Physical properties and chemical bonding of advera® modified asphalt binder

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Abstract. Modification of asphalt to improve the overall performance of pavements has been the focus of numerous researchers in recent years. This paper discovered whether the use of chemical additives namely Advera® is possible to influence the physical and chemical bonding of asphalt binder grade 80/100 subjected to different aging conditions. The fundamental characteristics of modified binder containing 4%, 5%, 6% and 7% of Advera® were determined by conventional methods while chemical characterisation was assessed by conducting Fourier tTransform iInfrared sSpectroscopy (FTIR). With the aid of image tool, scanning electron microscopy (SEM) was employed to study the surface texture and morphology of Advera® modified binder.The results indicated that, the Advera® modified binder had improved the physical and chemical properties over base binder for both aging condition. The SEM images show that the microstructure of Advera® modified asphalt binder changed compared to the control asphalt binder. A good dispersion of Advera® particles in the asphalt binder matrix is observed. This is proved by the FTIR results which indicate that the stretching of hydroxide is increase when the Advera® is added in the virgin asphalt binder.

1 Introduction

Asphalt binders are derived from the residual fractional distillation of crude oil. The performance of a binder is determined by its physical properties which are determined by the chemical composition. A broader range of chemical properties is demonstrated by asphalt binders depending on the source of crude oil and processes used to produce the asphalt binder. Asphalt binder is a thermoplastic liquid which behaves as an elastic solid at low service temperatures and at high temperatures, it behaves as a viscous liquid [1]. According to Yero and Hainin [2], the binder forms about 4 - 6% of the weight of the mixture, while the aggregate comprises between 94 - 96% by weight asphalt concrete mixture. Hamzah et al., [3] stated that the production process of crude oil is not only pricey, but also creates pollution to the environment. Hence the growth of a clean technology through low-carbon technology united with sustainable technology is necessary

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to overcome this problem. Production at lower temperatures, if workable, has the potential to use less fuel, resulting in reduced costs and lower emissions.

Asphalt mixtures (WMA) is a technology that has gained popularity, which is developed in response to the rise in crude oil prices, the asphalt binder and the mix [3]. WMA is a new and emerging technology that tries to reduce the emission and energy consumption through lowering the binder viscosity which resulted in reducing the mixing and compacting temperature during the production and placement process [5] compared to the traditional Hot Mix Asphalt (HMA) [6]. Modification of asphalt to improve the overall performance of pavements has been the focus of numerous researchers over the past few decades [7]. The modification of bitumen with foamed asphalt additive namely Advera® has enable the reduction of the mixing and compaction temperature that translates to the reduction in emission of greenhouse gases and energy saving.

It is reported that the use of Advera® lead to reduced odour and blue smoke production with up to 60% reduction in volatile organic compounds, carbon dioxide, sulphur dioxide and nitrogen oxide emissions and energy savings up to 30% [8]. However, researchers mentioned that by adding Advera® into the binder will results in a more consistent mixture [9] but it is understood that the proper way of using Advera® is to add them directly into mixture during mixing phase in order to provide adequate expansion of bitumen [10]. Thus, the study of the rheological properties enables the proper understanding of the performance of bitumen with or without the additive.

Modification of asphalt to improve the overall performance of pavements has been the focus of numerous researchers. Thus, this paper discovers the potential of Advera® foamed asphalt additive in reducing the aging of the asphalt binder using Superpave^{TM} asphalt binder test under unaged and short term aged condition.

2 Materials and Methods

2.1 Materials and sample preparation

In this study, Advera® WMA additive is acquired from PQ Corporation (Thailand). Advera® WMA is aluminosilicate that developed for warm mix asphalt application and also a synthetic mineral in powder form containing 18-20% moisture which is chemically and structurally bound. The properties of Advera® bulk density measured ranging 300-480 kg/m^3 which the value of moisture loss at 800^{o}C around 22% . Table 1 shows the chemical composition of Advera® that consists of Sodium Oxide, Aluminium Oxide and Silicon Oxide.

Table 1. Average Chemical Compositions

Type of Chemical	Composition
Sodium Oxide (Na_2O)	17-19%
Aluminium Axide (Al_2O_3)	28-35%
Silicon Oxide (SiO_2)	31-34%

Advera® modified asphalt binder were prepared by blending base binder 80/100 with Advera® in a concentration of 4% to 7% at 1% interval by weight of binder using high shear silverson mixer. The binder was pre-heated in the oven at 110^{o}C prior to blending process. Before adding the Advera®, the binder was stirred for 2 minutes to obtain a uniform temperature distribution and then the addition was performed manually and slowly to attain a homogenous distribution of the additive [11]. The additive was stirred at a rotational speed of 3000 rpm for 20 minutes at a temperature 130ºC to allow complete homogenization of Advera® within the binder. The samples were prepared by two aging condition which were unaged and short-term aged binder..

