Evaluation of Thermal Oxidative Aging Effect on the Rheological Performance of Modified Asphalt Binders

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ABSTRACT

Modified asphalt binder, which is combined by base binder and additive modifier, has been implemented in pavement industry for more than 30 years. Recently, the oxidative aging mechanism of asphalt binder has been studied for several decades, and appreciable finding results of asphalt binder aging mechanism were achieved from the chemistry and rheological performance aspects. However, most of these studies were conducted with neat binders, the research of aging mechanism of modified asphalt binder was limited. Nowadays, it is still highly necessary to clarify how the asphalt binder aging happens with the modified asphalt binder, what is the effect of the different modifiers (additives) on the binder aging process, how the rheological performance changes under the thermal oxidative aging conditions and so on.

The objective of this study was to investigate the effect of isothermal oxidative aging conditions on the rheological performance change of the modified and controlled asphalt binders. There were totally 14 different sorts of asphalt binders had been aged in the PAV pans in the air-force drafted ovens at 50°C, 60°C and 85°C for 0.5 day to 240 days. The Fourier-Transform Infrared Spectroscopy (FT-IR) and Dynamic Shear Rheometer (DSR) were used to perform the experiments.

The analysis of rheological indices (Low shear viscosity-LSV, Crossover modulus-G*c, Glover-Rowe Parameter-G-R, DSR function-DSR Fn) as a function of carbonyl area (CA) was conducted. With the SBS modification, both of the hardening susceptibility of the rheological index-LSV and G-R decreases compared with the corresponding base binder. The TR increased the hardening susceptibility of all the
rheological indexes. While for the G\*c, SBS increases the slope of the most modified asphalt binders except A and B_TR_X series binders.

The multiple linear regression statistical analysis results indicate that the oxidative aging conditions play an important role on the CA, and rheological performance indexes. The modifiers-SBS and TR have different directional effect on these parameters.

The field asphalt binder carbonyl area prediction was conducted. The pavement temperatures which were calculated by TEMP software were input into MATLAB™ as a parameter with other factors, e.g the asphalt binder oxidative aging parameters, the binder film thickness, the air void radius, etc., to calculate the field asphalt CA value as a function of time out to 20 years. It was found that the different rheological index method resulted different conclusion with the asphalt binder. The SBS modified asphalt binders of A, C version and B version had close average increasing rate of LSV, higher average decreasing rate of G\*c, lower average increasing rate of DSR Fn compared with the corresponding base binders. D_HPM had lower average increasing rate of LSV, G\*c and DSR Fn than base binder Base D. The tire rubber modified binder B_TR had higher average increasing rate of LSV, DSR Fn, and higher average decreasing rate of G\*c than base binder Base B.

The main finding of this study was that the modifier SBS and tire rubber can reduce the thermal oxidation aging rate (k_f and k_c) compared with the corresponding base binder, the activation energy was asphalt binder source dependent. For the hardening susceptibility, the modifiers-SBS, X, Y, Z reduced the HS of LSV and G-R. The tire rubber slightly increased the HS of LSV and G-R. A_PM, B_TR_X_PM reduced the HS of G\*c and other modified binders increased the HS of G\*c.
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CHAPTER 1 INTRODUCTION

1.1 General Introduction

Asphalt binder aging is an important factor that influences the whole life performance of asphalt pavement in the field. For example, within the asphalt binder aging, the pavement surface becomes brittle and loses the stress relaxation capability, and then fatigue and thermal cracking occurs under the traffic loading or environmental condition. As such, the mechanism of binder aging addressed on the chemical reaction or the effect on rheological performance has been studied for more than one century (Hubbard and Reeve, 1913). However, due to the natural complexity of the asphalt binder combination and the added modifier, and the numerous variables of asphalt mixture (i.e. air void content, asphalt film thickness, aggregate mineralogy, gradation, etc.), as well as the field environment labile conditions (i.e. temperature, radiation, moisture, pressure, etc.), thus these combined variables unfortunately lead to the aging mechanism becoming more difficult to characterize. Even though there are so many variables, the progress of asphalt binder aging studies made in the past decades is prodigious.

The pavement research group of Western Research Institute (WRI) had taken tremendous efforts on the study of oxidation aging effect on the asphalt binder chemical component and the performance-related physical properties change from the micro and macro scale level, respectively. It has been found that the sensitivity of asphalts to oxidation aging that induced hardening is highly source (chemical composition) dependent (Petersen, 2009). Others have also studied the primary mechanism of asphalt
binder oxidation aging, modified asphalt binder aging, field asphalt mix aging modeling, and the technology (seal coat) of resistance on asphalt binder aging in recent decades (Lunsford, 1994; Liu et al., 1996; Ruan et al., 2003; Glover et al. 2005, 2008; Prapaitrakul, 2009; Han, 2011).

Simultaneous and large scale studies have systematically studied the asphalt binder thermal oxidation aging effect with different asphalt binder sources, asphalt binder content, air void level and aggregate sources on the laboratory mix performance, such as thermal cracking, rutting, fatigue and moisture damage resistant ability and binder rheological performance under the ARC programs (Morian, 2014; Alavi, 2014).

A widely accepted agreement is that under the asphalt binder aging condition, the nonpolar fractions, naphthene aromatics, become polar fractions, polar aromatic and asphaltenes, which play an important role on asphalt binder flow property-viscosity (Petersen, 2009). Asphalt oxidation aging causes the binder becomes stiffer and more brittle, then decreases the capability of releasing tensile stress and the effective adhesion strength between asphalt and aggregate.

Currently a significant portion of the overall effort put forth as part of the asphalt binder aging study not only includes the thermal oxidation aging, but also extends to the radiation aging, weather aging, moisture aging, RAP aging, porous asphalt mix aging, WMA aging, antioxidant agent and recycling agent study, etc. (Lu et al., 2002; Durrieu, et al., 2007; Moouillet et al., 2008a, 2008b; Hagos, 2008; Xiao et al., 2015).
1.2 Problem Statement

Nowadays, more and more modified asphalt binders are used in the pavement industry to improve specific performance, such as resistance to rutting, fatigue cracking, or low temperature cracking, etc. Undoubtedly, these modifiers have an influence on the chemical reaction between base asphalt binders and ubiquitous oxygen, which definitely increases the complexity of the asphalt binder aging mechanism. Further, these questions, such as what is the extent of this influence and what are the main factors to determine these effects, are still not clearly understood. It is highly necessary to have more related projects, i.e. SHRP 2, NCHRP project 9-10, 9-23, 9-36, 9-52, and 9-54, to be proposed to study the asphalt binder aging issues.

1.3 Objective of Study

The objective of this study was investigating the effect of different asphalt modifiers (SBS, tire rubber, and additional base binder sources-X, Y, and Z) on the asphalt binder rheological performance under specific oxidation aging conditions. This objective can be divided into three aspects: 1) the asphalt binder kinetic reaction performance; 2) the asphalt binder physical rheological properties, such as the shear modulus, phase angle, and the hardening susceptibility; 3) the relationship between the base binder or modifier and the corresponding behavior; 4) the field binder oxidation aging CA prediction.

1.4 Scope of Study

Based on the interest of this study, there are 14 different asphalt binders, which include Base A, Base C, Base D and corresponding SBS modified asphalt binders, and Base B, with combinations of SBS, TR, X, Y, and Z modified asphalt binders, selected to conduct
the isothermal forced-draft oven aging and evaluated the related physiochemical performance change under the effect of thermal oxidative aging.
CHAPTER 2 LITERATURE REVIEW

2.1 Asphalt Binder Modification

Asphalt, which is also called “bitumen”, is defined as “A dark brown to black cementitious material in which the predominating constituents are bitumens which occur in nature or are obtained in petroleum processing.” by American Society for Testing and Material (ASTM) institute (ASTM Designation D8). The first implementation event of asphalt was recorded about 6000 B.C., a thriving shipbuilding industry produced and used asphalt (The asphalt handbook 1989). This reference also documented that the rock asphalt was used in France for floor, bridge, and sidewalk surfacing in 1802. In United States, the first bituminous mixtures were used for sidewalks, crosswalks and even roads starting in the late 1860s. Then later the well-known trial asphalt mix paving projects, such as AASHO, SHRP, WesTrack etc. were conducted to evaluate the applicability of asphalt mix in the United States.

Asphalt is one of the most common materials used in the pavement industry due to its particular advantage of adhesive, highly waterproof and durable properties. However, different types of distress, i.e. rutting, cracking, moisture damage etc. eventually happened after several (2-5) years of service. Therefore, seeking a higher bonding strength and more durable, cost-effective asphalt material aroused the interest of pavement engineers in recent decades, especially since more and more heavy trucks are running on the highway which is taking a toll on the pavement structure.

Asphalt binder modification is one of the prevailing ways to improve the specific physical performance of base asphalt binder by using different modifiers and
modification processes. Compared with the base binder, the benefit of the modified asphalt binder are improving the stiffness to resistant rutting, extending the tensile stress range to make it more resistant to cracking, and increasing the adhesive strength with the aggregate to decrease the probability of moisture damage. NCHRP Project 9-10 “Superpave Protocols for Modified Asphalt Binders,” systemically studied the characterization of different modified asphalt binders in Superpave mix design (Bahia et al., 2001). It was found that the current AASHTO MP1 specification does not adequately characterize the performance of modified asphalt binders and the potential performance of asphalt binder is underestimated. The studies also indicated that the current Superpave mixture tests, such as AASHTO TP7, TP9, can satisfactorily characterize the performance of modified HMA mixtures. It has also been summarized that the asphalt binder original resource has a major effect on the properties of the final modified product, such as the compatibility of the asphalt, which are mainly governed by the continuous phase morphology and the modifier molecular weight (McNally, 2011).

Polymer modification of asphalt binders is not a new concept and has been progressively more commonplace over the past several decades. While several agencies utilize unmodified asphalts, many have increasingly become reliant upon polymer-modified asphalt binders with a fair portion of those located in climatic regions that experience significantly higher levels of oxidation, such as the western and southwestern United States, for example. The accelerated aging in these regions is often attributed to elevated temperatures during the summer months, lack of an extended hard freeze in the winter months, and increased solar exposures, both temperature and ultraviolet (UV) radiation, as a result of the reduced moisture and atmospheric humidity levels.
Due to the increased levels of aging taking place in such locales where modified asphalt binders are becoming more prevalent, it is becoming increasingly important to characterize the benefits afforded with the polymer modification process. It is critical for state highway agencies (SHAs) as well as other municipalities to be able to quantify the benefits of modification in order to adequately utilize the dwindling transportation budgets and to justify the additional cost of the polymer.

In comparison to neat asphalt binders, the implemented modifiers have specific enhancements to the physical properties and rheological performance of asphalt binders, such as improving the ductility, expanding the relaxation spectra, and increasing the overall strength. For instance, the triblock styrene-butadiene-styrene (SBS), diblock styrene-butadiene-rubber (SBR), and ethylene-vinyl acetate (EVA) have been known to make asphalt binders more ductile at low temperature which increased the resistance to thermal cracking and decreased the rutting potential at high temperatures by stiffening the asphalt binders (Woo et al., 2007a, b). In general, improvement in asphalt binder ductility in conjunction with the improved elastic behavior due to polymer modification can have a positive influence on the cracking resistance of asphalt mixtures (Woo et al, 2007a, 2007b; Airey, 2003; McDaniel and Bahia, 2003; and Sebaaly et al. 2002).

Previous studies have shown the capability of polymer modifiers to lessen the deteriorative oxidative aging hardening effects (Lu and Isacsson, 1999; Glover et al., 2005). Accordingly, more durable asphalt pavements can be expected from the use of polymer modification (Glover et al., 2005).
Similar efforts to increase performance of asphalt binders and to capitalize on the development of recycling technologies, the usage of waste materials in infrastructure construction, namely the inclusion of tire rubber or ground tire rubber has earned a good deal of attention from pavement researchers. Studies searching into the mechanism of these modification techniques have indicated that the blending mechanism between the rubber and neat asphalt binders is largely attributable to the penetration of the asphalt binder into the polymer particles, specifically the styrene domain which tends to swell the rubber particle (Navarro et al. 2010; Airey, 2004; Bahl et al. 1993). This complex interaction tends to create a strong link between the asphalt binder and the rubber, which may give rise to significant changes in the behavior of the modified asphalt binder.

2.2 Asphalt Binder Oxidation Aging Study Methods

As mentioned previously, the asphalt binder aging has earned the attention of pavement researchers or engineers for several decades. Due to the complex field environmental condition, it is impractical to study the asphalt binder aging factors independently in the outside environment. Therefore, a significant amount of effort has been focused on the laboratory asphalt binder aging method study to evaluate the variable factors separately and comparably, and to simulate the field asphalt mix aging during the construction and in-service phases.

Chronologically speaking, as shown in the Table 2-1, there are more than 8 different asphalt binder aging experimental methods that have been studied in the laboratory (Hoppel et al., 1991; Bell, 1989; Hanson et al., 2000; Verhasselt, 2003; Zaniewski, 2004; Anderson et al., 2012; Dongre, 2004; Airey, G.D., 2003). Most of them
are designed for either short term or long term aging separately, except the RCAT method is standardized for both aging. In the Superpave PG system, the rolling thin-film oven test (RTFOT) and pressure aging vessel (PAV) tests are used to simulate the plant mixing, laydown short-term aging, and the field long-term service aging, are the most commonplace used methods in the laboratory or road construction industry.

However, the current asphalt binder aging method also has its own problem when the asphalt binder is modified. NCHRP Project 9-36 mentioned that the RTFOT is not applicable to age some modified binders because it can’t roll the bottle uniformly during the test, e.g. HPM binder. Another problem should be noted here is that some modified asphalt binder spills out of the bottle during the test, e.g. TR modified binder (Verhasselt et al., 2003; Anderson et al.; 2012).

With the flaws of the current asphalt binder aging methods, it is necessary to find a uniform and practical way to study the asphalt binder aging in the laboratory. Based on the previous asphalt binder studies, the modified the POV procedure by using 1 mm thickness asphalt binder which was distributed evenly in the steel trays to conduct the aging process (Lau et al., 1992; Lunsford, 1994; Morian, 2014). There was one methodology that was designed to minimize the oxygen diffusion effect on the asphalt binder when the aging process occurs, and it was found a strong relationship between the oxygen diffusivity and the low-shear rate limiting viscosity (Han, 2011). This method was implemented in this modified asphalt binder aging study, the details were discussed in the following chapter.
The Mechanistic-Empirical Pavement Design Guide (MEPDG) is a state-of-the-art design approach which is implemented by State Highway Agencies (SHA) in the United States. This semi-mechanistic based method uses the global aging system models to take account of the asphalt binder aging effect on the pavement performance. There are four asphalt binder aging models considered in Global Aging System (GAS) according to the MEPDG guide: 1) Original to mix/lay-down model; 2) Surface aging model; 3) Air void adjustment; and 4) Viscosity-depth model. These models mainly predict the viscosity as a function of surface aging, air void level, depth to evaluate the aging extent at any time and depth in the pavement system (Mirza and Witczak, 1995). The viscosity of the aged binder has an effect on the master curve of the mixture and corresponding shift factors by using the sigmoidal function. However, the applicability and accuracy of these GAS models still need to be evaluated.

In the MEPDG, there are three binder oxidation hypotheses: 1) binders oxidative aging only occurs at the top one inch of pavement layer; 2) asphalt binder aging hardening to a limited viscosity and then terminated; and 3) concerning the impact of binder oxidation on asphalt mixture performance, the design guide assumes that binder oxidation does not fundamentally affect the resistance to fatigue of the mixtures as a function of loading cycle (AASHTO, 2004). Obviously, these considerations are not fully consistent with the field of asphalt pavement aging or at least it underestimates the asphalt binder aging extent which leads to the mistaken prediction of the pavement duration life (Glover et al., 2007). The calibration or further research of the GAS models is beyond this study.
Except the leading asphalt binder aging study conducted by the SHRP program, the ongoing research projects funded by the National Cooperative Highway Research Program, such as NCHRP 9-23, NCHRP 9-52, and NCHRP 9-54, were proposed to refine the laboratory long-term aging procedure for asphalt binder and short-term and long term aging procedure for asphalt mix, respectively. There is no doubt that these projects should consider the protocol that needs to work for the modified asphalt binder or mix.
<table>
<thead>
<tr>
<th>BINDER AGING TYPE</th>
<th>TIME</th>
<th>AGING CONDITION</th>
<th>STANDARD</th>
<th>COMMENT</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thin-film Oven Test (TFOT)</td>
<td>1960</td>
<td>50g binder, 5h at 163°C</td>
<td>AASHTO T149/ASTM D1754</td>
<td>Short-term aging</td>
<td>SHRP A-305</td>
</tr>
<tr>
<td>Rolling Thin-Film Oven Test (RTFOT)</td>
<td>1970</td>
<td>35g binder, 163°C for 85 mins</td>
<td>AASHTO T240/ASTM D2872</td>
<td>Short-term aging</td>
<td>FHWA/TX-02/1742-1 Report</td>
</tr>
<tr>
<td>California Tilt-Oven Durability Test (TODT)</td>
<td>2000</td>
<td>35g binder, 111°C for 168h OR 113°C for 72h.</td>
<td>California Test 374</td>
<td>Simulate the effect of four years of desert aging</td>
<td>Douglas I. Hanson et al., 2000</td>
</tr>
<tr>
<td>Thin-film Accelerated Aging Test (TFAAT)</td>
<td>1989</td>
<td>0.16mm binder thickness, atmospheric pressure, 113°C for 72h</td>
<td>TxDOT Draft</td>
<td>Long-term aging</td>
<td>SHRP A-305</td>
</tr>
<tr>
<td>Rotating Cylinder Aging Test (RCAT)</td>
<td>2001</td>
<td>0h, 17h, 65h and 140h at 90°C, cylinder rotation rate of 1 rv/min, an oxygen inflow rate of 4.5 L/h</td>
<td>BBRC ME70/01</td>
<td>Short and Long-term aging</td>
<td>BRRC ME70/01 and A. Verhasselt, 2003</td>
</tr>
<tr>
<td>Pressure Aging Vessel (PAV)</td>
<td>2000</td>
<td>50g binder, 20h at 90°C or 100°C or 110°C under 2.1 Mpa</td>
<td>AASHTO R 28/ASTM D6521</td>
<td>Long-term aging</td>
<td>John P. Zaniewski et al, 2004</td>
</tr>
<tr>
<td>Stirred Air Flow Test (SAFT)</td>
<td>2001</td>
<td>250g binder, 700 rpm, 30 mins and 72h at 163°C</td>
<td>TxDOT Draft</td>
<td>Short-term aging</td>
<td>NCHRP 709, FHWA/TX-02/1742-2 Report</td>
</tr>
<tr>
<td>Modified German Rotating Flask (MGRF)</td>
<td>1991</td>
<td>200 g binder, 2000 ml flask, 45° tilt, 2000 ml/min air flow, at 163°C, 165°C and 168°C bath, 10,20,30 rpm, 201 min</td>
<td>Report by Hoppel et al. as guideline</td>
<td>Short-term aging, advance for PMA binder aging</td>
<td>Hoppel et al., 1991; Raj Dongre, 2004 and NCHRP 709</td>
</tr>
</tbody>
</table>

Table 2.1 Laboratory Asphalt Binder Aging Methods
2.3 The State of Asphalt Binder Aging

The basic asphalt binder composition proportion change is the primary reason to take account of the asphalt binder aging hardening. So far, there is a lot of effort to study the physiochemical reaction during the asphalt binder aging process (Corbett et al., 1975; Pfeiffer et al., 1940; Petersen et al., 1986, 1993; Lin et al., 1995; Liu, 1996; Domke et al., 1999, 2000; Glover et al., 2005; Han et al., 2013; Morian et al. 2013, 2014, 2015). Even though most of the pavement engineers are more concerned with the field pavement performance, the micro chemical-physical properties of these materials are the fundamental issue impacting on the macro performance change and such related studies are limited. Therefore, understanding the mechanism of the reaction between asphalt binder molecule and oxygen is the key point to accurately evaluate and predict the pavement performance over time.

Due to the complex nature and composition of asphalt binder, it is difficult to get detailed information on the binder microstructure at the molecular level. However, it is practical to analyze the asphalt component which has similar molecular weight or physical properties and separate the asphalt binder into several proportions by aid of a chemical solvent extraction process, such as SARA-saturate, aromatic, resin, asphaltene. (Corbett, 1969). Compared with these four fractions, the polarity in the increasing order saturates, aromatics, resin and asphaltenes. A general reaction occurred between the asphalt binder and the surrounding oxygen is that the non-polarity or soft component, i.e. the aromatic, or resin, oxidized to produce the heavier molecular component-asphaltenene by several processes. (Petersen, 2009; Glover, 2013). Usually, the chemical functional
group analysis (FGA) was conducted to evaluate the component proportion by utilizing microscopic approach, such as NMR, FT-IR. (Jennings et al., 1993). FT-IR is a common tool to identify the functional group in organic material science due to its high sensitivity, accuracy, repeatability and productivity. And the final oxidation products of asphalt binder are carbonyl and sulfoxide groups (Jin, 2011).

Additional studies on oxidized polymer-modified asphalt binders by analyzing the oxygen related chemical functionalities with FT-IR approach using attenuated total reflectance (ATR) measures, determined that the polymer concentration remained constant in the asphalt binder during an oxidation process thus refuting portions of the polymer degradation complaint (Yut et al., 2014).

Physical properties, i.e. ductility, softening point, specific gravity, penetration, etc. and rheological properties, i.e. viscosity, dynamic shear modulus, multiple stress creep recovery, etc. are commonly used to study the effects of oxidative aging on asphalt binders (Zhang et al., 2005; McNally, 2011). Evaluations of the influence of various modifiers, such as SBR, SBS, ground tire rubber (GTR), on the oxidative aging and corresponding physical property changes indicated that the modifiers have the potential to significantly reduce oxidative aging rates and hardening susceptibility parameters, though the benefits were found to be asphalt binder dependent (Ruan et al., 2003). Furthermore, it was also concluded that the oxidative aging can result in damage to the polymer network which then can significantly reduce the effectiveness of the polymer on the ductility of the asphalt binder. Consequently, a significant reduction in ductility improvement of selected SBS-modified asphalt binders has also been reported (Woo et al,
Nevertheless, lower hardening susceptibility associated with lower oxidation rate in SBS-modified asphalt binders in comparison with the corresponding base binder has also been reported (Ruan et al., 2003).

