework FHWA has also developed some tools which are publicly available. They are;

- Assessing Criticality in Transportation Adaptation Planning
- Transportation Climate Change Sensitivity Matrix
- CMIP Climate Data Processing Tool
- Vulnerability Assessment Scoring Tool (VAST)

NCHRP in 2014 published, A Guide to Regional Transportation Planning for Disasters, Emergencies, and Significant Events which also has important information addressing how to make transportation infrastructure more resilient to climate events (NCHRP, 2014). They have used the *Circle of Principles* as the frame work in their approach. The circle includes Comprehensive, cooperative, informative, coordinated, inclusive, exercised, flexible and continuous/iterative strategies with communication and collaboration.

## TASK 2. LABORATORY TESTING OF ASPHALT BINDERS

### Test Methods

The laboratory binder testing program for this research was provided by the TxDOT State Planning and Research (SPR) project 0-6747 that provided matching funds for this study *(4)*. The asphalt binder samples used for testing under this program were collected from the field at the time actual seal coat projects were being constructed. Eight asphalt binders were included in this testing program, and the binder sources were picked based on actual quantities of seal coat binder supplied to TxDOT projects. The binder grades included in the testing program were AC-10, AC-10 2TR (two sources), AC-15P, AC-20 5TR (two sources), and AC-20 XP (two sources). As for the notations used in binder grades, AC corresponds to the viscosity grading system, 2TR and 5TR corresponds to two and five percent tire rubber blended in, respectively, P and XP both refer to polymer modified binder.

Two tests were conducted on these binders, the strain sweep test and the Multiple Stress Creep Recovery (MSCR) test, both using the Dynamic Shear Rheometer (DSR). The strain sweep test helped to evaluate the rheological characteristics of each binder under a range of strain intensities, and its results show the elastic, viscoelastic and viscous response regions using the dynamic modulus (G*) of the binder as the basis. The MSCR test conducted according to the standard test AASHTO TP 70-12), is a relatively new test method originally introduced to help characterize the rutting potential of a binder by using short-term creep and recovery potential as a mechanism. Flushing, which is one of the two primary distresses in seal coats, being high-temperature distress similar to rutting in asphalt concrete, the researchers considered the MSCR test to evaluate the flushing potential of the binder. Both the strain sweep and MSCR tests were conducted on the un-aged and rolling thin film oven (RTFO)-aged binder. The RTFO aging method was selected based on performance data suggesting that the other major seal coat distress, the aggregate loss (raveling), typically occurs during the first winter season after the seal is placed, typically in a few months.

An asphalt binder is considered to be in the linear viscoelastic region when it’s dynamic modulus (G*) obtained from the strain sweep test is within 95 percent of the maximum G*that is recorded at very small strains when the binder displays predominantly elastic behavior. The test was conducted up to 100 percent strain at 64 °C, which is the standard high testing temperature for the commonly used performance-graded (PG) binder in Texas. The standard MSCR test calls for 10 creep-relaxation cycles, each with a total duration of ten seconds comprising of one second of creep shear stress followed by nine seconds of recovery under zero stress. The creep shear stress is applied at three levels; 0.1kPa and 3.2 kPa to represent different levels of traffic loading. In this testing program, a variation of the standard MSCR protocol was adopted to accommodate a longer recovery period of 59 seconds to simulate low truck traffic volumes in roads that typically get seal coat treatments. Furthermore, a 10 kPa shear stress level was added to the other two because the researchers believe that higher stress level would better represent the response of seal coated pavements under summer conditions. The MSCR test produces the non-recoverable creep compliance (Jnr) that is used as a high-temperature distress parameter to compare different binders as well as to correlate with pavement performance data. It is calculated using the following equation,

$$J_{nr} = \frac{\varepsilon_{10}}{\sigma}$$

Where, $\varepsilon_{10}$ is the un-recovered accumulated strain at the end of 1the $0^{th}$ cycle, and $\sigma$ is the applied creep shear stress.

**Results**

Table 1 provides a summary of the results from strain sweep tests on the six binder types used in this study. The only un-modified binder, AC 10, exhibits the lowest stiffness followed by AC 10-2TR, AC 15P, AC 20-5TR, AC 20XP, and AR. The desired binder will have high G* value at the high design temperature and higher strain levels at 0.95G* indicating that the binder will remain at elastic or delayed elastic levels unto higher strain levels. The results clearly show that binder modification can help with the high-temperature performance in binders even at low modification levels such as in AC-10 2TR with only two percent crumb rubber. Even though the strain at 0.95G* for AR binder is relatively low (at 20*), its stiffness values are at a higher level than any other binder tested even at a very high 100% strain (approximately 3700 Pa for original binder – see Figure 2).

Table 1. Strain sweep results.

| | G* (Pa) | G* (Pa) | G* (Pa) | Strain @ 0.95G* | Strain @ 0.95G* | Strain @ 0.95G* | Slope of Drop in G* from 0-100% Strain | Slope of Drop in G* from 0-100% Strain | Slope of Drop in G* from 0-100% Strain |
|---|---|---|---|---|---|---|---|---|---|
| Binder | Original Binder | RTFO Binder | G* Rank (Hi-Lo) | Original Binder | RTFO Binder | %Change | Original Binder | RTFO Binder | %Change |
| AC-10 | 742 | 1229 | 6 | 16% | 110% | 587% | 7.2% | 4.6% | -36.7% |
| AC-10 2TR | 1351 | 2874 | 5 | 51% | 58% | 14% | 7.3% | 9.0% | 22.5% |
| AC-15P | 1480 | 3366 | 4 | 23% | 16% | -30% | 9.3% | 13.6% | 45.6% |
| AC-20 5TR | 1618 | 3937 | 3 | 41% | 37% | -8% | 9.7% | 11.9% | 22.8% |
| AC-20 XP | 2227 | 5007 | 2 | 69% | 86% | 26% | 6.7% | 8.7% | 30.2% |
| A-R | 5169 | 7127 | 1 | 20% | 20% | 0% | 27.3% | 23.0% | -15.8% |

Note - Specification requirement of G* for asphalt concrete at 64 °C = 1000 Pa

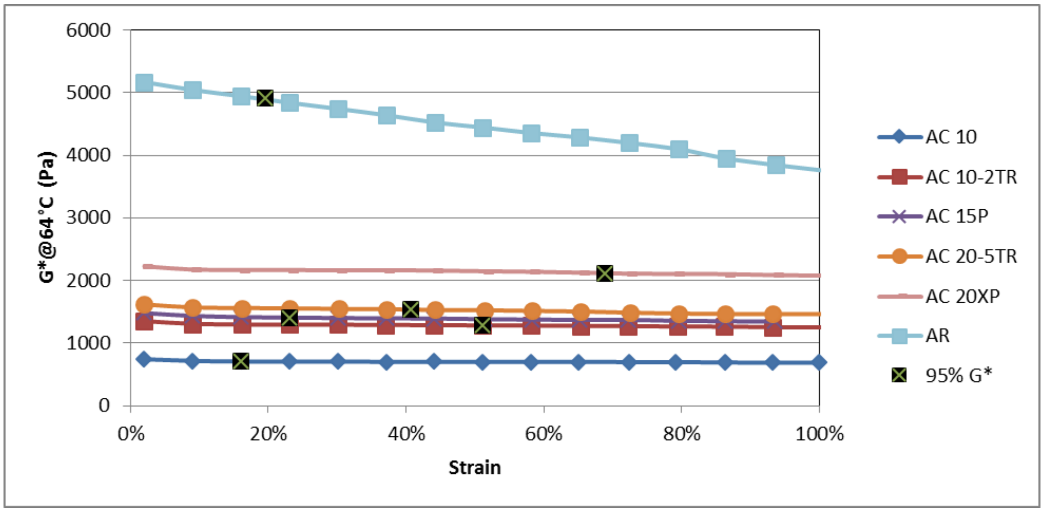

Figure 2. Strain Sweep Results for Unaged Binders.

Table 2 shows the $J_{nr}$ values obtained from the MSCR test conducted on unaged and aged binder at all three shear stress levels while Figure 3 illustrates Jnr values at the shear stress of 10kPa for both unaged and aged binders. A lower $J_{nr}$ value is expected to project better high-temperature performance (lower flushing) in seal coats. As expected, the unmodified AC-10 binder shows the highest Jnr values and with asphalt rubber (AR) binder exhibits the lowest values. At different stress levels, several modified binders such as AC-20 XP and AC-20 5TR resulted in different Jnr values varying according to the applied shear stress.  Looking at the data from Table 2, it is clear that Jnr values increases as the stress level goes up. This indicates that the strain is increasing at a higher rate than the stress as the stress level goes up. Several researchers found out that higher stress levels provide a better representation of the binder quality and also better repeatability of test results. The Jnr data for unaged and aged binder provides a good indicator of the rate of aging of different binders.