2.2 Test Methods

i. Penetration test: The penetration test provides a measure of the consistency or hardness of the bitumen. In this test, a needle of specified dimensions was allowed to penetrate a sample of bitumen, under a 100 g load at 25°C temperature for 5 seconds as outlined in ASTM D5 [12]. The specimens were prepared in sample containers and placed in a water bath at 25°C for 1.5 hours prior to testing. Loading of 100 ± 0.05g was brought to the surface of the specimen at right angles, allowed to penetrate the bitumen for 5 ± 0.1s, while the temperature of specimen was maintained at 25 ± 0.1°C

ii. Softening Point test: The softening point temperature was designated as the softening point of the bitumen and represents an equi-viscous temperature. In this test, a ring and ball apparatus was immersed in the water and left in room temperature for half an hour. A standard 3.5 g steel ball was placed onto a sample of bitumen confined in a brass ring that was suspended in a water bath. The water bath temperature was raised at 5°C per minute, the bitumen was softened and eventually deformed slowly with the ball moving through the ring. At the moment the bitumen and the steel ball touch a base plate 25 mm below the ring, the temperature was recorded. This The test was carried out to conformed ASTM D36 [13]. The temperature was used in conjunction with the penetration value to obtain the Penetration Index (PI).

iii. Rotational Viscosity Test: A brookfield rotational viscometer (RV) was used to determine the mixing and compaction temperature according to Asphalt Institute recommendation. The effects of Advera® contents on the viscosity of unaged and aged asphalt binders were carried out according to ASTM D4402 [14]. The mixing temperatures in the RV tests were commenced at 120°C up to 160°C at 20°C increments for both unaged and short term aged binder. In this test, 8.5g of binder sample was tested when the digital indicator on the temperature controller shows that the sample temperature has equalized. During the test, the spindle size, S21 was lowered into a chamber containing the hot sample operated at 20 rpm, and the spindle was coupled with the viscometer. A waiting period, 15 minutes was required to allow the temperature return to 120°C. Viscometer motor was turned-on and the operator observed the viscosity reading during the waiting period. The viscosity was recorded at 1-minute intervals.

v. Fourier Transform Infrared Spectroscopy: The chemical nature and composition with respect to the functional group present in the asphalt were evaluated using FTIR. In the experimental study, chemical characterizations of modified binders with Advera® before and after ageing will be performed using conventional method Fourier Transform Infrared Spectroscopy – attenuated total reflectance (FTIR-ATR). FTIR-ATR is a beneficial technique because it requires little to no sample preparation and ideal analytical tool for evaluating the presence of solvent in asphalt because of the simplicity of analysis [15]. FTIR spectras were recorded by PerkinElmer model Spectrum. All spectras were obtained by 32 scans with 4 cm^{-1} resolution in wavelengths ranging from 600 - 4000cm^{-1}. In this study, sulfoxide band and carbonyl band in the infrared spectra related were investigated to determine aging effect of modified asphalt binders.

3 Results and Discussions

3.1 Penetration and Softening Point Test

Figure 1 illustates the relationship between penetration and Advera® content for unaged and short-term aged binder. General trend shows that every contents of Advera® added on the asphalt binder is not significantly reduces the penetration value for both aging condition in camparison to virgin binder. The result indicates that the specimens incorporating 5% Advera® experiences the lowest penetration value compared to control binder and other percent of Advera® modified binders. Adding 5% of Advera® in unaged and short term aged binder, the penetration value reduces from 84.6d-mm to 80.1 d-mm and 62 d-mm to 51.1 d-mm respectively. Meanwhile asphalt binder modified with 7% Advera® is found as the highest penetration value compared to other modified binders for both unaged and short term aged binder. Overall, the penetration value of Advera® modified binder for both aging conditions are lower than control binder regardless of Advera® dosage. The bar chart also shows the penetration value for unaged binder is found to be higher than the short-term aged irrespective of Advera® contents. This is due to the fact that the specimen after aging were more hardened compared to the fresh binder because the aging was exposed to the high temperature and pressure [16].

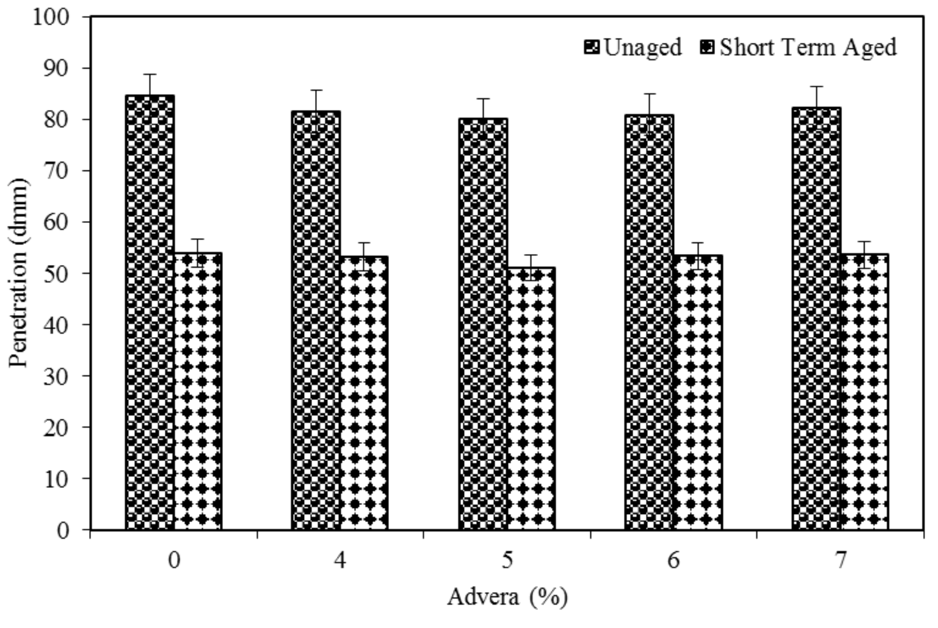

Fig. 1. Relationship between Advera® content and penetration for unaged and short term aged binder.

