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Rheological investigation of asphalt binder modified with nanosilica

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Abstract

The study investigates the use of nanosilica as a potential binder modifier. Nanosilica can be produced from rice husk and silica fumes and therefore is a cost-effective and environment-friendly modifier. Different percentages of nanosilica (0%, 0.5%, 1% and 3% by weight of asphalt binder) were added to VG-10 binder in a high-speed mixer. The influence of temperature, strain rate and frequency on viscosity was evaluated. Different rheological tests like time-temperature sweeps, Superpave rutting parameter ($G^*/sin\delta$), Multiple Stress Creep and Recovery (MSCR) Test, Creep tests, and Zero shear viscosity (ZSV) tests were performed on base asphalt binder and nanosilica modified asphalt binders. The addition of nanosilica enhanced the rutting potential of the asphalt binder. Fatigue evaluation using Linear Amplitude Sweep test showed that incorporation of nanosilica arrests the micro crack nucleation and therefore enhanced the fatigue performance of asphalt binder. Nanosilica particles act as a potential heating barrier and protect the host polymeric chains of the asphalt binder, thus improving its aging resistance. Nanosilica modified binders also showed an enhanced self-healing capability.

Keywords: Nanosilica; Shear thinning behaviour; Superpave rutting parameter; MSCR; ZSV; Self-healing; Linear amplitude sweep

1. Introduction

The pavements experience diverse kinds of distresses; amongst which high-temperature rutting, intermediate temperature fatigue and low temperature cracking are the most important from the design standpoint of flexible pavements. The type and extent of these distresses are influenced by loading, axle configurations, temperature variations, mixture parameters and rheological properties of the asphalt binders. There arises a need to overcome various distresses to make the pavements more durable. There have been continuous efforts to make pavements more durable against different types of failures by using diverse kinds of asphalt modifiers [1-6]. Besides the conventional modifiers, the use of different nanomaterials like nanoclays, nanotubes, nano alumina, as asphalt binder modifiers is being explored [7-11]. High specific surface area, high functional density, and high strain resistance make nanomaterials viable alternatives for binder modification [12]. The addition of nano-sized additives improves the performance of the asphalt binder and overcomes the drawbacks of the conventional polymers such as phase separation problems, storage instability problems, low resistance to heat, oxidation and higher costs. Organo-montmorillonite (OMMT) modified asphalt binders showed higher a resistance against thermo-oxidative aging [13]. Aging resistance of CL-30B nanoclay modified binders measured by means of rheological aging index showed that addition of CL-30B nanoclay enhances the aging resistance of the asphalt binders [14]. The addition of nanoclay significantly enhances the storage stability of the polymer modified asphalt binders [15]. Improvement in aging and storage stability of asphalt binders was enhanced after the addition of nanosilica [16]. A significant improvement in the aging resistance of the SBS modified asphalt binder was observed after the addition of carbon nanotubes [17]. Carbon nanotube modified asphalt binders showed an improvement in aging resistance and storage stability [18].

Adding nanosilica to asphalt binder had a positive effect on the physical and rheological properties of the asphalt binder. The available literature has mostly concentrated on evaluating the rutting resistance of the nanosilica modified asphalt binders by utilizing Superpave ($G^*/sin\delta$) rutting parameter. Previous research based on Superpave rutting parameter($G^*/sin\delta$), showed that the addition of nanosilica enhanced the rutting resistance asphalt binders. The addition of nanosilica improves the storage modulus and elasticity of the asphalt binder, besides an improvement in aging resistance [19]. It makes the asphalt binder stiff and improves temperature susceptibility as shown by decrease in penetration and increase in softening point. An enhancement in the PG grade of the asphalt binder is also observed after the addition of nanosilica [20]. Nanosilica improves the self-healing capacity of the asphalt binders and mixes, therefore making the pavements more durable and lasting [21]. An improvement in the elastic behaviour of the asphalt binder leading to an improvement in

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fatigue resistance, rutting resistance and creep performance of the asphalt binder has also been reported. Indirect tensile strength significantly increases after the addition of nanosilica [22]. The resilient modulus, split tensile strength and fatigue life of the asphalt mixes improved after introduction of nanosilica, it also improved the moisture susceptibility [23]. The addition of nanosilica slows down the oxidative process and thereby improves the aging resistance of asphalt binders. An improvement in high and intermediate temperature performance was observed but the low temperature performance did not show an improvement [24]. Introduction of nanosilica improves the permanent deformation characteristics of the asphalt binder. An improvement in the intermediate and low temperature performance has also been seen [25]. Nanosilica forms an inorganic network in the asphalt binder as was confirmed by X-ray diffractometry and Scanning Electron Microscopy. This leads to the crack arrests and improves the fatigue performance of the nanosilica modified asphalt binders [26].

Although $G^*/sin\delta$ is widely used to assess the rutting performance of the asphalt binders, but this parameter does not account for the delayed elastic response shown by modified binders. $G^*/sin\delta$ does not show good correlation with the rutting performance of mixtures. So advanced characterization methods such as Multiple stress creep and recovery (MSCR) test, Zero shear viscosity (ZSV), and creep tests may also be utilized to investigate the rutting potential of nanosilica modified binders [27-33]. Employing ZSV, MSCR and creep tests can help in better evaluation of the rutting potential of nanosilica modified binders. Zero-shear viscosity is a theoretical concept and is defined as the viscosity measured when shear rate is approaching zero. The ZSV concept is based on the fact that the purely dissipative viscous component is solely responsible for the nonrecoverable deformation. ZSV is an indicator of stiffness of the binder and permanent deformation under long-term loading [34]. Rutting of the asphalt mixes has been identified as a non-linear viscoelastic phenomenon, and therefore the measurements for binder rutting parameter in linear viscoelastic region will not relate well with asphalt mixture rutting. The Superpave rutting parameter failed to capture the true performance characteristics of modified binders, therefore to overcome the inadequacies of the existing rutting parameter Multiple stress creep and recovery test was proposed [35-37]. Different studies have shown this method to be applicable for both unmodified and modified asphalt binders [38-40]. MSCR test relates very well with the rutting performance of asphalt mixes evaluated from different rut tests [41-47]. Fatigue distress has been evaluated using different approaches. Linear Amplitude sweep (LAS) test has been found to be most effective approach in evaluating the fatigue distress. LAS test uses viscoelastic continuum damage approach for fatigue characterization of asphalt binders [48-51].

