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Rheological and nanomechanical characterization of aging in polymer modified asphalt

Seyed Saleh Yousefi

Seyed Saleh Yousefi
Candidate

Civil Engineering
Department

This thesis is approved, and it is acceptable in quality and form for publication:

Approved by the Thesis Committee:

Dr. Rafi Tarefder, Chairperson

Dr. Arup Maji

Dr. Percy Ng

RHEOLOGICAL AND NANOMECHANICAL CHARACTERIZATION OF AGING IN POLYMER MODIFIED ASPHALT

BY

SEYED SALEH YOUSEFI

B. Sc. in Civil Engineering

University of Tehran, Tehran, Iran

THESIS

Submitted in Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE
Civil Engineering

The University of New Mexico
Albuquerque, New Mexico

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DEDICATION

To my parents

AKNOWLEDGEMENTS

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ABSTRACT OF THESIS

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ABSTRACT

In this study, change in rheological and nanomechanical properties of asphalt due to aging is determined in the laboratory. Asphalt binders are aged using Rolling Thin Film Oven (RTFO), Pressure Aging Vessel (PAV), and draft ovens. Asphalt binder includes an unmodified base binder, Styrene-Butadiene (SB) and Styrene-Butadiene-Styrene (SBS) polymer modified binders. Rheological properties such as viscosity, phase angle, shear modulus, creep compliance, stiffness, etc. are determined using Dynamic Shear Rheometer (DSR) test, Multiple Stress Creep Recovery (MSCR) test, Bending Beam Rheometer (BBR) test, Rotational Viscosity (RV) test and the Direct Tension (DT) test. Nanomechanical properties such as hardness and reduced elastic modulus are determined using a nanoindenter. Laboratory test results are expressed in terms of Aging Index (AI) defined by relative change in specific rheological or nanomechanical property of aged and unaged binder.

As it was expected binder rheological properties such as stiffness increases and phase angle and creep compliance decrease due to aging. Based on aging index defined by

complex shear modulus (G^*), increase in percentage of polymer results in decrease in the AI value for both SB and SBS modified binder. It means percent increase of polymer is not good for long term stability but may be good for fatigue. When comparing AI defined by G^* of SB and SBS, it is shown that SBS has higher AI than SB. Aging index of RTFO condition binder does not vary as significantly as it varies in PAV conditioned sample. When comparing AI defined by G^*, elastic modulus (G'), viscous modulus (G''), of oven aged sample, base binder ages more than modified binder and G' changes exponentially compared to the linear change of G''. At low temperature, the difference in creep compliance of unaged and aged binder is small compared to that at high temperature. This confirms that temperature significantly affects aging. Based on AI defined by BBR stiffness, original binder shows AI value similar to the modified binder. Again, SBS has higher AI defined BBR stiffness than SB. Based on ductility measured in DT test, it can be said as sample ages its ductility reduces.

Nanoindentation is conducted on thin asphalt binder film deposited on glass slides. For both unmodified and modified binders, hardness and reduce modulus increase exponentially due to aging. Nanoindentation results show similar trend obtained by rheological test. Aging decreases the creep compliance defined by indentation depth, similar trend is observed in MSCR test by DSR.

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Aging is a phenomenon in which asphalt binder's stiffness increases due to changes in temperature and oxidation. Aging can be categorized into two stages. They are short term aging and long term aging. Short term aging occurs at high temperature (above 150 °C) which is usually required for compaction of asphalt mix during construction. Aging that occurs during the service life of a pavement is called long term aging. Short term aging is related to rutting. Long term aging is believed to be responsible for asphalt pavement cracking especially for top down cracking.

Understanding the aging phenomena has become one of the most challenging topics in pavement engineering. Several researchers have preformed chemical and mechanical aging tests but still aging is a poorly understood phenomenon. Because previous studies have not attempted to study hardness and stiffness at nano-scale due to aging which is done in this study.

Traditionally, laboratory simulation of aging has been performed through Rolling Thin Film Oven (RTFO) for short term aging and Pressure Aging Vessel (PAV) for long term aging. These ovens simulate aging through a combined temperature and air flow and pressure. These ovens are used in this study. In addition, a draft oven is used for aging simulation. Oven aging represents the field condition temperature and air on binder aging, however it time consuming. Previous study attempted by Mallick and Brown (2004) to validate the laboratory aging methods. They found that RTFO and PAV aging methods are capable of simulating short term and long term aging. They also conclude that using RTFO residue for PAV aging makes much difference in results than using unaged binder. Several researchers characterized the aging properties at low temperature or high temperature (Kandhal et al. 1996, Lee et al. 2008). Our study covers both high and low temperature for aging of asphalt binder.

Traditionally, aged and unaged binder's mechanical and rheological properties are obtained from Dynamic Shear Rheometer (DSR) test, Bending Beam Rheometer (BBR) test, Direct Tension (DT) test and viscosity test. The DSR measures the binder's mechanical properties at both high and medium temperatures. At low temperature, BBR and DT tests are used to measure the stiffness. The present study uses a new test method called Multiple Stress Creep Recovery (MSCR) test in addition to DSR, BBR, DT and viscosity.

A common practice in asphalt technology is that there is a continues effort on modifying asphalt binders for improved properties. Modifiers affect on both aged and unaged binder's properties. So it is important to determine the changes in properties of modified asphalt binder with aging. Some researchers warned against using modifiers increase the viscosity and stiffness of aged and unaged binders at low temperature (Da Silva et al. 2004). The modifiers which are being used these days can be listed as styrene-butadiene (SB), styrene-butadiene-styrene (SBS), elvaloy, ethylene vinyl acetate (EVA) and ethylene styrene interpolymer (ESI). Among these polymers SBS is reported to be the most common and beneficial modifier (Becker et al. 2001). Usually 3 to 5 % polymers are added to binders. For economical concerns it is important to know the exact percent of modifier for a specific use. Refineries usually perform their own test to find out the optimum amount of the polymer. Effect of percentage polymer on binder properties due to aging process can be useful for modification of asphalt binder. In this study, effects of aging on percent polymer modification are examined.

To this study, most of laboratory tests for asphalt binders are conducted at macro and micro scales. For complete characterization of asphalt binder aging, recently developed nanoindentation test can be very useful. While of these new test methods such as infrared spectrum and atomic force microscopy have been done to limited extent Nanoindentation has not been done to study aging in asphalt binder yet (Huang 2008, Tarefder and Arif 2010). In this study nanoindentation is preformed to examine aging factors of asphalt binder.

1.2 Objectives

Objectives of this study are to:

- Determine the difference in mechanical properties of unaged asphalt binder with aged asphalt binder by conducting conventional tests such as DSR, BBR and MSCR on aged and unaged binder.
- Examine the change in properties of asphalt binder as a function of percent of asphalt modifier and polymer type by conducting nanoindentation on asphalt binder film.

1.3 Organization of Thesis

Chapter 1 defines aging and aging related problems such as occurring top down cracking because of increased stiffness at low temperature due to aging. Literature review of recent works on aging of asphalt is presented in chapter 2. Chapter 3 explains the methodology of this study. Two next chapters are about results and discussions on different tests performed in this study. In Chapter 4, traditional test results are discussed and evaluated. Chapter 5 is about nano-indentation test of asphalt aging. At the end, conclusions and recommendations are made in chapter 6.

CHAPTER 2

LITERATURE REVIEW

2.1 Asphalt Binder

Asphalt is produced from petroleum distillation residue. The most important elements of an asphalt molecule structure are carbon and hydrogen. Other elements are sulfur, nitrogen and oxygen. Asphalt binder structure is made up of three different parts; Aliphatic, which is straight or branched chains of hydrocarbons, saturated rings of hydrogen-carbon called naphthenic, and aromatic, which is stable unsaturated hydrogen-carbon ring. Molecules of asphalt binder have polar components which is the main reason of oxidation aging.

2.2 Polymer Modified Asphalt Binders

Due to ever increasing traffic volume and loading, there is a continuing effort by pavement community to improve asphalt binder. Mechanical properties of asphalt binder can be adjusted to help extend the service life of asphalt pavement as well as minimize the potential pavement distress. The addition of polymer to asphalt binder can reduce potential rutting and fatigue cracking as well as increase cohesion and decrease temperature susceptibility. However, the addition of polymer to asphalt binder increase viscosity and stiffness thereby reduces the workability of asphalt mixture. It is not known how binder modification affects the long term aging properties of asphalt binder. The production of PMBs is done in two ways; by mechanical or chemical processes. Seventy five percent of the binders are modified by using elastomeric materials such as styrenic block copolymers (SBS, SB, etc). Fifteen percent of the modified binders use plastomeric and 10% use rubber (Diehl 2000). Polybutadiene, polyisoprene, isobutene isoprene copolymer and polychloropren can be mentioned as other elastomeric materials to modify asphalt binder. Plastomeric polymers include ethylene-vinyl acetate (EVA), low density polyethylene (LDPE), high density polyethylene (HDPE) and ethylene-propylene-diene (EPDM). Of the polymer type listed above poly-butadiene-base is the most commonly used modifier due to higher performance of aged and unaged binders at lower cost. The properties of PMB need more studies because of complex structure of bitumen and its interaction with polymer.

2.3 Styrene-Butadiene-Styrene Rubber

Styrene-Butadiene-Styrene (SBS**)** is a thermoplastic elastomer material. These modifiers have an elastic behavior at room temperature yet behave like plastic materials at higher temperature. Its structure contains SBS tri-block chains. The first and last blocks are spherical polystyrene ($C_6H_5CH=CH_2$) with a matrix of polybutadiene ($CH_2=CH-CH=CH_2$) between them (Collins 1991). SBS is known for its high elasticity, air permeability and wet-skid resistance.

SBS is widely used in modifying asphalt binder as it improves asphalt binder at softening point, stiffness, elasticity and impact resistance (Becker et al. 2001). Shell Chemical Company was the first to use SBS copolymers to modify asphalt binder in the 1960s. For mixing procedure the temperature was kept at 185°C or below. Rapid is done in order to reduce potential aging while ensuring complete mixing of the polymer and binder.

Lu and Isacsson (1997) did a research on the effects of bitumen source/grade, SBS copolymer content and structure on rheological behavior of PMB (Lu and Isacsson 1997). For characterizing the binder they used dynamic mechanical analysis. They discovered that SBS-modified asphalt has more elasticity at high temperatures and better flexibility at low temperature. These improvements provide resistance to rutting and fatigue cracking. Different percentages of SBS were used varying from 3% to 6% by weight. Higher polymer content shows improvement in viscoelastic properties of PMB but the improvement is not linear with the amount of polymer added. This paper also concludes that using SBS reduces temperature susceptibility of asphalt binder. The other conclusion of this study is that the source of the binder and polymer structure affect the degree of modification (Lu and Isacsson 1997).

A study is done by Airey (2003) on viscoelastic behavior of PMBs. He used dynamic mechanical analysis (DMA) as well as conventional asphalt binder tests (Airey 2003). Binder tests includes such as penetration, softening point, Fraass breaking point, ductility, elastic recovery test and rotational viscosity test. In addition, Airey determined the effects of bitumen source, SBS polymer content, bitumen-polymer compatibility and aging on the viscoelastic behavior of PMBs. He observed that makes a statement that conventional tests are not adequate to quantify the unique rheological characteristics of different PMB asphalts. According to this research, aged binders with high polymer content show higher viscous behavior instead of increasing elasticity (Airey 2003).

2.4 Styrene-Butadiene Rubber

Emulsion polymerized SBR was produced in Germany by I. G. Farbenindustrie in the 1930's. SB is one of the most commonly used copolymers in the asphalt industry. Styrene-Butadiene (SB) or Styrene-Butadiene Rubber (SBR) is a rubber copolymer where the styrene ($C_6H_5CH=CH_2$) and butadiene ($CH_2=CH-CH=CH_2$) chain make up its molecular structure. The advantage of using SBS in binder modification is that it has has excellent aging stability and decreases the changes of binder properties such as stiffness due to aging. One of the most important roles of SB in asphalt binder is increasing its ductility. SB copolymer also helps the aging by decreasing the rate of oxidation, adhesion and cohesion. The difference between SBR and SBS is their reaction type, behavior with different base asphalt binder, storage and handling, temperature sensitivity and final properties of mixes.

2.5 Aging

Aging is changing in asphalt binder mechanical properties due to oxidation. Aging increases the stiffness of asphalt binder which is called hardening. Several studies have shown that aging changes the rheological properties of asphalt binders. The aging process increases the elasticity and stiffness.

2.5.1 Aging Factors and Mechanism

There are six factors that have been reported to contribute to the aging; oxidation, volatilization, polymerization, thixotropy, syneresis and separation. Oxidation is reaction of oxygen and asphalt binder due to temperature. Oxidation is the main factor for aging. Volatilization is the evaporation of lighter components of asphalt binder. This kind of aging occurs during the short term aging due to high temperature. Polymerization is combining of asphalt molecules and forming larger molecules. Thixotropy is formation of a structure within the asphalt binder during long term period. This kind of hardening occurs in the pavements with little traffic. Syneresis is a reaction in which thin oily liquids cover the surface of pavement. Asphalt binder becomes stiffer by loosing these oily components. Separation is loosing of resin or asphaltenes from asphalt binder by absorption of some porous aggregates.

2.5.2 Type of Aging

Asphalt binders age during the construction and the pavement service life. Aging occurs during the construction because of high mixing and compaction temperatures. This asphalt aging is called short term aging. High temperature expedites the air oxidation and more volatile components are lost. Long term aging occurs during the service life of the pavement and is mostly associated with oxidative aging at intermediate and low temperatures. The oxygen reacts with asphalt and makes a stiffer structure. SHRP developed two laboratory methods to simulate short and long term aging. According to AASHTO T240, the rolling thin film oven (RTFO) is used for short term aging (Figure

2.1). RTFO residue is conditioned in a Pressurized Aging Vessel (PAV) for long term aging according to AASHTO R28 (Figure 2.2).

2.5.3 Adverse Effect of Aging

Asphalt binders requires testing after short term aging to measure its resistance for rutting and again after long term aging to determine potential fatigue cracking. There are two other factors to determine the rutting potential for RTFO binder and fatigue potential for PAV binder. Complex modulus divided by Sinδ (G*/Sinδ) measured at high temperature for short term aged binder shows the rutting potential. Multiplying complex modulus by Sinδ (G*xSinδ) which is obtained at intermediate temperature for long term aged binder, fatigue factor can be measured. Few years ago Dongre, D'Angelo and Reinke (2005) used the DSR to determine a new binder parameter to replace the current Superpave Specification parameter (G*/Sinδ). They believe that G*/Sinδ is not applicable to polymer-modified asphalt binders.

2.5.4 Recent Study on Aging

Molenaar et al. (2010) investigated the effect of common aging laboratory methods on rheological properties of binder. They compared lab results to results of field aged binders. They found that laboratory methods for long term aging are not capable of simulating the field aging. Molenaar et al. (2010) also studied the aging effects on binders in porous concrete. Aging increases tensile strength, resistance to fatigue cracking and decrease stress relaxation capacity. (Molenaar et al. 2010)

Zhange et al. (2011) studied the influence of short term and long term thermal oxidative aging on dynamic viscosity and thermal stability of SBS-modified binder and storage-stable SBS/sulfur-modified binder. the results show that adding sulfur results in more changes of binder’s viscous behavior due to aging compared with SBS-modified binder without sulfur. (Zhange et al. 2011)

DSR is one of the methods in this study to characterize the aging effects on binder’s mechanical properties. There are some other aging methods than common ones which are proposed by AASHTO. One of these methods is ultraviolet aging which is used in a study by Wu et al. (2009). They found that UV light aging improves thermal behavior of asphalt binder. They also concluded that this aging method can change complex modulus and phase angle (Wu et al. 2009).

Huang (2008) studied the effect of long term oxidative aging on rubber-modified asphalt binder. Findings show that a significant increase in elasticity of aged rubber-modified asphalt binder (Huang 2008).

Kumar et al. (2010) studied on aging characterization at high temperature of two different modified-binders; SBS as an elastomer and EVA as a plastomer. Various amount of polymers are used to modify asphalt binder, changing from 3% to 9%. The testing temperature range adjusted from 46 to 82 °C. The results show that SBS-modified binder has lower viscosity temperature susceptibility than the other modified asphalt binders and it has more resistance to cracking and rutting (Kumar et al. 2010).

Most studies have concentrated on improving the properties of asphalt binder, few studies been done on the effect of PMB properties due to aging. Modifiers will significantly affect both aged and unaged binders. So it is important to monitor the changes of modified asphalt binders during the aging period to ensure expected performance under traffic loading.

Some researchers have evaluated Superpave binder aging methods such as Mallick and Brown (2004). Their findings show that RTFO and PAV are capable of simulating short and long term aging. Ala Abbas (2002) used both base binder and RTFO residue for PAV aging to determine if the suggested sequence of these two aging procedure is necessary. This study used DSR and BBR tests to evaluate the binder's properties and determine that using RTFO residue for PAV has a significant effect on measured rheological properties. The Aging performance of modified binder has been widely researched in recent years with studies dedicated to find new methods of evaluating the aging effect on modified asphalt binder. The use of infrared spectrum and atomic force microscopy (AFM) are the examples of the new methods (Huang 2008, Wu et al., 2009).

2.6 Macro-Scale Test Methods of Aging

Conventional asphalt binder tests such as the penetration test have many limitations in terms of to characterization. For example, these tests are performed at one specific temperature and there is no specification or test method for long term aging of asphalt binder. So, because of this, in 1987, the US Congress dedicated $150 million for the Strategic Highway Research Program (SHRP). In 1993 SHRP came up with new series of specifications and test methods. This group of tests is called superpave tests and purposed a grading system of performance grading (PG) system. Superpave tests consist of several test methods and equipments for different performance related temperatures. It suggests using the DSR to characterize asphalts binder stiffness and elasticity properties at high and intermediate temperature. At low temperature BBR is recommended to measure stiffness and DT test is done to determine the elasticity. Another test method which is related to binder properties at high construction temperatures is Rotational Viscometer test.

2.6.1 Dynamic Shear Rheometer

The DSR test is the most common test method to measure the stiffness and viscoelastic behavior of asphalt binder by applying dynamic shear loading (Figure 2.4). The complex shear modulus (G*) represents binder's stiffness. The DSR also measures the phase angle (δ) in order to determine the elastic response of the binder. The following equation is used to calculate G*.

$$G^* = \frac{\tau_{max}}{\gamma_{max}} \quad 2.1$$

where,

$$\tau_{max} = \frac{2T}{\pi r^3} \quad 2.2$$

$$\gamma_{max} = \frac{\theta r}{h} \quad 2.3$$

T = maximum applied torque, r = radius of binder specimen/plate, θ = deflection (rotation) angle, h = specimen hight

There are two other factors in determining the rutting potential for RTFO binder and fatigue potential for PAV binder.

$$\text{Rutting Factor} = G^* / \sin\delta \qquad 2.4$$

$$\text{Fatigue Factor} = G^* \times \sin\delta \qquad 2.5$$

Rutting factor is measured measured at high temperature for short term aged binder and fatigue factor is measured at intermediate temperature for long term aged binder.

Elastic recovery is the ability of deformed binder to be recovered and to be returned to its original form. The elastic recovery of asphalt binder was traditionally measured by a ductilometer but recently DSR is taking place which has a significant role in this study.

2.6.2 Multiple-Stress Creep-Recovery Test

Multiple-Stress Creep-Recovery (MSCR) test method relies on asphalt binder creep recovery performance. This test basically determines the rutting performance of an asphalt binder. Previously G*/Sinδ was used as an indicator of rutting potential of asphalt binder at high temperatures. DSR rutting factor, G*/Sinδ is measured at low shear strain under an oscillating load. Dongre et al. (2005) used DSR to determine a new parameter called creep compliance to replace Superpave Specification factor for rutting. They believe G*/Sinδ is not applicable to polymer-modified asphalt binders. In DSR testing, the very low stress and strain levels are unable to activate the polymer network (Anderson et al.

2005). To that end, MSCR is used to determine the rutting potential of asphalt binder, especially for modified asphalt binders. In MSCR test, higher stress and strain levels are applied. To determine the effect of polymer on asphalt binder, higher stresses are applied and the response of the binder's stiffness as well as elastic behavior is recorded. This test method considers the true effect of traffic loading and has a different specification unlike for medium, high and very high traffic loadings. This test method includes a recovery period which indicates the elastic response of asphalt binder. Higher delayed elastic response shows higher elastic potential of asphalt binder. Compared with the conventional DSR test the creep compliance (J_{nr}) measured with MSCR test represent a better rutting potential than G*/Sinδ factor. In this study, J_{nr} is used to understand asphalt aging. Another advantage of this method is that it can measure the sensitivity of the asphalt binder where by pervious test methods were not capable of doing. Figure 2.4 shows a creep recovery cycle. Creep part lasts for 1 second and is followed by a 9 second recovery. The creep compliance is defined by:

$$J_{nr} = \frac{\gamma_u}{\tau} \qquad 2.4$$

where J_{nr} = non_recoverable compliance, γ_u = unrecovered strain, τ = shear stress.

2.6.3 Rotational Viscosity

Rotational viscosity (RV) is the most common test to measure asphalt binder's viscosity. Viscosity is one of the fundamental rheological properties of asphalt binder and is important for pavement construction procedure such as mixing, laying and compacting (Sybilski 1994). Different types of viscosity tests are used in many countries and this in turn provides different measurements and grading systems. Bitumen states differ by temperature. When the temperature is greater than 135°C, the asphalt binder is considered as a Newtonian liquid (Roberts et al. 1991). This means that the viscosity is not dependent on shear rate. Here characterization of the asphalt binder based on viscosity is very important. Figure 2.5 shows a Brookfield rotational viscometer which is so common.

