Technical Note

ISSN 1997-1400 Int. J. Pavement Res. Technol. 2(4):162-165

Study of Mechanism of Flame-Retardant SBS-Modified Asphalt

Da-Liang Liu[1+], Yun-Yong Huang[2], Jian-Long Zheng[1], Jian-Bo Yuan[1], and Ye-Qiu Liu[2]

Abstract: A complex flame retardant was applied to Styrene-Butadiene- Styrene Block Copolymer (SBS)-modified asphalt to test flame capability, followed by a conventional pavement-performance and flame-performance test. The results showed that the softening point and the penetration of the flame-retardant SBS-modified asphalt did not change significantly. However, the ductility of the asphalt decreased as the blending amount of complex flame retardant increased. A mixture of 7% SBS-modified asphalt and 12% fire retardant met the performance requirement of the polymer-modified asphalt SBS category I-D technical specification. The limited oxygen index (LOI) reached 26.2%, and the Underwriters Laboratory Vertical Burning (UL94) classification reached V0 grade. The flame retardant mixed with the SBS-modified bitumen can reduce the combustion heat release; however, the response of flame retardants to different temperatures, such as the precipitation of hydrogen bromide, can slow down the termination of combustion.

***Key words**: Experimental research; Flame retardant mechanism; Flame retardant SBS modified asphalt; Limited oxygen index (LOI); Road engineering.*

Introduction

The number of highway tunnels has increased substantially with the rapid development of highways in China. Currently, a great number of domestic and international highway tunnels have cement concrete pavement. The deficiencies of cement concrete pavements may include increased skidding, traffic noise, and micro cracking [1-3]. However, using bituminous concrete pavement in highway tunnels introduces safety concerns. To decrease the potential damage of a tunnel fire disaster, flame-retardants are applied to the bituminous material. To improve the flame resistance of bituminous material, both domestic and international organizations have researched flame-retardant technology in recent years. Yu et al. [4] investigated the influence of a compound flame retarder on flame resistance and the physical properties of Styrene-Butadiene- Styrene Block Copolymer (SBS) modified asphalt. With specific regulations of tunnel deck pavement in mind, Li et al. [5] invented an advanced technology of flame retardant for tunnel deck pavement and evaluated the mechanism of asphalt flame-resistance. Kong et al. [1] studied the effects of the blending amount of flame retardant on the characteristics of the SMA pavement. The authors developed a complex flame-retardant and fire-retardant SBS-modified asphalt. We have also applied different analytical tests such as the limited oxygen index (LOI), the Underwriters Laboratory Vertical Burning (UL94), the thermogravimetric analysis (TGA), the differential scanning calorimetry (DSC), and the (Py - FTIR) analysis to investigate the mechanism of the flame-retardant SBS modified asphalt and the flame retardant itself.

Raw Materials and Experimentation

[1] Professor, Highway Institute of Changsha University of Science and Technology, Changsha, China.
2 Associate Professor, Highway Institute of Changsha University of Science and Technology, Changsha, China.
+ Corresponding Author: E-mail liudaliang18@yahoo.com.cn
Note: Submitted September 3, 2008; Revised November 21, 2008; Accepted March 31, 2009.

Main Materials

The bitumen used in this experiment is AH-70. The flame retardant consists of a ratio of organic brominates, antimony trioxide, molybdenum trioxide, and other materials. The SBS modifier is of the type of YH-791 produced by Yue Yang General Petrochemical Works. It is the liner structure and its styrene/butadiene ratio is 30/70.

The Preparation of SBS

The basic bitumen was heated to 170℃ before 7% of SBS was added. At the temperature of 170 to 180℃, a high-speed homogenizer was applied at a shear rate of 4,000 to 6,000*rev/min* to homogenize the mixture for approximately 30 minutes.

The Experimental Method

The LOI Experiment

The experiment was carried out in accordance with the method of polymeric material's LOI. First, the SBS-modified bitumen was put into two-roll open mill plastication mastication for 10 minutes, then, 70% of multiple flame retardants and 30% of super-small calcareous rocks were added into the mill for another 20 minutes. The sample was then cut to the size of $100 \times 10 \times 4 mm$, according to the method regulated by GB/T2406-1993 [6].