The authors found very limited literature discussing MSCR, ZSV, creep tests and linear amplitude sweep test for rutting and fatigue evaluation of nanosilica modified asphalt binders, and therefore it is necessary to evaluate the performance of nanosilica modified asphalt binders using these approaches. The present study will be a good addition to the existing repository of information about performance of nanosilica modified asphalt binders.

The addition of nanosilica affects rheological properties and the flow behaviour of the asphalt binder, and therefore it is important to study the change in behaviour at different temperatures and shear rates. The present study aims to examine the influence of temperature, strain rate and frequency on rheological properties of the nanosilica modified asphalt binders. Based on the literature review, it was found that nanosilica has been utilized in the range of 1 to 6% for asphalt binder modification [52]. Studies have shown that using nanosilica in higher concentrations can have an adverse effect on the intermediate and low temperature performance of asphalt binders [53]. Therefore, in this study, 0%, 0.5%, 1%, and 3% nanosilica, by the weight of asphalt binder has been used. The maximum concentration of nanosilica used in this study was 3%, the maximum concentration was chosen on the basis of the study conducted by Leiva-Villacorta and Vargas-Nordcbeck 2019 [54]. They, in their study, evaluated the performance of nanosilica modified asphalt binders at low, intermediate and high temperatures and concluded that 3% content was the optimum percentage of nanosilica to be used for asphalt binder modification.

2. Objectives and scope of the study

The primary objective of this study was to evaluate the effect of nanosilica on various physical and rheological characteristics of the asphalt binder. The sub-objectives are enlisted below:

1. Evaluate the effect of nanosilica on the viscosity of the asphalt binder in different temperature domains and shear rates.
2. Investigate the effect of adding nanosilica on different rheological properties by means of time and temperature sweep tests.
3. Estimate the rutting potential of the nanosilica modified binders using the Superpave rutting parameter $G^*/sin\delta$, MSCR and creep tests.
4. Evaluate the fatigue resistance of the control and nanosilica modifiers utilizing Linear Amplitude sweep.
5. Assess the aging resistance potential of the nanosilica modified binders by means of a rheological parameter.
6. Investigate the self-healing potential of the nanosilica modified binder by means of ductility test.

3. Materials and experimental methodology

3.1. Materials

A soft grade binder of viscosity grade VG-10 was used in the study as the base binder. The basic properties of the base asphalt binder are enlisted in Table 1. Nanosilica used in the study as modifier was supplied by Platonic Nanotech private limited. The basic properties and elemental composition of nanosilica are listed in Table 2 and Table 3.

Table 1
Basic properties of the base binder.

Properties	Standard code	Values	Specification limit (minimum)
Penetration 0.1mm at 25°	IS: 1203	89	80
Softening point (°C)	IS: 1205	48	40
Ductility at 25°C	IS: 1208	100+	75
Dynamic viscosity	IS: 1206 (Part II)	1063	800
Kinematic viscosity	IS: 1206 (Part III)	282	250

Table 2
Physical properties of nanosilica.

Specification	Value
Purity	99.50%
Average size of the particle	30-50 nm
Specific surface area	200-250 m^2/g
Bulk density	0.10 g/cm^3
True Density	2.5 g/cm^3
Morphology	Porous

3.2. Sample preparation

The main challenge in the preparation of nanosilica modified binders is the proper dispersion of nanosilica particles in the asphalt binder. The high shear mixing technique is effective in dispersing nanosilica particles in the asphalt binder. Initially, the control asphalt binder was heated to a temperature of 150±5°C, and then nanosilica was added to the base binder in different concentrations (0, 0.5, 1 and 3% by weight of the base binder) in a high-speed mixer. The highest concentration of nanosilica chosen in the study was 3% by weight of the asphalt binder. The highest concentration of nanosilica was limited to 3%, based on a previous study conducted by Leiva-Villacorta and Vargas-Nordcbeck 2019 [54]. Small quantities of nanosilica were added to the asphalt binder over a time period of 15 minutes to prevent the agglomeration of nanosilica particles. The temperature during the mixing process was maintained at 150±5°C by using a thermostat. The high-speed mixer was maintained at the maximum rotational speed of 3500 rpm for 2 hours. Samples from high-speed mixer were taken after every 15 minutes and complex modulus was evaluated, complex modulus values increased as the mixing time increased, however; no change in complex modulus values was observed after mixing for 2 hours, and hence 2-hour mixing time was selected for preparation of nanosilica modified binders.

The mixing was carried out in presence of oxygen at high temperature that accelerates the aging process. This leads to the stiffening of the asphalt binder and affects the rheological properties of the asphalt binder. In order to remove any bias in the measurement of rheological properties that may incur due to aging of modified binder, the base asphalt was mixed under the same conditions without nanosilica to obtain the same set of conditions for all the samples before testing.

3.3. Aging of asphalt binders

The base asphalt and modified asphalt binders were made to undergo short-term aging by conditioning in a Thin Film Oven (TFO) at 163°C for 5 hours as per ASTM: D 1754 [55]. Long term aging of the asphalt binders was carried out in a pressure aging vessel. The pressure aging vessel was maintained at a temperature 100°C and 2.1 MPa pressure for 20 hours as per ASTM:D 6521 [56].

4. Test methods

4.1. Scanning electronic microscope

The SEM analysis was conducted to investigate the morphology of the nanosilica powder and nanosilica modified asphalt binder. The SEM images were captured using HITACHI-3600 SEM device.

Table 3
Elemental composition of nanosilica particles.

SiO_2	Al	Fe	Mg	Ca
99.5%	0.02%	0.05%	0.1%	0.08%

4.2. Physical characterization of the binders

The basic properties of base binder and nanosilica modified binder were evaluated, including penetration (IS: 1203), softening point (IS: 1205) and ductility (IS: 1208) [57].

4.3. Rheological characterization of the binders

4.3.1. Temperature and strain sweep

To investigate the variation in viscosity of base and nanosilica modified asphalt binders with change in temperature, a temperature sweep was carried out in the temperature range of 60-135°C. Anton Paar MCR 102 Dynamic Shear Rheometer (DSR) with a parallel plate geometry of 25 mm diameter and a 1 mm gap was used.

