Construction and Building Materials 159 (2018) 578–586

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Effects of ZnO particle size on properties of asphalt and asphalt mixture

Hongliang Zhang [a,*], Yang Gao [a], Guihong Guo [a], Baojun Zhao [b], Jinyang Yu [a]

[a] Key Laboratory for Special Area Highway Engineering of Ministry of Education, Chang'an University, Xi'an, Shaanxi 710064, PR China
[b] Shaanxi Province Transportation Construction Group Co., Ltd., Xi'an City, Shaanxi Province 710075, PR China

HIGHLIGHTS

- Three sized ZnO nanoparticles were made.
- The decrease of ZnO size in asphalt can change its properties.
- The smaller ZnO size could change the properties of asphalt mixture.

ARTICLE INFO

Article history:
Received 18 May 2017
Received in revised form 2 November 2017
Accepted 7 November 2017

Keywords:
Micro and nano ZnO
Size
Asphalt
Asphalt mixture
Laboratory performance

ABSTRACT

Micro or nano zinc oxide (ZnO), as a modifier, can significantly improve some properties of asphalt and asphalt mixture, but the effect of ZnO particle size is still unclear. In this paper, three different spherical sized ZnO nanoparticles (2 μm, 80 nm and 350 nm in average diameter) were made by homogeneous precipitation method and sol-gel method. Asphalt binders and asphalt mixtures modified by ZnO and ZnO/SBS (styrene-butadiene-styrene) were produced by means of a high shear mixer. The effects of ZnO particle size on physical properties of asphalt were analyzed through penetration test, softening point test, ductility test, dynamic shear rheological test (DSR), bending beam rheometer test (BBR) and aging test; and the effects on asphalt mixtures were characterized using the Marshall test, freeze-thaw splitting test, rutting test and a three-point bending beam test. Results show that the decrease of ZnO size in asphalt binder can weaken its creep stiffness, and increase its softening point, ductility, viscosity, anti-rutting factor, creep rate and anti-aging ability. In addition, with the decrease of ZnO size, the high temperature stability, water stability and low temperature crack resistance of asphalt mixture are improved. Finally, based on the test results, the optimum size of ZnO particle is determined as 80 nm.

1. Introduction

Today researches on nanostructures are very popular because they are being used and pursued for optics, optoelectronics, catalysis, biological sciences and piezoelectricity. Atoms at the surface of particles will have highly activeness when materials are at the nanometer size, and the resulting materials are significantly different from macroscale materials composed of the same substance. Research in the nanostructures of materials has skyrocketed over the last decade.

A variety of micro and nano materials have been used and studied to modify asphalt and concrete engineering, and the effects of nano materials were discussed. Amir et al. [1] found that nano clay and nano hydrated lime (HL) cloud enhance the tensile strength ratio (TSR) of asphalt mixes. Khodary et al. [2] proved that nano-size cement bypass could increase the physical, chemical, and rheological properties of modified nanomaterial-asphalt mixture for its high surface area. Khodary et al. [3] analyzed the impact of nano scale CaO on the stiffness properties of asphalt. Liu et al. [4] discovered that the nano $CaCO_3$ had an advantage influence on the high temperature stability of the asphalt and asphalt mixtures. Tang et al. [5] found that nano-montmorillonite (Nano-MMT)/SBS can improve the high-temperature anti-deformation ability and decrease the softening point of the aged asphalt. Yao et al. [6] explored the effects of nano silica on the rutting and fatigue cracking resistance of asphalt binders. Xiao et al. [7] showed that carbon nanoparticles was helpful in enhancing the failure temperature, complex modulus, and elastic modulus values and in increasing rutting resistance of the RTFO binder. Guo et al. [8] prepared modified nano TiO_2 by co-precipitation method and studied the influence of nano TiO_2 on the properties of coal tar pitch. Zhang et al. [9] made spherical nano Fe_3O_4 particles modified asphalt successfully. In addition, nano-SiO_2 has been reported to enhance concrete

* Corresponding author.
E-mail address: zhliang0105@163.com (H. Zhang).

https://doi.org/10.1016/j.conbuildmat.2017.11.016
0950-0618/

workability and compressive strength [10–12], to improve resistance to water penetration [13], and to contribute to control the leaching of calcium [14]. Nano-TiO_2 could act as a trigger with the photocatalytic degradation of pollutants when it was contained in concrete [15,16]. Nano-Al_2O_3 has been shown to obviously improve the modulus of elasticity of asphalt [17].

However, the micro or nano materials with single size were often used in those researches listed above. Only several scholars had studied the effects of the size of HL on the properties of asphalt or asphalt mixture. Shen et al. [18] reported that sub nano-sized HL can improve about 10% in tensile strength ratio (TSR) for HMA. Aboelkasim et al. [19–21] suggested that the nano sized hydrated lime (NHL) could perform potential benefits compared with regular-sized hydrated lime (RHL) as a modifier of asphalt.

ZnO, non-toxic, odorless, gender-based oxide, is an important semiconductor material. And it has been used in different areas for its special characteristics [22,23]. Recently, some scholars have focused on the effects of ZnO on the properties of asphalt and asphalt mixture. Gholam et al. [24] found that adding nano ZnO could improve the total surface free energy (SFE) of the asphalt binder. Zhang et al. [25] showed that ZnO could change the compatibility between asphalt and polymer and further affect the dispensability of polymer in asphalt binder. Xiao et al. [26] found that ZnO nanoparticles played an effective role in decreasing creep potentials of the asphalt mix samples. Kang et al. [27] found that the nanocoating could improve the tensile strength ratio of the hot mix asphalt. Liu et al. [28] studied the functions principles of the ZnO and SBS modified asphalt. In summary, the recent researches showed that ZnO could significantly improve the properties of asphalt and asphalt mixture. However, the effects of ZnO particle size on properties of asphalt and asphalt mixture are still unclear.

The aim of this paper is to study the effects of ZnO particles size on property of asphalt and asphalt mixture. In this paper, the spherical ZnO particles with different size were made in laboratory. Then, the ZnO particles were used to prepare micro and nano ZnO modified asphalt and ZnO/SBS modified asphalt. The effects of ZnO particle size on the properties of asphalt and asphalt mixture were analyzed by a serious of tests.