Thermal Analysis Test

The samples were subjected to TGA and DSC tests using the comprehensive thermal analyzer of type STA 449 produced by Netzsch (Germany). The heating rate was 10℃/*min*. The test specification was normal temperature (about 600℃) under atmosphere pressure.

PY-FTIR Analysis Test

The acquired samples of fire-retardant SBS-modified asphalt and

Table 1. Conventional Pavement Performance Test Results of Different Kinds of Flame-Retarded SBS Modified Asphalt.

Performance Indicators		7%SBS Modified Asphalt＋9% Flame Retardant Compound	7%SBS Modified Asphalt＋10% Flame Retardant Compound	7%SBS Modified Asphalt＋11% Flame Retardant Compound	7%SBS Modified Asphalt＋12% Flame Retardant Compound	7%SBS Modified Asphalt＋13% Flame Retardant Compound
Penetration (100*g*, 5*s*, 0.1*mm*)	30℃	62	59	57	55	54
	25℃	43	41	40	39	38
	15℃	20	19	18	18	18
Penetration Index（PI）		1.02	1.00	1.20	1.42	1.56
Correlation Coefficient		0.999	0.999	0.999	0.999	0.999
Ductility (5℃, 5*cm/min*)/*cm*		38.5	37.2	36.5	34.4	33.2
Softening Point /℃		85.9	85.8	84.7	85.2	84.8
Elastic Recovery /%		100	100	100	100	100

Table 2. LOI Test Results of Different Kinds of Flame-Retarded SBS Modified Asphalt.

Sample #	Flame Retardant in /%	LOI/%
0#	0	22.2
1#	9	23.8
2#	10	24.3
3#	11	25.0
4#	12	26.2
5#	13	27.4

neat asphalt with modification were subjected to the Vector22 infrared spectrophotometer, which is produced by Brucker (Germany). The heating rate is 20℃/*min*. The test specification is 23 to 600℃ under air atmosphere. The velocity of flow is 20*ml/min*.

The Result and Argumentation

The Common Technical Functions of Flame-Retardant SBS-Modified Bitumen

Table 1 shows the basic physical properties (penetration, softening points) of different modified materials. As seen from Table 1, the penetration and softening point of the flame retardant do not change significantly when multiple flame retardants are added, but the ductility is reduced slightly. This indicates that the addition of multiple flame retardants influences the low-temperature properties of bitumens. All of the main capabilities can satisfy the technical standard criterion of SBS-polymer-modified asphalt when the flame-retardant content is approximately 9 to 13%.

The Test of Flame Retardant LOI

Table 2 shows the results of the LOI test for different flame retardant content. LOI is the lowest volume fraction that can maintain a stable candle flame after sample ignition under a mixed draught of oxygen and nitrogen. It is the commonly used target to evaluate the flame retardancy of a high polymer content material. The test indicates that the amount of oxygen required to burn the materials is large. Therefore, it is concluded from the LOI test that the flame resistance of SBS-modified bitumen will increase with the content of flame retardant. When the content of flame retardant reached 12%, the sample's LOI numerical value was 26.2%, which is a favorable capability of flame retardancy and fire prevention.

The Underwriters Laboratory Vertical Burning Test

The UL94 vertical burning test is also applied to the sample of flame-retardant SBS-modified bitumen under different retardant contents. The results are shown in Table 3. Usually, the UL94 vertical burning test is used to inspect the flames' spreading tendency or tendency to extinguish after the materials are burned. The materials' flame resistance was divided into three levels (UL94V-0, UL94V-1, and UL94V-2) according to the test results, such as sample burning time, whether a molten drop will lead ignite absorbent cotton, and so on. As seen from the results, the UL94 vertical burning level will reach V-0 when the flame-retardant content reaches 12% and the sample possesses favorable flame resistance.

TGA and DSC tests were also performed on fire-retardant modified asphalt and on non-fire-retardant neat asphalt. Figs. 1 to 3 show the results from the TGA, DTG, and DSC tests, respectively.

Table 3. UL94 Test Results of Different Kinds of Flame-Retarded SBS Modified Asphalt.

