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Performance properties of polymer modified asphalt binders containing wax additives

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Abstract

The study presents an experimental evaluation of the rheological properties of control and polymer modified asphalt (PMA) binders containing wax additives and a comprehensive comparison between these two binder types. The control and PMA binders with the additives were produced using two of the available warm asphalt processes (i.e., LEADCAP and Sasobit) and then artificially short-term and long-term aged using the rolling thin film oven (RTFO) and pressure aging vessel (PAV) procedures. Superpave binder tests were carried out on the binders through the rotational viscometer (RV), the dynamic shear rheometer (DSR), and the bending beam rheometer (BBR). In general the results of this study indicated that (1) the addition of wax additives into the control and PMA binders decreases the viscosity, as expected; (2) the reduction rate of viscosity was quite similar for both the binders with wax additives; (3) the percentage increase of rutting resistance due to the additives was much higher for the control binder, compared to the PMA binder; (4) both the control and PMA binders showed the similar trends in terms of fatigue cracking and low temperature cracking behavior after the addition of wax additives.

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Keywords: PMA; Wax additives; Viscosity; Rutting; Fatigue cracking; Stiffness

1. Introduction

According to Environmental Protection Agency (EPA) in 2013, direct industrial greenhouse gas emissions accounted for approximately 21% of total emissions in the United States, making it the third largest contributor to this field, after the Electricity and Transportation sectors due to a rise in population, economic growth, the fluctuating price of energy, technological changes and many other factors. The paving industry has its own share of emission concerns with its use of hot mix asphalt (HMA), with the

major source coming from the production facility. HMA plants, regardless of its manufacturing technique (drum or batch) emit between 56,000 lbs/yr and 83,000 lbs/yr, depending on their fuel type (natural gas and oil, etc). As a result, warm mix asphalt (WMA) technologies have been introduced to reduce the mixing and compaction temperatures for asphalt mixtures as a means of reducing production cost, energy, and most importantly pollutant emissions.

In order to improve the quality of asphalt pavements, the asphalt industry incorporated polymers into asphalt as a way to mitigate the major causes for asphalt pavement failures, including permanent deformation at high temperatures and cracking at low temperatures [7,26]. When a polymer and virgin asphalt are blended, the polymer strands absorb part of the low molecular weight oil fraction of the virgin asphalt and become swollen. Of the polymer

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modifiers, styrene butadiene styrene (SBS) originally developed by Shell Chemical Co. is widely used in the majority of the asphalt binder industry and probably the most appropriate polymer for asphalt modification ([25,3]. SBS creates a three dimensional network within virgin asphalt phase resulting in excellent bonding strength to aggregates which leads to a durable and long lasting pavement [18,2]. According to [3], it is the most appropriate and used polymer for asphalt modification, followed by reclaimed tire rubber. It is the formation of critical network between the binder and SBS that increases the complex modulus, resulting the increase in rutting resistance. In 2004, Florida Department of Transportation and FHWA report that SBS benefited the cracking resistance by reducing the rate of micro-damage accumulation [30].

Due to high viscosity and improved binder coating, polymer modified asphalt (PMA) pavements have better pavement performance under high traffic applications. Polymer modifications are becoming important factors in paving industry due to their proven effects such as better resistance to rutting, fatigue damage, stripping, and thermal cracking in asphalt pavements [33,29,7]. However, there have been difficulties in workability of PMA because of high viscosity of the modified binders and concern about the health issues due to high level of toxic fumes and continuous exposure of workers to high temperatures during paving operations. Also, high temperature can thermally degrade the polymer as well as cause high economic cost due to the increased fuel consumption [30,4,35,27].

WMA technologies allow significant reduction of mixing and compaction temperatures of asphalt mixes using proprietary chemicals. In addition, the WMA provides better working condition based on reduction in emissions in asphalt plants and fields, and there are many other promising benefits including less fuel consumption, longer paving seasons, longer hauling distances, earlier traffic opening, reduced binder aging, and reduced cracking [1,6,8,12,13,24]. WMA technology can be used as a method of reducing the heat requirement for pavement operations while at the same time maintaining the integrity of the PMA binder. Several studies have been performed on the incorporation of wax additives into the PMA binder [11,5,15,14,17,16,20,19,21,32,13]. Most of the studies investigated the rheological properties of PMA binder by incorporating Sasobit into the binder. Based on this review, it appears that the addition of LEADCAP into the PMA binder and a comprehensive comparison between the two binder types (control and PMA) with two wax additives (LEADCAP and Sasobit) in terms of compatibility has not been reported in the previous study. This study can provide a substantial body of knowledge on such observations which may be of interest to the asphalt industry.

The objective of this study was to investigate the performance properties of PMA binders containing wax additives

through Superpave binder tests. Control binders with wax additives were used to compare with the PMA binders. The warm PMA binders were produced with two commercial wax additives, LEADCAP and Sasobit, and artificially aged using rolling thin film oven (RTFO) and pressure aging vessel (PAV) procedures. The viscosity properties for the binders were evaluated in the original state through rotational viscometer (RV) test using different testing temperatures (135 °C and 120 °C) and periods (30, 120, and 240 min). Rutting resistance properties in the original state and after RTFO aging as well as the fatigue cracking properties at intermediate temperature after RTFO + PAV aging methods were evaluated by dynamic shear rheometer (DSR) test. Low temperature cracking properties after RTFO + PAV procedures were evaluated by bending beam rheometer (BBR) test. Fig. 1 illustrates a flow chart of the experimental design used in this study.

