Selection of Optimum Nano-Modifier Content to Ensure Proper Performance of the 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, adhesiveness and moisture damage. Nano-structured materials have taken a scientific-industrial boom as asphalt modifiers due to their mechanical, thermal and electrical properties, among others. The chemistry of the nano-material, and thus their inherent physical properties, ends up in each one having specific effects on the asphalt and variable blending forms depending on their nature.

This paper evaluates the effect of the incorporation of nano-silica into a PG64-22 binder at various contents from 0.5% to 6.0%. Morphological, rheological and thermal analysis techniques were used to quantify the effect of asphalt binder modification. Such techniques were Differential Scanning Calorimetry (DSC), thermogravimetric (TGA) analysis, as well as Fourier transform infrared spectroscopy (FTIR) and Atomic Force Microscopy (AFM). Selection of the optimum modifier content was mainly based on DSR asphalt fatigue and rutting tests and work of adhesion analysis.

Keywords: Rheology, Asphalt, Nano-silica, TGA, FTIR, DSC

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 behavior of binders by the use of nano technology (*Yildirim, 2007*).

Silicon dioxide, also known as silica is a chemical compound that is an oxide of silicon with the chemical formula SiO_2. Silica is most commonly found in nature as sand or quartz, as well as in the cell walls of diatoms (*Shriver and Atkins, 2010*). 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 (*Lazzara and Milioto, 2010, Yao et al, 2012*).

Techniques such as Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry Analysis (DSC), Fourier Transformed Infrared

Spectroscopy (FTIR), atomic force microscopy (AFM), and Iatroscan thin film chromatography have been used to characterize the chemical composition and thermo dynamical behavior of asphalt binders (*Leiva-Villacorta et al, 2014*). The previous techniques can also be used as complement to rheological analysis to better understand the behavior of the material.

Dynamic shear rheometry (DSR) methods have been refined recently, to better predict modified binder properties related to rutting at high temperatures and fatigue cracking at intermediate temperatures. Current asphalt test standards now include Repetitive Creep test, Multiple Stress Creep Recovery (MSCR) Test and repetitive fatigue test of asphalt binders (*Bahia et al, 2001*). Asphalt-aggregate adhesion has also been previously characterized by means of the Bitumen Bond Strength (BBS) test *(Aguiar-Moya et al, 2013, Moraes et al, 2011)*. The test is performed following AASHTO TP-91 using the Pneumatic Adhesion Tensile Testing Instrument (PATTI).

In this study, nano-silica was used to modify the control asphalt binder. It was added into the control asphalt binder at concentrations ranging from 0.5% to 6% by weight of the asphalt binder. This report 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.

OBJECTIVE

The objective of this study was the selection of the optimum nano-modifier content based on binder performance tests.

Scope of Work

To accomplish the objective of this study, Dynamic Shear Rheometer (DSR) fatigue and rutting tests, along with BBS tests, were used to analyze the effect of the nano-material on binder performance. Fourier Transform Infrared Spectroscopy (FTIR), Differential Scanning Calorimetry (DSC), Thermogravimertric Analysis (TGA) and Atomic Force Microscopy (AFM) tests were used to analyze physical-chemical interaction and stability of the modified binder.

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 asphalt binder was also modified with nano-silica (nano-SiO_2) at 0.5%, 3.0% and 6.0%.

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.

Factor	Levels	Description
Asphalt	4	PG64-22*
		PG64-22 + 0.5% nano SiO2 (PG70-25)
		PG64-22 + 3% nano SiO2 (PG76-25)
		PG64-22 + 6% nano SiO2 (PG82-25)
Aggregate Source	4	River Gravel 1 – Central Pacific
		River Gravel 2 – Central Caribbean
		Limestone 1 – Central Valley
		Limestone 2 – North Pacific

