Binder performance and testing

Improving Mixture Performance with Nano-silica Modified Asphalt Binder

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Abstract

There is a growing need to improve the performance properties of asphalt binders in order to minimize the occurrence of failure mechanisms such as permanent deformation, fatigue and moisture damage. Nano-structured materials have taken a scientific-industrial boom as asphalt modifiers used to improve performance due to their mechanical, thermal and electrical properties, among others. The chemistry of the nano-material, and thus its inherent physical properties affects the asphalt binder in a comparable form as polymers at a lower or similar cost. The objective of this study was to evaluate and quantify the effect on binder modification with nano-silica on binder and mixture properties and performance. Nano-silica was selected because it is widely used in the painting industry to improve adhesion of the paint to the walls and provides and impermeable coat. The effect of the incorporation of nano-silica into a PG64(22, intermediate temperature) binder at various contents from 3.0% and 6.0% was evaluated. Rheological and chemical analysis techniques were used to quantify the effect of asphalt binder modification. The study included determination of the engineering properties of laboratory-produced asphalt mixtures. The laboratory testing program evaluated mixture stiffness over a wide temperature range (Dynamic Modulus), moisture susceptibility, fatigue cracking (cyclic SCB), and permanent deformation (Hamburg Wheel Tracking Test). In conclusion, modification of the neat binder with nano-silica demonstrated significant improvements in physical and thermal properties. A significant increase in stiffness at low frequencies/high temperatures were obtained with modified binders. In addition, a significant improvement in resistance to permanent deformation and resistance to moisture damage were obtained. No statistical effect on fatigue resistance was obtained.

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1. INTRODUCTION

Asphalt pavements are currently subjected to high performance requirements. In many cases the high traffic volume, traffic loads, and tire pressures that a flexible pavement will have to support require that the asphalt binders that are readily available be modified. In the past, the alternative for binder modification was the use of polymers such as styrene–butadiene–styrene (SBS), styrene–butadiene–rubber (SBR), ethylene glycidyl acrylate (EGA) and crumb rubber. Nowadays, the tendency is to modify the binder at the molecular level by the incorporation of nano materials and to perform more in depth analysis of the chemical and thermal behaviour of binders by the use of nano technology [1].

Nanotechnology is playing an important role in modifying several existing conventional technologies. There are several examples of addition of nanoparticles such as nano-ZnO, nano-alumina, nano silica etc. which have helped in enhancing properties such as corrosion resistance, mechanical properties and UV blocking effect [2]. Silicon dioxide, also known as silica is a chemical compound that is an oxide of silicon with the chemical formula SiO2. Nanosilica improves the properties of the paints by increasing the water repellence and provide extra protection of surfaces, against microbial, physical and chemical deterioration, as alternative to conventional organic based additives [3]. Due to properties such as greater surface area, strong adsorption, good dispersal ability, high chemical purity, and excellent stability the nano-silica has been used as an additive, catalyst carrier, rubber strength agent, plastic filler, graphite viscosity agent and most recently as a modifier for improving asphalt performance [4-5].

Due to its mechanical and thermal properties (higher modulus of elasticity and higher degradation temperatures), the effect of nanosilica on the asphalt binder was to improve (increase) the performance grade of the binder at the high critical temperature and to increase the intermediate critical temperature. This effect has been widely observed also when polymers have been used with asphalt binders [6-7, 1, 8-9].

In this study, nano-silica was used to modify the control asphalt binder. It was added into the control asphalt binder at two concentrations 3.0% and 6.0% by weight of the asphalt binder. This paper summarizes a comprehensive investigation on the effect of the incorporation of nano-silica on chemical composition and rheological properties of a typical asphalt binder in Costa Rica. In addition, two dense graded mixtures with nominal aggregate size of 9.5mm and 12.5mm were used to analyze the effect of the nano-silica on mixture properties and performance.

2. OBJECTIVE AND SCOPE

The main objective of this study was to evaluate and quantify the effect on binder modification with nano-silica on binder and mixture properties. A secondary objective was to select the top performer asphalt mixture that could provide a more balanced mixture in terms of performance.

