Technical Note

ISSN 1997-1400 Int. J. Pavement Res. Technol. 2(4):166-170

Effect of Montmorillonite on Oil Resistance of SBS Modified Bitumen

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Abstract: Styrene–butadiene–styrene (SBS) modified bitumen was mixed with different kinds of mineral materials including montmorillonite (MMT), limestone powder (LSP), and nano-calcium carbonate (n-$CaCO_3$). The effects of MMT, LSP, and n-$CaCO_3$ on diesel resistance of SBS modified bitumen were investigated. The results showed that the addition of LSP to SBS modified bitumen increased the percent weight loss of SBS modified bitumen, while the addition of n-$CaCO_3$ and MMT decreased the percent weight loss of SBS modified bitumen. As compared with n-$CaCO_3$, MMT exhibited better effect on improving diesel resistance of SBS modified bitumen. MMT/SBS modified bitumen displayed good resistance to diesel when the optimum MMT content is 3% (in weight). The engine oil resistance of MMT/SBS modified bitumen was also investigated. The results showed that the addition of MMT to SBS modified bitumen can reduce the swelling of SBS modified bitumen in engine oil. The effect of MMT on oil resistance of SBS modified bitumen can be explained by the formation of intercalated structure in MMT/SBS modified bitumen. It is believed that the formation of intercalated structure in MMT/SBS modified bitumen provides SBS modified bitumen with good barrier property to oil.

***Key words**: Bitumen; Intercalated structure; Montmorillonite; Oil resistance.*

Introduction

Asphalt pavement is widely used all over the world due to its properties of low noise, smoothness, and ease to maintenance and so on [1, 2]. However, the adhesion of asphalt-aggregate mixtures can be easily broken up by the seepage of vehicle oil, particularly in airports, gas stations, bus stations, and other places where the pavement often exposed to oil. The oil may gradually penetrate into asphalt pavement, and the bitumen components will be dissolved by the oil. Thus, the asphalt pavement will become soften and loose, the bond among the aggregate reduced. Moreover, holes will be found on the surface of the pavement. These will result in the deterioration of pavement performance, and therefore the reduction of service life occurs. With this respect, further efforts should be made for enhancing oil resistance of asphalt pavement.

In recent year, a few reports about oil resistance of asphalt pavement have been reported. Previous research showed that compounded asphalt pavement exhibited better oil resistance than regular asphalt pavement [3, 4]. Sealing material could also greatly improve oil resistance of the asphalt pavement [5]. Compounded asphalt pavement is generally described as an open-graded asphalt concrete mixture filled with cement grout. Sealing material of asphalt pavement is composed of silicone resin solution, penetrating agent and tackifier or consists of refined resin binder and fuel and oil-resistant, high molecular weight rubber. Coating the asphalt pavement with the sealing material helps fill the porous areas of the pavement, which can resist petroleum products and other damaging elements. However, as compared with regular asphalt pavement, the resistance to low temperature deformability of compounded asphalt pavement is poor [6]. The sealing material covered on asphalt pavement reduces the anti-slip performance of the pavement, and thus limits its application [7, 8]. But the improvements on the oil resistance of bitumen have not been reported since then.

Montmorillonite (MMT) is a mineral with low cost and abundance in quantity, which consists of layers of tetrahedral silicate sheets and octahedral hydroxide sheets [9, 10]. In recent years, the MMT has been widely used for the modification of polymers. Polymer chains can intercalate into the interlayer of MMT, which disperse the MMT into the polymer matrix at nanometer-scale [11-15]. Significant improvements in the thermal, mechanical and barrier properties are achieved [16, 17]. Nowadays, MMT has been successfully used to modify bitumen. Studies show that MMT can improve the high-temperature storage stability of asphalt, increase both the softening point and viscosity of bitumen [18, 19]. However, the effects of MMT on oil-resistant property of bitumen are not reported in the literatures.

