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2 **Aggregate/Asphalt Adhesion Properties for** 3 **Modified and Aged Binders**

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15 **ABSTRACT.** *The interaction between the asphalt binder and the aggregate is fundamental in*
16 *ensuring the adequate performance of asphalt mixtures, mainly under the presence of water.*
17 *The work of adhesion that is generated by both materials directly affects the resistance of the*
18 *asphalt mixture to moisture damage since it clearly quantifies the ease with which water can*
19 *displace the asphalt binder from the aggregate surface. However, the effect of moisture and*
20 *the physical-chemical interaction between asphalt and aggregate depends on the specific*
21 *properties of each material and the conditions at which the asphalt mixture is produced and*
22 *expected to perform.*

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24 *The study looks to characterize the bond strength between the asphalt and several*
25 *aggregate sources that are typically used in Costa Rica. Additionally, because only one neat*
26 *binder type is used in the Country, it was modified with several additives to determine the*
27 *effect of the modifier: polymers (SBR, SBS), nanomaterials (CNT, SiO₂, Diatomite), and*
28 *adhesion promoters (liquid antistriper, lime). Each binder was characterized by means of the*
29 *Superpave performance grade, Thermogravimetric Analysis (TGA) and Differential Scanning*
30 *Calorimetry Analysis (DSC).*

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32 *To measure the strength of adhesion, the Bitumen Bond Strength (BBS) test was*
33 *used. The results were also verified by means of goniometry which allows for measurement of*
34 *the contact angle between asphalt binder and the aggregate surface. The same principles*
35 *were used to estimate the surface energy of the asphalt and the aggregate, with and without*
36 *the presence of water. All testing was performed on the neat and modified binders, as well as*
37 *on each binder - aggregate combination after RTFO and RTFO + PAV aging.*

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39 *The BBS results identify significant differences in the bond strength due to moisture*
40 *conditioning and aging. The differences are highly dependent on the aggregate source.*
41 *Furthermore, depending on the type of aggregate, different failure types were observed:*
42 *cohesive vs. adhesive. The type of binder is also highly significant in determining strength of*
adhesion. The results also indicate an increase in the strength of addition associated to the
aging process, where the main increase in resistance is observed after RTFO aging. Similar
results were obtained when analyzing contact angles and work of adhesion based on the

1 *surface energy of the aggregates and binders. The changes in bond strength between asphalt*
2 *binder and aggregate, where also compared to the functional composition changes associated*
3 *to aging of the asphalt binders by means of FTIR spectroscopy. The changes in functional*
4 *groups such as sulfoxides and ethers were monitored and related to changes in performance.*
5 *Finally, adhesion properties were compared to Dynamic shear rheometry (DSR) fatigue and*
6 *rutting performance tests. The results indicated that the selection of the optimum modifier can*
7 *be based not only on DSR performance tests but also with an aggregate/binder interaction*
8 *analysis.*

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11 **KEYWORDS:** *Adhesion, surface free energy, performance, physical-chemical analysis.*
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14 **1.0 Introduction**

15 The most common manifestation of distress associated to the presence of moisture in
16 the HMA layer is known as stripping, a phenomenon that involves the loss of asphalt
17 coating from the aggregate surface (Roberts et al, 2009). The process is typically
18 followed by a progressive loss of aggregate particles from the HMA layer surface as
19 a results of stresses associated to wheel loads traveling over the material (raveling).
20 The previous distress modes are related in that they are originated by a loss of
21 adhesion at the asphalt binder - aggregate interface.

22 Several laboratory testing methods have been developed to quantify the
23 susceptibility of asphalt mixtures to moisture damage. The most typical tests are:
24 boiling test (ASTM D3625), Texas boiling test (Tex-530-C), static-immersion test
25 (AASHTO T 182), Lottman test, modified Lottman (AASHTO T283), Tunncliff
26 and Root Conditioning test (Tunncliff and Root, 1984), immersion-compression test
27 (AASHTO T 165), Texas freeze thaw pedestal test, Hamburg wheel tracking device
28 (HWTD) test (AASHTO T 324), and the Superpave simple performance tests (static
29 creep, repeated load permanent deformation, and dynamic modulus) with an
30 environmental conditioning system (ECS).

31 In Costa Rica, the modified Lottman or indirect tension test is used to
32 evaluate the susceptibility of HMA to moisture damage (Aguiar-Moya et al, 2013).
33 Similarly, many DOTs at the international level use the test to ensure a minimum
34 resistance to moisture damage, and to justify the need for adhesion promoters (Hicks
35 et al, 2003). However, in several cases it has been reported that the test is not
36 representative of field performance (Epps et al, 2000). Moreover, the testing
37 methodology has been highly criticized by experts due to its inability to reproduce
38 actual field failure mechanisms and changes associated to aging in the HMA
39 (Choubane et al, 2000, Kandhal and Rickards, 2002, Kringos et al, 2009).

40 Even though the test is simple to perform, it can suggest erroneous results
41 negatively affecting the true performance of the HMA. To avoid the potential issue,
42 methodologies based on the measurement of fundamental material properties
43 becomes necessary to ensure an adequate characterization of damage caused by the

1 presence of moisture in the asphalt mixture. The latter approach also allows for
2 determining how the material properties associated to moisture damage can change
3 during the service life of the pavement structure, when aging of the HMA is taken
4 into consideration.

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6 **2.0 Background**

7 Moisture damage is highly related to the cohesion bond which involves the internal
8 cohesion of the asphalt matrix, and with the adhesion bond which is related to the
9 interaction strength between asphalt and aggregate (Cheng, 2002). However, as of
10 currently implemented material design procedures, the previous properties are not
11 accounted for to the degree of importance that is required. Because of this reason, a
12 strong trend to study and understand the processes involved in aggregate-asphalt
13 adhesion and asphalt binder internal cohesion is being undertaken.

14 Deterioration associated to moisture damage is a function of various
15 thermodynamic processes. Several studies indicate different factors are the feasible
16 causes of the phenomenon that generates at the interface between the mastic and the
17 aggregate surface (adhesion failure) and within the internal structure of the mastic
18 (cohesion failure). In general, it is agreed that the failure type depends primarily on
19 the material properties. However, several factors other than the asphalt mastic affect
20 the susceptibility of the asphalt mixture: use of asphalt modifiers, and the use of
21 adhesion promoters such as liquid antistrip or hydrated lime (Howson et al, 2007). It
22 has also been observed that an increase in water pH present at the asphalt-aggregate
23 interface has an important effect on the weakening of the adhesive bond between the
24 two materials (Scott, 1982).

25 A literature review by Tarrer and Wagh (1991) identified at least 6 different
26 failure mechanisms that can be associated to moisture damage and aggregate
27 detachment, and can occur individually or simultaneously. The mechanisms are:
28 detachment, displacement, spontaneous emulsification, pore pressure, hydraulic
29 scouring, and environmental factors. Additionally, other factors such as rupture of
30 the asphalt film and pH instability have been highlighted.

31 Detachment occurs when a thin layer of water displaces the complete
32 asphalt film from the aggregate surface, without a break in the asphalt film
33 (discontinuity in asphalt film that allows the flow of moisture that can result from
34 inadequate coating). This is a consequence of lower free surface energy of water as
35 compared to the asphalt binder, resulting in a higher wettability (ability of a liquid to
36 maintain contact with a solid surface) of the aggregate (Majidzadra and Brovold,
37 1968). Displacement differs from detachment because water penetrates the aggregate
38 surface by a break in the asphalt binder film caused by inadequate coating or asphalt
39 film rupture (Scott, 1982, Fromm, 1974). Spontaneous emulsification results when
40 water and asphalt binder combine to form an emulsion, phenomenon that is
41 amplified by the presence of emulsifiers such as some mineral clays and asphalt
42 binder additives (Scott, 1982, Fromm, 1974). Pore pressure can also generate
43 moisture damage in asphalt mixtures with high air void contents, typically open

1 graded mixtures where water can circulate through the interconnected voids. As
 2 traffic loading continues, water pressure increases and can generate microcracks in
 3 the asphalt film. The problem worsens if water becomes trapped in the impermeable
 4 voids (Tarrer and Wagh, 1991, Asphalt Institute, 1981). Hydraulic scouring occurs
 5 only at the pavement surface and is a result of the effect of vehicle tires on wet
 6 pavement surfaces which generate high water pressures ahead of the tire and suction
 7 behind the tire (Scott, 1982, Fromm, 1974, Asphalt Institute, 1981).

