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Preparation and properties of isocyanate and nano particles composite modified asphalt

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HIGHLIGHTS

- Using isocyanate and nano particles as composite modifier.
- Samples are prepared under conditions of different addition of modifiers.
- The effects of nano particle on isocyanate modified asphalt properties were tested.
- The thermal stability of composite modified asphalt has a further promotion.

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ABSTRACT

Isocyanate modified asphalt samples were got by adding quantitative isocyanate into the base asphalt. Isocyanate and nano particles composite modified asphalt samples were produced by adding quantitative isocyanate and three different kinds of inorganic nanoparticles (Silicon dioxide, Titanium dioxide, Zinc oxide) into the base asphalt respectively. Isocyanate modified asphalt, isocyanate and nanoparticles composite modified asphalt were characterized by taking physical tests, SEM, fluorescence microscopy, TG and FTIR tests, which demonstrated that the high and low temperature performance of isocyanate and nano particles composite modified asphalt had been improved effectively. From the microscopic view, the modification of the base asphalt was very significant. Results also indicated that the temperature sensitivity of composite modified asphalt had been decreased. Meanwhile, the thermal stability had been improved when compared with the base asphalt and isocyanate modified asphalt.

1. Introduction

Asphalt is a dark brown complex mixture of hydrocarbons and their derivatives with different molecular weights of non-metallic composition. Asphalt has several physical forms such as liquid, semi-solid or solid products [1–4]. Modified asphalt is asphalt binder which was produced by mixing together with rubber, resins, polymers, finely ground rubber powder or other external additive (modifier) or taking lightly oxidized asphalt processing. There are many kinds of asphalt modifiers and the most widely used is the polymer modifying agent. Isocyanate modifier can improve the stability of the modified asphalt due to the isocyanate which contains unsaturated bond with highly activity, so that it can easily reacts with some organic or inorganic groups and finally forms a polyurethane elastomer [5]. Singh et al. [6] proved that ammonia ester bond was produced because of chemical reaction between –OH, –NH and other reactive groups of isocyanate, so that the softening point of modified asphalt rose and penetration declined. Phase separation of modified asphalt was small at low temperature through DSC and DSR testing. Rheological curves demonstrated that the rigidity and elasticity of modified asphalt had been improved effectively. Izquierdo et al. [7] had taken the experiment that ethylene glycol was mixed with isocyanate in a ratio of 1:5 and kept for 48 h, used the light brown liquid polymer as modifier, and then added water. Rheological properties of high temperature area had been improved owing to generating CO_2 and producing stable foam in chemical reaction. Due to the reaction between –OH, –H and other reaction groups of isocyanate, a small amount of ammonia ester bond was generated which made the stability of the modified asphalt with a little improvement. Nano materials are a three-dimensional space in which there is at least one dimension in the nanometer scale (1–100 nm) or take them as the material basic unit. The surface effect of nano particles can be used to improve the reaction rate among different groups and enhance the stability of modified asphalt. Nano materials have the surface

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effect, small size effect, quantum size effect and macroscopic quantum tunneling effect [8,9], which are widely used in the asphalt modification technology.

Galooyak et al. [10], Jahromi et al. [11] pioneered the use of montmorillonite (MMT) as modifier and the modified object was SBS modified asphalt, which indicated that the rheological performance of asphalt was improved on account of the layered structure of the MMT. Goh et al. [12] studied the modification of pitch based carbon fiber and finally enhanced the mechanical strength of asphalt. Further study using the layered nano material as modifying agent showed that the water resistance had been observably increased. Sureshkumar et al. [13] researched the performance of bitumen/polymer/nano materials triple system. Polacco et al. [14] also investigated the viscoelasticity and rheological properties of SBS modified asphalt which was modified by nano materials. Polacco et al. [14], Zhang et al. [15,16], Yu et al. [17] and other experts and scholars invented that the structure of nano materials dispersed in the asphalt binder had existed with two types which were plug-type and exfoliated layer. Exfoliated structure played a significant role in isolating the oxygen and water at the surface of asphalt, as well as preventing the evaporation of light components.

The compatibility between nano particles and asphalt, dispersion and stability in the asphalt are the pivotal issues to improve the modified asphalt performance. Nano particles with modification showed excellent compatibility, strengthening and toughening the asphalt properties, which had a good effect in extending the pavement performance of asphalt mixture. Nano particles added to the isocyanate modified asphalt would make the number of reactive groups in surface rapidly increasing. A large amount of ammonia ester bond was produced after reaction between –OH, –H and other reactive groups in isocyanate, while the stability of composite modified asphalt was greatly improved. The surface area and surface energy of atomic particle gathered rapidly. Then the mismatch phenomenon between the surface area and bonding occurred with a high activity, so the structure and motion between atoms were changed. Thus it is wise to select isocyanate and nano particles as a composite modifier.

2. Experimental

2.1. Materials

Base asphalt is the primary material for the modified asphalt production. The physical and chemical properties of the base asphalt determine the difficulty degree in the modified asphalt's production process, product quality technology and production costs [18]. In this study we choose 90A# asphalt as the base asphalt which was purchased from Xi'an Petroleum & Chemical Corporation.

