Technical Note

ISSN 1997-1400 Int. J. Pavement Res. Technol. 7(5):376-380

Aging Characteristic of Styrene-Butadiene-Styrene Modified Asphalt under Thermal-Humidity Conditions

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Abstract: The investigation of aging characteristic of Styrene-Butadiene-Styrene (SBS) modified asphalt binder (PMA) under thermal-humidity conditions is helpful for the application of PMA and the selection of anti-aging technology. Simulated aging tests on styrene-butadiene-styrene (SBS) and SBS-modified asphalt were compared for wet and dry conditions, and the effect of water on the aging of the modified asphalt was investigated using infrared spectroscopy. Aging under wet conditions changed the asphalt performance and caused a more pronounced color change in SBS. An infrared spectral analysis showed that aging under wet conditions increased the carbonyl content of the asphalt and SBS. The presence of water was shown to accelerate the aging of asphalt and SBS under the action of heat and oxygen. This enhanced aging was primarily related to the asphalt components with carbonyl groups, which were further oxidized to carboxylic acids by reacting with water. The double bonds in the SBS chains were also transformed into polar groups via a hydration reaction under thermal-humidity conditions.

DOI: 10.6135/ijprt.org.tw/2014.7(5).376

***Key words**: Aging mechanism; Infrared spectroscopy; SBS-modified asphalt; T2344hermal-humidity conditions.*

Introduction

Polymer-modified asphalt binder (PMA) consists of asphalt binder blended with a styrene-butadiene-styrene block copolymer (SBS) and has been widely used as a flexible pavement material because of its superior performance compared to base asphalt binder (BA) [1-3]. SBS-modified asphalt binders age during their production and service life. Asphalt binder aging from heat, water, oxygen, and other effects decreases the performance and shortens the service life of asphalt pavement [2-10]. Aging is an important consideration in selecting SBS-modified asphalt binder applications.

However, current testing methods for asphalt binders aging, which include PAV (pressure aging vessel test) and RTFO (rolling thin film oven test), are only related to the thermal oxidative aging of asphalt binder. The actual aging process over the service life of asphalt pavement is also affected by water [11-21]. The previous studies focused primarily on the influence of water on the performance of asphalt mixtures. Cheng, Airey, et al. [11-12] considered the factor of moisture in the damage evaluation of asphalt mixtures. A few studies have investigated the impact of water during the laboratory aging of base asphalt binder, and concluded that the water could accelerate the aging of asphalt binder [13, 14]. But Huang's study showed that moisture had no significant effect on the oxidation rate at atmospheric pressure [15]. The anti-aging ability of SBS modified asphalt binder is better than that of base asphalt binder. The aging mechanism of SBS modified asphalt binder is very complex because of various aging conditions and reactions between SBS and asphalt binders. Under thermal-humidity conditions, the water reacts with asphalt and SBS respectively, and the aging mechanism is more complicated than that in base asphalt binder. Therefore, it is critical to study the effect of water on aging of SBS modified asphalt binder.

In this study, asphalt binder was modified using SBS copolymers. Simulated aging for SBS and SBS-modified asphalt binders were compared under wet and dry conditions. The mechanical properties of the SBS-modified asphalt binders, including penetration, dynamic shear behavior, and low temperature rheological properties, were measured. The effect of water on the aging of the modified asphalt binder was investigated using infrared spectroscopy.

Experimental Program

Materials

Asphalt binder from China (penetration-grade 70#) was used as the base asphalt (BA) in preparing the polymer modified asphalt binder (PMA). Grade 4303 SBS with a radial structure was manufactured by the Yueyang Petrochemical Co., Ltd., in China and used as the asphalt modifying agent in the study. The PMA binder had an SBS content of 4% by weight.

The asphalt binders and SBS were blended at 170℃ - 180℃ using a high-speed shearing mixer. To prevent the SBS from separating out of the asphalt binder, a solubilizer and a stabilizer were added to the SBS-modified asphalt. The shear impeller speed ranged between 5,000 and 6,000 rpm, and the asphalt was mixed for 60 min. The final step in the blend processing of SBS and the asphalt involved swelling for 30 min at 150℃. The physical performance indexes of the BA and PMA are shown in Table 1.

