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Rheological Properties and Application of Molasses Modified Bitumen in Hot Mix Asphalt (HMA)

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Abstract

The high volume of water in molasses has made this study serious. The reason is that using molasses as a partial replacement without treatment significantly affects the rheological properties of the neat bitumen and increases the likelihood of moisture susceptibility of the hot-mix asphalt (HMA) pavement structure and create fractures of aggregate particles. Therefore, to use molasses as a partial replacement without affecting the structural integrity of the pavement, this study proposed a treatment method before blending it with petroleum-based bitumen. A series of experiment was conducted to accomplish the objective of this paper, including convectional tests, Fourier transform infrared (FTIR) test, amplitude and frequency sweep test, performance grade (PG) determination test, and multiple stress creep recovery (MSCR) tests. The IR spectra show that carbonyl index decreased with increasing molasses percent. There was PG improvement from the control grade to PG64 and PG70 when the base binder modified with 5-20% molasses and aged with rollingl thin film oven (RTFO) respectively. At the temperature 58°C nonrecoverable creep compliance at 3.2 kPa ($J_{nr3.2kPa}$) was decreased for each percent replacement. This led to improving the rutting potential. As well, at a temperature of 64°C the J_{nr} value was decreased only for 5% replacement, and then the J_{nr} value was gradually increased for the remaining percent replacement. Overall, this study revealed that treated molasses can be used as a partial replacement to enhance the rheological properties of the base bitumen and thus it can potentially be used to produce a sustainable bio-asphalt binder.

Keywords: MMB; DSR; FTIR; hot mix asphalt.

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1. Introduction

The role of using bio-asphalt in new asphalt mixtures is currently considered as one of the main alternatives for the reduction of environmental and health effect, the final cost of hot-mix asphalt (HMA) pavement construction, and minimize strong demand of conventional asphalt binder[1–10]. Some of these bio-binders studied and showed promising results include: sugar cane molasses [11–14], beet molasses[15], swine manure[1,16–18], waste cooking oil[6], [19–21], and wood waste [22,23]. However,the study shows that bio-asphalts are highly moisture susceptible due to high volume water content and moisture can have a profound effect on the durability of HMA pavement. Therefore, this study designed to show how can be used sugar-cane molasses in HMA without affecting the rheology and the structural integrity ofpavement.The use of sugar cane molasses as a replacement for bitumen in pavement construction has a lesser environmental impact and cheap construction cost than that of bitumen. It reduces the greenhouse gas emission by up to 30%, and it is also cost-effective and improves the thermal durability of asphalt pavement [24].A few research studies have been conducted on partial replacement of bitumen with molasses inHMA to determine the optimum percentage replacement.Some of the values claimed to be optimum values include 4.7% [13] and 13-15% [25] for 30 viscosity grade bitumen, 0-3% [26] and 9% [12] for 60/70 penetration grade bitumen, and 0-10% [15] and 5-20% [11] for 50/70 penetration grade bitumen. The agreement between the research outcomes is that the partial replacement of bitumen with molasses can improve the performance of the pavement. Even if, the studies have been valuable, but the studies did not provide any solution or information about the significant negative effects of high volumewater content in molasses. Also, they did not provide in-depth and sufficient information on the rheological properties and chemical composition of molasses modified bitumen. Whereas, this study examines, (a) the effect of water in molasses on adhesion and cohesion properties of the binder and its solution, (b)the chemical and rheological properties of molasses and molasses modified petroleum-based asphalt.

2. Materials and methods

2.1. Materials

2.1.1. Bitumen

According to thetemperature zone mapping of Ethiopia forthe binder performance grading (PG) system, bitumen grade PG58-10 is the commonly usedasphalt binder in most parts of the country[27]. Therefore, the same bitumen grade was used in this research study.The properties of the PG58-10 bitumen are discussed under the methodologies section.Bitumen PG58-10 is referred as a base binder (BB) henceforth.

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2.1.2. Molasses

Molasses (M) is a thick, sticky, dark borown syrup obtained from sugar industries as a waste of sugar cane or sugar beet processing [14]. The molasses used in this research study was obtained from Kuraz Sugar Factory in Ethiopia, located about 760 km south of Addis Ababa city [28].Sugar cane molasses was used as a partial replacement for petroleum-based neat asphalt (BB) to prepare bio-asphalt binder or molasses-modified binder (MMB). The water content of the molasses, which was 24.9% by weight, was reduced before blending with (BB) using distillation processes.Molasses was selected as the bio-rejuvenator of the BB, because molasses is compatible with the BB[11], [29], and [30].

The properties of the BB and molasses are discussed with togher with the results of the research study to comparethem with those of the MMB's.

2.1.3. Aggregate

The aggregates used in this research study were granite obtained from Deneba, about 350 km south west of the city of Addis Ababa, Ethiopia. The selection of the gradation was done followingSuperPave®[31] procedure with a nominal maximum aggregate size of 19mm. SuperPave is a mix design procedure and binder specification developed by a strategic highway research program (SHRP). SuperPave® gradation curve was selected for good particle interlocking, sufficient voids in mineral aggregate (VMA), and dense-graded HMA[31,32]. All properties of the aggregate were determined in accordance with ASTM or BSI standard procedures, and the test results are presented in Table 2 and Fig.1.

Table 1Characteristics of aggregate

Sieve Size (mm)	Properties	Result	Specification	Standard Test Method
25-4.75	Bulk specific gravity (SG)	2.74 g/cm3	*	ASTM C-127–68
	Apparent SG	2.85g/cm3	*	ASTM C-127–68
	Water absorption	1.1%	<2%	ASTM C-127–68
	Soundness	4.63%	10-20%	ASTM C-88
	Flakiness index	4.00%	<10%	BS 812
	Elongation index	6.50%	<10%	BS 812
	Impact value (IV)	6.59%	<30%	BS 812:112.

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	Crushing value (CV)	12.65%	<35%	BS 812:110
	Los-Angeles Abrasion LAT	9.46%	35-45%	ASTM C:131-69
4.75-0.075	SG	g/cm3	*	ASTM C-127–68
	Apparent SG	g/cm3	*	ASTM C-127–68
	Water absorption	1.2 %	<2%	ASTM C-127–68
	Angularity	78%	>45%	AASHTO T33
0.075	SG	2.706 g/cm3	*	ASTM C-127–68

*NA=Not applicable

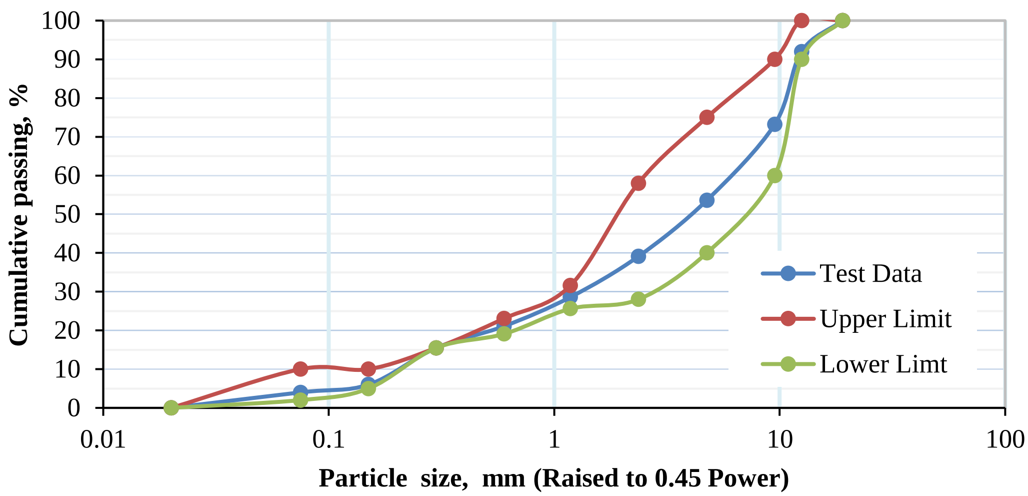

Figure 1 Aggregate particle size distribution curve

2.2. Methodologies

The first phase of the research study involved the determination of the properties of the materialsused,and the results were compared with the relevant specifications. Water content, penetration, softening point, ductility, flash and fire point tests were some fo the tests carried out on the binders.In the second phase, the optimal binder content was determined to be 5.5%, and this value was used as a control for the binder content of the mix; bio-asphaltbinder mix containing 5%, 10%, 15%, and 20%by weight of molasses as a partial placementfor the base bitumen were prepared.The study sample range matrix is presented inTable 2.Then, Fourier transform infrared (FTIR) spectrometer test was carried out on the molasses, BB, and MMB to

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know the functional group and change in chemical composition before and after blending the modifier.