Table 3 presents data for percent strain recovered during the 10th cycle of the MSCR test on all binders. This parameter presents a direct correlation to the better anticipated performance of the seal coat in terms of flushing, and the order of preference of binders in appears to remain the same as that from Jnr results. Figure 4 illustrates the percent strain recovery values for unaged and aged binder of all grades at the 10 kPa stress level. Figure 5 shows a plot of accumulated percent strain vs. time for all binders at unaged stage tested at 0.1 kPa stress level. Again, the ranked order of binders from best to worst stayed the same as before for Jnr and % Recovery. A closer look at the curve for a stiffer polymer-modified binder such as AC-20XP (Figure 6) show that it will take a longer time to recover and the standard testing protocol with a nine-second recovery period may not reflect the true response in the case of seal coats applied on low-traffic roadways.

Table 2. Jnr of Unaged and aged binder.

| | **0.1kPa** | **0.1kPa** | **3.2kPa** | **3.2kPa** | **10kPa** | **10kPa** |
|---|---|---|---|---|---|---|
| **Binder** | **Original $J_{nr}$** | **RTFO $J_{nr}$** | **Original $J_{nr}$** | **RTFO $J_{nr}$** | **Original $J_{nr}$** | **RTFO $J_{nr}$** |
| AC-10 | 13.67 | 7.23 | 14.80 | 8.37 | 15.77 | 8.91 |
| AC-10 2TR 1 | 5.65 | 2.48 | 7.88 | 3.65 | 9.10 | 4.24 |
| AC-10 2TR 2 | 8.43 | 6.55 | 10.25 | 8.36 | 11.41 | 9.22 |
| AC-15P | 2.14 | 0.79 | 4.61 | 1.20 | 7.68 | 1.91 |
| AC-20 5TR 1 | 1.82 | 0.52 | 4.45 | 1.03 | 6.16 | 1.56 |
| AC-20 5TR 2 | 1.58 | 1.49 | 3.85 | 2.41 | 6.57 | 3.40 |
| AC-20XP 2 | 1.87 | 0.55 | 2.50 | 0.81 | 3.64 | 1.11 |
| AC-20XP 1 | 1.01 | 0.47 | 1.71 | 0.78 | 3.23 | 1.11 |
| A-R | 0.00 | 0.00 | 0.53 | 0.28 | 1.99 | 1.48 |

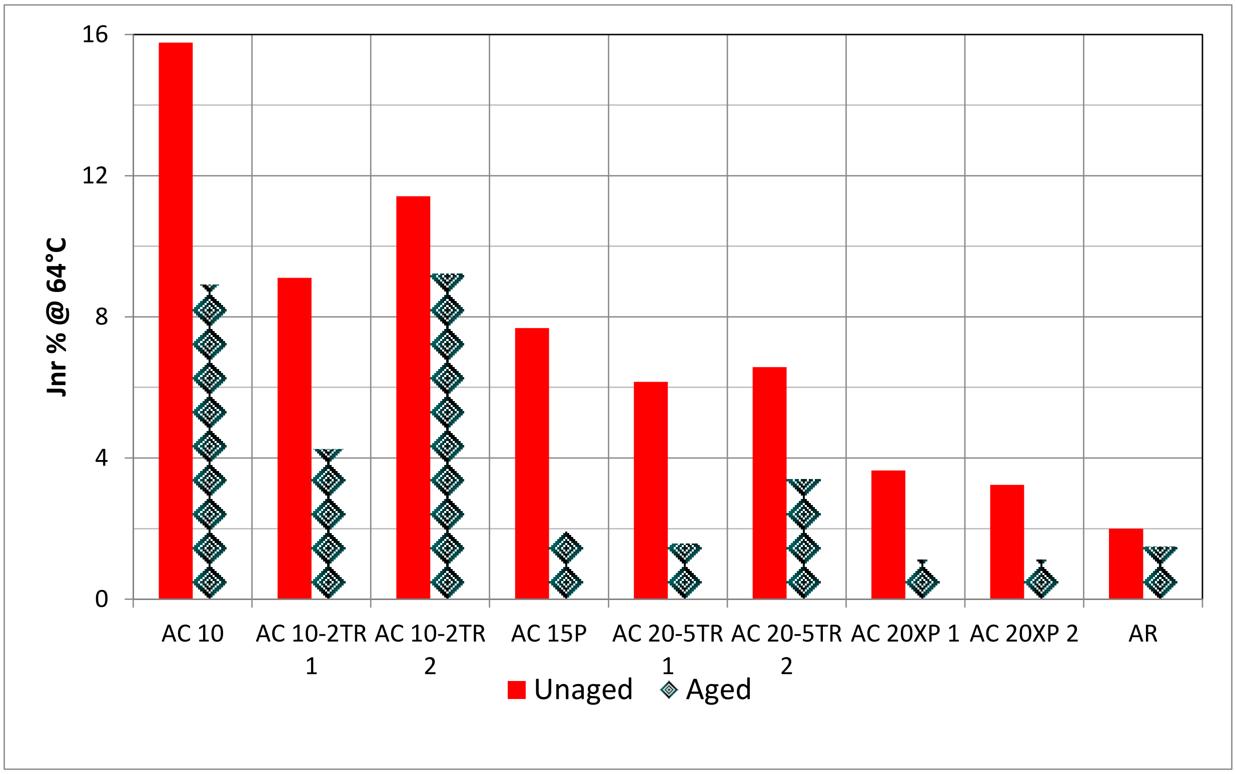

Figure 3. Jnr at 10kPa Stress Level for Unaged and Aged Binders.

Table 3. $J_{nr}$ of Unaged and aged binder 5 1. Percent Strain Recovery of Unaged and Aged Binder.

| | **0.1kPa** | **0.1kPa** | **3.2kPa** | **3.2kPa** | **10kPa** | **10kPa** |
|---|---|---|---|---|---|---|
| **Binder** | **Unaged %Recovery** | **RTFO %Recovery** | **Unaged %Recovery** | **RTFO %Recovery** | **Unaged %Recovery** | **RTFO %Recovery** |
| AC-10 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| AC-10 2TR 1 | 0.00 | 0.03 | 0.00 | 0.00 | 0.00 | 0.00 |
| AC-10 2TR 2 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| AC-15P | 0.13 | 0.11 | 0.03 | 0.06 | 0.00 | 0.01 |
| AC-20 5TR 1 | 0.11 | 0.19 | 0.01 | 0.07 | 0.00 | 0.02 |
| AC-20 5TR 2 | 0.17 | 0.07 | 0.02 | 0.01 | 0.00 | 0.00 |
| AC-20XP 2 | 0.06 | 0.13 | 0.03 | 0.07 | 0.00 | 0.03 |
| AC-20XP 1 | 0.19 | 0.16 | 0.08 | 0.07 | 0.01 | 0.02 |
| A-R | 0.98 | 0.93 | 0.08 | 0.15 | 0.00 | 0.01 |

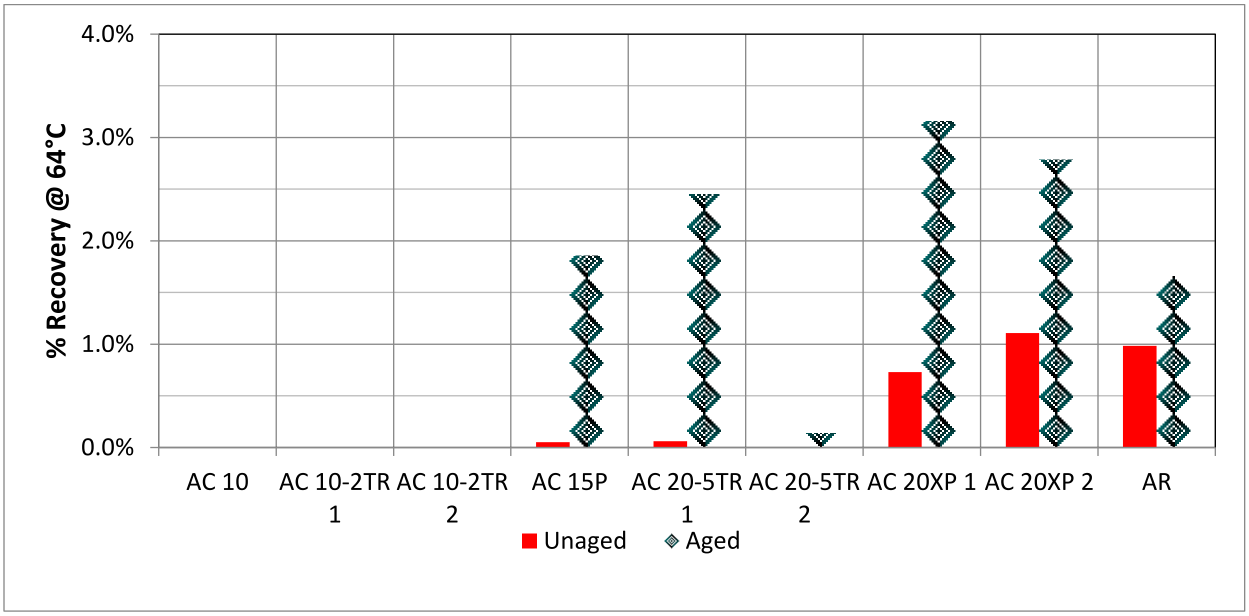

Figure 4. Percent Recovery at 10kPa Stress Level for Unaged and Aged Binders.

