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Examining the Efficacy of Promising Antioxidants to Mitigate Asphalt Binder Oxidation: Insights from a Worldwide Interlaboratory Investigation

Oxidative aging induces significant stiffening of asphalt binders that leads to a pronounced reduction in the overall durability of asphalt pavements. The strategic implementation of antioxidant additives provides a potential solution to alleviate this issue. Antioxidants can theoretically reduce oxidative aging rate and extend the operational lifespan of pavements. This work presents results from the second phase of the global consortium for antioxidants research aimed at investigating the effectiveness of potential antioxidants in increasing the durability of asphalt binders. Sixteen laboratories around the world participated in this effort and a total of 28 binders from diverse geographical regions were tested. Two promising antioxidants, namely zinc diethyldithiocarbamate (ZDC) and kraft lignin were evaluated in this phase and blended with the binders at specific proportions. Subsequently, a comprehensive investigation was conducted to assess rheological characteristics and chemical properties of the various blends, utilizing Dynamic Shear Rheometer (DSR) measurements and Fourier Transform Infrared (FTIR) Spectroscopy. The findings indicate that additives such as ZDC hold considerable promise as an effective antioxidant, particularly when considering a wide diversity of binders. In general, its incorporation does not compromise the rutting performance of the binders and significantly improves fatigue performance. Therefore, research efforts should be focused on exploring additional facets to assess its practical applicability in field. On the contrary, kraft lignin demonstrated more varied performance outcomes, with results being promising but generally not as effective as ZDC. This highlights the necessity for further investigation to comprehensively grasp the intricate nature of interaction of antioxidants with binders.

Keywords: asphalt oxidation; binder aging; antioxidant additives; binder rheology; binder chemistry

Introduction

Asphalt binder is the binding material that holds aggregates together and provides strength and durability to asphalt concrete mixtures. However, over time, asphalt binder undergoes aging and oxidative degradation due to exposure to environmental oxygen. This degradation significantly compromises the mechanical properties of asphalt concrete, leading to various pavement distresses such as cracking, raveling, and loss of flexibility (Petersen, 2009). As a result, the lifespans of pavements are reduced, necessitating frequent repairs and maintenance, which not only incur substantial costs but also contribute to environmental concerns through increased energy consumption and greenhouse gas emissions (Tauste et al., 2018). To address this challenge, researchers and industry professionals have turned their attention to the utilization of antioxidants in asphalt pavements (B. D. Beitchman, 1960; Herrington, 1995). Antioxidants are chemical additives that in theory mitigate or decrease the rate of oxidation by inhibiting the oxidation process in binders. Successful deployment of antioxidants in pavement applications can have significant effects as it would be possible to prolong service life of pavements, enhance its resistance to aging related damage, and ultimately ensure the sustainability and longevity of infrastructure (Camargo et al., 2021).

The use of antioxidants in asphalt binder dates back several decades with earliest reported studies from the late 1960s (B. Beitchman, 1960). The addition of antioxidants to binders as modifiers serves to regulate oxidation by capturing or eliminating free radicals and associated species, which are responsible for initiating and spreading the oxidation process (Dessouky et al., 2015). Additionally, certain antioxidants also interact with polar compounds and oxidation catalysts, including metals found in asphalt, to further enhance their protective effects (Sirin et al., 2018). When considering the large number of antioxidant-related studies in the literature over the past several decades, the reported results have been mostly empirical in nature with no clear explanations of the contradictory and inconsistent results presented. For instance, there has been significant research conducted on the effectiveness of organic phenylamines and zinc dithiocarbonates as antioxidants (Januszke, 1971; Wurstner et al., 1960). However, its extent of effectiveness and efficacy to be used in practical applications is still not known. Similarly, investigations have also explored the antioxidant capabilities of additional additives such as lime, lignin, and various synthetic polymers without any real tangible outcomes (Chachas et al., 1971). Critically, the correlation between the binder chemistry and observed rheology of antioxidant-modified binders remains poorly elucidated. When examining a diverse range of binders, it remains uncertain whether the observed antioxidant effect from a chemical standpoint after aging can be linked to alterations in rheological properties (Apeagyei, 2011; Santucci et al., 1981). Gaining insight into these intricate relationships will facilitate the comprehension of underlying mechanisms and pave the way for practical engineering applications.

Overall, it can be summarized that despite the abundance of numerous peer-reviewed research works on the subject, the understanding of the effectiveness and broad applicability of antioxidants remains limited in the asphalt research community, especially when considering the variations in geographical and chemical characteristics of different binders. In recent times, a global consortium was started with over fifteen different laboratories around the world with the aim of building upon the prior research on antioxidants and aging, and to substantially improve the understanding of the science and ultimately employ this understanding to validate the possibility for practice-level applications. The first phase (Phase -1) of the consortium tested seven different binders from five participating laboratories and evaluated their efficacy with four promising antioxidants (Adwani et al., 2023). Following the results from the previous study, the second phase of the consortium with sixteen consortium members continued this effort. This present work documents the results and findings from the second phase of this unique and large-scale global collaborative effort among universities from around the world.

Insights from previous study (Phase-1)

In Phase-1 of the consortium, the effectiveness of four promising antioxidant additives, namely kraft lignin, calcium hydroxide, zinc diethyldithiocarbamate (ZDC) and phenothiazine was evaluated using seven different binders from various geographical regions: Texas (USA), Vienna (Austria), Illinois (USA), Antwerp (Belgium), and Delft (Netherlands), blended at two additive proportions (3% and 5%). The study evaluated performance using Fourier Transform Infrared (FTIR) Spectroscopy and Dynamic Shear Rheometer (DSR) to identify and correlate relevant tendencies in oxidative behavior and rheological properties. The investigation revealed that the majority of antioxidants employed exhibited a certain degree of effectiveness in reducing the formation of carbonyls functional groups, as assessed through FTIR analysis. However, this correlation did not hold when considering indicators of binder stiffening and rheology. This disparity was attributed to the presence of multiple mechanisms that are specific to the additive-binder combination and their compatibility, which potentially influence the overall rheological behavior. Among the antioxidants examined, ZDC and kraft lignin demonstrated generally promising outcomes when considering the diversity of binders tested and hence were considered for further analysis in Phase 2 with sixteen participating laboratories. ZDC is expected to work as a peroxide decomposer, i.e., reacting with peroxide, an important precursor in binder oxidation (James, 2002; Sreeram et al., 2022). Kraft lignin on another hand has a chemical structure that makes it likely effective as a free radical scavenger (de Lima Neto et al., 2023). Free radicals are formed during the breaking of carbon-carbon bonds within the molecular structure of asphalt binder during oxidation and these free radicals react with oxygen to form oxidative bonds (Petersen, 2009).

Scope

This work presents results from Phase-2 of a global collaborative effort conducted to examine the efficacy of promising antioxidants to mitigate the oxidation of asphalt binders. In total, 28 binders were tested from various geographical regions. These binders were blended with two antioxidants, namely zinc diethyldithiocarbamate (ZDC) and kraft lignin at two specific proportions. Subsequently, a thorough investigation was undertaken to evaluate the chemical composition and rheological attributes of the different blends utilizing techniques such as Fourier Transform Infrared (FTIR) Spectroscopy and Dynamic Shear Rheometer (DSR) measurements. The main objective of the analysis included identifying and establishing significant trends relating rheological properties and oxidative behavior of antioxidant modified binders, in order to facilitate its widespread use in the future. Overall, this research is expected to offer valuable perspectives on the efficacy of antioxidants in relation to a wide range of geographically diverse binders. The outcomes presented are also anticipated to serve as a significant resource for informing the selection of promising antioxidants and offer insights into the direction for further exploration in the subject for the research community.

Materials And Procedures

This phase involved the use of 28 different binders from North America, South America, Europe, and Asia; the source locations are shown in the map in Figure 1. The high PG grade of these binders varied from 58°C to 76°C and Table 1 lists the binders along with the nomenclature used to denote these binders in this work. Two antioxidants, namely zinc diethyldithiocarbamate (ZDC) and kraft lignin (called lignin in this study) were used as the modifiers for the various binders. Table 2 illustrates the details of these antioxidants with the nomenclature used. The antioxidants additives used were standardized to ensure the uniformity of the additives used by any participating laboratory. In other words, the only material that varied from one laboratory to another was the base binder. Figure 2 shows the chemical structure and physical appearance of the additives. Furthermore, for such a large dataset, a well-defined nomenclature of binders was set up as listed in Table 1 and Table 2. For example, UT1_3%L refers to UT1 binder from the University of Texas at Austin blended with 3% kraft lignin (base binders are denoted by code B after the underscore).

