

Rheological Properties of Hot and Warm Asphalt Binder Modified with Nanosilica

Dania ALOTHMAN*, Hüseyin GÖKÇEKUŞ, Shaban Ismael ALBRKA ALI

Civil Engineering Department, Faculty of Civil and Environmental Engineering, Near East University, Near East Boulevard, Nicosia, 99138 North Cyprus

crossref <http://dx.doi.org/10.5755/j02.ms.30170>

Received 22 November 2021; accepted 02 March 2022

The impact of base and zycotherm binders modified with various proportions of nanosilica (i.e., 2 %, 4 %, and 6 %) based on the weight of the binder at high-temperature performance was investigated. Brookfield viscosity, penetration, softening point, and storage stability tests were all conducted on base and modified binders. Moreover, the Superpave rutting parameter ($G^*/\sin \delta$) and Multiple stress creep recovery (MSCR) were utilized to assess the resistance of binders to rutting. By observing the outcomes of the modified binder tests, the incorporation of nanosilica into the base and zycotherm binders improved temperature susceptibility. Binders modified with nanosilica showed remarkable storage stability at elevated temperatures, as the variation in softening point between the upper and bottom parts was less than 2.5 °C for all binders. Based on the outcomes of the Superpave rutting parameter, the inclusion of nanosilica enhanced the stiffness of the modified binders up to 130 % for 6 % of nanosilica, while the improvement was caused by 6 % of nanosilica with zycotherm was nearly 92 % at 70 °C. The MSCR test revealed that the base and zycotherm binders' recovery ($R\%$) was 27.72 % and 25.99 % for 6 % of nanosilica and 6 % nanosilica with zycotherm, respectively, while the nonrecoverable creep compliance (J_m) decreased by 56.87 % for 6 % of nanosilica, and 43.23 % for 6 % nanosilica with zycotherm at 100 MPa. The results show that the incorporation of nanosilica is capable of improving the rutting potential regardless of the levels of stress. The rheological characteristics of modified base and zycotherm binders were improved at all concentrations of nanosilica, with the optimal concentration being 6% nanosilica.

Keywords: MSCR, nanosilica, rheological behavior, superpave rutting parameter, zycotherm.

1. INTRODUCTION

For road construction, various grades of asphalt are usable based on their penetration of 30/40, 60/70, and 80/100. The continual increase in high traffic volume with regard to commercial vehicles, as well as significant daily and weather temperature variations, has resulted in the development of road properties [1]. Asphalt pavement must have the ability to withstand various loads during its service life to ensure optimal effectiveness for flexible pavements. Rutting a significant source of distress in bitumen mixtures, rendering it one of the most important design factors for flexible pavements [2]. In the most essential design circumstances of flexible pavements, rutting is recognized and exploited as the initial failure mechanism. However, rutting is considerably aided by the total persistent deformation caused by the accumulation of strain in various layers of the asphalt pavement. One of the most important qualities that determine how long asphalt pavements last is their resistance to rutting [3]. Rutting accelerates pavement deterioration, raises the cost of maintenance and replacement costs, decreases user comfort and safety, reduces pavement serviceability, and increases overall road infrastructure costs [4]. Traditional tests like softening point, ductility, and penetration, as well as rheological techniques like Dynamic Shear Rheometer (DSR), Rotational Viscosity (RV), and Bending Beam Rheometer (BBR) have been extensively utilized to assess the physical and rheological characteristics of bitumen binder [5]. Traditional linear viscoelastic assessment using DSR by

assessing the Superpave rutting parameter and contemporary tests, including MSCR, which is generally conducted in DSR, are examples of asphalt binder tests that may be connected to rutting resistance [6].

Recently, the need for excellent asphalt binder performance has led to the increased application of modifiers like synthetic waxes, polymers, and nanoparticles [7]. Other than conventional modifiers, several nanomaterials such as nano-alumina, nano-tubes, and nano-clays have been investigated for use as asphalt binder modifiers [8–10]. The inclusion of nanomaterial enhances the physical and/or chemical characteristics of bitumen, resulting in nano-modified bitumen with improved performance [9]. Nano-materials such as nanosilica have been shown to enhance the binder characteristics in recent studies [11]. Inorganic additives such as nanosilica have been widely utilized to improve the characteristics of bitumen binders [12]. Because of its large surface area as well as stability, nanosilica has been considered a promising material for developing and synthesizing new multifunctional materials [13]. The application of nanosilica allows the asphalt binder to stiffen and enhances the susceptibility of high temperatures, as shown in the decreased penetration and increased softening point. Moreover, it can be observed that the performance grade of the asphalt binder is also improved after the addition of nanosilica [14]. According to existing research on nanosilica, the addition improves temperature stability as well as moisture susceptibility resistance [15], and also

* Corresponding author. Tel: +962789890000.

E-mail address: 20177819@std.neu.edu.tr (D. Alothman)

leads to improvements in complex shear modulus (G^*) [16]. The use of nanosilica with 2 %, 4 %, and 6 % by the weight of asphalt was examined. A rolling thin film oven (RTFO) was used to age the bitumen binder for a short period. As a consequence, it was revealed that applying nanosilica to asphalt improves its complex modulus and viscosity, G^* and η^* , respectively [17]. The addition of nanosilica into the bitumen binder at percentages of 4% and 6% by weight resulted in improved rutting resistance, fatigue cracking, and aging performance of nanosilica modified binders [18]. Lushinga et al. showed that the inclusion of nanosilica to PMB increased viscosity, enhanced storage stability, increased complex shear modulus, and decreased binder rutting [19]. Many previous studies have found that the incorporation of nanosilica into the neat binder enhances its rut resistance [20–22].

The use of the Superpave rutting parameter $G^*/\sin \delta$ has been the focus of the majority of studies conducted to assess rutting resistance [12, 23, 24]. While $G^*/\sin \delta$ is commonly utilized to evaluate the rutting ability of asphalt binders, the rutting resistance of asphalt mixes is not well correlated with $G^*/\sin \delta$ [25]. As a result, sophisticated characterization techniques like the Multiple Stress Creep Recovery (MSCR) test are used [26–28]. To further assess the performance of bitumen binders at elevated temperatures, the MSCR test and the non-recoverable creep compliance (J_{nr}) were suggested. J_{nr} can correctly assess the asphalt binder's rutting resistance as a substitute to the rutting parameter. Shafabakhsh et al. showed that at various levels of stress, increasing the nanosilica dose boosts percent recovery ($R\%$) and reduces J_{nr} . In addition, it was revealed that the addition of 3 % of nanosilica had no effect on rutting resistance; however, the addition of 7% of nanosilica greatly improved the control asphalt binder's elevated temperature performance [20]. Ghanoon and Tanzadeh conducted research on modified asphalt binder utilizing 2 %, 4 %, and 6 % of nanosilica to evaluate how this modifier affects rutting performance while employing MSCR. The results demonstrated that in comparison to the base sample, the nanosilica modifier raised the percent of creep recovery ($R\%$), lowered the J_{nr} value, and reduced the cumulative strain [21]. Bhat and Mir demonstrated that nanosilica modified binders displayed increased rutting resistance in comparison to unmodified binders. In their research, the rutting resistance was analyzed by utilizing various methods such as MSCR, $G^*/\sin \delta$, and creep assessments. All the methods revealed that the application of nanosilica improved the rutting resistance of the neat binder [22]. Sukhija et al. investigated the rutting resistance of neat asphalt binder after adding 2 % and 4% nanosilica. According to their findings, the inclusion of nanosilica raised the performance grade (PG), reduced J_{nr} , increased $R\%$, and reduced stress susceptibility [29].