Table 2Asphalt binder sample range matix and definition

Binder	Definition
BB	Base bitumen, traditional petroleum asphalt
M	Molasses
MMB	molasses-modified binder
MMB5	95%Base Bitumen Blended With 5% Molasses
MMB10	90%Base Bitumen Blended With 10% Molasses
MMB15	85%Base Bitumen Blended With 15% Molasses
MMB20	80%Base Bitumen Blended With 20% Molasses

In the third phase, experiments were settled to conduct a compressive range of SuperPave® binder specification tests such a rotational thin film oven (RTFO) test, dynamic shear rheometer (DSR) test, frequency sweep test (FST), amplitude sweep test (AST), multiple stress creep recovery (MSCR) test, and PG determination test. These tests were carried out to evaluate the high, intermediate, and low-temperature rheological properties and performances of the BB and MMB’s. The entire sequence of the experimental program is presented in Fig. 2.

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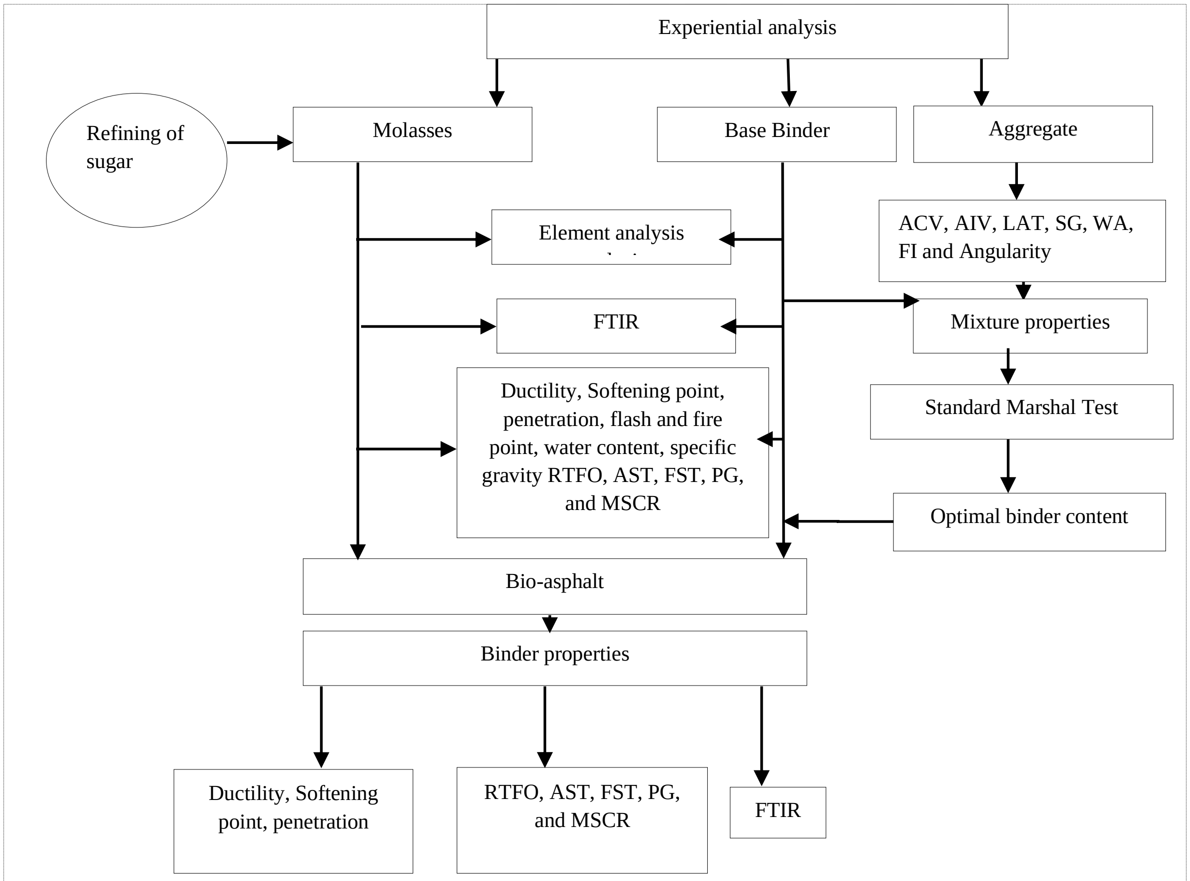

FTIR=Fourier transform infrared, RTFO=Rotation tiny film oven, AST=Amplitude sweep test, FST=Frequency sweep test, PG=Performance grade, MSCR=Multiple stress creep recovery ACV=Aggregate cursing value, AIV=Aggregate impact value, LAT=Loss-angels abrasion test, SG= Specific gravity

Figure 2 Experimental flow chart of the research study

During the distillation process, molasses was heated to a temperature close to, but not exceeding, 80 °C to avoid foaming. Then, the BB was uniformly heated at a temperature of 110°C until it turned into a liquid phase and immediately blends with the heated molasses per the specified percentages (5, 10, 15, and 20% of molasses). Each blend was mixed in a shear mixer at a speed of 4000 rpm for 30 min to get homogeneously mixed blend of MMB[6], [33–35]. The steps followed in the preparation of the bio-asphalt binder are shown in **Error! Reference source not found.**.

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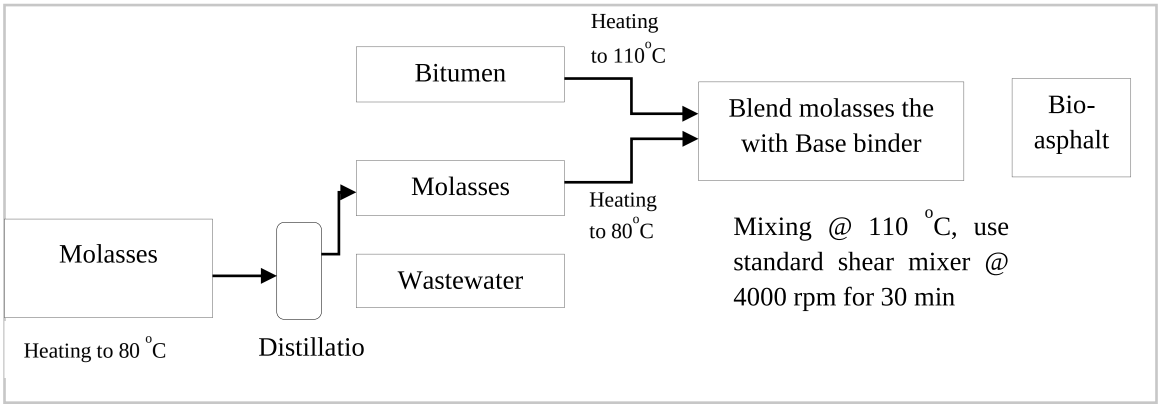

Figure 3 Molasses modified bio-binder (MMB) preparation

2.2.2. Fourier transform infrared (FTIR) spectrometer

FTIR is a common method used by organic chemistry to identify the various functional groups, areas, and levels of the peak in a single chemical compound. FTIR graph illustrates absorbance/transmittance versus wave number. In this respect, the Y-axis shows absorbance ranging from 0-100% and X-axis represent wave number ranging from 4000-500 cm-1(>1500 called functional group region and <1500 fingerprint region). The peak is classified as strong, moderate, and weak[36,37].