Blending and laboratory aging of binders

The antioxidants were blended with the base binders in the respective laboratories at two different proportions, 3% and 5% by weight of the binder. Different blending temperatures were adopted for the two additives based on their melting points. For lignin, blending was conducted at 165℃ and 600 rpm for a period of 60 minutes. ZDC was blended at 190℃ for 20 minutes followed by 165℃ for 40 minutes at constant rotation of 600 rpm. The volume of binders used for blending was around 500 mL for all the blends. It is acknowledged and understood that the use of the two modification percentages and same blending conditions for each binder may not be sufficient to fully illustrate the effectiveness of the antioxidants with respect to each individual binder. However, these percentages were chosen based on results from Phase-1 as well as practical considerations. The binders were short-term aged at 163℃ for 85 minutes using the rolling thin-film oven (RTFO) in accordance with ASTM D2872. The binders were then subsequently long-term aged for 20 hours at 2.1 MPa pressure and 100℃ using the pressure aging vessel (PAV) in accordance with ASTM D652.

Experimental Methods

Firstly, it is important to emphasize that this was a voluntary collaborative effort across multiple laboratories around the world. Consequently, only the most foundational methods and metrics were used to evaluate the influence of aging at this stage of this study. The experimental program included rheological and chemical investigations and the experiments were conducted in each participating laboratory with their respective equipment. It is acknowledged that different equipment manufacturers were used by the various laboratories when considering the suite of tests. Nevertheless, it was ensured that exactly the same testing procedures were followed in all the laboratories using standardized protocols. Further, in order to minimize bias between laboratories in relation to FTIR tests, all results were analyzed by normalizing the results using the spectral base lines measured in respective laboratories. Additional details regarding the methods are provided in the respective sections of the paper. Lastly, for both DSR and FTIR evaluations, at least two replicates were tested, and the results presented are the average values.

Rheological evaluations

DSR performance grading

The high and intermediate temperature evaluation of the binders were conducted following Superpave performance grading methods using the DSR in accordance with ASTM D7175 and AASHTO T315. The high temperature analysis was conducted for unaged and short-term aged binders at temperatures ranging from 58°C to 88°C. The complex modulus (G*) and phase angle (δ) were measured using oscillation testing at an angular frequency of 10 rad/s and strain amplitude of 12% for unaged and 10% for short-term aged binders. The high temperature testing was conducted using a 25 mm diameter and 1 mm gap parallel plate geometry. The intermediate temperature testing was performed on PAV aged binders at temperatures ranging 28°C to 16°C using an 8 mm diameter and 2 mm gap parallel plate geometry. G* and δ were measured from the oscillation testing at an angular frequency of 10 rad/s and strain amplitude of 1%.

Stiffening index based on oscillation testing

Apart from Superpave performance testing, testing was conducted on RTFO aged and PAV aged binders to establish a rheology based aging index denoted as "stiffening index" in this study. For calculating this index, the G* was obtained from the oscillation testing of binders at a particular temperature. The oscillation testing on DSR was conducted using a 25 mm diameter and 1 mm gap parallel plate geometry at a strain amplitude of 1%, and an angular frequency of 10 rad/s. The test was conducted at two temperatures, 30°C and 40°C, selected to reflect normal pavement service temperatures (Han et al., 2011). Using this, the stiffening index (SI) was defined as the ratio of complex modulus for the aged state to the unaged or lower aged state (i.e., PAV to RTFO) and represented in Eq (1).

$$SI = {G^*_{aged1}}\Big/{G^*_{aged2}} \quad (1)$$

In the above equation, G^*_{aged1}, is the complex modulus for higher aged condition, which is PAV aging in this case, and G^*_{aged2}, is the complex modulus for lower aged condition, i.e., RTFO aged condition.

FTIR spectroscopy

FTIR spectroscopy is one of the widely used methods to assess the aging effects in asphalt binders through the analysis of infrared active functional groups that form upon aging. Although FTIR spectroscopy is a semi-quantitative tool, in the context of this study, it is sufficient to evaluate and compare binders in different aging states (Sreeram et al., 2018b). In the present study, the participating laboratories used the attenuated total reflection (ATR) method for spectroscopy measurements, owing to the practicality of the method for faster evaluations (Mirwald et al., 2022). A testing guideline was prepared based on the previous literature and used by all the laboratories to ensure uniformity in the testing procedure (Mirwald et al., 2022; Sreeram et al., 2018b). The method to calculate the functional group band values was based on a well-known method (Sreeram et al., 2018b). In this method, analysis of the FTIR spectra involved the integration of areas, normalized spectra, and absolute baseline (Mirwald et al., 2022). It is generally accepted that carbonyl band (C=O) defined from 1666 cm^{-1} to 1746 cm^{-1} and sulfoxide band (S=O) defined from 944 cm^{-1} to 1066 cm^{-1} are good indicators of oxidation induced aging. Specifically, the C=O band has shown better correlation with respect to long-term aging compared to the S=O band (Sreeram and Leng, 2019). Due to specific antioxidant bands appearing near the S=O region, a sufficient integration and evaluation method has not yet been found. Therefore, the present work used the C=O band area calculated through the baseline integration method. Equation 2 demonstrates C=O band area calculation of each spectrum.

$$A = \int_{w_l,\,1666}^{w_h,\,1746} A_n(w)\,dw \quad (2)$$

In the above equation, A is the area under the band, w_h is the high wavenumber threshold for the functional group, defined at 1746 cm^{-1}, w_l is the low wavenumber threshold, defined at 1666 cm^{--1}, $A_n(w)$ is the normalized absorbance at wavenumber w. To compare binders and analyze the effects of long-term aging, an aging index (AI_{CO}) was defined as the ratio of the carbonyl band area for PAV aged to RTFO aged condition. Equation 3 shows the definition of AI_{CO}.

$$AI_{CO} = \frac{CO_{aged1}}{CO_{aged2}} \qquad (3)$$

In the above equation, CO_{aged1} is the carbonyl band area for PAV aged binder, and CO_{aged2} is the band area for RTFO aged binder.

Results and Discussion

The tests carried out by various laboratories resulted in a substantial volume of data to be analyzed, exhibiting both subtle and significant variations in results. Such discrepancies are to be anticipated considering the inherent diversity arising from the utilization of base binders from different geographical regions. It is important to note that despite using asphalt binders of identical grades, their chemical compositions remain distinct which can lead to varied interactions with the various additives (White et al., 1970). The results analysis presented in the following sections are derived from overarching trends obtained from the data, in accordance with the defined scope and objectives of this phase of the consortium.

Stiffness based on high temperature PG (High PG)

Figure 3 and Figure 4 show the High PG results of the various base binders modified using ZDC (Figure 3 (a) and 4(a)) and Lignin (Figure 3 (b) and 4(b)). As per AASHTO T316, the analysis for high temperature PG involves utilizing the G*/sinδ parameter, also commonly denoted as "Superpave rutting parameter." For unaged binders, the true high PG grade is defined as the temperature at which the G*/sinδ value equals 1 kPa. On the other hand, for RTFO aged binders, the true high PG grade is determined by determining the temperature at which the G*/sinδ value equals 2.2 kPa. Generally, these are interpolated between measurements taken at typical PG values, which occur every 6℃. The results for the true high PG at the unaged state are shown in Figure 3. To show a generalized effect of binder modification with these additives, the average of true PGs was calculated for the suite of binders and plotted in the figure along with the individual binders' High PG. In general, the results indicated that at the unaged state, the addition of ZDC had a minimal effect on the rheology of unmodified binder whereas the addition of lignin seemed to have a slight stiffening effect. The average high PG results show an average nominal reduction of 0.3℃ for ZDC modified binders compared to the base binder average. Similar results were obtained in a prior study that used this antioxidant and indicates the importance of choosing an optimum dosage to avoid the possibility of excessive deformation or rutting with excessively high dosages (Haghshenas et al., 2021).

The addition of lignin was seen to increase the average high PG by around 1.8℃ compared to the base binders' average. However, this addition was generally not drastic enough to change the nominal PG of the binder. Similar trends were also seen in the Phase-1 study conducted with lesser diversity of binders (Adwani et al., 2023). When considering the use of lignin, it is important to consider the mechanisms which lead to a rise in stiffness when used. Lignin constitutes a class of polyphenolic compounds characterized by a variety of functional groups, including aliphatic groups, diverse phenolic hydroxyl groups, and carboxyl groups. These structural attributes potentially enable the formation of robust intermolecular hydrogen bonds within the lignin matrix, thereby exerting noticeable influence on its intermolecular interactions with binder constituents. These interactions are postulated to decrease the molecular mobility of the binder, thereby increasing its stiffness (Zhang et al., 2021).

