

# Analysis of Asphalt Oxidation by Means of Accelerated Testing and Environmental Conditions

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## Abstract

The chemical changes that occur to asphalt with oxidation include an increase in oxygen content, as well as the unsaturation of the molecules. This change raises the polarity and stiffness of the material. As a consequence, the elastic response increases, altering its rheology. These transformations are essential to determine pavement performance during its service life. However, the characterization of these chemical and rheological processes cannot be completed because of the inefficiency of current procedures that simulate asphalt oxidation. For this reason, the objective of this study is to characterize asphalt oxidation fundamentally and to relate the observed changes in the materials' mechanical response. To achieve this goal, a representative group of asphalt samples has been exposed to environmental oxidation, and alternatively to thermal and ultraviolet aging in the laboratory. The samples were characterized chemically and rheologically before the start of the experiment. It was possible to find a correlation between the content of specific chemical species in the material and their mechanical behavior at low and intermediate temperatures. In addition, the present study helps to understand the oxidation phenomena, and helps verify the ineffectiveness of traditional aging techniques, so that they can be modified to simulate the environmental process better.

Asphalt oxidation occurs in two stages: (1) during the extraction, production of the asphalt mixture, and placement of the upper layer of the pavement, and (2) during the service life of the pavement (1). The reactions that occur during these stages are dependent on the chemical composition of the asphalt (2, 3). However, increases in the amount of oxygenated functional groups, double bonds, and aromaticity are expected (4–7).

Specifically, oxidation promotes the formation of aromatic structures and unsaturations (carbon-carbon double bonds), which increase the rigidity of the asphalt. Such chemical changes can be monitored by Fourier transform infrared spectroscopy (FTIR) (8–10). Also, after oxidation, there is an increment in polarity of molecules because of the presence of oxygen and double bonds in the molecules of the material, which in turn increase the number and magnitude of intermolecular interactions. As a consequence, the elastic component of the asphalt is expected to become dominant as the oxidation in the binder advances: this is usually accompanied by a reduction in the viscous component of the material. Therefore, the correct interpretation of the contribution of the elastic and viscous components to the asphalt

rheology is useful in the characterization and prediction of its performance. For example, a high contribution of the elastic component could represent an increase in the susceptibility of the binder to the fracture, which in turn is related to the energy dissipation capacity of the material: a rigid (oxidized) asphalt is expected to be less efficient in energy dissipation by flow, since its molecules will have reduced mobility, compared with a less rigid (non-oxidized) asphalt. In other words, an oxidized asphalt dissipates energy through the fracture.

Asphalt oxidation is characterized by the oxygenation of molecules, as well as by the increase in the number of double bonds and aromaticity (11). These transformations alter the rheological and mechanical responses of the material by increasing its fragility and susceptibility to fracture (12). In the laboratory, asphalt oxidation is

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simulated with thermal treatments performed in specially designed ovens, such as the rolling thin-film oven (RTFO) and the pressure aging vessel (PAV). In these procedures, asphalt is subjected to high temperatures, continuous airflow, and pressure (13). For example, after being exposed to the PAV, the asphalt sample is expected to oxidize to the equivalent of 7–10 years of in-field service (14). However, several studies suggest that thermal treatments do not achieve complete oxidation of asphalt as they ignore the contribution of ultraviolet (UV) radiation (photo-oxidation) (15). Consequently, photo-oxidation has been proposed to complement and improve this type of simulation. An example of such a procedure consists in subjecting the asphalt that has been previously oxidized by the conventional thermal method, to UV radiation. Although this additional treatment has proved to be a more accurate approximation of oxidation, it is still an incomplete simulation because several environmental factors that could contribute to oxidation are not considered, such as water, impurities in the air, and radiation of the entire electromagnetic spectrum. Consequently, the present study intends to analyze the chemical changes that occur to asphalt under environmental conditions and to relate them to the mechanical consequences of oxidation in the material. In addition, based on the results, the efficiency of the accelerated aging treatments (RTFO, PAV) commonly applied in the laboratory will be analyzed (16).

## Objective

The objective of this study is to analyze the chemical and rheological transformations that occur in the asphalt binder after environmental oxidation. In addition, and based on the previous, the efficiency of accelerated aging procedures commonly applied in the laboratory (such as PAV) in simulating oxidation of asphalt binder were analyzed.

## Methodology

### Materials

The materials analyzed in this study are neat binders denoted as Costa Rica 1 (PG 64-22), Costa Rica 2 (PG 70-25), Guatemala 1 (PG 64-22), Guatemala 2 (PG 64-22), Nicaragua (PG 64-25), El Salvador (PG 64-22), and Bolivia (PG 64-22), according to their origin country.

### Oxidation of Samples

The asphalts were subjected to thermal aging in RTFO and subsequently oxidized in the PAV, based on Superpave specifications. The Costa Rica 2 asphalt was also subjected to three and five consecutive PAV cycles, to induce a more severe oxidation in the material.

In the case of environmental oxidation, a fixed amount of Costa Rica 2 asphalt was poured into non-stick molds to produce a 1 mm-thick film, which has been chosen to simulate the film thickness of binder that coats the aggregate in an asphalt mixture. The films were exposed to the weather for two years in order to subject the binder to environmental oxidation (Figure 1). The samples were kept to 1200 MASL (meters above the sea level), and the temperature ranged between 20 and 27°C during such period.

Samples were removed from these conditions and analyzed monthly. An asphalt sample was maintained as a control. It is necessary to clarify that RTFO-treated asphalt was used in the preparation of the films, to simulate the short-term aging that occurs before the binder is placed on the pavement layer.

## Asphalt Characterization

Chemical changes induced by oxidation were determined by quantifying the particular signal area of the infrared spectrum of the samples. In the case of the environmental-oxidized films, infrared spectra were performed on the exposed and non-exposed surfaces of each film. The quantified signals were the following: oxygenated compounds ( $3500\text{ cm}^{-1}$ , hydroxyl,  $1700\text{ cm}^{-1}$ , carbonyl and  $1030\text{ cm}^{-1}$ , sulfoxide), aromatic and unsaturated compounds (containing C=C) ( $3050\text{ cm}^{-1}$  and  $1600\text{ cm}^{-1}$  respectively), and saturated compounds (containing C-H) ( $2800, 2900\text{ cm}^{-1}$ ).