Shear rate dependency allows the flow behavior of the asphalt binder under varying strain rates to be better understood [58,59]. A shear rate sweep in the range of 0.1 to 100 1/s was carried out to understand the behaviour of unmodified and modified asphalt binders. The sweep was carried out at temperatures of 60°C, 100°C, and 135°C.

4.3.2. Frequency sweep

Frequency sweep test is one of the most common method for evaluating the rheological characteristics of the asphalt binder. The test was conducted within the LVE range to measure the viscoelastic parameters at different temperatures and frequencies. The frequency sweep was carried at 0.1% strain rate and in the frequency range of 0.1-100 rad/sec. The temperature was increased from 40°C to 76°C, with 6°C increment.

The dependence of complex modulus and phase angle on temperature and frequency or loading time can be shown in the form of isochronal and isothermal plots respectively [60].

Black diagrams provide a useful tool in analyzing rheological data for the identification of possible discrepancies in experimental results. It verifies the time-temperature equivalency, and thermo-rheological simplicity [61]. The Black diagram is a plot between complex modulus G^* and phase angle δ obtained from a dynamic test. A black diagram is independent of temperature and frequency and allows all the oscillatory data to be reported in a single graph. A smooth curve in a black diagram indicates time-temperature equivalency. A disjointed curve indicates the breakdown of time-temperature equivalency, thus indicating a high degree of modification [62].

4.3.3. Rutting resistance using Superpave rutting parameter

Rutting resistance of the base asphalt and nanosilica modified asphalt was evaluated by means of Superpave rutting parameter as per ASTM-D7175-15 [63]. This parameter is used to determine the high-temperature failure of the asphalt binder. As per the Superpave specifications, a binder is considered to fail when the value of $G^*/\sin\delta$ drops below 1 kPa for the unaged binder. This test was performed on unaged binders using a dynamic shear rheometer with a parallel plate geometry. The plate diameter was 25 mm and 1 mm gap was used. The test was carried out at a frequency of 10 rad/sec in the temperature range of 52°C to 76°C with 6°C temperature bumps.

4.3.4. Multiple stress creep and recovery

The MSCR test was performed on TFO-aged samples as per ASTM-D7405-15 [64]. The two parameters obtained from the MSCR test are the average non-recoverable creep compliance (J_{nr}) and the average percentage recovery. The test was done at standard stress levels of 0.1 kPa and 3.2 kPa. Non-recoverable creep compliance is defined as the ratio between non-recoverable shear strain and shear stress applied during the loading cycle. J_{nr} is capable to characterize stress dependence of modified binders as well as unmodified asphalt binders. The two parameters are specified in Eqs. 1 and 2 respectively.

$$J_{nr(\sigma)} = \sum_{i=1}^{10} \frac{\left(\frac{e_{10}}{\sigma}\right)_i}{10} \quad (1)$$

where, J_{nr} denotes non- recoverable creep compliance (1/kPa), e_{10}= residual strain at the end of the loading cycle; σ = Standard stress level of 0.1 kPa and 3.2 kPa.

$$Percent\ Recovery\ (\sigma) = \sum_{i=1}^{10} \frac{\left(\frac{e_1 - e_{10}}{e_1}\right)_i}{10} \times 100 \quad (2)$$

where, e_1 and e_{10} denote strain at the end of the loading and recovery cycle, respectively.

4.3.5. Creep Test

Creep refers to the increase in deformation over time under sustained stress. The behavior of unmodified and modified asphalt binders under sustained loading has been evaluated in this study. The stress of 100 Pa was applied for a loading period of 10 minutes and the resulting strain at the end of loading period was measured. The stress level in this study is same as used in the study conducted by Anwar Parvez et al. 2014 [65] and also 100 Pa stress level is a standard loading level for MSCR test [64].

4.3.6. Linear Amplitude Sweep

The fatigue evaluation of the control and nanosilica modified asphalt binders have been evaluated by utilizing LAS test as per AASHTO TP 101. The test was performed at 25°C on a DSR with an 8mm assembly and a gap of 2mm. LAS test consists of two steps, in the first step, a frequency sweep test is conducted with frequency varied from 0.2 to 30 Hz at 0.1% strain rate. The second step consists of performing an amplitude sweep 0.1-30% at 10 Hz frequency. The data from the frequency sweep test is used in the estimation of undamaged parameter α and consequently parameter B. Amplitude sweep data is used to obtain the asphalt binders damage property which can be written as,

$$D(t) \cong \sum_{i=1}^{N} [\pi \gamma_o^2 (C_{i-1} - C_i)]^{\frac{\alpha}{1+\alpha}} (t_i - t_{i-1})^{\frac{1}{1+\alpha}} \quad (3)$$

where, *D(t)* is the damage accumulation in the specimen; C_i = ratio of complex modulus at any time (t) to the initial complex modulus = $G^*(t)/G^*$ (initial); γ_o = applied strain level (%); α= inverse of the slope of the line plotted between log of storage modulus and log of applied frequency.

The relationship between *C(t)* and *D(t)* is fitted using the power law:

$$C_t = C_O - C_1 (D)^{C_2}$$

$$C_{(t)} = C_0 - C_1 (D)^{C_2} \quad (4)$$

where, *C(t)* is the integrity parameter, C_0, C_1, and C_2 are the curve fitting parameters. *C* at peak shear stress is used to calculate failure point D_f by using the relation

$$D_f = \left(\frac{C_0 - C_{peak\ stress}}{C_1}\right)^{\frac{1}{C_2}} \quad (5)$$

Number of load cycles to failure N_f is calculated by using the equation,

$$N_f = A(\gamma_{max})^{-B} \quad (6)$$

where, *A* and *B* are regression coefficients and

$$A = \frac{f(D_f)^{1+(1-C_2)\alpha}}{(1+(1-C_2)\alpha)\times(\pi C_1 C_2)^{\alpha}};$$

$$B = 2\alpha$$

γ_{max} = maximum strain level

4.4. Effect of nanosilica on ageing resistance

Aging refers to the oxidative aging of the asphalt binders. Binders experience oxidation during the mixing and laying stage and also during their service life. During this process of aging, some of the lighter and volatile components of the binder evaporate, making the binder brittle which can lead to pavement deterioration. Therefore, binders with a lower degree of oxidation are sought after. The present study evaluates the aging resistance of the unmodified and modified binders by means of rheological aging indices [66]. The aging index is given in Eq. 7.