*Intermediate temperature

ADVANCED MATERIAL CHARACTERIZATION

Fourier Transform Infrared Spectroscopy (FTIR) Analysis

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 (*Daly et al, 2010, TNC, 2001*). Typically the obtained results are compared to a previously developed spectrum of similar materials in order to determine the nature of the analyzed material and to allow for interpretation of the spectrum bands *(Kuptsov, 1994)*. The functional composition changes associated to modification of the asphalt binder by means of FTIR spectroscopy are shown on Figure 1. 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 asphalt binders. As expected the intensity of these groups increased as the amount of nano-silica increased for the modified binders and also provided evidence of the proper incorporation of the modifier into the binder.
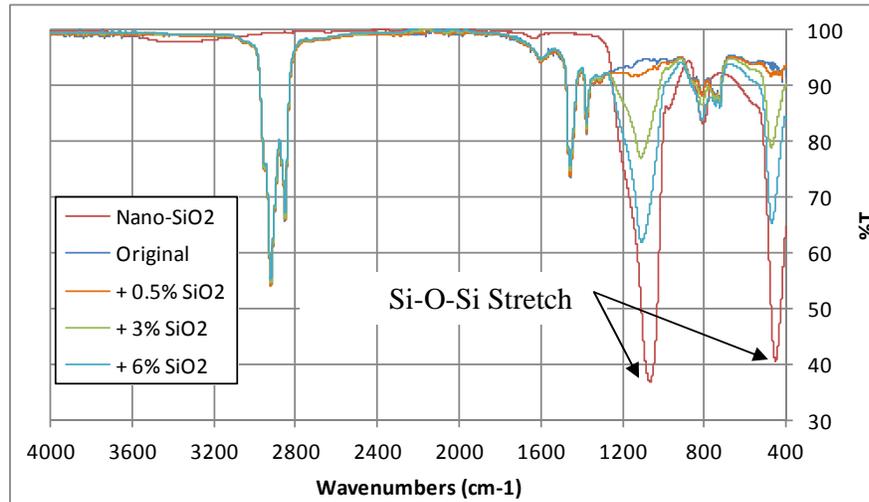
Figure 1. FTIR Analysis.

Atomic Force Microscopy (AFM)

The analysis of the modifier distribution on the asphalt was performed by means of AFM analysis. This test shows information on the topography and tridimensional environment of the sample, and also on the roughness of the material (*Allen, 2010*). The AFM images of the distribution of modifiers within the asphalt matrix are shown in Figure 2. These images indicate a good uniformity of the modified binder and a homogeneous dispersion of the modifier within the binder matrix. Addition of nano-silica to the neat binder increases the roughness of the surface (peak texture value) which is related to particle interlocking and stiffness of the binder.

