Differences in asphalt binder variability quantified through traditional and advanced laboratory testing

Allex E. Alvarez [a],*, Leidy V. Espinosa [a], Silvia Caro [b], Eduardo J. Rueda [b], Jose P. Aguiar [c], Luis G. Loria [c]

[a] *Program of Civil Engineering, Universidad del Magdalena, Carrera 32 # 22-08, Bloque VIII, Piso 2, Santa Marta D.T.C.H., Colombia*
[b] *Department of Civil and Environmental Engineering, Universidad de los Andes, Carrera 1 Este # 19A-40, Edificio ML Piso 6, Bogotá D.C., Colombia*
[c] *Laboratorio Nacional de Materiales y Modelos Estructurales, Universidad de Costa Rica, Ciudad de la Investigación, Finca 2. San Pedro de Montes de Oca, San José, Costa Rica*

HIGHLIGHTS

- Asphalt binder (AB) variability could induce uncertainty in the behaviour of asphalt mixtures.
- Variability of a Pen 60–70 AB was quantified through both traditional and advanced asphalt testing.
- Advanced testing captured higher variability than traditional testing used during production.
- Results encourage the need of new strategies to reduce current AB variability.

ARTICLE INFO

ABSTRACT

The variability in the properties of asphalt binders used for road construction could induce uncertainty in the response, performance, and degradation of flexible pavements. Although in the last 25 years some countries have adopted performance-based classification systems and stricter quality control procedures to reduce the variability of the material during its production, the reality is that most countries—including emerging economies that are extensively investing in road infrastructure—continue using classification techniques based on traditional indexes (i.e. penetration and viscosity). The objective of this paper is to assess the variability of traditional indexes and fundamental properties among eighteen asphalt specimens produced in the same refinery and classified as penetration 60–70 $^{1}/_{10}$ mm. The results show that the variability of the fundamental properties (i.e. rheological, thermodynamic, and chemical) among specimens is substantially higher than that of traditional asphalt-tests indexes (i.e. penetration, softening point, and penetration index). These results support the necessity for enhancing current classification and production practices in those countries that still use these traditional indexes.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

The service life of an asphalt pavement depends on different factors, including the properties of the materials, the design of the structure, construction and quality control processes, management strategies, operational conditions, and the occurrence of extreme weather or loading events. Regarding the role of the materials, the properties of the asphalt binder (or asphalt) are of paramount importance to ensure proper performance and durability of both asphalt mixtures [1] and asphalt surface treatments [2,3].

In terms of the production of the asphalt binders, a common practice at several refineries consists in loading the distillation towers with crude oils from different field sources, in proportions or 'recipes' that change as a function of the individual production rates at each oil field, market demand conditions, and/or specific technical requirements related to the refinery operation processes. The quality control system used during these processes is expected to guarantee a reduced variability of the material through time, which is crucial in determining the structural reliability of the pavement structure and corresponding durability of road networks. However, those control procedures are highly dependent on the specific asphalt classification system used in each country. Indeed, after demonstrating that traditional quality assessment, classification, and specification systems based on traditional indexes (e.g. penetration, softening point, ductility, and viscosity) were not sufficient to assure proper field performance of the

* Corresponding author.
E-mail addresses: aalvarez@unimagdalena.edu.co (A.E. Alvarez), scaro@uniandes.edu.co (S. Caro), ej.rueda117@uniandes.edu.co (E.J. Rueda), jose.aguiar@ucr.ac.cr (J.P. Aguiar), luis.loriasalazar@ucr.ac.cr (L.G. Loria).

asphalt mixtures, several countries have adopted new performance-based systems to control and classify these materials. These procedures, among which the Superpave system developed in North America [4] is the most popular, aim at classifying asphalt binders based on fundamental material properties so that they can fulfil the required performance in a specific road project.

Nevertheless, the reality is that with the exception of North America and some few other countries, classification systems based on traditional indexes continue being the most extended practice in the world [1]. This is particularly concerning in emerging economies, like those in Asia and Latin America, that are currently allocating unprecedented investments in the construction of road infrastructure. In the case of Colombia, for example, despite the fact that the asphalt binders comply with the penetration specifications adopted by the National Roads Institute (INVIAS by its acronym in Spanish) [5], changes in both the recipes and operation conditions at the refineries are believed to cause significant variability in the chemical, mechanical, and thermodynamic properties of the material. As a matter of fact, several main road contractors in the country have manifested variations in the workability, response, and/or performance of asphalt mixtures fabricated with virgin asphalts classified within a single penetration category. This situation motivated the Colombian Infrastructure Chamber to fund a study to quantify the chemical fraction composition of two asphalts (i.e. penetration 60–70 and 80–100 $^1/_{10}$ mm) produced in two local refineries [6]. The results demonstrated that asphalts produced under the same category during several consecutive days presented significant differences in their chemical composition.

Within this context, the objective of this paper is to quantify and compare the differences in the variability of traditional indexes and fundamental properties among several specimens of an asphalt binder produced at a single refinery using the penetration classification system. Asphalt variability, quantified using a penetration 60–70 $^1/_{10}$ mm asphalt (or Pen 60–70 asphalt), was evaluated through: (i) traditional characterization tests, (ii) rheological characterization of both unaged- and short term aged-asphalts, (iii) determination of surface free energy (SFE), (iv) computation of energy-based parameters derived from SFE measurements (i.e. adhesion quality and wettability of asphalt-aggregate interfaces), and (v) chemical characterization by means of asphalt Fourier Transform Infrared spectroscopy (FTIR).

It is important to stress that several of the properties quantified in this work were not evaluated during the development of the SHRP program that resulted in the Superpave methodology [4], since they were not available or used at the time. In addition, there are few published works that have evaluated the variability of asphalt binders using either traditional or advanced characterization asphalt testing (e.g. [6,7]). Therefore, the results obtained from this work offer relevant and up-to-date data that could be used to support improvements in current asphalt production practices and strategies in several countries and, consequently, they constitute a relevant contribution in the area of pavement engineering.

2. Materials and test methods

2.1. Experimental materials

Asphalt sampling was performed at two secondary facilities that continuously received Pen 60–70 asphalt produced at the main refinery in Colombia, located at the north-east of the country. In this manner, eighteen asphalt specimens were gathered between March 2013 and January 2017 for laboratory characterization. Specimens were collected at the secondary facilities within few days after receiving the asphalt from the refinery, shipped to the laboratory and kept until testing in a freezer at −18 °C to minimize aging effects. This procedure helped assuring undisturbed materials in order to obtain reliable results. In addition, six Colombian aggregates, commonly used in road projects in the country, were used to evaluate the quality of the adhesive bond that they develop with the asphalt binder specimens.