Fourier Transform Infrared (FTIR) Spectrometer analysis was carried out on the BB, molasses, and bio-asphalt binders using Spectrum Two™ equipment. The functional group and area of the peak were determined, and the fully absorbed and decreased indexes were detected.

The FTIR spectrometer test was performed to evaluate the chemical structure of the aged binder samples, before and after the addition of molasses. This study uses the parameter such as carbonyl index($I_{C=O}$) and sulphoxide index ($I_{S=O}$) to characterize the oxidation of the binder [38]. The researchers proposed a quantitative analysis for the two indexes as follow:

$$I_{C=O} = \frac{Area\ of\ the\ carbonyl\ bond\ around\ 1{,}700cm^{-1}}{Area\ of\ the\ spectral\ band\ between\ 2000cm^{-1}\ and\ 600\ cm^{-1}} \quad (1)$$

$$I_{S=O} = \frac{Area\ of\ the\ \text{sulphoxide}\ bond\ around\ 1{,}030\ cm^{-1}}{Area\ of\ the\ spectral\ band\ between\ 2000cm^{-1}\ and\ 600cm^{-1}} \quad (2)$$

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2.2.3. Rotational thin film oven (RTFO) test

Short-term aging and loss on heating tests were conducted using RTFO test, according to AASHTO T 240[39]for the BB and MMB[20]. Eight samples were heated in RTF oven at 163 °C for 85min, and the loss in mass was determined for each sample.

2.2.4. Dynamic shear rheometer (DSR) test

Bohlin dynamics shear rheometer instrument was used to characterize the rheological properties (Viscous and elastic behaviors) of the aged and un-aged BB and BBM's at low and high temperature gradients using 8 mm and 25mm movable plates[9,17,40]. The rutting indexes (G*/sinδ) and phase angles of the binders at 0.1 Hz, 1 Hz and 10 Hz were also determined. The phase angle and rutting index were used to characterize the viscoelastic properties and to predict the rutting resistance of the binders, respectively.

2.2.5. PG determination test

Performance-grade (PG) test was performed on RTFO-aged and un-aged BB and MMB's using DSR equipment in accordance with AASHTO T-315[41]testing procedure. The test was carried out in 25 mm diameter plates spaced at 1 mm moving at a constant frequency of 10 rad/sec with 10% strain for the RTFO-aged binders and 12% strain for the un-aged binders. The test temperature started at 52 °C and was gradually increased until the test was completed. The test was used to determine the permanent deformation parameter (G*/sinδ) and to categorize the PG.

2.2.6. Frequency sweep test (FST)

A frequency sweep test was performed using DSR SuperPave instrument for the RTFO-aged and un-aged BB & MMB's in accordance with AASHTO-315 [41]A strain-controlled test with frequency between 0.1Hz and 25Hzwas carried out at a temperatures of 10°C, 21.1°C, 37.8°C, 52°C, 58°C, 64°C, and 70°Cand with a constant strain amplitude. Before conducting the FST, a strain sweep test was performed to measure the limit of the linear viscoelastic (LVE) region for all the binders and the test temperatures. The FST test results were used to construct the isothermal plot, black space diagram, and master curve used to evaluate the rheological property of the binders at different temperatures and frequencies.

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2.2.7. Dynamics modulus master curve

The master curve of the complex modulus of the BB and MMB with 5, 10, 15 and 20 % by weight molasses were constructed using the time-temperature equivalent principle[42,43]. The reference temperature was 58◦C (high), 37.8◦C (intermediate), and 10◦C (low). In this study, a sigmoidal function were used to fit and smoothen the test results at different temperatures and construct the master curve[44] of complex modulus by means of Microsoft excel solver; the principle is shown in Equation (3).

$$\log|G*| = \delta + \frac{\alpha}{1+e^{\beta+\gamma(\log f_t)}} \quad (3)$$

Where α, β, δ, and γ are sigmoid function constants, f_t isreduced frequency, and |G*| is complex shear modulus.

2.2.8. Multiple stress creep recovery (MSCR) test

Bohlin Dynamic Shear Rheometer (DSR) instrument was used to perform MSCR test for RTFO-conditioned BB and MMB's in accordance with AASHTO T-350 standard procedure[45]. The test was used to evaluate the non-recoverable creep compliance (J_{nr}), which is the measure of the binder's potential for a permanent deformation (rutting) under cyclic loading[46,47]. During the test, the applied stress level started witha 0.1 kPa and, after 10 creep/recover cycles, the stress level was increased to 3.2 kPa. The J_{nr} was calculated as a residual strain in a specimen after creep/recover cycles divide by the applied stress.

3. Results and Discussions

3.1. FTIR test results

The FTIR test results for the BB, molasses and MMB's containing 5% and 10% molasses are presented in

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Table 3.To identify the MMB with a specific molasses content is represented by the acronym MMB followed by a numeral representing the percent of molasses. MMB5, for example, represents a molasses-modified binder containing 5% molasses.

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Table 3Typical index from FTIR test for BB, MMB5, and MMB10

Index	BB	Molasses	MMB5	MMB10
$I_{C=0}$	0.0059	0.0068	0.0062	0.0067
$I_{S=0}$	0.0011	0.0029	0.0013	0.0013

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Table 3illustrates that the MMB recorded higher carbonyl and sulphoxide indices then the BB (PG58-10). This indicates that the stiffness behavior and potential of aging of PG58-10 are improved.

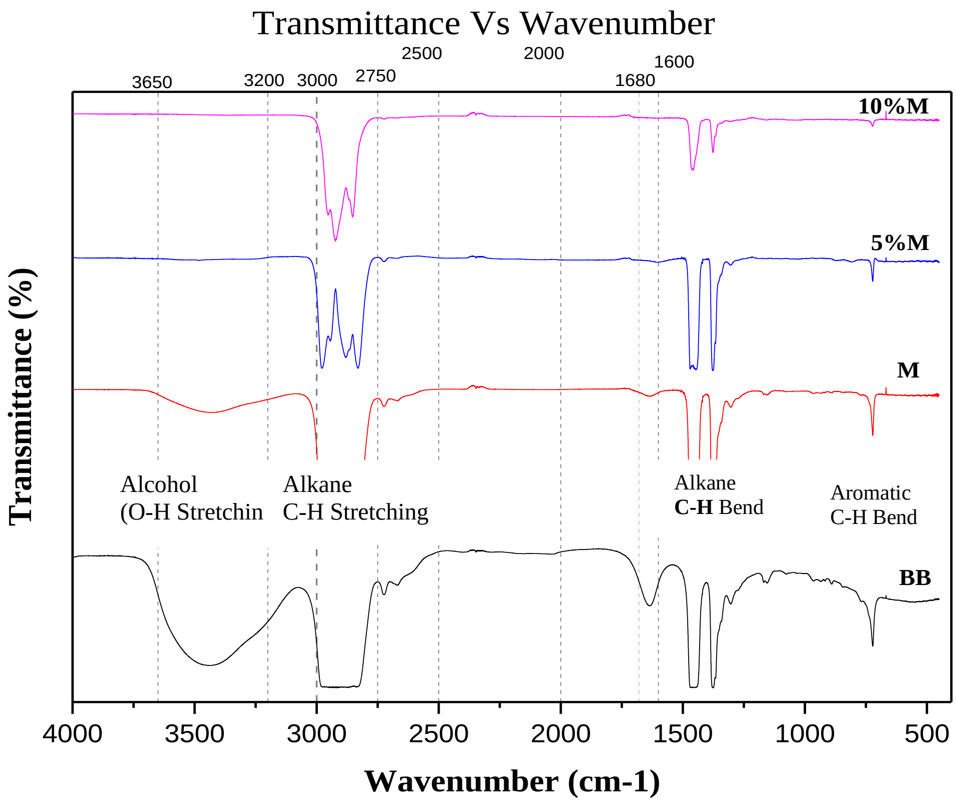

Figure 4 FTIR Spectra of un-aged BB, M, MMB5, and MMB10

The FTIR spectroscopy test results are also elaborated in **Error! Reference source not found.**. The results indicate that the observed absorbance peaks for M and BB are similar. This could be an indication that there were no significant variations between the functional groups, even if any chemical reaction took place during the mix of the molasses with the control binder BB. In the case of MMB5 and MMB10, peak functional groups between wave numbers 3550 cm^{-1} and 3425 cm^{-1} (Alcohol) were fully disappeared. This exemplifies that the alcohol reacted with oxygen at high temperature while preparing the MMB. Those around wave number 750cm^{-1}(Aromamins) are partially absorbed. The functional groups determined based on the FTIR test is presented in **Error! Reference source not found.**.

