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Rheological Performance of ZycoTherm/Nano-Silica Composite Modified Binders at High and Low Temperatures

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ABSTRACT

This study aims to investigate the impact of control and warm mix binders modified with nano-silica on the asphalt binder functioning to resist rutting endurance and low-temperature cracking. The percentages of nano-silica employed in this research were 2%, 4%, and 6% of asphalt binder weight. The control and modified binders were evaluated by performing conventional and rheological tests. The rheological properties were examined by master curves, isochronal plots, multiple stress creep recovery (MSCR), Superpave rutting parameter, and bending beam rheometer. The outcomes implied that the performance of the asphalt binder (with or without ZycoTherm) improved when nano-silica was added concerning ($G^*/\sin \delta$) parameter. The MSCR test demonstrated that the recovery *(R %*) of the control and warm mix binders improved whereas the non-recoverable creep compliance (J_{nr}) dropped, implying that nano-silica boosted the rutting potential. Moreover, it was observed at different temperatures that the values for the complex shear modulus increased when the phase angle values were reduced. Furthermore, at low temperatures, it is presumed that the performance of nano-silica modified asphalt binders will have minimal performance as opposed to the binders prepared with ZycoTherm, which prevents low-temperature cracking.

Keywords: nano-silica, ZycoTherm, modified asphalt binders, rheological behavior, rutting resistance, MSCR, BBR.

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1. INTRODUCTION

Asphalt pavement must have the ability to withstand various loads during its service life to ensure optimal effectiveness for flexible pavements. Pavements are subjected to various forms of distress including high-level temperature rutting, middling-temperature fatigue, and minimal-level temperature cracking. A significant form of distress in asphalt pavements is known as rutting. Rutting is prevalent in elevated - temperatures areas owing to the asphalt's decreased stiffness as well as the materials flow caused by their viscoelastic characteristics [1]. Asphalt is the primary cause of rutting distress, especially in low and intensive traffic at elevated – temperatures [2]. The existence of shear deformation and increased density are the main causes of rutting within the asphalt pavement layers. Furthermore, the build-up of enduring strain in the various asphalt layers due to permanent deformation extensively influences rutting. On the other hand, thermal cracking is a serious problem that occurs in cold-weather asphalt pavements. Because of the thermal shrinkage of asphalt, thermal cracking generally develops in the asphalt pavement layer [3]. The asphalt layer is prevented from being moved by friction between both the asphalt and bottom layers, leading to tensile stresses in the asphalt layers. The levels of these stresses rise as the temperature falls. Once these stresses exceed the asphalt mixture's tensile strength, initial cracks appear at the base of the asphalt layer [4, 5].

The pavement performance is affected by the conventional physical and rheological features of the asphalt mixtures at elevated and reduced environmental temperatures, which influence the final function of the mixture. Therefore, it is crucial to discover the enhanced asphalt that offers exceptional road operation, easy construction and is cost-effective. The application of various nanomaterials such as nano-alumina, nano-tubes, and nano-clays has been studied for use as modifiers for asphalt binders [6-9]. Nano-silica is considered to be one of the most significant nano-materials that is effective for modifying the attributes of asphalt and asphalt mixtures. The important advantages of nano-silica are its high-performance features and its low production costs. It also has many advantageous properties including suitable dispersing capacity, high stability, elevated purity percentages, high specific area, and strong absorption [10].

Permanent deformation is one of the most common types of asphalt pavement deterioration. Previous studies have advocated for the use of nano-silica in asphalt binders to improve rutting resistance [11-13]. Many researchers have employed nano-silica to modify the asphalt features and observed that the asphalt modified with nano-silica had greater complex modulus (G^*) and lesser phase angle (δ) values [14-15]. Therefore, by adding nano-silica to improve binder properties, the permanent deformation and fatigue distress performance of asphalt can be enhanced [10]. Saltan *et al.*, [16] applied nano-silica at three different percentages of 0.1%, 0.3%, and 0.5%. The results showed that the asphalt binder's elastic behavior improved, resulting in improved fatigue and rutting resistance. Shafabakhsh *et al.,* [11] discovered that the inclusion of 3% nano-silica did not affect the elevated temperature performance of asphalt binder while the inclusion of 5% and 7% nano-silica improved the asphalt binder's elevated temperature performance by one and two grades, respectively. Bhat and Mir [13] demonstrated that nano-silica 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 nano-silica improved the rutting resistance of the neat binder. Arshad *et al.,* [17] incorporated nano-silica at various concentrations (1-5%), and the results revealed that 2% nano-silica was the optimal dose with greater effect in terms of non-recoverable creep compliance (J_{nr}) and percentage recovery (R %). At low temperatures, the performance of asphalt modified with nanoparticles may be a disadvantage. Onochie et *al.,* [15] tested the control asphalt with 2% and 4% nano-silica using a BBR and discovered that the modifications resulted in 6% and 14% greater creep stiffness, respectively. Nejad *et al.,* [14] reported the same findings, the incorporation of nano-silica into the asphalt caused higher creep stiffness and lowered the m-value, demonstrating the inefficiency of nano-silica on the low-temperature cracking resistance. Therefore, higher nano-silica doses may increase rutting resistance but have a negative impact on low-temperature performance [18].

Other than the utilization of nano-silica, the use of Nano-ZycoTherm as an additive for warm mix binder is a promising alternative. Warm mix asphalt (WMA) technologies are applied to decrease the asphalt production temperature to 120-135 ˚C and compaction temperature to 105-120 ˚C [19]. WMA is considered one of the ideal options for paving as it is eco-friendlier compared to conventional HMA. Warm mix additives lead to a reduction in fumes, while preserving the environment and the well-being of people. Recently, numerous studies have been conducted on warm mix asphalt technologies wherein the utilization of various forms of additives. For instance, nano-technology ZycoTherm was proposed as a silane-based anti-striping agent, which has the potential to minimize temperatures without negatively affecting the compaction at low-temperature levels [20]. Ziari *et al.,* [21] studied the features of ZycoTherm-modified binders through physical and rheological assessments of asphalt. The outcomes revealed that applying ZycoTherm did not significantly influence the elastic responses, fatigue, and rutting properties of the binder. However, Mirzababaei *et al*., [22] conducted a study using the MSCR test for asphalt binders of asphalt with 85/100 grade. The results gathered implied that ZycoTherm reduced the non-recoverable compliance values (J_{nr}), which indicates lower susceptibility against rutting distress for asphalt binders. According to the results obtained from the evaluations, the binder prepared with ZycoTherm (0.1%) was found to have the greatest effect on the asphalt binder's performance with 85/100 penetration grade facing permanent deformation. Raufi *et al.,* [23] studied the after-RTFO (short-term aging) performance of ZycoTherm modified binder. The ZycoTherm-modified binder showed an improvement in rutting property and led to increasing $G^*/\sin \delta$ rates in comparison to the control binders at various frequencies and temperature ranges. In addition, it was observed that an enhancement of the asphalt binder concerning the rutting performance was attained as a result of nano-ZycoTherm adjustments. Ibrahim and Mehan [24] conducted a study involving DSR and BBR assessments. The study revealed an increment in the 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.

Individually, ZycoTherm and nano-silica are effective asphalt binder modifiers. However, their compatibility as a couple is an area of research that needs to be looked into more. The following research focuses on examining the rheological features of asphalt modified with ZycoTherm given that there have been few studies conducted on the MSCR and frequency sweep tests of ZycoTherm-modified binders. Furthermore, studies on nano-silica have been carried out in recent years, but the effect of ZycoTherm/nano-silica concerning the rutting resistance and low-temperature cracking has yet to be determined. Hence, it is decisive to analyze the performance of ZycoTherm modified with several percentages of nano-silica utilizing these approaches.

2. THE STUDY'S OBJECTIVES

1. Examine the effects of ZycoTherm, nano-silica, and ZycoTherm / nano-silica on the viscosity of the asphalt binder at various temperature ranges.

2. Evaluate the effects of adding ZycoTherm, nano-silica, and ZycoTherm / nano-silica on various rheological characteristics of the asphalt binder using a frequency sweep test.

3. Assess the permanent deformation of ZycoTherm, nano-silica, and ZycoTherm / nano-silica modified binders utilizing Superpave rutting resistance parameter ($G^*/\sin\,\delta$) and MSCR.

4. Investigate the effect of adding ZycoTherm, nano-silica, and ZycoTherm/nano-silica on the low-temperature performance using BBR.

