Interpreting the effectiveness of antioxidants to increase the resilience of asphalt binders
A global interlaboratory study

Adwani, Dheeraj ; Sreeram, Anand; Pipintakos, Georgios; Mirwald, Johannes ; Wang, Yudi ; Hajj, Ramez ; Jing, Ruxin; Bhasin, Amit

DOI
10.1016/j.conbuildmat.2022.130231

Publication date
2023

Document Version
Final published version

Published in
Construction and Building Materials

Citation (APA)
Adwani, D., Sreeram, A., Pipintakos, G., Mirwald, J., Wang, Y., Hajj, R., Jing, R., & Bhasin, A. (2023). Interpreting the effectiveness of antioxidants to increase the resilience of asphalt binders: A global interlaboratory study. *Construction and Building Materials*, *366*, Article 130231. https://doi.org/10.1016/j.conbuildmat.2022.130231

Construction and Building Materials 366 (2023) 130231

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Interpreting the effectiveness of antioxidants to increase the resilience of asphalt binders: A global interlaboratory study

Dheeraj Adwani [a], Anand Sreeram [a,*], Georgios Pipintakos [b], Johannes Mirwald [c], Yudi Wang [d], Ramez Hajj [d], Ruxin Jing [e], Amit Bhasin [a]

[a] Department of Civil, Architectural and Environmental Engineering, University of Texas at Austin, TX, USA
[b] Department of Construction Engineering, University of Antwerp, Antwerp, Belgium
[c] Christian Doppler Laboratory for Chemo-Mechanical Analysis of Bituminous Materials, Institute of Transportation, TU Wien, Vienna, Austria
[d] Department of Civil and Environmental Engineering, University of Illinois at Urbana Champaign
[e] Faculty of Civil Engineering and Geosciences, Delft University of Technology, the Netherlands

ARTICLE INFO

Keywords:
Antioxidants
Aging
Binder Chemistry
Resilience
Oxidation

ABSTRACT

The design and use of antioxidant additives to reduce or slow down the aging of asphalt binders can bring about tremendous benefits to the asphalt industry. Despite many isolated and scattered research efforts showing mixed results, the application of this science to engineering-based solutions has been limited due to variability in results and conflicting data available. This work presents the results from a global interlaboratory study to test the effectiveness of promising antioxidant additives, namely kraft lignin, calcium hydroxide, zinc diethyldithiocarbamate and phenothiazine to increase the resilience of asphalt binders and provide insights towards understanding the complex intricacies between chemistry and rheology. Specifically, seven different binders from various geographical regions in the world i.e., Texas (USA), Vienna (Austria), Illinois (USA), Antwerp (Belgium), and Delft (Netherlands) were blended with the antioxidants at two proportions. Subsequently, the chemical and rheological properties of the blends were evaluated using Fourier transform infrared (FTIR) spectroscopy and dynamic shear rheometer (DSR). The results indicate that although some antioxidants may reduce oxidation based chemical indices, their effect on rheology is more complicated and possibly related to unique physicochemical interactions in each binder. From a macro-perspective, zinc diethyldithiocarbamate showed promising results with a good correlation between rheology and chemistry for the majority of the binders. These additives or other additives with the same working principles should be investigated further. Additionally, significant research efforts must also be directed towards approaches aimed at understanding mechanisms of interaction and relating results with specific binder compositions.

1. Introduction

The study of aging or the oxidation of asphalt binders has been a focal point of research for asphalt researchers over the past several decades. Its significance can be mainly attributed to the fact that oxidation is a major factor that reduces the lifetime of pavements due to the negative impact it has on binder rheology. Oxidation leads to the increase in stiffness and embrittlement, increase in tensile strength, decrease in the ability to relax, and decrease in ductility of binders [1]. From chemical perspective, oxidation introduces oxygen containing functionalities in the binders which results in increased molecular agglomeration and immobilization of molecules. These increased associations make it more vulnerable to mechanical stress and increase its cracking propensity [2]. As oxidation results in simultaneous changes in the properties of binders over the service life of pavements, any approach to predict the performance properties of mixtures would need to consider this continually changing nature. Hence, understanding the chemistry and chemical changes that occur during asphalt binder oxidation has been the focus of extensive research. Despite widespread efforts, there are still fundamental gaps in knowledge that have prevented the application of this science into practical use in pavements.

Studies on understanding the chemistry of aging in asphalt binders have mainly focused on two areas: the kinetics of aging and the chemical pathways of aging. These areas are fundamentally dissimilar with

---

* Corresponding author.
E-mail address: anand.sreeram@austin.utexas.edu (A. Sreeram).

https://doi.org/10.1016/j.conbuildmat.2022.130231
Received 19 August 2022; Received in revised form 21 November 2022; Accepted 24 December 2022

distinct final objectives. Investigating the kinetics of aging can potentially be used to forecast the rate of oxidation of binders and its effect on performance, both at the binder and mixture level. However, it can be argued that from an engineering perspective, the most significant changes, and improvements to the lifetime of asphalt pavements can be brought about by understanding the chemical pathways of aging, and ultimately controlling the oxidation phenomenon. In that regard, extensive research has been conducted to investigate the various aspects of the oxidation process and on corresponding methods to prevent it using oxidation retarding additives i.e., antioxidants [3]. Antioxidants are chemical additives that can be added to organic materials to defer or lower the rate of degradation caused by the reaction with atmospheric oxygen. In theory, antioxidant additives can be used to prevent or slow down the aging of asphalt binders for pavement applications and improve the long-term durability of asphalt pavements. Therefore, their widespread application could naturally bring about massive benefit to the asphalt industry. When considering the use of antioxidants, the chemistry and chemical composition of asphalt binders would play a major role as it determines its propensity to oxidation, products formed, and other important parameters. Since asphalt binders consist of millions of different hydrocarbon molecules, they are typically separated into four polarity-based fractions, i.e., saturates, naphthalene aromatics, polar aromatics, and asphaltenes (in increasing order of polarity). The relative amounts of these fractions can vary depending on the crude source and refining process, and are susceptible to change as oxidation and aging take place over the course of its life cycle [4]. It is understood that the composition of binders and relative extents of polar fractions will strongly dictate the rate of oxidation and oxidation related chemistry of binders [5,6].