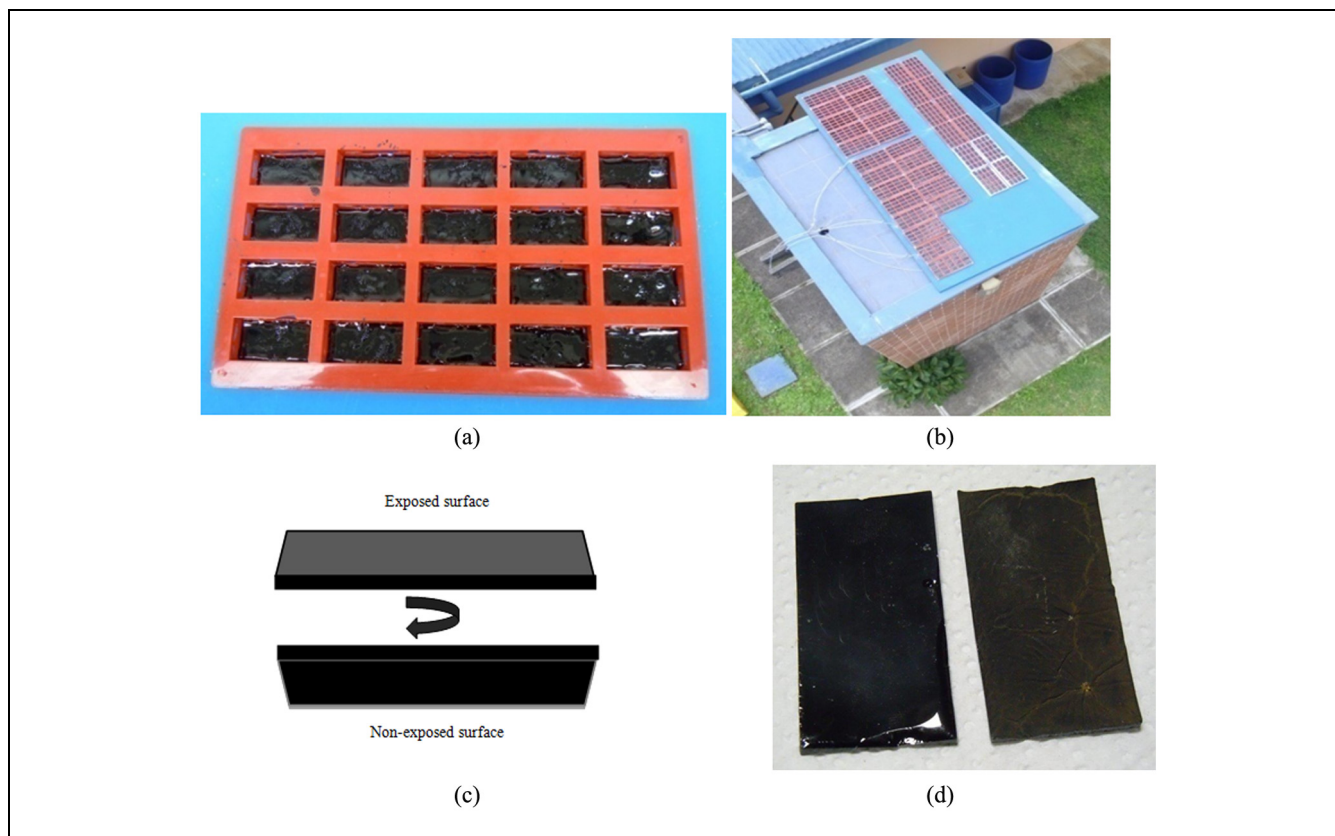
The rheological analysis consisted of two stages. First was a temperature sweep ( $5\text{--}64^\circ\text{C}$ ) at controlled strain (1%) and a frequency of 10 rad/s, which allows finding the region where the asphalt becomes susceptible to fatigue. For the second stage, after finding the fatigue-susceptible region, the behavior of the samples was evaluated under controlled stress (1 MPa) at a frequency of 10 rad/s and  $10^\circ\text{C}$ , to ensure that the asphalt will show fatigue susceptibility. In both tests, the 8 mm geometry was used for all samples.

## Results and Discussion

### Chemical Transformations in Asphalt during Oxidation

The signal area of a chemical species in an infrared spectrum is directly related to the concentration of such species (17). Therefore, this technique was used to quantify the extent of oxidation in the proposed asphalt samples. The results are listed in Table 1.

*Environmental Oxidation.* Based on Table 1, the exposed surface of the asphalt films was found to be significantly more oxidized than the RTFO sample (corresponding to the initial condition of the films). The data show an



**Figure 1.** (a) Asphalt samples placed in non-stick molds, (b) location of samples for environmental oxidation, (c) diagram of exposed/non-exposed surface of asphalt films, and (d) asphalt film after six months of environmental oxidation (non-exposed [left] and exposed [right] surfaces).

increase in oxygenated functional groups, such as hydroxyl, carbonyl, and sulfoxide. In addition, an increase in carbon-carbon double bonds and aromatization was observed, which in turn comes with the consequent decrease of aliphatic carbon-hydrogen bonds. These changes may increase the rigidity of the material, as double bonds and aromatic molecules are structures with less flexibility than those composed of carbon-carbon single bonds. On the other hand, the non-exposed surface shows an increase in oxygenated compounds mainly, which points out that oxygen penetrates the film by reacting with the asphalt along the film and producing such compounds, perceptible even on the unexposed surface. In contrast, UV radiation, responsible for the formation of unsaturations in the material, does not appear to penetrate the film sufficiently as no significant increase in the signal of the C–C double bond or the signal corresponding to aromatic compounds is observed.

*Comparison of Thermal and Environmental Oxidative Aging.* Comparing the oxidation of samples exposed to the weather and those treated in PAV, a significant difference was observed in the hydroxyl, carbonyl, sulfoxide,

aromaticity, and carbon-carbon double bonds. The previous is accompanied by a corresponding reduction in carbon-hydrogen bonds, being the environmental-oxidized samples the most affected. This finding suggests that the surface of asphalt exposed to environmental conditions during a short period undergoes a more severe oxidation than the asphalt subjected to thermal + pressure treatment, which intends to simulate up to 10 years of environmental conditions. On the other hand, the unexposed surface of the asphalt films experienced a slight increase in aromaticity and unsaturations. However, no significant increase in the number of oxygen compounds was observed. The data from Table 1 indicate that the thermal treatment (PAV) is not able to completely simulate asphalt oxidation: it is observed that PAV promotes the formation of oxygenated compounds but is insufficient in simulating the production of unsaturations and aromatic compounds in the material. The fact that the PAV does not simulate the environmental oxidation of binders has been highlighted in prior studies (18). To justify such observation, it is necessary to quantify the signal areas of the asphalt in original condition (non-oxidized) and compare them with the signal areas