3. MATERIALS AND EXPERIMENTAL DESIGN

The examined materials' specifications are presented in this section. Fig. 1 shows a tree diagram displaying the experimental system applied to demonstrate the complete scope of this research study.

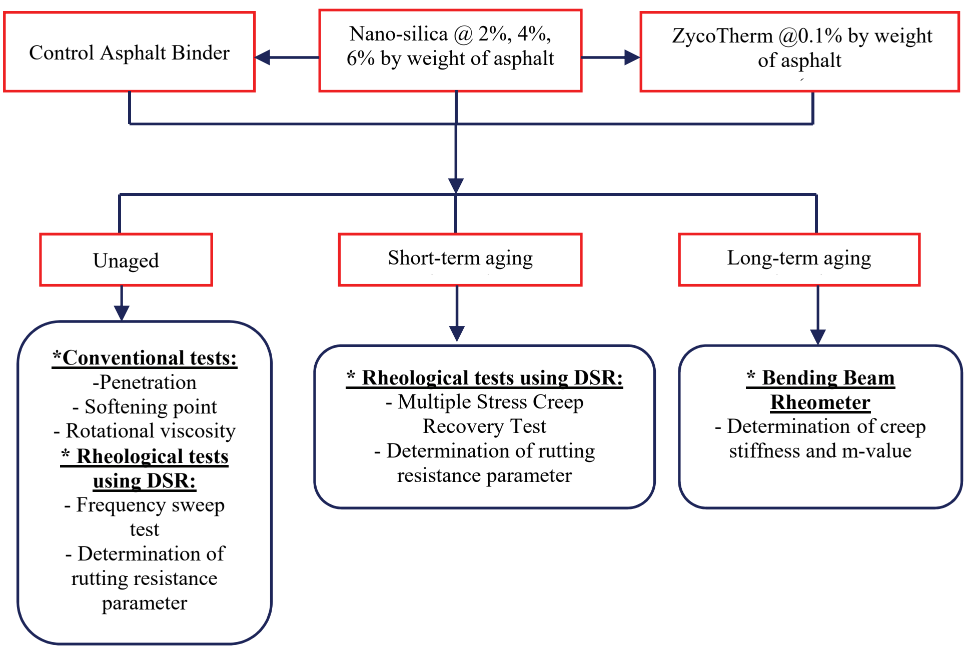

Figure 1 - The flowchart of the study

3.1. Asphalt Binder

The control asphalt binder utilized in this research was 60/70 grade. Table 1 below displays the characteristics of the asphalt binder.

Table 1 - Physical properties of control asphalt binder

Test	Test method	Unit	Result	Criteria
Penetration at 25˚C	ASTM D5	0.1 mm	67	60-70
Softening point	ASTM D36	˚C	50	48-56
Ductility at 25˚C	ASTM D113	cm	100	100 minimum
Flash point	ASTM D92	˚C	322	230 ˚C minimum
Rotational viscosity at 135 ˚C	ASTM D4402	Pa.s	0.5672	3 Pa s maximum

3.2. Nano-Silica

The silica composite is available globally and is applicable in the manufacturing of colloidal silica, silica gel, fumed silica, and other substances [25]. SiO_2 is the chemical compound for silica and is similar to the compound structure of diamonds. SiO_2 exists in nature in both crystalline and amorphous forms. Silica is white and has relatively high melting and boiling points [26]. There are various functional characteristics of nano-silica including high precise surface area, intense absorption, effective dispersal capability, high-level stability, and high chemical purity [10]. The addition of nano-materials offers various benefits including reduced manufacturing costs and increased performance [27]. The nano-silica features are shown in Table 2.

Table 2 - Physical properties of nano-silica

Property	Value
Appearance	Translucent liquid
pH	6.71
Viscosity (20 ˚C)	3.05mPa.s
Particle size	11 nm

3.3. ZycoTherm

ZycoTherm is a chemical warm mix additive that provides significant benefits as a result of WMA technologies. ZycoTherm lowers the mixing and compaction temperatures. ZycoTherm is considered to be an antistrip warm-mix chemical additive to stipulate moisture endurance for asphalt pavements. Moreover, it is also a scent-free substance. At room temperature, ZycoTherm has been identified as a warm mix additive that is integrated at 0.1% - 0.15% of the weight of the asphalt binder [28]. ZycoTherm, a silane-base technology, was employed and is considered to be more efficient than other well-known chemical WMA additives that are amine-based due to the fact the silane-based additives produce a molecular level hydrophobic zone that is water-resistant. The characteristics of ZycoTherm are shown in Table 3.

Table 3 - Physical properties of ZycoTherm

Property	**Value**
Physical state	Liquid
Color	Pale yellow
Viscosity	1-5 Pa.s
Specific gravity (25°C)	0.97g/cm^3
Odor	Odorless
Flash point	>80 °C
pH	10 % solution in water neutral or slightly acidic

3.4. Preparing the Modified Binder

The asphalt binder was combined with 2-6% of nano-silica, using 2% increments of the original weight for the binder, to produce nano-silica modified asphalt binder. The asphalt binder was heated to 160 °C, while the asphalt binder was modified with the aid of a mechanical mixer. Approximately 400g of binder was placed in a cylinder-shaped container and set on a hot plate. To preserve the viscosity of the binder within the blending process, the hot plate was adjusted at 160 °C. The heated asphalt binder was progressively infused with nano-silica while the mixture was stirred with a mechanical mixer. The stirring speed was adjusted to 1800 rpm for 60 minutes. To ease the reference of each sample, the nano-silica modified asphalt binders were identified by utilizing the following acronyms: 2% NS, 4% NS, and 6% NS. According to the manufacturer's suggestion, the WMA binder was prepared by using an additive content set at 0.1% of the binder's weight. The mechanical stirrer was set up at a speed sufficient to create a 15-30 mm deep vortex within the liquefied asphalt. The ZycoTherm was then added to the center of the vortex in a drop-wise method, while the asphalt was stirred at 130 °C with a pace of 10 drops per minute with a 1 ml syringe. The stirring continued for 15 minutes to complete the mixing procedure. Furthermore, to prepare WMA modified with nano-silica (ZycoTherm/nano-silica), the control asphalt was blended first with 0.1% ZycoTherm as mentioned previously, and then the nano-silica was gradually added to the mix by 2, 4, and 6% and blended with asphalt binder at 1800 rpm. The modified binders were labeled as, 0.1%Z+2%NS, 0.1%Z+4%NS, and 0.1%Z+6%NS.

3.5. Aging Conditions of Asphalt Binder

The control asphalt and modified binders were conditioned under short and long-term aging phases. To simulate the conditions of the short-term aging, a rolling thin film oven (RTFO) was utilized. The standard assessment method ASTM D 2872 indicates that 35 grams of asphalt must be set in open-mouthed cylinder bottles and then positioned into a heated carousel prepared oven at a temperature of 163 °C, which revolves beneath air- blown pressure at 15 rpm for 85 minutes. The test samples were utilized in the rheological evaluation of the RTFO-aged asphalt. According to ASTM D 6521, the asphalt binders were aged for 20 hours in a pressure aging vessel at 100 °C and a pressure of 2.1 MPa in terms of long-aging.

4. EXPERIMENTAL METHODS

4.1. Basic Physical Binder Tests

The fundamental properties of the control asphalt binder and the modified binders were identified by using the following tests: penetration test (ASTM D5), softening point test (ASTM D36), and viscosity test using a Brookfield Rotational Viscometer (ASTM D4402).

4.2. Temperature Susceptibility

Asphalt binder is composed of thermoplastic material, which means that when temperatures increase, it becomes softer, and when temperatures decrease, it hardens. This feature is one of the traits of asphalt binders known as temperature susceptibility. As the physical traits of asphalt transform at increased temperatures, the consistency and temperature susceptibility are specified by using the PI parameter, or penetration index. To compute the PI, the temperature susceptibility for binders is calculated by using the penetration at a temperature of 25 °C and softening point outcomes, as shown in Eq. 1 [29].

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

Where Pen(25) denotes the value of the penetration of the asphalt binder at 25 °C in 0.1mm and (SP) is the softening point value of the asphalt binder in °C.