Table 4 FTIR Spectra Functional Group

Asphalt binder	Region	Wave number (cm^{-1})	Functional group	Intensity	Signal

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BB	Diagnostic or Functional group region (FGR)	3600-3300	O-H stretching	Alcohol	Strong	Broad
		3000-2840	C-H Stretching	Alkanet	Strong	Broad
		2800-2750	C-H Bend	Aldehyde	Weak	Sharp
		2720-2700	C-H Stretching	Aldehyde	Weak	Sharp
		1680-1600	C=C Stretching	Alkene	Medium	Sharp
	Finger Print region (FPR)	1470-1450	C-H Bend	Alkane	Strong	Sharp
		1365-1350	C-H Bend	Alkane	Strong	Sharp
		1300-1260	C-N Bend	Aromamins	Weak	Sharp
		775-725	C-H Bend	Aromatic	Medium	Sharp
M	FGR	3600-3300	O-H stretching	Alcohol	Strong	Broad
		3000-2840	C-H Stretching	Alkane	Strong	Broad
		1680-1600	C=C Stretching	Alkene	Weak	Board
	FPR	1470-1450	C-H Bend	Alkane	Strong	Sharp
		1365-1350	C-H Bend	Alkane	Strong	Sharp
		775-725	C-H Bend	Aromatic	Weak	Sharp
MMB5	FGR	29090-2940	C-H Stretching	Alkane	Strong	Sharp
		2925-2875	C-H Stretching	Alkane	Strong	Sharp
	FPR	1425-1375	C-H Bend	Alkane	Strong	Sharp
		1350-1320	C-H Bend	Alkane	Strong	Sharp
		775-725	C-H Bend	Aromatic	Weak	V.Sharp
MMB10	FGR	2960-2875	C-H Stretching	Aldehyde	Strong	Broad
	FPR	1450 1400	C-H Bend	Alkane	Medium	Sharp

3.2. RTFO test results

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The RTFO test results as a percentage loss in mass of BB and MMB's specimens are presented in Table 5.The results of two specimens for each mix are presented.

Table 5 Loss on heating for BB and MMB's

Binder	BB		BB5		BB10		BB15		BB20	
Specimen	S1	S2	S1	S2	S1	S2	S1	S2	S1	S2
Change in mass (%)	0.10	0.07	1.022	0.971	1.907	1.977	2.096	2.048	2.103	2.134
Average loss (%)	**0.623**		**0.996**		**1.94**		**2.048**		**2..118**	

According to AASHTO M-320 PG specifications, the mass change in the asphalt binder should not exceed 1%[48]. Based on the specification limit, BBM5 meets the requirements. The results indicate that the loss in mass increases with the increase in the content of molasses. This could be due to high water content of molasses and the loss of the water due to evaporation during aging in the RTFO (163°C for 85mints). The loss of mass is expected to increase with the increase in the content of molasses. Therefore, a high percent of replacements at high temperatures should be considered with serious cautions due to the high water content of molasses.

3.3. Performance grade (PG)

The rutting resistance parameter G*/Sinδ of the un-aged and RTFO-aged MMB's are shown in Table 6 and Table 7, and the G*/Sinδ of the MMB's versus temperature effects were plotted as shown in Figures 5 and 6. These results were compared with the final control PG rheological parameter (G*/Sinδ)[48].

Table 6 Performance grade determination test result for un-aged binders

Binder	Temp. (°C)	Phase Angle (°)	Complex Modulus (Pa)	G*/sinδ (KPa)	Pass/Fail Temp (°C)	Remark	PG
BB	58	86.90	1913	1.92	58	Pass	
	64	87.75	848	0.85	62.2	Fail	58

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MMB5	64	87.81	1261	1.26	64	Pass	
	70	88.49	595	0.60	65.9	Fail	64
MMB10	64	86.94	1100	1.10	64	Pass	
	70	87.73	541	0.54	64.6	Fail	64
MMB15	64	85.69	1022	1.03	64	Pass	
	70	85.79	507	0.51	64.2	Fail	64
MMB20	64	87.37	1193	1.02	64	Pass	
	70	87.90	572	0.50	65.4	Fail	64

Table 7 Performance grade determination test result for RTFO-aged binders

Binder	Temp. (°C)	Phase Angle (°)	Complex Modulus (Pa)	G*/sinδ (KPa)	Pass/ Fail Temp (°C)	Remark	PG
BB	58	83.26	4988	4.95	58	Pass	
	64	85.30	2067	2.04	63.6	Fail	58
MMB5	76	87.71	4185	4.18	76	Pass	
	82	88.44	2099	2.10	82	Fail	76
MMB10	70	86.83	3360	3.35	70	Pass	
	76	87.71	1620	1.62	73.5	Fail	70
MMB15	70	86.40	3929	3.92	70	Pass	
	76	85.54	2105	2.10	75.6	Fail	70
MMB20	70	85.16	2289	1.53	70	Pass	
	76	85.28	1087	1.08	70.4	Fail	70

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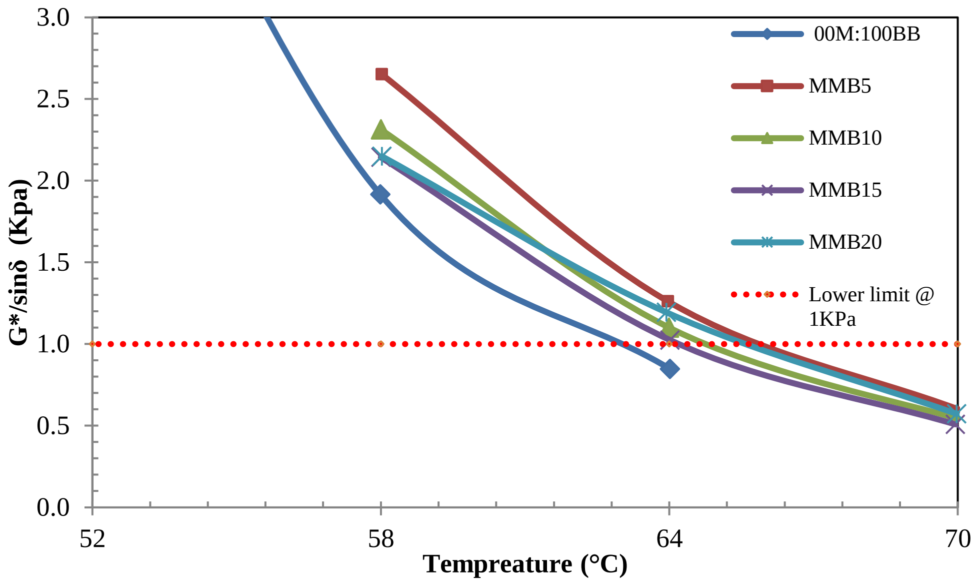