2.6.4 Bending Beam Rheometer

In areas of wide ranging temperatures, asphalt pavements are susceptible due to thermal cracking. Thermal cracking is related to the stiffness of asphalt binder at low temperature. BBR is a simple test to measure the flexible creep stiffness of the asphalt binder at low temperature range of -40 °C to 0 °C. An asphalt beam used for this test has dimensions of 125×6.25×12.5 mm. The point load of 980 mN is applied on the asphalt beam for 240 seconds. By measuring beam deflection, stiffness can be calculated.

$$S(t) = \frac{PL^3}{4bh^3\delta(t)} \qquad 2.5$$

where S(t) = creep stiffness at time, t = 60 seconds, P = applied constant load, 100 g (980mN), L = distance between beam supports, 102 mm, b = beam width. 12.5 mm, h = beam thickness, 6.25 mm, δ (t) = deflection at time, t = 60 seconds. BBR also records m-value which determines the changing rate of changes of creep stiffness with loading time. Figure 2.6 (a) show a schematic of BBR and Figure 2.6 (b) shows a BBR apparatus.

2.6.5 Direct Tension Test

The Direct tension test (DTT) measures the ductility of asphalt binder at low temperatures. Stiffer asphalt binders are more brittle where softer binders behave more ductility. This DTT test is an additional test to the BBR test to characterize asphalt binders at low temperatures. The DTT also measures the ultimate tensile strain at the same temperature BBR test.

$$\varepsilon_f = \frac{\Delta L}{L_e} \qquad 2.6$$

where ε_f = Failure Strain, ΔL = Change in length, L_e = Effective gauge length

The test procedure consists of applying a constant strain rate on a dog bone shaped sample at a rate of 1 mm/min. The strain that corresponds to the peak stress is not necessarily the strain at which the sample breaks.

2.7 Nanoindentation of Aging

The most useful test to measure asphalt properties is nano indentation test (Figure 2.7). This test includes a low load range (milli-Newton) which is applied on a smooth surface of an asphalt material with a diamond tip. There are several shapes for the indentation tips. Tips can be at the conical, spherical or pyramid shape. Load is applied on several points at the asphalts surface and the indentation depth is measure by load increment up to a certain load amount. Then the load stays constant and creep load is applied on the sample for a period of time. The loading and unloading curves determine the reduced elastic modulus and the hardness of asphalt samples by using Oliver and Pharr methods (1992). Indentation tests have only recently been done on modified asphalt binders with varuing PG grades (Tarefder et al. 2010).

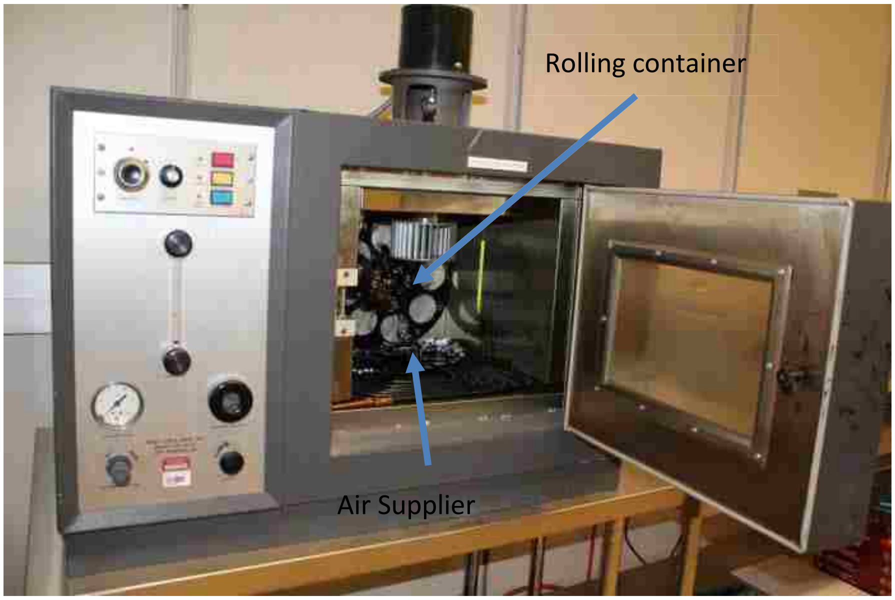


Figure 2.1: RTFO

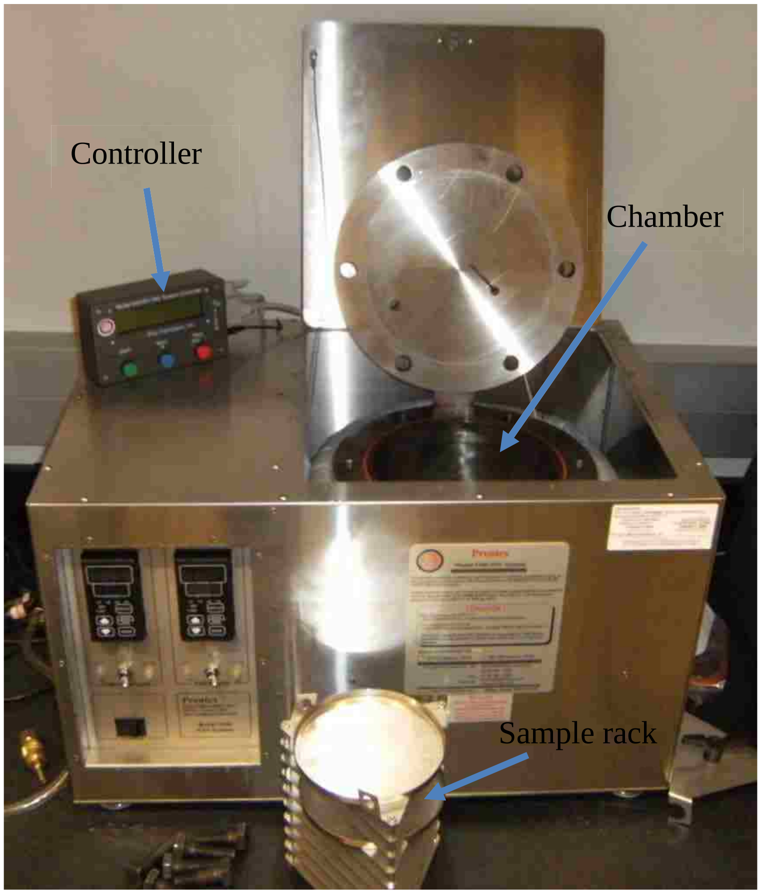
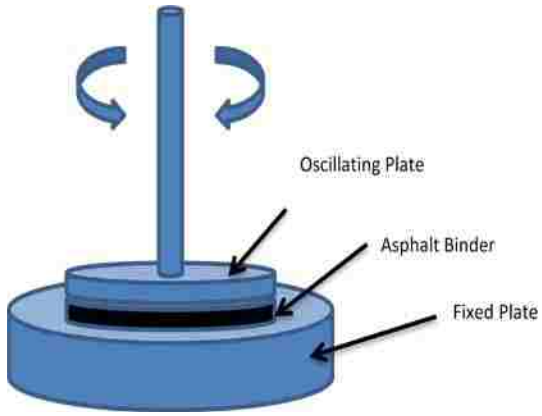
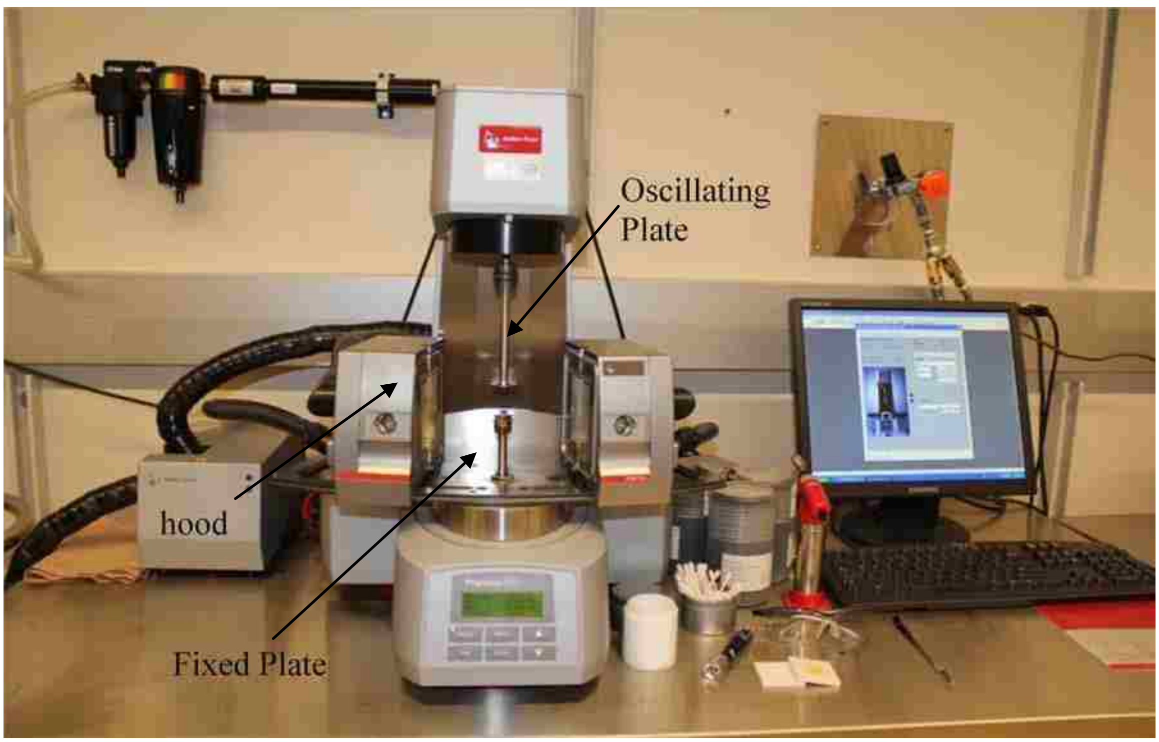


Figure 2.2: PAV



(a): Basics of DSR



(b): DSR apparatus

Figure 2.3: Dynamic Shear Rheometer

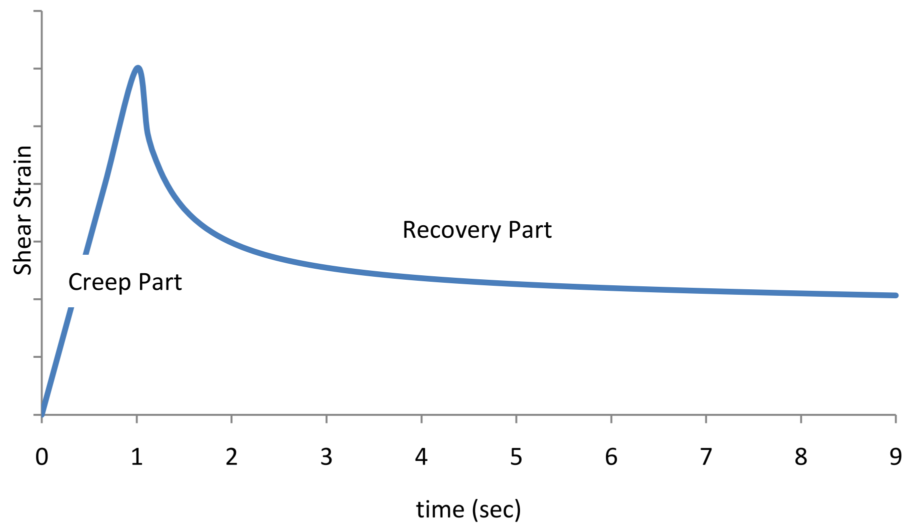
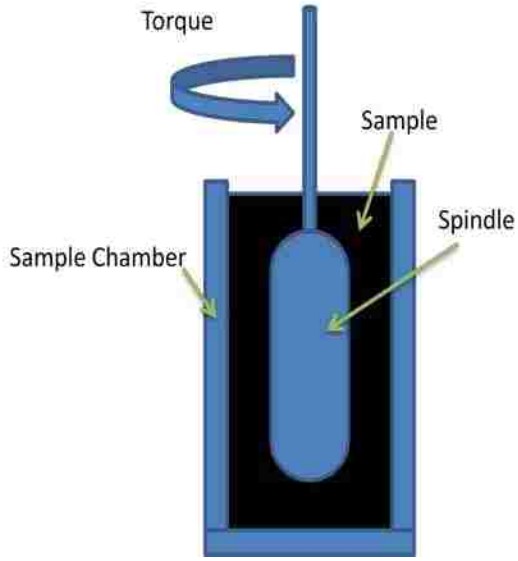


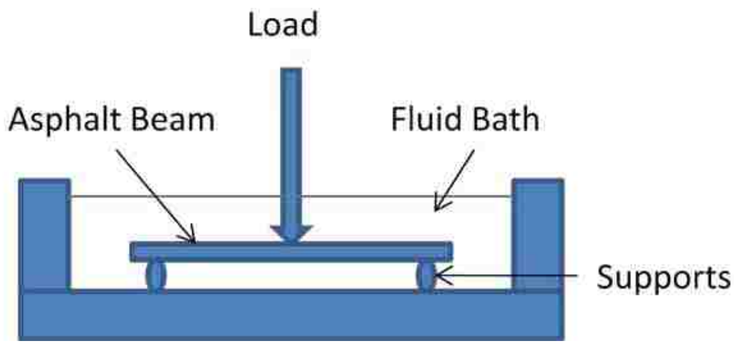
Figure 2.4: One creep recovery cycle

(a) Brookfield viscometer



(b) RV basics

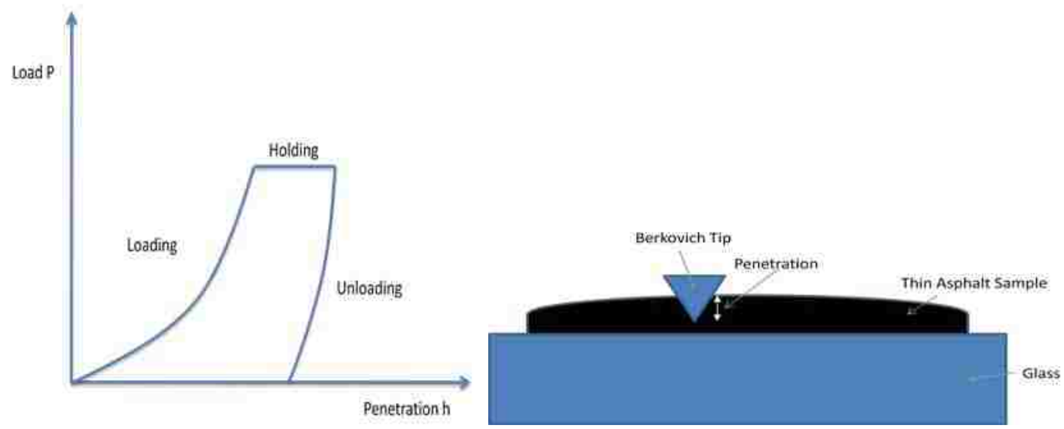
Figure 2.5: Rotational viscometer



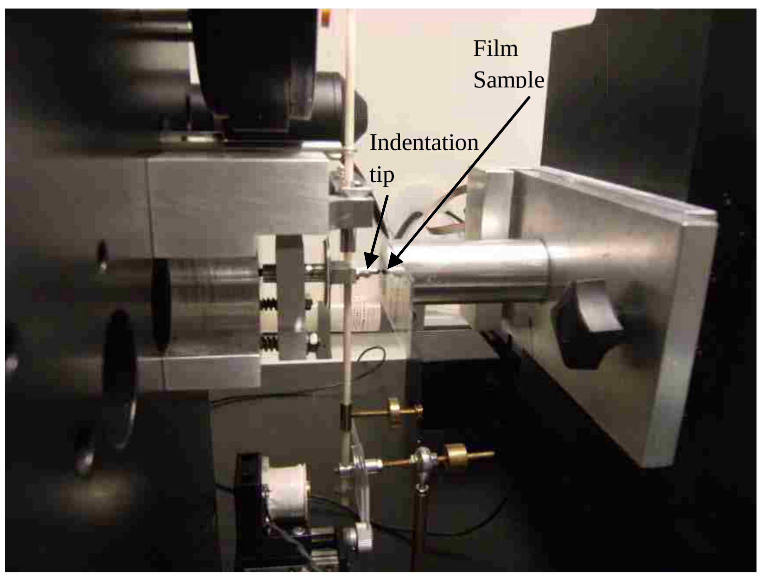
(a) BBR schematic

(b) BBR apparatus

Figure 2.6: BBR



(a) Nano indentation schematic



(b) Nano indentation apparatus

Figure 2.7: Nano Indentation

CHAPTER 3

METHODOLOGY

3.1 Materials

An unmodified asphalt binder designated as "PG 58-28" was collected from Holy Asphalt Refinery, Albuquerque, NM. Base binder was then modified using two styrene-based copolymers; styrene-butadiene and styrene-butadiene-styrene. Both copolymers were collected from Holy Asphalt Refinery, too (Holly Asphalt, 2008).

3.2 Modifying Asphalt Binder

Different percent of SB and SBS polymers were used to modify binders. About 3%, 4% and 5% polymers are used. Base binders are preheated up to 190° C in one gallon metal tin cans. Each of them contains about 2 kg of asphalt binder. Then the certain amount of polymer for each mix added while the binder was mixed by high shear mixer. Polymer should be added slowly to make sure that it is melted and mixed properly. Mixing of the binders and polymers should be done rapidly as the effect of high temperature on binder's properties will be significant. Adding stage for this amount of binder takes about 20 to 30 minutes. After adding the polymers, the modified binder needs to stay under the mixer for an extra 10 minutes. Then the binder stays at room temperature to be cooled.

3.3 Aging of Modified Binder

Two different methods are used to age asphalt binders. One method is standard test procedure for short term and long term aging and the other is for oven aging. According to AASHTO T240, binders are aged short term using the RTFO test. Binder samples aged at a temperature of 163 °C for 85 minutes in a rolling oven under constant air flow. Then residue of RTFO is used to prepare long term aged binder. The standard for long term aging is AASHTO R28. The RTFO residue is aged in a PAV which simulates aging approximately 10 years. The PAV applies 2.1 atm using air pressure at a constant temperature of 100 °C for 20 hours. The binder samples are then vacuumed at 170 °C for 30 minutes to make sure that all of the air bubbles caused by pressure were out of binder. The method of oven aging of binder samples is much simple. Binders aged in uncovered metal tin cans that contain about 50 g of asphalt binder. Binder samples are placed in the oven for varying time periods at 100 °C. The only factor in this aging procedure is temperature. Oven aged binders are useful in studying the effect of temperature on binder for long periods of time. The timings for aging the binder in oven are 1 week, 2weeks, 1 month, 2 months, 3 months, 4 months and 5 months for unmodified binder and 1 week, 2weeks, 1 month, 2 months and 3 months for SB 4% modified binder.

3.4 Testing Parameters

3.4.1 DSR Test

The DSR test followed AASHTO T 315 standard. The Oscillation temperature sweep test is preformed using the DSR test. Asphalt binder is subjected to shear stress at temperature ranges of 52°C to 76°C with 6° intervals. This test is done to determine the binders stiffness (G*), phase angle (δ), storage modulus (G') and loss modulus (G″). The strain rate for all DSR tests assigns 10% and the frequency is 10 rad/s. At each temperature, 30 points are measured and the mean value of G* and δ are recorded.

3.4.2 MSCR Test

The MSCR test is done according to AASHTO TP 70 standard. The test temperatures are identical to the DSR Test (52°C to 76°C with 6° intervals). The MSCR test is done to determine the creep compliance (J_{nr}). This parameter is measured at two shear stress levels, 100 kPa and 3200 kPa, where each temperature creep-recovery cycle is repeated 10 times and the mean value for creep compliance is recorded. The difference between the measured compliances (ΔJ_{nr}) for different shear stresses is calculated. ΔJ_{nr} represents the sensitivity of binder to changes in the shear stress.

3.4.3 BBR Test

The bending beam rheometer test is used to study the stiffness of binder at low temperature according to AASHTO T 313 standard. This test shows the change in binder’s properties at low temperature as compared with previous results at higher temperatures. All samples are tested at -18°C and the stiffness and the m-value is determined. A constant creep load of 980 mn is applied on an asphalt beam for 240 seconds. According to the standard, measured values for stiffness and m-value at 60 sec are used for analysis.

3.4.4 Brookfield Viscosity

This test measures the viscosity of asphalt binder at mixing and compaction temperature. Following AASHTO T 316 standard an 8-11 g of asphalt binder is tested at 135 °C at a speed of 20 rpm. The viscosity measurements are collected after 10 minutes rotation of the spindle in the chamber which contains the asphalt binder. For three minutes the viscosity is then measured at one minute intervals.

3.4.5 DT Test

Direct tension test is a complementary test for the BBR test at low temperatures. This test measures the ductility or brittleness of asphalt binder at low temperatures. According to AASHTO T 314 standard the test temperature is the same as BBR test (-18 °C). A dog bone shape sample is loaded in tension at 1 mm/min until it breaks. The failure stress is determined by recording the change in length at the maximum value of load (peak stress) on specimen.

3.4.6 NanoIndentation

3.4.6.1 Sample preparation

There is no specific standard for asphalt indentation test at nano scale. The test samples are prepared of thin film asphalt binder on glass slides. Glass slides are taped in such a way as to leave a small gap between them. A few drops of hot binder are poured between this gap. By scratching the poured binder, a thin film of asphalt binder remains in the gap. After cooling for 5 minutes, the tapes are tacked off. The samples are then placed in the oven at 160 °C for 10 minutes to smoothen the sample surface.

3.4.6.1 Test Apparatus

Nanoindentation test is performed by using a nanoindentor supplied by MicroMaterials Ltd. Wrexham, UK. This tests equipment conducts the indentation in a horizontal direction. Two Berkovich and Conical indentation tips were made available. By Trial and error tests, the numbers of successful indentations using Berkovich tips were more than those obtained using the conical tip. Therefore, the Berkovich tip was found to be more suitable for asphalt binder indentation. The Berkovich tip has a pyramidal shape with a semi angle of 65.27 °. The resolution of load and displacement for the indenter are 1 nN and 0.01 nm respectively.