In addition to using nanosilica, using nanozycotherm as a warm mix binder additive is a potential option. The asphalt concrete industry has been criticized for its excessive use of natural resources and energy, as well as its high emissions, particularly CO_2 . As a result, emerging countries should adopt materials that are environmentally friendly [30]. The emission of toxic components into the environment as a result of heavy traffic has an impact on the atmosphere's climatic potential [31]. Therefore, warm mix asphalt

(WMA) has been explored and investigated in several nations because of its lower energy consumption and lower hazardous chemical impacts [32]. Warm mix asphalt technologies are applied to decrease the asphalt production temperature to 120–135 °C and compaction temperature to 105–120 °C [33]. Fuel usage and the emissions of greenhouse gases are the two primary advantages of such a reduction. Longer transport distances, as well as an extended construction period and improved workability of asphalt mixtures are all benefits of WMA technology [34].

In recent years, extensive research has been performed on WMA technologies relating to the use of various kinds of additives. For instance, the impacts of zycosoil were studied by Arabani et al. for both dry and wet circumstances; the use of zycosoil increased the surface energy of adherence between both the bitumen binder and aggregate, according to their research [35]. To test WMA, Goh et al. utilized cecabase at 0.20, 0.30, and 0.35 percent by weight of bitumen binder. According to the findings of the tests, the addition of cecabase did not influence the dynamic modulus or moisture damage susceptibility of the mixture [36]. Moreover, Yang et al. evaluated the mechanical and environmental characteristics of crumb rubber modified with evotherm. According to the findings, the crumb rubber modified with evotherm performed much better and was more environmentally-friendly than hot mix asphalt (HMA) [37]. Shafabakhsh et al. utilized zycotherm to enhance the aggregate and asphalt binder adhesive bonding. Their findings showed that zycotherm decreased the asphalt mixture's sensitivity to moisture degradation [38]. The impacts of zycotherm in bitumen binder and asphalt mixes were the focus of another investigation. The findings revealed that WMA mixes with 0.1 percent of zycotherm performed similarly to or better than typical HMA mixes [39]. Ibrahim and Mehan conducted a study involving DSR and BBR assessments. The study revealed increments in rutting parameter ($G^*/\sin \delta$), fatigue parameter ($G^* \sin \delta$), creep stiffness, and also the m-values for each zycotherm-modified asphalt binder, and when 0.5 % of zycotherm was added, all these outcomes reflected higher values [40].

Many researchers have extensively utilized nanosilica to enhance asphalt binder through conventional and rheological testing with and without additions [14, 18, 41, 42]. Individually, zycotherm and nanosilica are effective asphalt binder modifiers. However, their compatibility as a couple is an area of research that requires further investigation. As a result, this research aims to investigate the possibility of modifying the asphalt binder containing zycotherm by adding varying concentrations of nanosilica. The following research focuses on investigating the physical and rheological characteristics of bitumen modified with nanosilica, zycotherm, and zycotherm/nanosilica given that the effect of zycotherm/nanosilica on rutting resistance has yet to be identified.

2. MATERIALS

2.1. Bitumen

The 60/70 grade bitumen binder was used as a reference in this study. Table 1 lists the properties of the bitumen binder.

Table 1. The physical properties of base bitumen binder

Test	Unit	Result	Test method
Penetration	0.1 mm	67	ASTM D5
Softening point	°C	50	ASTM D36
Ductility	cm	100	ASTM D113
Flash point	°C	322	ASTM D92
Rotational viscosity at 135 °C	Pa.s	0.5672	ASTM D4402

2.2. Nanosilica (NS)

This study utilized colloidal nanosilica to modify the properties of bitumen. Table 2 lists the nanosilica characteristics.

Table 2. The physical properties of nanosilica

Property	Unit	Value
Appearance		Translucent liquid
pH	-	6.71
Density (20 °C)	g/cm ³	1.2050
Viscosity (20 °C)	mPa.s	3.05
Particle size	nm	11

2.3. Zycotherm (ZT)

Zycotherm is a nano organic addition to asphalt derived from the silanol group (Si-OH). Zycotherm is a chemical warm mix additive that reaps substantial benefits from WMA technologies. In this study, a concentration of zycotherm of 0.1 % by weight of bitumen was selected. Table 3 lists the attributes of zycotherm.

Table 3. The physical properties of zycotherm

Property	Value
Ingredients	Hydroxyalkyl-alkoxy-alkylsilyl compounds, benzyl alcohol, and ethylene glycol
Color	Pale yellow
Physical state	Liquid
Odor	Odorless
pH	10 % solution in water neutral or slightly acidic
Viscosity	1–5 Pa.s
Specific gravity (25 °C)	0.97 g/cm ³
Flash point	> 80 °C

3. EXPERIMENTAL METHODOLOGY

To determine the appropriateness of nanosilica for bitumen modification, a set of experiments were conducted on various mixes of unmodified and modified bitumen binder. The experimental system used to exhibit the full scope of this research study is depicted in Fig. 1.

3.1. Modified bitumen preparation

Firstly, to achieve the processing viscosity, the base bitumen binder was heated to 160 °C. To prepare a nanosilica modified bitumen binder, the binder was blended with different percentages (2 %, 4 %, and 6 % of nanosilica) of the original binder weight. The nanosilica was gradually integrated into the hot binder while the mixture was agitated using a mechanical mixer. For 60 minutes, the rotational stirring speed was maintained at 1800 rpm.

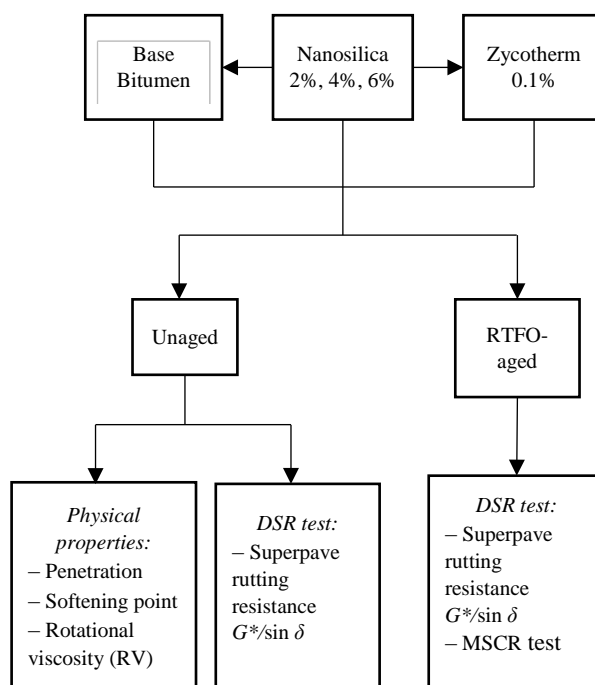


Fig. 1. The flowchart of the present study

The modified bitumen binder samples were placed in the oven before being used in the tests to eliminate unwanted bubbles. Zycotherm binder was produced using a content of 0.1 % of the binder's weight, as recommended by the manufacturer. The mechanical stirrer was configured to generate a 15–30 mm deep vortex within the bitumen at a sufficiently high speed. The zycotherm was then dropped into the center of the vortex, while the asphalt was agitated at 130 °C using a 1 ml syringe at a rate of 10 drops per minute. The mixing operation was completed after 15 minutes of stirring. To produce zycotherm/nanosilica composite modified binders, base bitumen was blended with 0.1 % zycotherm by weight of bitumen binder using the warm melting process, and then the nanosilica was gradually added to the mix by 2, 4, and 6 % and blended with bitumen binder at 1800 rpm at 130 °C. The softening point test was used to assess the homogeneity of the produced mixes. Specimens were obtained every 20 minutes to assure homogeneity. After the softening point readings were almost stabilized, it was determined that 1 hour was the best mixing time.