From the perspective of practice, the long-term aging of binders is initiated with the laying of pavement and continues throughout the service life. Therefore, it can be argued that the properties of the binders after RTFO aging are essentially the starting point when studying long-term aging and antiaging characteristics i.e., the effectiveness of antioxidants. When considering the RTFO aged binders, the High PG results were slightly amplified for one modifier. The average High PG of ZDC modified binders showed a reduction of 1.7℃ (from 66.8℃ to 65.1℃) when compared to the base binder. This indicates that during short-term aging simulation, the rate of the increase of stiffness is likely lower on average than in the base binders. For the lignin modified binders, the results for RTFO aged binders were similar to the unaged condition i.e., an increase of 1.5℃ in the average high PG with lignin addition (from 66.8℃ to 68.3℃). Short-term aging is characterized by the volatilization of certain components and accelerated aging phenomena occurring concomitantly with the mixing process. Consequently, this process induces a considerable increase in the binder stiffness. The mechanisms of oxidation during short-term aging are significantly different than long-term aging due to the increased temperatures (Kim et al., 2018) and there is inadequate research regarding the efficacy of such antioxidants to limit the extent of short-term aging.

Stiffness based on intermediate temperature PG (Intermediate PG)

The primary objective behind incorporating antioxidants in asphalt applications is to enhance the longevity of pavements by extending their durability and resistance against cracking. Consequently, it can be contended that the evaluation of the rheological properties after long term aging (LTA) is the most crucial criterion for assessing the efficacy of antioxidants. In this work, the stiffness of antioxidant binders was assessed using the G*.sinδ parameter. Widely known as the “fatigue parameter” in Superpave specifications, this parameter is typically associated with resistance to fatigue cracking (Deacon et al., 1997). In rheological terms, lower values of this parameter correspond to reduced binder stiffness, signifying improved resistance to fatigue-induced cracking. The parameter is also used to calculate the intermediate PG (termed as Intermediate PG in this study) for the PAV aged binders tested with a limiting criterion of G*.sinδ as 5000 kPa. It is important to recognize here that although contemporary literature clearly and rightfully recognizes that this is not an accurate indicator of fatigue cracking resistance, for the purposes of this study, this parameter can be used as a qualitative indicator for the extent of oxidative aging.

Figure 5 shows the intermediate PG of the various binders tested in this study. The average Intermediate PG of the virgin binder was around 22℃ whereas the binders modified with ZDC showed a considerably lower Intermediate PG of close to 19℃, i.e., a change of one intermediate temperature grade. This indicates that in general these binders will have a lower propensity to fatigue cracking, and indirectly also signifies the effectiveness of the antioxidant in reducing aging. However, it should be noted that the higher content of ZDC did not necessarily imply a higher effectiveness against cracking, at least when considering a global average. For the lignin modified binders, the results were not as promising as the Intermediate PG averages were slightly higher than the base binder average (1℃ increase in Intermediate PG). Nevertheless, it is important to point out that in general, lignin addition increased the stiffness of the binder at the unaged and short-term aged conditions. So, the comparison of Intermediate PG of lignin modified binders with the base binders may not be an appropriate approach. Lastly, is important to highlight that the findings presented herein are derived from overarching trends observed across all tested binders in the study, and not from individual cases, as certain variations were observed for specific binders.

To further illustrate the effect of the antioxidants on the binder rheology after LTA, some salient results of the G*.sinδ parameter at 25℃ are presented in Figure 6 and Figure 7. For clarity, the figures are divided into binders for each additive resulting in Intermediate PG greater than 25℃ and those less than 25℃. The effect of ZDC to lower the Intermediate PG of most of the binders is clearly visible in these results. In some cases, such as UIUC1, UIUC2, UT3, BUT1, UNot1, HKPU1, and UBol2 binders, the value of this parameter was remarkably reduced by about 50%. These results indicate that ZDC can likely improve the intermediate temperature cracking resistance without any significant effect on the rutting performance of the binder (as per the high PG evaluation).

When considering the lignin modified binders, the results were more varied. In some cases, the modification slightly increased the G*.sinδ value, whereas in most cases it seemed to have a negligible effect. Such results further illustrate the complexities when deliberating the large-scale applicability of such antioxidants. It is evident that the addition of lignin will likely increase the rutting related properties of binders, however, its effect as an effective antioxidant is debatable when considering a global suite of binders. Further, lignin is a highly complex polymer with high heterogeneity and its interaction with asphalt binder is a sophisticated process which may account for the high variability observed in results here (Zhang et al., 2021).

Statistical analysis of high and intermediate temperature PG

In addition to the global averages representing the general trend in properties, the changes in stiffness parameters for the unaged, RTFO, and PAV aged binders on modification were also studied using statistical tools. For the unaged and RTFO aged binders, the relative change in stiffness in terms of G*/sinδ at 64°C on antioxidant addition was calculated for each binder. Similarly, the relative change in stiffness in terms of G*.sinδ at 25°C on antioxidant addition was calculated for the PAV aged binders. Accordingly, a relative stiffness parameter was defined as shown in equation (4). In the equation, G* and δ represent complex modulus and phase angle at the specific testing temperature and conditions, respectively.

Relative stiffness parameter for:

$$\text{Unaged and RTFO aged binders (\%)} = \frac{\frac{G^*}{\sin\delta}\text{(modified)} - \frac{G^*}{\sin\delta}\text{(base)}}{\frac{G^*}{\sin\delta}\text{(base)}} \text{ x } 100$$

$$\text{PAV aged binders (\%)} = \frac{G^*.\sin\delta(\text{modified}) - G^*.\sin\delta(\text{base})}{G^*.\sin\delta(\text{base})} \text{ x } 100 \qquad (4)$$

The distributions of the relative stiffness parameter for the three aging conditions were plotted for the suite of modified binders considering normal distribution, as shown in Figure 8. The Mean and Standard Deviation (SD) for the distributions are also shown in the plots. The distribution plots in Figure 8 (a) and (b) suggest that the addition of ZDC itself did not alter the average stiffness of the unaged binders, as apparent from the negligible relative stiffness parameter for the unaged binders. For the RTFO and PAV aged binders, the relative stiffness reduces significantly for the ZDC modified binders. For example, the 3% and 5% ZDC addition showed mean relative stiffness parameter of -35% to -37% after PAV aging, which suggests a significant reduction in stiffness after aging as compared to the control binder. In the case of lignin, the distribution plots in Figure 8 (c) and (d) suggest that on average, addition of lignin increased the stiffness of unaged binders by 27% to 29%. Post RTFO and PAV aging, the relative stiffness parameter for lignin modification decreased, yet the mean of all binders remains positive. This indicates the small extent of the antioxidant effect with lignin addition. However, for all the aging conditions, the modified binders are stiffer than the base binders, which is not desirable for a prospective antioxidant additive.

Pairwise t-Test analysis

Furthermore, to statistically analyze the impact of modification with antioxidant additives, a pairwise t-test was performed on the stiffness parameters for different aging conditions between base and modified binders. For unaged and RTFO aged binders, the stiffness parameter was $G^*/\sin\delta$ at 64°C, and for PAV aged binders the corresponding stiffness parameter was $G^*.\sin\delta$ at 25°C. The results for the statistical analysis from the t-test are summarized in Table 3.

From the statistical analysis, it was observed that for the unaged condition, the p-value for base vs ZDC modified binders was greater than 0.05, implying that the test did not reject the null hypothesis at the 5% significance level. In other words, the stiffness parameters for the base and modified binders are not statistically different, suggesting negligible impact of ZDC addition on binder stiffness. On the contrary, lignin addition stiffens the base binder, as supported by the low p-values. For the RTFO aged binders, all the base vs modified binder combinations showed a p-value less than 0.05 suggesting rejection of null hypothesis at the 5% significance level. It suggests that the stiffness parameter values for base and modified binders (both lignin and ZDC) are different. Also, from the rheological results, it was observed that in general, lignin modified RTFO aged binders were stiffer than base binders and ZDC modified RTFO aged binders were softer than base binders.

Interestingly, PAV aged base vs lignin modified binders showed a p-value greater than 0.05. From a rheological perspective, lignin addition is stiffening the binders in unaged condition; however, after long-term aging, the rate of gain in stiffness in lignin modified binders is less than that for the base binders. This suggests a small antioxidant effect on lignin addition. Another critical observation is the considerably low p-values for PAV aged base vs ZDC modified binders indicating significantly lower stiffness of PAV aged ZDC modified binders.

Analysis using FTIR spectroscopy and stiffening index

The rheological tests and statistical analysis conducted using Performance Grade (PG) results shed significant insights into the aging behavior of the antioxidants-modified binders at a broad level. To strengthen and corroborate these findings, further investigations were undertaken for a subset of binders.

