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# High and low temperature properties of nano-particles/polymer modified asphalt



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#### HIGHLIGHTS

• Three kinds of nano-particles/polymer systems were proposed to modify SK-70 asphalt.

- Influences of nano-particles/polymer on the properties of SK-70 asphalt were tested with TFOT, DSR and BBR tests.
- Morphologies of modified asphalts and SK-70 asphalt were measured with SEM.
- The chemical bondings of modified asphalts and SK-70 asphalt were analyzed through FTIR.

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## ABSTRACT

At present, most asphalts and modified asphalts cannot meet requirements of both high temperature stability and low temperature cracking resistance simultaneously. Hence, the objective of this paper is to find new modification system to improve the high and low temperature properties of SK-70 base asphalt. In this paper, nano-zinc oxide (nano-ZnO) particles, nano-titanium dioxide (nano-TiO<sub>2</sub>) particles, nano-calcium carbonate (nano-CaCO<sub>3</sub>) particles, styrene-butadiene-styrene (SBS) and styrene-butadienerubber (SBR) were selected as modifiers. The modified asphalt samples with three or two kinds of modifiers were prepared, and the softening point, ductility and penetration of modified asphalt samples were measured and compared. Eventually, three optimal nano-particles/polymer modification systems for SK-70 base asphalt including 3%nano-ZnO/0.5%nano-TiO2/3.7%SBS, 5%nano-ZnO/4.2%SBS, 5%nano-CaCO<sub>3</sub>/4%SBR were proposed. To study the effects of these three optimal modification formulations on high and low temperature properties of base asphalt, dynamic shear rheometer (DSR), thin film oven test (TFOT), and beam bending rheometer (BBR) tests were conducted on the asphalt of SK-70 and the nanoparticles/polymer modified asphalts. The micro-morphology of SK-70 and the modified asphalts was examined using scanning electron microscope (SEM) and the reactions between modifiers and SK-70 base asphalt were studied by infrared spectrum instrument. From the test results, it was observed that the nano-materials were well dispersed in base asphalt, and could increase the dispersibility of polymer in base asphalt and improve the compatibility between polymer and base asphalt. Furthermore, the nano-materials could improve the high and low temperature properties of SK-70 base asphalt. Additionally, the results also revealed that for polymer modified asphalts the physical reaction between polymers and asphalt played the dominant role in the modification process, while for nano-particles/ polymer modified asphalts, both physical and chemical reaction occurred in the modification process.

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### 1. Introduction

Asphalt binder is one of critical components in the construction of asphalt pavement. Over 90% of the freeways in China are paved with asphalt. The regions with hot summer and cold winter have

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http://dx.doi.org/10.1016/j.conbuildmat.2016.03.118 0950-0618/© 2016 Elsevier Ltd. All rights reserved. more strict requirements on asphalt properties. However, it is not easy to find the base asphalt which can meet the requirements of both high temperature stability and low temperature cracking resistance simultaneously. Therefore, it's necessary to find some approaches to improve these properties of base asphalt.

The polymer modification is the most widely used approach to improve the properties of base asphalt. Currently, styrenebutadiene-styrene (SBS), styrene-butadiene-rubber (SBR) and polyethylene (PE) have been become popular modifiers to improve the elasticity and ductility of asphalt pavement [1]. Studies conducted by Khodaii and Mehrara [2], Lu and Isacsson [3] showed that SBS increased the binder elasticity at high temperatures, and asphalt modified with SBS had better permanent deformation susceptibility compared to unmodified asphalt. Li et al. [4] evaluated the low temperature rheological performance (LTRP) of SBS modified asphalt through dynamic shear rheometer (DSR) test, the results showed that SBS could improve the LTRP significantly when the temperature ranged from -10 °C to 10 °C. Good properties of SBS modified asphalt were due to that SBS could absorb low molecular weight oil fraction of asphalt and brought asphalt more stable structures. Wang et al. [5] tested the influence of SBR polymer on 160# base asphalt, the ductility at 5 °C increased about 28 cm compared to that of base asphalt. Becker et al. [6] reported that SBR polymers increased the ductility of asphalt, which could allow the pavement to be more flexible and crack resistance at low temperature. PE is one of the most popular plastics and is renowned for its good fatigue resistance [7,8]. Punith [9] proved that the addition of PE could reduce creep rate of asphalt mixture at high temperature. The researches of Jun et al. [10] and Nuñez et al. [11] indicated that PE could also increase the complex modulus of base asphalt and reduce the susceptibility of the asphalt to rutting. From the review of polymer modified asphalt, it could be concluded that SBS could improve high and low temperature properties to some extent. However, the properties of SBS modified asphalt are not good enough to resist very high temperature and very low temperature at the same time. Therefore, severe rutting or cracking sometimes occur in SBS modified asphalt pavement in the area where is very hot in summer and very cold in winter. Although SBR can improve the rutting resistance of base asphalt to a large extent, fail to improve the high temperature properties of base asphalt significantly. For PE polymer, the modification effect on base asphalt is in contradiction to that of SBR.