To accomplish the objective of this study, Dynamic Shear Rheometer (DSR) fatigue and rutting tests on the binder, along with BBS tests, were used to analyse the effect of the nano-material on binder performance. Fourier Transform Infrared Spectroscopy (FTIR), Differential Scanning Calorimetry (DSC) tests were used to analyse physical-chemical interaction and stability of the modified binder. Dynamic modulus, tensile strength ratio, Hamburg wheel tracking and a cyclic semi circular bending tests were used to analyse engineering properties of asphalt mixtures.

3. MATERIALS USED IN THE STUDY

The different materials that were used in this study are summarized in Table 1. Only one asphalt binder source was selected for the study since the Costa Rican National Petroleum Refinery (RECOPE) produces only one type of asphalt: PG64+22 or PG 64(22) (high and intermediate temperatures).

The selected aggregate sources are some of the most widespread aggregate sources used in Costa Rica. Two of the aggregate sources correspond to limestone materials. The remaining aggregate sources correspond to river gravels of complex mineralogy from different geographical locations in Costa Rica. However, the latter can be classified as siliceous materials from igneous formations that have been subjected to some sedimentary processes. The Central Caribbean material has historically performed well with regards to moisture damage. The materials from the Pacific Coast have been known to result in stripping problems.

Table 1. Materials Selection Summary

Material	Description
Binder	Original Un-modified PG64 (22)*
	PG64 (22) + 3% nano SiO2 (PG76 (25))
	PG64 (22) + 6% nano SiO2 (PG82 (25))
Aggregate Source	River Gravel 1 – Central Pacific
	River Gravel 2 – Central Caribbean
	Limestone 1 – Central Valley
	Limestone 2 – North Pacific

*Intermediate temperature

The type of silica used in this study was a fumed silica also known as pyrogenic silica because it is produced in a flame, consists of microscopic droplets of amorphous silica fused into branched, chainlike, three-dimensional secondary particles which then agglomerate into tertiary particles. The resulting powder has an extremely low bulk density and high surface area. Its three-dimensional structure results in viscosity-increasing, thixotropic behavior when used as a thickener or reinforcing filler. It has a BET surface between 175 - 225 m2/g and a density at 20 °C of approximately 2.2 g/cm3.

Mixing of the binder and nanosilica was performed in a high shear, high frequency blender at 180 °C for approximately one hour. This process was repeated several times in maximum quantities of 1 gallon per batch.

4. PERFORMANCE TESTS AND ANALYSIS OF BINDERS

4.1. Asphalt Binder Rheological Analysis

Figures 1 and 2 show the G* black space diagram and mastercurves of the control and the two modified binders. Three temperatures (4, 20 and 40 C) and five frequencies (0.1, 0.5, 1.5, 10, and 25 rad/s) were used to generate these data. The results indicated that inclusion of nano particles of silica produced a hardening effect on the binder. A significant reduction of the phase angle and a significant increase of the complex shear modulus obtained at high temperatures and low frequencies were also obtained. This behavior is more evident at high temperatures and low frequencies. On the other hand, no significant differences in G* values were observed at low temperatures and high frequencies.