Aging Tests

The SBS-modified asphalt binder samples were aged using the RTFO and PAV tests to simulate short-term aging in the production

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Note: Submitted February 09, 2014; Revised June 12, 2014; Accepted June 16, 2014.

Table 1. Physical Performance Indexes of Asphalt Binders.

Samples	Penetration at 25℃ [0.1 mm]	Softening Point [℃]	Ductility at 15℃ [cm]	$G^*/\sin\delta$ at 70℃ [kPa]	Creep Stiffness at -12℃ [MPa]
Base Asphalt (BA)	72	46	＞100	0.70	110
Polymer-modified Asphalt (PMA)	57	80	37	2.17	98

of an asphalt mixture and long-term aging in the service life of asphalt pavement. In the RTFO test (ASTM D2872), the SBS-modified asphalt binder samples were aged at 163℃ for 75 min using a P877 rotary thin film oven. The samples were then aged further using the PAV test (ASTM D6521) at a temperature of 100℃ and an air pressure of 2.1 MPa in a PR9300 pressure aging instrument for a duration of 10 or 20 h.

To evaluate the effect of water on the aging of the binder, a small amount of water was added to the asphalt binders that were subjected to the RTFO test before the PAV test was conducted, and the physical performance indexes of the binders were determined.

Mechanical Properties Test

The index of penetration at 25℃ of the asphalt binder in different aging states was determined following current Chinese test specifications (Standard Test Method of Bitumen and Bituminous Mixtures for Highway Engineering, T0604-2000). The dynamic shear properties of the asphalt binder were tested using a dynamic shear rheometer (RDA III, Rheometrics) at 10 rad/s. The G*/sin δ index of the binders was measured following standard testing methods (ASTM TP5) with a 25.0 mm diameter parallel plates and a 1.0mm gap. Low temperature creep tests were conducted using a bending beam rheometer (BBR) that was manufactured by the Cannon Instrument Company. Asphalt binder beams (with dimensions of 125 mm×12.5 mm×6.25 mm) were prepared, and a creep test was conducted at -12℃ (ASTM TP1) to obtain the creep stiffness (S Value) of the asphalt binders.

Infrared Spectral Analysis

Fourier transform infrared spectroscopy (FTIR) was used to investigate the aging mechanism of the SBS-modified asphalt binder under thermal-humidity conditions. Asphalt samples were aged using different methods for different times and were subsequently cast as films onto potassium bromide (KBr) pellets for analysis by FTIR using a TENSOR 27. The pure SBS samples were powdered and tableted with KBr. The infrared spectra of the asphalt binders and the SBS were obtained at a 4 cm^{-1} resolution. The carbonyl index (CI) was calculated by comparing the ratios of the absorption peak areas of the carbonyl (1650 cm^{-1} - 1740 cm^{-1}) bonds to that of the saturated C-H (1365 cm^{-1} - 1455 cm^{-1}) bonds.

Results and Discussion

Mechanical Properties

Figs. 1 – 3 show the test results for the following physical properties of the SBS-modified asphalt binders and BA samples: penetration at 25℃, the dynamic shear properties, and the low temperature rheological properties. The test results showed that the penetration of asphalt decreased, and the creep stiffness (S value) and the G*/sinδ of binders increased following RTFO aging and PAV aging for different times.

For the PAV test using hot oxygen, the penetration increased by 3-5 units (0.1 mm) in the presence of water. The G*/sinδ values of the BA and PMA that were aged under wet conditions increased by 17.5% and 12.5%, respectively, after 10 h of PAV aging and by 26.3% and 15.6%, respectively, after 20 h of PAV aging. Similar results are shown in Fig. 3, proving that the presence of water increased the aging of the asphalt binders. The amount of moisture significantly promoted hot oxygen aging reactions. These results show that less time was required to age asphalt binders with similar performances to the same degree under wet conditions than under dry conditions. Thus, the presence of water could shorten the service life of asphalt binders.

