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Effect of DLTDP and furfural on asphalt binders: Optimal dosage and PG grading

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ABSTRACT

The addition of anti-aging additives to asphalt binders has increased drastically over the last decade. Two candidates, dilauryl thiodipropionate (DLTDP) and furfural have been highlighted in some recent studies, as they showed promising results. However, the determination of the optimal content of each one of the compounds still needs to be better elaborated. In this matter, a new method for the dosage of furfural and DLTDP, based on the minimum rheological aging index, is presented in this paper. In addition, the Superpave asphalt binder characterization is used to investigate the effect of the anti-aging compound additives (composed by furfural and DLTDP) on the high, intermediate, and low temperatures of two asphalt binders. The achieved results reveal that furfural is partially lost during the short-term and long-term aging due to the high temperatures considered during each aging procedure. This demonstrates that the use of furfural may not be suitable for the preparation of hot mix asphalt. In addition, the combination of DLTDP and furfural (at the obtained optimal contents, for each binder) leads to a softening of the binders and a decrease of the continuous PG span. Thus, the combined use of these additives as anti-aging agents could not be proved by this study.

1. Introduction

The increasing pressure on the environment and extreme climate events lead to the demand for more sustainable practices and solutions towards the reduction of greenhouse gas emissions and the use of natural resources. In the sphere of road infrastructure, the increase of durability of the asphalt pavements may promote the reduction of energy consumption, greenhouse gas emission, and waste generation. The durability of asphalt roads is negatively affected by the oxidative aging of asphalt binders which leads to the increase of their stiffness, brittleness, and thus cracking, which promotes the premature collapse or deterioration of the pavement structure. [1–4].

The reason for hardening is well documented by researchers around the world who have captured the increase in the stiffness and viscosity of asphalt binders. For instance, physicochemical characterization studies correlated the increase of stiffness and viscosity to the increase of high polarity species and carbonyl groups on asphalt binders, respectively [5–14]. Consequently, a clear understanding of mechanisms related to the formation of these species will enable us to identify the problems and lead us to solutions to improve the aging resistance of asphalt binders.

Among others, free radical chain reaction, oxycyclic reaction, and dual oxidation are some of the mechanisms previously investigated to unravel the pathways linked to the oxidative aging of asphalt binders [2,15–18]. Between the mechanisms previously mentioned, the dual sequential asphalt binder oxidation mechanism provides valuable insights related to the chemical interaction between asphalt binders and atmospheric oxygen [12,19].

According to the dual oxidation mechanism, the oxidation takes place in the initial spurt phase (fast oxidation reactions) followed by a constant rate phase (slow oxidation reactions). The initial phase is characterized by the reaction between oxygen and highly reactive hydrocarbons providing hydroperoxides which can either react with sulfides or decompose resulting in the formation of sulfoxides and free radicals, respectively. Still at this stage, the oxygen can also react with precursor hydroaromatic increasing the aromaticity which may be most probably responsible for the initial viscosity increase, since few ketones are formed at this stage (especially at low temperatures).

During the slow oxidation phase, the oxidation of benzylic carbon culminates in the replacement of its hydrogen and in the formation of free radicals which oxidize resulting in hydroperoxide. Depending on the characteristics of the asphalt binder (composition and microstructure) and external factors (temperature and oxygen concentration), the

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formed hydroperoxides can either decompose to form ketones or react with sulfides resulting in sulfoxides. In addition to the main products (ketones and sulfoxides), scientific investigation reported the formation of carboxylic acids, dicarboxylic anhydrides, and alcohol functional groups during the oxidation of asphalt binders [19–20].

Anti-aging additives are substances that retard or slow down the aging of asphalt binders. Free radical scavenging (primary antioxidant), ultraviolet absorbing, peroxide decomposing (secondary antioxidant), and chain-breaking are the main mechanisms that improve the aging resistance of asphalt binders [15,21–22].