A considerable amount of research has been conducted on the use of antioxidants to reduce the extent1 and rate of aging in binders. For example, organic phenylamines and zinc dithiocarbonates have been extensively studied to gage their effectiveness as antioxidants [7,8]. Apart from this, research also exists on the use of other additives such as lime, lignin and different synthetic polymers, and their antioxidant capabilities [9,10]. Overall, despite of several hundred peer-reviewed research papers on this topic, very little is known about the effectiveness of antioxidants and widespread applicability when considering geographically (and chemically) different binders. The reported findings are also dispersed and sometimes conflicting which has limited their use in practice. Other than the complex chemical mechanisms involved, this can be attributed to the various approaches and materials used to assess the impact of antioxidant additives when contemplating the general nature of variability of bituminous materials. Moreover, there is limited understanding regarding the relationship between the chemistry and rheology of antioxidant modified binders. For example, when considering a varied suite of binders, it is still unclear if the antioxidant effect seen from a chemical perspective after aging can be correlated to changes in rheological properties such as binder stiffening [11,12]. Understanding these complexities will help unlock some of the mechanisms in action and provide a pathway for engineering applications.

With the onset of climate change, the increased focus on pavement resilience by transportation agencies has put focus on antioxidants in asphalt pavement applications once again. As mentioned, several decades of myopic research in this area have not yielded significant results for the community. In consideration of the potentially remarkable innovations possible with validation of such a technology, a global collaborative effort is required to advance the understanding of the science and make progress in this area. Hence, the objective of this work is to conduct a global interlaboratory study with a wide range of diverse materials to improve the understanding of the science; and to ultimately employ this understanding to validate the possibility for practice level applications. It is expected that this unprecedented team effort will also accelerate progress in addressing some of the fundamental gaps in knowledge in the area of asphalt oxidation and effective use of antioxidant additives.

2. Scope

This study presents the initial results from a global collaborative effort to test the effectiveness of four promising antioxidant additives to increase the resilience of asphalt binders and further provide insights towards understanding the complex intricacies between chemistry and rheology of such modified binders. Specifically, seven binders originating from different crude oil sources and used in different geographical regions in the world were blended with the antioxidants at two different proportions. Following this, the chemical and rheological properties of the various blends were evaluated using Fourier transform infrared (FTIR) spectroscopy and dynamic shear rheometer (DSR) based methods to identify and correlate relevant trends in oxidative behavior and rheological properties. Overall, the work conducted is expected to shed significant insights into the effectiveness of antioxidants when considering a diverse suite of chemically different binders. The results presented are also expected to help guide material selection in the future and provide outlook for further research in this topic. In view of the aims of the study, it must be noted that the results and analysis are presented from a macro-perspective in order to evaluate the potential use of antioxidants on a large scale in routine field applications.

3. Materials and procedures

Based on an extensive literature review conducted by the authors, four different antioxidants were selected in this study namely kraft lignin, calcium hydroxide, zinc diethyldithiocarbamate and phenothiazine. These additives were selected specifically as several prior extensive studies in this domain have indicated their potential to be used as effective antioxidants for asphalt binders [12,13,14]. It should be noted that these positive effects were reported based on the respective test materials and analyses conducted in the various studies. The chemical structure and images of the different additives used are presented in Fig. 1 and Fig. 2 respectively. Additionally, Table 1 lists the additional details regarding the additives.

When comparing the working principle of the additives, in theory zinc diethyldithiocarbamate and phenothiazine are expected to act as peroxide decomposers, whereas, kraft lignin has chemical properties that can make it effective as a free radical scavenger. Lastly, calcium hydroxide is a chemical additive that can be used to inhibit agglomeration of oxidation products. All additives were used in two different dosages (3 and 5 binder wt.%) as per the recommendations in the

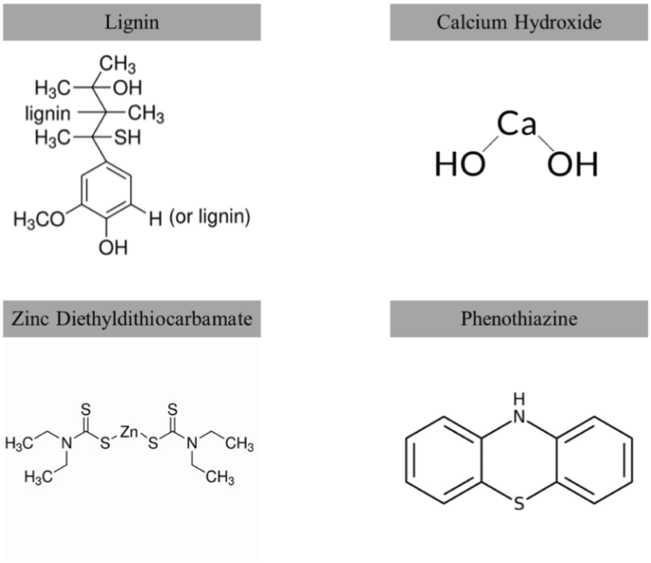


Fig. 1. Chemical structure of antioxidants used in the study.

Fig. 2. Pictures of antioxidants used in the study.

Table 1
Details of antioxidants used in the study.

Name	Manufacturer	CAS No.	Dosages (binder wt.%)	Code (used in study)
Kraft Lignin	Sigma Aldrich	8068–05-1	3 % & 5 %	Lig
Calcium Hydroxide	Sigma Aldrich	1305–62-0	3 % & 5 %	CaH
Zinc Diethyldithiocarbamate	Sigma Aldrich	14324–55-1	3 % & 5 %	ZDC
Phenothiazine	Fisher Scientific	92–84-2	3 % & 5 %	Pheno

various studies reviewed. Seven different unmodified binders were chosen from the various participating laboratories in Texas (USA), Illinois (USA), Vienna (Austria), Antwerp (Belgium), and Delft (Netherlands). These participating laboratories are a subset of a larger collaborative team working on the subsequent phases of this study. These binders were specifically sourced from different producers and geographical locations, and hence expected to have varying chemical compositions. The geographical location of the binders is important in the context of this work as the source of crude can significantly affect binder's chemical properties. The details of the binders along with the nomenclature used in this study are listed in Table 2. The binders are designated as per the Superpave performance grading in accordance with ASTM D6373 and AASHTO M320.

3.1. *Blending procedures*

Two dosages of each additive, 3 % and 5 % by weight of the binder were blended with different base binders. Based on the melting point of the selected antioxidants, different blending protocols were adopted for the four additives. For Lig and CaH, mixing of the additives with base binders was done at 165 °C for a period of 60 min at 600 rpm. For the remaining two additives ZDC and Pheno, the blending was carried out at 190 °C for a period of 20 min followed by reduced temperature of 165 °C for a period of 40 min at 600 rpm. Following blending, the binders were short-term aged using the rolling thin-film oven (RTFO) aging procedure at 163 °C for 85 min as per ASTM D2872. Subsequently, the binders were long-term aged using the pressure aging vessel (PAV) aging procedure at 100 °C for 20 h as per ASTM D652.

Table 2
Details of binders used in the study.