8 Changes in pH, or instability in acidity has the capacity to affect the
 9 chemical bonds at the material interface level y consequently the adhesiveness
 10 between asphalt and aggregate (Scott, 1982). The previous has been observed by
 11 measuring the changes in contact angle and wettability at the aggregate-asphalt
 12 interface. Finally, climatic factors such as relative humidity, temperature (air and
 13 water) and precipitation play an important role on material performance (Terrel and
 14 Shute, 1991).

15 All of the previous mechanisms are the consequence of water having lower
 16 surface free energy than asphalt binder, which translates to water presenting higher
 17 wettability of aggregates (Majidzadra and Brovold, 1968). The surface free energy
 18 (γ) is a physical-chemical property that corresponds to the amount of energy
 19 required to create a new unit of material surface area, under vacuum conditions.
 20 Surface free energy is a fundamental property of every material and affects
 21 superficial characteristics and interactions with other materials such as adsorption,
 22 wettability, adhesion and cohesion. Consequently, thermodynamic changes in
 23 surface free energy can be related to possible separation between the asphalt binder
 24 and the aggregate, and with cracks that can develop within the mastic structure.
 25 Similarly, these changes can be directly related to healing of fractures at the asphalt
 26 aggregate interface or within the mastic structure (Cheng, 2002).

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28 **2.1 Effect of aging on moisture damage**

29 The physical-chemical properties of an oxidized asphalt promote the occurrence of
 30 micro-cracks, which in turn become paths through which water can more freely
 31 penetrate the asphalt-aggregate interface, accelerating the moisture damage process.
 32 However, there are mixed results regarding the effect of an aged binder on the
 33 adhesion between asphalt and aggregate (Chávez-Valencia et al, 2007). If the
 34 strength of the interaction is reduced, the resistance of the asphalt-aggregate system
 35 will be compromised, increasing the sensibility to moisture (Miller et al, 2012).
 36 Negative consequences associated to the aging process can be predicted by
 37 characterizing the surface free energy of the affected material: asphalt. This in turn
 38 allows the design of aggregate-asphalt combinations that optimize the adhesion
 39 between the materials (Kim et al, 2003, Howson et al 2007, Sarsam and Azawee,
 40 2013).

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1 **3.0 Objective**

2 The main goals of the research project were: 1) quantify the adhesion between the
3 asphalt source available in Costa Rica with different aggregate types typically used
4 in HMA construction, 2) characterize the effect of different additives on moisture
5 damage susceptibility, and 3) determine the effect of aging on adhesion for the
6 analyzed materials. The Bitumen Bond Strength (BBS) test was used to evaluate the
7 asphalt-aggregate adhesion and the internal cohesion of the asphalt structure.
8 Contact angle measurements were also performed for all asphalt-aggregate
9 combinations by means of goniometry. Additionally, goniometry was used to
10 estimate the total surface free energy for the analyzed asphalts and aggregate
11 sources, to quantify the work of adhesion between asphalt and aggregate, as well as
12 the susceptibility to moisture.

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14 **4.0 Materials Used In The Study**

15 The different materials that were used in this study are summarized in Table 1. Only
16 one asphalt binder source was selected for the study since the Costa Rican National
17 Petroleum Refinery (RECOPE) produces only one type of asphalt: PG64-22 or PG
18 64[22] (high and intermediate temperatures). The asphalt binder was also modified
19 with 7 distinct additives to evaluate the impact on adhesion: two elastomeric
20 thermoplastic polymers [Styrene-Butadiene-Rubber (SBR) and Styrene-Butadiene-
21 Styrene (SBS)], three nanomaterials [multiwall carbon nanotubes (CNT), nano silica
22 (SiO_2), and diatomite (Dia)], and two adhesion promoters [liquid antistrip (AS) and
23 hydrated lime].

24 Each additive content was design in the laboratory previous to the current
25 study and the optimum contents are indicated in Table 1. All the additives were
26 incorporated using a low shear stirrer at 175 °C for 3 hours. The PG analysis results
27 is shown in Table 1. The vast majority of the analyzed modifiers increased the high
28 temperature grade. The highest change was shown by the 3% CNT modified asphalt
29 which increased by 24 °C.

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

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Table 1. Materials Selection Summary.

Factor	Levels	Description
Asphalt	8	PG64-22*
		PG64-22 + 3% SBR (PG76-19)
		PG64-22 + 3% SBS (PG76-25)
		PG64-22 + 3% CNT (PG88-25)
		PG64-22 + 6% nano SiO ₂ (PG82-25)
		PG64-22 + 6% Diatomite (PG70-25)
		PG64-22 + 10% Hydrated Lime (PG70-25)
		PG64-22 + 0.5% Liquid Antistrip (PG64-25)
Aging Conditions	3	Unaged
		RTFO Aged
		RTFO + PAV Aged
Aggregate Source	4	River Gravel 1 – Central Pacific
		River Gravel 2 – Central Caribbean
		Limestone 1 – Central Valley
		Limestone 2 – North Pacific

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*Intermediate temperature

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

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4.1 Thermogravimetric analysis (TGA)

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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 1 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.

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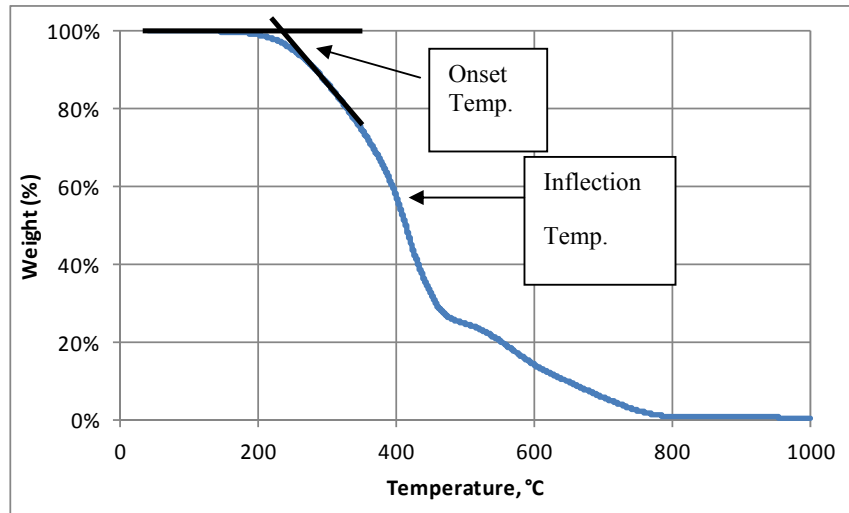


Figure 1. TGA definitions.

Table 2 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 parameters indicates on Figure 1 and the residual amount of material for all binders. The 3% SBR modified binder was the more stable binder with a mass loss of 0.18% while the least stable binder was the 0.5% Liquid Antistrip modified binder with 2.37 % mass loss. The onset temperature, also known as decomposition temperature, of the neat binder was 255.3 °C. This value decreased with the addition of SBS, Diatomite, Hidrated lime and Liquid antistrip. The behavior can be attributed to volatilization or evaporation of the lighter components. Conversely, higher decomposition temperatures and higher quantities of residual material can be attributed to formation of stronger molecular crosslinks.

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Table 2. *Materials TGA properties.*

Material	% Loss @ 200 °C	Onset Temperature, °C	Inflection Point, °C	Residue, %
PG64-22	0.917	255.31	416.31	0.67
3% SBR	0.179	319.27	433.82	11.65
+ 3% SBS	2.064	221.62	435.25	0.89
+ 3% CNT	0.398	298.55	449.43	7.16
+ 6% nano SiO ₂	0.709	273.15	439.03	18.96
+ 6% Diatomite	2.212	231.64	439.97	4.58
+ 10% Hydrated Lime	2.354	226.56	423.90	8.41
+ 0.5% Liquid Antistrip	2.371	233.39	439.97	0.74

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4.2 Differential Scanning Calorimetry Analysis (DSC)

4 DSC is widely used for determination of thermal transitions brought about by the
5 first order transitions, such as melting and crystallization of crystallizable species
6 (Elseifi et al, 2010). Glass transition, T_g, credited as a second order phenomenon
7 taking place in the amorphous region of the sample, can also be defined by DSC, but
8 it depends largely on the nature of the material and its content of crystallizable
9 fractions. Below the glass transition temperature, asphalt behaves like a glass and
10 appears brittle, affecting the fatigue performance of the binder and the mix. Figure 2
11 shows an example of DSC definitions utilized for characterization purposes. The
12 onset temperature denotes the temperature at which the glass transition begins. The
13 parameter T_m represents the peak melting temperature.

