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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 Xi̇an 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.

3. Results and discussion

3.1. Physical properties

Penetration of samples 2#–3# increased remarkably when SiO_2 nano particles were added to isocyanate modified asphalt but the penetration was lower than base asphalt as shown in Fig. 1a. It was confirmed the viscosity of modified asphalt became smaller. Compared with penetration of samples 2#–3# and there was some great contributions on the penetration with the decline of trace SiO_2. As shown in Fig. 1b, the softening point of 3# was greater than that of 1# while the softening point of samples 2# and 1# were essentially flat. The softening point elevated with the increase of SiO_2 content, which elucidated that the high temperature performance of SiO_2 modified asphalt was obviously improved. The ductility of SiO_2 modified asphalt was shown in Fig. 1c, which was generally considered to reflect the flexibility of asphalt. The greater the ductility was, the better the flexibility and the anti cracking performance of asphalt were. The ductility of 2# rose to 60 cm when the mass fraction of SiO_2 was 0.25%, which was far more than the ductility of sample 1#. The ductility of 3# whose mass fraction was 0.5% had improved observably, but no more than the ductility of 2#. It was identified that the addition of trace amount of nano SiO_2 could enhance the low temperature cracking resistance of the modified asphalt.

Penetration of modified asphalt had a huge effect as TiO_2 nano particles were added to isocyanate modified asphalt as seen from Fig. 1a. Penetration of 4# was almost back to the levels of base asphalt. With the increase of addition TiO_2, penetration of 5# diminished but it was still higher than that of 1#, which characterized that modification of nano TiO_2 to isocyanate modified asphalt was not satisfactory. However, the softening point of TiO_2 modified asphalt had a great influence, shown in Fig. 1b. The softening point of samples 4#, 5# had been evidently improved and the sample with bigger mass fraction of TiO_2 had better high temperature performance. It was due to the huge specific surface area and strong surface activity. Nano particles had a strong adsorption to the asphalt, so that the light components in asphalt were reduced and the temperature sensitivity of asphalt was changed. The improvement of the ductility was roughly same as that of SiO_2, but it was slightly worse than that of SiO_2.

Penetration was little affected after ZnO nano particles were added to 1# modified asphalt, as shown in Fig. 1a. Penetration of 6# had a little increase compared to 1#, which demonstrated that traces of ZnO nano particles had an impact on the penetration of asphalt. The role of modification was not only simple physical adsorption but existence of more complex chemical reactions. Softening point had a slight raise with increasing the ZnO content as shown in Fig. 1b. It was proposed that there was a hardening effect after adding ZnO and the softening point was improved. The ductility of ZnO modified asphalt was shown in Fig. 1c. When the mass fraction of ZnO was 0.5%, ductility of sample 7# was the same as the sample 1#. The ductility of 6# had increased, which proved that trace ZnO can improve the low temperature properties of asphalt.

Comprehensive Fig. 1(a–c), the high and low temperature performance of modified asphalt had improved because of the incorporation of nano particles to isocyanate modified asphalt. The surface of the nano particles had high activity and it could be easily modified by some special physical or chemical reactions, so as to

