Jurnal
Teknologi

Full Paper

The Influence of Polymer on Rheological and Thermo Oxidative Aging Properties of Modified Bitumen Binders

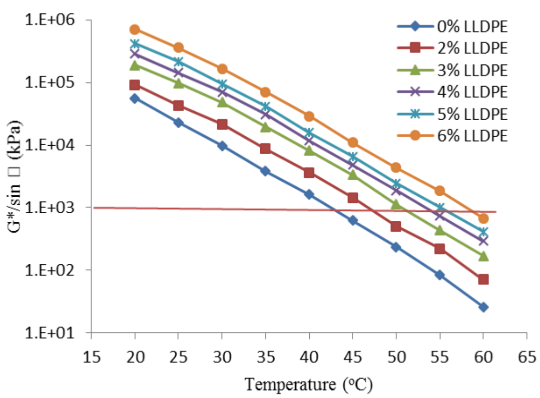
Article history
Received
10 December 2016
Received in revised form
14 June 2017
Accepted
15 August 2017

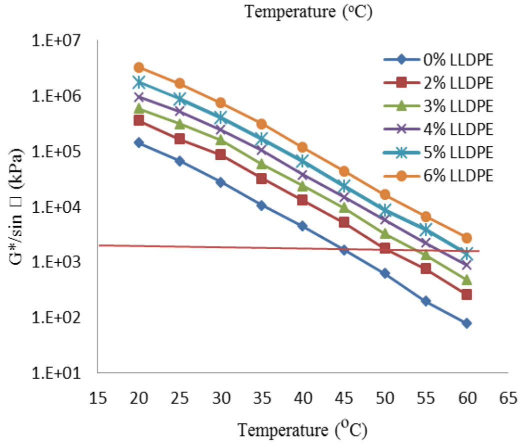
Nura Bala*, Ibrahim Kamaruddin, Madzlan Napiah

Department of Civil & Environmental Engineering, Universiti Teknologi PETRONAS, 32610 Bandar Seri Iskandar Perak Malaysia

*Corresponding author
madzlan_napiah@utp.edu.my

Graphical abstract





Abstract

Polymer modified bitumen (PMB) has been used for many years to improve the performance of asphalt concretes against premature pavement defects. In this research, modified samples were prepared with 2%, 3%, 4%, 5% and 6% Linear Low Density Polyethylene (LLDPE) polymer by weight of bitumen binder. The influence of LLDPE polymer was evaluated through binder properties test which includes penetration, softening point, storage stability, temperature susceptibility, rutting, fatigue and thermal oxidative aging resistance from a dynamic shear rheometer (DSR) measurements at a temperature of 20 °C to 60 °C. Results show that LLDPE polymer has a significant effect on binder properties. Penetration decreases and softening point increases with increasing LLDPE content on the modified binder after aging, which implies LLDPE improves the thermo oxidative aging resistance of the binder. Furthermore, the storage stability test shows that at higher LLDPE concentrations phase separation may occur. DSR analysis shows that modified binders have lower temperature susceptibility and higher aging resistance with increased stiffness and elastic behavior compared with unmodified binders. In addition, modified binders show enhanced resistance against high temperature rutting and at low temperature fatigue performance. It was found that the optimum LLDPE content is 6%.

Keywords: Bitumen, polymer, aging, rheology, storage stability

Abstrak

Polimer bitumen yang diubahsuai telah digunakan selama bertahun-tahun untuk meningkatkan prestasi konkrit asfalt terhadap kecacatan pramatang kaki lima. Dalam kajian ini, sampel-sampel yang diubahsuai telah disediakan dengan 2%, 3%, 4%, 5% dan 6% polimer Linear Low Density Polyethylene (LLDPE) secara kiraan berat bitumen pengikat. Pengaruh polimer LLDPE telah dinilai melalui ujian sifat pengikat termasuk penembusan, titik lembut, kestabilan penyimpanan, suhu kerentanan, perubahan bentuk, keretakan dan rintangan penuaan oksidatif haba terma dari ukuran reometer ricih dinamik (DSR) pada suhu 20 °C to 60 °C. Keputusan menunjukkan bahawa polimer LLDPE mempunyai kesan yang besar ke atas sifat pengikat. Penembusan menurun dan titik lembut meningkat dengan peningkatan kandungan LLDPE pada pengikat yang diubah suai selepas penuaan, yang menunujukkan bahawa LLDPE meningkatkan rintangan penuaan oksidatif haba terma pengikat. Bitumen yang diubahsuai menunjukkan kecenderungan suhu yang lebih rendah, menandakan bahawa rintangan suhu yang lebih tinggi berbanding dengan pengikat yang tidak diubahsuai. Tambahan pula, ujian kestabilan penyimpanan menunjukkan bahawa kepekatan LLDPE yang lebih tinggi menyebabkan fasa pemisahan. Analisis DSR menunjukkan bahwa pengikat yang diubahsuai mempunyai kecenderungan suhu yang lebih rendah dan rintangan penuaan yang lebih tinggi dengan peningkatan kekerasan dan sifat elastik berbanding pengikat yang tidak diubahsuai. Di samping itu, pengikat yang diubahsuai menunjukkan penigkatan rintangan berbanding rutting dan fatigue performance. Kandungan optima LLDPE yang telah ditemui adalah 6%.

Kata kunci: Bitumen, Polimer, Reologi, penuaan, penyimpanan kestabilan

1.0 INTRODUCTION

Pavements during their service life are generally associated with different types of premature failures, such as rutting under high temperature, fatigue and thermal cracking under low temperature conditions [1]. This adversely decreases the performance and durability of pavements and subsequently reduces their life cycle [2]. Binder failures can occur at different stages, during the processing or production of the bitumen, storage after production, or during laying and compaction of bituminous mixtures [3]. In addition, bitumen exposure to oxygen, especially for a longer period, can also result in oxidation which can be influenced by different factors such as the binder properties [4]. A bituminous pavement undergoes distresses not only to binder properties [5] but also due to increase in heavy traffic loads which also causes a rapid deterioration of pavements. Therefore, with these challenges modification of bitumen becomes necessary [6].

Recently, among the best process for improving properties and performances of bitumen is the incorporation of polymers at a range of 3 to 7% by weight of the binder [1,4,7,8]. Eventhough, improvements can be achieved at lower polymer percentages, but blending small quantities of the polymer into bitumens only leads to partial alleviation of fatigue and rutting defects [9]. Therefore, ascertaining the thermo oxidative aging and degradation of the polymer modified bitumens at all stages becomes an important parameter to enhance the performance of pavement bituminous mixtures [10]. Generally, bitumens when modified, especially if polymers are used, usually becomes thermodynamically disturbed, which makes it be unstable, and phase separation easily occurs if kept or stored under high temperature conditions, thus limiting their applications in pavement construction [11].

Polymers applied for bitumen modification generally falls into one of the following classes: reactive polymers, thermoplastic plastomers, and thermoplastic elastomers. Thermoplastic elastomers are generally employed due to their ability in enhancing elastic properties of the binder modified; and the remainings are generally used due to their ability to improve rigidity and reduce deformations under load [12, 13]. Most common plastomers applied for bitumen modification includes polyethylene (HDPE, LLDPE, and LDPE), ethylene butyl acrylate (EBA) and ethylene vinyl acetate (EVA) [13,14].

Rheological examinations of modified binders are very essential to ensure good long lasting field performances or to address specific pavement distress. Based on this, it becomes necessary for a fundamental method for binder testing as normal consistency tests fail to describe the full viscoelastic properties needed for a detail rheological evaluation of a modified binder. A dynamic shear rheometer (DSR), introduced during the Strategic Highway Research Program (SHRP) campaign in the early 1990s were employed as a fundamental test for determining both elastic, viscous and viscoelastic behaviors of all bitumens [15].

Chemical structures and the rheological behaviors of bitumens, especially if modified, change with aging [16, 17]. The main mechanisms of aging in bitumen are volatilization of light components, steric hardening, and oxidation during service life stage [18, 19]. Volatilisation and oxidation generally are irreversible process as they are associated with changes that are chemical in nature [20], but steric hardening, on the other hand, can be reversed either through heat or mechanical work because it entails structural reorganization of the molecules, which are produced by changes in temperature [21].