A complete literature review about the different substances used as an anti-aging additive to asphalt binders and aging mechanisms is beyond the scope of this study, given the copious available studies that competently cover these topics [4,15–16,21,23]. Moreover, the mechanical, rheological, and chemical characterizations presented in recent studies show the potential of using an anti-aging additive composed of an aromatic aldehyde (furfural) and a thioester/ peroxide decomposer (dilauryl thiodipropionate (DLTDP)) as an anti-aging additive for asphalt binders [24–27]. Apeagyei et al., [24] investigated several anti-aging additives and found that a compound of furfural and DLTDP (in presence of a catalyst) showed to be the most effective (about 40% reduction) to reduce the oxidative hardening of two different types of asphalt binders. Similarly, the addition of 2% of furfural and 1.5% DLTDP (in presence of catalytic acid) improved the aging resistance of the studied binder (PG 67–22 asphalt binder). However, the addition of this compound impacted the aging resistance of a PG 64–22 asphalt binder in a negative way [25]. In addition, the compound additive seemed to increase the fatigue resistance and reduce the formation of carbonyl functional groups in asphalt binders [26–27].

Given the potential of this anti-aging compound additive in boosting the aging resistance of asphalt binders, this study provides useful information on the determination of the optimal content of each component (furfural and DLTDP) which leads to the best aging reduction. Moreover, this study also presents the effect of the anti-aging compound additives (composed by furfural and DLTDP, at their optimal contents) on the performance grading of two asphalt binders. For that, the study was divided into two phases. In the first phase, a feasible dosage methodology of each additives based on the rheological aging index was introduced. In the second phase, the effect of the anti-aging compound additives on the performance of the asphalt binders based on the Superpave specification was presented.

2. Materials and methods

2.1. Materials

Two unmodified 70/100 penetration grade asphalt binders (referred to as A and B), supplied by two different refineries, were used in this study. A previous study showed discrepancies (in aging susceptibility and fatigue resistance) between the two asphalt binders with similar penetration and chemical composition [28]. Therefore, the selection of two asphalt binders with the same penetration grade aimed to investigate if the penetration grade plays a significant role in the determination of the optimal content of furfural and DLTDP. The properties of both binders are presented in Table 1.

Different contents of DLTDP, furfural, or the compound (furfural + DLTDP) were added to the asphalt binders (A and B) to evaluate their effectiveness as anti-aging additives. The properties of furfural and DLTDP are presented in Table 2. Fig. 1 shows the appearance and chemical structure of both additives (furfural and DLTDP).

Exposure to furfural is harmful to human health, therefore, it is highly recommended the use of special personal protective equipment during its handling, such as butyl rubber gloves, safety glasses, and mask fitted with A2P3 filter. Moreover, the handling of furfural should be only performed under a chemical hood fume.

Table 1
Physical and chemical properties of unaged asphalt binders used in this study.

Binder Properties	Units	Specifications	Results	
			Binder A	Binder B
Penetration (@25 °C)	0.1 mm		79	88
Softening point	°C	EN 1426	47.2	45.0
Density (@15 °C)	g/cm^3	EN 1427	1.02	1.02
Viscosity (@135 °C)	mPa·s		355	371
Chemical composition (wt%)	-	*	-	-
Saturates	-		22.9	24.9
Aromatics	-		51.5	45.8
Resins	-		9.5	11.1
Asphaltenes	-		16.1	18.2

(*). More details of the methodology can be found in [28–29].

Table 2
Properties of furfural and DLTDP.

Characteristic	Unit	Furfural	DLTDP
Chemical formula	–	$C_5H_4O_2$	$C_{30}H_{58}O_4S$
Molar mass	g/mol	96.07	514.84
Density (@25 °C)	g/cm^3	1.16	0.915
Boiling point	°C	161.7	704.8 ± 45.0
Melting point	°C	–	41 ± 1.0
Appearance (form)	–	Liquid (oil)	Powder
Appearance (color)	–	Colorless to very dark yellow	White

2.2. Preparation of modified asphalt samples

Firstly, a modified asphalt binder was prepared by adding weighed unmodified binder (A or B) into a metallic can. Then, the filled can was placed into a universal heating oven at 150 °C for 40 min prior to the blending process, to assure that the asphalt binder was fully melted. During the oven storage, the can was covered with a metallic lid to minimize oxidative aging. Secondly, the can was removed from the oven and a given mass of additive was added (wt% of unmodified asphalt binder) to the melted binder. During the preparation of the modified binders, the additive was added slowly to the binder to prevent any agglomeration. Then, the prepared blend was stirred using a shear mixer at 135 °C for 60 min at a rotation speed of 1100 rpm, to ensure the required homogeneity of the sample. During the mixing process, the can was placed on a sand bath and covered by an electric heating jacket (with a temperature controller), both at 135 °C, to ensure the uniform temperature of the sample by the constant heating. The temperature (135 °C), mixing speed (1100 rpm), and mixing duration (60 min) were selected based on the values reported in the literature review [24,30,25].