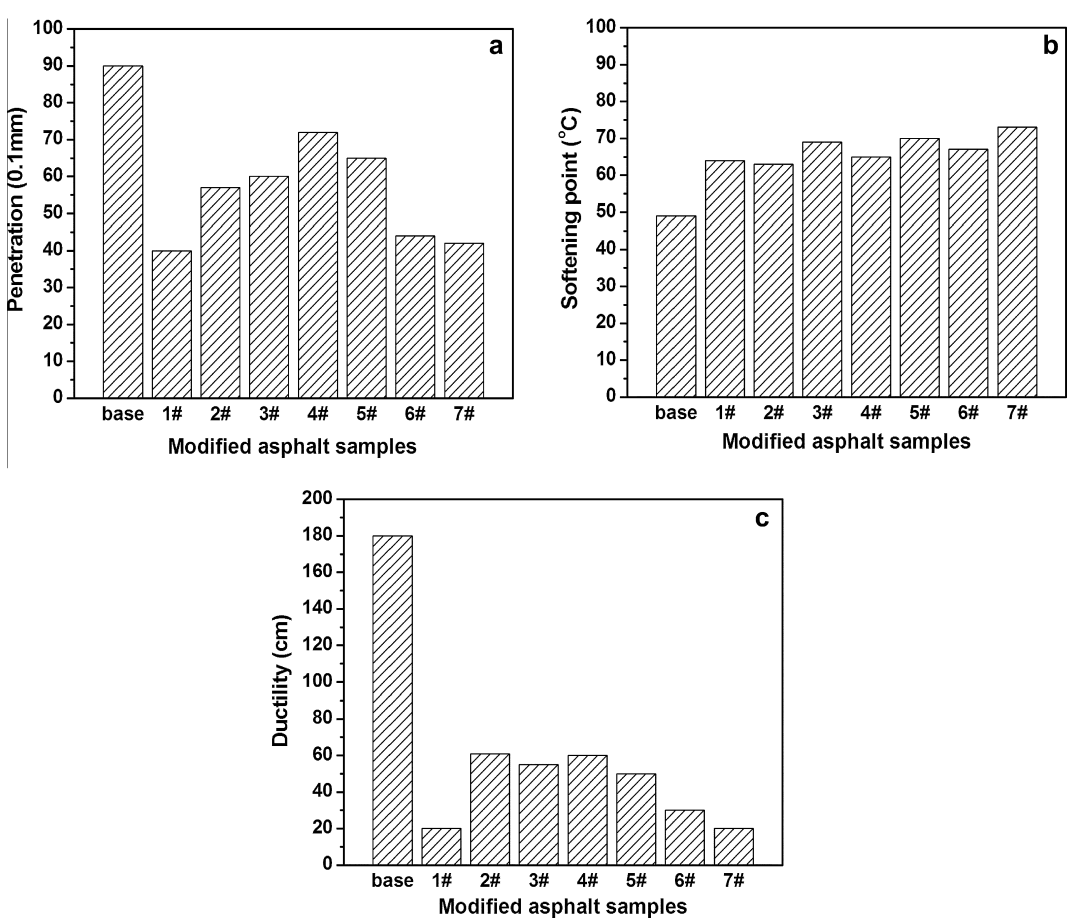

Fig. 1. Physical indexes of modified asphalts. a: Penetration at 25 °C; b: softening point; c: ductility at 5 °C.

ameliorate the performance of asphalt. The specific surface area of nano particles was large and the asphalt had a strong adsorption effect. So the light components of asphalt were reduced and the temperature sensitivity of asphalt was changed. The addition of inorganic nano particles can improve the deformation ability of asphalt, which was the result of the decline of ductility. However, there existed an optimum value of dosage. Trace amounts of addition can enhance the ductility of asphalt and a relatively large dose can ameliorate the softening point of asphalt. As for the penetration, it was not very satisfied to modify by nano particles. In summary, only quantitative of nano particles can be employed to make full use of the role of the modified agent to improve the performance of asphalt.

3.2. Fluorescence microscope analysis

Fluorescence microscopy images of base asphalt and 1#–7# modified asphalt are shown in Fig. 2. Sample of 1# had a uniform and orderly dispersion when compared with the fluorescence microscope images of base asphalt. It was due to reaction exactly between isocyanate and the deionized water, giving full play to the role of isocyanate. Analysis of 2# and 3#, it was occurred to a large area of reunion after the addition of SiO_2. When the dosage was 0.5%, the block area of dispersion was obviously more than that of 0.25%. It was suggested that the addition of SiO_2 nano particles can change the crystalline morphology of the original asphalt. Images of 4# and 5#, modified by TiO_2 nano particles, were opposite to the situation of SiO_2. Sample of 0.25% doses had a large area of reunion. TiO_2 nano particles acted as a nucleating agent, which also further explained why the high softening point of sample 5# was. The diameter of single particle in the image of 4# was reduced and made the crystal more refined. Although the dispersion was not very uniform, the number of dispersion increased significantly. At last, it was observed in the images of 6#–7# that microscopic morphology of ZnO nano particles composite modified asphalt was almost the same as that of TiO_2. It was illustrated that the results of 6# was better because of the increasing number of dispersed particles and bigger particle diameter. The most important reason was the uniform distribution of particles. From the point of view, the effect of nano particles on the modified asphalt was very observable, and the function of the modification of the 0.25% ZnO was the best.

