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FM analysis of aging properties of UV531/SBS modified bitumen

FENG Zhengang [1,2], CAI Fengjie[2], YAO Dongdong[3], LI Xinjun[2]

[1] Guangxi Key Lab of Road Structure and Materials, Nan'ning, 530007
[2] School of Highway, Chang'an University, Xi'an, 710064
[3] Jilin Provincial Transport Scientific Research Institute, Changchun, 130012
Corresponding author: FENG Zhengang
E-mail: zgfeng@chd.edu.cn

Abstract. Ultraviolet absorber UV531 and linear SBS modified bitumen were selected to prepare SBS modified bitumen via melt blending. Thermal-oxidative and ultraviolet (UV) aging of SBS modified bitumen were simulated by the film oven test (TFOT) and accelerated UV aging. The influence of UV531 on the micromorphology of SBS modified bitumen before and after aging was analyzed by fluorescent microscopy (FM). Combined with the three indicators and aging properties of modified bitumen, the relationship between microstructure and properties of SBS modified bitumen and UV531/SBS modified bitumen was discussed. The FM images show that the UV531 improves the thermal-oxidative aging property of SBS modified bitumen, but it has little effect on UV aging.

1. Introduction

SBS modified bitumen is more and more widely used in the construction of high-grade highway in the world. Some road agencies and petrochemical departments have invested a lot of manpower in the development, performance evaluation and application of SBS modified bitumen [1,2]. As for the problem that the service life of SBS modified bitumen is easily affected by aging, researchers have carried out a lot of anti-aging studies for SBS modified bitumen [3,4]. Adding anti-aging agents, such as antioxidant, layered silicate, nanometer material and ultraviolet absorber to SBS modified bitumen is the most widely used way to improve its aging resistance [5-7]. The results show that SBS modified bitumen with appropriate dosage of anti-aging agent possesses better aging resistance to heat, oxygen or ultraviolet (UV) light.

As a highly effective aging resistant agent, UV531 has been used in the modification of SBS modified bitumen. It is reported that UV531 can effectively improve the thermal-oxidative and UV resistant aging properties of SBS modified bitumen through conventional test and rheological property test method [8]

The physical properties and aging resistance of UV531/SBS modified bitumen must relate to its structural characteristics, so the microstructure of UV531/SBS modified bitumen needs to be analyzed to reveal action mechanism of UV531 on SBS modified bitumen. So far, the methods to analyze the microstructure of SBS modified bitumen include scanning electron microscopy (SEM), atomic force microscope (AFM), fluorescence microscope (FM) and other digital image processing technology [9,10]. Among these methods, the fluorescence microscope is the quickest, most acceptable and convenient method to analyze morphology of SBS modified bitumen, because it can observe the homogeneity and structure of SBS modified bitumen in the raw state, and investigate the morphology of the SBS modified bitumen by determining the dispersion state of bitumen and SBS modifier, and characterize the nature of the continuous and discontinuous phase [11]. Even though, the compatibility and the action mechanism of UV531 on SBS modified bitumen is still not very clear at present due to the extremely complicated chemical composition and structure of SBS modified bitumen.

In view of these, this paper prepared UV531/SBS modified bitumen via melt blending with base bitumen, SBS, and UV531. The thermal-oxidative and UV aging processes of UV531/SBS modified bitumen were simulated by the thin film oven test TFOT) and accelerated UV aging test. FM was used to evaluate the morphology and distribution of UV531/SBS modified bitumen before and after aging by assessing the state of dispersion of SBS modifier and bitumen phases. Combining with the fundamental properties (penetration, ductility, softening point) of UV531/SBS modified bitumen by using conventional test methods, the effect of UV531 on the micromorphology of SBS modified bitumen before and after aging was confirmed.

2. Materials and Methods

2.1. Materials

The bitumen, AH-70, was provided by Panjin Northern Bitumen Co., Ltd., China. Physical properties of the bitumen are shown in Table 1.

Table 1. Physical properties of the AH-70

Bitumen	Penetration (25℃，0.1mm)	Ductility (10℃，cm)	Softening point (℃)
AH-70	64	60.1	47.4

SBS modifier, linear SBS 1401, was supported by Hunan Yueyang Baling Petrochemical Co., Ltd. The physical properties are shown in Table 2.