The processing of the modified asphalt binders might induce aging of the material. In that regard, the unmodified asphalt binders were also proceeded under equal heating and mixing conditions to ensure the comparison between the modified and unmodified binders. For all binders, the heating and mixing were repeated twice to assure the reliability of the sample preparation and mixing process.

The prepared asphalt binders were tested at unaged, short-term aged, and long-term aged conditions. The short-term aging protocol was simulated according to RTFOT (EN 12607–1) [31] protocol. Consequently, PAV (EN 14769) [32] was performed on short-term aged samples to simulate long-term aging. The asphalt binders at different aging conditions were transferred into small metallic cans for further analysis.

The content of additives by total weight of modified bitumen and the codification of unaged binders are presented in Table 3. The letters “R” and “P” were added to the sample name to identify the short-term aged (RTFOT) and long-term aged (PAV) samples, respectively.

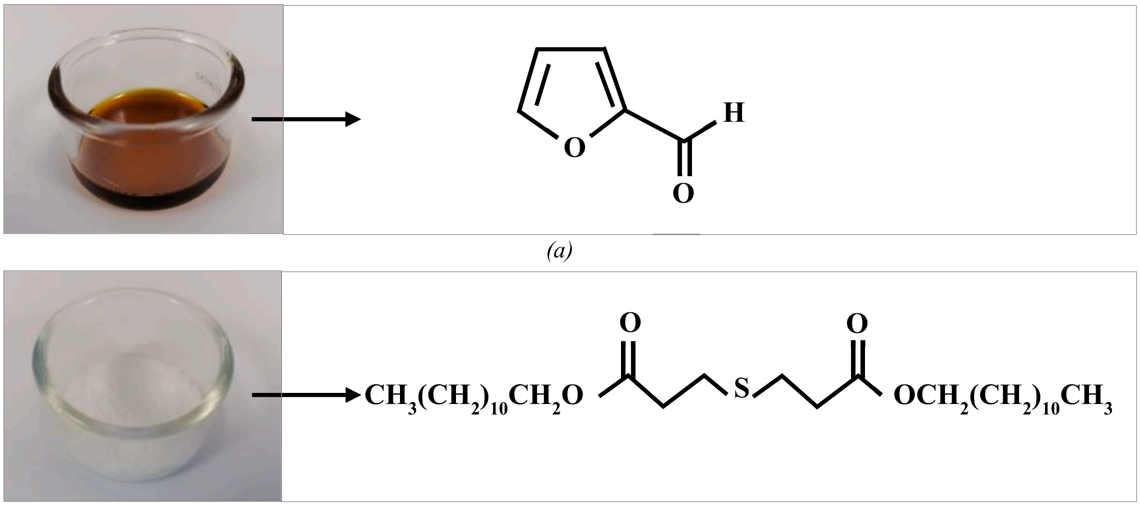


Fig. 1. Anti-aging additives. (a) furfural; and (b) DLTDP.

Table 3
Codification adopted to unaged asphalt binders.

Additive Content (wt%)*	Sample code	
	Binder A	Binder B
0% DLTDP + 0% Furfural	A_0D0F	B_0D0F
1% DLTDP + 0% Furfural	A_1D0F	B_1D0F
2% DLTDP + 0% Furfural	A_2D0F	B_2D0F
6% DLTDP + 0% Furfural	A_6D0F	B_6D0F
10% DLTDP + 0% Furfural	A_10D0F	B_10D0F
0% DLTDP + 1% Furfural	A_0D1F	B_0D1F
0% DLTDP + 2% Furfural	A_0D2F	B_0D2F
0% DLTDP + 6% Furfural	A_0D6F	B_0D6F
7.5% (4:1 – DLTDP: Furfural)	A_C1	–
2.5% (2:3 – DLTDP. Furfural)	–	B_C2

(*). wt% of unmodified asphalt binder.

2.3. Performance methods

The evaluation of the performance of the unmodified and the modified asphalt binders was executed according to the Superpave binder specification [33]. Brookfield rotational viscosity (RV) test, Dynamic Shear rheometer (DSR) test, and Bending Beam Rheometer (BBR) test were performed to assess the effect of the anti-aging additives on the properties of the asphalt binders. In addition, Attenuated Total Reflection-Fourier transform infrared (ATR-FTIR) spectroscopy was used to investigate the effect of oxidative aging on the chemical composition of asphalt binders.