The nano-material modification is another important approach to improve the properties of asphalt binder [12]. Many researches about nano-material modified asphalt had been done and considerable findings were obtained. Sarsam [13] suggested that nanoparticles could strongly absorb the asphalt, and a special physicochemical interaction occurred, as a result the asphalt temperature sensitivity was changed. Ye [14] reported the influence of nanotitanium dioxide (nano-TiO<sub>2</sub>) particles on the temperature properties of AH-70 base asphalt, and found that softening points of the modified asphalt with 0.5% nano-TiO<sub>2</sub> increased by 5 °C, the ductility at 5 °C decreased about 2.25 cm compared to those of base asphalt. The study of Tanzadeh et al. [15] illustrated that nano-TiO<sub>2</sub> could improve the capability of rutting resistance of asphalt binder. Sun et al. [16] showed that nano-TiO<sub>2</sub> modified asphalt possessed more stable ductility and smaller softening point changing ratio than base asphalt, and it could be concluded that nano-TiO<sub>2</sub> particles actively enhanced the photooxidation properties of asphalt and nano-TiO<sub>2</sub> modified asphalt was capable of resisting photooxidation aging. Arabani et al. [17] investigated the effect of nano-zinc oxide (nano-ZnO) on improving mechanical properties of hot mix asphalt (HMA) through laboratory experiments, and

#### Table 1

Properties of SK-70 base asphalt.

the results showed that nano-ZnO particles could decreased the permanent deformation of HMA pavement. Liu et al. [18] showed that surface modified nano-ZnO particles had satisfied dispersion in asphalt and could improve the ultraviolet aging resistance of asphalt. The researches on nano-calcium carbonate (nano-CaCO<sub>3</sub>) modified asphalt indicated that softening points of modified asphalt with 5%nano-CaCO<sub>3</sub> increased by 1.7 °C, and enhanced the ruttingresistance of base asphalt [19,20]. Moreover, compared to other nano-materials, nano-CaCO<sub>3</sub> is fairly inexpensive and natural abundant. Many researchers have studied performance and rheological properties of nano-montmorillonite (nano-MMT) modified asphalt [21-24]. Yu et al. [25] indicated that the addition of nano-MMT was able to increase the softening point and viscosity of the asphalt. The results of Zhang et al. [26] demonstrated that nano-MMT as an additive could increase ductility retention rates of asphalt and improve the aging resistance of asphalt. Zhang et al. [27] conducted research on nano-ferroferric oxide (nano-Fe<sub>3</sub>O<sub>4</sub>) modified asphalt. the softening point of modified asphalt increased by 2.5 °C and the ductility at 5 °C increased by 2 cm than those of base asphalt. Though these nano-additives effectively improve the cracking or rutting resistance of asphalt pavement, unfortunately, pure nanomaterial modified asphalt still can't meet the strict requirements of the area where is very hot in summer and very cold in winter.

For most pure polymer modifiers, thermo-dynamical incompatibility with asphalt is one of the major shortcomings, which results in delamination of the composite during thermal storage. However, nano-materials can improve the compatibility between polymer and asphalt, so nano-material/polymer modified asphalt also becomes more and more popular. Nano-CaCO<sub>3</sub>, nano-ZnO and nano-MMT were combined with SBS to modify base asphalt by several researchers [28–30]. Jerome [31] discussed the influence of nano-clays on the rheological properties of SBS modified asphalt and base asphalt. Kebritchi et al. [32] initially coated polymers on the surface of nano-CaCO<sub>3</sub> and this nano-particle/polymer composite was employed as modifier and the rheological properties of the modified asphalt were reported. Compared to pure nano-materials or pure polymer modifier, nano-particle/polymer composite exhibited better effects on the mechanics properties of asphalt.

This paper aimed to put forward new nano-particles/polymer composite modification systems which can meet the requirement of the area where is very hot in summer and very cold in winter. Polymers including SBS, SBR and PE, and nano-materials including nano-CaCO<sub>3</sub>, nano-ZnO, nano-TiO<sub>2</sub>, nano-Fe<sub>3</sub>O<sub>4</sub> and nano-MMT were used to modify SK-70 base asphalt. The modified asphalt samples with three or two kinds of modifiers were prepared, and the penetration, softening point and ductility of these samples were measured and compared. Several optimal nano-particles/ polymer modification formulations were selected to modify SK-70 base asphalt. Then the effect of these new modification formulations on the high and low temperature properties of SK-70 base asphalt was studied by thin film oven test (TFOT), DSR and beam bending rheometer (BBR) tests. Furthermore, the micromorphology and modification mechanism of nano-particles/ polymer modified asphalt were investigated by scanning electron microscope (SEM) and fluorescence microscope techniques.

Properties		Values	Specification limits in China	Test standard
Penetration (25 °C, 100 g, 5 s) (0.1 mm)		74.4	60-80	Specification of China (JTGE-20-2011)
Softening point (°C)		49.8	≥45	
Ductility (cm)	5 cm/min, 5 °C	6.8	≥15	
	5 cm/min, 10 °C	68.3	≥0	
TOFT	Mass loss (%)	0.64	-0.8-+0.8	
	Penetration ratio (%)	72.7	≥61%	
	Ductility (5 cm/min, 10 °C) (cm)	9.6	≥6	

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