Table 2. Physical properties of the SBS

SBS	300% constant elongation stress (MPa)	Tensile strength (MPa)	Elongation at break (%)	Hardness (HA)	Permanent set at break (%)	Melt mass flow rate (g/10 min)
1401	⩾3.0	⩾20.0	⩾680	⩾85	⩽60	0.10~5.00

The UV absorber UV531 was supplied by Nanjing Milan Chemical Co., Ltd., China. The physical properties of the UV531 are shown in Table 3.

Table 3. Physical properties of the UV531

UV absorber	Appearance	Melting point（℃）	Light transmittance（%）	
			450nm	500nm
UV531	Light yellow needle-like powder	48	90	≥95

2.2. Preparation of UV531/SBS modified bitumen

The UV531/SBS modified bitumen was prepared via melt blending using a high shear mixer. To begin with, the AH-70 matrix bitumen was heated to 180℃. Then the 4wt% SBS modifier and 0.1wt% sulfur were added into matrix bitumen, and the mixture was blended at 4000rpm for 1h. Then, high shear mixer was used to shear for 1h at 4000rpm. It was further stirred by mechanical mixer for 1.5h to complete the preparation of SBS modified bitumen. After that UV531 with a dose of 0.6% by mass of SBS modified bitumen was added into SBS modified bitumen slowly. The temperature was maintained at 180℃, and the high-speed shearing machine was kept at 2500rpm for 0.5h to obtain the UV531/SBS modified bitumen. The SBS modified bitumen without UV531 was treated by the same preparation method to obtain the control sample.

2.3. Aging experiment

According to ASTM D1754, the thin film oven test (TFOT) was carried out in type 82 bitumen film oven. The well-mixed bitumen weighed (50±0.5) g was placed in iron pan with inner diameter of 140mm and depth of 9.5mm, and the thickness of bitumen film was about 3.2mm. Then, the samples were heated in the oven for 5h with temperature at (163±1) ℃.

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The UV aging test was performed in a chamber (50×60×50 cm) with an UV lamp of 300W, and the wavelength of UV radiation was 280～400nm. The UV intensity of the UV lamp was (25±0.4) W/m2. The oven was equipped with digital automatic temperature-control system. The UV aging test process was as follows: the TFOT aged bitumen samples were placed in the ultraviolet aging oven to continue the test. The aging temperature was kept at 60℃ and the aging time was 6 days.

2.4 Fluorescent microscopy (FM)
The change of shape, size, quantity and distribution of SBS modifier in the blending and aging processes of SBS modified bitumen was tested by fluorescence microscopy. SBS modified bitumen samples were examined at room temperature under the microscope with fluorescent light (generated from a high pressure Xenon lamp) at magnification levels of 400×. A drop of hot bitumen was placed on the glass microscope slide to form a transparent film. Then a coverslip was covered on the film to observe the phase morphology under fluorescent microscopy.

2.5 Physical properties test
The penetration (25°C), ductilty (5°C) and softening point of the SBS modified bitumen before and after aging were tested according to the standards ASTM D5, ASTM D113 and ASTM D36, respectively.

3. Results and Discussion

3.1. Effect of UV531 on morphology of SBS modified bitumen before aging
The bitumen material will not appear fluorescence under the ultraviolet light emitted by the fluorescence microscope, while SBS modifier can emit fluorescence under the ultraviolet light. Therefore, the appearance and phase state of SBS modifier in the bitumen can be visually observed by using the fluorescence microscopy.

The microstructure of SBS and UV531/LSMB before aging is shown in figure 1 and figure 2. The small particles are evenly distributed, the bitumen is continuous phase and presented as black, the modifier is dispersed phase and presented as fluorescent yellow, and the SBS modifier is evenly dispersed in the modified bitumen. The figure shows that the addition of UV531 makes the SBS modifier particles in LSMB smaller and the number increased, and the contact area between the modifier and bitumen increased, indicating that UV531 changes the dispersion state of SBS polymer in bitumen.

