Technical Paper

ISSN 1997-1400 Int. J. Pavement Res. Technol. **7**(2):109-114

Effect of Flame Retardants on Long-term Aging Characteristics of Asphalt Binders

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Abstract: This work investigates the effects of flame retardants on long-term aging and rheological characteristics of modified asphalt binder containing Styrene-Butadiene-Styrene triblock copolymer (SBS) and flame retardants. The flame retardants included #A (decabromodiphenyl ether, antimony trioxide, and zinc borate with the ratio of 3:1:1 by mass) and #B (tetrabromobisphenol A bis (2, 3-dibromopropyl ether), antimony trioxide with the ratio of 2:1 by mass). Modified asphalt binders were aged according to the Pressure Aging Vessel (PAV) and Fluorescent Ultraviolet aging test (UV). Aged and unaged asphalt binders were characterized using limited oxygen index (LOI), and viscosity and dynamic shear rheology (DSR), respectively. Experimental results indicated that flame resistance of asphalt binder increases after PAV and UV aging processing, and the complex modulus and viscosity also increases. The UV aging brings a plateau region of the phase angle master curves over the intermediate temperature range. This behavior is very weak in the studied PAV aging and unaged asphalt binder. These changes were mainly due to the ultraviolet crossing linked to the asphalt. Compared with #B modified asphalt binder, #A modified asphalt binder showed better flame retardancy and rheological characteristics before and after aging.

DOI:10.6135/ijprt.org.tw/2014.7(2).109

***Key words**: Asphalt; Flame retardant; Long-term aging; Rheological characteristics.*

Introduction

Asphalts are mixtures of aliphatic, aromatic and naphthenic hydrocarbons and small quantities of organic acids, bases and heterocyclic components containing nitrogen, oxygen, sulphur, and some metal atoms [1, 2]. Asphalt can be used as a construction material and in pavements. A drawback in asphalt application is its flammability. An expanded growth of asphalt application concurrent with the proliferation of safety standards being set by government and private agencies has indicated that it is of prime importance to reduce the flammability of asphalt materials. Flame retardant modified asphalt binders may show different combustion properties due to the different mechanisms of various flame retardants [3]. Previous investigation has indicated that the compound flame retardants can improve the flame retardancy of asphalt binder [4, 5]. Asphalt binders with better flame retardancy and pavement performance have been prepared successfully by the addition of flame retardants such as decabromodiphenyl ether, antimony trioxide, and zinc borate [6].

Asphalt aging is one of the principal factors causing the deterioration of asphalt pavements. The aging includes the short-term aging during the mixing, transportation, and application, and the long-term aging during service in the field. The rolling thin film oven test (RTFOT), as described by the ASTM standard methods D2872, has been accepted as a reliable procedure to simulate short-term aging. Further aging is usually carried out on the RTFOT residue using the pressure aging vessel (PAV) to simulate long-term aging. But the long-term aging is a complex process; ultraviolet radiation and rainwater in particular have an important effect on asphalt performances in different zones. Ultraviolet radiation is a well known trigger of signaling responses in materials aging. Thus, the ultraviolet aging test method was employed to simulate the long-term climate aging of the asphalt binders in the field. Simulations of field climate aging process include temperature, film thickness, light intensity, and rainwater effects [7-9]. To evaluate asphalt binder performance after aging, flame retardancy, complex modulus (G*), phase angle (δ), and viscosity were tested in the laboratory [10-16].

In this paper, two kinds of flame retardants, #A (decabromodiphenyl ether, antimony trioxide, and zinc borate=3:1:1) and #B (tetrabromobisphenol A bis [2, 3-dibromopropyl ether], antimony trioxide=2:1), were employed to prepare modified asphalt binder. The RTFOT was used to simulate the short-term aging. The PAV and ultraviolet aging test (UV) were employed to simulate the long-term aging of asphalt binders. The effects of long-term aging on flame retardancy and rheological characteristics of the asphalt binder were evaluated by limiting oxygen index (LOI), dynamic shear rheometer, and Brookfield viscometer.