2. Experimental design

2.1. Materials

Performance grade (PG) 64–22 asphalt base binder and PMA binders containing SBS (approximately 3% by the weight of binder) were used in this study. Table 1 shows the properties of base binder and PMA binder.

Two types of commercial wax additives were used in this study. The first one is an organic additive of a polyethylene wax-based composition that includes crystal controller and artificial materials known as LEADCAP. The wax used in LEADCAP additive has approximately 110 °C melting point [34]. It is to adjust crystalline degree of wax material at the low temperature [24]. The second one is a Fischer-Tropsch (FT) wax, Sasobit, manufactured by Sasol Wax. It is a long chain aliphatic hydrocarbon obtained from coal gasification using the Fischer-Tropsch process. It is completely melted into the asphalt binder at a temperature in excess of 115 °C which can reduce the binder viscosity. After crystallization, it forms a lattice structure in the binder which is the basis of the structure stability of the binder containing Sasobit [31]. Fig. 2 shows the images of the wax additives used in this study.

2.2. Production of warm asphalt binder containing wax additives

LEADCAP and Sasobit were used in this study for producing the warm binders. The process involved the addition of two wax additives at specified concentration (1.5% by weight of the binder) followed by hand mixing for 1 min at 170 °C in order to achieve consistent mixing. Table 2 explains the arrangement of binders with wax additives used in this study. Binder aging process were then conducted by rolling thin film oven (RTFO) for 85 minutes at 163 °C (ASTM D 2872) and pressure aging vessel (PAV) for 20 h at 100 °C (ASTM D 6251).

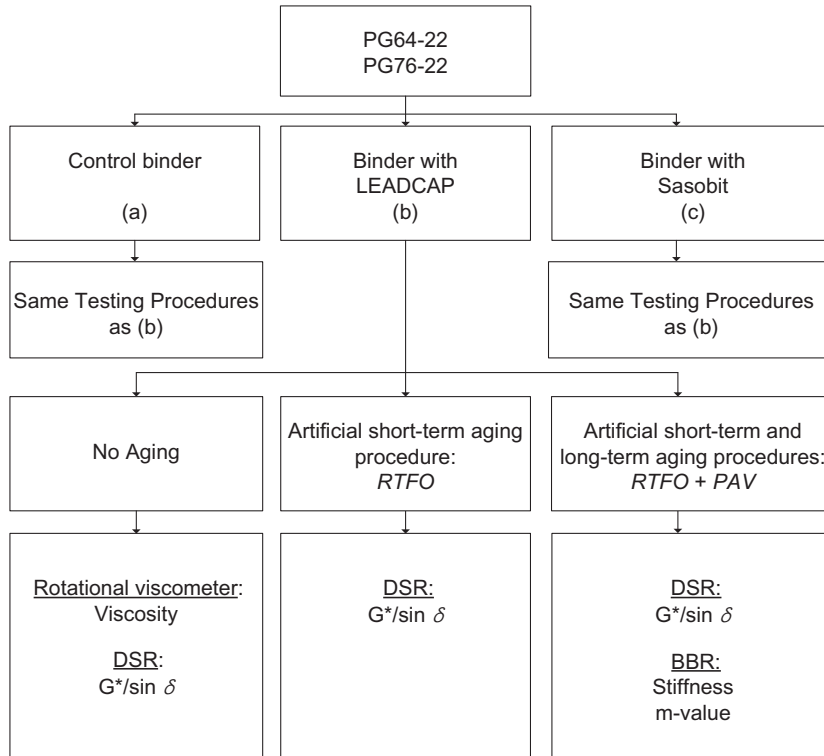


Fig. 1. Flow chart of experimental design procedures.

2.3. Superpave binder testing

The Superpave asphalt binder tests are used to measure the asphalt’s performance at three stages of its life: in its original state, after mixing and construction, and after in-service aging. In this study the selected binder test procedures included the viscosity test (AASHTO T 316), the DSR test (AASHTO T 315), and the BBR test (AASHTO T 313). Three replicate samples were tested and the results were reported as the average of these tests.

A 8.5 g sample of the control binders and a 10.5 g sample of PMA binders were tested with a number 21 spindle and with a number 27 spindle in the Brookfield rotational viscometer at 135 °C (the standard test temperature) and at 120 °C (the mixing temperature generally used for warm mix asphalt), respectively. Three testing periods (i.e., 30, 120, and 240 min) were used to evaluate the viscosity change in different testing periods.

In the DSR test, the binders (Original, RTFO residual, and RTFO + PAV residual) were tested at a frequency of 10 radians per second which is equal to approximately 1.59 Hz. Each asphalt binder both in the original state (unaged) and short-time aged state used to determine the $G^*/\sin \delta$. The $G^*\sin \delta$ at intermediate temperature was measured to evaluate the fatigue cracking property for RTFO + PAV residual binders. The BBR test was conducted on asphalt beams (125 × 6.35 × 12.7 mm) at -12 °C, and the creep stiffness (S) of the binder was measured at a load-

ing time of 60 s. A constant load of 100 g was then applied to the beam of the binder, which was supported at both ends, and the deflection of center point was measured continuously. Testing was performed on RTFO + PAV residual samples.

2.4. Statistical analysis method

A statistical analysis was performed using the Statistical Analysis System (SAS) program to conduct an analysis of variance (ANOVA) and Fisher’s Least Significant Difference (LSD) comparison with an $\alpha = 0.05$. The primary variables included the wax types (Control, LEADCAP, and Sasobit) and the binder types (Control and PMA).