2. Materials

2.1. Nano ZnO

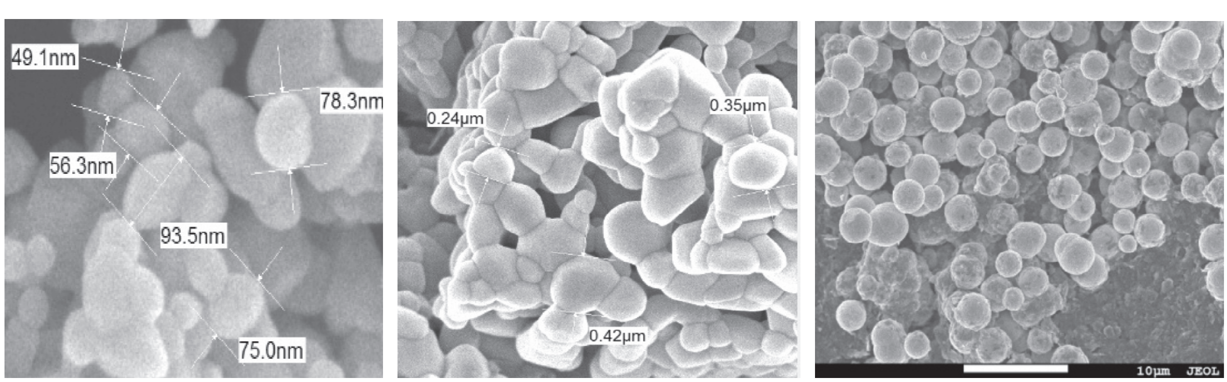
Over the past few years, various methods have been directed towards achieving micro or nano structured ZnO, such as sol-gel method, homogeneous precipitation method, micro emulsion method, combustion synthesis method and hydrothermal method. This paper used homogeneous precipitation method and sol-gel method to synthesize micro or nano structured ZnO, because the reactions in those two methods could occur at room temperature and do not require expensive equipment [29–32].

With zinc acetate, zinc nitrate and absolute alcohol as the starting materials, oxalic acid and urea as precipitating agents, acetyl trimethylammonium bromide as the modifier, the micro and nano ZnO particles were obtained by homogeneous precipitation method and sol-gel method. ZnO particles with average diameter of 80 nm, 350 nm and 2 μm were got by changing the reaction conditions.

ZnO particle with the size of 80 nm was produced by the following procedures: (1) 6.6 g of zinc acetate was dissolved completely into 50 ml deionized water at 75 °C to get acetate solution, and 0.13 g of acetyl trimethylammonium bromide was dissolved completely into zinc acetate solution; (2) 8 g of oxalic acid was dissolved completely into 150 ml absolute alcohol at 75 °C to get anhydrous ethanol solution with oxalic acid; (3) anhydrous ethanol solution with oxalic acid was slowly distributed into the zinc acetate solution to get the mixed solution; (4) rotors was kept stirring in the mixed solution at 75 °C until the white wet gel was got; (5) the white wet gel was rinsed for two times with deionized water and absolute alcohol and then dried at 80 °C; and (6) the powders obtained after dried were calcinated at 450–550 °C for 3 h. Finally, the nano powder with the average particle size of 80 nm was got (Fig. 1(a)).

ZnO particle with the size of 350 nm was produced as follows: (1) 3.5 g of zinc acetate was dissolved completely into 80 ml deionized water of 45 °C to get zinc acetate solution, and 1.44 g of oxalic acid was dissolved completely into 160 ml deionized water of 45 °C to get oxalic acid solution; (2) oxalic acid solution was slowly distributed into the zinc acetate solution to get anhydrous ethanol solution with oxalic acid; (3) the rinsed and dried steps were same with those when the ZnO with the size of 80 nm was produced; and (4) the powders obtained after dried were calcinated at 600 °C for 4 h. Finally, the nano powder with the average particle size of 350 nm was got (Fig. 1(b)).

ZnO particle with the size of 2 μm was produced by the following steps: (1) 30.7 g of zinc nitrate was dissolved completely into 200 ml deionized water to get zinc acetate solution, and 12 g of urea was dissolved completely into 200 ml deionized water to get urea solution; (2) the two solutions were poured into a sealed container and were stirred continuously at 80 °C for 2–3 h; (3) the rinsed and dried steps were same with those when the ZnO with the size of 80 nm was produced; and (4) the powders obtained after dried were calcinated at 600 °C for 4 h. Finally, the powder with the average particle size of 2um was got (Fig. 1(c)).



(a) ZnO particle with the size of 80nm (b) ZnO particle with the size of 350nm (c) ZnO particle with the size of 2um

Fig. 1. Spherical ZnO particles with different sizes.

Table 1
Technical properties of matrix asphalt.

Properties	Values	Test standard
Penetration (25 °C, 100 g, 5 s) (0.1 mm)	64.3	ASTM D5 [33]
Softening Point (°C)	45.6	ASTM D36 [34]
Ductility (cm)		ASTM D1754 [35]
5 cm/min, 10 °C	23.2	
5 cm/min, 5 °C	6.8	
Thin film oven test (TFOT)		ASTM D1754
Mass change (%)	0.64	
Penetration ratio (%)	62.7	
Ductility (5 cm/min, 10 °C) (cm)	8.7	

2.2. Asphalt

A matrix asphalt graded as PG 64–16 was used, and its properties are listed in Table 1. Linear SBS was used also for the tests.

ZnO modified asphalts and ZnO/SBS composite modified asphalts were made in this part. The surfaces of ZnO particles (80 nm, 350 nm and 2um) were modified by silane coupling agent [36]. ZnO particles (2%, 3% and 4% by weight of matrix asphalt) and the matrix asphalt were sheared together in a high shear mixer with the rotation speed of 1500 rpm at 160 °C for 20 min. Then, the mixture was stirred with the shear rotation speed of 4000 rpm at 170 °C for 40 min to get the ZnO modified asphalts. ZnO particles (2%, 3% and 4% by weight of matrix asphalt), SBS (3% and 4% by weight of matrix asphalt) and the matrix asphalt were sheared together in a high shear mixer with the rotation speed of 1500 rpm at 160 °C for 20 min. After that, the mixture was stirred with the shear rotation speed of 4500 rpm at 170 °C for 40 min to get the ZnO/SBS modified asphalt.

2.3. Aggregates

The aggregates were made from basalt. Mineral powder was made of finely ground limestone. Properties of aggregate (coarse and fine) are listed in Tables 6 and 7. And the gradation of AC-20 was used.

2.4. Asphalt mixture

The dosage of ZnO in modified asphalt mixture were determined by the tests of the ZnO modified asphalt, and the negative effects of micro and nano ZnO particles on the ductility of asphalt were compensated to a certain extent by SBS, the dosage of the ZnO is determined as 4% in ZnO modified asphalt mixture, and both of the dosage of ZnO and SBS are 4% also in ZnO/SBS modified asphalt mixture. The optimal bitumen content for asphalt mixtures were determined by Marshall Method (ASTM D6926 [38]). As a result, the optimal asphalt aggregate ratios of matrix asphalt mixture, ZnO modified asphalt mixture, SBS modified asphalt mixture and ZnO/SBS modified asphalt mixture were determined as 4.69%, 4.80%, 4.73% and 4.85% respectively.

