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Synthesis and characterization of organic intercalated layered double hydroxides and their application in bitumen modification

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HIGHLIGHTS

- XRD, FTIR and SEM were used to confirm the successful intercalation.
- SDBS–LDHs show superior UV protective ability.
- SDBS–LDHs improved the anti-ageing properties of bitumen.

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ABSTRACT

Organic layered double hydroxides (LDHs) intercalated by sodium dodecylbenzenesulfonate (SDBS) were prepared by anion-exchange method and applied to modify bitumen aiming at improving ageing resistance of bitumen. The organic LDHs (SDBS–LDHs) were characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and Ultraviolet and visible (UV–vis) spectrophotometry. The effect of SDBS–LDHs and LDHs on physical and anti-ageing properties of bitumen was evaluated by means of conventional and rheological test. The results of XRD, FTIR and SEM show that SDBS is successfully intercalated into interlayer of LDHs, and the UV–vis reflectance and absorbance curves illustrate that intercalation of SDBS enhances the UV shielding effect of LDHs. The addition of SDBS–LDHs or LDHs has little influence on physical properties of bitumen because SDBS–LDHs and LDHs are physically mixed in bitumen. Compared with pristine bitumen after TFOT and UV irradiation ageing, the introduction of SDBS–LDHs and LDHs significantly improves thermal- and photo-oxidative ageing resistance of bitumen. Notably, bitumen with SDBS–LDHs exhibits better anti-ageing performance than that with LDHs, implying more effective modification of SDBS-LDHs which is due to the enhanced UV protective ability and compatibility with bitumen of SDBS–LDHs.

1. Introduction

Layered double hydroxides (LDHs), also known as hydrotalcite-like compounds, are new kinds of functional materials with potential applications in varied fields [1]. LDHs possess host–guest supramolecular structures consisting of positively charged metal hydroxide basal layers of brucite-like and electrically balanced anions along with hydration water molecules in the interlayer galleries. The ideal formula of LDHs is often represented as $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}[A^{n-}_{x/n}\cdot yH_2O]^{x-}$, where M^{II} and M^{III} are divalent and trivalent metal cations, respectively, x is the molar ratio $M^{III}/(M^{III}+M^{II})$ with value ranges between 0.20 and 0.33, A^{n-} is an exchangeable n-valent anion [2,3].

Owing to the multi-selection of anion in the interlayer, a large variety of LDHs endowed with different functions could be tailored [4]. LDHs have received considerable attention in recent years because the versatility in chemical composition and physical chemical properties of LDHs provides matrix materials with a wide range of applications [5], for example, polymer containing LDHs can possess enhanced thermal stability, flame retardancy, mechanical properties, UV photostability [6–16], and so on.

Bitumen is widely used as adhesive materials in the construction of flexible pavement and building waterproofing due to its good viscoelastic properties, which plays a prominent role in determining many aspects of bitumen-based materials [17]. However, like all organic substances, bitumen is vulnerable to ageing

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due to being exposed to heat, oxygen, ultraviolet (UV) light during its mixing, paving and compaction, as well as service life, resulting in the age-hardening of bitumen and sacrifice of desirable physical properties, consequently, the aged bitumen materials would fail to meet the performance requirements [18]. Therefore, it is of pragmatic significance to increase durability of pavement by improving the binder with respect to anti-ageing-related properties.

In order to enhance the durability of bitumen, many attempts have been made to obtain bitumen with excellent ageing resistance performance. The most frequently employed method is modification by adding anti-ageing additives. For examples, antioxidants are added into bitumen to retard the oxidation of bitumen [19,20], light stabilizers/ultraviolet absorbers can weaken or even eliminate the high energy of UV [21,22], carbon black possessing high UV reflectance screens the UV light to prevent UV ageing of bitumen [23], layered silicate can efficiently hinder permeability of oxygen and loss of volatile component which obstruct the oxidation and hardening of bitumen [24,25].

Meanwhile, LDHs are also employed as UV screening agent of bitumen, and the results showed that LDHs could indeed enhance the UV ageing resistance of bitumen [26,27]. However, because of special characteristics of LDHs with high charge density, small gallery height, strong hydrophilicity and integrated hydrogen-bonding network between the hydroxide layers, intercalated anions and water molecules, bitumen molecules cannot penetrate the LDHs layers nor can LDHs layers be easily homogeneously dispersed in a hydrophobic bitumen matrix, consequently, it is difficult to obtain homogeneous and stable dispersion of bitumen/LDHs composite. Therefore, it is very essential and significant to convert hydrophilic LDHs layers into more hydrophobic LDHs layers [8,9,28]. Usually, the organic intercalation of LDHs is considered as a feasible and effective method to achieve the conversion. The organic intercalation of LDHs would on one hand cause the expansion of the interlayer distance and on the other make the LDHs particles more compatible with organic bitumen [29].