4.3. Dynamic Shear Rheometer (DSR)

The rheological characteristics of asphalt have been identified through its vicious and elastic features at low, moderate, and elevated temperatures. The DSR was utilized to perform Superpave rutting resistance, frequency sweep, and multiple stress creep recovery (MSCR) consistent with ASTM D7175, AASHTO T315, and ASTM D7405, respectively. The assessments were carried out to analyze the rheological features of control asphalt and warm mix binder that were modified by using various degrees of nano-silica. A frequency sweep assessment was employed to analyze the linear rheological features of the control and modified binders. The rheological indicators that are frequently acquired from the DSR experiment are the complex modulus (G^*) and phase angle (δ). The following indicators were applied to analyze the binder's elasticity characteristics. Moreover, the MSCR test was employed to identify the recovery (*R %*) and the non-recoverable creep compliance (J_{nr}) for the control and warm mix binder modified with nano-silica in RTFO aged state.

4.3.1. Frequency Sweep Test

The asphalt pavement structures under traffic loads displayed a dynamic loading influence and the blacktop material demonstrated various viscoelastic attributes when placed under various load frequencies. The assessment of the frequency sweep was performed where the load frequency was changed from 1 Hz to 15 Hz. Moreover, the assessment was conducted under strain-regulated states and the temperatures ranged between 10 ˚C and 82 ˚C with a temperature gap of 6 ˚C. During the assessment, an 8 mm plate was applied for temperatures under 40 ˚C, while a 25 mm plate was utilized for temperatures higher than 40 ˚C. The G^* and δ results obtained from the frequency assessment were employed to establish master curves for the control and warm mix binder modified with nano-silica. Additionally, the isochronal plots were plotted to assess how the modification process affected the performance features of both the control and warm mix asphalt binder.

4.3.2. Multiple Stress Creep Recovery (MSCR) Test

On the RTFO-aged specimens, a DSR was utilized to perform the MSCR test. The test evaluates the rutting performance of a binder by assessing both the recovery percent (*R %*) and the non-recoverable parameter of creep compliance (J_{nr}). At 0.1kPa and 3.2kPa levels of stress, the MSCR test comprises 10 cycles of stress creep with a 1-second duration and a 9-second recovery time. The samples were tested utilizing a 25 mm plate and a 1 mm spacing at a temperature of 64 ˚C. After releasing the imposed stress, the (*R %*) denotes the binder's elastic recovery. An asphalt binder with a high elastic tendency may result in minimal lasting asphalt deformation. A high value of (J_{nr}) implies a binder's susceptibility to rutting and conversely is right. The (J_{nr}) values might show the stress dependency of both unmodified and modified binders. Eqs. 2 and 3 are used to quantify (J_{nr}) and (*R %*), respectively.

$$J_{nr} = \frac{\varepsilon_{nr}}{\sigma} \tag{2}$$

Where J_{nr} represents the non-recoverable creep compliance (kPa^{-1}), ε_{nr} symbolizes the unrecoverable strain at the end of the recovery period, and σ symbolizes the stress (kPa) utilized during the loading period.

$$R\ \% = \frac{\varepsilon_1 - \varepsilon_{10}}{\varepsilon_1} \times 100 \tag{3}$$

Where *R %* is the percentage recovery, ε_1 symbolizes the value of the strain at the end of the creep stage, and ε_{10} denotes the strain rate at the end of the recovery stage.

4.3.3. Superpave Rutting Resistance Parameter

The Superpave rutting parameter ($G^*/\sin\delta$) was performed per ASTM D 7175-15 to measure the resistance to rutting of the control and modified binders. $G^*/\sin\delta$ parameter is used to determine whether asphalt binders fail when exposed to high temperatures. The binder deformation is avoided at loading as $G^*/\sin\delta$ rises. The $G^*/\sin\delta$ ratio for an unaged asphalt binder must be greater than 1kPa, whereas the $G^*/\sin\delta$ ratio for RTFO-aged binder must be greater than 2.2kPa based on ASTM D 2872. On both unaged and RTFO- aged binders, the assessment was carried out utilizing a DSR and a 25-mm-diameter parallel plate shape and a spacing of 1 mm. The test procedure was done at a frequency of 10 rad/sec in a range of temperature of 58 ˚C to 76 ˚C, at temperature intervals of 6 ˚C.

4.4. Bending Beam Rheometer (BBR) Test

The BBR method was applied to evaluate the low-temperature function of asphalt binders under ASTM D6648. The creep stiffness and m-value were attained by applying the BBR method for 60 seconds at varying temperatures: 0 ˚C, - 6 ˚C, -12 ˚C, and -18 ˚C. As stated by the requirement sets for Superpave, the creep stiffness has an ultimate value of 300 MPa and at least 0.3 is required for the m-value. To compute the creep stiffness and m-value, the control asphalt and the modified binders were all evaluated. All binder samples were subject to short-term aging (RTFO) and long-term aging (PAV).

5. RESULTS AND DISCUSSION

5.1. Conventional Physical Properties

The softening point and penetration tests' findings are shown in Table 4. The penetration test was conducted to assess the consistency of the control asphalt and modified binders, and the softening point test was conducted to validate the asphalt binders' high-service temperature.

The effect of adding nano-silica to the control and ZycoTherm binders is illustrated in Table 4. The penetration diminishes and the softening point rises, as can be seen. In comparison to the control and ZycoTherm binders, each nano-modified asphalt binder sample had a lower penetration and a greater softening point. The decrease in penetration values reveals that the binder has a stiffening influence, with stiffening increasing in proportion to the rise in nano-silica concentration. The binder's softening point is also increased when nano-silica is added, which improves its temperature susceptibility. The higher the penetration index value is, the lower the temperature susceptibility for the asphalt binder. Table 4 shows the PI outcomes.

Table 4 - Physical properties of control asphalt and modified binders

Binder Type	Penetration at 25 ˚C (0.1mm)	Softening point (˚C)	PI
Control Binder	67	50	-0.495
2%NS	52.65	55.30	0.165
4%NS	49.36	57.85	0.555
6%NS	46.51	59.40	0.727
0.1% Z	55	52.82	-0.296
0.1% Z+ 2%NS	50.50	56.50	0.325
0.1% Z+ 4%NS	48.94	58.75	0.719
0.1% Z+ 6%NS	45.30	60.60	0.9003

The viscosity of the control and nano-modified binders was measured utilizing a Brookfield rotational viscometer (RV) at a range of high temperatures between 135 °C and 195 °C with 10 °C increments. According to Fig. 2, all of the samples of asphalt binder had low viscosity values at elevated temperatures. Typically, when the temperature increases, the viscosity values are reduced. The inclusion of nano-silica in the control binder leads to increased viscosity values for the nano-silica modified asphalt binders. Moreover, according to the Superpave criteria, at 135 °C the viscosity values were within the limits, and the nano-silica modified asphalt binders acquired lower viscosity values in comparison to the maximum limit at 3 Pa s. However, looking at 4% NS, one can infer from the mixing procedure of the nano-silica modified asphalt binders that chemical reactions and physical diffusions might occur in which a new structure may be developed because of the nano-silica's temperature resistance resulting in the reduction in viscosity value as compared to other percentages. Moreover, nano-silica can intensify the control binder and enhance the recovery capability upon applying stress. Conversely, the viscosity value was decreased when nano-silica was added to the warm mix binders, which is part of the warm mix additive ZycoTherm that greatly affects the reduction of viscosity. As a result, the ZycoTherm resulted in a reduction in viscosity values, for example; a viscosity reduction of roughly 11.5% and 15% at 135 and 165 °C, respectively, in the binder containing both 0.1% ZycoTherm and 6% NS. ZycoTherm is regarded as an advantageous attribute for an additive, especially when assessing its effectiveness, given that it minimizes the functional temperatures that assist in preparing potential cost-effective and sustainable pavements. When ZycoTherm is in a liquid condition, it is considered one of the elements that influence the reduction of viscosity [23].