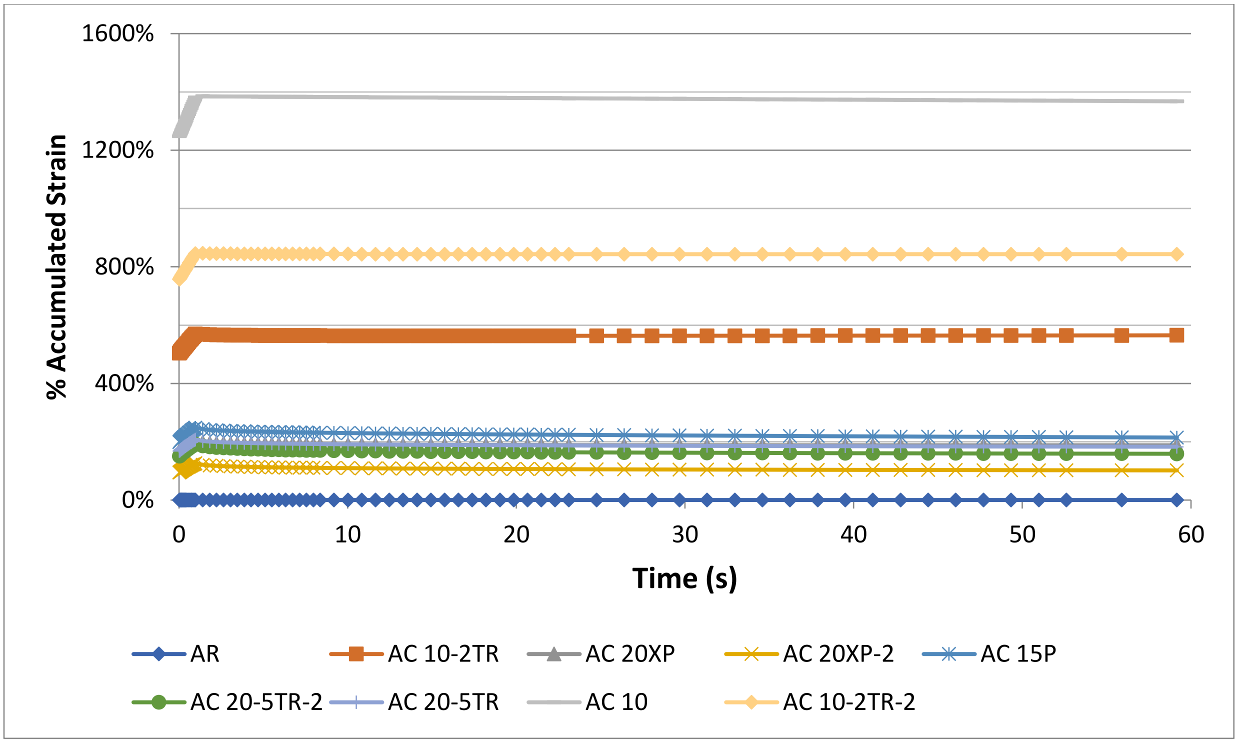

Figure 5. Accumulated percent strain at the 10th cycle for a shear stress of 0.1 kPa.

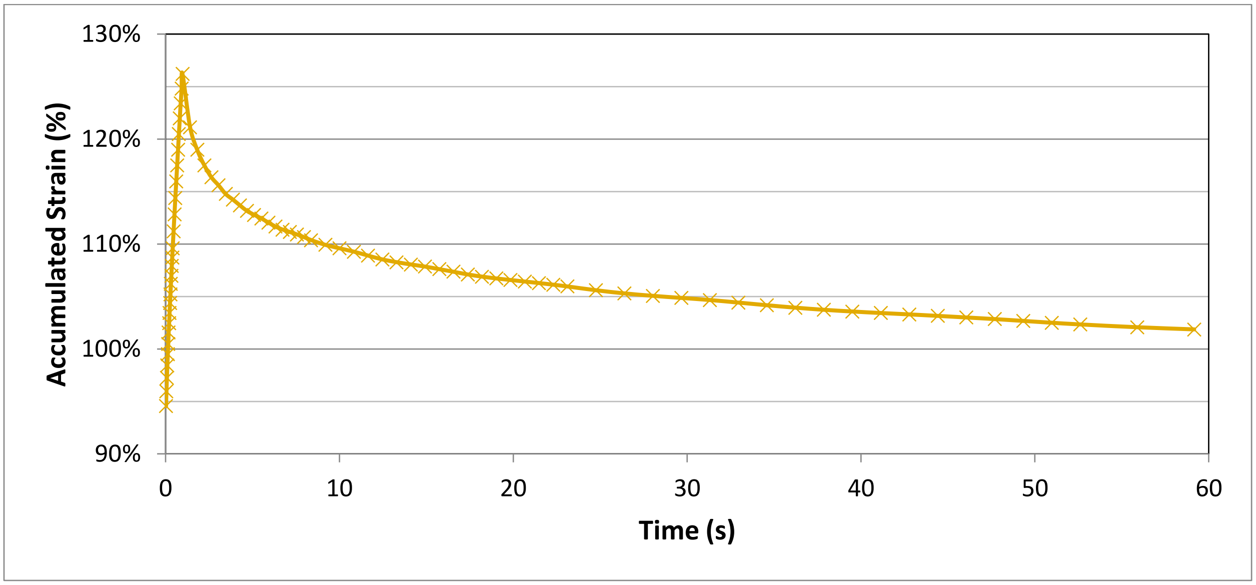

Figure 6. % Accumulated Strain vs. Time for AC-20 XP at 10th loading cycle and stress of 0.1 kPa.

## TASK 3. DETERMINE DESIRED THRESHOLD BINDER PROPERTY VALUES

This study used the surface condition index (SCI) criterion used in TxDOT Project 0-1710 for performance evaluation and rating of pavements with seal coat surfaces *(13)*. The actual rating is based on SCI scores, which range from 0.0 percent (very poor performance) to 100 percent (perfect performance) calculated from field test section survey data. For each distress, the SCI score can be calculated as an equal-weighted function of the distress area coverage (DAC) and the degree of severity of distress (DSD), expressed as a percentage by using the equation below.

$$SCI_{Distress} = 0.5\,(PDAC + PDSD)$$

where:
$SCI_{Distress}$ = SCI score as a percentage for given distress.
PDAC = distress area coverage as a percentage.
PDSD = degree of severity of distress in percentage.

The test section pavement evaluation results are typically presented for the two primary distresses in seal coats; aggregate loss, also known as raveling ($SCI_{AL}$) and bleeding ($SCI_{BL}$). Seal coat surfacings used for pavement evaluation came from TxDOT projects 0-1710, 0-6616 and 0-6747, and the time since seal coat application ranged from one to five years *(14).* A detailed presentation of results from the field evaluation can be found in the research report. For TxDOT project 0-6747 *(4)*. Of the test sections evaluated in this research, most of the unmodified binders (CRS-2, AC-10) were used on low volume roadways. In terms of aggregate loss, eight of the 15 roadways had a $SCI_{AL}$ less than 70. Five of these eight used unmodified binders, either CRS-2 or AC-10. In terms of bleeding, half of the unmodified binders had an $SCI_{BL}$ over 70 and the other half below 70. A total of eight test sections used an unmodified binder, and five performed poorly in terms of aggregate loss, two test sections performed poorly in terms of bleeding, and two test sections performed poorly in both aggregate loss and bleeding. Seven of the eight unmodified binder test sections performed poorly either from bleeding, aggregate loss, or both.

Fourteen of the test sections used in the field evaluation were on moderately trafficked roadways and used binders with grades AC-20-5TR, AC-15P, CRS-2P, CRS-2H, and AC-10. In terms of aggregate loss, half of the roadways had $SCI_{AL}$ below 70 and all, but one of these was constructed with polymer modified premium binders (AC-20-5TR, AC-15P, CRS-2P). In terms of $SCI_{BL}$, half of the sections performed poorly (below 70). Two of these were constructed with unmodified binders. Of the 14 total test sections, three were constructed with unmodified binders and all three performed poorly in terms of either bleeding or aggregate loss. Twelve test sections were constructed on high traffic roadways, and all these sections were constructed using modified binders. Only one of these sections had an $SCI_{AL}$ less than 70, and it was constructed with AC-20-5TR. Four sections had a $SCI_{BL}$ less than 70, and these sections were constructed with HFRS-2P, two with AC-20-5TR and AC-15P. The overall SCI for pavement test sections is calculated by averaging the values of $SCI_{AL}$ and $SCI_{BL}$. The predominantly used binder by TxDOT is the AC-20-5TR, so most of the test sections are constructed using this binder. The median overall SCI values for all of the binder types are follows:

- *Polymer Modified Binders (AC-10 2TR, AC-20 5TR, CRS-2P, HFRS-2P): Median SCI = 78.5*
- *Unmodified Binders (AC-10, CRS-2, CRS-2H): Median SCI = 72.5*

While the polymer modified binders overall performed at a higher level, the test section with the highest score happened to be constructed using an unmodified binder (AC-10). As is well known, there are many factors that can influence the performance of seal coats, and material selection is only one. If constructed properly and if the roadway is a good candidate for a seal coat treatment, unmodified binders may also perform well. For higher volume facilities, it still seems that polymer modified binders are likely to give better success.

