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Effect of etched Layered double hydroxides on anti ultraviolet aging properties of bitumen

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HIGHLIGHTS

- Layered double hydroxides (LDHs) was etched by nitric acid used to modify bitumen.
- The dispersity of LDHs in bitumen had been improved after etching treatment.
- Etched LDHs is more beneficial to enhance the UV aging resistance of bitumen than LDHs.

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ABSTRACT

Layered double hydroxides (LDHs) etched by nitric acid was characterized by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), zeta potential potentiometer, scanning electron microscopy (SEM) and ultraviolet and visible (UV–Vis) spectrum. TEM suggests that etching treatment causes the formation of some defects on the surface of etched LDHs and XPS shows that some hydroxyl groups are eliminated from the surface of LDHs after etching. The zeta potential of LDHs is enhanced from 12.02 mV to 17.21 mV for etched LDHs, which suggests etching treatment of LDHs can enlarge repulsion force between particles of LDHs. SEM confirms that the etching treatment is helpful to reduce the agglomeration of LDHs. UV–Vis curves indicates that the absorption UV capacity of LDHs is significantly improved by etching treatment. Moreover, the impact of etching treatment on the physical properties and dynamic rheological characteristics of LDHs modified bitumen during the process of aging was thoroughly investigated. Investigation results indicate that the etching treatment of LDHs is favorable for improving the ductility of LDHs modified bitumen. And the etched LDHs modified bitumen shows the smaller variations of physical properties and dynamic rheological properties as well as structural indexes after UV aging than those of LDHs modified bitumen, revealing that etched LDHs is more beneficial to enhance the anti-ultraviolet aging properties of bitumen since the improvement of dispersity and UV shielding capability of LDHs after etching.

1. Introduction

Asphalt mixture is broadly applied in the field of pavement construction attributed to its driving comfort and excellent road performance, for bitumen is a viscoelastic material as an important binder in the asphalt mixture [1–5]. However bitumen is a kind of organic material natively, thus it is susceptible to aging under the action of oxygen, ultraviolet (UV) light and heat during the process of construction and service, resulting in a decrease of road performance and service life [6–8]. Particularly, the weak bonds in the molecules of bitumen are easy to break and produce free radicals under the UV radiation, which will accelerate the aging of bitumen [9,10]. For organic material, especially for bitumen, the improvement of anti UV aging property counts for a great deal.

Aiming to solve this problem, some researches have been reported in publication. For instance, Feng et al. [11] studied on the application of UV absorbents as anti UV aging agent in bitumen, found that bumetrizole showed better performance in depressing the aging of bitumen than that of octabenzone, however, UV absorbents as organic molecules were also easy to be degraded. Zhang and his coworkers [12] found that the hardening trend of bitumen in long-term aging was slowed down by organo-montmorillonite since the formation of intercalated nanostructure of organo-montmorillonite modified bitumen, however, the anti-aging effect of organo-montmorillonite was limited for its poor UV shield property. A study by Liao et al. [13] suggested that carbon black could play an important role in restraining aging of

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bitumen due to the good UV absorption of carbon black, but reduced the low-temperature property of bitumen greatly.

In recent years, excellent UV shielding property of LDHs has attracted considerable attention because of its special lamellar structure [14]. It is reported that LDHs has been used for the study of modifying bitumen and enhancing its anti-aging property, and showed great performance [15,16]. However like other inorganic nanoparticles, LDHs is apt to agglomerate spontaneously as the result of large specific surface area [17], and bad compatibility with bitumen. To solve this problem, some works have been done. Xu et al. [18] reported that sodium dodecylbenzenesulfonate were favorably intercalated into the interlamination of LDHs, and found that LDHs intercalated with sodium dodecylbenzenesulfonate could improve the compatibility with bitumen as well as its UV aging performance. Zhang et al. [19] provided another method, LDHs was surface modified by triethoxyvinylsilane, which made the surface of LDHs coated with triethoxyvinylsilane, leading to a better dispersion in the bitumen.

LDHs is a hydrophilic powder particle with numerous surface active hydroxyl groups, which has strong hydrogen bonding effect, resulting in a serious agglomeration of LDHs particles and a weak compatibility with bitumen. Therefore, the reduction of hydroxyls on the surface of LDH and the decline of hydrogen bonding force between LDHs particles would lead to the improvement of dispersity of LDHs in the bitumen. According to this point, reducing the hydrophilicity of LDHs and improving its dispersity can be achieved by acid etching. Through acid etching, the reaction between hydrogen ion in acid and active hydroxyl groups on the surface of LDHs could cause a decline of these hydroxyl groups. Meanwhile, the oxygen atoms of hydroxyl would take away plentiful lone pairs of electrons, leading to the increase of electrostatic repulsion between LDHs particles. That would be helpful for enhancing the dispersion of LDHs in bitumen. This way is simpler as compared with the method of organic modified LDHs, and etched LDHs would have excellent dispersity in the bitumen.

Nitric acid is a kind of strong acid that always acts as an etching agent [20,21]. In this paper, LDHs was etched by nitric acid and the microstructures and properties of etched LDHs was characterized by X-ray diffraction (XRD), transmission electron spectroscopy (TEM), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), zeta potential potentiometer and UV–vis spectrophotometer. And the influence of etching treatment of LDHs on the physical properties, dynamic rheological characteristics and chemical composition of LDHs modified bitumen during the process of aging was thoroughly investigated.