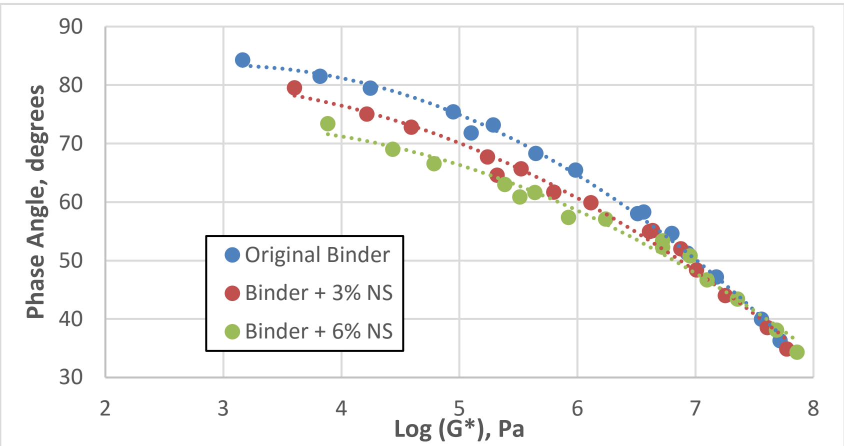


Figure 1. G* Black Space Diagrams

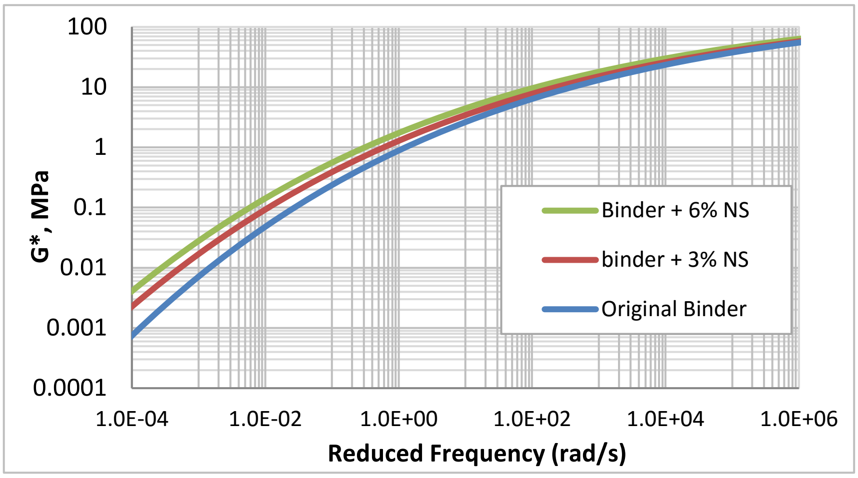


Figure 2. Binder MasterCurves

4.2. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analyses were performed on each of the studied binders. The analysis allows the study of the sample molecular structure based on the infrared spectrum. In this technique, infrared radiation is passed through a sample; some of this radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample [10]. The functional composition changes associated to modification of the binder by means of FTIR spectroscopy are shown on Figure 3.

There are three characteristic bands that define the nano-silica. One of high intensity at 1050 cm-1, a second with low intensity at 850 cm-1 and the last one of high intensity at 450 cm-1. These high transmittance (intensity) groups are not formed in unmodified binder. As expected the intensity of these groups increased as the amount of nano-silica increased for the modified binders without exceeding the intensity of the silica itself, thus and also providing evidence of the proper incorporation and dispersion of the modifier into the binder. Another important aspect obtained from FTIR analysis was the lack of presence of the carbonyl and sulfoxide peaks, which reveals that the modified binder did not age due to the incorporation of the modifier.