2.2. Asphalt traditional characterization tests

The asphalt specimens were subjected to the following tests—used in several countries, including Colombia—to quantify the variability of the traditional characterization indices used to control and classify the material: softening point (INV E 712-13), penetration (INV E 706-13), and ductility (INV E 702-13) [5]. In addition, the penetration index (I_p)—a quantitative measurement of the changes in asphalt consistency due to changes in its temperature—was determined in accordance with the testing method INV E 724-13 [5]. This computation is based on the eq. 1, proposed by Pfeiffer and Van Doormal [1].

$$I_p = \frac{20 - 10f}{1 + f} \tag{1}$$

where f is calculated as per Eq. (2), using the values of both penetration at 25 °C (P; $^1/_{10}$ mm) and softening point (T_{SP}; °C) of the asphalt binder.

$$f = \frac{50 \; Log\left[\frac{800}{P}\right]}{T_{SP} - 25} \tag{2}$$

2.3. Asphalt rheology characterization

Rheological characterization was conducted on the asphalt specimens to quantify the variability of the linear viscoelastic material properties (i.e. dynamic shear modulus, $|G^*|$, phase angle, δ, and shear viscosity, μ) through Dynamic Shear Rheometer (DSR) testing, using a TA2000ex rheometer. Thus, strain-controlled oscillatory shear tests were conducted at frequencies ranging between 1 Hz and 20 Hz, and temperatures ranging between 25 °C and 75 °C, in intervals of 1 Hz and 10 °C, respectively. In addition, the impact of aging on the magnitude and variability of these properties was assessed by testing the asphalts in two different conditions: (i) unaged, and (ii) short-term aged—obtained through the Rolling Thin Film Oven test or RTFO (AASHTO T240 [8]).

2.4. Asphalt- and aggregate-surface free energy (SFE) and Energy-Based parameters

The SFE properties of the asphalt specimens and of some selected aggregates were determined, and these values were used to compute several energy-based parameters to quantify the variability in the adhesion quality at the asphalt-aggregate interfaces. The SFE is defined as the work required to create a new unit of surface in a material, under vacuum conditions [9]. In this research, SFE was computed by applying the Good-Van Oss-Chaudhury theory [10], which defines three SFE components as follows: nonpolar or Lifshitz-van der Waals, Γ^{LW}; monopolar acid, Γ^+; and monopolar basic, Γ^-. The combination of these components yields the total SFE, Γ, of a material (e.g. asphalt or aggregate) through Eq. (3).

$$\Gamma = \Gamma^{LW} + 2\sqrt{\Gamma^+\Gamma^-} \tag{3}$$

These SFE components were computed for the asphalt specimens by means of the Wilhelmy plate method, which allows measuring the contact angle between a probe liquid (i.e. liquid with known SFE components) and a solid asphalt surface [9]. Following existing recommendations [9], the liquids used in this study were formamide, ethylene glycol, distilled water, and glycerol; and the laboratory procedure corresponded to that proposed by Hefer et al. [9]. In addition, the aggregates SFE testing was conducted through the methodology proposed by Bhasin and Little [11], using the Universal Sorption Device (USD).

Based on the known SFE components of both asphalts and aggregates, several energy-based parameters were computed as indicated in Table 1. The first parameter is the asphalt work of cohesion, W_{AA} (i.e. energy required to fracture an asphalt material creating two new surfaces of unit area), which can be computed using the asphalt (subscript A) SFE components in Eq. (4). The work of adhesion between aggregates and asphalts in both dry condition (Eq. (5)), W_{AS}^{dry}, and wet condition (Eq. (6)), W_{WAS}^{wet}, can be calculated using the SFE components of asphalt, aggregate (subscript S), and water (subscript W). The work of adhesion in dry condition is defined as the energy required to propagate an existing crack at the interface of two materials by creating two new surfaces of unit area, whereas the work of adhesion in wet condition refers to the work done to disrupt, in a unit area, an asphalt-aggregate interface by the water. The calculation of the interfacial energies (i.e. γ_{AW}, γ_{SW}, and γ_{AS} values in Eq. (6)) was performed through Eq. (7) as a function of both the total SFE and SFE components of water, asphalt, and aggregate.

Eq. (8) was applied to determine the ER_1 index [12], to quantify the moisture damage susceptibility of the asphalt-aggregate interfaces. In general, higher values of this index are desirable, since they represent asphalt-aggregate systems that simultaneously develop good quality adhesive properties in dry conditions and that are more resistant to the deleterious action of water. In addition, the asphalt wettability was assessed by means of both the spreading coefficient (Eq. (9)) [13] and the ER_2 index (Eq. (10)) [12]. The spreading coefficient evaluates the wettability, or ability of the asphalt to coat the aggregate, while the ER_2 index allows identifying material combinations that can develop simultaneously proper wettability and resistance to moisture damage.

Table 1
Energy parameters computed.

Energy parameter	Equation for quantification	Unit
Work of cohesion, W_{AA}	$W_{AA} = 2\Gamma_A^{LW} + 4\sqrt{\Gamma_A^+\Gamma_A^-}$ (4)	J/m²
Work of adhesion in dry condition, W_{AS}^{dry}	$W_{AS}^{dry} = 2\sqrt{\Gamma_A^{LW}\Gamma_S^{LW}} + 2\sqrt{\Gamma_A^+\Gamma_S^-} + 2\sqrt{\Gamma_A^-\Gamma_S^+}$ (5)	J/m²
Work of adhesion in wet condition, W_{WAS}^{wet}	$W_{WAS}^{wet} = \gamma_{AW} + \gamma_{SW} - \gamma_{AS}$ (6)	J/m²
Interfacial energy, γ_{ij}	$\gamma_{ij} = \Gamma_i + \Gamma_j - 2\sqrt{\Gamma_i^{LW}\Gamma_j^{LW}} - 2\sqrt{\Gamma_i^+\Gamma_j^-} - 2\sqrt{\Gamma_i^-\Gamma_j^+}$ (7)	J/m²
Energy ratio 1 index (or ER_1)	$ER_1 = \frac{W_{AS}^{dry}}{W_{WAS}^{wet}}$ (8)	–
Spreading coefficient (or SC)	$SC = W_{AS}^{dry} - W_{AA}$ (9)	J/m²
Energy ratio 2 index (or ER_2)	$ER_2 = \frac{W_{AS}^{dry} - W_{AA}}{|W_{WAS}^{wet}|}$ (10)	–

Legend: Γ_A^{LW} = asphalt nonpolar component; Γ_A^+ = asphalt monopolar acid component; Γ_A^- = asphalt monopolar basic component; Γ_S^{LW} = aggregate nonpolar component; Γ_S^+ = aggregate monopolar acid component; Γ_S^- = aggregate monopolar basic component; Γ_i = total surface free energy of the material i.