Table 1. Area of the Infrared Signals Related to Asphalt Oxidation

Asphalt: Costa Rica 2	Wavelength (cm <sup>-1</sup> )						
	3500 <sup>a</sup>	3050	2900	2800	1700	1600	1030
Original	0.19 ± 0.07 <sup>b</sup>	0.029 ± 0.002	8.37 ± 0.71	2.76 ± 0.19	0.010 ± 0.006	0.76 ± 0.035	0.107 ± 0.038
RTFO	0.16 ± 0.04	0.028 ± 0.003	8.61 ± 0.15	2.83 ± 0.04	0.019 ± 0.005	0.75 ± 0.01	0.194 ± 0.004
PAV (1 cycle)	0.38 ± 0.09	0.028 ± 0.002	8.36 ± 0.21	2.73 ± 0.07	0.129 ± 0.005	0.66 ± 0.07	0.672 ± 0.040
PAV (3 cycles)	0.54 ± 0.15	0.027 ± 0.003	8.07 ± 0.43	2.64 ± 0.14	0.323 ± 0.060	0.66 ± 0.03	1.025 ± 0.065
PAV (5 cycles)	0.39 ± 0.09	0.025 ± 0.004	7.10 ± 1.00	2.33 ± 0.34	0.399 ± 0.054	0.64 ± 0.08	0.920 ± 0.140
Outdoors 6 months (exposed surface)	5.25 ± 0.83	0.043 ± 0.008	4.10 ± 1.10	1.31 ± 0.37	2.960 ± 0.450	1.52 ± 0.29	1.388 ± 0.204
Outdoors 6 months (non-exposed surface)	0.33 ± 0.04	0.033 ± 0.002	8.60 ± 0.20	2.83 ± 0.05	0.073 ± 0.011	0.80 ± 0.02	0.543 ± 0.022
Outdoors 12 months (exposed surface)	4.89 ± 1.16	0.027 ± 0.004	3.89 ± 0.74	1.23 ± 0.25	1.006 ± 0.289	2.10 ± 0.42	1.446 ± 0.217
Outdoors 12 months (non-exposed surface)	0.68 ± 0.21	0.033 ± 0.005	8.46 ± 0.15	2.79 ± 0.06	0.123 ± 0.022	0.97 ± 0.05	0.879 ± 0.057
Outdoors 24 months (exposed surface)	2.52 ± 0.24	0.017 ± 0.002	3.42 ± 0.85	1.12 ± 0.28	0.286 ± 0.067	1.36 ± 0.10	1.910 ± 0.245
Outdoors 24 months (non-exposed surface)	0.70 ± 0.22	0.038 ± 0.004	8.10 ± 0.30	2.66 ± 0.10	0.148 ± 0.047	1.02 ± 0.08	1.198 ± 0.245

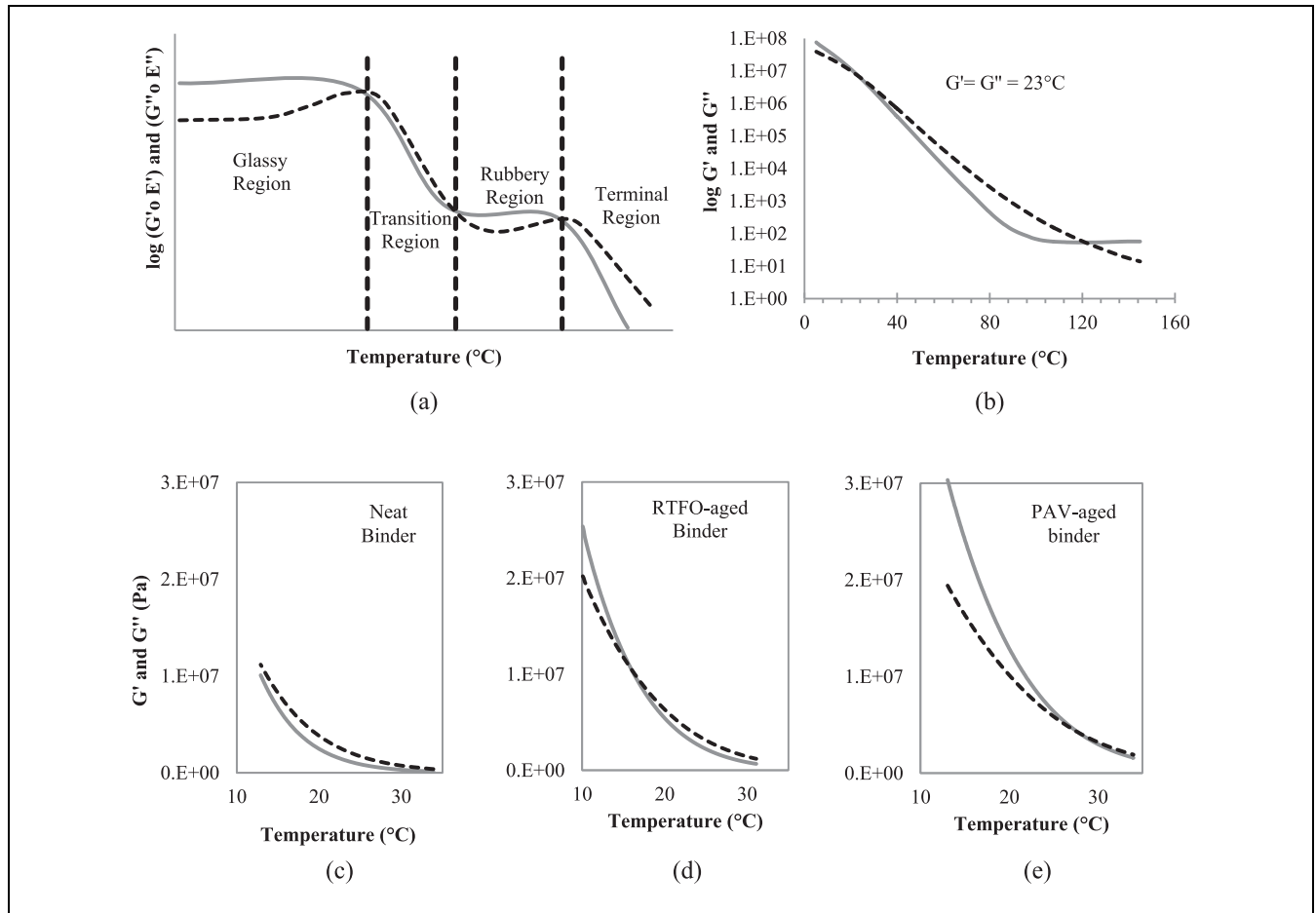
<sup>a</sup>Average of seven replicas.<sup>b</sup>Confidence interval 95%.

of the thermally treated asphalt. The results show that the only significant difference is the increase in oxygen compounds after PAV treatment. The differences can be attributed to the fact that the severe conditions of air pressure and high temperature to which the asphalt is subjected to during the PAV force the oxygenation reactions. Furthermore, it should be emphasized that the oxidation procedure in PAV does not consider the photo-oxidation of the asphalt, which promotes the formation of double bonds and aromatic compounds.

In addition, the asphalt was subjected to three and five consecutive aging cycles in the PAV. The areas of the signals of the spectra corresponding to these samples were quantified, and the results were quantitatively compared with those of the environmental-oxidized samples. It was found that three and five consecutive PAV cycles are not sufficient to produce the amount of carbonyls and sulfoxides formed after exposure of the asphalt to environmental conditions. This suggests that not even five consecutive PAV cycles correctly simulate the oxidation experienced by asphalt film outdoors. These observations reinforce the idea that heat treatments oxidize the binder only through the incorporation of oxygen into its molecules. In this way, subjecting the material to this type of treatment before mechanical evaluation could compromise the correct characterization of the asphalt. As a result, information regarding the performance of the binder throughout its service life might be lost. The following sections will address this issue.