Short term aging which usually occurs at the stages of mixing, paving and compaction, and long term aging process usually took place during service life stage of pavement [22]. Rolling thin film oven test (RTFOT), has been recognized as the reliable method for simulating short term aging process, while a long term aging stage is simulated by using a device known as Pressure Aging Vessel (PAV) [23, 24].

Despite the several investigations on using plastomeric polymers for bitumen modification, there are limited experimental studies on detail evaluation of thermo oxidative aging effects on polyethylene modified binders. Therefore, this research aims at characterizing the properties of the LLDPE modified binders through the application of conventional and empirical test techniques as well as evaluation of the storage stability and aging properties by assessing the aging indices of the modified binders.

2.0 METHODOLOGY

This section describes the materials and methods used for the research

2.1 Materials

Control base bitumen 80/100 penetration grade is used for this research which was supplied from PETRONAS refinery located in MelaKa, Malaysia. The Various properties of bitumen used for the research are described in Table 1.
LLDPE polymer in its pellet form was used for bitumen modification. The polymer was obtained from Etilinas Polyethylene factory in Kerteh, Malaysia.

Table 1 Physical properties of base binder

Bitumen Property	Value	Unit
Grade	80/100	Pen
Penetration (25°C and 0.1 mm)	84	dmm
Softening point temperature	42	°C
Ductility at 25°C	>150	cm
Viscosity at 135°C	0.65	Pa.s
Specific gravity	1.03	

2.2 Preparations of Modified Sample

Modified samples used in this research were prepared accordingly by adding 2%, 3%, 4%, 5% and 6% LLDPE polymer by weight of base bitumen. A multi mix laboratory bench top high shear mixer was used for mixing. The samples were prepared at a high shearing rate of 4000rpm and shearing temperature condition of about 150 ± 10 °C for the duration of 2 hours. These conditions were applied for the purpose of obtaining a uniform and homogenous mixture [3]. Control base bitumen was also passed the same conditions as the modified samples in order to have uniformity for all the samples throughout the research.

2.3 Experimentation Procedures

2.3.1 Conventional Properties Tests

Conventional properties of the base bitumen and polymer modified bitumen (PMB) were analyzed using Softening Point Test (Ring and Ball test) and Penetration test. Penetration test method (ASTM D5-13) describes the use of a standardized needle with a load of 100 g to evaluate the penetration of a given material at 5 seconds time period. The penetration of the material analyzed is taken as the depth of penetration of the needle expressed in units of 1/10 mm measured at a temperature of 25°C. Penetration test is used to define the penetration grade of the binder.

Ball and Ring softening point test is a consistency measure that characterizes binder base on softening temperature. According to ASTM: D36-12 used in this research, the softening point test defines a temperature under which a steel ball of weight 3.5g over a bitumen film when heated under a uniform temperature rate of 5°C/ min produces a deformation of 25.4 mm on the bitumen tested.

2.3.2 Temperature Susceptibility

Penetration and softening point values obtained for a binder sample are used to estimate penetration index (PI) which describes temperature susceptibility of the bitumen. PI is an important parameter for pavement design as it relates to the famous Van Der Poel nomograph, which is use in obtaining bitumen stiffness.

Binder temperature susceptibility is one of the most influential properties of bitumen binder as the behavior of binder depends entirely on the loading rate and temperature; therefore, temperature susceptibility of bitumen binder is described as the change in rheology of the binder with a change in temperature. Penetrations and softening points are used for evaluation of penetration index (PI) as described in Shell Bitumen Hand Book [25] based on Eq. 1.

$$PI_{TR\&B} = \frac{1952 - 500\log P_{25} - 20T_{R\&B}}{50\log P_{25} - T_{R\&B} - 120} \qquad (1)$$

Where $PI_{TR\&B}$ is penetration index, P_{25} is bitumen penetration at 25 °C, $T_{R\&B}$ is ring and ball softening point temperature of the bitumen. PI was evaluated in this research to compare the effect of various polymeric concentrations on temperature susceptibility of LLDPE modified bitumen.

2.3.4 High Temperature Storage Stability

For examining the stability of LLDPE polymer modified binders under high temperature conditions, European specification tube test [PN-EN 13399] was used for both fresh and modified bitumen. Under this method, binders were poured inside the aluminum foil tube (diameter of 35mm, a height of 170 mm) and immediately placed in an oven at 180°C for the duration of 72 hours. At the end of the period, the tube was then brought out and cools in a vertical position at room temperature. It was later stored in a freezer at −20°C for 6 hours. The samples are then divided into three parts and samples from the bottom and top parts were taken and examine through evaluating their softening point temperatures for stability during hot storage. The binder will be stable under high temperature storage if the difference between the top and bottom softening points of the specimen was less than 4°C [26].

2.3.5 Dynamic Shear Rheometer Test

DSR was applied for characterization of the viscoelastic behavior of bitumen binders at varying service temperature conditions. DSR measurements were performed using a Kinexus Malvern Instruments rheometer model 7106199 (United Kingdom). An 8mm diameter parallel plate geometry and 2mm diameter gap for testing were applied for low and intermediate temperature tests from 10°C to 35°C. At higher temperatures beyond 35°C, a parallel plate of 25mm diameter and 1mm gap for testing were applied. Temperature sweeps were performed within the linear viscoelastic region (LVE) at temperatures ranging from 20°C to 60°C within an interval of 5°C. Samples for rheological tests were prepared using both silicone mould and hot pour method.

Amplitude sweep tests were first conducted before temperature sweeps to determine the linear viscoelastic region (LVE) region of the bituminous binders. LVE were evaluated based on a point with 95% decrease in initial value of average complex modulus $|G^*|$ [27, 28]. After determining the limiting strain at that point, temperature sweep tests were conducted based on conditions stated in Table 2:

Table 2 Rheological test conditions

Parameter	Condition
Mode of loading	Controlled strain
Test temperatures	20–60°C (with the interval of 5°C)
Frequency	10 rad/sec
Temperature rise rate	2°C/min
Spindle geometries	8mm diameter with 2mm testing gap (20–35°C)
	25mm diameter with 1mm testing gap (35–60°C)
Strain	(0.2%) within the LVE response

2.3.6 Aging Methods

The short term and long term aging of the binders were simulated respectively by both Rollin Thin Film Oven Test (RTFOT) and Pressure Aging Vessel (PAV). RTFOT model B1 manufactured in Italy by CONTROL Co., Ltd., was used for simulation of short term aging during mixing in accordance with ASTM D2872 specification. Based on this specification, binder samples of 35g weight were placed in RTFOT glass bottles with a narrow opening on top. The bottles were placed in RTFOT carriage with the horizontal axis of revolution such that, the bottles top openings were directly facing a jet of air inside the oven. A temperature of 163°C was kept constant and the bottle carriage was set to rotate for 85 minutes at a speed of 15 rpm.

PAV model PR9300 manufactured in America by Prentex Co., Ltd., was employed for rapid aging of binders during service life. PAV test was conducted based on ASTM D6521 specification. Under this specification, a sample of weight 50±0.5g from RTFOT test was placed into two marked PAV pans and immediately kept all in the same PAV for a single test run. An applied air pressure of 2.1±0.1 Map which maintained for 20h ± 10 min after the inside PAV temperature was around ±2 °C of the aging temperature (109°C), The PAV pans were removed after 20 hours and poured into separate containers for subsequent tests.

3.0 RESULTS AND DISCUSSION

3.1 Conventional Properties (Penetration and Softening Point Test)

Penetration represents consistency and is used to describe the flow and deformation properties of binders; Figure 1 shows the effect of LLDPE polymer modification on physical properties of the control binder both before and after aging.