3.3. SEM analysis

Scanning electron microscopy micrographs of the samples 1#–7# are shown in Fig. 3. Samples of 2#–3# SiO_2 nano particles composite modified asphalt had changed markedly when compared with sample 1#, which described that the SiO_2 nano particles were well dispersed in the composite modified asphalt. It was observed from 3# SEM image that agglomeration of nano particles was due to the more amount addition of SiO_2 nano particles and forming a new network structure after chemical reaction. The SiO_2 nano particles in the asphalt dispersed uniformly, which could be concluded that SiO_2 nano particles dispersed in asphalt may have a positive effect on the improvement of modified asphalt in modulus and delaying or weakening the aging effect. TiO_2 nano particles, as a kind of particle with minimum specific surface area, have an evident effect on the elastic modulus and yield stress of asphalt. It can be clarified from images of 4#–5# that isocyanate modified asphalt after adding TiO_2 nano particles formed a new structure because of large area agglomeration. The dispersion of TiO_2 nano

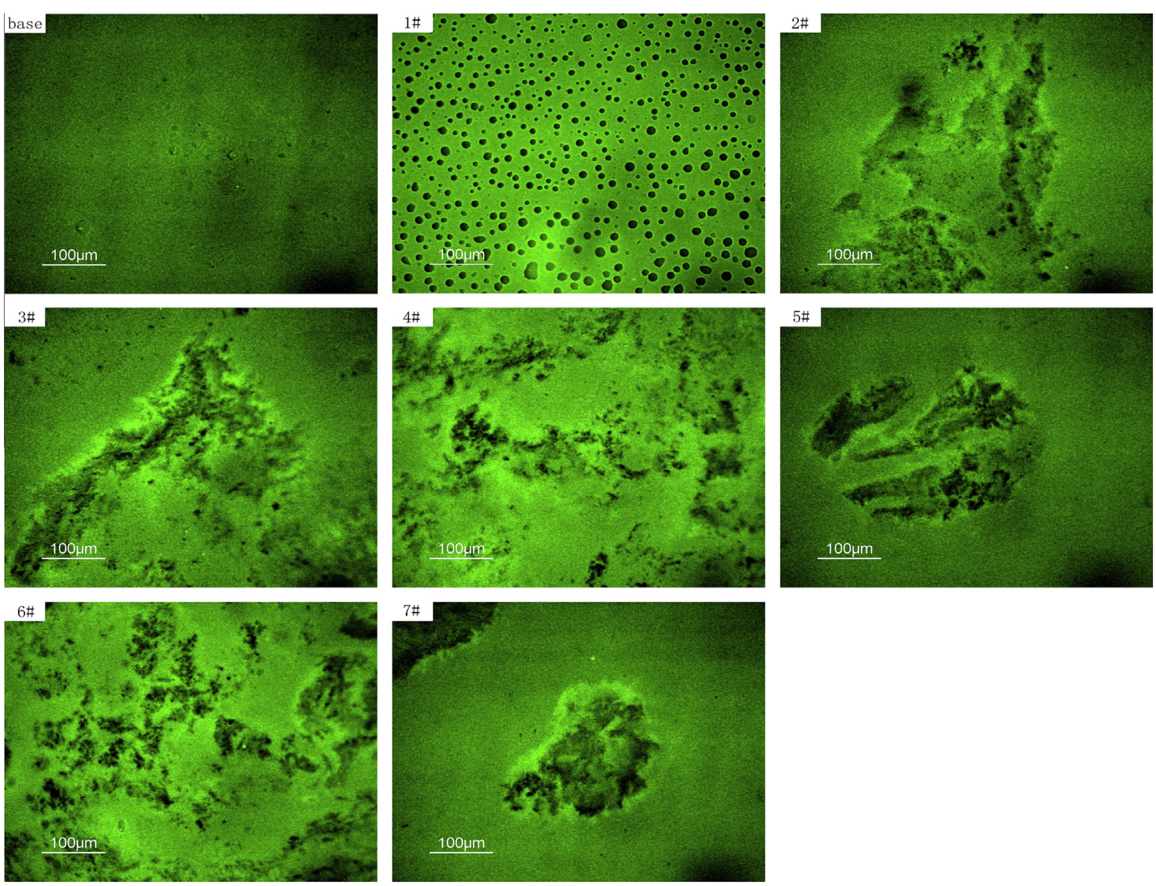

Fig. 2. Fluorescence microscopy images of base asphalt and 1#–7# modified asphalt.