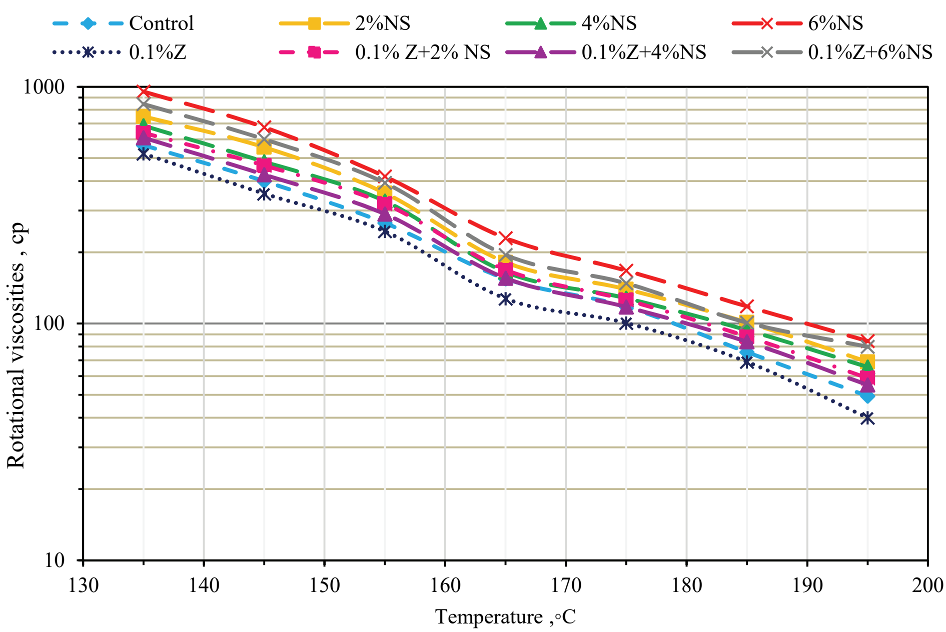

Figure 2 - Rotational viscosities for control and modified binders

5.2. Multiple Stress Creep Recovery (MSCR) Test

5.2.1. Cumulative Strain

The usual strain outputs from the MSCR assessment of control and modified asphalt at 64 °C with two levels of stress are displayed in Figs. 3a and 3b, respectively. In Fig. 3a, the low-stress level (100 Pa) for the first 100 seconds is displayed, while Fig. 3b shows the high-stress level (3200 Pa) for the next 100 seconds. The outcomes obtained from the MSCR consist of two stages, namely the creep stage and the recovery stage, to finish a cycle. It can be shown by analyzing the gathered strain and stress levels, the accumulated creep compliance at 100Pa is lesser than at 3200Pa, which signifies that when stress levels increase, the accumulated strain increases as well. Moreover, the addition of 0.1% ZycoTherm on the control asphalt led to a slight decrease in the gathered strain. However, when adding nano-silica to the binders, it can be observed that the gathered strain decreases considerably when compared to the control and ZycoTherm binders. As a result, the nano-silica can enhance the stiffness of the binder at elevated temperatures. From the outcomes gathered, it is shown that 6% NS has the lowest accumulated strain followed by a 0.1%Z +6%NS compared to the other percentages.

5.2.2. Recovery Percentage (R %)

The recovery percentage strain assists in identifying the elastic characteristic of the asphalt when subject to loading. The percentage recoverable strain is an essential constraint for assessing the recovery capability of the asphalt after it has deformed. The increase in the percentage of asphalt recovery (*R %*) represents minimal exposure to permanent deformation. This occurs during the 9-second rest period within each cycle, which allows more strain to return to its former condition. This constraint is crucial when analyzing the asphalt binder resistance to rutting as it denotes the hindered asphalt elasticity. As shown in Fig. 3c, the recovery percentage strain at 100 Pa and 3200 Pa stress levels for control asphalt and modified binders. According to the analysis of the outcomes obtained at each stress level, the value marginally declined at 3200 Pa as opposed to the value at 100 Pa.

The following results imply that by adding nano-silica to control asphalt, the elastic recovery and rutting resistance for the asphalt binder is improved. Adding nano-silica increases the recovery value and this is evident in the data gathered. By observing the data collected at 100 Pa stress level, the recovery of the control binder is 6.6% and it increases to 24.28%, 20.56%, and 27.72% once nano-silica was added at 2%, 4%, and 6%, respectively. While the warm mix binder (0.1% Z) shows a 7.84% recovery, and this recovery jumps to 20.54%, 15.14, and 25.99% when 2%, 4%, and 6% nano-silica were added, respectively. The same type of improvement was observed at the 3200 Pa stress level. As a consequence, the inclusion of nano-silica improves the asphalt binder's elasticity, resulting in a better recovery response.

5.2.3. Non-recoverable Creep Compliance (J_{nr})

The non-recoverable creep compliance (J_{nr}) constraint is used to determine the impact of the binder on rutting performance. When J_{nr} values are low, it represents improved rutting resistance, and when J_{nr} values are high, it represents poor rutting resistance. In Fig. 3d, the J_{nr} outcomes are shown for the control and ZycoTherm binders, which have been modified with nano-silica at both 100 Pa and 3200 Pa stress levels. According to the data, the J_{nr} increases as the stress level transitions from 100 Pa to 3200 Pa, at 100 Pa results show the decline of J_{nr} for the control binder from 3.058 to 1.643, 1.76, and 1.319 when nano-silica was added at 2%, 4% and 6% of, respectively. The J_{nr} for warm mix binder (0.1%Z) is 2.644, with the addition of 2, 4, and 6% of nano-silica the J_{nr} values dropped to 1.791, 2.512, and 1.501, respectively.