### Rheological Consequences of Oxidative Aging

The viscoelastic behavior of polymeric materials is governed by the variation of the magnitude of viscous and elastic components with temperature. Figure 2a illustrates this behavior, in which four regions are distinguished: glassy region, transition region, rubbery region, and terminal region. The movement and final arrangement of the molecules define the mechanical characteristics of the polymer in the different regions of the viscoelastic behavior. In the glassy region, molecular motion is reduced; there are only vibrational or short translational movements. In this region, the deformations are associated with elongation and shortening of the bonding distance and bonding angles. The transition region is, as the name implies, a transition from the vitreous region of restricted movement to the rubbery region, where more complex configurations occur. In this region, there are translational and configurational movements. The increase in temperature promotes the mobility and flexibility of the molecules, and therefore, they begin to behave as a fluid. In the rubbery region, the molecular chains begin to move in a more rapid and coordinated way. This rapid mobility causes deformation



**Figure 2.** Variation of elastic component,  $G'$  (continuous line) and viscous component  $G''$  (dotted line) with temperature in (a) polymeric materials, (b) environmental-oxidized asphalt, (c) neat binder, (d) RTFO-aged binder, and (e) PAV-oxidized binder.

and relaxation to occur almost instantaneously. In this region, the material modulus varies little with temperature. Finally, in the terminal region, the molecules have a greater freedom of movement and the secondary bonds break and re-establish. At this point, unrecoverable deformations occur as a result of long-range configurational changes (19–21).

To assess the mechanical behavior of asphalt binder, a sweep of the elastic and viscous components was performed at different temperatures (5–145 $^{\circ}\text{C}$ ) for the Costa Rica 2 asphalt exposed to environmental aging for six months. The sweep was performed at a frequency of 10 rad/s and a strain of 1%. The results are shown in Figure 2b.

According to Figure 2b, it is possible to observe in the asphalt a behavior similar to a polymeric material. However, it is important to note that because of the heterogeneous composition of the asphalt, the regions shown in Figure 2a could overlap or elongate in the case of the binder. Therefore, in asphalt, several phase

transitions can be found, such as melting and glass transitions, covering a wide temperature range. In other words, these transitions do not occur at specific points in the asphalt, as is the case in homogeneous materials.

The importance of this analysis is that the location of the intersection points between  $G'$  and  $G''$  (23 $^{\circ}\text{C}$  in Figure 2b) determines the behavior of the asphalt at a given temperature. For example, the first point where  $G' = G''$  in Figure 2b indicates the boundary between the glassy and transition regions on the asphalt. Consequently, it is expected that below this temperature, the material behaves rigidly: the material becomes more elastic and increases the probability of fatigue cracking. In this sense, and considering the polymeric behavior of asphalt (16), it is expected that the temperature at which  $G' = G''$  can be an important indicator of oxidation in the asphalt: an oxidized binder exhibits a  $G' = G''$  point at a higher temperature, as compared with a non-oxidized one.

**Table 2.** Crossover Temperature of Asphalt Samples at Different Oxidation Levels

Asphalts	T (°C) ( $G'' > G'$ )			
	Original	RTFO	PAV	Outdoors
Guatemala 1	<10°C	12.1	22.5	–
Guatemala 2	<10°C	13.1	25.1	–
Nicaragua	<10°C	13.2	22.5	–
Bolivia	<10°C	17.2	27.9	–
Costa Rica 1	<10°C	12.5	25.5	–
Costa Rica 2	<10°C	16.4	27.7	–
Costa Rica 2 (3 PAV cycles)	–	–	45.1	–
Costa Rica 2 (5 PAV cycles)	–	–	63.4	–
Costa Rica 2 (6 months outdoors)	–	–	–	23.4
Costa Rica 2 (1 year outdoors)	–	–	–	30.3
Costa Rica 2 (2 years outdoors)	–	–	–	33.8

The previous observation is illustrated after monitoring the elastic and viscous components for the Costa Rica 2 asphalt samples at different levels of oxidation. In the analysis, a temperature sweep from 5 to 34°C was used. In the case of non-oxidized asphalt (Figure 2c), only the transition region was identified, indicating that the rheology of such material is governed by the viscous component ( $G''$ ) at these temperature ranges. However, as aging progresses, the elastic component ( $G'$ ) becomes more important: it was found that the crossover temperature in the RTFO-aged asphalt is significantly lower than for the PAV-treated asphalt (Figure 2, *d* and *e*, respectively). Therefore, for the laboratory-treated samples the elastic component governs the mechanical response of the asphalt material aged in RTFO below 16.4°C, and for the asphalt aged in PAV, below 27.5°C. This implies that the binder is more susceptible to fracture at temperatures at which the elastic component dominates. In these regions the molecular motion is reduced, a condition that becomes more important in oxidized samples.

Asphalt samples from different countries in Latin America were used to extend the analysis of the Costa Rica 2 asphalt and corroborate the findings from Figure 2, *c* through *d*. The analyzed samples consisted of neat, RTFO, and PAV-aged binders, in order to relate the location of the crossover point to the oxidation level in the samples. Furthermore, by comparison, the Costa Rica 2 sample was analyzed after being exposed to 6, 12 and 24 months of environmental oxidation. The results are shown in Table 2.

Based on Table 2, the crossover temperature of the viscous and elastic components is below 10°C for the non-aged asphalt samples. On the other hand, RTFO-aged samples show crossover temperatures higher than 10°C. It is worth noting that at this level of thermal aging an increase in the amount of sulfoxides in the material and the formation of the carbonyl in a smaller amount is expected. This trend can be observed in Table 3, which

**Table 3.** Carbonyl ( $1700\text{ cm}^{-1}$ ) and Sulfoxides ( $1030\text{ cm}^{-1}$ ) Signal Areas for Selected Asphalts