3. Experiment methods

3.1. Penetration, softening point, ductility and viscosity test

The conventional physical properties of ZnO modified asphalt and ZnO/SBS modified asphalt, including penetration (0.1 mm at 25 °C, 100 g, and 5 s), softening point, ductility (5 cm/min, 10 °C) and Brookfield rotational viscosity, were tested following by ASTM D5, ASTM D36, ASTM D1175 respectively.

3.2. Dynamic shear rheological (DSR) test

The relaxation of shear stress of ZnO modified asphalt and ZnO/SBS modified asphalt binders was tested in a dynamic shear rheometer (DSR) following by ASSHTO TP5. The parallel plates geometry with a diameter of 8 mm and gap size 1 mm were used in the test at different temperatures (64 °C, 70 °C, 76 °C, 82 °C). The target shear strain was put up to 1% of the sample thickness, and the range of the time to reach the target strain was 60 s. Relaxation time was 1000 s. After the asphalt binder sample was sandwiched between the fixed plate and the spindle, the desired test temperature has to control at 0.1 °C using a water bath. When the spindle was oscillated back and the forthwith constant stress, the resulting strain was monitored.

3.3. Bending beam rheometer (BBR) test

Bending beams rheometer (BBR) was carried out to test the low temperature creep of ZnO modified asphalt and ZnO/SBS modified asphalt binders. The asphalt binder beams (125 mm in length, 6.25 mm in width and 12.5 mm in height) were prepared in molds. And the experiment was followed by ASTM D 790 at −18 °C. The beam specimens were removed from the mold after cooling the mold assembly in freezer for 10 mins. The beam was then kept in the test bath for 60 ± 5 mins before test. After per-loading procedures, a 100-gram load was applied to the beam for a total of 240 s.

3.4. Thin film oven test (TFOT)

The penetration and ductility of ZnO modified asphalt and ZnO/SBS modified asphalt binders before and after TFOT were measured following ASTM D1754 [39]. 50 g sample of asphalt cement in a cylindrical flat-bottom pan. The asphalt cement layer in the pan is about 3 mm deep. The shelf rotates at to 6 rpm at 163 °C. The sample was kept in the oven for 5 h, and then transferred to a suitable container for measuring penetration and ductility of the aged asphalt cements.

3.5. Marshall test

Marshall test was conducted to evaluate Marshall stability and flow of ZnO modified asphalt mixtures and ZnO/SBS modified asphalt mixtures in accordance with ASTM-D 6926. Cylindrical specimens (101.6 mm in diameter and 63.5 mm high) were prepared, and those specimens were applied with a compressive load. The load was applied at a rate of 2 inches per minute. Marshall stability was the load that must be applied to cause the specimen to fail, and the flow index was the total vertical deformation of the specimen at the maximum load.

3.6. Freeze-thaw splitting test

The splitting strength of ZnO modified asphalt mixtures and ZnO/SBS modified asphalt binder mixtures were tested by freezing-thawing splitting test. In this test, the former Marshall specimens with 50 hammer striking times for two sides were used. Freezing-thawing splitting test was carried out by following progress: the specimens were kept in water at vacuum condition of 98 kPa for 15 mins; and the specimens were then transferred into a chamber at −18 °C for 16 h; after that, the specimens were immersed in water at 60 °C for 24 h; finally, the specimens were kept in water at 25 °C for 2 h. The applied loading rate was kept in 50 mm/min. Tensile stress along the vertical diametric plane was got until those specimens failed.

3.7. Rutting test and three-point bending beam test

Rutting test was carried out to test the high-temperature stability of the ZnO and ZnO/SBS modified asphalt mixtures in accordance with ASTM E 1703 [40]. A three-point bending beam test at −10 °C was conducted to discuss low-temperature crack resistance of the ZnO and ZnO/SBS modified asphalt mixtures. The slab specimens (300 mm × 300 mm×50 mm) were fabricated using a rolling wheel compactor, and the beam specimens (30 mm × 35 mm×250 mm) for the three-point bending beam test were sawed from slabs specimens. In three-point bending beam test, the beam specimens were loaded at a ratio of 50 mm/min until failing. Flexural strength and strains of the beam specimens were measured.

4. Results and discussion

4.1. Effects of ZnO particle size on properties of asphalt

4.1.1. Effects of ZnO particle size on penetration, softening point, ductility of asphalt

The results of Penetration test (0.1 mm at 25 °C, 100 g, and 5 s), softening point test and ductility test (5 cm/min, 10 °C) for ZnO modified asphalt and ZnO/SBS modified asphalt are shown in Figs. 2-4. It can be seen that, for both of ZnO modified asphalt and ZnO/SBS modified asphalt, when ZnO particle size decreases, the penetration decreases slightly, the softening point and ductility increase slightly. For these two modified asphalts, with the increase of the dosage of ZnO particles, the penetration and ductility decrease to a small extent and the softening point increases to a small extent. When the dosage of ZnO particles is 4%, the softening point is the highest. Although the ductility in this case is less than those when the dosage of ZnO particles is low, it is still very large. For example, it is greater than 170 cm for ZnO modified asphalt and greater than 240 cm for ZnO/SBS modified asphalt which can meet the requirement of low temperature cracking resistance very well. As a result, 4% will be adopted as the dosage of ZnO particle in the viscosity, dynamic shear rheological test (DSR), bending beam rheometer test (BBR) and aging test afterwards.

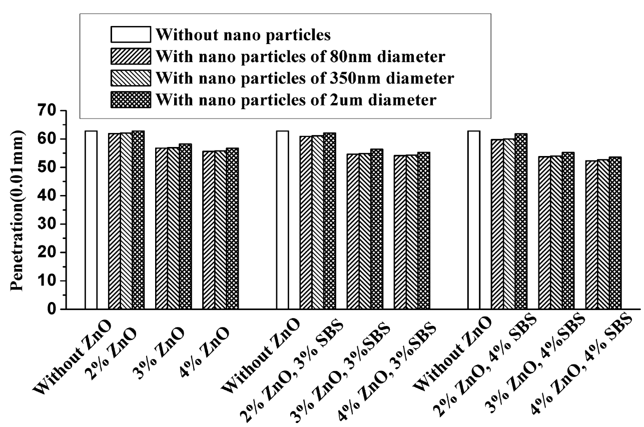


Fig. 2. Effects of ZnO particle size on penetration of asphalt.