FTIR spectroscopy

The aging indices were derived from the C=O bands, as elaborated in earlier sections and notable findings are illustrated in Figure 9. Firstly, understanding the significance of the aging index is important. The C=O primarily reflects the transformation of benzylic carbons into carbonyl groups as a consequence of aging (RTFO to PAV). When comparing both sets of antioxidant-modified binders, it could be observed that in general, the use of antioxidants largely reduced the aging index in most of the binders. For ZDC modified binders, an obvious reduction in aging indexes was also evident. The mechanism attributed to ZDC involves its hypothesized role as a peroxide decomposer, which effectively curtails the generation of free radicals during the initial stages of oxidation (Petersen, 1998). This, in turn, decelerates the overall oxidation process. Notably, the introduction of ZDC at a dosage of 5% demonstrated a more pronounced effect in diminishing the aging index. However, certain deviations from the anticipated trend were also observed, underscoring the complexity associated with assessing the global effectiveness of antioxidants.

Similarly, in the context of lignin modified binders, a notable reduction in the aging index was consistently observed across the majority of the examined binders. These findings imply that lignin demonstrates antioxidant properties by effectively scavenging free radicals that may arise during the oxidation process of benzylic carbon. When considering possible mechanisms, it is plausible that lignin undergoes oxidation in place of the binder itself. During this oxidation process, it is postulated that lignin donates hydrogen, leading to the formation of a ketone containing a carbonyl group (Azadfar et al., 2015). However, when utilizing FTIR to quantify the carbonyl index, the specific origin of the carbonyl is not discerned. As a result, it is essential to consider the possibility that a portion of the carbonyl band observed in the FTIR spectrum may originate from the lignin present in the binder. Consequently, the actual carbonyl content of the binder may be even lower than the calculated value, owing to the contribution of lignin-derived carbonyls (Batista et al., 2018). Overall, the FTIR results indicate that the oxidation behavior of each binder seems intimately connected to its distinct chemical composition. Consequently, when using the same antioxidant, the degree of reduction in oxidation indices varies among different binders. This observation underscores how the specific chemical properties inherent to each binder could play a crucial role in determining the efficacy of the antioxidant treatment.

Stiffening index from oscillation testing

As described in previous sections, an aging index was defined based on G* and referred to as "stiffening index" in this study. Firstly, it is crucial to acknowledge the importance of such an index. Many studies have mistakenly relied on similar rheology-based indices to showcase how antioxidants and similar additives can mitigate aging. However, it must be recognized that the inclusion of antioxidants inherently transforms the rheological properties of the original binder. Consequently, when evaluating the rheological performance of different binders at the same temperature, the resulting ratio (unaged or short-term aged vs. long-term aged) serves as an indicator of how stiffness changes over time and should not be directly construed as a measure of aging behavior. Instead, this ratio primarily reflects how the presence of additives affect the binder's stiffness characteristics over time, when tested at a particular temperature. Although this parameter cannot be directly linked to extent of oxidation, it is still useful to gauge antioxidant effectives in terms of rheology as the increase in stiffness of binders with time can be directly linked to a decrease in binder ductility which consequently influences pavement longevity and cracking resistance (Sreeram et al., 2018a). Some interesting observations from the analysis are shown in Figure 10.

When considering the SI, the positive effect of lignin and the remarkable effect of ZDC in reducing the stiffening rate of binders is clearly visible. For most binders, ZDC addition showed significant reduction in stiffening index at both dosages. For some binders, the SI for binders with ZDC was around 50% lower as compared to the respective base binders. This reduction signifies that the rate of stiffness gain due to long-term aging is much lower in comparison to the unmodified binder as their initial stiffness would be generally similar as observed from the high PG results. Such an effect may lead to a more balanced pavement performance and overall longevity, particularly when considering the moderate testing temperatures used in this study to match conventional pavement service temperatures (Aragão and Kim, 2012). It is also evident that the rate of stiffness change differs for each binder which suggests distinctive chemical interactions between the antioxidants and the individual binders, which is likely based on their unique compositions. Additionally, the findings from both FTIR testing and stiffening index analysis imply that the physicochemical processes governing the antioxidant behaviors in the binders may be exceedingly intricate and extend beyond mere reduction of oxidative groups. This complexity indicates that the mechanisms driving the beneficial effects of antioxidants in binders encompass multifaceted physicochemical transformations and warrant further investigation and comprehension.

Key Insights and Takeaways

The primary goal of this study was to identify and establish notable trends concerning the rheological properties and oxidative behaviors of antioxidant-modified binders. This study followed a unique "inverted round-robin" approach, i.e., each participating laboratory used different binders that were local to their region but used the same antioxidant and dosage, with the ultimate goal of measuring the broad scale or global efficacy of candidate antioxidants.

As expected, this study revealed diverse outcomes suggesting that the physicochemical processes governing antioxidant behaviors in binders are exceedingly complex and extend far beyond a reduction of oxidative groups. In this context, it is important to reevaluate the fundamental purpose of employing antioxidants. In practical terms, the primary objective of using antioxidants is to extend the service life of pavements by enhancing their durability and ability to withstand long-term cracking. In this regard, the crucial parameter to focus on are related to the rheological behavior of the binder, with the reduction of oxidation serving as a precursor driving mechanism. Accordingly, it becomes imperative to thoroughly consider the potential rheological effects induced by the binder modification itself when assessing the efficacy of antioxidants. Such considerations are paramount in comprehending the overall performance and effectiveness of antioxidants in pavement applications. Based on the findings of this study, it is evident that ZDC is a highly effective additive, exhibiting strong effectiveness with most of the asphalt binders used. The incorporation of ZDC does not compromise the rutting performance of the binders and significantly improves their resistance to oxidative aging and brings about concomitant benefits such as resistance to fatigue cracking by up to 35% when considering a global average.

Conversely, lignin also demonstrates some potential as an effective additive, albeit to a much lesser extent. The addition of lignin leads to an increase in the binder's stiffness by around 29% on average, thereby enhancing its rutting resistance. However, the ability of lignin-modified binders to withstand fatigue cracking remains unclear based on the results obtained in this investigation which suggest only a small improvement when considering global averages. Regarding the reduction of oxidative groups, both additives demonstrated significant potential. Lastly, it is important to note that the statements presented above represent the general trend observed across the various tested binders. Certain anomalies were naturally observed in the results, indicating that the interaction between antioxidants and binders is indeed intricate and multifaceted. Further comprehensive research is required in various aspects, as elaborated in the subsequent section.

Future Research

Based on the outcomes of this study, it is evident that the ZDC additive exhibits significant potential as an effective antioxidant for a wide range of geographically diverse binders. To explore its practical applicability, further studies should focus on evaluating the performance of mixtures containing such modified binders including evaluating aspects such as optimum dosage, safety, cost, etc. Additionally, the implementation of trial sections utilizing this additive could also serve as a fast-track approach, potentially yielding significant benefits to the industry.

Regarding the use of lignin, additional research is imperative as a result of the complex nature of the additive-binder interaction and the diversity of results observed in this study. It is important to note that although the same source and type of lignin was used in this study, the term lignin itself may refer to a very diverse family of organic compounds. Further research is also essential to understand the fundamental chemistry and mechanisms involved when using different antioxidants. As a starting point, research must also be undertaken to comprehensively study the effect of binder chemical composition on antioxidant effectiveness and investigate correlations between observed rheology and chemistry. Lastly, it must be noted that that this work did not evaluate possible differences resulting from equipment biases when considering various testing equipment. Future work should address this by conducting tests on a single binder.

Conclusions

This study presented the results from Phase-2 of a collaborative global research initiative focused on examining the efficacy of two high potential antioxidants in mitigating the oxidation of asphalt binders. A total of 28 binders, sourced from diverse geographical regions were used in the analysis. These binders were blended with two specific antioxidants, zinc diethyldithiocarbamate (ZDC) and kraft lignin, at predetermined proportions. The evaluation basis focused on a broader perspective, aiming to discern the widespread applicability of this technology. The main conclusions from the study were as follows:

- The introduction of ZDC into the binders typically did not cause any significant negative impact on their rutting performance. Conversely, a significant improvement in aging reduction and consequently the fatigue performance of the binders was observed following its incorporation.
- The addition of lignin in binders resulted in an increased stiffness and rutting performance. However, the effectiveness of lignin modified binders in mitigating fatigue cracking remains uncertain, as the outcomes of this investigation yielded mostly unremarkable results in this regard.
- Analysis using FTIR indicated that on average, the uses of different antioxidants showed some tendencies to lower the content of carbonyl functional groups, thus lower the aging indices of the binders. However, its relationship with reducing aging related effects on binder rheology is uncertain as there are likely multiple mechanisms in action that could be unique to the additive-binder pair and may impact the overall rheological behavior.