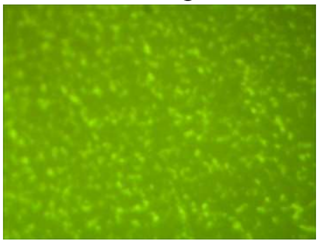

Figure 1. The FM image of unaged SBS modified bitumen

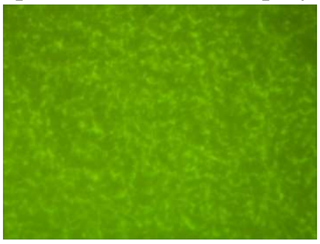

Figure 2. The FM image of unaged UV531/ SBS modified bitumen

As shown in Table 4, the addition of UV531 increased the penetration and elongation of SBS modified asphalt, while the softening point decreased. The increase of penetration degree of SBS modified asphalt indicated that the addition of UV531 reduced the viscosity of SBS modified asphalt, and the increase of its elongation indicated that UV531 could improve the low temperature ductility of SBS modified asphalt and improve the low temperature performance of SBS modified asphalt. The addition of UV531 had an adverse effect on the high-temperature performance of SBS modified asphalt, but the effect was small. In general, the addition of UV531 improved the physical properties of SBS modified asphalt, which was consistent with the conclusion obtained by fluorescence microscope.

Table 4. Physical properties of the SBS modified bitumen

Content of UV531(%)	Penetration (25℃，0.1mm)	Ductility (5℃，cm)	Softening point (℃)
0	46	19.0	53.1

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0.6	56	19.5	50.0

3.2. Effect of UV531 on morphology of SBS modified bitumen after TFOT aging

The microstructure of TFOT aged samples is shown in figure 1 and figure 2. After TFOT aging, SBS modifiers in SBS modified bitumen and UV531/ SBS modified bitumen agglomerate, crosslink and degrade, the number of SBS modifiers decreases and the size of particles becomes larger. In the two states, the bitumens are both continuous phases, and the SBS modifiers are both dispersed phases. However, the particles of SBS modifier increase after UV531 is added to the modified bitumen, which indicates that UV531 prevents the degradation of SBS modifier and improves the performance of SBS modified bitumen. It implies that UV531 has a promoting effect on the heat and oxygen aging resistance of SBS modified bitumen.

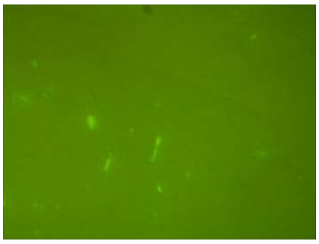

Figure 3. The FM image of TFOT aged SBS modified bitumen

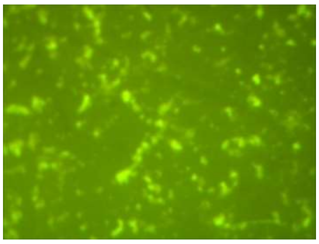

Figure 4. The FM image of TFOT aged UV531/ SBS modified bitumen

Combined with residual penetration ratio (PRR) and softening point increment (△S), the influence of UV531 on aging performance of SBS modified bitumen is verified and calculated. PRR and △S can reflect the susceptive degree of aging. The formulas are as (1)~(2)

$$\mathrm{PRR} = \frac{Aged\ penetration\ value}{Unaged\ penetration\ value}\ x\ 100 \quad (1)$$

△S=*Aged softening point value-Unaged softening point value* (2)

As illustrated in table 5, after TFOT aging, the PRR of modified bitumen with UV531 increases and the SPI decreases compared with the modified bitumen without UV531. It demonstrates that the addition of UV531 improves the heat aging performance of SBS modified bitumen, which is consistent with the results obtained by FM.

Table 5. The influence of UV531 on TFOT aging performance of SBS modified bitumen

Content of UV531（%）	PRR	△S（℃）
0	85	7.8
0.6	90	4.8

3.3. Effect of UV531 on morphology of SBS modified bitumen after UV aging

In figure 5 and figure 6, there is almost no SBS modifier in the fluorescence micrograph after UV aging. The reason lies in that the aging of modified bitumen dissolves the insoluble polybutadiene segment in SBS modifier into matrix bitumen, thus showing the disappearance of polymer particles.