14 Table 3 shows the calculated parameters for all binders. The onset
15 temperature for the neat binder was -45.7 °C, while for the modified binders the
16 results varied between -50 and -40 °C. The glass transition temperature showed
17 significant differences with respect to the neat binder. The trend was to lower the T_g
18 by the addition of the modifiers with the exception of the SBR polymer. No
19 significant differences were obtained among binders in terms of the melting peak
20 temperature which ranged between 23.4 and 26.5 °C (similar to the intermediate
21 performance grade temperatures for all binders).

22 Finally, the total enthalpy of the melting transition increased compared to
23 the neat binder result. A high crystallinity may increase the hardness and bring about
24 a more rubber-like consistency and a better resistance to flow at high temperatures
25 (Harrison et al, 1992). In this case, the higher content of crystallizable fractions was
26 obtained for the 3% SBR modified binder.

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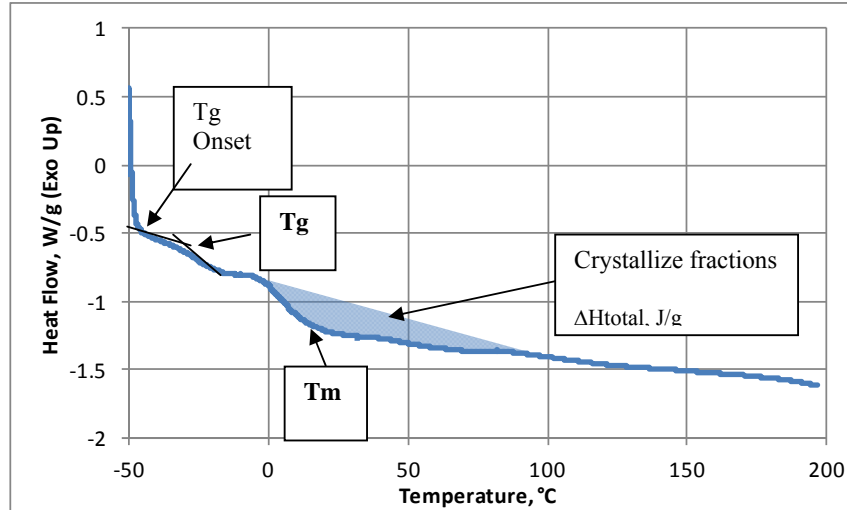


Figure 2. DSC definitions.

Table 3. Materials DSC properties.

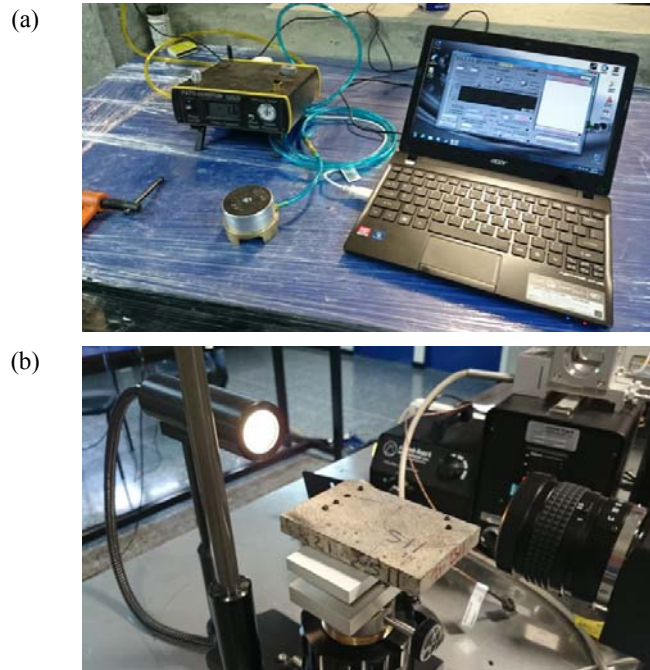
Material	Tg Onset, °C	Tg, °C	Tm, °C	ΔH_{total} , J/g
PG64-22	-45.71	-27.56	24.48	7.85
+ 3% SBS	-46.92	-29.68	26.53	7.99
+ 3% SBR	-40.32	-35.76	26.31	12.16
+ 3% CNT	-45.42	-37.25	25.53	9.95
+ 10% Hydrated Lime	-49.23	-38.95	23.43	8.83
+ 0.5% Liquid Antistrip	-50.62	-36.68	25.52	10.59
+ 6% Diatomite	-43.92	-34.15	24.56	9.26
+ 6% nano SiO ₂	-40.29	-35.39	23.54	10.72

5.0 Description of the Adhesion Test Methods

As part of the study, asphalt-aggregate adhesion was characterized by means of 3 different methodologies. The first method is based on the BBS test (Aguiar-Moya et al, 2013). 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 (Figure 3).

1 The aggregate samples are cut or cored from large rocks. The aggregate
 2 sample faces are then polished using 280-grit material to ensure uniform roughness
 3 between samples (the mechanical interlock between asphalt-aggregate is minimized
 4 to ensure adhesion measurements correspond to thermodynamic interaction between
 5 the materials). The samples are then placed in an ultrasonic bath to remove any
 6 surface residue. An asphalt sample of $0.4 \pm 0.05\text{g}$ is placed on metallic stubs of
 7 known diameter (20 mm). The stubs containing the asphalt sample are then pressed
 8 against the aggregate surface without applying torsion.

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11 **Figure 3.** (a) PATTI Testing Equipment and (b) Goniometer.

12

13 The BBS measures the pull-off tensile strength (POTS) of the asphalt-
 14 aggregate system when it is subjected to a constant load rate of 100 psi/s and is
 15 analyzed after 24 hours of conditioning at room temperature ($POTS_{Dry}$) and 48 hours
 16 conditioning in a water bath at $40\text{ }^{\circ}\text{C}$ ($POTS_{Wet}$). A minimum of 2 replicates were
 17 used for each of the material combinations. Additionally, the percent loss in bond
 18 strength can be estimated as:

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$$[POTS_{Dry} - POTS_{Wet}] / POTS_{Dry} \quad [1]$$

1 To complement the empirical BBS test, contact angle (θ_{SL}) measurements
2 were taken to characterize asphalt wettability of the aggregate surface. Testing was
3 performed to quantify the strength of the interaction between the asphalt and
4 aggregate molecules, relative to the intermolecular interaction within each material.
5 θ_{SL} was measured at 25 °C using a Ramé-hart 250 goniometer (Figure 3).

6 The goniometer is an optical equipment capable of capturing the profile of
7 an asphalt drop over an aggregate substrate, and works based on the Sessile Drop
8 principle (Kwok et al, 1997). θ_{SL} is the angle formed between the liquid/solid and
9 liquid/gas interface. The samples are prepared in a manner similar to the BBS test
10 but differ in that the asphalt drop is placed directly over the aggregate surface
11 (Figure 4). A minimum of 5 replicas for each asphalt-aggregate combination are
12 evaluated for estimating θ_{SL} .

14 **6.0 Testing Results And Data Analysis**

15 **6.1 BBS Test**

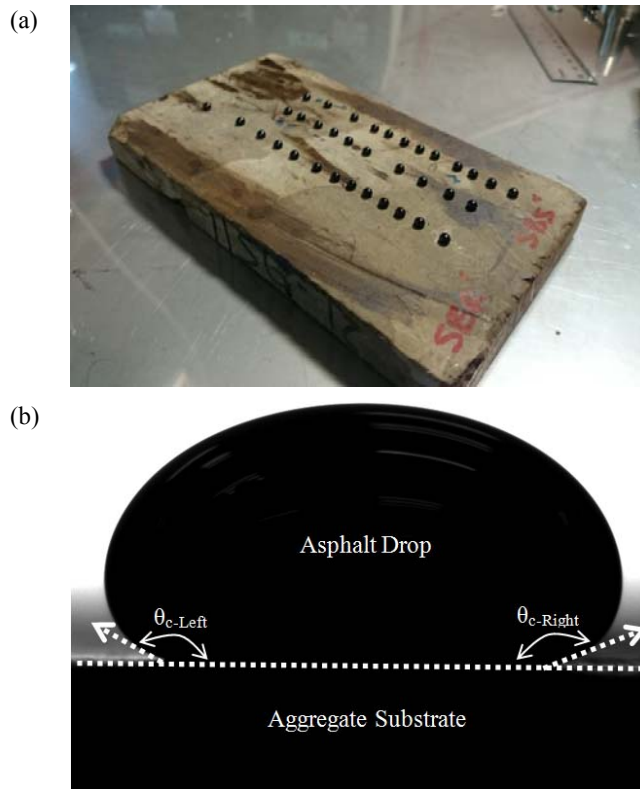
16 Figures 5 to 7 shows the dry and wet POTS for the analyzed asphalt binders in
17 original and aged conditions, while Figure 8 shows the loss of adhesion as per [Eq.
18 1]. For the unaged binders, under dry conditions, the 3% SBR modified asphalt and
19 Limestone 1 combination required the least amount of strength for inducing failure.
20 Additionally, the use of SBR resulted in POTS consistently lower than that
21 associated to the original binder, and to most of the modified binders. The variability
22 in results reduced when conditioning was applied to the samples. However, the
23 conditioned samples exhibit a significant loss in POTS.