In this paper, Styrene–butadiene–styrene (SBS) modified bitumen was mixed with different kinds of mineral materials including MMT, limestone powder (LSP), and nano-calcium carbonate (n-$CaCO_3$). The effect of MMT, LSP, and n-$CaCO_3$ on diesel resistance of SBS modified bitumen was compared. Moreover, the effects of MMT content and soaking time on diesel resistance of MMT/SBS modified bitumen as well as the engine oil resistance of MMT/SBS modified bitumen were investigated.

Experimental Program

Materials

Modified bitumen with 4.8% (in weight) linear-like SBS was provided

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Note: Submitted September 8, 2008; Revised October 6, 2008; Accepted March 31, 2009.

Table 1. Physical Properties of SBS Modified Bitumen.

Physical Properties	SBS Modified Bitumen
Penetration (25 °C, 0.1*mm*)	57
Softening Point (°C)	68
Ductility (5 °C, *cm*)	40.5
Viscosity (135°C, *mPa.s*)	2,600

by Guochuang New Materials Factory, China. The physical properties of SBS modified bitumen were listed in Table 1. The MMT, with interlayer cation of Na^+ and having a cation exchange capacity (CEC) of 90*meq*/100*g*, was supplied by Fenghong Clay Chemical Factory, China. The LSP (800mesh) was provided by Wuhan Jinsan Mining Factory, China. n-$CaCO_3$ (60 to 80*nm*) was supplied by Shitong New Material Science and Technology Factory, China.

Preparation of SBS Modified Bitumen

The SBS modified bitumen with different mineral materials was prepared using a high shear mixer. SBS modified bitumen was first heated until it fully became liquid at around 175°C in the mixer, and then MMT, LSP, or n-$CaCO_3$ was added into SBS modified bitumen, respectively. The mixture was blended at 3,000rev/min rotation speed for about 30 minutes to ensure a thorough dispersion of mineral materials.

Oil Resistant Test of Modified Bitumen

The mixture of modified bitumen was first poured into a 25×50 ×10*mm* mould and cooled at the room temperature for 1hr. Then the sample was weighed. The modified bitumen in the mould was then soaked in diesel or engine oil for certain period of time. The oil residue with a filter paper was removed and weighed again.

Percent weight loss was calculated according to the following equation:

$$\omega = (m_1 - m_2)/m_1 \times 100\% \quad (1)$$

Where ω is percent weight loss of sample; m_1 is the weight of the mould contained modified bitumen samples before soaking, *g*; m_2 is the weight of the mould contained modified bitumen samples after soaking, *g*.

X-Ray Diffraction Test

The structures of pristine MMT and MMT/SBS modified bitumen were investigated by X-ray diffraction (XRD). XRD graphs were obtained using a Rigaku D/max 2400 diffract meter with Cu-Ka radiation (λ=0.154*nm*; 40*kV*, 120*mA*) at room temperature. The diffraction to grams were scanned from 1.5° to 40° in the 2θ range in 0.02° steps and scanning rate was 2°/min.

Results and discussion

Effect of Different Modifications on Diesel Resistance of Modified Bitumen

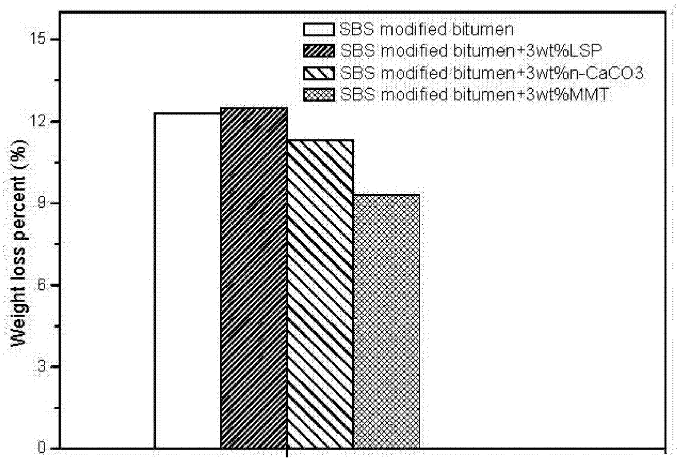

Fig. 1. Effects of Different Modifications on Diesel Resistance of Modified Bitumen.