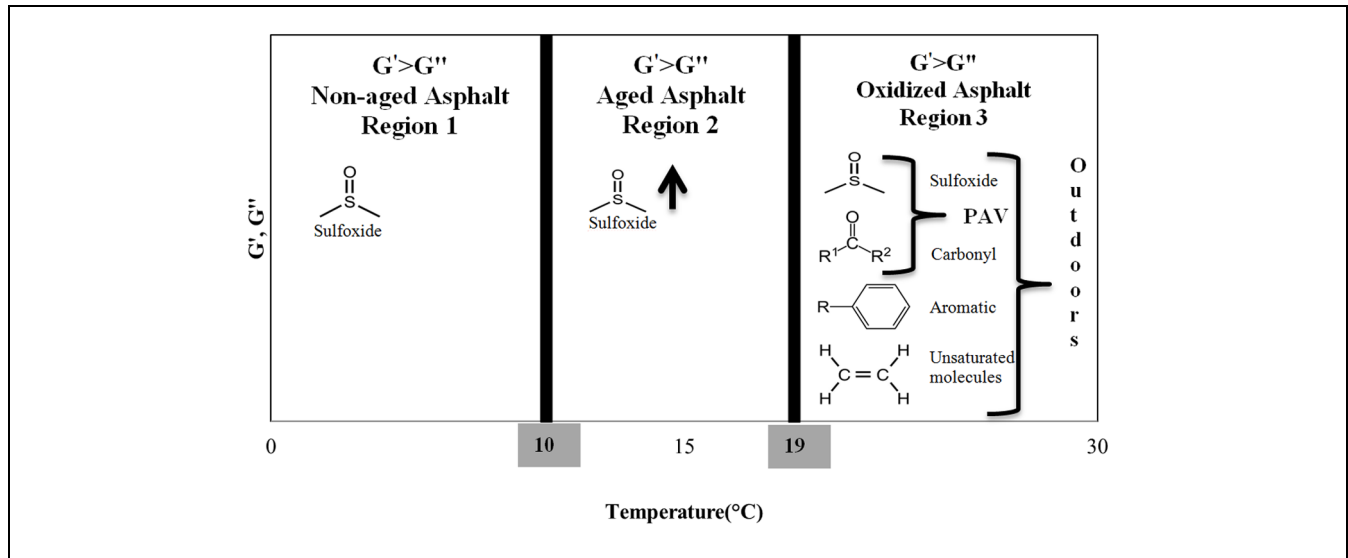
Asphalt	Wave length ( $\text{cm}^{-1}$ )	
	1700	1030
Costa Rica 2 original	0.010	0.107
Costa Rica 2 RTFO	0.019	0.194
Costa Rica 2 PAV	0.129	0.672
Nicaragua original	0.020	0.173
Nicaragua RTFO	0.048	0.201
Nicaragua PAV	0.133	0.760
Bolivia original	0.001	0.161
Bolivia RTFO	0.018	0.192
Bolivia PAV	0.153	0.515

illustrates the content of these chemical species for the asphalts under different aging and oxidation conditions.

When the samples are subjected to thermal oxidation in the PAV, the crossover temperatures exceed 19°C, which is accompanied by a significant increase in the number of carbonyls and sulfoxides, as expected for this type of oxidized sample. It must also be noted that for highly oxidized binders (five consecutive PAV cycles) the crossover point occurs at a temperature at which deformation is expected. This is consistent with the data in Table 3.

It is important to note that the crossover temperature of asphalt placed outdoors for one year period exceeds the value corresponding to PAV-oxidized asphalts, which is intended to simulate the oxidation of asphalt after ten years of service. The previous can be explained by the chemical analysis summarized in Table 1, where it was observed that the oxidation of the asphalt in the PAV is incomplete compared with the environmental oxidation. Photo-oxidation of asphalt produces rigid structures with greater polarity, which could generate an increase in rigidity of the material as the level of environmental





**Figure 3.** Rheological evaluation of the level of aging and oxidation of asphalt and its relationship with the chemical composition. Here “aged” refers to short aged binder (RTFO) and “oxidized” refers to a more severe oxidized binder (i.e., PAV).

oxidation advances. This would explain the significant increase in crossover temperature of environmental-oxidized films compared with thermal aging. The former suggests that aging in PAV is a less severe method in simulating the oxidative conditioning of the asphalts, as photo-oxidative reactions are not accounted for: valuable information is lost regarding the chemical composition of the binder and its final mechanical response.

#### *Relationship between FTIR and Dynamic Shear Rheometer (DSR) in Oxidized and Aged Asphalts*

Figure 3 summarizes the findings from Tables 2 and 3 and shows the relationship between the rheology and the chemical composition of asphalts.

Based on Figure 3 and data in Table 2, asphalts in non-aged condition were found to exhibit a crossover temperature ( $G' = G''$ ) below 10°C (Region 1). At temperatures below 10°C, the elastic component ( $G'$ ) dominates over the viscous component ( $G''$ ). A material with lower crossover temperature is expected to have a longer service life at intermediate temperatures. On the other hand, asphalts having a crossover temperature between 10 and 19°C generally have a higher sulfoxide content than a non-aged asphalt (Tables 2, 3). Therefore, it is expected that the asphalts with a crossover temperature within this range can be short-term aged. Consequently, materials within this range of crossover temperatures can oxidize at a higher rate, mainly in asphalt samples with crossover temperatures near the top of the range. Finally, if the crossover temperature is above 19°C, there is a high probability that the asphalt has been oxidized. This is

because samples that exhibit this behavior show the presence of chemical species such as carbonyls and an important content in sulfoxides, as is the case of PAV-aged samples. For samples exposed to environmental conditions, an increase in aromatic and unsaturated molecules, accompanied by the increase in carbonyls and sulfoxides is observed.

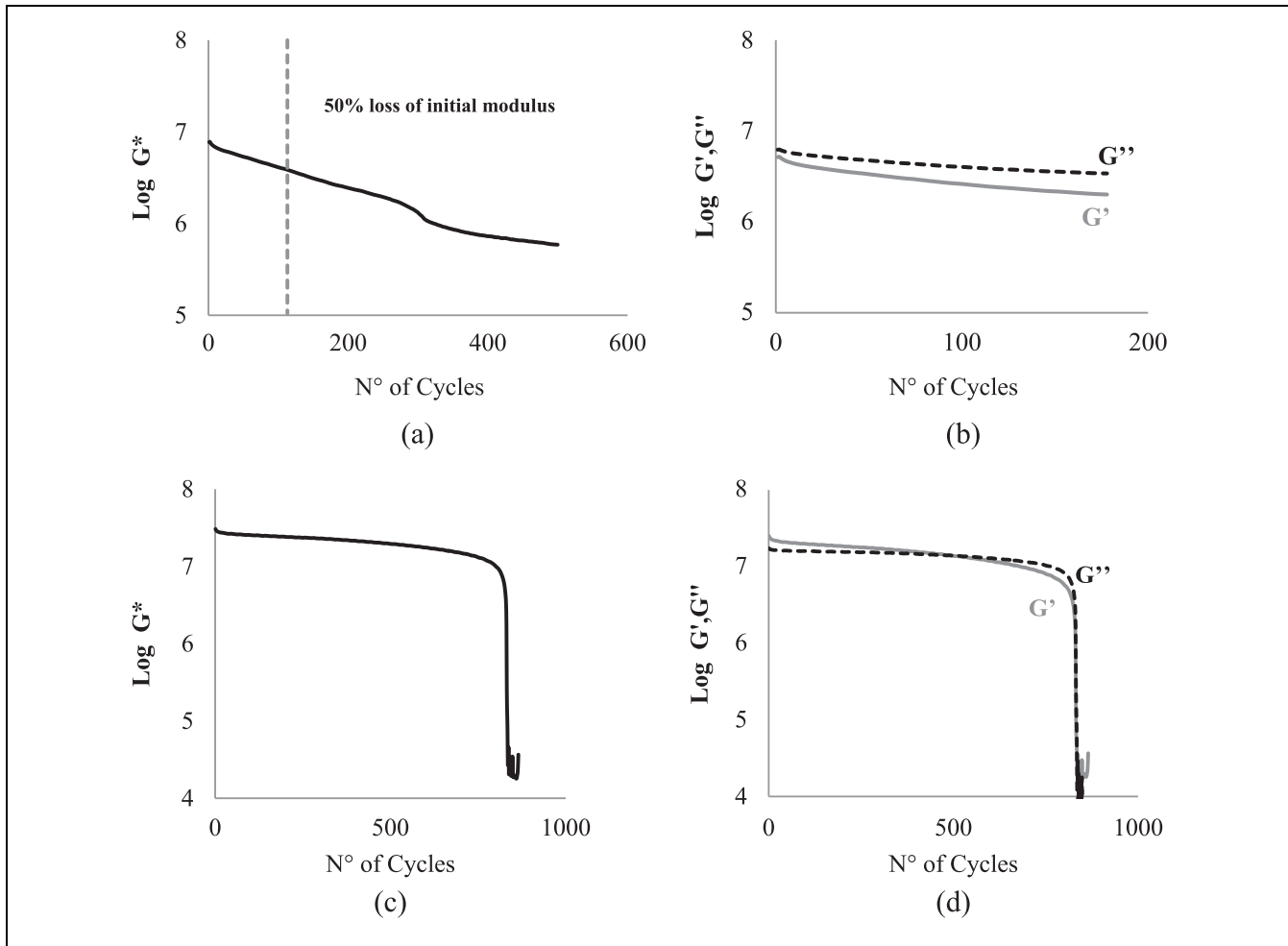
The most important contribution of Figure 3 is that it relates the chemical composition of the asphalt binder to its mechanical response. It should be noted that rheological tests do not replace chemical analyses. However, in the specific case of the findings of Figure 3, a simple rheological analysis can facilitate the material selection.