2.3.1. Brookfield rotational viscosity

The viscosity at high temperatures is an important parameter to assign the fluid properties of asphalt binders such as pumpability at the plants, mixability with the aggregate, workability, placement, and compaction of asphalt binder's mixtures [34–35].

Based on that, Superpave specification limits the viscosity of the asphalt binder (at 135 °C) to a value of 3 Pa·s to assure the pumpability of the asphalt binder at the HMA plant [33]. Furthermore, the viscosity-temperature chart allows the determination of the mixing and compaction temperatures of asphalt mixtures. The mixing and compaction range temperatures are correlated with the viscosity range equal to 0.17 ± 0.02 Pa·s and 0.28 ± 0.03 Pa·s, respectively [33–34].

The Brookfield rotational viscometer (Model DV-III) was employed to determine the viscosity of the unaged asphalt binders at 135, 150, and 165 °C according to EN 13302 [36]. For each binder tested the coefficient of variation was within 6%. The results were reported based on the average value of the two replicated samples.

2.3.2. Dynamic shear rheometer (DSR)

Asphalt binders are viscoelastic materials, therefore, their properties are dependent on time, temperature, and frequency [34,37]. The linear viscoelastic characteristics of these materials can be measured over a wide range of frequencies and temperatures using a DSR. In this study, the frequency sweep test was performed based on the relationship between applied stress and measured strain to obtain the viscoelastic parameters such as the norm of the complex modulus ($|G^*|$) and phase angle (δ).

The rheological test was performed with a DSR (Anton Paar Inc., MCR 302, Austria) at the temperature range from – 8 °C to 82 °C with increments of 6 °C. For intermediate temperatures (– 8 °C to 40 °C), parallel plate geometry with a diameter of 8 mm and sample height equal to 2 mm were considered. For temperatures above 40 °C, 25 mm diameter and 1 mm gap were used. Two replicate specimens were tested for each type of asphalt binder studied. For each type of asphalt binder tested, the coefficient of variation was below 15%.

The master curves ($|G^*|$ and δ) were constructed based on the time–temperature superposition principle (TTSP) at 25 °C reference temperature. The detailed methodology adopted for the construction of the curves can be found in a previous study of the authors [28].

2.3.3. Bending beam rheometer (BBR)

BBR test evaluates the ability of asphalt binders to resist transverse cracking formation due to thermal stress at low temperatures [38]. The test consists of a three-point bending test where a constant load is applied to an asphalt binder beam and the respective deflection is measured as a function of time [39].

Flexural creep stiffness (S) and m-value are the main parameters calculated from the BBR results. The S parameter represents the material stiffness while the m-value expresses the stress dissipation/ relaxation capacity due to the temperature variation. The lower S and higher m-value would contribute to the better low temperature performance of asphalt binders.

The Superpave specification specifies (@60 s of the loading time) a maximum value to S (300 MPa) and a minimum value to m-value (0.30) to minimize the risk of thermal cracking.

In this study, the BBR test was performed in RTFOT + PAV aged asphalt binders at three different temperatures (−18 °C, −24 °C, and −30 °C), according to protocols given in EN14771 [40] and using a BBR instrument (Coesfeld, Germany). For each binder tested, the results for each temperature were reported based on the average value of four replicated samples, the coefficient of variation of S and m-value were within 6% and 12%, respectively.

2.3.4. Fourier-transform infrared (FTIR) spectroscopy

Attenuated Total Reflectance-Fourier Transform Infrared spectroscopy technique (ATR-FTIR) is commonly used to track the effect of oxidative aging and polymer additives on the chemical composition of asphalt binders, at surface level [41–46].

In this study, FTIR analyses were performed using an FTIR spectrometer fitted with a single reflection diamond ATR-crystal (Bruker Optics Inc., Model Alpha II, Ettlingen, Germany). Each ATR-FTIR spectrum was recorded in the wavenumber range from 4000 to 400 cm^{-1} with an instrument resolution of 4 cm^{-1} and 24 scans were performed. Before each measurement, a background spectrum of the clean ATR crystal was recorded. The produced absorbance spectra were normalized (at band 2919 cm^{-1}) using Bruker OPUS software.