Binder No.	Binder Grade	Source	University/Lab	Nomenclature
Binder 1	PG 64–22	Texas	University of Texas at Austin	T1
Binder 2	PG 64–22	Texas	University of Texas at Austin	T2
Binder 3	PG 64–22	Texas	University of Texas at Austin	T3
Binder 4	PG 64–22	Antwerp	University of Antwerp	A1
Binder 5	PG 58–22	Vienna	Vienna University of Technology	V1
Binder 6	PG 64–22	Delft	Delft University of Technology	D1
Binder 7	PG 64–22	Illinois	University of Illinois Urbana-Champaign	I1

4. Experimental methods

The flowchart in Fig. 3 shows the experimental program of this study. Both chemical and rheological analyses were conducted to identify the various facets associated with the use of antioxidants in binders. It is important to note that the different tests mentioned here were conducted separately in the respective laboratories of the participating institutions as listed in Table 2. However, the impact of aging is assessed by normalizing results from the same binder and laboratory, and therefore the collective results are less susceptible to interlaboratory biases.

4.1. *Dynamic shear rheometer*

The high temperature stiffness of various binders was assessed using a DSR at temperatures of 58 °C, 64 °C, and 70 °C. The instrument was used to measure the complex shear modulus and phase angle at a static frequency of 10 rad/s, strain amplitude of 12 % for unaged and 10 % RTFO aged binders. A 25 mm plate was used in a parallel plate geometry at three different temperatures, and the gap between the two circular plates was set at 1 mm. Likewise, to calculate the intermediate temperature rheology and associated parameters of the PAV aged binders, an 8 mm plate was used with the gap between the two plates set at 2 mm. The testing was conducted at a strain amplitude of 1 % and at three temperatures depending on the grade of the binder. The DSR testing was conducted as per ASTM D7175 and AASHTO T315. All tests were conducted in two replicates and the results show the average value.

4.2. *FTIR spectroscopy*

FTIR spectroscopy has been widely used as a method to understand aging in asphalt binders through assessing changes in oxidation related functional groups in the absorbance spectra. In particular, the implementation of the attenuated total reflection geometry (ATR) has increased the practicability of the method since the binder can directly be applied onto the crystal. For sample preparation, a small binder quantity was heated and homogenized following recommendations from an earlier study [15]. Prior to each measurement a background spectrum of the empty and clean ATR crystal was recorded. The FTIR spectra for each binder were recorded from wavenumbers 600 cm^{-1} to 4000 cm^{-1} using different instruments in the respective laboratories. All tests were

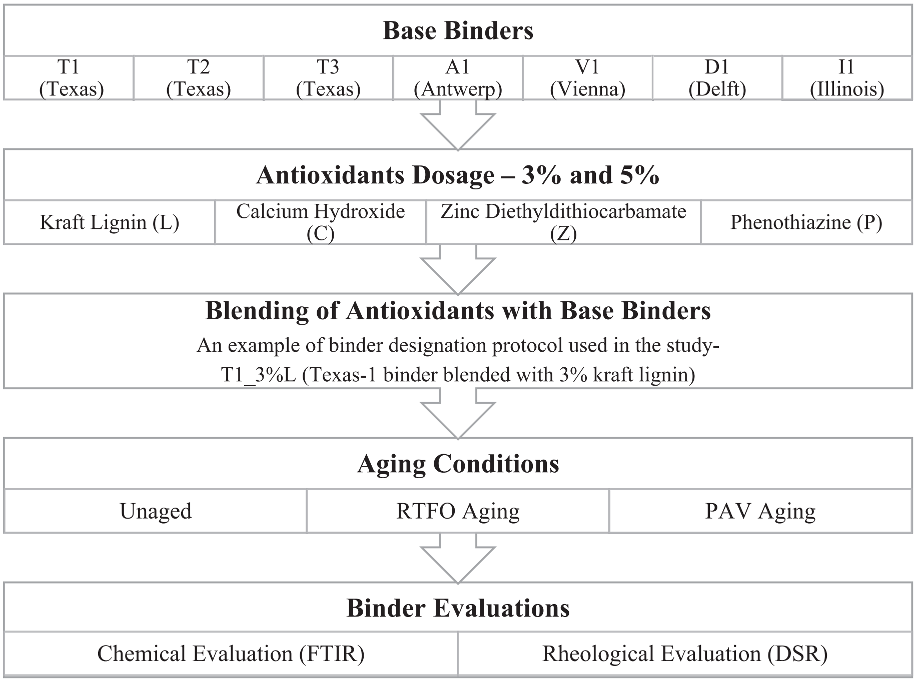


Fig. 3. Experimental program of the study.

conducted on at least two replicates and the results show the average value. A method reported in a previous study was used to quantify the oxidation related functional group bands [16]. In this study, area under C=O band (defined from 1666 cm^{-1} to 1746 cm^{-1}) and S=O band (defined from 944 cm^{-1} to 1066 cm^{-1}) were calculated using full baseline integration. However, the C=O band was primarily used to study the aging levels of different binders as it is known to correlate better with long-term aging as compared to the S=O band [17]. Also, some additives may interfere with the S=O band. A higher area under the carbonyl band indicates higher levels of oxidative aging. The area under each FTIR spectrum was calculated after normalization as per the following equation:

$$S = \int_{N_{l,os}}^{N_{u,os}} VS_{norm}(N)dw \tag{1}$$

where S is total area, $N_{u,os}$ is the threshold for higher wavenumber of the structural group, $N_{l,os}$ is the threshold for the lower wavenumber of the structural group, and $VS_{norm}(N)$ is the absorbance at wavenumber N that is normalized. Based on the carbonyl indices of the binders, an aging index (AI_{CO}) was defined as

$$AI_{CO} = \frac{CO_{PAV}}{CO_{RTFO}} \tag{2}$$

where CO_{PAV} is the area under carbonyl band for PAV aged binder and CO_{RTFO} is the area under carbonyl band for RTFO aged binder.