Overall, this study marked an interlaboratory initiative on a global scale conducted to investigate the use of diverse antioxidants and their wide effectiveness when considering binder diversity. The use of certain additives such as ZDC show remarkable potential to increase the lifetime of pavements., Further work is required to expedite the widespread adoption of this technology and provide a solid foundation for informed material selection decisions. In the forthcoming phases, the consortium is poised to address these concerns through cohesive efforts, aiming to accelerate the broad implementation of this technology while simultaneously generating greater interest on this subject in academic and industrial circles.

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.

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Figure 1. World map showing locations and diversity of binder sources used in the study

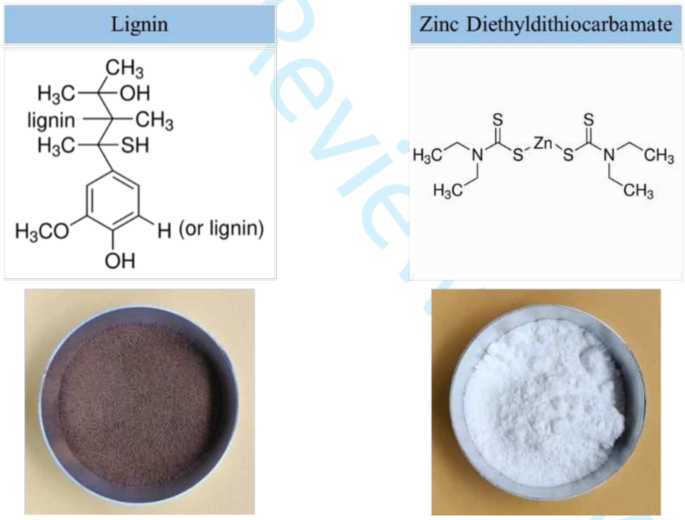
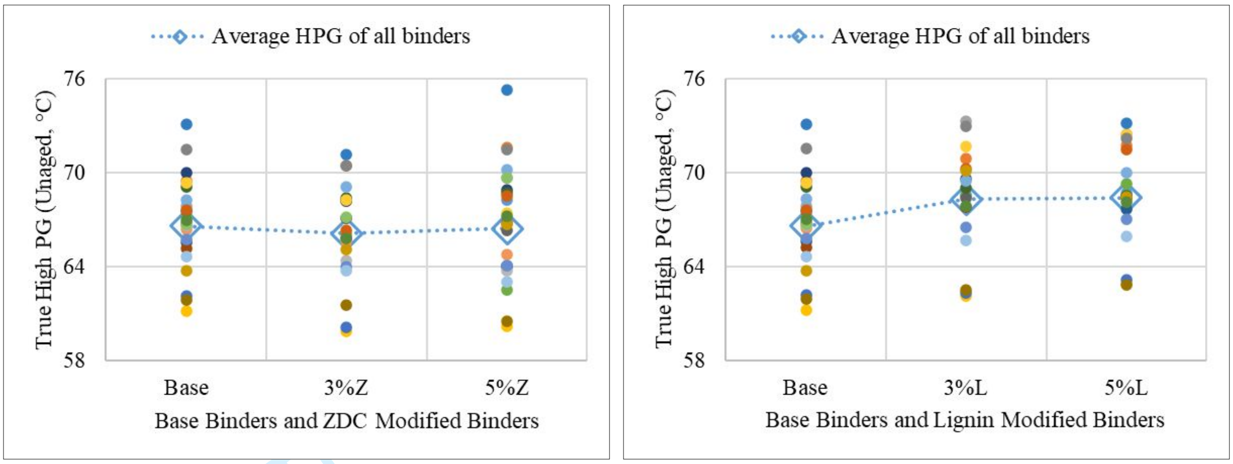
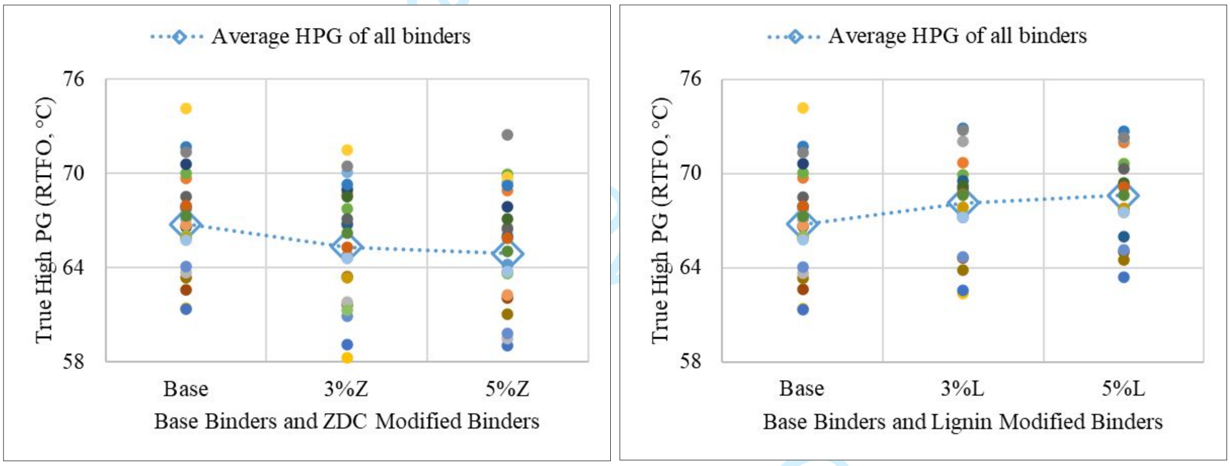


Figure 2. Chemical structure and pictures of the antioxidants used in the study



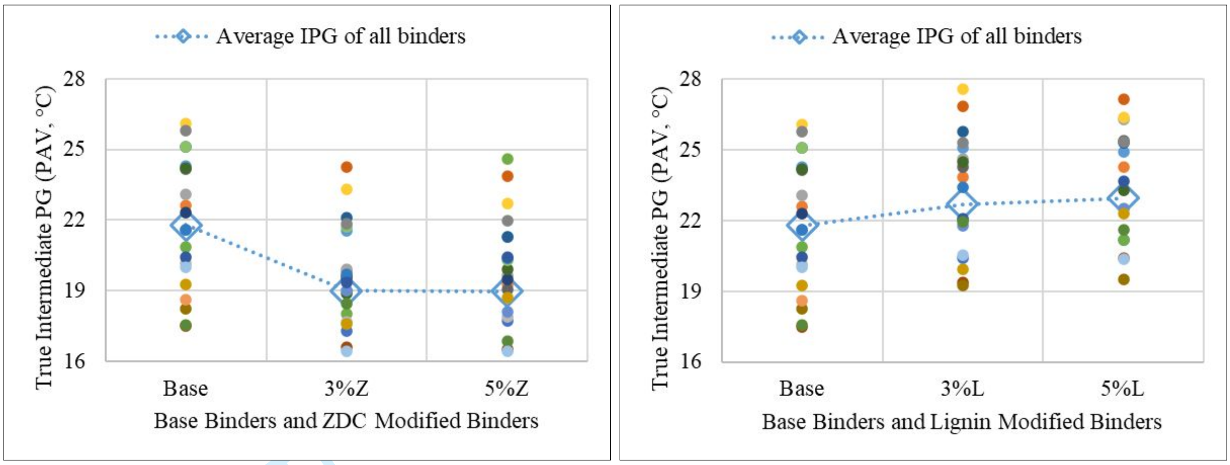
(a) (b)

Figure 3. True high PG for unaged base binders compared with (a) ZDC modified binders, (b) Lignin modified binders (including binders from all labs)



