Effect of Aging on Adhesion Properties of Asphalt Mixtures with the Use of Bitumen Bond Strength and Surface Energy Measurement Tests

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The interaction between asphalt binder and aggregate is fundamental to ensure adequate performance of asphalt mixtures, mainly in the presence of water. The work of adhesion generated between both materials directly affects the resistance of asphalt mixture to moisture damage, because it measures the ease with which water can displace asphalt binder from the aggregate surface. The objective of this study was to characterize the bond strength between asphalt and several aggregate sources. A PG 64-22 neat binder was modified with several additives to determine the effect on adhesion: polymers, nanomaterials, and adhesion promoters. To measure the strength of adhesion, the bitumen bond strength (BBS) test and contact angle measurements between asphalt binder and the aggregate surface by means of goniometry were used. The surface energy of the asphalt and the aggregate, with and without the presence of water, was estimated also. Testing was performed on all binders and on each binder–aggregate combination after (*a*) rolling thin-film oven (RTFO) aging and (*b*) RTFO and pressure aging vessel aging. The BBS results identified differences in bond strength as a result of moisture conditioning and aging. The differences depended on the aggregate source and binder type. Different failure modes were also observed (i.e., cohesive, adhesive). The results also indicated an increase in strength of adhesion associated with the aging process: the main resistance gain was observed after RTFO aging. Finally, changes in bond strength were compared with functional composition changes associated with the aging process and related to changes in performance.

The most common form of distress associated with the presence of moisture in a hot-mix asphalt (HMA) layer is known as stripping, a phenomenon that involves the loss of the asphalt coating from the aggregate surface (*1*). Typically, the process is followed by a progressive loss of aggregate particles from the HMA layer surface as a result of stresses associated with wheel loads that traveled over the material (i.e., raveling). Previous distress modes are related in that they originated from a loss of adhesion at the asphalt binder–aggregate interface.

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Historically, several laboratory testing methods have been developed to quantify moisture damage. The most common tests are the boiling test (ASTM D3625), Texas boiling test (Tex-530-C), static-immersion test (AASHTO T 182), Lottman test, modified Lottman (AASHTO T 283), Tunnicliff and Root conditioning test (*2*), immersion-compression test (AASHTO T 165), Texas freeze–thaw pedestal test, Hamburg wheel tracking device test (AASHTO T 324), and the Superpave® simple performance tests (i.e., static creep, repeated load permanent deformation, and dynamic modulus) with an environmental conditioning system.

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

Even though the test is simple to perform, it can yield erroneous results that affect the true performance of the HMA negatively. To avoid this possibility, methodologies with their basis in the measurement of fundamental material properties became necessary to ensure an adequate characterization of damage caused by the presence of moisture in the asphalt mixture. Such an approach makes it possible to determine how the material properties associated with moisture damage can change during the service life of the pavement structure, when aging of the HMA is taken into consideration.

BACKGROUND

Moisture damage is highly related to the cohesion bond, which involves the internal cohesion of the asphalt matrix, and to the adhesion bond, which is related to the interaction strength between asphalt and aggregate (*9*). As part of currently implemented material design procedures, these properties are not accounted for to the degree of importance required. For this reason, a broad effort is under way to study and understand the processes involved in aggregate–asphalt adhesion and asphalt binder internal cohesion.

Deterioration associated with moisture damage is a function of various thermodynamic processes. Several studies indicated different

factors were feasible causes of the phenomenon that generated at the interface between the mastic and the aggregate surface (adhesion failure) and within the internal structure of the mastic (cohesion failure). In general, it was agreed that the failure type depended primarily on the material properties. However, several factors other than the asphalt mastic affected the susceptibility of the asphalt mixture, such as the use of asphalt modifiers, as well as adhesion promoters, such as liquid antistrip or hydrated lime (10). It has also been observed that an increase in water pH present at the asphalt–aggregate interface has an important effect on the weakening of the adhesive bond between the two materials (11).

A literature review by Tarrer and Wagh identified at least six failure mechanisms that could be associated with moisture damage and aggregate detachment and that could occur individually or simultaneously (12). The mechanisms were detachment, displacement, spontaneous emulsification, pore pressure, hydraulic scouring, and environmental factors. Other factors, such as rupture of the asphalt film and pH instability, have been highlighted.

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

Changes in pH, or instability in acidity, can affect the chemical bonds at the material interface level and consequently the adhesion between asphalt and aggregate (11). This occurrence has been observed through the measurement of the changes in contact angle and wettability at the aggregate–asphalt interface. Finally, climatic factors [e.g., relative humidity, temperature (air and water) and precipitation] play important roles in material performance (16).

All of the previous mechanisms are the consequences of water having higher surface free energy (γ) than asphalt binder, which translates into water presenting higher wettability of aggregates (13). The surface free energy is a physical–chemical property that corresponds to the amount of energy required to create a new unit of material surface area, under vacuum conditions. Surface free energy is a fundamental property of every material and affects superficial characteristics and interactions with other materials (e.g., adsorption, wettability, adhesion, cohesion). Consequently, thermodynamic changes in surface free energy can be related to possible separation between the asphalt binder and the aggregate, and to cracks that can develop within the mastic structure. Similarly, these changes can be directly related to the healing of fractures at the asphalt aggregate interface or within the mastic structure (9).