5. Results and discussion

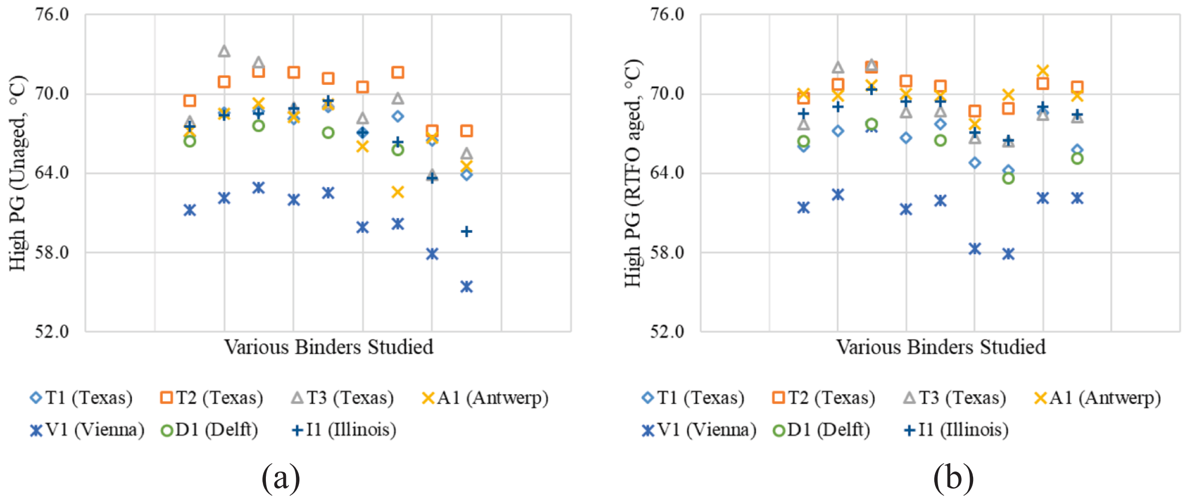
5.1. Diversity in data

The tests conducted by the different laboratories generated a large amount of data with considerable variation in results. This is expected due to the general variability when contemplating the use of different base binders. Although the asphalt binder used could be of the same grade, its chemical constitution would be unique, and hence its interaction with different additives is expected to be distinct. Additionally, the tests were conducted on different equipment and by different operators from individual laboratories, so the variances in results would also be exacerbated in that regard.

The G*/sinδ parameter as covered in AASHTO T316 was used to evaluate the data in terms of high temperature performance grade (PG) and the results are shown as per the unaged binder criteria and RTFO aged binder criteria in Fig. 4. The high PG grade of unaged binders is defined as the temperature where the value of G*/sinδ is 1 kPa. Similarly, for RTFO aged binders, the high PG grade is the temperature where the same value is 2.2 kPa. It could be observed that most of the high PG values were between 64 °C and 70 °C respectively even after antioxidant modification, which indicates minimal effect on initial stiffness of the base binders. However, for the binders from Vienna, the PG results were between 58 °C and 64 °C respectively. This is expected as its original binder grade was PG 58–22. Interestingly, some of the high PG results were higher for the RTFO aged binder as opposed to the unaged binder which shows that different antioxidants have varying effects on stiffness during short-term aging. This is discussed in detail in the next section. Similarly, the C=O and S=O indices were calculated for the different binders as described in previous sections and the results are shown in Fig. 5. Different values for the indices were observed which were then used to calculate the aging indices. It should be noted that although FTIR based indices are not necessarily quantitative measurements, they can be used to semi-quantitatively estimate the relative change in oxidation related properties when comparing individual binders in different aging states [18,19].

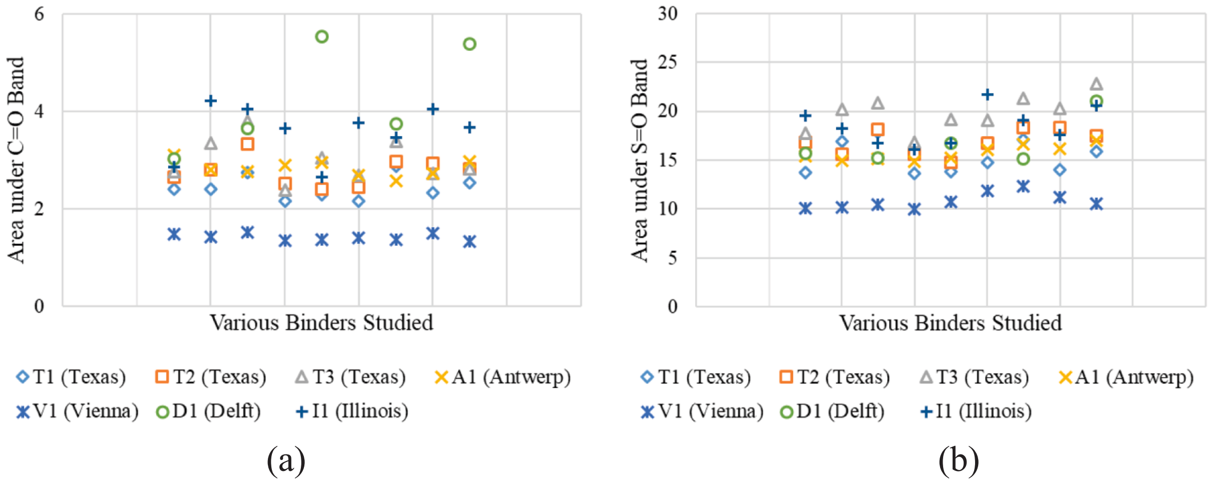
5.2. *Effect of antioxidants on binder stiffness after blending and short-term aging*

Antioxidants are expected to chemically interact with asphalt binders and hence may change their physical properties. The initial effect of the antioxidants on base binder stiffness can be observed by looking at the respective stiffness indicators of the binders, such as the high PG grade. The high PG grades for the different binders in the unaged and RTFO aged state are shown in Fig. 6. Generally speaking, the addition of the antioxidants had minimal effect (less than 5 %) on the unaged and RTFO high PG grade of the base binders used in this study. Specifically, ZDC and CaH modified binders showed similar values as



(a) (b)

Fig. 4. Global data set of high PG of a) Unaged, b) RTFO aged binders.



(a) (b)

Fig. 5. Global data set of FTIR index of a) C=O Band, b) S=O Band.

compared to the respective base binders whereas Lig modified binders showed a very marginal increase. Overall, the results indicate that their addition has insignificant effects on initial binder stiffness and may not provide additional significant rheological benefits at high temperature, such as in terms of rutting resistance etc. However, for the case of Pheno, an opposite trend could generally be observed wherein the initial base binder stiffness was seen to be decreasing with its addition indicating a softening of the binder with modification.

When considering the stiffness properties of the binders after RTFO (short-term) aging, some interesting results could be noticed. Short-term aging is generally characterized by loss of volatiles and rapid aging during the mixing process which results in an increase in stiffness [20]. Therefore, comparison of high PG grades in these two aging states is a direct measurement of the rate of increase in the stiffness of the binders. Comparable results were observed for the Lig and CaH modified binders, i.e., their rate of increase in stiffness was seen to be generally similar to the base binder. However, for the ZDC and Pheno modified binders, the results were more varied. Pheno modified binders, which were initially seen to have lower stiffness after blending (unaged state), significantly increased stiffness after short-term aging for most of the evaluated binders. Contrary to that, the rate of increase in stiffness was seen to be considerably lower for the ZDC modified binders. This was observed for the *T*-series as well as the V1 binder. For the A1 binder, the opposite trend was observed especially at 5 % additive modification. Moreover, the rate of change of stiffness was also observed to be varied for each binder which shows the effect of bitumen variability on antioxidant effectives, even at the short-term aging level. It is understood that more robust rheological analysis should be conducted to effectively quantify the differences in stiffness. However, this is beyond the scope of this work and further studies will be directed in that regard.