Styrene-Butadiene-Styrene (SBS) is a well-recognized elastomer which has been commonly used in asphalt pavements. Remarkable strength and elasticity of SBS-modified asphalt binders can be created from the physical cross-linking of the molecules into a three dimensional network (Airey, 2003). Nonetheless, the degree of SBS modification depends on the composition of the asphalt binder, SBS concentration and structure, as well as binder-polymer compatibility (Lu et al., 1998 and 1999, Airey, 2003). Others have investigated the aging characteristics of polymer-modified binders in porous asphalt pavements utilizing X-ray tomography, gel permeation chromatography (GPC), Fourier-transform infrared spectroscopy (FT-IR), and dynamic shear rheometer (DSR) measures (Lu et al., 2010). A general conclusion indicated that the degradation of the polymer had occurred mainly during the production and early in-service life of the pavement. However, the polymer did provide a benefit to the hardening effect due to oxidation of the base asphalt binder to some extent, and that the base binder was an important component to obtain a durable modified asphalt binder.

Rheological evaluations based upon master curve development can be a very useful method to evaluate the influence of the oxidative aging on multiple physical characteristics of asphalt binders. Correspondingly, black space diagrams, defined as complex modulus versus phase angle, provides a robust evaluation methodology for the rheological evaluation of asphalt binders. Recent work in the field of non-load related
oxidative aging-induced cracking has utilized this evaluation technique to quantify the dramatic loss in the relaxation properties of asphalt binders with the oxidative aging (Rowe, 2011).

2.4 Summary

The pavement industry can improve the specific performance of base binder by adding different modifiers and conducting different modification process. This chapter mainly focuses on the literature review, which includes the asphalt binder modification, the development of asphalt binder aging methods, and the currently research state of the asphalt binder aging study from chemical and physical aspects.
CHAPTER 3 RESEARCH METHODOLOGY AND SCOPE

The physicochemical characterization of asphalt binders has been extensively developed with advanced technology improvement. In the 1990s, under the contract with the Strategic Highway Research Program (SHRP), many different microscopic technical tools such as Nuclear Magnetic Resonance (NMR), Infrared (IR) Microscopy, Size Exclusion Chromatography (SEC) and so forth were commonly implemented to investigate the chemical composition and molecular structure of asphalt binders at the microscale level (Jennings et al., 1993; Branthaver et al., 1993). At the same time, the macro performance tests were also explored to characterize the rheological properties with asphalt binders, especially with the ever-increasing capability of high resolution equipment. During this research study, the Fourier-Transform Infrared Spectroscopy (FT-IR) and Dynamic Shear Rheometer (DSR) were utilized to investigate the change in the chemical bonds of the functional groups and the rheological performance with different oxidative-aged asphalt binders.

3.1 FTIR Test with Pavement Material

3.1.1 Brief Theory of FT-IR

The electromagnetic spectrum is an advanced science in the physics field. Figure 3.1 shows the electromagnetic spectrum distribution. It indicates that the electromagnetic spectrum is classified as radio waves, microwaves, infrared, ultraviolet, X-ray and gamma rays (Stuart, 2005). For the specific infrared spectrum, it is classified into three categories based on the wavelength or wavenumber range: far-infrared spectra (400-4 cm\(^{-1}\)), mid-infrared spectra (4,000-400 cm\(^{-1}\)), and near-infrared spectra (14,000-4,000 cm\(^{-1}\)).
The fundamental theory of infrared spectroscopy is that infrared radiation passes through the material, and some fraction of the radiation is absorbed which excites vibrations or rotations of the atoms at a molecular level, and the remaining radiation is transmitted to the material or reflected by the material surface. The frequency of the specific energy input causing the excitation is indicated as the peak in an absorption spectrum. However, not all of the infrared radiation absorption is shown in the spectrum. The infrared absorptions should satisfy the requirement which is that the dipole moment should changes as bond expands and contracts. Figure 3.2 presents a general example of the movement modes of the molecular bond. FT-IR can be used to analyze materials in various physical states, e.g. gas, liquids and solids in bulk, or thin film forms.

![Electromagnetic Spectrum Radiation Type Distribution](image)

*Figure 3.1 Electromagnetic Spectrum Radiation Type Distribution (Courtesy of NASA)*
The spectrometer of Fourier-Transform Infrared Spectroscopy-Nicolet 6700 which was manufactured by Thermo Scientific Inc. was used to get the infrared absorption spectrum with oxidative aged asphalt binder (see in Figure 3.3). The accessory part depicted in the Figure is called attenuated total reflectance (ATR) which allows a beam of laser radiation to pass through the crystal to touch the subject material, which then becomes decreasingly reflected by the material absorption. As such, the crystal implemented here is a kind of stable diamond-material and below the diamond is another material which is named ZnSe. The standard of AASHTO T-302 is used to quantify the polymer content by IR spectrum analysis. AASHTO T-319 was designed to quantify the asphalt binder which is extracted and recovered from the asphalt mixtures.
3.1.2 Pavement Material Spectra

FT-IR is widely used to identify the material composition change by analyzing the related bond peak ratio under different conditions. FT-IR and other microscopic tools have been used to characterize the asphalt binders based on chemical and physical properties (Wei et al., 1996). Others have commonly used FT-IR, specifically with ATR, to study the kinetic oxidation with asphalt binder for more than 20 years (Glover et al., 1989). The aging effect on asphalt-rubber binders based upon the functional group analysis and rheological performance point of view has also been investigated (Lima et al., 2005). Still others have successfully applied FT-IR spectroscopy through transmission measures to study the asphalt binder molecular structure and to understand the mechanism of the relation between fractions and physical properties (Branthaver et al., 1993).
Table 3.1 is a brief summary of the IR assigned bands for several asphalt modifiers. With advanced technology development, a lot of specific binder modifiers are available now, i.e. SBS, SBR, EVA, SEBS, lime, anti-stripping additive, antioxidant additive and emulsifiers.

Table 3.1 IR Absorption Band for Some Asphalt Modifiers

<table>
<thead>
<tr>
<th>Compound</th>
<th>Assigned band (cm(^{-1}))</th>
<th>Origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>699 and 750</td>
<td>C-H bending in monoalkylated aromatic</td>
</tr>
<tr>
<td>PB</td>
<td>730-650</td>
<td>C-H wagging of cis-alkene</td>
</tr>
<tr>
<td></td>
<td>911</td>
<td>C-H bending of terminal-alkene</td>
</tr>
<tr>
<td></td>
<td>966</td>
<td>C-H bending of trans-alkene</td>
</tr>
<tr>
<td></td>
<td>993</td>
<td>C-H bending of cis-alkene</td>
</tr>
<tr>
<td>EVA</td>
<td>1240 and 1740</td>
<td>acetate ester</td>
</tr>
<tr>
<td>C=O</td>
<td>1650-1820</td>
<td>Carbonyl</td>
</tr>
<tr>
<td>S=O</td>
<td>1030</td>
<td>Sulfoxide</td>
</tr>
<tr>
<td>Lime</td>
<td>1384-1388</td>
<td>CaCO(_3)</td>
</tr>
</tbody>
</table>

The analysis of the IR spectra requires a significant effort to deduce the chemical functional composition in the interested matter based on the spectrum peak height, peak shape and peak location. Usually, there are some references or libraries which are applicable when attempting to determine the component fraction of the material. For
instance, Sadtler IR library is one of the most prevalent libraries and it has more than 225,000 referenced spectra.

Figures 3.4 to 3.10 indicate FT-IR ATR spectra for different asphalt binders. These Figures which are plotted by OMNIC™ software contain the control asphalt binders identified as Base binders and the corresponding modified versions of each. For the B-TR series, the right part of the spectra moves up and the possible reason for this is that the carbon black in the asphalt absorbs most of the radiation which makes the absorbance value higher than other compositions. Several differences are indicated by the ellipse cycles. The asphalt binders studied in this research are carefully defined by chapter 4.

Figure 3.4 FTIR-ATR Spectrum for Base_A and A_PM Original Binder
Figure 3.5 FTIR-ATR Spectrum for Base_B and B_TR Original Binder

Figure 3.6 FTIR-ATR Spectrum for Base_C and C_PM Original Binder

Figure 3.7 FTIR-ATR Spectrum for Base_D and D_HPM Original Binder
Figure 3.8 FTIR-ATR Spectrum for B_TR_X and B_TR_X_PM Original Binder

Figure 3.9 FTIR-ATR Spectrum for B_TR_Y and B_TR_Y_PM Original Binder

Figure 3.10 FTIR-ATR Spectrum for B_TR_Z and B_TR_Z_HPM Original Binder
3.2 Asphalt Binder Rheological Performance Test

The rheological characteristics of asphalt binder has a tremendous effect on the properties of the asphalt mix and pavement in-situ performance. In most cases, the asphalt binder tests are focused on the flow resistance properties characterization under specific temperatures, loading frequencies and loading levels. Chronologically speaking, the underlying changes of the rheological advanced tests are developed from empirical to empirical-mechanistic with the new available technology. The following section describes the general procedures of asphalt binder rheological tests.

3.2.1 Binder Empirical Rheological Test

In the asphalt pavement industry, there is a large amount of effort put forth on the development of performance based specification. Before the Strategic Highway Research Program (SHRP) 1990, the penetration grading system, which was introduced by Federal Highway Administration (FHWA) in 1918, was utilized widely all over the world. However, the evaluation of the grades, which were based on the magnitude of the penetration of a standard needle (100 gram) to the binder at 25°C (77°F) in 5 seconds, was an empirical test with weak correlation to the field pavement performance and was described by AASHTO T149 or ASTM D5. Figure 3.11 shows the failure characterization of the penetration grading system, it is possible that the three asphalt binders have same penetration value but different temperature susceptibility.
Figure 3.11 Example of Penetration Grading Failure Identification

At the same time, another flow performance asphalt binder test is the ring and ball softening point test. From the ASTM standard D36-95 document, two stainless steel balls are utilized to each envelop on the top of the binder which is constrained by a ring under a constant rate of heating. The softening point is defined by the temperature when the ball falls a distance of 25 mm from the ring. It should be clearly noted that this test is a kind of simulative phenomenon characterization and has been outdated for decades.

In the 1960s, a new asphalt binder grading system-Viscosity Grading was created to fix the penetration grading system shortcoming. AASHTO M226 indicates how the viscosity grading system works and it solves the previous problem to some extent. AASHTO T316 or ASTM D4402 documents the viscosity determination procedure by using rotational viscometer. Rotational devices have the capability to evaluate the flow properties of various asphalt binders. However, neither of these measurements considers
the low temperature properties of asphalt binder nor has a satisfied consistency with modified asphalt binders.

3.2.2 Asphalt Binder Performance Related Rheological Tests

In order to find more mechanistic methods to characterize the asphalt binder rheological performance, SHRP asphalt programs were started in the late 1980s resulting in the current performance grading (PG) system. The PG system attempts to mechanistically address the main pavements distress types noted in the field, namely rutting (high temperature), fatigue cracking (intermediate temperature) and thermal cracking (low temperature).

The bending beam rheometer (BBR) test is mainly utilized to characterize the flexural creep stiffness or compliance of asphalt binder under low temperature conditions. It is well known that asphalt binder is a kind of viscoelastic material and its performance depends upon loading time and temperature. Under low temperature conditions, asphalt binder becomes stiff and elastic and the challenge is to evaluate the modulus property. Fortunately, BBR can measure the deflection under a constant load (980±50 mN) at temperatures corresponding to its lowest pavement in-service temperature plus 10°C. In the analysis, the creep compliance is calculated by the elastic-viscoelastic correspondence principle, which assumes that the stress distribution is the same as that in a linear elastic beam under the same load (AASHTO T313). Equation 3.1 describes the stiffness calculation.

\[ S(t) = \frac{PL^3}{4bh^3}\delta(t) \]  

Equation 3.1
Where, $S(t) = \text{time-dependent flexural creep stiffness, MPa}$;

$P = \text{constant load, N}$;
$L = \text{span length, mm}$;
$b = \text{width of beam, mm}$;
$h = \text{thickness of beam, mm}$;
$\delta(t) = \text{deflection of beam over time, mm}$.

Another asphalt binder low temperature performance test is the direct tension test (DTT), which is conducted by using PAV aged binders to get the ultimate tensile strain. This test is required when the BBR creep stiffness is greater than 300 Mpa but smaller than 600 Mpa, because the asphalt binder, especially SBS modified, may have high creep stiffness but will not crack, which means it is more ductile (Chowdhury et al., 2002; AASHTO T314, 2013).

The dynamic shear rheometer (DSR) is a common tool that has been utilized in the food science, cosmetics, plastic and polymer industry for many years. Both the loading time (frequency), loading level, and temperature effects can be evaluated. In this study, oscillatory shear loading is selected as the loading mode for the asphalt binder test. As shown in Figure 3.12, the asphalt binder is sandwiched between a fixed plate and a moveable plate that oscillates back and forth.
The greatest advantage with the DSR is that it can accurately measure the asphalt binder rheological properties in the complex domain, i.e. complex shear modulus, complex viscosity, phase angle, stress relaxation and strain creep performance, etc., being utilized worldwide. Equations 3.2 and 3.3 indicate the stress and strain calculation. The frequency of oscillation is the cycle number of the moving back and forth (A to B, B to A, A to C and C to A) in one second. For instance, if the oscillation happened two cycles in
one second, then the related frequency is 2 Hz. Another common unit of oscillation frequency is radians per second which by defining one radian corresponds to about 57 degrees. As such, 10 radians per second which is corresponding to 1.59 Hz is performed for Superpave Performance Grading test at high and intermediate temperatures according to AASHTO M320.

\[
\tau = \frac{2T}{\pi r^3} \quad \text{Equation 3.2}
\]

\[
\gamma = \frac{\theta r}{h} \quad \text{Equation 3.3}
\]

Where, \( \tau \) = shear stress, pa;

\( T \) = the loading torque, mN;

\( \gamma \) = the shear strain, mm/mm;

\( r \) = the radius of the center to the loading point, mm;

\( h \) = the thickness of the asphalt binder, mm.

In the majority of cases, there are two different categories test loading control mode: constant stress and constant strain. For the constant stress control situation, a constant torque is applied to move the plate from point A to point B. However, this constant maximum torque is asphalt binder material, test frequency and temperature dependent, i.e. the stiffer asphalt binder, high frequency and low test temperature require more torque. On the other hand, the constant strain control mode is setting the distance of the plate moving to be fixed and the torque is measured. Commonly, the constant strain mode is conducted for the Superpave binder test in PG system.
In the PG system, the parameter of $G/\sin(\delta)$ at high temperature is adapted to evaluate the asphalt binder performance of resisting rutting, i.e. $G^*$ and $\delta$ (phase angle) are interacted to make the asphalt binder performances more elastic at high field service temperature (as shown in Figure 3.13). In the same way, the value of $G^*\sin(\delta)$ at intermediate temperature is conducted to control the maximum stiffness that the asphalt pavement should be soft enough to resistant the fatigue cracking (AASHTO M320, 2015). Figure 3.13 shows two different asphalt binders which have completely different behaviors. Binder 1 has a higher phase angle compared with binder 2, it means that binder 1 performs more liquid like relative to the second binder at the same condition.

![Figure 3.13 Examples of Asphalt Binder Viscoelastic Behaviors](image)

**Figure 3.13 Examples of Asphalt Binder Viscoelastic Behaviors**

Last, and perhaps most importantly, the relationship between rheological parameters obtained from the DSR test data should be addressed. The Kramers-Krong relationship, shown in Equation 3.4, present the integral transform relationships between the real and
imaginary parts of a complex function which meets the Bolzmann superposition and causality principles (Chailleux et al., 2006). As presented in Figure 3.13, \( G' \), \( G'' \) and \( G^* \) can be converted to each other, as presented by Equation 3.5. And the complex shear modulus is the ratio of peak shear stress over the peak shear strain.

\[
G^*(i\omega) = G'(\omega) + iG''(\omega) = |G^*|e^{i\delta(\omega)} \\
G' = G^* \cos(\delta) \quad \text{Equation 3.5 (a)}
\]

\[
G'' = G^* \sin(\delta) \quad \text{Equation 3.5 (b)}
\]

\[
\tan(\delta) = \frac{G''}{G'} \quad \text{Equation 3.5 (c)}
\]

Where, \( G' \)= Elastic shear modulus or storage shear modulus, psi; \( G'' \)=Viscous shear modulus or loss shear modulus, psi; \( G^* \)=Complex shear modulus, psi; \( \delta \)= Phase angle, radians; \( i = \sqrt{-1} \).

Equation 3.6, which is known as the Cox-Merz rule, which indicates the relationship between complex shear viscosity and complex shear modulus. The so called Cox-Merz rule was founded in polymer science and it has been found to hold for almost all polymer melts, concentrated or semi-dilute solutions, i.e. asphalt binder material (Cox et al., 1958).

\[
\eta^* = \frac{G^*}{i\omega} \quad \text{Equation 3.6 (a)}
\]

\[
\eta' = \frac{G''}{\omega} \quad \text{Equation 3.6 (b)}
\]

\[
\eta'' = \frac{G'}{\omega} \quad \text{Equation 3.6 (c)}
\]

Where, \( \eta^* \)= complex shear viscosity, poise; \( \eta' \)= elastic shear viscosity or storage shear viscosity, poise; \( \eta'' \)= viscous shear viscosity or loss shear viscosity, poise;
\( \omega \) = shear rate, radian/second;
\( i \) = imaginary number, is equal to \( \sqrt{-1} \).

The ability of the DSR to study the asphalt binder rheological performance, much further beyond the Superpave PG system, has had a pronounced benefit on asphalt research in recent decades. The related reference is elsewhere with the expressed acknowledgement of the contribution of G.D. Airey, G.M. Rowe, Hussain Bahia, Donald Christensen, D.A. Anderson, Mihai Marasteanu, Shinche Huang, Elie Y. Hajj, Nathan Morian and so forth.

**Frequency sweep**

The DSR was used to evaluate the asphalt binder properties in the laboratory (Marasteanu et al., 2000). As noted, the original binders were tested at the high PG temperature and the high PG temperature+6°C and the test were run on 25 mm parallel plates with a 1.0 gap. For the RTFO aged samples, the temperatures range were from 34 °C to the high PG temperature+6 °C and the plate and gap were same with the original binders. While, the PAV samples were tested over a range from 4 °C to the high PG temperature+6°C, and the tests were performed on 8 mm plate with 2 mm gap. During all the tests, the sample was allowed to equilibrate for ten minutes at each temperature prior to testing to eliminate the transition effect. The frequencies conducted were from 1 to 100 rad/s. The controlled strain was adjusted at each temperature to make sure the oscillating torque remained under 2 mN-m which indicate the test was performed in the linear viscoelastic (LVE) range. Usually, the controlled strain would be doubled for every 6°C increment. Table 3.4 shows the recommendation for the strain used in frequency test.
Table 3.2 Recommended Strain Levels for Frequency Sweep Tests (courtesy to M.O. Marasteanu)

<table>
<thead>
<tr>
<th>Test Condition</th>
<th>Strain Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original, 25 mm plates</td>
<td>5-15%</td>
</tr>
<tr>
<td>RTFOT, 25 mm plates</td>
<td>0.1-8%</td>
</tr>
<tr>
<td>PAV, 25 mm plates</td>
<td>0.1-4%</td>
</tr>
<tr>
<td>PAV, 8 mm plates</td>
<td>0.02-3.5%</td>
</tr>
</tbody>
</table>

In this study, all the frequency tests were conducted with the thermal oxidation aged asphalt binder at multiple temperatures. The strain level was constant as 1% and the frequency range were 0.1 to 100 rad/s and 0.01 to 100 rad/s for 8 mm and 25 mm plates, respectively.

**Strain amplitude sweep test**

Strain sweep test is used to characterize the linear viscoelastic range under specific condition. As mentioned, only RTFOT and PAV samples were conducted the strain test (*Marasteanu et al., 2000*). For the RTFOT aged asphalt binder, the strain sweeps were performed at the high PG temperature+6°C. The initial strain was set at 2 percent to increase at 2 percent interval until 200 percent and the frequency was set at 10 rad/s. The complex modulus was measured until it dropped at least 20 percent from the initial modulus. For the PAV aged asphalt binder, 34°C and 6°C above the PG temperature were performed by using 8 mm parallel plates with 2 mm gap. The strain conducted from 0.2 percent to 2 percent at 0.2 percent interval and then from 2 percent to 200 percent at 2 percent increments.
However, typically asphalt binder is viscoelastic material, i.e. temperature, loading time (frequency) and stress level (non-linear) dependent, resulting that the strain sweeps test condition should be asphalt binder specific.

**Time sweep test**

Time sweep test is also called repeated cyclic loading test at constant amplitude to measure the fatigue life of asphalt binders. However, it is recognized that the time sweep is a very time-consuming test. Efforts have been made to investigate a procedure to decrease the evaluation time by accelerating the damage accumulation in the asphalt binder specimen (*Martono et al.*, 2008).