The result in Figure 1 describes that LLDPE decreases penetration of the binders and the decrease in penetration increased with increase in LLDPE. At 6% LLDPE content it was observed that penetration decreases by almost 50% compared with unmodified binder. It was also observed that LLDPE has a strong effect on control binder as indicated through penetration values reduction and stiffness increase. These can enhance the binder resistance against high temperature effects and makes it more resistant to pavement failures such as deformations. The decrease in Penetration after aging implies an increase in consistency and higher resistance to aging of the LLDPE modified binders. The large difference in penetration values after thermo oxidative aging in all the modified binder samples clearly indicates an increase in binders hardening and higher resistance against failures.

The large reduction observed between the penetration values of aged and unaged binders shows that LLDPE polymer within the bitumen rapidly increases the hardness of the binders. This was due to strong network formation of dispersed polymer as the viscoelastic properties of the control binder is strongly influenced by factors which include; temperature, polymer concentration, and binder penetration grade. Furthermore, the decrease in penetration is also related to diffusion of oil fraction within the bitumen (maltenes) in the polymeric phase which causes higher interactions and swelling between the LLDPE polymer modifier and polar molecules of the binder (asphaltenes). A similar phenomenon was also reported by Perez et.al [29].

Softening point test was used to describe the plastic flow of binders. It was also used to evaluate the stability of paving binders under conditions of high service temperature. For paving applications, a higher value of bitumen softening point temperature describes the higher stability of the binder under high service temperatures. Figure 2 shows softening point values of base and LLDPE modified binders before aging and after RTFOT aging.

From Figure 2, it can be seen that LLDPE addition raises softening point values for all the modified binders. Observing the binders after RTFOT aging, the softening point values enhanced for all LLDPE modified binders. This simply describes that the ability of the aged modifies binders to become soft quickly under conditions of high service temperature reduces greatly. This makes it be less susceptible to temperature and more resistant to permanent deformation.

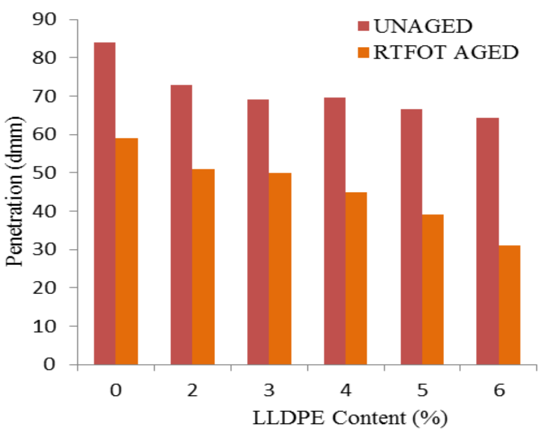


Figure 1 Penetration of base and LLDPE modified binder before aging and after RTFOT aging

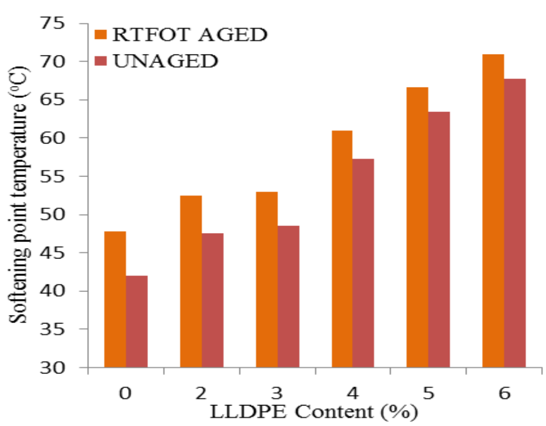


Figure 2 Softening point of base and LLDPE modified binder before aging and after RTFOT aging

3.2 Susceptibility to Temperature

Bituminous binder materials are generally very sensitive to variations in temperature, these makes them display diverse properties under a varying service temperature conditions. Penetration index (PI) describes bitumen deviation in behavior from Newtonian to non-Newtonian. For paving applications the bitumen usually used has a PI value between -2 (high temperature susceptible bitumen) and +2 (low temperature susceptible bitumen). A bitumen Having PI value lower than -2 describes Newtonian behavior with brittleness at a lower value and bitumens having PI values higher than +2 are generally less brittle and under high strains exhibit higher elastic properties [30].

Figure 3 shows the plot of penetration index of base and LLDPE modified binder before and after RTFOT aging. It can be seen that modification of bitumen with LLDPE polymer significantly enhanced the susceptibility of the binder towards a temperature. A higher penetration index (PI) values indicate less susceptibility to temperature and more rubbery elastic behavior [31]. It was observed that the PI values of the base bitumen and 6% LLDPE polymer before and after aging is -1.9 and -1.7 respectively. However, after aging, the PI values increases to 1.65 and 1.9 for base bitumen and 6% LLDPE respectively. This increase in PI values implies enhancement in temperature susceptibility for the modified binders. These enhancement increases with polymer addition and the susceptibility to temperature among the binders are much higher for the modified samples using greater LLDPE content. Higher temperature susceptibility by LLDPE modified binders indicates that polymer modification of binders induces a behavior to the bitumen which is rubbery elastic in nature, this makes it more resistant to temperature cracking and permanent deformation.

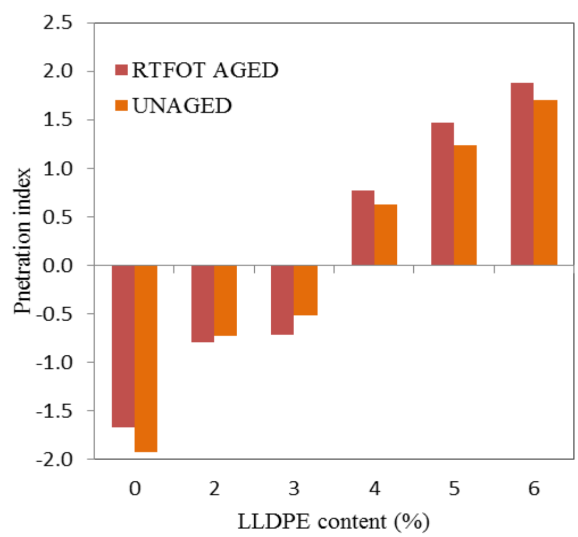


Figure 3 Penetration index of base and LLDPE modified binder before and after aging

3.3 Storage Stability

Test for stability during storage is generally conducted to confirm that, effectiveness of the polymer used for modification were not changed through some processes such as high temperatures, contamination or any form of degradation under transportation and storage conditions, Figure 4 shows the effect of LLDPE polymer on high temperature storage stability

From Figure 4, it can be observed that the storage stability of the base bitumen was affected by LLDPE polymer modification and the effect increases with increase in polymer content. Further observations indicate that, among all the samples, only base bitumen and bitumen sample modified with 2% LLDPE shows 2 ^{O}C and 3.5 ^{O}C differences in softening point values. This result implies that the two binders can be stable under storage. Comparing unmodified and modified binders, only 2 % LLDPE binder yields a stable modified binder as the top and bottom sample sections show a 3.5^{O}C difference in softening point temperatures.

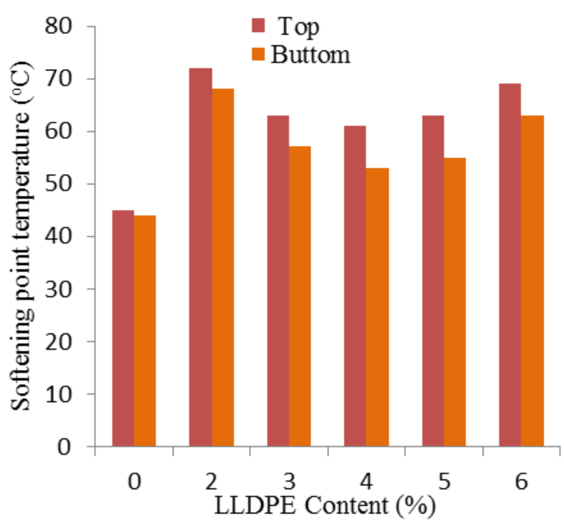


Figure 4 Effect of LLDPE on high temperature storage stability

It was observed that the stability during storage of LLDPE polymer modified binders is governed by several factors which include the difference in densities, polarity, molecular weights, other factors include viscosity difference between polymer and the binder and the structure of the bitumen phase. A similar phenomenon was also reported by Lu and Isacsson et.al [16].