3.2. Aging conditions of bitumen binders

Short-term aging was employed to condition the base bitumen and modified binders. A rolling thin film oven (RTFO) was utilized to mimic the circumstances of short-term aging. According to ASTM D 2872, 35 grams of bitumen must be deposited in open-mouthed cylinder bottles and then placed in a heated carousel-ready oven at a temperature of 163 °C, which rotates at 15 rpm under air blown pressure for 85 minutes. The test specimens were used in the RTFO-aged bitumen's rheological assessment.

3.3. Physical properties tests

The following tests were used to determine the basic characteristics of the base bitumen and the modified binders: penetration test (ASTM D5), softening point test

(ASTM D36), and viscosity test with a Brookfield Rotational Viscometer (ASTM D4402).

3.4. Temperature susceptibility

The bitumen binder is made of thermoplastic material, which means it softens as the temperature rises and hardens as the temperature drops. The temperature susceptibility of base and modified binders was examined using a penetration index (PI). To determine the PI, the temperature susceptibility of binders was estimated using penetration at 25 °C and softening point findings, as given in Eq. 1 [43].

$$PI = \frac{1952 - 500 \log(Pen_{25}) - 20SP}{50 \log(Pen_{25}) - SP - 120}, \quad (1)$$

where (Pen_{25}) is the value of asphalt binder penetration in 0.1 mm at 25 °C, and (SP) is the value of asphalt binder softening point in °C.

3.5. Storage stability

The bitumen high-temperature storage stability was assessed using a hot storage stability method. This method is used to assess a binder's stability to withstand phase separation at elevated temperatures. Separately prepared binders were placed into a 140 mm high, 30 mm diameter aluminium foil tube. For 48 hours, the tube was maintained upright in a 163 °C oven. Following the previous conditioning time, the aluminium tubes were placed vertically in a -10 °C freezer. The tubes were then divided into three halves of similar lengths. The softening points of the upper and bottom portions then were tested in line with ASTM D36. Once the difference between both the softening points of the upper and bottom portions reaches a maximum of 2.5 °C, the blend is deemed stable [44].

3.6. Dynamic shear rheometer (DSR) test

The rheological characteristics of asphalt were identified through its viscous and elastic features at elevated temperatures. The DSR was utilized to perform Superpave rutting resistance and multiple stress creep recovery tests (MSCR) consistent with ASTM D7175 and ASTM D7405, respectively. The assessments were conducted to analyze the rheological features of base bitumen and zycotherm binder that were modified by using various percentages of nanosilica. The assessments were performed by using the binder models that were set between two parallel DSR plates with the following dimensions: 25.0 mm in diameter and 1.0 mm in thickness. The rheological indicators that are frequently acquired from the DSR experiment are the complex modulus (G^*) and phase angle (δ). Moreover, the MSCR test was employed to identify the non-recoverable creep compliance (J_{nr}) and the recovery percentage ($R\%$) for the base and zycotherm binders modified with nanosilica in RTFO aged state.

3.6.1. Rutting resistance parameter

To evaluate the base and modified binders' resistance to rutting, the Superpave rutting parameter was utilized according to ASTM D 7175-15. The Superpave criterion is used to identify asphalt binders that fail at high temperatures. When $G^*/\sin \delta$ rises, the binder deformation is minimized during loading. Concerning the non-aged

asphalt binder, the $G^*/\sin \delta$ ratio must exceed 1kPa ($G^*/\sin \delta > 1$ kPa), while for the aged binder on a short-term basis, the $G^*/\sin \delta$ must be greater than 2.2 kPa ($G^*/\sin \delta > 2.2$ kPa) based on ASTM D 2872. On both unaged and RTFO-aged binders, the evaluation was performed using a dynamic shear rheometer with a parallel disc that had a diameter of 25 mm and a distance of 1 mm. The test technique was conducted at a frequency of 10 rad/sec with temperatures varying from 58 °C to 76 °C with 6 °C temperature gaps.

3.6.2. Multiple stress creep recovery (MSCR) test

The multiple stress creep recovery test while using a DSR was applied to the RTFO-aged specimens. The MSCR test can be undertaken at various levels of stress. Due to their remarkable consistency among the rutting outcomes of asphalt binders and mixtures, D'Angelo *et al.* recommended the use of 100 and 3200 Pa levels of stress [45]. The testing of the samples was done in replicas by utilizing a 25 mm plate and 1 mm distance with a temperature of 64 °C, while the levels of stress were 100 and 3200 Pa. For ten cycles at each stress stage, invariable stress creep with a duration of 1 second and a recovery time of 9 seconds was conducted by applying the MSCR test. The percent recoverable ($R\%$) and non-recoverable factor of creep compliance (J_{nr}) were identified at the end of the ten cycles. J_{nr} is known as the proportion of nonrecoverable shear strain to shear stress utilized in the loading period. The J_{nr} values can reflect both the modified and base asphalt binders' stress dependence. Eq. 2 and Eq. 3 quantify the two constraints, respectively.

$$J_{nr} = \frac{\varepsilon_r - \varepsilon_0}{\sigma}, \quad (2)$$

where J_{nr} represents the nonrecoverable creep compliance (kPa^{-1}), ε_r symbolizes the strain value at the end of the recovery stage, ε_0 symbolizes the value of strain at the beginning of the creep stage, and σ symbolizes the utilized stress throughout the loading period (kPa).

$$R\% = \frac{\varepsilon_c - \varepsilon_r}{\varepsilon_c - \varepsilon_0} \times 100, \quad (3)$$

where $R\%$ is the percentage recovery, and ε_c symbolizes the end-of-creep stage strain value.

4. RESULTS AND DISCUSSION

4.1. Physical properties binder tests

Fig. 2 illustrates the effect of adding nanosilica to the base and zycotherm binders. It can be observed that the penetration decreases and the softening point increases. Furthermore, each nano-modified asphalt specimen attained a lower penetration and higher softening point in contrast to the base and zycotherm binders. The reduction in the penetration values implies the stiffening impact of the binder, whereby the stiffening increases in line with the increased nanosilica concentration.