Figure 5 PG grade limit for un-aged binders

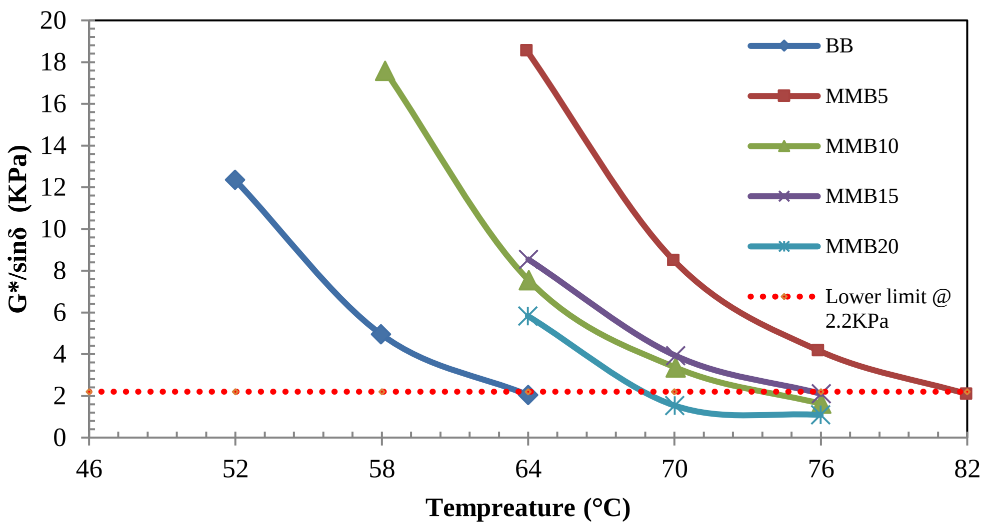

Figure 6 PG grade limit for RTFO-aged binders

The un-aged binder test results show an improvement in the performance grade from the control grade PG58 to PG64 in all MMB's, while those of RTFO-aged improved to PG-70. This result clearly shows that partially replacing base bitumen with sugar cane molasses increases the stiffness of the bases binder, which led to an increase in the rheological parameter. Complex shear modulus increased due to the addition of molasses and RTFO-aging, those parameter lead

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to improved rutting performance. To confirm this increment quantitatively, rutting resistance parameters (G*/Sinδ) of the un-aged MMB5, MMB10, MMB15, and MMB20 were increased by 38.02%, 20.32%, 11.98%,and 11.46%, respectively, at a temperature of 58^{o}C and by 48.67%, 29.8%, 29.76%, and 20.7%, respectively, at a temperature 64^{o}C. The RTFO-aged samples became stiffer, which led to an increased rutting résistance factor.

However, studies show that there is a weak relationship between stiffness parameter (G*/Sinδ) and rutting potential and recommend MSCR test for the strong relationship and to measure the rutting potential accurately[49]. Therefore, the MSCR test was performed to measure the rutting performance and correlate the result with SHRP-PG[50].

3.4. FST results

The major rheological parameters, complex modulus and phase angle, were determined using FST. Using the obtained parameters, isothermal plots, black space diagram and master curves were plotted to characterize the shear stiffness of the binder, to evaluate the effect of added molasses in the base binder and to characterize the binder for a wide range of temperature and frequency. A sample of the black space diagram and isothermal plot for MMB20 are shown Figure 7 Figure 8.

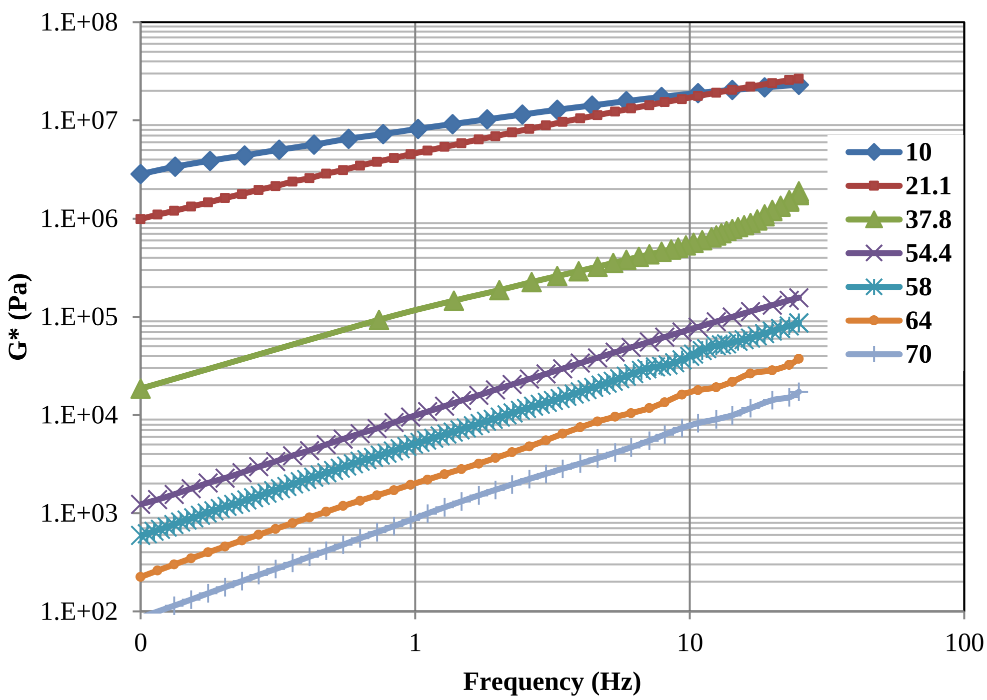

Figure 7 Log-log Isothermal plot of MMB20

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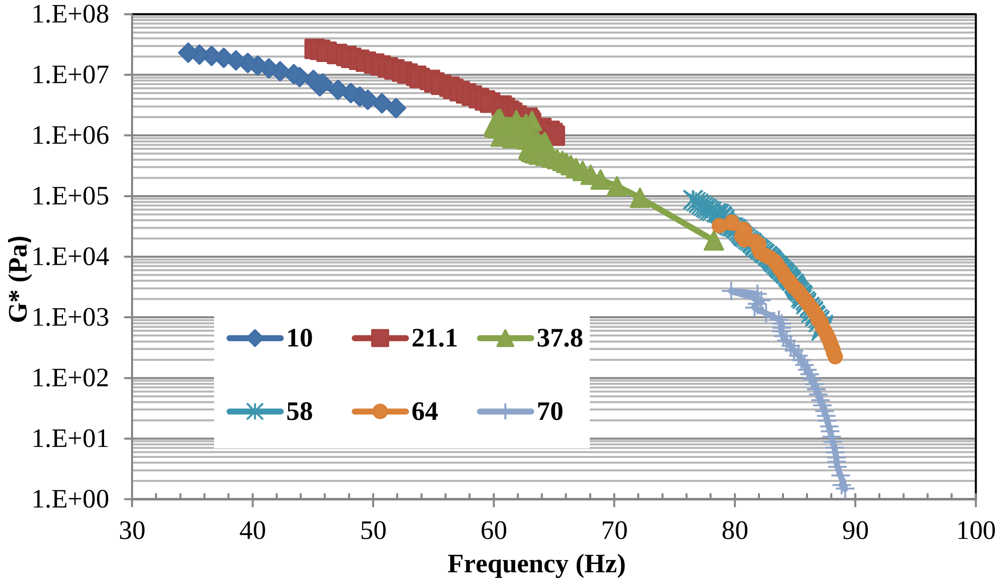

Figure 8 Semi-log black space diagram of MMB20

From the frequency sweep test result, the black space diagram, isothermal plot and the master curve was developed and presented in Figure 7 through 11. The figures indicate that at a lower temperature, higher frequency and percentage replacement led to higher complex shear modulus. But, at a higher temperature, the result was the opposite. An increase in the percentage replacement of molasses from 5% to 20% at higher temperature led to a decrease in the complex shear modulus. At lower to higher temperature and frequency, the phase angle (δ) of MMB5 and MMB10 gradually increased and then decreased slowly for MMB15 and MMB20.

