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► **To cite this version:**

Rodrigo Shigueiro Siroma, Mai Lan Nguyen, Pierre Hornych, Emmanuel Chailleux. A Literature Review of Bitumen Aging: From Laboratory Procedures to Field Evaluation. *Journal of Testing and Evaluation*, 2022, 50 (2), pp.20210235. 10.1520/JTE20210235 . hal-04312837

HAL Id: hal-04312837

<https://univ-eiffel.hal.science/hal-04312837>

Submitted on 28 Nov 2023

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A literature review of bitumen aging: from laboratory procedures to field evaluation

Rodrigo Shigueiro Siroma¹, Mai Lan Nguyen², Pierre Horny³, and Emmanuel Chailleux⁴

ABSTRACT

Because bitumen aging is behind the major pavement distresses, a better understanding of it is of utmost importance for tailoring longer-lasting roads and developing more effective maintenance strategies. For this purpose, this paper presents an in-depth review of the relevant literature on the aging phenomenon of neat (unmodified) bitumen. The main accelerated laboratory aging procedures as well as some recent ones, for both bitumen and asphalt mix, are presented and their effectiveness in reproducing the effects corresponding to field aging are discussed. Then, the main laboratory tests used to track the evolution of bitumen aging and some values proposed as end-of-life criteria that reflect poor pavement performance are outlined. Finally, a promising method whereby the colloidal structure of bitumen can be estimated from its rheological behavior is presented.

Keywords

Bitumen aging, Pavement durability, Laboratory aging, Field aging, Failure criteria

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1. Introduction

The major applications of bitumen as a construction material are in paving and roofing sectors, accounting for 85 and 10%, respectively, of the approximately 87 million tons produced annually worldwide.¹ Apart from those found in natural deposits, bitumen (also called asphalt, asphalt cement, or asphalt binder depending on the geographical location) is a complex hydrocarbon product that corresponds to the heaviest fraction obtained from the distillation of crude oil during refining.² The elemental composition of bitumen is highly dependent on the source of its crude oil, processes employed during manufacturing, and aging.^{2,3}

Bitumen has widely been employed as the main binding component in road construction due to its desirable engineering characteristics. For this end-use, bitumen must meet a set of specifications that are traditionally related to physical—or rather rheological—properties,⁴ thus affording asphalt pavements optimum serviceability and durability.⁵ Hence, any substantial changes in rheology that may take place are usually undesirable since this implies poorer performance and, consequently, faster deterioration of the asphalt material.

However, these alterations are likely to happen due to the organic nature of bitumen that makes it highly prone to oxidative aging when in contact with oxygen and other reactive oxygen species (ROS) naturally present in the atmosphere. The so-called aging phenomenon is a combination of several mechanisms, where an extensive list can be found in Traxler.⁶ Among these, oxidation, volatile loss by evaporation, exudation of the oily component from the bitumen into the mineral aggregate, and steric hardening are the most recognized aging mechanisms.^{2,7,8}

Depending on the conditions to which the bituminous material is exposed, the aging phenomenon can be divided into two stages: short- and long-term aging. The first takes effect already in the very early stages of hot asphalt mix manufacture when bitumen is brought to high

temperatures and is intensely exposed to oxygen due to the increased surface area observed during mixing, transporting, laying, and compaction of asphalt mix. Long-term aging starts shortly thereafter and, unlike the previous stage, it occurs at temperatures found in situ throughout the pavement service life. In this scenario, the irreversible changes triggered by this phenomenon in bitumen chemistry and molecular structure accumulating over time cause bitumen to stiffen and embrittle, thus impairing pavements' durability as they become more susceptible to cracking.

Given the inevitability of hardening of bitumen due to its aforementioned intrinsic characteristics, a better comprehension of the detrimental effects of aging on bitumen properties is of pragmatic importance for tailoring longer-lasting asphalt pavements and developing more effective maintenance strategies. For this purpose, this paper presents an in-depth review of the relevant literature regarding the aging phenomenon of neat (or unmodified) bitumen. The main accelerated laboratory aging protocols, for both bitumen and asphalt mix, are presented and their effectiveness in reproducing the effects yielded in the field are discussed. Also, methods proposed in recent works that either overcome limitations of the classic aging procedures or whose aging conditioning are more realistic are evaluated. Then, a comprehensive analysis of the laboratory tests to track the evolution of bitumen aging with the highest incidence in the technical literature are presented. Furthermore, some end-of-life criteria proposed in several research works that correspond to poor pavements performance are presented and their feasibility are discussed. Finally, a promising method that estimates the colloidal structure of bitumen from its rheological behavior is presented.

2. Accelerated Laboratory Aging Protocols

Several attempts have emerged over the decades striving to reproduce the effects of aging

in the field as accurately as possible through accelerated laboratory procedures. Some of them were summarized and discussed in Bell⁷ and Airey⁹. The vast majority of these laboratory aging procedures, however, were designed for bitumen, while relatively few were intended for asphalt mix.⁷ Most of these conditioning protocols consist of extended exposure of bitumen or asphalt mix to high temperatures as it accelerates their oxidation rate, which is desirable; however, laboratory aging procedures employing excessively high temperatures might generate considerably different effects than those yielded in the field at surrounding temperatures.^{3,5}

2.1. AGING PROTOCOLS FOR BITUMEN

Consisting of relatively thin film samples exposed to high temperatures, these procedures aim to simulate the aging of the bitumen thin film coating the aggregates. Of the several procedures proposed, the Rolling Thin-Film Oven Test (RTFOT) and Pressure Aging Vessel (PAV) have been widely used over the past decades as they are prescribed by the main bitumen specifications, such as the European standard EN 12.591:2009¹⁰ and American Association of State Transportation and Highway Officials (AASHTO) M320-17,¹¹ to reproduce, in an accelerated manner in the laboratory, the effects of age-oxidation that take place in bitumen during short- and long-term aging, respectively.

RTFOT has a fundamental advantage over its predecessors due to the continuous flow of bitumen around the inner surface of each bottle, which results in a relatively thin film of 1.25 mm.^{7,9} This attenuates the problem found in its previous versions where a thicker film sample could result in a more aged surface, creating a “skin” that would prevent homogeneous aging. RTFOT is generally in line with short-term aging¹² yet does not aim to faithfully reproduce the conditions to which the bitumen is submitted.^{12,13} Factors such as origin and grade of bitumen have

a great influence on the hardening, while processes in the plants as well as asphalt mix composition seem to be not so significant during short-term aging.^{13,14} Although RTFOT-aging is sometimes more aggressive^{13,14} or milder¹⁵ than aging that takes place in asphalt mix plants, it can provide crucial information on the aging susceptibility of a given bitumen during short-term aging and the risk of premature hardening of asphalt mixes.^{13,14} This is the only aging procedure stipulated by EN 12.591:2009 where limiting values for parameters, such as penetration and softening point are proposed. By contrast, AASHTO M320:2017 establishes the maximum temperature under which the bitumen displays a minimum resistance to rutting. One of the main drawbacks of RTFOT is, however, when bitumen does not attain low enough viscosity to produce the moving film, as occurs with hard grade,¹² polymer-modified,¹⁶ and warm mix binders.¹⁷

Adopted by the Strategic Highway Research Program (SHRP) as the main protocol to simulate long-term aging,^{3,18} PAV adopts high pressure to grow the diffusion rate of oxygen into a 3.2-mm thin film sample of RTFOT-aged bitumen. Depending on the conditions to which the pavement will be subjected throughout its service life, different temperatures can be employed for PAV: 90°C for cold climates, 100°C for moderate climates, and 110°C for hot climates (desert areas).¹⁹ The European standard does not include limiting values for PAV-aged bitumens, while the AASHTO standard utilizes the PAV-aged bitumen to assess its performance at intermediate (fatigue) and low (thermal cracking) temperatures. Despite being well propagated that the PAV aging method is able to reproduce 5–10 years of in-service aging,²⁰ its performance according to previous works is, however, ambiguous: with some endorsing works, either in part or in full,^{15,21–23} and others questioning its effectiveness,^{24–27} as seen in Table 1. It is worth mentioning that the depth of the sample coring has a considerable impact on the aging level of the reclaimed bitumen due to the presence of a strong aging gradient below the pavement surface. In spite of using lower

temperatures than those currently practiced (first version of the PAV protocol), Button and Little²⁸ stated that factors such as temperature, film thickness, and bitumen origin strongly influence the oxidation rate. In this case, a higher temperature and a smaller thickness lead to a higher aging level. To achieve this, attempts such as reducing the thickness of bitumen film to attenuate the formation of a protective “skin” on the surface of the bitumen sample that could hinder the free diffusion of oxygen²⁹ and the use of several 20-hour PAV protocols in a row (extended PAV)^{24,25,30} are found in the literature.