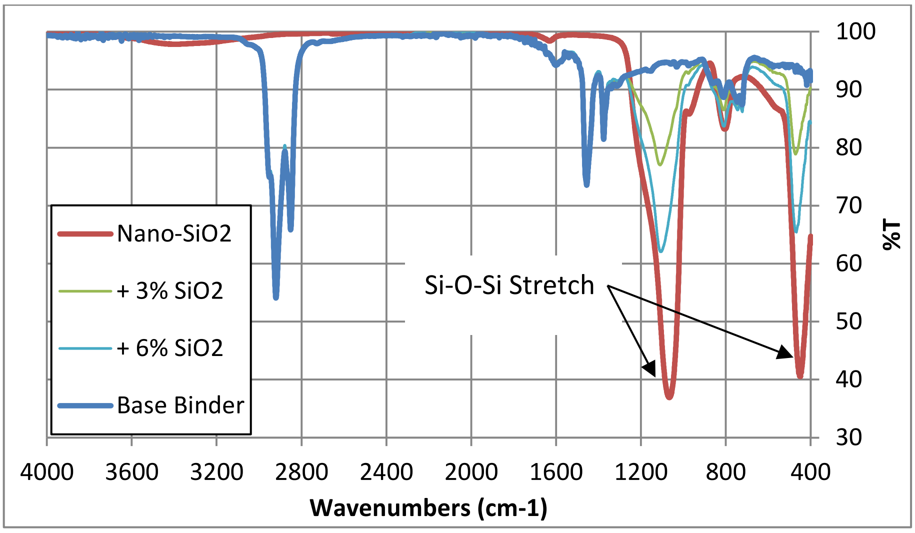


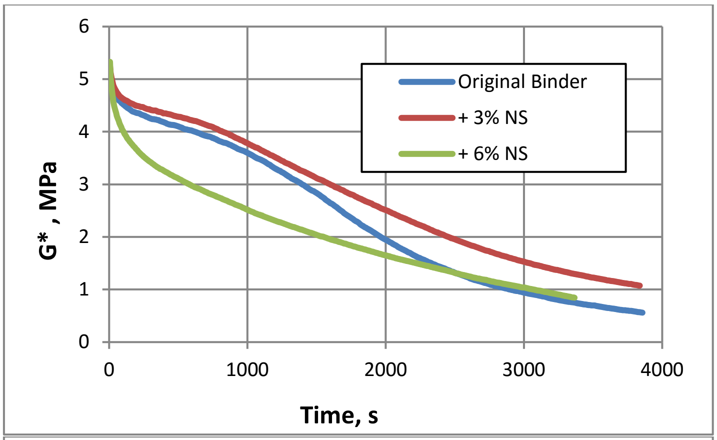
Figure 3. FTIR Analysis

4.3. Effect of Modifier Content on Fatigue at binder level

To characterize the fatigue performance of the binders, a DSR repetitive fatigue analysis was used. The test was performed at a temperature of 22 °C (neat binder intermediate performance grade temperature) and consists of subjecting the sample to an angular frequency of 10 rad/s, under controlled mode (10 %) following NCHRP 459 recommendations [11]. A 2 mm thick and 8.0 mm in diameter sample geometry was used due to the relatively low temperature. The test was performed to a point close to 100% damage of the sample and the results are exhibited on Figure 4. A primary damage zone with an initial modulus decay rate (viscoelastic range) and after that a secondary zone with an accelerated damage zone are exhibited for all samples. It was determined that the inflection point between the primary and secondary zones occurred when the slope of the "Phase angle vs. Time" curve equals zero.

For each fatigue curve the inflection point in terms of time was computed along with the associated G* value. Table 2 shows the average and standard deviation of three samples tested with the DSR. On average, addition of 3% and 6% nano-SiO2 to the original binder improves its fatigue resistance. However, these results, in terms to average time to reach the inflection point, were not statistically different at $\alpha = 0.05$ (p-value = 0.455). It was also observed that in all cases the samples reached the inflection point prior to losing 50% of their original stiffness.

a



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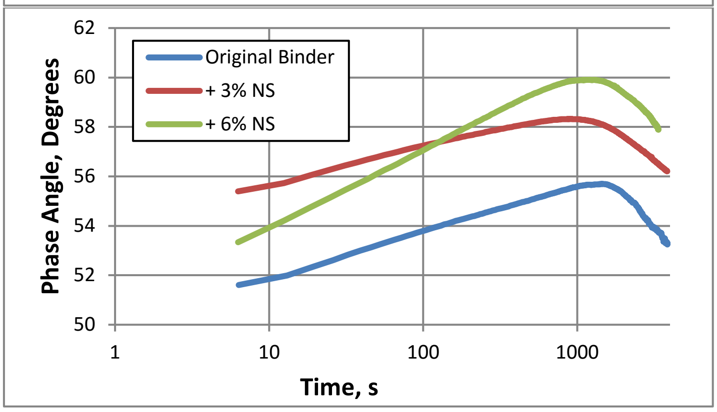

Figure 4. Fatigue test results, a. G* vs. Time, b. Phase angle vs. Time

Table 2. Binder Fatigue Analysis.

Material	G* Initial, MPa		Time to Inflection, sec		G* @ Inflection, MPa		% G* @ Inflection
	Ave.	Std. dev.	Ave.	Std. dev.	Ave.	Std. dev.	
Original	5.03	0.22	1475	296	3.03	0.88	60%
+ 3% SiO2	5.57	0.09	2172	1877	2.83	1.16	51%
+ 6% SiO2	5.47	0.20	2018	1176	2.96	0.90	54%

4.4. Effect of Modifier Content on Rutting at binder level

To characterize the rutting performance of all the binders, the repetitive creep test was conducted. The repetitive creep test is performed at the high PG grade temperature and consists of subjecting the sample to 300 load cycles with a shear stress of 100 Pa. The defined creep time is 1.0 seconds and the recovery time is 9.0 seconds according to test specifications [11]. This test was performed at 64 °C and the results are shown on Figure 5. A 1 mm thick and 25 mm in diameter sample geometry was used due to the high testing temperature. All the modified binders showed lower permanent deformation than the original or neat binder. As expected, an increase in the stiffness of the binder and the higher content of crystallisable fractions have positive effects on permanent deformation.

