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Effect of organic layered silicate on microstructures and aging properties of styrene–butadiene–styrene copolymer modified bitumen

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HIGHLIGHTS

- This work evaluates a novel bitumen modification through the use of organic layered silicate.
- A new approach to determine the microstructures of OLS/SBS modified bitumen is reported.
- Thermal and ultraviolet aging properties of OEVMt/SBS modified bitumen are evaluated.
- Aging mechanism of the binders is revealed by using optical microscopy.

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ABSTRACT

A new approach to determine the microstructures of organic layered silicate/SBS modified bitumen was adopted by combining the results from X-ray diffraction analysis of organic layered silicate/SBS modified bitumen and the dissolving–filtrating procedure. The effect of thin film oven test (TFOT) and ultraviolet (UV) aging on the morphology of binders was characterized by using optical microscopy. The results show that organic montmorillonite/SBS modified bitumen and organic rectorite/SBS modified bitumen form the semi-exfoliated nanostructure, while organic expanded vermiculite/SBS modified bitumen forms the exfoliated nanostructure. The high temperature properties of SBS modified bitumen and the compatibility between SBS and bitumen are improved with the introduction of organic layered silicate. Compared with SBS modified bitumen, organic layered silicate/SBS modified bitumen shows the lower viscosity aging index and the higher retained ductility after TFOT and UV aging. Aging influences the morphology of SBS modified bitumen significantly. There is a single phase trend of SBS modified bitumen during TFOT, which is accelerated by UV radiation. However, the morphological changes are prevented obviously with the introduction of organic layered silicate, indicating the good aging resistance of organic layered silicate/SBS modified bitumen. Additionally, the influence of organic layered silicate on these physical properties of SBS modified bitumen before and after aging depends on its nature.

1. Introduction

Styrene–butadiene–styrene (SBS) copolymer modified bitumen has been widely used in road construction as a binder [1–3]. SBS exhibits a two-phase morphology consisting of glassy polystyrene (PS) domains connected together by the rubber polybutadiene (PB) segments at the temperatures between glass transition temperatures of the PB and PS, so SBS exhibits crosslinked elastomer network behavior. Above the glass transition temperature of PS, the PS domains soften and SBS becomes melt processable. This behavior of a thermoplastic elastomer has allowed SBS to become one of the promising candidates in bitumen modification [4]. It has been recognized that the physical and mechanical properties and rheological behaviors of conventional bitumen can be improved by the addition of SBS [5]. Furthermore, as other plain bitumens, SBS modified bitumen is also subjected to aging, which influences its chemical structures and physical properties. Aging of SBS modified bitumen is one of the principal factors causing the deterioration of asphalt pavements. Important aging related modes of failure are traffic and thermally induced cracking, and ravelling [6]. However, most published studies reported on the aging process and mechanism of SBS modified bitumen [7–9]. There were relatively few reports on improving the aging resistance of SBS modified bitumen [10].

Recently, layered silicates have been used to modify SBS modified bitumen. The main layered silicate includes montmorillonite (Mt), rectorite (REC), vermiculite (VMt) and kaolinite clay. The sheet

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structure of Mt consists of tetrahedral silicate layers and octahedral alumina layers. The tetrahedral silicate layer consists of SiO_4 groups linked together to form a hexagonal network of repeating units of Si_4O_{10}. The alumina layer consists of two sheets of closely packed oxygens or hydroxyls, between which octahedrally coordinated aluminum atoms are imbedded in such a position that they are equidistant from six oxygens or hydroxyls. The two tetrahedral layers sandwich the octahedral layer, sharing their apex oxygens with the latter. A single silicate layer with a sandwiched structure has a thickness of around 1 nm and a cross-sectional area of about 100 nm^2 [11,12]. REC is a 1:1 regular interstratification of a dioctahedral mica and a dioctahedral Mt. Like Mt, VMt is a mica-type silicate, belongs to the general family of 2:1 layered silicates. Each layer consists of octahedrally coordinated cations (typically Mg, Al and Fe) sandwiched by tetrahedrally coordinated cations (typically Si and Al). The isomorphous substitution of Si^{4+} by Al^{3+} leads to a net negative surface charge that is compensated by an interlayer of exchangeable hydrated cations (Ca^{2+}, Mg^{2+}, Cu^{2+}, Na^{+}) [13,14]. When pristine VMt flakes are strongly heated at high temperature (about 900 °C) during a short period of time, the water situated between layers is quickly converted into steams, exerting a disruptive effect upon the structure. As a consequence, a highly porous material named expanded vermiculite (EVMt) is formed and it is an efficient thermal insulator [14].

More attention of the researchers has been paid to Mt/SBS modified bitumen [15–17]. To increase the compatibility between the Mt and SBS modified bitumen, Mt is commonly exchanged with organic cations, particularly alkylammonium ions, making the Mt become lipophilic, and the interlayer spacing is also enlarged. It has been found that physical properties, rheological behaviors of SBS modified bitumen could be obviously improved due to the introduction of Mt. Even more exciting is that Mt can significantly improve the thermo-oxidative and ultraviolet aging resistance of SBS modified bitumen, which was attributed to the barrier properties of Mt [18,19]. However, there were relatively few reports on the effect of different layered silicate on the properties of SBS modified bitumen. In addition, few researchers paid attention to the microstructures of the Mt/SBS modified bitumen except the using of X-ray diffraction (XRD). New analytical methods should be taken to better understand the interaction of layered silicate with SBS modified bitumen. The investigation of mechanism and microstructures between SBS modified bitumen and different layered silicates is significant to improve the aging properties of SBS modified bitumen and expand modifiers for SBS modified bitumen, which also can contribute to the application of nanotechnology in road materials.