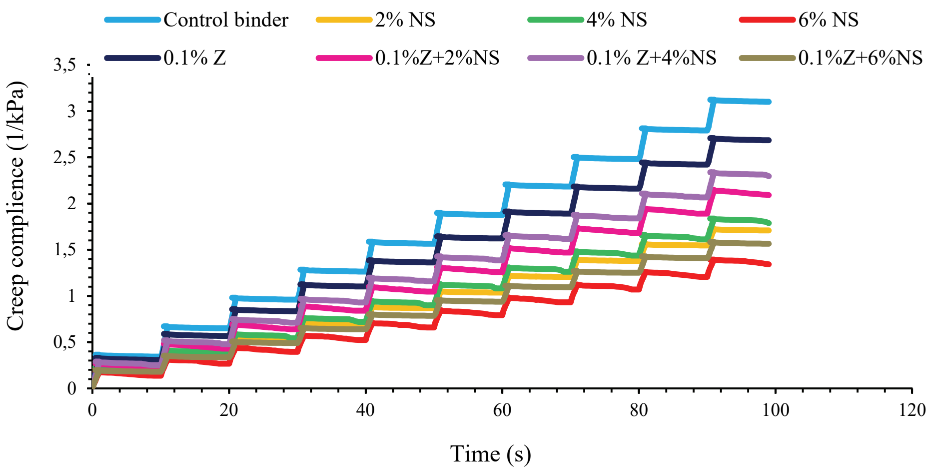

Figure 3a -The accumulated creep compliance at 100 Pa

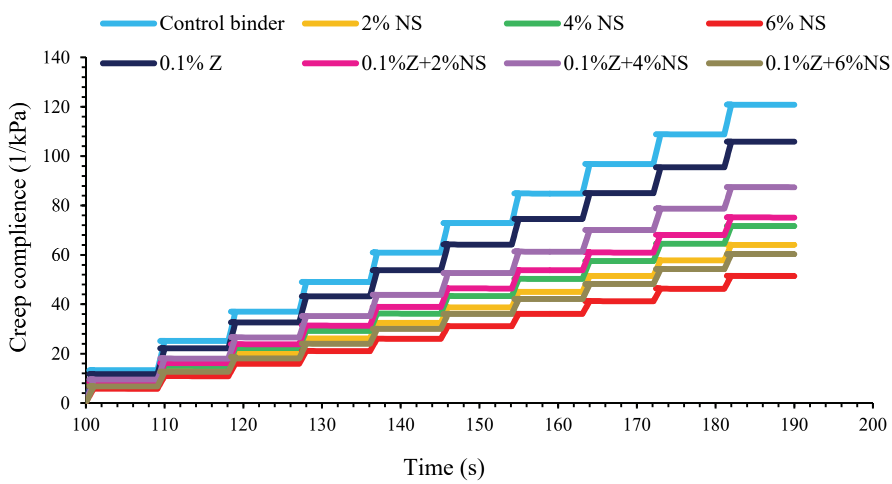

Figure 3b - The accumulated creep compliance at 3200 Pa

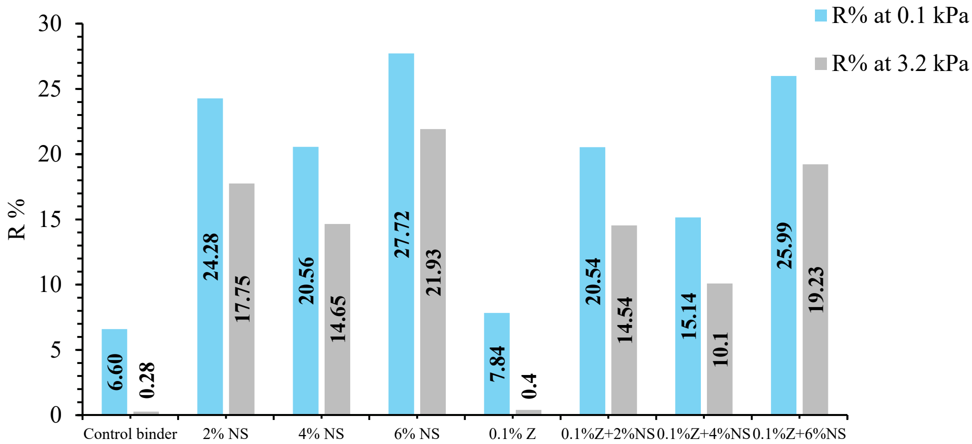

Figure 3c - R% at 100 Pa and 3200 Pa levels of stress

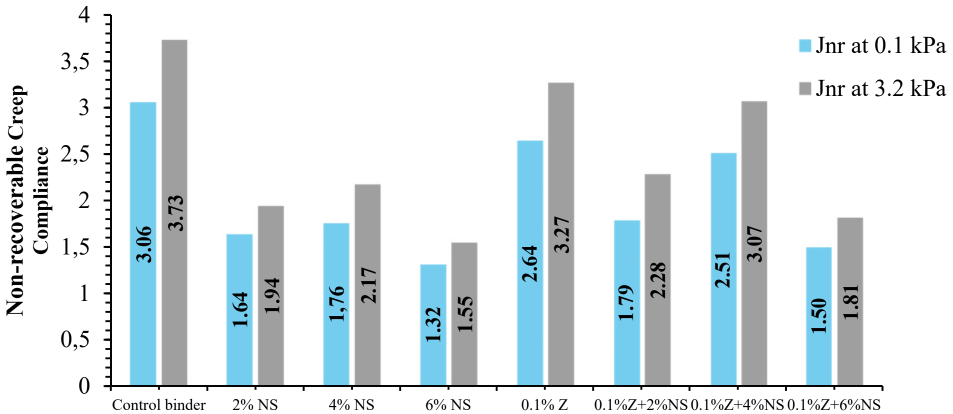

Figure 3d - J_{nr} at 100 Pa and 3200 Pa levels of stress

The higher stiffness of the modified binders might explain the drop in the J_{nr} value with the presence of nano-silica. The recovery strain percent (*R %*) revealed an inverse relation with non-recoverable creep compliance (J_{nr}). The reduction in non-recoverable creep compliance along with the increase in recovery values revealed that the modified binders with nano-silica have a greater impedance to permanent deformation.

According to AASHTO T350, J_{nr} at 3200 Pa is used as a criterion to categorize asphalt depending on a specified traffic volume and loading rate, as shown in Table 5. According to the J_{nr} results, control, 4%NS, 0.1%Z, 0.1%Z+2%NS, and 0.1%Z+4%NS modified binders were determined to be appropriate for standard loading (S), whereas 2%NS, 6%NS, and 0.1%Z+6%NS were determined to be suitable for heavy loading (H). As a result, the inclusion of nano-silica improves the asphalt binder's traffic loading grade. Moreover, the decrease in J_{nr} values with the addition of nano-silica might be explained by the greater stiffness of the modified asphalt binders.

Table 5 - Grade category of Jnr at 3200Pa based on traffic loading

Grade Category	J_{nr} at 3200 (1/kPa)	Traffic loading level (ESALs)
E (Extremely loading)	0.0 < 0.5	> 30 million and speed of traffic<20Km/h
V (Very high loading)	0.5 < 1.0	> 30 million or speed of traffic<20Km/h
H (High loading)	1.0 <2.0	10-30 million or speed of traffic 20-70Km/h
S (Standard loading)	2.0 < 4.0	<10 million and speed of traffic >70Km/h

5.3. Frequency Sweep Test

5.3.1. Isochronal Plots

The use of isochronal plots allowed the viscoelastic attributes of the control and modified asphalt like the G^* and δ against temperature, to be illustrated at specific frequencies. Figs 4a-4d show the temperature ranges plotted against the phase angle and complex modulus for the unaged control binder, warm mix binder, and nano-silica modified binders at 1 Hz and 15 Hz. Figs.4a and 4b show the isochronal plots for the control asphalt modified with nano-silica at 1 and 15 Hz, respectively. The G^* value rises and the δ value reduces at all temperatures as a result of the addition of NS to the control binder for up to 6%. This implies that the dispersion of nano-silica within the mixture results in an improvement in the strength of the modified asphalt and considerably improves the asphalt's elevated-temperature performance. The complex modulus of nano-silica modified binders has increased significantly, enhancing the binders' rutting resistance. This increase becomes more pronounced at higher frequencies. Moreover, when temperature increases, the phase angle of the binders increases, and the modified binders with nano-silica exhibit lower phase angles than the control asphalt. The phase angle of the 6% NS decreases significantly at both low and high temperatures. Furthermore, the phase angle of nano-silica modified binders decreases at low (1 Hz) and high (15 Hz) frequencies, showing that the modified binders seem to be elastic [13,30].

Figs. 4c and 4d show the isochronal plots for the control, ZycoTherm, and ZycoTherm/nano-silica binders at 1 and 15 Hz, respectively. It is shown that asphalt modified with 0.1% ZycoTherm is capable of insignificantly increasing the G^* and reducing the δ values in comparison to the control binder, implying that its behavior at high temperatures is quite similar to that of control asphalt. However, when nano-silica was added to the warm mix binder at various proportions, this resulted in a significant increase in the G^* values and a

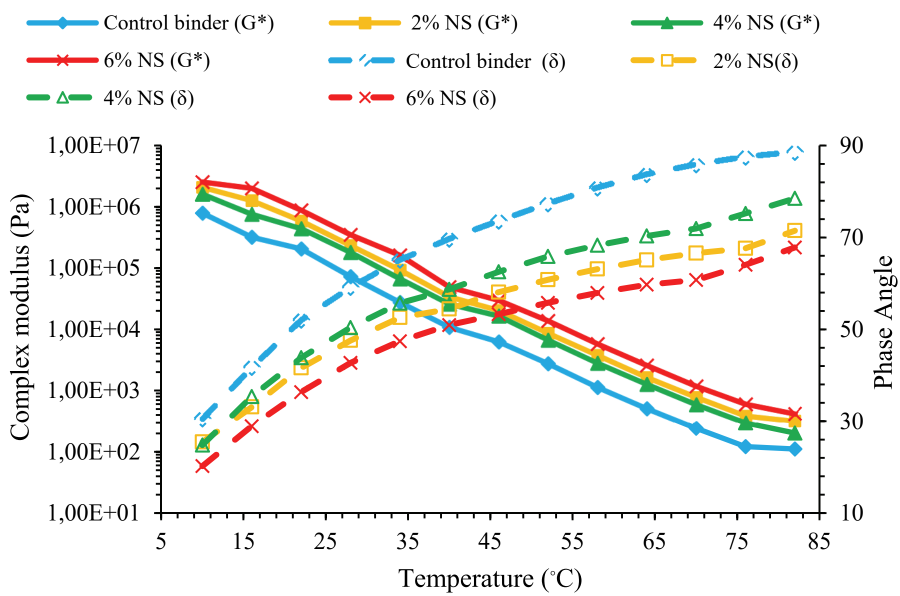

Figure 4a - Isochronal plot of G and δ of control binder modified with NS at 1 Hz*

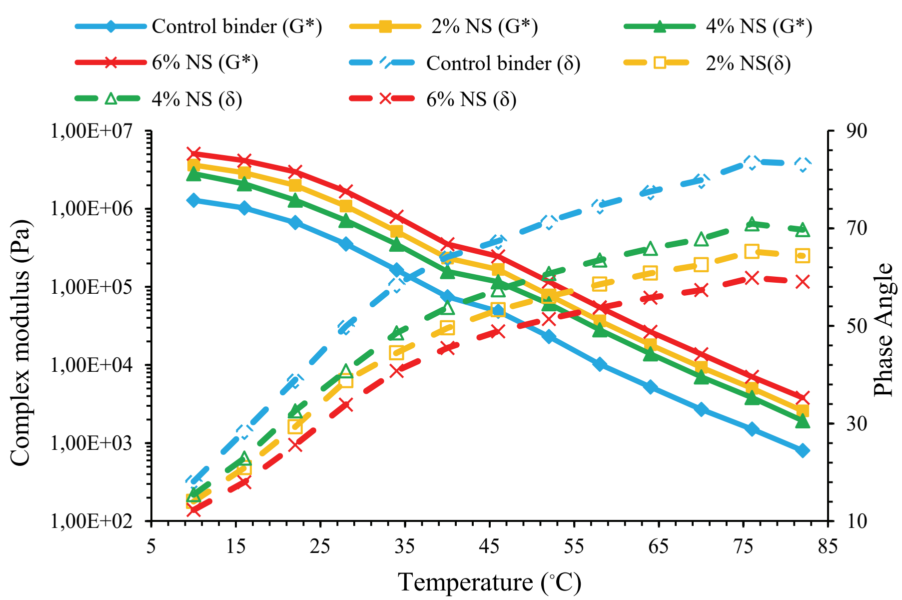

Figure 4b - Isochronal plot of G and δ of control binder modified with NS at 15 Hz*