$$\text{Rutting aging index} = \left(\frac{\text{Aged rutting factor} - \text{Unaged rutting factor}}{\text{Unaged rutting factor}}\right) \times 100 \quad (7)$$

4.5. Self-healing potential of nanosilica modified binder

The Self-healing phenomenon takes place at the molecular level and is mainly affected by the Van der Waals forces and hydrogen bonding molecules. Different types of additives can be added to the asphalt binder to enhance the self-healing capacity of the asphalt binders. These materials include Ionomers, nanoparticles, and super molecular rubber [67]. The self-healing phenomenon takes place at the molecular levels, i.e. at the nano level. Therefore, modification of asphalt binder at the nano-level can help to improve the self-healing potential of the asphalt binders. In this study, the self-healing potential of the nanosilica modified asphalt binders was evaluated by using a special ductility test. The methodology used to carry out the test was as given by Qui *et al.* 2009 [67]. The ductility samples of nanosilica modified asphalt binders were prepared and then cut in the middle by using a sharp knife. After cutting the samples, the specimens were placed on a glass plate in a proper orientation. A small force was applied at the ends of the briquettes for about 10 seconds. It was ensured that the two cut surfaces of the asphalt binder are properly in contact with each other. Finally, the samples were allowed to self-heal at room temperature for a period of 4 hours. After 4 hours of healing, self-healed nanosilica modified samples and base asphalt samples were placed in a ductility machine, with the water bath maintained at a temperature of 5°C. The ductility test was performed at a displacement rate of 5 cm/min. The healing percentage is calculated as follows:

$$SH_{Ductility}\% \frac{L_{healed}}{H_{original}} \times 100 \quad (8)$$

where, $SH_{Ductility}\%$ = self-healing percentage in ductility test; $L_{Healed}\%$ = length of the healed sample when it breaks; $L_{original}\%$ = length of the original ductility samples when it breaks;

5. Results and discussions

5.1. SEM analysis

Figs. 1 and 2 show SEM images of nanosilica and 3% nanosilica modified asphalt binder. As is evident from Fig. 1, nanosilica particles tend to agglomerate and form bundles of nanosilica particles. In Fig. 2, no agglomeration of nanosilica particles can be seen and thus the mixing technique used was successful in dispersing the nanosilica particles in the asphalt binder.

5.2. Conventional binder tests

As shown in Table 4, there is a decrease in the penetration of asphalt binder with the addition of the nanosilica. The decrease in penetration indicates the stiffening effect of the asphalt binder, and the stiffening increases with an increase in nanosilica concentration. The Softening point can be used as an indicator of temperature susceptibility of the asphalt binder. The addition of nanosilica increased the softening point of the asphalt binder, indicating an improvement in its temperature susceptibility. Ductility is a measure of elasticity of the asphalt binder. Ductility test result values showed a decreasing trend after the addition of nanosilica. The stiffening effect of the nanosilica leads to a decrease in the ductility. The high specific surface area of the nanosilica enhances the interaction with the asphalt.

Higher Penetration index indicates lower temperature susceptibility of the asphalt binder. Penetration index was calculated using Eq. (9) [68].

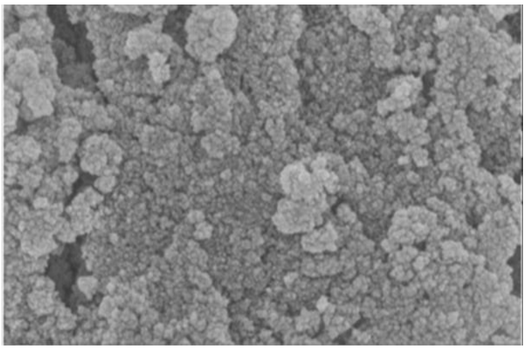

Fig. 1. SEM images of nanosilica.

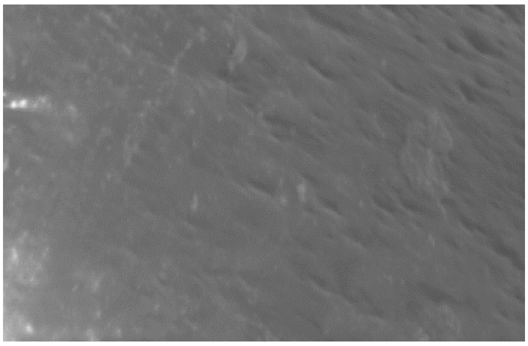

Fig. 2. SEM image of 3% nanosilica modified binder.

Table 4
Physical properties of nanosilica modified asphalt binder.

SiO_2 concentration (%)	Penetration (mm)	Softening point (°C)	Ductility (mm)	Penetration index
0	92	52	>100	0.94
0.5	78	60	86.4	2.22
1	61	66	71.2	2.55
3	54	72	68.3	3.33

$$PI = \frac{1952-500\log pen-20SP}{50\log pen-SP-120} \tag{9}$$

5.3. Temperature and strain sweep

5.3.1. Temperature dependence of viscosity

Viscosity is dependent on the force of cohesion. With an increase in temperature, the cohesive force decreases and hence the binder viscosity also decreases. Fig. 3 shows the effect of change in temperature on the viscosity of the unmodified and nanosilica modified asphalt binders. The results show a consistent increase in the viscosity with an increase in the nanosilica content. The viscosity decreases with an increase in temperature for unmodified as well as modified binders.

5.3.2. Shear rate dependence

Asphalt binder is subjected to varying strain levels in bituminous mix preparation and compaction stages. So, it becomes imperative to investigate the effect of varying strain rates on the binder. Figs. 4, 5 and 6 show the effect of varying strain rates on the viscosity of the binder at temperatures of 60°C, 100°C and 135°C. At 60°C, the base binder shows Newtonian behavior up to a strain level of 10 1/s. The viscosity then starts to decrease with an increase in strain rate indicating a shift towards non-Newtonian behaviour. As the dosage of nanosilica is increased, the shear rate dependency increases and the binder behaves as Newtonian fluid for a narrower shear rate region. At 100°C, base binder and 0.5% nanosilica modified binder show Newtonian behavior. 1% nanosilica modified binder shows Newtonian behaviour up to a shear rate of ≈ 90 1/s, and 3% nanosilica modified binder showed Newtonian behavior for a narrower strain region of ≈10 1/s. At 135°C, the change in strain rate doesn't affect the viscosity and thus the unmodified and nanosilica modified binders show Newtonian behaviour at this temperature.

