

1                   **ADHESION PERFORMANCE OF NANO-SILICA MODIFIED BINDER**  
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32                   **Word Count: Abstract (259) + Body (4,355) + Figures and Tables (11x250) = 7,364**  
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1 **ABSTRACT**

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3 The interaction between the binder and the aggregate is fundamental in ensuring the adequate  
4 performance of asphalt mixtures, mainly under the presence of water. The work of adhesion that is  
5 generated by both materials directly affects the resistance of the asphalt mixture to moisture damage  
6 since it clearly quantifies the ease with which water can displace the binder from the aggregate  
7 surface. However, the effect of moisture and the physical-chemical interaction between binder and  
8 aggregate depends on the specific properties of each material and the conditions at which the asphalt  
9 mixture is produced and expected to perform. The study looks to characterize the bond strength  
10 between nano-silica modified asphalt and several aggregate sources that are typically used in Costa  
11 Rica. Each binder was characterized by means of the Superpave performance grade,  
12 Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry Analysis (DSC). To  
13 measure the strength of adhesion, the Binder Bond Strength (BBS) test was used. All testing was  
14 performed on the neat and modified binders, as well as on each binder - aggregate combination after  
15 RTFO and RTFO + PAV aging. The BBS results identify significant differences in the bond strength  
16 due to moisture conditioning and aging. The differences are highly dependent on the aggregate source.  
17 Furthermore, depending on the type of aggregate, different failure types were observed: cohesive vs.  
18 adhesive. The type of binder is also highly significant in determining strength of adhesion. The results  
19 also indicate an increase in the strength of adhesion associated to the aging process, where the main  
20 increase in resistance is observed after RTFO aging.

21  
22 **INTRODUCTION**

23 The most common manifestation of distress associated to the presence of moisture in the HMA layer is  
24 known as stripping, a phenomenon that involves the loss of binder coating from the aggregate surface  
25 (1). The process is typically followed by a progressive loss of aggregate particles from the HMA layer  
26 surface as a result of stresses associated to wheel loads travelling over the material (ravelling). The  
27 previous distress modes are related in that they are originated by a loss of adhesion at the binder -  
28 aggregate interface.

29 Several laboratory testing methods have been developed to quantify the susceptibility of asphalt  
30 mixtures to moisture damage. The most typical tests are: boiling test (ASTM D3625), Texas boiling  
31 test (Tex-530-C), static-immersion test (AASHTO T 182), Lottman test, modified Lottman (AASHTO  
32 T283), Tunncliffe and Root Conditioning test (2), immersion-compression test (AASHTO T 165),  
33 Texas freeze thaw pedestal test, Hamburg wheel tracking device (HWTDD) test (AASHTO T 324), and  
34 the Superpave simple performance tests (static creep, repeated load permanent deformation, and  
35 dynamic modulus) with an environmental conditioning system (ECS).

36 In Costa Rica, the modified Lottman or indirect tension test is used to evaluate the susceptibility of  
37 HMA to moisture damage (3). Similarly, many DOTs at the international level use the test to ensure a  
38 minimum resistance to moisture damage, and to justify the need for adhesion promoters (4). However,  
39 in several cases it has been reported that the test is not representative of field performance (5).  
40 Moreover, the testing methodology has been highly criticized by experts due to its inability to  
41 reproduce actual field failure mechanisms and changes associated to aging in the HMA (6-8).

42 Moisture damage is highly related to the cohesion bond which involves the internal cohesion of the  
43 asphalt matrix, and with the adhesion bond which is related to the interaction strength between binder  
44 and aggregate (9). However, as of currently implemented material design procedures, the previous  
45 properties are not accounted for to the degree of importance that is required. Because of this reason, a  
46 strong trend to study and understand the processes involved in aggregate-binder adhesion and binder  
47 internal cohesion is being undertaken.

48 Deterioration associated to moisture damage is a function of various thermodynamic processes.  
49 Several studies indicate that different factors can be considered as feasible causes of the damage  
50 caused at the interface between the mastic and the aggregate surface (adhesion failure) and within the  
51 internal structure of the mastic (cohesion failure). In general, it is agreed that the failure type depends  
52 primarily on the material properties. However, several factors other than the asphalt mastic affect the  
53 susceptibility of the asphalt mixture: use of binder modifiers, and the use of adhesion promoters such  
54 as liquid antistriper or hydrated lime (10). It has also been observed that an increase in water pH present

1 at the asphalt-aggregate interface has an important effect on the weakening of the adhesive bond  
2 between the two materials (11).

3 Tarrer and Wagh (12) identified at least 6 different failure mechanisms that can be associated to  
4 moisture damage and aggregate detachment, and can occur individually or simultaneously. The  
5 mechanisms are: detachment, displacement, spontaneous emulsification, pore pressure, hydraulic  
6 scouring, and environmental factors. Additionally, other factors such as rupture of the asphalt film and  
7 pH instability have been highlighted.