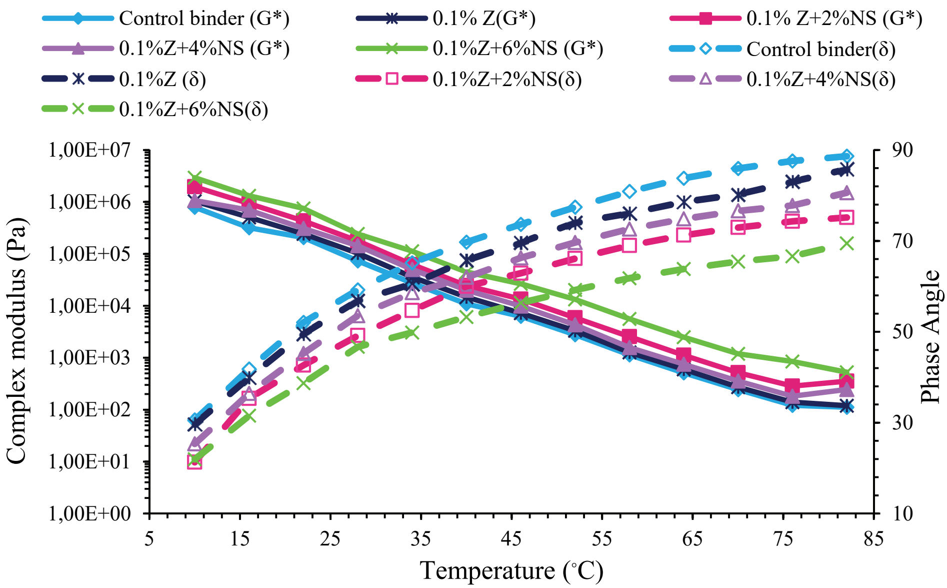

Figure 4c - Isochronal plot of G and δ of control binder, warm mix binder and warm mix binder modified with NS at 1 Hz*

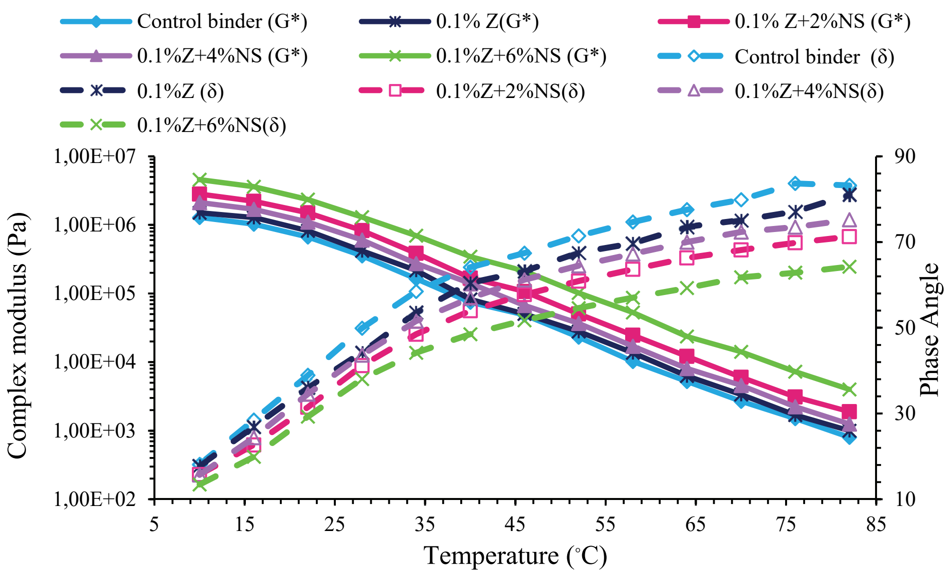

Figure 4d - Isochronal plot of G and δ of control binder, warm mix binder and warm mix binder modified with NS at 15 Hz* decrease in the δ values. The variations found in the G^* and δ values at 15 Hz for the control, warm mix, and nano-silica modified binders at 2%, 4%, and 6% were much more significant than those at 1 Hz but followed the same pattern, demonstrating that the effect of additives was more pronounced at higher frequencies. Because all modified binders with nano-silica show higher stiffness at both high and low temperatures, it can be stated that nano-silica modified binders with or without ZycoTherm were able to enhance the performance of the elevated temperatures (resistance to rutting) of control asphalt but were ineffective in enhancing the performance of the low-medium temperature.

5.3.2. Master Curves

A master curve can be described as a curve that reflects the binder's time dependence by displaying rheological parameters, such as G^* and δ, across a selection of temperatures and frequencies. The established curve is capable of distinguishing the various assessed binders. Developing the master curve required a time-temperature superposition, where 22 °C was selected as the reference temperature. Furthermore, upon plotting a smooth curve at other temperatures, the rheological outcomes were shifted horizontally using related factors. Fig.5 shows the master curves for the G^* and δ of the control binder, warm mix binder, and nano-silica modified binders for the unaged samples. In Fig. 5a, the complex shear modulus, G^*, for the control asphalt modified with nano-silica modified is shown. It is demonstrated that adding nano-silica to the asphalt resulted in higher values of complex modulus over the whole range of frequency and temperature. Because of the presence of nano-silica, an increase in the complex modulus values indicates that the asphalt binder becomes stiffer and can considerably improve the asphalt's high-temperature performance. The degree of increase in complex modulus values for 6% NS is greater than for the other percentages. This tendency, however, is observed to be more evident at lower frequency ranges. Generally, lower frequencies indicate slower-moving vehicles, making the pavement more susceptible to rutting [31]. On the other hand, Fig. 5b illustrates the complex shear modulus, G^*, for the control asphalt binder, warm mix binder, and warm mix binder modified with nano-silica. It is evident that the complex modulus of ZycoTherm-asphalt was marginally higher than the control asphalt, but not significantly; however, when NS was added at any percentage to the ZycoTherm-asphalt binder, the G^* significantly increased. This might contribute to the stiffening effect of nano-silica particles. In Fig. 5c, the master curves for the phase angle of the control asphalt modified with various NS percentages are shown. As shown in the figure that the phase angle declines across all frequencies. In comparison, the phase angle of the control asphalt approaches 90°, meaning that the asphalt will lose its elasticity and enter the viscous flow phase. The nano-silica modified binders have a phase angle of no greater than 75°, guaranteeing that the asphalt is resistant to rutting. In Fig. 5d, the master curves of the phase angles for the control asphalt, warm mix binder, and warm mix modified with nano-silica are illustrated. It is shown that the control asphalt had the highest phase angle value; however, this parameter was slightly decreased when 0.1% of ZycoTherm was added; the drop-in phase angle values in the middle and low-frequency ranges are more noticeable. When NS was added to binders containing ZycoTherm, the phase angle values were significantly reduced in comparison to those of the control asphalt and warm mix asphalt. Logically, the nano-silica modified binders displayed the largest variation degrees in raising the complex modulus and lowering the phase angle.