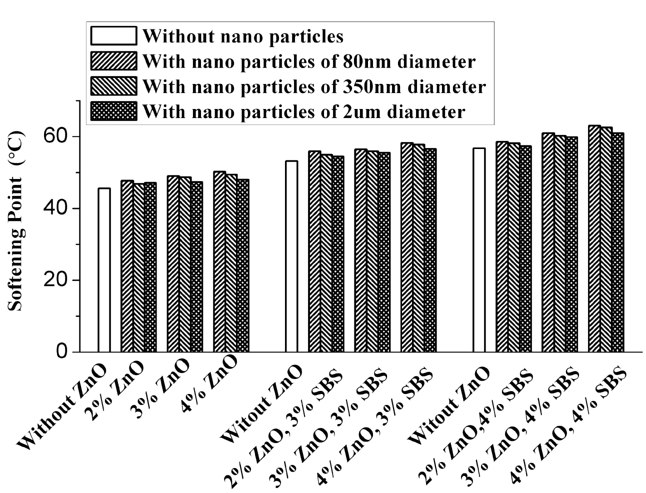


Fig. 3. Effects of ZnO particle size on softening point of asphalt.

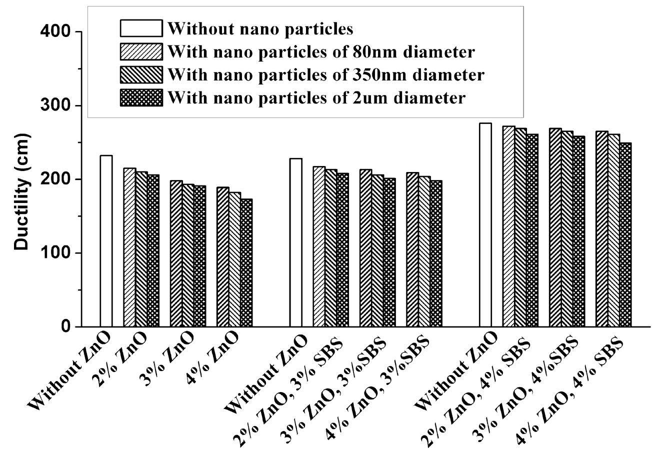


Fig. 4. Effects of ZnO particle size on ductility of asphalt.

Penetration can reflect the hardness or softness of asphalt. With the decrease of particle size, the Van der Waals interaction energy and the non-bonding interaction between nano-ZnO particles and the asphalt molecules increase [41,42], as a result the asphalt structure becomes more stable and the corresponding penetration of asphalt may decrease. In addition, it is easier to fill the pores between the asphalt molecules with the smaller particle of nano-ZnO, which makes the asphalt more compact and stable, and improves the high temperature performance of asphalt. So, the softening point of asphalt is improved. The reason why the ductility of the modified asphalt increases with the decrease of particle size can also be attributed to that the Van der Waals interaction energy and the non-bonding interaction between the asphalt molecules and nano-particles may be greater with the decrease of ZnO particles sizes [43,44].

4.1.2. Effects of ZnO particle size on viscosity of asphalt

Viscosities of ZnO and ZnO/SBS modified asphalt are shown in Fig. 5. The results indicate that the adding of ZnO particles and

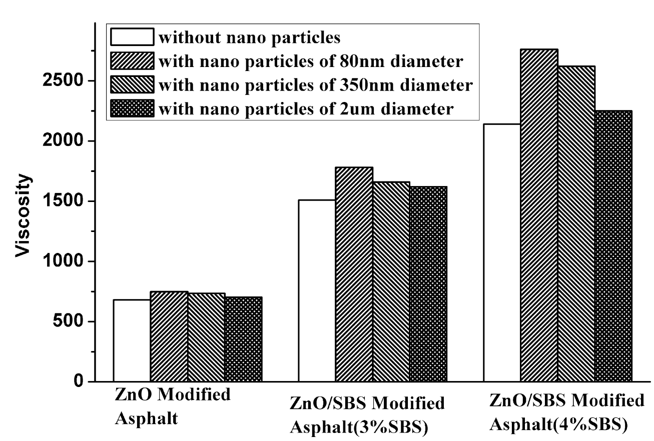


Fig. 5. Results of viscosity test (Pa·s).

the decrease size of ZnO particle can improve the viscosity of asphalt. When ZnO diameter is reduced from 2 μm to 80 nm, for the dosages of SBS of 0%, 3% and 4%, the viscosities of asphalts increase by 6%, 10% and 23%, respectively. At the same time, ZnO particles combined SBS play an advantage role in the viscosity of asphalt than ZnO particles. The influence mechanism nano ZnO size on the viscosity of modified asphalts is similar to that on the penetration.

4.1.3. Effects of ZnO size on rutting resistance of asphalt

The rheological behaviors of ZnO and ZnO/SBS modified asphalt binders at high temperatures were characterized by DSR test. In the DSR test, the dynamic shear modulus (G∗), phase angle (δ) and anti-rutting factor (G∗/sinδ) of the asphalt binder at the specified testing temperature and loading frequency were tested.

The DSR test results are listed in Table 2 and Table 3. Results indicate that the adding of ZnO particles can improve the anti-rutting factors of these two asphalts, and the decrease of ZnO size has large positive effects on anti-rutting factor of asphalts at all of the four temperatures. For example, when the ZnO particle sizes are reduced from 2 μm to 80 nm, for ZnO modified asphalt the anti-rutting factor at 64 °C is improved up to 22.3%; for ZnO/SBS modified asphalt with the dosages of SBS of 3% and 4%, the increase amplitudes of anti-rutting factors are the greatest at 64 °C, which are 35.5% and 8.5% respectively. The principle of improving anti-rutting factors and the stability may be similar to that of improving softening point.

Table 2
DSR test results of ZnO modified asphalt.

Property Factor	Temperature (°C)	Matrix asphalt	ZnO Modified Asphalt 80 nm	350 nm	2 μm
G (kPa)	64	1.0164	1.605	1.489	1.312
	70	0.4917	0.7321	0.6667	0.617
	76	0.2892	0.3641	0.345	0.3171
	82	0.1293	0.1958	0.1822	0.1763
δ (°)	64	88.12	85.71	85.51	85.79
	70	85.85	85.24	84.07	84.42
	76	83.77	82.25	81.36	81.01
	82	76.81	73.61	73.11	74.64
$G^*/\sin\delta$ (kPa)	64	1.0169	1.6095	1.4936	1.3155
	70	0.4930	0.7346	0.6703	0.6199
	76	0.2909	0.3675	0.3490	0.3210
	82	0.1328	0.2041	0.1904	0.1828

4.1.4. Effects of ZnO size on low temperature creep properties of asphalt

Bending Beam Rheometer (BBR) Test is a measurement tool which can provide the creep characteristics of asphalt binders at low temperature. In addition, creep stiffness(S) and creep rate (m) are two important outputs of BBR test. A tensile thermal stress is produced in asphalt mixtures with the contraction during the nighttime. And the lower mixture stiffness (S) reflects a less tensile stress; the higher creep rate (m) means a more stress relaxation.