Sample #	Flame Retardant in /%	UL94 Vertical-Burning
0#	0	flame
1#	9	V-2
2#	10	V-1
3#	11	V-1
4#	12	V-0
5#	13	V-0

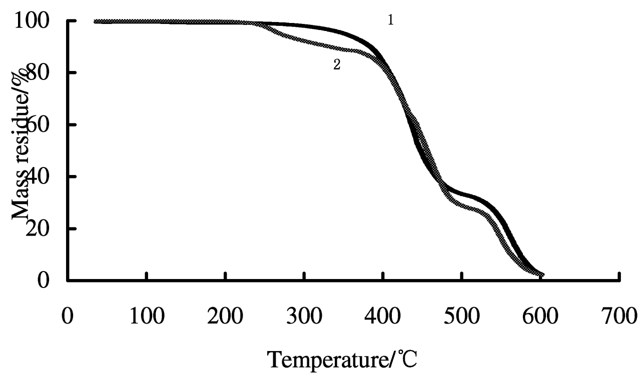

Fig. 1. TGA Curves of Fire-Retardant and Non-Fire-Retardant SBS Modified Asphalt, 1 for Non-Flame-Retardant SBS-Modified Asphalt and 2 for Flame-Retardant SBS-Modified Asphalt.

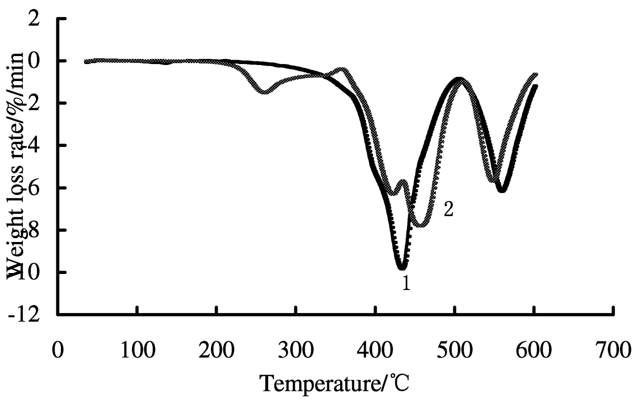

Fig. 2. DTG Curves of Fire-Retardant and Non-Fire-Retardant SBS Modified Asphalt, 1 for Non-Flame-Retardant SBS-Modified Asphalt and 2 for Flame-Retardant SBS-Modified Asphalt.

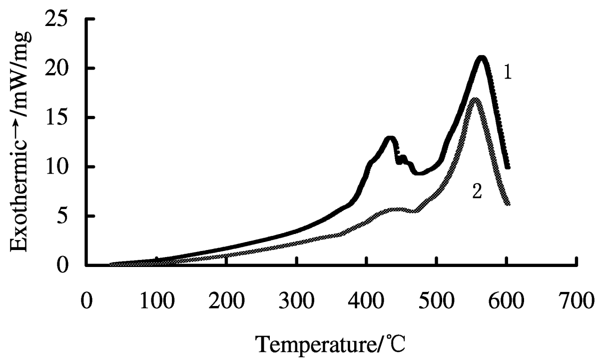

Fig. 3. DSC Curves of Fire-Retardant and Non-Fire-Retardant SBS Modified Asphalt, 1 for Non-Flame-Retardant SBS-Modified Asphalt and 2 for Flame-Retardant SBS-Modified Asphalt.

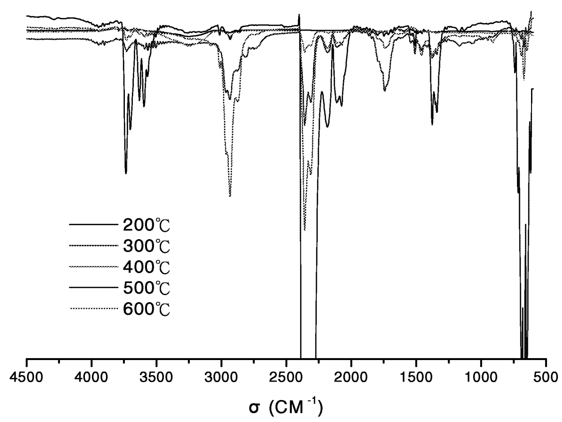

Fig. 4. SBS-Modified Asphalt Pyrolysis Gas FTIR Spectra at Different Temperatures.