Experiments

Raw Materials

The 60/80 pen grade asphalt, with penetration of 69 mm at 25°C, softening point of 49.8°C, ductility of 150 cm at 15°C, and viscosity of 0.45 Pa.s at 135°C, was used to prepare modified asphalt binder. Styrene-Butadiene-Styrene triblock copolymer (SBS), Grade YH791, was produced by Yueyang Petrochemical Co., Ltd. of Hunan Province, China. It is a linear SBS, containing 30% styrene,

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Note: Submitted April 25, 2013; Revised July 28, 2013; Accepted July 29, 2013.

and the average molecular weight of SBS is 120,000. All flame retardants are a commercial product (industrial grade).

Methods

Asphalt was heated to 175±5^{o}C in an oil-bath heating container until it flowed fully and 4.5% SBS was added slowly. The mixture was sheared at the speed of 5,000 rpm for 2 h using a high shear mulser (Model 100L, Shanghai Weiyu electromechanical Co., Ltd., China), and the blend became essentially homogenous. A given part of the stabilizer and 8% mix flame retardants was blended into the asphalt under 2,000 rpm, stirring for 1 hour continuously using stirrer (Model JJ-1, Jiangsu Wenhua instruments Co., Ltd., China).

The Rolling Thin Film Oven (Model B1, CONTROL Co., Ltd., Italy) was employed to simulate short-term aging according to ASTM D2872. The Pressure Aging Vessel (Model PR9300, Prentex Co., Ltd., America) was used for the accelerated aging of asphalts according to ASTM D6521.

UV aging tests were performed in a QUV accelerate weather-resistance tester (Q-panel Co., Ltd., US). As soon as the time of RTFOT of asphalt binder was over, each asphalt sample was immediately poured into the pans, and approximately 3 mm thickness film was obtained. The sample was placed together in the UV weather equipment to undergo UV aging. The temperature was set to 50^{o}C and air atmosphere was used for testing.In this procedure, samples of approximately 1.5 mm film thicknesses were subjected to actinic light of 1.19 W/m^2 of 340 nm to 8h after spraying water 10 min, then condensation for 4 h at 10^{o}C; all these processing times are one complete cycle. The samples were carried on circularly for 15 days, 30 days, 45 days, and 60 days, respectively, and their related performance was tested.

Flame retardancy of modified asphalt binder was evaluated by the limited oxygen index (LOI, HC-2, Jiangning Instruments Co., Ltd., China). Limiting oxygen index methods are widely used to measure the flammability of polymers and to investigate the effectiveness of flame retardants. Flame retardancy was assessed by the LOI according to ASTM D-2863. For testing, the top of the sample was ignited by a gas flame, which was stopped once ignition has occurred. Then, the lowest oxygen concentration in a flowing mixture of nitrogen and oxygen, which just supports sustained burning, can be determined. The effectiveness of flame retardants is measured by the changes in the critical oxygen concentration. The LOI is defined in Eq. (1):

$$LOI = \frac{\Phi_{cr}(O_2)}{\Phi_{cr}(O_2) + \Phi(N_2)} \tag{1}$$

where: $\Phi_{cr}(O_2)$ and $\Phi(N_2)$ are the minimum oxygen concentration and the relevant nitrogen concentration in the inflow gases, respectively.

Dynamic shear properties were measured with a dynamic shear rheometer (DSR, MCR 101, Anton Paar Co. Ltd of Austria) in a parallel plate configuration with a gap width of 1 mm. Rheological tests were performed under controlled strain conditions. Principal rheological parameters obtained from the DSR were complex modulus (G*), storage modulus (G'), loss modulus (G''), and the phase angle (δ). G* is defined as the ratio of maximum shear stress to the maximum strain and provides a measure of the total resistance to deformation. The δ is the phase shift between the applied stress and strain responses during a test and is a measure of the viscoelastic balance of the material behavior. Temperature sweeps (from 25 to 95^{o}C) with 1^{o}C/min increments applied at a fixed frequency of 10 rad/s.