TABLE 1

Correlation between PAV hours at 100°C and 2.1 MPa after RTFOT aging and in-service years

Location	PAV hours	Equivalent years	Depth (cm)	Bitumen grade	Reference
USA	11, 21 and 45	1, 2 and 4, respectively	top 1.3	PG67-22	Smith et al. ²⁴
	3 and 14	2 and 4	5.0–6.3		
	20		top 1.3		
USA	20	< 8	top 12.5 mm	PG64-28	Zhang et al. ²⁷
USA	20	8	75 mm depth	PG70-22	Qin et al. ²¹
USA	20	< 5	100 mm depth	PG58-28	Li et al. ²⁶
USA	20	3	surface	various	Mallick&Brown ¹⁵
NL	20	3	surface	70/100	Jing et al. ²²
France	20	> 7	surface	35/50	GNB ²³

Regarding the limitation of RTFOT and also PAV, it is worth mentioning the Universal Simple Aging Test (USAT), which is a 300-µm film test, developed by the Western Research Institute (WRI)¹⁷ as an optimized alternative to the standard RTFOT and PAV procedures. Despite

being a static thin-film test, which could develop a protective “skin” that would prevent homogeneous oxidation of the sample, the extremely thin film is somewhat similar to the thickness of the bitumen film on granular, in which oxidation can be considered as kinetics-controlled, i.e., absence of an oxidation gradient.³¹

2.2. AGING PROTOCOLS FOR ASPHALT MIX

Compared to research on bitumen aging, relatively little has been dedicated to the aging of asphalt mixes.⁷ Despite being simpler, laboratory protocols for bitumen aging are somehow limited by not considering complex factors that may influence aging of bitumen in asphalt mixes, such as the bitumen-aggregate physicochemical interactions. Laboratory aging procedures for asphalt mixes were then proposed for this purpose. However, a heavier workload is required to age asphalt mix, such as manufacturing the asphalt mixes themselves, going through all the steps of the aging procedures, and at the end of each aging level, extracting and recovering the bitumen.

Laboratory aging procedures for asphalt mixes can be classified according to the specimen state (loose or compacted), acceleration factor (forced-draft oven, modified pressure, etc.), and aging factor (oxygen, ozone, actinic light, etc.). Some of them are presented and discussed in Bell,⁷ Airey,⁹ de la Roche et al.,³² and Kim et al.³³

Among the various methods, the one proposed by AASHTO R30:2002³⁴ is widespread for producing aged specimens for performance testing. As the manufacture of asphalt mixes in the laboratory is considerably less aggressive than the procedures to which the asphalt material is submitted in the asphalt mix plant, transport, and laying in the field, this standard document proposes a short-term aging protocol after mixing at 135°C for 4 hours. Then the asphalt mix is compacted to initiate the long-term aging routines. In this setup, the oxidation rate is significantly

low due to the difficult access of the air in the bowels of the compacted specimen. Despite the incidence of the aging gradient in compacted samples aged in the laboratory, it is noteworthy that its direction is different from what is observed in the field. In the first, the aging gradient goes from the periphery toward the center of the specimen, while in the second it goes downward.^{33,35} Furthermore, the exposition to high temperatures and eventually pressures, depending on the aging procedure, can compromise the integrity of the sample with a possible distortion that can alter its geometry, e.g., void content.³⁵ To mitigate this issue, Houston et al.²⁰ proposed some methods, such as confining the sample by wrapping it in wire mesh secured with clamps.³⁶ Further discussions as well as some correlations of long-term aging duration in the laboratory with equivalent in-service years in various types of climates found in the United States are presented in Bell et al.³⁷

Unlike the previous approach, laboratory aging procedures for loose asphalt mixes, such as the one proposed by RILEM TC 206-ATB TG5,³² is considerably more efficient due to the greater ease of air circulation throughout the loose asphalt mix, thus ensuring more homogeneous aging with a higher oxidation rate. The procedures and temperatures are similar to those described in AASHTO R30:2002. The only difference however is during long-term aging that, instead of being compacted, the asphalt mix is disaggregated. It is worth mentioning that the RILEM TC 206-ATB TG5 protocol was proposed to produce well-controlled reclaimed asphalt (RA)-like material in the laboratory and no correlation with field aging was proposed.³² In seeking to optimize loose asphalt mix aging, Rad et al.³⁸ proposed the optimal temperature of 95°C that increases the oxidation rate without affecting the chemical and rheological relationship of the bitumen. Applying this optimal temperature, Elwardany et al.³⁹ proposed a method to determine the duration of the laboratory aging protocol for loose asphalt mix that reproduces the same aging

level found at a given time, climate, and depth within any pavement located in the United States. One of the main drawbacks of aging loose asphalt mix is the poor adhesion and cohesion during the compaction of the specimens for performance testing, which may confound the results.^{32,35} Some alternative for this problem is discussed in Kim et al.³³

Besides the traditional methods that use high temperatures as an aging acceleration factor, it is worth mentioning innovative approaches whose employed procedures get closer to the conditions found in the field, such as the Viennese Aging Procedure (VAPro). Based on Bell's recommendations,⁷ Steiner et al.⁴⁰ proposed a method that consists of simulating the long-term aging effects in compacted specimens through a triaxial cell with compressed air—enriched with ozone and nitric oxides, both highly oxidative gases present in the atmosphere but in smaller concentration, at 45°C–75°C (temperatures usually reached on surface layers in summer). Maschauer et al.⁴¹ observed that the complex modulus of the bitumens extracted and recovered from a VAPro-aged compacted asphalt mix for 6 and 12 days corresponded satisfactorily with those of the RTFOT- and RTFOT+PAV- aged bitumens, respectively. It is worth mentioning that a procedure similar to the one described above was also developed for bitumen aging: the Viennese Binder Aging (VBA).⁴²

3. Aging Indexes and Proposed End-of-Life Criteria

The relentless pursuit of sound laboratory tests and indexes that can be employed not only to track the evolution of the aging level in bitumen but also to accurately estimate the level of pavement performance has been intense over the last decades. Apart from the traditional empirical tests, most of the tests that have been used are classified as chemical and rheological.

As bitumen makes up approximately 5 wt% of asphalt mixes, extracting a large amount of

bitumen not only requires extra time and effort but also a copious amount of organic solvent that implies the overexposure to such element, which is harmful to humans. Therefore, the amount of bitumen needed must be one of the main parameters to be taken into account when assessing the quality and feasibility of a laboratory test.

3.1. EMPIRICAL INDEXES

Empirical tests such as the Needle Penetration and Softening Point have historically been used to quantify the consistency of bitumen, although they do not represent any fundamental engineering properties. The first is the backbone of the most widespread bitumen classification method: the Penetration Grading system. The changes due to bitumen aging are represented by the decrease in penetration and increase in softening point.⁴³⁻⁴⁶ Given the frequent use of both parameters, several limiting values to monitor if unmodified bitumens still perform satisfactorily after aging were proposed not only in previous works but also in technical standards. The European standard EN 12.591:2009¹⁰ presents the specifications for fresh bitumen according to its penetration grade and limits the acceptable variation in penetration and softening point values considering exclusively the RTFOT aging. This, therefore, ensures a certain softness of the newly laid asphalt pavement.

For the Zaca-Wigmore test road built in the mid-1950s in California (USA), a limiting value of 30 was stated for penetration (originally 200–300) as a pavement failure criterion.⁴⁷ In a review study carried out by Finn et al.⁴⁵ on the relationship between asphalt material (with an emphasis on bitumen) properties and pavement performance (test roads), it is observed that this value of 30 is not in agreement with those found in other test road studies, where in some cases lower penetration values were found in extracted bitumen from sites with little or no cracks.

In France, Information Note number 26 published by “Service d’Étude Techniques des Routes et Autoroutes” (SETRA)⁴⁸ presents the following failure criteria determined from bitumens extracted from zones with a high incidence of top-down cracking:

- Penetration at 25°C < 20 (0.1 mm),
- Softening point $\geq 70^{\circ}\text{C}$,
- Fraass breaking point temperature $\geq 0^{\circ}\text{C}$,
- n-heptane-asphaltene content > 0.2.