2.5. Asphalt chemical analysis

Fourier Transform Infrared Spectroscopy (FTIR) was used to capture the chemical variability among asphalts. The result from the FTIR test is a 'material fingerprint', expressed as an infrared spectrum, consisting of absorption bands of different molecular components and structures present in the specimen of interest.

In this work, FTIR results of the asphalt binders were obtained using a Thermo Nicolet iS50 spectrometer, coupled with Attenuated Total Reflectance (ATR). The ATR allows the user to place the specimen directly on the instrument, without previous treatment. A subset of eight asphalt specimens out of the eighteen analysed in this work was tested for FTIR. These asphalt specimens were selected as those that presented maximum differences in the energy-based parameters. As a result, 64 spectra were collected per specimen by applying the procedures stated in previous research [14,15].

Several functional groups were identified from the Infrared (IR) spectra to quantify the chemical variability among asphalts, and the area under the IR spectra for each functional group was then estimated. Finally, a functional group index (FGI) was computed to standardize the functional group areas so that they can be directly compared. The FGI was defined as per Eq. (11), in terms of the absorbance of the IR bands (A_{FG}) that are characteristic to each functional group and the total absorbance under the FTIR spectra for each asphalt (A_{Total}).

$$FGI = \frac{A_{FG}}{A_{Total}} \tag{11}$$

3. Results and discussion

The following sections present the results and corresponding analyses of the experimental tests conducted, followed by a comparison of the coefficients of variation (COV; ratio between the standard deviation and the mean) of each parameter assessed.

3.1. Asphalt traditional characterization tests

Fig. 1a and b show, respectively, the softening point values—mean values based on the temperatures reported for two rings—and the penetration values—mean values based on three penetrations per specimen—for the eighteen asphalt specimens assessed. In these figures, as well as in all other figures presented in this work, the codes for the asphalt specimens correspond to the month and year of production; thus, specimen '03–13', for example, was produced in March 2013. As in several other countries, local specifications in Colombia recognize the softening point as a useful indicator of asphalt variability [5]. The use of this index for this purpose has been justified based on [1]: (i) the existence of an inverse linear functional relationship between the softening point and the penetration values for distilled asphalt binders, (ii) the fact that higher softening points are associated with an increase in the asphaltene content, and (iii) the fact that softening point values are related to the oxidation stability of the asphalt binder (i.e. short-term aging).

As shown in Fig. 1a, most of the specimens evaluated met the corresponding specification limits required for this index by INVIAS. The mean value of these results, μ, was 50.8 °C and the corresponding COV was 5%. These results suggest low variability in the asphalt specimens in terms of this consistency index. On the other hand, the results of penetration (i.e. Fig. 1b) show, as expected, that most of the specimens evaluated met the local penetration specification, with a mean value, μ, of 65 $^1/_{10}$ mm and a COV of 5.5%. Therefore, the penetration values also suggest low variability in the asphalt consistency at intermediate temperatures.

Fig. 2 presents the penetration index results. In accordance with the INVIAS specifications [5] for this type of asphalt binder, admissible penetration index values range between −1.2 and +0.6. Asphalts with penetration index values higher than +0.6 or smaller than −1.2, are respectively, deemed as materials with low and high susceptibility to temperature changes, whereas intermediate
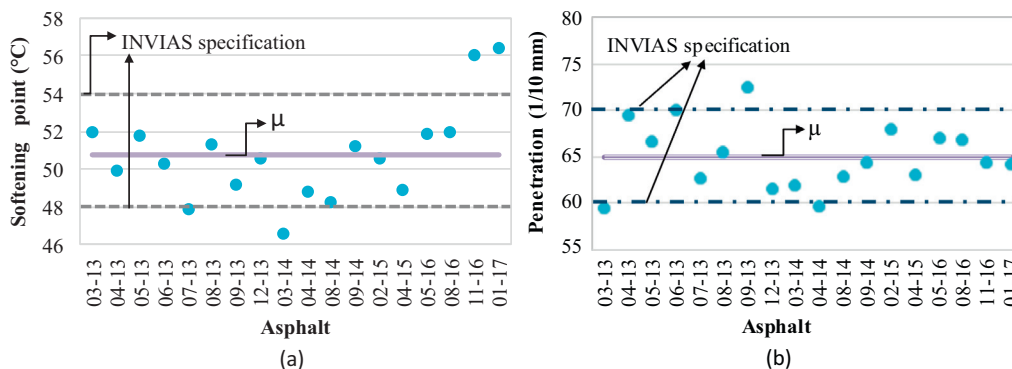

Fig. 1. Values of (a) softening point, and (b) penetration.
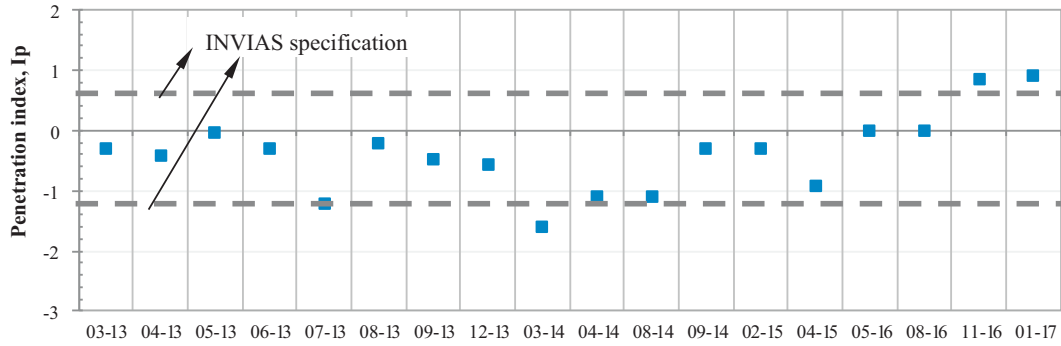
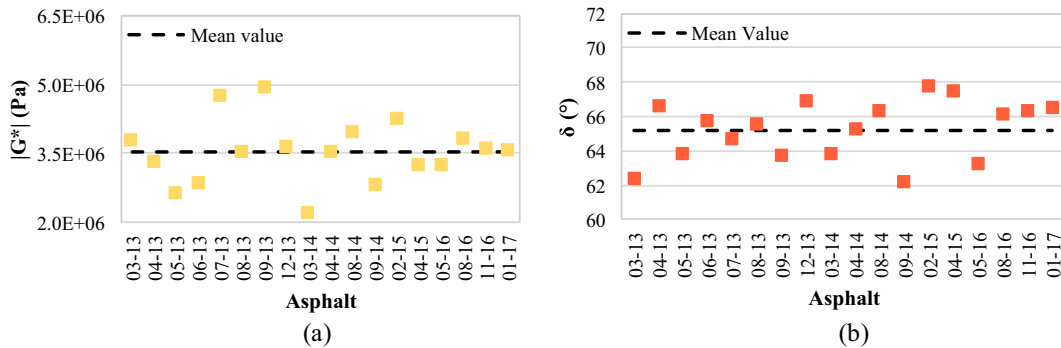Fig. 2. Values of penetration index.