It was observed that phase separation occur within LLDPE modified binders due to density and polarity differences between control binder and LLDPE polymer during storage. During high temperatures, melted droplets of LLDPE polymer which were dispersed in the bitumen will be accumulated on the top of the modified binder and float. Similarly, maltenes fraction within the binder also swells and absorbed by elastic LLDPE fraction, this results in competition between bitumen asphaltenes and LLDPE polymer for the maltenes absorption which consequently causes instability. After 48 hours of high temperature storage, the softening point values for the upper section of binder modified was generally greater than that of the lower section. This was caused by instability which forces the polymer rich phase to migrate to the upper part and polymer rich phase segregates to the lower part. Therefore, there is higher polymer concentration on the top section compared to the lower section.

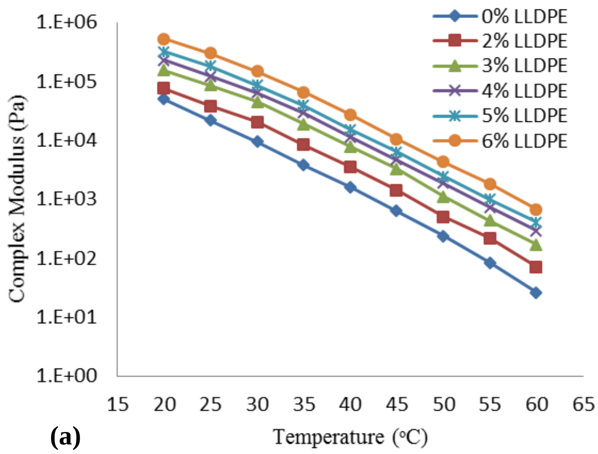
3.4 Rheological Properties of LLDPE Modified Bitumens

3.4.1 Isochronal Plots of LLDPE Modified Binders

An isochronal plot basically describes viscoelastic variables at constant loading time or frequency, such as phase angle or complex modulus against varying temperature ranges. Therefore, viscoelastic properties can be analyzed at a given frequency over a varying range of service temperatures. The isochronal plots allow for the comparison between different viscoelastic parameters such as phase angle and complex modulus under varying conditions of temperatures.

Figures 5, 6 and 7 show the values for complex modulus, phase angle and complex viscosity of LLDPE modified binders as a function of temperature and LLDPE concentration under a constant frequency of 1.59 Hz for both unaged and aged samples. From these figures, it is observed that the binder complex modulus and complex viscosity increase with an increase in the LLDPE polymer content and in all cases, their values are greater than that of the unmodified binder. On the other hand, the phase angle presents a different phenomenon whereby a decrease with an increase in LLDPE polymer content was observed. Comparing unaged and aged binders, Figure 5 and Figure 6 indicate that the complex modulus and complex viscosities of all aged samples were larger than those of the unaged binders. On the other hand, Figure 7 shows that the phase angles of all aged samples were lower than those of the unaged binders.

The increase in complex modulus values and reduction in values of phase angle observed implies the ability of the polymer when dissolved in bitumen to form a continuous elastic network that depends on polymer content and physical or chemical properties of polymer and binder. Furthermore, the result shows that the modified binders exhibit higher elastic properties than the unmodified binders, and aging will not have much influence, which in turns implies LLDPE polymer can improve the binder resistance.



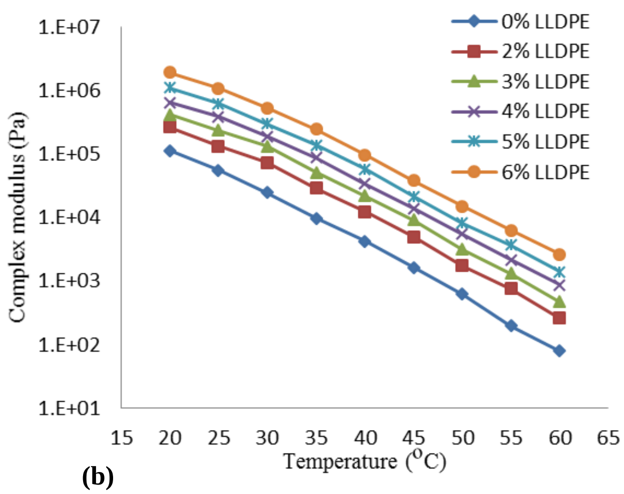
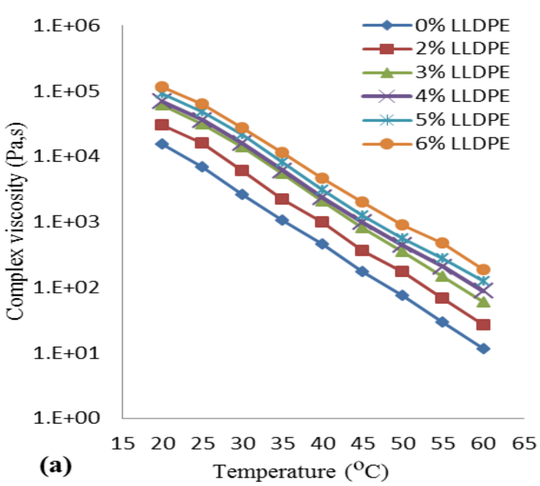


Figure 5 Isochronal plots of temperature and complex modulus: (a) Unaged base and LLDPE modified binder; (b) Aged base and LLDPE modified binder



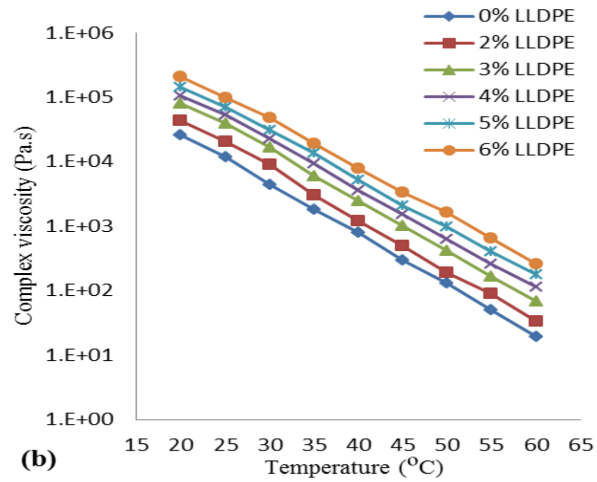
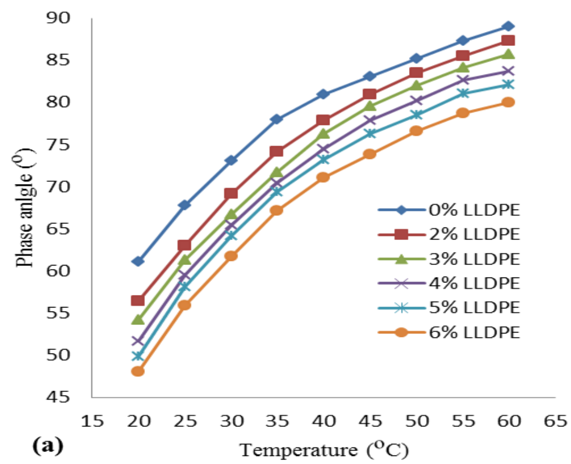


Figure 6 Isochronal plots of temperature versus complex viscosity: (a) Unaged base and LLDPE modified binder; (b) Aged base and LLDPE modified binder



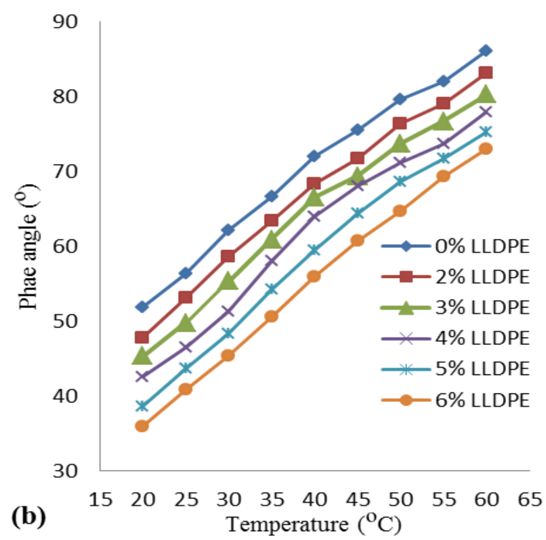


Figure 7 Isochronal plots of temperature versus complex modulus: (a) Unaged base and LLDPE modified binder; (b) Aged base and LLDPE modified binder

3.4.2 Black Diagram

Black diagram generally describes a relationship between phase angle and complex modulus found from rheological examinations. In black diagram, viscoelastic data are also represented over a varying range of service temperatures. Deviations can occur within the black diagram due to some factors which includes changes in composition, measurement errors and also variations in structures of the binders [32].