The functional indices (carbonyl, sulfoxide, and aromatics) were determined to assess possible changes in the asphalt binders' chemical composition due to the aging and/ or addition of additives. For the determination of each one of the functional indices (I_{CO}, $I_{SO,}$ and $I_{C=C}$) the normalized spectra and absolute baseline were considered. The calculation of each index was based on the ratio of the integrated absorbance around the given functional group band region (carbonyl, sulfoxide, or aromatics) to the integrated absorbance band of a reference group. At least three replicates were used to calculate the FTIR indices, for each type of tested asphalt binder. Also, the coefficient of variation was within 5% for I_{SO} and $I_{C=C}$ and within 20% for I_{CO}, for all binders tested. The wavenumbers integration limits considered for the calculation of the three FTIR indices are given in Table 4.

2.3.5. Aging indices

The physical, mechanical, and chemical changes on properties of asphalt binders due to oxidative aging can be evaluated by aging indices [24,47–49]. Generally, aging indices are defined as (i) the ratio of a given property after aging to the same property before aging [47,50–55]; (ii) the difference between the property value of aged binder and the same property of the binder at unaged condition [52,56–59]. The details of the aging indices used to evaluate the aging susceptibility of asphalt binders are given in Table 5.

3. Results and discussion

Several authors indicated that the anti-aging compound additive made by the combination of DLTDP and furfural showed potential in improving the aging resistance of asphalt binders [24,26–27,25]. This study aims to evaluate the effect of this compound on the PG performance grading and aging resistance of asphalt binders. For that, the research was divided into two phases. In phase I, the contents of anti-aging additives (DLTDP and furfural) that showed the best improvement on the short-term aging resistance of a specific asphalt binder, were determined. The optimal contents of DLTDP and furfural (obtained in phase I) were considered to produce modified binders containing both additives. In phase II, Superpave binder specification was considered to verify the effects of this compound anti-aging additive on the low, intermediate, and high performance of the asphalt binders.

Table 4
Integration limits used in FTIR indices calculation.

Functional group	Upper wavenumber limit (cm^{-1})	Lower wavenumber limit (cm^{-1})
Carbonyl	1800	1660
Sulfoxide	1045	985
Aromatics	1635	1560
Reference (aliphatic)	1525	1355

Table 5
Aging indices. Calculation methods.

Aging index	Index equation	Reference
Rutting parameter aging index (RAI)	$RAI=(\lvert G^*\rvert/\sin\delta)_{Aged}/(\lvert G^*\rvert/\sin\delta)_{Unaged}$	[24,47,60]
Fatigue parameter aging index (FAI)	$FAI=(\lvert G^*\rvert.\sin\delta)_{Aged}/(\lvert G^*\rvert.\sin\delta)_{Unaged}$	[24–25]
Carbonyl aging index (CAI)	$CAI = I_{CO\ Aged} / I_{CO\ Unaged}$	[61–62]
Sulfoxide aging index (SAI)	$SAI = I_{SO\ Aged} / I_{SO\ Unaged}$	[61]
Aromatics aging index (ArAI)	$ArAI = I_{C=C\ Aged} / I_{C=C\ Unaged}$	–

3.1. Phase I: Determination of optimal dosage

In the first phase of the study, four contents of DLTDP (1%, 2%, 6%, and 10%) and three contents of furfural (1%, 2%, and 6%) were added to each type of the binders (A and B). Given, the broad range of the asphalt binder blends produced, it was chosen to focus the investigation of aging on short-term aging resistance of binders in order to optimize resources. Once the short-term aging resistance has been successfully used as a precursor of the long-term performance of asphalt binders [24].

For that, each one of the prepared blends was submitted to the RTFOT aging procedure. Then, a frequency sweep test was conducted on the unaged and short-term aged binders to determine the rheological parameters such as the Superpave rutting parameter ($\lvert G^*\rvert/\sin\delta$). This parameter can be determined at different temperatures and a fixed frequency of 1.59 Hz. The increase of this parameter increases the rutting resistance of the asphalt binder [33,63]. Moreover, RAI (Table 5) was calculated based on the rutting parameter to evaluate the short-term aging resistance of the asphalt binders.