8 Detachment occurs when a thin layer of water displaces the complete binder film from the  
9 aggregate surface, without a break in the binder film (discontinuity in binder film that allows the flow  
10 of moisture that can result from inadequate coating). This is a consequence of lower free surface  
11 energy of water as compared to the binder, resulting in a higher wettability (ability of a liquid to  
12 maintain contact with a solid surface) of the aggregate (13). Displacement differs from detachment  
13 because water penetrates the aggregate surface by a break in the binder film caused by inadequate  
14 coating or binder film rupture (11, 14). Spontaneous emulsification results when water and binder  
15 combine to form an emulsion, phenomenon that is amplified by the presence of emulsifiers such as  
16 some mineral clays and binder additives (11, 14). Pore pressure can also generate moisture damage in  
17 asphalt mixtures with high air void contents, typically open graded mixtures where water can circulate  
18 through the interconnected voids. As traffic loading continues, water pressure increases and can  
19 generate microcracks in the binder film. The problem worsens if water becomes trapped in the  
20 impermeable voids (12, 15). Hydraulic scouring occurs only at the pavement surface and is a result of  
21 the effect of vehicle tires on wet pavement surfaces which generate high water pressures ahead of the  
22 tire and suction behind the tire (11-15).

23 Finally, the physical-chemical properties of oxidized binder promote the occurrence of micro-  
24 cracks, which in turn become paths through which water can more freely penetrate the binder-  
25 aggregate interface, accelerating the moisture damage process. However, there are mixed results  
26 regarding the effect of an aged binder on the adhesion between asphalt and aggregate (16). If the  
27 strength of the interaction is reduced, the resistance of the asphalt-aggregate system will be  
28 compromised, increasing the sensibility to moisture (17). Negative consequences associated to the  
29 aging process can be predicted by characterizing the surface free energy of the affected material:  
30 binder. This in turn allows the design of aggregate-binder combinations that optimize the adhesion  
31 between the materials (10, 18, 19).

### 32 33 **OBJECTIVE**

34 The main goals of the research project were: 1) quantify the adhesion between the binder source  
35 available in Costa Rica with different aggregate types typically used in construction, 2) characterize  
36 the effect of different modifier contents on moisture damage susceptibility, and 3) determine the effect  
37 of aging on adhesion for the analyzed materials. The Binder Bond Strength (BBS) test was used to  
38 evaluate the binder-aggregate adhesion and the internal cohesion of the binder structure.

### 39 40 **MATERIALS USED IN THE STUDY**

41 The different materials that were used in this study are summarized in Table 1. Only one binder  
42 source was selected for the study since the Costa Rican National Petroleum Refinery (RECOPE)  
43 produces only one type of binder: PG64-22 or PG 64[22] (high and intermediate temperatures). The  
44 binder was also modified with nano silica (SiO<sub>2</sub>) at 0.5%, 3% and 6% by mass of binder. All the  
45 additives were incorporated using a low shear stirrer at 175 °C for 3 hours. The PG analysis results are  
46 shown in Table 1. The vast majority of the analyzed modifiers increased the high temperature grade.

47 The selected aggregate sources are some of the most widespread aggregate sources used in  
48 roadways construction in Costa Rica. Two of the aggregate sources correspond to limestone materials.  
49 The remaining aggregate sources correspond to river gravels. All of these have complex mineralogy  
50 and come from different geographical locations in Costa Rica. Both river gravel sources can be  
51 classified as siliceous materials from igneous formations that have been subjected to some  
52 sedimentary processes. The Central Caribbean material has historically performed well with regards to  
53 moisture damage. The materials from the Pacific Coast have been known to result in stripping  
54 problems.

1 **TABLE 1. Materials Selection Summary**

Material	Description
Binder	PG64-22*
	PG64-22 + 0.5% nano SiO <sub>2</sub> (PG70-25)
	PG64-22 + 3% nano SiO <sub>2</sub> (PG76-25)
	PG64-22 + 6% nano SiO <sub>2</sub> (PG82-25)
Aggregate Source	River Gravel 1 – Central Pacific
	River Gravel 2 – Central Caribbean
	Limestone 1 – Central Valley
	Limestone 2 – North Pacific

2 \*Intermediate temperature  
3

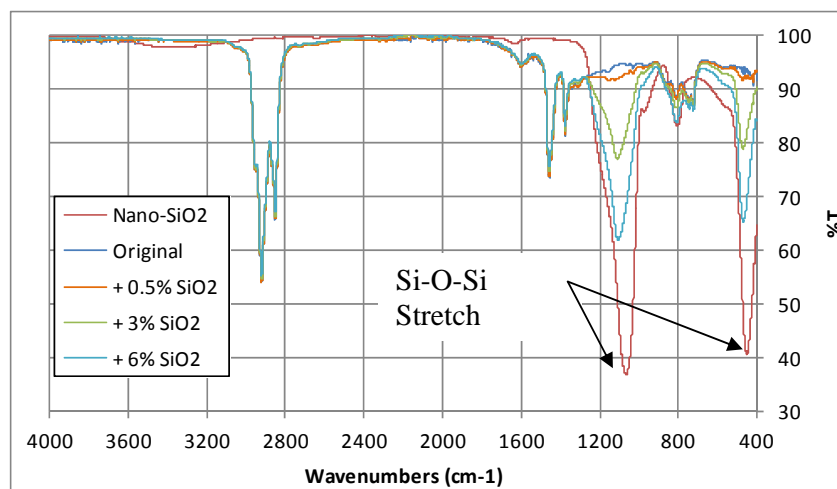
4 The asphalt binder aging variable is intended for simulating the changes in adhesion due to changes in  
5 asphalt properties associated to the aging process. Three distinct aging conditions have been evaluated:  
6 1) neat binder, 2) RTFO aged binder to simulate the aging associated to the plant mixing and HMA  
7 field construction process, and 3) PAV aging to simulate aging and oxidation in the asphalt binder  
8 during the initial 7 to 10 years of service life.  
9

