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Physical properties and microstructures of organic rectorites and their modified asphalts

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HIGHLIGHTS

- Only 1831-OREC in modified asphalt forms exfoliated nanostructure.
- 1831-OREC has the best modification effect on asphalt.
- Na-REC and ORECs in asphalt act as nucleators contributing to heterogeneous nucleation of asphaltenes.

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ABSTRACT

Three kinds of organic rectorites (ORECs) were prepared by selecting dodecyl trimethyl ammonium chloride (1231), lauryl dimethyl benzyl ammonium chloride (1227) and stearyl trimethyl ammonium chloride (1831) as organic modifiers to modify Na-REC. Na-REC and ORECs modified asphalts were prepared by using the melting intercalation method. The effect of organic reagents on hydrophilicity of Na-REC was investigated by using hydrophilicity test. The result indicates that 1831-OREC shows the best lipophilicity. Microstructures of Na-REC, ORECs and their modified asphalts were characterized by X-ray diffraction (XRD), fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM) tests. Results show that 1831-OREC has the largest interlayer spacing, followed by 1227-OREC. Only 1831-OREC in modified asphalt forms part-exfoliated nanostructure. Effects of ORECs on physical properties, thermal storage stability were studied by penetration, softening point, ductility and viscosity test. It is concluded that introduction of Na-REC and ORECs enhances high temperature property but has the bad effect on low temperature cracking resistance of asphalt. 1831-OREC has the best modification effect on asphalt. Moreover, the 1831-OREC modified asphalt shows the best thermal storage stability. Morphologies of modified asphalts were investigated by atomic force microscope (AFM) test. The result shows that Na-REC and ORECs in asphalt matrix act as nucleators which can contribute to heterogeneous nucleation of asphaltenes.

1. Introduction

Asphalt is used in road pavement widely as one of building materials. However, base asphalt is easy to soften at high temperature and brittle at low temperature, which hardly meets the demand of modern traffic. In this respect, base asphalt should be modified to improve its properties [1,2]. The most commonly used modifier is the polymer modifier. However, a great deal of researches have indicated that the polymer has poor compatibility with asphalt matrix because of their difference in parameters such as molecular weight, density and solubility [3,4]. The polymer and asphalt are only coexistence in physical sense, so the polymer modified asphalt belongs to an unstable system and has poor thermal storage stability [5–9]. Therefore, it is necessary to deeply study the existing modification technologies of asphalt and research some new modification technologies of asphalt.

Layered silicate, as a kind of material with nanometer scale, has been widely used in the modification of asphalt in recent years [8,10–14]. The most commonly used layered silicate is montmorillonite (MMT) because its interlayers have lots of hydrated cation which could have some chemical reactions with molecule chains of asphalt, forming a composite system with excellent storage stability, good thermal stability, good flame retardant properties and so on [14,15]. OMMTs can be obtained by the organic modification to MMT, which can enlarge interlayer spacing of MMT and make MMT more lipophilic, so OMMTs generally have better compatibilities with base asphalt and improve some properties of asphalt

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better than MMT [14,16,17]. However, REC has a layered structure similar to MMT. In comparison, interlayers of REC have less hydrated cation than MMT, but interlayer spacing of REC is two times larger than that of MMT, so molecular chains of asphalt are easier to insert into the REC gallery space. In addition, compared with MMT, REC has a larger aspect ratio which can more efficiently hinder the movement of the molecule chains in asphalt. Therefore, REC probably has a better application prospect than MMT. More and more attention has been paid to researching REC modified asphalt [18–21].

Current researches on organic rectorite (OREC)/asphalt nanocomposites mainly focus on the preparation of OREC, preparation and properties of OREC modified asphalts. However, there are few studies on the influence of molecular structure of organic reagents on asphalt properties. In fact, there are many kinds of organic reagents, and the cost of them is significantly higher than that of REC, so how to choose organic reagents which are economic and suitable for asphalt matrix is the key to popularization and application.

In this paper, three kinds of representative organic quaternary ammonium salts were selected among organic reagents to prepared three types of ORECs. ORECs were used to modify base asphalt. Effects of ORECs on the properties of asphalt were studied. Moreover, effects of organic reagents on the properties of modified asphalt were studied in the molecular structure level.

2. Experimental

2.1. Materials

The Na-REC was supplied by Shunhehuatao Co., Hubei, China, and its chemical compositions and technical indexes are listed in Tables 1 and 2, respectively. Three kinds of organic reagents were supported by Sinopharm Chemical reagent Co., Ltd., and their basic information is shown in Table 3. The 80/100 penetration grade asphalt was supplied by SK Co., Korea, and its conventional physical properties are listed in Table 4.