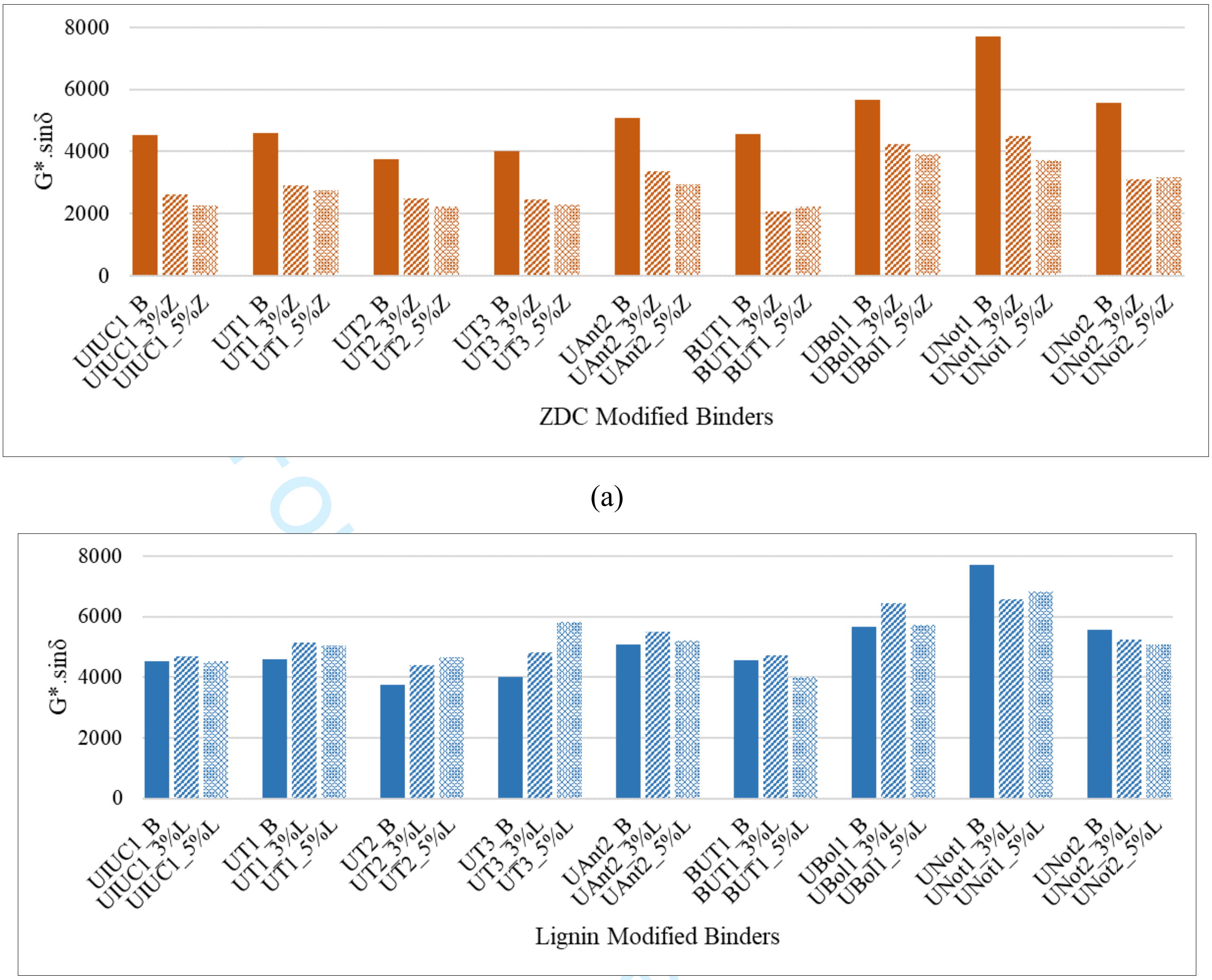
(a) (b)

Figure 4. True high PG for RTFO aged base binders compared with (a) ZDC modified binders, (b) Lignin modified binders (including binders from all labs)



(a) (b)

Figure 5. True intermediate PG for PAV aged base binders compared with (a) ZDC modified binders, (b) Lignin modified binders (including binders from all labs)



(a)

(b)

Figure 6. Superpave parameter G*.sinδ at 25℃ for binders having IPG≥25℃ modified with (a) ZDC, and (b) Lignin (selected binders)

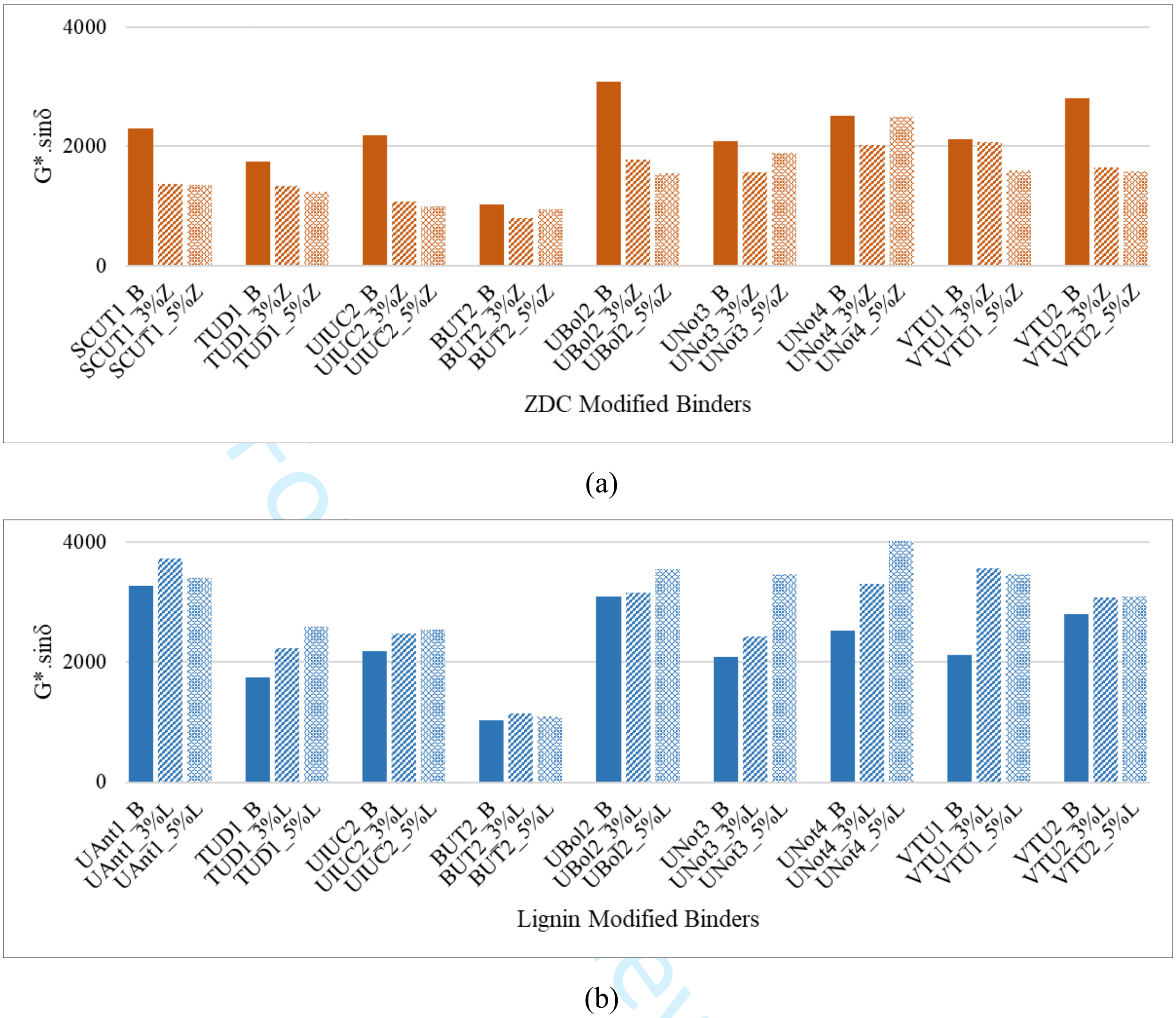
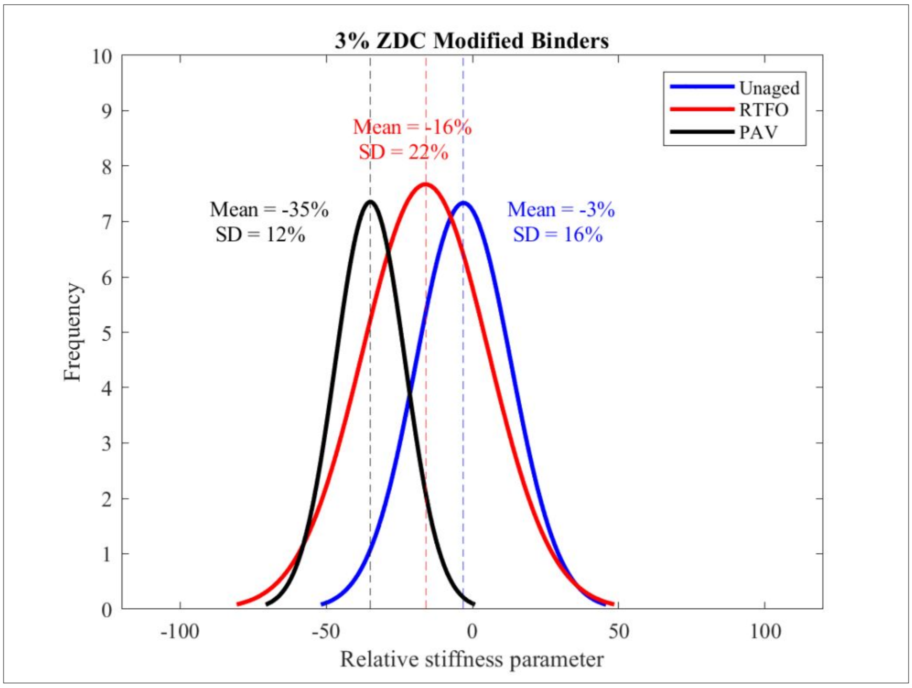
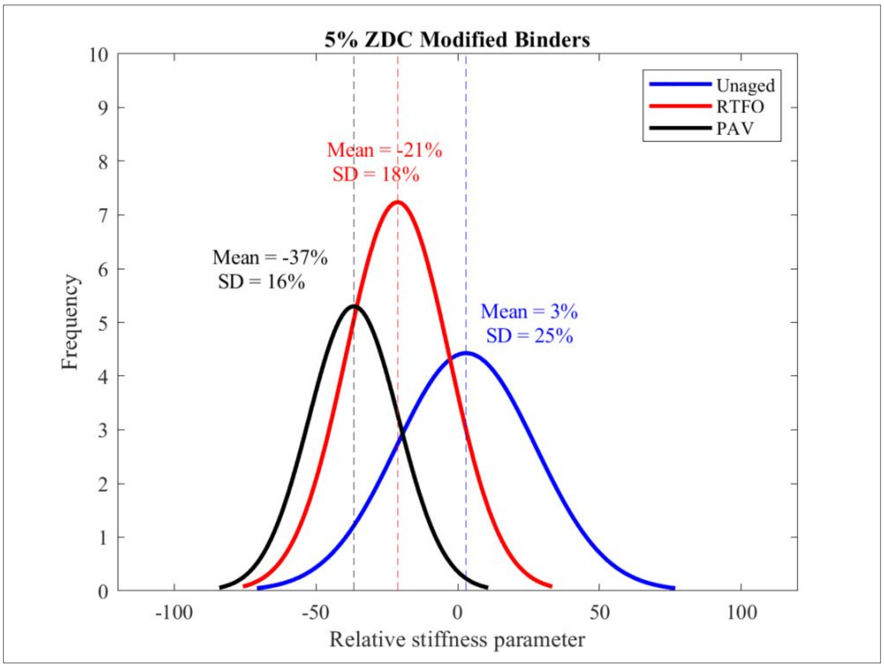