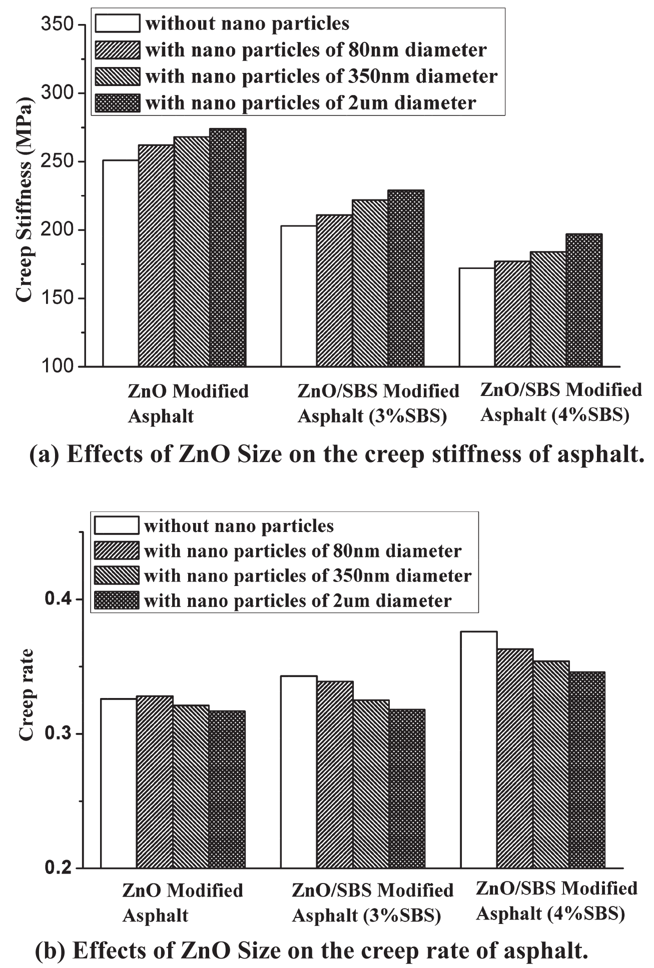


Fig. 6. BBR test results of asphalt.

Table 3
DSR test results of ZnO/SBS modified asphalt.

Property Factor	Temperature (°C)	SBS Modified Asphalt (3%SBS)	ZnO/SBS Modified Asphalt (3%SBS) 80 nm	350 nm	2 μm	SBS Modified Asphalt (4%SBS)	ZnO/SBS Modified Asphalt (4%SBS) 80 nm	350 nm	2 μm
G^* (kPa)	64	3.03	4.67	3.91	3.44	4.03	4.77	4.63	4.51
	70	1.54	2.27	1.93	1.76	2.07	2.51	2.47	2.29
	76	0.75	1.14	0.98	0.93	1.14	1.37	1.39	1.21
	82	0.41	0.54	0.53	0.51	0.68	0.81	0.85	0.69
δ (°)	64	78.0	76.2	77.1	76.1	74.9	70.2	69.9	75.1
	70	79.6	79.1	79.3	77.0	75.4	72.5	70.4	77.4
	76	79.2	79.8	79.5	76.7	73.7	72.2	68.7	77.1
	82	76.3	78.6	77.7	74.8	70.2	69.5	65.2	75.3
$G^*/\sin\delta$ (kPa)	64	3.12	4.81	4.01	3.55	4.18	5.07	4.93	4.67
	70	1.58	2.31	1.97	1.81	2.14	2.64	2.62	2.34
	76	0.77	1.16	1.00	0.96	1.19	1.44	1.49	1.25
	82	0.43	0.63	0.54	0.53	0.72	0.87	0.94	0.71

Table 4
Aging test results of ZnO modified asphalt.

Size of ZnO	Penetration			Ductility		
	Before aging (0.01 mm)	After aging (0.01 mm)	Penetration ratio (%)	Before aging (mm)	After aging (mm)	Ductility ratio (%)
–	64.3	40.3	62.7	232	87	37.5
80 nm	59.7	40.9	68.5	189	72	38.1
350 nm	60.6	40.8	67.3	182	68	37.4
2 μm	61.8	39.7	64.2	173	61	35.3

So, the low stiffness and high creep rate at low temperature are desirable for asphalt binder. Test results are shown in Fig. 6. When ZnO particles are added into the matrix asphalt, the cracking resistance properties of asphalt binders are reduced under low temperature. But with the decrease of ZnO particle size, the creep stiffness of asphalt decreases slightly, and the creep rate of asphalt increase to a small extent. It implies that the decrease of ZnO particle size can improve the low temperature cracking resistance of asphalt slightly. When the nano particles are incorporated into asphalt evenly, the smaller the particle size is, the higher the activation energy is, and the higher the external damage energy may be required at the low temperature [45,46].

4.1.5. Effects of ZnO size on aging property of asphalt

Test results of ZnO and ZnO/SBS modified asphalts are listed in Tables 4 and 5. It can be seen that the penetration ratios and ductility ratios of ZnO and ZnO/SBS modified asphalts increase to a very small extent as the size of ZnO particles decreases. It implies that the decrease of the size of ZnO particles has slight positive influence on the aging property of asphalt.

4.2. Effects OF ZNO SIZE on properties of asphalt mixture

The effects of the variation of ZnO size on the water stability, rutting resistance and low temperature cracking resistance of asphalt mixture would be studied in this section.

Immersion Marshall test and freeze-thaw splitting test were carried out to demonstrate the effects of nano ZnO and ZnO/SBS on the water stability of modified asphalt mixture. Retained stability is the ration of Marshall stability soaked for 48 h and Marshall stability soaked for 0.5 h in the immersion Marshall test. The value of retained stability soaked can reflect the stripping resistance of asphalt mixtures, further influence the water stability. At the same time, the measured tensile strength ratio (TSR) in the freeze-thaw splitting test was mainly used for evaluating water stability of nano ZnO and ZnO/SBS modified asphalt mixture. The tensile strength ratio (TSR) was determined using the following equation:

$$TSR = \frac{S_W}{S_D} \tag{1}$$

Table 7
Properties of fine aggregates.

Property	Values	Requirements	Test standard
Coarse aggregates abrasiveness (%)	26.5	≯ 30	ASTM D 692
Coarse aggregates crushing value (%)	22.4	≯ 24	
Rubble content of coarse aggregates (%)	11.7	≯ 15	
Soft stone content (%)	0.8	≯ 3	

Table 5
Aging test results of ZnO/SBS modified asphalt.