10 **Advanced Material Characterization**

11 There are an important number of well-known tests that have been used as methods to characterize the  
12 chemical composition and thermo dynamical behavior of asphalt binders. The following are some of  
13 the techniques currently used in Costa Rica:  
14

15 **Fourier Transform Infrared Spectroscopy (FTIR) Analysis**

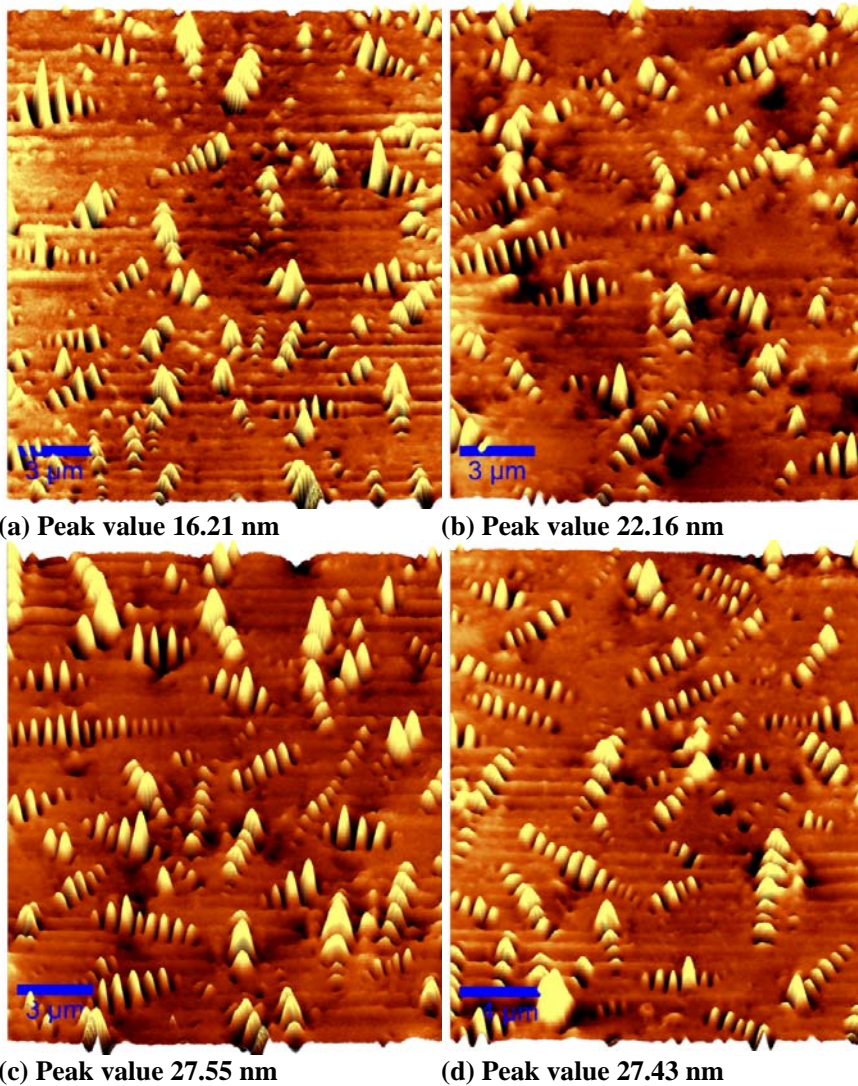
16 In this technique, infrared radiation is passed through a sample; some of this radiation is absorbed by  
17 the sample and some of it is passed through (transmitted). The resulting spectrum represents the  
18 molecular absorption and transmission, creating a molecular fingerprint of the sample (20). Typically  
19 the obtained results are compared to a previously developed spectrum of similar materials in order to  
20 determine the nature of the analyzed material and to allow for interpretation of the spectrum bands  
21 (21). The functional composition changes associated to modification of the binder by means of FTIR  
22 spectroscopy are shown on Figure 1. There are three characteristic bands that define the nano-silica.  
23 One of high intensity at 1050 cm<sup>-1</sup>, a second with low intensity at 850 cm<sup>-1</sup> and the last one of high  
24 intensity at 450 cm<sup>-1</sup>. These high transmittance (intensity) groups are not formed in unmodified  
25 binder. As expected the intensity of these groups increased as the amount of nano-silica increased for  
26 the modified binder and also provided evidence of incorporation of the modifier into the binder.  
27



28 **FIGURE 1. FTIR Analysis**  
29  
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1 **Atomic Force Microscopy (AFM)**