Fig. 3. Mean values for asphalts in unaged condition, at 25 °C, and 10 Hz loading frequency, of (a) $|G^*|$, and (b) δ.

responses are to be expected for values among +0.6 and −1.2. As shown in this figure, three asphalt specimens did not meet the local specifications, which are the same ones that fail to meet the softening point specification, although their penetration values—used for controlling the asphalt binder production—are between the specified limits. Overall, the penetration index values suggest low variability in the temperature susceptibility considering that most of the specimens met the current specification limits.

Ductility wise, all the asphalts registered rupture at 148 cm (i.e. maximum distance of testing at the equipment used), meeting the minimum local specification of ductility (i.e. 100 cm; [5]). Despite the fact that ductility is related to asphalt adhesiveness—unmodified asphalts with low ductility generally exhibit poor adhesive properties and poor field performance [5]—, these results did not permit to differentiate the material response, as the previous parameters did, or provide any information on the variability of the asphalts tested.

3.2. Asphalt rheology characterization

The variability of $|G^*|$ obtained among the three replicate tests performed for a single asphalt specimen, at both unaged and aged conditions, ranged in values of COV between 4.10% and 6.76%. As for δ, the variability among replicates was even lower, with values of COV between 0.18% and 2.41%. This variability among replicates of a single asphalt specimen are in good agreement with those reported in the literature (e.g. maximum COV of 5.1% for $|G^*|$ and 0.4% for δ, for binders type ABD-1 and AAM-1, respectively, of the Strategic Highway Research Program, SHRP, materials reference library [7]).

To quantify the variability among the eighteen asphalt specimens, the mean values of $|G^*|$ and δ were analysed. In all cases, the variability of these mean values was notably higher than that reported among the three replicates performed for a single asphalt, proving that the differences of the linear viscoelastic properties of the eighteen asphalts are statistically significant. As an example of the results, Fig. 3 shows the mean value for both material properties of the eighteen unaged specimens, determined at 25 °C and 10 Hz. Data in Fig. 3a shows that the mean value of $|G^*|$ among the eighteen specimens was 3.53×10^6 Pa Pa, with a standard deviation of 6.72×10^5 Pa, which resulted in a COV of 19%. Regarding δ, the mean value among specimens was 65.21°, with a standard deviation of 1.65°, and a related COV of 2.53%.

In general, for a constant temperature of 25 °C, the COV of $|G^*|$ among specimens for different frequencies ranged from 19% to 25%, being higher at high loading frequencies. A similar trend was found for the values of $|G^*|$ obtained at a constant frequency and different temperatures. On the other hand, at a constant value of frequency, the variability of δ among the asphalt samples decreased when the test temperature increased (i.e. COV ranging from 2.81% at 25 °C to 0.86% at 75 °C), whereas the variability of δ increased—at a given constant temperature—when the testing frequency decreased, within a range of 0.49 to 3.47%.

Regarding the short-term aged asphalts, the increase in the dynamic shear modulus of the RTFO samples with respect to the corresponding unaged asphalts was variable among specimens, suggesting chemical differences—subsequently discussed—that lead to a different aging impact on the linear viscoelastic properties of the materials. For example, as shown in the Fig. 4, the mean value of $|G^*|$ for the 09-13 asphalt increased between the unaged- and aged-condition in a range of 45% to 68%, depending on the loading frequency; whereas for the 09–14 asphalt these increments in modulus were between 102% and 147%.

In general, the mean values of $|G^*|$ for the short-term aged asphalts presented COV values varying between 18% and 24%, as a function of temperature (Fig. 5a). These ranges are slightly
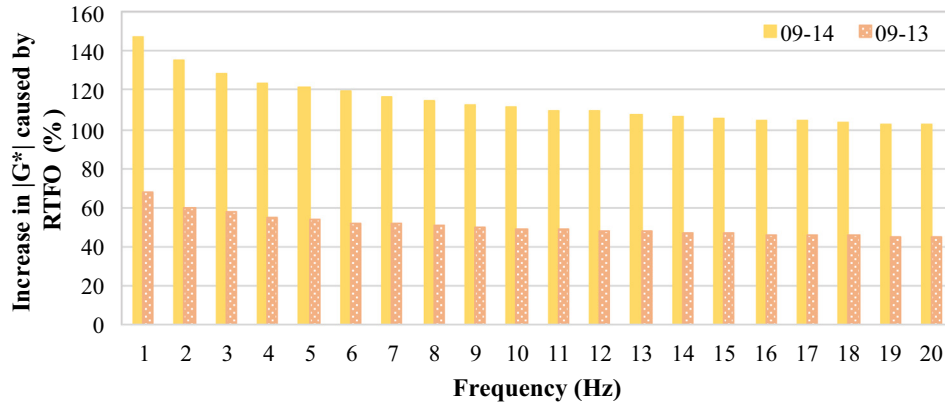
Fig. 4. Comparison between the increase in $|G^*|$ induced by the short-term aging condition with respect to the unaged condition for both the 09–13 and 09–14 asphalts.
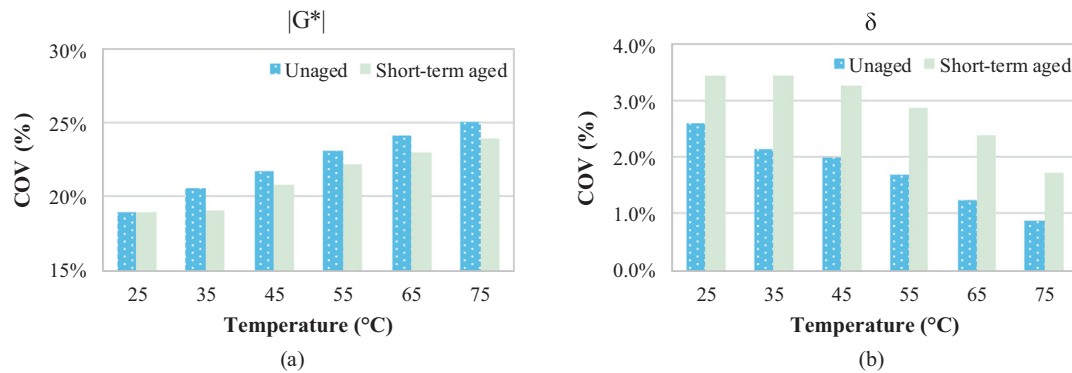

Fig. 5. Comparison between the COV of the (a) dynamic shear modulus, and (b) phase angle, in unaged and short-term aged conditions (10 Hz loading frequency).

smaller than those obtained for the unaged specimens, suggesting that short-term aging did not notably affect the variability of $|G^*|$. On the contrary, Fig. 5b shows that short-term aging did increase the variability of δ with respect to the unaged asphalt condition for the set of asphalts studied.