EFFECT OF AGING ON MOISTURE DAMAGE

The physical–chemical properties of oxidized asphalt promote the occurrence of microcracks, which in turn become paths through which water can more freely penetrate the asphalt–aggregate interface, which accelerates the moisture damage process. However, results are mixed as to the effect of an aged binder on the adhesion between asphalt and aggregate (17). If the strength of the interaction is reduced, the resistance of the asphalt–aggregate system is compromised, which increases moisture susceptibility (18). Negative consequences associated with the aging process can be predicted through the characterization of the surface free energy of the affected material: asphalt. This in turn allows the design of aggregate–asphalt combinations that optimize the adhesion between the materials (19–20). Consequently, the purpose of the study presented in this paper was to measure the compatibility between asphalt and aggregate to ensure adequate durability.

OBJECTIVE

The main goals of the research project were to (a) quantify the adhesion between the asphalt source available in Costa Rica with different aggregate types typically used in HMA construction, (b) characterize the effect of different additives on moisture damage susceptibility, and (c) determine the effect of aging on adhesion for the analyzed materials. The bitumen bond strength (BBS) test was used to evaluate the asphalt–aggregate adhesion and the internal cohesion of the asphalt structure. Contact angle measurements also were performed for all asphalt–aggregate combinations by means of goniometry. In addition, goniometry was used to estimate the total surface free energy for the analyzed asphalts and aggregate sources, to quantify the susceptibility to moisture.

MATERIALS USED IN STUDY

The various materials used in this study are summarized in Table 1. Only one asphalt binder source was selected for the study, because the Costa Rican National Petroleum Refinery produces only one type

TABLE 1   Materials Selection Summary

Factor	Level	Description

Asphalt	8	PG 64-22
		PG 64-22 + 3% SBR (PG 76-19)
		PG 64-22 + 3% SBS (PG 76-25)
		PG 64-22 + 3% CNT (PG 88-25)
		PG 64-22 + 6% nano SiO_2 (PG 82-25)
		PG 64-22 + 6% diatomite (PG 70-25)
		PG 64-22 + 10% hydrated lime
		    (PG 70-25)
		PG 64-22 + 0.5% liquid antistrip
		    (PG 64-25)

Aging conditions	3	PG 64-22 RTFO aged PAV aged[a]
Aggregate source	4	River Gravel 1, Central Pacific River Gravel 2, Central Caribbean Limestone 1, Central Valley Limestone 2, North Pacific

NOTE: PG = performance grade; SBR = styrene–butadiene–rubber; SBS = styrene–butadiene–styrene; CNT = carbon nanotube; SiO_2 = silicon dioxide; RTFO = rolling thin-film oven; PAV = pressure aging vessel.
[a]PAV-aged binders were previously subjected to RTFO aging.

of asphalt: PG 64-22. The asphalt binder was modified with seven additives to evaluate their impact on adhesion: two elastomeric thermoplastic polymers (i.e., SBR and SBS), three nanomaterials [i.e., multiwall carbon nanotubes, nano silica (silicon dioxide), and diatomite], and two adhesion promoters (i.e., liquid antistrip and hydrated lime).

The optimum content for each additive was determined in the laboratory before the current study and is shown in Table 1. All of the additives were incorporated with the use of a low shear stirrer at 175°C for 3 h. The resulting performance grades also are shown in Table 1. The vast majority of the analyzed modifiers increased the high temperature grade. The greatest change was in the 3% carbon nanotube modified asphalt, which increased the high temperature by four performance grades.

The aggregate sources selected were some of the most widespread aggregate sources used in Costa Rica. Two of the aggregate sources corresponded to limestone materials, while the remainder corresponded to river gravels of complex mineralogy from various geographical locations in Costa Rica. However, both groups could be classified as siliceous materials from igneous formations that had been subjected to some sedimentary processes. Historically, central Caribbean material has performed well with respect to moisture damage. Materials from the Pacific Coast have been known to result in stripping problems.

The asphalt binder aging variable was intended to simulate the changes in adhesion that resulted from changes in asphalt properties associated with the aging process. Three distinct aging conditions were evaluated: (*a*) neat (unaged) binder, (*b*) rolling thin-film oven (RTFO)-aged binder to simulate the aging associated with the plant mixing and HMA field construction process, and (*c*) pressure aging vessel (PAV) aging to simulate aging and oxidation in the asphalt binder during the initial 7 to 10 years of service life.

DESCRIPTION OF TEST METHODS

As part of the study, asphalt–aggregate adhesion was characterized by means of three methodologies. The first method had its basis in the BBS test (*3*). The test was performed in accordance with AASHTO TP-91 and with the use of a pneumatic adhesion tensile testing instrument, a piece of equipment initially developed by the paint and sealant industries (Figure 1).