It is worth noting that the limiting value of 20 proposed for penetration can be achieved by a 35/50 pen grade bitumen (widely employed in road construction in France) or harder subjected to the RTFOT aging protocol and yet fall within the specification limits found in EN 12.591:2009. Regarding softening point, a similar situation could only occur with 20/30 pen grade bitumen.

Ramond et al.⁴⁴ compared these limiting values proposed by SETRA with those obtained from field-aged bitumens from non-cracked and cracked (top-down cracking) sites on the French tollway A 07 and trunk roads RN 6 and RN 7. He found that among these 4 criteria proposed, both the softening point and asphaltene content appeared to be the parameters that best correlate with the incidence of cracking. Then comes the penetration, which according to the author can be left out, since the sections indicated as cracked were the same as those obtained by softening point, yet with a lower degree of precision. And finally, the Fraass breaking point temperature presented the worst performance among all these criteria for this purpose. Through non-parametric statistical analyses, Ramond et al. settled the softening point at 68°C and the temperature corresponding to the phase angle of 45° of 40°C (further discussed in subsection 3.3.3.3) as the bitumen parameters capable of better distinguishing asphalt mixes according to their cracking state.

Moreover, some studies carried out by the “Groupe National Bitumen” (GNB)^{23,46} on different roads across France emphasize the lack of precision in penetration when bitumen is considerably aged (high viscosity). The penetration value reduces in the first 2 years after construction and then seems to stabilize thereafter. The softening point, on the other hand, increases continuously, where a limit value of 65°C was proposed due to its precision in classifying cracked roads. Besides, the fact that the softening point test requires much less bitumen than penetration makes it much more attractive.

3.2. CHEMICAL INDEXES

3.2.1. Saturate, Aromatic, Resin, and Asphaltene (SARA) fraction

Formed predominantly by hydrocarbon molecules, bitumen also presents some heterocyclic species, functional groups containing sulfur, nitrogen, and oxygen atoms as well as traces of metals.^{3,4,49} However, given its extremely complex chemical composition, researchers have focused over the past decades rather on fractionating bitumen components into generic groups according to their reactivity and/or polarity. Among these, Corbett⁵⁰ proposed a scheme well-known as “SARA fraction” that consists of using solvents with increasing polarity to separate bitumen into 4 groups: saturate, aromatic, resin, and asphaltene. Alternative solvents have since been adopted for safety and convenience reasons⁵¹ and the procedures are described in ASTM D-4124-09(2018)⁵². The reactivity of those toward oxidation increases with their polarity. While the nonpolar saturate fraction content remains practically unchanged due to its low chemical reactivity, the components of the three remaining fractions tend to move from aromatics through resins to asphaltenes.^{5,43,53,54} It is also common to detect a positive net production of the resin fraction, i.e., the decrease in the aromatic fraction causes a significant increase in resin and a slight growth in

asphaltene.^{54,55} Both cases imply an increase in the polarity of the lower molecular weight intermicellar environment (maltene). This intensifies intermolecular bonds—causing a reduction of mobility between them—⁸ that hinders the dissipation of mechanical and thermal stresses, thus increasing the cracking susceptibility of asphalt materials.

Proposed by Gaestel et al.⁵⁶, the Colloidal Instability Index (CI) uses the content of each SARA fraction to quantify the colloidal stability of the bitumen and is given by Equation 1:

$$CI = \frac{\text{Saturates} + \text{Asphaltenes}}{\text{Aromatics} + \text{Resins}} \quad (1)$$

The increase in IC value with aging represents the growth in asphaltene content and the decrease in the amount of peptizing molecules, such as resins, causing asphaltenes aggregation that makes bitumen more prone to cracking. Care must be taken as it not uncommon to find the numerator and denominator of the CI switched.⁵⁷

Huet⁵⁸ investigated bitumens from the top 5-mm core slices from French and Belgian roads with cracking incidence and proposed the limiting value of 0.6 for the IC as an end-of-life criterion. According to the studied bitumens, this represents an asphaltene content of 0.23–0.26, which is in accordance with the limit values of 0.20 proposed by SETRA⁴⁸ and 0.22 settled in a study carried out by GNB²³ on 7-year-old French roads with a significant incidence of top-down cracking.

When the increase in resin is greater than that of asphaltene, the CI index does not grow as expected despite the increase in bitumen polarity with aging. Perhaps the increase in polarity would be better represented by the (resin+asphaltene)/(saturate+aromatic) ratio, as employed in Mirwald et al.⁵⁴ The lack of a clear trend is the main argument that shows the unfeasibility of the CI > 0.6 index for a wide range of bitumens.

Some serious limitations of the SARA test are often stated in previous works, such as the lack of reproducibility,^{59,60} different correlation between methods,⁵⁹ groupings of aromatics that

are often classified as resins,^{60,61} among others. Attempting to circumvent these issues, it is worth mentioning alternatives such as the fully automated Saturates, Aromatics, Resins, and Asphaltene Determinator (SAR-AD) proposed by Boysen and Schabron⁶² and the low-cost and repeatable protocol designed by Sakib and Bhasin.⁶³ Despite the promising results, these novel methods need to be further validated and developed to be able to better correlate the chemical components with the physical properties of bitumen.

3.2.2. Fourier Transform Infrared (FTIR) Spectroscopy

Given its vocation for identifying molecular components and structures, FTIR is widely used to track the oxidation level of bitumen through the changes of the two functional groups: carbonyl (C=O) and sulfoxide (S=O). In the carbonyl IR absorption region, ketone accounts for most of the growth observed with oxidative aging.^{3,5,8,64} The first stage of aging, also called spurt, is marked by a rapid formation of both, where the increase rate of sulfoxide is higher than that of carbonyl; then, sulfoxide appears to stabilize, whereas carbonyl continues to grow.^{5,65-67}

Mirwald et al.⁵⁴ investigated three laboratory-aged 70/100-pen-grade bitumens from different crude oil sources through the SARA method and then analyzed each fraction thereof with the FTIR procedure. The saturate fraction does not change with aging, which is in accordance with the previous subsection. The aromatics, however, display an increase in ketone, yet the sulfoxide remains stable—the molecules when forming the sulfoxide with aging are probably eluted in fractions of higher polarity. The resins of the fresh bitumens display three functional groups within the carbonyl bands: carboxylic acid (1730 cm^{-1}), ketones (1700 cm^{-1}), and 2-quinolones (1675 cm^{-1}). The first and third decrease after aging, while the ketone increases. This is likely due to the various chemical reaction, such as condensation, or a prevailing ketone formation that overlaps the

two functional groups. In the fresh stage, the sulfoxide already has a high content that does not evolve much with aging. Finally, the spectrum of asphaltene presents an increase in ketone and sulfoxide. Although it is an interesting analysis, the question that remains is: Do the changes caused by aging seen in the spectrum of each SARA fraction correspond to the increase in polarity of the molecules already present in that fraction? Or, is this rather explained by molecular displacements that may occur toward more polar fractions? Further investigations are needed to confirm these assumptions.

Lau et al.⁶⁸ stated that the growth rate of the carbonyl index is directly proportional to the aging temperature and this index has frequently been taken into account due to its well-known linear relationship with the log viscosity. Sulfoxide, in contrast, has been regarded with skepticism due to its apparent pseudo-steady state after the spurt²⁰ that implies the net result of sulfoxide production from oxidation and its loss through thermal decomposition.³ This sulfoxide decay is considerably affected by the aging temperature and the diffusion rate of the oxygen into the bitumen, which is controlled, for instance, by the bitumen film thickness.^{5,69} Although the aging temperatures of various procedures recently proposed are below 100°C, care must be taken during bitumen extraction and recovery. In this latter, bitumen is brought to high temperatures for hours for the total evaporation of the solvent. This disbelief reflects the considerable number of studies that consider only the carbonyl index.^{53,70} However, a more fundamental investigation into the role of sulfoxide in the physical aspect of bitumen carried out by Petersen and Glaser⁶⁴ underlines that the alcohols yielded from sulfoxide reaction are the principal factor that leads to increased viscosity, especially for high sulfur content bitumen. Lu et al.⁷¹ observed the aforementioned high dependence on the aging temperature during the production of both indexes. The bitumens aged in the field, at temperatures lower than those frequently practiced in the laboratory, show higher

sulfoxide levels and lower contents of carbonyl when compared to those aged in the laboratory. Different temperatures employed during the PAV procedure presented the same trend. These results highlight the different mechanisms that may occur during the field- and laboratory-aging, which would hinder the estimation of the field-aging level through these FTIR indexes.