In view of this point, the hydrophobization of LDHs is used to improve compatibility between hydrophilic inorganic particles and lyophobic organic bitumen. In the present work, hydrophobic organic LDHs were prepared by anion exchange and applied to modify bitumen for improving ageing resistance of bitumen. The effect of organic LDHs on physical and anti-ageing properties of bitumen was evaluated by means of conventional and rheological test.

2. Materials and methods

2.1. Materials

CO_3^{2-}–LDHs (MgAl–CO_3^{2-}–LDHs with Mg/Al = 2.0) were commercially available LDHs provided by Beijing Tech-layer Co., Ltd., Beijing, China. Sodium dodecylbenzenesulfonate (SDBS, analytically pure) and anhydrous ethanol (analytically pure) were purchased from Sinopharm Chemical Reagent Co., Ltd, Shanghai, China. Bitumen, referred to as SK-70, was produced by SK Corp., Korea. The physical properties of bitumen were as follows: penetration, 78 dmm at 25 °C (ASTM D5); softening point, 44.4 °C (ASTM D36); ductility, 17.1 cm at 10 °C and >150 cm at 15 °C (ASTM D113); viscosity, 0.49 Pa s at 135 °C and 227 Pa s at 60 °C (ASTM D4402).

2.2. Intercalation of LDHs

The organic intercalated LDHs were prepared by the anion-exchange method. Prior to the intercalation, the powdery LDHs were converted to slurry form. MgAl–CO_3^{2-}–LDHs powders (7.00 g), CO_2-free deionized water (100 mL) and anhydrous ethanol (100 mL) were added in a three-necked flask, and the mixture were stirred for 1 h at 70 °C to make LDHs disperse in mixed solvent sufficiently. Then SDBS solution (10.00 g SDBS dissolved in 400 mL CO_2-free deionized water) was directly added into the slurry for the anion exchange, the pH value of the mixture in the flask was adjusted to around 3 by adding adequate amount of HCl. The anion exchange reaction took place by stirring at 70 °C for 3 h under N_2 stream. After reaction and cooling down, the solid product was then separated and thoroughly washed with CO_2-free deionized water and finally dried at 70 °C in a vacuum oven for 24 h. The dried product was then ground to obtain organic intercalated LDHs (denoted as SDBS–LDHs) with a particle size of 200 mesh.

2.3. Preparation of modified bitumen

The modified bitumens were prepared by melt blending. Firstly, the weighed bitumen was poured into an iron container and heated to a well fluid at around 140 °C. Secondly, LDHs (3 wt.% and 5 wt.%) were added into the bitumen. Finally, the mixtures were blended at 4000 rpm for about 60 min to ensure the uniform dispersion of LDHs in the bitumen, LDHs and SDBS–LDHs modified bitumen are denoted by LMB and SLMB, respectively. The pristine bitumen was also prepared under the same conditions in order to compared with the modified bitumen preferably.

2.4. Bitumen ageing procedures

The short-time ageing was carried out in a thin film oven test (TFOT) at 163 °C for 5 h, following the standard method of ASTM D1754. This technique is applied to simulate the thermal-oxidative ageing of bitumen that occurs in processing of mixing with aggregates and compaction. The UV ageing of bitumen samples aged by TFOT were carried out in an oven with an UV lamp of 500 W to simulate the photo-oxidative ageing of bitumen in service life. The melted bitumen was placed on a Ø140 ± 0.5 mm iron pan which was put on bottom of the chamber, and the thickness of bitumen film was about 3.2 mm. The height from the pan to the lamp was adjustable to keep the average intensity of UV irradiation reaching to the bitumen's surface was about 1200 $\mu W/cm^2$. The bitumen underwent UV irradiation 9 days under 60 °C in the oven.

2.5. Characterization and measurement

The X-ray diffraction (XRD) patterns of LDHs, SDBS-LDHs and modified bitumen were recorded using a D8 Advance diffractometer (Bruker Corporation, Germany) with Cu-Kα radiation (λ = 0.15406 nm, 40 kV, 40 mA) at room temperature. The diffractive angle was scanned from 1.5° to 60° in the 2θ range of 0.02° steps, scanning rate was 2°/min.

A Fourier transform infrared (FTIR) spectrometer (Nexus, Thermo Nicolet Corp., U.S.) was used to record the spectra of LDHs and SDBS-LDHs. All spectra were recorded in wavenumber ranging from 4000 to 400 cm^{-1}. The number of scan was 64, and the spectral resolution was 4 cm^{-1}.

Morphological features of LDHs and SDBS-LDHs samples were studied using a field emission scanning electron microscope (FE-SEM, Hitachi S4800, Japan). SEM images were taken on the microscope at a voltage of 5 kV.

The reflectance and absorbance of the LDHs samples were measured using an ultraviolet and visible (UV–vis) spectrophotometer (UV-3600, Shimadzu, Japan). The spectra were recorded in wavelength ranging from 200 to 800 nm, and the spectral resolution was 1 nm. $BaSO_4$ was used as a reflectance standard in the UV–vis diffuse reflectance experiment.

The physical properties of pristine and modified bitumens,