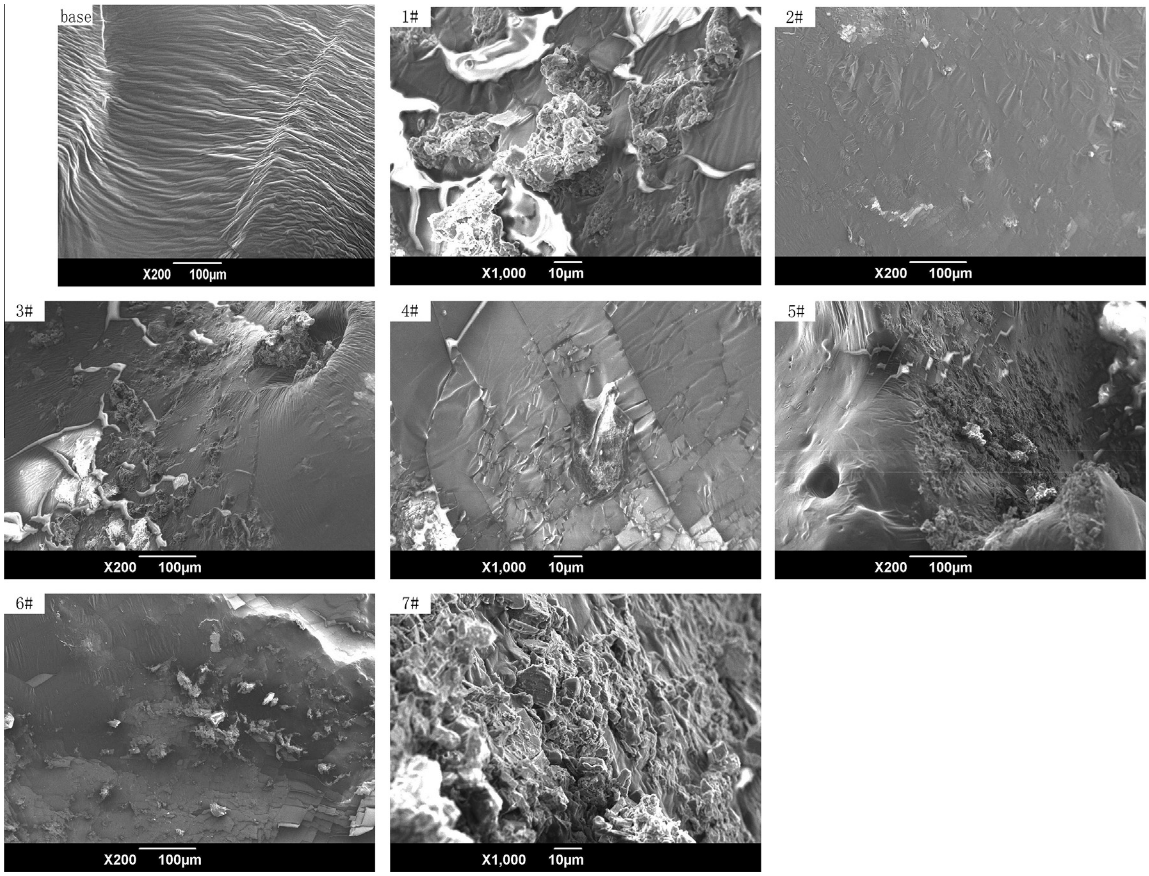

Fig. 3. SEM images of 1#–7# modified asphalt.

particles was not as good as SiO_2 whether the addition of TiO_2 nano particles was small or large. We can consider from the images 6#–7# that the particle size of 6# was comparatively large in the range of 10 μm, while the particle in the image of 7# had a small size in the same range and the dispersion was very uniform after enwrapping and high dispersion of ZnO nano particles. Analysis of the microscopic structure, the results were mainly due to the effect of the interaction between the ZnO nano particles and the isocyanate. The impact of adding a small amount of ZnO was not obvious, which was consistent with 1#. It was indicated that a bigger dose of ZnO nano particles could play a great role of the effect of high dispersion.

3.4. Thermal analysis

It was summarized that when the three kinds of nano particles with the mass fraction of 0.5% were added to isocyanate modified asphalt, the performance of modified asphalt was better according to the previous softening point tests. So we choose the 1#, 3#, 5#, 7# and base asphalt for comparison and the TG curves are shown in Fig. 4. The thermal decomposition of the nano particles and isocyanate composite modified