Asphalt	Size of ZnO	SBS (%)	Penetration			Ductility		
			Before aging (0.01 mm)	After aging (0.01 mm)	Penetration ratio (%)	Before aging (mm)	After aging (mm)	Ductility ratio (%)
Matrix asphalt	–	3	59.1	38.1	64.5	228	104	45.5
ZnO modified asphalt	80 nm	3	53.7	41.5	77.3	209	103	49.3
	350 nm	3	54.0	40.8	75.6	204	99	48.5
	2 μm	3	55.2	41.2	74.6	198	90	45.9
SBS modified Asphalt	–	4	57.4	39.8	69.3	276	137	49.6
ZnO/SBS modified asphalt	80 nm	4	52.3	44.1	84.3	263	146	55.5
	350 nm	4	52.7	43.6	82.7	261	142	54.4
	2 μm	4	53.6	40.6	75.7	249	127	51.1

Table 6
Properties of coarse aggregates.

Property	Result			Requirements	Test standard
	13.2–26.5 mm	4.75–13.2 mm	0–4.75 mm		
Crushing value (%)	22.4	20.7	–	≯ 24	ASTM D692 [37]
Loss values of Losangels abrasion (%)	26.5	25.3	–	≯ 30	
Apparent relative density(g/cm^3)	2.794	2.755		≮ 2.6	
Bulk relative density (g/cm^3)	2.759	2.716	2.593	–	
Water absorption (%)	0.46	0.52	–	≯ 2.0	
<0.075 Particle (water washing) (%)	0.8	0.9	1.0	≯ 1.0	

Table 8
Results of immersion marshall tests and freeze-thaw splitting tests.

Asphalt	Size of ZnO	Immersion marshall test			freeze-thaw splitting test		
		MS soaked for 48 h (kN)	MS soaked for 0.5 h (kN)	Retained stability (%)	Splitting strength before freezing and Thawing (MPa)	Splitting strength after freezing and thawing (MPa)	TSR (%)
Matrix asphalt	–	7.76	9.51	81.60	0.865	0.652	75.38
ZnO modified asphalt	80 nm	9.52	11.34	83.95	0.935	0.733	78.40
	350 nm	9.31	11.17	83.53	0.948	0.741	78.16
	2 μm	8.65	10.45	82.78	0.927	0.709	76.48
SBS modified asphalt	–	10.98	12.51	87.77	0.980	0.818	83.47
ZnO/SBS modified asphalt	80 nm	13.42	14.72	91.17	1.107	0.992	89.61
	350 nm	12.77	14.05	90.89	1.074	0.948	88.27
	2 μm	12.23	13.68	89.40	1.009	0.878	87.02

where S_w is average tensile strength value of wet modified asphalt mixture and S_D is average tensile strength value of dry modified asphalt mixture.

Dynamic stability (DS), the number of times of standard axle load with 1 mm deformation, was used to represent the high-temperature stability in the rutting tests. The higher DS value was, the stronger rutting resistance ability of mixture would be.

Beam bending tests at low temperature were conducted to discuss low-temperature crack resistance of mixture. The flexural strength of asphalt mixture (σ_N) and the corresponding strain (ε_N) were calculated using Eqs. (2) and (3) based on the dimensions of the beam specimen [28].

$$\sigma_N = \frac{3P_N L}{2bh^2} \tag{2}$$

$$\varepsilon_N = \frac{6\sigma_N h}{L^2} \tag{3}$$

where σ_N is the nominal strength; ε_N is the strain at failure; P_N is the maximum measured load; L is the span length; b is the width of the beam; h is the thickness of the beam and δ_N is the deflection of the beam corresponding to maximum load P_N.

Results are listed in Table 8 and Figs. 7 and 8.

These results indicate that after ZnO particles are added into matrix asphalt or SBS modified asphalt, the water stabilities and dynamic stabilities of asphalt mixtures are enhanced, but the low temperature bending strains and the flexural strengths are reduced. In addition, as ZnO particle size decreases, these indexes increase to a large or small extent. For example, when the particle size is reduced from 2 μm to 80 nm, for the ZnO and ZnO/SBS modified asphalt, the dynamic stabilities of asphalt mixture are improved by 17.9% and 14.9% respectively.

Nano-ZnO could fill the gap between the aggregate in the asphalt mixture. With the gradual reduction of particle size, it is easier for nano-ZnO to enter the gap which makes the mixture more dense and stable. In addition, nano-ZnO changes to a certain extent the surface structure of asphalt. When nano-ZnO particle size decreases, the surface roughness of asphalt may be improved, the combined force and adhesion between asphalt and aggregate

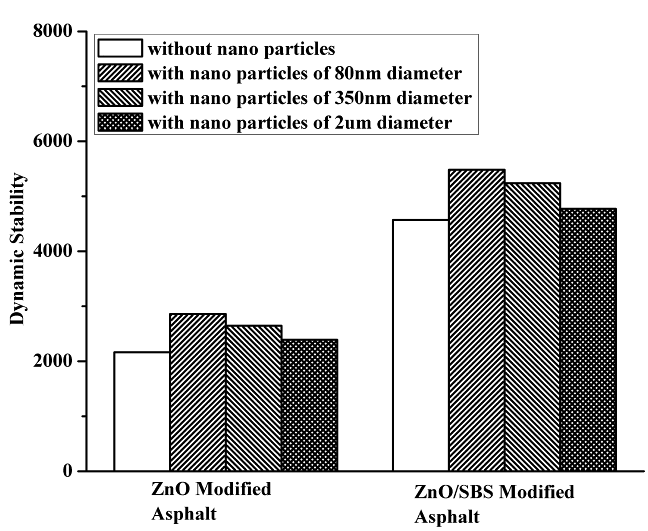


Fig. 7. Results of rutting test (times mm^{-1}).

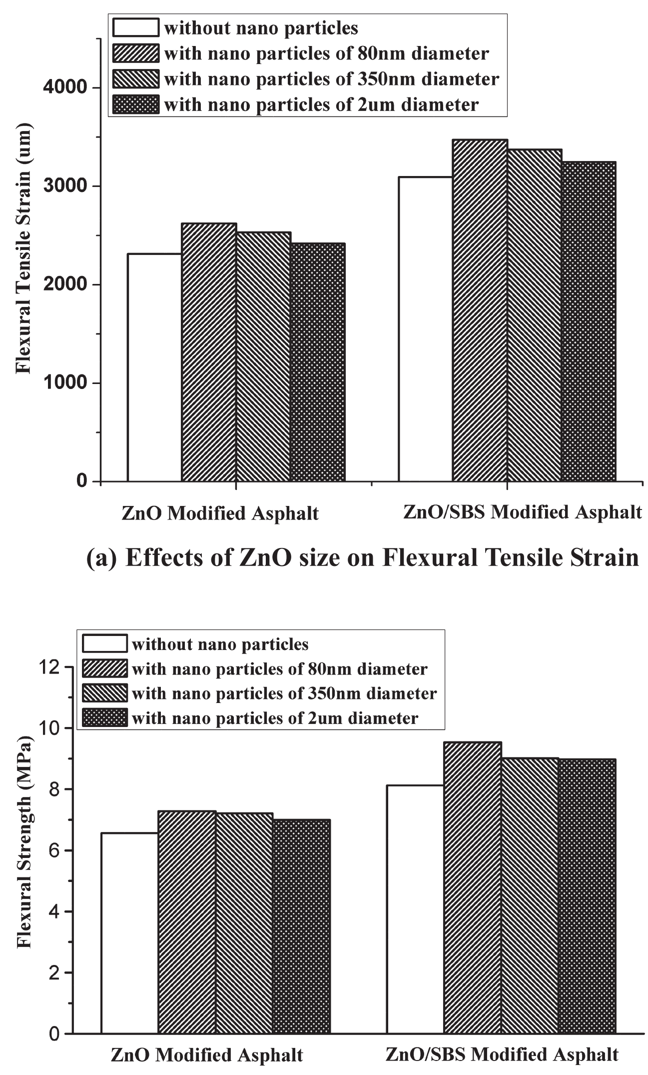


Fig. 8. Results of the three-point beam bending test.