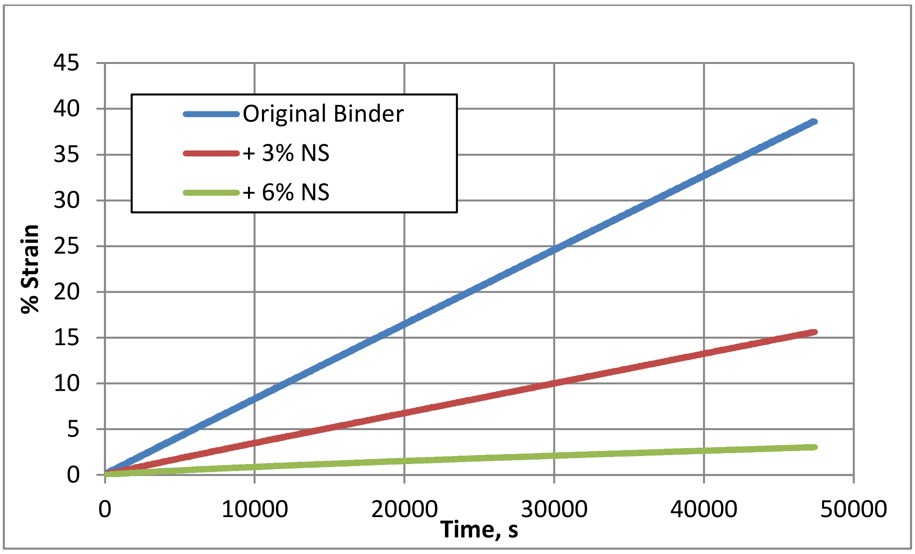

Figure 5. Repetitive creep test results.

5. ASPHALT MIXTURE DESIGN AND PERFORMANCE

5.1. Mix design

Six mix designs were developed for the purposes of this research using the Superpave volumetric mix methodology. Table 3 shows two aggregate gradations using River Gravel 1 – Central Pacific (known for historic stripping problems). Both gradations were created to comply with Superpave specifications for a 12.5 mm and 9.5 mm NMAS. All six mixtures were design under AASHTO R35 to meet the requirements of AASHTO M323 for high traffic level (over 10 million ESALs) with Ndesign of 75 gyrations. Table 4 shows all the volumetric properties along with the respective requirement.

Table 3. Aggregate Particle Size Distributions

Sieve No	Sieve Size (mm)	12.5 mm NMAS		9.5 mm NMAS	
		% Passing	Criteria	% Passing	Criteria
3/4"	19.00	100.00	100	100.00	-
1/2"	12.50	95.86	90-100	100.00	100
3/8"	9.50	84.68	-	94,66	90-100
N° 4	4.75	48.48	-	49.02	90
N° 8	2.36	32.57	28-58	32.68	32-67
N° 16	1.18	22.42	-	22.47	-
N° 30	0.60	16.03	-	16.02	-
N° 50	0.30	11.40	-	11.36	-
N° 100	0.15	7.89	-	7.83	-
N° 200	0.08	5.60	2-10	5.57	2-10

A slight increase in the optimum binder content was obtained when adding the nano-silica. Any differences in the volumetric properties of these two sets of mixtures could be attributed to an increase in binder content to provide workability and compactability in the mixture when a stiffer binder is used. In addition, the aggregate source is highly absorptive (over 2.5% absorption of the blend); therefore, absorption of the modified binders may be slower than the mixtures without nano-silica, such mixtures might be over-asphalted also producing and increase in effective binder content and VMA.