2 This test shows information on the topography and tridimensional environment of the sample, and also  
3 on the roughness of the material (22). AFM images of the distribution of modifiers within the binder  
4 matrix are shown in Figure 2. These images indicate a good uniformity of the modified binder and a  
5 homogeneous dispersion of the modifier within the binder matrix. Addition of nano-silica to the neat  
6 binder increases the roughness of the surface which is related to particle interlocking and stiffness of  
7 the binder. Therefore, the surface texture of the binder obtained from AFM images is expected to be  
8 related to the tensile strength of the binder. In addition, these images illustrate the so-called Bee-  
9 structures in binder. There is very little difference in the AFM when comparing unmodified versus  
10 modified binders, as an indication that the Bee-structures are related to natural species of the binder  
11 rather than the modifier.  
12

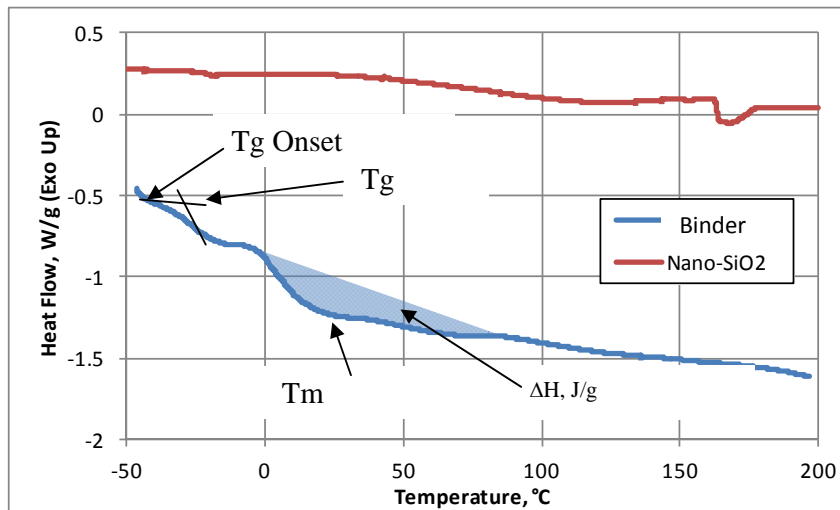


13  
14 **FIGURE 2. AFM topography (a) unmodified, (b) +0.5% SiO<sub>2</sub>, (c) +3% SiO<sub>2</sub>, (d) +6% SiO<sub>2</sub>**  
15 **binder**

16  
17 **Differential Scanning Calorimetry Analysis (DSC)**

18 DSC is widely used for determination of thermal transitions brought about by the first order  
19 transitions, such as melting and crystallization of crystallizable species (23). Glass transition, T<sub>g</sub>,  
20 credited as a second order phenomenon taking place in the amorphous region of the sample, can also  
21 be defined by DSC (Figure 3), but it depends largely on the nature of the material and its content of

1 crystallizable fractions ( $\Delta H$  - enthalpy). Below the glass transition temperature, binder behaves like a  
 2 glass and appears brittle, affecting the fatigue performance and tensile strength of the binder and the  
 3 mix. The onset temperature denotes the temperature at which the glass transition begins. The  
 4 parameter  $T_m$  represents the peak melting temperature. As seen on Figure 3 the binder clearly exhibits  
 5 these properties within the range of -50 to 200 °C. On the other hand, the inorganic material  $\text{SiO}_2$   
 6 which already behaves as a crystal only exhibits minor transitions and it is more stable at the same  
 7 temperature range.  
 8



9  
 10 **FIGURE 3. DSC analysis of the neat binder and modifier.**

11  
 12 Table 2 shows the calculated parameters for all binders. The onset temperature for the neat binder was  
 13 -45.7 °C, while for the modified binders the results varied between -50 and -40 °C. The glass  
 14 transition temperature showed significant differences with respect to the neat binder. The trend was to  
 15 lower the  $T_g$  by the addition of the modifiers. No significant differences were obtained among binders  
 16 in terms of the melting peak temperature which ranged between 23.5 and 24.4 °C. The transition  
 17 temperature  $T_g$  in silicates is related to the energy required to break and re-form covalent bonds in an  
 18 amorphous or random network of covalent bonds  $T_g$  (24). Addition of some elements found in the  
 19 asphalt binder with a valency less than 4 to the silica helps in breaking up the network structure, thus  
 20 reducing the  $T_g$ .

21 Finally, the total enthalpy of the melting transition increased compared to the neat binder result. A  
 22 high crystallinity may increase the hardness, the tensile strength and bring about a more rubber-like  
 23 consistency and a better resistance to flow at high temperatures (25). In this case, the higher content of  
 24 fractional crystallization was obtained for the 6% nano  $\text{SiO}_2$  modified binder.  
 25