The ANOVA was performed first to determine whether significant differences among sample means existed. In the analyses of this study, the significance level was .95 ($\alpha = 0.05$), indicating that each finding had a 95% chance of being true. Upon determining that there were differences among sample means using the ANOVA, the LSD was then calculated. The LSD is defined as the observed differences between two sample means necessary to declare the corresponding population means difference. Once the LSD was calculated, all pairs of sample means were compared. If the difference between two sample means was greater than or equal to the LSD, the population means were declared to be statistically different [28].

Table 1
Properties of asphalt binders.

Aging states	Test properties	PG 64–22 (unmodified)	PG 76–22 (SBS modified)
Unaged binder	Viscosity @ 135 °C (cP)	531	3244
	$G^*/\sin \delta$ @ 64 °C (kPa)	1.4	5.9
	$G^*/\sin \delta$ @ 76 °C (kPa)	–	1.9
RTFO aged residual	$G^*/\sin \delta$ @ 64 °C (kPa)	2.5	13.7
	$G^*/\sin \delta$ @ 76 °C (kPa)	–	3.3
RTFO + PAV aged residual	$G^*\sin \delta$ @ 25 °C (kPa)	2558	3650
	Stiffness @ –12 °C (MPa)	287	285
	<i>m</i> -value @ –12 °C	0.307	0.302

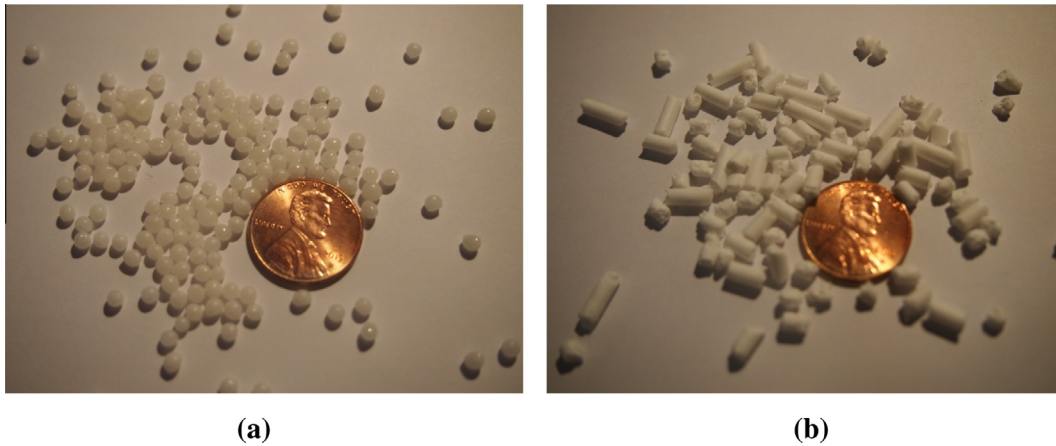


Fig. 2. Wax additives; (a) Sasobit and (b) LEADCAP.

Table 2
Designation and description of the binders.

Designation	Description	Method
Control	Base binder	–
Control + L	Binder with 1.5% LEADCAP	Hand mix
Control + S	Binder with 1.5% Sasobit	Hand mix
PMA	PMA binder	–
PMA + L	PMA with 1.5% LEADCAP	Hand mix
PMA + S	PMA with 1.5% Sasobit	Hand mix

3. Results and discussion

3.1. Rotational viscosity (high temperature)

The viscosity of asphalt binder at high temperatures is considered to be an important property to decide working temperature because it reflects the binder’s ability to be pumped through an asphalt plant, thoroughly coat aggregate in a HMA mixture, and be placed and compacted to form a new pavement surface. Fig. 3 shows the standard RV test results for all binders used in this study. It is clear that the addition of SBS into the asphalt binder greatly increases the binder viscosity, as expected. This potential problem can be solved by addition of wax additives. The results indicate that the addition of wax additives results in decreasing the mixing and compaction temperatures

for all binders containing the additives. LEADCAP and Sasobit were observed to be effective to reduce the viscosity of control binder by 9.7% and 13.6%, respectively and this reduction rate remained similar in both testing temperatures. Sasobit has significant effects in reducing the viscosity of PMA binder [11,13,20,21,15,14,17,32,22]. The viscosity reduction rate of PMA binder at 135 °C with Sasobit was approximately twice compared to the PMA binder with LEADCAP whereas at 120 °C decreasing rate was 13.3% and 10.5% by the addition of Sasobit and LEADCAP, respectively. The viscosity values of PMA binders at 120 °C do not meet the current maximum requirements set forth by Superpave (i.e., 3,000 cP). Although at 135 °C the PMA binder shows the higher values than the requirement, the PMA binder with wax additives satisfies the requirement. A similar decreasing trend and rate of viscosity were observed at both temperatures for the control and PMA binders with wax additives.

The statistical significance of the change in the viscosity as a function of WMA additive and binder types was examined and results are shown in Table 3. The data indicated that the binder types have a significant effect on the viscosity value at both testing temperatures (135 °C and 120 °C). In most cases (except for control binder: Control + L vs. Control + S), the results showed that, within each binder type, the binders have a significant difference in the viscosity depending on the WMA additive.