3.4.6.1 Test Configuration

All binder samples are tested at a controlled temperature of 27±0.1 °C. Five points with a distance of 1 mm from each other are selected on each sample for indentation. The test consists of three parts: Loading, maintaining the load and the unloading. The indentation test applied a controlled load at a maximum of 0.20 mN. The initial loading is then adjusted 0.05 mN and the tip indented at a loading and unloading rate of 0.025 mN. At the holding stage the load is maintained for 30 s. Oliver and Pharr (1992) developed a method which uses depth verses loading, to calculate reduced elastic modulus and hardness of the asphalt samples. The data for dwell loading is then used to calculate creep compliance by varying the time.

3.5 Test Matrix

Table 3.1 presents a test matrix created to study the effect of aging on the rheological properties of original and modified binder. This table lists tests methods performed on both unmodified and modified asphalt binders for aged and unaged conditions. Both SB and SBS samples are divided into different modifier percentages (3, 4 and 5%) of asphalt binder. The First column presents the test methods. The second column presents the different aging methods used for each sample. The numbers listed in the cells represents the number of each preformed test on the sample. From this test matrix, a total of 345 tests are predicted. Table 3.2 presents a matrix for oven aged samples with varying aging times.

Table 3.1 Test Matrix

Test Matrix		Base		Modified Binder											
				SB						SBS					
				3%		4%		5%		3%		4%		5%	
		Aged	Un Aged	Aged	Un Aged	Aged	Un Aged	Aged	Un Aged	Aged	Un Aged	Aged	Un Aged	Aged	Un Aged
DSR			3		3		3		3		3		3		3
	RTFO	3		3		3		3		3		3		3	
	PAV	3		3		3		3		3		3		3	
	Oven	14				10									
BBR			3		3		3		3		3		3		3
	RTFO	3		3		3		3		3		3		3	
	PAV	3		3		3		3		3		3		3	
	Oven	21				15									
Nanoindentation			2		2		2		2		2		2		2
	RTFO	2		2		2		2		2		2		2	
	PAV	2		2		2		2		2		2		2	
Brookfield Viscosity			3		3		3		3		3		3		3
	RTFO	3		3		3		3		3		3		3	
	PAV	3		3		3		3		3		3		3	
	Oven	7				5									
DT			2		2		2		2		2		2		2
	RTFO	2		2		2		2		2		2		2	
	PAV	2		2		2		2		2		2		2	
												Total		345	

Table 3.2 Oven Aged Test Matrix

Oven Aged Test Matrix	Aging Time	Base	Modified Binder
			SB 4%
DSR	1 week	2	2
	2 weeks	2	2
	1 month	2	2
	2 months	2	2
	3 months	2	2
	4 months	2	
	5monthes	2	
BBR	1 week	3	3
	2 weeks	3	3
	1 month	3	3
	2 months	3	3
	3 months	3	3
	4 months	3	
	5monthes	3	
Brookfield Viscosity	1 week	1	1
	2 weeks	1	1
	1 month	1	1
	2 months	1	1
	3 months	1	1
	4 months	1	
	5monthes	1	

CHAPTER 4

Rheological Experimentation of Aging in Polymer Modified Asphalt

4.1 Introduction

This chapter characterizes polymer modified asphalt binders' rheological properties at aged and unaged conditions. For high temperature properties, binders are tested from 52°C to 76°C using DSR for measuring viscoelastic properties such stiffness, phase angle. For low temperature properties, binders are tested using BBR and DT. Elastic recovery of the binders is determined through MSCR test. For measuring viscosity, Brookfield rotational viscometer is used. Two polymers, SB and SBS are used to modify the binder. In addition, this chapter includes some other method of aging in addition to short and long term aging.

4.2 Laboratory Testing

4.2.1 Dynamic Shear Rheometer

Temperature sweep test is conducted in DSR. In temperature sweep test, a sample of liquid asphalt is subjected to shear stress at sweep of temperature (52°C to 76°C) with 6° intervals. The test is performed to determine the binders stiffness (G^*), phase angle (δ), storage modulus (G') and loss modulus (G''). acoording to AASHTO T 315, Table 2, the strain rate for all DSR tests were is assigned 10% and the frequency is 10 rad/s. Table 4.1 shows the rheological properties for unmodified binder at both unaged and aged conditions. Table 4.2 presents the same properties for SB-modified binder and Table 4.3 present the results for SBS-modified binder.

4.2.2 Results and Discussion for the DSR Test

Figure 4.1(a) shows the G* varying with the temperature for original binder. This figure shows that aging increases the G* value and makes the binder stiffer. It also shows that the increase in temperature reduces the G* value. Phase angle changes due to aging and temperature. The values for δ are presented at Figure 4.1(b). Phase angle increases with temperature while reduces with aging. Increasing in phase angle means that the binder is going from elastic behavior toward the viscous behavior. It can be concluded that the aging as well as low temperature, makes the binder to behave more elastic. Figure 4.2 shows the G* versus temperature for SB-modified binder and SBS-modified binder and Figure 4.3 shows the δ varying with temperature for the modified binders. The results for the modified binders are similar as the original binder for aging.

The effect of different percent of polymers on G* is presented in Figure 4.4 and on δ is presented in Figure 4.5. These properties are varying with temperature. As the temperature increases asphalt binder becomes softer and looses the stiffness against the shear stress, so the little percent of polymer which is solid at the tested temperature improves the binder resistance to the shear stress. At lower temperatures polymers helps the binder to show more strength against the shear stress. Modifiers also have a significant effect on phase angle of the binder. Figure 4.5 shows that by having more amounts of polymers in the binder the phase angle reduces. This means that modified binder has more elastic response to the shear stresses. At Figure 4.5 it can be seen that by changing the temperature, the difference between the phase angles for several percent of binders stays constant. SBS-modified binder has the similar effects to the SB-modified binder. The stiffness and the phase angle for the both modified binders are presented in Figure 4.6 as a function of temperature to see which one of the SB or SBS polymers is more effective. At a specific percent, SBS-modified binder shows more stiffness and lower phase angle than SB-modified binder.

The original binder and SB 4% modified binder are oven aged, too. Table 4.5 presents The DSR test results for original binder as well as Table 4.6 for SB 4% modified binder. Figure 4.7 (a) shows the stiffness varying with aging time at 58 °C. It can be seen that by aging the stiffness increases as well as the slope of the stiffness curve. Figure 4.7 (b) presents the phase angle varying by aging time. It shows that phase angle reduces by aging time and having more elastic behavior. It can be understood that phase angle has a linear relationship with the aging time. Figure 4.7 also shows the effect of modification on G* and δ which will increase the stiffness and reduces the phase angle. If the original binder results of oven aged binder is compared with the results of PAV aged binder, it can be concluded that the same results for the PAV aging can be obtained by oven aging for a time between 1 and 2 month.

For both SB and SBS modified binders aging index (AI) has been calculated at 58°C with the following equation.

$$AI = \frac{G^* \, aged \, binder}{G^* \, unaged \, binder} \qquad 4.1$$

The aging index for different percent of SB-modified binder is compared at Figure 4.8 (a). For both RTFO and PAV binders it can be seen that the AI increases by adding 3% of SB polymer and after that by adding more polymer AI decreases. This shows that more percent of polymer in the asphalt binder will reduce the aging affect, so for the high modified binders, the stiffness changes so less than low modified binders. Figure 4.8 (b) shows the similar trend for the SBS-modified binder. Figure 4.9 compares the effect of polymer types on aging. At a specific percent of polymer content, for both RTFO and PAV binders, SB-modified binder shows lower aging index than SBS-modified binder. This can be mentioned as an advantage of using SB instead of SBS. AI is also calculated for storage and loss modulus of all binder types. This can show the effect of aging on elastic and viscous behavior of binders. Figure 4.10 shows the AI that is calculated based on storage modulus of modified binders. It shows that except than 3% polymer content, the storage modulus for SB-modified binder changes more than SBS-modified binder for both RTFO and PAV aging conditions. So, elastic behavior of SB-modified binder changes more than elastic behavior of SBS-modified binder through the aging process. Loss modulus for both modified binders is compared in similar way at Figure 4.11. Here, the loss modulus for SBS-modified binder changes more than SB-modified binder for both RTFO and PAV aging conditions. It can be concluded that viscous behavior of SBS-modified binder changes more than viscous behavior of SB-modified binder through the aging process.

For the oven aging, AI is calculated for both oven aged binders based on G*. Figure 4.12 compares the AI for both binders. It can be seen that modification reduces the aging effect on stiffness. So, the original binder gets stiffer through the aging process than modified binder. The stiffness for unaged modified binder is higher than original binder (Figure 4.7 (a)) but after the aging original binder shows the higher stiffness than modified binder. AI is also calculated for the original binder based on G' and G″ to see the effect of aging on elastic and viscous behavior of asphalt binder. The AI for different oven aging times is presented at Figure 4.13 for both G' and G″. This figure shows that G' is highly effected by oven aging time compared with G″. It can be concluded that oven aging is changing the elastic behavior of the asphalt binder more than its viscous behavior.

4.2.3 Significance of Test Results for DSR Test

ANOVA statistical analysis is preformed on G* results of the asphalt binders at aged and unaged conditions at 58 °C and 70 °C. The calculated P-values are presented in Table 4.6. If the P-value is less than 0.05, means that inputs are significant to the outputs. From the results, it can be seen that inputs are so significant but they don’t have the same P-values at different aging conditions. It can be seen that P-value for PAV binders are lower than the other ones. So, it can be concluded that PAV aging has higher effect to the stiffness of modified binder compared with the other aging conditions.

4.2.3 Multiple Stress Creep Recovery Test

For the MSCR test, the temperatures are as same as the DSR Verification Test (The temperatures are from 52°C to 76°C with 6° intervals). At this test, creep compliance is measured for two shear stress levels, 100 kPa and 3200 kPa. Then the difference between the measured compliances (ΔJ_{nr}) for different shear stresses is calculated and reported in percent. ΔJ_{nr} is used to understand the sensitivity of the binder to the changes of the shear stress. All the results for the MSCR test are presented at Table 4.6 for original binder, Table 4.7 for SB-modified binder and Table 4.8 for SBS-modified binder.

4.2.4 Results and Discussion for the MSCR Test

The effect of SB on binder's creep compliance (J_{nr}) at the applied shear stress of 3200 Pa can be seen at Figure 4.14 for unaged, RTFO and PAV binders. Modifying the binder with SB polymer decreases the $J_{nr.}$ value. It means that SB-modified binder has more resistance against the rutting. The figure also shows that, the creep compliance changes with the temperature. Higher values are obtained for the creep compliance at high temperatures. So, At higher temperatures the pavement is more susceptible to rutting. From the same figure, it can be concluded that adding more polymer to the binder results in reducing the creep compliance value and high modified binders also show less changes in J_{nr} with the change of temperature. This can be seen by the slope of 5% SB-modified binder curve which is lower than the other binders at Figure 4.15.

For studying the sensitivity of the modified binder to the changes of shear stress, ΔJ_{nr} values are calculated. Equation 4.2 is used to calculate ΔJ_{nr}.

$$\Delta J_{nr}\ (\%) = \frac{J_{nr\ \tau=3200\ Pa}}{J_{nr\ \tau=100\ Pa}} * 100 \qquad 4.2$$

Figure 4.16 shows the changes of ΔJ_{nr} verses temperature for SB-modified binder at aged and unaged conditions. The high value for ΔJ_{nr} indicates the high sensitivity of binder to changes of shear stress. For SB-modified binder, the results show that the more polymers are added to the binder the more sensitive it becomes. This figure also shows that at higher temperatures the binder becomes more sensitive to the change of shear stress. SBS-modified binder shows the similar results in creep compliance to the SB-modified binder results. SBS improves the creep properties by decreasing the creep compliance which can be seen in Figure 4.17, but on the other hand it gives more sensitivity to the binder (Figure 4.18).

To compare the effect of polymer type on creep compliance, J_{nr} versus temperature is presented at Figure 4.19 (a) for RTFO aged binder. It shows that for a specific amount of polymer, SBS reduces the creep compliance more than SB or in other words, SBS polymer gives more resistance to the binder against the rutting. The sensitivity of two different modified binders to shear stress is compared at Figure 4.19(b). ΔJ_{nr} is presented as a function of temperature for both SB and SBS-modified binder at RTFO aging condition. It shows that most of the binders modified with SBS have less sensitivity to the changes of shear stress than the binders modified with SB.

4.2.5 BBR Test

Bending beam rheometer test is used to study the stiffness of polymer modified binder at unaged and aged conditions at low temperature. The test results are used to calculate the changes of the binder's properties at low temperature. All samples are tested at -18 °C and the results for the stiffness (S) and the m-value are collected. The BBR test results for unmodified binder are presented in Table 4.9 and for the SB and SBS-modified binder are presented in Table 4.10 and Table 4.11.

4.2.6 Results and Discussion for the BBR Test

Stiffness and m-value for the SB-modified binders are presented in Figure 4.20. It shows that the SB-modified binders have higher stiffness than unmodified binder. It can be concluded that regardless to the temperature, modifying the binder results in increasing the stiffness. At medium and high temperatures, having a high stiffness is desirable. However, increasing in stiffness at low temperature may lead to thermal craking. The m-value has the opposite trend than stiffness. Modified binder shows lower m-value than unmodified binder. It means that the rate of changes in stiffness by loading for modified binder is lower than unmodified binder. This can be mentioned as a disadvantage of using this kind of modified binders. Figure 4.21 shows the results of same properties for the SBS-modified binder. At a certain amount of polymer, SBS is increasing the stiffness more than SB. Similar to the high temperatures, SBS increases the stiffness more than SB polymer at low temperatures, too.

Aging index is calculated base on BBR stiffness at -18 ° C to see if the similar results can be obtained to the DSR test.

$$AI = \frac{S\ aged\ binder}{S\ \ unaged\ binder} \qquad 4.3$$

Figure 4.22 (a) shows the AI for SB-modified binder and Figure 4.22 (b) shows the AI for SBS-modified binder. Same as DSR test result it can be seen that higher percent of polymer content in the asphalt binder ages it less.

Aging effect of polymer types are compare at different modification degree for RTFO condition at figure 4.23 (a) and for PAV condition at figure 4.23 (b). Similar to the DSR test results, BBR test shows that the binder modified with SB is aged less than the binder modified with SBS polymers.

4.2.7 Viscosity Test

Viscosity test is conducted by using Brookfield rotational viscometer. The test temperature is set to be at 135 °C. Only one kind of spindle is used to measure the viscosity which is appropriate for asphalt binder. This spindle is not applicable to the materials with a viscosity more than 25 Pa.s, even for the aged modified asphalt which has a high viscosity. For each sample 3 readings collected and the mean value is reported.

4.2.8 Results and Discussions for the Viscosity test

The results for viscosity test at unaged, RTFO and PAV conditions are presented in Table 4.12. There are no measurements for some of the PAV binder samples. This is because of high viscosity of those samples which are not at the capacity range of the spindle. It can be seen that through the RTFO aging the viscosity increases 1.1~1.5 times through the

PAV aging it increases 2.7~3.1 times. Figure 4.24 shows the increasing of viscosity by aging for original binder, SB-modified binder and SBS-modified binder. Higher viscosity is also obtained by increasing the modification degree. By comparing the results for different modified binders it can be concluded that SBS-modified binder has higher viscosity at a same modification degree of SB-modified binder.

4.2.9 Direct Tension Test

DT test is to measure the ductility of asphalt binder at low temperatures. It is complimentary test to the BBR test. Some binders at low temperatures have stiffness more than maximum value which is allowed by AASHTO M 320 standard (S > 300 MPa). DT test is then preformed to measure the ductility to see if the binder can be used. In this study, the effect of aging and modification degree on the asphalt binder is considered.

4.2.10 Results and Discussion for the Direct Tension Test

The test results for DT test are presented in Table 4.13 and Figure 4.25 shows the failure strain for original binder at different aging conditions. It can be seen that by aging the binder breaks at lower strain. This means that aging reduces the ductility of asphalt binder. It can be concluded that aged asphalt binder is more susceptible to the thermal cracking than the unaged binder.

4.3 Conclusions

- The use of SBS in binder modification has a greater effect on the mechanical performance that of SB. Binder modification with SBS increases binder stiffness and decreases phase angle and creep compliance to a large extend than SB. As the polymer amount increases, the effects of modification are amplified. However, the effect of polymer is temperature-dependent. For example, at low temperatures, G* is greater than that at high temperatures and J_{nr} is much lower at high temperatures than that at low temperatures.
- Based on G*, S and viscosity results, SB reduces the effect of aging more than SBS.
- Aging increases the elastic component of complex shear modulus more than the viscous component.
- Results show that creep compliance decreases with aging. This results may explain why rutting usually occurs during the earlier stages times of a pavement life. However, with binder modification there is increased of the creep compliance due to changes of shear stress (loading).
- Short term aging with the RTFO increases binder viscosity by 110-150 percent. Long term with the PAV aging increases the viscosity by 270-310 percent. Therefore, viscosity increases twice as much due to long term aging when compared to short term aging.
- Base on the rheological properties of unmodified binder (G*), it takes approximately 1.5 months of draft oven aging at 100 °C to simulate long term

aging using a PAV. However, modified binder requires additional time in a draft oven to simulate long term aging.

- Over all, the results show that polymer modification improves the binder performance at high temperatures by reducing the creep compliance, and by increasing stiffness at intermediate temperatures. It can also be seen that polymer mentioned that modification reduces the effect of aging.

Table 4.1: Rheological properties for original binder

Binder		T (˚C)	G* (KPa)	G' (Kpa)	G″ (Kpa)	δ(˚)
Original Binder	Unaged	52	4	0.36	3.98	84.9
		58	1.8	0.11	1.80	86.5
		64	0.865	0.03	0.86	87.9
		70	0.437	0.01	0.44	88.8
		76	0.234	0.00	0.23	89.5
	RTFO	52	8.74	1.35	8.63	81.1
		58	3.87	0.44	3.85	83.5
		64	1.78	0.14	1.77	85.5
		70	0.865	0.04	0.86	87.1
		76	0.442	0.01	0.44	88.3
	PAV	52	35.1	11.43	33.19	71
		58	15.5	4.12	14.94	74.6
		64	6.95	1.43	6.80	78.1
		70	3.21	0.49	3.17	81.2
		76	1.54	0.17	1.53	83.7

Table 4.2: Rheological properties for SB-modified binder

Binder			T (˚C)	G* (KPa)	G' (KPa)	G″ (KPa)	δ(˚)
SB	3%	Unaged	52	6.43	1.14	6.33	79.8
			58	3.09	0.45	3.06	81.7
			64	1.55	0.18	1.54	83.3
			70	0.819	0.07	0.82	84.8
			76	0.449	0.03	0.45	86.1
		RTFO	52	17.2	4.68	16.55	74.2
			58	7.92	1.81	7.71	76.8
			64	3.81	0.73	3.74	78.9
			70	1.92	0.30	1.90	80.9
			76	1.01	0.13	1.00	82.8
		PAV	52	51.6	22.54	46.42	64.1
			58	26.7	10.22	24.67	67.5
			64	13.2	4.34	12.47	70.8
			70	6.54	1.82	6.28	73.8
			76	3.34	0.77	3.25	76.6
	4%	Unaged	52	7.32	1.50	7.17	78.2
			58	3.57	0.62	3.52	80
			64	1.83	0.27	1.81	81.6
			70	0.979	0.12	0.97	83.2
			76	0.544	0.05	0.54	84.7
		RTFO	52	16.2	4.57	15.54	73.6
			58	7.79	1.94	7.55	75.6
			64	3.91	0.85	3.82	77.4
			70	2.04	0.38	2.00	79.3
			76	1.1	0.17	1.09	81.3
		PAV	52	46.9	20.49	42.19	64.1
			58	25.2	10.01	23.13	66.6
			64	13.5	4.75	12.64	69.4
			70	7.18	2.17	6.84	72.4
			76	3.79	0.96	3.67	75.3
	5%	Unaged	52	8.86	2.04	8.62	76.7
			58	4.43	0.87	4.34	78.7
			64	2.3	0.39	2.27	80.3
			70	1.25	0.18	1.24	81.7
			76	0.71	0.08	0.71	83.3
		RTFO	52	13.7	4.46	12.95	71
			58	7.44	2.04	7.16	74.1
			64	3.87	0.92	3.76	76.3
			70	2.1	0.44	2.05	78
			76	1.18	0.21	1.16	79.8
		PAV	52	45	20.01	40.31	63.6
			58	24.4	9.89	22.31	66.1
			64	13.4	4.80	12.51	69
			70	7.29	2.26	6.93	71.9
			76	3.95	1.04	3.81	74.7

Table 4.3: Rheological properties for SBS-modified binder

Binder			T (˚C)	G* (KPa)	G' (KPa)	G″ (KPa)	δ(˚)
SBS	3%	Unaged	52	5.85	0.94	5.77	80.8
			58	2.69	0.31	2.67	83.4
			64	1.3	0.11	1.30	85.3
			70	0.665	0.04	0.66	86.7
			76	0.357	0.02	0.36	87.5
		RTFO	52	16.1	4.98	15.31	72
			58	7.55	1.76	7.34	76.5
			64	3.58	0.58	3.53	80.6
			70	1.73	0.19	1.72	83.7
			76	0.876	0.06	0.87	85.9
		PAV	52	66.9	29.64	59.97	63.7
			58	31.6	12.85	28.87	66
			64	15.3	5.51	14.27	68.9
			70	7.48	2.22	7.14	72.7
			76	3.74	0.87	3.64	76.6
	4%	Unaged	52	10.2	3.71	9.50	68.7
			58	5.23	1.61	4.98	72.1
			64	2.69	0.67	2.60	75.5
			70	1.42	0.30	1.39	77.6
			76	0.786	0.16	0.77	78.5
		RTFO	52	25.2	9.81	23.21	67.1
			58	12.3	4.43	11.48	68.9
			64	6.12	1.95	5.80	71.4
			70	3.19	0.86	3.07	74.4
			76	1.69	0.37	1.65	77.4
		PAV	52		0.00	0.00	
			58	42	19.98	36.95	61.6
			64	21.2	9.39	19.01	63.7
			70	11	4.30	10.13	67
			76	5.73	1.85	5.42	71.2
	5%	Unaged	52	13.5	5.64	12.26	65.3
			58	7.03	2.52	6.56	69
			64	3.65	1.05	3.49	73.2
			70	1.92	0.46	1.86	76
			76	1.05	0.23	1.02	77.4
		RTFO	52	27.3	11.88	24.58	64.2
			58	13.6	5.53	12.42	66
			64	7.09	2.62	6.59	68.3
			70	3.72	1.22	3.51	70.8
			76	2.02	0.60	1.93	72.6
		PAV	52		0.00	0.00	
			58	43.6	23.10	36.97	58
			64	23.1	11.76	19.88	59.4
			70	12.6	5.95	11.10	61.8
			76	6.97	2.99	6.30	64.6