The TxDOT Seal Coat Material Selection Table (SCMST) has been used as a guideline to select binders based on a tiered approach in terms of traffic levels *(1)*. However, the service conditions of roadways with seal coat surfaces have changed over the years with higher speed limits and heavy truck traffic even on minor collector roadways where this treatment is commonly used. Even though the truck traffic volumes are not as high as on other major collectors and arterials, minor collectors such as Texas Farm-to-Market (FM) roads do take a beating from even low volumes of heavy traffic. This is further accentuated by extreme climate conditions such as the extended drought during summer 2011that are becoming increasingly common. Field evaluation data indicated $SCI_{BL}$ values at unacceptable levels (less than 60) on highways that had a wide range of truck volumes from very low to very high. In low truck volume roadways, the softer asphalt binders recommended in the SCMST may not be able to withstand even low levels of heavy traffic.

The non-recoverable creep compliance values calculated from the MSCR test for commonly used seal coat binders such as AC-10, AC-10 2TR, AC-15P, AC-20 5TR, AC-20 XP, and A-R showed significantly different laboratory performances from binders tested at 64°C. Softer asphalt cement binders such as AC-10 and softer but modified binders such as AC-10 2TR showed significant non-recoverable strain build-up during the 10 cycles of MSCR test for both un-aged and RTFO-aged conditions. The stiffer binders such as A-R, AC-20 XP, AC-20 5TR, and AC-15P showed much better performance in terms of bleeding/flushing behavior as indicated by lower non-recoverable creep compliance values. This shows that using low-cost softer binders in low ADT highways with even small amounts of truck traffic will result in bleeding/flushing leading to wet-weather traffic safety problems. There are many factors that can influence the performance of seal coats, and material selection is only one. If constructed properly and if the roadway is a good candidate, unmodified binders may perform well. For higher volume facilities, it still seems that polymer modified binders are likely to give better success.

Based on results from laboratory tests presented under Task 2, the strain sweep and MSCR tests are capable of identifying seal coat binders that can perform well in high-temperature conditions. Even though the material selection is only one of several factors that are necessary to ensure seal coats that perform well for the anticipated performance period, using the suitable binder appears to be a required element for good seal coat performance. Research findings from this research show that modified binders have a much higher likelihood pf performing well in hot weather conditions common to Region 6 states. There is a wide array of modifiers used in asphalt ranging from latex, copolymers such as Styrene-Butadiene-Rubber (SBR) and Styrene-Butadiene-Styrene (SBS), phosphoric acid, waste crumb rubber and combinations of them just to name a few. The current industry specifications try to pre-screen the type(s) of modifiers that are allowed in seal coat and asphalt concrete binders. However, the control of the modifier use and the assessment of their implications (both positive and negative) over an extended period is a very challenging task even if they are backed up by solid research. Therefore, more fundamental approaches may be needed to better understand the modification process, the effectiveness of modification practices, and their effectiveness and reliability in performance. One such method is a molecular simulation of the asphalt binder modification. This allows the assessment of how the modifier interacts with the asphalt at a molecular level, and how those interactions can lead to better or worse performance. Such a technique will not only allow highway agencies such as State DOTs to more effectively screen asphalts, but it will also allow binder suppliers to develop more effective asphalts by simulating both asphalt cement and the modifier. That way, the binder producer can evaluate asphalts obtained from different crude oil sources and plant types. Under Task 4 of this report, the methodologies and the results of research on molecular simulation are presented. This study, though small in scope, allowed the research team to assess the feasibility of using molecular simulation for more effective evaluation of modified asphalt binders.

TASK 4. MOLECULAR MODELING OF ASPHALT BINDER

## Research Plan

The main tasks in the molecular modeling part of the work were as follows:

### Preparation and Characterization of Realistic Model Structures

*Structure preparation:* Asphalt is a mixture of a very large number of organic molecules that fall in one of the following categories: saturated alkanes, asphaltenes, and polar and naphthene aromatics. *(15)* Some representative examples of these molecules as suggested in the literature *(15, 16)* are shown in Figure 7. In this work, the "model asphalt" was prepared by simply mixing the representative component molecules from each category in the compositions suggested in the literature. *(15)* An important aspect of the work is to determine the effect of polymeric additives such as styrene-butadiene rubber (SBR) on the mechanical properties of asphalt. The model generation procedure is non-trivial when these polymeric component or topological complexities such as cross-links are present in the system. In such cases, the required model structures are prepared by applying the simulated polymerization technique developed by this research team for this purpose. *(17-19)* In this approach, one starts with the required molecular composition of the mixture and then uses either simulated annealing algorithm or directed diffusion to connect the spatially close monomers.

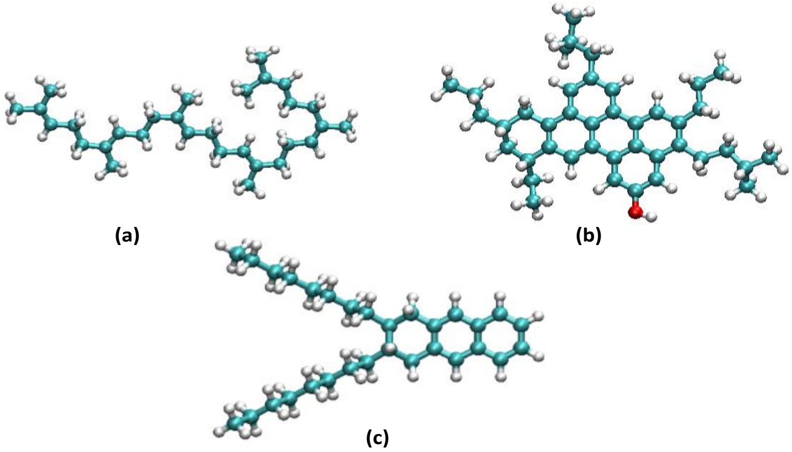

Figure 7. Representative molecules in asphalt, namely: (a) squalane, (b) asphaltene, and (c) dioctyl-cyclohexane-naphthalene. Carbon, oxygen and hydrogen atoms are shown in cyan, red and white colors.

Prior work has shown that such a simulated polymerization technique can be used to prepare well-relaxed model structures of polymers containing linear chains such as polystyrene$^3$ as well as complex topologies such as highly cross-linked epoxy. *(18-21)*. As a proof of concept, in preliminary work, we used the directed diffusion based simulated polymerization approach described above to build a model structure of asphalt containing SBR molecules (Figure 8).

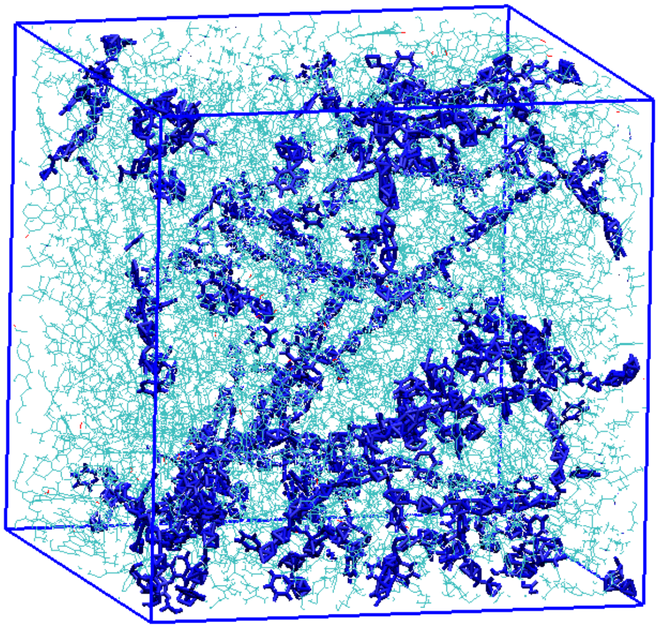

Figure 8. Model structure of asphalt (light blue color) containing SBR molecules (dark blue color).