may be stronger, and thus the water stability and low temperature cracking resistance of asphalt mixture are improved [47]. As discussed earlier, the reduction of nano-ZnO asphalt particles improves the high temperature performance of asphalt, reduces the penetration of asphalt and increases the viscosity of asphalt, so the decrease of nano-ZnO particle can improve the high temperature stability of asphalt mixture.

5. Conclusions

The ZnO particles with different sizes were made in this paper. The penetration, softening point, ductility, rheological and aging property of asphalts were measured through penetration test, softening point test, ductility test, DSR test, BBR test and aging test; and the high temperature stability, water stability and low temperature crack resistance of asphalt mixture were measured through Marshall test, freeze-thaw splitting test, rutting test and a three-point bending beam test. The effects of ZnO size on the properties of asphalt and asphalt mixture were discussed, and the following conclusions can be drawn.

(1) For both of ZnO modified asphalt and ZnO/SBS modified asphalt, the penetration decreased slightly but softening point and ductility increase obviously as the ZnO particle size decreases.
(2) In rheological tests, when the particle size is reduced from 2 μm to 80 nm, for dosages of SBS of 0%, 3% and 4%, the anti-rutting factors of asphalt are improved by 22.3%, 35.5% and 8.5% respectively. In low temperature creep test, with the decrease of ZnO particle size, the creep stiffness of asphalt decreased to a small extent, and the creep rate of asphalt increased to a small extent. In aging test with the decrease of ZnO size, the penetration ratio and ductility ratio increase to a small extent. In summary, when the ZnO size is 80 nm, the anti-rutting factor and ductility after aging of asphalt are the best.
(3) In the laboratory performance tests of asphalt mixture, when the particle size is reduced from 2 μm to 80 nm, for the dosages of SBS of 0% and 4%, the dynamic stabilities of asphalt mixture were improved by 17.9% and 14.9% respectively. In addition, the water stabilities, flexural tensile strengths and low temperature bending strains of asphalt mixtures are enhanced also when ZnO particle size decreases. In summary, when the ZnO size was 80 nm, the laboratory performances of asphalt mixture are the best.
(4) According to the analysis above, the size of 80 nm is recommended for ZnO particles.

Acknowledgements

This research was supported by National Natural Science Foundation of China (NSFC) (Grant No. 51208043), Natural Science Basic Research Plan in Shaanxi Provincial Communication Department (No. 2013-01 K). This support is gratefully acknowledged.