Table 4.4: Rheological properties for oven aged original binder

Binder	Aging Time	T (˚C)	G* (KPa)	G' (KPa)	G" (KPa)	δ(˚)
Original Binder	Unaged	52	4.00	0.36	3.98	84.9
		58	1.80	0.11	1.80	86.5
		64	0.87	0.03	0.86	87.9
		70	0.44	0.01	0.44	88.8
		76	0.23	0.00	0.23	89.5
	1 week	52	6.26	0.76	6.21	83
		58	2.75	0.24	2.74	85.1
		64	1.28	0.07	1.28	86.7
		70	0.63	0.02	0.63	88
		76	0.33	0.01	0.33	89
	2 weeks	52	11.90	2.13	11.70	79.7
		58	5.14	0.67	5.10	82.5
		64	2.33	0.22	2.32	84.7
		70	1.11	0.07	1.11	86.5
		76	0.56	0.02	0.55	87.9
	1 month	52	21.70	5.42	21.00	75.6
		58	9.41	1.82	9.24	78.8
		64	4.21	0.61	4.17	81.7
		70	1.96	0.20	1.95	84.2
		76	0.95	0.06	0.95	86.1
	2 month	52	49.00	17.50	45.70	69
		58	21.60	6.38	20.60	72.8
		64	9.62	2.23	9.35	76.6
		70	4.39	0.76	4.33	80
		76	2.07	0.26	2.05	82.9
	3 month	52	93.10	41.60	83.30	63.5
		58	43.20	17.00	39.70	66.9
		64	19.90	6.59	18.80	70.6
		70	9.25	2.46	8.91	74.5
		76	4.37	0.89	4.27	78.2
	4 month	52	152.00	77.10	131.00	59.6
		58	74.60	34.50	66.20	62.4
		64	36.00	14.70	32.90	65.9
		70	17.30	5.97	16.20	69.8
		76	8.26	2.30	7.93	73.8

Table 4.5: Rheological properties for oven aged original binder

Binder	Aging Time	T (˚C)	G* (KPa)	G' (KPa)	G″ (KPa)	δ(˚)
SB 4%	Unaged	52	7.32	1.50	7.17	78.2
		58	3.57	0.62	3.52	80
		64	1.83	0.27	1.81	81.6
		70	0.98	0.12	0.97	83.2
		76	0.54	0.05	0.54	84.7
	2 weeks	52	12.40	3.26	11.90	74.7
		58	5.91	1.33	5.76	77
		64	2.90	0.54	2.85	79.3
		70	1.48	0.22	1.46	81.5
		76	0.78	0.09	0.78	83.6
	1 month	52	14.30	4.25	13.60	72.6
		58	6.80	1.83	6.55	74.4
		64	3.36	0.79	3.27	76.4
		70	1.73	0.34	1.70	78.8
		76	0.92	0.14	0.91	81.4
	2 month	52	23.80	9.75	21.70	65.8
		58	11.90	4.60	11.00	67.3
		64	6.19	2.21	5.78	69.1
		70	3.32	1.07	3.14	71.2
		76	1.81	0.51	1.74	73.6

Table 4.6: P-value calculated by ANOVA for both aged and unaged binders

P-value	SB			SBS		
T (°C)	Unaged	RTFO	PAV	Unaged	RTFO	PAV
58	0.00114	0.000439	0.009337	0.013116	0.005959	0.002163
70	0.0026	0.001112	0.000772	0.019609	0.011724	0.006349

Table 4.7: MSCR test result for original binder

Binder		T (˚C)	Jnr (1/kPa) (τ=100Pa)	Jnr (1/kPa) (τ=3200Pa)	ΔJnr (%)
Original Binder	Unaged	52	2.2583	2.4098	6.71
		58	5.1616	5.5733	7.98
		64	11.1323	11.9549	7.39
		70	22.4816	23.9168	6.38
		76	42.2863	44.9303	6.25
	RTFO	52	0.9439	1.013	7.32
		58	2.3225	2.5227	8.62
		64	5.3123	5.7998	9.18
		70	11.3676	12.3464	8.61
		76	22.6004	24.3552	7.76
	PAV	52	0.1232	0.1282	4.13
		58	0.3517	0.3815	8.47
		64	0.9344	1.0571	13.14
		70	2.2766	2.6414	16.02
		76	5.1984	6.026	15.92

Table 4.8: MSCR test result for SB modified binder

Binder			T (˚C)	Jnr (1/kPa) (τ=100Pa)	Jnr (1/kPa) (τ=3200Pa)	ΔJnr (%)
SB	3%	Unaged	52	1.0671	1.2983	21.67
			58	2.4375	3.0736	26.1
			64	5.2537	6.6104	25.82
			70	10.7342	13.2288	23.24
			76	20.4714	24.8952	21.61
		RTFO	52	0.9315	1.0519	12.92
			58	2.2575	2.5879	14.63
			64	5.0603	5.8088	14.79
			70	10.6031	12.0463	13.61
			76	20.7709	23.4377	12.84
		PAV	52	0.0438	0.0465	6.25
			58	0.1134	0.1365	20.38
			64	0.3019	0.4023	33.27
			70	0.7755	1.105	42.49
			76	1.7689	2.708	53.09
	4%	Unaged	52	0.8337	1.0671	28
			58	1.9303	2.5306	31.1
			64	4.1448	5.5734	34.47
			70	8.5421	11.2325	31.5
			76	16.4689	21.1535	28.45
		RTFO	52	0.2893	0.3485	20.44
			58	0.6833	0.9272	35.69
			64	1.6138	2.29	41.9
			70	3.5203	5.1119	45.21
			76	7.1937	10.4277	44.96
		PAV	52	0.0377	0.0399	5.91
			58	0.0947	0.1202	26.91
			64	0.2571	0.3785	47.219
			70	0.6533	0.9909	51.68
			76	1.5426	2.4014	55.67
	5%	Unaged	52	0.5924	0.7927	33.82
			58	1.4594	1.9284	32.14
			64	3.0006	4.2347	41.13
			70	6.1804	8.6126	39.35
			76	12.1306	16.4271	35.42
		RTFO	52	0.2382	0.3502	47.02
			58	0.5579	0.9314	66.95
			64	1.3498	2.1196	57.03
			70	2.9653	4.5942	54.93
			76	5.946	9.1919	54.59
		PAV	52	0.0352	0.0369	4.76
			58	0.0881	0.1159	31.54
			64	0.2496	0.4195	68.07
			70	0.6484	1.0402	60.43
			76	1.4779	2.3397	58.31

Table 4.9: MSCR test result for SBS modified binder

Binder			T (˚C)	Jnr (1/kPa) (τ=100Pa)	Jnr (1/kPa) (τ=3200Pa)	ΔJnr (%)
SBS	3%	Unaged	52	0.4533	1.3368	194.87
			58	1.5916	3.3756	112.08
			64	4.0726	7.6228	87.17
			70	12.0471	15.8638	31.68
			76	26.182	30.3546	15.937
		RTFO	52	0.3449	0.3715	7.71
			58	0.8921	1.0222	14.58
			64	2.2209	2.5428	14.49
			70	5.0093	5.6951	13.69
			76	10.4834	11.8429	12.97
		PAV	52	0.04	0.0404	1.09
			58	0.1123	0.1181	5.11
			64	0.3049	0.3419	12.16
			70	0.7847	0.9347	19.11
			76	1.9091	2.339	22.52
	4%	Unaged	52	0.3811	0.4752	24.69
			58	0.8845	1.1648	31.69
			64	1.9668	2.7554	40.09
			70	4.4528	6.1432	37.96
			76	9.4502	12.8807	36.3
		RTFO	52	0.1446	0.1688	16.96
			58	0.2801	0.4309	53.82
			64	0.5466	1.0441	91
			70	1.091	2.4239	122.18
			76	2.4424	5.7562	135.68
		PAV	52	0.0122	0.0122	0.01
			58	0.031	0.0332	7.03
			64	0.0808	0.0916	13.4
			70	0.2038	0.2493	22.35
			76	0.5072	0.6632	30.76
	5%	Unaged	52	0.0861	0.3138	264.58
			58	0.2932	1.0296	251.13
			64	0.8542	2.5914	203.38
			70	2.4694	6.0297	144.18
			76	7.558	13.4102	77.43
		RTFO	52	0.1557	0.1785	14.61
			58	0.3657	0.4681	28.02
			64	0.8757	1.1751	34.2
			70	2.0779	2.7901	34.28
			76	4.8476	6.3425	30.84
		PAV	52			
			58	0.0297	0.0334	12.37
			64	0.0613	0.0863	40.72
			70	0.1446	0.2409	66.64
			76	0.3656	0.6914	89.13

Table 4.10: BBR test results for original binder

Binder		Sample	T (˚C)	Load (mN)	Δ (mm)	Measured Stiffness (Mpa)	m-value	Mean Stiffness (Mpa)	Mean m-value
original binder	Unaged	1	-17.9	978	0.5734	137.5303	0.421607	124.0826	0.430092
		2	-18	977.9	0.7127	110.6349	0.438576		
		3							
	RTFO	1	-18	950.1	0.5405	141.7175	0.387267	141.7004	0.389115
		2	-17.9	954.1	0.543	141.6832	0.390963		
		3							
	PAV	1	-17.9	977.1	0.3623	217.4657	0.317212	218.7654	0.314971
		2	-18	971.7	0.352	222.5916	0.313843		
		3	-17.9	968.4	0.3611	216.2388	0.313858		

Table 4.11: BBR test results for SB modified binder

Binder			Sample	T (˚C)	Load (mN)	Δ (mm)	Measured Stiffness (Mpa)	m-value	Mean Stiffness (Mpa)	Mean m-value
SB	3%	Unaged	1						108.58	0.4110
			2	-17.9	964.7	0.7164	108.5792	0.411015		
			3							
		RTFO	1	-18	698.2	0.5136	152.0132	0.36546	154.16	0.3655
			2	-17.9	970.3	0.5151	151.8853	0.366018		
			3	-17.9	964.9	0.4906	158.5799	0.364929		
		PAV	1						202.53	0.3016
			2	-17.9	964.4	0.3819	203.6257	0.300951		
			3	-17.9	967.1	0.3871	201.4338	0.302231		
	4%	Unaged	1	-17.9	694.2	0.6672	116.5233	0.403421	120.87	0.3974
			2	-17.9	966.9	0.6044	128.9909	0.394407		
			3	-18	973.6	0.6705	117.0862	0.394356		
		RTFO	1	-17.9	974.9	0.4798	163.8341	0.333604	163.94	0.3422
			2	-17.8	971.5	0.4911	159.49	0.349561		
			3	-18	973.6	0.4659	168.4962	0.34333		
		PAV	1	-17.9	674.5	0.3549	221.4095	0.283919	223.38	0.2858
			2	-17.9	973.8	0.3484	225.358	0.287646		
			3							
	5%	Unaged	1	-17.9	968.7	0.6679	116.9369	0.395843	124.91	0.3876
			2	-17.9	979.4	0.5662	139.4733	0.378956		
			3	-17.9	964	0.657	118.3067	0.388092		
		RTFO	1	-17.9	974.4	0.4905	160.1645	0.343005	166.31	0.3373
			2	-17.9	970.4	0.4763	164.269	0.339218		
			3	-17.8	967.5	0.447	174.5049	0.329812		
		PAV	1	-18	969.3	0.3367	232.1441	0.275994	234.19	0.2698
			2	-17.9	973.4	0.3314	236.8437	0.269991		
			3	-18	968.7	0.3344	233.5749	0.263403		

Table 4.12: BBR test results for SBS modified binder

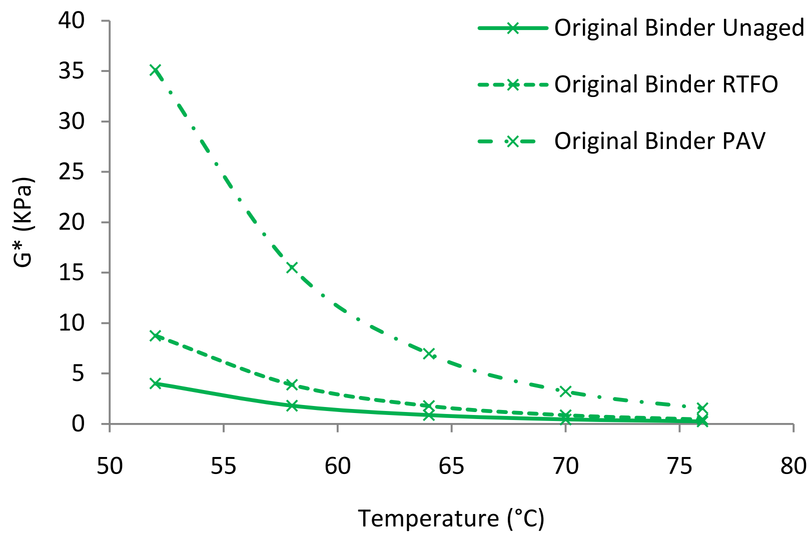
Binder			Sample	T (˚C)	Load (mN)	Δ (mm)	Measured Stiffness (Mpa)	m-value	Mean Stiffness (Mpa)	Mean m-value
SBS	3%	Unaged	1	-17.9	979	0.6891	114.5439	0.413947	104.4042	0.356381
			2	-17.9	950.9	1.0963	69.9358	0.243092		
			3	-17.9	956.2	0.5989	128.7328	0.412105		
		RTFO	1	-17.9	954.3	0.4315	178.3078	0.346661	173.2475	0.348434
			2	-17.9	950.3	0.4523	169.4254	0.35447		
			3	-17.9	953.6	0.447	172.0094	0.344171		
		PAV	1						246.4073	0.292061
			2	-17.9	970.1	0.3241	241.3455	0.294064		
			3	-17.9	972.1	0.3117	251.4691	0.290057		
	4%	Unaged	1	-17.9					108.2505	0.390723
			2	-17.9	981.7	0.7022	112.7272	0.389331		
			3	-18	962.3	0.7477	103.7738	0.392114		
		RTFO	1	-17.9	960.2	0.4566	169.563	0.349128	165.6361	0.347158
			2	-17.9	972.9	0.4912	159.7083	0.34768		
			3	-17.9	972.9	0.4679	167.6369	0.344665		
		PAV	1	-17.9	966.3	0.3151	247.3032	0.283486	245.9283	0.279521
			2	-17.9	965	0.3153	246.7585	0.277308		
			3	-17.9	965.7	0.3195	243.7232	0.277769		
	5%	Unaged	1	-17.9	938.1	0.6414	117.9271	0.378872	124.2197	0.38293
			2	-17.9	951.5	0.6152	124.7016	0.382754		
			3	-17.9	934.8	0.5796	130.0305	0.387163		
		RTFO	1	-17.9	969.2	0.5393	144.8959	0.329939	146.5371	0.337282
			2	-17.9	967.2	0.5316	146.6952	0.34384		
			3	-17.9	955.1	0.5203	148.0202	0.338066		
		PAV	1	-17.9	948	0.3048	250.8158	0.262554	255.0001	0.265428
			2	-17.9	948.7	0.2951	259.1843	0.268301		
			3							

Table 4.13: Viscosity test results for standard aging conditions

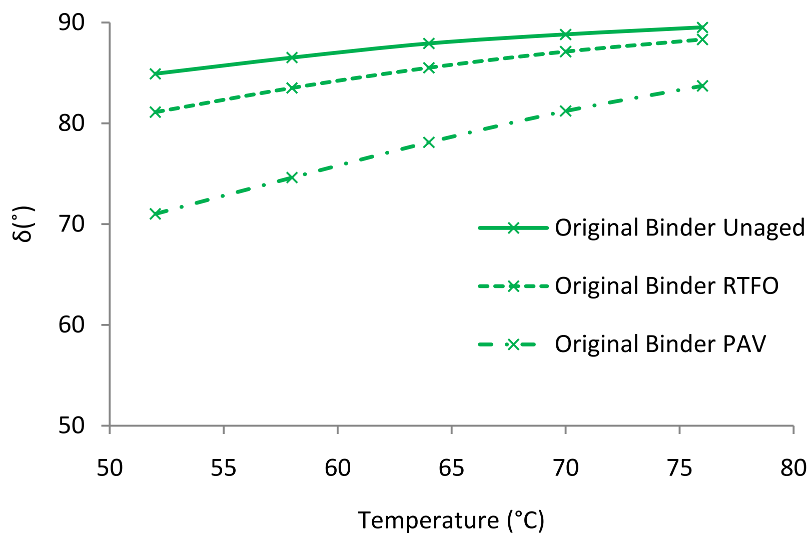
Viscosity (Pa.s)		Aging Condition		
Binder		Unaged	RTFO	PAV
original binder		3.02	4.07	9.01
SB	3%	6.70	9.00	17.13
	4%	7.06	10.88	22.07
	5%	10.01	13.97	
SBS	3%	5.76	8.45	
	4%	9.31	10.03	
	5%	9.76	11.11	

Table 4.14: DT test results for standard aging conditions

Failure Strain (%)		Aging Condition		
Binder		Unaged	RTFO	PAV
original binder		2.93	2.59	0.83
SB	3%	1.57	4.52	1.20
	4%	16.36	4.91	1.62
	5%	4.10	3.95	2.20
SBS	3%	3.33	1.75	1.04
	4%	1.06	1.40	1.87
	5%	0.97	1.16	1.12

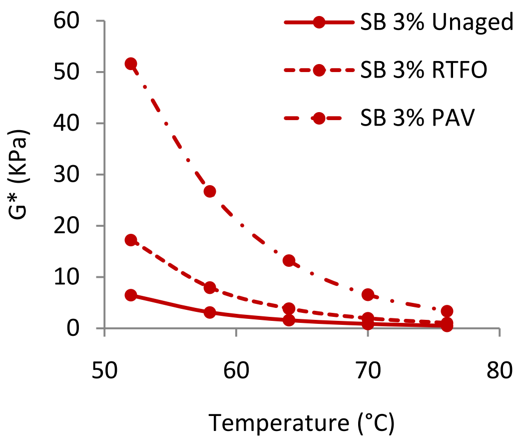


(a) Complex shear modulus (G*)

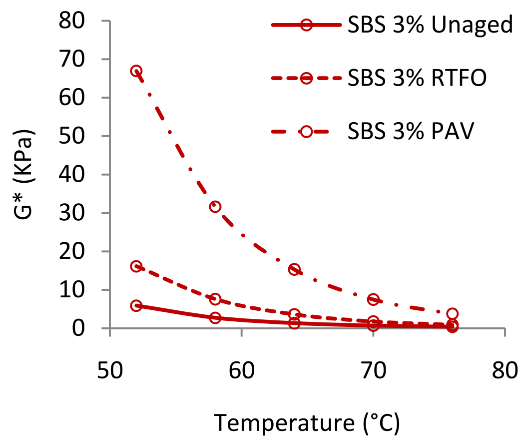


(b) Phase angle (δ)

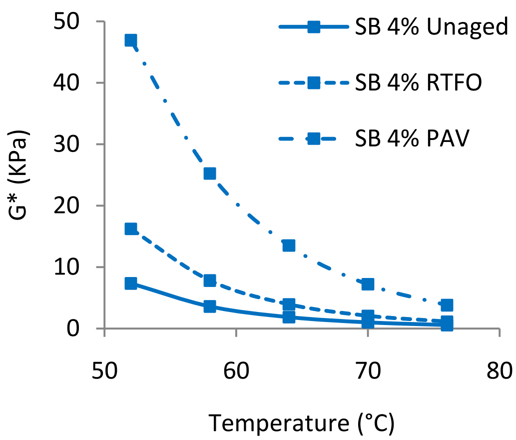
Figure 4.1: G* and δ vs. temperature for original binder at aged and unaged conditions at 58 °C