*Model validation:* Before calculating the viscoelastic moduli of these model structures, it is important to validate the structures. This is achieved by determining the thermal and volumetric data of the systems and comparing the simulated values with the experimental data. In particular, the process starts with the model structures at a high value of temperature and cool these in a stepwise fashion using molecular dynamics (MD) simulations while monitoring the volume and the enthalpy of the system. This exercise yields values of the following volumetric and thermal properties: room temperature density, the coefficient of volume thermal expansion (CVTE), and glass transition temperature ($T_g$). (1*8-21*). The MD simulations are carried out using the LAMMPS simulation package. (*22*) The quantitative accuracy of the simulation results is determined by the force field parameters used to represent the interatomic interactions. For a large number of cross-linked polymer systems, previous simulation work *(18-21)* conducted by this research team has shown that the simulation results for thermal, volumetric and mechanical properties obtained using the general AMBER force field (GAFF) (*23-24*) are in excellent quantitative agreement with experimental data. The GAFF force field is used in this work as well; if a disagreement is found with experimental data, the force field parameters will be adjusted to achieve the agreement for the properties listed above. The validated model structures and the force field parameters are then used to determine the mechanical properties of these systems as described in the next section.

### Viscoelastic Moduli of the Asphalt Model Systems

The main viscoelastic properties of asphalt of interest are the storage (*G′*) and the loss moduli (*G′′*). In this work, the non-equilibrium molecular dynamics (NEMD) approach was used for determining the viscoelastic properties of the model structures. (*25*) Specifically, in this approach, the system will be subjected to oscillatory deformation by a modification of the equation of motion and the use of sliding brick periodic boundary conditions. The values of *G′* and *G′′* can then be determined by monitoring the time-dependent stress developed in the system in response to the imposed strain. Such simulation approach has been used in the literature (*26-27*) for determining the viscoelastic properties of polymeric systems, and the research team has used the steady shear version of the method for determining the viscosity of alkanes. *(28)*. The molecular modeling techniques described above was used to perform the following studies.

*Effect of additives:* This approach can be used to correlate the rheological properties of asphalt systems with the chemistry of the additives. As an example, the mechanical properties of model structures of the neat asphalt will be compared with those of the asphalt containing styrene-butadiene rubber (SBR) as the additive. Such a study will allow for a systematic investigation of the effect of the chemical functional groups in the additive molecules on the mechanical performance of asphalt. Furthermore, the effect of composition (i.e., the mass fraction of additives) on the mechanical properties of asphalt can also be readily characterized by studying asphalt containing different amounts of the additive.

*Effect of temperature change:* An important consideration in the process application is the ability of asphalt to sustain its performance characteristics through large temperature changes. The typical temperature range of interest for this purpose is -23 °C (~ -10 °F) to 70 °C (~ 158 °F). Once the asphalt model structures are prepared, these can be readily used to study the effect of temperature change on the viscoelastic properties of various asphalt compositions. This is achieved by using molecular simulations to determine the viscoelastic properties at selected temperatures at either end of the given temperature range. In addition to mechanical properties, the knowledge of the CVTE of the asphalt will also be important for determining its performance characteristics; specifically, a smaller value of CVTE should lead to a lower tendency for cracking. The CVTE of these asphalt systems can be readily determined from the volume-temperature data of these systems as described in the previous section.

In summary, the goal of this initial work will be to demonstrate the feasibility of using molecular simulations to characterize the viscoelastic properties of asphalt. Simulations allow for the scanning of large parameter space in a cost-effective manner; the simulation predictions help reduce the number of experiments to be performed for the targeted design of asphalt for given process conditions.

Molecular dynamics simulations have the ability for deciphering the mechanisms underlying the structural, dynamic, and rheological properties of asphalt. In this study, the atomistic model of AAA-1 asphalt as proposed by Li and Greenfield *(29)* was utilized to investigate the effect of the addition of SBR on the aggregation of asphaltene molecules, dynamics of asphalt constituents, and the viscoelastic properties of the system. The model structures of AAA-1 and AAA-1-SBR systems were validated by determining their volumetric properties (specific volume and glass transition temperature). *(28)* These model structures were then used to determine the structural, dynamic and rheological properties of neat asphalt and the SBR modified asphalt systems.

In what follows, the simulation methodology and the details of the results for the volumetric, structural, dynamic and rheological properties are presented. The results for the volumetric, structural and dynamic properties of AAA-1 asphalt and SBR modified AAA-1 asphalt was described in a recent publication by members of this research team. *(28)*

## Simulation Methods

We used the twelve-component model of AAA-1 asphalt as proposed by Li and Greenfield *(29)* that comprises the four major types of the constituent molecules (asphaltene, polar aromatics, naphthene aromatics and saturates). The intra- and inter-molecular interactions were determined using the general AMBER force field (GAFF). *(30, 31)* The AM1-BCC method *(15, 16)* was utilized to calculate the atomic charges. A cut-off distance of 9 Å was employed to calculate interactions between atoms. The long-range parts of the Lennard-Jones and electrostatic interactions were determined by the tail correction and the particle-particle-particle-mesh (PPPM) algorithms, respectively. *(17)* Initially, the molecules were placed in a cubic box with low density, and the density of the system was increased by applying a pressure of 100 atm. Finally, the systems were relaxed using molecular dynamics (MD) simulations under conditions of a constant number of molecules, pressure, and temperature (constant NPT) for a duration of 2 ns at T = 600 K and atmospheric pressure. The temperature and pressure of the systems were held constant by Nosé-Hoover thermostat and barostat. *(18, 19)* All simulations were performed by using the LAMMPS package, *(20)* and five replicas for each system were built for increasing the statistical accuracy.

In order to prepare the model structures of SBR modified asphalt, styrene and butadiene monomers were added to the AAA-1 asphalt system with a mole ratio of $x_s = 0.3\, x_b$, where $x_s$ and $x_b$ are the values of mole fraction of styrene and butadiene. Initially, the mixture of monomers and asphalt components was relaxed by using constant NPT MD simulations. The reaction between the styrene and butadiene monomers was then simulated by connecting the spatially closest monomers using the simulated annealing polymerization technique.[11-12] A representative snapshot of the structure of polymer modified asphalt is shown in Figure 9.

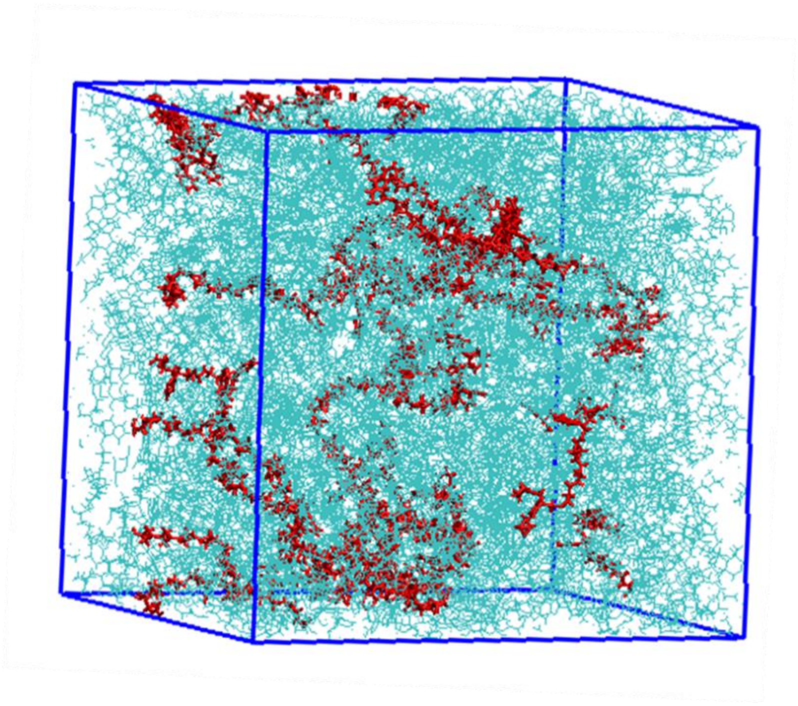

Figure 9. Simulation box of AAA-1-SBR system. Asphalt constituents and SBR chain are shown in cyan and red colors respectively.

## Results and Discussion

### Volumetric Properties

The model structures of AAA-1 and AAA-1-SBR (all of the results are presented for systems with SBR mass fraction = 0.065) systems were cooled down from 600 K to 80 K in a step-wise fashion using a cooling rate of 5 K/ns. It was found that the addition of SBR did not cause a significant change in the volumetric properties (specific volume and the glass transition temperature) of neat asphalt.[2] We note that the values of the glass transition temperature ($T_g$) determined from MD simulation are higher than the experimentally reported values due to the utilization of a very high cooling rate in the simulations. *(28)* This expected shift in the $T_g$ due to this high cooling rate can be calculated by using the Williams-Landel-Ferry (WLF) equation:[13] $\log a_T = \frac{-C_1(T-T_0)}{C_2+T-T_0}$, where $a_T$ is the normalized relaxation time of the system with respect to the relaxation time at temperature $T_0$, and $C_1$ and $C_2$ are the WLF equation parameters. If the shift in $T_g$ due to the cooling rate difference is considered, the corrected value of $T_g$ is in a close agreement with the value determined from the experiment. *(28)*