The aggregate samples were cut or cored from large rocks. The aggregate sample faces were then polished with 280-grit material to ensure uniform roughness between samples. (The mechanical interlock between the asphalt–aggregate was minimized to ensure that adhesion measurements corresponded to the thermodynamic interaction between the materials.) The samples were then placed in an ultrasonic bath to remove any surface residue. An asphalt sample of 0.40 ± 0.05 g was placed on metallic stubs of a known diameter (20 mm). The stubs that contained the asphalt sample were pressed against the aggregate surface without the application of torsion.

The BBS measured the pull-off tensile strength (POTS) of the asphalt–aggregate system when it was subjected to a constant load rate of 0.689 MPa/s (100 psi/s) and was analyzed after 24 h of conditioning at room temperature ($POTS_{dry}$) and after 48 h of conditioning in a water bath at 40°C ($POTS_{wet}$). A minimum of two replicates were used for each of the material combinations. The percentage loss in bond strength could be estimated as

$$\frac{\left[POTS_{dry} - POTS_{wet}\right]}{POTS_{dry}} \tag{1}$$

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

The goniometer is an optical instrument that can capture the profile of an asphalt drop over an aggregate substrate. It works on the basis of the sessile drop principle (*21*). θ_{SL} is the angle formed between the liquid–solid and liquid–gas interface. The samples were prepared in a manner similar to the one used to prepared samples for the BBS test but differed in that the asphalt drop was placed directly over the aggregate surface (Figure 2). A minimum of five replicates for each asphalt–aggregate combination were evaluated to estimate θ_{SL}.

TESTING RESULTS AND DATA ANALYSIS

BBS Test

Figure 3 shows the dry and wet POTS for the analyzed asphalt binders in original and aged conditions, while Figure 4 shows the loss of adhesion as set out in Equation 1. For the unaged binders, under dry conditions, the 3% SBR modified asphalt and limestone 1 combination required the least amount of strength to induce failure. The use of SBR resulted in a POTS level that was consistently lower than that associated with the original binder as well as with most of the
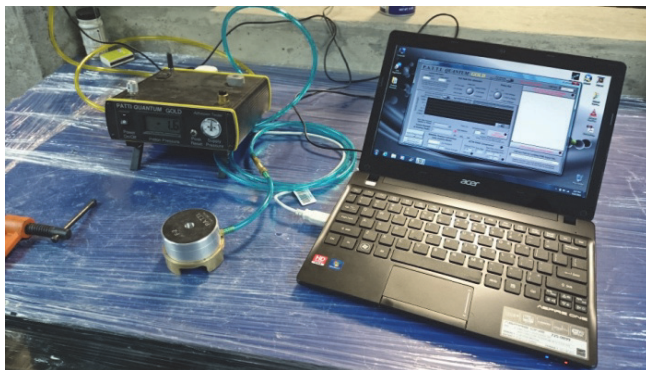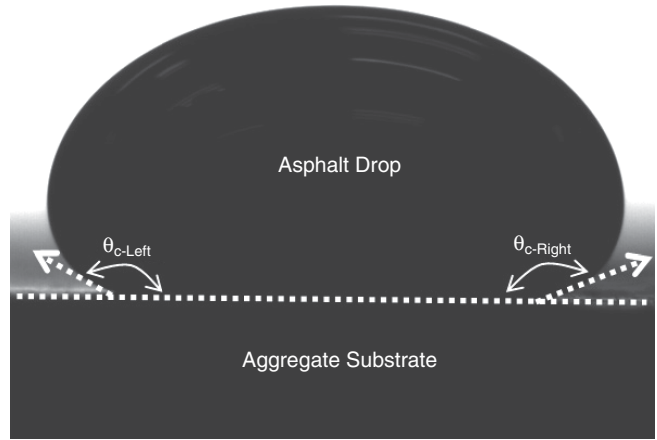

(a)
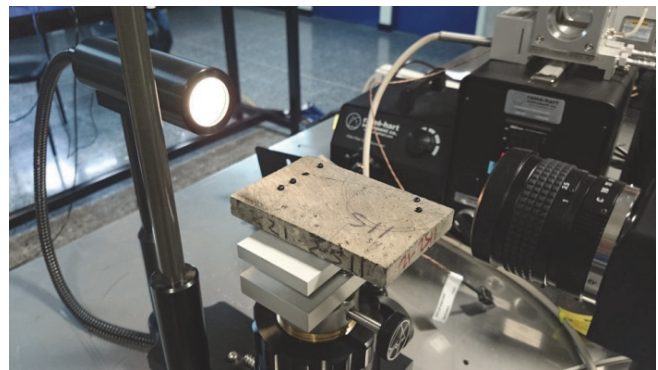
(b)