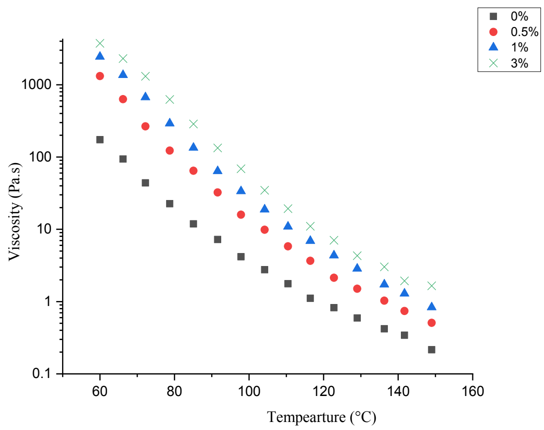

Fig. 3. Temperature dependence of viscosity.

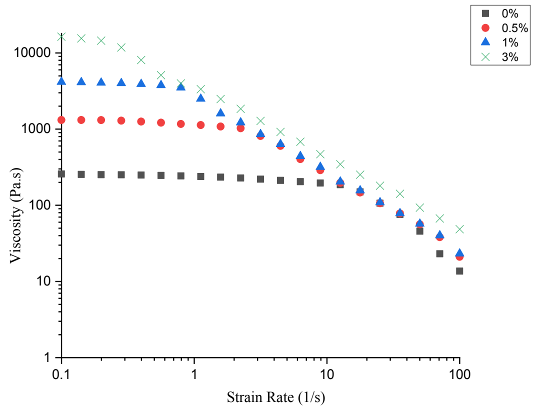

Fig. 4. Strain rate sweep at 60°C.

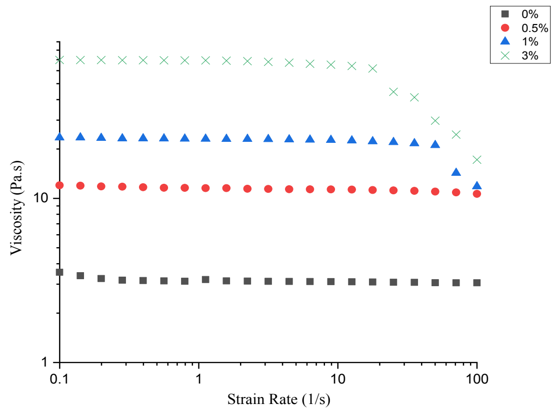

Fig. 5. Strain rate sweep at 100°C.

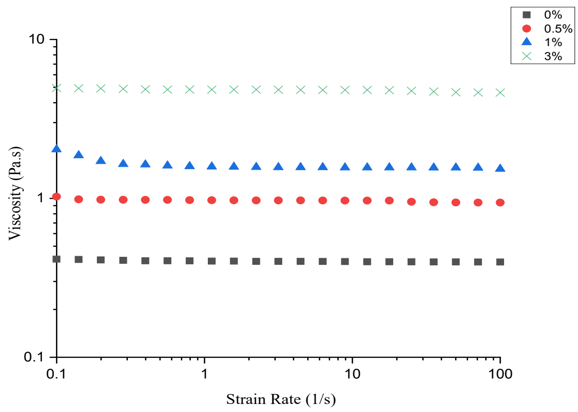

Fig. 6. Strain rate sweep at 135°C.

The shear-thinning behaviour of the nanosilica modified asphalt binders can be modelled by using Carreau's model, as shown in Eq. (10) [69-71]. Carreau's model overcomes the drawbacks of power-law model in very low and high shear rate regions. In Carreau's model, viscosity depends upon the shear rate. Carreau's viscosity model is useful in describing the flow behaviour of fluids in high shear rate region. This model is capable of describing both the shear thinning and shear thickening phenomenon. Carreau presented the rheological equations from molecular network theories [72]. As can be seen from Fig.7, the model was found to have a good fit with the obtained results (with R2 equal to 0.9851, 0.9962, 0.9784 and 0.9682 for 0, 0.5, 1 and 3% respectively).

Table 5
Carreau model parameters.

Binder	η_0(Pa.s)	η_∞ (Pa.s)	γ_c (s-1)	s
Base	257.83	0	16.63	0.71
0.5% Nanosilica	1319.55	8.29	2.50	0.55
1% Nanosilica	4169.73	20.65	1.45	0.66
3% Nanosilica	17146.74	40.68	0.34	0.57

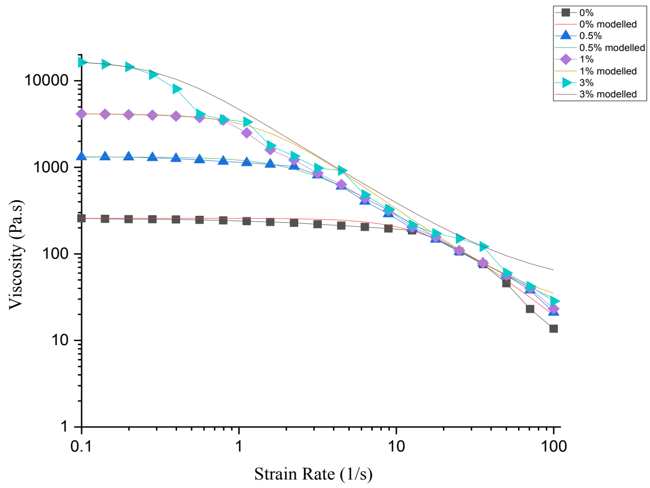

Fig. 7. Model fitted curves.

$$\eta = \eta_\infty + \frac{\eta_0 - \eta_\infty}{\left(1+\left(\frac{\gamma}{\gamma_c}\right)^2\right)^s} \quad (10)$$

where, η_∞ is infinite shear viscosity, η_0 is zero shear viscosity, s is the parameter related to the slope of the shear-thinning region and γ_c is the critical shear rate for the onset of shear thinning. The different carreau model parameters have been shown in Table 5. In this model, a zero shear Newtonian plateau was assumed at the beginning up until the critical shear rate γ_c is reached when the shear thinning behaviour starts. With the increase of the shear rate, the viscosity gradually reached an infinite-shear Newtonian plateau. The addition of nanosilica to the control binder caused a significant increase in zero shear viscosity. A higher value of zero shear viscosity at high temperature implies the fluidic nature of the asphalt that would lead to a better coating of aggregates by asphalt binder. The shear-thinning occurs due to the alignment of the asphalt particles in the direction of the applied stress, which leads to a decrease in the viscosity.