To obtain the viscosity values of the base and nano-modified binders, the Brookfield rotational viscometer was used at a range of temperatures between 135 °C and 195 °C. At elevated temperatures, all of the asphalt binder samples exhibited low viscosity values, as shown in Fig. 3.

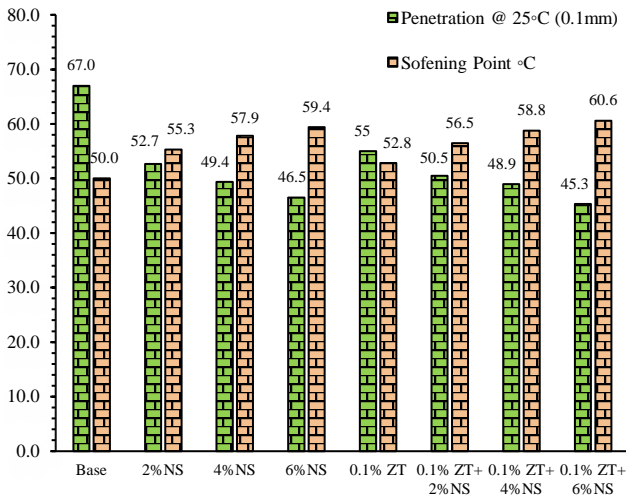


Fig. 2. Penetration and softening point of base and modified bitumen binders

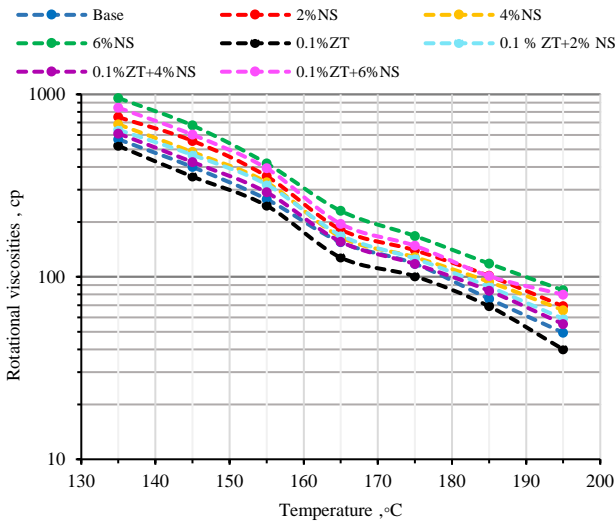


Fig. 3. The viscosity of base and modified bitumen binders

The viscosity values are often lowered as the temperature rises. The addition of nanosilica to the base binder causes the viscosity of the nanosilica modified binders to increase. Furthermore, according to the Superpave criteria, at 135 °C the viscosity values were within the limits, and the nanosilica modified binders acquired lower viscosity values in comparison to the maximum threshold at 3 Pa s. However, with regard to the 4 % NS, chemical changes and physical diffusions may occur during the process of mixing the nanosilica modified binders, resulting in the development of a new structure and a reduction in viscosity as compared to other percentages. Additionally, when stress is applied, nanosilica can strengthen the base binder and improve the recovery capabilities.

When nanosilica is added to zycotherm binder, however, the viscosity is reduced significantly. Zycotherm binder has a significant impact on viscosity reduction.

Table 4. PI of base and modified bitumen binders

Binder	Base	2% NS	4% NS	6% NS	0.1% ZT	0.1% ZT + 2% NS	0.1% ZT + 4% NS	0.1% ZT + 6% NS
PI	-0.495	0.165	0.555	0.727	-0.296	0.350	0.719	0.900

Zycotherm is a beneficial feature for an addition, especially when evaluating its efficacy because it reduces functioning temperatures, which aids in the preparation of possible cost-effective and sustainable pavements. When zycotherm is in a liquid state, it is one of the factors that causes the viscosity to decrease.

4.2. Temperature susceptibility

The penetration index (PI) is a tool used for estimating bitumen's temperature susceptibility. For base asphalt, the PI value varies from (-3) to (+7), with smaller values indicating a more temperature-sensitive bitumen and vice versa. Table 4 shows that adding nanosilica stiffened the base and zycotherm binders, with max and min PI values of 0.900 and -0.495, respectively. Increased PI values indicate that the penetration value has decreased and the softening point has increased. Moreover, the lower the temperature susceptibility of the bitumen binder, the greater the penetration index value. All percentages of nanosilica utilized in this research are appropriate for road construction because all the PI values are within the range of +1 and -1 [46].

4.3. Storage stability

Storage stability was conducted to determine the modifier's stability and suitability with a bitumen binder at high temperatures. The softening points of the base and the modified binders are shown in Fig. 4.

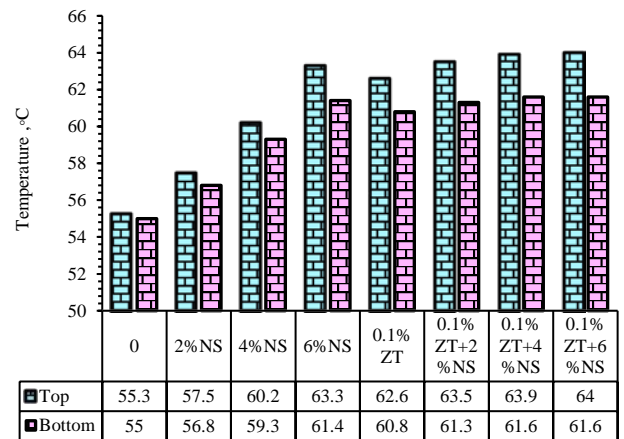


Fig. 4. The softening point difference between the top and bottom portions of the base and modified bitumen binders

For all nanosilica concentrations, the storage stability of nanosilica modified samples was increased. Furthermore, the stability of bitumen samples with 0.1 % zycotherm was acceptable. The variation in softening point between the upper and bottom parts was below 2.5 °C for all binders, as shown in the figure, demonstrating that all these binders may be kept at high temperatures and remain stable. As a result, it can be inferred that nanosilica is a stable substance that can be utilized to modify the bitumen binder.

4.4. Superpave rutting resistance parameter

As depicted in Fig. 5, the Superpave rutting parameter ($G^*/\sin \delta$) was examined at various temperatures to determine the improvement in the binder's rutting resistance following the inclusion of nanosilica to base and zycotherm binders. The obtained $G^*/\sin \delta$ parameter for un-aged binders can be observed in Fig. 5 a. Nanosilica modified binders have higher $G^*/\sin \delta$ values than the base and zycotherm binders. Furthermore, as compared to base bitumen at 70 °C, the zycotherm modified binder exhibited an improvement of 8.14 % in terms of potential rutting resistance. Previous studies have revealed similar findings, indicating that the addition of zycotherm has an impact on rutting resistance [40, 47], but this value rose dramatically after the addition of nanosilica. According to the outcomes of the modified binders, the incorporation of nanosilica to base and zycotherm binders resulted in considerable enhancement levels at all temperatures. Fig. 5 b depicts the $G^*/\sin \delta$ parameter for RTFO- aged binder, $G^*/\sin \delta \geq 2.2$ kPa can be utilized to evaluate the binder's rutting performance. The $G^*/\sin \delta$ value of all nanosilica modified binders is greater than those of the base and zycotherm binders, which is similar to the un-aged condition. The greatest $G^*/\sin \delta$ value was observed in base and zycotherm binders containing up to 6 % NS by weight of the binder, followed by binders containing 2 % NS, while the lowest $G^*/\sin \delta$ value was observed in binders containing 4 % NS. Meanwhile, 4 % NS has the lowest $G^*/\sin \delta$ despite passing the Superpave criteria under unaged and RTFO aged conditions. It's possible that the chemical reactions of nanosilica were to cause [48]. It is important to note that the Superpave rutting parameter is dependent on bitumen binder stiffness. The addition of nanosilica makes bitumen binders stiffer, and this is

beneficial for rutting. The rutting improvement is due to nanosilica dispersion inside the bitumen binder, where the nanosilica particles adhere to the binder's surface, generating a new nanosilica modified binder network structure. This improved structure can absorb and transmit extra load to the bitumen binder, resulting in enhanced rutting resistance [18].