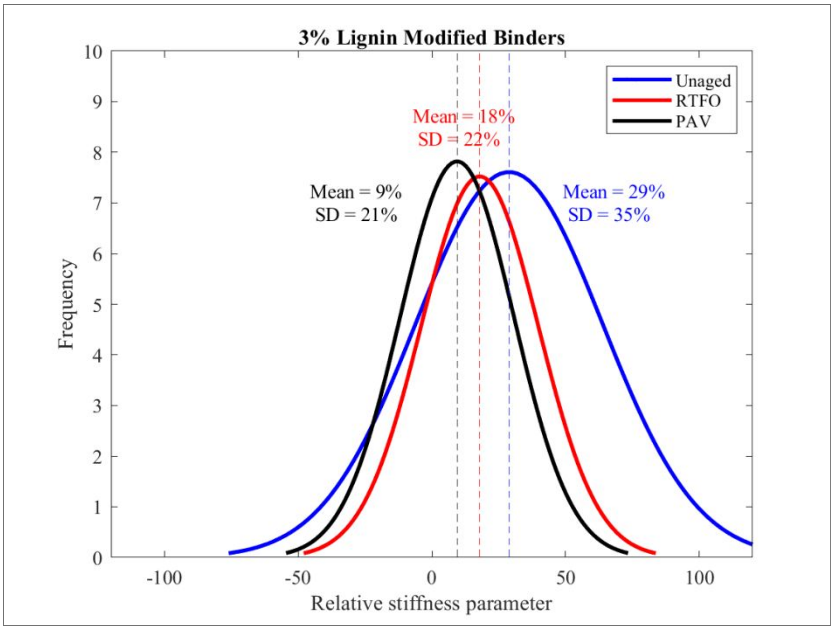
Figure 7. Superpave parameter G*.sinδ at 25℃ for binders having IPG≤25℃ modified with (a) ZDC, and (b) Lignin (selected binders)


3% ZDC Modified Binders
Unaged
RTFO
PAV
Mean = -16%
SD = 22%
Mean = -35%
SD = 12%
Mean = -3%
SD = 16%
Frequency
0
1
2
3
4
5
6
7
8
9
10
-100
-50
0
50
100
Relative stiffness parameter

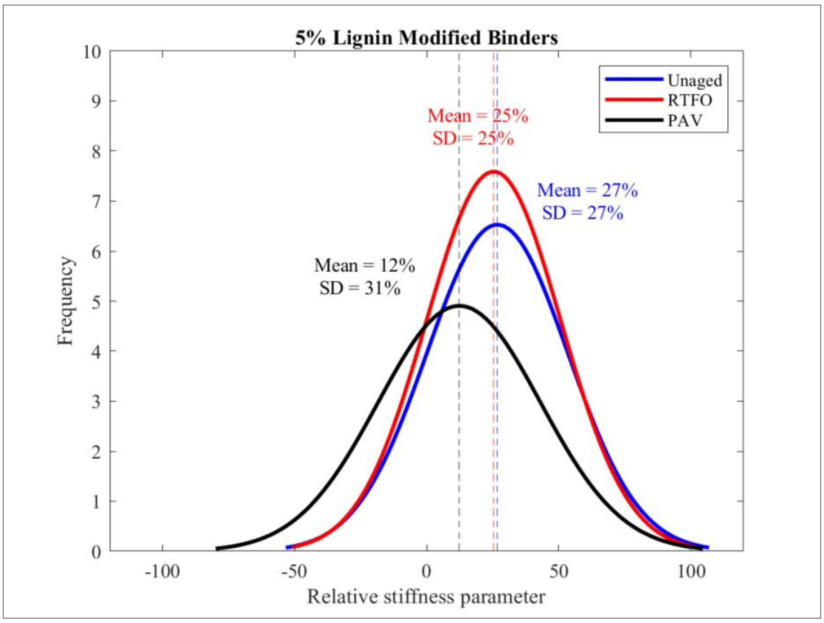
(a)


5% ZDC Modified Binders
Unaged
RTFO
PAV
Mean = -21%
SD = 18%
Mean = -37%
SD = 16%
Mean = 3%
SD = 25%
Frequency
0
1
2
3
4
5
6
7
8
9
10
-100
-50
0
50
100
Relative stiffness parameter

(b)