**Linear Amplitude Sweep Test**

The linear amplitude sweep (LAS) test is a new performance test which determines the resistance of asphalt binders to damage by means of cyclic loading employing linearly increasing load amplitudes by utilizing DSR at the intermediate pavement temperature as outlined in AASHTO TP 101 (*AASHTO, 2015*). The LAS test is conducted on a DSR in strain-controlled mode at the same temperature and loading frequency as the time sweep (*Johnson, 2010*). The loading amplitude is systematically increased to accelerate damage in the specimen. The first 100 cycles is applied to 0.1% strain to evaluate the undamaged linear viscoelastic properties. Then each subsequent load step consists of 100 cycles at a rate of increase or 1% applied strain per step for 20 steps, beginning at 1% and ending at 20% applied strain. The viscoelastic continuum damage (VECD) numerical approach is applied to analysis the asphalt binder fatigue performance.
3.3 Complex Shear Modulus Master Curve

Asphalt binder complex shear master curve is a useful tool to provide the relationship between the binder stiffness property and reduced frequency over a range of temperatures and frequencies which are difficult to measure directly from the test. Like the asphalt mix dynamic modulus master curve, a representative function can be applied to predict the modulus at specific reference temperature and reduced frequency. With the resulting data from each isothermal frequency sweep, the measures can be shifted to a single smooth curve at the reference temperature by applying the time-temperature superposition (TTSP) principle (Ferry, 1980). The following section investigates the different master curve fitting functions and related shift factors functions.

3.3.1 Binder Master Curve Construction

As addressed previously, the asphalt binder shear master curves play an important role on the characterization of the rheological performance, such as low shear limit viscosity or zero shear viscosity, phase angle temperature and frequency susceptibility, glass modulus and transition region, etc. Chronologically speaking, the shear master curve can be stratified three groups: monographs, mathematical models and mechanical models (Yusoff, 2012). Before processing the master curve shifting, there are some assumptions and principles should be clarified and satisfied.

First of all, it is should be clear that the frequency sweep test would be conducted in the linear-viscoelastic (LVE) region. As noted previously, the asphalt binder belongs to viscoelastic material category and its rheology properties are temperature (T) and frequency (f) dependent within a small strain level. In the nonlinear viscoelastic region
often obtained through large strain levels or deformations, the related performance is highly affected by the level of stress or strain. However, the measurements in the study at hand, focused on the development of the master curves within the LVE region, even though there are numerous studies regarding nonlinear rheological performance of asphalt binder available nowadays (Polacco et al., 2006).

Secondly, the time-temperature superposition principle (TTSP) should be hold in the master curve modeling. From Ferry, TTSP holds should satisfy three requirements: 1) each exact matching isothermal curve (time or frequency) is obtained; 2) the shift factor $\alpha T$ has the same value for all viscoelastic functions; 3) the temperature dependence of $\alpha T$ can be expressed as a reasonable form, such as Arrhenius, WLF, Kaelble (Van et al., 1998). On the other hand, the material to which this technique is applicable is said to be “thermorheologically simple”. This means that at all the frequency test conditions (different isothermal temperature and frequency), the material should have the same temperature dependency. A step further to say, the micro-structure rearrangement and phase amorphous change do not occurred during the running test.

Thirdly, with the complexity of the modified asphalt binder structure, there is not a universal master curve function to be suitable for all kinds of asphalt binder material. Table 3.5 depicts several master curve functions. For the most part, these master curve models are able to characterize the rheological properties of neat asphalt binder effectively. However, many researchers observed that during the master curve construction for binders with high asphaltene content, crystalline asphalt, or modified asphalt binder, particularly those that are highly modified, i.e. SBS, EVA, tire rubber,
nano-clay, etc., the models lack the ability to predict the rheological properties during phase transitions, e.g. plateau range. In the black space diagram, some phase transition occurred in the phase angle range between 45°C to 60°C due to the SBS microstructure takes the main role to resistant the shear loading at high temperature compared with the low temperature.

With the advanced technology development, there are a lot of master curve fitting functions and related shift factors functions available nowadays. Each one should considered with respect to the development origin as it applies to application limitations relative to specific materials or characteristics. Within the appropriate application of each model, each one in particular presents inherent advantages and disadvantages compared with the others. Appendix C summarized the master curve fitting functions and shift factor functions.

With the extensive amount of effort put forth into the study of asphalt binder rheology properties, e.g. linear or non-linear viscoelasticity, viscoelastic-plasticity, and others, presents an appreciation of the advancement in the industry. studied the linear viscoelastic domain relationship between asphalt binders and mixes by using general “2S2P1D” (2 springs, 2 parabolic, 1 dashpot element) model based on physical analogical elements (Benedetto et al., 2004). Other researchers evaluated the thermo-viscoelastic property of asphalt mix with oxidation aging (Morian et al., 2013).

3.3.2 Rhea Software Version 1.2.9

RHEA™ version 1.2.9 package is the rheological analysis software that was used to perform the initial shifting of the complex shear modulus master curves (Rhea, 2011). In
general, the software shifts the isothermal frequency sweep data into the master curve using a modified non-linear Marquadt-Levenburg least square optimization and followed by a numerical analysis using the discrete relaxation and retardation spectra (Baumgaertel et al., 1989). A maximum of 32 relaxation modes can be calculated for the data sets.

The Rhea™ software shifts the isothermal frequency sweep measured data to fit a smooth master curve utilizing methods of “free shifting.” Following the development of the master curve, subsequent calculations determine the fit of the master curve to Christensen-Anderson-Sharrock (CAS) or prony series master curve forms. The corresponding shifting is then fit to the shift functions according to using Arrhenius, Williams-Landel-Ferry (WLF), and Keable functional forms according to the time-temperature superposition principle, see Figure 14 to 16. The term “free shifting” indicates that the master curve data are shifted to the since master curve which is then fit to the equation forms, i.e. master curve and shift function. This is different than most common methods of shifting the data to fit a particular master curve function and a corresponding shift function, which is less desirable from a true rheological measurement standpoint (Morian, 2014).

In this study, compared with the CAS model, the Prony series function model fits the modified asphalt binder much better. Generally, Prony series functions are mechanical element modeling and combined by generalized Maxwell-Weichert (a spring and n number of elements of a spring and a dashpot in series) and Generalized Kelvin-Voigt models (a spring and a dashpot in series and m number of elements of a spring and
a dashpot connected in parallel). Equation 3.7 and 3.8 are the relaxation modulus and creep compliance functions used by RHEA™ software and the Kaelble shift function was implemented in the master curve shifting process.

\[
E(t) = E_e + \sum_{i=1}^{n} E_i e^{-(t/\rho_i)} \quad \text{Equation 3.7}
\]

\[
D(t) = D_g + \frac{t}{\eta_0} + \sum_{j=1}^{m} D_j (1 - e^{-(t/\tau_j)}) \quad \text{Equation 3.8}
\]

Where, 

- E(t)- relaxation modulus as a function of time;
- D(t)- creep compliance as a function of time;
- Ee- equilibrium modulus;
- Dg- Glassy compliance;
- Ei- relaxation strength;
- Dj- retardation strength;
- \(\eta_0\)- zero shear or long time viscosity;
- \(\rho_i\)- relaxation time;
- \(\tau_j\)- retardation time;
- n- number of Maxwell elements;
- m- number of Voigt elements;
- t- time of applied loading.
Figure 3.14 Example of WLF Shift Factor of Base A_Orig Binder

Figure 3.15 Example of Kaelble Shift Factor of Base A_Orig Binder
3.4 Thermal Aging Kinetic Analysis Parameters

3.4.1 Carbonyl and Sulfoxide

As noted above, asphalt binder aging is a ubiquitous phenomenon in the field and it accelerates the deleterious rate of asphalt pavement. Basically, during the oxidative aging process, the light molecular aromatic and resin reacted with accessible oxygen to produce increasingly polar functional groups materials, such as ketones, anhydrides, carboxylic acids, sulfoxides and so forth. At the same time, the solubility and mobility are reduced, leading to increases in viscosity as the asphalt binder becomes stiffer and brittle.

It is mounted that the chemical functionality formed during the thermal aging process can be represented by carbonyl and sulfoxide, which represent the major oxidation products. In this study, it was found that the sulfoxide area decreased when the aging temperature is high, such as 85°C, and under the long term aging duration. In order
to accurately investigate the relationship of the chemistry functional group change and the rheological performance change, it was decided that only the carbonyl functional group was taken consideration.

The macro function of the OMNIC™ software was used to calculate the value of carbonyl area and sulfoxide area. All the CA and SO area value from the infrared spectra of the aged binders was automatically calculated by the same procedure which was coded in Macro function. The six measured raw spectra were conducted by the automatic baseline correction in OMNIC™ software in Process tab to make the spectra flat to touch the baseline. Then the corrected spectra were dealt with the other corrections-atmospheric suppression correction in the same Process tab. After the corrections, the spectra were averaged by selecting the average and variance data format in statistical spectra function under analyze tab and also select to add the average spectra to a new window. At last, the area values were calculated by the following description with the average spectra. Figure 3.17 shows the peaks area of carbonyl functional group in the infrared spectra which was measured by the FTIR-ATR machine. The carbonyl area wavenumber range is from 1650 to 1750 cm\(^{-1}\) (should be avoid of the effect of the C=C bond around 1600 cm\(^{-1}\)), and the base line is the line between the two points on the spectra which the wavenumber are 1750 and 1524 cm\(^{-1}\), respectively. The sulfoxide area are set as the wavenumber range is 1080 to 980 cm\(^{-1}\), and the base line is the line between the two points on the spectra at the wavenumber of 1080 and 980 cm\(^{-1}\).
3.4.2 Aging Kinetics Parameters

Previously, oxidation kinetics have been extensively studied by many researchers (Petersen et al., 2009; Liu et al., 1996; Glover et al., 2014, Morian, 2014). Usually, the growth rate of the carbonyl functional group can be described by an Arrhenius functional form presented in Equation 3.9. This relationship is selected to indicate component reaction rate of the carbonyl functional group during the oxidative aging process. Figure 3.18 presents an example of the carbonyl growth represented as the carbonyl area (CA) as defined in previous sections with different aging durations exposed to different isothermal temperatures.

\[ r_{CA} = \frac{\partial CA}{\partial t} = AP^a e^{-E/RT} \quad \text{Equation 3.9} \]

Where, \( A \) = the frequency factor,
P = the oxygen partial pressure in this study,
\( \alpha \) = the reaction order,
E = the activation energy (kJ/mol),
R = the gas constant (8.314 J.mol/°K),
T = the absolute temperature, °K.

The result shows that the carbonyl growth rate increases with temperature and also at a nonlinear rate at the same environment condition and after some specific point, the carbonyl content increases at a constant rate. This change in oxidation rate, in particular led to fast and constant rate notations in the carbonyl area described by the following kinetic model represented in Equation 3.9 (Lin et al., 1995; Liu, 1996; Domke et al. 1999, 2000; Glover et al., 2005; Han et al., 2013):

\[
CA = M(1 - e^{-k_f/\alpha}) + k_c \times t + CA_{tank} \quad \text{Equation 3.10}
\]

Where the parameter \( k_f \) and \( k_c \) are the fast and constant kinetic reaction rate, individually, M is the gap between the \( CA_0 \) and \( CA_{tank} \) (see Figure 3.18), \( CA_0 \) is the intercept of the constant rate line and \( CA_{tank} \) is the carbonyl content of original asphalt binder. Furthermore, both of the rate factors \( k_f \) and \( k_c \) are modeled utilizing the Arrhenius function presented in Eqn 3.10.
Figure 3.18 Aging Model Fitting with the Measurement Data of Base A Binder

\[ C_A = M(1-e^{-\frac{t}{\tau}}) + k_\text{f} \cdot t + C_{A_\text{fit}} \]

Figure 3.19 Arrhenius Reaction Parameters of B_TR_X Binder
A much more fundamentally chemistry based model has recently been developed (Huang et al., 2012). This model is a dual sequential mechanism approach for oxidation of asphalt binder proposed by (Petersen 1998). The fast reaction path which was governed by the reactive material (polycyclic hydroaromatics) goes through several steps to produces free radical and the slow reaction which was driven by benzyl carbon produces a benzyl radical for hydrogen abstraction. This model based the short-term aging asphalt binder study, and this was different with the aging method used in this study. So it was not considered during the latter analysis.

\[
[P(t)] = M(1 - \frac{k_2}{k_1})(1 - e^{-k_1 t}) + k_2 Mt + [P_{1,0}] \quad \text{Equation 3.11}
\]

\[
[Sulfoxide+ Carbonyl] = M(1 - \frac{k_2 P_{O_2}^n}{k_1 P_{O_2}^m})(1 - e^{-k_2 P_{O_2}^m t}) + k_2 P_{O_2}^n Mt + [P_{1,0}] \quad \text{Equation 3.12}
\]

Where,

- \([P(t)]\)-the extent of oxidation metric, usually S=O and C=O absorbance sums;
- \(M\)-the reactive material concentration for the fast reaction;
- \([P_{1,0}]\)-the RTFO time zero value of \(P\);
- \(k_2, k_1\)- the slow and fast reaction rate constants for isothermal aging, temperature dependent according to the Arrhenius equation;
- \(P_{O_2}^n, P_{O_2}^m\)-the partial oxygen pressure, \(n, m\) is the pressure exponent for the slow and fast reaction, respectively.
3.4.3 Rheological Performance Parameters

3.4.3.1 Low Shear Viscosity (LSV)

Low shear viscosity (LSV) is an important rheological indicator of asphalt binder to represent the capability of asphalt mix to resist the shear deformation at high temperatures. Prior to LSV, zero Shear Viscosity (ZSV), which was defined as the complex viscosity at the shear rate of zero and equivalent to the elastic modulus, was explored to characterize the rutting resistant properties of asphalt binders. However, zero shear viscosity is just a theoretical concept and it is impractical to test the asphalt binder at zero shear rate directly. So a newly approach was proposed to replace ZSV which is referred to as low shear viscosity (shear rate is close to zero).

The study of the applicability of using low shear viscosity was conducted to evaluate the asphalt binder rheological behavior. It concluded that LSV is inadequate to characterize the creep performance when the asphalt binder was modified with SBS additive (Zoorrob et al., 2012). Some researchers investigated the relationships between zero shear viscosity, low shear viscosity and MSCR tests and EN 12697-22 rutting test. The results shown that polymer modified binders and crumb rubber binder had a better potential to resist the permanent deformation than the conventional binder and a relationship existed between the asphalt mixes and asphalt binder tests (Antonio Paez Duenas et al., 2012).

However, the low shear rate for LSV is defined differently by various researchers. For instance, it was set the shear frequency at 0.001 rad/s as the LSV point and Glover team set the rate of 0.1 rad/s as the point (Morian et al., 2013). Usually, this setting point
is limited to the test equipment resolution, another concern is that it is very time consuming to test the asphalt binder at such low shear frequency, and the TTSP is a sound tool to shift the other frequency data to 0.001 rad/s by using related shift function. Figure 3.20 shows the LSV point in a dynamic viscosity curve.

![Figure 3.20 LSV point of Base A-orig](image)

**3.4.3.2 Crossover Modulus**

Crossover modulus, the cross point between the viscous modulus ($G''$) and elastic modulus ($G'$) curve, is defined as the shear modulus at phase angle of $45^\circ$ (shown in Figure 3.18). Equation 3.13 and 3.14 is a master curve which was developed by Christensen and Anderson, referred as the “CA model” (Christensen and Anderson, 1992).
\[ G^*(\omega) = G_g \left[ 1 + \left( \frac{\omega_c}{\omega} \right)^{\frac{\log 2}{R}} \right]^{\frac{-R}{\log 2}} \]  \hspace{1cm} \text{Equation 3.13}

\[ \delta(\omega) = \frac{90}{\log 2} \left[ 1 + \left( \frac{\omega}{\omega_c} \right)^{\frac{\log 2}{R}} \right] \]  \hspace{1cm} \text{Equation 3.14}

**Figure 3.21 Crossover Frequency of Base A-orig**

3.4.3.3 Black Space Diagram

Black space diagram is a plot of shear complex modulus \(G^*\) versus phase angle \(\delta\) as shown in Figure 3.22. Researchers used the black space diagram to evaluate the phase change in asphalt binder and the field block cracking with R value which is used in CA model and denoted in the following Equation 3.15 \((\text{King et al., 2012; Rowe et al., 2011})\).

\[ R = G_g^* - G_c^* \]  \hspace{1cm} \text{Equation 3.15}
3.4.4 Hardening Susceptibility

Hardening susceptibility is defined as the relationship between rheological measurements as a function of the aging of an asphalt binder. While this definition may fit several evaluation protocols, this study will focus on the four rheological indices discussed previously as a function of the increase in the carbonyl functional groups, i.e. CA, as a measure of the oxidation.

Utilizing the low shear viscosity (LSV) as an example, Equations 3.16 and 3.17 present the format for the semi log relationships commonly used to characterize the hardening susceptibility plots also depicted in Figure 3.23.

\[
\ln \eta_0^* = HS \ast CA + m \quad \text{Equation 3.16}
\]

\[
\eta_0^* = e^{HS \ast CA} e^m \quad \text{Equation 3.17}
\]
Where, $\eta_0^* =$ low shear viscosity of the asphalt binder;

$HS =$ hardening susceptibility, slope of relationship;

$CA =$ carbonyl area, arbitrary units - unit less;

$m =$ intercept of log $\eta_0^*$ and CA relationship.

Utilizing this format, the hardening susceptibility of the other rheological indices (RI) may be evaluated simply by replacing the LSV term with the crossover modulus ($G^*_c$), the DSR function (DSRFn), or the Glover-Rowe parameter ($G - R$) along with the corresponding CA measures of oxidation as indicated in Equation 3.18.

$$RI = e^{HS\cdot CA}e^m \quad \text{Equation 3.18}$$

Utilizing this format, the hardening susceptibility (HS) of the asphalt binder will be represented by the slope of the relationship. Likewise the intercept term of the HS relationship in the semi-log scale will be evaluated as the quantity of $e^m$ numerically.
3.4.4.1 LSV vs CA

Figure 3.23 Example of Hardening Susceptibility-LSV vs CA of Base A

With the asphalt binder aging, both of the carbonyl area and low-shear viscosity increased. The Figure 3.23 shows that the Ln(LSV) has a good correlation with carbonyl area value. This chart is a good tool to evaluate the sensitivity of LSV increasing rate based on the carbonyl area change.
3.4.4.2 Glover DSR function vs CA

Figure 3.24 Example of Hardening Susceptibility-DSR Fun. vs CA of Base A

The DSR function, which was developed by Dr. Glover from University of Texas A&M, is used widely to evaluate the asphalt binder fatigue property. DSR function combining with ductility value becomes DSR map which was used to indicate the asphalt binder cracking event. Usually, the asphalt binder starts to block cracking at the ductility of 5 cm (test temperature at 4°C), and has severe blocking cracking at the ductility of 3 cm for unmodified asphalt binders. DSR function increased with the oxidative aging processing. All of the DSR function parameters were at condition of 15°C, 0.005 rad/s.
3.4.4.3 Crossover modulus-CA

![Graph showing Crossover modulus vs Carbonyl Area](image)

**Figure 3.25 Example of Hardening Susceptibility-G*c vs CA of Base A**

Crossover modulus, which was the shear modulus at the phase angle of 45°, decreased with the CA increasing. The crossover frequency was also dropped under the aging effect. It is necessary to evaluate the evolution of the crossover modulus G*c with oxidative aging and G*c is a parameter in the Christensen-Anderson (CA) which was used to predict the complex modulus and phase angle. The condition of G*c was at 25°C.
3.4.4.4 G-R vs CA

**Figure 3.26 Example of Hardening Susceptibility-G-R vs CA of Base A**

Glover-Rowe (G-R) parameter was developed from Glover DSR function by Dr. Rowe to evaluate the field asphalt pavement block cracking. G-R vs CA has similar trend with DSR function vs CA curve. The corresponding G-R value to the block cracking and severe cracking are 180 kPa and 450 kPa at condition of 15°C, 0.005 rad/s.

### 3.5 Field Asphalt Pavement Oxidation Modeling

In this study, the field asphalt pavement aging prediction was conducted with the investigated asphalt binders. At first, the pavement temperature profiles were produced by TEMPS software which was developed by the pavement research group of University of Nevada, Reno. The behind heat transfer theory was elaborated in the following
sections. Then the transport pavement oxidative aging model was used to predict the asphalt pavement carbonyl area growth over time and with depth.

In order to predict the field asphalt pavement aging accurately, it is highly necessary to have the precise pavement real temperature profile over time and with depth. Historically, the pavement temperature models can be stratified to statistically-based, such as LTPP temperature equations; numerically-based, such as Enhanced Integrated Climate Model (EICM); and analytically-based predictive models, such as Laplace Transformation Model (Mohseni, 1998; Larson et al., 1997; Liu et al., 1996; Wang, 2012).

In this study, the heat transfer model was used to predict the asphalt pavement temperature profile, as shown in Figure 3.27. This model included three parts-thermal convection model, thermal radiation model and thermal conduction model (Han et al., 2011; Alavi, 2014). The finite control volume method (FCVM) which is a numerical approach for solving the diffusion equations was used to capably describe the heat transfer mechanism (Versteeg et al., 1995; Kolditz, 2002).
The solar radiation heat flux ($Q'$), which is defined by equation 3.19, is the net radiation absorbed by the pavement surface. The global radiation intensity is specified by the location, such as latitude, day time and the incident angle between pavement surface and the sun radiation. The albedo ($\sigma'$) is the ratio of the reflected radiation from the surface to the incident radiation.

$$Q_{\text{solar}} = (1 - \sigma')Q_{\text{solar}}$$  \hspace{1cm} \text{Equation 3.19}

Where, $Q'$solar-the global radiation intensity;

$\sigma'$- albedo, i.e. unit-less reflection coefficient, from 0 to 1.

The thermal infrared radiation was calculated by equation 3.20 which included the incoming and outgoing long-wave thermal radiation (Han et al., 2011).
\[ Q_{\text{radiation}} = Q_{\text{incomming}} - Q_{\text{outgoing}} = \varepsilon_a \sigma T_{\text{air}}^4 - \varepsilon \sigma T_{\text{surface}}^4 \quad \text{Equation 3.20} \]

Where, \( \varepsilon_a \) - the absorption coefficient of pavement surface;

\( \varepsilon \) - the emissivity of pavement surface;

\( \sigma \) - the Stefan-Boltzmann constant \( (5.67 \times 10^{-8} \text{ W.m}^{-2}.\text{K}^{-4}) \);

\( T_{\text{air}} \) - air temperature pavement surface temperature;

\( T_{\text{surface}} \) - pavement surface temperature.