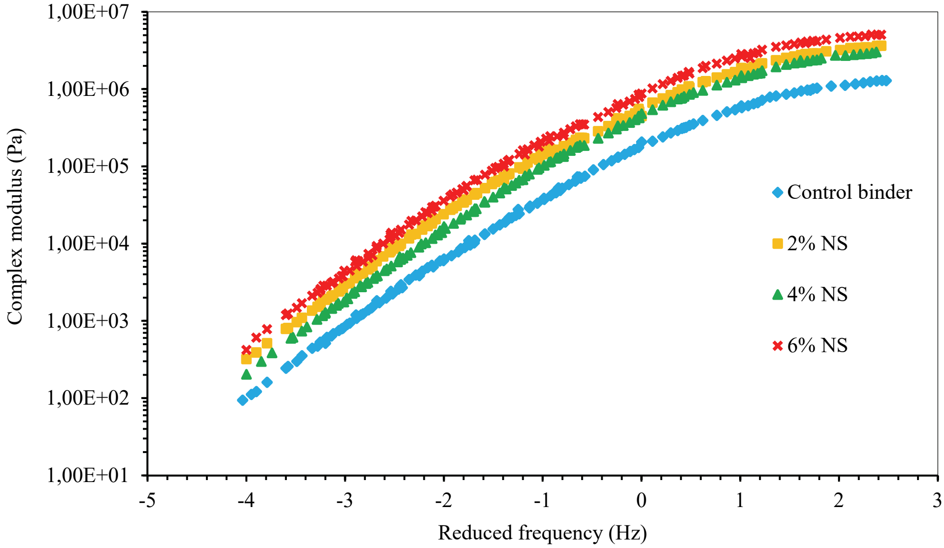

Figure 5a - G master curve of control binder modified with NS*

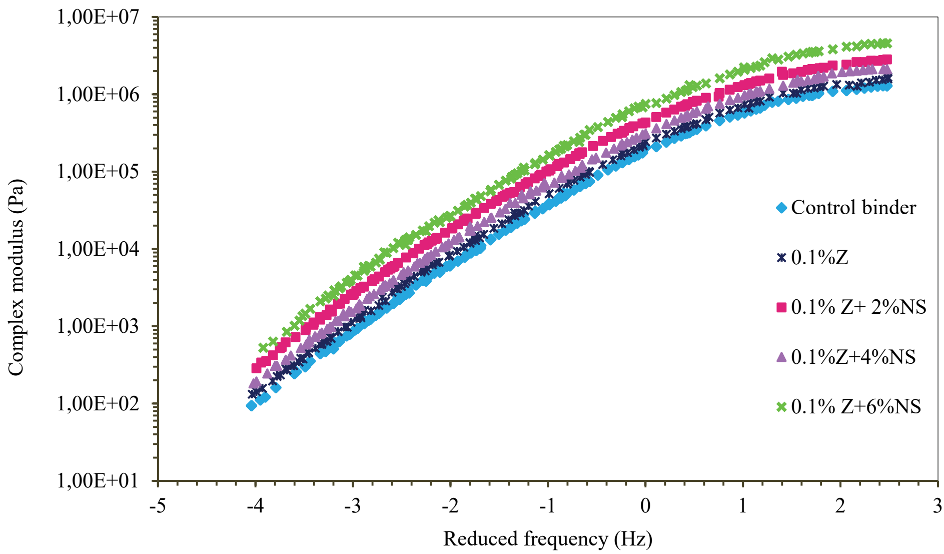

Figure 5b - G master curve of control binder, warm mix binder and warm mix binder modified with NS*

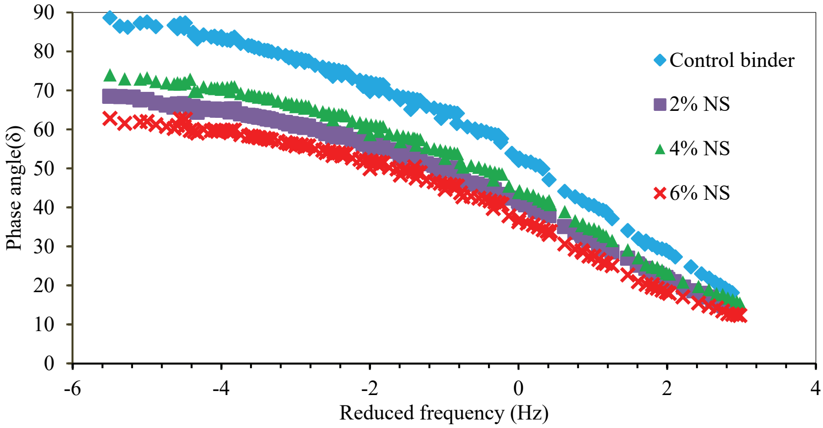

Figure 5c - δ master curve of control binder modified with NS

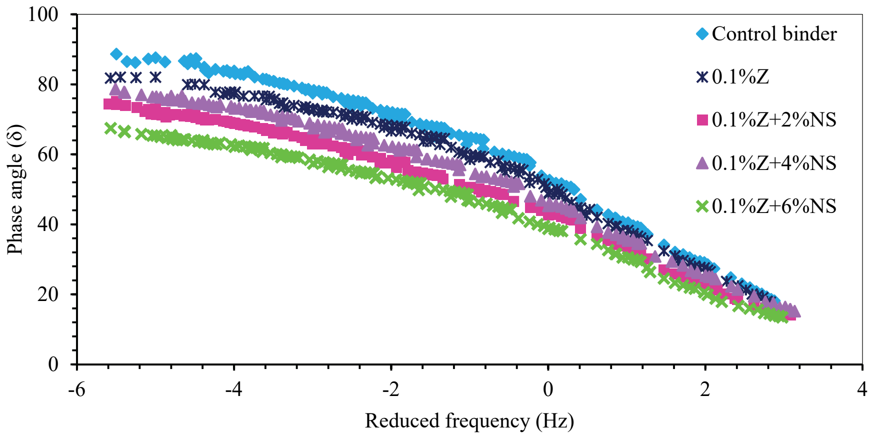

Figure 5d - δ master curve of control binder, warm mix binder and warm mix binder modified with NS

5.4. Superpave Rutting Parameter

Because the majority of the asphalt binder's permanent deformation occurs during the early phases of pavement construction, the Superpave standard mandates that the DSR test be performed on unaged and RTFO-aged asphalt at high -temperatures to determine rutting resistance. The Superpave rutting parameter ($G^*/\sin\delta$) is utilized to define the enhancement of the binder's rutting resistance when adding nano-silica to the control and warm mix binders at various temperatures, as depicted in Fig. 6. Fig. 6a shows that all the unaged nano-silica modified binders have higher $G^*/\sin\delta$ values than control and warm mix binders, while the ZycoTherm-modified binder revealed insignificant resistance towards potential rutting in comparison to the control binder and that this resistance increased significantly following the inclusion of nano-silica. By observing the outcomes of the modified binders, the addition of nano-silica to control and warm mix binders the enhancement levels at all temperatures are significant. The rutting enhancement is the result of nano-silica dispersion within the asphalt binder, where the NS particles adhere to the binder's surface, forming a new network structure of NS-modified asphalt binder. Fig. 6b shows the *G*/sin δ* values for RTFO-aged binders. Despite this, all nano-silica modified binders have a higher *G*/sin δ* than the control and warm mix binders, which is identical to the unaged condition. Control and warm mix binders having up to 6% NS by weight of binder had the greatest *G*/ sin δ* value, followed by binders containing 2% NS, while binders containing 4% NS had the lowest *G*/ sin δ* value. The incorporation of nano-silica into asphalt binder improves rutting resistance at elevated - temperatures in general, with the effects of 6% NS being the most substantial.

