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Effect of expanded vermiculite on microstructures and aging properties of styrene–butadiene–styrene copolymer modified bitumen

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HIGHLIGHTS

- ▶ EVMT/SBS modified bitumen forms the phase-separated structures.
- ▶ OEVMT/SBS modified bitumens form the exfoliated nanostructures.
- ▶ OEVMTs improve the high temperature stability and physical properties of the binders.
- ▶ OEVMT/SBS modified bitumens show the more pronounced aging resistance compared with EVMT.

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ABSTRACT

Organic expanded vermiculites (OEVMTs) were prepared using cetyltrimethyl ammonium bromide (CTAB) and octadecyl dimethyl benzyl ammonium chloride (ODBA) as intercalation agents. Effect of EVMT organic modification on physical and aging properties of styrene–butadiene–styrene (SBS) modified bitumen was investigated. The microstructures of the binders were characterized by X-ray diffraction (XRD) and atomic force microscopy (AFM), respectively. EVMT/SBS modified bitumen forms a phase-separated structure, while OEVMT/SBS modified bitumens form the exfoliated nanostructures according to XRD analysis. OEVMTs show the more obvious influence on physical properties of SBS modified bitumen in comparison with EVMT. The compatibility between the EVMT and SBS modified bitumen is also improved after organic modification of EVMT. AFM analysis indicates that the contrast between the dispersed phase and the matrix phase in SBS modified bitumen increases with the addition of ODBA-EVMT. As a result of thin film oven test (TFOT), the viscosity aging index of SBS modified bitumen decreases, while the retained ductility and penetration increase obviously with the introduction of EVMT and OEVMTs. ODBA-EVMT/SBS modified bitumen has more pronounced improvements in aging resistance of SBS modified bitumen in comparison with CTAB-EVMT/SBS modified bitumen by preventing the phase-separated trend of the SBS modified bitumen during TFOT.

1. Introduction

Bitumen has been widely used as the binder of aggregate in road pavement due to its good viscoelastic properties [1]. However, the increasing demands of traffic on road building materials have resulted in a search for binders with improved performance relative to conventional bitumens in recent decades. Consequently, more and more modified bitumens are used in road pavement [2]. Quite often, these initiatives are achieved by adding polymeric modifiers into the binders [3]. Pavement with polymer modification exhibits greater resistance to rutting and thermal cracking, and decreases fatigue damage, stripping and temperature susceptibility [4]. One of the most successful polymers is the styrene–butadiene–styrene (SBS) block copolymer, which can retard low-temperature thermal stress cracking and improve resistance to high-temperature rutting with a finely dispersed polymer phase in the bitumen binders [5–7].

Bitumens, as other organic substances, evolve with time, which is called aging. Bitumen aging mainly occurs during the mixing process, laying on the road and the service life in the pavement [8]. Meanwhile, SBS tends to be degraded by exposing to heat and ultraviolet light causing discoloration and surface embrittlement due to the sensitivity of the double bonds of polybutadiene segment to light, heat and oxide, which would impact its performance [9]. In this case, it is necessary to improve the aging

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resistance of SBS modified bitumen both during manufacturing and laying of SBS modified bitumen at high temperature as well as in pavement application.

In recent decades, polymer/layered silicate nanocomposites have attracted the interest of polymer and materials scientists in filled polymers. Due to the addition of layered silicate, some properties of polymers, such as stiffness, fire resistance, fluid and gas barrier properties are superior to those of unmodified polymers [10]. The main layered silicates include montmorillonite (MMT), rectorite, vermiculite (VMT) and kaolinite clay. In order to make the layered silicate more compatible with the polymer, some surfactants, particularly alkylammonium ions, are usually used to modify the layered silicate by replacing the hydrated interlayer cations. In this way, the hydrophilic silicate surface became organophilic [11]. It has been found that the nature of the organic modifiers has an obvious effect on the morphology and properties of the nanocomposites [12,13].

Recently, layered silicates have been used to modify bitumen. More attention of the researchers has been paid to MMT modified bitumen. It has been found that physical properties, rheological behaviors of bitumen and polymer modified bitumen could be obviously improved due to the introduction of MMT. Even more exciting is that MMT can largely improve the aging resistance of bitumen [14–17]. Like MMT, VMT is a mica-type silicate, belongs to the general family of 2:1 layered silicates. 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 [18]. It has been clarified that the heat resistance and barrier properties of EVMT layers are more obvious than that of MMT due to its much higher aspect ratio [19].

In the present work, EVMT and two OEVMTs were used to modify the SBS modified bitumen. The effect of EVMT organic modification on physical and aging properties of SBS modified bitumen was investigated. The microstructures and modification mechanism of the binders were also proposed.