The effects of different modifications on diesel resistance of modified bitumen blends are shown in Fig. 1. As seen in Fig. 1 that the percent weight loss of LSP/SBS modified bitumen in diesel is larger than that of pristine SBS modified bitumen, while the percent weight loss of both n-$CaCO_3$/SBS modified bitumen and MMT/SBS modified bitumen are lower than that of pristine SBS modified bitumen. Furthermore, MMT/SBS modified bitumen shows lower percent weight loss than that of n-$CaCO_3$/SBS modified bitumen.

Different particle size, surface properties of mineral materials, and the dispersed structure in modified bitumen may lead to the above results. LSP consists of micro-particles (average particle size is 15*μm*), and the surface of LSP is hydrophilic, which results in poor interaction between LSP particles and bitumen matrix. When the bitumen around the LSP particles is dissolved by diesel, the LSP particles exfoliate from the bitumen matrix and leave big holes in the matrix, which promote the permeation of diesel to bitumen. As a result, the percent weight loss of LSP/SBS modified bitumen is larger than that of pristine SBS modified bitumen. So the addition of LSP decreases the diesel resistance of SBS modified bitumen. On the other hands, n-$CaCO_3$ consists of nano-particles (particle size is 60 to 80*nm*), and the surface becomes organophilic due to the modification of some surfactants. Moreover, the nano-particles exhibit larger specific surface area and higher surface activity, so the interaction between n-$CaCO_3$ particles and bitumen matrix is much stronger than that of LSP particles/bitumen matrix. In addition, the nano-particles of n-$CaCO_3$ can lead to stronger space obstacles effect on diesel molecules, which can decrease the permeation of diesel molecules to bitumen. As a result, n-$CaCO_3$ can improve the diesel resistance of SBS modified bitumen.

MMT is a very soft phyllosilicate mineral with a 2:1-type layer structure. It has 2 tetrahedral sheets sandwiching a central octahedral sheet. If bitumen chain intercalates into the interlayer of MMT, MMT modified bitumen may form two structure types, namely intercalated structure and exfoliated structure. XRD curves for pristine MMT and MMT/SBS modified bitumen are shown in Fig. 2. The interlayer spacing can be calculated according to the Bragg equation ($2d\sin\theta = \lambda$), which are given in Table 2. It can be found that the d_{001} peak of the pristine MMT is at 2θ = 5.88° (d_{001} = 1.50*nm*) while the d_{001} peak of the MMT in SBS modified bitumen is shifted towards a lower θ, that is 2θ = 3.02° (d_{001} = 2.92*nm*).

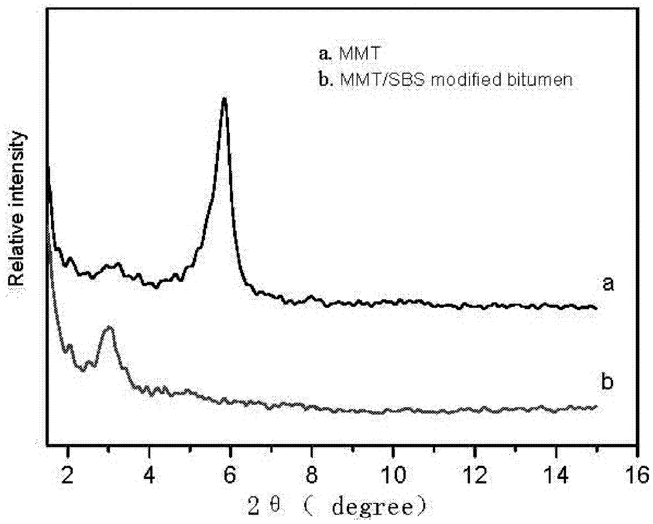

Fig. 2. XRD Patterns of MMT and MMT/SBS Modified Bitumen.