(a) Peak value 16.21 nm

(b) Peak value 22.16 nm

(c) Peak value 27.55 nm

(d) Peak value 27.43 nm
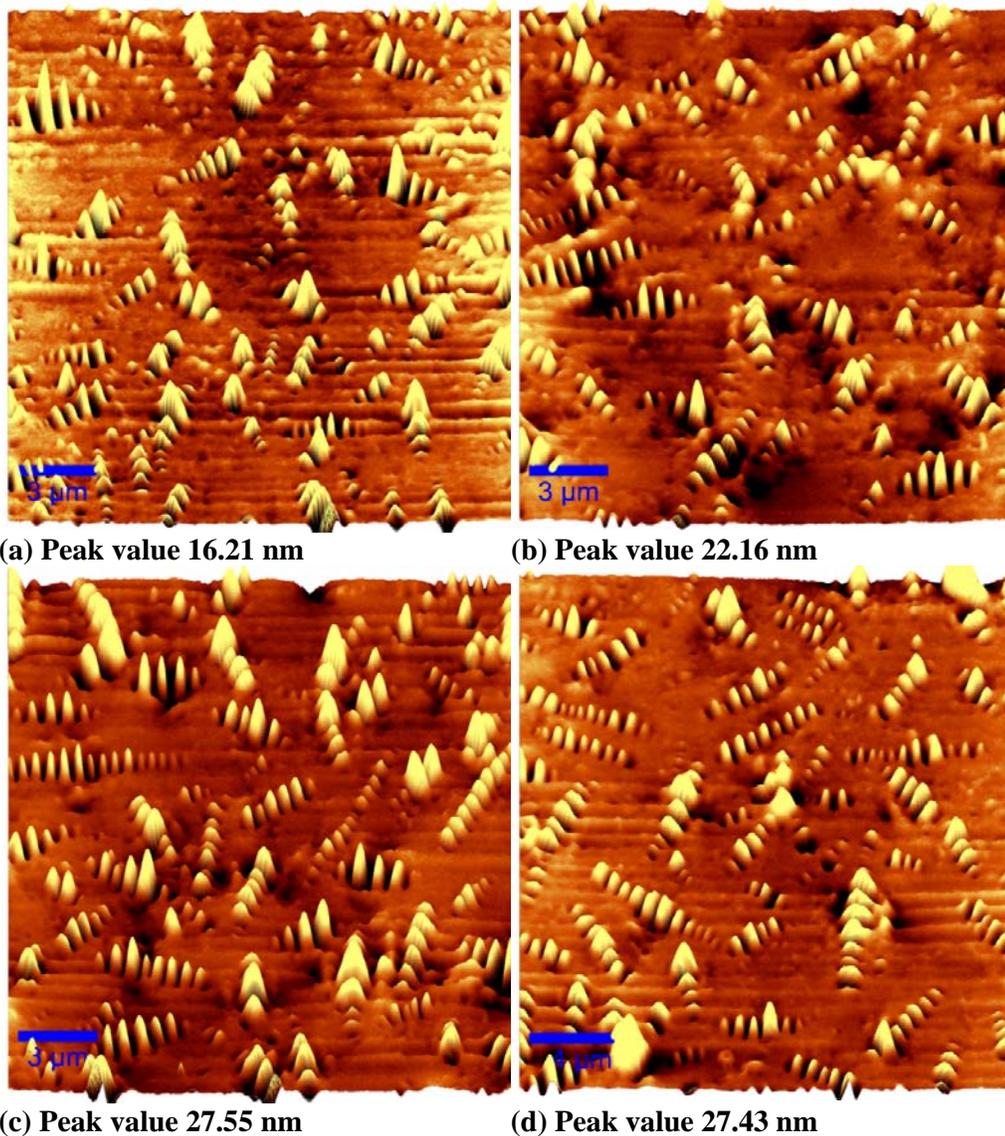
Figure 2. AFM topography (a) unmodified, (b) +0.5% SiO$_2$, (c) +3% SiO$_2$, (d) +6% SiO$_2$.

Differential Scanning Calorimetry Analysis (DSC)

DSC is widely used for determination of thermal transitions brought about by the first order transitions, such as melting and crystallization of crystallizable species (*Elseifi et al, 2010*). Glass transition, Tg, credited as a second order phenomenon taking place in the amorphous region of the sample, can also be defined by DSC (Figure 3), but it depends largely on the nature of the material and its content of crystallizable fractions (ΔH - enthalpy). Below the glass transition temperature, asphalt behaves like a glass and appears brittle, affecting the fatigue performance of the binder and the mix. The onset temperature denotes the temperature at which the glass transition begins. The parameter Tm represents the peak melting temperature. As seen on Figure 3 the asphalt binder clearly exhibits these properties within the range of -50 to 200 °C. On the other hand, the inorganic material SiO_2 which already behaves as a crystal only exhibits minor transitions and it is more stable at the same temperature range.
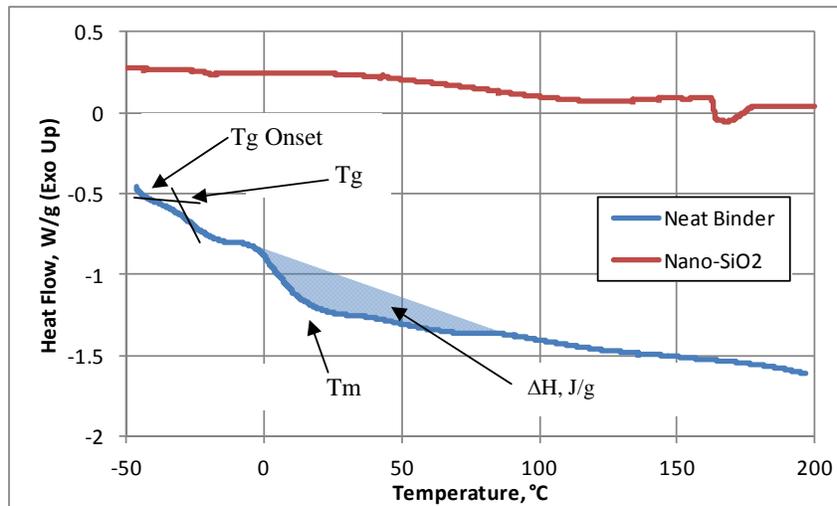
Figure 3. DSC analysis.