3.5. Multiple stress creep recovery (MSCR) test result

3.5.1. Low temperature (T_{ref}=10°C)

As observed in Figure 9, the complex modulus and the rutting factor of MMB10 and MMB20 are increased from low to high frequency range. In the case of MMB5 and MMB15, the complex modulus and rutting factors decreased with the lower frequency (0.1to 10 Hz.), and the complex modulus increased with the increase in frequency.

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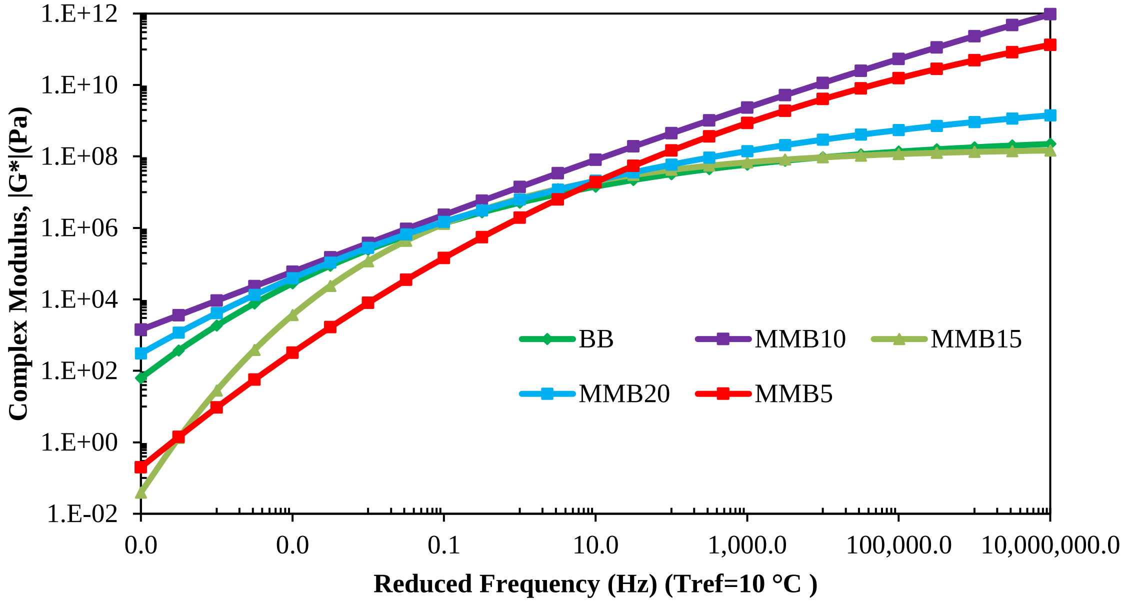

Figure 9 Lower temperature complex modulus master curve (Tref=10 °C)

3.5.2. Intermediate temperature (T_{ref}= 37.8°C)

As shown in *Figure 10*, in the lower frequency range of 0.1 to 1000 Hz, the complex modulus and rutting factors of all MMB's were consistent with that of BB. This result indicates that the MMB's have almost the same resistance to rutting as the BB. In the high frequency range exceeding 1050 Hz, the complex modulus of MMB's reduced, to some extent, compared to the control BB.

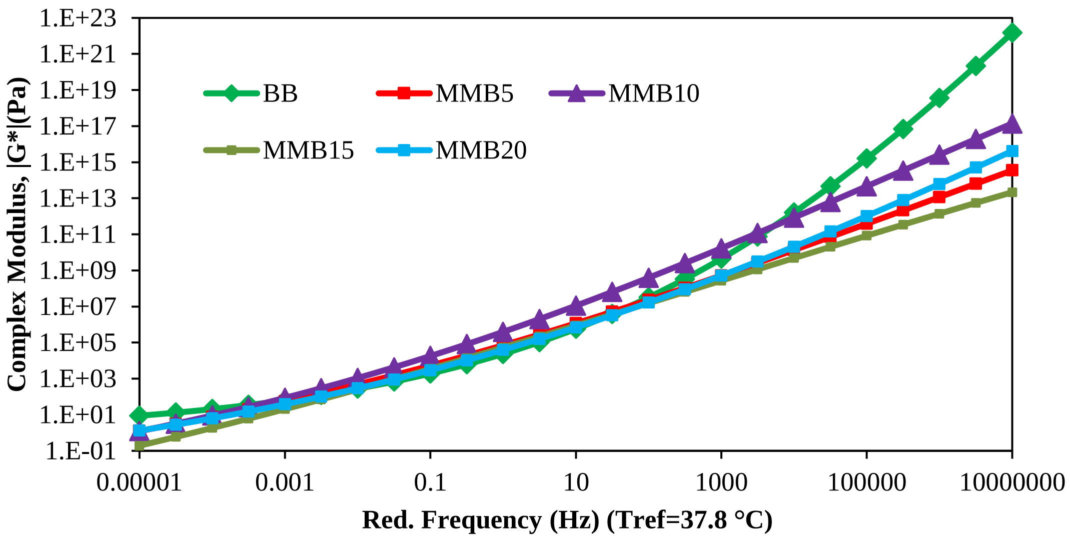

Figure 10 Intermediate tempreature complex modulus master curve (T_{ref} = 37.8 °C**)**

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3.5.3. High temperature(T_{ref}= 58 °C)

Figure 11 indicates that, in the lower to higher frequency range, the complex modulus and rutting factors of all MMB's were significantly decreased relative to that of the BB. This result indicates that the MMB's have less resistance to rutting than the BB at high temperatures.

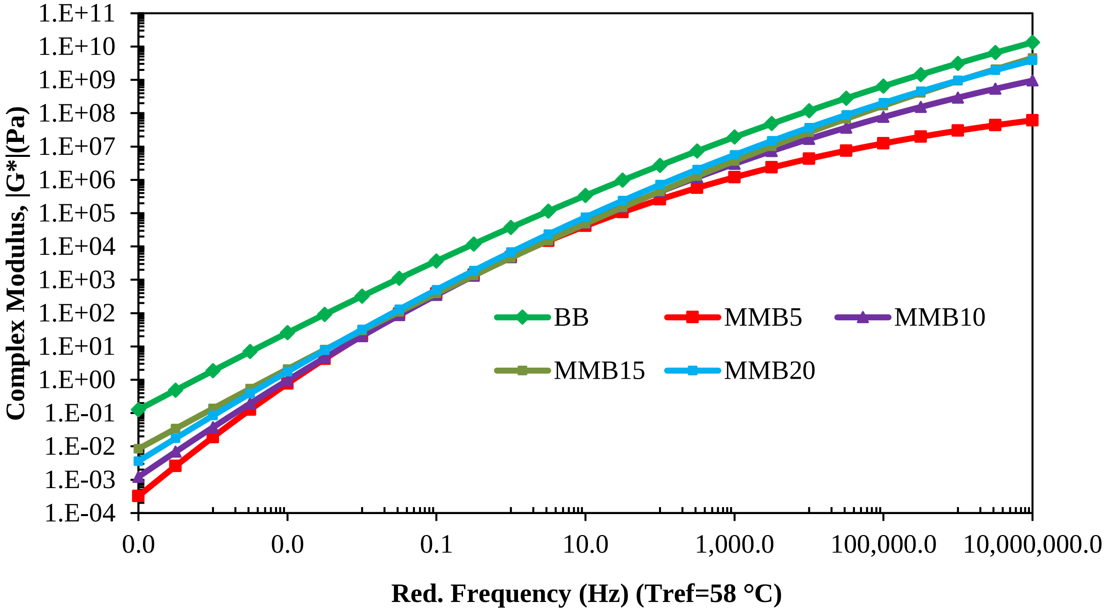

Figure 11 High Temperature Complex Modulus Master Curve (Tref=58 °C)

3.6. Multiple stress creep recovery (MSCR) test result

From the obtained test results, the average percent recovery, non-recoverable compliance (J_{nr}), and non-recoverable compliance difference ($J_{nr\ Diff.}$) were determined in two stress levels (0.1 kPa and 3.2 kPa). J_{nr} at 3.2kpa is a critical constraint to evaluate the rutting potential and summarized in Table 8 and Figure 12.