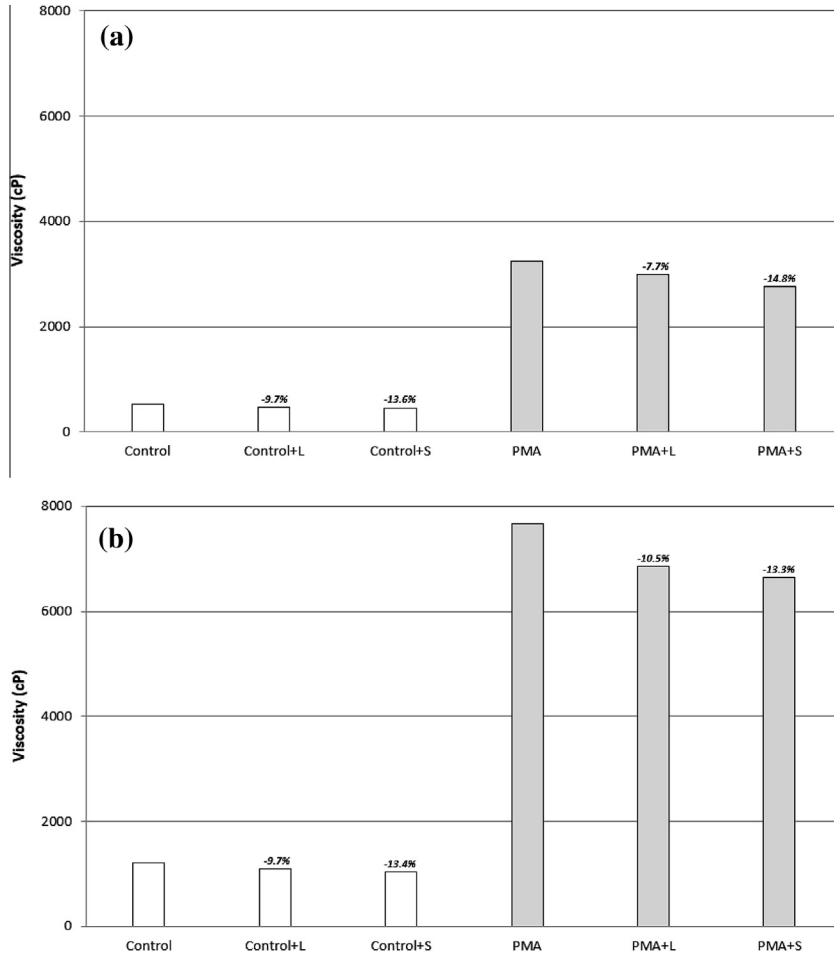


Fig. 3. Viscosity of the binders with wax additives (a) 135 °C and (b) 120 °C.

Table 3
Statistical analysis results of the viscosity value as a function of binder and wax additives; (a) 135 °C and (b) 120 °C.

Viscosity	PG 64–22			PG 76–22		
	Control	Control + L	Control + S	PMA	PMA + L	PMA + S
<i>(a)</i>						
Control	–	S	S	S	S	S
Control + L		–	N	S	S	S
Control + S			–	S	S	S
PMA				–	S	S
PMA + L					–	S
PMA + S						–
<i>(b)</i>						
Control	–	S	S	S	S	S
Control + L		–	N	S	S	S
Control + S			–	S	S	S
PMA				–	S	S
PMA + L					–	S
PMA + S						–

N: non-significant, S: significant.

3.1.1. Rotational viscosity as a function of time at 135 °C

One of the benefits of WMA binder is a longer hauling distance and period. The hauling management of asphalt mixture usually depends on the binder viscosity. The

viscosity test was performed for 240 min to evaluate the longer hauling management of control and PMA binders. This is demonstrated in Figs. 4 and 5, which depict the time versus viscosity curve for 240 min at 135 °C. As expected,

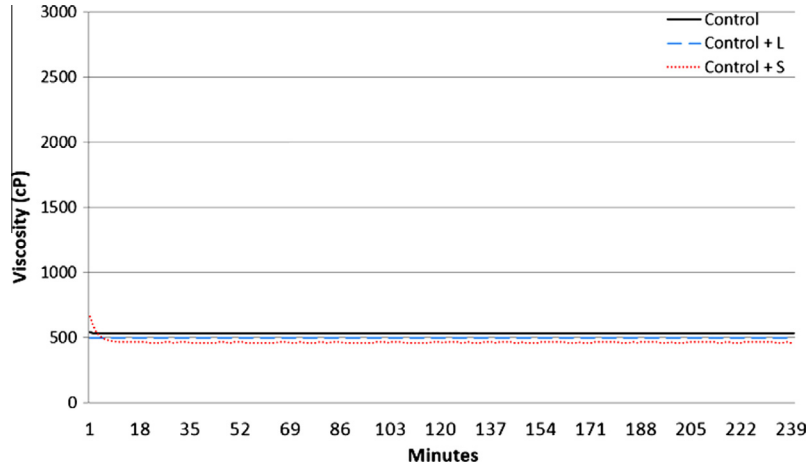


Fig. 4. Viscosity change of control binder during 240 min at 135 °C.

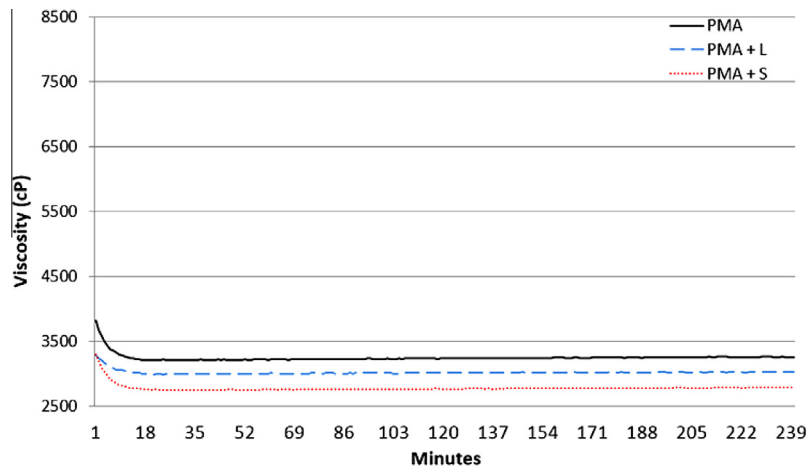


Fig. 5. Viscosity change of PMA binder during 240 min at 135 °C.