FIGURE 1   Test equipment used: (*a*) pneumatic adhesion tensile testing instrument and (*b*) goniometer.
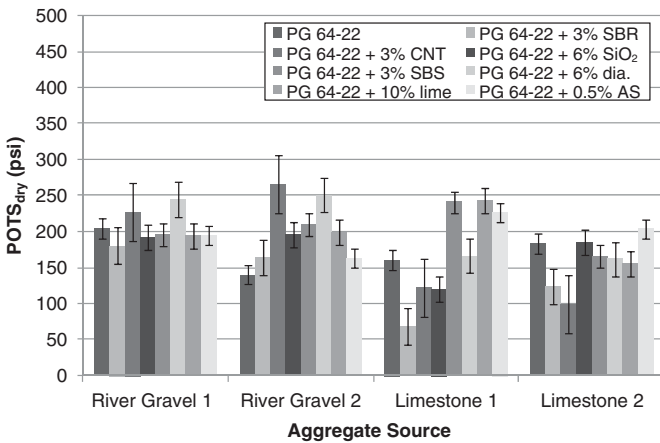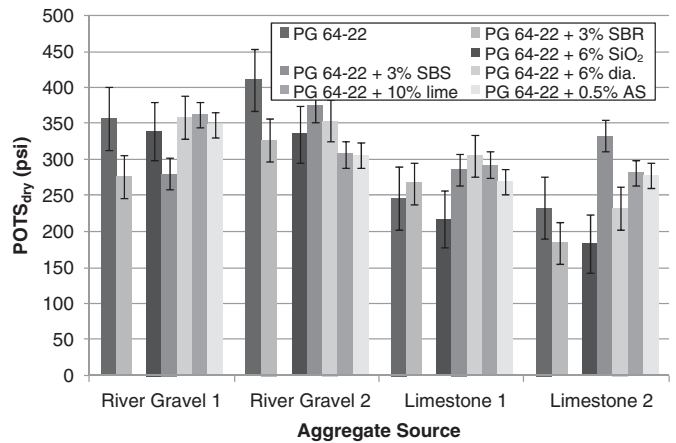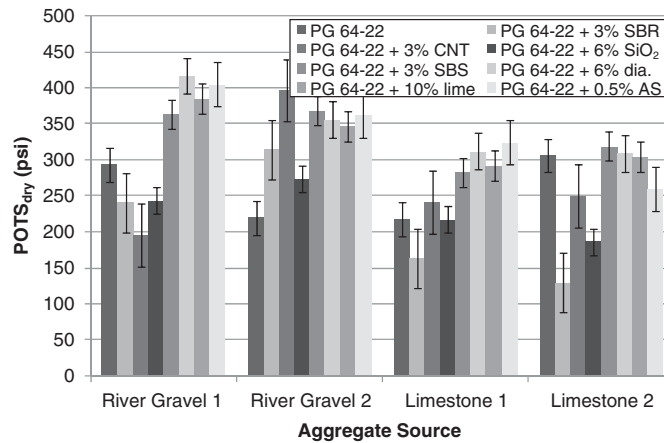
(a)

(b)

FIGURE 2   Elements of sample preparation: (*a*) asphalt binder drop samples for contact angle measurement and (*b*) contact angle images used in measurements.

(a)

(b)

(c)