Despite being a handy and effective tool to track the oxygen uptake in bitumen, the procedures adopted between laboratories diverge considerably due to the lack of standardization to date. To address this issue, several works propose ways to converge the main steps thereof, such as bitumen storage,⁷² sample preparation,⁷³ raw spectra treatment,^{67,74} and indexes calculation.^{65,67,70,73}

3.2.3. Size Exclusion Chromatography (SEC)

Also known as Gel Permeation Chromatography (GPC), this method classifies bitumens based upon their molecular size, or weight, distribution. Bitumen is initially dissolved into a solvent and this resulting solution represents the mobile phase that will pass through a porous matrix of spherical particles (stationary phase). Under the hypothesis of a total absence of reactivity and absorbance between the phases, the elution time of the dissolved bitumen molecules will depend exclusively on their size. Resembling a Gaussian distribution curve, the chromatogram obtained is usually divided into three parts: small (intermicellar environment), medium (isolated asphaltene molecules), and large (asphaltene agglomeration) molecular size.

Laboratory-^{53,75,76} and field-^{45,77}aging have a considerable impact on molecular size distribution, where a marked increase is often seen in the large molecular size (LMS) population. This is due to the increase in polarity in the intermicellar environment (maltene) that seems to favor the agglomeration of molecules (asphaltene micelles).^{5,8} This hampers the bitumen's ability

to disperse stresses, thus making asphalt materials more susceptible to cracking. Finn et al.⁴⁵ present a survey carried out in the Montana Big Timber test road where the bitumens extracted from cracked zones were those that displayed the higher LMS. Martin et al.⁷⁷ point out that SEC can be useful; however, the chromatograms of distinct bitumens are hardly comparable to one another as they depend not only on their source but also on the procedures employed.

Several drawbacks of SEC are usually stated in the literature, such as the insolubility of the studied material in some commonly used solvents^{78,79} and the undesirable interactions that may occur between the stationary and the mobile phase, thus generating adsorption of small molecules.⁸⁰ Yet its premise seems to be the biggest problem in quantifying the colloidal system with aging. The fact of merely breaking weak bonds that may have resulted from processes triggered by the aging phenomenon prevents potential insights that could be gained regarding the structural changes that take place in bitumen with aging. Besides, the molecular weight distribution (MWD) obtained experimentally does not necessarily correspond to that of the bulk, or undiluted, bitumen, which determines its mechanical behavior. To attenuate this issue, Brûlé, Ramond, and Such⁸¹ present an alternative technique for SEC that aims to preserve intermolecular bonds (asphaltenes agglomerations) as much as possible and therefore resulting in chromatographs closer to what is expected for the bitumen colloidal structure. Another possible solution to work around this issue is to estimate the MWD of a given bitumen from its rheological response and is further discussed in subsection 4.1.

3.3. RHEOLOGICAL INDEXES

Unlike empirical tests, which only measure bitumen properties within a limited and narrow domain, the robustness of rheological parameters to encompass a wide range of temperatures and

frequencies where bitumen behaviors vary from viscous liquid to elastic solid explains its almost ubiquitous presence in papers over the past decades. Unlike the European standard, the SHRP bitumen specifications are based on the results of the frequency-sweep test, such as Dynamic Shear Rheometer (DSR), and Bending Beam Rheometer (BBR) tests to validate the use of a given bitumen under a given condition.

3.3.1. Creep Modulus - Bending Beam Rheometer (BBR)

For evaluating the bituminous materials' ability to resist low-temperature cracking, the Bending Beam Rheometer (BBR) test consists of applying a constant load on a bitumen beam (3-point bending test) at temperatures corresponding to the lowest expected one to be found in the field during the pavement service life, i.e., under which bitumen behaves like an elastic solid. The two outputs of the BBR test are flexural creep stiffness (S) and the creep rate (m-value) after 60 seconds. The first measures the resistance of the bitumen to the thermal stresses that gradually take place in pavements when the temperature drops and the second quantifies the relaxation properties of the bitumen.² At low temperatures, the aging phenomenon impairs the relaxation ability (m-value) more than the stiffness (S).⁸²⁻⁸⁴ As will be seen in subsection 3.3.3.1, limiting values for both parameters were established by the AASHTO M320-17¹¹ standard for RTFOT+PAV-aged bitumen. In this case, it will be determined the low-temperature stiffness (T_S), which is the temperature at $S \leq 300$ MPa, and $T_{m\text{-value}}$ that is represented by the slope of the log-stiffness versus log-time ($m\text{-value} \geq 0.3$). Observing the good correlation that the m-value had with Glover's fatigue criterion,⁸⁴ which in turn corresponds satisfactorily with Kandhal's ductility,⁸⁵ Anderson et al.⁸⁶ proposed the ΔT_C parameter that is the difference between the T_S and $T_{m\text{-value}}$, that is, $\Delta T_C = T_S - T_{m\text{-value}}$. ΔT_C is highly dependent on the rheological index (R-value) and temperature

susceptibility parameters.^{87,88} As bitumen ages, the BBR curve flattens and ΔT_C becomes increasingly negative.^{89,90} Limiting values of $\Delta T_C \leq -2.5^\circ\text{C}$ (possible risk of cracking) and $\Delta T_C \leq -5^\circ\text{C}$ (more urgent remediation) was proposed. It is worth mentioning that some early works define $\Delta T_C = T_{m\text{-value}} - T_S$ (resulting in an inverse trend).⁸⁹

One of the major criticisms of the BBR procedures is undoubtedly the excessive amount of bitumen needed. In the early 1990s, when the SHRP specification was first proposed, its use was justified by the lack of precision of the DSR device at low temperatures.⁹¹ However, in the past decades, it has been observed an increase in the robustness of rheometers, which has made possible attempts toward interrelationship between BBR and DSR data.⁹²⁻⁹⁵ The lack of sensitivity of the BBR test due to the short conditioning time has long been discussed by Hesp and coworkers.⁹⁶⁻⁹⁸ Khan et al.⁹⁹ mentioned that this, and even premature failure observed in previous studies,^{96,100,101} is often because the specimen is in a non-equilibrium state due to the short conditioning time, which may favor low-performance materials by not taking their degradation over the years into consideration. The Extended Bending Beam Rheometer (EBBR) was proposed in this context to mitigate this issue. Proposing the measurements after 1, 24, and 72 hours of conditioning, the accuracy of the performance grading improved considerably,^{97,99} although this extra time can be problematic.

3.3.2. Complex Modulus – Temperature-frequency sweep test

Frequency sweep test at multiple temperatures is employed to measure the bitumen's complex modulus Bitumen ($G^* = G' + iG'' = |G^*|e^{i\phi}$). When submitted to a small number of loading cycles whose strain or stress is kept small enough, bitumen behavior can be regarded as linear viscoelastic (LVE).¹⁰² Within this domain, the experimental measurements of the bituminous

material tend to generate a unique curve regardless of the temperature and frequencies employed during the experimental measurements, thus displaying the so-called thermorheologically simple behavior.^{103,104} This implies that the bitumen can display the same rheological response when subjected to different sets of frequency and temperature, i.e., the Time-Temperature Superposition Principle (TTSP) is applied. This hypothesis allows the construction of a smooth and continuous master curve of both modulus $|G^*|$ and phase angle (ϕ) by shifting horizontally (along the reduced frequency axis) the measured isotherms based on their corresponding shift factors (aT) that can be computed through several methods,¹⁰⁵ such as the William, Landel, and Ferry (WLF)¹⁰⁶ method. The possibility of constructing master curves overcomes the limitations of laboratory tests by permitting the results to be extrapolated to more realistic situations. With aging, the increase in modulus that takes place mainly in conditions where bitumen previously presented a more viscous-like behavior—at high temperatures and/or low frequencies—results in an overall decrease in phase angle, indicating an increasingly elastic-like and less viscous-like material. Several LVE models have been proposed to describe the rheological measurements with few parameters that evolve with aging. The definition of these parameters is achieved by mathematical optimization that reduces as much as possible the differences between the modeled curve and the experimental data.