Figure 2 illustrates the presence of Advera® on softening point of asphalt binder. Overall, softening point for Advera® modified binder is slightly higher than the base binder for both aging condition. Based on the bar chart, unaged binder containing 5% Advera® depicts the highest softening point followed by 0%, 4%, 7% and 6%. Meanwhile, same trend is observes for short them aging where 5% of Advera had increase the softening point compared to base binder from 47ºC to 48.1ºC. However, 4% and 7% result in similar value of softening point after aging. Incorporating 5% Advera® results in 4.8% and 2.3%

increases over base binder for both aging condition. This finding is constant with the previous study which claim that addition of Advera® does not significantly influence the softening point [17]. According to Mahrez and Karim [18], asphalt binder with high softening point may be less susceptible to permanent deformation.

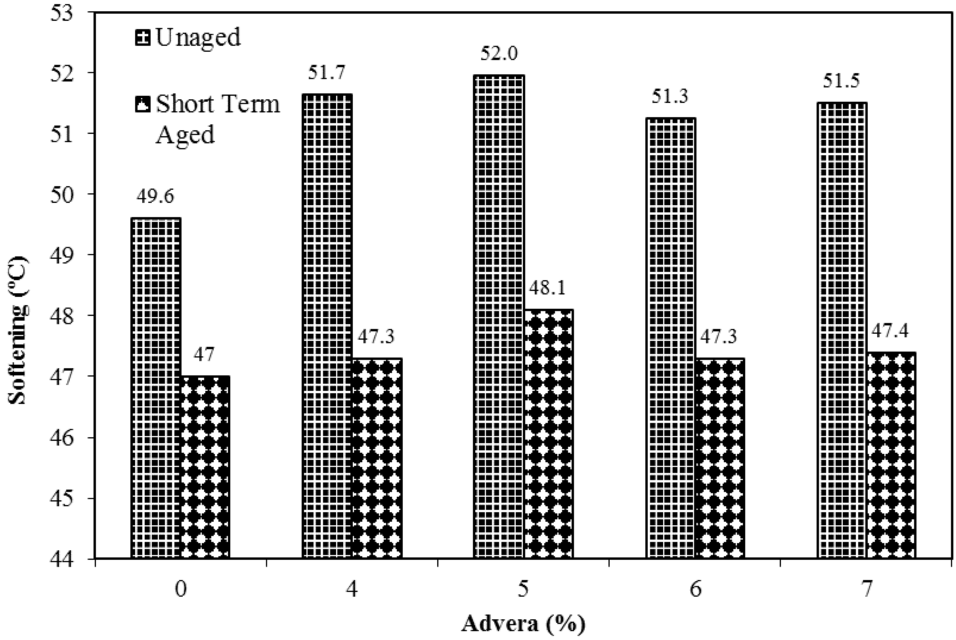

Fig.2. R.elationship between Advera® content and softening point for unaged and short term aged binder.

3.2. Penetration Index

The penetration index for all modified binders are depicted in Figure 3 which shows the effect of Advera® content and aging condition on penetration index. Overall trend found that, the addition of Advera® increases the PI for unaged and short term aged binder. The result indicates that adding 5% Advera® into the unaged binder depicts the highest value of PI followed by 4% 7% and and 6% of Advera® content. After simulated into the RTFO oven, the PI for incorporating 5% Advera® decreases to -1.64 but still remains the highest value compared to the base binder and other modified binders. Incorporating 5% Advera® increases the PI from -0.10 to 0.51 and -1.81 to -1.64 for unaged and short term aged respectively compared to the base binder. The increase in PI will enhance the temperature susceptibility of the bitumen. According to Hadavand [19], asphalt mixtures containing bitumen with higher PI are more resistant to low temperature cracking as well as permanent deformation.

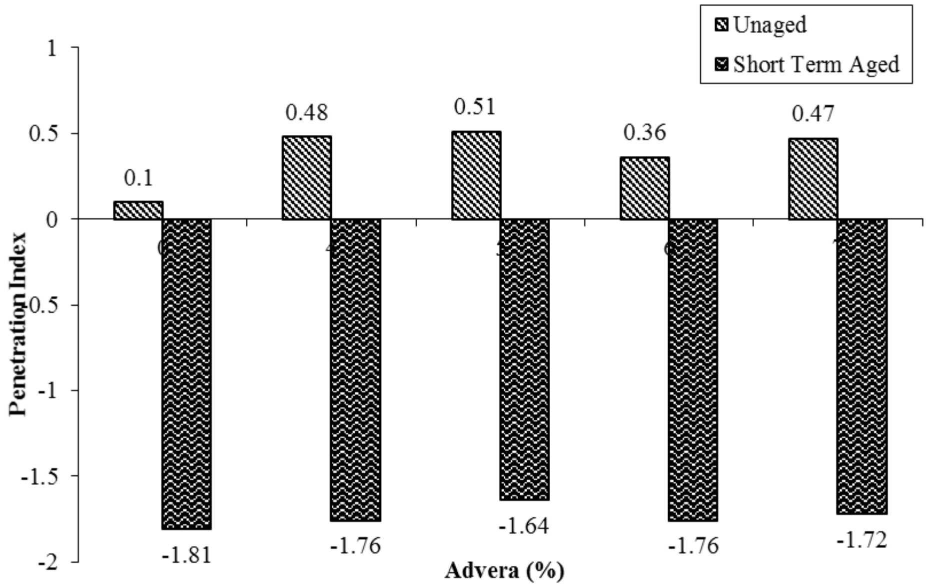

Fig. 3. Effect of Advera® content on penetration index.