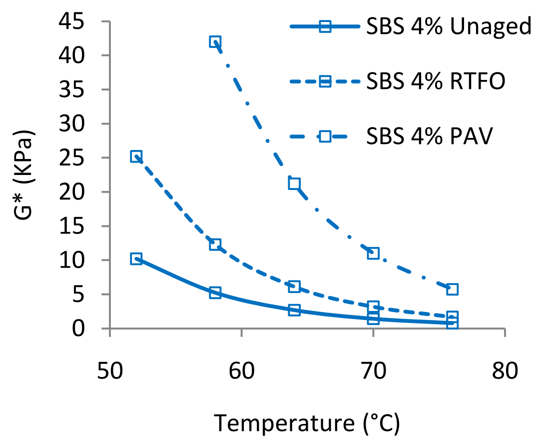
(a) SB 3%



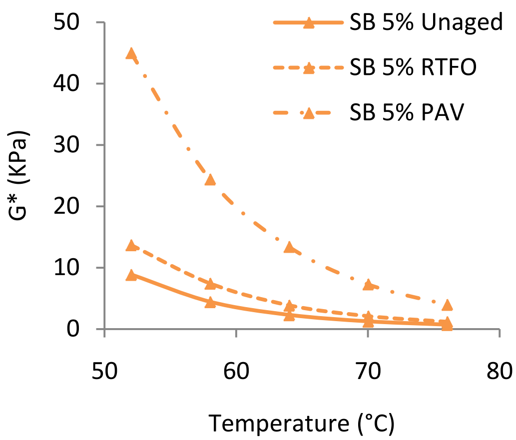
(d) SBS 3%



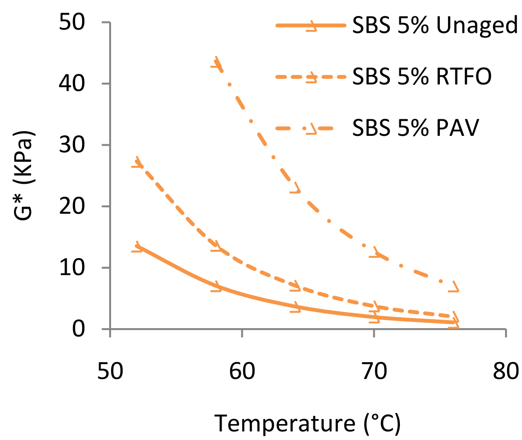
(b) SB 4%



(e) SBS 4%

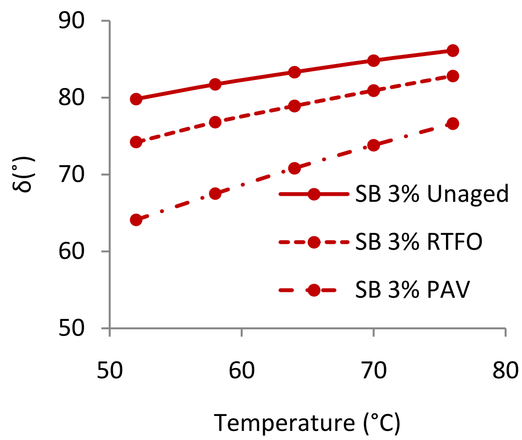


(c) SB 5%

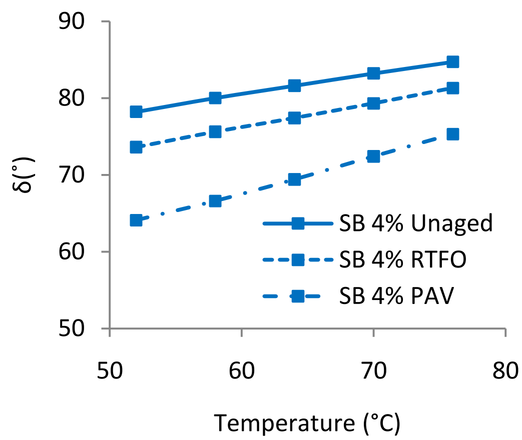


(f) SBS 5%

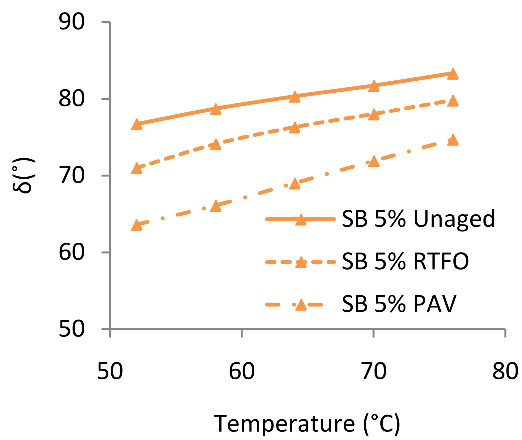
Figure 4.2: G* vs. temperature for SB and SBS-modified binders at aged and unaged conditions



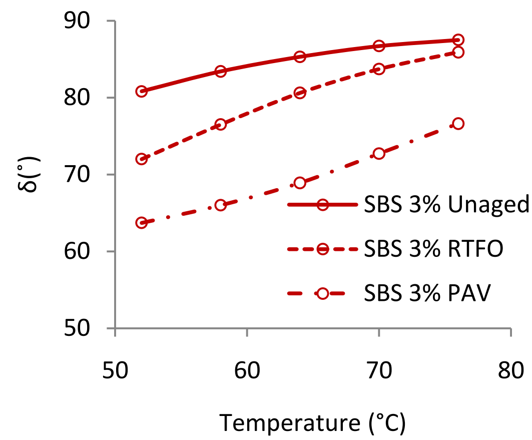
(a) SB 3%



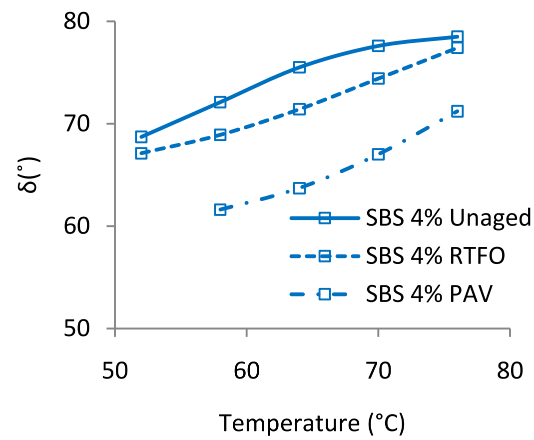
(b) SB 4%



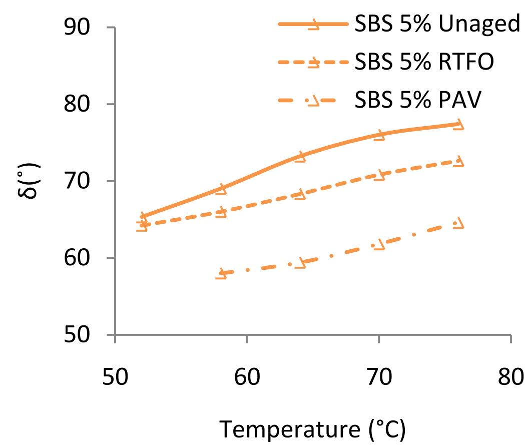
(c) SB 5%



(d) SBS 3%

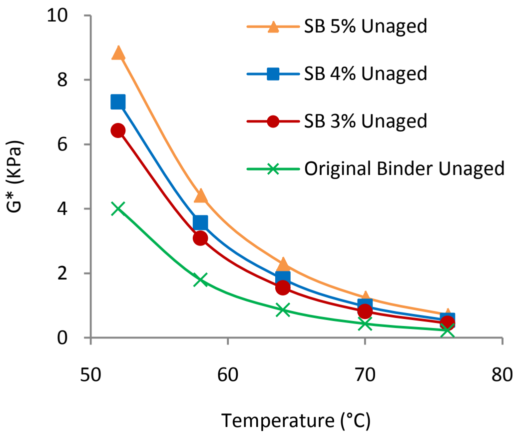


(e) SBS 4%

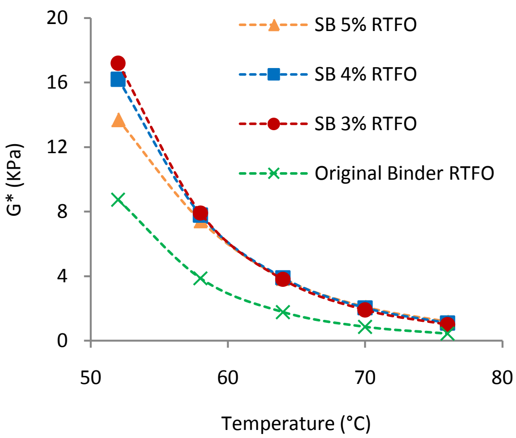


(f) SBS 5%

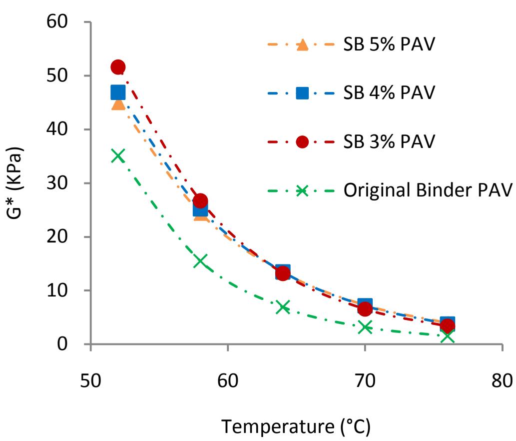
Figure 4.3: δ vs. temperature for SB and SBS modified binders at aged and unaged conditions



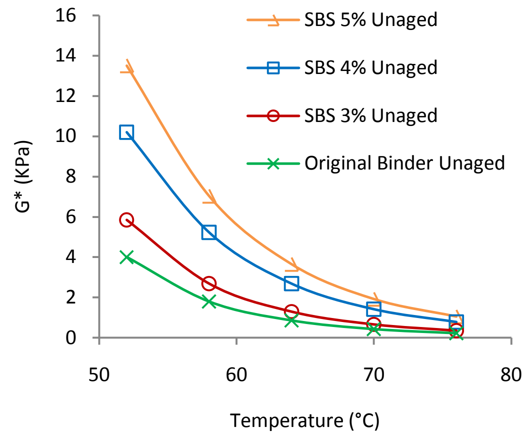
(a) Unaged SB-modified binder



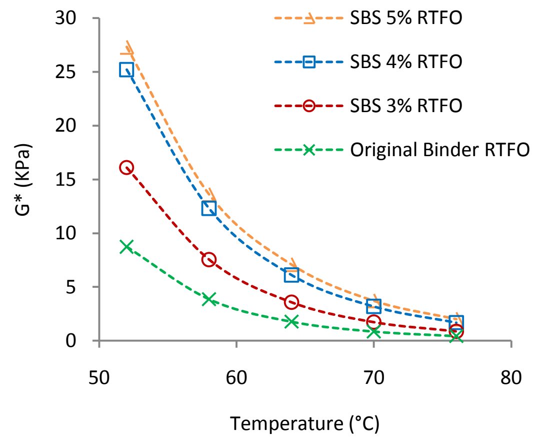
(b) RTFO aged SB-modified binder



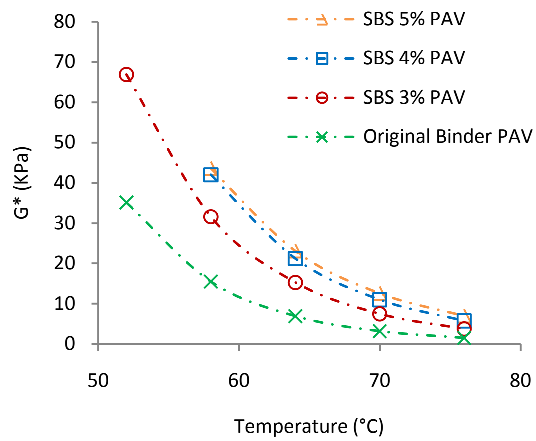
(c) PAV aged SB-modified binder



(d) Unaged SBS-modified binder

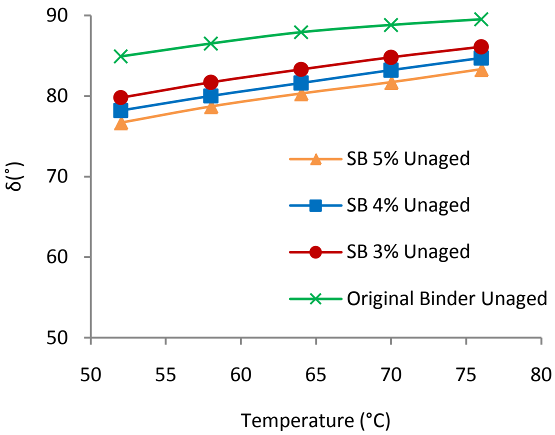


(e) RTFO aged SBS-modified binder

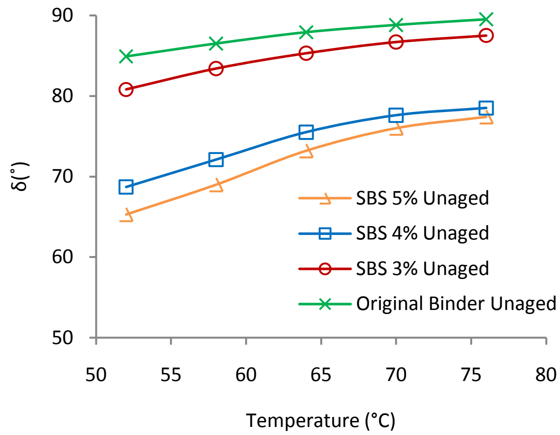


(f) PAV aged SBS-modified binder

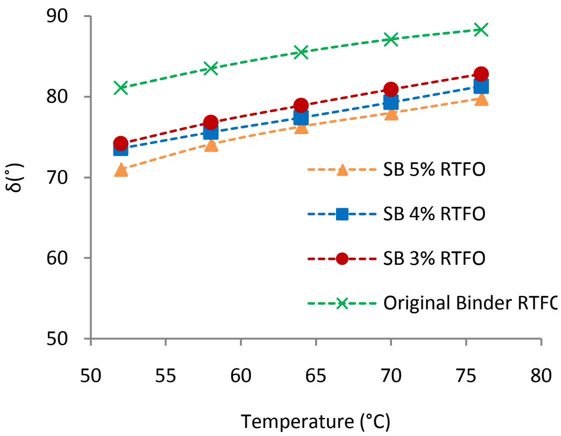
Figure 4.4: G* as a function of temperature for SB and SBS-modified binders



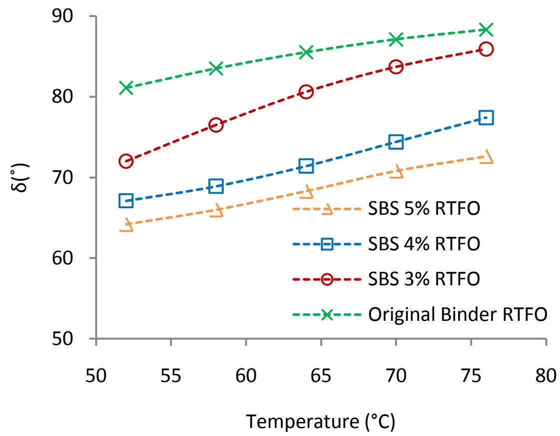
(a) Unaged SB-modified binder



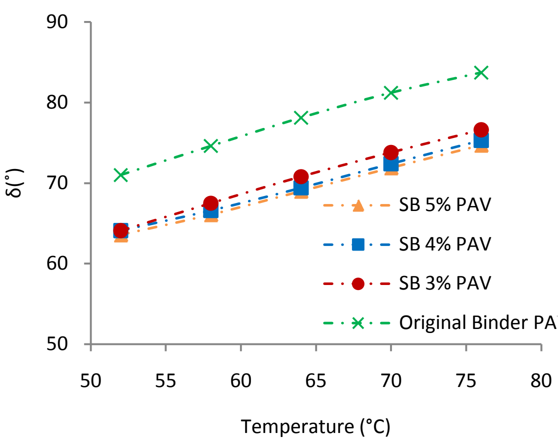
(d) Unaged SBS-modified binder



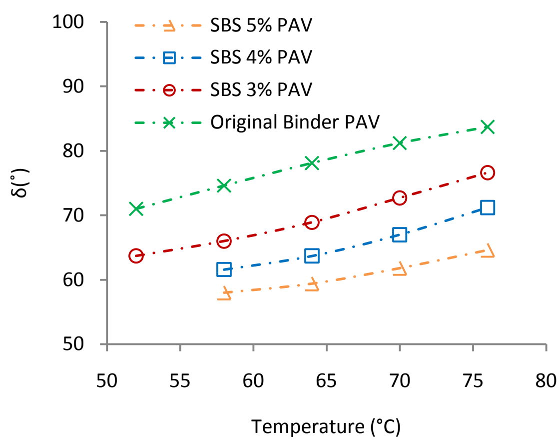
(b) RTFO aged SB-modified binder



(e) RTFO aged SBS-modified binder

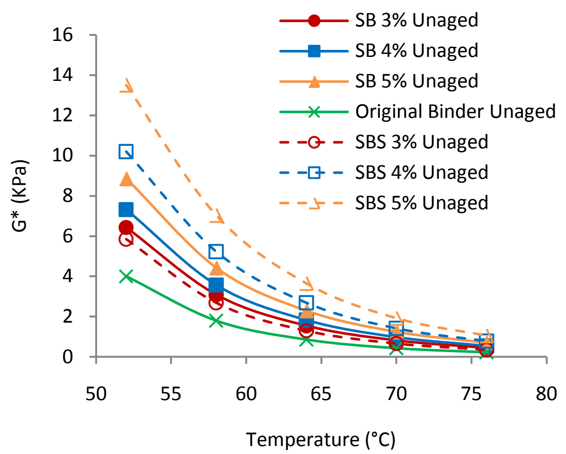


(c) PAV aged SB-modified binder

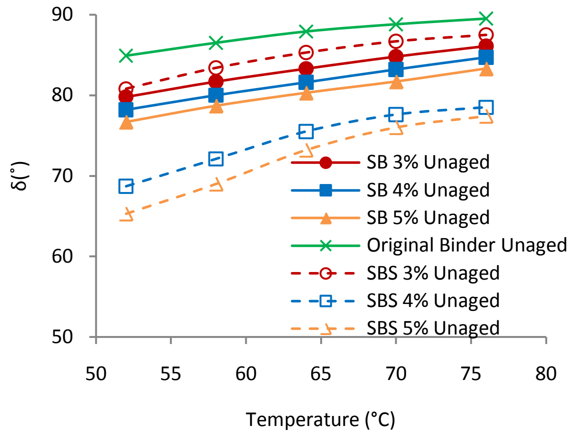


(f) PAV aged SBS-modified binder

Figure 4.5: δ as a function of temperature for SB and SBS-modified binders

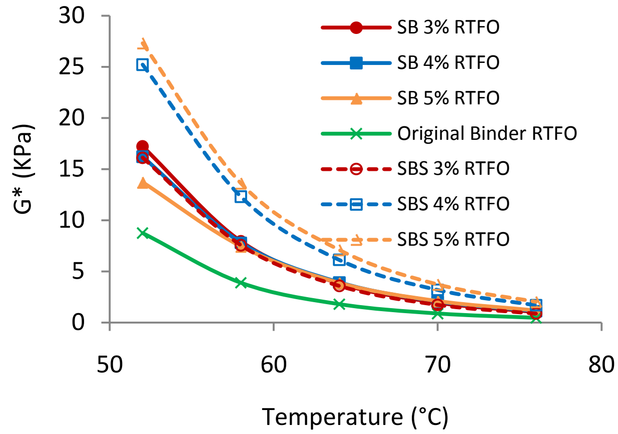


(a) Stiffness

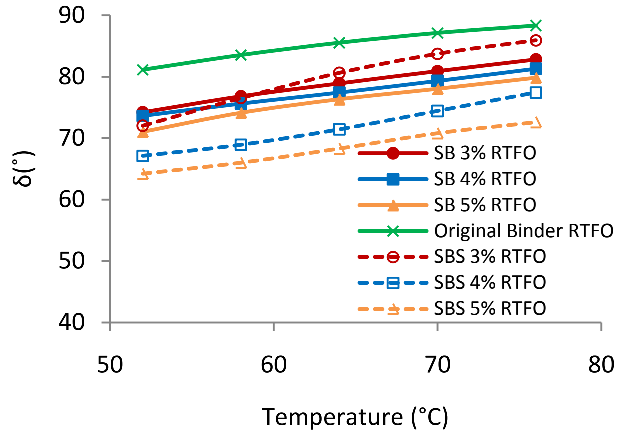


(b) Phase angle

Figure 4.6: Comparing original binder, SB and SBS modified binders at unaged condition

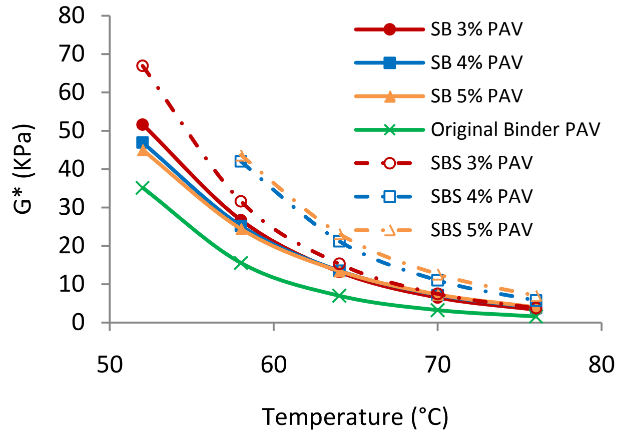


(a) Stiffness

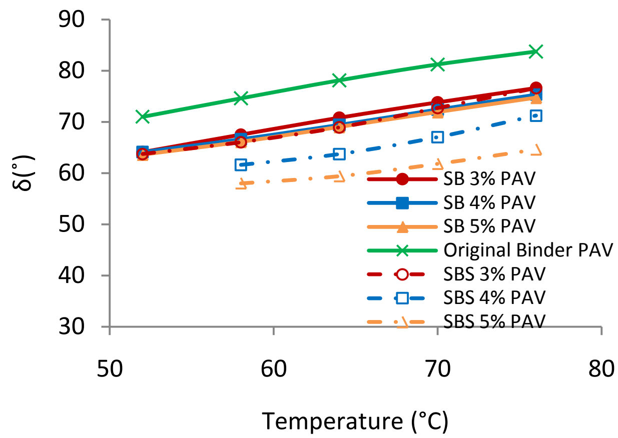


(b) Phase angle

Figure 4.7: Comparing original binder, SB and SBS modified binders at RTFO condition