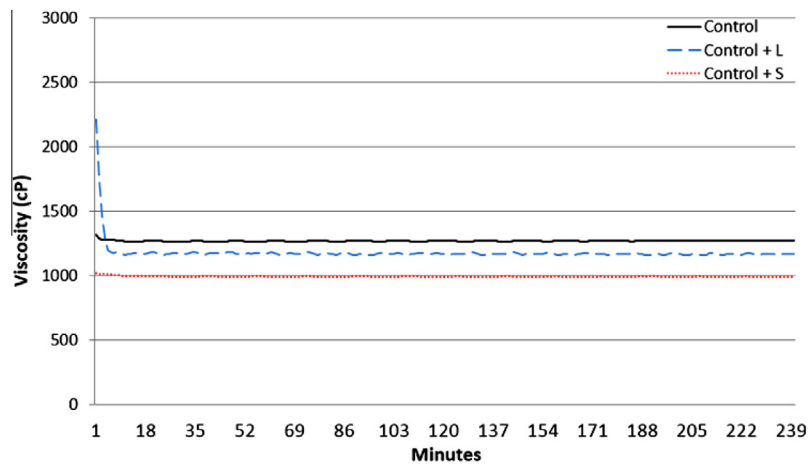


Fig. 6. Viscosity change of control binder during 240 min at 120 °C.

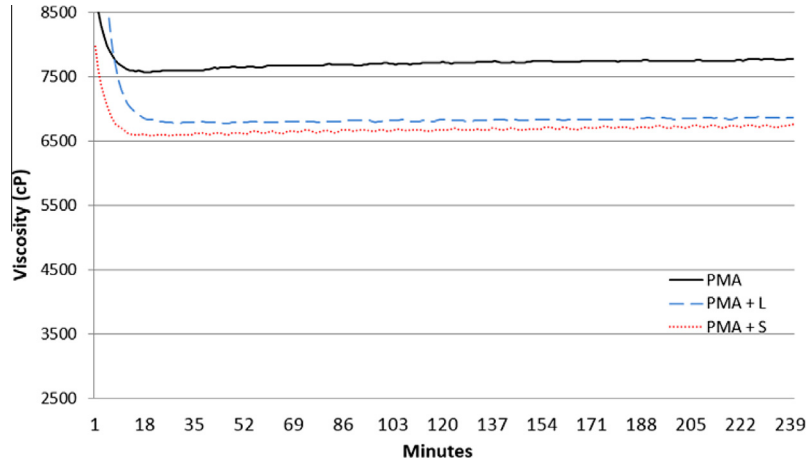


Fig. 7. Viscosity change of PMA binder during 240 min at 120 °C.

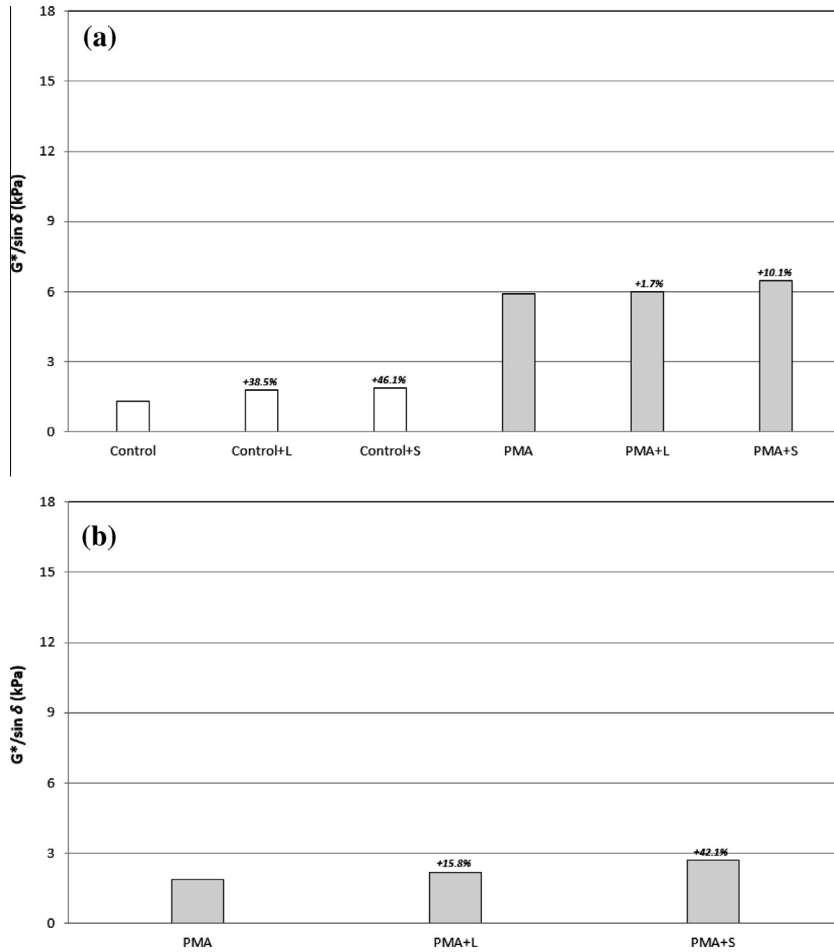


Fig. 8. $G^*/\sin \delta$ of the binders with wax additives (No aging); (a) 64 °C and (b) 76 °C.