5.4. Time and temperature sweep tests

5.4.1. Isochronal plot

The Isochronal plot of complex modulus (G^*) and phase angle at a frequency of 10 rad/sec is shown in Fig.8. The addition of nanosilica to the asphalt binder increases the complex modulus of the binder. This increase can be observed in the entire temperature domain. The establishment of the plateau region in the isochronal plot suggests the high degree of modification that the binder has undergone [73]. The Phase angle of the binder increases with an increase in temperature and the nanosilica modified binders show lower phase angles as compared to the base binder. As the concentration of nanosilica increases, a significant decrease in the phase angle is observed at lower as well as at higher temperatures.

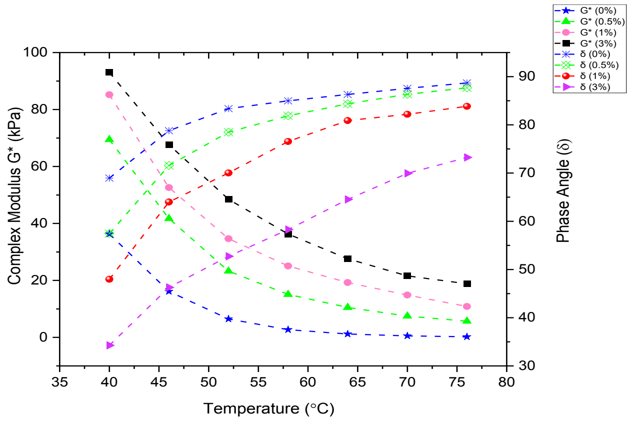

Fig. 8. Isochronal plot for complex modulus and phase angle.

The mechanism responsible for improvement in complex modulus can be explained as follows. Incorporation of nanosilica in asphalt binder leads to the formation of a miscible system. The high temperature and high-speed preparation aids in making it a uniform and stable miscible system. The nanosilica particles possess higher melting point as compared to the temperature used during the mixing process, therefore it remains uniformly dispersed in asphalt binder without dissolving in it. The uniform dispersion of nanosilica particles in the asphalt binder enhances the strength of the asphalt binder. The improvement in shear modulus can be explained by Orowan mechanism and Hall-Petch reinforcement mechanisms. According to Orowan mechanism the addition of nanosilica restricts the motion of asphalt. This improves the load bearing capacity of the asphalt binder, leading to enhancement in its shear complex modulus. Due to the smaller size of the nanosilica particles the average distance between the particles decreases, thereby leading to an increase in the yield strength. The Orowan mechanism can be expressed using the following equation.

$$\tau = \frac{\mu b}{d}$$

where, τ is the yield stress, μ is the shear modulus of matrix, b is Burgers vector of matrix, and d is the average distance between the particles.

According to Hall-Petch reinforcement there exists a mismatch in atomic arrangement at the interface of asphalt binder and nanosilica. This mismatch in atomic arrangement disrupts the dislocation movement of the asphalt binder by generating repulsive stress fields. Higher the applied stress required to overcome the repulsive stress fields, higher the yield strength of the asphalt binder. This leads to a decrease in the plastic deformation of the asphalt binder. As per Hall-Petch equation, the smaller size of nanosilica particles will generate higher phase interface that prevents the dislocation of the asphalt binder, and thus improves its strength. Hall-Petch equation is shown as follows.

$$\sigma = \sigma_o + K.d^{-\frac{1}{2}}$$

where, σ is the yield strength of the material, k is a constant, d is the particle size [74-78].

5.4.2. Isothermal plots

Frequency dependence of complex modulus and phase angle has been illustrated in Fig.9. A significant increase in the complex modulus of nanosilica modified asphalt binders can be seen, thus improving the rutting resistance of the binders. This increase is more significant at higher frequencies and a plateau is formed when the frequency is decreased. The phase angle of nanosilica modified binders shows a decrease at low and high frequencies, implying that the modified binders are more elastic in nature.

5.4.3. Black diagram

The effect of the addition of nano nanosilica on the complex modulus and phase angle has been shown in the form of the black diagram as shown in Fig.10. As is evident from Fig.10, the complex modulus and phase angle show a monotonic trend of complex modulus increasing and phase angle decreasing. Nanosilica modified asphalt binder has a smaller phase angle value as compared to base asphalt binder for the same complex modulus. As the measure of nanosilica is increased, the value of phase angle decreased. This indicates an improvement in the elastic behaviour of the asphalt binder and better rutting resistance.

5.5. Superpave rutting parameter

To identify the improvement in the rutting resistivity of the binder after the addition of nanosilica, Superpave rutting parameter (*G*/sinδ*) has been evaluated at different temperatures and presented in Fig.11. As can be seen in Fig. 11, there is an increase in *G*/sinδ* values with the addition of nanosilica at each performance grade temperature. A significant improvement is observed at all the temperatures for a nanosilica content of 3%. The improvement in rutting is because when nanosilica is dispersed in

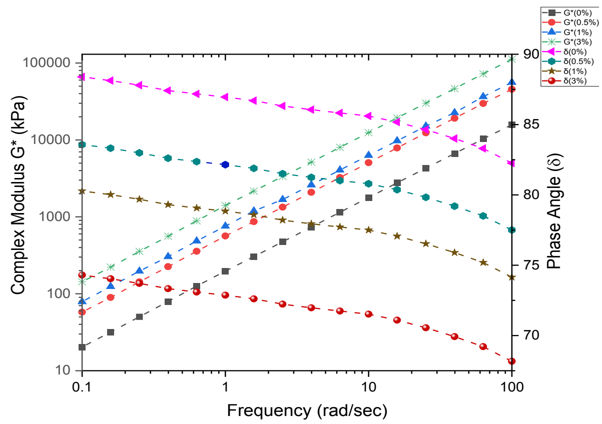

Fig. 9. Isothermal plot for complex modulus and phase angle.