This study aims at determining the effect of different organic layered silicate on the microstructures, physical and aging properties of SBS modified bitumen. The microstructures of organic layered silicate/SBS modified bitumen were characterized by combining XRD and dissolving–filtrating method. Aging properties and mechanism of organic layered silicate/SBS modified bitumen were investigated by optical microscope and the physical properties changes of the binders before and after thin film oven test and ultraviolet aging.

2. Experimental details

2.1. Materials

The 80/1000 pen grade bitumen was used as base binder in this study. The physical properties and chemical compositions of the bitumen are listed in Table 1. The SBS, Grade 1301, was a linear-like SBS, containing 30 wt% styrenes, and the average molecular weight of SBS was 120,000. The interlayer spacing of Mt, EVMt and REC is 1.53 nm, 1.42 nm and 2.25 nm, respectively. Chemically pure octadecyl dimethyl benzyl ammonium chloride (ODBA) was used as intercalation agents for cation exchange to modify the Mt, EVMt and REC interlayer surface. Information on the characteristics of the organic layered silicates is given in Table 2.

Table 1
Physical properties and chemical compositions of pristine bitumen.

Physical properties and chemical compositions		Measured values
Physical properties	Penetration (25 °C, 0.1 mm)	63
	Softening point (°C)	49.1
	Ductility (15 °C, cm)	130.1
	Viscosity (60 °C, Pa s)	253
	Viscosity (135 °C, Pa s)	0.52
Chemical compositions (%)	Saturates	23.43
	Aromatics	32.26
	Resins	33.73
	Asphaltenes	10.58

Table 2
Characteristics of the used organic layered silicates.

Organic layered silicates	Interlayer spacing (nm)	ODBA content (wt%)
OMt	2.31	10.5
OREC	4.58	13.1
OEVMt	5.33	18.6

2.2. Preparation of organic layered silicate

A 500-mL round-bottom, three-necked flask with a mechanical stirrer, thermometer, and condenser with a drying tube was used as a reactor. Layered silicate (Mt, EVMt or REC, 10 g) was gradually dissolved in 200 mL deionised water and stirred for 30 min. Then a certain amount of ODBA was added into this solution. The resultant suspension was vigorously stirred for 10 h. The treated layered silicate was repeatedly washed with deionised water. The filtrate was titrated with 0.1 N $AgNO_3$ until no precipitate of AgCl was formed. The filter cake was then placed in a vacuum oven to dry at 80 °C for 24 h. The dried cake was then ground to obtain organic layered silicate with a particle size of 300 mesh.

2.3. Preparation of organic layered silicate/SBS modified bitumen

The organic layered silicate/SBS modified bitumens were prepared using a high shear mixer at 175 °C and a shearing speed of 4000 rpm. First, bitumen was heated to become a fluid in an iron container, then upon reaching about 175 °C, SBS (3 wt%, the amounts were based on 100 parts bitumen) and sulfur powder (0.12 wt%) were added to the bitumen and sheared for 45 min to produce SBS modified bitumen. After that, a certain amount of organic layered silicate was added into this mixture, and the mixture was blended at a fixed rotate speed about 30 min, then the mixture was blended using a common mixer at a rotation speed of 2000 rpm for about 90 min to produce organic layered silicate/SBS modified bitumens. The SBS modified bitumen in the absence of organic layered silicate was prepared under the same condition in order to compare with the organic layered silicate/SBS modified bitumens.

2.4. High-temperature storage stability test

The binders were poured into a toothpaste-shaped aluminum tube with a diameter of 25.4 mm and a length of 140.0 mm. The specimen was placed vertically in an oven for 48 h at 163 °C. Once cooled, the tubes were cut into three sections, and samples were taken from the top and bottom portions and reheated at 150 °C to take samples for the ring-and-ball (R&B) softening point test. The stability of the binders was assessed by investigating the difference in softening point between the top and bottom samples.

2.5. Aging procedures

Aging of the bitumen was performed using thin film oven test (TFOT) and UV radiation, respectively. TFOT was executed in accordance with ASTM D 1754 [20]. The residue from the TFOT was UV-aged for 12 days in a draft oven (850 mm × 600 mm × 600 mm, together with fresh air) with an UV lamp of 500 W. The intensity of UV radiation was about 800 $\mu w/cm^2$. The melted bitumen was placed on a $\Phi 150 \pm 0.5$ mm iron pan which was placed at the bottom of the chamber, and the thickness of bitumen film was about 2.0 mm. The vertical distance from the pan to the lamp was 500 mm. The working temperature was controlled at 80 °C. The aged binders were evaluated by measuring physical properties and optical microscope analysis.