2. Experimental

2.1. Materials

The 80/100 pen grade bitumen was supported by SK Corp., Korea, and the physical properties of the bitumen are listed in Table 1. The SBS, Grade 1301, was produced by the Yueyang Petrochemical Co., Ltd., China. It was a linear-like SBS, containing 30 wt% styrenes, and the average molecular weight of SBS was 120,000. EVMT, 300 mesh, was supplied by Jinli Mineral, Co., Ltd., Hebei, China. Organic expanded vermiculites (OEVMTs), CTAB-OEVMT and ODBA-OEVMT, 300 mesh, an EVMT modified by cetyltrimethyl ammonium bromide (CTAB) and octadecyl dimethyl benzyl ammonium chloride (ODBA) (chemically pure, supplied by Tianjin Yuanhang Chemicals Co., Ltd., Tianjin, China.) as organic modifiers, respectively, were prepared by our laboratory.

Table 1
Physical properties of bitumen.

Physical properties and chemical compositions	Measured values
Penetration (25 °C, 0.1 mm)	91
Ductility (15 °C, cm)	>150
Softening point (°C)	46.0
Viscosity (60 °C, Pa s)	178
Viscosity (135 °C, Pa s)	0.30
Saturates (%)	13.48
Aromatics (%)	49.78
Resins (%)	25.31
Asphaltenes (%)	11.43

Table 2
The interlayer spacing of EVMT and OEVMTs.

EVMT and OEVMTs	Interlayer spacing (nm)	Ammonium content (wt%)[a]
EVMT	1.42	0
CTAB-EVMT	5.28	17.0
ODBA-EVMT	5.33	18.6

[a] Determined by thermogravimetric analysis under helium atmosphere.

2.2. Preparation of OEVMTs

A 500-mL round-bottom, three-necked flask with a mechanical stirrer, thermometer, and condenser with a drying tube was used as a reactor. EVMT (10 g) was gradually dissolved in 200 mL deionised water and stirred for 30 min. Then CTAB or ODBA was added into this solution. The resultant suspension was vigorously stirred for 10 h. The treated EVMT was repeatedly washed with deionised water. The filtrate was titrated with 0.1 N $AgNO_3$ until no precipitate of AgBr or 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 OEVMTs with a particle size of 300 mesh.

2.3. Preparation of EVMT- and OEVMT/SBS modified bitumen

The EVMT- and OEVMT/SBS modified bitumens were prepared using a high shear mixer (model BME 100 L, Shanghai Weiyu Mechano-electronic Manufacturing Co., Ltd., China) 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 was added to the bitumen and sheared for 45 min to produce SBS modified bitumen. After that, a certain amount of EVMT or OEVMT 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 EVMT- or OEVMT/SBS modified bitumens. The SBS modified bitumen in the absence of EVMT was prepared under the same condition in order to compare with the EVMT- and OEVMT /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 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 procedure

Aging of the binders was performed using thin film oven test (TFOT) according to ASTM D 1754. TFOT is used to simulate aging of bitumen during the plant hot mixing, transport and the lay down process. TFOT is executed in an oven with a plat and an axis, and the rotation of plat is carried out by the axis. Binders were heated for 5 h at 163 °C. The aged binders were evaluated by measuring physical properties and AFM analysis.

2.6. Characterization

XRD graphs of EVMT, OEVMT and EVMT/SBS modified bitumens were obtained using a Rigaku D/max D/MAX-IIIA diffractometer with Cu Kα radiation (λ = 0.15406 nm; 40 kV, 50 mA) at room temperature. The scanning rate was 2 deg/min. The diffractograms were scanned from 0.5° to 10°.

AFM (Model DI Nanoscope IV, American Veeco Company) was applied to investigate the micro-morphology of the binders. A hot liquid drop of bitumen (175 °C) was carefully placed on a 10 mm × 10 mm × 1 mm steel disk, then cooled to ambient temperature (about 5 °C), covered by a glass cap to prevent dust pick-up and annealed for a minimum of 24 h before imaging. Topographic and phase images were scanned using an etched silicon probe. Cantilever was 125 μm long with curvature radius at 5–10 nm and height at 15–20 μm. The drive frequency was 260 kHz and the drive amplitude was 56 mw. Test was operated in tapping mode. All the microphotographs show a 15 μm × 15 μm region.

2.7. Physical properties test

The physical properties of the binders, including softening point, penetration (25 °C), and ductility (5 °C), were tested according to ASTM D 36, ASTM D 5, and ASTM D 113, respectively. Brookfield viscometer (Model DV-II+, Brookfield Engineering Inc., USA) was employed to measure the viscosity of the binders at 135 °C and 60 °C according to ASTM D 4402.