Based on the elucidation above, the minimum value of RAI index was taken as the main criterion for the selection of optimal content of DLTDP and furfural for the asphalt binders considered in this study. In addition, the potential of using FTIR aging indices (CAI, SAI, and ArAI) as a criterion for dosage of the anti-aging additives (DLTDP and furfural) was also investigated.

3.1.1. DLTDP: Rheological characterization

The rheological properties of the modified and unmodified asphalt binders (at the unaged and short-term conditions) are presented in Fig. 2 (a)-(d).

From the master curves of complex modulus, it can be seen that the increase of the content of DLTDP led to a downward shift in master curves (reduction of material stiffness) of both asphalt binders (A and B), regardless of the aging condition of the material.

The reduction of the stiffness may negatively impact the rutting resistance of the asphalt binders. In this matter, Fig. 3 (a) displays the effect of the addition of DLTDP on the rutting parameter of asphalt binders A and B (@ 58 °C), at unaged and RTFOT aging conditions. While in Fig. 3 (b) is shown the change in the continuous high-performance grade of asphalt binders (A and B) due to the addition of DLTDP.

As can be seen in Fig. 3 (a), the addition of DLTDP led to a reduction in the rutting parameter of the unaged and RTFOT aged binders (A and B). Similar observations have already been reported in other studies [24–25].

Furthermore, the rutting parameter increased after the RTFOT (for both unmodified binders). However, the increase observed for binder A (164%) was higher than the observed for binder B (103%), indicating that the first one was more susceptible to short-term aging than the second one. On the other hand, the addition of 2% of DLTDP led to a reduction of the rutting parameter of binder A (RTFOT aged) by 49% while the same content of additive reduced the parameter observed for binder B (RTFOT aged) by 28%, resulting in the approximation between