The convection heat transfer model was used to evaluate heat convection efficiency between the pavement surrounding atmosphere and the pavement surface, as indicated in Equation 3.21 and 3.22. The parameter \( h_{\text{convection}} \) is the convection heat transfer coefficient. \( U \) is the wind speed in \( \text{m.s}^{-1} \) and \( a, b \) are constant equal to 1.4 and 0.5, respectively.

\[ Q'_{\text{convection}} = h_{\text{convection}} (T_{\text{air}} - T_{\text{surface}}) \quad \text{Equation 3.21} \]

\[ h_{\text{convection}} = 698.24 \times a \times 0.00144 \left[ \frac{T_{\text{surface}} + T_{\text{air}}}{2} \right]^{0.3} \times U^d + 0.0009 \sigma (T_{\text{surface}} - T_{\text{air}})^{0.3} \quad \text{Equation 3.22} \]

The conduction heat transfer model, or diffusion model, which describes the heat transfer between the pavement top surface and underneath layers, follows the Fourier’s law \((Han et al., 2011)\). In the below equation 3.23, the factor \( K_{\text{surface}} \) is the thermal conductivity of the pavement surface material. The Equation 3.24 is the pavement surface thermal heat balance equation which defines the surface
boundary condition. The factor $\delta$ is the pavement surface thickness, $\rho_{\text{surface}}$ is the material density and $c_{\text{surface}}$ is the heat capacity of the asphalt mixture.

$$Q_f = -k_{\text{surface}} \frac{\partial T}{\partial z} \bigg|_{\text{surface}}$$  \hspace{1cm} \text{Equation 3.23}

$$Q_{\text{solar}} + Q_{\text{radiation}} - Q_{\text{convection}} - Q_f = \delta (\rho_{\text{surface}} \times c_{\text{surface}}) \frac{\partial T_{\text{surface}}}{\partial t}$$  \hspace{1cm} \text{Equation 3.24}

In this study, 1-D partial differential equation (PDE) was conducted to calculate the heat diffusion into the pavement structure by converting the temperature change over time to the temperature change with considering depth, as depicted by equation 3.25. Gui et al., 2007 evaluated the relationship between climate air temperature and pavement structure temperature. It was found that the temperature variation decreased with the pavement depth and the boundary condition was that the temperature change beyond 3 meters obeys linear function in equation 3.26.

$$\frac{\partial T}{\partial t} = \alpha \left( \frac{\partial T}{\partial z} \right), \alpha = \frac{k}{\rho c}$$  \hspace{1cm} \text{Equation 3.25}

$$\frac{\partial T}{\partial z} \bigg|_{3-m} = \text{constant}$$  \hspace{1cm} \text{Equation 3.26}

The asphalt binder carbonyl area (CA) during the constant-rate oxidative aging period under the isothermal condition is calculated by the linear relationship expressed in equation 3.27. The related kinetic parameters and hardening susceptibility equation were described in previous section in this chapter.

$$CA(t) = CA_0 + r_{Ca} \times t$$  \hspace{1cm} \text{Equation 3.27}
\[ LSV = e^{HS \cdot CA + m} \]  

Equation 3.28

Where,

- **HS** - the asphalt binder hardening susceptibility;
- **m** - the intercept with no physical meaning.

The requirement of determining the asphalt binder carbonyl area (CA) value for the specific location is that the temperature and the localized oxygen pressure should be known at first. Therefore, Figure 3.28 shows the oxidative aging path in the asphalt binder thin film. Equation 3.29 expressed the numerical solution of the CA calculation. Equation 3.29 is the partial differential equation (PDE) for calculating the oxygen pressure at the specific depth location. The boundary and initial condition for the oxygen diffusion PDE calculation, are defined as that the surface oxygen pressure is equal to the surrounding air oxygen pressure; the diffusion rate at the bottom \((z=L)\) is zero; and the initial condition of oxygen pressure is zero.

![Figure 3.28 Asphalt Binder Thin Film Aging](Han, 2011)
\[ CA(t) = \int_{0}^{t} r_{CA} dt + CA_0 \] \hspace{1cm} \text{Equation 3.29}

Where,

- \( r_{CA} \)- constant rate of carbonyl growth, i.e., Figure 3.18;

- \( CA_0 \)- carbonyl Area (CA) content at the start of constant-rate aging period;

- \( t' \)- variable of integration.

\[ \frac{\partial P}{\partial t} = \frac{\partial}{\partial z} \left( D_{O_2} \frac{\partial P}{\partial z} \right) - \left( \frac{cRT}{h} \right) r_{CA} \] \hspace{1cm} \text{Equation 3.30}

Where,

- \( P \)- oxygen pressure as a function of time \( t \) and depth \( z \);

- \( Do2 \)- oxygen diffusivity of asphalt binder;

- \( c \)- model parameter (constant), \( 2.75\times10^{-4} \) to \( 4.59\times10^{-4} \) gmol O2/ml/CA;

- \( h \)- model parameter (function of temperature);

- \( R \)- gas constant (8.314 Joul/mol/°K).

In the equation 3.30, the factor \( h \) is the dimensionless Henry’s law constant which is defined by equation 3.31. The parameter \( h_0 \) is Henry’s law constant at the reference temperature \( Tr \) and it was reported to be 0.0076 at 30°C reference temperature (Dickinson, 1984). Equation 3.31 is an empirical equation to estimate the \( Do2 \) from LSV, in poise, and aging temperature, in kelvin (Han et al., 2013).

\[ h = h_0 [1 + 0.00215(T-Tr)] \] \hspace{1cm} \text{Equation 3.31}
The air oxygen flows from the surrounding atmosphere to the inter-connected air voids of the asphalt mixture and diffuses into the adjoining asphalt-aggregate matrix to react with the asphalt binder to produce the carbonyl functional groups. Usually, the oxygen partial pressure in the air void can be fairly assumed to be constant. Equation 3.33 was used to solve the oxygen partial pressure in the cylindrical system. The boundary and initial conditions are $P= P_{\text{gas}}$ at air void radius ($r=r_{\text{in}}$); $\frac{\partial P}{\partial r} = 0$ at the end of effective aging radius ($r=r_{\text{out}}$); and the initial condition is $P= 0$ at $t=0$.

Figure 3.29 Schematic of Asphalt Binder Aging in Mixture (Han, 2011).

$$\frac{\partial P}{\partial t} = \frac{1}{r} \left( \frac{\partial}{\partial r} \right) \left( r D_{o_2} \frac{\partial P}{\partial z} \right) - \left( \frac{cTR}{h} \right) r_{CA} \quad \text{Equation 3.33}$$
When the calculated time period is short, i.e. one hour for days of aging, the calculation equation 3.28 can be replaced by equation 3.34 which is based on the trapezoidal rule of integration.

\[
CA(t) = \left[ \frac{r_{CA}(t - \Delta t) + r_{CA}(t)}{2} \right] + \int_{t-\Delta t}^{t} r_{CA} dt' + CA_o \quad \text{Equation 3.34}
\]

The following equations are the numerical calculation of oxygen diffusion PDE for the control volumes at different depth locations for the thin-film and asphalt-aggregate matrix situations. The FCVM was implemented in these calculations. Equation 3.35 to 3.37 express the control volume calculation for the thin-film at the exposed surface, middle and bottom locations, shown in Figure 3.30. Equation 3.38 to 3.40 express the calculations for the effective oxidative aging zone for the asphalt-aggregate matrix at the different locations. Additional information would be included in the related reference.

Figure 3.30 Schematic of Thin-film Asphalt Binder (Alavi, 2014)
\[
\frac{P'_t - P^0_t}{\Delta t} - \frac{\Delta \mathbf{z}}{\Delta \mathbf{z}} = -\frac{(D_n^0)^0 + (D_n^0)^{0}}{2} \times \left( \frac{P'_t - P^0_t}{\Delta \mathbf{z}} - \frac{(D_n^0)^0 + (D_n^0)^{0}}{2} \right) \times \left( \frac{P'_t - P^0_t}{\Delta \mathbf{z}} \right) + \frac{cRT'}{h'} \times A \times e^{-E_{at}/RT'} \times \frac{\Delta \mathbf{t}}{2} \int (P'_t)^0 d\mathbf{z}
\]

Equation 3.35

\[
\frac{P'_t - P^0_t}{\Delta t} - \frac{\Delta \mathbf{z}}{\Delta \mathbf{z}} = -\frac{(D_n^0)^0 + (D_n^0)^{0}}{2} \times \left( \frac{P'_t - P^0_t}{\Delta \mathbf{z}} - \frac{(D_n^0)^0 + (D_n^0)^{0}}{2} \right) \times \left( \frac{P'_t - P^0_t}{\Delta \mathbf{z}} \right) + \frac{cRT'}{h'} \times A \times e^{-E_{at}/RT'} \times \frac{\Delta \mathbf{t}}{2} \int (P'_t)^0 d\mathbf{z}
\]

Equation 3.36

\[
\frac{P'_{\text{bottom}} - P^0_{\text{bottom}}}{\Delta t} - \frac{\Delta \mathbf{z}}{\Delta \mathbf{z}} = -\frac{(D_n^0)^0 + (D_n^0)^{0}}{2} \times \left( \frac{P'_{\text{end}} - P^0_{\text{end}}}{\Delta \mathbf{z}} - \frac{(D_n^0)^0 + (D_n^0)^{0}}{2} \right) \times \left( \frac{P'_{\text{end}} - P^0_{\text{end}}}{\Delta \mathbf{z}} \right) + \frac{cRT'}{h'} \times A \times e^{-E_{at}/RT'} \times \frac{\Delta \mathbf{t}}{2} \int (P'_t)^0 d\mathbf{z}
\]

Equation 3.37

Figure 3.31 Schematic of Effective Aging Zone Mesh for Asphalt-Aggregate Matrix
(Aliva, 2014)

\[
\frac{P'_t - P^0_t}{\Delta t} \times \Delta r = \frac{(D_n^0)^0 + (D_n^0)^{0}}{2} \times \left( \frac{P'_t - P^0_t}{\Delta \mathbf{z}} - \frac{(D_n^0)^0 + (D_n^0)^{0}}{2} \right) \times \left( \frac{P'_t - P^0_t}{\Delta \mathbf{z}} \right) + \frac{cRT'}{h'} \times A \times e^{-E_{at}/RT'} \times \frac{\Delta \mathbf{t}}{2} \int (P'_t)^0 \Delta r
\]

Equation 3.38
\[
\frac{P'_e - P^{0}_e}{\Delta t} \times r_e \times \Delta r = r_e \times \left[ \frac{(D_{e_1})^0_{e+1} + (D_{e_2})^0_{e+1}}{2} \times \left( \frac{P'_e - P^0_e}{\Delta r} \right) - \frac{(D_{e_1})^0_{e} + (D_{e_2})^0_{e}}{2} \times \left( \frac{P'_e - P^0_e}{\Delta r_{e+1}} \right) \right] - \frac{cRT_e^2}{h^2} \times A \times e^{\frac{-Ea}{RT_e}} \times \int_{\Delta r_{e+1/2}}^{r_e} (P'_e) \, rdr
\]

Equation 3.39

\[
\frac{P'_{end} - P^{0}_{end}}{\Delta t} \times r_{end} \times \Delta r = r_{end} \times \left[ \frac{(D_{e_1})^0_{end} + (D_{e_2})^0_{end-1}}{2} \times \left( \frac{P'_{end} - P^0_{end}}{\Delta r} \right) - \frac{(D_{e_1})^0_{end} + (D_{e_2})^0_{end-1}}{2} \times \left( \frac{P'_{end} - P^0_{end}}{\Delta r_{end-1}} \right) \right] - \frac{cRT_e^2}{h^2} \times A \times e^{\frac{-Ea}{RT_e}} \times \int_{\Delta r_{end-1/2}}^{r_{end}} (P'_e) \, rdr
\]

Equation 3.40

3.6 Multi Linear Regression Statistical Analysis

Multivariate linear regression techniques was used in this study to analyze the significance of each factor which might play an important role on the kinetic reaction and rheological performance. For other statistical analysis, ANOVA analyses are available to many statistic software, such as PASS, R, and Minitab, etc.

The related theory of linear regression evaluation is everywhere (Neter et al. 1996). The requirement for the multivariate linear regression evaluation is that the data set should avoid the exhibit multicollinearity between the predictor variables which should result in random experimental errors with normal distribution and the variance of each statistical grouping should exhibit homogeneity of variance.

The general linear regression model (GLM) was selected in these comparisons to perform the data analysis. The considerations in this model includes qualitative predictor variable, transformed variables, and interaction terms, such as the following Equation 3.41 shows an example of GLM model. This equation has two variables as \( X_1 \) and \( X_2 \), the interaction effect is also considered as \( X_1 \times X_2 \) form. Figure 5.53 shows an example of GLM analysis model.

\[
E(Y) = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_1 X_2 \quad \text{Equation 3.41}
\]
Where, \( E\{Y\} \)- predicted dependent variable in the analysis;
\( \beta_0 \)- intercept of the base equation (condition A);
\( \beta_1 \)- slope of the base equation (condition A);
\( \beta_2 \)- modification to the intercept of the base equation due to condition B;
\( \beta_3 \)- modification to the slope of the base of the equation due to condition B;
\( X_1 \)- independent predictor variable (quantitative in this example);
\( X_2 \)- qualitative predictor variable (dummy variable);

\[ X_2 = 0, \text{ for condition A,} \]
\[ X_2 = 1, \text{ for condition B,} \]

Figure 3.32 An Example of GLM Analysis Model

In this study, the asphalt binder material and aging conditions are the two main aspects that affect the kinetic reaction or asphalt binder’s rheological performance. The statistical analysis software-Minitab version 16 was implemented to conduct the multiple linear regression analysis to identify the significance of the modifier on the rheological performance. These results were performed in the rheological data analysis during chapter 5 part.
3.7 Summary

This chapter describes the details about specific test methods to characterize the chemical composition change (Carbonyl functional group) and rheological physical property change which is indicated by the rheological performance parameters-LSV, G*c, DSR function and G-R based on the shifted master curve of the selected asphalt binder under the isothermal oxidation aging condition. On the other hand, the general information of the asphalt binder rheological test, analysis parameters, asphalt binder aging kinetics and hardening susceptibility are also explained in this chapter. Lastly, the behind fundamental theory of the field asphalt pavement carbonyl area (CA) prediction was also elaborated carefully.
CHAPTER 4 EXPERIMENTAL PLAN

There are a lot of different factors that affect binder aging, such as solar radiation, temperature, moisture content, aggregate mineralogy, binder chemical component and so forth. However, it is not practical to consider all of these factors in one laboratory study. This chapter elaborates the experimental details such as the objective binder materials, aging methodology, rheology performance test and kinetic parameter test procedures.

The objective of this research was to investigate: (1) the effect of thermal oxidation aging (different temperature and aging duration) on the rheological performance and kinetic properties with base binder, polymer modified and tire-rubber modified binder; and (2) the mechanism of the binder modifiers (SBS, SBR, TR) resistant oxidative aging behavior.

4.1 Material

In this research, there are 14 different types of binders to be investigated in this study. Table 4.1 shows the nomenclature of the objective binders.
### Table 4.1 Nomenclature of Investigated Binders in This Study

<table>
<thead>
<tr>
<th>Base Binder</th>
<th>Modifier $^a$</th>
<th>Additional Base $^b$</th>
<th>Binder ID $^c$</th>
<th>Commercially Available $^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base A</td>
<td>--</td>
<td>--</td>
<td>Base A</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>SBS</td>
<td>--</td>
<td>A_PM</td>
<td>PG64-28NV</td>
</tr>
<tr>
<td>Base B</td>
<td>--</td>
<td>--</td>
<td>Base B</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>TR</td>
<td>--</td>
<td>B_TR</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>TR</td>
<td>X</td>
<td>B_TR_X</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>TR, SBS</td>
<td>X</td>
<td>B_TR_X_PM</td>
<td>PG64-28NVTR</td>
</tr>
<tr>
<td></td>
<td>TR</td>
<td>Y</td>
<td>B_TR_Y</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>TR, SBS</td>
<td>Y</td>
<td>B_TR_Y_PM</td>
<td>PG76-22NVTR</td>
</tr>
<tr>
<td></td>
<td>TR</td>
<td>Z</td>
<td>B_TR_Z</td>
<td>PG58-22TR</td>
</tr>
<tr>
<td></td>
<td>TR, SBS</td>
<td>Z</td>
<td>B_TR_Z_HPM</td>
<td>PG58-22TR +7.5%</td>
</tr>
<tr>
<td>Base C</td>
<td>--</td>
<td>--</td>
<td>Base C</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>SBS</td>
<td>--</td>
<td>C_PM</td>
<td>PG76-22NV $^e$</td>
</tr>
<tr>
<td>Base D</td>
<td>--</td>
<td>--</td>
<td>Base D</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>SBS</td>
<td>--</td>
<td>D_HPM</td>
<td>PG58-28 +7.5%</td>
</tr>
</tbody>
</table>

*a- TR denotes terminally blended Tire Rubber; SBS denotes Styrene-Butadiene-Styrene.
b- Certain formulations include additional base binders, which may or may not be the same as one another, --signifies no addition or modification.
c- PM denotes Polymer; HPM denotes High Polymer dosage rate.
d- The “NV” extension indicates that the asphalt binder meets the NDOT PG-plus system.
e- NDOT specification requires a minimum of 3% SBS.

From this table, the relationship of the asphalt binders is clearly indicated. There are four different kinds of base binders, Base A, B, C and D. PM represents polymer modified with the base binder, e.g. A_PM is SBS modified based on base A binder. TR represents the tire-rubber modified binder, and there are also three undisclosed binder component X, Y, Z which are added to B_TR to combine with polymer (SBS) to get the modified binders of B_TR_X_PM, B_TR_Y_PM and B_TR_Z_HPM. HPM indicates the binder TR_B_Z and Base D are modified with 7.5% content of SBS polymer.
It is should be noted that the modified asphalt binders used in this study were provided by the Paramount Nevada in combination with Wright Asphalt Products for the terminally blended rubber products. At the time of writing, the information of the modification process was not disclosed by the asphalt binder supply company due to the proprietary nature of the terminal blend and formulation processes. As shown in the Figure 4.1 a, the terminally blended asphalt binder studied in this project is more uniform and does not contain large particulate rubber as is present in the example shown in (b) which is an example wet process crumb rubber asphalt binder and its rubber particle size is evident to identify.

![Figure 4.1 Tire Rubber Modified Asphalt Binder Used in this Study (a), not (b)-Crumb Rubber Binder.](image)

4.2 Aging Conditions

The asphalt binder aging was conducted on three different temperatures of 50°C, 60°C and 85°C which were set on specialized forced draft ovens. The aging samples were prepared in standard pressure aging vessel (PAV) pans with the dimensions of 140 mm
(5.5 in.) diameter by 9.5 mm (3/8 in.) deep as specified in AASHTO R28 and T179 (AASHTO, 2006). The samples were aged in PAV pans however without the high pressure vessel. The pressure in the draft ovens is equal to the local atmospheric air pressure.

Utilizing the specific gravity of each asphalt binder, an appropriate mass of asphalt binder was added to each pan to result in an asphalt film thickness of 1 mm (0.04 in.) according to Equation 4.1, which generally results in about 15.7 grams of binder in each PAV pan (Morian, 2014).

\[
M_b = \frac{G_b \rho_w \pi d^2 h}{4}
\]

Equation 4.1

The sample pans were placed on multiple racks, with eight samples per rack as standard practice. In the consideration of uniform aging in the air force-drafted oven, the location of the PAV pans was arranged properly, each sample was blended by two aged PAV pans asphalt binder. One pan was located on the top front rack and another one was located on the bottom back rack. The reason of doing like this was to minimize the discrepancy in the aging process due to inconsistent temperature and oxygen recirculation rate.

| Table 4.2 Asphalt Binder Laboratory Aging Condition |
|---------------|-----------------|-----------------|-----------------|
| Aging Temperature | 50°C | 60°C | 85°C |
| Aging Duration | 4, 8, 15, 30, 60, 120, 180, 240 days | 2, 4, 8, 15, 30, 60, 100, 160 days | 0.5, 1, 2, 4, 8, 15, 25, 40 days |
4.3 DSR Frequency Sweep Test

Frequency sweep tests were performed on the aged asphalt binders by using Dynamic Shear Rheometer (DSR) which were manufactured by Anton Paar Company. In WRSC asphalt lab, there are two DSR equipment: MCR 301 and MCR 302 (see Figure 4.2). As mentioned previously in Chapter 3, the frequency sweep tests were conducted with 8 and 25 mm diameter spindles. There are 8 different isothermal frequency sweep templates: 15 to -2°C, 46 to 22°C, 52 to 64°C, 60 to 80°C, 85 to 100°C, 100°C, and 100 to 110°C.

Usually, the amplitude test (strain sweep test) should be conducted at the beginning to find the LVE region for the specific binder at fixed temperature. Based on the previous study experience, 1% strain level can make sure the tests of all the studied asphalt binders were running under the LVE region. For each asphalt binder case, there were two replicate samples conducted at each test temperature condition. Table 4.3 shows the matrix of frequency sweep test condition for each binder.
(a) DSR equipments

(b) MCR302

(c) MCR301

Figure 4.2 The DSR equipment in UNR asphalt lab.
Table 4.3 Matrix of DSR Frequency Sweep Test Conditions

<table>
<thead>
<tr>
<th>DSR Geometry</th>
<th>8mm dia.</th>
<th>2mm gap&lt;sup&gt;1&lt;/sup&gt;</th>
<th>25mm dia.</th>
<th>1mm gap&lt;sup&gt;2&lt;/sup&gt;</th>
<th>0.5mm gap&lt;sup&gt;2&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base A</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>52-60-64</td>
<td>60-70-80</td>
</tr>
<tr>
<td>A_PM</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Base B</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>B_TR</td>
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<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>B_TR_X</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>B_TR_Y</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>B_TR_Z</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>B_TR_X_PM</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>B_TR_Y_PM</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>B_TR_Z_HPM</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Base C</td>
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<td>✓</td>
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<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Base D</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>D_HPM</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

1 – 1% shear strain, 0.1-100 rad/s (verify) with 6 points/decade (19 total data points per isotherm).