5.3. *Effect of antioxidants on long-term aging*

The main purpose of using antioxidants in binders is to delay or reduce the extent of oxidation over the course of its lifetime. Hence, its effectiveness (or lack of) can only be judged after long-term aging of binders. In this study, long-term aging of the binders was conducted using the PAV aging method as described in previous sections. The effects of the different antioxidants on the aging behavior of binders were assessed through both chemical and rheological methods. For the sake of brevity and conciseness, some relevant results from the analysis conducted are presented in the next sections.

5.3.1. *Evaluation of oxidation metrics using FTIR*

The long-term aging of the various binders considerably increased their oxidation-based indices when evaluated using the FTIR. The

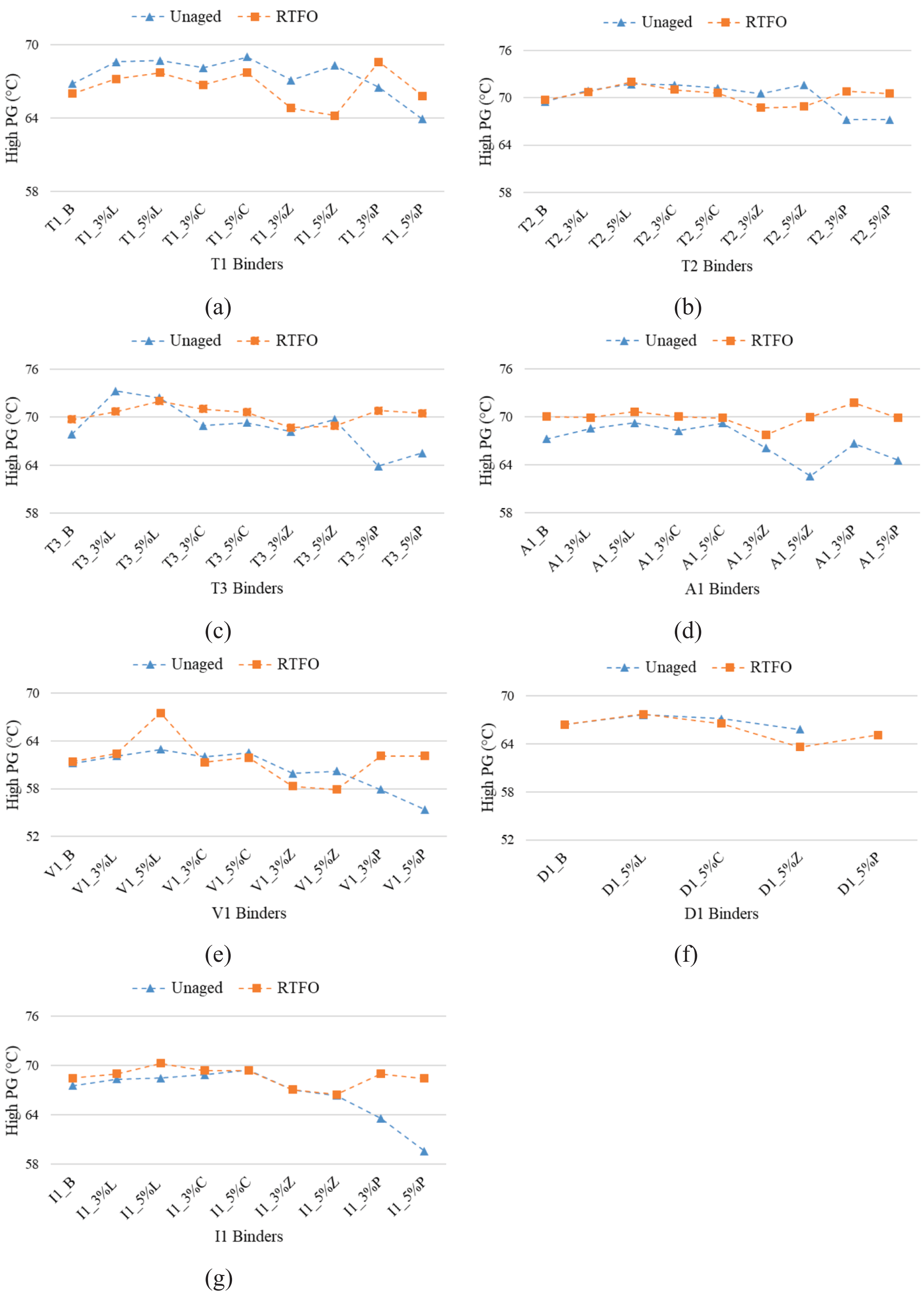


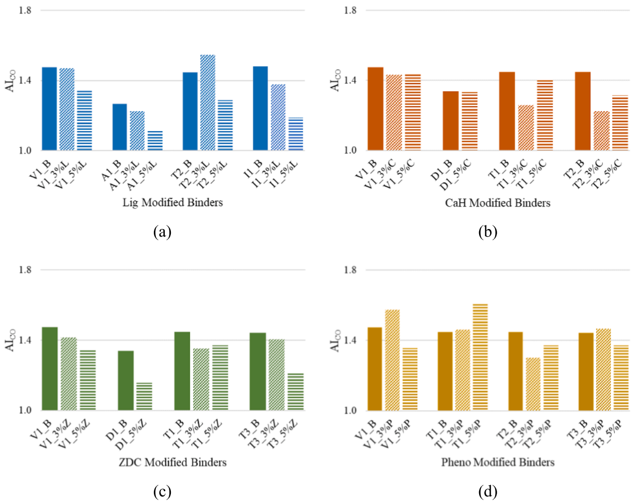
Fig. 6. High PG under unaged and RTFO aged state for (a) T1 binders, (b) T2 binders, (c) T3 binders, (d) A1 binders, (e) V1 binders, (f) D1 binders, and (g) I1 binders.

increase in these indices over time is a well reported phenomenon. The chemical pathways responsible have been studied in detail by researchers, detailing the conversion of aliphatic sulphides to sulphoxides and benzylic carbon to carbonyl groups [1]. In this process, the molecular structuring in the binders is transformed through the dissociation, isomerisation, and fragmentation of the asphaltene molecules, the dissociation of aromatics molecules, and the association, cyclisation, and dissociation of saturate molecules [21]. The aging indices, which are measure of relative aging extent were calculated for the different binders as described in previous sections and some of the important results are shown in Fig. 7.