Results of Infrared Spectral Analysis of Binders

Infrared spectroscopy is one of the most important analytical techniques in materials research. This technique is indispensable for

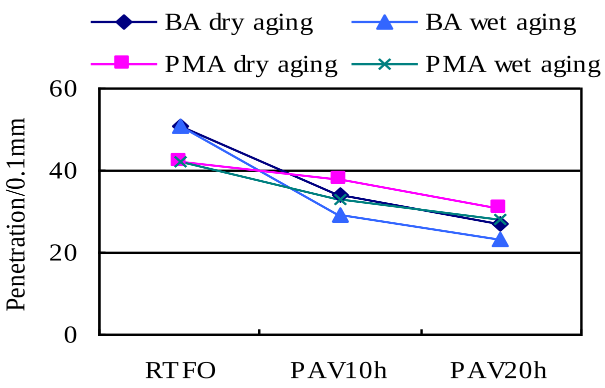


Fig. 1. Penetration of Asphalt Binders at 25℃.

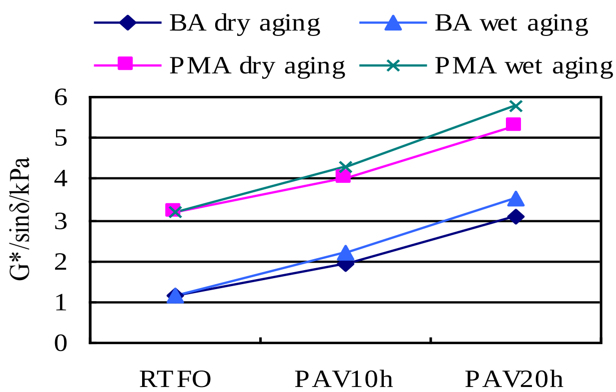


Fig. 2. G*/sin δ of Asphalt Binders at 70℃.

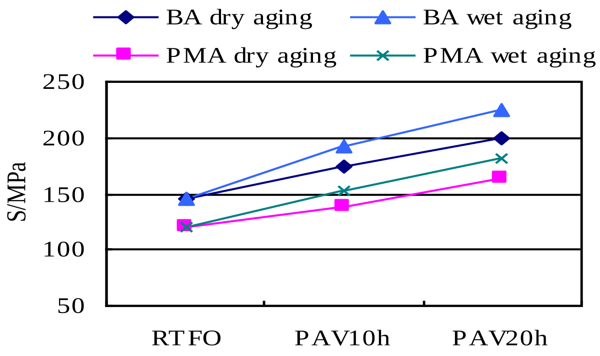


Fig. 3. Stiffness of Asphalt Binders at -12℃.

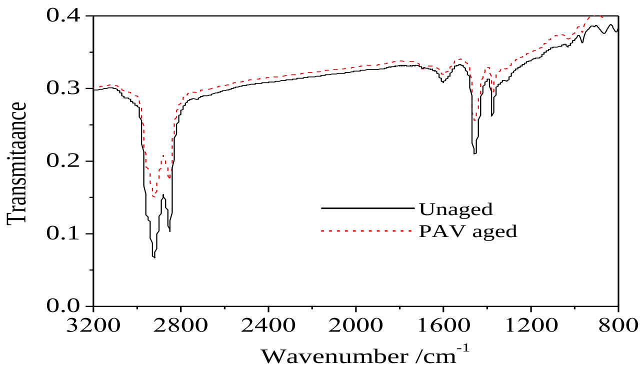


Fig. 4. FTIR Spectra of Asphalt Binders.

determining the characteristics of the functional groups in asphalt binder. Tracking the changes in the absorption peaks of the primary functional groups in asphalt binder can be used to obtain a deeper understanding of the asphalt binder aging process.

Fig. 4 shows the infrared spectra of the different types of the asphalt binders. For all of the asphalt binders, strong peaks were observed in the 2850 cm^{-1} - 2980 cm^{-1} region, which correspond to C-H stretching vibrations. The C-H asymmetric deformation peaks and the C-H symmetric deformation peaks were observed at 1,400 cm^{-1} – 1,500 cm^{-1} and 1,370 cm^{-1} – 1,390 cm^{-}1, respectively.

In addition to these typical vibrations represented by the observed absorption peaks, other peaks were observed for the aged asphalt binder. After PAV aging, additional absorption peaks appeared at 1,698 cm^{-1}, which were attributed to the increase in the carbonyl content of the asphalt binders. The carbonyl group occurs in products, such as aldehydes, ketones and esters, of the chemical reaction between asphalt molecular and oxygen [3, 7-8, 22]. In the asphalt binder aging process, the formation of polar carbonyl groups enhanced intermolecular interactions in the asphalt. Compositional changes of the asphalt binders can change the physical performance of asphalt: for example, hardening and increased stiffness of the asphalt may result.