2 – 1% shear strain, 0.01 – 100 rad/s 2.25 pts/decade (10 total data points per isotherm).

4.4 FTIR-ATR Spectra Test

Fourier transform infrared spectroscopy test (FTIR) was conducted to investigate the asphalt binder chemistry functional groups change under different thermal oxidation aging condition. The succinct theory of FT-IR was described in chapter 3. Compared with the solvent dissolved asphalt binder, or KBr pellet samples, the Attenuated Total Reflectance (ATR) mode was convenient to conduct the test without needing to other assistance. It is considered crucial to get the representative asphalt binder sample to achieve a qualified spectra.

In this regard, the single-beam reflection diamond ATR accessory was employed as an innovative tool to evaluate the asphalt binder microstructure change with oxidation.
aging effect. In this study, the IR absorption was set as the test mode, and the wavenumber range of 4000 to 400 cm\(^{-1}\) at a resolution of 4 cm\(^{-1}\) was selected as the default setting. For each spectra, forty scans were averaged as the resultant spectrum which was recorded by the OMNIC™ software and preview checking was conducted to get a stable and consistent spectra before the final scanning. The following schematic diagram described the FT-IR ATR test procedure.

**Figure 4.3 Schematic Diagram of FT-IR ATR Test Procedure**

- **Step 1:** Put the small can in big can, then put in the oven for 5 mins

- **Step 2:** Stirring the binder, drop around 0.5 g on the diamond, cover with paper, and put a fixed load

- **Step 3:** Wait for 5 mins, scan the spectra for 3 times

- **Step 4:** Repeat step 1 to 3, get the replicate spectra
4.5 Summary

In this chapter, the information of the fourteen different types of asphalt binder selected as the objective study materials was explained. DSR and FT-IR ATR were the fundamental equipment to evaluate the asphalt binder rheological performance and chemistry functional groups information. The test conditions are summarized as below:

1. The objective asphalt binder was poured in the PAV pans with 1 mm thickness film and aged in the air force-drafted oven at 3 different temperature which went through eight different duration individually.

2. During the DSR test, isothermal frequency sweep test was conducted at 1% strain level. However, different asphalt binder had different temperature range.

3. The single-beam reflection diamond ATR accessory was employed to achieve the representative spectrum. And the test detail was described herein.
CHAPTER 5 TEST RESULTS AND DATA ANALYSIS

Based on the Dynamic Shear Rheometer (DSR) isothermal frequency sweep test result, the master curve which is shifted under the time-temperature superposition principle was developed, then the different rheological indices (low shear viscosity-LSV, Crossover shear modulus-G*c, Glover DSR function-G’/η’/G’, and Glover-Rowe parameter-G-R) were picked up from the master curve under specific condition (i.e. reference temperature and loading frequency). Simultaneously, based on the spectra result of the Fourier Transform Infrared Spectroscopy (FTIR), the area of the chemistry functional group-carbonyl (CA) which represents the asphalt binder oxidation extent was calculated by utilizing macro model in the OMNIC™ software.

It is practical to analyze the relationship between the change in carbonyl functional group and the related rheological parameters at the same oxidative aging state. At first, the least square regression by Excel Solver Function was implemented to get the best fit curve which was used to achieve the kinetic aging factors, such as k_f, k_c, E_ac, E_af, A_ac, and A_af. In this section, the effect of the different modifier (i.e. tire rubber, SBS) and base binder on these factors was evaluated.

Later on, the hardening susceptibility, which indicates asphalt binder resistant oxidation capability, was evaluated in this chapter.

5.1 Oxidation Rate Parameters

The Nicolet 6700 infrared spectrometer supplied by Thermo Fisher Scientific Inc. was used to measure the spectra to track the oxidized asphalt binder chemistry functional group change after the specific thermal oxidation duration. The test was conducted on the
Attenuated Total Reflectance (ATR) accessory and the interested functional groups (Carbonyl and Sulfoxide) area were calculated by the macro function in the OMNIC™ software, version 8. The macro function calculation theory was described in Chapter Three. For each oxidative aged asphalt binder sample, a minimal six (6) spectra were averaged to increase the measurement accuracy. The average carbonyl and sulfoxide area results are tabulated in Table 5.1-5.3.

Appendix A shows the figures of the carbonyl measurement result which is indicated by the single symbol and the predicted regression curve. From all the figures, the carbonyl area is sensitive to the aging temperature, especially at 85°C, the duration of fast rate is much shorter than other low temperatures and the magnitude of constant rate is also higher, which is consistent with the chemistry principle-Arrhenius Reaction Function (Equation 3.9). The statistical data will be analyzed in other section of this chapter.
Figure 5.1 Fast-rate kinetics for asphalt binders with Base A and A_PM.

From the Figure 5.1, it shows that both of the base binder A and polymer modified binder A_PM had the similar trend—the fast rate of the reaction increases with the temperature increasing from 50°C to 85°C. Compared with base binder A, binder A_PM had lower reaction rate and the difference became larger with the increasing temperature. The slope, or the $E_{af}$ terms were observed to be slightly different, which were 47 and 39, respectively. The term $E_{af}$, which is called activation energy, can be used to indicate the reaction sensitivity to the surrounding environment. The higher value means more friendly environment is needed during the reaction. It is well known that the activation energy is independent of the temperature but material resource dependent.
Figure 5.2 Fast-rate Kinetics for Asphalt Binders with Base C and C_PM.

The binder Base C and C_PM had similar trend like binder Base A version, from the Figure 5.2, while the slightly difference is that the difference is larger than the former binder, such as the activation energy changed from 60 to 36 rather than from 47 to 39. This phenomenon might be caused by the different modifier- any other polymer modifier or other combined interaction and those results need to be verified. However, the Figure 5.3 indicates the high content polymer increased the activation energy, even though the fast rate of the oxidation aging process decreased compared with the base binder Base D.
For the binder of Base B series, the consideration of the fast-rate kinetics should include the influence of the terminal blend tire rubber, TR, other unknown binder component-X, Y, Z, and polymer. The related fast-rate kinetic results are indicated in the following Figures 5.4 to 5.8. The first comparison made was between Base B and the binder B_TR, and from Figure 5.4, it shows that the tire rubber reduced the fast rate reaction. It also indicates that the difference between the two binders was slightly different with the various temperatures, i.e. 50, 60, and 85°C. This also can be seen from the close activation energy-$E_\text{af}$, which was 54 and 60, respectively. Figure 5.5 shows the influence of the additions of the secondary base asphalt binders X, Y, and Z led to modest variations in the $k_f$ terms, but only very minor influence on the $E_\text{af}$ terms, which were 60, 61, 57 and 57, respectively. The additions X and Y increased the fast rate by a slight
margin compared with the binder B_TR. However, the addition of asphalt Z decreased the fast-rate oxidation reaction.

Figure 5.4 Fast-rate Kinetics for Asphalt Binders with Base B and B_TR.

Figure 5.5 Fast-rate Kinetics for Asphalt Binders with B Series.
The effect of the polymer on the base binders which were treated by the tire rubber were shown in Figure 5.6 to 5.8. Both of the polymer-modified binders exhibited an increased in the oxidation rate under the specific temperatures in the fast-rate oxidation period. This phenomenon is different than the previous binders-Base A, Base C and Base D where the polymer presented a reduction in the fast-rate period.

As shown in Figure 5.6, compared with the binder B_TR_X and B_TR_X_PM, the fast-rate increased when the additive of polymer was added, and the activation energy decreased from 61 to 47. At the same time, the $k_f$ of the two binders became closer with the increasing temperature. While this trend was slightly different with the binder B_TR_Y and B_TR_Y_PM, the activation energy value was a little larger than the latter binder. As mentioned previously, the 7.5% content polymer was categorized as high content. The binder B_TR_Z_HPM for each of temperatures included in this study.

For an interim summary of the fast-rate kinetics parameter $k_f$, the only polymer modified asphalt binder showed lower levels of the fast-rate $k_f$ term than the based binder, such as Base A, Base C, and Base D. However, the terminal blended rubber reduced the oxidation rate and the subsequent polymer modification increased the levels back closer to the original binder at the same specific aging temperatures. This means that the tire rubber and the polymer had opposite or neutralized influence on the oxidation process when both of them were blended together to the base binder and this combined influence was different with the single additive effect.
Figure 5.6 Fast-rate Kinetics for Asphalt Binders with B_TR_X and B_TR_X_PM.

Figure 5.7 Fast-rate Kinetics for Asphalt Binders with B_TR_Y and B_TR_Y_PM.
Figure 5.8 Fast-rate Kinetics for Asphalt Binders with B_TR_Z and B_TR_Z_HPM.

Figure 5.9 Constant-rate Kinetics for Asphalt Binders with Base A and A_PM.
Similar to the fast-rate kinetic analysis, the Figure 5.9 to 5.16 indicate the constant-rate-kc measurement, specific to the inclusion of the terminal blend TR rubber and polymer additives.

From Figure 5.9, the Base A and A_PM binders presented fairly similar constant oxidation rates, which means in the long period view, the effect of this type of polymer on the oxidation aging was minimized. The activation energy was also dropped from 80 to 72 with the modification. Compared to Figure 5.10 and 5.11, which shows that both of the polymer modified asphalts had lower constant rate than the respective base binders. The activation energy value jumped up slightly from 93 to 98 for Base C series, and increased from 79 to 89 for Base D series which has the high polymer content.

![Figure 5.10 Constant-rate Kinetics for Asphalt Binders with Base C and C_PM.](image-url)
Figure 5.11 Constant-rate Kinetics for Asphalt Binders with Base D and D_HPM.

For the binder Base B version, the measured constant rate oxidation parameters were presented in Figure 5.12 to 5.16. At first, the variation between the modified binder and control binder was more consistent and smaller compared the fast-rate oxidation measures. Figure 5.12 indicates that the tire rubber modified binder B_TR had lower constant rate kinetic value than the binder Base B and the magnitude became closer with the increasing temperatures. The secondary binder additions of X, Y, and Z were added to B_TR to make the intermediate binder B_TR_X, B_TR_Y and B_TR_Z. Figure 5.13 shows that all of the constant rate parameters increased with the addition of the secondary base asphalts. However, the change in activation energy had variable directions, B_TR_Y decreased from 93 to 84, while another increased from 93 to 98 and 99, respectively.

Comparing the polymer modified binder with the tire rubber and the control binder-secondary binder addition modified binder in Figure 5.14 to 5.16, the effect of the
modifier on the kinetic parameter was different with different modified asphalt binder. Both of the binder B_TR_X_PM and B_TR_Z_HPM had higher level of constant rate than the X, Y, Z versions binder. The binder B_TR_Y_PM had lower rate under the polymer modification. While both of the three polymer modified binder had lower level of activation energy. All the measured CA and Sulfoxide data was figured in Appendix A.

![Figure 5.12 Constant-rate Kinetics for Asphalt Binders with Base B and B_TR.](image-url)
Figure 5.13 Constant-rate Kinetics for Asphalt Binders with B_TR, B_TR_X, B_TR_Y and B_TR_Z.

Figure 5.14 Constant-rate Kinetics for Asphalt Binders with B_TR_X and B_TR_X_PM.
Figure 5.15 Constant-rate Kinetics for Asphalt Binders with B_TR_Y and B_TR_Y_PM.

Figure 5.16 Constant-rate Kinetics for Asphalt Binders with B_TR_Z and B_TR_Z_HPM.
Table 5.1 Carbonyl and Sulfoxide Area at 50°C Measurement Result.

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|        |            | 15     | 0.5425 | 0.3163 | 0.5479 | 0.4357 | 0.4604 | 0.3795 | 0.4204 | 0.2066 | 0.3888 | 0.2848 | 0.5594 | 0.2848 | 0.5911 |
|        |            | 30     | 0.6511 | 0.3877 | 0.6344 | 0.5712 | 0.5419 | 0.4558 | 0.5139 | 0.2712 | 0.4629 | 0.3617 | 0.6338 | 0.3282 | 0.6930 |
|        |            | 60     | 0.7235 | 0.451  | 0.7503 | 0.7034 | 0.6364 | 0.5646 | 0.6228 | 0.3669 | 0.5128 | 0.4395 | 0.7021 | 0.3984 | 0.7163 |
|        |            | 120    | 0.8467 | 0.5242 | 0.841  | 0.8485 | 0.7054 | 0.6859 | 0.7217 | 0.4039 | 0.5666 | 0.5051 | 0.8537 | 0.4465 | 0.8331 |
|        |            | 180    | 0.8006 | 0.5394 | 0.8177 | 0.9126 | 0.7681 | 0.7172 | 0.7694 | 0.4281 | 0.6414 | 0.5199 | 0.8779 | 0.4693 | 0.9209 |
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Table 5.2 Carbonyl and Sulfoxide Area at 60°C Measurement Result.

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Table 5.3 Carbonyl and Sulfoxide Area at 85°C Measurement Result.

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<td>0.6798</td>
<td>0.5046</td>
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<td>0.8716</td>
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<td>0.8223</td>
<td>0.9150</td>
<td>0.5079</td>
<td>0.7439</td>
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<td>1.0920</td>
<td>0.6620</td>
<td>1.0165</td>
<td>0.7954</td>
<td></td>
</tr>
</tbody>
</table>
In previous chapter, the details regarding the background about the asphalt binder aging kinetic factors was described. Equation 3.8 shows the oxidation reaction relation of the factors, while table 5.4 includes the oxidation aging parameters with the analysis discussed in the following section.

### Table 5.4 Asphalt Binder Oxidation Aging Parameters.

<table>
<thead>
<tr>
<th>Binder ID</th>
<th>Eac (KJ/mol)</th>
<th>Aac (CAg/day)</th>
<th>Eaf (KJ/mol)</th>
<th>Aaf (Cag/day)</th>
<th>k&lt;sub&gt;f&lt;/sub&gt; (CA/day)</th>
<th>k&lt;sub&gt;c&lt;/sub&gt; (CA/day)</th>
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</thead>
<tbody>
<tr>
<td>Base_A</td>
<td>80.1</td>
<td>5.93E+09</td>
<td>46.8</td>
<td>6.35E+06</td>
<td>0.171</td>
<td>0.2878</td>
</tr>
<tr>
<td>A_PM</td>
<td>71.8</td>
<td>3.10E+08</td>
<td>38.9</td>
<td>2.00E+05</td>
<td>0.103</td>
<td>0.1589</td>
</tr>
<tr>
<td>Base_B</td>
<td>84.4</td>
<td>2.37E+07</td>
<td>53.8</td>
<td>1.92E+07</td>
<td>0.039</td>
<td>0.0702</td>
</tr>
<tr>
<td>B_TR</td>
<td>93.3</td>
<td>3.68E+11</td>
<td>60.1</td>
<td>6.24E+07</td>
<td>0.012</td>
<td>0.0236</td>
</tr>
<tr>
<td>B_TR_X</td>
<td>98</td>
<td>2.54E+12</td>
<td>61.1</td>
<td>1.09E+08</td>
<td>0.014</td>
<td>0.0286</td>
</tr>
<tr>
<td>B_TR_X_PM</td>
<td>82.1</td>
<td>1.30E+10</td>
<td>47.5</td>
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<td>0.043</td>
<td>0.0728</td>
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<tr>
<td>B_TR_Y</td>
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<td>2.17E+10</td>
<td>57.4</td>
<td>3.48E+07</td>
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</tr>
<tr>
<td>B_TR_Y_PM</td>
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<td>1.34E+09</td>
<td>61.2</td>
<td>2.38E+08</td>
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<td>0.0615</td>
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<tr>
<td>B_TR_Z</td>
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<td>3.56E+12</td>
<td>56.9</td>
<td>1.63E+07</td>
<td>0.010</td>
<td>0.0195</td>
</tr>
<tr>
<td>B_TR_Z_HPM</td>
<td>90.9</td>
<td>2.45E+11</td>
<td>51.1</td>
<td>6.34E+06</td>
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<td>0.0614</td>
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<tr>
<td>Base_C</td>
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<td>5.12E+11</td>
<td>60.3</td>
<td>6.06E+08</td>
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<td>0.2116</td>
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<tr>
<td>C_PM</td>
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<td>2.04E+12</td>
<td>36.5</td>
<td>4.43E+04</td>
<td>0.056</td>
<td>0.0848</td>
</tr>
<tr>
<td>Base_D</td>
<td>78.8</td>
<td>3.69E+09</td>
<td>36</td>
<td>6.98E+04</td>
<td>0.104</td>
<td>0.1558</td>
</tr>
<tr>
<td>D_HPM</td>
<td>89</td>
<td>8.89E+10</td>
<td>45.2</td>
<td>5.34E+05</td>
<td>0.026</td>
<td>0.0434</td>
</tr>
</tbody>
</table>

From Figure 5.17 to 5.20, the results of the oxidation parameters, such as A<sub>af</sub>, A<sub>ac</sub>, E<sub>af</sub> and E<sub>ac</sub>, are presented as bar chart format. The factors A<sub>af</sub> and A<sub>ac</sub>, which are specific to those of the rate constant, are mathematically the interception of the oxidation reaction equation. These factors will vary depending on the order of the reaction. If the reaction is first order it has the units s<sup>-1</sup>, and for this reason it is often called the frequency factor or attempt frequency of the reaction. Compared the Figure 5.17 and Figure 5.18, the
magnitude of $A_{ac}$ value is multiple orders of magnitude higher than the comparative $A_{af}$ value.

Comparing the parameters of $A_{af}$ and $A_{ac}$, these two factors do not follow the exactly same trend for each binder. It shows that most of the binders have the same direction, except the binders, B_TR_Y and B_TR_Y_PM, Base C and C_PM. For the $A_{af}$, the data increased with the polymer modification for B_TR_Y and significantly dropped down with another polymer modification for Base C binder. However, for the $A_{ac}$ factor, the trends changed the direction.

The similar phenomenon was found for the activation energy parameters-$E_{af}$ and $E_{ac}$, only of the binders B_TR_Y and B_TR_Y_PM, and, Base C and C_PM had different direction.

Figure 5.17 Kinetic Parameter Pre Exponent-$A_{af}$. 

![Aaf graph](image-url)
Figure 5.18 Kinetic Parameter Pre Exponent-\( A_{ac} \).

Figure 5.19 Kinetic Parameter Activation Energy-\( E_{af} \).
Figure 5.20 Kinetic Parameter Activation Energy-E_{ac}.

Previous research has found that there was a good correlation between the kinetics parameters for 15 different modified and unmodified asphalt binders (Jin et al., 2011). The correlation analysis was also conducted here.

Figure 5.21 shows the correlation between the activation energy of the fast-rate and constant-rate oxidation parameters. There is not a good correlation for these two factors for the binders in this study, the correlation coefficient is only 0.1165. Interestingly, the correlations between the parameters, $A_{af}$ and $E_{af}$, $A_{ac}$ and $E_{ac}$ are very good, which the correlation factor is 0.9428 and 0.997, respectively (Jin et al., 2011). And the correlation equations are indicated as below:

$$A_{af}=0.6873\exp(0.3157E_{af}) \quad \text{Equation 5.1}$$

$$A_{ac}=0.0088\exp(0.3386E_{ac}) \quad \text{Equation 5.2}$$
It should be noted that the exponent and intercept values are primarily consistent with the previous study conclusion, even though the specific number is different (Jin et al., 2011).

**Figure 5.21** Correlation between Kinetics Parameters $E_{af}$ and $E_{ac}$.
Figure 5.22 Correlation between Kinetics Parameters $A_{af}$ and $E_{af}$.

Figure 5.23 Correlation between Kinetics Parameters $A_{ac}$ and $E_{ac}$.

Therefore, an overall summary of the change in the oxidation measures as result of the modification process is indicated in the following table. The influence of binders
which contains terminally blended rubber on the fast-rate and constant-rate oxidation parameters were observed to be somewhat inconsistent with one another. Further, the overall reduction in the level of \( k_f \) terms were much more obvious than the constant-rate \( k_c \) for the rubber modified asphalt binders.

**Table 5.5 Influence of Asphalt Binder Modification on Oxidation Kinetics Parameters.**

<table>
<thead>
<tr>
<th>Asphalt Binder</th>
<th>Modifier</th>
<th>Influence of Modification on ( k_f )</th>
<th>Influence of Modification on ( E_{af} )</th>
<th>Influence of Modification on ( k_c )</th>
<th>Influence of Modification on ( E_{ac} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>SBS</td>
<td>↓</td>
<td>↓</td>
<td>↓</td>
<td>↓</td>
</tr>
<tr>
<td>C</td>
<td>SBS</td>
<td>↓</td>
<td>↓</td>
<td>↓</td>
<td>↑</td>
</tr>
<tr>
<td>D</td>
<td>SBS</td>
<td>↓</td>
<td>↑</td>
<td>↓</td>
<td>↑</td>
</tr>
<tr>
<td>B</td>
<td>TR</td>
<td>↓</td>
<td>↓</td>
<td>↓</td>
<td>↑</td>
</tr>
<tr>
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<td>↑</td>
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</tr>
<tr>
<td>B_TR_Y</td>
<td>SBS</td>
<td>↑</td>
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<td>↓</td>
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<td>B_TR_Z</td>
<td>SBS</td>
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<td>↓</td>
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5.2 Master Curve

In this study, all the master curves were shifted from the isothermal frequency sweep tests by the aiding of RHEA™ Version 1.2.9 software. The reference temperature was set as 60°C, and the isothermal frequency sweep curves were shifted by prony series function, the shift factor function was Kaelble modeling. At the time of writing, the master curve information of the studied asphalt binder was not disclosed by the supplier.