asphalt was roughly divided into three stages: the first two stages of the mass loss were in the temperature range of 490–300 °C and 490–550 °C. TG curves ended at 650 °C at last. During the first mass loss at 300 °C, the weight of base asphalt reduced in the first place while the others had not started. It was time to 330 °C, 3#, 7#, 5# begin to have a mass reduction in turns. It was proved that the addition of nano particles had delayed the first time of mass decomposition. In the process of mass loss, though the weight of 7# started to decrease at last, the slope of curve was the largest. 3# began to be mass loss relatively late and the curve was flatter. This was because that 3# had a good adsorption capacity, which could adsorb the isocyanate and oil in the surface of asphalt. While the specific surface effect, volume effect, quantum size effect of nano materials can make the nano particles penetrate into the nearby of isocyanate unsaturated bond and form a network structure through the chemical reaction between a large number of residual bonds and isocyanate in the surface. The rest curves were basically coincident except for 3#

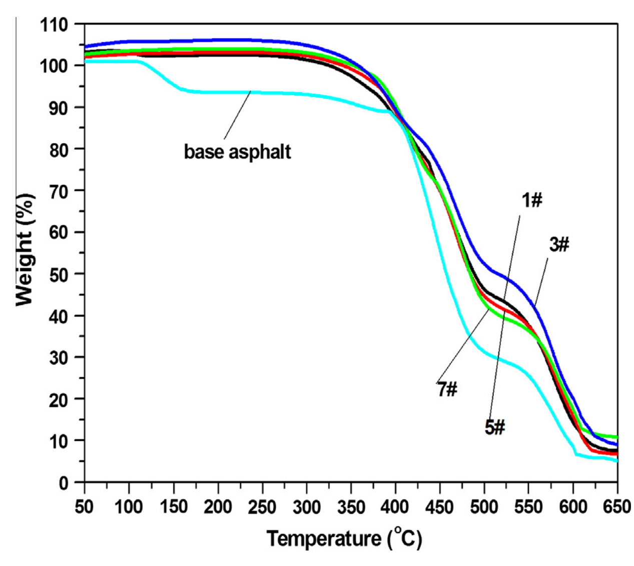

Fig. 4. TG curves of base asphalt and 1#, 3#, 5#, 7# modified asphalt.