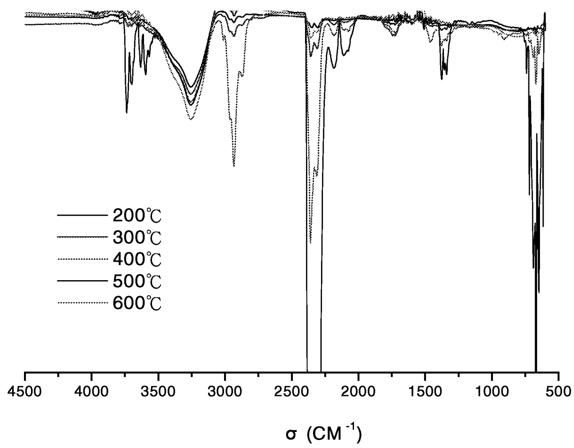

Fig. 5. Flame-Retarded SBS Modified Asphalt Pyrolysis Gas FTIR Spectra at Different Temperatures.

The TGA test for neat asphalt without fire retardant at atmospheric oxygen is divided into two steps. The maximal temperature of the thermogravic velocity is 440℃. The first weightless period top is 300 to 500℃. The temperature of the second weightless period is 500 to 600℃ and the maximum temperature of the thermogravic velocity is 560℃. When the temperature reaches 600℃, the sample has already been over-decomposed and the remaining carbon volume is almost zero. The TGA test for the fire-retardant SBS-modified asphalt is divided into three steps. When the temperature is between 250 and 350℃, there exists a weightless period during which the fire retardant decompounds. For the other two steps, the weightless temperature intervals do not change. As seen from the results of TGA, the carbon residue volume is almost zero after multiple fire retardants decompound at 250 to 350℃ and the fire-retardant SBS-modified asphalt decompounds at 600℃. This indicates that the function of multiple fire retardants is carried out primarily through gas-phase reactions. The decomposition of fire retardant precedes that of bitumen and is more favorable for its gas phase fire-retardant function's plenitude exertion. As seen from the results of DSC and DTG, the maximum weightless velocity and decomposed exotherm for fire-retardant SBS-modified asphalt fell.

Fire-Retardant SBS-Modified Asphalt (Py–FTIR) Analytic Test

Figs. 4 and 5 show the analytical pyrolysis gas phase curve for un-modified asphalt and 12% fire-retardant SBS-modified asphalt. As seen from Fig. 4 that the performance of SBS-modified asphalt will be the volatilization of ounce moisture and small molecule hydrocarbon substance at 200℃. From the offspring FTIR spectra separated out at pyrolysis at the initial stage of 300°C, the water vapor absorption peak can be observed to be within the wave numbers 3,964 to 3,038cm^{-1}; the saturation alkane absorption peaks within 2,940 to 2826cm^{-1}; the CO_2 absorption peaks at both 2,359cm^{-1} and 737 to 613cm^{-1}; the CO absorption peaks at 2,179 to 2109cm^{-1}; the carbonyl absorption peaks at 1,740cm^{-1}; the aromatic hydrocarbon absorption peaks at 1,550 to 1,257cm^{-1}; and alkane, CO_2, carbonyl exhibit strong absorption peaks. Hence, the weightlessness in the first stage is primarily caused by the separation of alkane, aldehyde, and ketone. The group of aromatic hydrocarbons is divided into partition to precipitate whose molecular weight is lower. The existence of CO_2 and CO in the gas may be due to the separating out of the reaction of oxygen and small molecule organic matter. As seen from the table of SBS-modified asphalt pyrolysis product separation at 400°C, the ingredients of pyrolysis gas are similar to the pyrolysis product at 300°C. Through the deuteric offspring and the separation of the spectral configuration of SBS-modified asphalt pyrolysis, we can observe the saturation-alkane absorption peak at 2,940 to 2826cm^{-1}. Additionally, the intensity of the carbonyl absorption peak at 1,740cm^{-1} is visibly depressed when compared to the pyrolysis at the initial stage. This shows that component of SBS-modified asphalt with lesser molecular alkane, aldehyde, and ketone have separated out completely in this stage. However, the appearance of the strong absorption points at 3,964 to 3,038cm^{-1}, 2,359cm^{-1} and 737 to 613cm^{-1} is due primarily to the decarburization of hydrocarbon chains of organic matter in the SBS-modified asphalt followed by dehydrogenation, oxygenation, and so on, which result in substantial H_2O and CO_2 in the gas. The intensity of the aromatic hydrocarbon absorption peak at 1,550 to 1257cm^{-1}, as compared to the initial pyrolysis stage, is visibly enhanced. This supports the existence of a large amount of aromatic hydrocarbon divided into groups to precipitate, which have high molecular weight.