It should be noted that, in addition to the previously analyzed asphalts, LanammeUCR has a database of almost 20 years of asphalts from different countries and, in general, the consistency of Figure 3 has been observed.

#### *Stress-Controlled Fatigue Test*

Historically, the most common method to evaluate fatigue of asphalt binders in the DSR is to apply a 10% strain at a 10 rad/s frequency, using an 8 mm geometry with a sample thickness of 2 mm. The temperature to be used is at the discretion of the user (ASTM D 2872). The most commonly used failure criterion is to consider that a 50% reduction of the initial modulus is indicative of fatigue damage. Figure 4 compares the results of the previous fatigue test under strain-controlled conditions (Figure 4, a, b) and under stress-controlled conditions (Figure 4, c, d) for Costa Rica 2 PAV-oxidized sample.

Based on Figure 4a (strain-controlled), it is emphasized that the behavior of the material be log-linear as



**Figure 4.** (a) Strain-controlled fatigue test (dotted line denotes a 50% loss in initial modulus), (b) behavior of elastic (gray) and viscous (black) components, (c) stress-controlled fatigue test, and (d) behavior of its elastic (gray) and viscous (black) components for PAV-oxidized Costa Rica 2 in DSR.

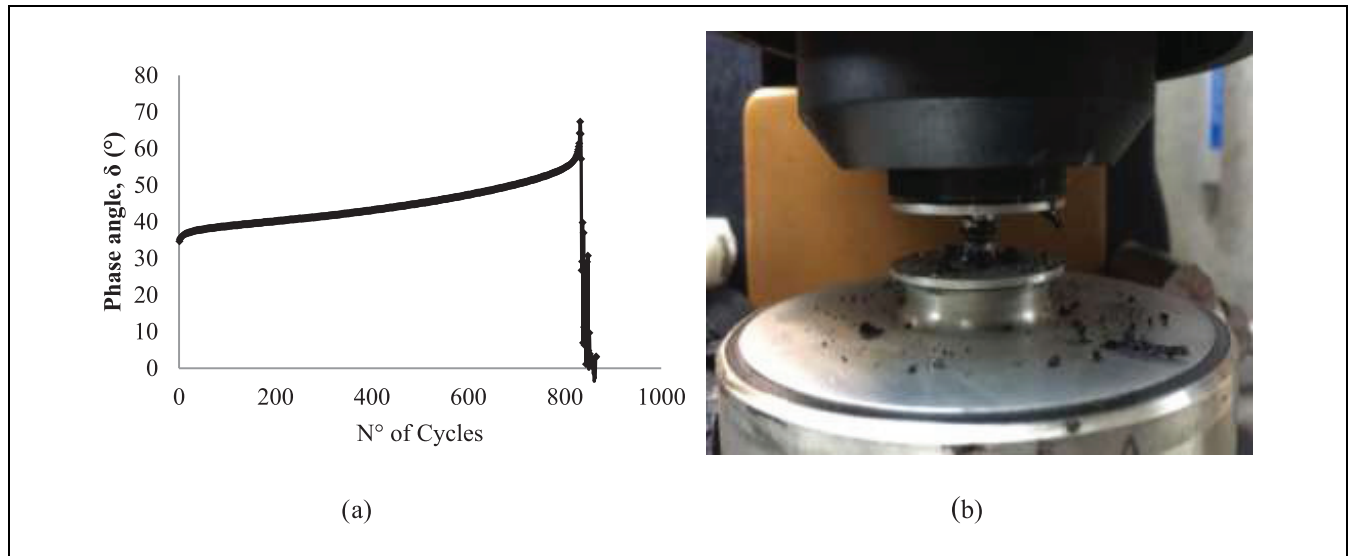
evidenced by its correlation coefficient. In the region where the material loses 50% of its modulus, there is still a high degree of linearity in its response: this shows that with each load application the modulus decreases linearly, suggesting that after each deformation cycle the material relaxes and enters flow. On the other hand, as shown in Figure 4c (stress-controlled), the material exhibits a small decrease in its modulus as a result of a deformation of its structure, but after approximately 800 load cycles a significant decrease in the modulus is observed, evidencing fatigue in the asphalt binder. Therefore, according to the results obtained, the fatigue phenomenon at intermediate temperatures is a process in which the material deforms slightly in the initial cycles of the test, and the presence of fatigue can be associated with an abrupt drop in the modulus after which it does not recover again.

As observed in the strain-controlled test (Figure 4b), the viscous component ( $G''$ ) dominates over the elastic

component ( $G'$ ) from the start of the test, and this behavior is accentuated as the number of cycles increases. This phenomenon shows that the asphalt binder tends to be susceptible to deformation throughout the test. On the other hand, under stress-controlled conditions (Figure 4c), the response of the material is entirely different: the modulus drops abruptly, and the elastic and viscous components compete to dominate the behavior. Figure 4d shows that during the first load cycles the elastic component dominates the behavior of the asphalt. However, as the load cycles increase, there is an increasing influence of the viscous component and, therefore, the drop in modulus observed might be occurring as a result of damage in the sample, until it breaks.