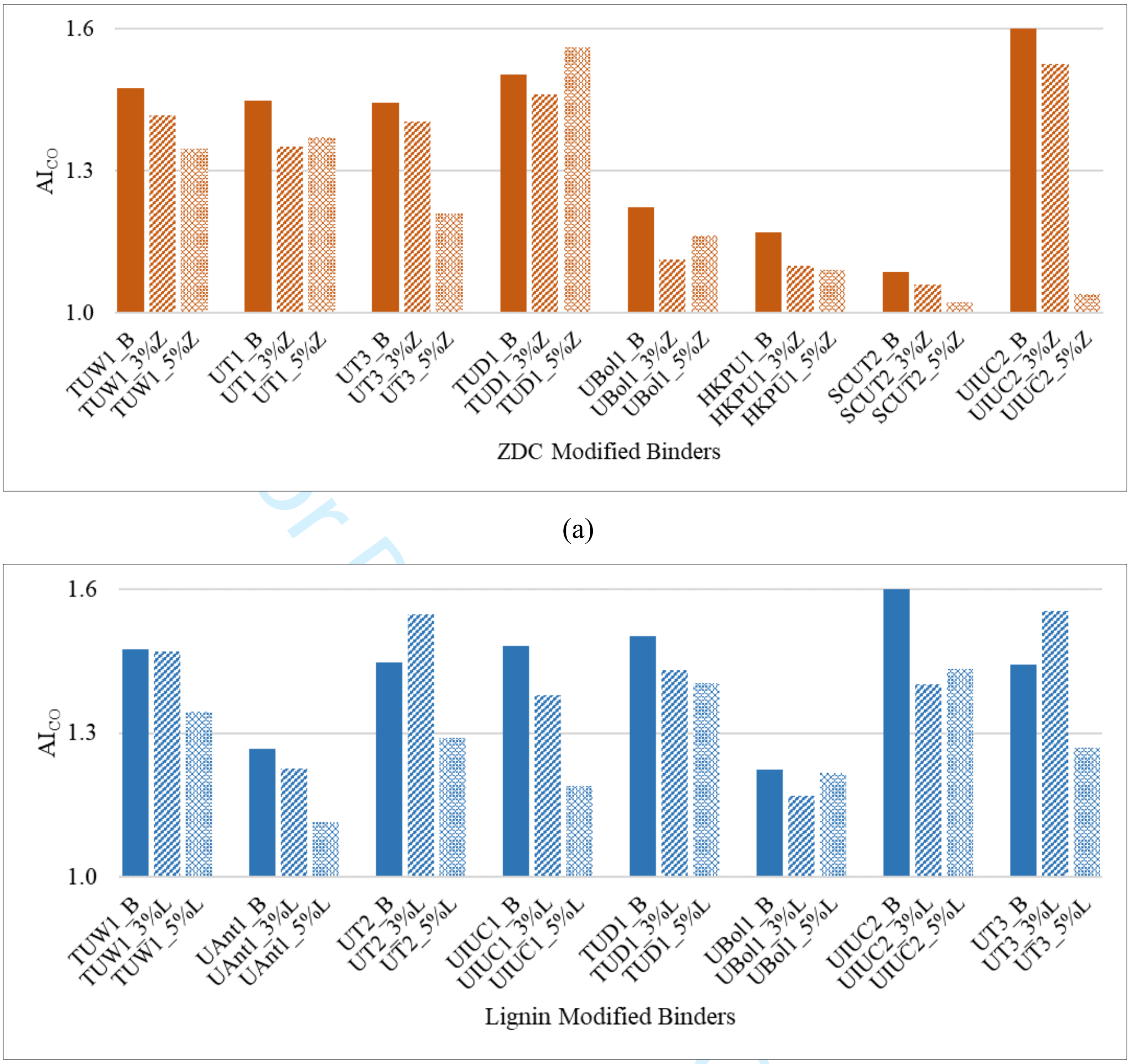


(c)



(d)

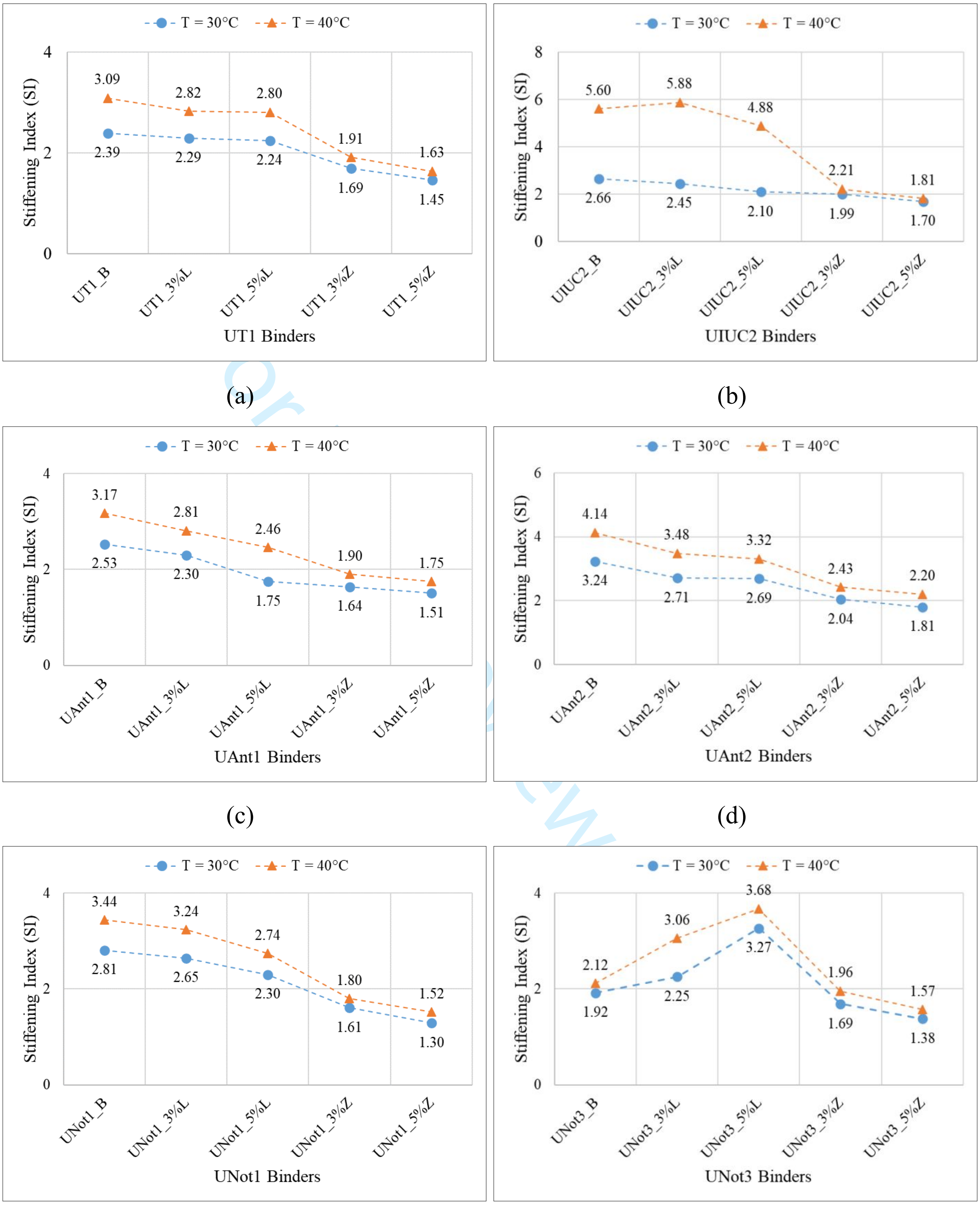
Figure 8. Distribution plots of relative stiffness for the antioxidant modified binders with (a) (b) ZDC, (c) (d) Lignin



(a)

(b)

Figure 9. Aging Indices (AI$_{CO}$) based on C=O band for selected binders modified with (a) ZDC, and (b) Lignin



(a) (b)

(c) (d)

(e) (f)

Figure 10. Stiffening Indices (SI) based on time sweep testing at two temperatures for selected binders modified with ZDC and Lignin

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Table 1. Details of the participating labs and the binders used in the study

S. No.	University/Lab	Source	No. of Binders	Binder Nomenclature	High Temperature PG Grade (°C)
1	University of Texas at Austin	Texas (USA)	3	UT1, UT2, UT3	64
2	Vienna University of Technology (TU Wien)	Vienna (Austria)	2	TUW1, TUW2	58
3	University of Antwerp	Antwerp (Belgium)	2	UAnt1, UAnt2	64
4	Delft University of Technology (TU Delft)	Delft (Netherlands)	1	TUD1	58
5	University of Illinois Urbana-Champaign	Illinois (USA)	2	UIUC1, UIUC2	64, 58
6	Universidad de los Andes	Bogota (Colombia)	1	UAndes1	70
7	Beijing University of Technology	Beijing (China)	2	BUT1, BUT2	64
8	South China University of Technology	Guangzhou (China)	2	SCUT1, SCUT2	64, 58
9	University of Bologna	Bologna (Italy)	2	UBol1, UBol2	64
10	Hong Kong Polytechnic University	Hong Kong SAR	1	HKPU1	64
11	University of Gustave Eiffel	France	1	UGE1	70
12	University of Nottingham	Nottingham (UK)	4	UNot1, UNot2, UNot3, UNot4	58, 64,70,76
13	Vilnius Gediminas Technical University	Vilnius (Lithuania)	2	VTU1, VTU2	64

14	Bundesanstalt für Materialforschung und – prüfung (BAM)	Berlin (Germany)	1	BAM1	76
15	Wuhan Institute of Technology	Wuhan (China)	1	WIT1	64
16	Belgian Road Research Centre (BRRC)	Brussels (Belgium)	1	BRRC1	64

Table 2. Details and nomenclature of the antioxidant additives used in the study

Name	Manufacturer	Chemical Abstract Service (CAS) No.	Dosages (binder wt.%)	Code (used in study)
Kraft Lignin	Sigma Aldrich	8068-05-1	3% & 5%	L
Zinc Diethyldithiocarbamate	Sigma Aldrich	14324-55-1	3% & 5%	Z

Table 3. Summary of pairwise t-test between stiffness parameters for base and modified binders

	Hypothesis test result 'h'			p-value		
	Unaged	RTFO	PAV	Unaged	RTFO	PAV
Base vs 3% Lignin Modified Binders	1	1	0	0.0021	0.0243	0.1592
Base vs 5% Lignin Modified Binders	1	1	0	0.0052	0.0177	0.1946
Base vs 3% ZDC Modified Binders	0	1	1	0.3462	0.0026	1.15E-07
Base vs 5% ZDC Modified Binders	0	1	1	0.9865	0.0035	1.50E-06