Varying results were obtained when considering the aging indices of the modified binders with respect to the base binder. Pheno in general showed poor results and the aging indices observed were comparable or higher in some cases. However, the other modified binders with ZDC, Lig and CaH showed considerable reduction in the aging indices as compared to the base binders. When looking at dosages, a higher dosage of 5 % seemed to a have a greater effect in reducing the aging index for ZDC and Lig modified binders. It should be noted that these results are based on general trends observed for all the binders tested in the study and not individual cases as some variation was seen for specific binders. Nevertheless, it is interesting to note that although the mechanisms of action would be different for each antioxidant, its use seemed to largely reduce the formation of oxidation related functional groups through binder modification. For example, it is anticipated that preventive oxidants such as ZDC would act as peroxide decomposers and reduce the formation of free radicals in the oxidation initiation step, thereby slowing down the oxidation process [22]. Contrary to that, CaH would reduce the formation of oxidative groups in different ways such as through the chemisorption of pro-oxidant species and absorption of some oxidative species [23]. The oxidation propensity of each binder is unique to its chemical composition and the variations seen in the reduction of oxidation indices for different binders (when considering the same antioxidant) indicates that the specific chemical properties of each binder could be affecting its effectiveness. This needs further deliberation, and its implications are reflected upon in the later sections of this study.

5.3.2. Effect of long-term aging on rheology using DSR

Ultimately the purpose of using antioxidants in asphalt applications is to prolong the lifespan of pavements through increased resilience and fatigue cracking resistance. Therefore, it could be argued that the rheological properties after aging are the most important criteria to evaluate the effectiveness of antioxidants. In this study, the G*.sinδ parameter was used to evaluate the stiffness of the antioxidant binders. This parameter is commonly referred to as the “fatigue factor” in the Superpave specification and lower values of this parameter are desired from the standpoint of resistance to fatigue cracking, characterized in rheological terms by lower binder stiffness. Some important results of the various binders are presented in Fig. 8 and show the value of G*.sinδ for the different binders at 25 °C. Firstly, it is important to interpret these results in relation with the previous results of the study. It was seen from the high PG results that the change in stiffness with the addition of the antioxidants was generally marginal for CaH, Lig and ZDC modification and the increase in stiffness with the addition of Pheno was evident (after RTFO aging). Therefore, it can be assumed the value of G*.sinδ for ZDC, Lig and CaH modified binders is an indirect measurement for the antioxidant effectiveness to reduce age related hardening in terms of binder rheology.



(a) (b)

(c) (d)

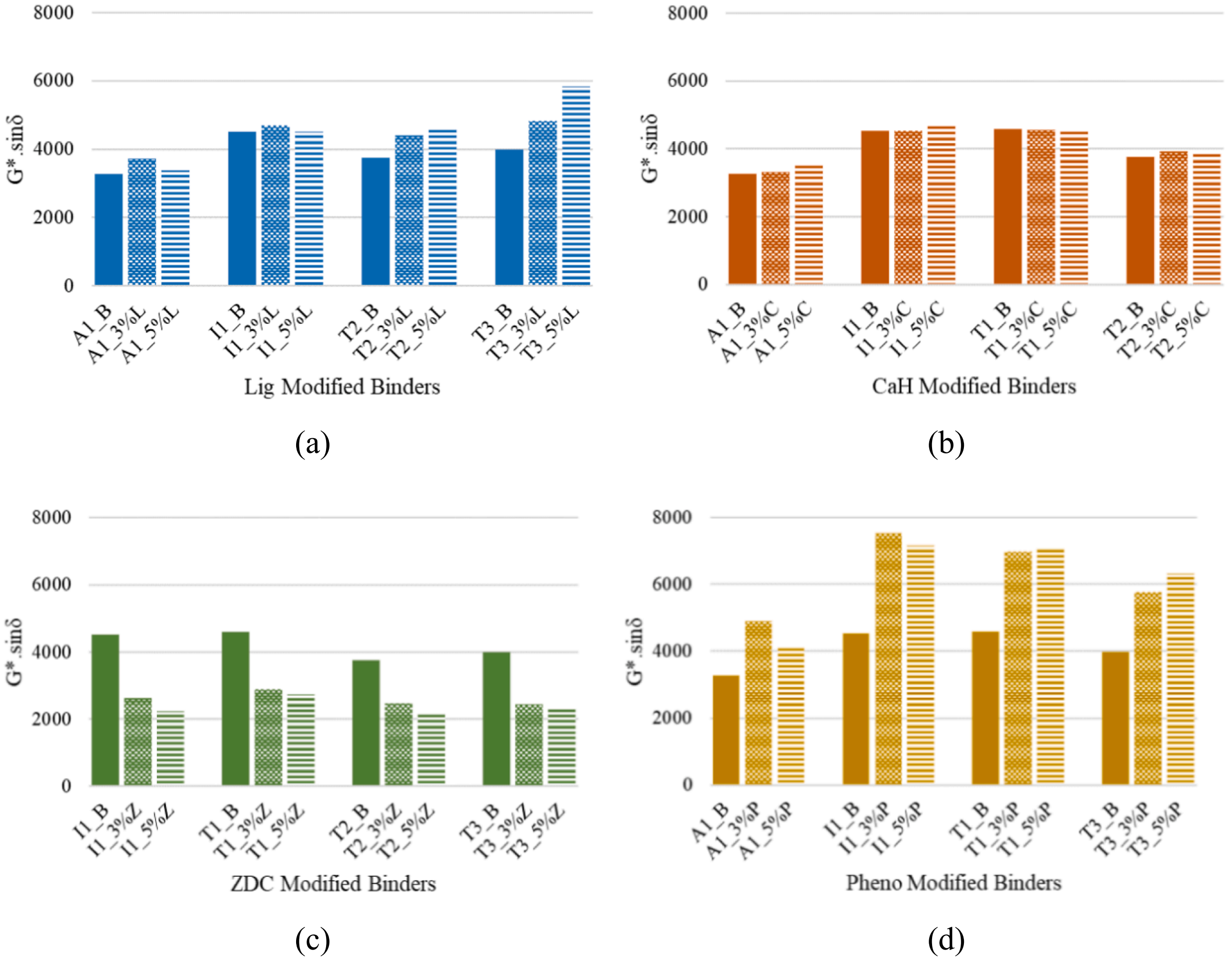
Fig. 7. Aging indices based on $C{=}O$ band for selected binders with (a) Lig, (b) CaH, (c) ZDC, and (d) Pheno.