5.3 Aging Rheological Performance Indices

With the asphalt binder aging, the asphalt binder becomes more brittle and stiffer which can be observed by the shear modulus increases under the same condition, i.e. temperature and loading time. Usually, the rheological indices, e.g. LSV, \( G^*c \), R value, DSR function, and G-R parameters, are selected to evaluate the asphalt binder rheological
performance under isothermal oxidation aging effect. These parameters are quite informative and each of them have their own advantage and disadvantage during the rheological performance analysis (Morian et al., 2015). While the scope of this study mainly focuses on the representation of these parameters with respect to the oxidation measures represented as hardening susceptibility parameters. The multi linear regression analysis was conducted to evaluate the significance of the binder modification on the rheological performance change. The results were tabulated in Appendix B.

5.3.1 Hardening Susceptibility – Low Shear Viscosity (LSV)

Beginning with the LSV values based upon the referenced methodology noted in Equation 3.16 utilizing the measurements of Base A, C, and D and their respective modified versions, the hardening susceptibility relationships are considered in Figure 5.24 to Figure 5.26. Similar to the oxidation kinetics measures, the Base B and respective modified versions are presented separately in the following Figure 5.27 to Figure 5.30. In the interest of space, the actual HS parameters, i.e. slope (HS) and intercept (m) terms, have been summarized in Table 5.6 for each of the respective rheological indices, e.g. LSV, $G_\ast^c$, DSR Fn and G-R parameters.
Figure 5.24 Hardening Susceptibility-LSV for asphalt binders with Base A and A_PM.

Figure 5.25 Hardening Susceptibility-LSV for asphalt binders with Base C and C_PM.
Referencing the Base A, C, and D asphalt binders presented in Figure 5.24 to Figure 5.26 and summarized in Table 5.6, it is clear that the influence of the polymer modification significantly increases the stiffness, e.g. LSV, of the asphalt binders at a given oxidation level, i.e. CA value. This is a highly expected result given the fixed measurement conditions, i.e. 60°C and 0.001 rad/s coupled with the known benefit of polymer modification, i.e. increasing the rutting resistance at high temperatures without disrupting the low-temperature properties of the asphalt binder. This influence has been quantified in the intercept of the HS relationship (e^m) presented in Table 5.6. More thorough evaluations of the e^m term based upon LSV suggested that the magnitude of the stiffening effect was proportional to the assumed polymer loading rate discussed in the previous section. Specifically, the higher the SBS polymer loading rate, the greater the increase in the viscosity of the asphalt binder, as would be expected given the

**Figure 5.26 Hardening Susceptibility-LSV for asphalt binders with Base D and D_HPM.**
relatively high temperature of 60°C utilized for these LSV determinations. It was further noted that the slope of the HS relationship for these particular binders was also significantly reduced with SBS modification, though not by the same order magnitude as the intercept. From the statistical view of point, the SBS modification significantly affect the rheological performance which the P value is less than 0.05 for the intercept and the slope, as shown in Appendix B table 1.

Figure 5.27 Hardening Susceptibility-LSV for asphalt binders with Base B and B_TR.
Figure 5.28 Hardening Susceptibility-LSV for asphalt binders with B_TR_X and B_TR_X_PM.

Figure 5.29 Hardening Susceptibility-LSV for asphalt binders with B_TR_Y and B_TR_Y_PM.
Hardening Susceptibility - LSV for asphalt binders with B_TR_Z and B_TR_Z_HPM.

Similar observations of the variation of Base B asphalt binder considered in Figure 5.27 to Figure 5.30 and Table 5.6 indicate a similar trend with an increase in the viscosity, i.e. LSV, and a decrease in the slope, i.e. HS parameters with the SBS modification of these asphalt binders. Comparing the influence of the rubber modification, i.e. B_TR to Base B, indicated a similar increase in viscosity, but also a substantial increase in the HS of the B_TR asphalt binder. This result is suspected to be the combined effect of the terminally blended process by which the rubber has been added to the Base B asphalt binder. This process, though not fully disclosed due to proprietary limitations, is not the simple addition of tire rubber to an asphalt binder, but is a more involved digestion procedure. Regardless of the process utilized, the end result in an increase in both the $e^m$ and HS parameters. However, once the B_TR asphalt binder was utilized in additional binder formulations, e.g. blended with Bases X, Y, or Z, the HS
parameters were slightly reduced from the level of the B_TR asphalt binder. Further consideration of the polymer modification of the blended base asphalt binders notes a similar reduction in the HS and the corresponding increase in the viscosity, i.e. $e^m$, noted with the previous asphalt binders which did not contain the TR material. In short, the addition of the TR binder into the process did not noticeably influence the benefit of the polymer modification process. The statistical analysis results indicated that the tire rubber, Y, Z and SBS polymer can significantly influence the LSV performance of the studied asphalt binders. The binder B_TR_X did not change the LSV slope compared with the base binder B_TR and the p value is 0.104.

It has been observed that such considerations of the HS in terms of LSV have commonly been utilized in more comprehensive oxidation modeling efforts (Lunsford, 1994, Han et al, 2013). Many of these more robust oxidation calculations include a correlation of various forms between the LSV and the diffusivity of the modeled asphalt binder as an input parameter to in-place oxidation rate, such as equation 3.30. However, the majority of these correlations have not been developed to include the substantial increase in LSV and the subsequent calculated reduction in diffusivity, due to the polymer modification process.

5.3.2 Hardening Susceptibility – Crossover Modulus

Considering the methodology based upon the crossover modulus relationships associated with Equation 3.14, the HS parameters of Base A, C, and D and their associated modified version are presented in Figure 5.31 to Figure 5.33 and in Table 3.
Similar evaluations of the Base B set of asphalt binders are likewise considered in Figure 5.34 to Figure 5.37 and again in Table 5.6.

Figure 5.31 to 5.37 indicate the expected relative reduction in the crossover modulus (G*c) with the increased levels of oxidation, i.e. Carbonyl Area. It should be noted here is that the drop of crossover modulus is not same as the drop of the asphalt binder modulus. Another similar rheological index (R) which is comparable to crossover modulus-G*c as R+G*c=Gg (glass modulus, default value as 1*10^9 pa, but other define it as 3*10^9 pa) has been defined (Christensen and Anderson, 1992). So it is understandable that this trend is the result of the systematic shift of the asphalt binder master curve toward higher shear modulus with the increased aging levels. This shifting results in a reduction in defining crossover frequency in order to maintain the phase angle of 45°, i.e. the magnitude of loss moduli is equal to storage moduli, eventually resulting the drop of the crossover modulus as noted in the following Figures 5.31 to 5.37.
Figure 5.31 Hardening Susceptibility-$G^*c$ for asphalt binders with Base A and A_PM.

Figure 5.32 Hardening Susceptibility-$G^*c$ for asphalt binders with Base C and C_PM.
Figure 5.33 Hardening Susceptibility-$G^*_c$ for asphalt binders with Base D and D_HPM.

More concentrated observations of Figure 5.31 to 5.33 considering Bases A, C, and D and their associated modified versions indicate relatively similar trends of $G^*_c$ with oxidation, with the exception of the C_PM asphalt binder. This binder in particular exhibited a much higher HS compared to the others in the Figure and in Table 5.6, even if the highest CA point were removed as an anomalous measure for the C_PM asphalt binder. More careful observations of Figure 5.31 to 5.33 and Table 5.6 attempting to differentiate the other $G^*_c$ HS measures indicated much less variation and a lack of systematic influence of the polymer modification between the respective asphalt binders, as compared to that of the LSV determinations. However, two of the three binders, Base A and D, presented fairly similar HS values while Base C exhibited nearly double the HS value with $G^*_c$ as a result of the polymer modification process. The multi linear regression
analysis shows that the SBS modification can significantly influence the $G^*c$ value of the asphalt binders.

Figure 5.34 Hardening Susceptibility-$G^*c$ for asphalt binders with Base B and B_TR.
Figure 5.35 Hardening Susceptibility-$G^\ast c$ for asphalt binders with B_TR_X and B_TR_X_PM.

Figure 5.36 Hardening Susceptibility-$G^\ast c$ for asphalt binders with B_TR_Y and B_TR_Y_PM.
Figure 5.37 Hardening Susceptibility-G*c for asphalt binders with B_TR_Z and B_TR_Z_HPM.

Considerations of $G_c^*$ with the Base B family of asphalt binder presented in Figure 5.34 to 5.37 indicated a greater degree of separation between the HS of the asphalt binders. Referencing Table 5.6, it can be observed that the HS of all but the B_TR_X asphalt binder increased to varying levels with binder modification, including the rubber modification of Base B. However, the rubber modification of Base B and the polymer modification of B_TR_X resulted in fairly similar values of HS, again noting the strict statistical evaluations was also performed. Those findings are countered by the nearly doubling in the HS term of $G_c^*$ with the modification of both the B_TR_Y and BTR_Z asphalt binders. For the statistical view of point, the polymer SBS and binder component Z can significant affect the G*c performance while the component X and Y did not change the G*c vs CA slope.
Overall, considerations of the HS parameters resulting from $G_c^*$ were found to be asphalt binder source dependent, but not necessarily consistently influenced by the terminally blended rubber asphalt binder, TR. As a brief summary, five of the seven HS determinations were increased with binder modification, with the results ranging from marginal amounts to more than doubling of the HS values for certain asphalt binders.

5.3.3 Hardening Susceptibility – Glover-Rowe Parameter

Additional considerations based upon the Glover-Rowe parameter methodology presented in Equation 3.15, the HS relationships are presented in Figures 5.38 to 5.44 and in Table 5.6 in graphical and tabular forms, respectively. Acknowledging the fact that alternative testing conditions have been considered and may be beneficial (Rowe et al., 2014), this analysis has been conducted at 15°C and a testing frequency of 0.005 rad/s, as is the current standard of practice associated with this methodology. As such, the HS comparisons based upon the G-R parameter for Base A, C, and D and their associated modified versions are presented in Figure 5.38 to 5.40 and in Table 5.6. Similarly, the evaluations of the Base B set of asphalt binders are likewise considered in Figure 5.41 to 5.44 and again in Table 5.6.
Figure 5.38 Hardening Susceptibility-G-R for asphalt binders with Base A and A_PM.

Figure 5.39 Hardening Susceptibility-G-R for asphalt binders with Base C and C_PM.
Beginning with the HS relationships resulting from the G-R methodology on Base A, C, and D presented in Figure 5.38 to 5.41, a systematic influence of the addition of the polymer to the asphalt binder is readily apparent, similar to that of the LSV evaluation previously. In general, the polymer modified version of each respective binder exhibited a higher intercept, i.e. $e^{m}$, and a lower slope, i.e. HS term compared to the unmodified versions as evidenced by the relevant section of Table 5.6. The multi linear regression analysis results show that the tire rubber and component X, Y did not significantly affect the G-R parameters comparing with the base binder B_TR. In the other cases, the modifiers, such as SBS, Z, can significantly influence the G-R performance.
Figure 5.41 Hardening Susceptibility-G-R for asphalt binders with Base B and B_TR.

Figure 5.42 Hardening Susceptibility-G-R for asphalt binders with B_TR_X and B_TR_X_PM.
Figure 5.43 Hardening Susceptibility-G-R for asphalt binders with B_TR_Y and B_TR_Y_PM.

Figure 5.44 Hardening Susceptibility-G-R for asphalt binders with B_TR_Z and B_TR_Z_HPM.
Similar observations of the Base B and related asphalt binders presented in Figure 5.41 to 5.44 indicated quite similar findings with nearly identical HS relationships for Base B, B_TR_X, and B_TR_Y. B_TR_Z presented only moderate variation from these three base asphalt binders. Table 5.6 also indicated a significant reduction in the HS value based upon the G-R parameter of the all the polymer-modified asphalt binders compared to their unmodified origins, i.e. all four base asphalt binders. The rubber modification process indicated a slight increase in the HS, but only marginally so. While both modification processes resulted in a marked increase in the intercept term, i.e. $e^m$, of the HS relationship based upon the G-R parameter determinations. This increase in stiffness has, at times led to alternative measurement protocols, e.g. temperatures or frequencies, specific to each asphalt binder being evaluated. However, this study maintained the standard protocol of 15°C and 0.005 rad/s given the sensitive and undisclosed characteristics of each of the evaluated asphalt binders (Morian et al., 2015).

5.3.4 Hardening Susceptibility - Glover DSR function

Both the G-R and DSR functions are used to assess the asphalt pavement cracking extent through correlations with ductility measures that has been observed to correlate with the field cracking. This study was studied by several asphalt pavement researchers (Glover et al., 2015, Rowe et al., 2014), which correlated that the asphalt binder cracking at the measured ductility of 5 cm and severe cracking at the ductility of 3 cm. G-R is a revised representation of the DSR function. Therefore, it is highly expected that the finding of the trend is similar to the G-R for all the asphalt binders. The statistical analysis shows that the same direction was found with the G-R parameters.
Table 5.6 Hardening Susceptibility Parameters of Evaluated Asphalt Binders.

<table>
<thead>
<tr>
<th>Binder ID</th>
<th>LSV (Pa.s, 60°C, 0.001 rad/s)</th>
<th>Ge* (kPa, 25°C)</th>
<th>G-R Parameter (kPa, 15°C, 0.005rad/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>e^m</td>
<td>HS</td>
<td>e^m</td>
</tr>
<tr>
<td>Base A</td>
<td>8</td>
<td>11.1</td>
<td>54,503</td>
</tr>
<tr>
<td>A_PM</td>
<td>327</td>
<td>7.9</td>
<td>27,635</td>
</tr>
<tr>
<td>Base B</td>
<td>47</td>
<td>7.4</td>
<td>24,703</td>
</tr>
<tr>
<td>B_TR</td>
<td>243</td>
<td>10.0</td>
<td>13,479</td>
</tr>
<tr>
<td>B_TR_X</td>
<td>55</td>
<td>9.1</td>
<td>23,558</td>
</tr>
<tr>
<td>B_TR_X_PM</td>
<td>1,190</td>
<td>6.6</td>
<td>15,982</td>
</tr>
<tr>
<td>B_TR_Y</td>
<td>104</td>
<td>8.0</td>
<td>28,945</td>
</tr>
<tr>
<td>B_TR_Y_PM</td>
<td>16,536</td>
<td>5.1</td>
<td>21,971</td>
</tr>
<tr>
<td>B_TR_Z</td>
<td>218</td>
<td>7.4</td>
<td>23,562</td>
</tr>
<tr>
<td>B_TR_Z_HPM</td>
<td>17,940</td>
<td>4.8</td>
<td>15,176</td>
</tr>
<tr>
<td>Base C</td>
<td>11</td>
<td>9.6</td>
<td>54,166</td>
</tr>
<tr>
<td>C_PM</td>
<td>11,481</td>
<td>8.0</td>
<td>59,321</td>
</tr>
<tr>
<td>Base D</td>
<td>33</td>
<td>9.8</td>
<td>33,750</td>
</tr>
<tr>
<td>D_HPM</td>
<td>92,337</td>
<td>5.2</td>
<td>26,352</td>
</tr>
</tbody>
</table>

For each respective Rheological Index (RI), RI = e^m*+e^m
The range of R^2 values for the evaluated asphalt binders were:
LSV: 0.81-0.98, G*: 0.88-0.98, and G-R: 0.88-0.99

As an overall summary of the hardening susceptibility relationships based upon the respective rheological indices, Table 5.7 presents the relative change in the HS parameter specifically with respect to the modification of each of the asphalt binders in this evaluation.

In a general overview, Table 5.7 indicates that there was general agreement between the influence of the modification processes between the LSV and G-R parameter determinations representing binder characteristics at the high and lower end of the intermediate temperature range, i.e. 15°C. However the crossover modulus determinations presented less distinct deviations in the HS parameter specifically.

Despite these noted differences, each of the evaluation techniques indicated an increase in the HS of the Base B asphalt binders due to the addition of the terminally
blended rubber. However, it is important to recall that the addition of the rubber is not simply the addition of the rubber and other materials or processes utilized to include the rubber materials may have an influence. Due to the proprietary nature of this process, further details regarding the addition of the terminal blending process are not fully disclosed. However, this influence should be considered along with the addition of the SBS polymer as this condition would represent the commercially available products. In this manner, the polymer modification still consistently reduced the HS of the regardless of the inclusion of the rubber.

**Table 5.7 Influence of Asphalt Binder Modification on Hardening Susceptibility Parameters.**

<table>
<thead>
<tr>
<th>Binder</th>
<th>Modifier</th>
<th>LSV (pa.s, 60°C, 0.005 rad/s)</th>
<th>G*c (25°C)</th>
<th>G-R (15°C, 0.005 rad/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Int.</td>
<td>HS</td>
<td>Int.</td>
</tr>
<tr>
<td>A</td>
<td>SBS</td>
<td>↑</td>
<td>↓</td>
<td>↓</td>
</tr>
<tr>
<td>C</td>
<td>SBS</td>
<td>↑</td>
<td>↓</td>
<td>0.01</td>
</tr>
<tr>
<td>D</td>
<td>H-SBS</td>
<td>↑</td>
<td>↓</td>
<td>0.005</td>
</tr>
<tr>
<td>B</td>
<td>TR</td>
<td>↑</td>
<td>↑</td>
<td>↓</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B_TR</td>
<td>X</td>
<td>↓</td>
<td>0.104</td>
<td>↑</td>
</tr>
<tr>
<td></td>
<td>Y</td>
<td>↓</td>
<td></td>
<td>↑</td>
</tr>
<tr>
<td></td>
<td>Z</td>
<td>↓</td>
<td></td>
<td>↑</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B_TR_X</td>
<td>SBS</td>
<td>↑</td>
<td>↓</td>
<td>↑</td>
</tr>
<tr>
<td>B_TR_Y</td>
<td>SBS</td>
<td>↑</td>
<td>↓</td>
<td>↑</td>
</tr>
<tr>
<td>B_TR_Z</td>
<td>H-SBS</td>
<td>↑</td>
<td>↓</td>
<td>↑</td>
</tr>
</tbody>
</table>

Note: the number in the above table is P value, the P value of black cell is 0.
5.3.5 Correlation between the HS parameters

Even though the four rheological parameters represent differing performance direction with respect to the different modifier and base binder combinations, it is interesting to compare them to one another. Figure 5.45 presents the relationship between the LSV, G*c, and DSR function. Apparently, the unmodified binders, e.g. Base A, Base C and Base D have practically the same correlation for these parameters as shown in Figure 5.46. The correlation coefficients are 0.9225 and 0.9027, respectively.

However, for the modified asphalt binders, i.e. A_PM, C_PM and D_HPM, all of them exhibit the same relation forms, such as the form as LSV=A*(DSR Fn)^B and G*c=C*(DSR Fn)^D, but with different regression coefficients, as shown in Table 5.8. A_PM and C_PM have similar slopes (0.7947 and 0.8088) but different intercept (166.19 and 1482.1), while D_HPM has a higher interception of 7198.1 and lower slope of 0.6971 compared with A_PM and C_PM. Figure 5.47 indicated the correlation between the DSR Fn and G-R parameter for Base A, Base C and Base D series binders noting there is a strong correlation between them as the form as G-R=E*(DSR Fn)^F. This phenomenon was also can be observed for the Base B series binders, except the binder B_TR_X_PM, which has higher scatter data and low correlation factor as 0.2558.

Generally speaking, at the same level of DSR function, the LSV results observed to systematically increase from A_PM, C_PM to the highly modified binder-D_HPM. It is also noted that the crossover modulus has same trend that the G*c of binder D_HPM
(7.5% SBS) is higher than binder A_PM (3%SBS) and C_PM (3%SBS). The difference between them decreased with increasing DSR function value.

**Figure 5.45** Comparison of Selected Rheological Indices of Base A, Base C and Base D Version Binder.
Figure 5.46 Rheological Indices Relation of Base A, Base C, Base D Binders.

Figure 5.47 Correlation between G-R and DSR Fun. of Base A, Base C, and Base D Version Binder.
Due to the complexity of Base B series of binders, the plots were separated into two Figures to make them much easier to identify. As shown in the Figure 5.48, the LSV-DSR Fn slope increases from 0.474 to 0.6151 compared between the binder of Base B and B_TR, this effect should be contributed by the tire rubber. It also indicates that the LSV values of modified asphalt binder are higher than the unmodified base binder which is logical. Compared the modified asphalt binder with the base binders, the slope of LSV-DSR Fn is higher. The high content polymer modified asphalt binder D_HPM has the highest sensitivity with the DSR Fn change.

Figure 5.48 Correlation between LSV and DSR Fn. of Base B Series Binder.
Figure 5.49 Correlation between $G^\ast c$ and DSR $F_n$ of Base B Series Binder.

Figure 5.50 Correlation between $G-R$ and DSR $F_n$ of Base B Series Binder.
### Table 5.8 Comparison between Selected Rheological Indices.

<table>
<thead>
<tr>
<th>Binder ID</th>
<th>LSV(^1) (60°C, 0.005 rad/s)</th>
<th>G(^*)c (25°C)</th>
<th>G-R (15°C, 0.005 rad/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>Diff.(^2)</td>
</tr>
<tr>
<td>Base A</td>
<td>105.72</td>
<td>0.62</td>
<td>0.9191</td>
</tr>
<tr>
<td>A_PM</td>
<td>166.19</td>
<td>0.7947</td>
<td>28%</td>
</tr>
<tr>
<td>Base B</td>
<td>105.72</td>
<td>0.474</td>
<td>0.9708</td>
</tr>
<tr>
<td>B_TR</td>
<td>116.94</td>
<td>0.6151</td>
<td>30%</td>
</tr>
<tr>
<td>B_TR_X</td>
<td>151.84</td>
<td>0.5865</td>
<td>0.9223</td>
</tr>
<tr>
<td>B_TR_X_PM</td>
<td>271.33</td>
<td>0.7316</td>
<td>25%</td>
</tr>
<tr>
<td>B_TR_Y</td>
<td>192.62</td>
<td>0.5581</td>
<td>0.9521</td>
</tr>
<tr>
<td>B_TR_Y_PM</td>
<td>3884.30</td>
<td>0.542</td>
<td>3%</td>
</tr>
<tr>
<td>B_TR_Z</td>
<td>163.75</td>
<td>0.6018</td>
<td>0.9566</td>
</tr>
<tr>
<td>B_TR_Z_HPM</td>
<td>1871.60</td>
<td>0.7511</td>
<td>25%</td>
</tr>
<tr>
<td>Base C</td>
<td>144.39</td>
<td>0.5596</td>
<td>0.9355</td>
</tr>
<tr>
<td>C_PM</td>
<td>1482.10</td>
<td>0.8088</td>
<td>45%</td>
</tr>
<tr>
<td>Base D</td>
<td>100.46</td>
<td>0.6375</td>
<td>0.9212</td>
</tr>
<tr>
<td>D_HPM</td>
<td>7198.10</td>
<td>0.6971</td>
<td>9%</td>
</tr>
</tbody>
</table>

Note: 1-both of these correlations are based on DSR Fn.
2-the difference percentage is defined as Diff.=difference (Base binder-Modified binder)/Base binder
3-R\(^2\)=correlation coefficient.
The below Table 5.9 summarized the effect of the modifiers, such as tire rubber, SBS or both, on the sensitivity of the rheological parameters in relation to the DSR Fn. Associated with the table 5.8, both of these modifiers increase the slope of LSV and G*c, and without the influence of G-R, except the binder of B_TR_X which the data of B_TR_X_PM is highly variable.