Fig. 6 synthesizes the rheological results through the 'envelopes' of the eighteen asphalt master curves of $|G^*|$. The extreme master curves in these envelopes correspond to the 06–13 and 09–13 asphalts for the unaged condition, and for the 03–14 and 08–14 asphalts for the aged condition. These data prove that the magnitude of $|G^*|$ varies among the set of asphalts from 67%, at low frequencies, up to 98%, at high loading frequencies, for the unaged condition, and from 124%, at low frequencies, up to 67% at high loading frequencies, for the RTFO condition. These results demonstrate that even though the eighteen different asphalts share the same penetration classification category, their individual

mechanical response under specific field conditions (i.e. temperature and loading frequency) could be radically different.

DSR results were also used to evaluate the variability in the dynamic shear viscosity of the asphalt binders in both unaged- and aged-condition. The results at 25 °C and 10 Hz show that this property present a mean value of 5.69×10^4 Pa.s and a COV of 21% in unaged condition. Short-term aging increased the mean value of this property in 65% (i.e. 8.93×10^4 Pa.s), although this condition did not modify its variability (i.e. COV of 20%). Since the COV values of this property among replicates of a single asphalt were always lower than 6.7%, it is possible to conclude that this property is statistically different among the asphalt specimens.

3.3. Asphalt- and aggregate-surface free energy (SFE) and energy-based parameters

Table 2 presents the SFE components and the total SFE of the six aggregates used in this work to evaluate the variability in the quality of the adhesive bonds developed with the set of eighteen asphalts. The ALB-, BCM-, and RIS-aggregates were characterized in previous works [16,17]. In addition, Table 3 presents the values of SFE components, total SFE, and work of cohesion in dry condition (W_{AA}) for the eighteen asphalts evaluated. As previously discussed, higher values of the work of cohesion are related to asphalt materials with a higher resistance to fracture.

The COV computed for the total SFE values of the eighteen asphalts assessed—and their corresponding work of cohesion values—was 20%. This variability suggests the existence of actual differences in the thermodynamic properties of the asphalts. Furthermore, as supported in previous research [18], these differences
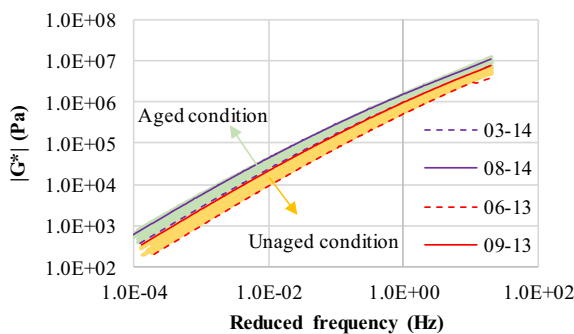

Fig. 6. Asphalt master curves envelopes (reference temperature 25 °C).

Table 2
SFE characterization of the aggregates (J/m^2).

Aggregate code	Geology	SFE components and total SFE				
		Γ^{LW}	Γ^-	Γ^+	Γ^{AB}	Γ
GUA	Gravels, with predominance of sandstone and shale	0.0428	0.0021	0.7372	0.0794	0.1222
RIO	Gravels, with predominance of amphibolite	0.0371	0.0025	0.5630	0.0755	0.1125
RUT	Quartz-latite, latite, and tuff	0.0367	0.0018	0.5761	0.0646	0.1013
ALB	Gravels, with predominance of sandstone and siltstone [16]	0.0359	0.0003	0.3635	0.0194	0.0554
BCM	Gravels, with predominance of sandstone and mudstone [16]	0.0416	0.0042	0.7652	0.1138	0.1554
RIS	Gravels, with predominance of basalt [17]	0.0521	0.0035	1.8548	0.1600	0.2121

Table 3
SFE characterization of the asphalt specimens (J/m^2).

Asphalt	Γ^{LW}	Γ^-	Γ^+	Γ^{AB}	Γ	W_{AA}
03–13	0.0115	0.0000	0.0010	0.0000	0.0115	0.0230
04–13	0.0104	0.0112	0.0004	0.0042	0.0146	0.0292
05–13	0.0058	0.0045	0.0025	0.0068	0.0125	0.0251
06–13	0.0174	0.0036	0.0000	0.0000	0.0174	0.0348
07–13	0.0056	0.0076	0.0018	0.0073	0.0129	0.0258
08–13	0.0046	0.0068	0.0030	0.0090	0.0136	0.0273
09–13	0.0071	0.0000	0.0028	0.0000	0.0071	0.0141
12–13	0.0064	0.0049	0.0020	0.0062	0.0126	0.0252
03–14	0.0185	0.0023	0.0000	0.0000	0.0185	0.0370
04–14	0.0173	0.0026	0.0000	0.0007	0.0179	0.0359
08–14	0.0083	0.0043	0.0023	0.0063	0.0146	0.0292
09–14	0.0134	0.0045	0.0010	0.0043	0.0177	0.0355
02–15	0.0022	0.0085	0.0058	0.0140	0.0162	0.0325
04–15	0.0166	0.0019	0.0001	0.0010	0.0176	0.0353
05–16	0.0164	0.0007	0.0001	0.0004	0.0168	0.0335
08–16	0.0038	0.0097	0.0045	0.0052	0.0134	0.0269
11–16	0.0069	0.0068	0.0026	0.0084	0.0153	0.0306
01–17	0.0035	0.0067	0.0049	0.0114	0.0149	0.0297

in the SFE components are believed to be related to differences in the chemical composition of the samples.