Analogical or lumped-element models combine discrete analogical elements to simplify the description of a complex mechanical behavior by mathematical approximation, such as the 2 Springs, 2 Parabolic elements, and 1 Dashpot (2S2P1D) model proposed by Olard et al.¹⁰⁷ This model consists of one spring associated in parallel with a branch formed by the association in series of one spring, two parabolic creep elements, and one dashpot. The complex modulus is then given by Equation 2:

$$E^*(i\omega\tau) = E_0 + \frac{E_\infty - E_0}{1 + \delta(i\omega\tau)^{-k} + (i\omega\tau)^{-h} + (i\omega\beta\tau)^{-1}} \quad (2)$$

where:

i = imaginary unit,

ω = frequency in radian per second,

E_0 = static modulus when $\omega\tau \rightarrow 0$ (for binder, $E_0 = 0$),

E_∞ = glassy modulus when $\omega\tau \rightarrow \infty$,

δ = dimensionless calibration constant,

k = ratio $E_{\text{imag}}/E_{\text{real}}$ when $\omega \rightarrow 0$,

h = ratio $E_{\text{imag}}/E_{\text{real}}$ when $\omega \rightarrow \infty$,

β = viscosity at high temperature and/or low frequency,

τ = characteristic time.

Aged bitumens^{108,109} and those extracted from aged asphalt mixes^{55,110}, both in the laboratory, result in changes in the other terms of Equation 2: G_∞ remains unchanged; δ tends to increase, k remains unchanged^{55,109,110} or decrease¹⁰⁸, h remains unchanged¹⁰⁹ or decrease^{55,108,110}; β and τ considerably increase. Comparing trends in the evolution of each model parameters can sometimes be inconclusive, since depending on the optimization method, some parameters may be privileged over others.

During the SHRP, Christensen and Anderson¹¹¹ proposed the CA model based on the shape of the relaxation spectra to draw the master curves of the stiffness modulus and the phase angle. Unlike the previous model, this model is based on analytical equations (skewed logistic function) whose parameters have physical meaning, such as the Rheological Index (R-value) that describes the overall shape of the master curves and the crossover frequency (ω_c) that is the pulsation

equivalent to the phase angle of 45°. To improve accuracy when the phase angle is greater than 45°, Marasteanu and Anderson¹¹² refined the previous model with the CAM model, described by Equation 3:

$$|G^*(\omega)| = G_{\infty} \left[1 + \left(\frac{\omega_c}{\omega} \right)^k \right]^{-\frac{m}{k}} \quad (3)$$

where ω is the frequency in radian per second. When bitumens are submitted to accelerated laboratory aging protocols^{109,113}, their initial parameters of the CAM model evolve: glassy modulus (G_{∞}) remains unchanged; parameter (k) that is equivalent to the $\log 2/R$ of the CA model decreases as R increases; crossover frequency (ω_c) decreases; and parameter (m) that indicates the velocity at which the phase angle converges to the two asymptotes slightly increases.

The results, whether experimental, modeled, or both, are illustrated by different graphical representations that underline different aspects of rheological behavior as bitumen ages. Among these, several researchers have pointed out the high sensitivity of the Black Space Diagram (phase angle versus G^*) in detecting subtle changes in bitumen, which can provide valuable insights in the prediction of failure mechanisms associated with excessively aged bitumen.^{82,114,115} King et al.⁸² stressed the importance of assessing the evolution of the age-induced cracking performance of bitumen based on its positioning in Black Space. Furthermore, he also proposed the determination of a damage region in Black Space that correlates with the creep stiffness and slope value from the BBR. Following this line, Rowe⁹² proposed this correlation and his findings will be presented in the next subsections.

3.3.3. Rheology-based failure criteria

3.3.3.1. SHRP/Superpave Bitumen Specification

Striving to establish more rational parameters than those previously used for bitumen classification, SHRP proposed in the early 90s a performance-based specification.¹⁸ Also known as Superior Performing Pavements (Superpave), this specification is embodied in AASHTO M320-17¹¹ and categorizes bitumens according to their performance when subjected to several environmental conditions. In this context, the SHRP specification determines the range of temperatures—and thus the geographic area—to which the bitumen can be subjected without jeopardizing the pavement performance. Therefore, bitumen must meet the limits proposed by the SHRP specification not only under different conditions but also at different laboratory aging levels:

1. $|G^*| / \sin\phi$ (at T_1 and 10 rad/s) ≥ 1.0 kPa (fresh bitumen),
2. $|G^*| / \sin\phi$ (at T_1 and 10 rad/s) ≥ 2.2 kPa (RTFOT-aged bitumen),
3. $|G^*| * \sin\phi$ (at T_2 and 10 rad/s) ≤ 5.0 MPa (RTFOT+PAV-aged bitumen),
4. $S(t)$ (at T_3 and $t = 60$ s) ≤ 300 MPa (RTFOT+PAV-aged bitumen),
5. $m\text{-value}(t) = d \log[S(t)]/d \log(t)$ (at T_3 and $t = 60$ s) ≥ 0.3 (RTFOT+PAV-aged bitumen).

These parameters address the main distresses found in asphalt pavements: rutting (2) at high temperatures (T_1), fatigue cracking (3) at intermediate temperatures (T_2), and thermal cracking (4 and 5) at low temperatures (T_3). It is worth mentioning that two pieces of apparatus are required to fulfill all the criteria: the Dynamic Shear Rheometer (DSR) for the parameters (1), (2), and (3); and the Bending Beam Rheometer (BBR) for (4) and (5).

Among these parameters, the one related to fatigue resistance that is based on a dissipated energy concept ($G^*\sin\delta$) has been increasingly criticized due to its inconsistency with the “true” fatigue performance of bitumen.^{82,116–119} Subhy¹¹⁸ stated that the conditions in which the G^* and phase angle are determined (LVE domain) do not represent the magnitude of those experimented

by bitumen within pavements. Other arguments are related to inaccuracies during its conception as well as technological restraints at that time.^{117–119}

The SHRP specification has led researchers from several countries to revisit the procedures routinely used for this purpose. Such and Ramond¹²⁰ tried to transpose the Superpave criteria, which uses the concept of limiting temperatures, to European bitumen specification—where the softening point is a crucial parameter for the employment of a given bitumen. Relying on some simplified hypotheses, some softening point limiting values corresponding to the SHRP parameters (1), (2), and (3) shown above were proposed. They stated that despite the great divergences between the specifications at first, both have the same core: to control bitumen consistency over time to prevent major distresses of pavements. The main difference is that the SHRP methodology does so by controlling the moduli, while the European specification uses rather the softening temperature. Ramond and Such¹²¹ pointed out that direct transposition of the SHRP specification to Europe—without taking into account the different particularities, such as the climatic asphalt—could result in the use of excessively soft bitumens in a French context.

3.3.3.2. Glover-Rowe (G-R) cracking parameter

The Glover-Rowe (G-R) parameter, proposed by Rowe¹²², has widely been employed to assess the non-load cracking resistance of bituminous materials. This method was conceived by rearranging the equation proposed as a surrogate for tensile strain at the failure by Glover et al.⁸⁴, which in turn was based on Kandhal's findings⁸⁵ regarding the good correlation found between ductility and cracking incidence on several roads in Pennsylvania in the early 1970s. The G-R parameter is expressed by Equation 4:

$$G - R = \frac{|G^*|(\cos\delta)^2}{\sin\delta} \quad (4)$$

where $|G^*|$ and φ are the norm or the complex modulus and phase angle, respectively, computed at 15°C and 0.005 rad/s. Based on the ductility limiting values proposed by Kandhal, Rowe proposed that the damage onset and significant cracking due to non-load-related cracking are likely to arise when the value computed is higher or equal to 180 and 450 kPa (updated to 600kPa), respectively. As this parameter is in terms of modulus (G^*) and phase angle (φ), its result is plotted on the Black Space Diagram. By rearranging Equation 4, it can be noted that the G-R parameter is the division of the storage modulus ($|G^*|\cos \varphi$) by the viscous/elastic ratio ($\tan \varphi$) at 15°C and 0.005 rad/s. With aging, the increase in $|G^*|\cos \varphi$ (numerator) and decrease in the viscous/elastic ratio value (denominator) causes the value or G-R to increase as bitumen ages, as seen in several works.^{82,99,116}

3.3.3.3. Limiting phase angle temperatures

In this subsection, limiting values corresponding to a given phase angle value proposed in the technical literature are presented. Roughly speaking, two values of phase angle are predominantly used for performance grading: $\delta=30^\circ$ (and approximate values) and $\delta=45^\circ$. These parameters will be presented chronologically.