As detailed in the previous section related to FTIR, ZDC, Lig and CaH showed considerable potential to reduce the aging indices of the base binders. It is generally understood that the lower the amounts of oxidative groups formed during aging, the lesser will be the rate of binder stiffening [1]. Noteworthy results were observed when correlating this to the G*.sinδ parameter from the DSR tests. Pheno showed higher stiffness which is understandable considering its higher stiffness after short-term aging and inconsistent ability to reduce the formation of oxidative functional groups. Lig and CaH modified binders showed interesting results as they exhibited higher or similar values of G*.sinδ as compared to the base binder. This was despite the fact that such modification resulted in lower aging indices for many of the binders tested. Such results suggest that the issues of binder stiffening of such modified binders may be more complicated, and beyond merely the reduction of oxidative groups. In the case of ZDC modified binders, G*.sinδ values observed were lower indicating that these binders have reduced propensity to age. Hence, ZDC modified binders showed a reasonable correlation between chemistry and rheology and is in general the best performing antioxidant on a global scale. Nevertheless, it must be noted again that these results have been summarized based on general trends and there is variability in the case of specific binders which illustrates the complexity when considering the use of such additives on an individual basis. The implications of these are discussed in the next section. It should also be mentioned that the G*.sinδ parameter cannot fully capture the rate of stiffening in terms of changes in binder rheology during aging. Therefore, further studies are planned in that regard.

5.4. Discussion

As mentioned in the scope of the study, this work investigated the effectives of antioxidants when considering a global suite of binders from various geographical locations. Firstly, it is important to note that the effectiveness of an antioxidant will likely be contingent on the significance of the process it inhibits in the overall binder oxidation chemistry, and hence depends on the different chemical interactions between the constituents in the modified binder [12]. The different results shown in this study indicate the physicochemical processes driving antioxidant behaviors in binders are highly complicated, and beyond merely the reduction of oxidative groups. In that regard, some previous studies have also suggested that some antioxidants may affect oxidative hardening of binders in other ways such as through influencing asphaltene dispersion and subsequently its fractional component compatibility [1]. Currently, there is limited understanding in this area and further research is required to understand its rheological implications, specific to each antioxidant.

When considering the various antioxidants evaluated in this study, ZDC seemed to be the most promising additive wherein it generally showed improved aging resistance for many of the different base binders used in this study. The other additives tested were generally a “hit or miss” and no clear trend could be observed between rheology and chemistry of the binders. Even for the most promising additives such as



(a) (b)

(c) (d)

Fig. 8. Superpave parameter G*.sinδ at 25 °C for selected binders with (a) Lig, (b) CaH, (c) ZDC, and (d) Pheno.

ZDC, the rate of change of rheological and chemical properties seemed to be unique to each individual binder. Understanding the mechanisms driving such behavior is critical when considering the use of such additives in practice. Without a fundamental comprehension of material interaction, engineering mixes to perform as required would be an unsystematic and futile approach. Lastly, there are other aspects to be considered such as costs. Some antioxidants may only provide some marginal benefits in terms of performance on an indiscriminate basis as per the current state of knowledge in this area. Therefore, their large-scale use may not make economic sense when considering other issues such as additional handling, processing, and safety requirements. Overall, the results from this work using a wide variety of globally procured base binders indicate that a “one size fits all” approach commonly used in asphalt research may not be suitable to study the effectiveness of antioxidants on a macro scale. Although some additives such as ZDC hold considerable promise, significant knowledge gaps in understanding its mechanisms of action and influence of bitumen composition needs to be addressed before considering its use in field-based applications. Additionally, this study focused on preliminary results from a larger collaborative effort planned over multiple phases. A known limitation in the aforementioned results is that when comparing the modified binder to the base binder, the effect of the additive on the rheology of the binder itself is not fully captured by the testing methods. This will be considered in future studies by conducting more comprehensive frequency-temperature sweep tests and further advanced rheological characterization.

6. Direction for future studies

Theoretically, the use of certain antioxidants can reduce the age hardening effect of binders and enhance its service life. However, bringing this theory into fruition for engineering applications requires extensive research in several fundamental areas with knowledge gaps. The findings from this study indicate that certain additives such as ZDC may hold more potential than other additives such as Pheno when considering their use as a high-performance antioxidant for different globally produced binders. Nevertheless, building on such promise to reach a level where such additives can be routinely used with confidence requires a considerable number of important questions to be answered.

Most research efforts in this area have generally investigated the effectiveness of a certain type of antioxidant using a small suite of locally available binders. As shown from the results presented here, there is a significant amount of variability in effectiveness depending on the source and composition of the binder. This variability must be embraced by researchers, and underlying factors or unique binder fingerprints that lead to this must be investigated. Specifically, it is important to comprehensively study the effect of binder chemical composition on antioxidant effectiveness. Only such strategies will allow the community to move away from the “hit or miss” approach and utilize the body of information to develop methodologies that can be deployed on a more routine basis. Lastly, the development of accurate characterization methods when considering the rheology and chemistry of such modified binders is also warranted. For example, more advanced chemical characterization approaches can be used to identify the difference of molecular structuring of binders (if any) when modified with specific antioxidants.

7. Findings and conclusions

This study presents the initial results from a global effort to test the effectiveness of four promising antioxidant additives to increase the resilience of asphalt binders and further provide insights towards understanding the complex intricacies between the chemistry and rheology of such modified binders. Specifically, seven different binders from various geographical regions in the world including Texas (USA), Vienna (Austria), Illinois (USA), Antwerp (Belgium), and Delft (Netherlands) were blended with four different antioxidants at various proportions. Following this, the chemical and rheological properties of the various blends were evaluated using Fourier transform infrared spectroscopy (FTIR) and dynamic shear rheometer (DSR) based methods to identify and correlate relevant tendencies in oxidative behavior and rheological properties. Varying results and trends were observed from the large amount of data gathered, and the results were analyzed using a macro-level lens considering practicability of this technology. It was seen that most of the antioxidants used showed some tendencies to lower the aging indices of the binders when evaluated using FTIR. However, this trend could not be matched when looking at binder stiffening indicators and rheology. This is likely due to multiple mechanisms that are unique to the additive-binder pair and their compatibility that may exist to impact the overall rheological behavior. Out of the different antioxidants tested, ZDC showed promising results with a good correlation between rheology and chemistry for the majority of the binders. These additives or other additives with the same working principle should be investigated further using an even wider suite of materials.

Overall, the work conducted in this study presents a first of its kind interlaboratory effort to study the effectiveness of different antioxidants. The results obtained in the study suggest that the current approaches commonly used in the community will be insufficient to raise this technology into a mature level for routine engineering applications. Research efforts must be directed towards approaches aimed at understanding fundamental mechanisms of interaction of the constituent materials and relating experimental data with specific binder compositions and fingerprints. As part of this global effort, ongoing work is being conducted in different aspects such as evaluating the effect of antioxidants on binder rheology using advanced rheological methods including characterization of low temperature properties. The results obtained here in regard to the most promising additives have also been used to start the second phase of testing of the most promising additives with eleven additional laboratories around the world. Lastly, the technical feasibility of using such additives in field needs to be explored after laboratory scale analysis.