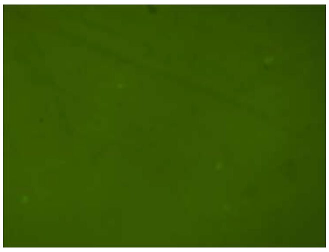

Figure 5. The FM image of UV aged SBS modified bitumen

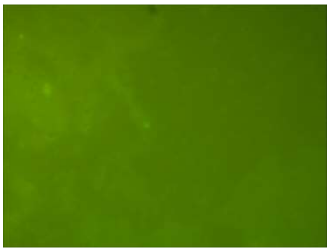

Figure 6. The FM image of UV aged UV531/ SBS modified bitumen

As can be seen from Table 6, after UV aging, UV531/SBS modified bitumen has only slight changes in PRR and SPI compared with SBS modified bitumen without UV531, which is also consistent with the FM images of SBS modified bitumen obtained after UV aging.

Table 6. The influence of UV531 on UV aging performance of SBS modified bitumen

Content of UV531（%）	PRR	△S（℃）
0	59	10.6
0.6	61	9.7

4. Conclusions

(1) The addition of UV531 changed the dispersive state of SBS modified bitumen and improved the physical properties of SBS modified bitumen to some extent. Before aging, SBS modifier particles in the UV531/modified bitumen become smaller and increase. The bitumen and modifier form a two-phase continuous network structure, which improves the physical properties of SBS modified bitumen. After TFOT aging, the addition of UV531 increases the number of SBS modifier particles, indicating that UV531 has degradation effect on the thermal-oxidative aging resistance of SBS modified bitumen. After UV aging, the polymer particles basically disappear, indicating that UV531 has little effect on the modified bitumen.

(2) The conclusions obtained from the conventional three indexes are basically consistent with the conclusions obtained from the FM images, which indicates that the microstructure of SBS modified bitumen has a good correspondence with its macroscopic properties and can qualitatively reflect the physical properties of modified bitumen.

Acknowledgements

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References

[1] Airey G D 2003 *Rheological properties of styrene butadiene styrene polymer modified road bitumens* Vol 82 (Amsterdam: Elsevie) pp 1709-1719
[2] Lee S, Amirkhanian S N and Kim K W 2009 *Laboratory evaluation of the effects of short-term oven aging on asphalt binders in asphalt mixtures using HP-GPC* Vol 23 (Amsterdam: Elsevie) pp 3087-3093
[3] Zhang D, Zhang H and Shi C 2017 *Investigation of aging performance of SBS modified asphalt with various aging methods* Vol 145 (Amsterdam: Elsevie) pp 445-451
[4] F Durrieu, Farcas F and Mouillet V 2007 *The influence of UV aging of a styrene/butadiene/styrene modified bitumen: comparison between laboratory and on site aging* Vol 86 (Amsterdam: Elsevie) pp 1446–1451
[5] Ouyang C 2006 *Improving the aging resistance of styrene-butadiene-styrene tri-block copolymer modified asphalt by addition of antioxidants* Vol 91 (Amsterdam: Elsevie) pp 795-804
[6] Yu JY et al 2009 *Effect of organo-montmorillonite on aging properties of asphalt. Construction and Building Materials* Vol 23 (Amsterdam: Elsevie) pp 2636–2640
[7] Feng Z G et al 2013 *Effect of ultraviolet aging on rheology, chemistry and morphology of ultraviolet absorber modified bitumen* Vol 46 (France: Rilem) pp1123–1132
[8] Feng Z G et al 2015 *Effect of Ultraviolet Absorber UV531 on Properties of SBS Modified Bitumen* Vol 37 (Wuhan: Journal of Wuhan university of technology) pp53-58
[9] Yu X, Burnham N A and Tao M 2015 *Surface microstructure of bitumen characterized by atomic force microscopy* Vol 218 (Amsterdam: Elsevie) pp17-33
[10] Sengoz B and Isikyakar G 2018 *Analysis of styrene-butadiene-styrene polymer modified bitumen using fluorescent microscopy and conventional test methods* Vol 150 (Amsterdam: Elsevie) pp424-432
[11] Dong F Q et al 2016 *Rheological behaviors and microstructure of SBS/CR composite modified hard asphalt* Vol 115 (Amsterdam: Elsevie) pp 285-293