Further analysis was performed using One-Way ANOVA to determine the effect of Advera® for Unaged Binder on PI at 95% confidence level (α=0.05). Table 2 show that Advera® slightly has not significant effect on increasing PI due to increases in softening point and penetration test with P-value more than 0.05.

Table 2. One way ANOVA Effects of Advera® for Unaged Binder on PI.

Source	DF	SS	MS	F	*p*-value
Advera	1	0.07420	0.07420	5.63	0.098
Error	3	0.03952	0.01317		
Total	4	0.11372			
R-Sq=65.25% R-sq (adj)= 53.67%					

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Table 3 summarizes the analysis results for short term aged binder on PI using One-Way ANOVA at 95% confidence level. It can be seen that the Advera® content does not significantly affected the penetration Index (PI), with *p*-value more than 0.05. According to Mannan [23], binder with higher PI are more resistant to low temperature cracking as well as permanent deformation.

Table 3. One way ANOVA Effects of Advera® for Short Term Aged Binder on PI.

Source	DF	SS	MS	F	*p*-value
Advera	1	0.005370	0.005370	1.50	0.307
Error	3	0.010710	0.003570		
Total	4	0.016080			
R-Sq=33.40% R-sq(adj)= 11.20%					

4.3. Effect of Advera® on Mixing and Compaction Temperature

The mixing and compaction temperatures of asphalt mix greatly depend on the viscosity of the binder. The ideal laboratory mixing and compaction temperature of asphalt concrete and other hot-mix type using conventional binder are the temperatures at which the binder achieves a viscosity of 0.17 ± 0.02 Pa.s and 0.28 ± 0.03 Pa.s, respectively [20]. Figure 4 illustrates the graph of the relationship between temperature and viscosity. General trend shows that the addition of Advera® increase the mixing and compaction temperature. However, Advera® modified binder only shows slightly different compared to control binder. Incorporating 4% and 6% of Advera show the highest mixing and compaction temperature which found in the range 158-162 and 145-149 Pa.s whereas the lowest mixing and compaction compared to all modified binder is 5% and 7% of Advera® which found in the range 160-165 Pa.s and 147-151 Pa.s respectively. Table 4 tabulates the result for mixing and compaction temperature for base binder and modified binders. The same result was recorded in previous studies which claimed that the addition of Advera® increases the mixing and compaction temperature of asphalt binder [21].

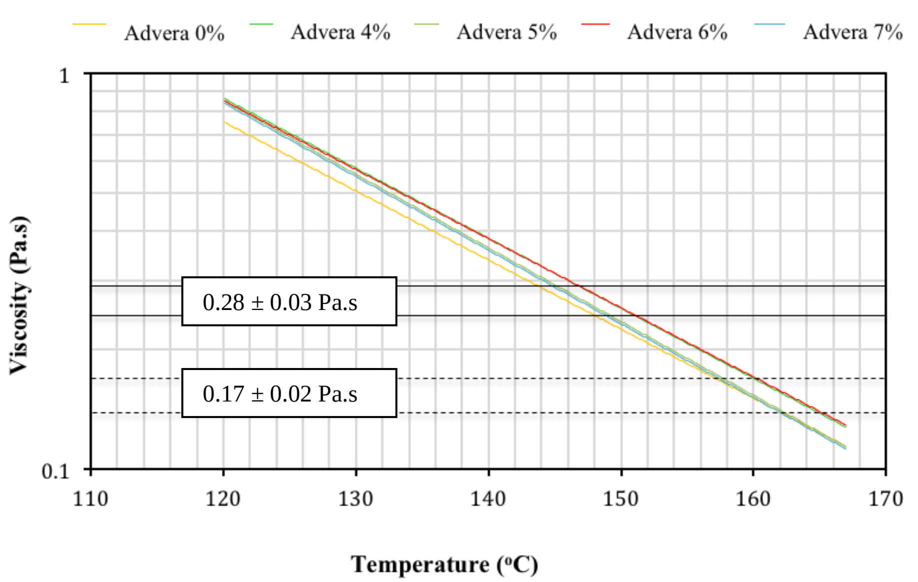

Fig. 4. Temperature-Viscosity Relationship.

Table 4. Mixing and compaction temperature.

Advera (%)	Mixing Temperature (°C)	Compaction Temperature (°C)
0	157 – 162	143.5 – 148
4	160 – 165	147 – 151
5	157.5 – 162	145 – 149
6	160 – 165	147 – 151
7	157.5 – 162	145 – 149

Figure 5 and 6 show the relationship between Advera® content and binder viscosity at different temperature. The result indicates a general trend that every content of Advera® results in a rise of the binder viscosity compared to the base binder whereas when the binder is aged the viscosity also increases except for binder modified by 5% and 6% of Advera® irrespective of the test temperature. The viscosities of the binder were observed at peak when temperature equivalent to 120°C for both aging condition. At similar temperature, the asphalt binder modified by Advera® is higher for unaged and aged binder except aged binder containing 6% Advera® compared to the base binder.