24 It is interesting to observe than even though the strength of adhesion
25 appears lower for limestone aggregates, the change when these materials are
26 subjected to wet conditioning is low in comparison to river gravels (specifically
27 River Gravel 1). A possible explanation to why River Gravel 1 shows greater losses
28 can e associated to a higher aggregate porosity which can result in faster water
29 filtration rates that can accelerate the displacement of the asphalt film. It is also
30 important to note that the analysis confirms the superiority of River Gravel 2, which
31 currently represents the preferred aggregate source, due to the field resistance to
32 moisture damage that mixtures produced with the material tend to exhibit. In
33 general, under dry conditioning, cohesive failures were typically observed. The
34 tendency was the same for wet conditioned samples, with the exception of the river
35 gravels that showed adhesive failure between asphalt-aggregate.

36 When the asphalt binders were aged, the number of adhesive failures was
37 considerably reduced. This suggests that in the long term special attention should be
38 given to ensuring the cohesion of the asphalt binder and the asphalt mastic, condition
39 that is difficult due to stiffening associated to the aging process. The POTS results
40 for aged binders indicate a 70%+ increase in POTS when RTFO aging is performed.
41 Consequently, the strength required to break the internal cohesion bond is practically
42 doubled. In the case of PAV aged binder, a considerable increase in POTS with
43 respect to the unaged binder is also observed (60%+). However, there is a small

1 reduction with respect to the POTS results under RTFO aging. The previous
2 suggests that the increase in polarity of short term aged asphalt improves the
3 compatibility with highly polar aggregates, but the change in polarity is
4 counterbalanced by stiffening of the material in the longer term. This can be an
5 indicator that adhesion is controlled by electrostatic forces in the short term but is
6 dependent of the mechanical behavior of the material in the long term (adhesion or
7 cohesion failure depends on material strength).

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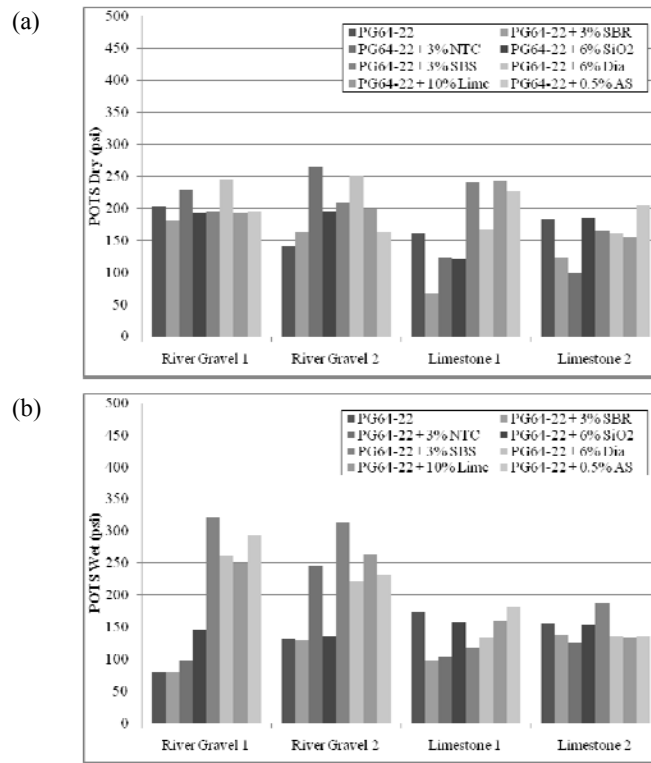
10 **Figure 4.** (a) *Asphalt Binder Drop Samples for Contact Angle Measurement and* (b)
11 *Contact Angle Images Used in Measurements*

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13 When evaluating the loss of adhesion associated to unaged binders, it can
14 be clearly observed that the loss is significantly affected by the aggregate source and
15 by the asphalt modifier, where an interaction between the two factors also exists. For
16 example, in the case of river gravels, the lower losses are associated to asphalts

1 modified with SBS, Diatomite, and as expected, adhesion promoters. However, the
 2 tendency is reversed when limestones are used. The previous can be explained by
 3 the differences in polarity between the types of aggregate. The data also confirms the
 4 optimum performance is shown by River Gravel 2, regardless of the type of asphalt
 5 that is used.

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8 **Figure 5.** POTS for different asphalt-aggregate combinations with asphalts in
 9 unaged condition (a) dry and (b) wet

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11 RTFO aged binders show a considerable reduction in loss of adhesion: the
 12 affinity of aggregate and asphalt improves with short term aging. However, the
 13 effect is reverted when long term aging is considered: especially for the case of river
 14 gravels. When comparing the loss of adhesion between unaged and PAV aged
 15 samples, the latter shows greater susceptibility to moisture (Figure 8).

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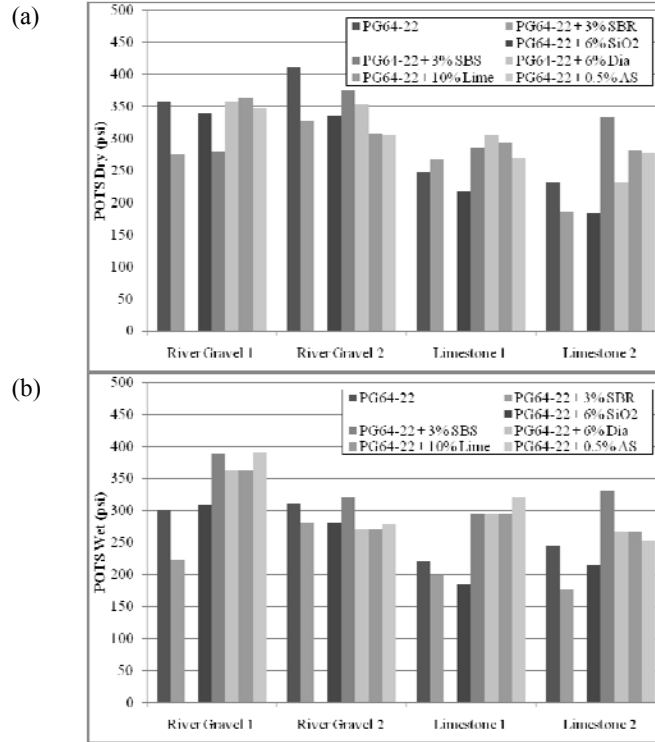
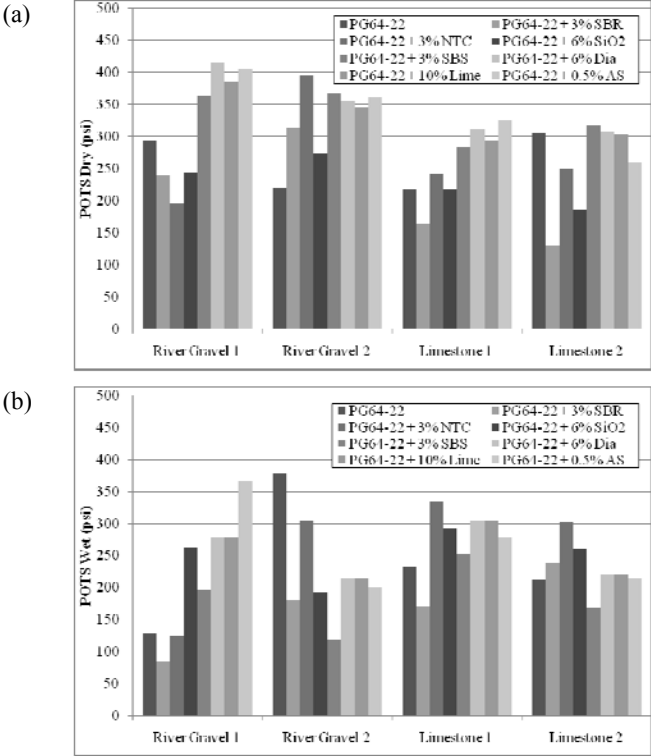


Figure 6. POTS for different asphalt-aggregate combinations with asphalts in RTFO condition (a) dry and (b) wet.