8. Disclaimer

The contents of the paper reflect the views of the authors, who are responsible for the data presented herein. This paper does not constitute a standard, specification, or regulation. Manufacturer names of the additives are presented as they are deemed essential to the work conducted in the study.

CRediT authorship contribution statement

Dheeraj Adwani: Investigation, Formal analysis, Writing – original draft, Writing – review & editing. **Anand Sreeram:** Conceptualization, Methodology, Investigation, Formal analysis, Writing – original draft, Writing – review & editing. **Georgios Pipintakos:** Methodology, Investigation, Formal analysis, Writing – review & editing. **Johannes Mirwald:** Methodology, Investigation, Formal analysis, Writing – review & editing. **Yudi Wang:** Investigation, Formal analysis, Writing – review & editing. **Ramez Hajj:** Investigation, Formal analysis, Writing – review & editing. **Ruxin Jing:** Investigation, Formal analysis, Writing – review & editing. **Amit Bhasin:** Conceptualization, Methodology, Formal analysis, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

References

[1] J.C. Petersen, A Review of the Fundamentals of Asphalt Oxidation: Chemical, Physicochemical, Physical Property, and Durability Relationships, Transp. Res. Board (2009), https://doi.org/10.17226/23002.

[2] A. Sreeram, Z. Leng, R. Hajj, A. Bhasin, Characterization of compatibility between aged and unaged binders in bituminous mixtures through an extended HSP model of solubility, Fuel. 254 (2019), 115578, https://doi.org/10.1016/j.fuel.2019.05.161.

[3] B.D. Beitchman, Effects of antioxidants on asphalt durability, J. Res. Natl. Bureau Standards. 64C (1959) 13–17.

[4] J. Mirwald, S. Werkovits, I. Camargo, D. Maschauer, B. Hofko, H. Grothe, Understanding bitumen ageing by investigation of its polarity fractions, Constr. Build. Mater. 250 (2020), 118809, https://doi.org/10.1016/j.conbuildmat.2020.118809.

[5] W.H. King, L.W. Corbett, Relative Oxygen Absorption and Volatility Properties of Submicron Films of Asphalt Using the Quartz Crystal Microbalance, Anal. Chem. 41 (1969) 580–583, https://doi.org/10.1021/ac60273a005.

[6] J. Knotnerus, Bitumen Durability—Measurement by Oxygen Absorption, Ind. Eng. Chem. Prod. Res. Dev. 11 (1972) 411–422, https://doi.org/10.1021/i360044a011.

[7] R.S. Wurstner, W.A. Higgins, W.G. Craig, Laboratory evaluation of factors influencing the performance of paving asphalts, in: Proceedings of the Association of Asphalt Paving Technologists, 1960, pp. 233–274.

[8] R.M. Januszke, Paving Asphalt Additives in Durability Determination, Ind. Eng. Chem. Prod. Res. Dev. 10 (1971) 209–214, https://doi.org/10.1021/i360038a021.

[9] C.V. Chachas, W.J. Liddle, D.E. Petersen, Use of hydrated lime in bituminous mixtures to decrease hardening of the asphalt cement, 1971.

[10] R.C. Williams, Using Lignin as an Asphalt Antioxidant, (2008). www.ctre.iastate.edu (accessed June 21, 2022).

[11] I.G.do N. Camargo, T. Ben Dhia, A. Loulizi, B. Hofko, J. Mirwald, Anti-aging additives: proposed evaluation process based on literature review, Road Mater. Pavement Des. 22 (2021) S134–S153, https://doi.org/10.1080/14680629.2021.1906738.

[12] P.R. Herrington, Antioxidants for Roading Bitumen (Report No. 50), 1995.

[13] H.F. Haghshenas, E. Fini, R. Rea, A. Khodaii, Increasing the efficacy of recycling agents with simultaneous addition of zinc diethyldithiocarbamate as an antioxidant, Constr. Build. Mater. 271 (2021), 121892, https://doi.org/10.1016/j.conbuildmat.2020.121892.

[14] S. Arafat, N. Kumar, N.M. Wasiuddin, E.O. Owhe, J.G. Lynam, Sustainable lignin to enhance asphalt binder oxidative aging properties and mix properties, J. Clean. Prod. 217 (2019) 456–468, https://doi.org/10.1016/j.jclepro.2019.01.238.

[15] J. Mirwald, D. Nura, B. Hofko, Recommendations for handling bitumen prior to FTIR spectroscopy, Mater. Struct./Materiaux et Constructions. 55 (2022) 1–17, https://doi.org/10.1617/s11527-022-01884-1.

[16] A. Sreeram, Z. Leng, Y. Zhang, R.K. Padhan, Evaluation of RAP binder mobilisation and blending efficiency in bituminous mixtures: An approach using ATR-FTIR and artificial aggregate, Constr. Build. Mater. 179 (2018) 245–253, https://doi.org/10.1016/j.conbuildmat.2018.05.154.

[17] A. Sreeram, Z. Leng, Variability of rap binder mobilisation in hot mix asphalt mixtures, Constr. Build. Mater. 201 (2019) 502–509, https://doi.org/10.1016/j.conbuildmat.2018.12.212.

[18] A. Sreeram, Z. Leng, R. Hajj, W.L.G. Ferreira, Z. Tan, A. Bhasin, Fundamental investigation of the interaction mechanism between new and aged binders in binder blends, Int. J. Pavement Eng. 23 (2022) 1317–1327, https://doi.org/10.1080/10298436.2020.1799208.

[19] B. Hofko, M.Z. Alavi, H. Grothe, D. Jones, J. Harvey, Repeatability and sensitivity of FTIR ATR spectral analysis methods for bituminous binders, Mater. Struct./Materiaux et Constructions. 50 (2017) 1–15, https://doi.org/10.1617/s11527-017-1059-x.

[20] L.D. Poulikakos, S. dos Santos, M. Bueno, S. Kuentzel, M. Hugener, M.N. Partl, Influence of short and long term aging on chemical, microstructural and macro-mechanical properties of recycled asphalt mixtures, Constr. Build. Mater. 51 (2014) 414–423, https://doi.org/10.1016/j.conbuildmat.2013.11.004.

[21] M.N. Siddiqui, M.F. Ali, Investigation of chemical transformations by NMR and GPC during the laboratory aging of Arabian asphalt, Fuel. 78 (1999) 1407–1416, https://doi.org/10.1016/S0016-2361(99)00080-0.
[22] J.A. Brydson, Plastics Materials, Elsevier Science, 1995.
[23] H. Plancher, E.L. Green, J.C. Petersen, Reduction of oxidative hardening of asphalts by treatment with hydrated lime - A mechanistic study, 45 (1976).