Table 4. Asphalt Mixtures Volumetric Properties

Property	Original Binder		+ 3 % NS		+ 6 % NS		Criteria	
	9.5 mm	12.5 mm	9.5 mm	12.5 mm	9.5 mm	12.5 mm	9.5 mm	12.5 mm
Pb	6.6	6.2	6.8	6.4	7.0	6.7	-	-
Va	4.1	4.0	4.0	4.0	4.0	4.1	3 – 5	
VMA	15.5	14.3	15.6	14.6	15.8	15.2	>15	> 14
VFA	73.9	73.9	74.4	72.8	74.7	73.0	65 – 75	
Db Ratio	1.13	1.24	1.13	1.23	1.11	1.17	0.8 – 1.3	
$\%G_{mm(Nini)}$	86.0	86.0	85.6	85.8	85.7	85.6	< 89	

5.2. Dynamic modulus test

Dynamic modulus testing was performed using AASHTO TP 79-13 in the Asphalt Mixture Performance Tester (AMPT). Figure 6 contains the E* mastercurves for all the different mixes. In this case, all mixtures had similar results at low temperatures and high frequencies as shown with the mastercurves. Maximum E* values were similar; however, minimum E* values did show significant differences as shown in the mastercurve plots. In terms of the steepness of the curve, all modified mixtures showed the lower slopes (less susceptible to changes in frequency) compare to the control mixtures.

In order to have a general idea of the temperature effect on E* values, the relative increase in dynamic modulus was analysed at 10 Hz and all tested temperatures. Table 5 shows that at 4 °C, relative changes in E* values were lower than 10%, at 20 °C relative changes were between 6.2 and 13.1% and at 40 °C relative changes were between 42.3 and 47.8%. It was observed that the 9.5mm NMAS control mixture experienced higher increments in E* values compared to the 12.5mm mixture.

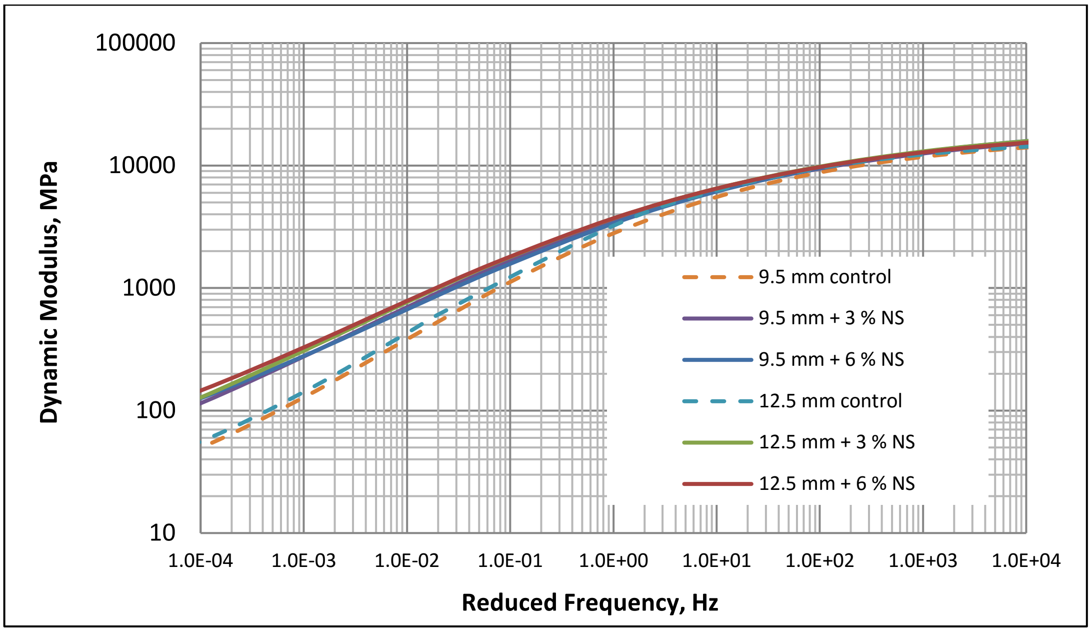

Figure 6. Mixture E* Mastercurves

Table 5. E* Change at 10 Hz.