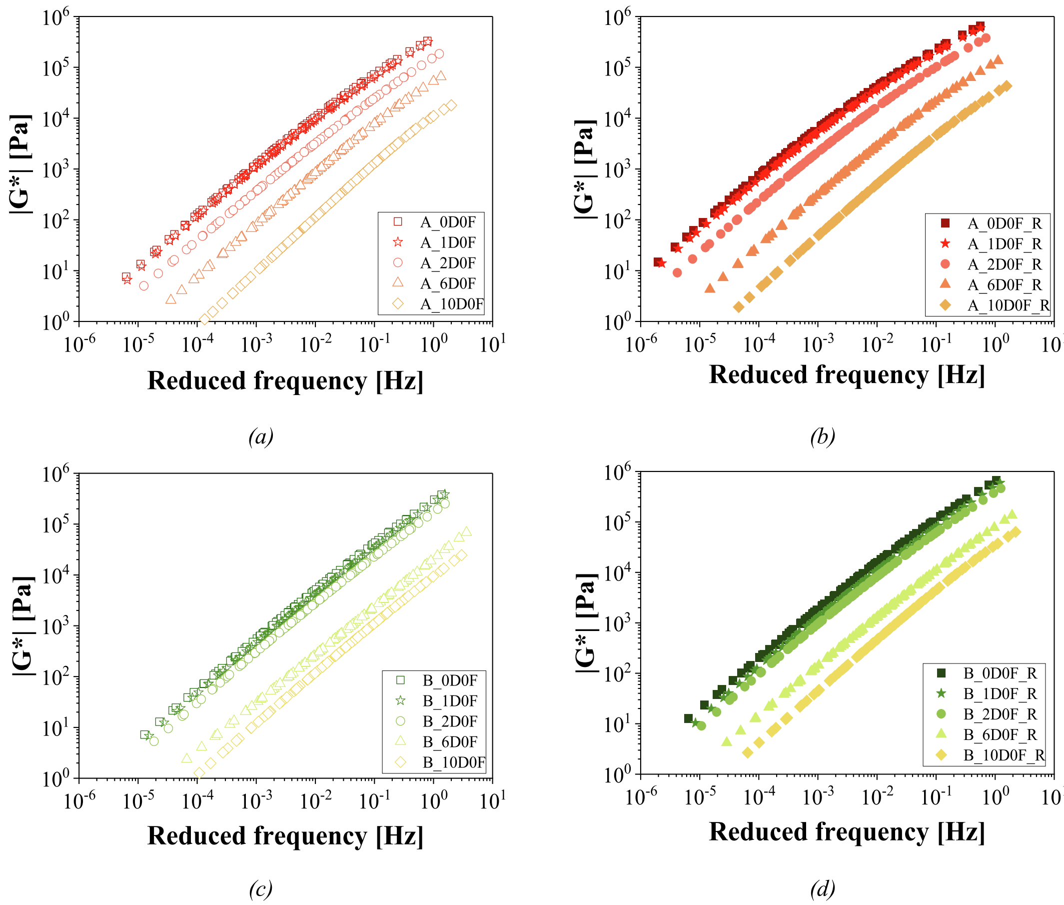


Fig. 2. |G*| master curves of asphalt binders (A and B) modified with different contents of DLTDP: (a) Binder A (unaged condition); (b) Binder A (RTFOT aged condition); (c) Binder B (unaged condition); (d) Binder B (RTFOT aged condition).

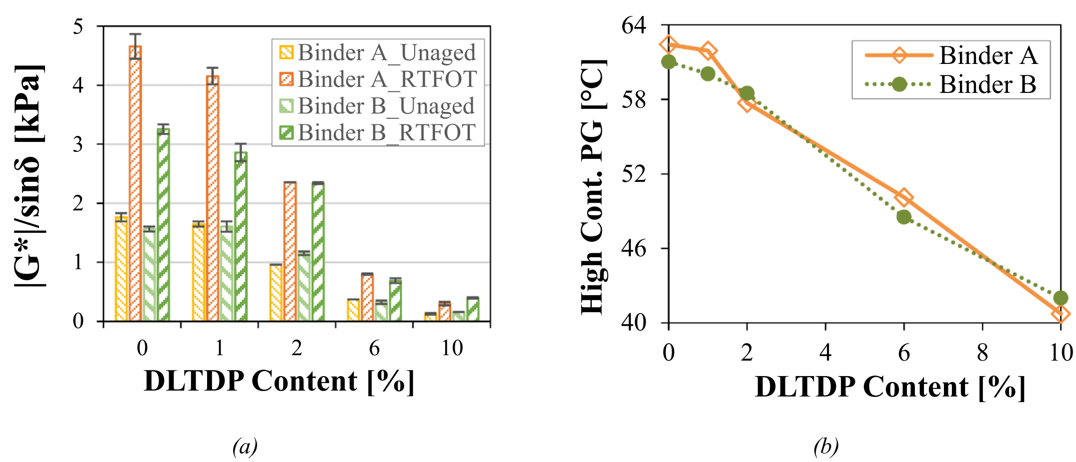


Fig. 3. (a) Rutting parameter of asphalt binders modified with DLTDP; (b) Effect of DLTDP on the continuous PG.

the values of the rutting parameter for both RTFOT aged binders. From those findings, it was possible to deduct that the addition of DLTDP is more likely to reduce the aging susceptibility of binder A than binder B, especially for added content equal to or higher than 2%.

In addition, based on the values of the rutting parameter and the limits set on Superpave specification it was determined the high continuous PG for each one of the contents of DLTDP of the binders (A and B). According to the curves presented in Fig. 3 (b), it can be concluded that there was a strong correlation between the increment of the content of DLTDP added and the reduction of the high continuous performance grade, regardless of the binder type. Also, the obtained results indicated the jeopardizing effect of the additive on the rutting resistance of both asphalt binders. Finally, it can be stated that the softening effect of DLTDP on the asphalt binders was dependent on the binder type and the added content of the additive.

3.1.2. DLTDP: Chemical characterization

FTIR analysis was performed on both binders (A and B) modified with different contents of DLTDP (Fig. 4 and Fig. 5), respectively. For reference purposes, an IR spectrum of the pure DLTDP is given in Fig. 6.

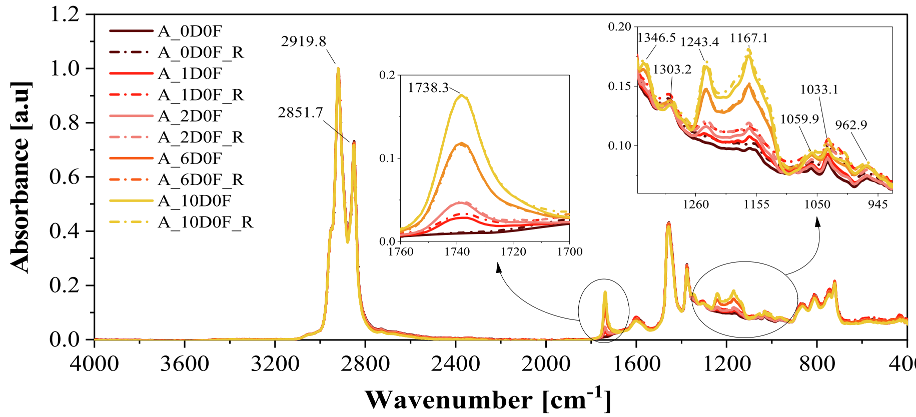


Fig. 4. FTIR spectra of binder A modified with different contents of DLTDP.