The behavior of the phase angle was also monitored through the stress-controlled test (Figure 5a), and it was observed that at the beginning of the test the phase angle is below  $45^\circ$ , indicating that the elastic component ( $G'$ )





**Figure 5.** (a) Phase angle response during the stress-controlled fatigue test for Costa Rica 2 asphalt and (b) observed failure condition.

dominates over the viscous response ( $G''$ ). As the number of load cycles increases the asphalt undergoes deformation, which is associated with the increase in the phase angle before failure occurs. The observed deformation is associated with the free volume of the binder molecules which, at such temperature, have enough space to move and tend to deform before the structure collapses. From the 800th cycle, this parameter drops abruptly, which confirms that there is a fatigue failure in the material. As shown in Figure 5b, the samples tested under stress-controlled conditions experienced an evident fracture, and their structure is completely broken upon failure.

#### *Comparison between Environmental Conditions and Multiple PAV Cycles on Asphalt Oxidation*

Fatigue on samples of asphalt Costa Rica 2 exposed to multiple PAV cycles and environmental oxidation were tested according to the previously described methodology. The obtained results are shown in Figure 6.

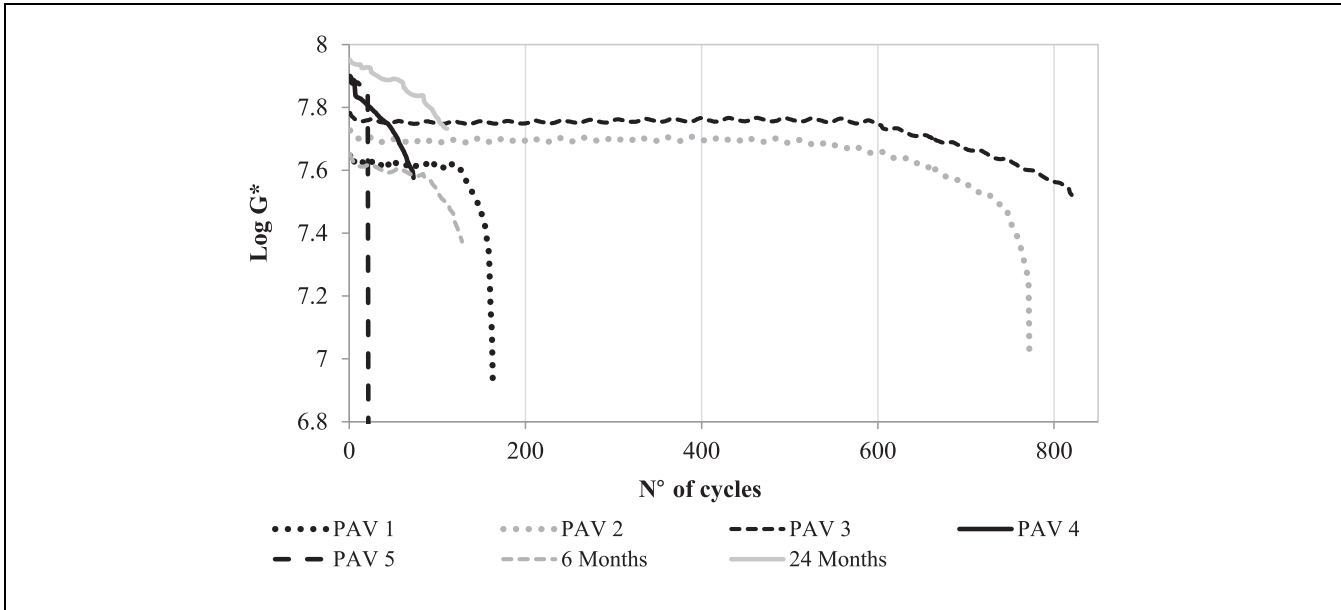
At this point, it is important to recall that according to the chemical analysis, the oxidation process caused by the PAV is incomplete compared with environmental oxidation. As shown in Figure 6, the oxidation achieved with the PAV is less drastic than 6 months of environmental oxidation. Consequently, this incomplete PAV oxidation means that the binder is more fatigue resistant than that exposed to environmental conditions. On the other hand, it was observed that the sample exposed for 24 months undergoes an increase in its modulus, but its resistance to fatigue cycles is reduced by an increase in its fragility.

A feasible solution to obtain a more drastic and realistic oxidation of asphalt could be to increase the number

PAV cycles to which the material is subjected. Figure 6 shows the effect of increased PAV cycles on fatigue life for Costa Rica asphalt 2, evaluated under stress-controlled conditions. As shown in Figure 6, as the asphalt is subjected to continuous PAV cycles, its modulus increases. In the case of the samples subjected to one, two, and three consecutive PAV cycles, the asphalt becomes increasingly resistant to fatigue, which is evidenced by the increasing resistance to load cycles. On the other hand, even if the modulus of the samples oxidized after four and five PAV cycles increases, the material becomes fragile and can withstand a lower number of load cycles compared with the less oxidized material. Therefore, trying to simulate the environmental oxidation of binders by increasing the number of PAV cycles should be done with caution, given that the increase in one, two, or three PAV cycles could favor the fatigue resistance of the asphalt. The same analysis was performed using several binder sources to validate the findings for the sample Costa Rica 2. The results are shown in Table 4.

#### **Conclusion**

The thermal oxidation simulated in the PAV is achieved by increasing the content of oxygenated molecules in the material. However, it was found that environmental oxidation is a more severe process. Therefore, it is concluded that laboratory PAV aging is deficient in simulating the chemical oxidation of asphalt because it does not consider the effect of UV radiation, which causes unsaturation and aromaticity in the material. UV radiation might be more severe than RTFO and PAV treatments. This



**Figure 6.** Comparison of stress-controlled fatigue test results for Costa Rica 2 samples oxidized under environmental conditions during 6 and 24 months (the curve of one cycle PAV-oxidized sample is shown for a simpler comparison), up to five PAV cycles.

**Table 4.** Stress-Controlled Fatigue Analysis Results

Asphalt	Condition	Initial modulus (MPa)	Failure modulus (MPa)	Number of cycles
Costa Rica 2	PAV 1	44.3	22.4	158
	PAV 2	53.4	22.8	762
	PAV 3	60.6	33.2	820
	PAV 4	76.6	37.7	73
	PAV 5	79.5	70.1	21
	6 months outdoors	44.9	23.6	128
	2 years outdoors	89.4	54.0	111
Bolivia	PAV 1	22.5	2.04	239
	PAV 2	26.3	2.62	381
	PAV 3	29.4	2.99	607
	PAV 4	31.7	7.53	36
	PAV 5	34.3	10.7	22
El Salvador	PAV 1	32.0	11.4	283
	PAV 2	47.9	20.4	893
	PAV 3	55.3	31.3	178
	PAV 4	57.7	42.0	15
	PAV 5	68.5	58.3	7
Nicaragua	PAV 1	33.3	12.4	539
	PAV 2	39.1	13.3	780
	PAV 3	42.2	28.3	1060
	PAV 4	44.5	33.7	153
	PAV 5	69.8	34.2	109

demonstrates the ineffectiveness of thermal treatments in simulating the oxidative aging that occurs to asphalt binders under environmental conditions. However, it must be recognized that oxidizing the material under environmental conditions for a complete characterization is a time-consuming process. Therefore, the results obtained

serve as starting point for the calibration of an aging method that more realistically simulates the oxidation of the binder. In this regard, it is necessary to note that relying on multiple PAV cycles must be carefully done since it was found that two and three consecutive PAV cycles increment the fatigue resistance of the material and still

do not emulate the photo-oxidative reactions that occur in the field. In summary, it is proposed to incorporate UV radiation, as well as humidity and temperature, in such an accelerated laboratory method, so that they can be adjusted to the climatic conditions of each region. The authors are currently working on an improved methodology that can simulate more efficiently the complete oxidation of the asphalt binder.