The results show that at 64 °C, both the base and zycotherm binders have a high-performance grade (PG). High-temperature performance grade is defined as the highest temperature where $G^*/\sin \delta \geq 1.0$ kPa. The results of $G^*/\sin \delta$ at various temperatures show that adding nanosilica to the base and zycotherm binders at any concentration (2–6 %) enhances the binder's performance grade at high temperatures, resulting in a one-grade increase.

4.5. MSCR test

The recovery percentages at 100 Pa and 3200 Pa stress levels for the base and modified binders are shown in Fig. 6 a. According to an analysis of the obtained results at each stress level, the value decreased at 3200 Pa compared to 100 Pa. According to the data acquired at 100 Pa stress level, the recovery of the base binder was 6.6 %, and it increased to 24.28 %, 20.56 %, and 27.72 % with the addition of 2 %, 4 %, and 6 % of nanosilica, respectively. While zycotherm binder (0.1%) showed 7.84 % recovery, it increased to 20.54 %, 15.14 %, and 25.99 % with the addition of 2 %, 4 %, and 6 % of nanosilica, respectively. At 3200 Pa stress level, a comparable enhancement was observed. The addition of nanosilica to the base and zycotherm binders improved the asphalt binder's elasticity, resulting in an improved recovery performance.

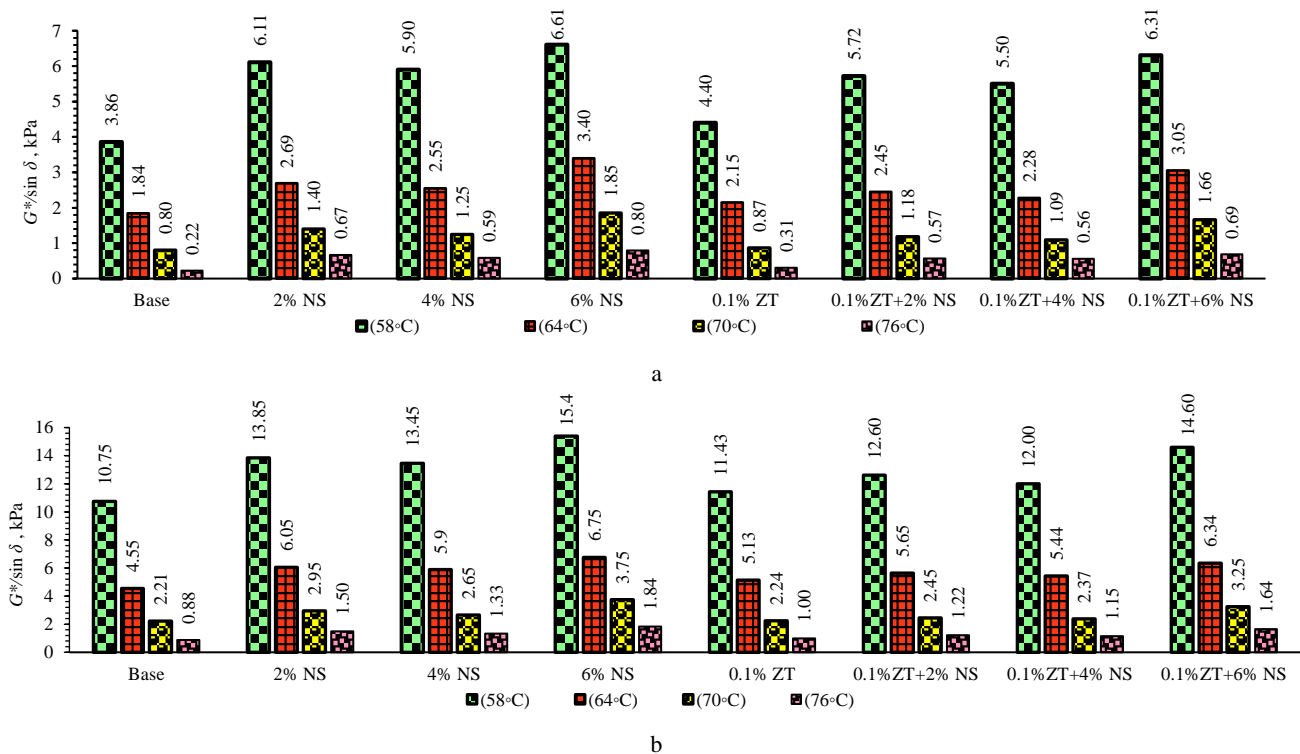


Fig. 5. The Superpave rutting parameter ($G^*/\sin \delta$) of base and modified bitumen binders: a – un-aged; b – after RTFO