## Structural properties

The mechanical properties of asphalt are affected by structural changes in asphalt. In this regard, asphaltene aggregation is believed to play a role in determining rheological properties of asphalt.[14-15] To characterize this, the molecular structure of the systems was studied by determining the radial distribution function (RDF), which gives the normalized probability of occurrence of a molecule or an atom at a given distance *r* from another molecule or atom of interest. Our results for the RDF between the asphaltene molecules in the unmodified (neat) asphalt system (see Figure 10a) *(28)* indicate a tendency for aggregation of asphaltene-phenol and asphaltene-pyrrole molecules. As seen in the Figure 10b, the increase in the height of the first peak in the RDF for these asphaltene-phenol and asphaltene-pyrrole molecules in SBR modified asphalt system indicates that addition of SBR to asphalt increases the aggregation of these molecules; the other type of asphaltene molecule (asphaltene-thiophene) does not show a strong tendency for aggregation in either system. *(28)*

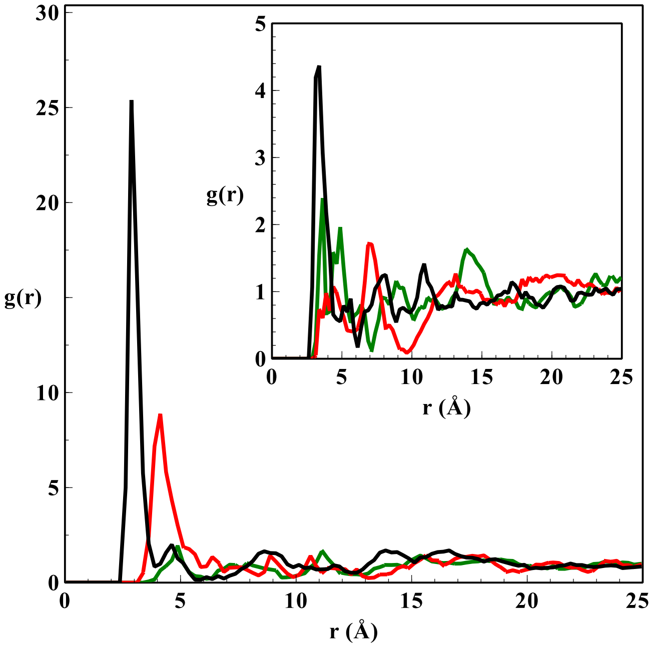

Figure 10a. RDFs of O-O atoms of asphaltene-phenol (black color solid line), N-N atoms of asphaltene-pyrrole (red color dot dash line), and S-S atoms of asphaltene-thiophene (green color dashed line) at a temperature T = 333 K in the AAA-1 asphalt system. Inset: RDF of O-N (black color solid line), O-S (red color dot dash line) and N-S (green color dashed line) atoms in the same system. (Taken from *(28)*).

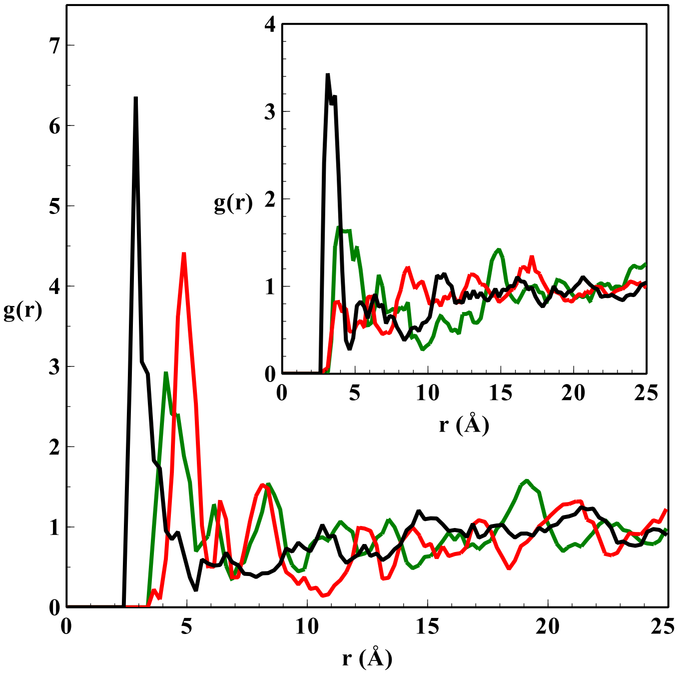

Figure 10b. RDFs in the SBR- AAA-1 asphalt system at a temperature T = 333 K. Lines have the same meaning as those in Figure 10a. (Taken from *(28)*).

Dynamic properties

In addition to the structure, molecular mobility also plays an important role in governing rheological properties of asphalt. The translational dynamics of different chemical components of asphalt was characterized by determining their mean-squared-displacement (MSD). Specifically, the MSD of asphaltene phenol, quinolinohopane, perhydrophenanthrene (PHPN), and squalane was monitored; these molecules were chosen as representatives of the asphaltene, polar aromatics, naphthene aromatics, and saturates constituent groups, respectively.

As seen in Figure 11, the MSD of the four selected components shows a size-dependent behavior. The asphaltene-phenol molecule, which has the highest molecular weight among the selected molecules, has the lowest translational mobility, while the squalane molecule shows the fastest dynamics due to its smaller molecular weight. Furthermore, as seen in Figure 12, the mobility of the component molecules of asphalt reduces by adding SBR to asphalt. This reduction in the mobility is more significant for larger molecules such as asphaltene phenol, compared to the smaller molecules.

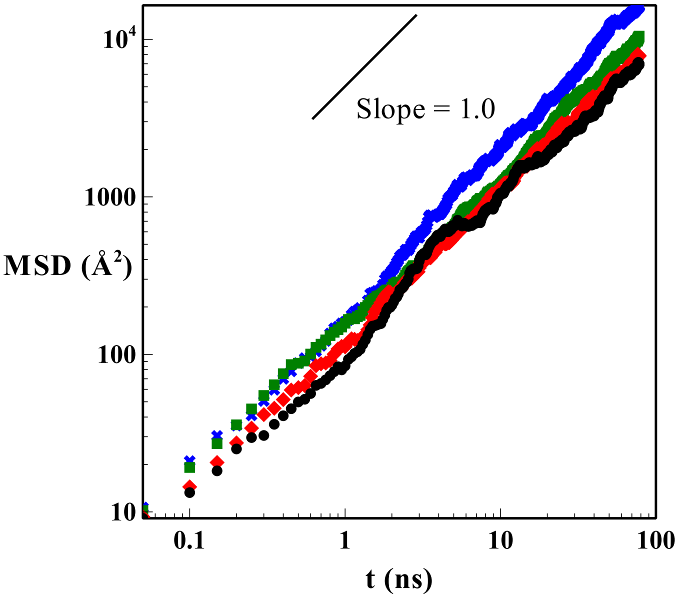

Figure 11. Time dependence of the MSD of asphaltene phenol (black circle), quinolinohopane (red diamond), PHPN (green square), and squalane (blue cross) molecules at temperature T = 520 K in the AAA-1 asphalt system. A line with slope = 1.0 (representative of diffusive behavior) is also shown as a guide to the eye. (Taken from *(28)*).

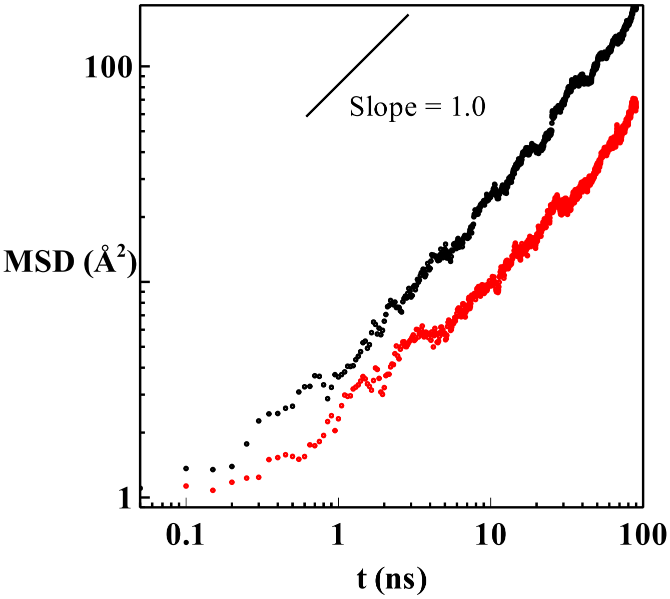

Figure 12. Comparison of the MSD of quinolinohopane molecules in the neat AAA-1 (black circle trendline above) and AAA-1-SBR (red circle trendline below) asphalt systems at temperature T = 400 K. A line with slope = 1.0 (representative of diffusive behavior) is also shown as a guide to the eye. (Taken from *(28)*).

The Einstein relation ( $D = \lim_{t \to \infty} \frac{\langle \Delta \vec{r}^2(t) \rangle}{6t}$ , where $\langle \Delta \vec{r}^2(t) \rangle$ is the mean-squared displacement (MSD) of the center of mass of each molecule) was used to calculate the diffusion coefficient of the selected components of asphalt. Assuming the validity of the Stokes-Einstein relationship, the Vogel-Fulcher-Tammann (VFT) equation *(26)* can be used to characterize the temperature dependence of the diffusion coefficient as follows:

$$\frac{1}{D} = \frac{1}{D_0} \exp\left( \frac{BT_0}{T - T_0} \right) \tag{1}$$

where $D_0$, $B$, and $T_0$ are the VFT equation constants.