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Aggregate/Asphalt Adhesion Properties



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Figure 7. POTS for different asphalt-aggregate combinations with asphalts in PAV condition (a) dry and (b) wet.

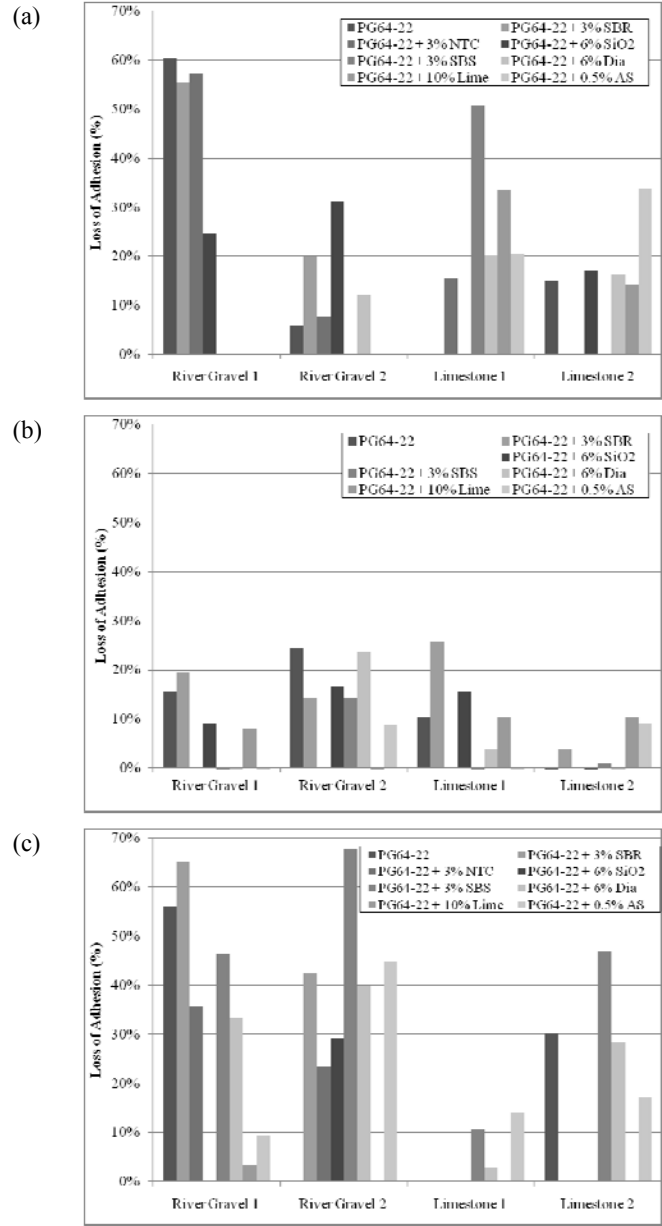


Figure 8. Loss of adhesion associated to (a) unaged binders, (b) RTFO aged binders, and (c) PAV aged binders.

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1 6.1.1 Effect of Modifier Content on BBS

2 In order to determine whether the additive content has an effect on work of
3 adhesion, nano SiO₂ was selected to perform BBS testing at different modifier
4 contents. Figure 9 shows the POTS results before and after the wet conditioning
5 process. It can be observed that as the additive content is increased, an increase in
6 adhesion is also obtained. However, the phenomena occurs up to a critical additive
7 concentration after which adhesivity begins to drop. In the case of SiO₂, the critical
8 concentration is above 3%. Consequently, an optimal adhesion/cohesion range can
9 be obtained for a given modifier to maximize the adhesivity, and consequently
10 moisture damage resistance.

11 The previous observation can be verified the loss in POTS when comparing the dry
12 and wet conditioned samples. In this case, it can be clearly observed that there is
13 practically no loss in POTS when the modifier is used in concentration between
14 0.5% and 3% by weight of asphalt. Furthermore, when no additive is used, important
15 losses are observed in the strength of adhesion when the samples are wet
16 conditioned.

17 The previous analysis was also repeated while changing the aging conditions of the
18 asphalt binder, as in the previous section. Similar trends (although at lower
19 magnitudes) were observed for the RTFO aged binders. The lower magnitude
20 responds to the increment in polarity associated to the short term aging process,
21 which positively affects the moisture damage resistance. For the case of PAV aged
22 binders, the trend is reverted and it was found that the losses associated with
23 adhesion increased considerably: higher moisture susceptibility. The previous
24 observation is consistent with what was previously observed and can be associated
25 to material stiffening, generation of micro-cracks and consequently ease with which
26 water can infiltrate to the asphalt-aggregate interface.

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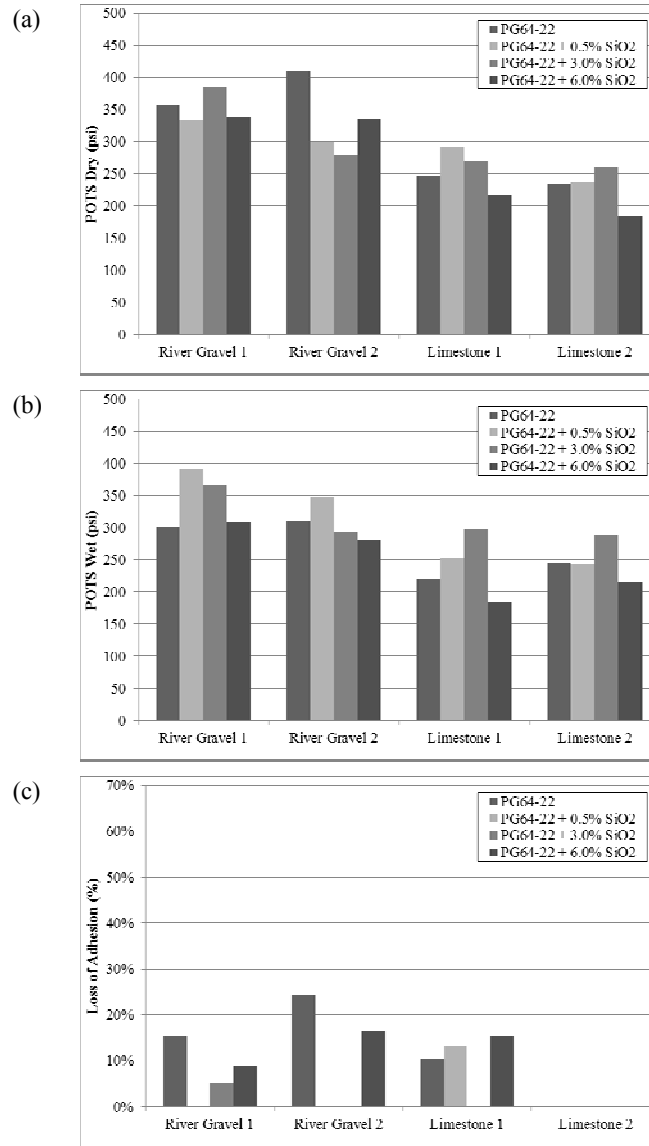


Figure 9. POTS for different modifier concentrations under (a) dry and (b) wet conditioning, and (c) loss of adhesion associated to changes in additive content.

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6.2 Contact Angle Measurements

Contact angle measurements were performed to measure the wettability of the asphalt to the various aggregate sources, and to observe the correlation with BBS test results. The contact angle was measured on an asphalt drop that is placed on the aggregate surface (asphalt is heated to 165 °C in a temperature controlled chamber and dropped from 25 mm height), 5 minutes after setting. Each drop is measured for a left and right contact angle (Figure 4) and the values are averaged. If the difference between angles for a given drop exceeds 5°, the measurements are discarded.

The results are shown on Figure 10. It is interesting to note that with the exception of the liquid antistripping modified asphalt, the contact angle between modified asphalt and all aggregate sources increased. This is consistent with what was observed in the BBS test based on POTS: higher contact angles (indicator of lower wettability) correlate to asphalt-aggregate combinations with higher loss of adhesion values.