FIGURE 3   POTS for different asphalt–aggregate combinations with asphalts in dry (*a*) unaged condition, (*b*) RTFO-aged condition, and (*c*) PAV-aged condition (dia. = diatomite; AS = liquid antistrip).
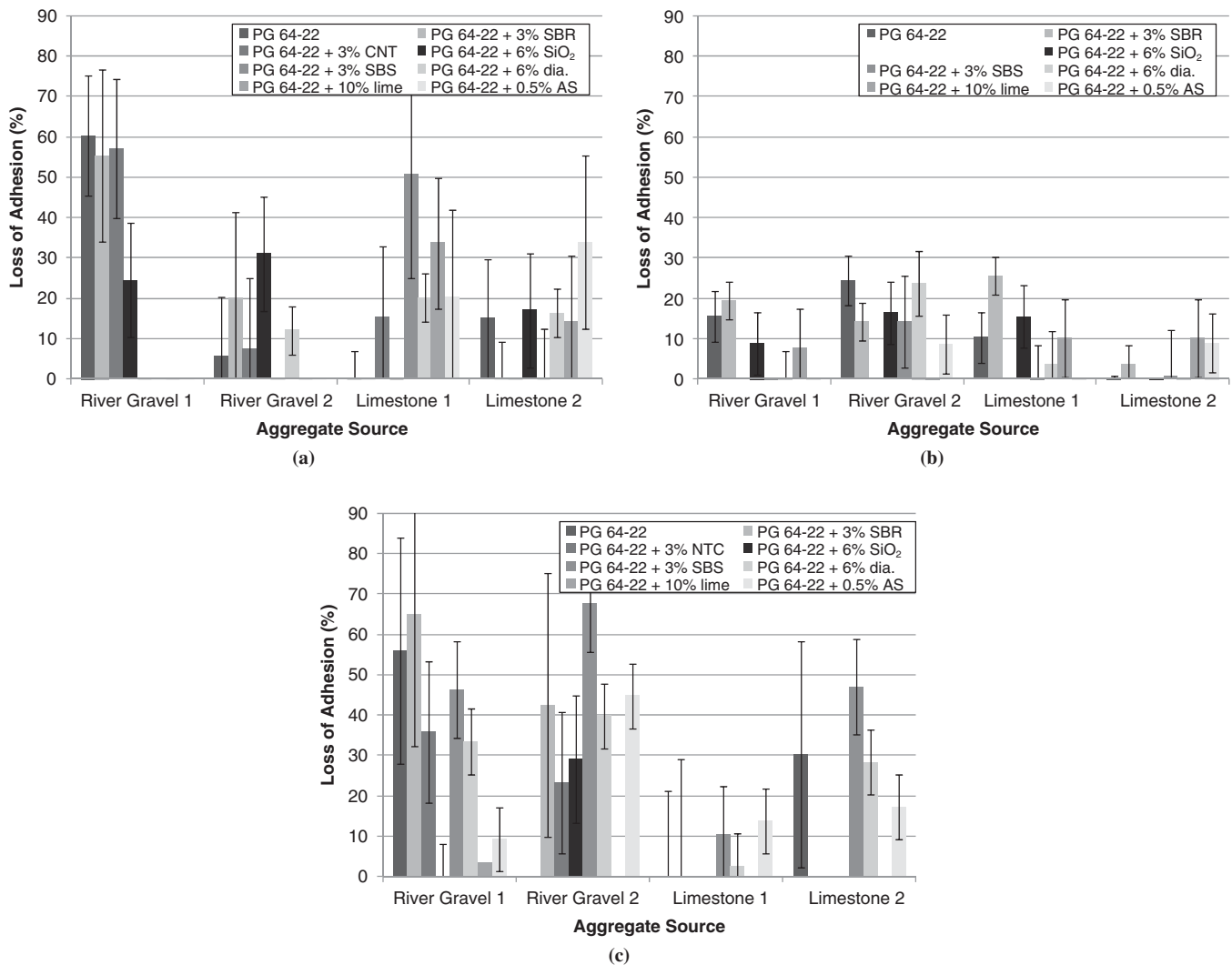
FIGURE 4 Loss of adhesion associated with (*a*) unaged binders, (*b*) RTFO-aged binders, and (*c*) PAV-aged binders.

modified binders. The variability in results diminished when the samples were subjected to conditioning. However, the conditioned samples exhibited a significant loss in POTS.

Although the strength of adhesion appeared lower for limestone aggregates, the change when these materials were subjected to wet conditioning was low compared with the river gravels (specifically, River Gravel 1). A possible explanation why River Gravel 1 showed greater losses might be related to the higher aggregate porosity that could result in faster water filtration rates and that could accelerate the displacement of the asphalt film. The analysis confirmed the superiority of River Gravel 2, which was the preferred aggregate source, given the field resistance to moisture damage that mixtures tended to exhibit when produced with the material. In general, under dry conditioning, cohesive failures typically were observed. The tendency was the same for wet conditioned samples, with the exception of the river gravels that showed adhesive failure between asphalt–aggregate.

When the asphalt binders were aged, adhesive failures were considerably fewer. This result suggested that, in the long term, special attention should be given to ensure the cohesion of the asphalt binder and the asphalt mastic. However, the previous requirement

was difficult to achieve, given the hardening associated with the aging process. The POTS results for aged binders indicated a 70%+ increase in POTS when RTFO aging was performed. Consequently, the strength required to break the internal cohesion bond practically doubled. In the case of PAV aged binder, a significant increase in POTS with respect to the unaged binder also was observed (60%+). However, a small reduction occurred with respect to the POTS results under RTFO aging. This finding suggested that an increase in the polarity of short-term aged asphalt improved the compatibility with highly polar aggregates. However, the change in polarity was counterbalanced by the hardening of the material over the longer term. This finding may indicate that adhesion is controlled by electrostatic forces in the short term but depends on the mechanical behavior of the material in the long term (adhesion or cohesion failure depends on material strength).

As was the case in previous studies, when the loss of adhesion associated with unaged binders was being evaluated, it was clear that the loss was highly dependent on the aggregate source, the asphalt binder, and the interaction between the two factors (*3*). For example, in the case of river gravels, the lower losses were associated with asphalts modified with SBS, diatomite, and as expected, adhesion promoters.

However, the tendency was reversed when limestone was used. This behavior could be explained by the differences in polarity between the types of aggregate. The data also confirmed that the optimum performance was shown by River Gravel 2, regardless of the type of asphalt that was used.

RTFO-aged binders showed a considerable reduction in loss of adhesion: the affinity of aggregate and asphalt improved with short-term aging. However, the effect reverted when long-term aging was considered, especially for river gravels. When the loss of adhesion was compared between unaged and PAV-aged samples, the latter showed greater susceptibility to moisture.

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 was placed on the aggregate surface (asphalt was heated to 165°C in a temperature-controlled chamber and dropped from a 1-in. height), 5 min after setting. Each drop was measured for a left and right contact angle (Figure 2), and the values were averaged. If the difference between angles for a given drop exceeded 5°C, the measurements were discarded.