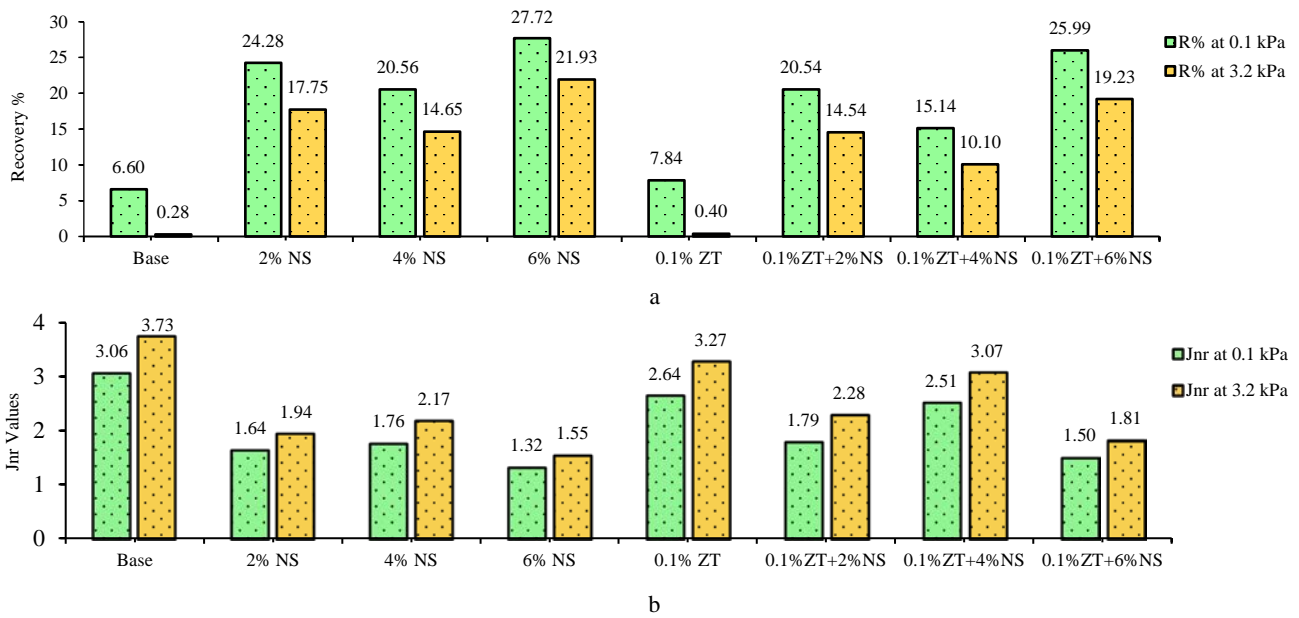


Fig. 6. The MSCR of base and modified bitumen binders: a – $R\%$ at 0.1 kPa and 3.2 kPa levels of stress; b – the non-recoverable creep compliance (J_{nr}) at 0.1 kPa and 3.2 kPa levels of stress

The use of nanosilica boosts the recovery value, as seen by the data collected. The elastic recovery improved at all concentrations, with 6 % nanosilica showing the greatest improvement; however, the improvement was minor when 4 % nanosilica was added. This is also consistent with the findings of Arshad et al. [49].

To assess the influence of the binder on rutting performance, the nonrecoverable creep compliance (J_{nr}) constraint was applied. Fig. 6 b demonstrates how the addition of nanosilica to the bitumen changes the J_{nr} . A smaller J_{nr} value is preferable in terms of rutting. Rutting resistance enhances with the addition of nanosilica. This is due to nanosilica's greater surface area, which causes an interconnected network to develop inside the underlying bitumen binder, thus boosting stiffness.

According to the findings, the J_{nr} increases as the degree of stress increases from 100 to 3200 Pa. At increasing levels of stress, the effectiveness of modification is proven to be more favorable. This demonstrates the efficacy of nanosilica in enhancing bitumen binders' stress sensitivity [29]. At 100 Pa, the decreases of J_{nr} in comparison with the base bitumen were 46.27 %, 42.44 %, and 56.87 % when nanosilica was added at 2 %, 4 %, and 6 %, respectively. Moreover, the zycotherm binder reduced the J_{nr} value by 13.54 % in comparison to base bitumen, indicating that the bitumen binder decreased the susceptibility of bitumen to permanent deformation. Mirzababaei et al. stated that 0.1 % of zycotherm can enhance binders' resistance to rutting by decreasing the non-recoverable values [47]. However, the reduction in J_{nr} for zycotherm binder was increased with the addition of 2 %, 4 %, and 6 % nanosilica by 41.43 %, 17.85 %, and 50.92 %, respectively in comparison to base bitumen. The reduction in J_{nr} revealed that nanosilica particles improved the rutting resistance of the zycotherm binder. The decline in the J_{nr} values with the inclusion of nanosilica might be explained by the modified bitumen binders' increased stiffness.

5. CONCLUSIONS

The physical and rheological characteristics of base and zycotherm binders modified with different percentages (i.e., 2 %, 4 %, and 6 %) of nanosilica were investigated in this research. Based on the findings and discussion provided above, the following conclusions may be derived.

1. According to the physical attributes (penetration and softening point) outcomes, adding nanosilica to the base bitumen reduces the penetration while increasing the softening point. The stiffness effect of the bitumen binder is indicated by the reduction in penetration, while the stiffness also improves as the nanosilica concentration rises. The bitumen binder's softening point increased, suggesting that its temperature susceptibility has improved. Furthermore, as compared to the base and nanosilica modified binders without zycotherm, the zycotherm binders modified with nanosilica showed superior enhancement.
2. The incorporation of nanosilica into the base bitumen increased its viscosity, which could be related to the stiffening of the nanosilica enhanced bitumen binder. However, the base binder modified with nanosilica had greater values than the zycotherm binders modified with nanosilica. As a result, adding zycotherm reduces viscosity. At 135 °C, the modified binders' viscosity values were all within the Superpave standards.
3. By adding nanosilica into the base binder, the high-temperature susceptibility decreased while zycotherm binders modified with nanosilica showed a superior performance.
4. By incorporating nanosilica into the base and zycotherm binders for storage stability, all modified binders containing nanosilica were shown to remain stable when maintained at elevated temperatures.
5. According to the Superpave rutting resistance parameter, it can be inferred that adding nanosilica to the base and zycotherm binders raises the complex

modulus (G^*) and lowers the phase angle (δ), resulting in a higher $G^*/\sin \delta$. The increase in $G^*/\sin \delta$ reflects the influence of nanosilica in stiffening and improving the elasticity of the base and zycotherm binders, rendering them more rut-resistant. Furthermore, adding nanosilica to the base and zycotherm binders resulted in a one-grade improvement in the performance grade.

6. With the incorporation of nanosilica, the recovery of the base and zycotherm binders was enhanced, while the non-recoverable creep compliance was reduced, indicating that the nanosilica particles improved the rutting resistance.
7. Generally, nanosilica modified binders enhanced physical and rheological characteristics at all percentages. The current research showed that adding nanosilica to the base and zycotherm binders could prevent bitumen from rutting at elevated temperatures. For all the rheological methods, the trend of enhancement in rutting resistance vs the percentage of the nanosilica used is the same.