For unaged binder (Fig.5) tested at 120°C, the binder containing 4% advera® increases 15% followed by 6% advera which shows 12.5% compared to the control binder while the binder containing 5% and 7% of Advera® depicts the same increase in viscosity which is 11.3% higher than the control binder. The same trend has been observed when tested at 140°C and 160°C which shows that the 4% and 6% of Advera® modified binder are higher than the control binder. After the binder were aged in RTFO for 163°C (Fig.6), the viscosity shows an increment with every content of Advera® except 6% which is lower than the control binder when tested at temperature 120°C. It is noticed that when tested at temperature 140°C and 160°C, 5% and 6% of Advera® exhibit similar viscosity value of 330mPa.s and 70mPa.s respectively. When 7% of Advera® is added to the binder, the viscosity is slightly increase from 180mPa.s to 190mPa.s and the result also shows that, for short term aged binder the 7% of Advera® modified binder shows the highest viscosity for every tested temperature compared to compared to the other binders.

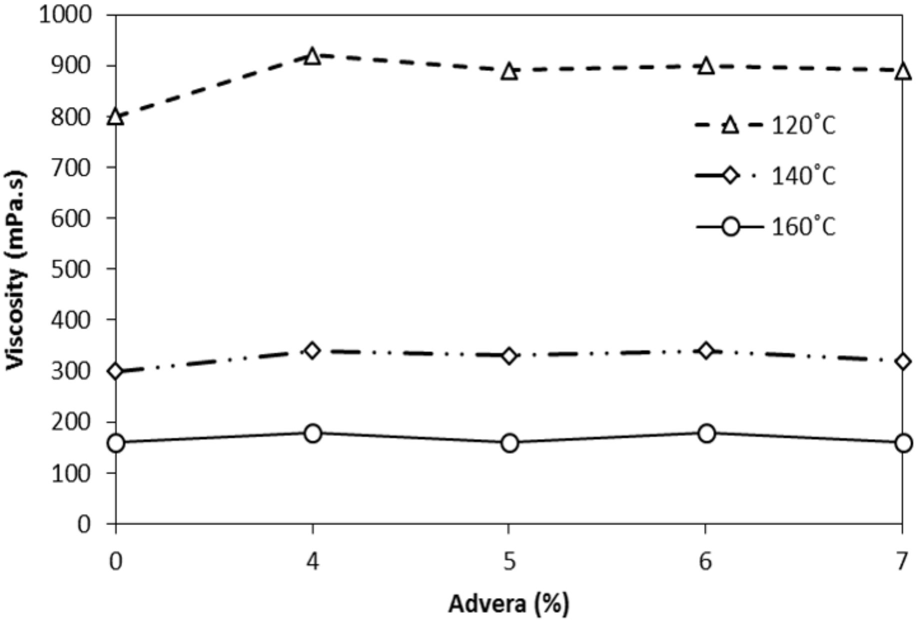

Fig.5. Relationship between viscosity and Advera® content for unaged binder.

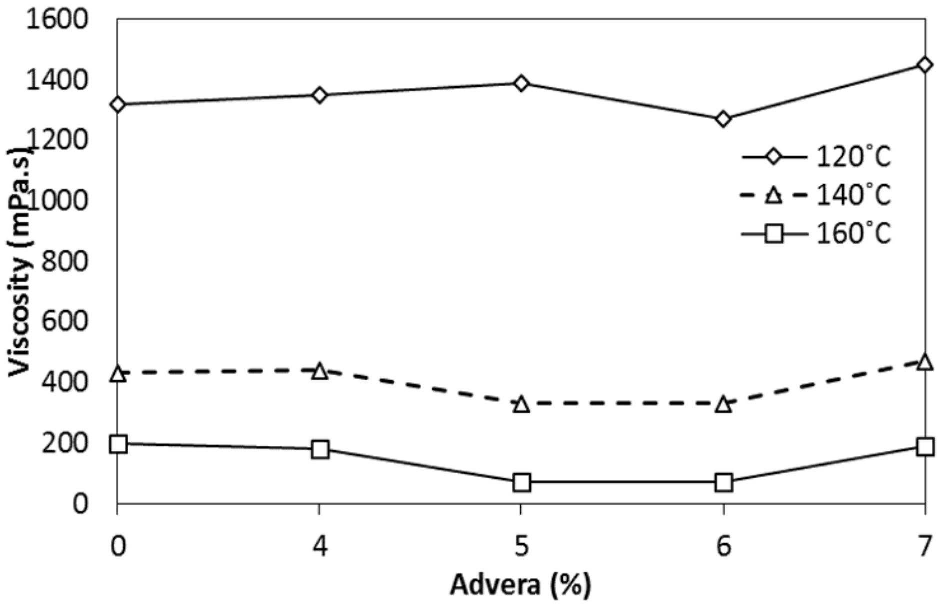

Fig.6. Relationship between viscosity and Advera® content for short term aged binder.

The increase in viscosity with Advera® is thought to be caused by the addition of fine powder to the binder which acts as a filler [11, 17, 22] . Gandhi and Amirkhanian [21] reported that the increase in viscosities of the binder after RTFO aging may not entirely due to increased aging of asphalt binder in the presence of Advera® but due to subsidence of the foaming effect of Advera® during the aging process. After initial foaming, the Advera® particle remain undissolved in the binder thereby increasing the viscosities of the binder. However, some previous finding shows that the addition of Advera® into the binder results in increase the viscosity of asphalt binder and some shows the opposite statement. This is mainly due to chemical structure and source of particular Advera® [17]. However, based on viscosity data, all modified asphalt binders are lower than 3Pa.s when tested at 135°C hence meet the standard specification of Superpave™.