### Table 5.9 Sensitivity of Rheological Indices Based on DSR Fun.

<table>
<thead>
<tr>
<th>Binder</th>
<th>Modifier</th>
<th>LSV (Pa.s, 60°C, 0.001 rad/s)</th>
<th>Gc* (kPa, 25°C)</th>
<th>G-R Parameter (kPa, 15°C, 0.005rad/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>SBS</td>
<td>↑</td>
<td>↑</td>
<td>≈</td>
</tr>
<tr>
<td>B</td>
<td>TR</td>
<td>↑</td>
<td>↑</td>
<td>≈</td>
</tr>
<tr>
<td>B_TR_X</td>
<td>SBS</td>
<td>↑</td>
<td>↑</td>
<td>≈</td>
</tr>
<tr>
<td>B_TR_Y</td>
<td>SBS</td>
<td>≈</td>
<td>↑</td>
<td>≈</td>
</tr>
<tr>
<td>B_TR_Z</td>
<td>SBS</td>
<td>↑</td>
<td>↑</td>
<td>≈</td>
</tr>
</tbody>
</table>

With increasing asphalt binder aging, the crossover modulus decreased and the low shear viscosity increased as shown in Figure 5.51 and 5.52. The base binder A, C, and D followed the similar trend with same parameters from Figure 5.51, while the modified asphalt binder also had good correlation between these two parameters but with different trend parameters. As shown in Figure 5.52, for the binder B series, the binder Base B, B_TR had close trend, while the SBS modified binder B_TR_Y_PM and B_TR_Z_HPM has lower slope, while B_TR_X, B_TR_X_PM, B_TR_Y, and B_TR_Y were the middle bridge between the previous trends.
Figure 5.51 Correlation between LSV and Crossover modulus G\textsuperscript{*}c for Base A, Base C, Base D version binders.

Figure 5.52 Correlation between LSV and Crossover modulus G\textsuperscript{*}c for Base B series binders.
5.4 Summary

This chapter mainly focuses on the analysis of the kinetic data set from the FTIR test and the rheological performance results from the DSR isothermal frequency sweep test. The kinetic results indicate that the oxidative aging rate increases with the aging temperature increasing and the asphalt modifier, such as SBS, TR, can dramatically decreases the oxidative aging rate.

For the rheological performance analysis, the master curve was created by shifting the isothermal frequency sweep data within the aid of the RHEA version 1.29 software. Then the rheological parameters, i.e. LSV, G*c, G-R, and DSR function, were set to evaluate the oxidative aging and the different modifier’s effect. There is a good correlation between these rheological parameters and the oxidative aging indicator-carbonyl area (CA). It was concluded that different modifier has different effect on the different rheological parameter for different asphalt binder resource.

Then the multiple linear regression analysis was conducted to determine the significant variables to these kinetic and rheological parameters. The results shows that the aging conditions play an important role on the CA and the rheological parameters. However, other kinetic parameters are not affected by the aging conditions and the modifiers. The behind possible reason still needs to be studied.
CHAPTER 6 FIELD AGING PREDICTION

In order to compare the laboratory asphalt binder isothermal oxidative aging with field asphalt binder aging which is impacted by various asphalt mixture and climate factors, such as asphalt mix air void, oxygen diffusion, asphalt binder film thickness, temperature, wind speed, solar radiation, etc., three different climate locations-Phoenix Sky Harbor International Airport, Reno-Tahoe International Airport, and Glasgow (Montana) Airport were selected to simulate the field asphalt pavement oxidative aging. TEMPS software, which was developed by the pavement research group of University of Nevada, Reno, was used to calculate the temperature of the asphalt pavement layer with the local weather data. Then the pavement asphalt CA prediction was conducted (Alavi, 2014). These pavement temperature prediction and CA prediction models were initially developed by several other asphalt pavement researchers (Han, 2011). Lastly, the output results were analyzed.

6.1 Pavement Structure and Climate Data

In order to compare the field aging performance of different modified asphalt binders, the same pavement structure and materials were assumed for the three different airport pavements. As shown in Figure 6.1, the layer thicknesses for the asphalt pavement and gravel base were 0.15 m and 0.35 m, respectively. The TEMPS software calculated the temperature in the pavement to the depth of 3 meters. Table 6.1 presents the pavement material properties, such as density, thermal conductivity, and specific heat capacity.
Before running the TEMPS software, the local climate data, such as the wind speed, air temperature, and solar radiation, were collected from the National Oceanic and Atmospheric Administration and National Solar Radiation Data Base website (NSRDB, 2015) as input files of TEMPS software. Figure 6.2 shows the air temperature of the three
locations. The location of Phoenix had higher summer and winter temperature than other two locations, and Reno and Glasgow has close temperature in summer, while Reno was warmer than Glasgow in winter, as shown in Figure 6.3 (January).

Figure 6.2 Air Temperature of the Three Locations in 2010.
The temperature of asphalt pavement changed with the surrounding environment condition. The related background was elaborated in chapter 3 section 5. Figure 6.4 shows the heat transfer balance between the pavement structure and its surrounding environment and this balance was presented by equation 3.24. These pavement
temperature models was accounted in TEMPS software. Based on input files combined by air temperature which was achieved from the national weather database and the pavement material parameters, the output was the pavement structure temperature over depth from January to December, 2010, as shown in Figure 6.5. From Figure 6.5, it is evident to observe that the pavement surface (0.01m) temperature was close to the air temperature and its variation was apparent, while the variation decreased with increasing pavement depth.

![Reno Pavement Temperature](image)

**Figure 6.5 Example of Reno Pavement Structure Temperature.**

6.2 Predicted Carbonyl Area and Calculated Rheological Indexes

The carbonyl area of the field asphalt pavement was calculated by the model which was described in chapter 3 and the model was programed with MATLAB™ software (Alavi, 2014).
Figure 6.6 shows the CA predicted value for different pavement depth at Reno. The relative increasing rate of CA decreased with the increasing depth. Generally, the asphalt binder oxidation aging rate was dependent on the surrounding air temperature. Figure 6.7 shows the predicted CA result of binder Base B at the three locations. It is apparent to conclude that the average CA increasing rate was higher for the warmer location of Phoenix than other two places, such as Reno and Glasgow.

![Reno A_PM CA Field Prediction](image)

Figure 6.6 Example of CA Prediction at Reno.
Based on the concept of oxidation prediction model, the HS was used to determine the physical properties represented as rheological indices as a function of in-service duration. The carbonyl area value of the specific binder has specific function of time with the oxidative aging reaction parameters, such as $E_c$, $E_{af}$, $k_c$, $k_f$, etc. Therefore, it is practical to deduce the relationship between the rheological index and the field aging time under specific environment condition, such as the air temperature, solar radiation and pavement depth. The analysis methodology was same for the three different locations, so Reno was selected to be the interest to perform the comparison.

**Figure 6.7 Example of CA Prediction of Base B.**
Figure 6.8 Predicted LSV of Base A and A_PM at Reno.

Figure 6.9 Predicted LSV of Base C and C_PM at Reno.
As shown in Figure 6.8, the binder Base A and A_PM has close slope function (LSV vs Time), while A_PM had higher magnitude level of LSV value than the base binder Base A. The same trend was found for the binder Base C, C_PM, and Base D, D_HPM (see Figure 8.9 and 8.10). Base C had slightly higher increasing rate than its modified asphalt binder C_PM, while the LSV magnitude level of C_PM was around 3 fold that of the Base C binder. The LSV slope of Base D was significantly higher than the high SBS modified asphalt binder D_HPM. The fundamental benefit of these modification was improving the capability of asphalt pavement to resistant the permanent deformation (rutting) under high temperature condition.
Comparing the base asphalt binder Base A, Base C, Base D presented in Figure 6.11, the LSV vs time slope by decreasing order were Base A, Base D, and Base C.
Evidently, the binder Base C had higher stiffness than asphalt binder Base A initially which means Base C was more preferable to resistant rutting distress during the early service life of the asphalt pavement, the figure indicates after probably two years, the LSV value of Base A became higher because of the higher oxidation aging rate. Therefore, it is rational to predict that the binder Base A will probably affect the performance of asphalt pavement more extensively. In the field pavement, other factors, such as the aggregate, the loading level, etc., in addition to the binder stiffness also should be considered. As shown in Figure 6.12, the modified asphalt binder D_HPM had the higher LSV value due to the high content of SBS (7.5%) modification, and it had the close increasing rate with binder C_PM. The binder A_PM had the smallest initial LSV value but the highest rate.

Figure 6.15 shows the comparison of the predicted LSV of some specific binders. Firstly, comparing the binder A_PM and B_TR_X_PM, both of them had the same PG grading, while A_PM stiffed much faster than B_TR_X_PM binder and other modified asphalt binders. The cause may be due to the B_TR_X_PM contains the tire rubber modifier or other original resource. Secondly, the binder C_PM and B_TR_Y_PM had close stiffness and C_PM had a slight smaller average slope than B_TR_Y_PM. Lastly, the two high content SBS modified asphalt binders-B_TR_Z_HPM and D_HPM had very close LSV increasing rate while D_HPM had higher magnitude level. However, these comparisons did not directly verify the causes behind these figures, other information, such as the asphalt binder resource, the binder production procedure, and the modifier difference, etc. were needed to explain these outcomes.
Figure 6.13 Predicted LSV of B Series 1 Binders at Reno.

Figure 6.14 Predicted LSV of B Series 2 Binders at Reno.
Figure 6.15 Comparison of Predicted LSV of Some Specific Binders at Reno.

Figure 6.16 Predicted G* c of A, C, D Series Binders at Reno.
Figure 6.17 Predicted $G^*c$ of B Series Binders at Reno.

Figure 6.18 Predicted $G^*c$ of Some Specific Binders at Reno.
Figure 6.16 to 6.18 indicate the calculated G*\(c\) from the predicted CA value by the hardening susceptibility function over time. For the A, C, D series binders, all of them had the close initial crossover modulus but different decreasing rate except binder C_PM, and it was found that the difference between C series binder was higher than other series. The methodology of G*\(c\) analysis is still under developing, the primary use of the G*\(c\) was to evaluate the asphalt binder master curve shifting (the G*\(c\) moves to the lower frequency under the same loading and temperature condition). The same trend was found for the binder B series. Generally, the base binder had higher crossover modulus than the corresponding modified asphalt binder. The tire rubber modified asphalt binder B_TR had close crossover modulus with the base binder Base B. From Figure 6.18, the G*\(c\) value of the binder A_PM decreased much faster than the binder B_TR_X_PM and they had close initial crossover modulus. The binder B_TR_Y_PM had higher level of G*\(c\) than the binder C_PM but slightly higher decreasing rate. The high SBS content modified asphalt binder D_HPM had higher G*\(c\) than B_TR_Y_HPM but smaller decreasing rate.
Figure 6.19 Predicted DSR Fn of A, C, D Series Binders at Reno.

Figure 6.20 Predicted DSR Fn of B Series Binders at Reno.
Figure 6.21 Predicted DSR Fn of Some Specific Binders at Reno.

Figure 6.19 and 6.21 indicate the DSR function results. Firstly, the figure 6.19 shows that the high SBS content modified asphalt binder had the highest DSR function value but the lowest increasing rate. Binder Base A and A_PM had close average increasing rate. As discussed in previous chapter, the DSR function has a good correlation to the ductility value by DSR map (Glover et al., 2005). Secondly, for the binder B series, under the effect of the additive of X, Y, Z, and the corresponding SBS modified asphalt binders had similar increasing rate with the base binder except the binder Base B and B_TR, as shown in Figure 6.20. Figure 6.21 shows the DSR Fn results for some specific asphalt binders. The DSR Fn of binder A_PM had the smallest initial value but the highest increasing rate comparing with other binders. The binder C_PM had higher initial DSR Fn value but slower increasing rate than the binder B_TR_Y_PM. For the high SBS content modified asphalt binders, they had close increasing rate, but
D_HPM had higher DSR Fn magnitude level. The G-R parameter was developed based on DSR function value, so the same conclusion would be draw for the objective binders. Therefore, there is no necessary to analysis the G-R parameter in this section.

Based on the discussion conducted in this chapter, it can be concluded that the rheological index was material resources dependent, the different modification also play an important role in changing the mechanical performance of the base binder. The different analysis results were found for the different rheological parameters which again proved the research finding (Morian et al., 2015).

For the LSV, the modified binder A_PM had higher LSV magnitude and close average increasing rate with base binder Base A, C_PM and Base C also had the same trend with the A series binders, D_HPM had higher LSV but slower increasing rate than base binder Base D, the binders which were SBS modified based on the X, Y, Z binder had close increasing rate but higher LSV level accordingly. The LSV of tire rubber modified binder B_TR had higher increasing rate but lower initial stiffness than the base binder Base B. Comparing the same SBS modified binders which had the same PG grading, the binder A_PM had lower initial LSV but higher average increasing rate than the binder B_TR_X_PM; binder C_PM and B_TR_Y_PM had close LSV, but the latter one had slight higher increasing rate; the two high content of SBS modified asphalt binders-D_HPM and B_TR_Z_HPM had similar increasing rate but the latter one had lower LSV magnitude level.

For the rheological index of G*c, the binder A, C, D version binders had different trend with each other. The binder A_PM had close G*c value but higher decreasing rate than base binder Base A; binder Base C had higher G*c value but slightly lower
decreasing rate than binder C_PM, binder Base D had higher $G^c$ value and higher decreasing rate than the high SBS content modified asphalt binder D_HPM; the B version binders had the close $G^c$ decreasing rate for each comparable binders and the SBS modified asphalt binder had lower $G^c$ value, except the binder Base B and B_TR which had close $G^c$ value and the B_TR had higher decreasing rate.

For the DSR Fn results, the SBS modified asphalt binder A_PM, C_PM and D_HPM had higher initial DSR Fn value but lower increasing rate than the corresponding base binders, it should be noted that the binder A_PM had slight lower increasing rate than base binder Base A. The SBS modified binders of B version had higher initial DSR value but close increasing rate with the corresponding X, Y, Z modified asphalt binders. This trend was different with the A, C, D version binders and the probably reason would be the complex interaction between the SBS modifier and the additive of X, Y and Z. The binder B_TR had smaller initial DSR Fn value but higher increasing rate than the binder Base B.
CHAPTER 7 CONCLUSION AND RECOMMENDATION

Asphalt binder, a sort of complex carbon-hydrogen mix, always undergoes temperature dependent oxidative aging at ambient oxygen pressures. The same situation also happened to the modified asphalt binder, while the oxidative mechanism and the effect of the specific modifier are not totally understood. This study was to investigate the isothermal oxidative aging effect on rheological performance of different modified asphalt binders.

7.1 Main Conclusion

Based on this objective, there were 14 inter-related asphalt binders being aged in the air-forced draft oven at 85°C for 0.5 to 40 days, 60°C for 2 to 160 days, and 50°C for 4 to 240 days. After the specific aging process, the aged asphalt binder was collected to conduct the FT-IR spectra test to characterize the chemical functional group change and DSR frequency sweep test to shift the master curve to get the rheological performance parameters.

After the data analysis, the main finding from this study can be concluded as follows:

- The aging conditions-temperature and aging duration play an important role on the asphalt binder aging hardening and its rheological performance change.
- With the aging temperature increasing, the asphalt binder oxidative aging rate jumped up. The carbonyl area increases with the oxidation aging development. From the carbonyl area curve, the asphalt binder initially went the fast rate
oxidative aging which was governed by the reactive material source and then the reaction dropped down to a constant rate.

- The asphalt binder oxidative aging follows the universal Arrhenius kinetic reaction principle. The general trend was that the SBS and TR can reduces the oxidative aging fast and constant rate for asphalt binder A, C, D, B_TR series. While with the additive X, Y, and Z, the oxidative rate increased for the SBS modified asphalt binder compared with the base binder. There is no uniform trend found for the activation energy which is asphalt binder resource dependent.

- Asphalt binder master curve is a useful methodology to evaluate the asphalt binder mechanic properties. Even though there are a lot of different master curve shift functions available now, there is necessary to develop robust function for the modified asphalt binder, especially for the high content additive modified asphalt binders.

- The analysis of rheological index as a function of carbonyl area (CA) was conducted. With the SBS modification, both of the hardening susceptibility of the rheological index-LSV and G-R decreases compared with the corresponding base binder. The TR increased the hardening susceptibility of all the rheological indexes. While for the G*c, SBS increases the slope of the most modified asphalt binders except A and B_TR_X series binders.

- The multiple linear regression statistical analysis results indicate that the oxidative aging conditions play an important role on the CA, and rheological performance indexes. The modifiers-SBS and TR have different directional effect on these parameters.
The field asphalt binder carbonyl area prediction was conducted. It was found that the different rheological index method resulted different conclusion with the asphalt binder. The SBS modified asphalt binders of A, C version and B version had close average increasing rate of LSV, higher average decreasing rate of G\*c, lower average increasing rate of DSR Fn compared with the corresponding base binders. D_HPM had lower average increasing rate of LSV, G\*c and DSR Fn than base binder Base D. The tire rubber modified binder B_TR had higher average increasing rate of LSV, DSR Fn, and higher average decreasing rate of G\*c than base binder Base B.

### 7.2 Recommendation

This study was an excellent research project to investigate oxidative aging resistance of the modified asphalt binders and the results was reasonable and appreciable. However, there are some limitations to this study, such as the asphalt binder aging conditions were limited to ambient pressure, 3 temperatures (85°C, 60°C, and 50°C) and 8 aging duration for each temperature, there were only 14 different asphalt binder and modifiers-SBS, TR, unknown asphalt components-X, Y, and Z studied, etc. Therefore, the following recommendations still needs to be proposed to the further research study:

- Other microscopic analysis tools, such as NMR, can compensate the FTIR to get more useful information, i.e. how is the modifier change during the aging.
- More details of the objective modified asphalt binder, i.e. the modifier type and composition, needs to be addressed to support the understanding of the oxidative aging mechanism.
• The related asphalt mixture aging and field pavement aging need to investigate the correlation between the laboratory binder aging and the real field mix oxidative aging.

• Definitely, more related asphalt binder aging researches and projects need to be proposed to study this complex but meaningful asphalt binder oxidative aging issues. For example, the alternative asphalt binder (bio-binder, engine oil binder) aging mechanism, the asphalt emulsion aging, and the aging effect on the asphalt pavement life and the cost, etc.
REFERENCES


King, Gayle, Mike Anderson, Doug Hanson, and Phil Blankenship. Using Black Space Diagrams to Predict Age-Induced Cracking. In 7th RILEM International Conference on Cracking in Pavements, pp. 453-463. Springer Netherlands, 2012.


Rowe, G.M.: Prepared Discussion following the Anderson AAPT paper cited previously. AAPT 80, 649–662 (2011)


APPENDIX

APPENDIX A-CARBONYL MEASUREMENT AND PREDICTION RESULTS

Figure A-1 Measurement Result and Predicted Result of Carbonyl Area of Base A.

Figure A-2 Measurement and Predicted Results of Carbonyl Area of A_PM.
Figure A-3 Measurement and Predicted Results of Carbonyl Area of Base B.

Figure A-4 Measurement and Predicted Results of Carbonyl Area of B_TR.
Figure A-5 Measurement and Predicted Results of Carbonyl Area of B_TR_X.

Figure A-6 Measurement and Predicted Results of Carbonyl Area of B_TR_X_PM.
Figure A-7 Measurement and Predicted Results of Carbonyl Area of B_TR_Y.

Figure A-8 Measurement and Predicted Results of Carbonyl Area of B_TR_Y_PM.
Figure A-9 Measurement and Predicted Results of Carbonyl Area of B_TR_Z.

Figure A-10 Measurement and Predicted Results of Carbonyl Area of B_TR_Z_HPM.
Figure A-11 Measurement and Predicted Results of Carbonyl Area of Base C.

Figure A-12 Measurement and Predicted Results of Carbonyl Area of C_PM.
Figure A-13 Measurement and Predicted Results of Carbonyl Area of Base D.