As seen from Fig. 5, the flame-retarded SBS-modified asphalt is different from pure SBS-modified asphalt in that the offspring of different flame-retardant SBS modified asphalt have separate spectral configurations, which appear as a Br-ionic strong absorption point at different temperatures in the offspring precipitation spectrogram at 3,250cm^{-1}. The organo-bromine fire retardant autolysis or HX occurred because of its reaction with antimony oxide or other organic matter. The latter can react with Sb_2O_3 again and spanning SbOX. The SbOX can endothermically decompose at a wider temperature range. Its offspring is $Sb_4O_5X_2$, Sb_3O_4X, SbX_3, and so on. On the one hand, they may catch active free radicals, which exist according to the combustion reaction and can slow or terminate the combustion. On the other hand, they can depress the systematic temperature and the rate of decomposition effectively through the reaction of the SbOX decompound endotherm and cover and dilute the effects of HX and SbX_3, thereby achieving the flame retardant effect.

Conclusions

1. The penetration and softening points of the fire-retardant SBS modified asphalt significantly changed with the addition of multiple flame retardants, but the ductility decreased substantially. Each characteristic satisfies the technical standard criterion for SBS-polymer-modified bitumen when the content of flame retardant is 9 to 13%.
2. The limited oxygen index of fire-retardant SBS-modified asphalt can reach 26.2% and the UL94 vertical burning can reach the V0 level when the content of flame retardant reached 12%. Using multiple flame retardant provides a favorable fire-retardant effect for SBS-modified asphalt that satisfies the demand of high-level highway tunnel and road surface pavements.
3. The result of a thermal analysis test indicates that the addition of flame-retardant can reduce the burning exotherm of the SBS-modified asphalt. The py-FTIR analysis test result indicates that the bromide of hydrogen bromide is precipitated by the flame retardant and can set a burning buffer or termination under different temperatures.

References

1. Kong, X.M., Yu, J.Y., and Cheng, S.B., (2007). Effect of Flame Retardant on Pavement Performance of SBS Modified Bitumen Mixtures, *Journal of Wuhan University of Technology*, 29(8), pp. 19-22.
2. Ou, Y.X, (2002). *Application Flame Retardant Technology*, pp. 50-59, Chemical Industry Press, Beijing, China.
3. Yang, Q., Guo, Z.Y., and LIN, X.X., (2005). Research on Fire-Retarded Open-Graded Friction Course Used in Road Tunnel, *Journal of Tong'ji University: Natural Science Edition*, 33(3), pp. 316-320.
4. Yu, J.Y., Luo, X.F., and Wu, S.P., (2007). Preparation and Properties of Flame-Retarded SBS Modified Asphalt, *Journal of Highway and Transport*, 20(2), pp. 35-39.
5. Li, Z.W., Chen, H.Q., and Mu, J.B., (2002). Study on Technology to Improve Flame Resistant SBS Modified Bitumen and Its Mechanism, *Journal of Changsha Cummunications University*, 18(4), pp. 44-47.
6. National Standards of the People's Republic of China, (1993). Plastics-Determination of Flammability by Oxygen Index, *GB/T2406-1993*, General Administration of Quality Supervision, Inspection, and Quarantine of the People's Republic of China, Beijing, China.