REFERENCES

1. **Cetin, M.** Landscape Engineering, Protecting Soil, and Runoff Storm Water *Advances in Landscape Architecture-Environmental Sciences* 2013: pp. 697–722. <https://doi.org/10.5772/55812>
2. **Bhat, F.S., Mir, M.S.** Performance Evaluation of Nanosilica-modified Asphalt Binder *Innovative Infrastructure Solutions* 4 (1) 2019: pp. 1–10. <https://doi.org/10.1007/s41062-019-0249-5>
3. **Shaheen, M., Al-Mayah, A., Tighe, S.** Effects of High Friction Aggregate and PG Plus Binder on Rutting Resistance of Hot Mix Asphalt Mixtures *International Journal of Pavement Engineering* 18 (4) 2017: pp. 292–302. <https://doi.org/10.1080/10298436.2015.1065996>
4. **Al-Sabaeci, A.M., Napiyah, M.B., Sutanto, M.H., Alaloul, W.S., Zoorob, S.E., Usman, A.** Influence of Nanosilica Particles on the High-temperature Performance of Waste Denim Fibre-modified Bitumen *International Journal of Pavement Engineering* 2020: pp. 1–14. <https://doi.org/10.1080/10298436.2020.1737060>
5. **He, R., Wu, S., Wang, X., Wang, Z., Chen, H.** Temperature Sensitivity Characteristics of SBS/CRP-Modified Bitumen after Different Aging Processes *Materials* 11 (11) 2018: pp. 2136. <https://doi.org/10.3390/ma11112136>
6. **Jing, R., Varveri, A., Liu, X., Scarpas, A., Erkens, S.** Rheological, Fatigue and Relaxation Properties of Aged Bitumen *International Journal of Pavement Engineering* 21 (8) 2020: pp. 1024–1033. <https://doi.org/10.1080/10298436.2019.1654609>
7. **Nejad, F.M., Nazari, H., Naderi, K., Karimiyan Khosroshahi, F., Hatefi Oskuei, M.** Thermal and Rheological Properties of Nanoparticle Modified Asphalt Binder at Low and Intermediate Temperature Range *Petroleum Science and Technology* 35 (7) 2017: pp. 641–646. <https://doi.org/10.1080/10916466.2016.1276589>
8. **You, Z.** Nanomaterials in Asphalt Pavements *International Journal of Pavement Research and Technology* 6 (3) 2013: pp. IV. [https://doi.org/10.6135/ijprt.org.tw/2013.6\(3\).iv](https://doi.org/10.6135/ijprt.org.tw/2013.6(3).iv)
9. **Li, R., Xiao, F., Amirhanian, S., You, Z., Huang, J.** Developments of Nano Materials and Technologies on Asphalt Materials – a Review *Construction and Building Materials* 143 2017: pp.633–648. <https://doi.org/10.1016/j.conbuildmat.2017.03.158>
10. **Martinho, F.C., Farinha, J.P.S.** An Overview of the Use of Nanoclay Modified Bitumen in Asphalt Mixtures for Enhanced Flexible Pavement Performances *Road Materials and Pavement Design* 20 (3) 2019: pp. 671–701. <https://doi.org/10.1080/14680629.2017.1408482>
11. **Arshad, A.K., Shaffie, E., Hashim, W., Rahman, Z.A.** Evaluation of Rutting Resistance of Dense Graded Asphaltic Concrete with Nanosilica Modified Binder *AIP Conference Proceedings* 2018: pp. 020025. <https://doi.org/10.1063/1.5062651>
12. **Enieb, M., Diab, A.** Characteristics of Asphalt Binder and Mixture Containing Nanosilica *International Journal of Pavement Research and Technology* 10 (2) 2017: pp. 148–157. <https://doi.org/10.1016/j.ijprt.2016.11.009>
13. **Senff, L., Labrincha, J.A., Ferreira, V.M., Hotza, D., Repette, W.L.** Effect of Nano-silica on Rheology and Fresh Properties of Cement Pastes and Mortars *Construction and Building Materials* 23 (7) 2009: pp. 2487–2491. <https://doi.org/10.1016/j.conbuildmat.2009.02.005>
14. **Ezzat, H., El-Badawy, S., Gabr, A., Zaki, E.S.I., Breakah, T.** Evaluation of Asphalt Binders Modified with Nanoclay and Nanosilica *Procedia Engineering* 143 2016: pp. 1260–1267. <https://doi.org/10.1016/j.proeng.2016.06.119>
15. **Cai, L., Shi, X., Xue, J.** Laboratory Evaluation of Composed Modified Asphalt Binder and Mixture Containing Nanosilica/Rock Asphalt/SBS *Construction and Building Materials* 172 2018: p. 204–211. <https://doi.org/10.1016/j.conbuildmat.2018.03.187>
16. **Shi, X., Cai, L., Xu, W., Fan, J., Wang, X.** Effects of Nanosilica and Rock Asphalt on Rheological Properties of Modified Bitumen *Construction and Building Materials* 161 2018: p. 705–714. <https://doi.org/10.1016/j.conbuildmat.2017.11.162>
17. **Zafari, F., Rahi, M., Moshtagh, N., Nazockdast, H.** The Improvement of Bitumen Properties by Adding Nanosilica *Study of Civil Engineering and Architecture* 3 (1) 2014: pp. 62–69.
18. **Yao, H., You, Z., Li, L., Lee, C.H., Wingard, D., Yap, Y.K., Goh, S.W.** Rheological Properties and Chemical Bonding of Asphalt Modified with Nanosilica *Journal of Materials in Civil Engineering* 25 (11) 2013: pp. 1619–1630. [https://doi.org/10.1061/\(ASCE\)MT.1943-5533.0000690](https://doi.org/10.1061/(ASCE)MT.1943-5533.0000690)
19. **Lushing, N., Cao, L., Dong, Z., Assogba, C.O.** Improving Storage Stability and Physicochemical Performance of Styrene-butadiene-styrene Asphalt Binder Modified with Nanosilica *Sustainability* 12 (21) 2020: pp. 8968. <https://doi.org/10.3390/su12218968>
20. **Shafabakhsh, G., Motamedi, M., Firouznia, M., Isazadeh, M.** Experimental Investigation of the Effect of Asphalt Binder Modified with Nanosilica on the Rutting, Fatigue and Performance Grade *Petroleum Science and Technology* 37 (13) 2019: pp. 1495–1500. <https://doi.org/10.1080/10916466.2018.1476534>
21. **Ghanoon, S.A., Tanzadeh, J.** Laboratory Evaluation of Nano-silica Modification on Rutting Resistance of Asphalt Binder *Construction and Building Materials* 223 2019: pp. 1074–1082.