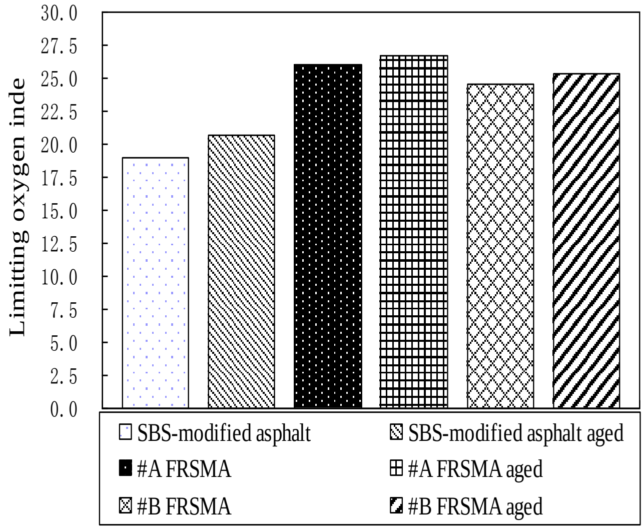

Fig. 1. Effect of PAV Aging on LOI of FRSMA and SBS-modified Asphalt Binder.

Brookfield viscometer (Model DV-Ⅱ+, Brookfield Engineering Inc., USA) was employed to measure the rotational viscosity of the modified asphalt binder according to ASTM D4402.

Results and Discussion

Flame Retardancy

Fig. 1 shows a comparison of LOI between SBS-modified asphalt binder and SBS-modified asphalt binder with flame retardants before and after PAV aging. The standard deviation of the results is lower than 5%. The results indicate that the LOI of asphalt binder increases after PAV aging. Compared with the SBS-modified asphalt binder, the increment of LOI of two kinds of modified asphalt binder is 0.7 for #A modified asphalt binder, and 0.8 for #B modified asphalt. The decomposition of asphalt is difficult in the asphalt burring process [17]. Consequently, the flame retardancy of asphalt binder is increased by PAV aging.

The effect of UV aging time on the flame retardancy of asphalt binders is shown in Fig. 2. The LOI of asphalt binders tends to increase as UV aging time increases. The LOI increment in asphalt is directly related to the flame retardants types. The LOI increment is 1.1%, 1.6%, and 1.0% for SBS-modified asphalt, SBS-modified asphalt with #A, and SBS-modified asphalt with #B after UV aging. The results indicated that ultraviolet radiation accelerates the asphalt binder to form a cross-linked network structure during UV aging. The cross-linked network structure needs more energy to crack or break. It means increasing the ignition temperature. Therefore, UV aging increases the flame resistance of the asphalt binder. #A modified asphalt binder shows the highest increment increase

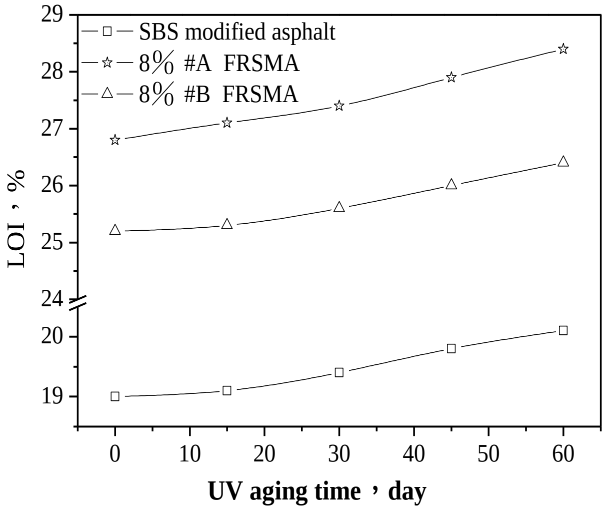

Fig. 2. Effect of UV Aging Time on LOI of Asphalt Binders.

among three kinds asphalt binders after UV aging.