Figure 8 shows the relationship between phase angle and a complex modulus of base and LLDPE modified binder. It can be observed that at lower phase angle 5% LLDPE content has a greater value of complex modulus compared to unmodified and other LLDPE modified binders. This implies that among all the modified binders 5% LLDPE will have better resistance against rutting defects.

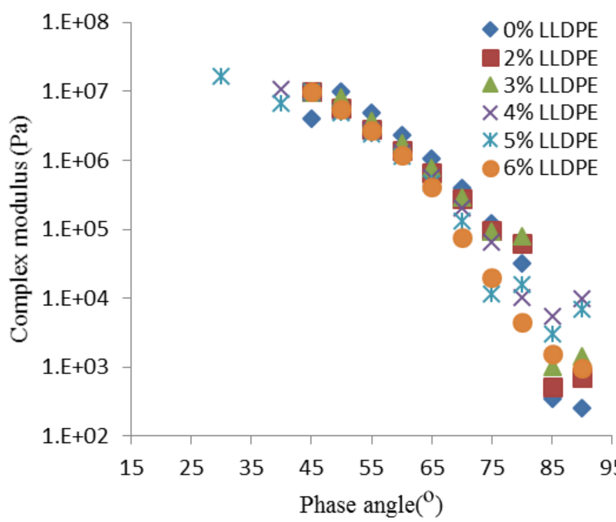


Figure 8 Black diagram for base and LLDPE modified binder

3.4.3 Effect of LLDPE on Rutting Resistance

Superpave criteria describe the use of ratio G*/sin δ for estimating rutting resistance of binders under high temperature conditions. The Superpave criteria specifies G*/sin δ ≥ 1 kPa and G*/sin δ ≥ 2.2 kPa to be the minimum required rutting parameter for unaged and RTFOT aged binders respectively. A binder with higher values of G*/sin δ ratio will have better permanent deformation resistance [23].

Figure 9 shows plots of G*/sin δ values against different temperatures before and after RTFOT aging. The results show that the minimum value of G*/sin δ was found in the unmodified binder. 6% LLDPE modified binder has the largest value of G*/sin δ. Moreover, it is also observed that 4% and 5% LLDPE samples have a similar behavior as their values of G*/sin δ ratio only slightly differs by not morethan 10%. For unaged samples (Figure 9a), it can be observed that at a temperature of 60 °C, 6% LLDPE sample almost have G*/sin δ values greater than the minimum required 1.0 kPa.

For aged samples (Figure 9b), under the same temperature, 6% LLDPE sample have G*/sin δ ratios greater than the minimum required of 2.2 kPa. This indicates that 6% binder sample will have better rutting resistance both before and after aging. Generally, it shows that introduction of LLDPE polymer to bitumen binder significantly increased the ratio G*/sin δ which can lead to an enhancement in pavement resistance to permanent deformation.

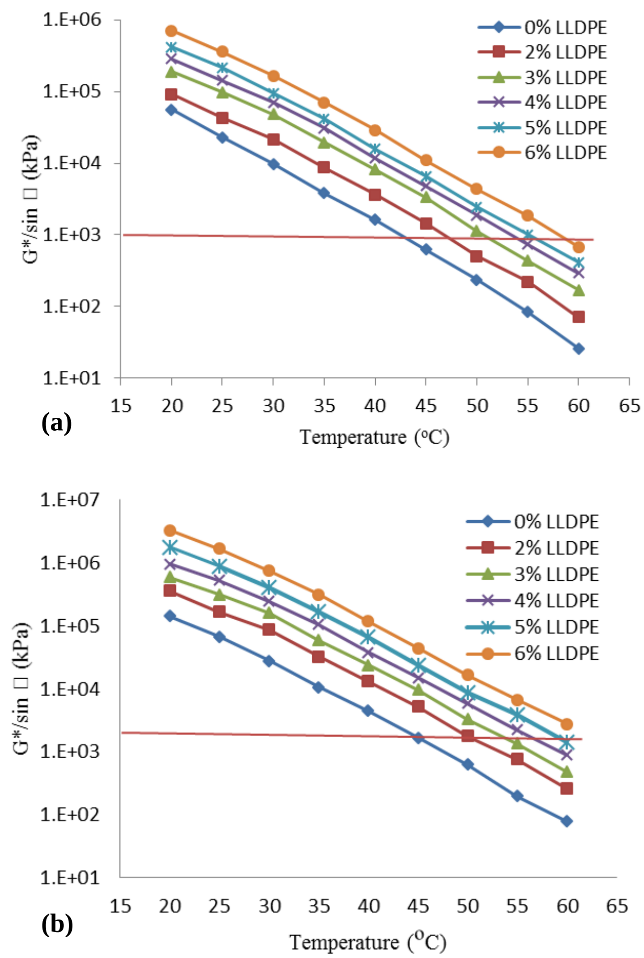


Figure 9 Temperature effects on the rutting parameter of (a) Unmodified and LLDPE modified binder before aging. (b) Unmodified and LLDPE modified binder after aging

3.4.4 Effect of LLDPE on Fatigue Resistance

Resistance of asphalt against fatigue defects was also estimated using results obtained from DSR tests. For estimating the fatigue resistance of the binder, DSR tests were carried out on PAV aged binders residue as described by Superpave criteria. To obtain the fatigue resistance, G*.sin δ of the binder were calculated, the Superpave criteria specifies a limitation value of 5000 kPa to be the highest fatigue cracking parameter [23].

Figure 10 shows the plot of temperature effect on fatigue resistance of unmodified and LLDPE modified binders. It is observed that, the minimum value for G*.sin δ was found in 6% LLDPE modified binder, and unmodified binder shows the largest value of G*.sin δ. It can be seen that G*.sin δ values for modified satisfied the minimum fatigue cracking parameter required by Superpave criteria at intermediate to the high temperature of 25 °C to 60 °C. The reduction in G*.sin δ value by increasing the LLDPE content indicates an improvement in the modified binder resistance against fatigue.

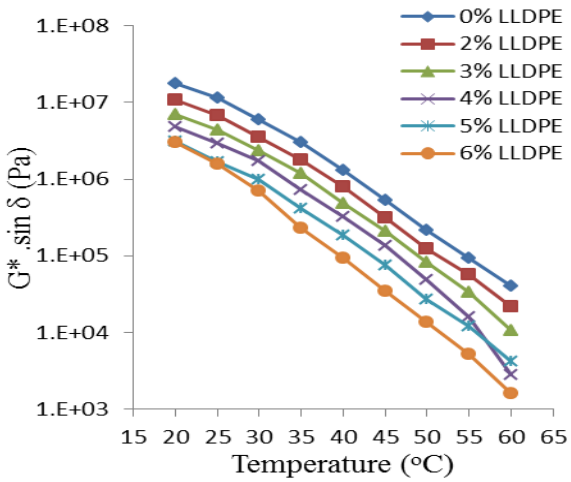


Figure 10 Temperature effect on fatigue parameter of unmodified and LLDPE modified binder after aging

3.4.5 Superpave Fail Temperature

Superpave fail temperature of bitumen binder is described as the temperature in which the ratio G*/sin δ falls under 1.0 kPa. The temperature at failure is used to describe the performance grade of bituminous binders [33]. Figure 11 shows the plot of the fail temperature of unmodified and LLDPE modified binders.