Table 3 shows the calculated parameters for all binders. The onset temperature for the neat binder was -45.7 °C, while for the modified binders the results varied between -50 and -40 °C. The glass transition temperature showed significant differences with respect to the neat binder. The trend was to lower the Tg by the addition of the modifiers. No significant differences were obtained among binders in terms of the melting peak temperature which ranged between 23.5 and 24.4 °C.

Finally, the total enthalpy of the melting transition increased compared to the neat binder result. A high crystallinity may increase the hardness and bring about a more rubber-like consistency and a better resistance to flow at high temperatures (*Harrison et al, 1992*). In this case, the higher content of crystallisable fractions was obtained for the 6% nano SiO_2 modified binder.

Table 2. Materials DSC properties.

Material	Tg Onset, °C	Tg, °C	Tm, °C	ΔH, J/g
PG64-22	-45.7	-27.5	24.4	7.8
+ 0.5% nano SiO$_2$	-49.9	-33.9	24.0	8.7
+ 3% nano SiO$_2$	-43.3	-35.5	24.3	9.9
+ 6% nano SiO$_2$	-40.3	-35.3	23.5	10.7

Thermogravimetric analysis (TGA)

TGA is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing or decreasing temperature cycles (with constant heating rate), or as a function of time (with constant temperature and/or constant mass loss) (*Coats and Redfern, 1963*). TGA is commonly used to determine selected characteristics of materials that exhibit either mass loss or gain due to decomposition, oxidation, or loss of volatiles of the asphalt binder. Figure 4 shows an example of TGA definitions. The extrapolated onset temperature denotes the temperature at which the weight loss begins. The point of highest weight loss change rate is known as the inflection point. It is obtained from the peak of the first derivative of the weight loss curve. While almost all the binder was decomposed around 750 °C, the mass loss experience by the nano-silica was 2.1% at the same temperature. This significantly higher thermal stability of the modifier was expected to positively affect the thermal behavior of the binder.
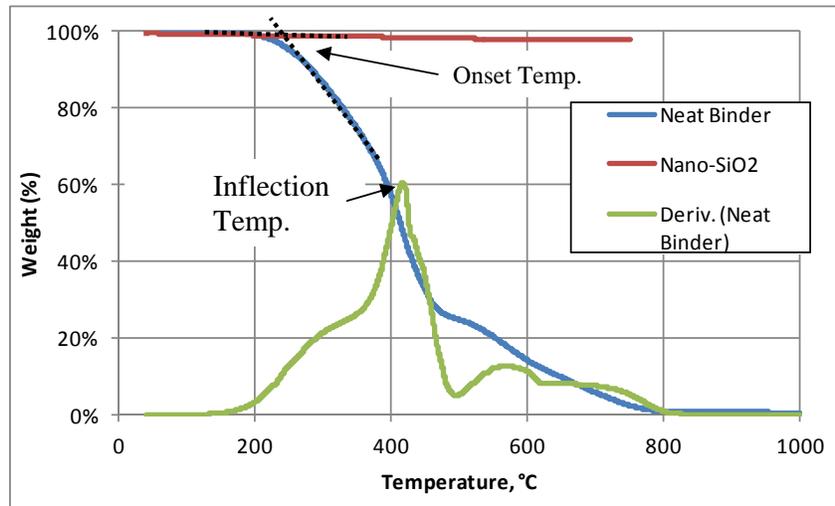
Figure 4. Thermogravimetric analysis.

Table 3 shows the percent mass loss at 200 °C in order to compare the stability of the binders at temperatures close to production conditions. This table also shows the extrapolated onset temperature, the inflection and the residual amount of material for all binders. The 6% nano-SiO$_2$ modified binder was the most stable binder (up to 200 °C) with a mass loss of 0.18%. The onset temperature, also known as decomposition temperature, of the neat binder was 255.3 °C. This value decreased with the addition of 0.5% of the modifier but

increased for higher nano-SiO_2 contents. An increase in the amount of modifier produced an increase in the overall stability of the binder since higher inflection points and higher quantities of residual material were obtained. This can be attributed to formation of stronger molecular crosslinks and higher particle interlocking as observed with the AFM images.

Table 3. Materials TGA properties.