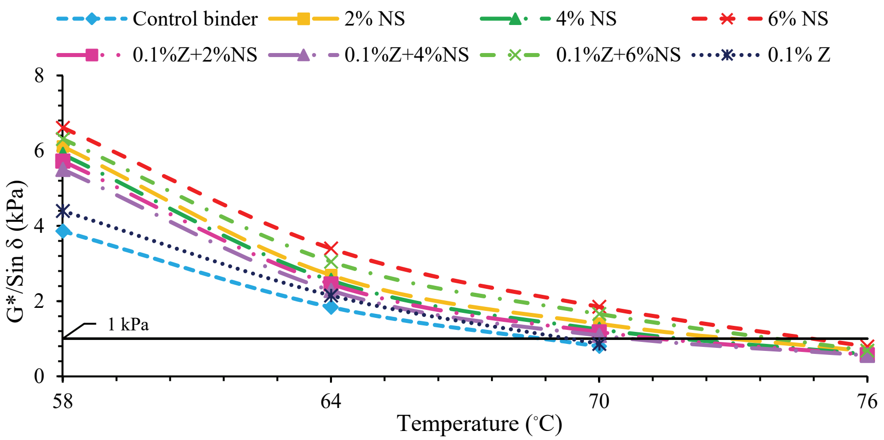

Figure 6a - G/sin δ for unaged control asphalt and modified binders*

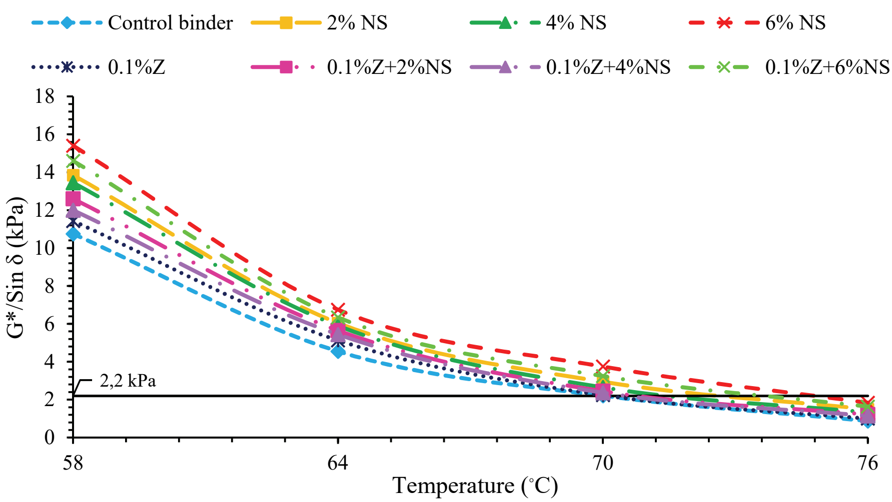

Figure 6b - G/sin δ after RTFO for control and modified binders*

5.5. Bending Beam Rheometer Test

The BBR test was utilized to assess the rheological features of the binders at low temperatures. As displayed in Fig. 7a and Fig.7b, at 60 seconds, all binders' creep stiffness and m-values were determined below 0 ˚C, -6 ˚C, -12 ˚C, and -18 ˚C. When the temperature was reduced from 0 ˚C to −18 ˚C for all asphalt binders, it is evident that the creep stiffness increased and the m-value decreased. Moreover, it is apparent that the creep stiffness of 2% NS, 4% NS, and 6% NS was higher than the control binder and the m-value for the binders was marginally less than that of the control binder. Nano-silica had a negative impact on binders' low-temperature performance, as evidenced by drop-in m- values and an increase in stiffness values. Additionally, the addition of nano-silica to the control asphalt in the absence of ZycoTherm did not effect on the control binder's low-temperature performance grade, despite changing the m-values and creep stiffness values. The insignificant influence of nano-silica on the low-temperature PG of binders was also documented in previous studies [10, 14, 32]. In comparison to the control binder, the creep stiffness is somewhat lower and the m-value higher for the warm mix binder containing 0.1% ZycoTherm. Furthermore, the ZycoTherm binder has a greater m-value as compared to control asphalt; a higher m-value indicates superior cracking resistance. The control asphalt met the low-temperature standards at -6 ˚C, whereas the ZycoTherm binder at -12 ˚C, as the m- value was more than 0.3. However, the creep stiffness increased and the m-values decreased when NS was added to the warm mix binder. As a result, adding nano-silica to the control asphalt does not effect on its low-temperature performance and is insufficient to change the low-temperature grade, whereas the ZycoTherm binder with or without nano-silica particles at low temperature is able of changing the performance grade for the control asphalt and cracking might be avoided. As a result of the findings, the control binder, warm mix binder, and nano-modified asphalt stiffnesses at 60 s were all below 300 MPa and the m-values for all the binders at the 60s were above 0.300. All the evaluated binders are within the Superpave™ specification.

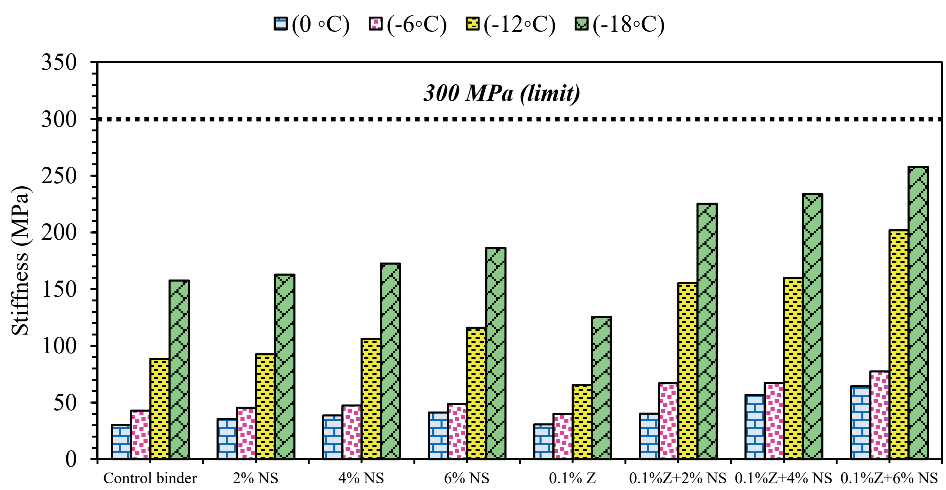

Figure 7a - Creep stiffness values for control and modified binders

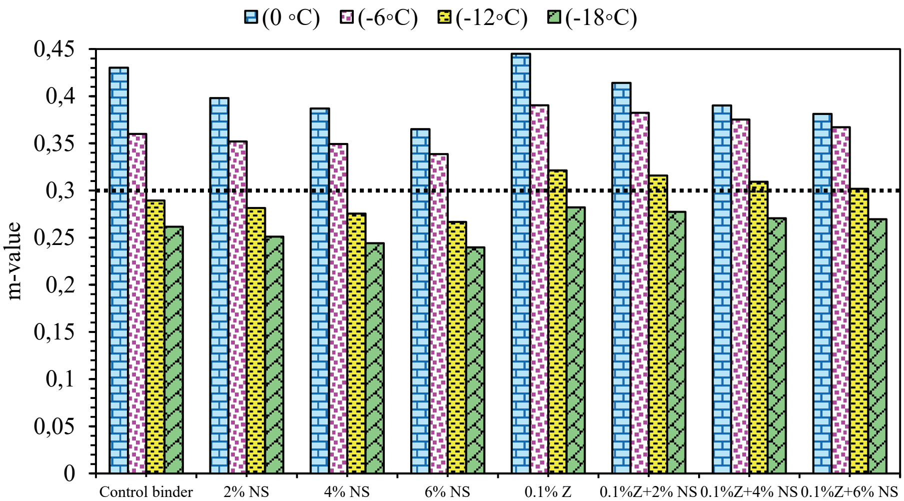

Figure 7b - m-values for control and modified binders

6. CONCLUSION

This research focused on analyzing the impacts of the various percentages of nano-silica (i.e., 2%, 4%, and 6%) on the basic physical features and the rheological features of the control and warm mix binders. Moreover, the research evaluated the impacts of various temperature and frequency ranges on complex modulus and phase angle values as well as the permanent deformation resistance by using the MSCR and Superpave rutting resistance parameter. The influence of low temperatures was utilized using the bending beam rheometer. The results obtained from this study are as follows.

The basic physical features reveal that by adding nano-silica to the control binder, the penetration values decreased while the softening point values increased. Additionally, the warm mix binders modified with nano-silica displayed better enhancement as opposed to the control binder and nano-silica modified binders without ZycoTherm.

By incorporating nano-silica into the control binder, the high-temperature susceptibility decreased and is better enhanced for warm mix binders modified with nano-silica.

The outcomes obtained from the rotational viscosity prove that nano-silica modified binders have higher values than warm mix binders modified with nano-silica. This implies that adding ZycoTherm decreases viscosity. The modified binders' viscosity values all fall within the Superpave specifications requirement at 135 ◦C.

The frequency sweep assessment reveals that the stiffness of the control and warm mix binders was enhanced with the inclusion of nano-silica, resulting in greater complex modulus (G*) values and lesser phase angle (δ) values and enhanced rutting resistance.

The MSCR evaluation displays the effect of nano-silica modified control and warm mix binders on improving the rutting resistance by boosting the recovery percentages and decreasing the J_{nr} values.

Based on the Superpave rutting resistance parameter $G^*/\sin\delta$, adding nano-silica to the control and warm mix binders increases the elasticity of the binder rendering it more resistant to rut.

The BBR test reveals that at low temperatures, applying nano-silica to the control asphalt increases creep stiffness, thus lowering the m-value. This demonstrates nano-silica's ineffectiveness at low temperatures, as well as its resistance to cracking. However, the inclusion of ZycoTherm material had a good influence on changing the grade from -16 °C to -22 °C, meaning that the ZycoTherm/ nano-silica modification had a greater effect on low-temp grade owing to the presence of ZycoTherm.

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