4.4 Effect of Advera® Content on Aging Index

Figure 7 shows the bar chart of aging indices for binder with Advera® tested at different temperature. The result indicates that the decreases in temperature results in increases the aging index for all binder containing Advera®. Aging indices tested at 120°C are higher than those tested at 140°C and 160°C. The addition of 6% Advera® significantly lower the aging index followed by 5%, 4% and 7% Advera® compared to control binder at every test temperature. The percentage decreases after adding 6% Advera® at 120°C, 140°C and 160°C is 14.6%, 32.2% and 68.8% respectively. It is also noticed that, the aging index for 5% and 6% Advera® is almost equal at temperature 140°C which shows 1.00 and 0.97. High aging index indicates a higher tendency to age when exposed to high plant temperatures and pavement service temperatures [23].

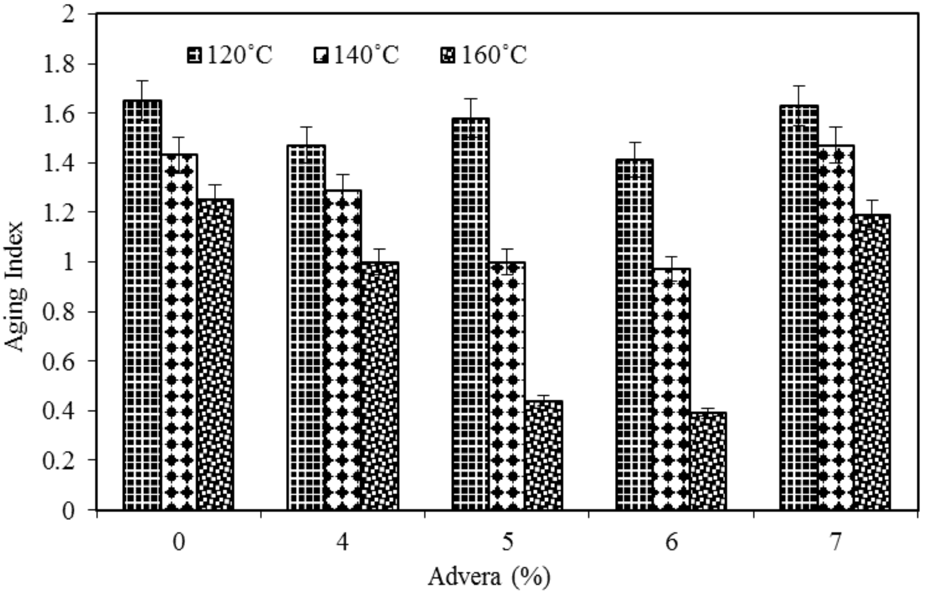

Fig.7. Effect of Advera® on Aging Index.

4.5 Fourier Transform Infrared Spectroscopy

The aging of asphalt binder is an oxidative chemical process that will lead to the formation of carbonyl compounds (C=O) and sulfoxides (S=O) [24]. The spectra of modified and unmodified binder tested in FTIR spectrometer for unaged and short term aged are displayed in Figure 8 and 9. The characteristic of functional groups in the carbonyl and sulfoxide regions at wavelength numbers 1030cm^{-1} and 1700cm^{-1} were observed which is often applied to evaluate the aging extent of bitumen during different aging processes. The IR absorbance of carbonyl bonds (Fig. 8) in the Advera® asphalt binder increases slightly compared to the base binder. However, IR absorbance of unmodified asphalt binder shows slightly higher compared to modified binders after RTFO aging (Fig. 9). Referring to Figure 8, asphalt binder modified by 7% of Advera® exhibit the highest IR absorbance of carbonyl bonds which equal to 0.0203 whereas for Figure 9 shows the base binder as the highest IR absorbance which equal to 0.1086. The corresponding sulfoxides bonds of these binders are 0.1119 and 0.0223 respectively. The result indicates that the addition of Advera® into the asphalt binder could reduce the aging process because it can delay the oxidation reaction. According to Lopes et al., [20] high C=O and S=O reflect to the aging of asphalt binder. Though the sulfoxide bonds for unaged modified binder with 7% Advera® shows higher than unmodified binder after aging, the previous study mention that the sulfoxide index is not considered as an aging index in the asphalt binder [25]. It can be summarized that the decreasing and increasing of carbonyl groups are due to the binder molecur chained at high temperature and react with ketones and anhydrides to reduce aging.