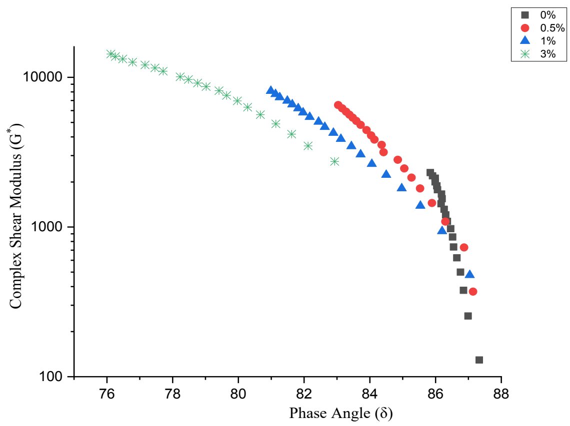

Fig. 10. Black diagram.

asphalt binder, the nanosilica particles are glued to the surface of the asphalt binder and a new structure of the nanosilica modified asphalt binders is formed. This new structure can absorb and transfer more load coming onto the asphalt binder and therefore improving the rutting resistance [24].

5.6. Multiple stress creep and recovery test

The impact of nanosilica addition on non-recoverable compliance J_{nr} and recovery is shown in Fig.12. It can be seen that the J_{nr} decreases with the addition of nanosilica. The base asphalt had the highest value of J_{nr} value at both the stress levels. As the concentration of nanosilica is increased J_{nr} value showed a decreasing trend. J_{nr} showed the same trend for both the stress levels. The decrease in the J_{nr} value with the addition of nanosilica may be attributed to the increased stiffness of the modified asphalt binder.

The addition of nanosilica enhances the elastic nature of the asphalt binder, which results in the improved recovery response. As can be seen from Fig.12, the recovery of the asphalt binder increases with the addition of nanosilica. Nanosilica modified binders showed a higher recovery response at both stress levels. The improved recovery response of the nanosilica modified binders' results in lesser strain accumulation in the binders and therefore enhances the rutting resistance.

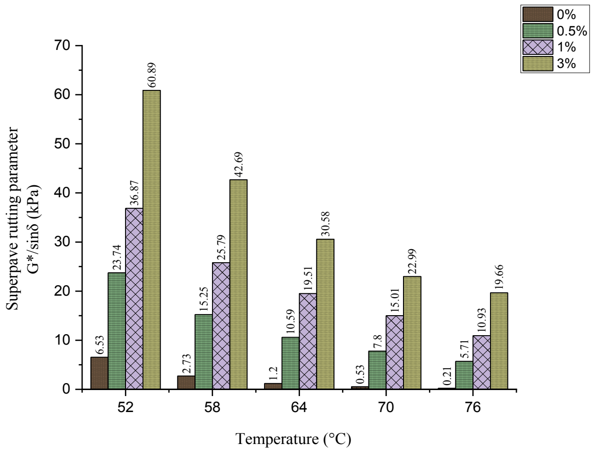

Fig. 11. Variation of Superpave rutting parameter with temperature.

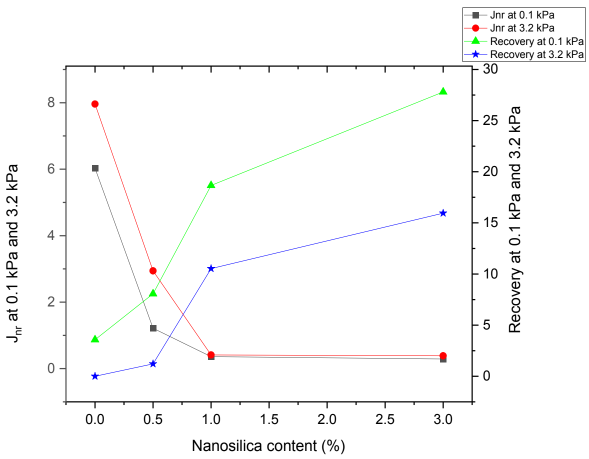

Fig. 12. Variation of J_{nr} and recovery values at 0.1 kPa and 3.2 kPa stress levels for different nanosilica contents.

5.6.1. Ranking of asphalt binders

As per AASHTO T350, non-recoverable creep compliance at 3.2 kPa can be used to determine the applicability of asphalt binder for a particular traffic level and load rate. Table 6 shows the different categories.

From the values of J_{nr}, it was found that control asphalt binder with 0% nanosilica failed at 64°C as per AASHTO M332-14. 0.5% nanosilica modified binder was found to be suitable for standard traffic grade "S". 1% nanosilica modified asphalt binder was found to be suitable for very heavy traffic grade "V". 3% nanosilica modified binder was found to be suitable for extreme grade "E". Thus, it may be concluded that addition of nano nanosilica significantly enhances the traffic grading capacity of the asphalt binder.

5.7. Creep test

Fig.13 shows the effect of creep loading on the strain values of base asphalt and nanosilica modified asphalt binders for a duration of 10 minutes at a temperature of 60°C. Strain shows a linear variation with the loading time and the slope of the line can be used as a parameter to evaluate the effect of loading on the deformation of the binder. A line with a higher slope indicates a higher rate of deformation and line with a lower slope indicates a lower rate of deformation. The base binder curve has the highest slope amongst the curves. With the addition of nanosilica the slope of the curve decreased as can be seen in Fig.13. The slope of the curve of the base binder was 41.57 s^{-1} and it decreased to 1.525 s^{-1} with 3% nanosilica content. This is due to a lower accumulation of strain in nanosilica modified binders. Thus, the addition of nanosilica to the asphalt binder improves its rutting resistance.

5.8. Linear amplitude sweep

Fig.14 shows the effect of nanosilica on the fatigue performance of asphalt binders at strain rates of 2.5% and 5%. The addition of

Table 6
Limiting values of J_{nr} for various traffic levels.

$J_{nr,3.2\ kPa}^{-1}$	Grade	Traffic designation	Load rate
$\le$ 4.5	Standard (S)	< 10 million ESAL	>70 km/h
$\le$ 2.00	Heavy (H)	10-30 million ESAL	20-70 km/h
$\le$ 1.00	Very heavy (V)	>30 million ESAL	<20 km/h
$\le$ 0.5	Extreme (E)	>30 million ESAL	<20 km/h

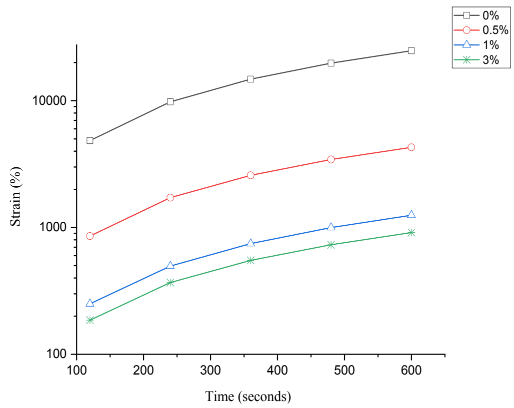

Fig. 13. Variation of strain with Creep loading for different nanosilica contents.