Material	% Loss @ 200 °C	Onset Temperature, °C	Inflection Point, °C	Residue, %
PG64-22	0.92	255.3	416.3	0.67
+ 0.5% nano SiO_2	1.14	247.6	425.8	0.51
+ 3% nano SiO_2	1.17	302.8	433.4	9.67
+ 6% nano SiO_2	0.71	273.1	439.0	18.96

PERFORMANCE EVALUATION

Effect of Modifier Content on Fatigue

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 (*Bahia et al, 2001*). The test was performed to a point close to 100% damage of the sample and the results are exhibited on Figure 5. 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 inflexion point between the primary and secondary zones occurred when the slope of the "Phase angle vs. Time" curve equals zero.
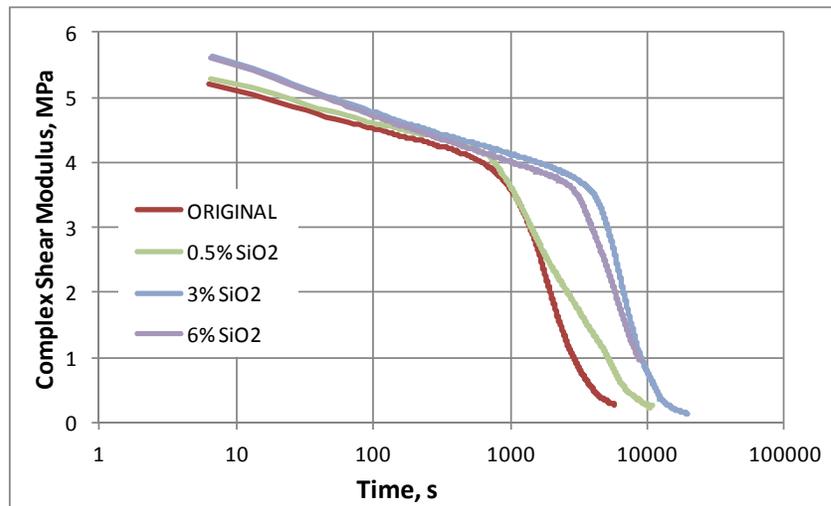
Figure 5. Fatigue test results.

For each fatigue curve the inflexion point in terms of time was computed along with the associated G* value. These results were compared against the time

required to reach 50% modulus drop and the outcomes are shown on Table 4. Based on the inflection point concept, addition of 0.5% affected negatively the fatigue resistance of the binder. On the other hand, addition of 3% and 6% nano-SiO_2 to the original binder significantly improves its fatigue resistance. When considering the time to reach 50% of the modulus, addition of 0.5% nano-SiO_2 slightly improves its fatigue resistance.

Even though, the 6% nano-SiO_2 modified binder showed a significant improvement in fatigue resistance, the best results were obtained for the 3% nano-SiO_2 modified binder. The stiffness of the binder and the content of crystallisable fractions seemed to start having negative effects of fatigue resistance for modifier contents around and above 6%.

Table 4. Fatigue Analysis.

Material	G* Initial, MPa	Inflection, sec	G* @ Inflection, MPa	Time @ 50% G*, sec
PG64-22	5.19	1270	3.20	1628
PG64-22 + 0.5% SiO2	5.29	780	3.97	1721
PG64-22 + 3% SiO2	5.64	3500	3.65	5424
PG64-22 + 6% SiO2	5.61	2850	3.59	4283

Effect of Modifier Content on Rutting

To characterize the rutting performance of all the binders, the repetitive creep test and Multiple Stress Creep Recovery (MSCR) analyses were used. 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 (*Bahia et al, 2001*). This test was performed at 64 °C and the results are shown on Figure 6. 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.
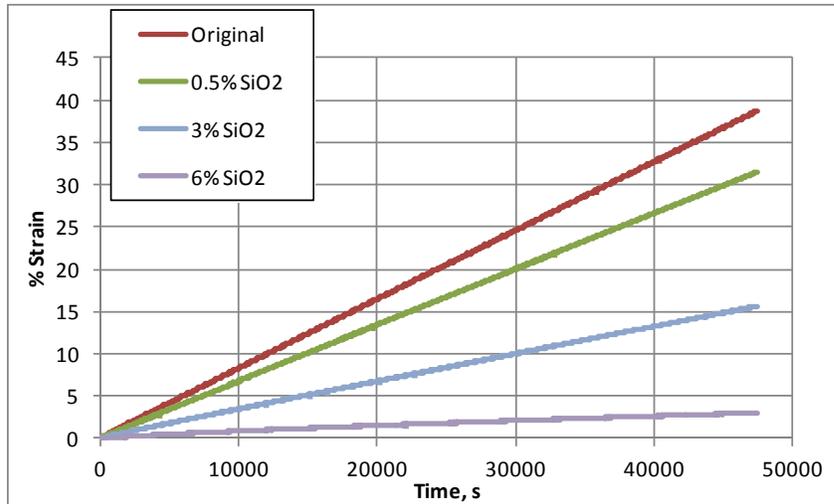
Figure 6. Repetitive creep test results.