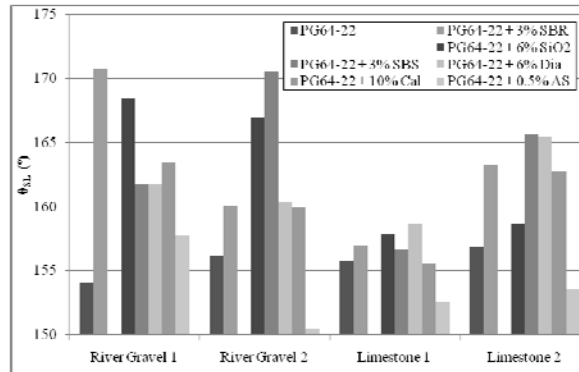


Figure 10. Contact angle results.

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Note however that in the BBS test, failure can be associated to adhesion of asphalt-aggregate system or internal cohesion of the asphalt matrix. On the other hand, contact angle measurements only address adhesion between the two system components. It is also important to note that the use of the goniometer for the measurement of contact angles between asphalt and aggregates is fairly new. Consequently there is no specification to standardize the conditions under which the asphalt drop is placed on the aggregate surface.

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6.3 Surface Free Energy

In order to assess the surface energy components of asphalts and aggregates, the contact angles formed by three probe liquids over the asphalt (or aggregate) surface were measured with a goniometer. The selection of an adequate liquid depends on that it must not dissolve or chemically react with the surface of interest, also the

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liquid must be pure and the three components of its surface energy according to Acid-Base theory, must be known [the dispersive (non-polar) component, γ^{LW} ; the acidic (electron receptor) component, γ^+ ; and the basic (electron donator) component, γ^- . In this study, the selected probe liquids were water, glycerol and diodomethane for aggregates and water, ethylene glycol and formamide for asphalts. In addition, the validity of liquid selection, and measured contact angles was performed based on existing references (Hefer et al, 2005, Bhasin et al, 2007, Wei, 2012). Equation 2 was used to relate the measured angles to the unknown surface energy components (Arabani and Hamed, 2014).

$$\gamma_L(1 + \cos \theta) = 2\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + 2\sqrt{\gamma_S^+\gamma_L^-} + 2\sqrt{\gamma_L^-\gamma_S^+} \quad [2]$$

where L refers to probe liquid and S refers to the solid surface of binder or aggregate. The results are shown in Tables 4 and 5.

From Table 4 it can be observed that the dispersive (non-polar) component is the major contributor to the total surface energy of the aggregates. Although the basic component is high in value for almost all the conditions, its contribution is not enough to provide a predominantly polar character to the aggregates, except for the River Gravel 2 which is highly polar. It should be noted however, that the previous observation is closely related to the instrument used to obtain the surface energy components. Higher values of basic component (and total surface energy) of aggregates have been reported for other authors who use different γ measurement procedures, such as the Universal Sorption Device (Little et al, 2004).

Table 4. Surface Free Energy of Aggregates.

Aggregate	γ^{TOTAL}		γ^{LW}		γ^+		γ^-	
	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.
Gravel 1	44.1	2.99	40.3	1.35	0.1	0.01	50.2	1.51
Gravel 2	51.2	5.13	23.3	1.16	5.9	0.25	33.2	2.32
Limestone 1	42.1	6.14	39.4	3.05	0.2	0.02	8.5	0.45
Limestone 2	54.7	1.96	46.9	0.7	0.6	0.01	26.5	2.3

The neat binder has higher dispersive character in comparison to the polar one (Table 5). By adding different additives these values change, depending on the chemical nature of the additive. Of the seven additives used, only hydrated lime and diatomite are polar, the rest are non-polar nature. It is expected that a non-polar additive will increase the dispersive component of the total surface energy of the neat binder and a polar one will decrease the same component but increase the acidic or basic component. This is generally observed in the data, with the exception of hydrate lime which, contrary to what was expected, increased the dispersive

Aggregate/Asphalt Adhesion Properties

1 character of the asphalt possibly due to reactions taking place during the
2 modification process.

3 The chemical changes that occur in the asphalt during aging have consequences in
4 terms of surface energy characteristics. The data indicates that in general the aging
5 process increases the dispersive component of the surface energy and decreases the
6 polar component. It is important to notice that this behavior is not applicable for all
7 the asphalts, as they might differ chemically from each other. Once the asphalts were
8 aged, the work of adhesion increased for all the cases. The ageing process causes
9 chemical changes that make the asphalt more compatible to the aggregate, and so the
10 interactions established between them will be stronger.

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Table 5. Surface Free Energy of binders.

Asphalt Binder	γ^{TOTAL}		γ^{LW}		γ^{+}		γ^{-}	
	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.
PG-64-22	13.4	0.53	9.5	0.24	0.8	0.01	4.9	0.13
PG-64-22 (RTFO)	12.3	0.37	7.1	1	1.7	0.39	4	0.16
PG64-22 (PAV)	16.3	0.33	14.7	0.16	0.2	0	2.6	0.05
+ 3% SBR	13.0	2.35	9.7	0.24	1.4	0.01	1.9	0.05
+ 3% SBR (RTFO)	17.3	0.47	16.1	0.77	0.2	0.08	2.6	0.16
+ 3% SBR (PAV)	17.3	4.1	16.9	0.15	0.01	0	2.9	0.06
+ 3% SBS	18.7	0.55	18	0.27	0.04	0.001	2.9	0.06
+ 3% SBS (RTFO)	14.7	1.1	12.7	2.7	0.2	0.31	6.3	0.58
+ 3% SBS (PAV)	19.5	0.97	19.4	0.48	0.002	0.00003	1.3	0.04
+ 3% NTC	14.7	0.44	12.9	0.2	0.9	0.01	1	0.05
+ 3% NTC (RTFO)	-	-	-	-	-	-	-	-
+ 3% NTC (PAV)	16.5	0.33	15.1	0.16	0.1	0.002	3.7	0.09
+ 6% SiO2	12.3	0.18	9.4	0.02	1.3	0.02	1.6	0.04
+ 6% SiO2 (RTFO)	14.0	1.8	12	2.6	0.6	0.46	1.7	0.17
+ 6% SiO2 (PAV)	17.6	0.23	16.7	0.11	0.1	0.001	1.9	0.05
+ 6% Dia	11.9	0.41	5	0.02	4.3	0.12	2.8	0.03
+ 6% Dia (RTFO)	11.6	0.8	7.7	1.4	2.6	0.64	1.5	0.12
+ 6% Dia (PAV)	16.2	0.24	14.5	0.11	0.2	0	3.3	0.03
+ 10% Lime	16.2	0.19	13.4	0.05	0.8	0.01	2.3	0.06
+ 10% Lime (RTFO)	13.1	0.44	8.8	0.98	1.3	0.28	3.8	0.15
+ 10% Lime (PAV)	15.7	0.16	14.3	0.08	0.4	0	1.4	0.01
+ 0.5% AS	13.7	0.21	8.9	0.07	1.5	0.02	3.7	0.04
+ 0.5% AS (RTFO)	11.9	0.15	3.3	0.14	4.7	0.14	4	0.18
+ 0.5% AS (PAV)	15.6	0.23	12.5	0.1	0.7	0.01	3.4	0.04

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1 **6.4 FTIR Analysis**

2 The analysis allows the study of the sample molecular structure based on the
3 infrared spectrum. Typically the obtained results are compared to a previously
4 developed DB of similar materials in order to determine the nature of the analyzed
5 material and to allow for interpretation of the spectrum bands (Kuptsov, 1994). The
6 functional composition changes associated to aging of the asphalt binders by means
7 of FTIR spectroscopy are shown on Figures 11 and 12.

8 The RTFO aged binder do not exhibit significant changes other than those associated
9 to the aging process. The neat binder shows 2 spectrum bands associated to
10 oxidation: 1032 cm^{-1} low intensity increase in sulfoxides and with less probability
11 ether groups, and a barely visible 1700 cm^{-1} indicates changes in carbonyl groups.
12 Because some modified binders show very low intensity in 1032 cm^{-1} band, they
13 could be considered as less prone to aging (process occurs at lower rate). This is
14 especially true when the increase in sulfoxides is low. It is expected that the previous
15 observations be highly related to changes in asphalt polarity and consequently on the
16 increase in asphalt-aggregate adhesion. In the case of PAV aged binders, the 1700
17 cm^{-1} increases in intensity for all binders.

18 To better comprehend the changes in the FTIR bands, the additives were also
19 measured individually. The 1050 cm^{-1} high intensity, 850 cm^{-1} low intensity, and
20 450 cm^{-1} high intensity bands are typical of vibration movements associated to SiO_2 .
21 The SBR and SBS bands near to 700 cm^{-1} and 980 cm^{-1} are typical of styrene and
22 butadiene respectively. In the case of CNT, typical high absorbance results in the
23 curvature associate to the spectrum. The spectra for inorganic materials such as lime
24 and Diatomite, as well as the antistrip liquid, show spectrums similar to those of the
25 neat binder.