- <https://doi.org/10.1016/j.conbuildmat.2019.07.295>
22. **Bhat, F.S., Mir, M.S.** Rheological Investigation of Asphalt Binder Modified with Nanosilica *International Journal of Pavement Research and Technology* 14 (3) 2021: pp. 276–287.
<https://doi.org/10.1007/s42947-020-0327-2>
 23. **Sun, L., Xin, X., Ren, J.** Inorganic Nanoparticle-modified Asphalt with Enhanced Performance at High Temperature *Journal of Materials in Civil Engineering* 29 (3) 2017: pp. 04016227.
[https://doi.org/10.1061/\(ASCE\)MT.1943-5533.0001750](https://doi.org/10.1061/(ASCE)MT.1943-5533.0001750)
 24. **Han, L., Zheng, M., Li, J., Li, Y., Zhu, Y., Ma, Q.** Effect of Nano Silica and Pretreated Rubber on the Properties of Terminal Blend Crumb Rubber Modified Asphalt *Construction and Building Materials* 157 2017: pp. 277–291.
<https://doi.org/10.1016/j.conbuildmat.2017.08.187>
 25. **Amini, A., Ziari, H., Goli, A.** Investigating the Performance of Rubberised Binders Used in Iran Based on Multiple Stress Creep Recovery and Performance Grading Systems *Road Materials and Pavement Design* 19 (4) 2018: pp. 803–818.
<https://doi.org/10.1080/14680629.2016.1274676>
 26. **Zoorob, S.E., Castro-Gomes, J.P., Oliveira, L.P., O'connell, J.** Investigating the Multiple Stress Creep Recovery Bitumen Characterisation Test *Construction and Building Materials* 30 2012: pp. 734–745.
<https://doi.org/10.1016/j.conbuildmat.2011.12.060>
 27. **Zhang, J., Walubita, L.F., Faruk, A.N., Karki, P., Simate, G.S.** Use of the MSCR Test to Characterize the Asphalt Binder Properties Relative to HMA Rutting Performance – a Laboratory Study *Construction and Building Materials* 94 2015: pp. 218–227.
<https://doi.org/10.1016/j.conbuildmat.2015.06.044>
 28. **Saboo, N., Kumar, R., Kumar, P., Gupta, A.** Ranking the Rheological Response of SBS-and EVA-modified Bitumen Using MSCR and LAS Tests *Journal of Materials in Civil Engineering* 30 (8) 2018: p. 04018165.
[https://doi.org/10.1061/\(ASCE\)MT.1943-5533.0002367](https://doi.org/10.1061/(ASCE)MT.1943-5533.0002367)
 29. **Sukhija, M., Saboo, N., Yadav, A.K., Rath, C.** Laboratory Study on the Suitability of Nano-silica as a Modifier for Asphalt Binders *Construction and Building Materials* 302 2021: p. 124406.
<https://doi.org/10.1016/j.conbuildmat.2021.124406>
 30. **Bayraktar, O.Y., Saglam-Citoglu, G., Belgin, C.M., Cetin, M.** Investigation of the Mechanical Properties of Marble Dust and Silica Fume Substituted Portland Cement Samples under High Temperature Effect *Fresenius Environmental Bulletin* 28 (5) 2019: pp. 3865–3875.
 31. **Bayraktar, O.Y., Saglam-Citoglu, G., Belgin, C.M., Cetin, S., Cetin, M.** Investigation of Effect of Brick Dust and Silica Fume on the Properties of Portland Cement Mortar *Fresenius Environmental Bulletin* 28 (11) 2019: pp. 7823–7832.
 32. **Jomoor, N.B., Fakhri, M., Keymanesh, M.** Determining the Optimum Amount of Recycled Asphalt Pavement (RAP) in Warm Stone Matrix Asphalt Using Dynamic Creep Test *Construction and Building Materials* 228 2019: p. 116736.
<https://doi.org/10.1016/j.conbuildmat.2019.116736>
 33. **Ziari, H., Moniri, A., Imaninasab, R., Nakhaei, M.** Effect of Copper Slag on Performance of Warm Mix Asphalt *International Journal of Pavement Engineering* 20 (7) 2019: pp. 775–781.
<https://doi.org/10.1080/10298436.2017.1339884>
 34. **Hurley, G.C., Prowell, B.D.** Evaluation of Sasobit for Use in Warm Mix Asphalt *NCAT Report* 5 (6) 2005: pp. 1–27.
 35. **Arabani, M., Roshani, H., Hamed, G.H.** Estimating Moisture Sensitivity of Warm Mix Asphalt Modified with Zycosoil as an Antistripping Agent Using Surface Free Energy Method *Journal of Materials in Civil Engineering* 24 (7) 2012: pp. 889–897.
[https://doi.org/10.1061/\(ASCE\)MT.1943-5533.0000455](https://doi.org/10.1061/(ASCE)MT.1943-5533.0000455)
 36. **Goh, S.W., Hasan, M.R.M., You, Z.** Performances Evaluation of Cecabase® RT in Warm Mix Asphalt Technology *Procedia-Social and Behavioral Sciences* 96 2013: pp. 2782–2790.
<https://doi.org/10.1016/j.sbspro.2013.08.311>
 37. **Yang, X., You, Z., Hasan, M.R.M., Diab, A., Shao, H., Chen, S., Ge, D.** Environmental and Mechanical Performance of Crumb Rubber Modified Warm Mix Asphalt Using Evotherm *Journal of Cleaner Production* 159 2017: pp. 346–358.
<https://doi.org/10.1016/j.jclepro.2017.04.168>
 38. **Shafabakhsh, G.H., Faramarzi, M., Sadeghnejad, M.** Use of Surface Free Energy Method to Evaluate the Moisture Susceptibility of Sulfur Extended Asphalts Modified with Antistripping Agents *Construction and Building Materials* 98 2015: pp. 456–464.
<https://doi.org/10.1016/j.conbuildmat.2015.08.123>
 39. **Ameri, M., Vamegh, M., Naeni, S.F.C., Molayem, M.** Moisture Susceptibility Evaluation of Asphalt Mixtures Containing Evonik, Zycotherm and Hydrated Lime *Construction and Building Materials* 165 2018: pp. 958–965.
<https://doi.org/10.1016/j.conbuildmat.2017.12.113>
 40. **Ibrahim, I., Mehan, H.N.A.** The Effect of Nano-materials on Hot Mixture “asphalt-concrete” *Open Journal of Civil Engineering* 5 (04) 2015: p. 419.
<https://doi.org/10.4236/ojce.2015.54042>
 41. **Shafabakhsh, G.H., Ani, O.J.** Experimental Investigation of Effect of Nano TiO₂/SiO₂ Modified Bitumen on the Rutting and Fatigue Performance of Asphalt Mixtures Containing Steel Slag Aggregates *Construction and Building Materials* 98 2015: pp. 692–702.
<https://doi.org/10.1016/j.conbuildmat.2015.08.083>
 42. **Saltan, M., Terzi, S., Karahancer, S.** Examination of Hot Mix Asphalt and Binder Performance Modified with Nano Silica *Construction and Building Materials* 156 2017: pp. 976–984.
<https://doi.org/10.1016/j.conbuildmat.2017.09.069>
 43. **Read, J., Whiteoak, D.** *The Shell Bitumen Handbook* Thomas Telford 2003.
 44. **Zani, L., Giustozzi, F., Harvey, J.** Effect of Storage Stability on Chemical and Rheological Properties of Polymer-modified Asphalt Binders for Road Pavement *Construction and Building Materials* 145 2017: pp. 326–335.
<https://doi.org/10.1016/j.conbuildmat.2017.04.014>
 45. **D'angelo, J., Dongre, R., Reinke, G.** Evaluation of Repeated Creep and Recovery Test Method as an Alternative to SHRP+ Requirements for Polymer Modified Asphalt Binders *Proceedings of the Fifty-first Annual Conference of the Canadian Technical Asphalt Association (CTAA): Charlottetown, Prince Edward Island, 2006.*
 46. **Arshad, A.K., Samsudin, M.S., Ahmad, J., Masri, K.A.** Microstructure of Nanosilica Modified Binder by Atomic Force Microscopy *Jurnal Teknologi* 78 (7–3) 2016: pp. 37–44.
<https://doi.org/10.11113/jt.v78.9480>
 47. **Mirzababaei, P., Nejad, F.M., Vanaei, V.** Investigation of Rutting Performance of Asphalt Binders Containing Warm

Additive *Petroleum Science and Technology* 35 (1) 2017: pp. 79–85.
<https://doi.org/10.1080/10916466.2016.1247173>

48. **Alhamali, D.I., Wu, J., Liu, Q., Hassan, N.A., Yusoff, N.I.M., Ali, S.I.A.** Physical and Rheological Characteristics of Polymer Modified Bitumen with Nanosilica Particles *Arabian Journal for Science and Engineering* 41 (4) 2016: pp. 1521–1530.
<https://doi.org/10.1007/s13369-015-1964-7>

49. **Arshad, A.K., Samsudin, M.S., Masri, K.A., Karim, M.R., Halim, A.A.** Multiple Stress Creep and Recovery of Nanosilica Modified Asphalt Binder *MATEC Web of Conferences* 103 2017: pp. 09005 EDP Sciences.
<https://doi.org/10.1051/mateconf/201710309005>



© Alothman et al. 2022 Open Access This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.