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Effect of nano-ZnO with modified surface on properties of bitumen

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HIGHLIGHTS

- Surface-modified inorganic nanoparticle nano-ZnO was developed.
- SMN-ZnO proved a good compatibility between surface-modified nano-ZnO and bitumens.
- The aging resistance of bitumen is improved obviously by SMN-ZnO.
- SMN-ZnOs could improvements in physical performance and aging resistance of bitumen.

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ABSTRACT

The effects of surface-modified inorganic nanoparticle nano-ZnO on the physical and ultraviolet aging resistance of bitumen were investigated as well as the microstructures of the binders. The compatibility between inorganic nanoparticle nano-ZnO and bitumen was studied by high temperature stability test. Fourier transform infrared spectroscopy shows that surface-modified coupling agent has been introduced to the surface of nano-ZnO through chemical bond. The mass change rate and viscosity aging index of the bitumen are decreased by nano-ZnO after thin film oven test and pressure aging vessel aging. Surface-modified nano-ZnO more pronounced improvements in aging resistance of bitumen.

1. Introduction

As is well known, bitumen has been widely used as the binder of aggregate in pavement construction due to its preferential viscoelastic properties [1–3]. However, with the increasing demands of road materials in recent years need to find binders owing better performance than normal grade bitumens. Moreover, bitumen is easy to become hard and brittle when exposed to heat, oxygen, and ultraviolet light during production, transportation, storage, and during subsequent placement of the mixture in the pavement [4]. Therefore, more and more modified bitumens are used in road materials. In recent ten years, polymer/inorganic nanoparticles nanocomposites have drawn the interest of materials scientists in polymers. Actually the addition of nanoparticles usually less then 5 wt% in a polymer matrix afford many properties, such as stiffness, electricity, fluid and gas absorption properties and so on [5–7]. However, inorganic nanoparticles of size small, large surface area, large surface polarity and extremely easy to reunite, and the general hybrid technology is difficult to obtain the nano-dispersion. Nanoscale dispersion is always a pervasive problem in the process of practical application [8]. To increase the uniformly of dispersion, inorganic nanoparticles is commonly surface-modified before preparation of nanocomposites with physical modification, particularly chemically modification, making the inorganic nanoparticles become stable, and the affinity with bitumen is strengthen. It has been concluded that the surface chemically modification has an effect on the morphology and properties of the nanocomposites [9].

Currently, inorganic nanoscale materials have been used to modify bitumen. More attention of the researchers has been paid to montmorillonite and rectorite modified bitumen. It has been found that physical properties, rheological behaviors and aging resistance of bitumen and polymer modified bitumen could be obviously improved due to barrier properties of layered silicates [10–14]. However, there is little report on the effect of inorganic nanoparticles on the properties of bitumen.

In this paper, inorganic nanoparticle nano-ZnO was used to prepare modified bitumens by melt blending. The nanostructure of nano-ZnO modified bitumens were characterized by Fourier transforms infrared spectra (FTIR) and scanning electron micrographs (SEMs). The effect of surface-modified nano-ZnO (SMN-ZnO) on

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the physical and aging properties of the modified bitumens were investigated. At the same time, in the process of high temperature storage or transportation, inorganic nanoparticles could gradually move, gather together and produce subsidence lead to the upper and lower performance of sample appear bigger difference, which affects the final performance. Therefore, storage stability is also an important indicator in bitumen/inorganic nano-ZnO composites.

2. Experimental

2.1. Materials

Grade bitumen, Ssangyong-70, was from H.I.T.C. Corp, the physical properties of grade bitumen were tested in accordance with GB/T 0604-2011, GB/T 0605-2011 and GB/T 0606-2011, and they are shown in Table 1.

Nano-ZnO was supplied by LONGi Silicon Materials Co., Shaanxi, China. Chemically pure methacryloxy propyl trimethoxyl silane (KH-570) used as silane coupling agents to modify the nano-ZnO was supplied by Xi'an Chemicals Co., Ltd., Shaanxi, China.

2.2. Preparation of SMN-ZnO

A certain amount of KH-570 put in toluene, while by means of acetic acid to adjust pH value. After hydrolysis of silane coupling agent, nano-ZnO were added in the toluene solution according to the mass fraction with a mechanical stirrer 3 h at 80 °C, and remove of toluene at room temperature. The separated solid were extracted for 3 h with acetone, and oven dry for 2 h at 130 °C, the dried cake was then ground to obtain surface-modified nano-ZnO with a particle size of 300 meshes.

2.3. Preparation of SMN-ZnO modified bitumen

The SMN-ZnO modified bitumens were prepared as follows: bitumen was heated to 150 ± 5 °C in a heating stirrer until it moved fully. The appropriate amounts of SMN-ZnO were added into the melting bitumen and mixed for 60 min with a lab mixer at 4000 rpm. And then stir the mixture in the ordinary blender for 1.5 h at 150 °C, namely the SMN-ZnO modified bitumens were obtained. The grade bitumen was also processed under the same conditions in order to compare with the SMN-ZnO modified bitumens.