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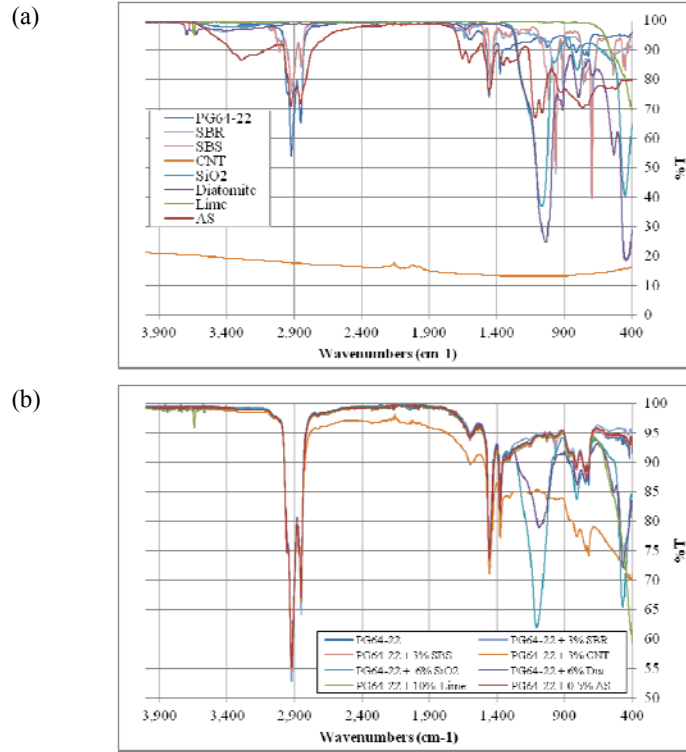


Figure 11. FTIR spectra for (a) additives, (b) unaged binder.

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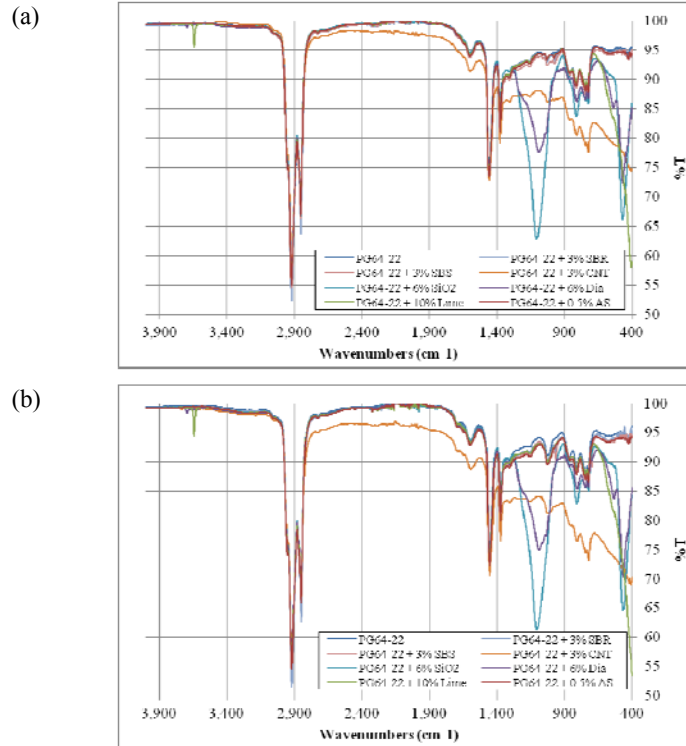


Figure 12. FTIR spectra for (a) RTFO aged binder, and (b) PAV aged binder.

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7.0 Binder Performance tests

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 using a Dynamic Shear Rheometer (DSR).

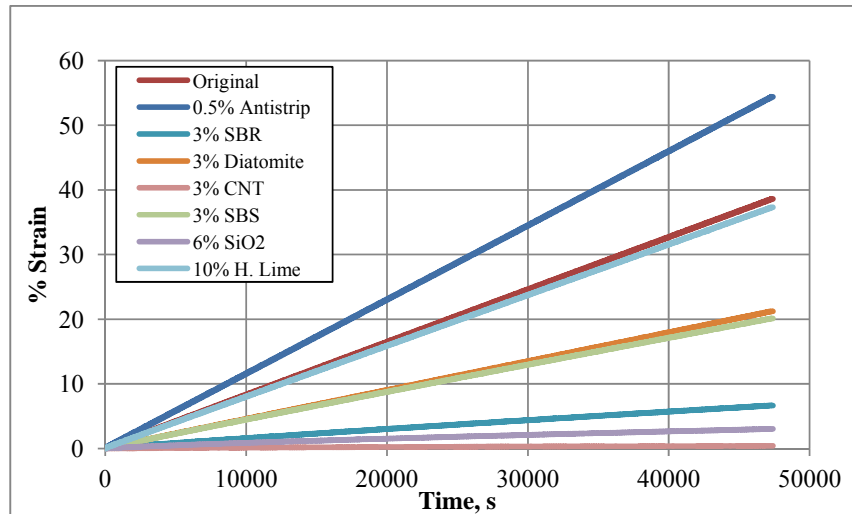
7.1 Repetitive Creep and MSCR tests

To characterize the rutting performance of all the binders, the repetitive creep test and MSCR analyses were used. The repetitive creep test is performed at the base PG grade high 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 (NCHRP Report 459). This test was performed at 64 °C and the results are shown on Figure 13. The majority of the

1 modified binders showed lower permanent deformation than the original or neat
 2 binder. The exception to this trend was obtained for the binder modified with the
 3 anti-stripping agent. The CNT modified binder at 3.0% exhibits the best overall
 4 rutting performance with a 95% reduction with respect to the neat binder. On the
 5 other hand, the binder modified with the anti-stripping agent affected negatively the
 6 permanent deformation resistance with a 41% increase with respect to the neat
 7 binder.

8 The MSCR test (ASTM - D7405/ AASHTO TP70) produces lab results that
 9 are closely correlated with actual mix performance. By dynamically loading the
 10 modified binder, and monitoring its accumulated "nonrecoverable creep compliance"
 11 (J_{nr}), the new test more accurately predicts polymer-modified binder performance,
 12 recognizing differences in polymer behavior at different temperatures and stress
 13 levels (Mooney, 2008). The MSCR test was also conducted at 64 °C. The same
 14 rolling thin film oven (RTFO) aged specimen utilized in the dynamic shear
 15 rheometer (DSR) test (conducted according to AASHTO T 315) was also used in the
 16 MSCR test. Table 6 summarizes the MSCR testing results. Based on MSCR test
 17 results, the neat binder did not meet the $J_{NR@3.2KPa}$ requirement but met the J_{NRdiff}
 18 requirement, consequently could not be graded at the lowest traffic level. On the
 19 other hand, all modified binders were graded at least as PG 64-22 "H" with the
 20 exception of the binder modified with the anti-stripping agent that was graded as PG
 21 64-22 "S".

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Figure 13. Repetitive creep test results.

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2**Table 6. MSCR Results.**

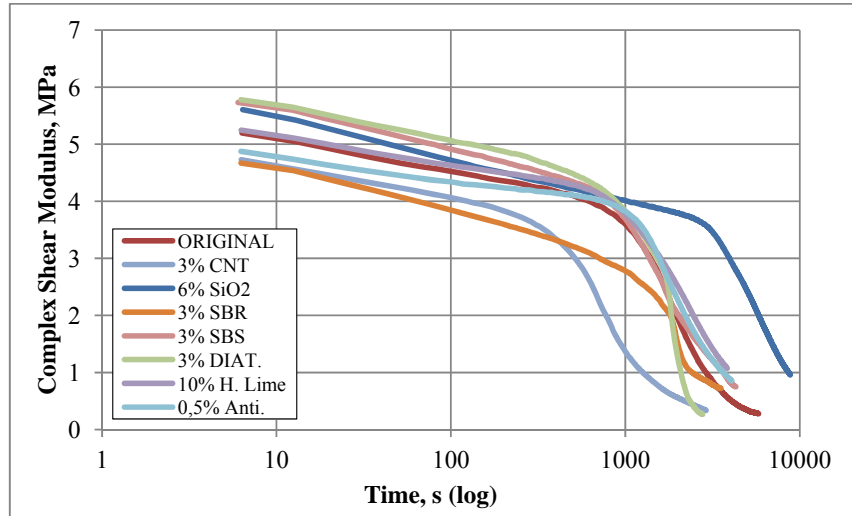
Material	Result	$J_{NR@3,2KPa}$	$\frac{(J_{NR@3,2KPa} - J_{NR@0,1KPa})}{J_{NR@0,1KPa}}$
PG64-22	PG 64 (22)	7.344	0,22
PG64-22 + 3% SBR	PG 64(22) E	0.311	0.36
PG64-22 + 3% SBS	PG 64(22) V	0.899	0.25
PG64-22 + 3% NTC	PG 64(22) E	0.064	0,75
PG64-22 + 6% SiO ₂	PG 64(22) E	0.292	0,36
PG64-22 + 6% Dia	PG 64(22) E	0.118	0.44
PG64-22 + 10% H. Lime	PG 64(22) H	1.476	0.16
PG64-22 + 0.5% AS	PG 64(22) S	2.148	0.17
Traffic		$J_{NR@3,2KPa}$	$\frac{(J_{NR@3,2KPa} - J_{NR@0,1KPa})}{J_{NR@0,1KPa}}$
Standard "S" ($< 1 \times 10^7$ 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	$< 0,75$