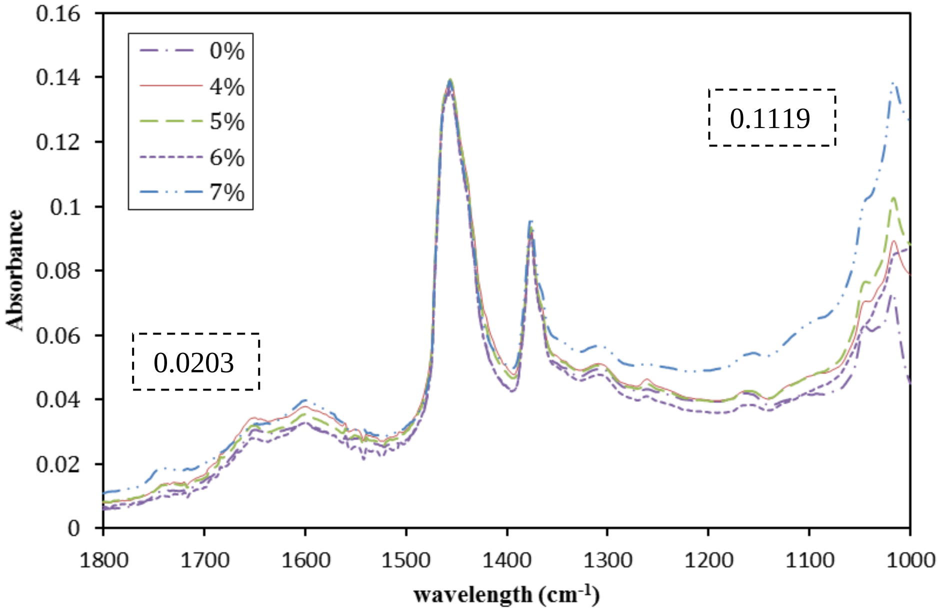

Fig.8. Characteristic peaks around the carbonyl and sulfoxide for unaged binder.

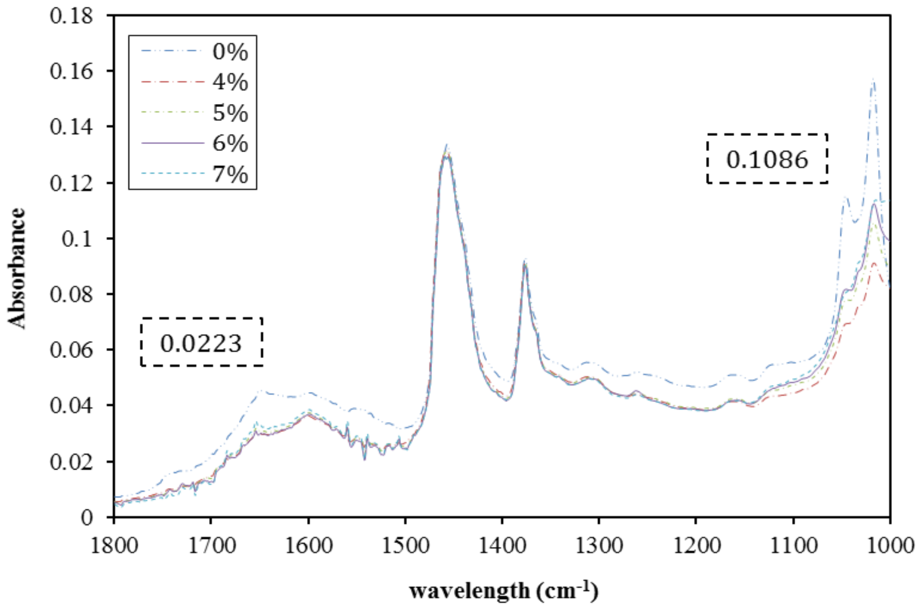

Fig.9. Characteristic peaks around the carbonyl and sulfoxide for aged binder.

4.6 Scanning Electron Microscopy

The SEM images of Advera® modified binder are helpful to understand the microstructure change of modified binder, as well as the physical dispersion of Advera® particles. As shown in Figure 10 the microstructure of Advera® modified asphalt binder was changed significantly compared to the control asphalt binder. The image shows that the microstructure change of the base binder is smaller compared to Advera® modified asphalt binder for every addition of Advera®. Morphological evaluation shows that Advera® modifier were thoroughly blended. In addition, from the FTIR (Fig. 8) of control and Advera® modified binder, the stretching OH group in the asphalt is centred around 3594cm^{-1} and 3735cm^{-1} is increased. It proves that Advera® is physically dispersed in the asphalt. The image also displays that the microstructure of asphalt binder was increased after blending with Advera®. The new structure of Advera® modified binder is formed, and the Advera® group, white particles in asphalt matrix, is glued uniformly with the asphalt binder. The surface of Advera® group reacts with the asphalt binder, and the size of Advera® group becomes bigger. This is an important factor that affects the viscosity of modified asphalt binder.