PMA binders exhibited much higher viscosity values than control binders. According to Fig. 4, the viscosity values of control binders were stabilized between 9 and 10 min and the viscosity values were found to have little change for the whole testing period. On the other hand, the viscosity of PMA binders steadily increased approximately after 30–40 min.

3.1.2. Rotational viscosity as a function of time at 120 °C

The viscosity test was performed at the lower temperature of 120 °C that is generally used for WMA. The viscosity changes for 240 min are illustrated in Figs. 6 and 7 at 120 °C. Generally, there was no considerable viscosity change at 120 °C, similar to 135 °C. However, the PMA binders showed much higher viscosity than the current

requirement at 120 °C. The viscosity curves of PMA binders containing LEADCAP or Sasobit were found to have increasing trends over time. Also, the differences between PMA binder and PMA binders with the additives were higher compared to those at 135 °C.

3.2. Rutting property ($G^*/\sin \delta$)

The higher $G^*/\sin \delta$ values from the DSR test indicate that the binders are less susceptible to rutting or permanent deformation at high pavement temperatures. The $G^*/\sin \delta$ values of binders in original state and after short time aging were measured at 64 °C and 76 °C. The results are shown in Figs. 8 and 9. In general, the PMA binders resulted in the higher $G^*/\sin \delta$ than the control binders regardless of aging state. However, the percentage improvement of rutting resistance due to the addition of wax additives were observed much higher for control binders compared to PMA binders. The reason might be the PMA binder was already modified with SBS for high temperature performance so the addition of wax additives has less effect compared to the unmodified control binder. The use of wax additives into binders was observed to increase the $G^*/\sin \delta$

δ values in both aging states except for PMA binder with LEADCAP at 64 °C during RTFO aging process. The binders with Sasobit showed the highest values within each binder type (Control binder or PMA binder) regardless of aging and temperature which is due to the presence of wax crystals [9,10]. This finding is consistent with the previous observations [14,20,19,21,16]. It means that the wax additive of Sasobit has a positive effect on the rutting resistance at high temperatures due to the presence of wax crystals in the binders which causes an increase in the complex modulus of the binders. In short, both the wax additives and the SBS polymer play a significant role in improving rutting resistance.

The statistical results of the change in the $G^*/\sin \delta$ values for no aging and RTFO aging at 64 °C are shown in Table 4. Regardless of aging, the data indicated that the binder types have a significant effect on the $G^*/\sin \delta$ values. For no aging, the differences between control binder and the control binder containing LEADCAP or Sasobit are statistically significant. For RTFO aging, the PMA binder with Sasobit was found to be significantly different in the $G^*/\sin \delta$ value when compared to other PMA binders.

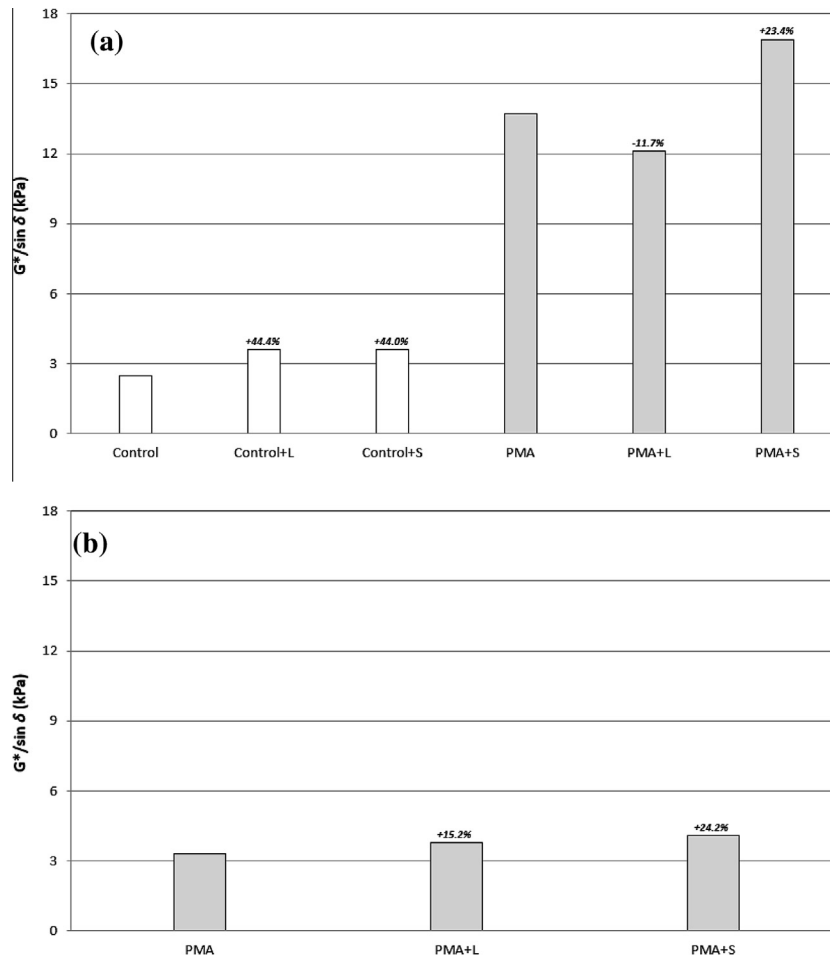


Fig. 9. $G^*/\sin \delta$ of the binders with wax additives (RTFO); (a) 64 °C and (b) 76 °C.