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5**7.2 Fatigue**

6 To characterize the fatigue performance of the binders, a DSR repetitive fatigue
7 analysis was used. The test was performed at a temperature of 22 °C (neat binder
8 intermediate performance grade temperature) and consists of subjecting the sample
9 to an angular frequency of 10 rad/s, under controlled mode (10 %) following
10 NCHRP 459 recommendations. The test was performed to a point close to 100%
11 damage of the sample and the results are exhibited on Figure 14. A primary damage
12 zone with an initial modulus decay rate (viscoelastic range) and after that a
13 secondary zone with an accelerated damage zone are exhibited for all samples. It
14 was determined that the inflexion point between the primary and secondary zones
15 occurred when the slope of the "Phase angle vs. Time" curve equals zero (Figure
16 15).

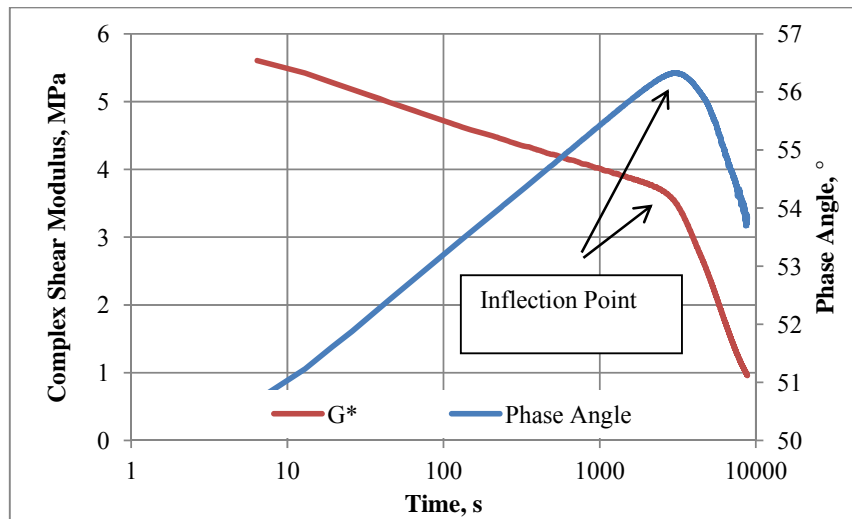
17 For each fatigue curve the inflexion point in terms of time was computed
18 along with the associated G^* value. These results were compared against the time to
19 reach 50% modulus drop and the outcomes are shown on Table 7. On average, the
20 time to reach 50% damage was 54% greater than the inflexion point. It can be seen
21 that the binder modified with 3% CNT and 10% hydrated lime presented lower
22 inflexion affecting negatively their fatigue resistance. This behavior matches the
23 results obtained from the rutting tests where the addition of materials typically used
24 to treat moisture damage tend to compromise the fatigue performance. On the other

1 hand, addition of 6% SiO₂ to the original binder significantly improves its fatigue
 2 resistance.
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Figure 14. *Fatigue test results.*



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Figure 15. *Fatigue Inflexion point definition.*

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3**Table 7. 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 + 3% SBR	4.67	1453	2.28	1499
PG64-22 + 3% SBS	5.73	1124	3.65	1453
PG64-22 + 3% NTC	4.72	577	2.79	679
PG64-22 + 6% SiO ₂	5.61	2850	3.59	4283
PG64-22 + 3% Diat.	5.77	1120	3.78	1596
PG64-22 + 10% H. Lime	5.24	776	4.05	1906
PG64-22 + 0.5% AS	4.87	1403	3.31	1883

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6**7.3 Combined Results**

7 Based on the performance test results and the use of adhesion parameters, a ranking
8 analysis was developed to select the most suitable asphalt binder to resist the three
9 major types of distresses for one aggregate source (river gravel 2). Table 8 shows all
10 the materials ordered from 1 to 8, 1 meaning best performance. This analysis
11 indicates that asphalt binders modified with NTCs and SiO₂ are good candidates
12 from the permanent deformation point of view. In terms of fatigue resistance,
13 binders modified with SiO₂ and SBR are the best candidates. Finally, binders
14 modified with SBS and Hydrated Lime are good candidates to resist the damage
15 produce by the presence of moisture for the river gravel 2. Notice how binders that
16 could performed well for rutting and fatigue tended to be have higher moisture
17 damage susceptibility and reciprocally.

18 The selection of a binder capable of resisting all three types of distresses is
19 complicated. However, depending on the function of the asphalt layer, a binder
20 could be selected to address two types of potential problems. For instance, if the
21 asphalt mixture would be used as surface layer moisture damage and rutting may be
22 address with the addition of the SBS polymer. Moreover, if the asphalt mixture
23 would be used as base layer fatigue cracking and rutting may be address with the
24 addition of the SiO₂. As a result, some of these modifiers serve as candidates for
25 further asphalt mixture performance tests and its selection will depend of the type of
26 distress to be analyzed.

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Table 8. Performance ranking analysis.

Material	Creep	MSCR	Fatigue	POTS Ratio RG2	WAB GR2	WBB GR2
PG64-22	7	8	4	4	5	5
+ 0.5% AS	8	7	3	2	3	4
+ 10% H. Lime	6	6	7	3	2	2
+ 3% Diat.	5	2	6	6	1	8
+ 3% SBS	4	5	5	1	4	1
+ 3% SBR	3	4	2	7	6	6
+ 6% SiO2	2	3	1	8	8	7
PG64-22 + 3% NTC	1	1	8	5	7	3

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8.0 Summary of Findings And Conclusions

8 The BBS results correlate fundamental material properties such as surface free
9 energy and work of adhesion. In general, it was observed that some modified binder-
10 aggregate combinations result in a reduction of the stress required to separate the
11 asphalt film from the aggregate surface. The cause can be associated to two factors:
12 stiffening of asphalt during the modification process, and 2) intrinsic chemical
13 properties of the additive and how its polarity interacts with that of the aggregate.
14 Such is the case of SBR which is the polymer that is typically used in Costa Rica.
15 The styrene is stiff and the rubber component is non adhesive, but in general SBR
16 modified asphalt shows high resistance to rupture and humidity.

17 Furthermore, due to the significant differences in strength of adhesion
18 between the different aggregate-binder combinations, the adhesion between the
19 materials cannot always be considered adequate based on limits established in the
20 literature: the $POTS_{Wet}/POTS_{Dry}$ ratio should not drop below 0.70. This non-
21 compliance typically occurred with Gravel 1 and Limestone 1, reason why the use of
22 the aggregate sources should be limited if there is previous history of moisture
23 damage related problems, even when antistripping agents are used. The benefits of the
24 adhesion promoter need to be verified for each condition.

25 Application the Sessile Drop method allowed calculation of surface energy
26 components for asphalts and binders and it was possible to relate the results with
27 different parameters associated to moisture damage. All of the additives proposed
28 improved the adhesion of the binder with the aggregate as they increase the
29 compatibility between them to form a stronger bond. However, the compatibility

1 ratios showed that the modified binders did not result in a significant difference in
2 resistance to moisture damage, compared to the neat binder. However, the
3 combinations including gravels show a higher degree of compatibility which
4 suggests that these mixtures will be more efficient in resisting stripping. This is
5 consistent with field experience associate to the use of this materials.

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

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