The MSCR test (ASTM - D7405/ AASHTO TP70) produces lab results that are closely correlated with actual mix performance. By dynamically loading the modified binder, and monitoring its accumulated "nonrecoverable creep compliance" (J_{nr}), the new test more accurately predicts polymer-modified binder performance, recognizing differences in polymer behavior at different temperatures and stress levels (Mooney, 2008). The MSCR test was also conducted at 64 °C. The same rolling thin film oven (RTFO) aged specimen utilized in the dynamic shear rheometer (DSR) test (conducted according to AASHTO T 315) was also used in the MSCR test. Table 5 summarizes the MSCR testing results. Based on MSCR test results, the neat binder did not meet the $J_{NR@3,2KPa}$ requirement but met the J_{NRdiff} requirement, consequently could not be graded at the lowest traffic level. On the other hand, all modified binders were graded at least as PG 64-22 "H". This results were consistent with the repetitive creep test results.

Table 5. MSCR Results.

Material	Result	$J_{NR@3,2KPa}$	$(J_{NR@3,2KPa}-J_{NR@0,1KPa})$ $/J_{NR@0,1KPa}$
PG64-22	PG 64 (22)	7.344	0.22
+ 0.5% SiO2	PG 64(22) H	1.227	0.18
+ 3% SiO2	PG 64(22) V	0.702	0.23
+ 6% SiO2	PG 64(22) E	0.292	0.36
Traffic		$J_{NR@3,2KPa}$	$(J_{NR@3,2KPa}-J_{NR@0,1KPa})$ $/J_{NR@0,1KPa}$
Standard "S" ($< 1 \times 107$ ESALs)		< 4	$< 0,75$
High "H" ($1 \times 10^7 – 3 \times 10^7$ ESALs)		< 2	$< 0,75$
Very High "V" ($> 3 \times 10^7$ ESALs)		< 1	$< 0,75$
Extremely High "E" ($> 3 \times 10^7$ ESALs) & standing		< 0.5	$< 0,75$

Effect of Modifier Content on Adhesion

Prior to performing the test, the aggregate samples are cut or cored from large rocks. The aggregate sample faces are then polished using 280-grit material to ensure uniform roughness between samples (the mechanical interlock between asphalt-aggregate is minimized to ensure adhesion measurements correspond to thermodynamic interaction between the materials). The samples are then placed in an ultrasonic bath to remove any surface residue. An asphalt sample of 0.4±0.05g is placed on metallic stubs of known diameter (20 mm). The stubs containing the asphalt sample are then pressed against the aggregate surface without applying torsion.

The BBS measures the pull-off tensile strength (POTS) of the asphalt-aggregate system when it is subjected to a constant load rate of 100 psi/s and is analyzed after 24 hours of conditioning at room temperature ($POTS_{Dry}$) and 48 hours conditioning in a water bath at 40 °C ($POTS_{Wet}$). A minimum of 2 replicates were used for each of the material combinations. In order to determine whether the additive content has an effect on work of adhesion, nano-SiO_2 was selected to perform BBS testing at different modifier contents. Figure 7 shows the POTS results before and after conditioning. It can be observed that as the additive content is increased, an increase in adhesion is also obtained. However, the phenomena occurs up to a critical additive concentration after which adhesivity begins to drop. In the case of SiO_2, the critical concentration is above 3%. Consequently, an optimal adhesion/cohesion range can be obtained for a given modifier to maximize the adhesivity, and consequently moisture damage resistance.