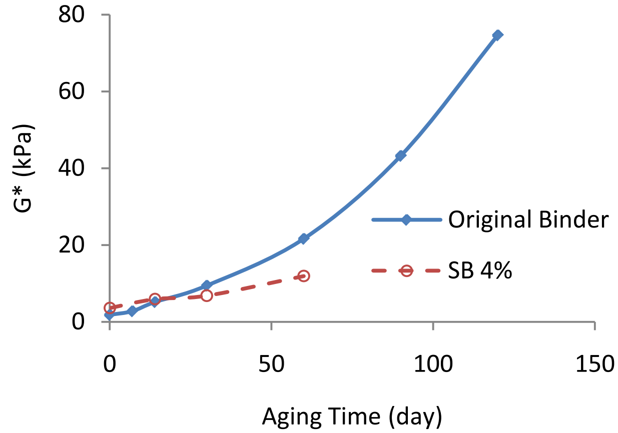


(a) Stiffness

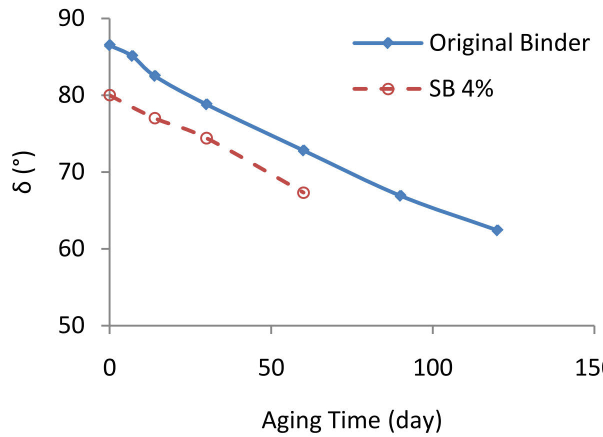


(b) Phase angle

Figure 4.8: Comparing original binder, SB and SBS modified binders at PAV condition

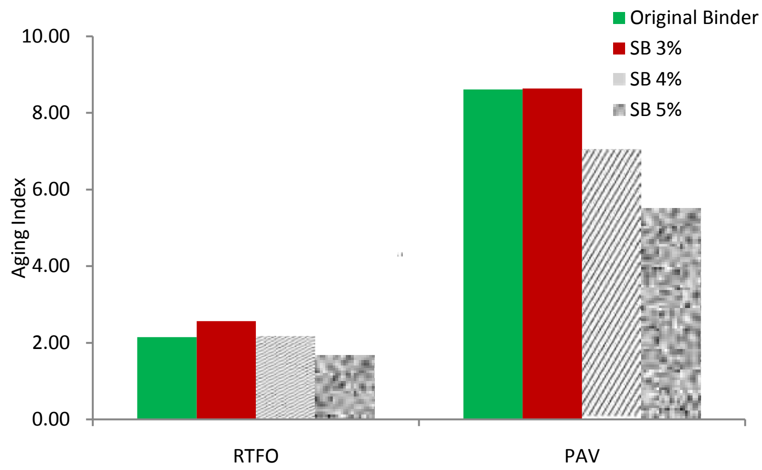


(a) Stiffness

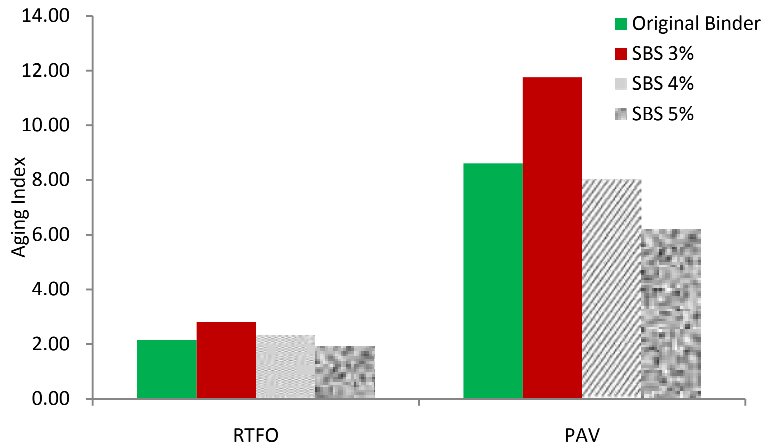


(b) Phase angle

Figure 4.9: Stiffness and phase angle vs. oven aging time for original binder and SB 4%-modified binders



(a) SB-modified binder



(b) SBS-modified binder

Figure 4.10: Aging Index of G* for different percent of SB and SBS-modifier binder at 58 °C

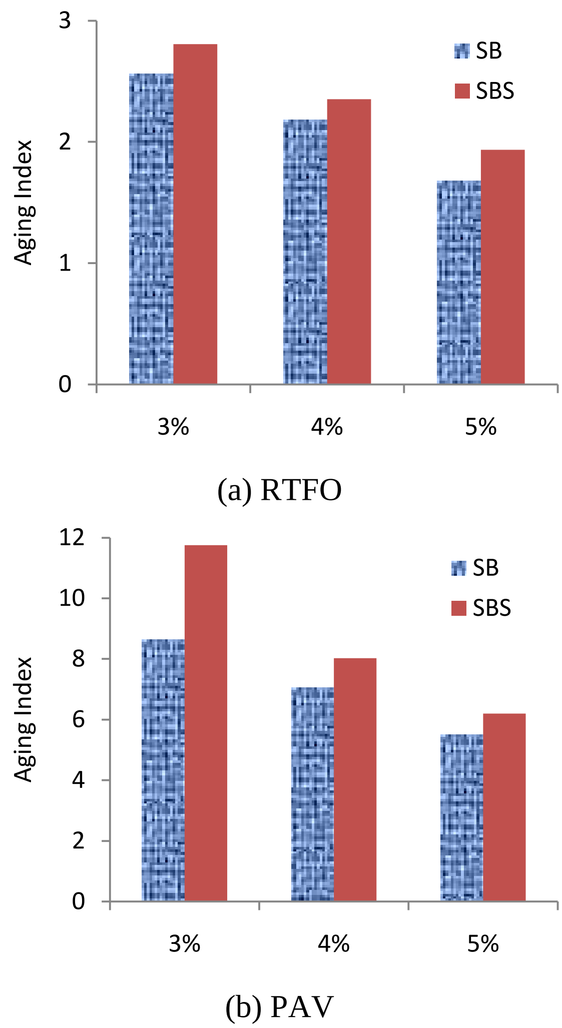
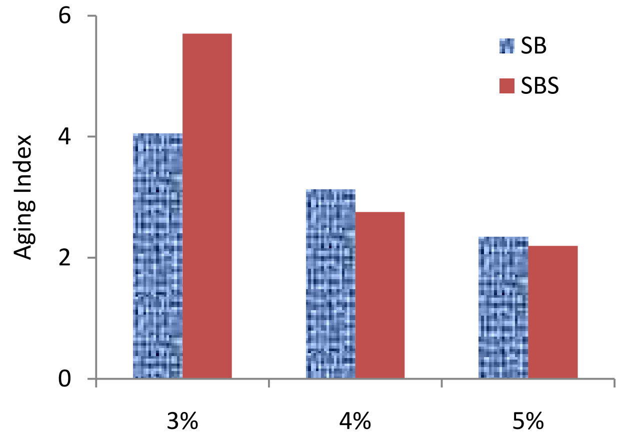
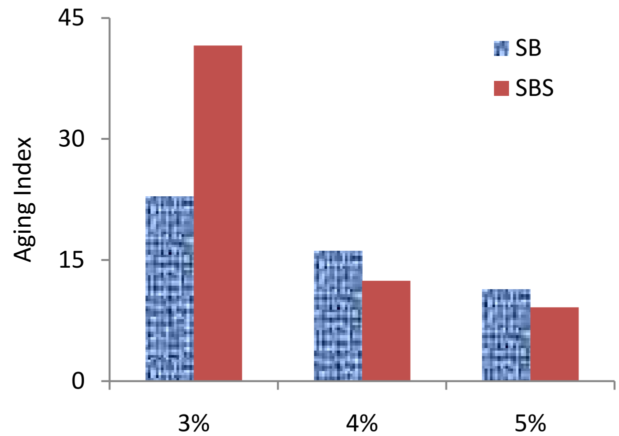


Figure 4.11: Aging Index of G* for RTFO and PAV modified binders at 58 °C

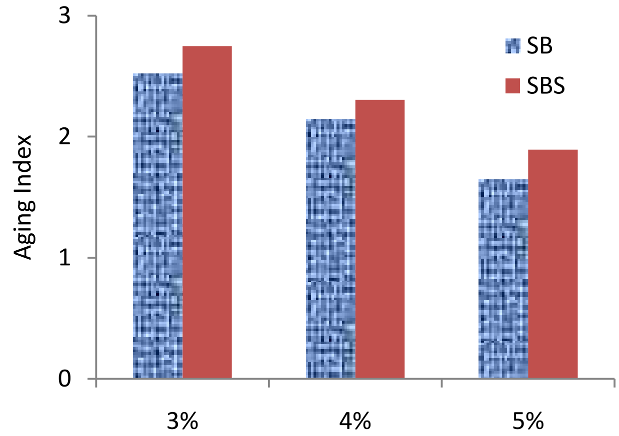


(a) RTFO

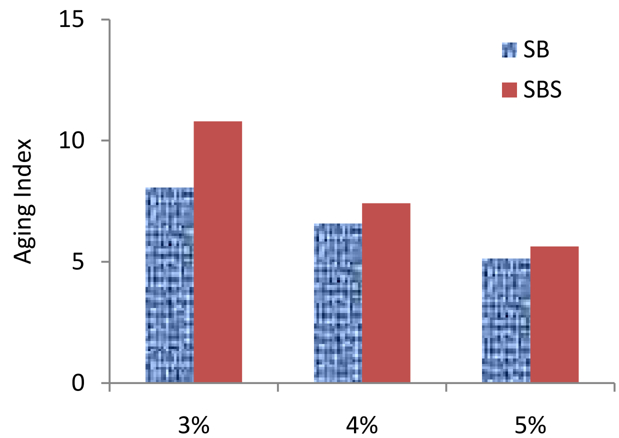


(b) PAV

Figure 4.12: Aging Index of G' for RTFO and PAV modified binders at 58 °C



(a) RTFO



(b) PAV

Figure 4.13: Aging Index of G″ for RTFO and PAV modified binders at 58 °C

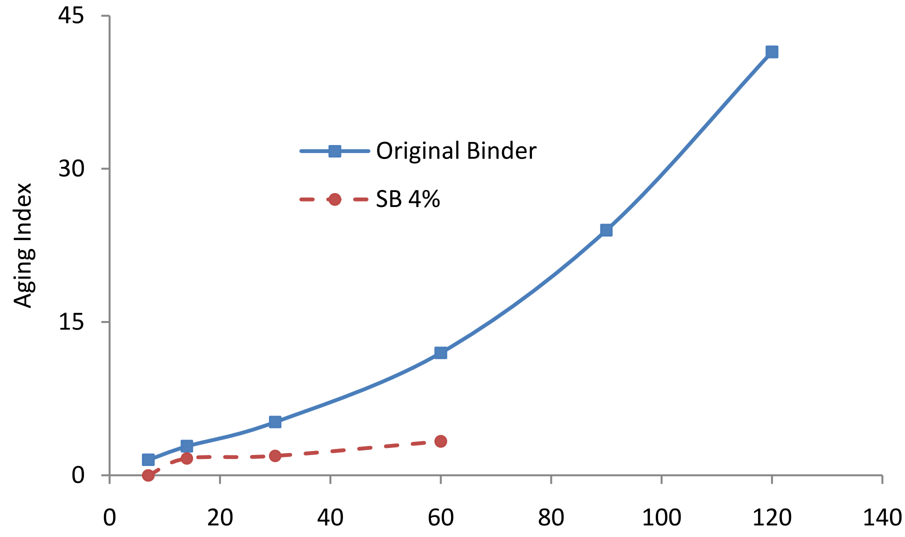


Figure 4.14: Aging Index for oven aged original binder and SB4%-modified binders based on G*

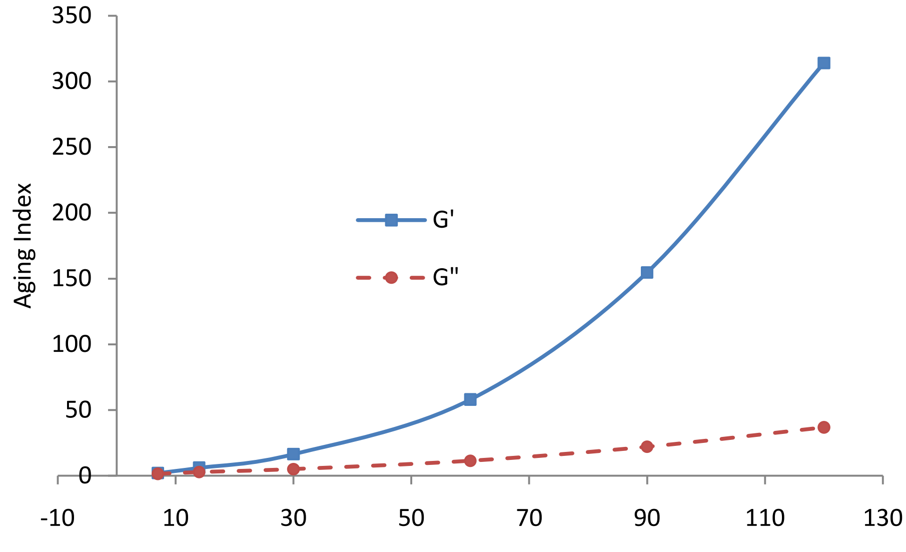
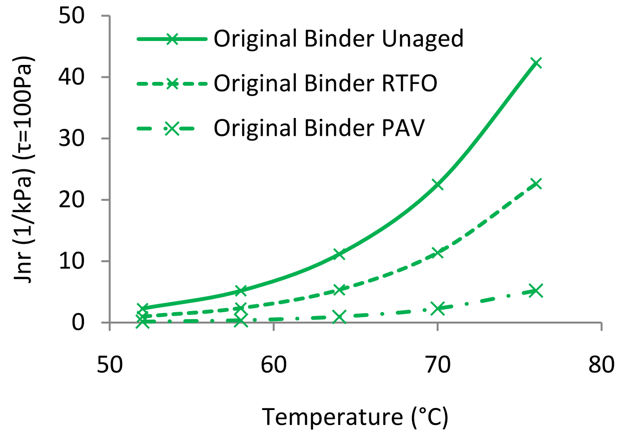
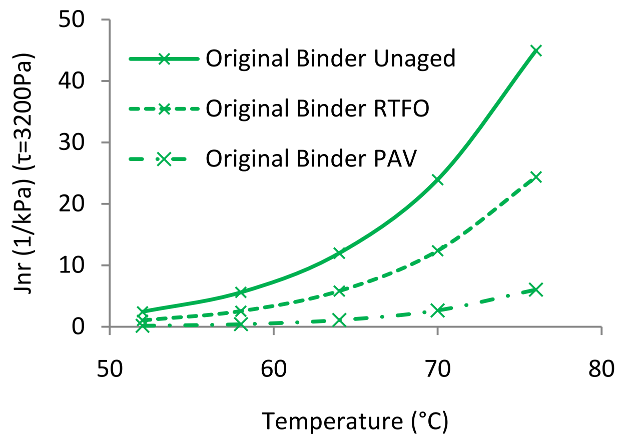


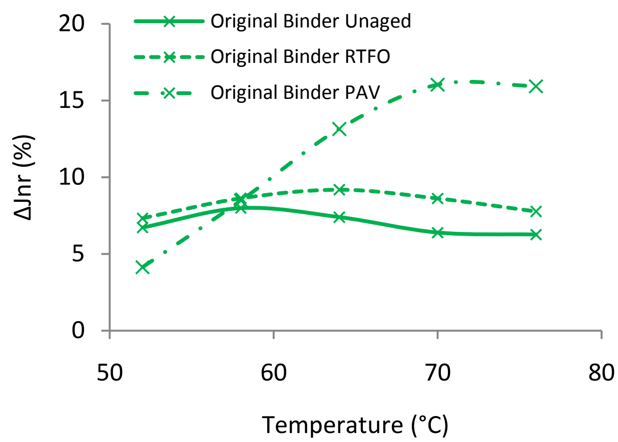
Figure 4.15: Aging Index for oven aged original binder based on G' and G″



(a) Jnr at τ=100Pa

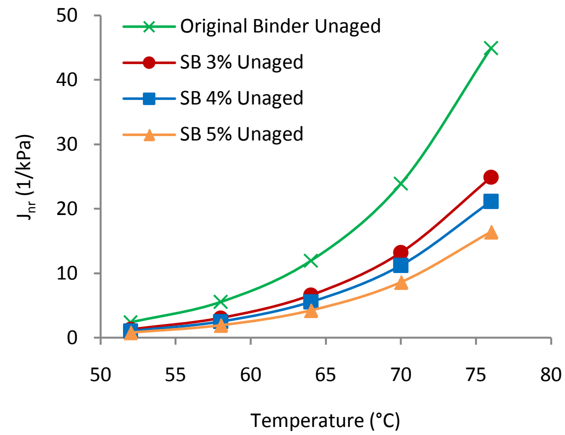


(b) Jnr at τ=3.200Pa

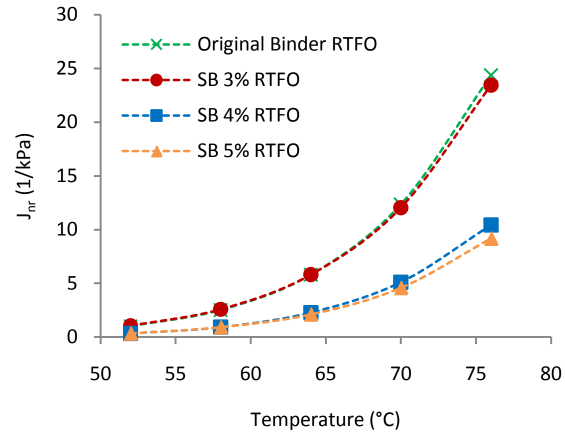


(c) Δ Jnr

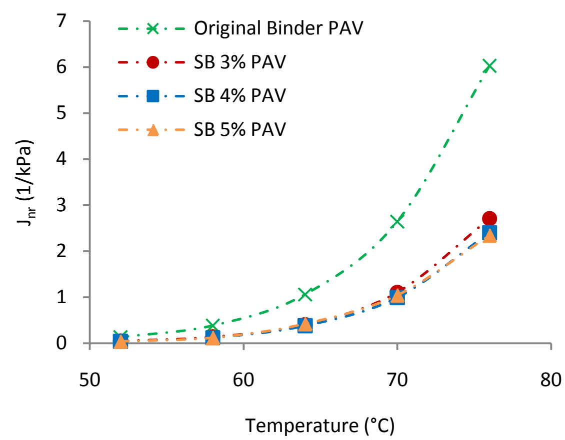
Figure 4.16: J_{nr} and ΔJ_{nr} vs. temperature for original binder at aged and unaged conditions



(a) Unaged

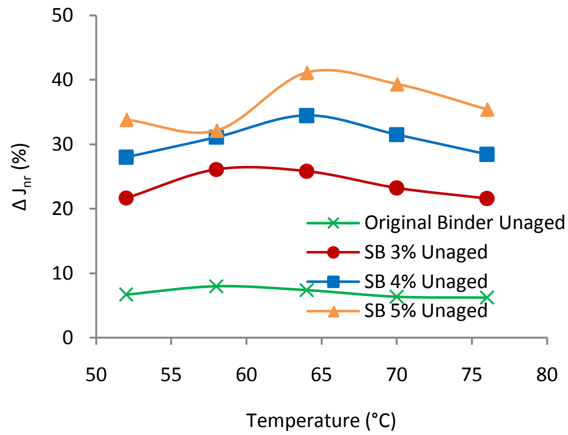


(b) RTFO

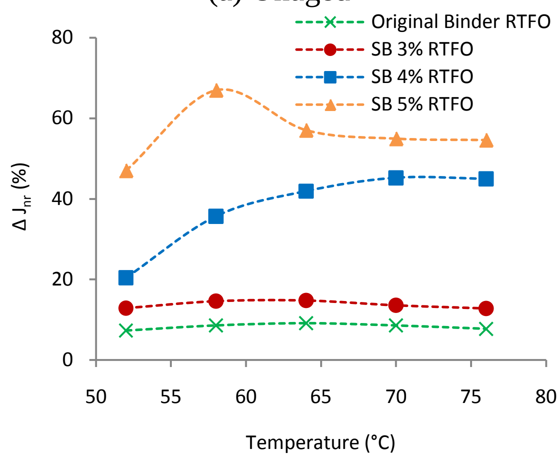


(c) PAV

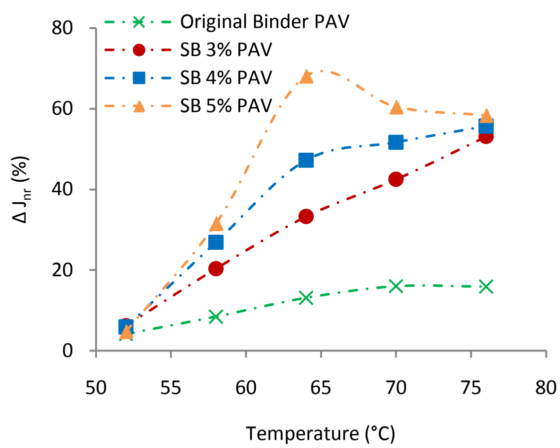
Figure 4.17: J_{nr} vs. temperature for SB-modified binder at τ=3.2 kPa for aged and unaged conditions



(a) Unaged

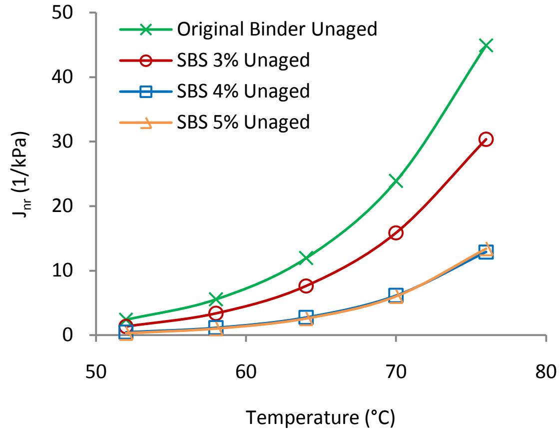


(b) RTFO

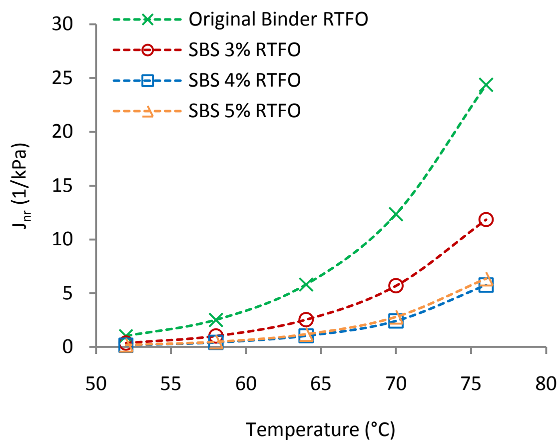


(c) PAV

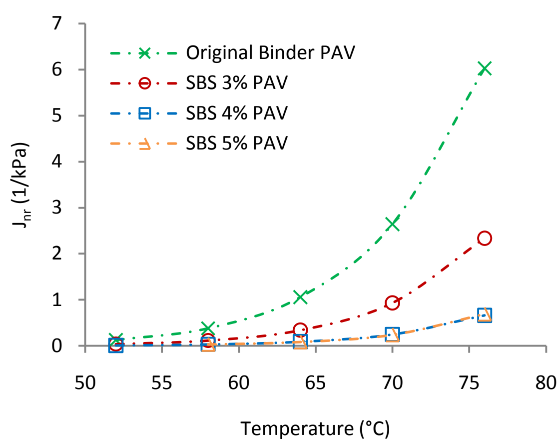
Figure 4.18: ΔJ_{nr} vs. temperature for SB-modified binder for aged and unaged conditions