The toluene 2,4-diisocyanate used in this paper was produced by Aladdin, which is colorless liquid with a strong pungent taste and the molecular weight is 174.16. Nano silica is also a material with a huge surface area, strong adsorption, good dispersal ability, high chemical purity and excellent stability. Silicon dioxide was prepared for these experiments whose molecular weight is 60.08 and the average particle size is 30 nm. Titanium dioxide needed in this paper was bought from Aladdin whose molecular weight is 79.87 and average particle size is 25 nm. Zinc oxide required in this paper was manufactured by Aladdin, whose molecular weight and average particle size are 79.87 and 30 ± 10 nm respectively.

2.2. Preparation of modified asphalt

300 g of base asphalt was placed in the iron container and heated to 90 °C. 6 g of the isocyanate was added into the base asphalt within five minutes, and then added 50 ml of deionized water in the process of stirring. Making the temperature constant and stirring was stopped until no bubble was generated. Sample 1# preparation was completed.

On the basis of the isocyanate modified asphalt samples, silica, titanium dioxide and zinc oxide were added to improve the modified asphalt properties and to explore the modification mechanism. The preparation method of isocyanate and nano particles composite modified asphalt is as the following: 300 g of base asphalt was heated to 90 °C in the iron container. 50 ml deionized water was added to mixture asphalt after 6 g isocyanate, and 0.75 g, 1.5 g silica were added to asphalt within 5 min while stirring. Samples of 2#, 3# were produced by heating and stirring until no bubble was created while the temperature was kept constant. Using the same method, samples of 4#–7# were prepared by adding 0.75 g, 1.5 g titanium dioxide and 0.75 g, 1.5 g zinc oxide to isocyanate modified asphalt. Preparation parameters of 1#–7# samples are shown in Table 1.

Table 1
Preparation parameters of modified asphalt samples (1#–7#).

Samples	Isocyanate (g)	Nano particles (%)	Deionized water (ml)
1#	6	0	50
2#	6	0.25% SiO_2	50
3#	6	0.5% SiO_2	50
4#	6	0.25% TiO_2	50
5#	6	0.5% TiO_2	50
6#	6	0.25% ZnO	50
7#	6	0.5% ZnO	50

2.3. Characterization

2.3.1. Physical measurements

Penetration of samples at 25 °C was used in this research to indicate the viscosity of asphalt. High temperature stability of asphalt was generally evaluated by its softening point. The ductility at 5 °C can be employed to reflect the low-temperature anti cracking performance of the asphalt.

The penetration of composite modified asphalts was measured according to Chinese national standard GB 0604-2000 [19] with a GS-IV automatic asphalt penetrometer supplied by Shuyang Highway Instrument Co., Ltd, China. The softening point of composite modified asphalts was tested in accordance with Chinese national standard GB 0606-2000 [19] with a SLR-C digital softening point tester supplied by Shuyang Highway Instrument Co., Ltd, China. The ductility was examined on the basis of Chinese national standard GB 0605-2000 [19] with a STYD-3 digital ductility testing machine from Shanghai Luda Instrument Co., Ltd, China.

2.3.2. Microstructure observation

Fluorescence microscopy was applied to discover the morphology and relative dispersion of polymer in the asphalt. The hot asphalt samples were dropped to the slide and then covered with cover slips. Uniform film thickness of asphalt samples was required to have a good detection of microstructure. Put the samples under the fluorescence microscopy and took tests. The measuring instrument used in the experimentation was Nikon 80i fluorescence microscope (Nikon Corporation, Japan).

2.3.3. Scanning electron micrographs (SEM) testing

Scanning electron microscope was employed to observe the microstructure changes of the modified asphalt, as well as the physical dispersion of the nano particles. A certain amount of modified asphalt was taken as the test samples and metal films were deposited on the surface of the samples under vacuum state by using JFC-1600 ion plating apparatus (JEOL, Japan). The prepared samples were put into the scanning electron microscope and set parameters with a magnification of 1000 or 200. The instrument used in the tests was a JSM-6390A scanning electron microscope (JEOL, Japan).

2.3.4. TG measurements

Thermal gravimetric analysis is a thermal analysis technique, which is used to measure the mass loss of the samples under the program control temperature. It was carried out in a METTLER TOLEDO TGA/DSC 1 analyzer with a Gos Controller GC10 STARe system. The samples whose mass was in a range from 4 to 10 mg were placed in an alumina ceramic crucible and took them into the test instrument. It is clearly to observe the mass changes of the samples according to the TG curves in the computer when heated under nitrogen (flow rate: 100 ml/min) from 50 °C to 650 °C with a heating rate of 15 °C/min.

2.3.5. FTIR testing

Fourier transform infrared spectroscopy (FTIR) spectra can be used to study the structure and chemical bonds of molecules. A certain amount of potassium bromide (KBr) was ground into fine powder and pressed into sheet with good transparency by using the tablet machine. A small quantity of modified asphalt was evenly coated on the sheet and the samples were put in the instrument which measured by using a Shimadzu FTIR-8400S Fourier transform infrared spectrometer whose scanning frequency of each spectrum was 20 times per minute.