The areas under the absorption peaks of the functional groups reflected the degree of aging of the asphalt binder. The larger the carbonyl index, the higher is the degree of aging of the asphalt binders. The areas of the characteristic absorption peaks were calculated for asphalt binders with different degrees of aging, and the relative carbonyl indexes were obtained. The results are shown in Table 2.

Table 2 shows that the carbonyl indexes of the asphalt binders increase with the aging time. This result was primarily attributed to the formation of carbonyl carbon from the reaction between the asphalt and oxygen. The chemical reaction continued uninterrupted under sustained heat and oxygen levels.

The carbonyl content of the aged SBS-modified asphalt binder was relatively lower than that of the BA binder. This result shows that the anti-aging performance of the SBS-modified asphalt binder was better than that of the BA. After 20 h of PAV aging, the BA carbonyl index was 0.104, whereas the carbonyl index of the SBS-modified asphalt was 0.049, which corresponded to a decrease of approximately 50%. This result showed that the SBS modifier slowed down the oxidation reaction of the asphalt binder.

Table 2. Carbonyl Indexes of Aged Asphalt Binders.

Asphalt Type	Aging Conditions	Aging Time		
		None	PAV 10 h	PAV 20 h
Base Asphalt (BA)	Dry	0	0.076	0.104
	Wet	0	0.092	0.137
Polymer-modified Asphalt (PMA)	Dry	0	0.029	0.049
	Wet	0	0.032	0.061

The results in Table 2 show that the area of the carbonyl absorption peak of the asphalt binders after PAV aging under wet conditions is clearly larger than that under dry conditions. Under wet conditions, the carbonyl indexes of the BA and the PMA increased by 30% and 20%, respectively, after 20 h of PAV aging relative to the carbonyl indexes obtained for dry conditions. This result shows that the presence of water promotes the oxidation reaction of the asphalt binders.

SBS Infrared Spectral Analysis

Fig. 5 shows the infrared spectra of SBS after aging in dry and wet environments. There were clear changes in the absorption peaks in the SBS spectra after PAV aging under hot, oxygenated conditions, and a carbonyl absorption peak with a large area appeared at 1,724 cm^{-1}. This result demonstrated that SBS underwent severe oxidation in the hot, oxygenated aging process. Oxygen aging in SBS primarily occurred in the polybutadiene segment, whereas the styrene segment remained relatively stable. This result was attributed to the instability of the polybutadiene double bond (C=C), especially at high temperatures. This double bond reacted with oxygen, resulting in an increase in the carbonyl concentration, as shown by the carbonyl absorption peak at 1,724 cm^{-1}. The segment structures of the SBS may have broken at the same time, which is the primary degradation mechanism of SBS in the aging of modified asphalt binders.

The curves in Fig. 5 show that the area of the carbonyl absorption peak of SBS aged in the presence of water is clearly larger than that under dry conditions. The carbonyl index of SBS under wet and dry conditions was 0.842 and 0.227, respectively. These results show that the presence of water promotes the oxidation reaction in SBS during PAV aging.

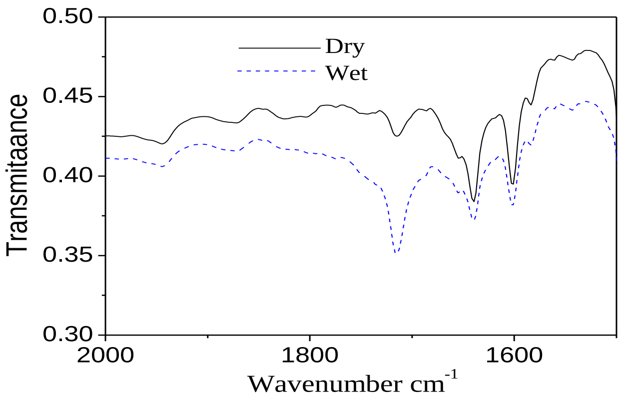


Fig. 5. FTIR Spectra of SBS.

