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Investigation of microstructures and ultraviolet aging properties of organo-montmorillonite/SBS modified bitumen

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Organo-montmorillonite(OMMT)/Styrene-butadiene-styrene(SBS) modified bitumen nanocomposites were prepared by melt blending. The microstructures of OMMT/SBS modified bitumen were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and atomic force microscopy (AFM), respectively. The effect of OMMT on ultraviolet (UV) aging properties of SBS modified bitumen was investigated. FTIR and XRD analyses indicate that the OMMT/SBS modified bitumen forms an intercalated structure. It is observed that the phase contrast between the dispersed domains and the matrix is inverted in SBS modified bitumen, which is decreased with the introduction of OMMT according to AFM analysis. As a result of UV aging, both viscosity aging index and softening point increment of OMMT/SBS modified bitumen decrease significantly. There is a single phase trend in the morphology of the bitumen after aging, which is accelerated by the existence of SBS. However, these changes can be effectively prevented under the influence of OMMT, indicating the good UV aging resistance of OMMT/SBS modified bitumen.

1. Introduction

Bitumen plays a prominent role in determining many aspects of road performance because of its viscoelastic property. However, because of continuously increasing traffic volumes and axle loads, conventional bitumens do not always perform as expected. Consequently, for certain applications, bitumen properties need to be improved [1]. Quite often, these initiatives are achieved by adding polymeric modifiers to the binders [2]. 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 [3–5].

Bitumens, as other organic substances, evolve with time, which is called aging [6]. Bitumen is prone to go fragile and stiff due to exposing to heat, oxygen, and ultraviolet (UV) light during storage, mixing, transport and laying down, as well as in service life. Bitumen aging is one of the principal factors causing the deterioration of bitumen pavements. The main aging mechanism is an irreversible one, which contributes to the oxidation, loss of volatile components and exudation of oily components from the bitumen into the aggregate [7]. Those changes eventually lead to the physical hardening of bitumen during the aging periods. A number of laboratory methods have been used in the quantitative determination of bitumen aging at various stages of the production process as well as in service, which mainly include thin film oven test (TFOT), rolling thin-film oven test (RTFOT) and pressure aging vessel (PAV) aging. There is now an attention in ultraviolet (UV) aging, which has an obvious influence on the aging of the upper layers of wearing courses of a pavement [1,8]. It has been found that the same aging level as the one simulated by PAV is reached in a few hours when a thin film of bitumen is submitted to UV exposure after RTFOT [8]. Aging is already a very complex process in unmodified bitumens, and the degree of complexity increases after modification by SBS which also evolves with time [9]. However, the UV aging mechanism of bitumen is still not well understood. Thus, understanding the process of UV aging, especially the role and effect of SBS in this process is very important for real application.

With the rapid development of nanotechnology, layered clay/polymer composites with nanometer dimensions have recently become a hot direction for new materials development. Polymer/montmorillonite (MMT) nanocomposites are a kind of composites in which nanosize layers of MMT are dispersed in the polymer matrix [10,11]. Recently, MMT has been used to modify bitumen. MMT can obviously improve the physical properties, rheological behaviors and thermo-oxidative aging properties of bitumens and SBS modified bitumens. Compared with sodium montmorillonite (Na^{+}-MMT), organo-montmorillonite (OMMT) exhibited better modification effects to the bitumen [12]. However, the influence of MMT on UV aging properties of SBS modified

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Table 1
Physical properties of bitumen.

Physical properties	Measured values
Penetration(25 °C, 0.1 mm)	70
Softening point (°C)	48.2
Ductility (15 °C, cm)	91.1
Viscosity (60 °C, Pa s)	274
Viscosity (135 °C, Pa s)	0.54

bitumen has not been taken into account. Furthermore, most of published studies were limited in the physical or rheological properties of the MMT modified bitumens, few researchers paid attention to the microstructures of the binders except the using of X-ray diffraction (XRD) [12–14].

In this paper, the microstructures of OMMT/SBS modified bitumen were characterized by XRD, Fourier transform infrared spectroscopy (FTIR) and atomic force microscopy (AFM), respectively. The effect of OMMT on ultraviolet (UV) aging properties of SBS modified bitumen was investigated. The relationship between microstructures and UV aging properties of the binders was also analysed.

2. Experimental details

2.1. Materials

The 60/80 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. OMMT, the Na^+-MMT (cation exchange capacity was 90 meq/100 g, supplied by Fenghong Clay Chemical Factory, China) modified by hexadecyl dimethyl benzyl ammonium chloride (HDBA), was prepared by our laboratory.