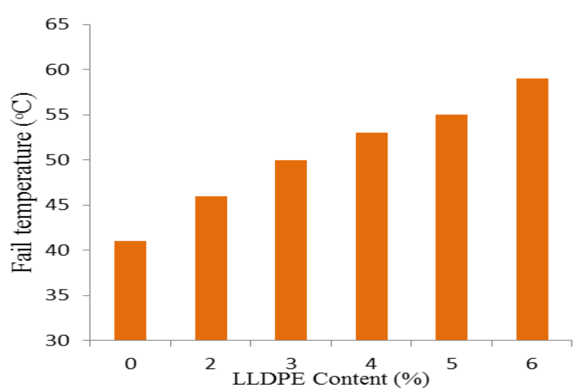


Figure 11 Superpave Fail temperatures of unmodified and LLDPE modified binders

It is observed that all LLDPE modified binders have higher fail temperature values of more than 48 °C compared to the unmodified binder with a least fail temperature value of around 40 °C. The fail temperature improves with an increase in LLDPE content. 6% LLDPE have the greatest fail temperature of 60 °C which makes it be more stable compared to other LLDPE modified binders.

3.5 Effects of Thermal Oxidative Aging on Rheology

3.5.1 Complex Modulus

The thermo oxidative aging for both unmodified and modified binders was simulated using RTFOT, aging index for complex modulus was estimated to evaluate the binders resistance against aging defects. Lower values of complex modulus aging index describe better resistance to aging while greater values indicate less aging resistance complex modulus aging index can be obtained from Eq. 2:

$$CAI = \frac{G^*_{(RTFOTaged)}}{G^*_{(Unaged)}} \qquad (2)$$

where *CAI* is the complex modulus aging index of the binder, $G^*_{(RTFOTaged)}$ and $G^*_{(Unaged)}$ are aged and unaged complex modulus respectively. Figure 12 shows the effects of LLDPE content on complex modulus aging index before and after RTFOT aging. It is observed that LLDPE polymer decreases the complex modulus aging index of modified binders compared with unmodified binders. Comparing LLDPE modified binders, the binder containing 6% LLDPE displays the lowest complex modulus aging index, with that, the LLDPE content enhances greatly the binders resistance to thermo oxidative aging. The enhancement in thermo oxidative aging resistance of the binders can be as a result of exfoliated structure formation by the LLDPE polymer that serves as a barrier between the binder and oxygen molecules.

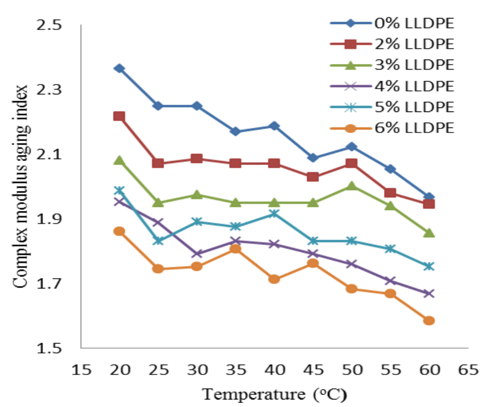


Figure 12 Complex modulus aging index of modified binders

3.5.2 Phase Angle

Phase angle aging index was evaluated to estimate the aging susceptibility for the modified binders. Under phase angle aging index, a lower value indicates a higher degree of binder aging. Phase angle aging index is evaluated using Eq. 3:

$$PAI = \frac{Aged_{(phaseangle)}}{Unaged_{(phaseangle)}} \quad (3)$$

where *PAI* is the phase angle aging index, *Aged* *(phaseangle)* and *Unaged* *(phaseangle)* are the phase angles before and after RTFOT aging. Figure 13 shows the effects of LLDPE content on the phase angle aging index before and after RTFOT aging. It is observed that LLDPE polymer increases the phase angle aging index of modified binders when compared with the unmodified binder. Similarly, comparing the LLDPE modified binders, the binder containing 6% LLDPE shows the largest phase angle aging index, due to that, binder's thermal oxidative aging resistance can be enhanced.

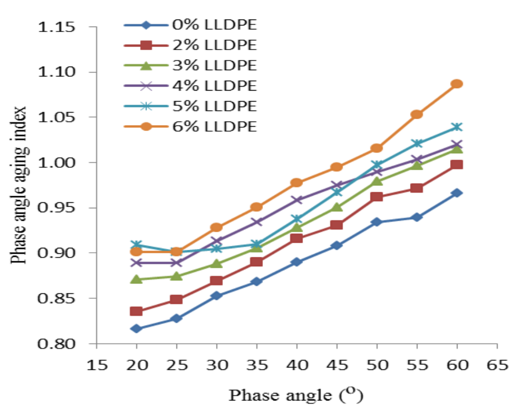


Figure 13 Phase angle aging index of modified binders

3.5.3 Viscosity

Generally, bitumen viscosity is dependent on test parameters which include temperature and shear rate [34]. Viscosity aging index (VAI) is another excellent parameter that fully describes the aging resistance properties of the binder; viscosity aging index is evaluated using Eq. 4:

$$VAI = \frac{Aged_{(viscosity)} - Unaged_{(viscosity)}}{Unaged_{(viscosity)}} \times 100 \quad (4)$$

where *VAI* refers to the viscosity aging index for the binders, *Aged* *(viscosity)* and *Unaged* *(viscosity)* are aged RTFOT viscosity and unaged viscosity of the binder. Figure 14 describes the aging effects on the viscosity of the binder after RTFOT aging.

Viscosity aging index of LLDPE modified samples is significantly less than that of unmodified samples. It is observed that VAI gradually reduces with increase in LLDPE contents. This shows that after aging LLDPE polymer can decrease viscosity and improve the resistance to thermal oxidative aging of modified binders. This might happens because, during the time of binder aging, naphthene aromatics are partly converted into polar aromatics, also the polar aromatics are converted into asphaltenes causing an increase in asphaltene content. Due to these changes in composition, the LLDPE polymer prevents loss of volatile components in the binder especially at high temperatures and disturbs the formation of large molecules. The finding corresponds to phenomena reported by McNally T. et al [35].

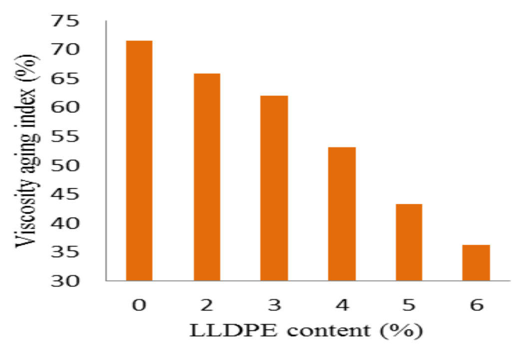


Figure 14 Viscosity aging index of modified binders

3.5.4 High Temperature Aging Index

High temperature aging indices (HTAI) is applied for evaluation of changes in rheological behaviors at different oxidation levels. A higher value of HTAI indicates less resistance of bitumen binder to aging as obtained from Eq. 7 [3].

$$HTAI = \frac{G^*/\sin\delta_{(RTFOTaged)}}{G^*/\sin\delta_{(Unaged)}} \quad (5)$$

where *HTAI* is the high temperature aging index for the binder, *G*/ sin δ* *(RTFOT aged)* and *G*/ sin δ* *(Unaged)* are G*/ sin δ ratios of RTFOT aged and unaged bitumen binders. Figure 15 shows the high temperature aging index of unmodified and LLDPE modified binders.

It can be seen that, 5 and 6% LLDPE modified binders have the least temperature aging index after RTFOT. It is evident that high temperature aging depends on the concentration of polymer used on bitumen modification and increasing polymer content tends to minimize the increase in stiffness after bitumen aging. Moreover, comparing with base bitumen, the LLDPE modified binders decreases high temperature aging susceptibility by almost 40% due to a decrease in oxidation in the binder.