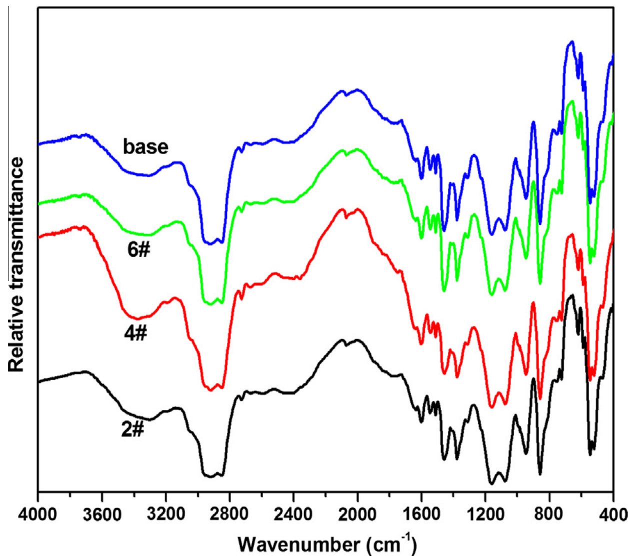

Fig. 5. FTIR images of base asphalt and 2#, 4#, 6# modified asphalt.

at the temperature of 400–500 °C but the slope of 3# was also consistent with the other samples. Ingredients of the mass loss in this stage were the same which were the light components, aromatic hydrocarbons and the water molecules of asphalt. The second stage began with the 1#, and the order for the starting of the nano particles was same as the first stage. The high-temperature stability of modified asphalt by adding nano particles mainly depended on its specific surface area, adsorption capacity, so as to improve the evaporation rate of the other components at high temperature. Furthermore the order of mass loss also represented the adsorption capacity of different nano particles. In accordance with the TG curves shown in Fig. 4, it can be clearly concluded that the high-temperature stability of nano particles and isocyanate composite modified asphalt had increased, while the adsorption capacity of the three kinds of nano particles was ZnO > SiO_2 > TiO_2.

3.5. FTIR analysis

Compared with the fourier infrared spectroscopy curves of 2#, 4#, 6# modified asphalt shown in Fig. 5, the new peak appeared in the range of 1500 cm^{-1}–637 cm^{-1}, which was due to the formation of the nano material layer. It was demonstrated that the new peak was the embodiment of the functional groups of nano particles from the infrared spectra of 2# and 4#, such as the stretching vibration of Si-O-Si at 1037 cm^{-1} and Ti-Ti bending vibration at 914 cm^{-1}. It was proved that there was no chemical reaction between SiO_2, TiO_2 and isocyanate according to the bending vibration of Si-O and Ti-O bonds at 520–470 cm^{-1}. It was not difficult to find that the absorption peaks between 3000 and 3500 cm^{-1} became relatively flatter compared with the fourier infrared spectroscopy curves of base asphalt and 6#, which showed some chemical reactions between oxhydryl groups of modified asphalt and ZnO. The weakening of characteristic peak intensity proved that there was mostly chemical reaction of ZnO with hydroxyl groups and the absorption peak of ZnO nano particles was disappeared at 460 cm^{-1}.

4. Conclusion

Isocyanate as asphalt modifier is a new modification method which is different from the ordinary polymers. The optimization of nano particles and isocyanate composite modified asphalt was remarkable: the sensitivity to temperature of composite modified asphalt had been reduced and the stability of asphalt binder had been enhanced. Among them, when the mass fraction of isocyanate and SiO_2 nano particles was 2% and 0.5% respectively, the composite modified asphalt had the optimal high-temperature stability. Low-temperature cracking resistance of isocyanate modified asphalt had improved significantly by adding 0.25% ZnO nano particles. Adding the right amount of nano particles allowed the thermal stability of isocyanate modified asphalt a further promotion and the isocyanate played a better role in the asphalt.

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