2.4. Structure characterization

The FTIR of SMN-ZnO modified bitumens were performed using an FTIR (NEXUS670, GMI, Inc., USA) spectroscope. The spectra were collected from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} and scanning rate was 64/min.

2.5. Scanning electron micrographs (SEMs) analysis

The mixed asphalt binder underwent a scanning electron micrograph (SEM) analysis to understand the microstructure change of the modified binder, as well as the physical dispersion of the nano-silica particles. SEM images of two samples that were obtained at different nano-ZnOs. It is observed that the agglomeration between nano-silica particles still occurs in the unmodified nano-ZnOs modified asphalt (Fig. 3a). However, the presence of nano-ZnOs still small enough compared to unmodified nano-ZnOs modified asphalt, and it is scattered uniformly in Fig. 3b.

2.6. Aging procedure

Laboratory aging of unmodified and SMN-ZnO modified bitumens was performed using the TFOT procedure and UV aging. TFOT was conducted in an oven with a rotating platform on an axis, and the bitumen was put on the platform and heated for 5 h at 163 °C. The UV apparatus consisted of a plat bottom and a UV light source. The UV aging procedure of SMN-ZnO modified bitumens at 60 °C for 10 d was used for measuring physical properties.

Table 1
The physical properties of bitumen.

Physical properties	Measured values
Penetration (25 °C, dmm)	72
Softening point (°C)	48.5
Ductility (15 °C/10 °C, cm)	140.0/15.9
Viscosity (60 °C, Pa s)	256
Viscosity (135 °C, Pa s)	0.52

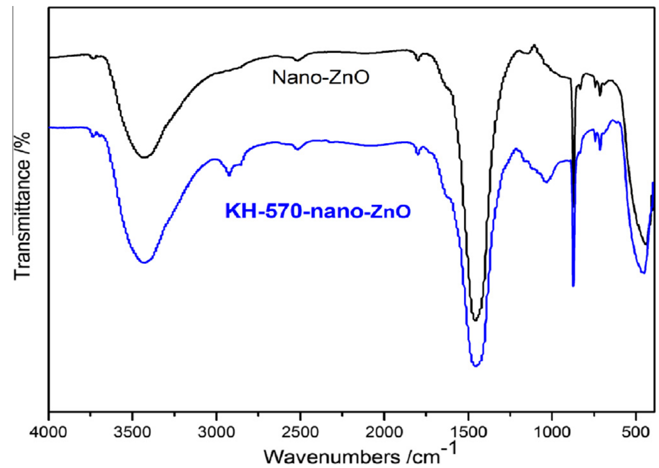

Fig. 1. FTIR spectra of nano-ZnO before and after surface modification by KH-570.

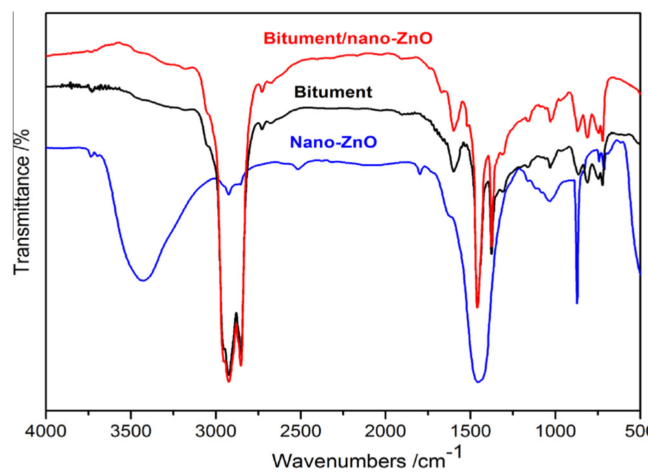

Fig. 2. FTIR spectra of nano-ZnO, bitumen and nano-ZnO/bitumen.

2.7. Physical properties test

The physical properties of unmodified bitumens and SMN-ZnO modified bitumens were tested according to ASTM D36, ASTM D5 and ASTM D113, respectively. Brookfield viscometer (Model DV-II+, Brookfield Engineering Inc., USA) was used to measure the viscosity of the binders according to ASTM D4402.

2.8. Compatibility test

The compatibility between bitumen with different unmodified and surface-modified nano-ZnO were tested reference to the polymer modified asphalt segregation test (JTGE 20-T, 0661-2011). Pour 50 g molten sample of into the vertically aluminum tube (d = 25.4 mm, h = 140 mm), and cool to room temperature, into the oven at 163 °C for 48 h, and then save in the refrigerator of below 2 °C for 5 h to cool completely. Aluminum tube from the sample surface can be divided into three parts. By comparing the differ softening point (ΔS) from between the upper and lower samples, as well as the upper and lower content (ΔC) of SMN-ZnO to evaluate the compatibility with asphalt and SMN-ZnO. The smaller ΔS, and the smaller ΔC, the better compatibility.

3. Results and discussions

3.1. Structure of SMN-ZnO modified bitumen

The FTIR of nano-ZnO were shown after the pre and post surface modification in Fig. 1. As can be seen from the Fig. 1, the absorption peak at 3435 cm^{-1} correspond to the –OH stretching vibration in the nano-ZnO, the absorption peak at 456 cm^{-1} is the result of