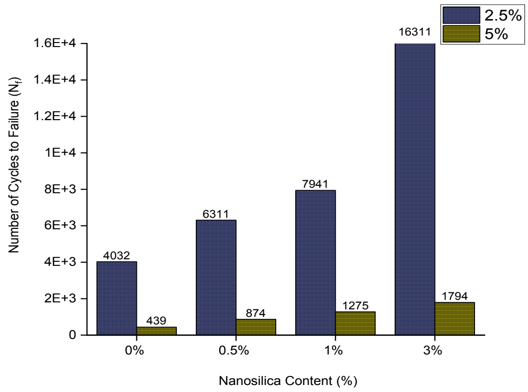

Fig. 14. Load cycles to failure at strain levels of 2.5% and 5% for control and nanosilica modified asphalt binders.

nanosilica significantly enhances the fatigue life of the asphalt binder. As is evident from the figure, addition of 3% nanosilica increases the number of failure cycles to 16311 from 4032 for control binder. The nanosilica particles have high specific surface area, and therefore have stronger interactions with different functional groups within the asphalt binder. This leads to the formation of a network within the asphalt binder that arrests the growth of microcracks and thereby enhances the fatigue performance.

5.9. Effect of nanosilica on aging resistance

Fig.15 shows the aging resistance of base asphalt binder and nanosilica modified asphalt binders. Results show that adding nanosilica to the asphalt binder decreases the rutting aging index of the binder. The improvement in aging due to the addition of nanosilica can be explained as follows. Asphalt being a polymer system is susceptible to aging, which is initiated by thermal scissions of carbon-carbon bonds associated with a transfer of hydrogen radical at the site of scission. When nanosilica is added to the control binder, due to its low surface potential work, it can migrate to the surface of the composite at higher temperatures and act as a potential heating barrier and protect the host polymeric chains of the asphalt binder [24]. With an increase in the nanosilica content, the oxidative process was found to slow down leading to a decrease in the aging resistance. For example, the addition of 3% nanosilica decreased the rutting aging factor from 185.83 to 10.22.

5.10. Self-healing potential of nanosilica modified binder

Fig.16 shows the variation in ductility self-healing values for base asphalt binder and nanosilica modified asphalt binders. The ductility test carried out after the 4-hour healing period showed that the base binder recovered by 64.41%. The binder recovery increases with incorporation of nanosilica particles in the asphalt binder. 3% of nanosilica improved the recovery by 82.48%. Thus, it can be concluded that the addition of nanosilica helps in the self-healing of the asphalt binder and hence in improving the service life of asphalt binders.

6. Conclusions

The study evaluated the effect of addition of nanosilica on the rheological properties of the asphalt binder. The effect of

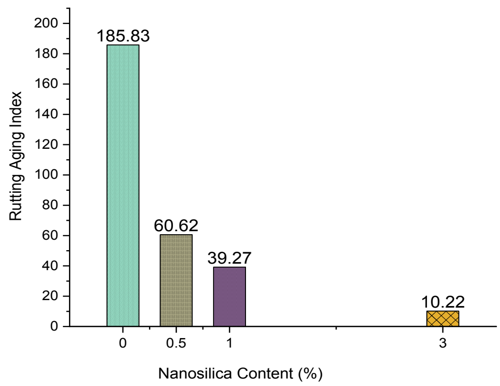

Fig. 15. Variation in rutting aging index with nanosilica content.

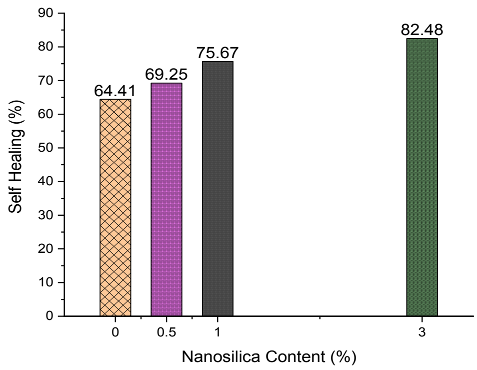

Fig. 16. Variation of ductility self-healing test for different percentages of nanosilica.

temperature and frequency on the complex modulus and phase angle has been studied. The resistance to permanent deformation has been evaluated by means of Superpave rutting parameter, MSCR, and creep tests. Linear amplitude sweep test was used for fatigue characterization of asphalt binders. The ageing resistance was evaluated by means of rutting ageing index. The following conclusions can be drawn from the study:

1. The addition of nanosilica increases the stiffness and improves the elastic nature of the control binder.
2. The addition of nanosilica decreases the temperature susceptibility of the binder.
3. Nanosilica modified binders showed shear thinning behaviour at certain temperatures. The base binder is a Newtonian fluid at 135°C, 100°C and at 60°C. It showed Newtonian behaviour up to shear rate of 10/s. Nanosilica modified binders show shear thinning behaviour at 60°C. Shear rate dependency increases with an increase in nanosilica content. Similar results are observed at a temperature of 100°C but to a lesser extent. The shear dependence of unmodified and Nanosilica modified binders vanishes at 135°C.
4. Complex modulus values increased and phase angle decreased with the addition of nanosilica, and the same was observed for the entire temperature and frequency range.
5. Nanosilica modified binders showed higher rutting resistance as compared to the unmodified binder. Rutting resistance was evaluated by using different approaches like $G^*/sin\delta$, MSCR, and creep tests. In all the approaches, it was found that the use of nanosilica enhances the rutting potential of the base binder.

6. The recovery aspect of the binder increased significantly when the concentration of nanosilica was increased to 3%, the improvement was seen for both the stress levels.
7. The linear amplitude sweep tests revealed that incorporation of nanosilica enhances the fatigue resistance of the asphalt binders by arresting the development of microcracks.
8. From investigations into the aging resistance, it was found that the aging resistance potential of the binder improves with the addition of nanosilica.
9. Nanosilica modified binders possess self-healing properties and therefore can help in improving the service life of the pavements.

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