The ratio G*/ sin δ increment after aging is also used to describe the susceptive aging degree in bitumen binder. G*/ sin δ increment is expressed as ΔG*/ sin δ which is calculated using Eq. 6:

$$\Delta G^*/\sin\delta = G^*/\sin\delta_{(Aged)} - G^*/\sin\delta_{(Unaged)} \quad (6)$$

where $\Delta G^*/\sin\delta$ is the increment in $G^*/\sin\delta$ ratio after aging. $G^*/\sin\delta_{(Aged)}$ and $G^*/\sin\delta_{(Unaged)}$ are $G^*/\sin\delta$ ratios of bitumen binders before and after aging respectively. Figure 16 shows the $G^*/\sin\delta$ increment after RTFOT aging Comparing the LLDPE modified with unmodified binders, the $G^*/\sin\delta$ increment decreased with increase in polymer content. This implies that LLDPE decreases oxidation in the binder, which in turns reduces hardening process within the binder during aging. It is evident that 5% and 6% LLDPE shows the least $G^*/\sin\delta$ increment, indicating that, this modified binders will be more resistance to aging.

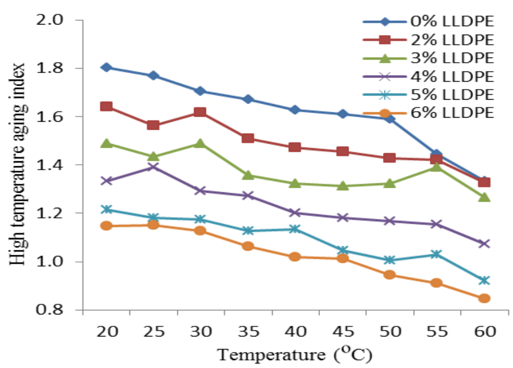


Figure 15 Effect of high temperature aging on unmodified and LLDPE modified binders

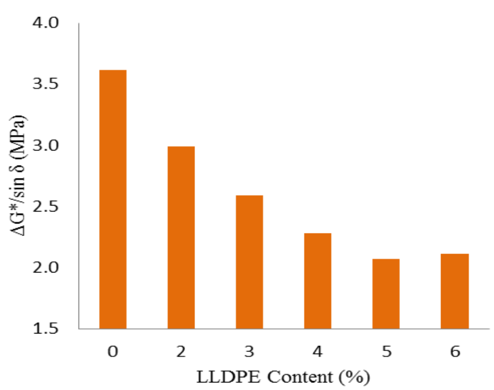


Figure 16 Effect of aging on $G^*/\sin\delta$ of unmodified and LLDPE modified binders

3.6 Effects of Thermal Oxidative Aging on Conventional Properties

3.6.1 Penetration Aging Ratio

The penetration aging ratio is also used to describe the aging effects of bitumen binder on the physical properties. Penetration aging ratio (PAR) reflects the changes in properties of bitumen binder after aging process; PAR is evaluated using Eq. 7:

$$PAR = \frac{Penetration_{(Aged)}}{Penetration_{(Unaged)}} \times 100 \quad (7)$$

where *PAR* is penetration aging ratio of bitumen binder. *Penetration* $_{(Aged)}$ and *Penetration* $_{(Unaged)}$ are aged penetration and unaged penetration of the bitumen binder. Figure 17 shows the aging effects on the penetration ratio of unmodified and LLDPE modified binders. From the results, it was observed that penetration of both modified and unmodified binders shows a reduction after thermo oxidative aging, which leads to decrease in the penetration ratio. Penetration aging ratio decrease with the addition of LLDPE polymer, this implies that the aging susceptibility of the binders decreases after modification and also the resistance of the binder to thermo oxidative aging was enhanced.

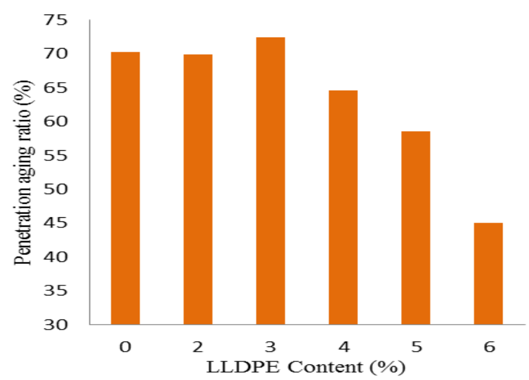


Figure 17 Penetration aging ratio of unmodified and LLDPE modified binders

3.6.2 Softening Point (Softening Point Increment Δ*S*)

The changes in softening point values before and after RTFOT aging are also investigated as a good indicator to measure the degree of aging in bitumen binder. The softening point increment defined by ΔS serves as an indicator to evaluate aging properties. Softening point increment is calculated using Eq. 8.

$$\Delta S = \text{Softening point}_{(Aged)} - \text{Softening point}_{(Unaged)} \quad (8)$$

where ΔS refers to increment in softening point, Softening point (aged) is aged softening point value, and Softening point (unaged) is the unaged softening point value. Figure 18 describes the effect of aging on modified and unmodified bitumen binder based on softening point changes after RTFOT aging.

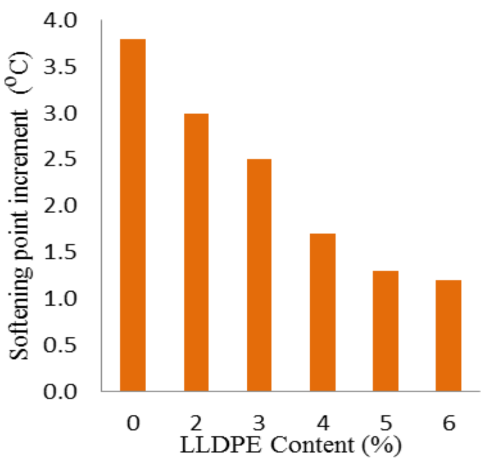


Figure 18 Softening point increment of unmodified and LLDPE modified binders

It can be seen that the softening point of unmodified binders and LLDPE modified binders shows an increase after RTFOT aging. However, comparing the binders, LLDPE modified binder shows the lowest softening point increment (ΔS). It is observed that 6% LLDPE binder having the highest polymer content shows the least softening point increment. This happened because during aging of bitumen, the content of fractions having the higher molecules increases, while content of the small molecules decreases and LLDPE in the binder restricts the oxidation within the binder, which in turns decreases the hardening process and improving the aging resistance. A similar phenomenon was also reported by Mashaan et.al [36].

4.0 CONCLUSION

Laboratory tests conducted were used to investigate rheological and aging properties of LLDPE modified binders. Based on these research outcomes, the overall conclusions achieved are summarized as follows:

a. Conventional properties tests (penetration, and softening point tests) showed that the hardness of modified binders increases, thus result leads to higher temperature susceptibility enhancement
b. From isochronal plots, it is revealed that an additional increase in stiffness (complex modulus) occurs due to enhanced temperature susceptibility for the modified binders, compared with the base bitumen which significantly shows a smaller complex modulus
c. Penetration index values obtained for the binders when LLDPE was added into indicates that, the temperature susceptibility of modified binders improved.
d. From fatigue and rutting parameters, it can be concluded that application of LLDPE polymer for binder modification improves the binder resistance against rutting defects under high temperatures and better resistance against fatigue.
e. RTFOT aging results indicate that LLDPE modified bitumens have the least complex modulus aging index and higher phase angle aging index compared with unmodified binders. This indicates their high ability to resist thermo oxidative aging.
f. The rheological aging indices obtained shows that addition of LLDPE polymer delays the thermo oxidative aging process within the binder modified binder; this was reflected through decrease in the rheological aging indices among all the binders
g. Based on effects of LLDPE polymer on both rheological and other physical properties tested before and after aging, it can be concluded that the optimum LLDPE content is 6%.

Acknowledgement

The authors like to express their gratitude to Universiti Teknologi PETRONAS (UTP) for providing all necessary facilities, with a conducive and well equipped laboratory in running the experiments and also to all technologist in Highway Laboratory of Civil Engineering Department.