The previous observation can be verified by comparing the dry and wet conditioned samples (Bond Strength Ratio - BSR). Results indicate that the use of modification improves resistance to moisture damage as BSR values of most modified binders are higher (improved moisture resistance) compared to the base binder. Additionally, the best overall improvement was obtained with the addition of 3% nano-silica. If a 70% minimum BSR was used as a pass/fail parameter, most treatments will comply with this criteria with the exception of the neat binder/River Gravel 1 and marginally the 6% NanoSiO2 modified binder/River Gravel 2.
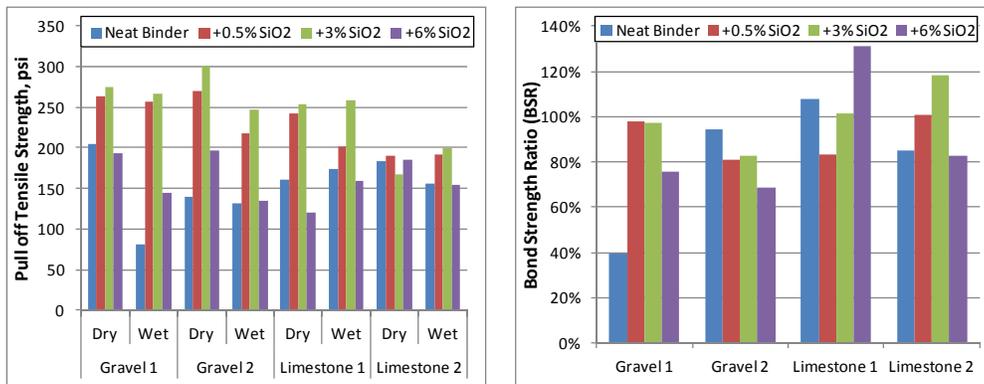
Figure 7. Evaluation of aggregate/binder interaction.

Selection of the optimum modifier content

Based on the results from performance and advanced material characterization tests, a ranking analysis was developed to select the most suitable asphalt binder. Table 6 shows all the materials ranked from 1 to 4, 1 meaning best performance. Asphalt binders modified with 3% and 6% nano-SiO_2 exhibited the most improvement in thermal and physical properties and performance. The higher thermal stability of the 6% nano-SiO_2 modified binder is related to the better resistance to permanent deformation. On the other hand, the low temperature stability improvement and higher surface roughness of the 3% nano-SiO_2 modified binder is related to better fatigue resistance and lower moisture damage susceptibility.

The selection of a binder capable of resisting all three types of distresses is complicated. However, depending on the function of the asphalt layer, a binder could be selected to address two types of potential problems. However, the 3% nano-SiO_2 content can be selected as optimum amount of modifier to be incorporated into the neat binder due to its overall performance. Further studies utilizing asphalt mixtures are necessary to validate these results.

Table 6. Performance ranking analysis.

Material	Roughness AFM	Low Temp. Stability DSC - Tg	Thermal Stability TGA	Rutting MSCR, DSC	Fatigue	BSR POTS
PG64-22	4	4	3	4	3	4
+ 0.5% SiO2	3	3	4	3	4	2
+ 3% SiO2	1	1	2	2	1	1
+ 6% SiO2	2	2	1	1	2	3

CONCLUSIONS

Modification of the neat binder with nano-silica demonstrated significant improvements in physical and thermal properties with higher thermal stability and higher particle interlock (roughness). Higher contents of crystallizable fractions and higher thermal stability seem to be responsible for stiffer and more resistant to permanent deformation binders. On the other hand, lower glass transition temperatures and higher surface roughness seem to be responsible for more fatigue resistance binders and less moisture damage susceptible binders.

Significant differences in strength of adhesion between the different aggregate-binder combinations were obtained. A minimum Bond Strength Ratio of 70% is recommended. Non-compliance occurred with River Gravel 1/neat binder, reason why the use of aggregate sources should be limited if there is previous history of moisture damage related problems.

Selection of the optimum modifier can be based not only on DSR asphalt fatigue and rutting tests (creep and MSCR) but also with an aggregate/binder interaction analysis and physical and thermal properties. Depending on the function of the asphalt mixture within the pavement structure, a modifier could be selected to address two types of typical distresses. Further evaluation of mixtures containing the studied modified binders is needed to corroborate the results of this research.

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