The results are shown in Figure 5. With the exception of the liquid antistrip modified asphalt, the contact angle between modified asphalt and all aggregate sources increased with respect to the neat binder. This finding was consistent with what was observed in the BBS test on the basis of POTS: overall higher contact angles (indicator of lower wettability) could be related to asphalt–aggregate combinations with higher loss of adhesion values.

In the BBS test, however, failure could be associated with adhesion of the asphalt–aggregate system or the internal cohesion of the asphalt matrix. Contact angle measurements addressed only the adhesion between the two system components. The use of the goniometer to measure contact angles between asphalt and aggregates is fairly new. Consequently, no specification exists to standardize the conditions under which the asphalt drop is placed on the aggregate surface.

Surface Free Energy

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 its capability not to dissolve or chemically react with the surface of interest. Also, the liquid must be pure and the three components of its surface energy, according to acid-base theory, must be known [the dispersive (nonpolar) 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, and ethylene glycol and formamide for asphalts. The validity of the liquid selection and measured contact angles was obtained on the basis of earlier research (22–24). Equation 2 was used to relate the measured angles to the unknown surface energy components (25):

$$\gamma_L \left(1 + \cos\theta\right) = 2\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + 2\sqrt{\gamma_S^+\gamma_L^-} + 2\sqrt{\gamma_L^-\gamma_S^+} \qquad (2)$$

where L refers to the probe liquid, and S refers to the solid surface of binder or aggregate. The results are shown in Table 2.

The surface energy values for the distinct aggregates sources differed from each other. This result was expected, given the variable chemical composition of aggregates, which would result in different surface characteristics. However, the previous observation was 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 by others who used different γ measurement procedures, such as the universal sorption device (26).

The surface energy of neat asphalt changes when modified. The resulting values depend on the chemical nature of the material used as an additive. Of the seven additives used in this study, only hydrated lime and diatomite were polar; the rest were nonpolar in nature. A nonpolar additive is expected to increase the dispersive component of the total surface energy of the neat binder. A polar additive decreases the same component but increases the acidic or basic component. In general, this expectation was observed in the data, with the exception of hydrated lime which, contrary to what was expected, increased the dispersive character of the asphalt, possibly as a result of reactions that took place during the modification process.

The chemical changes that occur in the asphalt during aging have consequences in terms of surface energy characteristics. Data indicate that in general the aging process increases the dispersive component of the surface energy and decreases the polar component. However, such behavior is not applicable to all of the asphalts, which may differ chemically from one another. Once the asphalts were aged, the work of adhesion increased in all cases. The aging process causes changes in polarity (i.e., chemical changes) that make the asphalt more compatible with the evaluated aggregate sources. Thus the interactions established between the two materials became stronger.

Fourier Transform Infrared Spectroscopy Analysis

The infrared spectrum of a sample helps to determine its molecular structure and to study the chemical changes that take place during a given process. Typically, an obtained sample spectrum is compared with a previously developed database of similar materials to associate the wavelength bands with different chemical groups that may compose the sample (27).

In Figure 6, b and d, the binders (i.e., original, RTFO, PAV) show bands typical of hydrocarbon-based compounds (i.e., below 3,000 cm^{-1}, about 1,400 cm^{-1}, below 900 cm^{-1}). Once the binder is modified, the presence of the additives causes changes in the infrared spectroscopy spectrum. To better comprehend these changes, the additives were
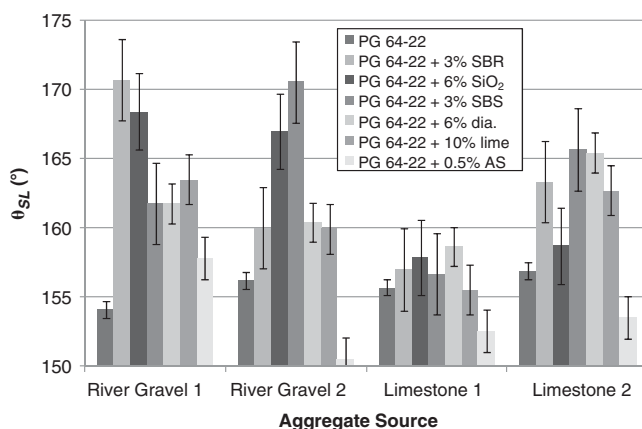

FIGURE 5   Contact angle results.