References

[1] Airey, G. D. 2002. Use of Black Diagrams to Identify Inconsistencies in Rheological Data. *Road Materials and Pavement Design*. 3(4): 403-424.
[2] J. Yu, L. Wang, X. Zeng, S. Wu, and B. Li. 2007. Effect of Montmorillonite on Properties of Styrene–butadiene–styrene Copolymer Modified Bitumen. *Polymer Engineering & Science*. 47: 1289-1295.
[3] S. Dessouky, C. Reyes, M. Ilias, D. Contreras, and A. Papagiannakis. 2011. Effect of Pre-heating Duration and Temperature Conditioning on the Rheological Properties of Bitumen. *Construction and Building Materials*. 25: 2785-2792.
[4] C. Fang, T. Li, Z. Zhang, and D. Jing. 2008. Modification of Asphalt by Packaging Waste-polyethylene. *Polymer Composite*. 29: 500-505.
[5] K. H. Mustafa, M. M. A. Aziz, M. Rosli, A. A. Z. Hainin, and M. N. M. Warid. 2016. A Review on Crack Relief Layer (crl) in Roads and Highways. *Jurnal Teknologi.* 78(7–3): 45–52.
[6] G. D. Airey. 2003. Rheological Properties of Styrene Butadiene Styrene Polymer Modified Road Bitumens. *Fuel.* 82: 1709-1719.
[7] T. A. Khan and D. Sharma. 2011. Effect of Waste Polymer Modifier on the Properties of Bituminous Concrete Mixes. *Construction and Building Materials*. 25: 3841-3848.
[8] N. Bala and I. Kamaruddin. 2016. Physical and Storage Stability Properties of Linear Low Density Polyethylene at Optimum Content. *Engineering Challenges for Sustainable Future: Proceedings of the 3rd International Conference on Civil, Offshore and Environmental Engineering (ICCOEE 2016, Malaysia*. 395.
[9] R.-m. Ho, A. Adedeji, D. W. Giles, D. A. Hajduk, C. W. Macosko, and F. S. Bates. 1997. Microstructure of Triblock

Copolymers in Asphalt Oligomers. *Journal of Polymer Science Part B Polymer Physics*. 35: 2857-2877.

[10] M. Cortizo, D. Larsen, H. Bianchetto, and J. Alessandrini. 2004. Effect of the Thermal Degradation of SBS Copolymers During the Ageing of Modified Asphalts. *Polymer Degradation and Stability*. 86: 275-282.

[11] F. Navarro, P. Partal, M. García-Morales, M. Martín-Alfonso, F. Martinez-Boza, C. Gallegos. 2009. Bitumen Modification with Reactive and Non-reactive (Virgin and Recycled) Polymers: A Comparative Analysis. *Journal of Industrial and Engineering Chemistry.* 15: 458-464.

[12] J. Zhu, B. Birgisson, and N. Kringos. 2014. Polymer Modification of Bitumen: Advances and Challenges. *European Polymer Journal*. 54: 18-38.

[13] E. Shaffie, J. Ahmad, A. K. Arshad, D. Kamarun, and H. Awang. 2016. Investigation on Rutting Performance of Nanopolyacrylate and Natural Rubber Latex Polymer Modified Asphalt Binder Mixes. *Jurnal Teknologi.* 78: 11-15.

[14] A. Al-Hadidy and T. Yi-qiu. 2009. Effect of Polyethylene on Life of Flexible Pavements. *Construction and Building Materials*. 23: 1456-1464.

[15] Y. Yildirim. 2007. Polymer Modified Asphalt Binders. *Construction and Building Materials*. 21: 66-72.

[16] G. Polacco, J. Stastna, D. Biondi, and L. Zanzotto. 2006. Relation between Polymer Architecture and Nonlinear Viscoelastic Behavior of Modified Asphalts. *Current Opinion in Colloid & Interface Science*. 11: 230-245.

[17] I. Gawel and K. Baginska. 2004. Effect of Chemical Nature on the Susceptibility of Asphalt to Aging. *Petroleum Science and Technology*. 22: 1261-1271.

[18] D. Lesueur. 2009. The Colloidal Structure of Bitumen: Consequences on the Rheology and on the Mechanisms of Bitumen Modification. *Advances in Colloid and Interface Science*. 145: 42-82.

[19] J. C. Petersen. 2009. A Review of the Fundamentals of Asphalt Oxidation: Chemical, Physicochemical, Physical Property, and Durability Relationships. *Transportation Research Board.* 140: 1-78.

[20] X. Lu and U. Isacsson. 2000. Artificial Aging of Polymer Modified Bitumens. *Journal of Applied Polymer Science*. 76: 1811-1824.

[21] D. Swiertz. 2010. *Asphalt Aging Characteristics, Rheological Implications and Laboratory Techniques*. University of Wisconsin-Madison.

[22] W. Fernández, H. Rondón, and F. Reyes. 2012. A Review of Asphalt and Asphalt Mixture Aging. *Ingeniería e Investigación*. 33: 5-12.

[23] T. W. Kennedy, G. A. Huber, E. T. Harrigan, R. J. Cominsky, C. S. Hughes, H. Von Quintus. 1994. Superior Performing Asphalt Pavements (Superpave): The Product of the SHRP Asphalt Research Program. Strategic Highway Research Program, *National Research Council*. Report No. SHRP-A-410.

[24] S. A. Hesp, S. Iliuta, and J. W. Shirokoff. 2003. Reversible Aging in Asphalt Binders. *Energy & Fuels*. 21: 1112-1121.

[25] J. Read and D. Whiteoak. 2003. *The Shell Bitumen Handbook*. Thomas Telford Publishers, Institution of Civil Engineers (ICE) United Kingdom.

[26] N. Dehouche, M. Kaci, and K. A. Mokhtar. 2012. Influence of Thermo-oxidative Aging on Chemical Composition and Physical Properties of Polymer Modified Bitumens. *Construction and Building Materials*. 26: 350-356.

[27] J. Petersen, R. Robertson, J. Branthaver, P. Harnsberger, J. Duvall, S. Kim. 1994. Binder Characterization and Evaluation: Volume 1. Rep. No. SHRP-A-367, Strategic Highway Research Program. National Research Council, Washington, DC.

[28] C. Vallés, R. J. Young, D. J. Lomax, and I. A. Kinloch. 2014. The rheological behaviour of concentrated dispersions of graphene oxide. *Journal of Materials Science*. 49: 6311-6320.

[29] A. Pérez-Lepe, F. Martínez-Boza, and C. Gallegos. 2005. Influence of Polymer Concentration on the Microstructure and Rheological Properties of High-density Polyethylene (HDPE)-modified Bitumen. *Energy & Fuels.* 19: 1148-1152.

[30] N. I. M. Yusoff, D. Mounier, G. Marc-Stéphane, M. R. Hainin, G. D. Airey, and H. Di Benedetto. 2013. Modelling the Rheological Properties of Bituminous Binders Using the 2s2p1d Model. *Construction and Building Materials*. 38: 395-406.

[31] X. Lu and U. Isacsson. 1997. Characterization of Styrene-Butdiene-styrene Polymer Modified Bitumens-comparison of Conventional Methods and Dynamic Chemical Analyses. *Journal of Testing and Evaluation*. 25: 383-390.

[32] G. D. Airey. 2002. Use of Black Diagrams to Identify Inconsistencies in Rheological Data. *Road Materials and Pavement Design*. 3: 403-424.

[33] F. Xiao, S. Amirkhanian, H. Wang, and P. Hao. 2014. Rheological Property Investigations for Polymer and Polyphosphoric Acid Modified Asphalt Binders at High Temperatures. *Construction and Building Materials*. 64: 316-323.

[34] M. S. Samsudin, A. K. Arshad, J. Ahmad, and K. A. Masri. 2016. Microstructure of Nanosilica Modified Binder by Atomic Force Microscopy. *Jurnal Teknologi*. 78: 33-44.

[35] T. McNally. 2011. Introduction to Polymer Modified Bitumen. *Polymer Modified Bitumen Properties and Characterisation*. Woodhead Publishing Limited, Cambridge.1-15.

[36] A. H. Ali, N. S. Mashaan, and M. R. Karim. 2013. Investigations of Physical and Rheological Properties of Aged Rubberised Bitumen. *Advances in Materials Science and Engineering.* 13: 1-7.