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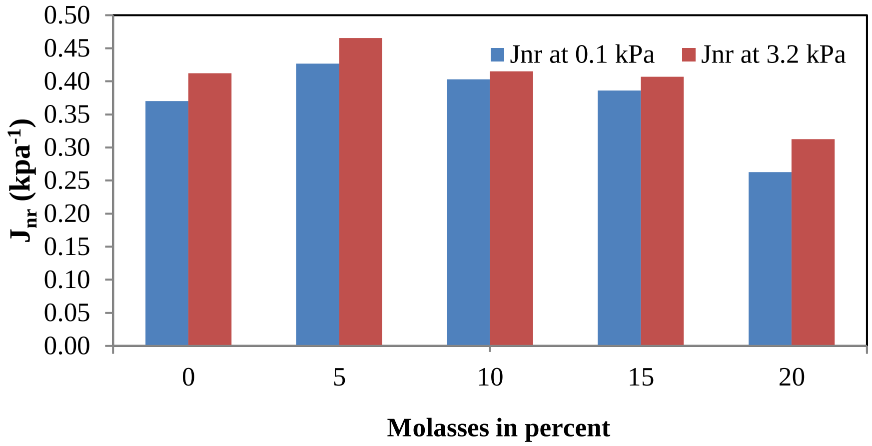
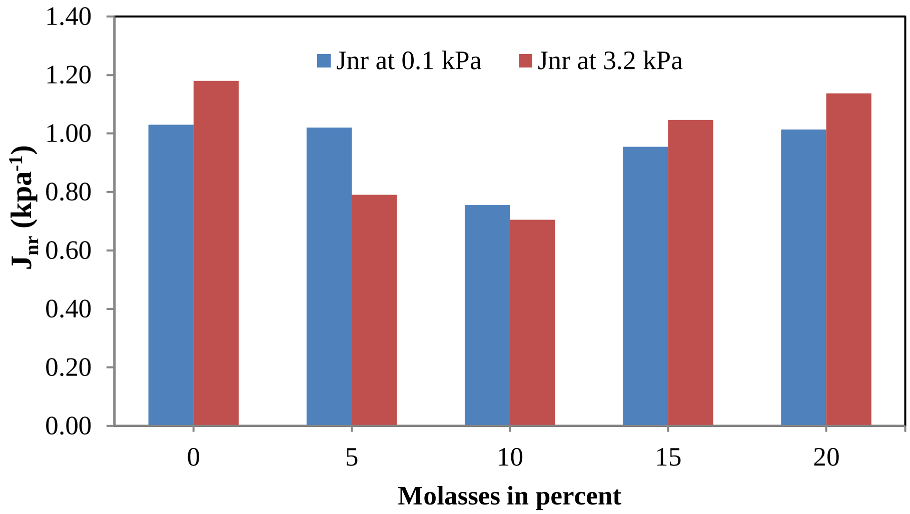


(a)



(b)

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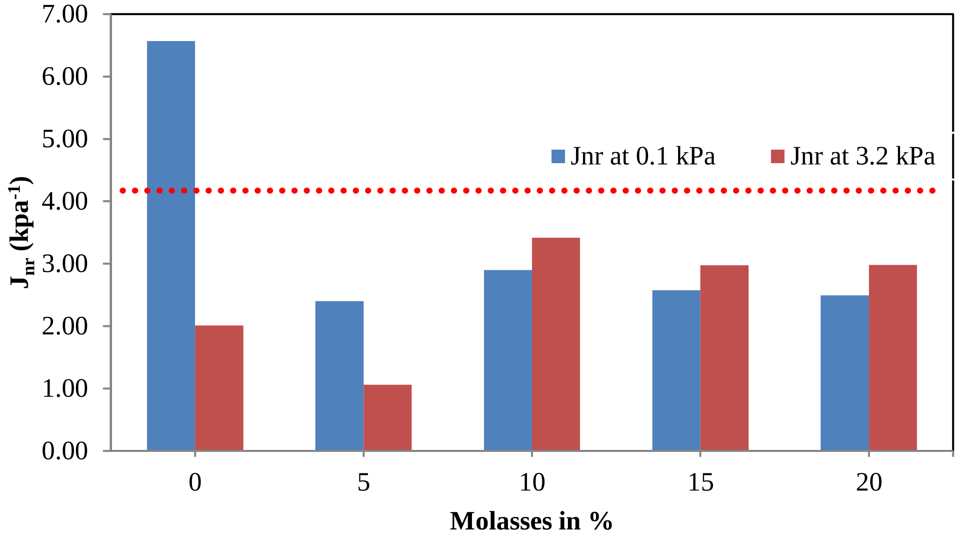

(c)

Figure 12 Non-recoverable compliance (Jnr) evaluations at (a) 52ºC, (b) 58ºC, and c) 64 º C

Figure 12 presents the calculated non-recoverable creep compliance ($J_{nr0.1KPa}$, $J_{nr3.2KPa}$) with the change in molasses percentage at high temperature. The result indicates that the J_{nr} value increases as the temperature increase for all binders. However, at a temperature of 58^{o}C, the J_{nr} value was decreased with the increase in the percent replacement of molasses for BB. This led to improving the rutting potential. Further, at a temperature of 64^{o}C the J_{nr} value was decreased only for MMR5, and then the J_{nr} value was gradually increased for the remaining percent replacements. However, the increment in the J_{nr} value was within the ASSHTO M-332 specification limit. Therefore, the rutting resistance of high percent replacements at high temperature should be considered with cautions.

According to AASHTO M-332 [51], the maximum $J_{nr3.2}$ value of the standard (S), heavy (H), very-heavy (V), and extremely heavy (E) traffic condition are 4 kPa^{-1}, 2kPa^{-1}, 1 kPa^{-1}, and 0.5 kPa^{-1}, respectively. This indicates that the $J_{nr3.2}$ value decreased from 4 to 0 kPa^{-1} when the traffic loading is increased from standard to extremely heavy. The MSCR result of this study has been presented in Table 8 and clearly defined the PG with a traffic designation for each of MMB and the BB. This result shows that $J_{nr3.2}$ value increases as the temperature increase, for all MMB's. At a temperature of 52^{o}C, the results indicate that there were no significant variations on traffic designation of all MMB's and the BB, PG52E. The traffic designation of BB, MMB15, and MMB20 exhibited similar PG and traffic PG58H, whereas for MMB5 and MMB10 the traffic loading was improved from PG58H to PG58E and PG58V respectively.

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Accumulated (total) strain with respect to time was calculated using a semi-empirical equation [46,52]and based on phase angle (δ) and shear complex modulus (G*).