As explained in Section 2.4, several energy-based parameters were computed to quantify the potential effect that the variability of the asphalt SFE values can induce on both the adhesion quality of asphalt-aggregate interfaces and wettability properties of these asphalts over the selected aggregates listed in Table 2. Overall, the analysis of the energy parameters provided evidence of high variability in the response of the asphalt-aggregate interfaces. Namely, the COV values for the work of adhesion in dry condition—computed for the combination of each aggregate with the eighteen asphalts—ranged from 23.7% to 36.6%, and the COV values for the work of adhesion in wet-condition varied from 18.8% to 21.9%.

In addition, Fig. 7 shows the ER_1 index values that result from combining the eighteen asphalts and the six aggregates. The corresponding COV values computed for the ER_1 index obtained for the combination of each aggregate with the eighteen asphalts varied between 42.7% and 52.3%; these extreme values were obtained for the ALB- and RIS-aggregates, respectively. These results permit to

conclude that the variability in the SFE for the set of Pen 60–70 asphalts strongly impact the adhesion quality of the resulting aggregate-asphalt systems. Furthermore, field performance variability of these material combinations is also expected, since previous research [19,20] has shown a direct relationship between this energy parameter and the performance of the asphalt mixtures in the field.

The ER_1 index values permit to analyse the variability of these Pen 60–70 asphalts by differentiating two response groups (or asphalt groups), identified in Fig. 7. The first group includes those asphalts that produce interfaces with ER_1 index values smaller than 0.5, while the second group includes asphalts related to ER_1 index values larger than 0.5. According to the thresholds proposed by Bhasin et al. [21] to assess the moisture damage resistance of hot-mix asphalt mixtures in the field (shown in Fig. 7), the first group has low resistance to moisture damage, while the second one presents medium to high resistance to this degradation phenomenon.

The COV values for the ER_2 index, calculated for the combination of each aggregate with the eighteen asphalts were
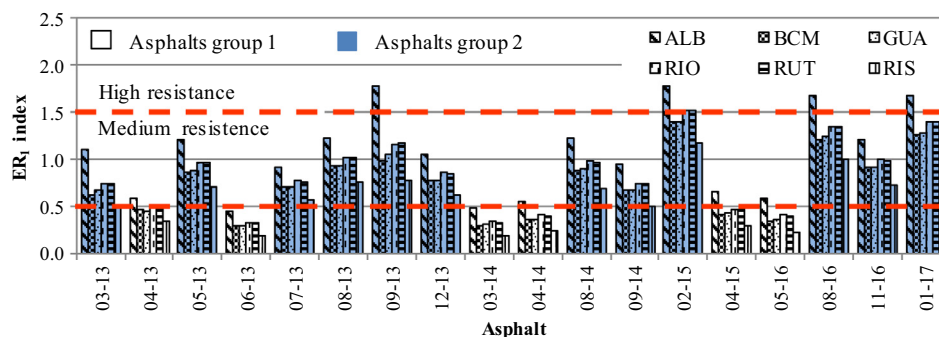
Fig. 7. Values of the ER_1 index for asphalt-aggregate interfaces.

meaningfully, ranging between 57.7% and 61.3%, and the COV values for the spreading coefficient ranged from 43.2% to 48%. Corresponding detailed results are not presented for briefness. This variability data permit to infer that road sections built with asphalt mixtures fabricated with a single source of aggregates and the Pen 60–70 produced in different days could have differentiable responses in terms of resistance to both fracture and moisture damage, as well as exhibiting different coating ability of the asphalt over the aggregate.

3.4. Asphalt chemical analysis

Fig. 8 shows the FTIR spectra results for the subset of eight asphalt specimens analysed. The signals of interest for the asphalt spectrum are listed in Table 4. The spectra of the eight asphalt specimens studied are expected to be similar. However, small changes in the intensity of the signals, or in the appearance of the signals other than those listed in Table 4, can be related to chemical changes among the materials, such as processes involving oxygenated functions. Indeed, Fig. 8 shows that there are mild differences in the intensity of the spectra near to the bands associated with the oxygenated functions (sulfoxides, carbonyls) and, to a lesser degree, changes in aromatics, aliphatics, and unsaturates [22]. The asphalts exhibiting a signal near 1700 cm^{-1} are believed to

have a larger presence of C-O bonds (carbonyls) than those in which the carbonyl signal is absent. The effect of these double bonds can be related to an increase in the stiffness of the material [23,24], and therefore, to changes in the asphalt viscosity—affecting the workability [25]—and rheological response of the material [26]. The reduced flexibility of the asphalt binders can also be attributed to C—C double bonds (unsaturates), as opposed to the aliphatic simple bonds (C—C), which allow for larger movement of the molecules.

The descriptive statistics for the functional groups listed in Table 4 are summarized in Table 5. These data confirm that the largest relative variability can be associated with the oxygenated functions and, more specifically, to the carbonyl bands. Fig. 9 presents the standardized FTIR areas associated with the carbonyl- and sulfoxide-functional groups for the asphalt specimens; these indexes were used to assess differences in the oxygenated functions between specimens.

Significant variations can be observed in both the carbonyl- and sulfoxide-functional groups within the asphalts. The range in values associated with carbonyl content is as large as 0.023 cm^{-1}, indicating that the specimens differ in up to 122% in this component, and the overall COV of this index was 21.8%. The specimens exhibiting higher carbonyl content—and therefore less molecular flexibility—are the 03–13-, 05–13, 02–15-, and 04–15. In the case of the sulfoxide content, variations were as large as 75% and the overall COV of this index among specimens was 15.6%. Higher sulfoxide content was observed in the 02–15-, 04–15-, 05–16-, and 08–16-specimens.
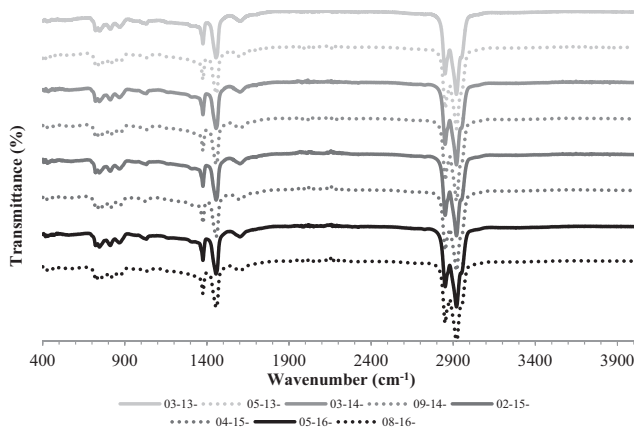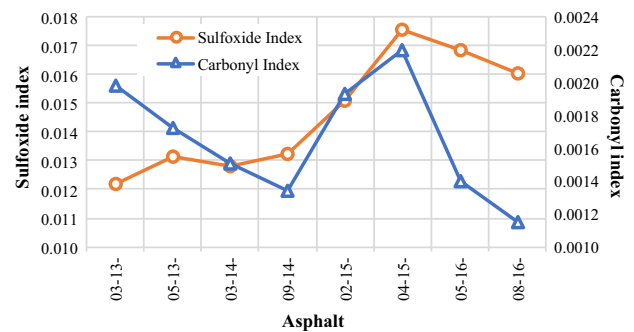

Fig. 8. FTIR spectra of analysed binders. Note: the base line for each observation has been shifted to allow a more detailed analysis of each individual spectra.