Pictures of Original SBS and Aged SBS are shown in Fig.6. Before the aging process, the color of original SBS was white. After the PAV aging, the color of SBS became yellow. However, under wet condition, the color change is more significant than that in dry condition. It suggests that the presence of water accelerated SBS aging.

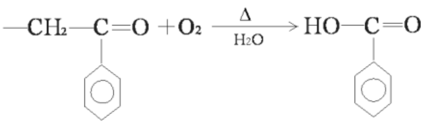
Aging Mechanism of Modified Asphalt in the Presence of Water

The test results for the physical properties and the infrared spectral analysis showed that the presence of water accelerated the aging reactions in the asphalt binders and SBS. Asphalt binders contain many polar groups, such as carbonyl, carboxyl, and ester groups, among others. The polar groups were hydrophilic, which caused the asphaltene molecules to move to the asphalt-water interface. The combined action of heat, oxygen, and water accelerated the aging process of the asphalt binders [23], which reacted with both oxygen and water.

Water promotes SBS aging via a complex mechanism. Olefin polymers are usually stable in the presence of water; however, polar bonds containing C-O groups can be generated under hot, oxygen-rich aging conditions. This type of material can easily be further oxidized in the presence of water, thereby increasing SBS aging. The infrared spectral analysis confirmed that water promoted the oxidation reaction.

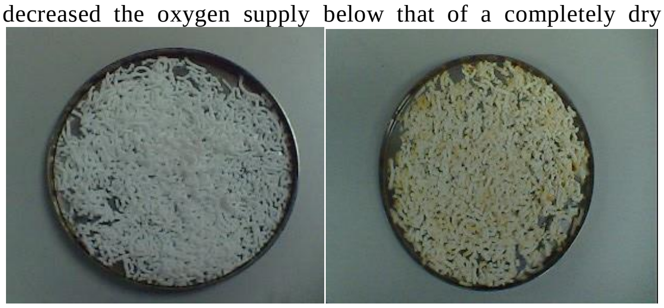
The carbonyl groups that formed during the aging of the asphalt binder or SBS was further oxidized to acid groups. The reaction mechanism consists of two simple equations, Eqs. (1) and (2), which are shown below.

$$R-\underset{\underset{O}{\|}}{CH} + O_2 \xrightarrow[H_2O]{\Delta} R-\underset{\underset{O}{\|}}{C}-OH \qquad (1)$$



(2)

Another reaction may have occurred. The presence of water vapor decreased the oxygen supply below that of a completely dry



(a) Original SBS (b) Aged SBS under dry condition

(c) Aged SBS under wet condition

Fig. 6. Picture of Original SBS and Aged SBS.

environment, which may have produced a small number of free radicals. However, free radical chain growth and disproportionation reactions were constantly occurring: thus, as more polymer molecules fractured, more polar groups with low molecular weights were produced. The polybutadiene segment in SBS also contained a large number of double bonds. The carbon-carbon double bond could have undergone a hydration reaction (Eq. (3)) in the hot and humid environment, which would also have increased the number of the polar groups [24].

$$-CH=CH- + H_2O \longrightarrow -CH_2-\underset{\underset{OH}{|}}{CH}- \qquad (3)$$

Conclusions

This study evaluated the effects of water on the aging of PMA. Simulated aging in SBS-modified asphalt binder was compared under wet and dry conditions. The main conclusions drawn from this study include:

1. The combined action of heat and oxygen affects the physical performance of the asphalt binder, and the aging process is accelerated under wet conditions. Thus, the presence of water would accelerate the aging process of asphalt binder and reduce the service life of asphalt pavement.
2. Aging under wet conditions results in a more pronounced color change in SBS than aging under dry conditions, showing that the presence of water accelerates SBS aging.
3. Infrared spectroscopy results demonstrate that the asphalt components containing carbonyl groups are further oxidized to carboxylic acid under wet conditions. The results also show that the double bond segment of SBS undergoes a hydration

reaction and generates polar groups under thermal-humidity conditions.

Acknowledgements

This work was funded by the National Natural Science Foundation of China (Grant No. 51108374, 51108375), West Light Foundation of the Chinese Academy of Sciences (12KJZRZMYO01), and the Special Fund for Basic Scientific Research of Central Colleges (Chang'an University, Grant No. CHD2011JC187, 2014G1311087).

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