Surveys in the mid-1980s conducted by researchers from former “Laboratoire Central des Ponts et Chaussées (LCPC)”, now Université Gustave Eiffel (UGE), in several experimental sections spread across France already emphasized the precision of the temperature corresponding to the phase angle of 45° ($T_{\delta=45^\circ}$) at 7.8 Hz (minimum frequency attained by the Metravib rheometer used in research works at that time) to describe the performance of the studied pavements built with 35/50 pen grade bitumens.^{23,44,46,103} In the GNB report,²³ it is mentioned that this value was suggested by Guy Ramond based on the assumption of self-healing of cracked

pavements, which from a rheological standpoint, this would only be possible when the viscous component of the bitumen is greater than its elastic one. The $T_{(\delta=45^\circ)}$ at 7.8 Hz increases with aging. As mentioned in subsection 3.1, through non-parametric statistical analyses, Ramond et al.⁴⁴ determined that once bitumen displays the $T_{(\delta=45^\circ \text{ at } 7.8 \text{ Hz})} \geq 40^\circ\text{C}$ the asphalt mix will be more prone to thermal cracking for 35/50 pen grade bitumen. In GNB,²³ this threshold value was lowered to 35°C.

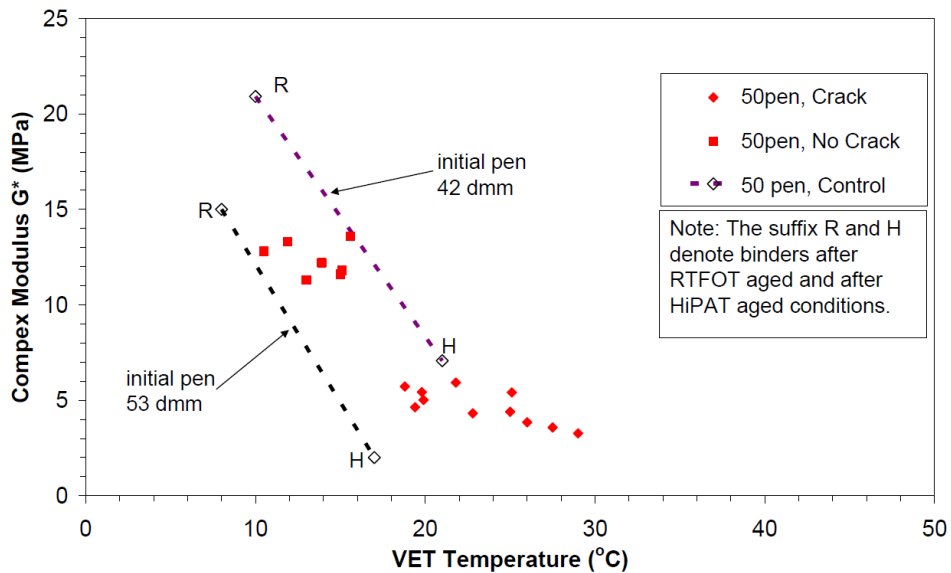
In trying to “translate” the SHRP specification presented in subsection 3.3.3.1 into the French context, Ramond and Such¹²¹ determined the softening point temperatures corresponding to each of the Superpave criteria using Van der Poel’s nomograph.¹²³ Grounded in simplifying assumptions, Ramond and Such determined that the 27° phase angle satisfactorily meets the low and intermediate temperature criteria adjusted to the milder French climate. Ramond and Such¹²¹ conclude that these simplifying hypotheses and the whole concept of the SHRP fatigue criterion may not necessarily correspond to reality and further studies would be necessary. The temperature at which the phase angle value is 27° ($T_{\delta=27^\circ}$) at 7.8 Hz was the parameter that best correlated, along with the BBR m-value, with the cracking incidence of several 7-year-old French pavements built with 35/50 pen bitumen.²³ The $T_{\delta=27^\circ}$ at 7.8 Hz increases with aging and a limiting value of 12°C was proposed in the above-mentioned survey.

Inspired by the ($T_{\delta=45^\circ}$) criterion used in France, Widyatmoko, Elliott and, Heslop¹²⁴ renamed it “Visco-Elastic Transition” (VET) temperature, included the crossover modulus (G^*_{VET}), and changed the frequency to 0.4 Hz. In the T_{VET} versus G^*_{VET} graph (Figure 1), core bitumens from several aged roads across the United Kingdom were placed in different “clusters” that correlated satisfactorily with the performance level observed in these sites. This study concluded that this graphical representation appears to be a useful preliminary screening tool for

assessing the cracking susceptibility of bitumen, although further study would be required to validate it. Moreover, following up his work, Widyatmoko and Elliot¹²⁵ proposed two threshold values, which have yet to be validated: For 15 pen grade bitumen, $T_{VET} < 35^{\circ}\text{C}$ and $G^*_{VET} > 5$ MPa; and for 50 pen grade, $T_{VET} < 20^{\circ}\text{C}$ and $G^*_{VET} > 10$ MPa.

FIGURE 1

T_{VET} VERSUS G^*_{VET} graph for recovered bitumens (50 pen grade) (Widyatmoko¹²⁵)



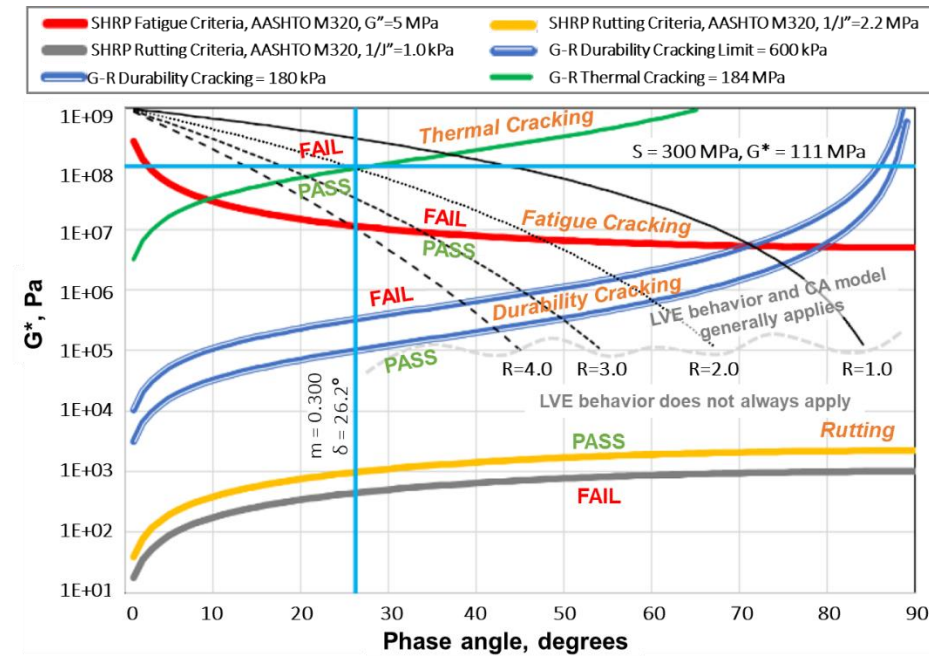
Soleimani, Walsh, and Hesp⁹⁷ stated that the loss tangent, $\tan(\delta)$, that represents the viscous/elastic ratio can provide valuable information on the relaxation ability of bitumen and could therefore serve as a surrogate for thermal fatigue investigation. They noted that the $\tan(\delta)=0.54$, that is, $\delta=28^{\circ}$, at -10°C and 0.1 rad/s after 2-hour conditioning is as accurate as the 72-hour conditioned EBBR in distinguishing good from poor performing sections. Angius, Ding, and Hesp⁹⁸ showed that the temperatures corresponding to phase angle values of 25° , 30° , and 35°

at 10 rad/s are highly correlated with the EBBR grade. Khan et al.⁹⁹ rounded $\delta=28^\circ$ to 30°C and then the $(T_{\delta=30^\circ})$ parameter determined using a regular DSR with 15 minutes conditioning steps has been due to its great correlation with the EBBR test after 72 hours of conditioning. The correlation is not so good for the traditional BBR though, which may be likely because of the confounding effects to which the classical BBR are susceptible, such as reversible hardening. As already mentioned in subsection 3.3.1, the EBBR protocol proved to be more accurate than the traditional BBR; however, the long conditioning time (3 days) could make it unfeasible. In this study, it was proposed two limiting values for $(T_{\delta=30^\circ})$: 0°C for PG -28 and -6°C for PG -34 locations.