Fig. 9. Carbonyl- and sulfoxide-functional group index based on FTIR.

Table 4
Typical FTIR signals of unaged- and unmodified-asphalts.

Functional group	Approximated wavelength (cm^{-1})	Number of signals	Intensity
C—H aromatic	3050	One	Low
C—H bonds	2900–2800	Two	High
C-O double bond (Carbonyls)	1680–1800	One	Low
C—C double bond (Unsaturates)	1600	One	Medium-low
C—C simple bonds (Aliphatics)	1350–1450	Two	Medium
S—O double bond (Sulfoxides)	1030	One	Low
Aromatic carbons (Aromatics)	700–900	Four	Medium-low

Table 5
Variation in functional group indexes for the asphalts analysed.

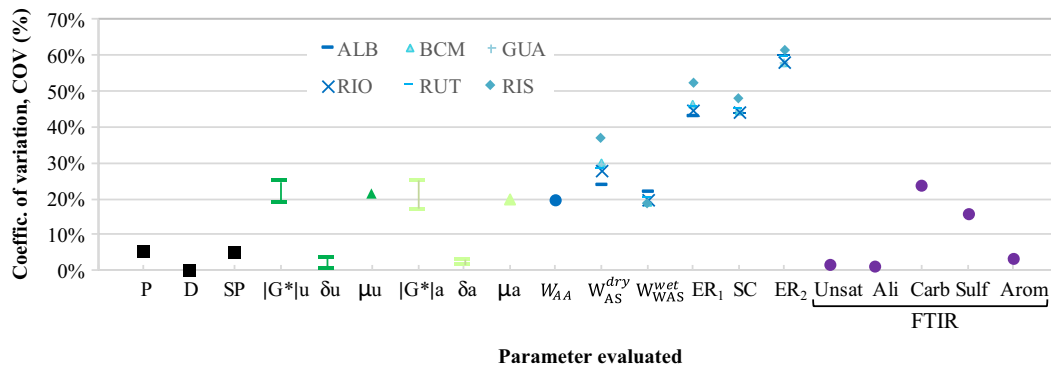| Functional group index	Mean	Standard deviation	COV	Minimum	Maximum
Unsaturates	0.0434	0.0006	1.45%	0.0424	0.0445
Aliphatics	0.2662	0.0024	0.92%	0.2626	0.2710
Carbonyls	0.0017	0.0004	21.76%	0.0010	0.0023
Sulfoxides	0.0146	0.0023	15.56%	0.0103	0.0179
Aromatics	0.0662	0.0024	3.59%	0.0622	0.0702

Fig. 10. Coefficient of variation (COV) values of the parameters evaluated. Note: P: penetration; D: ductility; SP: softening point; $|G^*|u$: $|G^*|$ unaged; δu: δ unaged; μu: shear viscosity unaged; $|G^*|a$: $|G^*|$ aged; δa: δ aged; μa: shear viscosity aged; W_{AA}: work of cohesion; W_{AS}^{dry}: work of adhesion-dry; W_{WAS}^{wet}: work of adhesion-wet; ER_1: energy ratio 1 index; SC: spreading coefficient; ER_2: energy ratio 2 index; FTIR: infrared spectroscopy: Unsat: unsaturates; Ali: aliphatics; Carb: carbonyls; Sulf: sulfoxides; Arom: aromatics.

These results suggest some degree of correlation to the SFE results: the carbonyl index has a -34.3% coefficient of correlation with the monopolar basic component (Γ^-) and the sulfoxide index shows correlation to both the total SFE (31.8%) and work of cohesion (31.7%). As expected, these previous analyses indicate that the higher contents in the oxygenated functional groups could result in higher total SFE and internal cohesion due to an increase in polarity.

3.5. Statistics Comparison

Fig. 10 presents the COV for the parameters evaluated in this study. These results show that the properties and parameters derived from rheology-, SFE-, and FTIR-tests of the asphalts analysed—originally classified as Pen 60–70—, are significantly variable, and that this variability is not fully captured or quantified by the traditional asphalt tests currently used in several countries. These differences are believed to be mainly due to changes in the chemical composition of the asphalts, as demonstrated through the FTIR results. This finding is in good agreement with a previous study [6], in which the SARA test was used to quantify the chemical fractions (i.e. saturates, aromatics, resins, and asphaltenes) of nine asphalt specimens classified under two different penetration categories. Such study showed that the percentages of resins varied between 20 and 50% and that the percentage of asphaltenes varied in a range of 9 to 27% among asphalt specimens classified as Pen 60–70. Furthermore, those results also showed low variability in the aromatics components among the asphalt specimens; an observation that is consistent with the FTIR testing results obtained as part of the present work.

4. Conclusions and recommendations

This paper quantified and compared the variability of asphalt binders, captured through both traditional indexes and fundamental material properties—including rheological, thermodynamic, and chemical properties—. The assessment included a set of 18 asphalts classified as Pen 60–70, produced between March 2013 and January 2017 at the main refinery of Colombia.

The experimental results showed that while the set of eighteen asphalts presented values of COV below 10% in the conventional indexes (i.e. penetration, softening point, and penetration index), further advanced characterisation demonstrated the existence of high variability in some of their fundamental material properties (i.e. rheological properties and influence of aging on these properties, SFE values, adhesive characteristics evaluated through SFE, and chemical composition), with COV values that were typically over 20%. Overall, this variability quantification shed light on the increased uncertainty that the material responses can actually exhibit in the field respect to those quantified using the conventional indexes. In this regard, future work should focus on quantifying the impact of the variability in the properties of Pen 60–70 asphalt herein reported on both the mechanical response and surface properties of asphalt layers fabricated with these asphalt binders, and, consequently, on the overall life-cycle costs of the corresponding pavement structures.