Temp. (°C)	Mixture	Dynamic Modulus |E*| (MPa)	% Increase with respect to control mixture
4	9.5 control	12 430.7	-
	9.5 + 3 % NS	13 035.5	4.9
	9.5 + 6 % NS	13 460.7	8.3
	12.5 control	13 153.0	-
	12.5 + 3 % NS	13 565.7	3.1
	12.5 + 6 % NS	13 381.7	1.7
20	9.5 control	5 331,0	-
	9.5 + 3 % NS	6 027.5	13.1
	9.5 + 6 % NS	6 000.3	12.6
	12.5 control	6 050.3	-
	12.5 + 3 % NS	6 423.0	6.2
	12.5 + 6 % NS	6 510.0	7.6
40	9.5 control	1 012.9	-
	9.5 + 3 % NS	1 497.0	47.8
	9.5 + 6 % NS	1 415.8	39.8
	12.5 control	1 134.3	-
	12.5 + 3 % NS	1 614.7	42.3
	12.5 + 6 % NS	1 628.9	43.6

5.3. Hamburg wheel-track testing (HWTT)

HWTT was performed in accordance with AASHTO T 324-14 at 50°C. Rut depths are automatically measured for each load cycle. Testing is terminated if rutting exceeds 12.5 mm (½-inch). All the mixtures complied with the 12.5 mm criteria with a maximum rut depth of 7.7 mm for the 12.5mm NMAS control mixture (Figure 7). In addition, no signs of moisture susceptibility were obtained due to the lack of the inflection point in any on the mixtures. A significant reduction in rutting susceptibility was obtained with the incorporation of the nano-silica with rut depths 50% lower than the control mixtures.

An analysis of variance was conducted to evaluate the effect of gradation type (NMAS), asphalt type (control vs. modified) and the interaction of these two factors. ANOVA results indicated that only the asphalt type was statistically significant at $\alpha = 0.05$. On average, the control mixtures had a rut depth of 7.61mm, the control +3% NS mixtures had a rut depth of 3.56mm, and the control + 6% NS had a rut depth of 2.89mm.

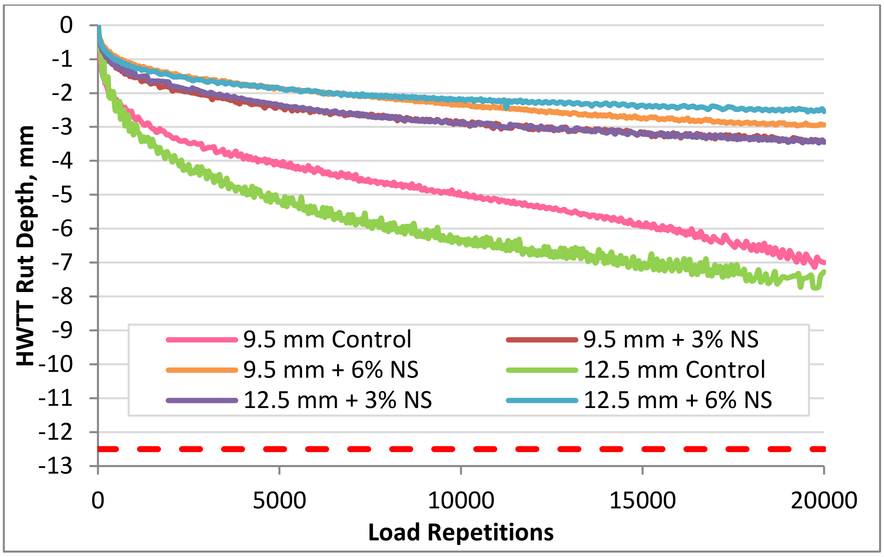

Figure 7. HWT Test Results

5.4. Dynamic Semi-circular Bending test

The Superpave gyratory compactor (SGC) was used to produce compacted samples of 150 mm in diameter and 170 mm of height with a target air voids of 7 ± 0.5%. SCB samples were then prepared with thickness of 50 mm with a notch of 15 mm long and 4 mm wide. It is noted that the introduced notch serves as crack initiator as this test is solely aimed at characterizing the fracture properties of AC mixtures during cracking propagation rather than by cracking initiation. Specimens were long term aged in a conventional oven (85 °C ± 3 °C for 120 hours). A set of three samples were tested on static mode at a rate of 5 mm/min to determine the yield load and the fracture energy.

To conduct the repetitive SCB testing, 50% of the yield load was applied using a 1 Hz haversine load. Table 6 shows the static and dynamic SCB test results. In terms of fracture energy and cycles to failure, the results did not follow any trend. An analysis of variance indicated that neither the type of gradation or NMAS nor the type of asphalt produced statistical differences in the cycles to failure. Therefore, no improvement or negative impact on fatigue resistance was obtained with the use of nan-silica.