Dynamic Shear Properties

At present, the most commonly used method of fundamental rheological testing of asphalt is by means of dynamic mechanical methods using oscillatory type testing. These oscillatory tests are undertaken using a dynamic shear rheometer (DSR), which applies oscillating shear stresses and strains to samples of asphalt sandwiched between parallel plates at different loading frequencies and temperatures. Figs. 3 and 4 show the effect of PAV aging on the dynamic shear properties of SBS and two kinds of flame retardant-modified asphalt binder. The results indicated that PAV aging increases complex modulus (G*), especially at high temperature. Compared to SBS-modified asphalt binder, the slope of the complex modulus master curve of SBS-modified asphalt binder with flame retardants is slightly larger. Therefore, flame retardants increase the temperature sensitivity and do not change the asphalt aging performances. Nevertheless, there is not a significant difference between the aged and unaged asphalt binder in G* values for both SBS-modified asphalt binder and SBS-modified asphalt binder with flame retardants.

Phase angle is also a very significant rheological parameter for asphalt binders. Figs. 3 and 4 shows phase angles (δ) master curves for SBS-modified asphalt and SBS-modified asphalt binder with flame retardants. The results show that the addition of flame retardants to asphalt decreases the phase angle value significantly at low temperatures, indicating that flame retardants bring elasticity to the SBS-modified asphalt binder. Nevertheless, phase angle value increases at higher temperatures. As a result, the slope of phase angles master curve increases with the increasing the temperature, and the slope of phase angles master curve decreases with aging. Therefore, aging makes asphalt binders less temperature sensitive.

Figs. 5 and 6 show the effects of UV aging time on the dynamic shear properties of #A and #B modified asphalt binder. The results show that the complex modulus increases and phase decreases after UV aging. The results indicate that UV aging makes the mechanical properties of the asphalt more solid-like, and the changes are dependent on aging time. A significant decrease in the phase angle is generally observed between 60 days UV aging and unaged asphalt binder, especially at high temperatures. Since the phase angle is a measure of the ratio between loss modulus and storage modulus, the decreased phase angle implies that aging leads to a greater increase in storage modulus than in loss modulus.