TABLE 2 Surface Free Energy of Aggregates and Asphalt Binders

Material	γ^{Total}		γ^{LW}		γ^+		γ^-	
	Average	SD	Average	SD	Average	SD	Average	SD
Aggregate								
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	0.70	0.6	0.01	26.5	2.30
Asphalt Binder								
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	1.00	1.7	0.39	4.0	0.16
PG 64-22 (PAV)	16.3	0.33	14.7	0.16	0.2	0.00	2.6	0.05
PG 64-22 + 3% SBR	13.0	2.35	9.7	0.24	1.4	0.01	1.9	0.05
PG 64-22 + 3% SBR (RTFO)	17.3	0.47	16.1	0.77	0.2	0.08	2.6	0.16
PG 64-22 + 3% SBR (PAV)	17.3	4.10	16.9	0.15	0.01	0.000	2.9	0.06
PG 64-22 + 3% SBS	18.7	0.55	18.0	0.27	0.04	0.001	2.9	0.06
PG 64-22 + 3% SBS (RTFO)	14.7	1.10	12.7	2.70	0.2	0.31	6.3	0.58
PG 64-22 + 3% SBS (PAV)	19.5	0.97	19.4	0.48	0.002	0.00003	1.3	0.04
PG 64-22 + 3% CNT	14.7	0.44	12.9	0.20	0.9	0.01	1.0	0.05
PG 64-22 + 3% CNT (RTFO)	NA	NA	NA	NA	NA	NA	NA	NA
PG 64-22 + 3% CNT (PAV)	16.5	0.33	15.1	0.16	0.1	0.002	3.7	0.09
PG 64-22 + 6% SiO_2	12.3	0.18	9.4	0.02	1.3	0.02	1.6	0.04
PG 64-22 + 6% SiO_2 (RTFO)	14.0	1.80	12.0	2.60	0.6	0.46	1.7	0.17
PG 64-22 + 6% SiO_2 (PAV)	17.6	0.23	16.7	0.11	0.1	0.001	1.9	0.05
PG 64-22 + 6% diatomite	11.9	0.41	5.0	0.02	4.3	0.12	2.8	0.03
PG 64-22 + 6% diatomite (RTFO)	11.6	0.80	7.7	1.40	2.6	0.64	1.5	0.12
PG 64-22 + 6% diatomite (PAV)	16.2	0.24	14.5	0.11	0.2	0.00	3.3	0.03
PG 64-22 + 10% lime	16.2	0.19	13.4	0.05	0.8	0.01	2.3	0.06
PG 64-22 + 10% lime (RTFO)	13.1	0.44	8.8	0.98	1.3	0.28	3.8	0.15
PG 64-22 + 10% lime (PAV)	15.7	0.16	14.3	0.08	0.4	0.00	1.4	0.01
PG 64-22 + 0.5% AS	13.7	0.21	8.9	0.07	1.5	0.02	3.7	0.04
PG 64-22 + 0.5% AS (RTFO)	11.9	0.15	3.3	0.14	4.7	0.14	4.0	0.18
PG 64-22 + 0.5% AS (PAV)	15.6	0.23	12.5	0.10	0.7	0.01	3.4	0.04

NOTE: SD = standard deviation; NA = not available.
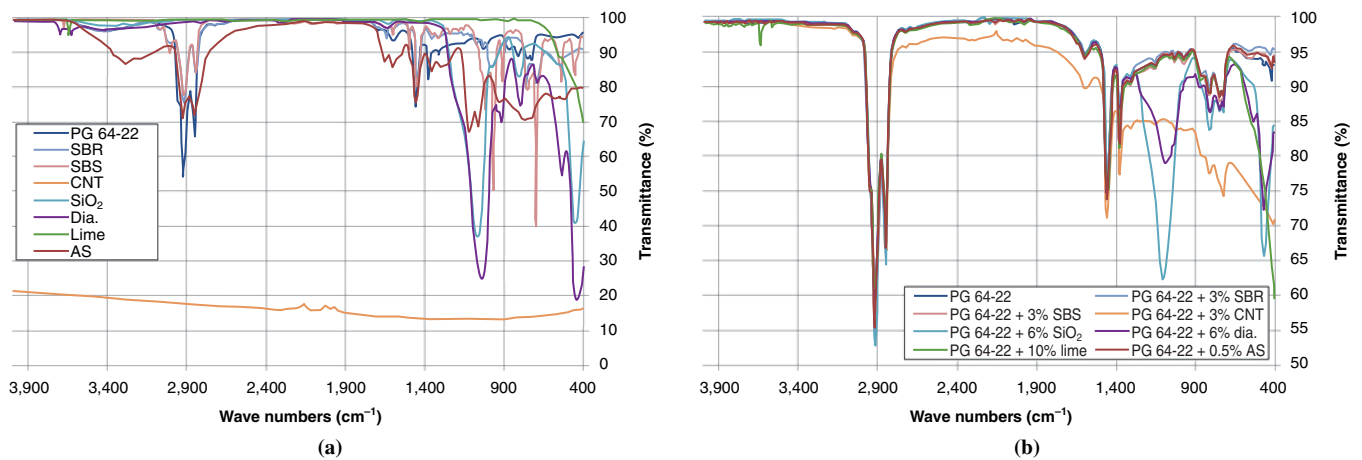