26 **TABLE 2. Materials DSC properties**

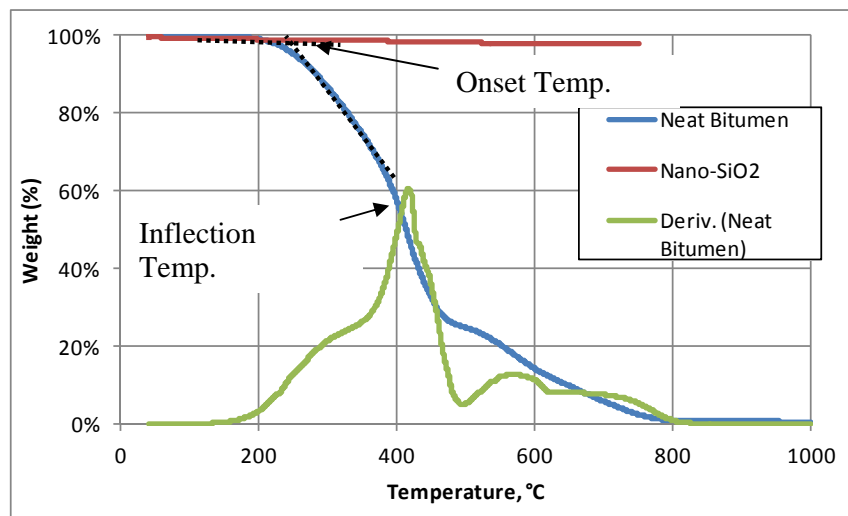
Material	Tg Onset, °C	Tg, °C	Tm, °C	ΔH, J/g
PG64-22	-45.7	-27.5	24.4	7.8
+ 0.5% nano $\text{SiO}_2$	-49.9	-33.9	24.0	8.7
+ 3% nano $\text{SiO}_2$	-43.3	-35.5	24.3	9.9
+ 6% nano $\text{SiO}_2$	-40.3	-35.3	23.5	10.7

27  
 28 **Thermogravimetric analysis (TGA)**

29 TGA is commonly used to determine selected characteristics of materials that exhibit either mass loss  
 30 or gain due to decomposition, oxidation, or loss of volatiles of the binder (26). Figure 4 shows an  
 31 example of TGA definitions. The extrapolated onset temperature denotes the temperature at which the  
 32 weight loss begins. The point of highest weight loss change rate is known as the inflection point. It is  
 33 obtained from the peak of the first derivative of the weight loss curve and it indicates when Pyrolysis  
 34 occurs. Pyrolysis is a thermochemical decomposition of organic material at elevated temperatures in

1 the absence of oxygen (or any halogen). It involves the simultaneous change of chemical composition  
 2 and physical phase, and is irreversible (27). This property is related to the bond strength and structure  
 3 of the material.

4 TGA can provide information about the relative thermal stabilities of these silica packing materials  
 5 which in turn provides an indication of the bond strength between the silica and the binder. Figure 4  
 6 exhibited a smaller total weight loss over the temperature range evaluated for the nano-silica compared  
 7 to the neat binder. While almost all the binder was decomposed around 750 °C, the mass loss  
 8 experience by the nano-silica was 2.1% at the same temperature. This significantly higher thermal  
 9 stability of the modifier was expected to positively affect the thermal behavior of the binder.  
 10



11 **FIGURE 4. Thermogravimetric analysis.**

12 Table 3 shows the percent mass loss at 200 °C in order to compare the stability of the binder at  
 13 temperatures close to production conditions. This table also shows the extrapolated onset temperature,  
 14 the inflection and the residual amount of material for all binders. The 6% nano-SiO<sub>2</sub> modified binder  
 15 was the most stable (up to 200 °C) with a mass loss of 0.18%. The onset temperature, also known as  
 16 decomposition temperature, of the neat binder was 255.3 °C. This value decreased with the addition of  
 17 0.5% of the modifier but increased for higher nano-SiO<sub>2</sub> contents. An increase in the amount of  
 18 modifier produced an increase in the overall stability and bond strength of the binder since higher  
 19 inflection points (Pyrolysis) and higher quantities of residual material were obtained. This can be  
 20 attributed to formation of higher particle interlocking as observed with the AFM images.  
 21

22 Based on this analysis, the results suggest a change in the mixing and compaction  
 23 temperatures in mixes with nano-silica modified binders. Higher onset temperatures and  
 24 higher inflection points measured for nano-silica modified binders indicate that more energy  
 25 (more heating) is required to start the thermochemical decomposition, which also means more  
 26 stable binders at typical working temperatures (mixing and compaction temperatures).  
 27  
 28  
 29

30 **TABLE 3. Material 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 <sub>2</sub>	1.14	247.6	425.8	0.51
+ 3% nano SiO <sub>2</sub>	1.17	302.8	433.4	9.67
+ 6% nano SiO <sub>2</sub>	0.71	273.1	439.0	18.96