2.2. Preparation of OMMT/SBS modified bitumen

The OMMT/SBS modified bitumens were prepared using a high shear mixer at 180 °C and a shearing speed of 4000 rpm. First, bitumen was heated to become a fluid in an iron container, then upon reaching about 180 °C, 4 wt.% SBS was added to the bitumen and sheared for 30 min to produce SBS modified bitumen. After that, 3 wt.% OMMT 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 OMMT/SBS modified bitumen composites. The SBS modified bitumen in the absence of OMMT was prepared under the same conditions in order to compare with the OMMT/SBS modified bitumen.

2.3. Aging procedure

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. 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 μw cm^{-2}. The melted bitumen was placed on a Φ150 ± 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 like viscosity (135 °C) and softening point as well as AFM analysis.

2.4. Characterization

XRD graphs of MMT, OMMT and OMMT/SBS modified bitumen were obtained using a Rigaku D/max D/MAX-ШA diffractometer with Cu Kα radiation (λ = 0.15406 nm; 40 kV, 50 mA) at room temperature. The data were collected in step-scan mode and the scanning rate was 0.002°/s. The diffractograms were scanned from 0.5° to 10°.

FTIR spectra of OMMT and the binders were obtained with a model Nexus FTIR spectrometer from Thermo Nicolet Corp. (New York, USA). The scan range was from 4000 cm^{-1} to 400 cm^{-1} with a resolution of 4 cm^{-1}.

AFM (Model DI Nanoscope IV, American Veeco Company) was applied to investigate the micro-morphology of the binders. A hot liquid drop of bitumen (140 °C for pristine bitumen and 180 °C for modified bitumen [15]) 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 [16]. 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.

The absorption edge and reflectance of the OMMT samples were measured using an ultraviolet and visible (UV–vis) spectrophotometer (UV2550, Shimadzu, Japan). $BaSO_4$ was used as a reflectance standard in the UV–vis diffuse reflectance experiment.

2.5. Physical properties test

The softening point of the binders was tested according to ASTM D 36. The Brookfield viscometer (Model DV-II+, Brookfield Engineering Inc., USA) was employed to measure the viscosity (135 °C) of the binders according to ASTM D 4402.

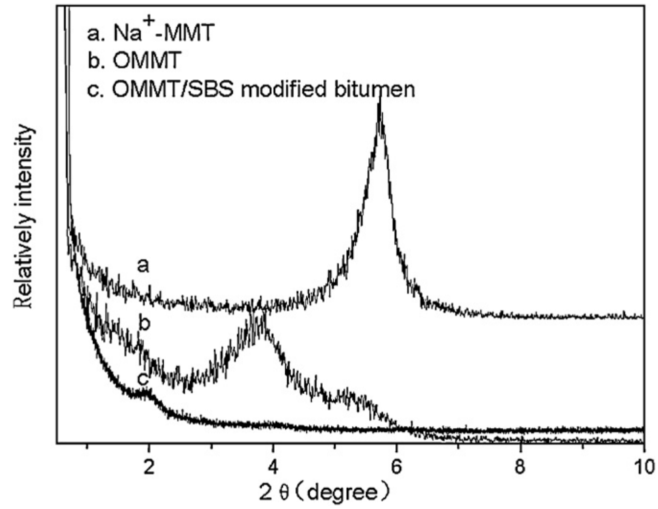

Fig. 1. XRD patterns of different MMTs.

3. Results and discussion

3.1. Microstructures of the binders

3.1.1. XRD analysis

The XRD patterns of the Na^+-MMT, OMMT and OMMT/SBS modified bitumen with 3 wt.% OMMT are shown in Fig. 1. According to our previous research, the high temperature stability and thermo-oxidative aging properties of the bitumen can be improved obviously without degrading the low temperature cracking properties of bitumen after the addition of 3 wt.% OMMT [12–14]. Consequently, in this paper, the chosen content of OMMT is 3 wt.% relative to bitumen. Fig. 1(a) shows a characteristic peak at $2\theta = 5.76°$, which is assigned to the 001 basal reflection of Na^+-MMT, while Fig. 1(b) shows a characteristic peak at $2\theta = 3.65°$ of OMMT. Compared with Na^+-MMT and OMMT, the diffraction peak of OMMT in SBS modified bitumen is further shifted to smaller angles (Fig. 1(c)). The data for Na^+-MMT, OMMT and OMMT/SBS modified bitumen, calculated by the Bragg formula ($n\lambda = 2d \sin\theta$), are summarized in Table 2.

MMT clay is a phyllosilicate mineral. Cations such as Na^+, K^+, and Ca^{2+}, compensate the negative charge that exists in the crystal lattice of each silicate layer in MMT [17,18]. Polar molecules such as hexadecyl dimethyl benzyl ammonium chloride, which can

Table 2
Interlayer spacing of MMT.

Samples	2θ (°)	d (nm)
Na^+-MMT	5.76	1.53
OMMT	3.65	2.42
OMMT/SBS modified bitumen	2.00	4.41