Table 6. Cyclic SCB Test Results

Mix type	Maximum Load (kN)	Fracture Energy (kN*mm)	Average Cycles to failure
9.5 control	2.29	6.78	647
9.5 + 3% NS	2.77	4.87	565
9.5 + 6% NS	2.80	3.43	579
12.5 control	2.62	5.69	616
12.5 + 3% NS	2.78	4.73	661
12.5 + 6% NS	3.25	5.56	411

5.5. Tensile Strength Ratio (TSR)

The moisture susceptibility of the mixtures was determined using AASHTO T 283-14. The indirect tensile strength was determined using a Marshall Stability press which loads the specimens at a rate of 2 in/min. The IDT strength was then calculated based on the failure loading and measured specimen dimensions. AASHTO M 323-14 recommends a tensile-strength ratio (TSR) value of 0.8 and above for moisture resistant mixtures.

Table 7 gives a summary of the results from the TSR testing of all mixtures. All mixtures met the 0.8 minimum criteria and the tendency was for the tensile strength ratio to increase with an increase of nano-silica content. Therefore, the improve adhesion capabilities provided by the nano-silica and its intrinsic protective properties helped reduce moisture susceptibility.

Table 7. TSR Test Results.

Mixture	Tensile Strength Dry (kPa)		Tensile Strength Wet (kPa)		TSR (%)
	Average	St. Dev.	Average	St. Dev.	
9.5 control	366	7	312	13	85.3
9.5 + 3% NS	977	33	956	10	97.8
9.5 + 6% NS	959	15	850	10	88.6
12.5 control	852	11	738	17	86.6
12.5 + 3% NS	1 034	43	986	56	95.4
12.5 + 6% NS	963	22	952	59	98.8

5.6. Performance Comparison and Analysis

Based on the results from mixture performance testing, a ranking analysis was conducted to select the most suitable asphalt mixture. Table 8 shows all the materials ranked from 1 to 3, 1 meaning best performance. A ranking analysis considering equal importance of all three performance tests, established as top performers the two modified 12.5mm NMAS mixtures, followed by the two modified 9.5mm NMAS mixtures and at last the 12.5mm and 9.5mm control mixtures. However, based on the conditions of the climatic region, where moisture damage (40% weight) and fatigue cracking (40% weight) are the main type of distresses, the top performer was the 12.5mm NMAS + 3% NS mixture. In addition, this relative importance ranking analysis allowed a more clear differentiation among mixtures. The cost of the nano-material can also be a factor to consider in the selection of the top performer mixture. In this case, a 3% NS modified mixture should provide the lowest cost to benefit ratio.

Table 8. Mixture Ranking Analysis.

Mixture	Performance Test			Final Rank	
	HWT	RSCB	TSR	Equal Importance	Relative Importance
9,5 control	5	2	6	3	5
9,5 + 3% NS	3	5	2	2	3
9,5 + 6% NS	2	4	4	2	4
12,5 control	6	3	5	4	6
12,5 + 3% NS	4	1	3	1	1
12,5 + 6% NS	1	6	1	1	2

6. CONCLUSIONS

Based on the experimental results of this study, it can be concluded that:

- Modification of the neat binder with nano-silica demonstrated significant improvements in physical and thermal properties. Superior binder performance at higher temperature along with higher thermal stability produced higher bond and tensile strength.
- A significant increase in asphalt and mixture stiffness at high temperature and low frequencies was obtained with the incorporation of nano-silica. A significant decrease in rutting susceptibility was observed at the asphalt and mixture level with the addition of nano-silica. In addition, the improved bonding strength between the modified binder and the aggregate was reflected with higher TSR values. On the other hand, no evidence of change in fatigue performance was obtained.
- In general, the intrinsic properties of the nano-silica, that help improve adhesive properties and help protect against harsh environmental conditions, can significantly improve thermal and physical properties of an asphalt binder. This benefit was also translated to the improved performance of asphalt mixtures. The results also indicated that adding 3% nano-silica could be recommended to modify asphalt binders at the lowest cost to benefit ratio.

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