Figure 13 and Figure 14 show that the accumulated strain was influenced by the percentage of the molasses used. Smaller values of accumulated strain was obtained for MMB5, followed by BB, MMB10, MMB15, and MMB20 for 3.2 kPa stress level and BB, MMB15, MMB20 and MMB10 for 0.1 kPa stress level. From this, it can be concluded that MMB5 could improve better the resistance to rutting phenomena compared to the MMB's with higher molasses contents. ,

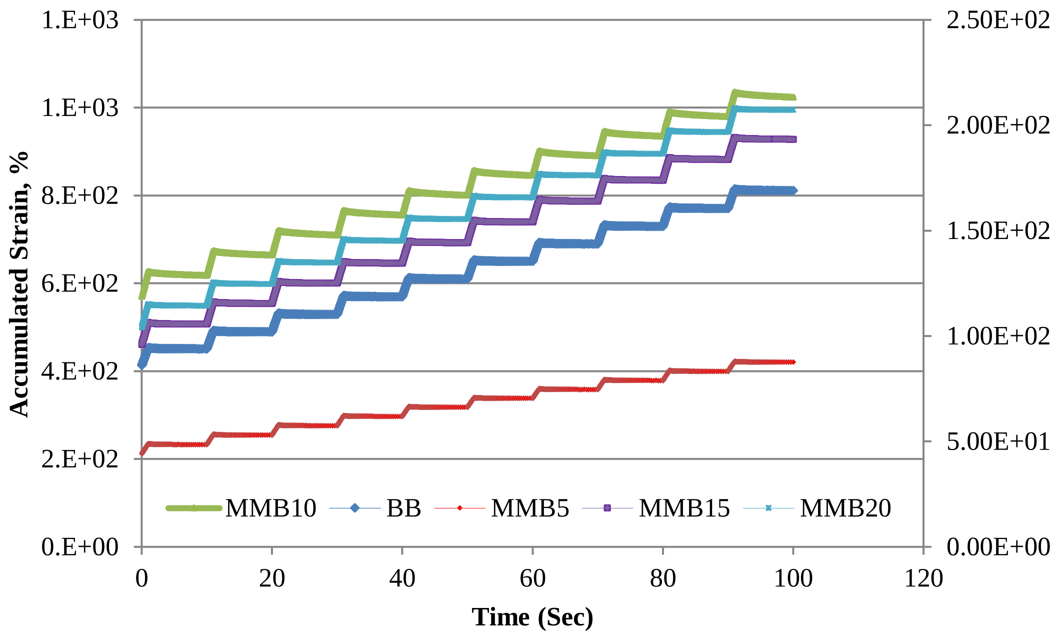

Figure 13 Effect of stiffness on total strain at 0.1kPa (58 °C) for all binders

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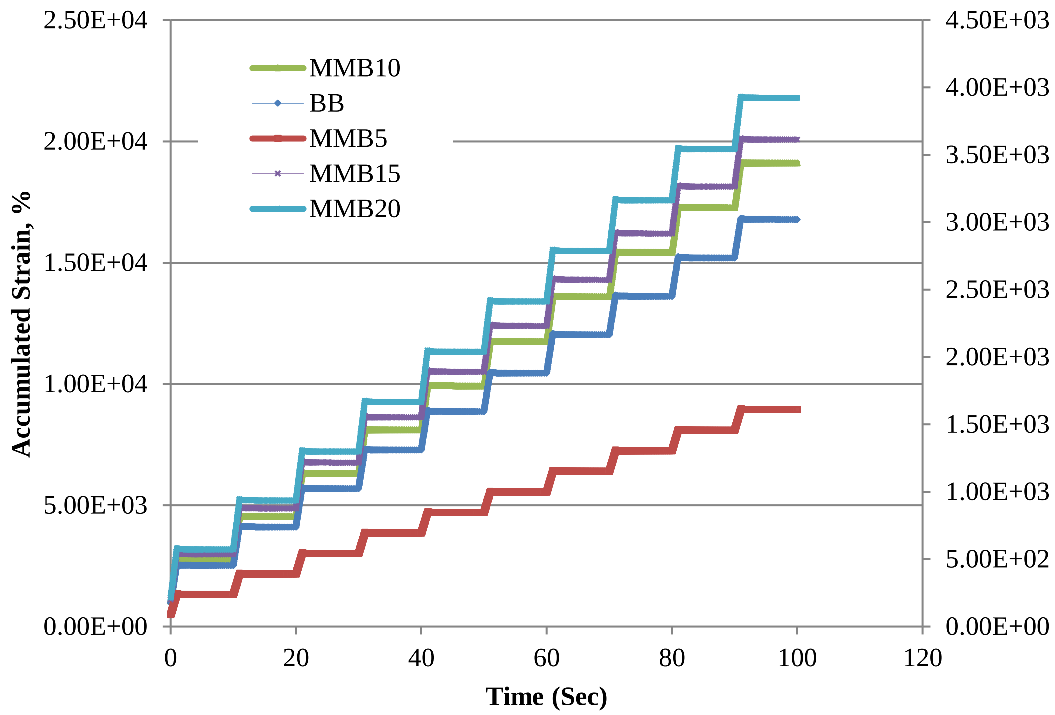

Figure 14 Effect of stiffness on total strain at 3.2kPa (58°C) for all binders

Table 8 Summary of MSCR test output

Binder Rating	BB			MMB5			MMB10			MMB15			MMB20		
Description	Test Temp. (˚C)			Test Temp. (˚C)			Test Temp. (˚C)			Test Temp. (˚C)			Test Temp. (˚C))		
	52	58	64	52	58	64	52	58	64	52	58	64	52	58	64
Percent Recovery at 0.1 kPa	11.4	7.41	6.43	11.3	8.4	16.5	11.1	7.92	8.0	12.7	7.94	4.18	12.2	7.5	5.23
Percent Recovery at 3.2 kPa	3.52	1.08	0.22	3.89	3.27	4.7	7.66	3.18	0.77	7.91	3.18	0.77	5.88	2.51	0.75
J_{nr} at 0.1 kPa	0.37	1.03	6.57	0.43	1.02	2.4	0.40	0.75	2.99	0.39	0.95	2.57	0.26	1.01	2.49
J_{nr} at 3.2 kPa	0.41	1.18	2.01	0.47	0.79	1.1	0.42	0.70	3.42	0.41	1.05	2.98	0.31	1.14	2.98
J_{nr} Difference (%)	10.7	13.9	10.8	13	9.16	11.5	2.99	9.57	17.9	5.43	9.57	15.6	19.2	12.3	19.8
PG Equivalent MSCR	52E	58H	64S	52V	58E	64H	52E	58V	64S	52E	58H	64S	52E	58H	64S

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4. Conclusion

This research comprehensively investigated the effect and the potential of using molasses as a modifier for neat bitumen through chemical and rheological approaches**.**

Specific findings from this study have been summarized as follows:

- Water content tests showed that 24.9% by weight water was obtained in molasses. This high volume water was reduced by distillation process before blended it with petroleum-based asphalt binder. After treating the molasses the bio asphalt was prepared.
- From FTIR spectrum strong peak within a wave-number range of 3550cm^{-1} and 3425cm^{1} wave number Alcohol (O-H stretching) were fully reacted with other functional group and around wave-number 750cm^{-1}Aromamins (C-H stretching) partially reacted.
- Frequency sweep tests demonstrated that as the percentage of molasses increases led to increasing the complex shear modulus only at lower temperatures. However, at high temperatures, the complex shear modulus was decreased. Therefore, molasses modified bio-asphalt a significantly improve the rutting potential at low temperature
- PG grade determination tests confirmed that neat bitumen does not have significant change in PG grade before and after RTFO aging. Whereas, the percentage of bio-binder increases, the complex shear modulus was increased. This led to improving the PG from PG58 to PG64. And after RTFO conditioned the PG to become PG70.
- Multiple recovery stress tests conducted by DSR revealed non-recoverable creep compliance (J_{nr}) increases as a temperature increases. But at a temperature of 58^{o}C a very good J_{nr} result is observed, for all binder replacement the J_{nr} value was decreased.
- Overall, this study revealed that treated molasses can be used as a partial replacement to enhance the rheological properties of the base bitumen and thus it can potentially be used to produce a sustainable bio-asphalt binder.

Author Contributions: Conceptualization, methodology, data collection and data analysis, validation, original draft writing, and editing – W.K.H.; Supervision and editing – T.T.G.

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and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the Ministry of Science and Higher Education.

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Conflict of Interest

The authors declare no conflict of interest.

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