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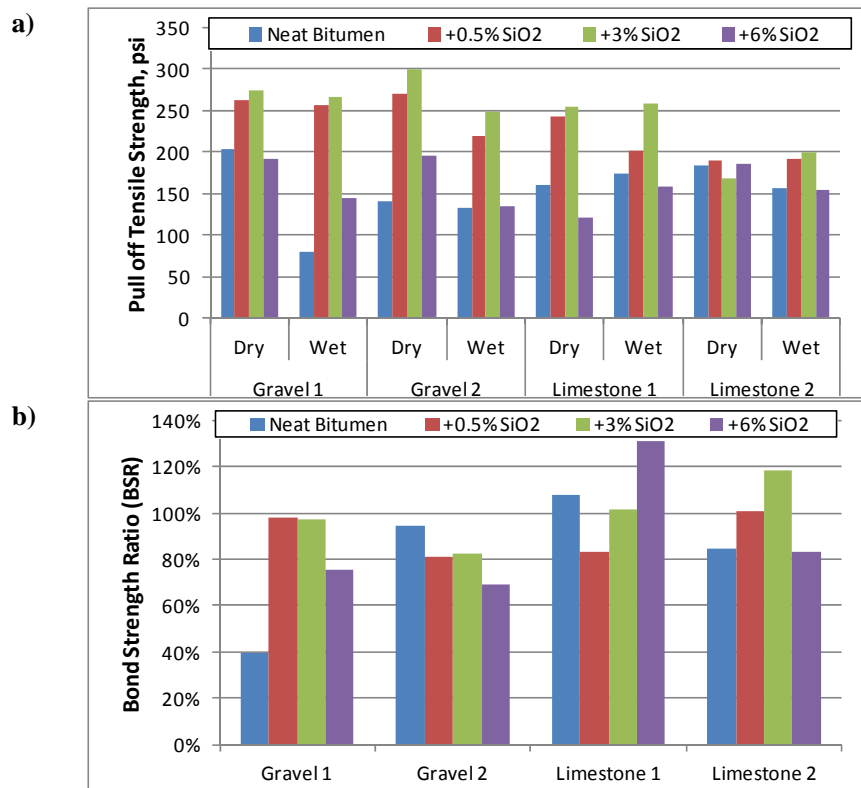
**Effect of Modifier Content, Aging and Aggregate Source on Adhesion**

**Description of the Adhesion Test Method**

Binder-aggregate adhesion was characterized based on the Binder Bond Strength (BBS) test (3). The test was performed following AASHTO TP-91 using a P.A.T.T.I., an equipment initially conceived by the paint and sealant industries. 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  $0.4 \pm 0.05g$  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 test is performed at room temperature (21 °C).

**Test results and analyses**

The BBS measures the pull-off tensile strength (POTS) of the binder-aggregate system when it is subjected to a constant load rate of 100 psi/s (690 kPa/s) and is analyzed after 24 hours of conditioning at room temperature (POTS<sub>Dry</sub>) and 48 hours conditioning in a water bath at 40 °C (POTS<sub>Wet</sub>). A minimum of 2 replicates were used for each of the material combinations. Figure 5 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 phenomenon occurs up to a critical additive concentration after which adhesivity begins to drop. In this case, 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. This behavior correlates to the increase in texture obtained from the previously discussed AFM images. An increase in surface texture of the binder (higher particle interlocking) could be responsible for the increase in tensile strength of the binder.



**FIGURE 5. Evaluation of aggregate/binder interaction, a) Strength, b) BSR**

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

8 When the binder was aged (Figures 6 and 7), the number of failures was considerably reduced. This  
9 suggests that in the long term special attention should be given to ensuring the cohesion of the binder  
10 and the asphalt mastic, condition that is difficult due to stiffening associated to the aging process. On  
11 average, the POTS results for aged binders indicate a 50% increase in POTS when RTFO aging was  
12 performed. Consequently, the strength required to break the internal cohesion bond is practically  
13 doubled. In the case of PAV aged binder, a considerable increase in POTS with respect to the unaged  
14 binder was also observed (40% on average). However, there is a small reduction with respect to the  
15 POTS results under RTFO aging (6% on average). The previous suggests that the increase in polarity  
16 of short term aged binder improves the compatibility with highly polar aggregates, but the change in  
17 polarity is counterbalanced by stiffening of the material in the longer term. This can be an indicator  
18 that adhesion is controlled by electrostatic forces in the short term but is dependent of the mechanical  
19 behavior of the material in the long term (adhesion or cohesion failure depends on material strength).  
20 RTFO aged binders show a considerable increment in the Bond Strength Ratio (reduction in loss of  
21 adhesion) which indicates that the affinity of aggregate and binder improves with short term aging.  
22 However, the effect is reverted when long term aging is considered: especially for the case of river  
23 gravels. When comparing the loss of adhesion between unaged and PAV aged samples, the last one  
24 shows greater susceptibility to moisture.

25 An analysis of variance (ANOVA) was performed to evaluate the effect of the aging, aggregate  
26 source and modifier content on the pull off tensile strength for the dry and wet conditions as well as  
27 the BSR. The results shown on Table 4 indicated that the variability observed for the response POTS-  
28 Dry can be explained by the statistical difference of the three treatments at a confidence level of 95%.  
29 On the other hand, only the aging treatment was statistically significant at the same confidence level.  
30 Finally, the variability of the response BSR cannot be statistically explained by any of the analyzed  
31 treatments. A second-level interaction ANOVA was also performed to evaluate the effect of combined  
32 treatments but all of them were not statistically significant.