The values of the reciprocal of the diffusion coefficient determined by the Einstein relation at different temperatures are shown in Figure 13 for different component molecules. As seen from the figure, the Arrhenius plot of the reciprocal of the diffusion coefficient shows a curvature at low temperatures, and the values follow the VFT equation functional form. The same behavior was also observed for the SBR modified asphalt system. The VFT equation parameter values obtained from fitting the diffusion data to equation (1) above are listed in Table 4.

Table 4. Results from the VFT equation fit to the diffusion data for the neat and SBR modified asphalts systems. (Taken from *(28)*).

| | $\log\left(1/D_0\right)$ | $\log\left(1/D_0\right)$ | $B$ | $B$ | $T_0$ | $T_0$ |
|---|---|---|---|---|---|---|
| Component | Neat | Modified | Neat | Modified | Neat | Modified |
| Asphaltene-phenol | 3.62 | 3.34 | 4.9 | 6.6 | 260.8 | 247.5 |
| Quinolinohopane | 3.34 | 3.39 | 6.0 | 5.8 | 247.1 | 255.5 |
| PHPN | 3.39 | 3.67 | 5.8 | 4.4 | 246.7 | 270.1 |
| Squalane | 3.61 | 2.73 | 4.4 | 14.2 | 261.4 | 167.2 |

## Rheological Characteristics

### Shear Viscosity

We used non-equilibrium molecular dynamics (NEMD) *(27)* method to obtain the shear rate dependence of asphalt viscosity. The values of the zero-shear viscosity of the neat AAA-1 asphalt system were determined at different temperatures over the range 380 K to 600 K. These values of the zero-shear viscosity follow the VFT functional form; this behavior is consistent with the results of the translational dynamics that also showed VFT behavior for the temperature dependence of the reciprocal of the diffusion coefficient of asphalt. The reduction in the mobility of different components of asphalt upon addition of SBR suggests that the AAA-1-SBR system will have a higher viscosity compared to the neat asphalt. Indeed, as seen in Figure 14, the values of the shear viscosity of the SBR modified system are higher than those of neat asphalt at lower shear rates.

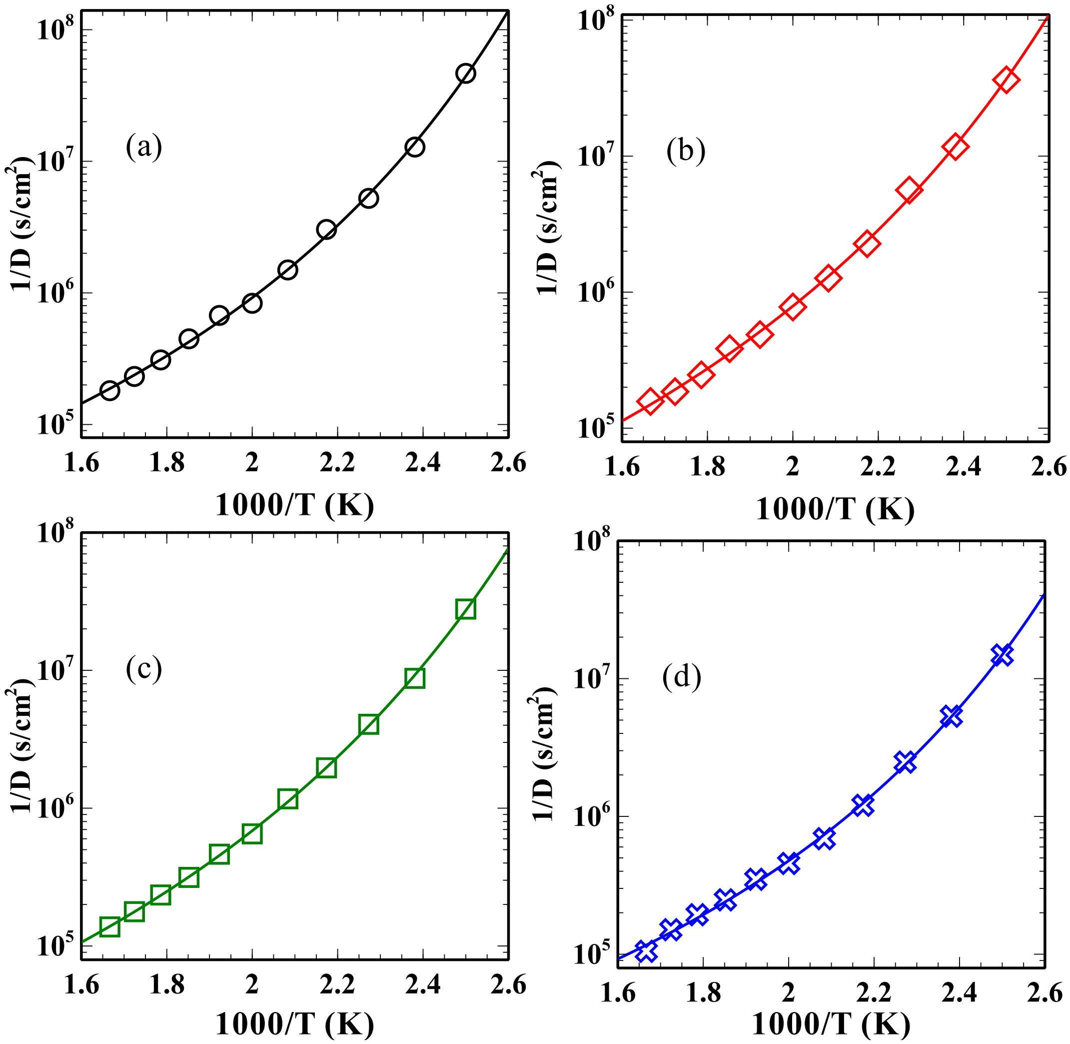

Figure 13. Reciprocal of self-diffusion coefficient for (a) asphaltene-phenol (black circle), (b) quinolinohopane (red diamond), (c) PHPN (green square), (d) and squalane (blue cross) molecules as a function of reciprocal temperature for the AAA-1 asphalt system. Error bars are of the same size as the symbols. The dotted lines show the VFT fits. (Taken from *(28)*).

## Viscoelastic Moduli

The viscoelastic moduli of the neat and SBR modified asphalt systems were also determined using the NEMD method. *(27)* A sinusoidal shear deformation ($\gamma(t) = \gamma_0 \sin(\omega t)$, where $\gamma_0$ is the amplitude of the applied strain and $\omega$ is the frequency) was imparted on the simulation box to determine the frequency response of the system at different temperatures. The response of the system was characterized by determining the shear stress in the system. The storage and loss moduli ($G'$ and $G''$) of these systems then were determined from the shear stress as follows

$$G' = \frac{\sigma_0}{\gamma_0}\cos(\delta)$$

$$G'' = \frac{\sigma_0}{\gamma_0}\sin(\delta)$$

Where, $\sigma_0$ is the magnitude of the stress response and $\delta$ is the phase angle of the stress response.

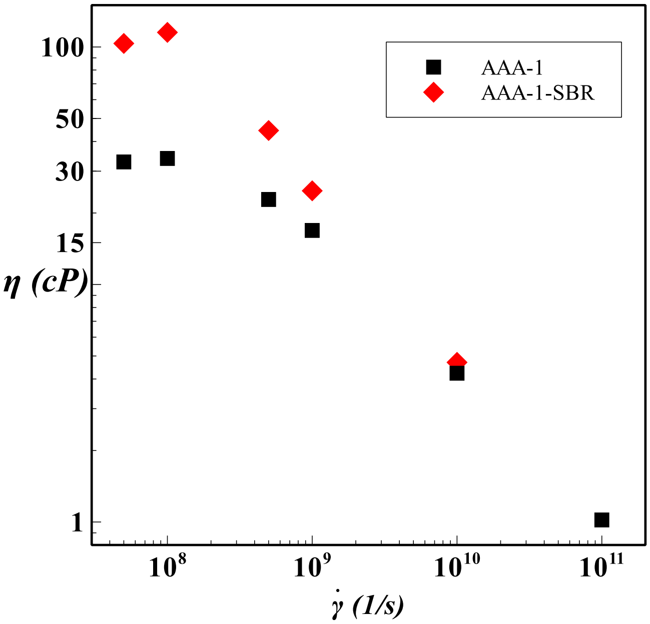

Figure 14. The viscosity of the AAA-1 and AAA-1-SBR asphalt systems as a function of shear rate at temperature T = 440 K.