Figs. 5 and 6 also indicate that the UV aging brings a plateau

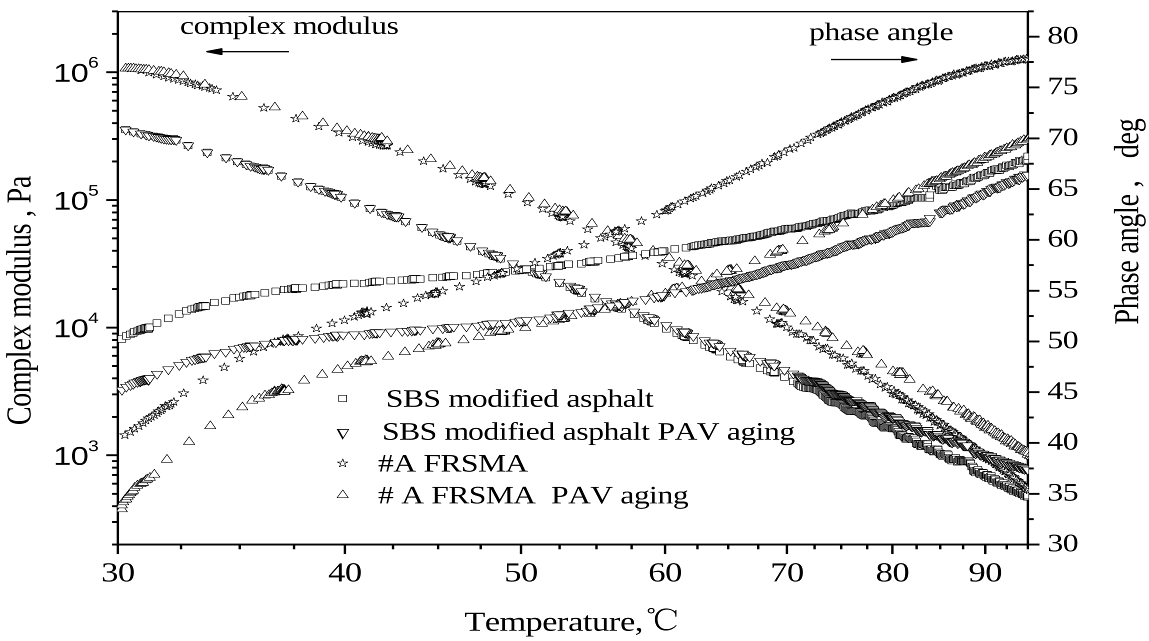

Fig. 3. Effect of PAV Aging on Complex Modulus and Phase Angle for #A FRSMA and SBS-modified Asphalt Binder.

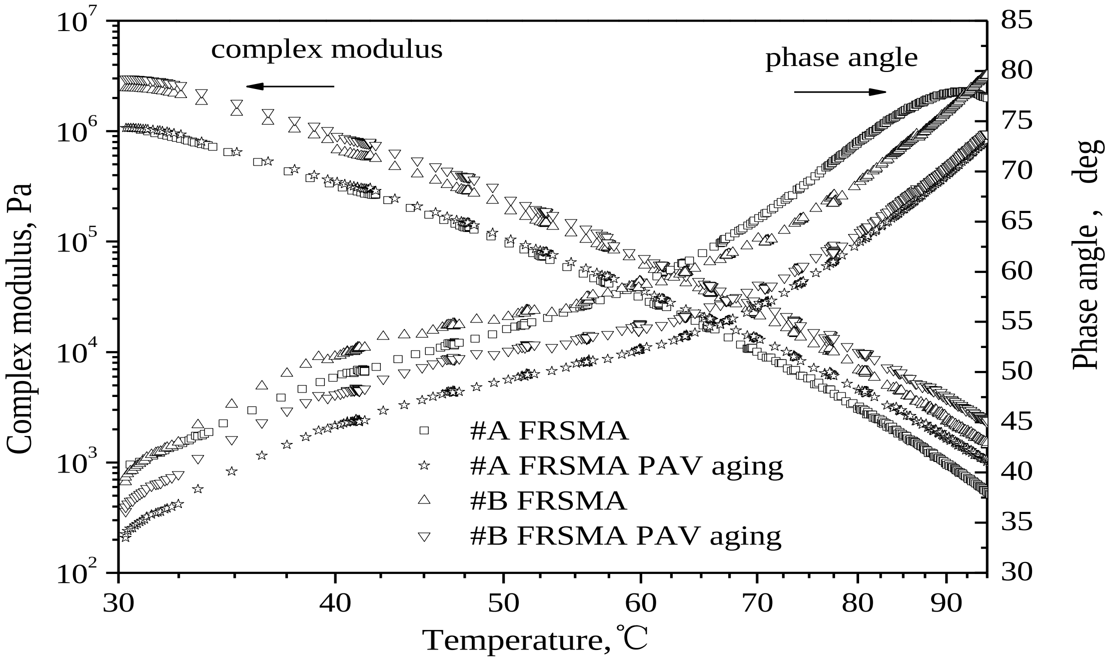

Fig. 4. Effect of PAV Aging on Complex Modulus and Phase Angle for #A FRSMA and #B FRSMA.