33 A Tukey-test was performed as a complement of the ANOVA to find the means that were  
34 significantly different from each other. The results in Table 4 indicate that the tensile strengths for the  
35 dry and wet conditions were not statistically different between RTFO and PAV aging stages but  
36 greater than the unaged stage. With regards to the aggregate source, the tensile strengths for the dry  
37 condition were not statistically different within types of gravel and types of limestone but different  
38 between them. In this case, the river gravel aggregate presented higher POTS than the limestone.  
39 Addition of the modifier content exhibit tensile strengths for the dry and wet conditions statistically  
40 different between two groups: 0.5% and 3.0% nano-SiO<sub>2</sub> against 6.0% and unmodified with greater  
41 values for the first group.  
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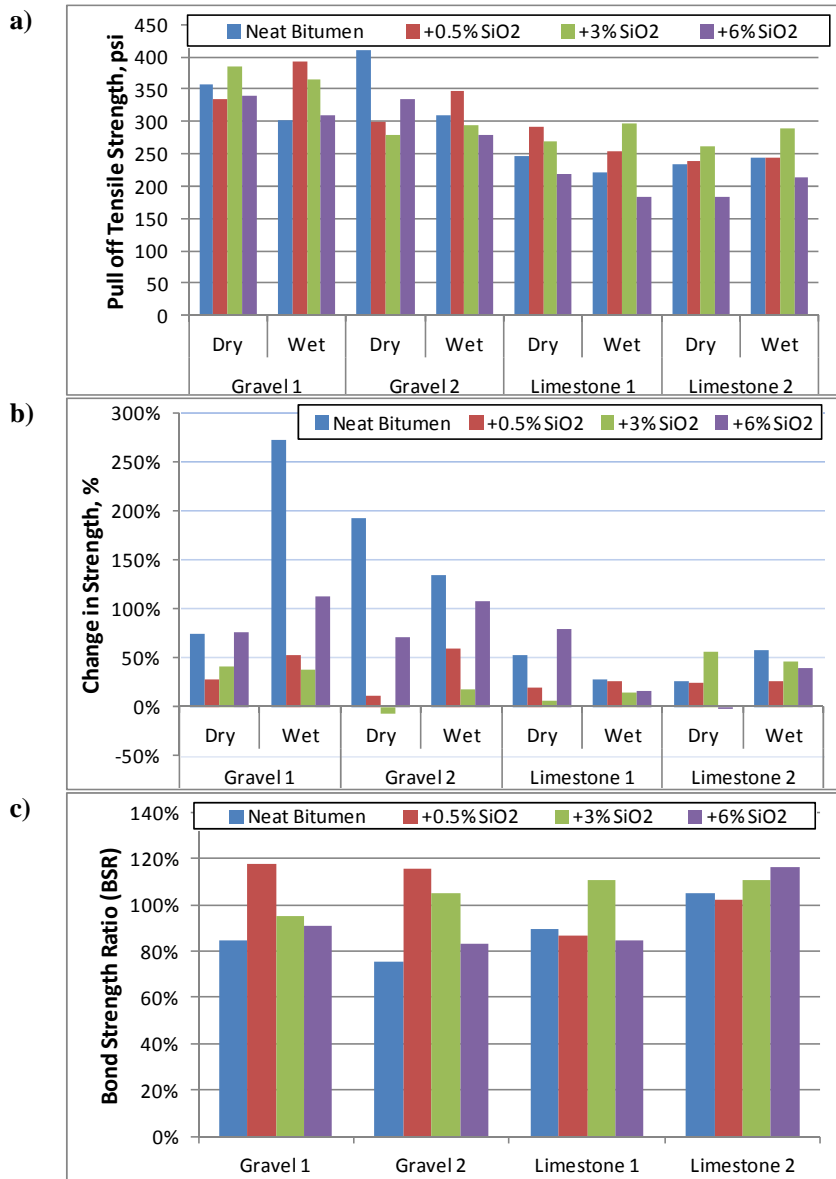


FIGURE 6. Aggregate/binder interaction RTFO condition a) Strength, b) Strength change, c) BSR