Table 4
Statistical analysis results of the $G^*/\sin \delta$ value as a function of binder and wax additives at 64 °C (a) No aging and (b) RTFO aging.

$G^*/\sin \delta$	PG 64–22			PG 76–22		
	Control	Control + L	Control + S	PMA	PMA + L	PMA + S
<i>(a)</i>						
Control	–	S	S	S	S	S
Control + L		–	N	S	S	S
Control + S			–	S	S	S
PMA				–	N	N
PMA + L					–	N
PMA + S						–
<i>(b)</i>						
Control	–	S	S	S	S	S
Control + L		–	N	S	S	S
Control + S			–	S	S	S
PMA				–	N	S
PMA + L					–	S
PMA + S						–

N: non-significant, S: significant

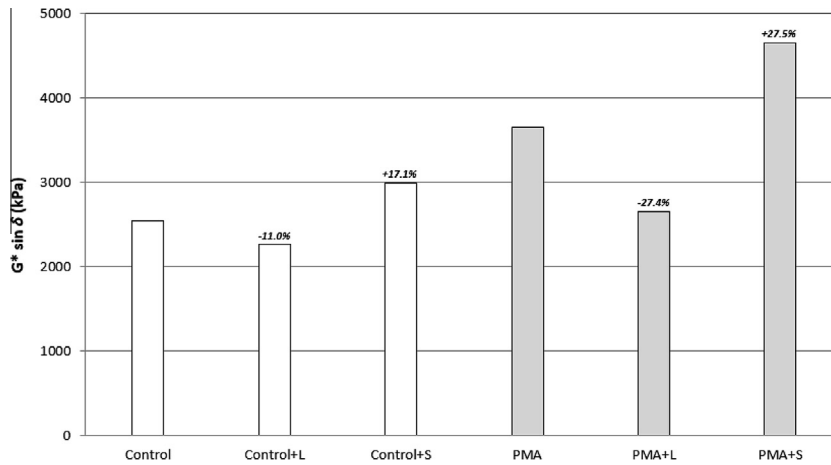


Fig. 10. $G^* \sin \delta$ at 25 °C of the binders with wax additives (after RTFO + PAV).

Table 5
Statistical analysis results of the $G^* \sin \delta$ value as a function of binder and wax additives at 25 °C after RTFO + PAV.

$G^* \sin \delta$	PG 64–22			PG 76–22		
	Control	Control + L	Control + S	PMA	PMA + L	PMA + S
Control	–	N	N	S	N	S
Control + L		–	S	S	N	S
Control + S			–	S	N	S
PMA				–	S	S
PMA + L					–	S
PMA + S						–

N: non-significant, S: significant.

3.3. Fatigue cracking property (intermediate failure)

The product of the complex shear modulus G^* and the sine of the phase angle, δ , is used in Superpave binder specification to help control the fatigue of asphalt pavements. The lower values of $G^* \sin \delta$ are considered desirable attributes from the standpoint of resistance of fatigue cracking. The $G^* \sin \delta$ values of the binders (RTFO + PAV residual)

were measured using the DSR at 25 °C and the results are illustrated in Fig. 10. The PMA binder exhibited the higher $G^* \sin \delta$ values than the control binder, indicating that the SBS polymer modification has little influence on the resistance of fatigue cracking. This finding may be explained that SBS modification increases the high temperature grade, but results in the same low temperate grade as the control binder. The binders with Sasobit showed the

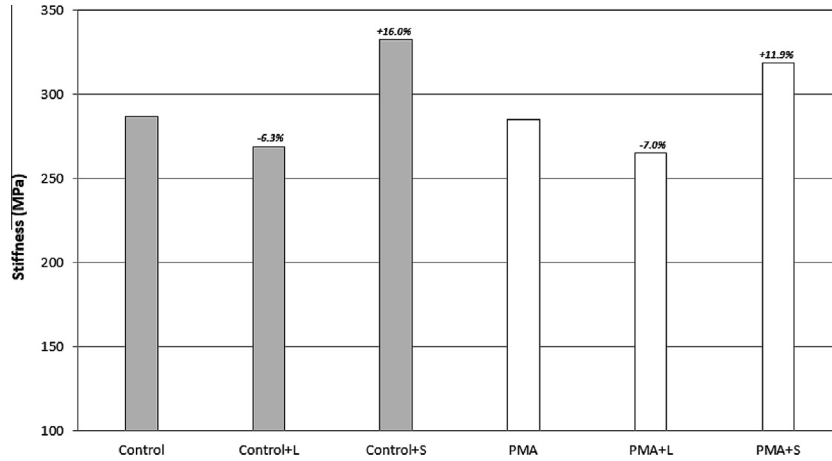


Fig. 11. Stiffness at -12 °C of the binders with wax additives (after RTFO + PAV).