Rowe⁹² proposed to simplify the SHRP specification by trying to establish intercorrelations between the BBR and DSR employing discrete relaxation spectra. By doing so, Rowe converted the low-temperature parameters $S \leq 300$ MPa and $m\text{-value} \geq 0.3$ at 60 s to corresponding $G^*=111$ MPa and $\delta=26.2^\circ$, respectively, that can now be plotted on the Black Space Diagram along with the other curves produced by the (G-R) parameter. The thermal cracking curve seen in Figure 2 illustrates the single-event thermal cracking phenomenon determined at 0.005 rad/s by the G-R parameter using the G^* and δ determined from the BBR parameters. As for the gray, yellow, and red curves, they represent the SHRP criteria $|G^*|/\sin\phi$ for fresh bitumen, $|G^*|/\sin\phi$ for RTFOT-aged bitumen, and $|G^*|\sin\phi$ for RTFOT+PAV aged bitumen, respectively, transposed to the G-R parameter conditions. Regarding the R-value curves plotted as well in Figure 2, King⁸² points out their similarities with the limiting curves established by the G-R parameter in the Black Space Diagram and states that these represent the increase in cracking susceptibility with the growth in the R-value as bitumen ages.

FIGURE 2

Black Space Diagram representing several failure criteria (adapted from Rowe⁸⁷)



3.3.4. Discussion on the rheological failure criteria

According to the ‘Point vs. Shape parameters’ discussion raised in Rowe¹²⁶, unlike the ΔT_c that is a shape parameter, i.e., it represents the bitumen master curve fully or partially, all other failure criteria presented in the previous subsection are point parameters—representing a single value at a given condition. It is worth mentioning that point parameters are the most used in existing bitumen specifications.

Despite their particularities, all these criteria that employ temperature corresponding to the phase angle of approximately 30° are highly correlated with the BBR and EBBR m-value, i.e., thermal cracking resistance. It is noteworthy that these phase angle values are in agreement with the relation $\delta/90$ (where δ is the phase angle in degree) proposed in Anderson et al.⁹⁴ to estimate the BBR m-value when it is 0.3. In this case, the advantages of the $T_{(\delta \approx 30^\circ)}$ over the BBR or EBBR are twofold: the conditioning time and the amount of bitumen needed.

In addition to the master curve construction method and rheological model employed, all these rheology-based criteria are entirely dependent on the bitumen stiffness (grade). In Siroma et al.,³⁰ different values for the G-R parameter were computed based on the grade of the studied bitumens. Moreover, different threshold values were proposed for the limiting phase angle temperatures based on the bitumen grade, which according to Rowe and Sharrock⁹¹ this could diminish their usefulness as specification parameters.

As for the limiting values, the ΔT_c and Glover-Rowe (G-R) parameters have the same common origin: Kandhal's ductility findings⁸⁵ in the early 1970s. Despite these parameters are already widespread in several countries, care must be taken when trying to directly transpose the limiting values recommended by these parameters to conditions considerably different from those observed in Pennsylvania (US) where Kandhal's investigations were carried out. Attention in this regard should not only be for these parameters but also all the others mentioned above, whose limiting values stipulated for each depend strongly on the particularities of the geographic area where the study was done.

4. Promising method for bitumen rheological-microstructural coupling: The δ -method

Despite the shortcomings of the Size Exclusion Chromatography (SEC) test raised in subsection 4.1.3, its premise itself appears to be a tremendous issue in determining the bitumen molecular weight distribution (MWD). An alternative to overcome this problem is to estimate the MWD of a given bitumen from its linear viscoelastic behavior, as widely practiced in the field of polymer science with encouraging results.^{78,127} This approach considers that each molecule that composes the material has a unique relaxation frequency below which this molecule ceases to

contribute to the overall mechanical resistance, yielding a reduction in the norm of complex modulus ($|G^*|$) and an increase in phase angle (δ). The intrinsic colloidal system that characterizes bitumen implies that its rheological behavior is influenced rather by molecular associations than individual molecules; therefore, the MWD of bitumen determined through this approach would be rather considered as Apparent Molecular Weight Distribution (AMWD).

For bitumen, Zanzotto, Stastna, and Ho¹²⁸ initially observed that, unlike what was seen for polymers, the $|G^*|$ has limitations in representing the higher molecular weight components (associates). Observing then that the phase angle is sensitive enough for this purpose, Zanzotto, Stastna, and Ho¹²⁹ calibrate the crossover frequency (ω_c) at $T=0^\circ\text{C}$ and the molecular weight (MW) measured via Vapor Pressure Osmometry of several regular bitumens. The equation proposed by Zanzotto, Stastna, and Ho¹²⁹, however, does not correspond with the linear regression seen in the figure where the aforementioned calibration is portrayed. Following up this work, Themeli et al.¹³⁰ present Equation 5 that corresponds better with the linear regression mentioned above:

$$\log(MW) = 2.88 - 0.06767 \log(\omega) \quad (5)$$

where MW is the molecular weight and ω the angular frequency.

Through Equation 5, the phase angle master curve is now represented as a function of molecular weight (MW). Considering the hypothesis presented in the first paragraph of this subsection, the Cumulative Molecular Weight Distribution (CMWD) is proportional to the phase angle master curve and is given by Equation 6:

$$CMWD = \frac{1}{90^\circ} \delta(MW) \quad (6)$$

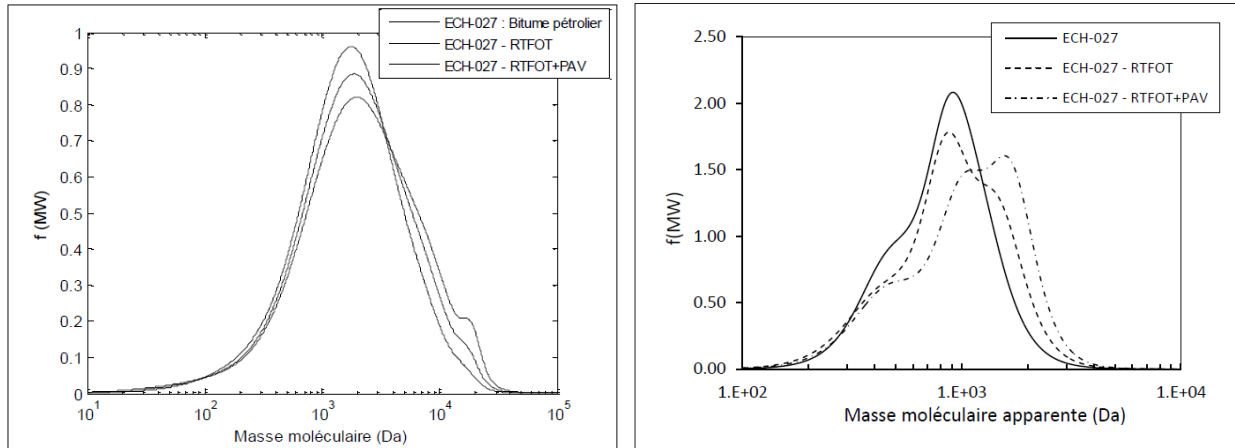
Finally, the fractions corresponding to each AMWD can be calculated through a numerical derivation of CMWD with respect to MW, as seen in Equation 7:

$$f(MW) = \frac{d(CMWD)}{d(\log(MW))} \cong \frac{\Delta(CMWD)}{\Delta(\log(MW))} \quad (7)$$