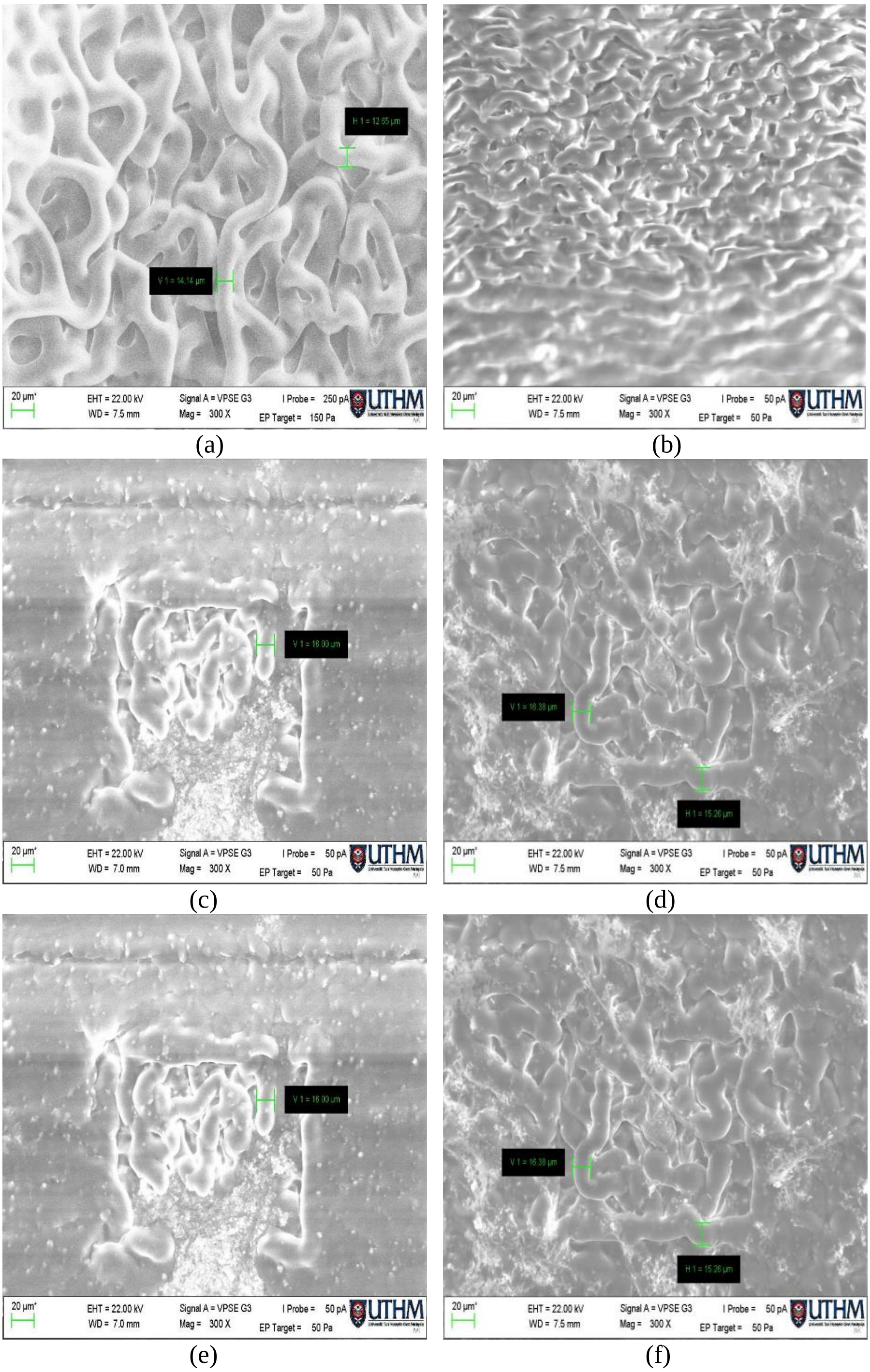

Fig.10. SEM images of (a) base binder, (b) base binder + 4% Advera®, (c) base binder + 5% Advera®, (d) base binder + 6% Advera®, (d) base binder + 7% Advera®, (e) Advera®.

5 Conclusion

This study aimed to evaluate the performance of asphalt binder after blending with foamed asphalt additive namely Advera®. It verified that the physical properties that the binder modified by Advera® causes increase in softening point and small reductions in penetration. Eventhough the penetration of modified binder shows small decrement in comparison to virgin binder, but an increased softening point temperature of modified binders indicate increased stiffness of the asphalt binder. Hence, the penetration index of asphalt binder increased with the increased of Advera® into the asphalt binder regardless of the aging state.

The addition of Advera® into the asphalt binder increases the viscosity of the binder at high and intermediate temperature regardless of the aging state. In addition, aged binder exhibits increased viscosity due to binder hardening that increased the binder stiffness. According to rotational viscosity results, the addition of Advera® increased the viscosity, therefore raising the mixing and compaction temperatures. The previous study claimed that, the increase in viscosity is mainly due to the Advera® that acts as a filler which remain undissolved in the asphalt binder. Thus, Advera® failed to exhibit a reduction temperature of the asphalt binder which is the main purpose of warm mix asphalt additive. However, the aging index which is the ratio between aged over unaged viscosity depicts that, adding Advera® into the asphalt binder could reduce the resistance to aging compared to control binder irrespective to the test temperature.

Chemical evaluation by FTIR verified that the aging could be quantified by its means.The chemical functional and structural changes are precisely analysed through infrared at vibration modes of C=O and S=O. The aging degree of Advera® modified binder is monitored by the changes of the carbonyl and sulfoxide bonds which indicate the functional characteristic of modified binder before and after aging. It can be observed that the absorbance value increases at every level of oxidation at carbonyl and sulfoxide regions. Based on absorbance peaks of carbonyl bonds, the addition of Advera®could delay the aging process of asphalt binder.

The SEM images show that the microstructure of Advera® modified asphalt binder changed compared to the control asphalt binder. A good dispersion of Advera® particles in the asphalt binder matrix is observed. This is proved by the FTIR results which indicate that the stretching of OH is increase when the Advera® is added in the virgin asphalt binder.

The authors would like to acknowledge the financial support from Universiti Tun Hussein Onn Malaysia (UTHM) and Ministry of Education Malaysia (MOE), which enabled this paper to be materialized. Also, assistance received from Mr Azuan Poharan@ Bunari Assiatant Engineer of the Highway Engineering Laboratory in the collection of data is gratefully acknowledged. Appreciation is also extended to PQ Chemicals (Thailand) Ltd Ltd. and Hanson Quarry Sdn. Bhd., for respectively supplying Advera® and aggregates.

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