References

[1] K. Amir, B. Peyman, The influence of nanomaterials on moisture resistance of asphalt mixes, Study Civ. Eng. Architecture (SCEA) 3 (5) (2014) 34–43.
[2] F. Khodary, M.S. Abd, H.S. El-Sheshtawy, Nano-size cement bypass as asphalt modifier in highway construction, J. Eng. Res. Appl. 6 (3) (2013) 645–648.
[3] F. Khodary, M.S.A. El-sadek, H.S. El-Sheshtawy, CaO/asphalt nano composite: synthesis and enhancement of stiffness properties for asphalt concrete mixtures, Int. J. Sci. Eng. Res. 6 (1) (2015) 444–448.
[4] D. Liu, A. Yue, L. Chen, A study of the performance of nano calcium carbonate modified asphalt and the mixture, J. Changsha Commun. Univ. 4 (2004) 016–021.
[5] X.D. Tang, X.L. Kong, Z.G. He, Nano-montmorillonite/SBS composite modified asphalt: preparation and aging property, Mater. Sci. Forum 68 (8) (2011) 175–179.
[6] H. Yao, Z. You, L. Li, Rheological properties and chemical analysis of nanoclay and carbon microfiber modified asphalt with fourier transform infrared spectroscopy, Constr. Build. Mater. 38 (2013) 327–337.
[7] F. Xiao, A.N. Amirkhanian, S.N. Amirkhanian, Influence of carbon nanoparticles on the rheological characteristics of short-term aged asphalt binders, J. Mater. Civ. Eng. 23 (4) (2010) 423–431.
[8] J.G. Guo, A. Ren, J.P. Guo, Study of the coal tar pitch paving on road modified by nano-material, Guangzhou Chem. Indus. 39 (23) (2011) 41–42.
[9] J.S. Zhang, Y.B. Gao, M.T. Li, Effects of Nano Fe_2O_3 Particles on the Three Indicators of Asphalt, Shandong Jiaotong Univ. 12 (4) (2004) 10–14.
[10] J. Shen, B. Huang, X. Shu, Size Effect of Sub Nano-scaled Hydrated Lime on Selected Properties of HMA, Int. J. Pavement Res. Technol. 4 (4) (2013) 112–117.
[11] A. Diab, Z. You. Rheological Properties of Short-term Aged Foamed Asphalt Modified with Nano Bydrated Lime, In: International Conference on Materials, Architecture and Engineering Technology (ICMAET) (2013) 19–20.
[12] A. Diab, Z. You. Rheological Characteristics of Nano-Sized Hydrated Lime-Modified Foamed Warm Mix Asphalt. International Conference on Materials, Architecture and Engineering Technology (ICMAET) (2013) 34–40.
[13] A. Diab, Z. You, Evaluation of foam-matrixd warm mix asphalt modified with nano-sized hydrated lime using multiple creep and recovery tests, Second Transportation Dev. Congress (2014) 21–28.
[14] S.I. Sarsam, Effect of nano-materials on asphalt cement properties, Int. J. Sci. Res. 1 (10) (2013) 422–426.
[15] C. Fang, R. Yu, S. Liu, Nano-materials applied in asphalt modification: a review, J. Mater. Sci. Technol 29 (7) (2013) 589–594.
[16] k.A. Hong, X. Peng, Z. Xin, Study on hot storage stability of nanometer ZnO/SBS, Modified Asphalt. Jiangsu Univ. (Nat. Sci. Ed.) 31 (4) (2010) 412–416.
[17] H.L. Zhang, C.Z. Zhu, Effect of nano-zinc oxide on ultraviolet aging properties of the asphalt with 60/80 penetration, Mater. Struct. 48 (10) (2015) 3249–3257.
[18] P. Xiao, X. Li, Microstructure and cross blend mechanism of nanometer ZnO/SBS modified asphalt, J. Jiangsu Univ. (Nat. Sci. Ed.) 6 (2006) 019–026.
[19] A.H. Kang, P. Xiao, X. Zhou, Study on hot storage stability of nanometer ZnO/SBS modified asphalt, J. Jiangsu Univ. Nat. Sci. Ed. 31 (4) (2010) 412–416.
[20] H.Y. Liu, H.L. Zhang, P.W. Hao, The effect of surface modifiers on ultraviolet aging properties of nano-zinc oxide modified asphalt, Pet. Sci. Technol. 33 (1) (2015) 72–78.
[21] F. MoghadasNejad, R. Tanzadeh, J. Tanzadeh, Investigating the effect of nano particles on the rutting behaviour of hot-mix asphalt, Int. J. Pavement Eng. 17 (4) (2016) 353–362.
[22] Y.H. Lin, D.S. Li, X.Y. Hou, Preptionof nanometer zincoxide powders by plasma pyrolysis and their applications, J. Am. Ceramic Soc. 31 (4) (2010) 412–416.
[23] L. Yang, J.E. Zhou, Preparation and characterization of nano-zinc oxide, J. Mater. Process. Technol. 189 (3) (2007) 379–383.
[24] Zhou Yan, Deng Jian, cheng, Guan Xiao, yan, Surface modification of nano-zinc oxide by silane coupling agents, Nat. Sci. J. Xiangtan Univ. 28 (4) (2006) 53–56.
[25] Giovanni Polaccoa, Antonio Muscentea, Dario Biondia, Simona Santinib, Effect of composition on the properties of SEBS modified asphalts, Eur. Polymer J. 42 (5) (2006) 1113–1121.
[26] Samuel Zapién-Castillo, José Luis Rivera-Armenta, María Yolanda Chávez-Cinco, Beatriz Adriana Salazar-Cruz, Ana María Mendoza-Martínez, Physical and rheological properties of asphalt modified with SEBS/montmorillonite nanocomposite, Constr. Build. Mater. 106 (1) (2016) 349–356.
[27] Ala R. Abbas, Umme Amina Mannan, Samer Dessouky, AbbasEffect of recycled asphalt shingles on physical and chemical properties of virgin asphalt binders, Constr. Build. Mater. 5 (2013) 162–172.
[28] Augusto Cannone Falchetto, Mihai O. Marasteanu, Sreelatha Balmurugan, Ioan I. Negulescu, Investigation of asphalt mixture strength at low temperatures with the bending beam rheometer, Road Mater. Pavement Design 15 (2017) 28–44.
[29] K. Sobolev, I. Flores, L.M. Torres-Martinez, P.L. Valdez, E. Zarazua, E.L. Cuellar, Engineering of SiO_2 nanoparticles for optimal performance in nano cementbased materials, in: Z. Bittnar, P.J.M. Bartos, J. Nemecek, V. Smilauer, J. Zeman (Eds.), Nanotechnology in construction: proceedings of the NICOM3 (3rd international symposium on nanotechnology in construction). Prague, Czech Republic, 2009, pp. 139–148.
[30] K. Sobolev, M. Ferrada-Gutiérrez, How nanotechnology can change the concrete world: Part 1, Am. Ceram. Soc. Bull. 84 (10) (2005) 14–17.
[31] H. Li, Xiao H-g, J. Yuan, J. Ou, Microstructure of cement mortar with nanoparticles, Compos. B Eng. 35 (2) (2004) 185–189.
[32] T. Ji, Preliminary study on the water permeability and microstructure of concrete incorporating nano-SiO_2, Cem. Concr. Res. 35 (10) (2005) 1943–1947.
[33] ASTM D5. Standard test method for penetration of bituminous materials. USA, ASTM International.
[34] ASTM D36. Standard test method for softening point of bitumen (Ring-and-Ball Apparatus). USA, ASTM International.
[35] ASTM D1754. Standard test method for effects of heat and air on asphaltic materials (Thin-Film Oven Test). USA, ASTM International.
[36] J.J. Gaitero, I. Campillo, A. Guerrero, Reduction of the calcium leaching rate of cement paste by addition of silica nanoparticles, Cem. Concr. Res. 38 (8–9) (2008) 1112–1118.
[37] ASTM D692. Standard Specification for Coarse Aggregate for Bituminous Paving Mixtures. USA, ASTM International.

[38] ASTM D6926-10. Standard Practice for Preparation of Bituminous Specimens Using Marshall Apparatus. USA, ASTM International.
[39] ASTM D1754. Standard Test Method for Effects of Heat and Air on Asphaltic Materials (Thin-Film Oven Test). USA, ASTM International.
[40] ASTM E1703. Standard Test Method for Measuring Rut-Depth of Pavement Surfaces Using a Straightedge. USA, ASTM International.
[41] J.P. Aguiar-Moya, J. Salazar-Delgado, V. Bonilla-Mora, et al., Morphological analysis of bitumen phases using atomic force microscopy[J], Road Mater. Pavement Des. 16 (sup.1) (2015) 138–152.
[42] P.K. Das, N. Kringos, V. Wallqvist, et al., Micromechanical investigation of phase separation in bitumen by combining atomic force microscopy with differential scanning calorimetry results[J], Road Mater. Pavement Des. 14 (sup.1) (2013) 25–37.
[43] F. Vallee, B. Ruot, L. Bonafous, L. Guillot, N. Pimpinelli, L. Cassar, et al. Cementitious materials for self-cleaning and depolluting facade surfaces, In: RILEM proceedings (2005), PRO 41 (RILEM international symposium on environment-conscious materials and systems for sustainable development), 2004. pp. 337–346.
[44] Y. Murata, T. Obara, K. Takeuchi, Air purifying pavement: development of photocatalytic concrete blocks, J. Adv. Oxidat. Technol. 4 (2) (1999) 227–230.
[45] Å.L. Lyne, V. Wallqvist, B. Birgisson, Adhesive surface characteristics of bitumen binders investigated by atomic force microscopy[J], Fuel 113 (2013) 248–256.
[46] R. Jahangir, D. Little, A. Bhasin, Evolution of asphalt binder microstructure due to tensile loading determined using AFM and image analysis techniques[J], Int. J. Pavement Eng. 16 (4) (2015) 337–349.
[47] J.F. Masson, V. Leblond, J. Margeson, et al., Low-temperature bitumen stiffness and viscous paraffinic nano-and micro-domains by cryogenic AFM and PDM[J], J. Microsc. 227 (3) (2007) 191–202.