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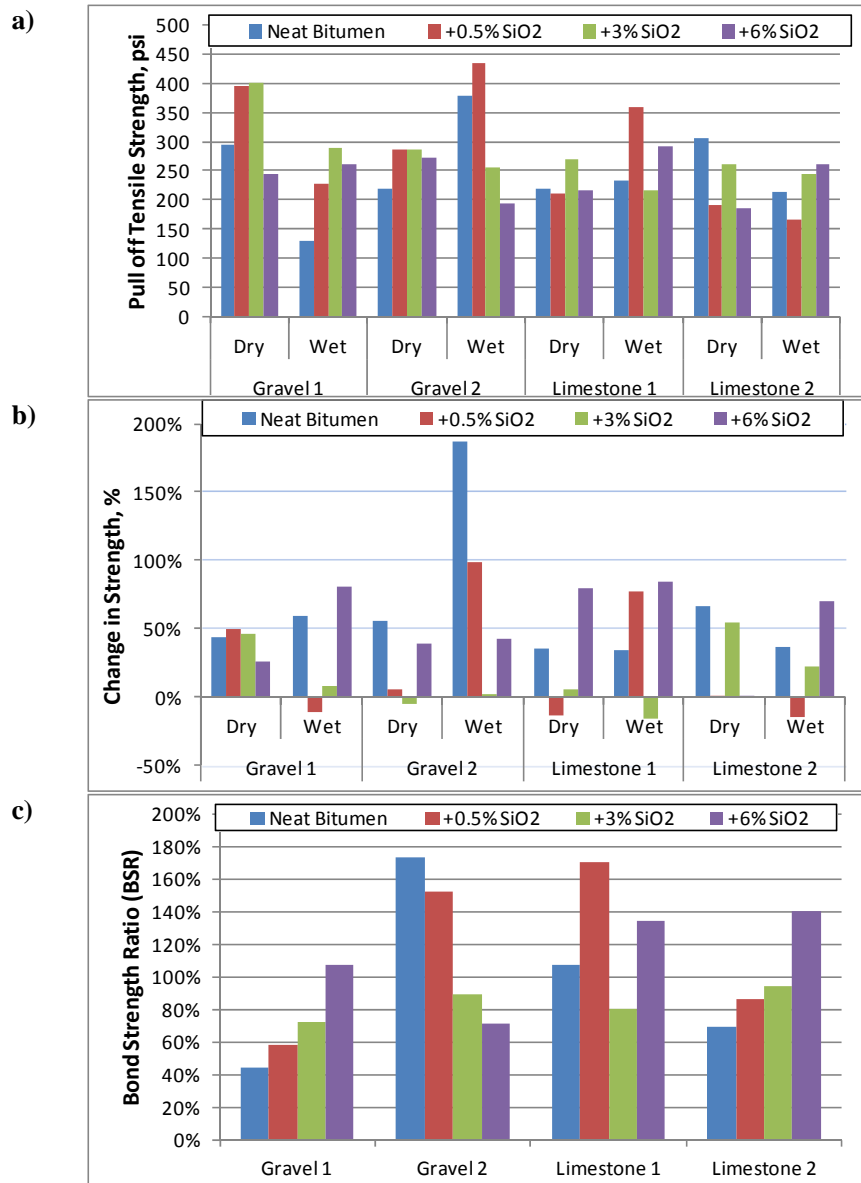


FIGURE 7. Aggregate/binder interaction PAV condition a) Strength, b) Strength change, c) BSR

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**TABLE 4. Analysis of variance and Tukey-test results**

Response						
Pull-off tensile strength - Dry						
Source	DF	Seq SS	Adj SS	Adj MS	F-statistic	P-value
Aging	2	57893	57893	28947	15.59	<<0.05
Agg. Type	3	65059	65059	21686	11.68	<<0.05
Mod. Cont.	3	23785	23785	7928	4.27	0.011
Error	39	72430	72430	1857		
Response						
Pull-off tensile strength - Wet						
Source	DF	Seq SS	Adj SS	Adj MS	F-statistic	P-value
Aging	2	83387	83387	41693	12.88	<<0.05
Agg. Type	3	18858	18858	6286	1.94	0.139
Mod. Cont.	3	38030	38030	12677	3.92	0.015
Error	39	126206	126206	3236		
Response						
BSR						
Source	DF	Seq SS	Adj SS	Adj MS	F-statistic	P-value
Aging	2	0.1288	0.1288	0.0644	0.91	0.412
Agg. Type	3	0.4366	0.4366	0.1455	2.05	0.123
Mod. Cont.	3	0.1336	0.1336	0.0445	0.63	0.601
Error	39	2.7675	2.7675	0.0709		
Treatment	Condition	Mean Tensile Strength		Grouping*		
		Dry	Wet			
Aging	RTFO	292.4	284.1	A		
	PAV	266.1	259.6	A		
	Original	209.2	186.1	B		
Mod. Cont.	3% SiO <sub>2</sub>	283.8	274.2	A		
	0.5% SiO <sub>2</sub>	267.6	268.5	A		
	Original	247.8	215.8	B		
	6% SiO <sub>2</sub>	224.3	214.6	B		
Agg. Type	River Gravel 1	306.8	NA	A		
	River Gravel 2	274.6		A		
	Limestone 1	226.5		B		
	Limestone 2	215.7		B		

\* Means that do not share a letter are significantly different

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**CONCLUSIONS**

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Based on the experimental results 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 (from TGA and DSC analyses). Higher particle interlock (roughness from AFM images) are among some of the benefits provided by the modification with nano-silica. Although these results may be an indication of the binder tensile strength due to the addition of nano-silica, the interaction binder/aggregate was the main point of concerned for this study and the results did not exactly follow the expected trend. Based on the thermal analysis conducted, the results suggest a change (increment) in the mixing and compaction temperatures in mixes with nano-silica modified binders.

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

5 The modifier content also affected significantly the strength of adhesion among the different  
6 aggregate-aging combinations. An optimal adhesion/cohesion performance can be obtained for the  
7 studied modifier to maximize the adhesivity, and consequently moisture damage resistance at a  
8 concentration near 3%.

9 Aging of the different asphalt binders produced significant changes in the strength of adhesion.  
10 RTFO aged binders showed a considerable increment in strength of adhesion which indicates that the  
11 affinity of aggregate and binder improves with short term aging.

12 In general, it was observed that some modified binder-aggregate combinations result in a reduction  
13 of the stress required to separate the asphalt film from the aggregate surface. The cause can be  
14 associated to two factors: stiffening of binder during the modification process and/or aging, and 2)  
15 intrinsic physical and chemical properties of the modifier and how its particle interlocking and polarity  
16 interacts with that of the aggregate.

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