(a) Unaged

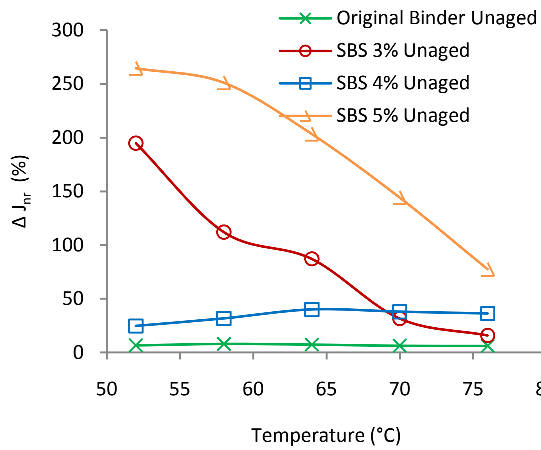


(b) RTFO

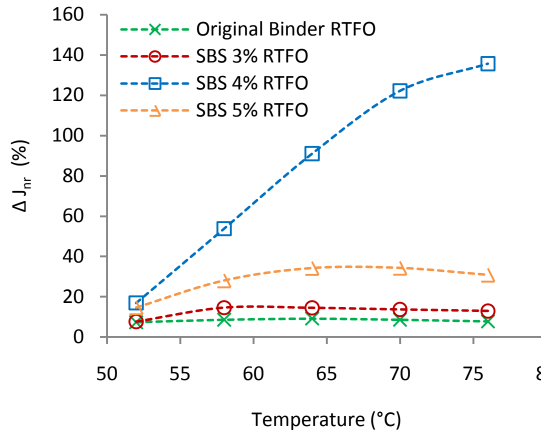


(c) PAV

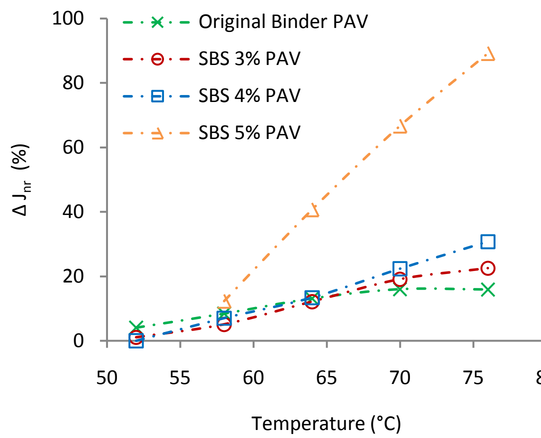
Figure 4.19: Jnr vs. temperature for SBS-modified binder at τ=3.2 kPa for aged and unaged conditions



(a) Unaged

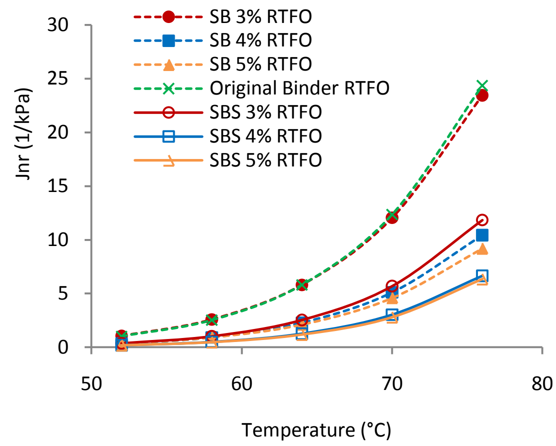


(b) RTFO

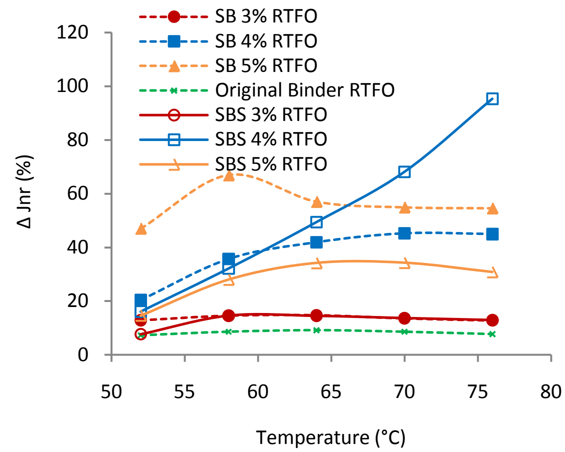


(c) PAV

Figure 4.20: Δ J_{nr} vs. temperature for SBS-modified binder for aged and unaged conditions

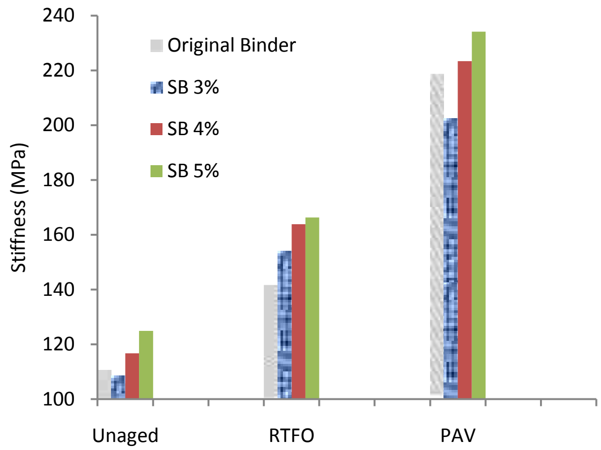


(a) J_{nr} at τ=3.2 kPa

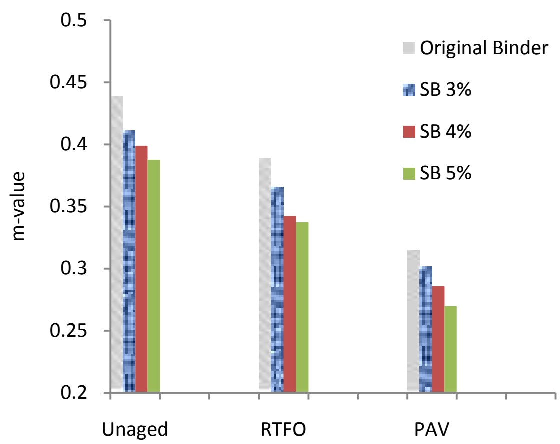


(b) ΔJ_{nr}

Figure 4.21: J_{nr} and ΔJ_{nr} vs. temperature for SB and SBS-modified binders for RTFO

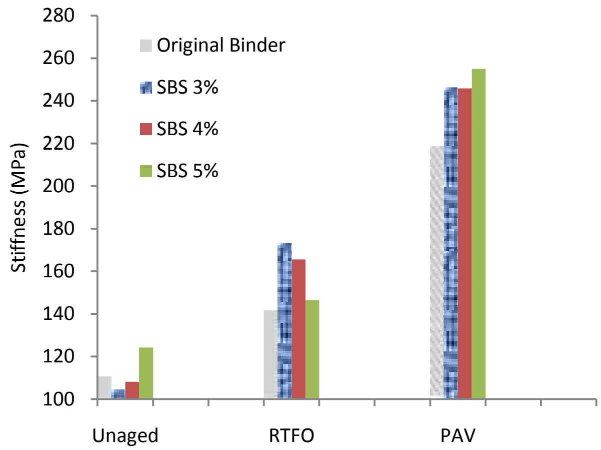


(a) Stiffness

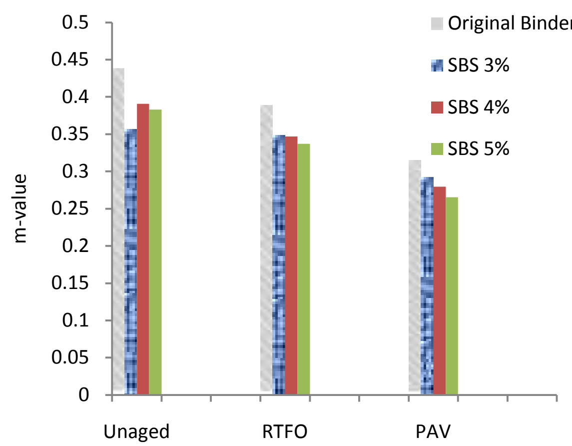


(b) m-value

Figure 4.22: Stiffness and m-value of SB-modified binder for aged and unaged conditions

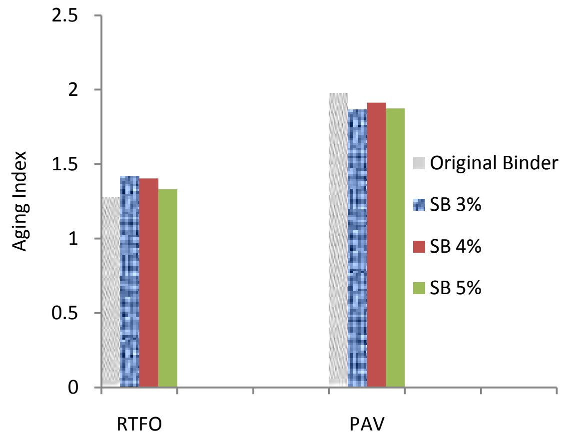


(a) Stiffness

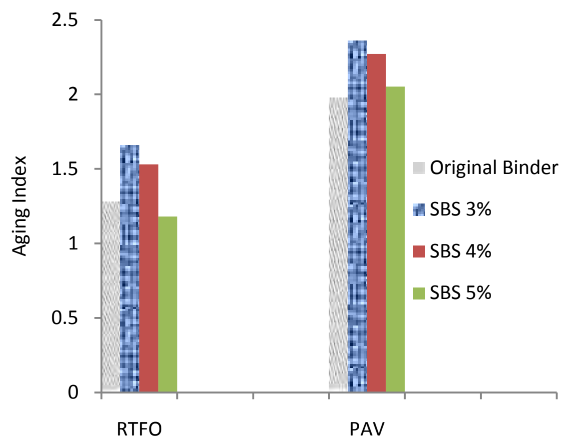


(b) m-value

Figure 4.23: Stiffness and m-value of SBS-modified binder for aged and unaged conditions

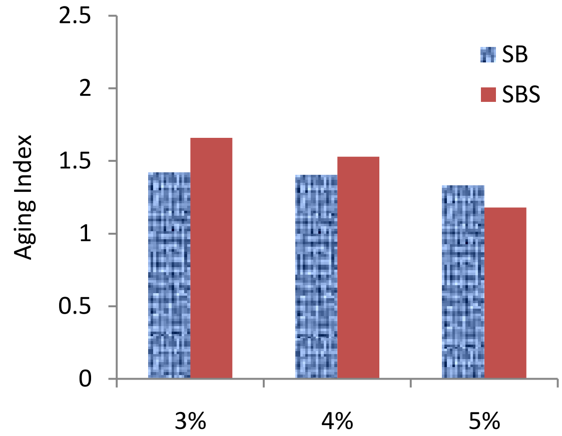


(a) SB-modified binder

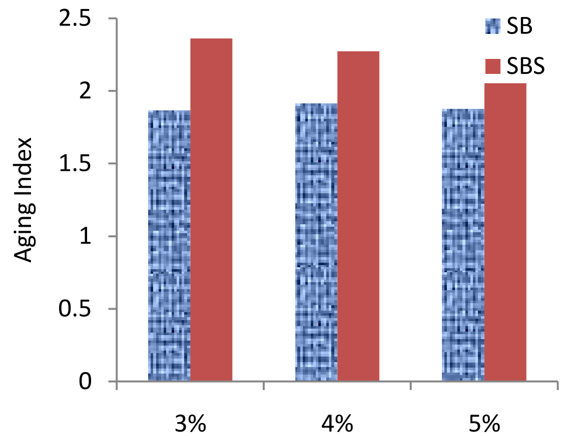


(b) SBS-modified binder

Figure 4.24: Aging Index for different percent of SB and SBS-modified binders for BBR test

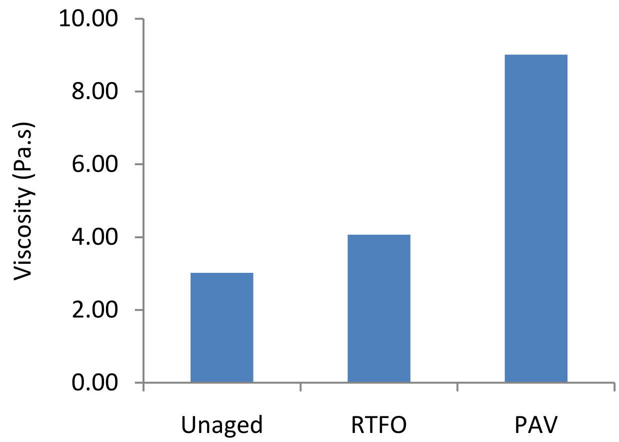


(a) RTFO

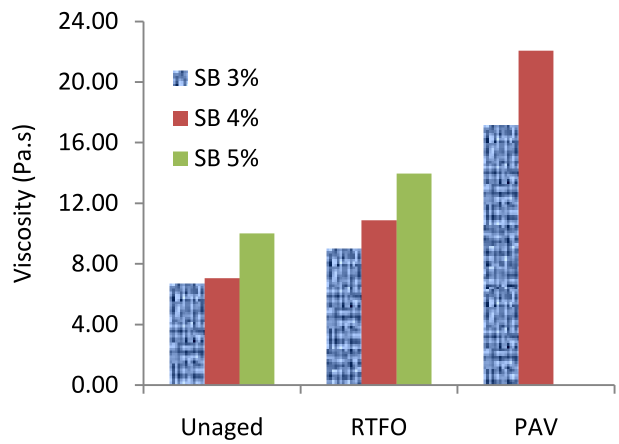


(b) PAV

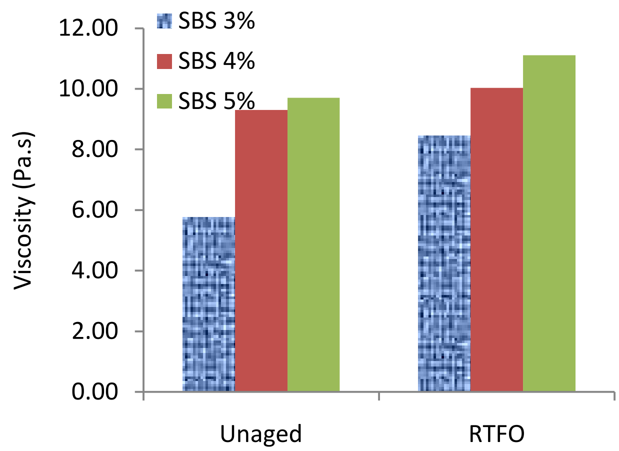
Figure 4.25: Comparing aging index for SB and SBS modified binders



(a) Original Binder



(b) SB-modified binder



(c) SBS-modified binder

Figure 4.26: Viscosity of original binder, SB and SBS-modified binder for aging

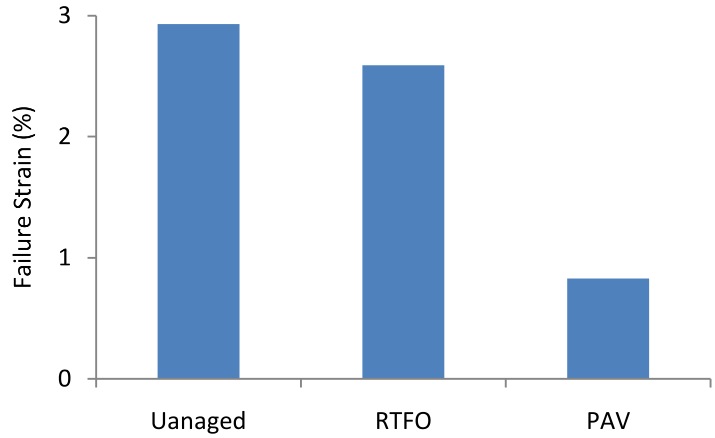


Figure 4.27: Failure strain of original binder at unaged and aged conditions

CHAPTER 5

Nanomechanical Experimentation of Aging on Polymer Modified Asphalt

5.1 Introduction

In this study, nanoindentation test is used to characterize the mechanical properties of asphalt binder at unaged and aged conditions. This chapter interprets the indentation test results.

5.2 Results and Discussions

Indentation is applied on a thin film of asphalt binder laid on a glass slide (Figure 5.1). The thickness of binder samples are more than 10 µm. To ensure that the glass is not indenting and all the penetration depth is in the binder sample, separate indentation is applied on glass surface with a same loading configuration on binder. Figure 5.2 shows a typical indentation result on a binder sample. Maximum Indentation depth for binder is approximately 8000 nm. The loading, holding and unloading curves are smooth, but glass indentation does not have smooth curves. Glass is much harder than asphalt binder and the maximum indentation depth is not more than 30 nm. Figure 5.3 shows two data series for an indentation test on glass slide. This is done to make sure that the tip just indented the asphalt binder

An indentation test contains three parts as shown in Figure 5.4. The first part is loading. Loading starts with initial value of 0.05 mN and increases at rate of 0.025 mN/s until it reaches to its maximum value of 0.25 mN. The second part is holding part. The maximum loading maintained on sample for 30 seconds. The third part is unloading part and the rate of unloading is same as loading part. The first and the third parts are used to calculate hardness and reduced modulus for each sample by using Oliver Pharr method (1992). Once Er is known, E is calculated using:

$$\frac{1}{E_r} = \frac{(1-\upsilon^2)}{E} + \frac{(1-\upsilon_i^2)}{E_i} \qquad 5.1$$

Contact area is then calculated as a function of indentation depth.

$$S = \frac{dP}{dh} = \frac{2}{\sqrt{\pi}} E_r \sqrt{A} \qquad 5.2$$

Here, S is measured stiffness of the upper portion of the unloading data (Figure 5.4), E_r is the reduced modulus and A is the area of the elastic contact. With contact area and maximum load hardness can be obtained.

$$H = \frac{P_{max}}{A} \qquad 5.3$$

Figure 5.4 shows calculated elastic modulus for base binder, SB5% and SBS 5% modified binders at unaged and aged conditions. It can be seen that by aging hardness of samples increases. RTFO aging increases the hardness of base binder approximately 7 times and PAV aging increases the hardness of RTFO residue approximately 4-6 times. This figure also shows that modification has significant effect on the aged binders. It can be concluded that polymers will increase hardness of RTFO and PAV aged binders. Figure 5.5 compares the effect of two different modified binders, too. With a same amount of polymer (5%), SBS-modified binder shows higher hardness than SB-modified binder.

It should be considered that asphalt binder is too soft to be indented. For running the test, the indentation tip needs to contact with the surface of binder. For soft binders same as unaged binders it is too difficult to introduce the surface to the indentation tip and the results will not be appropriate. Even if some data is collected for soft binders the calculated values will be too small to be considered. Most of the successful tests are for the aged binders. The results for the stiffer binders are more meaningful to be analized and compared with each other.

Reduced elastic moduli that are presented in Figure 5.6 are for the same binders which were compared previously. This figure shows that the aging increases the reduced modulus. This means that by aging, binder behavior changes from viscous to elastic. As it was expected, the results show that the modification increases the elastic modulus of aged binders. Between two different modified asphalt binders, SBS-modified binder has the higher modulus value than SB-modified binder.

Another measured property for binders at nano scale is creep compliance verses loading time. For conical indenter geometry, Tweedie (2006) recommends the following equation.

$$J_c(t) = \frac{8\tan(\alpha)h^2(t)}{\pi P_0} \qquad 5.4$$

Here, h (t) is the penetration depth at the time t, P_0 is the constant load at its maximum value and α is the semi angle for the conical tip. To Use the same equation for Berkovich tip the equivalent angle should be calculatedin in a way that the conical tip with the equivalent angle gives the same contact area as Berkovich tip. Qin proposes the equivalent angle by the following equation.

$$\alpha = tan^{-1}\left(\sqrt{\frac{3\sqrt{3}}{\pi}}tan\psi\right) \quad 5.5$$

The Berkovich tip corresponds to $\psi = 65.3°$. Qin equation gives $\alpha = 70.3°$. The creep compliance for each indentation is normalized after the calculation. Then the normalized creep compliance for different binders is used to compare the results with each other.

$$J_n(t) = \frac{J(t)}{J_0} \quad 5.6$$

At Figure 5.7 normalized creep compliance for SB 4% at different aging conditions are compared. The unaged binder curve has the highest slope. Creep compliance for unaged samples increases rapidly with time. On the other hand, PAV aged binder curve has the lowest slope and creep compliance increases slowly. Lower creep compliance indicates higher elasticity. The difference between unaged, RTFO aged and PAV aged binder increases with the creep time. At a specific time the difference in creep compliance between unaged and RTFO aged binder is much smaller than difference between RTFO and PAV aged binder. So, it can be concluded that long term aging highly affects the creep compliance and reduces it. Figure 5.8 presents the same curves for SBS 4% binder. The results are same as SB 4% binder. It should be mentioned that the presented curves, only shows the primary creep for the binder samples. Keeping the load on a binder makes the curve to merge to a constant value which is called secondary creep. In this study, for the depth considerations, keeping the load for more than 30 seconds was not possible and the tip might have indented the glass.