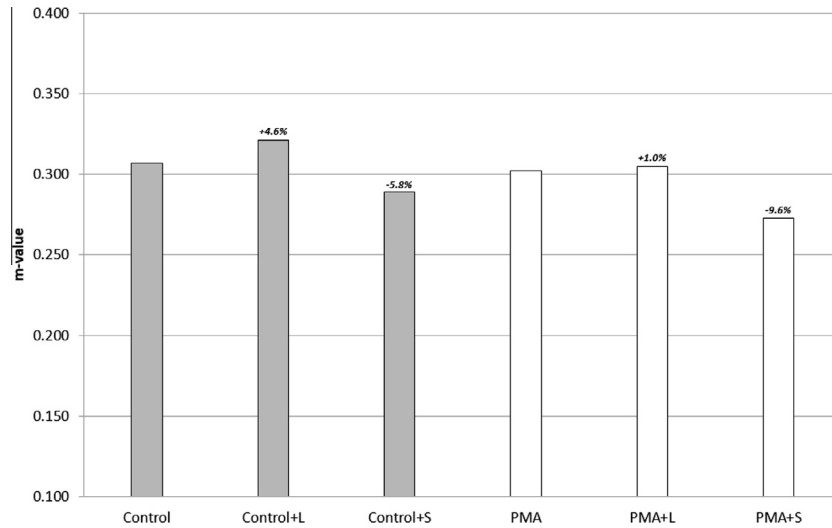


Fig. 12. *m*-value at -12 °C of the binders with wax additives (after RTFO + PAV).

highest values within each binder type (Control binder or PMA binder) which is consistent with the previous finding [20]. However, the addition of LEADCAP into control and PMA binders reduced the $G^* \sin \delta$ values by 11% and 27.4%, respectively. It means that the wax additive LEADCAP has a positive effect on the cracking resistance at intermediate temperature. Also, all the values satisfied the maximum requirements of 5,000 kPa by Superpave.

The statistical significance of the change in the $G^* \sin \delta$ value as a function of WMA additive and binder types was examined and results are shown in Table 5. The results showed that binder types have a significant effect in the $G^* \sin \delta$ value, except for PMA binder containing LEADCAP. The differences between control binder and the control binder with LEADCAP or Sasobit were statistically insignificant whereas the differences between PMA binder and the PMA binder with the wax additives were statistically significant.

3.4. Thermal cracking property (low temperature)

Superpave asphalt binder specification includes a maximum value of 300 MPa for creep stiffness and the decrease in stiffness is expected to lead to smaller tensile stress in the asphalt binder and less chance for low temperature. From the BBR tests at -12 °C, the stiffness and *m*-value of control and PMA binders with wax additives (RTFO + PAV residual) were calculated and the results are shown in Figs. 11 and 12. After the RTFO + PAV aging processes, the control and PMA binder stiffness values at -12 °C are measured to be 287 MPa and 285 MPa, respectively. The PMA binder with LEADCAP is found to have the lowest stiffness values of 265 MPa, which is approximately 7% lower than the PMA binder stiffness. The binders with Sasobit were found to have the highest stiffness value within each binder type [11,20,23]. All the control and PMA binders, except for the binders with 1.5% Sasobit,

Table 6
Statistical analysis results of the stiffness value as a function of binder and wax additives at -12°C after RTFO + PAV.

Stiffness	PG 64–22			PG 76–22		
	Control	Control + L	Control + S	PMA	PMA + L	PMA + S
Control	–	N	S	N	S	N
Control + L		–	S	N	N	S
Control + S			–	S	S	S
PMA				–	N	S
PMA + L					–	S
PMA + S						–

N: non-significant, S: significant

satisfied the requirement set forth by Superpave (maximum 300 MPa). In general, the use of SBS polymer to modify the asphalt binder in terms of thermal cracking properties is observed to have little influence. However, the PMA binder with LEADCAP is expected to have the best performance with regard to low temperature cracking resistance, among six binder types used in the study. Also, $G^*\sin\delta$ values at 25°C and the stiffness values of control and PMA binders with wax additives were found to have a similar trend.

The statistical results of the change in the stiffness value are shown in Table 6. In general, the data indicated that within each binder type, the differences between the binder and the binder containing LEADCAP are statistically insignificant. For both binders, the wax types were found to have significant differences on the stiffness values.

4. Summary and conclusions

To investigate the performance properties of control and PMA binders with wax additives, warm PMA binders were produced using two wax additives, LEADCAP and Sasobit, and artificially short-term and long-term aged in the laboratory. A series of Superpave binder tests were carried out using the rotational viscometer, the DSR, and the BBR to evaluate various performance properties (viscosity, rutting, fatigue cracking, and low temperature cracking) of the binders. From the test results, the following findings were drawn for the materials used in this study.

- (1) The addition of two wax additives into control and PMA binders can significantly decrease the viscosity at 135°C and 120°C and the reduction rate was quite similar for both the binders.
- (2) The viscosity of control binders were stabilized between 20 and 40 min and remained constant whereas the viscosity of PMA binders steadily increased after 30–40 min over the whole testing period at 135°C . The same trend was observed at 120°C .
- (3) Generally, both the additives were observed to be effective on increasing the rutting resistance. Irrespective of the aging state (no aging and RTFO), it was found that the control binders containing wax

additives have the higher percentage improvement in rutting resistance compared to the PMA binders with the additives.

- (4) From the DSR test at intermediate temperatures, it appeared that the binders with Sasobit were observed to have the higher $G^*\sin\delta$ values, meaning they were less resistant to fatigue cracking. Whereas, the addition of LEADCAP significantly reduced the $G^*\sin\delta$ values, suggesting that the use of LEADCAP was useful to improve the fatigue cracking resistance. These trends were similar for both the control and PMA binders.
- (5) The binders with Sasobit were found to have significantly higher stiffness values which relate to possible lower resistance on low temperature cracking. However, the addition of LEADCAP significantly reduced the stiffness values. Both the binders were found to have the similar trend in stiffness values. Also, the use of SBS polymer seemed to have little effect on the thermal cracking behavior.
- (6) Between these two wax additives, LEADCAP is observed to be better than Sasobit in terms of resistance to fatigue and low temperature crackings. On the other hand, for rutting resistance, Sasobit performs better than LEADCAP.
- (7) It is recommended to conduct a field study to generalize these findings with the field behavior.

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