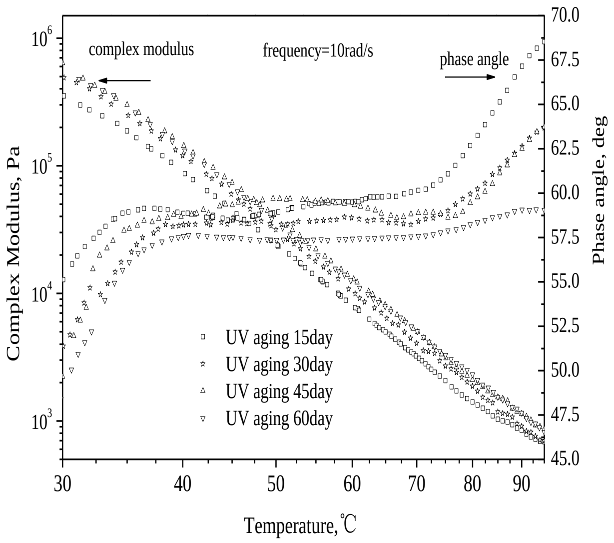

Fig. 5. Effect of UV Aging on Complex Modulus and Phase Angle for #A Modified Asphalt.

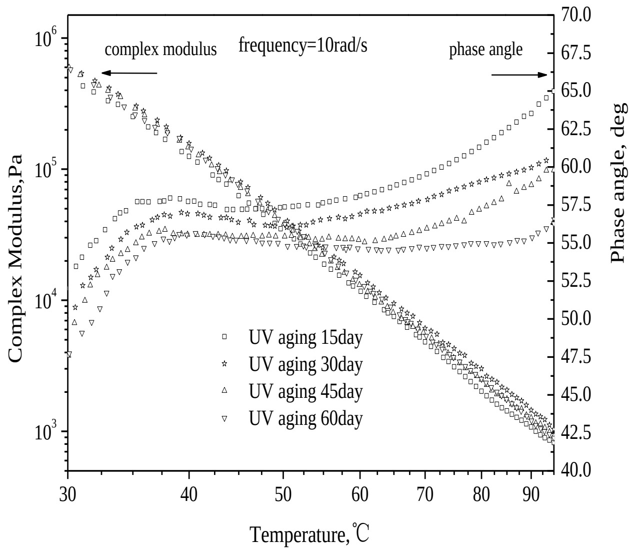

Fig. 6. Effect of UV Aging on Complex Modulus and Phase Angle for #B Modified Asphalt.

region of the phase angle master curves over the intermediate temperature range. It is assumed that the formation of a network of asphalt results in this plateau region. A true plateau region is absent for PAV aging, but for UV aging, there is a well defined plateau region, suggesting the formation of a strong network during UV aging. UV aging makes asphalt show more sol-like behavior. The plateau region disappears, and phase angle increases when the temperature is high enough. This phenomenon indicated that the effects of temperature on rheological properties are higher than the network formation in the asphalt binder.

Viscosity

The effect of PAV aging on the viscosity of the modified asphalt binder at 135°C is shown in Fig. 7. The standard deviation of the results is lower than 3%. The addition of flame retardants can increase the viscosity of the asphalt binder. The viscosity of the #B modified asphalt binder is higher than that of #A, which illuminates that the #B ingredient swells the light oil constituents in asphalt, indicating the interactions between asphalt and flame retardants. The viscosity of modified asphalt cannot be greater than 3 Pa.s at

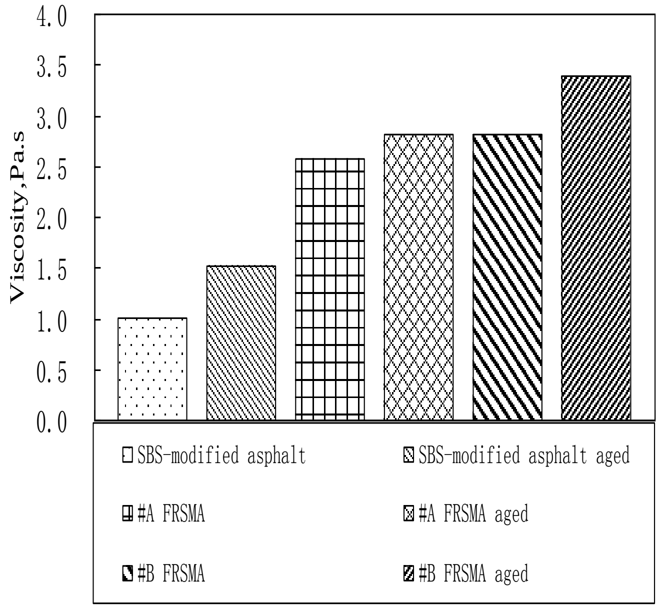

Fig. 7. Effect of PAV Aging on Dynamic Viscosity of Asphalt Binder at 135°C.