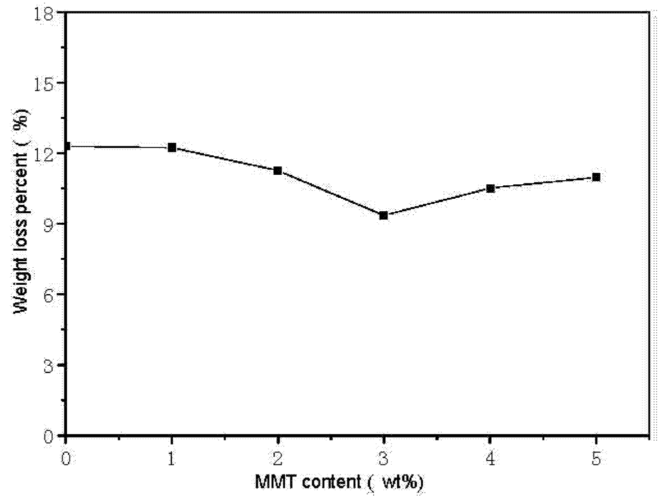

Fig. 3. Effects of MMT Content on Diesel Resistance of SBS Modified Bitumen.

Therefore we can conclude that bitumen intercalates into the MMT gallery and the MMT/SBS modified bitumen forms an intercalated structure. The intercalated structure provides modified bitumen with good barrier property, which can greatly decrease diesel permeability to modified bitumen. Therefore MMT can enhance the diesel resistance of SBS modified bitumen.

Effect of MMT Content on Diesel Resistance of SBS Modified Bitumen

The effect of MMT content on diesel resistance of SBS modified bitumen is shown in Fig. 3. It can be seen that the percent weight loss of SBS modified bitumen decreases when MMT content is less than 3%, however, when MMT content is higher than 3%, its percent weight loss increases. This result can be explained by the dispersed structure of MMT in SBS modified bitumen. For MMT/SBS modified bitumen, when MMT content is low, MMT is well dispersed in SBS modified bitumen and bitumen easily intercalates into the MMT gallery, the percent weight loss of SBS modified bitumen decreases with the increasing MMT content. When MMT content is more than 3%, complete intercalation of high aspect ratio silicate layers becomes harder to be produced because of geometrical constraints within the limited space remaining available in the bitumen matrix, the excess MMT is dispersed in bitumen matrix as filler. So the percent weight loss of SBS modified bitumen increases with the increasing MMT content.

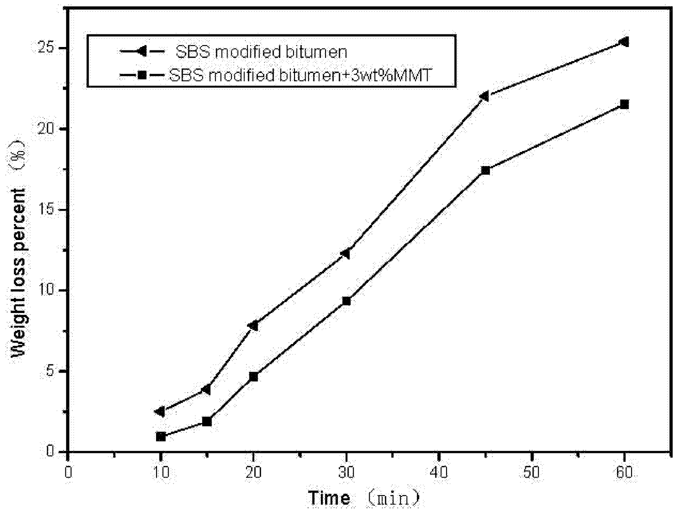

Fig. 4. Effects of Soaking Time on Diesel Resistance of Modified Bitumen.

Table 2. Interlayer Spaces of MMT and MMT in SBS Modified Bitumen.

Samples	2θ (°)	d (*nm*)
MMT	5.88	1.50
MMT in SBS Modified Bitumen	3.02	2.92

Effect of Soaking Time on Diesel Resistance of MMT/SBS Modified Bitumen

Two curves of percent weight loss versus soaking time for the MMT/SBS modified bitumen and pristine SBS modified bitumen are shown in Fig. 4. Note that the MMT content in MMT/SBS modified bitumen is 3%.