The effect of two different polymers on aging is compared at Figure 5.9. It can be seen that for the same aging condition SBS-modified binder has lower creep compliance than

SB-modified binder. It can be concluded that SBS polymer increases the elasticity of aged binder more than SB polymer.

5.3 Conclusions

- The use of nanoindentation test shows that aging increases elasticity as well as hardness of the binder while it decreases the creep compliance.
- Results from this study confirm that SBS has a greater effect than that of SB on binder mechanical properties (stiffness and elasticity).
- Results from micro and nano-scale testing show similar effects on asphalt binder mechanical properties through the aging.
- From this study, the author suggests using spherical tips for achieving more accurate results from nanoindentation testing, especially with soft binders. The spherical tip is not as sharp as Berkovich tip which makes it more adequate for softer binders.

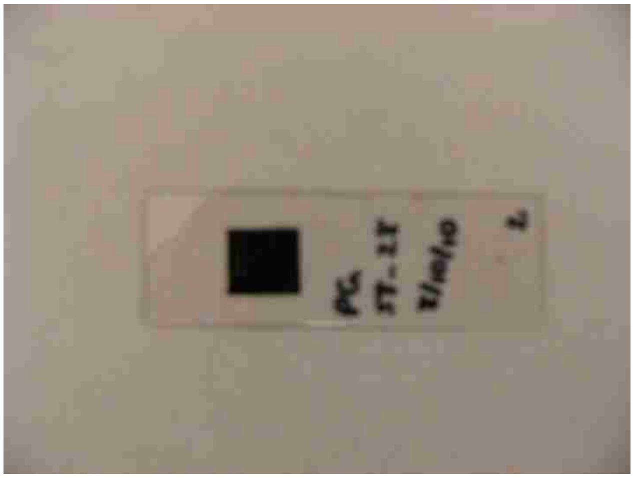


Figure 5.1: The asphalt sample for indentation test

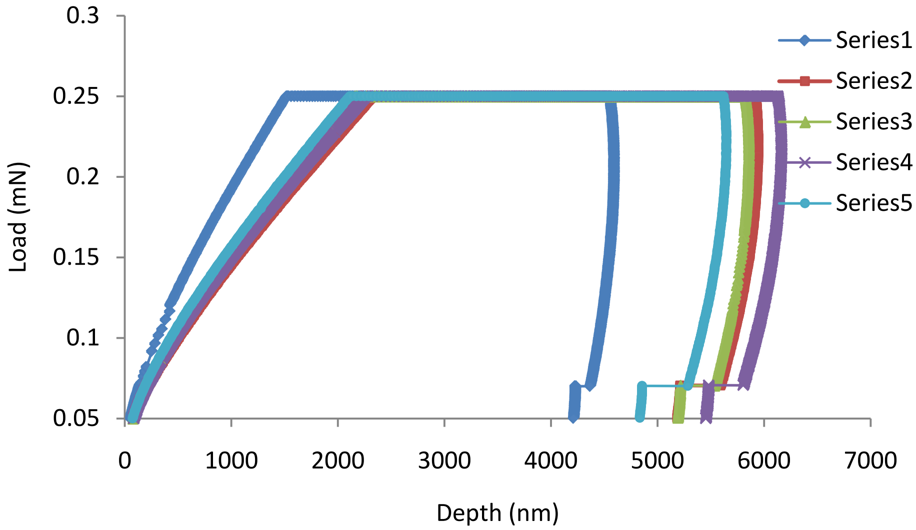


Figure 5.2: Indentation test on SB 5% at PAV aging condition

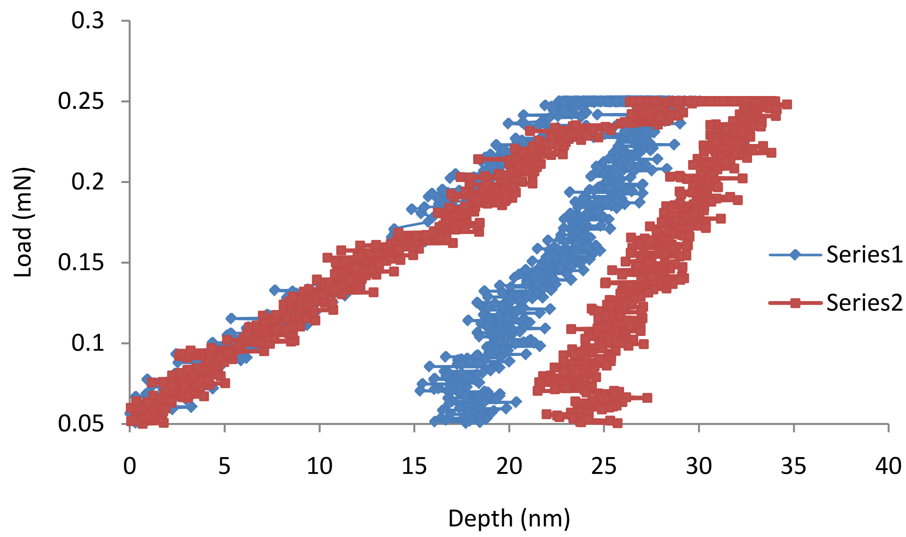


Figure 5.3: Indentation test on glass

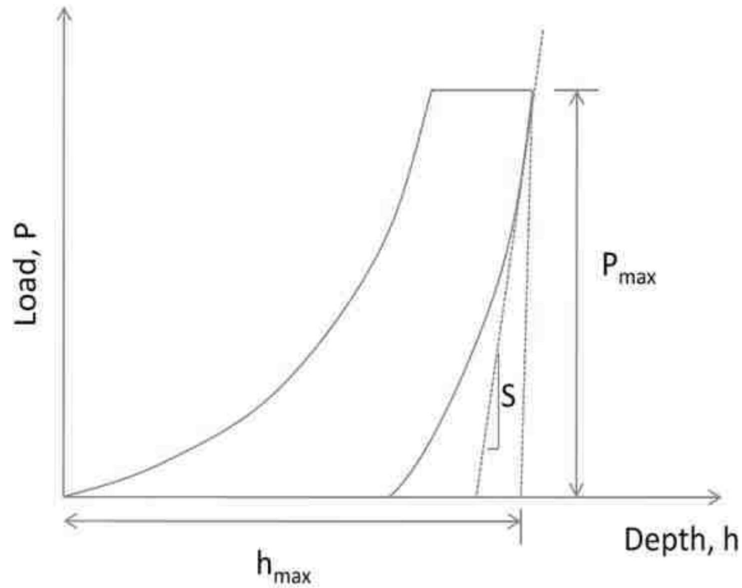


Figure 5.4: Typical indentation curve

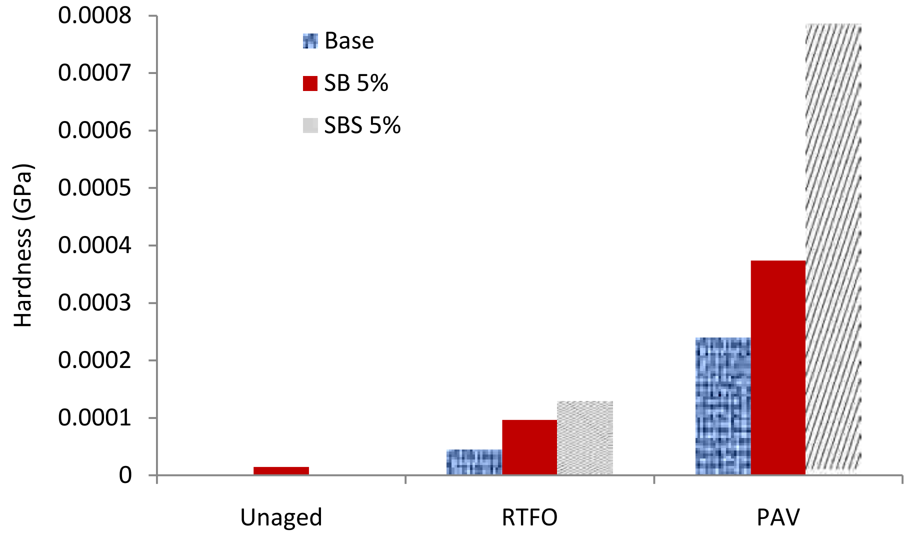


Figure 5.5: Hardness for Base, SB 5% and SBS 5% at unaged and aged conditions

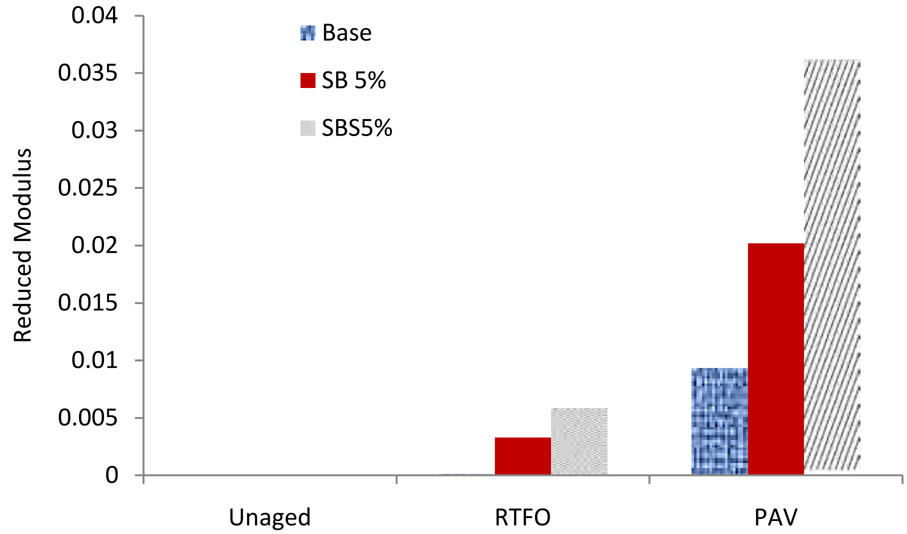
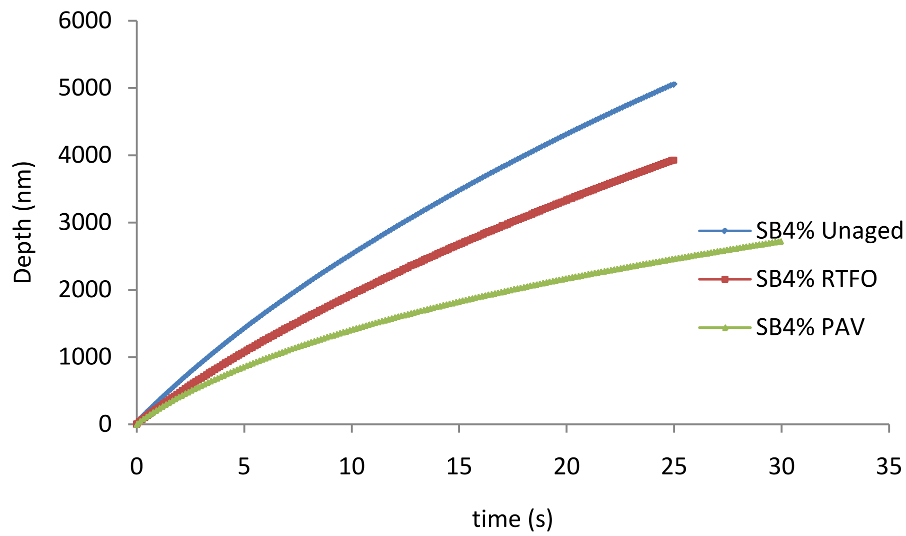
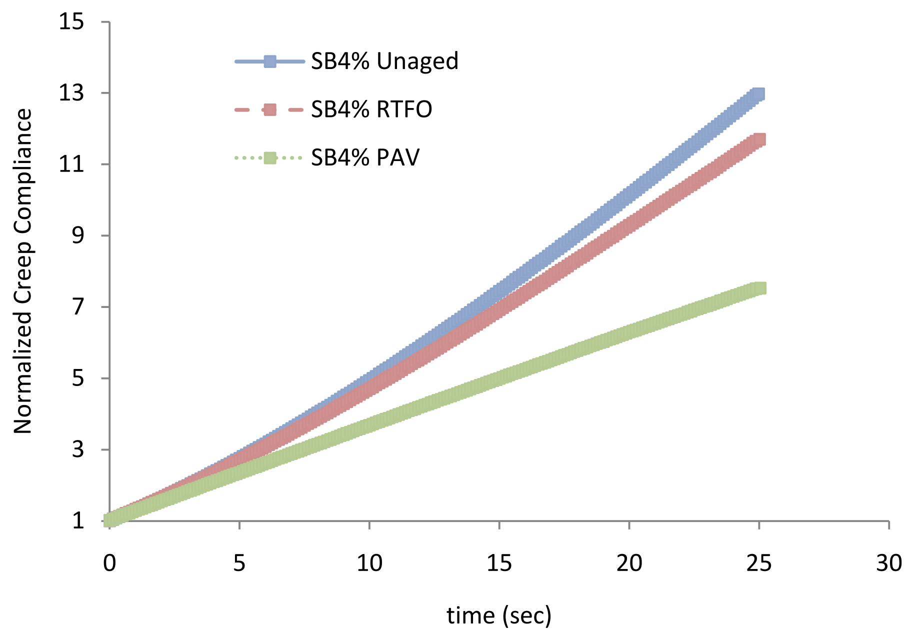


Figure 5.6: Reduced modulus for Base, SB 5% and SBS 5% at unaged and aged conditions

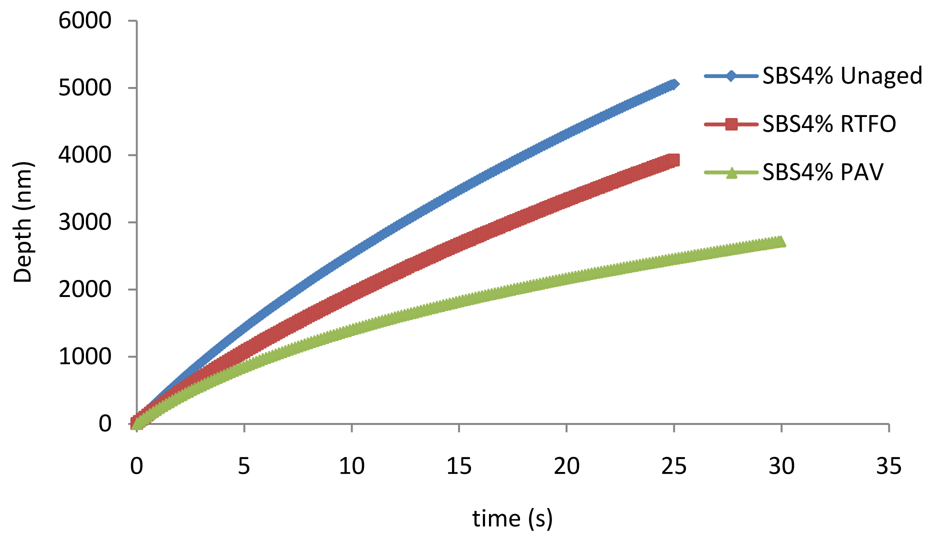


(a) Penetration depth vs. time

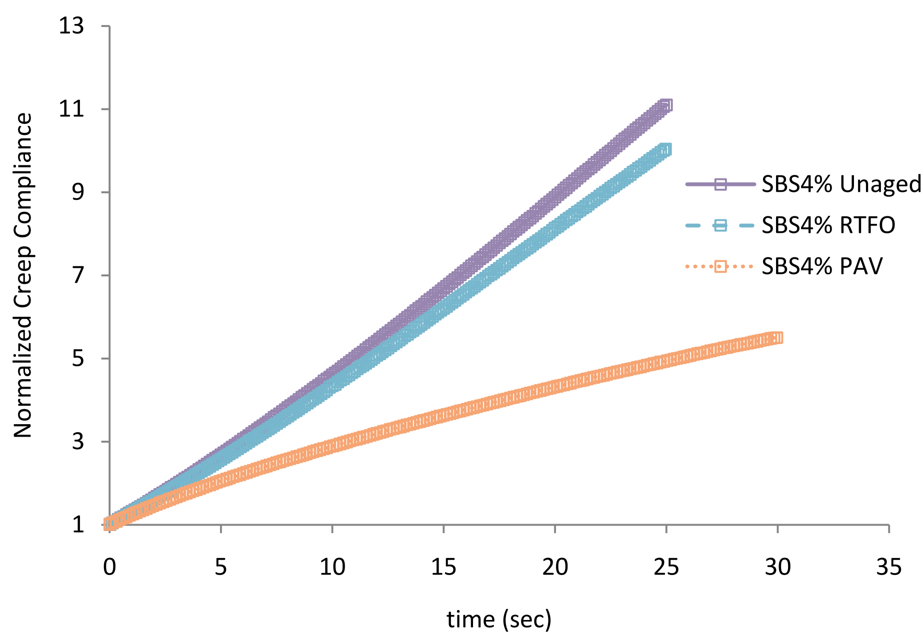


(b) Normalized creep compliance vs. time

Figure 5.7: Normalized creep compliance and penetration depth for SB4% vs. time at unaged and aged conditions



(a) Penetration depth vs. time



(b) Normalized creep compliance vs. time

Figure 5.8: Normalized creep compliance and penetration depth for SBS 4% vs. time at unaged and aged conditions

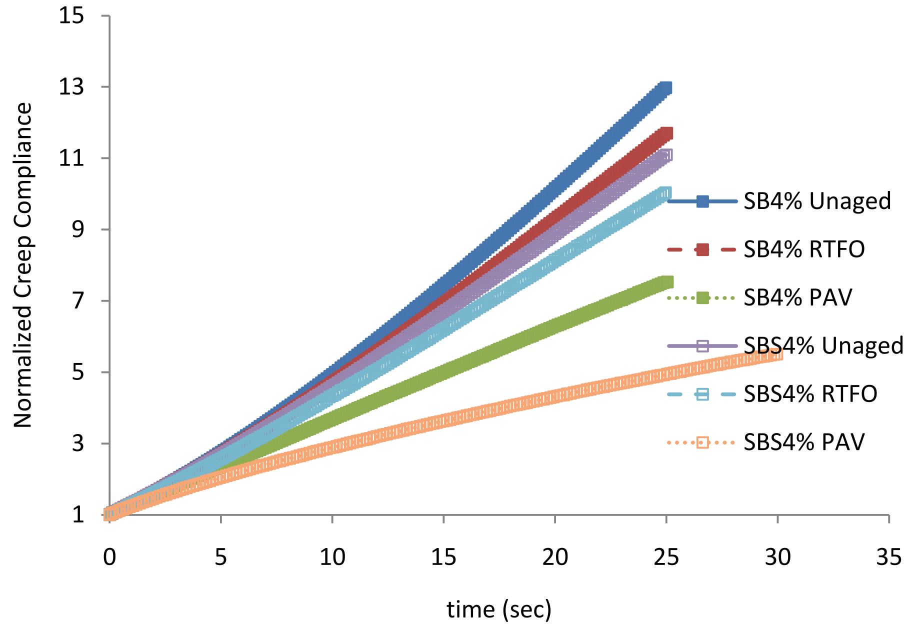


Figure 5.9: Comparing creep compliance of SB 4% and SBS 4%

CHAPTER 6

CONCLUSIONS

6.1 Summery

This study characterizes the aging properties of unmodified and modified asphalt using rheological and nanomechanical test methods. Binder aging leads to several problems in asphalt binder such as top down cracking and thermal cracking. The aging that occurs during the mixing and compaction is short term aging. The aging occurs during the pavement service life is long term aging. The main reason for the aging is oxidation. The binder becomes stiffer due to oxidation. This can result in fatigue cracking. In this study, binders are aged in laboratory using RTFO for short term aging and PAV for long term aging. In addition, draft oven is used to age the binders for various times. Modification is used to improve aging performance of asphalt binder. For binder modification, SB and SBS polymers are used at 3, 4 and 5%. Traditionally rheological tests such as DSR, MSCR, BBR, DT and RV are preformed to characterize the aged and unaged properties of modified binders such as complex modulus, stiffness and creep compliance. In addition, nanoindentation is used in this study to measure the hardness and reduced modulus. The results are analyzed by using relative aging index to compare the effect of polymer type and polymer amount on binder properties due to aging.

6.2 Conclusions

Based on the studies mentioned above the conclusion can be summarized as follows:

- At low temperature, aging, polymer type and polymer percent has effect on G* and the difference creep compliance of unaged and aged binder is small compared to that at high temperature. This confirms that temperature significantly affects aging.

- Based on aging index defined by complex shear modulus (G^*), increase in percent polymer results in decrease in aging index value for both SB and SBS modified binder.

- When comparing aging index defined by G^* SBS has higher aging index than SB. Overall, SB is better than SBS modifier.

- Aging index of RTFO sample is about 2 for G* and 8 for PAV. The PAV has about 4 times more aging effect. It can be concluded that in the field there will be 4 times of a aging during mixing and compaction.

- When comparing AI defined by G^*, elastic modulus (G'), viscous modulus (G''), of oven aged sample, base binder ages more than modified binder and G' changes exponentially compared to the linear change of G''.

- Based on AI defined by BBR stiffness, original binder shows AI value similar to the modified binder. Again, SBS has higher AI defined by BBR stiffness than SB.

- For both unmodified and modified binders, hardness and reduce modulus increase exponentially due to aging.

- Nanoindentation results show similar trend obtained by rheological test. Aging decreases the creep compliance defined by indentation depth, similar trend is observed in MSCR test by DSR.

6.3 Recommendation

The Following points can be recommended for the future studies:

- This study did not develop a basic understanding of how asphalt chemistry changes due to aging. Specifically, how chemistry relates to the rheological and indentation properties.
- Mechanical models can be developed base on the rheological and nanomechanical results to predict aging.

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