In summary, the results show the limitations of traditional asphalt tests to capture the actual variability in the produced asphalt. Consequently, they provide technical evidence on the importance of modifying or complementing both the classification- and characterization-asphalt tests currently used in several countries that share equivalent limited asphalt control production strategies, as a measurement for improving the overall variability of the material. This strategy could help reducing the uncertainty related to the performance of the asphalts in the field. In addition, given the limited information available in the literature on asphalt binder variability of traditional and advanced testing, the data reported in this study can serve as reference for future studies dealing with the characterization of this material.

Conflict of interest

There is no conflict of interest.

Disclaimer

This paper does not constitute a standard, specification, nor is it intended for design, construction, bidding, contracting, or permit purposes. Trade names were used solely for information and not for product endorsement.

References

[1] R.N. Hunter, A. Self, J. Read, The Shell Bitumen Handbook, sixth ed., London, 2015.

[2] F.G. Praticò, R. Vaiana, T. Luele, Macrotexture modeling and experimental validation for pavement surface treatments, Constr. Build. Mater. 95 (2015) 658–666.

[3] S. Shuler, A. Lord, A. Epps Martin, D. Hoyt, Manual for Emulsion-Based Chip Seals for Pavement Preservation, National Cooperative Highway Research Program-Transportation Research Board, Washington, D.C., 2011. NCHRP Report 680.

[4] Asphalt Institute, Superpave Asphalt Binder Specification-Performance Graded Asphalt Binder Specification and Testing, Superpave Series No. 1 (SP-1), Lexington, KY, 1996.

[5] INVIAS, Especificaciones Generales de Construcción de Carreteras y Normas de Ensayo Para Carreteras, Bogotá D.C., 2013.

[6] H.L. Arenas, Propuesta Técnica para Garantizar la Homogeneidad de los Asfaltos Producidos en las Refinerías Colombianas, Cámara Colombiana de Infraestructura, 2009.

[7] A. Abbas, E. Masad, T. Papagiannakis, A. Shenoy, Modelling asphalt mastic stiffness using discrete element analysis and micromechanics-based models, Int. J. Pavement Eng. 6 (2) (2005) 137–146.

[8] American Association of State Highway and Transportation Officials, AASHTO T 240-13, Standard Method of Test for Effect of Heat and Air on a Moving Film of Asphalt (Rolling Thin-Film Oven Test) (ASTM Designation: D 2872-04), 2013, pp. 1–12.

[9] A.W. Hefer, A. Bhasin, D.N. Little, Bitumen surface energy characterization using a contact angle approach, J. Mater. Civ. Eng. 18 (6) (2006) 759–767.

[10] C.J. Van Oss, Interfacial Forces in Aqueous Media, Marcel Dekker Inc., New York, 1994.

[11] A. Bhasin, D.N. Little, Characterization of aggregate surface energy using the universal sorption device, J. Mater. Civ. Eng. 19 (8) (2007) 634–641.

[12] A. Bhasin, D.N. Little, K.L. Vasconcelos, E. Masad, Surface free energy to identify moisture sensitivity of materials for asphalt mixes, Transp. Res. Rec. 2007 (2001) 37–45.

[13] N.M. Wasiuddin, M.M. Zaman, E.A. O'Rear, Effect of Sasobit and Aspha-min on wettability and adhesion between asphalt binders and aggregates, Transp. Res. Rec. 2051 (2008) 80–89.

[14] A. Baldi-Sevilla, M.L. Montero, J.P. Aguiar-Moya, L.G. Loria-Salazar, A. Bhasin, Influence of bitumen and aggregate polarity on interfacial adhesion, Road Mater. Pavement Des. 18 (2017) 304–317.

[15] A. Baldi-Sevilla, M.L. Montero, J.P. Aguiar-Moya, L.G. Loría-Salazar, Influence of nanosilica and diatomite on the physicochemical and mechanical properties of binder at unaged and oxidized conditions, Constr. Build. Mater. 127 (2016) 176–182.

[16] A.E. Alvarez, M.M. Caballero, Efecto del Llenante Mineral sobre la Calidad de las Interfases Asfalto-Agregado de Mezclas Asfálticas, 9 Jornadas Internacionales del Asfalto, Medellin (2014) 1–10.

[17] A.E. Alvarez, E. Ovalles, S. Caro, Assessment of the effect of mineral filler on asphalt-aggregate interfaces based on thermodynamic properties, Constr. Build. Mater. 28 (1) (2012) 599–606.

[18] J. Wei, F. Dong, Y. Li, Y. Zhang, Relationship analysis between surface free energy and chemical composition of asphalt binder, Constr. Build. Mater. 71 (2014) 116–123.

[19] A. Bhasin, J. Howson, E. Masad, D.N. Little, R.L. Lytton, Effect of Modification Processes on Bond Energy of Asphalt Binders, Transportation Research Board 86th Annual Meeting, Transportation Research Board, Washington, D.C., 2007, pp. 1–14.

[20] A. Bhasin, D.N. Little, K.L. Vasconcelos, E. Masad, Use of Surface Free Energy to Identify Moisture Sensitivity of Materials for Asphalt Mixes, Transportation Research Board 86th Annual Meeting, Transportation Research Board, Washington, D.C., 2007, pp. 1–15.

[21] A. Bhasin, E. Masad, D. Little, R. Lytton, Limits on adhesive bond energy for improved resistance of hot mix asphalt to moisture damage, Transp. Res. Rec. 2006 (1970) 3–13.

[22] M. Gong, J. Yang, J. Wei, T. Pauli, H. Yu, Quantitative characterisation of asphalt's composition-microstructure relationship based on atomic force microscopy, differential scanning calorimetry, and Fourier transform infrared spectroscopy tests, Road Mater. Pavement Des. 18 (2017) 207–532.

[23] J.P. Aguiar-Moya, J. Salazar-Delgado, A. Baldi-Sevilla, F. Leiva-Villacorta, L. Loria-Salazar, Effect of aging on adhesion properties of asphalt mixtures with the use of bitumen bond strength and surface energy measurement tests, Transp. Res. Rec. 2505 (2015) 57–65.

[24] J.P. Aguiar-Moya, J. Salazar-Delgado, A. García, A. Baldi-Sevilla, V. Bonilla-Mora, L.G. Loría-Salazar, Effect of ageing on micromechanical properties of bitumen by means of atomic force microscopy, Road Mater. Pavement Des. 18 (2017) 203–2015.

[25] X. Jin, R. Han, Y. Cui, C. Glover, Fast-rate constant-rate oxidation kinetics model for asphalt binders, Ind. Eng. Chem. Res. 50 (2011) 13373–13379.

[26] P. Juristyarini, R. Davison, C.J. Glover, Oxidation hardening kinetics of the rheological function G'/(η'/G') in asphalts, Pet. Sci. Technol. 29 (2011) 2027–2036.