On the other hand, the fatigue behavior of binders is governed not only by the modulus but also by fragility. The previous was observed with fatigue testing: the fatigue test performed under stress-controlled conditions is a better approximation to the actual fatigue process and is more reliable in representing fatigue in the material, compared with the test performed at strain-controlled conditions. This happens because with the stress-controlled condition, a rapid modulus decrease can be observed and the sample fails when tested in the DSR (Figure 5b).

Finally, the data also showed a good relationship between the crossover temperature and the oxidation level of the asphalt. This results in an important tool for the evaluation of asphalt binders, especially when the equipment required for chemical analysis is not readily available.

### Author Contributions

The authors confirm equal contribution to the paper. All authors reviewed the results and approved the final version of the manuscript.

### References

- Huang, S., and W. Grimes. Influence of Aging Temperature on Rheological and Chemical Properties of Asphalt Binders. *Transportation Research Record: Journal of the Transportation Research Board*, 2010. 2179: 39–48.
- Lu, X., and U. Isacson. Effect of Aging on Bitumen Chemistry and Rheology. *Construction and Building Materials*, Vol. 16, No. 1, 2002, pp. 15–22.
- Branthaver, J. F., J. C. Petersen, R. E. Robertson, J. J. Duvall, S. S. Kim, P. M. Harnsberger, T. Mill, E. K. Ensley, F. A. Barbour, and J. F. Schabron. *Binder Characterization and Evaluation, SHRP-A-368: Chemistry*. Transportation Research Board, National Research Council, Washington, D.C., 1993.
- Lamontagne, J., P. Dumas, V. Mouillet, and J. Kister. Comparison by Fourier Transform Infrared (FTIR) Spectroscopy of Different Aging Techniques: Application to Road Bitumens. *Fuel*, Vol. 80, No. 4, 2001, pp. 483–488.
- Mouillet, V., J. Lamontagne, F. Durrieu, J. P. Planche, and L. Lapalu. Infrared Microscopy Investigation of Oxidation and Phase Evolution in Bitumen Modified with Polymers. *Fuel*, Vol. 87, No. 7, 2008, pp. 1270–1280.
- Yao, H., Z. You, L. Li, S. W. Goh, C. H. Lee, and Y. K. Yap. Rheological Properties and Chemical Analysis of Nanoclay and Carbon Microfiber. *Construction and Building Materials*, Vol. 38, 2013, pp. 327–337.
- Yang, X., Z. You, and J. Mills-Beale. Asphalt Binders Blended with a High Percentage of Biobinders: Aging Mechanism Using FTIR and Rheology. *Journal of Materials in Civil Engineering*, Vol. 27, No. 4, 2015, pp. 04014157.
- Loría-Salazar, L. G. Evaluación de asfaltos modificados en laboratorio con distintos polímeros. *Infraestructura Vial*, Vol. 17, 2007, pp. 46–53.
- Liu, M., K. M. Lunsford, R. R. Davidson, C. J. Glover, and J. A. Bullin. The Kinetics of Carbonyl Formation in Asphalt. *American Institute of Chemical Engineers Journal*, Vol. 42, No. 4, 1996, pp. 1069–1076.
- Lui, M., M. A. Ferry, R. R. Davidson, C. J. Glover, and J. A. Bullin. Oxygen Uptake as Correlated to Carbonyl Growth in Aged Asphalts and Asphalt Corbett Fractions. *Industrial & Engineering Chemistry Research*, Vol. 37, No. 12, 1998, pp. 4669–4674.
- Yang, X., Z. You, and J. Mills-Beale. Asphalt Binders Blended with a High Percentage of Biobinders: Aging Mechanism Using FTIR and Rheology. *Journal of Materials in Civil Engineering*, Vol. 27, No. 4, 2015, pp. 1–11.
- Transportation Research Circular E-C140: A Review of the Fundamentals of Asphalt Oxidation*. Transportation Research Board of the National Academies, Washington, D.C., 2009. <http://onlinepubs.trb.org/Onlinepubs/circulars/ec140.pdf>.
- Bahia, H., and D. Anderson. The Pressure Aging Vessel (PAV): A Test to Simulate Rheological Changes Due to Field Aging. In *Physical Properties of Asphalt Cement Binders, STP18189S* (J. Hardin, ed.), ASTM International, West Conshohocken, PA, 1995, pp. 67–88.
- Wu, S., L. Panga, L. Mo, J. Qiu, G. Zhu, and Y. Xiao. UV and Thermal Aging of Pure Bitumen-comparison Between Laboratory Simulation and Natural Exposure Aging. *Road Materials and Pavement Design*, Vol. 9, 2008, pp. 103–113.
- Durrieu, F., F. Farcas, and V. Mouillet. The Influence of UV Aging of Styrene/Butadiene/Styrene Modified Bitumen: Comparison Between Laboratory and on Site Aging. *Fuel*, Vol. 86, No. 10–11, 2007, pp. 1446–1451.
- Polacco, G., J. Stastna, D. Biondi, and L. Zanzotto. Relation Between Polymer Architecture and Nonlinear Viscoelastic Behavior of Modified Asphalts. *Current Opinion in Colloid & Interface Science*, Vol. 11, No. 4, 2006, pp. 230–245.
- Walas, S. M. *Reaction Kinetics for Chemical Engineers: Butterworths Series in Chemical Engineering*. Butterworth-Heinemann, Newton, 2013.
- Qin, Q., J. F. Schabron, R. B. Boysen, and M. J. Farrar. Field Aging Effect on Chemistry and Rheology of Asphalt Binders and Rheological Predictions for Field Aging. *Fuel*, Vol. 121, 2014, pp. 86–94.

19. Brinson, H. F., and L. C. Brinson. *Polymer Engineering and Viscoelasticity: An Introduction*, 2nd ed. Springer US, New York, 2015.
  20. Rosen, S. *Fundamental Principles of Polymeric Materials*, 2nd ed. John Wiley & Sons, Inc., New York, 1993.
  21. Padmarekha, A., and J. Murali Krishnan. Viscoelastic Transition of Unaged and Aged Asphalt. *Journal of Materials in Civil Engineering*, Vol. 25, No. 12, 2013, pp. 1852–1863.
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