Figure A-14 Measurement and Predicted Results of Carbonyl Area of D_HPM.
## APPENDIX B- MULTI LINEAR REGRESSION ANALYSIS RESULTS

### Multi Linear Regression Statistical Results - LSV

<table>
<thead>
<tr>
<th>Binder</th>
<th>LSV (pa.s, 60°C, 0.005 rad/s)</th>
<th>Base Equation</th>
<th>Modifier</th>
<th>Int.</th>
<th>HS</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td>( \beta_0 )</td>
<td>( \beta_1 )</td>
<td>( \beta_2 )</td>
<td>( \beta_3 )</td>
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<tr>
<td>A</td>
<td></td>
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<td>11.109 (0.000)</td>
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<tr>
<td>C</td>
<td></td>
<td>2.416 (0.000)</td>
<td>9.615 (0.000)</td>
<td>SBS</td>
<td>6.933 (0.000)</td>
</tr>
<tr>
<td>D</td>
<td></td>
<td>3.488 (0.000)</td>
<td>9.837 (0.000)</td>
<td>H-SBS</td>
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<td>B</td>
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<td>7.357 (0.000)</td>
<td>TR</td>
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<tr>
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<td>X</td>
<td>-1.48 (0.000)</td>
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<tr>
<td></td>
<td></td>
<td>5.491 (0.000)</td>
<td>9.971 (0.000)</td>
<td>Y</td>
<td>-0.852 (0.000)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.491 (0.000)</td>
<td>9.971 (0.000)</td>
<td>Z</td>
<td>-0.107 (0.000)</td>
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<td>B_TR_X</td>
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<td>4.012 (0.000)</td>
<td>9.074 (0.000)</td>
<td>SBS</td>
<td>3.07 (0.000)</td>
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<td>SBS</td>
<td>5.074 (0.000)</td>
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<td>7.364 (0.000)</td>
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### Multi Linear Regression Statistical Results - G*c

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<td>Base Equation</td>
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<tr>
<td>A</td>
<td>17.814 (0.000)</td>
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<tr>
<td>C</td>
<td>17.808 (0.000)</td>
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<tr>
<td>D</td>
<td>17.335 (0.000)</td>
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<tr>
<td>B</td>
<td>17.022 (0.000)</td>
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<tr>
<td>B_TR</td>
<td>16.417 (0.000)</td>
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<tr>
<td></td>
<td>16.417 (0.000)</td>
</tr>
<tr>
<td></td>
<td>16.417 (0.000)</td>
</tr>
<tr>
<td>B_TR_X</td>
<td>16.975 (0.000)</td>
</tr>
<tr>
<td>B_TR_Y</td>
<td>17.181 (0.000)</td>
</tr>
<tr>
<td>B_TR_Z</td>
<td>16.975 (0.000)</td>
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</table>
### Multi Linear Regression Statistical Results-G-R

<table>
<thead>
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<th>Binder</th>
<th>Base Equation</th>
<th>Modifier</th>
<th>Int.</th>
<th>HS</th>
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<td></td>
<td>( \beta_0 )</td>
<td>( \beta_1 )</td>
<td>( \beta_2 )</td>
<td>( \beta_3 )</td>
</tr>
<tr>
<td>A</td>
<td>-5.587 (0.000)</td>
<td>17.172 (0.000)</td>
<td>SBS</td>
<td>4.772 (0.000)</td>
</tr>
<tr>
<td>C</td>
<td>-5.976 (0.000)</td>
<td>16.663 (0.000)</td>
<td>SBS</td>
<td>6.899 (0.000)</td>
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<tr>
<td>D</td>
<td>-3.254 (0.000)</td>
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<td>H-SBS</td>
<td>5.269 (0.000)</td>
</tr>
<tr>
<td>B</td>
<td>-2.852 (0.000)</td>
<td>13.84 (0.000)</td>
<td>TR</td>
<td>2.661 (0.000)</td>
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<td>B_TR</td>
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<td>X</td>
<td>-2.969 (0.000)</td>
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<td>B_TR</td>
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<td>14.712 (0.000)</td>
<td>Y</td>
<td>-2.438 (0.000)</td>
</tr>
<tr>
<td>B_TR</td>
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<td>14.712 (0.000)</td>
<td>Z</td>
<td>-0.845 (0.009)</td>
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<tr>
<td>B_TR_X</td>
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<td>14.769 (0.000)</td>
<td>SBS</td>
<td>3.584 (0.000)</td>
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<tr>
<td>B_TR_Y</td>
<td>-2.629 (0.000)</td>
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<td>SBS</td>
<td>3.602 (0.000)</td>
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<tr>
<td>B_TR_Z</td>
<td>-1.035 (0.000)</td>
<td>11.641 (0.000)</td>
<td>H-SBS</td>
<td>2.454 (0.000)</td>
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# Multi Linear Regression Statistical Results-DSR Fn

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<th>HS</th>
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<td>DSR Fn (15°C, 0.005rad/s)</td>
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<tr>
<td></td>
<td>( \beta_0 )</td>
<td>( \beta_1 )</td>
<td>( \beta_2 )</td>
<td>( \beta_3 )</td>
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<tr>
<td>A</td>
<td>-4.116 (0.000)</td>
<td>17.418 (0.000)</td>
<td>SBS</td>
<td>4.912 (0.000)</td>
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<td>C</td>
<td>-4.366 (0.000)</td>
<td>16.663 (0.000)</td>
<td>SBS</td>
<td>6.932 (0.000)</td>
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<tr>
<td>D</td>
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<td>H-SBS</td>
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<td>B</td>
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<td>15.349 (0.000)</td>
<td>TR</td>
<td>3.083 (0.000)</td>
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<td></td>
<td><strong>B_TR</strong></td>
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<tr>
<td></td>
<td>1.42 (0.000)</td>
<td>14.879 (0.000)</td>
<td>X</td>
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<td>1.42 (0.000)</td>
<td>14.879 (0.000)</td>
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<td>-0.85 (0.009)</td>
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<tr>
<td></td>
<td>0.569 (0.000)</td>
<td>11.814 (0.000)</td>
<td>H-SBS</td>
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APPENDIX C-ASPHALT BINDER MASTER FUNCTIONS AND SHIFT FACTOR FUNCTIONS

Master Curve Fitting Functions (a)

<table>
<thead>
<tr>
<th>Function name</th>
<th>Equation</th>
<th>Factors</th>
<th>Time</th>
<th>Comment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jongepier and Kuiman’s</td>
<td>[ \omega_r = \frac{\omega_0 \eta_0}{G_g} ] [ H(\tau) = G_g \frac{\exp(-\frac{H(\tau)}{\beta})^3}{\beta} ] [ G_g = \frac{1}{\beta} \int H(\tau) d\ln \tau ] [ \tau_m = \frac{\eta_0}{G_g} \exp\left(\frac{\beta^2}{4}\right) ]</td>
<td>( \omega_r ) is reduced frequency (rad/s), ( \eta_0 ) is zero shear viscosity (Pa.s) and ( G_g ) is the glassy modulus (Pa), ( H(\tau) ) is the relaxation spectrum distribution, ( \beta ) is the width parameter, ( \tau ) is relaxation time (s) and ( \tau_m ) is a time constant (which determines the position of the spectrum along the relaxation time ( \tau ) axis at a given temperature)</td>
<td>1969</td>
<td>Relaxation spectrum highly skewed on a logarithmic scale distribution, Calculation is challenge</td>
<td>Jongepier and Kuiman [1969], Anderson et al., 1994</td>
</tr>
<tr>
<td>Dobson’s Model</td>
<td>[ \frac{dy}{dx} = \frac{\tan \delta}{(1 + \tan \delta)(1 - 0.01 \times \tan \delta)} ] [ y = \log\left(\frac{</td>
<td>G^*</td>
<td>}{G_g}\right) ] [ x = \log\left(\frac{\eta_0 \alpha_\tau}{G_g}\right) ] [ \alpha_\tau = \frac{\eta_0 \alpha_\tau}{G_g} \log\left(1 + \tan \delta\right) = -by ] [ \log \alpha_\tau = \log G_g - \frac{1}{b} \left[ \log(1 - G_g^\prime) + \frac{20.5 - G_g^\prime - G_g^\prime}{230.3} \right] ]</td>
<td>( G_g^\prime ) is the complex modulus magnitude, ( G_g ) is glassy modulus, ( \eta_0 ) is the steady state or Newtonian viscosity and ( aT ) is the shift factor. ( b ) is a parameter describing the width of the relaxation spectrum, All the equations above are applicable for the value of ( \tan \delta = 9.5 )</td>
<td>1969/1972</td>
</tr>
<tr>
<td>Dickison and Witt’s</td>
<td>[ \log G_g^\prime = \frac{1}{2} \left[ \log \alpha_\tau - [(\log \omega_\tau)^2 + (2\beta)^\frac{1}{2}] \right] ] [ \beta = \frac{\pi - 2\delta}{4} - \left( 1 - \log \alpha_\tau \right) \left( \log \omega_\tau^2 + (2\beta)^\frac{1}{2} \right) ] [ G^\prime = \frac{</td>
<td>G^\prime</td>
<td>}{G_g} ] [ \log</td>
<td>G_g^\prime</td>
<td>= -\beta \left[ \frac{2(\delta - \delta^\prime)}{\pi - 2\delta^\prime} \right] ]</td>
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</tbody>
</table>
# Master Curve Fitting Functions (b)

<table>
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<tr>
<th>Function name</th>
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<th>Factors</th>
<th>Time</th>
<th>Comment</th>
<th>Reference</th>
</tr>
</thead>
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<tr>
<td>Christensen, Anderson (CA)</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>
\[ | G^* | = G_g \left[ 1 + \left( \frac{\omega}{\omega_c} \right)^{\frac{\lambda}{100}} \right]^{\frac{\delta}{\log 2}} \]  
\[ \delta = \frac{90}{1 + \left( \frac{\omega}{\omega_c} \right)^{\frac{\delta}{\log 2}}} \]  
\[ \omega_c = \frac{G_g}{G_g} \left( \frac{90 - \delta}{\delta} \right)^{\frac{\delta}{\log 2}} \]  
\[ \omega_f = \frac{G_g}{G_g} \left( \frac{90 - \delta}{\delta} \right)^{\frac{\delta}{\log 2}} \]  
\[ \delta_v = 90 \left( \frac{G_g}{G_g} \right)^{\frac{\delta}{(7 - 0.91)}} \]  |  
\[ G_g \text{-the glass complex modulus; } G_g \text{ is normally very close to } 1 \times 10^9 \text{ Pa in shear loading for most bitumen and can be used for most purposes. } \]  
\[ \omega_c \text{ or } \tau \text{ is the crossover frequency or crossover time. } R \text{ is the difference between the glass modulus, } G_g \text{ and the dynamic shear complex modulus at the crossover frequency. } \delta \text{ is transition phase angle, } \omega_f \text{ is the location parameter for the viscous flow region (rad/s)} \]  | 1992  | CA Model is relatively simple in shape and reasonably accurate as compared to the previous models. It is not able to model the rheological properties of modified bitumen.  | Silva et al., 2004, Anderson et al., 1994 |
| Fractional Model |  
\[ | G^* | = \prod_{i=1}^{n} \left( 1 + \left( \mu_i, \omega \right) \right)^{\frac{1}{1 + \left( \lambda_i, \omega \right)}}^{\frac{1}{1 + \left( \lambda_i, \omega \right)}} \]  
\[ \delta = \frac{\pi}{2} + \frac{1}{(n-m)} \sum_{i=1}^{n-m} a \tan(\mu_i, \omega) - \sum_{i=1}^{n-m} a \tan(\lambda_i, \omega) \]  | $\mu_k$ and $k$ are the relaxation times ($\mu_k > 0$, $k > 0$) and $m$ and $n$ are the numbers of relaxation time ($n > m$).  | 1994  |  | Stastna et al. [1999], Marasteanu and Anderson [1999a] |
| Christensen, Anderson and Marasteanu (CAM) |  
\[ | G^* | = G_g \left[ 1 + \left( \frac{\omega}{\omega_c} \right)^{\frac{\omega}{\omega_c}} \right]^{\frac{\omega}{\omega_c}} \]  
\[ \delta = \frac{90 \cdot \frac{\omega}{\omega_c}}{1 + \left( \frac{\omega}{\omega_c} \right)^{\frac{\omega}{\omega_c}}} \]  | $v = \log 2/R$, $w$ addresses the issue of how fast or how slow the $|G^*|$ data converge into the two asymptotes  | 1999  |  | Marasteanu and Anderson, 1999a |
# Master Curve Fitting Functions (c)

<table>
<thead>
<tr>
<th>Function name</th>
<th>Equation</th>
<th>Factors</th>
<th>Time</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Bahia and Co-workers’ Model</td>
<td>[ f_c = f_c \left( \frac{G_e}{G_s} \right)^{\frac{1}{\nu_k}} ] [</td>
<td>G'</td>
<td>= G_s + \frac{G_s - G_e}{\left[1 + \left( \frac{f_c}{f_c'} \right)^{\nu_k} \right]^{\frac{1}{\nu_k}}} ] [ R = \log \frac{2^{\nu_k/2}}{1 + \left( 2^{\nu_k/2} - 1 \right) \frac{G_s}{G_e}} ] [ R = {1 + \left( \frac{G_s}{G_e} \right) - 1} \times {1 + \left[ \left( \frac{G_s}{G_e} \right)^{1/\nu_k} \right]^{\nu_k/2} } ] [ \delta = 90I - (90I - \delta_m) \left{1 + \left[ \frac{\log \left( \frac{f_c}{f_c'} \right)}{R_g} \right]^{\nu_k/2} \right} ]</td>
<td>Ge=0 for binder when ( f=0 ), ( fc ) is a location parameter with dimensions of frequencies and ( f' ) is reduced frequency, ( k ) and ( me ) are the shape parameters.</td>
<td>2002</td>
</tr>
<tr>
<td>Al-Qadi and co-workers’ Model</td>
<td>[</td>
<td>G'</td>
<td>= G_s \left[1 - \frac{1}{1 + \left( \frac{\omega}{\omega_0} \right) \nu} \right] ] [ \delta = \frac{90}{\left[1 + \left( \frac{\omega}{\omega_0} \right) \nu \right]^{\nu}} ]</td>
<td>w0 is the scale parameter that defines the location of the transition along the frequency axis, ( \nu ) and ( \omega ) are the dimensionless model parameters.</td>
<td>2002</td>
</tr>
<tr>
<td>Di Benedetto and Neifar (DBN) Model</td>
<td>[ G_0^{*} = \left( \frac{1}{G_0} + \sum_{i=1}^{n} \frac{1}{G_i + i\omega \eta_i(T)} \right)^{-1} ]</td>
<td>( G_0 ) is the elastic modulus of the spring, ( \eta_i ) is a ciscosity. The number ( n ) is the elementary body.</td>
<td>2007</td>
<td>Good agreement with 2S2P1D</td>
<td>Di Benedetto et al., 2007</td>
</tr>
</tbody>
</table>
### Master Curve Fitting Functions (d)

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>General 2S2P1D</td>
<td>$J(t) = a \left(\frac{t}{\tau}\right)^h$</td>
<td>$h$-controlled the slope at low values of $G''$, $K$-controlled the slope at high values of $G''$, $\delta$ controlled the slope at low temp or high frequencies, $\beta$ controlled the slope at high temp or low frequency.</td>
<td>2003</td>
<td>Good agreement fitting</td>
<td>Olard and Di Benedetto, 2003</td>
</tr>
<tr>
<td>Sigmoidal Model</td>
<td>$\log</td>
<td>G^*</td>
<td>= \nu + \frac{\alpha}{1 + e^{\beta + \gamma {\log(\omega)}}}$</td>
<td>$w$ is the reduced frequency, $\nu$ is the lower asymptote, $\alpha$ is the difference between the values of the upper and lower asymptote, $\beta$ and $\gamma$ are shape parameters.</td>
<td>2002</td>
</tr>
<tr>
<td>Generalized Logistic Sigmoidal Model (RBS)</td>
<td>$\log</td>
<td>G^*</td>
<td>= \nu + \frac{\alpha}{\left[1 + \lambda e^{\beta + \gamma {\log(\omega)}}\right]^{1/\lambda}}$</td>
<td>Symbols are as previously defined.</td>
<td>2008</td>
</tr>
<tr>
<td>Huet Model</td>
<td>$J(t) = a \left(\frac{t}{\tau}\right)^h$</td>
<td>$G^* = \frac{(i\omega\tau)^h}{a \Gamma(h+1)}$</td>
<td>$G^* = \frac{G_p - G_0}{1 + \alpha(i\omega)^- + (i\omega)^++(i\omega)^--1}$</td>
<td>1963</td>
<td>It is unable to model modified bitumen.</td>
</tr>
</tbody>
</table>
## Master Curve Fitting Functions (e)

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>Huet-Sayegh Model</td>
<td>[ G' = G_0 + \frac{G_e - G_0}{1 + \alpha(i\omega)^{-\xi} + (i\omega)^{-\eta}} ]  [ \ln \tau = a + bT + cT^2 ]</td>
<td>[ G_0 ] is the limit of the complex modulus, ( 0 &lt; \xi &lt; 1, \alpha ) is a dimensionless constant</td>
<td>1967</td>
<td>It is not suitable for asphalt binder at the very low frequency</td>
<td>Sayegh, 1967, Olard and Di Benedetto, 2003</td>
</tr>
<tr>
<td>Prony Series</td>
<td>[ R(t) = E_0 + \sum_{j=1}^{L} E_j e^{-\tau_j} ] [ \Omega(t) = \frac{1}{E_0} + \sum_{j=1}^{L} \frac{1}{E_j} (1 - e^{-\tau_j}) ]</td>
<td>[ R(t) ] is relaxation modulus, ( \Omega(t) ) is creep compliance, ( \tau_j ) is the relaxation time, ( \tau_j = \eta_j/\tau_l ), ( l = 1, 2, \ldots, N ).</td>
<td>1999</td>
<td>It is a robust approach for different materials, but the calculation is complex.</td>
<td>Park and Schapery, 1999</td>
</tr>
<tr>
<td>Polynomial Model</td>
<td>[ \log</td>
<td>G'</td>
<td>= A(\log f)^3 + B(\log f)^2 + C(\log f) ]</td>
<td>( f ) is reduced frequency and A, B and C are the shape parameters</td>
<td>2005</td>
</tr>
<tr>
<td>Laboratoire des Ponts et Chaussées (LCPC)</td>
<td>[ \log</td>
<td>G'(\omega)</td>
<td>- \log</td>
<td>G'(\infty)</td>
<td>= -\frac{2}{\pi} \int \frac{u \delta(u) - \omega \delta(\omega)}{u^2 - \omega^2} du ]  [ \delta = \frac{2\omega}{\pi} \int \log</td>
</tr>
</tbody>
</table>
## Master Curve Shift Factor Functions (a)

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>Arrhenius</td>
<td>$\log a_T = C \left( \frac{1}{T} - \frac{1}{T_{ref}} \right) = 0.4347E_a \left( \frac{1}{R} \frac{1}{T} - \frac{1}{T_{ref}} \right)$</td>
<td>$c$-fitting coefficient, $E_a$-activation energy, $R$-gas constant (8.314 J/mol.k), $T$-interest temperature, $T_{ref}$-reference temperature.</td>
<td>6</td>
<td>Just temperature factor</td>
<td>Dongre, Raj et al., 2005</td>
</tr>
<tr>
<td>Williams, Landel and Ferry (WLF)</td>
<td>$\log a_T = -\frac{C_1(T-T_{ref})}{C_2 + (T-T_{ref})}$</td>
<td>$c_1, c_2$-fitting coefficients, $T$-interest temperature, $T_{ref}$-reference temperature</td>
<td>3</td>
<td>Accurately for neat binder</td>
<td>Rowe, Geoffrey et al., 2011</td>
</tr>
<tr>
<td>Kaelble</td>
<td>$\log a_T = -\frac{c_1(T-T_g)}{c_1 +</td>
<td>T-T_g</td>
<td>} = -\frac{c_2(T-T_g)}{c_2 +</td>
<td>T-T_g</td>
<td>}$</td>
</tr>
<tr>
<td>Modified Kaelble</td>
<td>$\log a_T = -c_1 \left( \frac{T-T_d}{c_2 +</td>
<td>T-T_d</td>
<td>} - \frac{T_g-T_d}{c_2 +</td>
<td>T_g-T_d</td>
<td>} \right)$</td>
</tr>
</tbody>
</table>
Master Curve Shift Factor Functions (b)

<table>
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<tr>
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</tr>
</thead>
<tbody>
<tr>
<td><strong>Laboratoire Central des et Chausées (LCPC) Approach</strong></td>
<td>$\delta_{\omega}(f_j) = \frac{2}{\pi} \log(\frac{G^<em>(T, f_j) / G^</em>(T, f_i)}{\log(f_j) - \log(f_i)})$</td>
<td></td>
<td></td>
<td>a-average of the two phase angles measured at $f_i$ and $f_j$</td>
<td>Chailleux et al., 2006</td>
</tr>
<tr>
<td></td>
<td>$\delta_{\omega}(T_j, f_j) = \frac{2}{\pi} \log(\frac{G^*(T_j, f_j)}{\log(a(T_j, f_j))})$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\delta_{\omega}(T_j, f_j) = \frac{2}{\pi} \sum_{j=1}^{n} \log(a(T_j, f_j))$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| **Numerical, Non-Linear Least Squares Shift** | $\log |G^*| = \nu + \frac{\alpha}{1 + e^{\beta - \gamma \log(\omega)}}$ | | | Shape parameters, the glass modulus, the equivalent modulus. | Yusoff et al., 2012 |
| | $\log |G^*| = \nu + \frac{\alpha}{[1 + \lambda e^{\beta - \gamma \log(\omega)}]^\frac{1}{\lambda}}$ | | | | |
## Master Curve Shift Factor Functions (c)

<table>
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<tr>
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</thead>
<tbody>
<tr>
<td>Log-Linear Equation (Polynomial Shift)</td>
<td>( \log \left( \frac{T}{T_{ref}} \right) = \beta(T - T_{ref}) )</td>
<td>fitting coefficient</td>
<td>7</td>
<td>Two factors, simple fitting</td>
<td>Witczak, 1996</td>
</tr>
<tr>
<td>Viscosity Temperature Susceptibility (VTS) Equation</td>
<td>( \log a_T = c \left( 10^{A+VTS \log T} - 10^{A+VTS \log T_{ref}} \right) )</td>
<td>Viscosity approach, MEPDG used.</td>
<td>5</td>
<td>Good fitting, but not accurate for the low temperature</td>
<td>Rasmussen, Robert Otto, 2002</td>
</tr>
<tr>
<td>Second-order Polynomial Shift Function</td>
<td>( \log f_r = \log f + a(T_r - T) + b(T_r - T)^2 ) [ \log a_T = aT^2 + bT + c ]</td>
<td>a, b, c</td>
<td>-</td>
<td>Good for some asphalt mixture</td>
<td>Witczak, 2005</td>
</tr>
</tbody>
</table>