2.2. Preparation of ORECs

Adding Na-REC (20 g) into deionized water (600 mL) and stirred at 300 rpm for 4 h. A certain type of the organic reagent was added into the solution at 80 °C. Then the resultant suspension continued to be stirred at 300 rpm for 2 h. The precipitate was repeatedly washed with deionized water until no precipitate of AgCl was produced when the filtrate was titrated with 0.1 N $AgNO_3$ [16]. Next, the precipitate was dried at 105 °C for 6 h. The dried precipitate was ground and then sieved to prepare the OREC with a particle size of 300 mesh.

2.3. Preparation of modified asphalts

The OREC modified asphalts were prepared by the melting intercalation method [14,16,17]. Base asphalt was heated to 150 ± 10 °C and then stirred at 2000 rpm. The Na-REC or OREC (1231-OREC, 1227-OREC or 1831-OREC) was gradually added into base asphalt, and then the mixture was blended at 3000 rpm for 1 h to obtain Na-REC or OREC modified asphalt.

2.4. Hydrophilicity test

Hydrophilicities of Na-REC and ORECs were evaluated by measuring hydrophilic coefficients of them. The measured procedures are as follows: 20 mL distilled water or kerosene was added into a cylinder (75 mL). The 2.5 g specimen was mixed with distilled water or kerosene in the cylinder. The mixture was then stirred using a stirring stick for 2 min to make sure that the specimen was dispersed evenly in the distilled water or kerosene. Next, the stirring stick was slowly rinsed with a washing bottle until the liquid surface height of cylinder reaches 50 mL. The volumes of sediments in distilled water and kerosene were recorded after 24 h, respectively. The hydrophilic coefficient (η) was calculated from Eq. (1):

$$\eta = \frac{V_B}{V_H} \quad (1)$$

where, V_B is the volume of sediment in water, and V_H is the volume of sediment in kerosene.

Table 1
The chemical compositions of Na-REC.

Chemical compositions	Content/%
Na_2O	2.76
MgO	0.385
Al_2O_3	37.4
SiO_2	52.6
K_2O	1.46
CaO	1.64
Fe_2O_3	0.241

Table 2
The technical indexes of Na-REC.

Parameters	Technical indexes
Appearance	Brown powder
Specific surface area, g/cm^3	73
Purity, %	81
Cation exchange capacity, mmol/100 g	43
X-rad d_{001} (nm)	2.22

2.5. Characterizations

The X-ray diffraction (XRD) patterns of samples were obtained using a Shimadzu XRD-6000 diffractometer with Cu-Ka radiation (λ = 0.154 nm, 40 kV, 30 mA) at room temperature. The diffractive angles (2θ) of Na-REC and OREC were all scanned from 3° to 10° in 0.02° steps, and the scanning rate was 2°/min, while the diffractive angles (2θ) of modified asphalts were all scanned from 0.6° to 10° with the scan rate of 2°/min and steps of 0.02°.

The Fourier transform infrared spectroscopy (FTIR) patterns of specimens were gained using a Nicolet-6770 spectrometer. Wave numbers ranged from 4000 cm^{-1} to 500 cm^{-1}.

The scanning electron microscope (SEM) images of samples were obtained by using the JSM-6360LV SEM made by JEOL Ltd. in Japan. The surface morphologies of Rectorite samples before and after modification were observed by two times electronic signals at different magnification and acceleration voltages. The test chose 20 kV acceleration voltages and magnification of 10,000 and 20,000.

2.6. Physical properties test

The physical properties of modified asphalts, including penetration (25 °C), softening point, ductility (15 °C) and viscosity were determined in accordance to ASTM D5, ASTM D36, ASTM D113 and ASTM D4402, respectively.

2.7. High temperature storage stability test

The high temperature storage stability test of modified asphalts was conducted as follows: the modified asphalts were poured into aluminum toothpaste tubes with a diameter of 32 mm and a length of 160 mm. Tubes were sealed and then maintained in vertical position at 163 °C for 48 h. Next, tubes were cut into three sections after the temperature of tubes dropped to the room temperature. Difference between softening points of samples at the top and bottom of tubes was measured to evaluate the storage stability of modified asphalts.

2.8. Atomic force microscope test

A DI Nanoscoper IV atomic force microscope was used to observe the morphology of Na-REC and OREC modified asphalts. A hot liquid drop of asphalt was smeared as thin as possible on a 20 × 20 × 1 mm glass slide and then cooled to the room temperature. Next, the slide was put in airtight containers for more than 24 h before imaging. This test was operated in tapping mode with the resonance frequency of 260 kHz and the scan rate of 0.8 Hz.

3. Results and discussion

3.1. Hydrophilicity analysis of Na-REC and ORECs

Dispersion effects of Na-REC and ORECs in distilled water are displayed in Fig. 1. As is seen in Fig. 1, Na-REC is dispersed well in distilled water, indicating that Na-REC has good compatibility with distilled water and belongs to a hydrophilic material. In comparison, ORECs are layered in distilled water, so ORECs are almost incompatible with distilled water and belong to hydrophobic