As seen in Fig. 4 that both percent weight losses of pristine SBS modified bitumen and MMT/SBS modified bitumen increase with the extended soaking time. As compared with pristine SBS modified bitumen, the percent weight loss of MMT/SBS modified bitumen is smaller than that of pristine SBS modified bitumen at the same soaking time, and the difference increases with the increase of soaking time.

It is well known that bitumen can be completely dissolved in diesel, so both percent weight losses of pristine SBS modified bitumen and MMT/SBS modified bitumen in diesel increase as the soaking time increases. Although the barrier property of intercalated structure of MMT/SBS modified bitumen can decrease the permeability of diesel, bitumen molecules in the surface of MMT/SBS modified bitumen are dissolved by diesel with the increase of soaking time, so the intercalated structure is gradually damaged. As a result, the percent weight loss of MMT/SBS modified bitumen increases with the increase of soaking time.

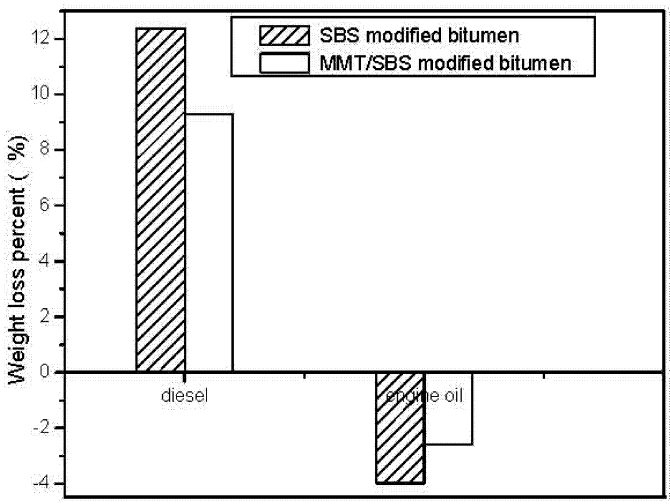

Fig. 5. Oil Resistance of MMT/SBS Modified Bitumen in Engine Oil.

Oil Resistance of MMT/SBS Modified Bitumen in Engine Oil

The percent weight loss of MMT/SBS modified bitumen in engine oil and in diesel is shown in Fig. 5. The soaking time in engine oil is 3hrs, while the soaking time in diesel is 0.5hr. As shown in Fig. 5, both weights of pristine SBS modified bitumen and MMT/SBS modified bitumen in engine oil increase, i.e. both MMT/SBS modified bitumen and SBS modified bitumen show swelling phenomenon in engine oil. However, the weight gained by MMT/SBS modified bitumen is less than that of pristine SBS modified bitumen, which can also be explained by the barrier property of intercalated structure in MMT/SBS modified bitumen. Hence, the addition of MMT reduces the swelling of SBS modified bitumen in engine oil.

Conclusions

Based on the test result and analyses of the effects of montmorillonite on oil resistance of SBS modified bitumen, the following conclusions are summarized.

1. The effects of MMT, LSP and n-$CaCO_3$ on diesel resistance to SBS modified bitumen are compared respectively. Both n-$CaCO_3$ and MMT enhance the diesel resistance to SBS modified bitumen, while LSP decreases the diesel resistance to SBS modified bitumen.
2. As compared with n-$CaCO_3$, MMT exhibited better effects on improving diesel resistance to SBS modified bitumen, which can be explained by the formation of intercalated structure in MMT/SBS modified bitumen and the intercalated structure provides SBS modified bitumen with better barrier property to diesel. MMT/SBS modified bitumen displays good resistance to diesel when the optimum MMT content is 3%.
3. The engine oil resistance to MMT/SBS modified bitumen is also investigated. Both SBS modified bitumen and MMT/SBS modified bitumen show swelling phenomenon in engine oil. However, due to the barrier property of intercalated structure in MMT/SBS modified bitumen, MMT can reduce the swelling of SBS modified bitumen in engine oil.

Acknowledgments

This work is part of a research Project 50773061 supported by National Natural Science Foundation of China. The authors gratefully acknowledge the financial support from National Natural Science Foundation.

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