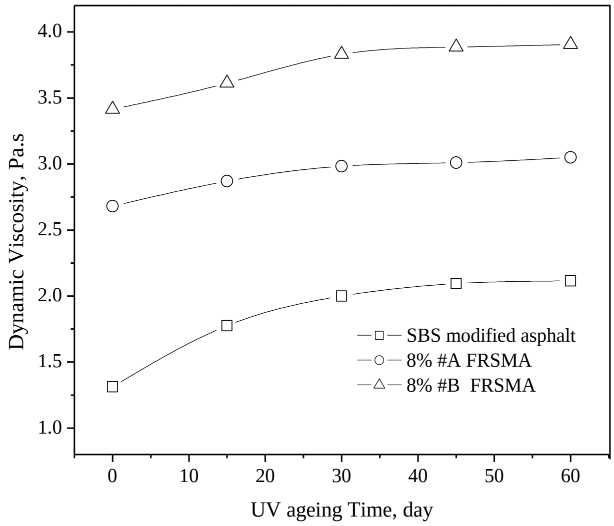

Fig. 8. Effect of UV Aging Time on Viscosity of Asphalt.

135°C according to Superpave binder specification limits. The results show that the viscosity is 2.58 Pa.s and 2.82 Pa.s for modified asphalt binder with #A and modified asphalt binder with #B when flame retardant contents are less than 8%. Therefore, addition of 8% flame retardants meets the requirement of Superpave binder specification. The PAV aging results indicated that viscosity of asphalt binder increases after aging, but viscosity increments have different change patterns. These phenomena are mainly due to flame retardant components. In other words, addition of flame retardant probably alters the mechanism of asphalt aging, and the aging is determined by the flame retardant types. The results indicate that #A modified asphalt binder performs better than #B modified asphalt binder before and after aging.

Relationships between UV aging time and viscosity of the asphalt binder at 135°C are shown in Fig. 8. It indicates that with the increasing of UV aging time, viscosity of SBS-modified asphalt binder without/with flame retardants presents an increasing trend, and SBS-modified asphalt binder is larger than others. It indicates that SBS-modified asphalt binder is sensitive to the UV rays and more serious aging. Flame retardants can improve the sensitivity to UV rays, decreasing the effect of UV aging on asphalt binder viscosity. So, flame retardants have the ability to counteract ultraviolet rays. Fig. 8 also shows that the viscosity of SBS-modified asphalt binder has no remarkable change between 45 days and 60 days aging. And increments of the viscosity decrease after 30 days, which implies that there was little cross linked network found in modified asphalt binder. Therefore, the cross linked network depends on UV aging time to a great extent.

Conclusions

Long-term aging properties of SBS modified asphalt binder and SBS modified asphalt binders with two kinds of flame retardant were evaluated in this paper. The flame resistance of asphalt binder increases after PAV and UV aging processing, and the complex modulus and viscosity also increases. The UV aging brings a plateau region to the phase angle master curves over the intermediate temperature range. However, this behavior is very weak in the studied PAV aging and unaged asphalt binder. The results indicate that ultraviolet promotes modified asphalt binder crossing-linked structure. Compared with #B modified asphalt binder, #A modified asphalt binder shows better flame retardancy and rheological characteristics before and after aging. By comparing the results of the PAV aging and UV aging, the asphalt binder aging due to the ultraviolet radiation must be considered in the study of the performance of asphalt pavement, especially in geographical regions with high solar radiation intensity and high relative humidity.

Acknowledgements

Supported by the National Natural Science Foundation of China (51208050) and Special Fund for Basic Scientific Research of the transportation department (2013 319 812 020).

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