Recently, Krolkral et al.¹⁰⁸ proposed an alternative method to determine the AMWD through analytical equations using the rheological parameters of the Huet-Such model. It is noted that both the SEC chromatogram (Figure 3 (left)) and AMWD obtained by the δ -method (Figure 3 (right)) display a similar average molecular weight of approximately 1000 Da, which underlines the soundness of this approach. In contrast, a larger MW range is found in the SEC chromatogram when compared to AMWD, which is due to the strong dependence of the first on the test method and conditions.^{131,132} For both cases, the curves shift toward larger molecular weights where a new molecular population emerges (at $MW \approx 20,000$ in SEC chromatogram and $AMWD \approx 2,000$ calculated through the δ -method). The fact that the molecular weight of asphaltene—the most aromatic of the heaviest components of crude oil—is between 500 to 1,000 Da¹³³ shows that the AMWD captures not only single molecules but also molecular agglomerations. Attempts to quantify the AMWD curves by decomposing them into 4 Gaussian curves emphasize the role of light and intermediate fractions in the creation of larger molecules (asphaltenes agglomeration) with aging.^{55,108}

FIGURE 3

Chromatograms (left) and AMWD (right) obtained through the SEC test and δ -method, respectively, for an unchanged bitumen at different aging levels (Themeli¹³⁴)



It is observed in Figure 3 (right) that the changes in the AMWD curves caused by aging are more pronounced, which validates the sensitivity of the δ -method for this purpose. To date, the δ -method proposed by Themeli et al.¹³⁰ has only been used to investigate natural and refined bitumens artificially aged, either by bitumen aging procedures^{108,130,134,135} or extracted and recovered from loose asphalt mix.⁵⁵ Although Zanzotto, Stastna, and Ho's pioneering work¹²⁹ was based on field-aged bitumens, their results are difficult to interpret due to the discrete rheological model used.

Besides providing valuable insights into the microstructural evolution that may occur within bitumen as it ages, the δ -method also underlines the high sensitivity of the phase angle for this purpose. Pauli, Farrar, and Huang¹³⁶ also showed a good correlation of the measured phase angle (at 25°C and 0.1 rad/s) with colloidal dispersed phases, e.g., asphaltenes or SEC fractions.

5. Summary

The end use of bitumen in the paving construction sector is as the binder component in asphalt mixes that compose the layers in a pavement structure. The combination of countless

factors and interactions with one another that will result in the overall response of the pavement structure to the traffic loadings combined with the surrounding environment goes far beyond the already complex understanding of bitumen. However, selecting high-quality bitumen will contribute positively to the asphalt mix performance throughout the years. By addressing efforts to obtain more durable materials and, consequently, preserving the serviceability of pavement structure for a longer time, the paving sector moves toward more sustainable development. Table 2 summarizes all the limiting values found in the technical literature during this review study (values found in bitumen specifications were not included).

TABLE 2

Summary of all failure criteria cited in this work (except for the SHRP bitumen specifications)

Indexes	End-of-life criterion	References
Penetration at 25°C	≤ 20 (0.1 mm)	SETRA ⁴⁸
	≤ 30 (0.1 mm)	Zube et al. ⁴⁷
Softening Point	$\geq 65^{\circ}\text{C}$	GNB ²³
	$\geq 68^{\circ}\text{C}$	Ramond et al. ⁴⁴
	$\geq 70^{\circ}\text{C}$	SETRA ⁴⁸
Asphaltene content	> 0.2	SETRA ⁴⁸
	> 0.22	GNB ²³
	$> 0.23\text{--}0.26$	Huet ⁵⁸
Colloidal Index (CI)	> 0.6	Huet ⁵⁸
ΔT_C (t = 60s)	$\geq -2.5^{\circ}\text{C}$	Anderson et al. ⁸⁶
	$\geq -5.0^{\circ}\text{C}$	
G-R at 15°C and 0.005 rad/s	≥ 180 kPa	Rowe ¹²²
	≥ 600 kPa	Rowe ⁸⁹

	$\geq 184 \text{ MPa}$	Rowe ⁹²
T($\delta=45^\circ\text{C}$) at 7.8 Hz	$\geq 35^\circ\text{C}$	GNB ²³
T($\delta=27^\circ\text{C}$) at 7.8 Hz	$\geq 12^\circ\text{C}$	
T($\delta=45^\circ\text{C}$) at 0.4 Hz (VET)	15 pen: $T_{\text{VET}} \leq 30^\circ\text{C}$ and $G^*_{\text{VET}} \geq 5 \text{ MPa}$	Widyatmoko and Elliot ¹²⁵
	50 pen: $T_{\text{VET}} \leq 20^\circ\text{C}$ and $G^*_{\text{VET}} \geq 10 \text{ MPa}$	
T($\delta=30^\circ\text{C}$)	$\geq -6^\circ\text{C}$ for a PG -28	Khan et al. ⁹⁹
	$\geq 0^\circ\text{C}$ for a PG -34	
ϕ at 15°C and 0.005 rad/s	$\leq 26.2^\circ$	Rowe ⁹²
G at 15°C and 0.005 rad/s	$\geq 111 \text{ MPa}$	

6. Conclusion

The detrimental effects of the aging phenomenon on the durability and, consequently, the serviceability of asphalt pavements are undeniable. In this case, a better understanding of it is of utmost importance for tailoring longer-lasting roads and developing more effective maintenance strategies. For this purpose, this paper presents an in-depth review of the relevant literature on the aging phenomenon of neat (unmodified) bitumen. Based on the review presented and discussed in this work, the following conclusions can be drawn:

- The irreversible changes triggered by aging in bitumen chemistry and molecular structure accumulating over time cause it to stiffen and embrittle, thus impairing pavements' durability as they become more susceptible to cracking.
- RTFOT does not accurately reproduce the processes that occur during short-term aging yet is still a great tool to quantify the aging susceptibility and premature hardening of asphalt mixes.
- PAV, on the other hand, has been the target of criticism regarding its ability to reproduce the expected effects of in-service years of aging, although it is not unanimous. Therefore,

two solutions to achieve higher aging levels are proposed in some previous works: to use of several 20-hour PAV protocols in a row (extended PAV) or reduce the thickness of bitumen film to attenuate the formation of a protective “skin” on the surface of the bitumen sample that would prevent the oxidation of bitumen below the surface.

- It is worth mentioning that the depth of sample coring has a considerable impact on the aging level of the reclaimed bitumen due to the presence of a strong aging gradient below the surface.
- The main problem in either compacted or loose asphalt mix aging procedures comes down to producing aged asphalt mix for performance testing. Although the first is widely used for this purpose, it is difficult to quantify the distortion of the compacted specimen during aging, while the second may present limited compaction of specimens.
- The amount of bitumen needed must be one of the main parameters to be taken into account when assessing the quality and feasibility of a laboratory test to avoid overexposure to organic solvent, which is harmful to humans.
- The advantages of using softening point over penetration to correlate with pavement performance are twofold: the lack of precision of the latter in the measurement of very aged bitumens (high viscosity) and the fact that the softening point test requires much less bitumen than penetration
- The increase in polarity verified by the SARA method can sometimes generate different trends of the colloidal instability index (CI) with aging. FTIR is an attractive test due to its sensitivity and practicality in detecting oxygen uptake in bitumen, although the procedures adopted between laboratories diverge considerably due to the lack of standardization to date. Through the SEC test an increase in larger molecular size (LMS) can be observed;

however, its premise of diluting the bitumen in a solvent, and thus breaking some molecular associations, may result in the loss of crucial information about the molecular structure changes within the bitumen caused by the aging phenomenon.

- The two major criticisms of the BBR test are undoubtedly the excessive amount of bitumen needed and the lack of sensitivity due to the short conditioning time. To address these issues, interconversion techniques between BBR and DSR as well as EBBR (extended BBR) that requires 72 h of conditioning are proposed. Despite improving considerably the accuracy, the extra time needed for EBBR can be problematic.
- Frequency sweep test at multiple temperatures shows an increase in modulus where bitumen previously displayed a more viscous-like behavior and an overall decrease in phase angle, thus indicating an increasingly elastic- and less viscous-like material.
- Several bitumen properties considered effective in classifying the performance of pavements have been proposed in the literature. It can be noted that the parameters related to phase angle can be grouped into two main values: 27° (determined from its good correlation with thermal cracking resistance) and 45° (viscous/elastic balance).
- Care must be taken when trying to directly transpose the limiting values recommended as they are strongly influenced by the particularities of the geographic area where the study was done.
- The results obtained show some similarities between the SEC chromatogram and the AMWD obtained by the δ Method. The fact that the changes in the AMWD curves are more pronounced than those obtained by SEC highlights the sensitivity of the δ Method for this purpose.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the French National Research Agency (ANR) for the financial support of the MoveDVDC project (ANR-17-CE22-0014).

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