FIGURE 6 Fourier transform infrared spectroscopy for (a) additives and (b) unaged binders.
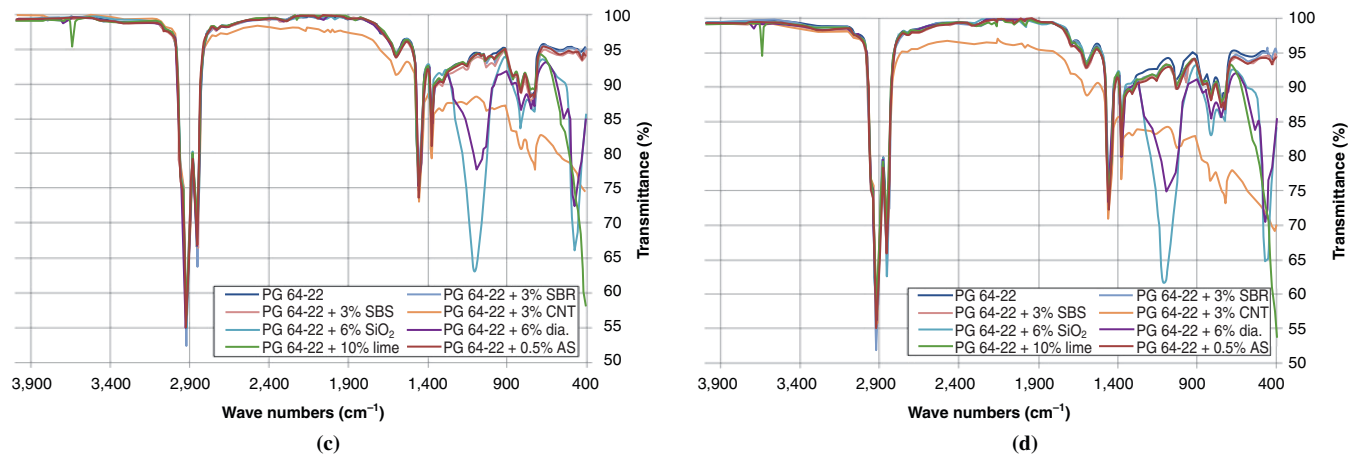
FIGURE 6 *(continued)*   Fourier transform infrared spectroscopy for (*c*) RTFO-aged binder and (*d*) PAV-aged binder.

measured individually (Figure 6*a*). The main bands observed on the additives were the 1,050 cm^{-1} high intensity, the 850 cm^{-1} low intensity, and the 450 cm^{-1} high intensity bands typical of vibration movements associated with nanosilica. These bands also were present on the diatomite because of its composition. The SBR and the SBS bands near 700 cm^{-1} and 980 cm^{-1} were typical of styrene and butadiene, respectively. The carbon nanotube showed a wide single band because of its absorption of all of the wavelengths contained on the spectrum.

The spectrum of aged asphalts also was measured (Figure 6, *c* and *d*). During the aging process, the formation of chemical groups, such as carbonyls and sulfoxides, became important and could be related to the oxidation process that occurred on the asphalt. The sulfoxides band was located at about 1,030 cm^{-1}, as seen in the unaged and aged binders (the higher intensity appeared in PAV-aged binders). The carbonyl band appeared at about 1,700 cm^{-1} and was visible only on the PAV-aged binders. These observations confirmed the increase in polarity of the aged asphalts, which was related to the increment in asphalt–aggregate adhesion observed throughout the study.

SUMMARY OF FINDINGS AND CONCLUSIONS

It was verified that BBS results correlated with fundamental material properties, such as surface free energy and work of adhesion. In general, it was observed that some modified binder–aggregate combinations resulted in a reduction of the strength required to separate the asphalt film from the aggregate surface. The cause could be associated with two factors: (*a*) the stiffening of the asphalt during the modification process and (*b*) the intrinsic chemical properties of the additive and how its polarity compared with that of the aggregate. Such was the case with SBR, which was the polymer typically used in Costa Rica. The styrene was stiff and the rubber component was nonadhesive, but in general SBR-modified asphalt showed high resistance to rupture and humidity.

Further, because of the significant differences in adhesion strength among the various aggregate–binder combinations, the adhesion between the materials could not always be considered adequate on the basis of the limits established in the literature: the POTS$_{wet}$/POTS$_{dry}$ ratio should not drop below 0.70. This noncompliance typically occurred with Gravel 1 and Limestone 1. For this reason, the

use of the aggregate sources should be limited if there is a history of moisture damage-related problems, even when antistrip agents are used. The benefits of the adhesion promoter need to be verified for each condition.

Application of the sessile drop method allowed for the calculation of surface energy components for asphalts and binders, and it was possible to relate the results to different parameters associated with moisture damage. All of the additives proposed improved the adhesion of the binder with the aggregate as they increased the compatibility between them to form a stronger bond. However, the combinations, including gravels, showed a higher degree of compatibility, which suggested that these mixtures would be more efficient in their resistance to stripping. This finding was consistent with field experience associated with the use of these materials.

On the basis of all of the results, it is highly recommended that agencies characterize the various sources in use of asphalt binders and mineral aggregates to determine the possibility of durability-related issues. Under such a scenario, an agency could reject the use of certain asphalt binder–aggregate combinations or require the use of adhesion promoters.

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