A comparison of the $G'$ and $G''$ values of the neat asphalt and SBR modified asphalt at two different temperatures is shown in Figures 15 and 16 respectively. The values of the moduli $G'$ and $G''$ increase with an increase in the frequency at a high temperature (i.e. in the rubbery state), while at a low temperature (i.e., in the glassy state), the values of these moduli show a very small change at the high frequencies that are accessible in molecular simulations. Furthermore, at a low temperature, the value of the storage modulus is higher than that of the loss modulus for both neat and SBR modified asphalt systems. This trend changes with an increase in the temperature such that the loss modulus has a higher value compared to the storage modulus for both the neat and the SBR-asphalt systems at the high temperature.

Our results show that the effect of the addition of SBR on viscoelastic moduli is only observed at the high temperatures. Specifically, as seen in Figures 15 and 16, at low temperatures, neat and SBR-modified asphalt have effectively the same values of the moduli. On the other hand, at high temperatures, both storage and loss moduli of SBR-modified asphalt are higher than the corresponding moduli values of the neat asphalt. We also observed that the time-temperature superposition (TTS) principle[13] which is commonly used for the analysis of experimental data could be used to collapse the viscoelastic property data from simulations onto master curves.

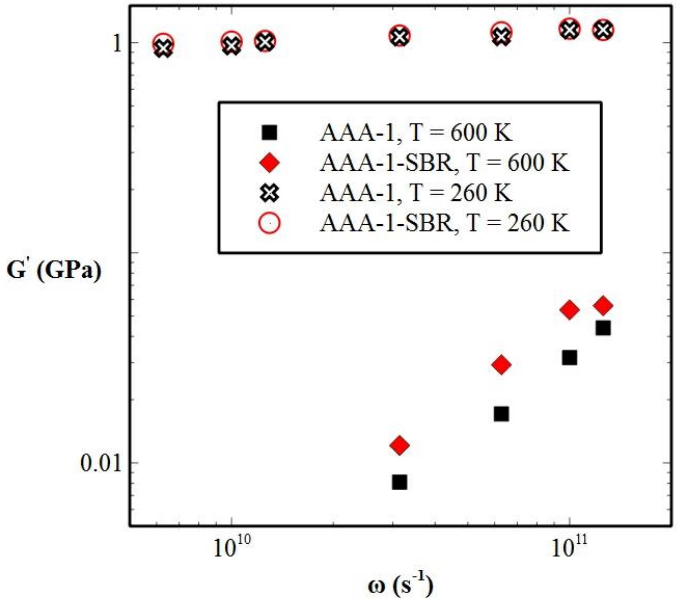

Figure 15. A comparison of the storage modulus of AAA-1 and SBR-AAA-1 asphalt systems at two different temperatures.

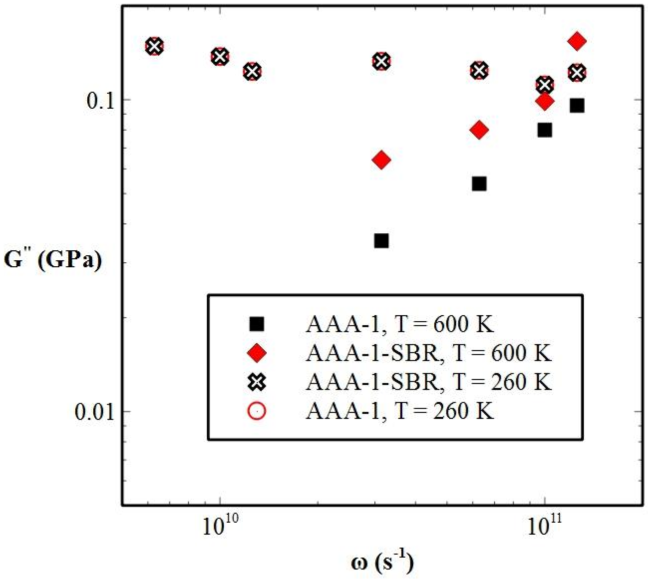

Figure 16. A comparison of the loss modulus of AAA-1 and SBR-AAA-1 asphalt systems at two different temperatures.

## Summary

MD simulations were used in this work to study the effect of the addition of SBR on the volumetric, structural, dynamic, and rheological properties of asphalt. It was found that addition of SBR increases the degree of asphaltene aggregation in the system. The temperature dependence of the reciprocal of diffusivities of various components of neat and SBR modified asphalt systems was consistent with the VFT functional form. A study of the translational dynamics of the asphalt constituents showed that the mobilities of the asphalt constituents reduce with the addition of SBR, the reduction being more prominent for the larger constituent molecules of asphalt.

The effect of the addition of SBR on the rheological properties of asphalt was also studied. The shear viscosity of the SBR modified system at a high temperature (i.e., in the rubbery state) was significantly higher than that of the neat asphalt system. This observation agrees with the diffusivity results that showed that the addition of SBR to asphalt reduced the translational mobility of the system constituents. The addition of SBR did not affect the moduli of asphalt at lower temperatures whereas both storage and loss moduli of asphalt increased on addition of SBR at higher temperatures.

## CONCLUSIONS AND RECOMMENDATIONS

This research project was conducted with two primary objectives. They are, (1) facilitate the development of new asphalt modification protocol(s) with the help of novel techniques to assess material quality, and (2) assess the feasibility of a molecular dynamics (MD) based protocol that can evaluate modified asphalts for enhanced performance. The work was carried out with a particular focus on improving binder performance and resilience under extreme high-temperature conditions in flexible pavements containing preventive maintenance treatments such as seal coats in the FHWA Region 6 States.

According to the EPA, depending on emission scenarios the global average temperature will rise by 2 to 11.5 °F, and the U.S average temperature will rise by 4 to 11 °F over the next century. The number of days above 90 °F projected to increase throughout the U.S, especially in the southeast and southwest areas that are also expected to see 150 or more days with temperatures 90 °F or above, under high emission scenarios. Such high temperatures are also projected to occur more frequently. (EPA, 2014) With these projections, in almost every scenario, the temperatures of the FHWA Region 6 states are projected to rise by significant levels from where they are today. Considering the extent of negative performance impacts from the 2009 and 2011 droughts in FHWA Region 6, It is prudent for the highway agencies to find new ways to develop novel material systems that can be resilient under forecasted high-temperature scenarios. With the sporadic but more frequent nature of extreme temperatures that are becoming more common, development of these novel materials also requires novel tools to predict material performance.

MD simulations were used in this work to study the effect of the addition of Styrene-Butadiene-Rubber (SBR) on the volumetric, structural, dynamic, and rheological properties of asphalt. It was found that addition of SBR increases the degree of asphaltene aggregation in the system. A study of the translational dynamics of the asphalt constituents showed that the mobilities of the asphalt constituents reduce with the addition of SBR, the reduction being more prominent for the larger constituent molecules of asphalt. The effect of the addition of SBR on the rheological properties of asphalt was also studied. The shear viscosity of the SBR modified system at a high temperature (i.e., in the rubbery state) was significantly higher than that of the unmodified (neat) asphalt system. This observation agreed with the diffusivity results that showed that the addition of SBR to asphalt reduced the translational mobility of the system constituents.

Based on results from laboratory tests presented under Task 2, the strain sweep and multiple stress creep recovery (MSCR) tests are capable of identifying seal coat binders that can perform well in extreme high-temperature conditions. Even though the material selection is only one of several factors necessary to ensure seal coats that perform well for the anticipated design life, using the suitable binder appears to be a crucial element to ensure well-performing and resilient seal coats. Findings from this research show that modified binders have a much higher likelihood of performing well in hot weather conditions common to Region 6 states. A wide array of modifiers used have been used in asphalt ranging from latex, copolymers such as SBR and Styrene-Butadiene-Styrene (SBS), phosphoric acid, waste crumb rubber and combinations of them just to name a few. The current industry specifications are developed to pre-screen asphalt modifiers that can be used with binders in seal coats and asphalt concrete. However, the assessment of the modifier impact over an extended period is a challenging task even if they are backed up by results from extensive standardized tests. Therefore, more fundamental approaches are needed to better understand the modification process, the effectiveness of modification practices, and their effectiveness and reliability in performance. One such method is a molecular simulation of the asphalt binder modification. This allows the assessment of how the modifier interacts with the asphalt at a molecular level, and how those interactions can lead to better or worse performance. Such a technique will not only allow highway agencies such as State DOTs to more effectively screen asphalts, but it will also allow binder suppliers to develop more effective asphalts by simulating both asphalt cement and the modifier. That way, the binder producer can evaluate asphalts obtained from different crude oil sources and plant types. Under Task 4 of this report, the methodologies and the results of research on molecular simulation are presented. This study, though small in scope, allowed the research team to assess the feasibility of using molecular simulation for more effective evaluation of modified asphalt binders.

This research has shown that MD simulations can be effectively used to evaluate the interaction of asphalt binder modifiers with asphalt cement, and the simulation results can also be used to more fundamentally evaluate the short- and long-term effects of modified asphalt binders under a wide array of service conditions, more specifically extreme high temperatures. The technique is ready for implementation in a controlled setting where modified binders, both conventional and novel, can be used in actual projects where field performance during a two-year period can be monitored and correlated with MD simulations as well as rheological and standard quality control tests.

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