2. Materials and experimental methods

2.1. Materials

SK-70# bitumen was produced by SK Corp., Korea, the physical properties of bitumen are presented as Table 1. LDHs (CO_3^{2-}-MgAl-LDHs) was provided by Beijing University of Chemical Technology, China, whose mean size is 450 nm with the atomic ratio of Mg^{2+}/Al^{3+} = 2.0.

2.2. Etching treatment of LDHs

3 g LDHs and 300 mL deionized water were taken into a three-necked flask, then 30 mL nitric acid with the concentration of 1.0 mol/L was added into the three-necked flask and stirred at the speech of 500 rpm for 1 h at room temperature, finally, centrifuged, filtered and washed, dried at 65° C for 24 h to obtain etched LDHs.

Table 1
Physical properties of the bitumen.

Penetration (25 °C, 0.1 mm)	Softening point (°C)	Ductility (10, cm)	Viscosity (135 °C, Pa·s)
73	50.1	13.8	0.55

2.3. Preparation of etched LDHs modified bitumen

Samples were prepared by melt blending method. First, 300 g pristine bitumen and etched LDHs or LDHs (3% by weight of bitumen) were taken into a pot, heated the mixture to 140 °C with oil-bath temperature control system. Then the mixture was stirred with the speed of 4000 rmp for one hour to ensure homogeneous blending, to obtain etched LDHs or LDHs modified bitumen. Finally, they were applied to do relevant experiments and test. Meanwhile, the pristine bitumen was prepared in the same process as the control sample. The bitumen modified by LDHs and etched LDHs were denoted by LMB, ELMB, respectively. And the pristine bitumen was denoted by PB.

2.4. Aging procedures

The thin film oven tests (TFOT) of PB, LMB and ELMB were carried out at 163 °C for 5 h following the standard of ASTM D1754. Then, the samples were put into an UV aging oven with the ultraviolet light intensity of 1200 $\mu W/cm^2$ for different days (3 d, 6 d and 9 d) at 60 °C.

2.5. Characterization and test

2.5.1. XRD

XRD graphs of the LDHs and etched LDHs were obtained from a D8 Advance diffractometer (Bruker Corporation, Germany) with Cu-Ka radiation (k = 0.15406 nm). The XRD graphs were taken with the diffractive angle from 5° to 65° with the 2θ range of 0.02° steps at room temperature.

2.5.2. TEM

TEM images of the LDHs and etched LDHs were taken by JEM-2100F (JEOL Ltd) with working voltage of 200 kV. The samples were prepared as follows: Small amount of LDHs or etched LDHs was added into the deionized water and ultrasonic dispersion for 20 mins, then a drop of prepared suspension was taken on the surface of Si_3N_4 film.

2.5.3. XPS

XPS of LDHs and etched LDHs sample were studied by ESCALAB 250Xi (Thermo Fisher Scientific Inc., Wellesley, MA, USA). The measurements were carried out under high vacuum (1.0×10^{-9} Pa) with an Al-Kα radiation (1486.6 eV).

2.5.4. Zeta potential potentiometer

Zeta potentials of LDHs and etched LDHs were tested by Malvern Zetasizer-2000 analyzer. The samples were prepared as follows: LDHs powders was added into the deionized water with the concentration of 0.5 g/L, and ultrasonic dispersion for 5 min.

2.5.5. SEM

SEM morphology of LDHs and etched LDHs was investigated by HitachiS-4800 with the operating voltage of 5 kV. The samples were prepared as follows: Small amount of LDHs or etched LDHs was taken into the deionized water and ultrasonic dispersion for 5 min, then drops of prepared suspension were dripped on the surface of aluminum foil, and dried for a moment. Finally, it was treated with gold spray.

2.5.6. Ultraviolet and visible (UV–Vis) spectrophotometer

PerkinElmer Lambda 750 S spectrophotometer was used to record the ultraviolet and visible absorption and reflectance spectra of LDHs and etched LDHs, the measurement ranged from 200 nm to 800 nm with the spectral resolution of 2 nm.

2.5.7. Physical properties test

The physical properties of the PB, LMB and ELMB, including softening point, penetration (25 °C), ductility (10 °C), and viscosity (135 °C) were tested based on the standard of ASTM D36, ASTM D5, ASTM D113, and ASTM D4402, respectively.

2.5.8. FTIR

The spectra of the PB, LMB and ELMB were obtained by Thermo Scientific Nicolet FT-IR spectrometer. The samples were prepared by liquid film method (the concentration was 5 wt%). The measurement was carried out in the range of 400 ~ 4000 cm^{-1} with the spectral resolution of 4 cm^{-1}, and the scanning rate of 64/min.

2.5.9. Dynamic shear rheometer (DSR) test

Dynamic shear rheometer (Anton Paar Company, Austria) was applied to test the dynamic rheological properties of PB, LMB and ELMB before and after aging. Temperature sweep test (frequency: 10 rad/s; increment: 2 °C/min) was implemented ranging from 30 °C to 80 °C under stress-controlled mode with the plates of 25 mm diameter and 1 mm gap.