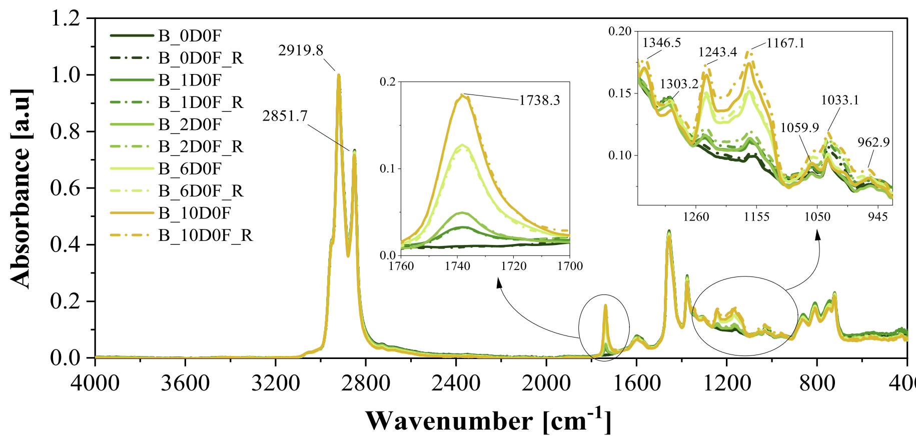


Fig. 5. FTIR spectra of binder B modified with different contents of DLTDP.

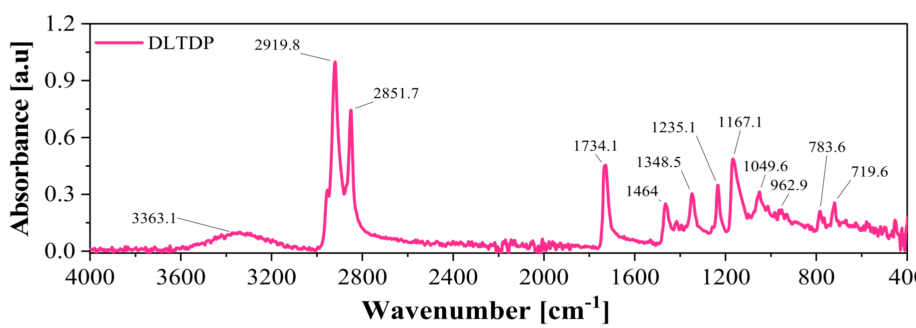


Fig. 6. FTIR spectra of DLTDP.

This enables the identification of DLTDP in the blends shown in Fig. 4 and Fig. 5.

By analyzing the absorbance spectra related to binders A and B (Fig. 4 and Fig. 5, respectively), it was noticed that the addition of DLTDP resulted in the increase of absorbance bands at the five locations of the spectra (1738, 1347, 1243, 1162 and 963 cm^{-1}) which may indicate the chemical reaction between DLTDP and the asphalt binders.

This assumption is based on the fact that the appearing/intensified bands were also observed on the spectrum of pure DLTDP (Fig. 6). For instance, the intensity of the peak found at the band (1760 – 1650 cm^{-1}) related to C=O stretching, and the two strong peaks found at bands (1260 – 1100 cm^{-1}) due to C-O stretching and C–C-O stretching, increased as the content of DLTDP was increased.

To quantify the effect of DLTDP on the binder's chemical composition and aging, functional groups indices (I_{CO}, I_{SO}, and $I_{C=C}$) were calculated. The results are given in Fig. 7 (a)-(c).

In general, the increment of DLTDP was followed by an increase of the sulfoxides functional groups, which was observable for both asphalt binders (A and B). In addition, an expected increase in I_{SO} values after the RTFOT aging can be seen. Considering these results, the utilization of the I_{SO} index needs to be treated with care as bands from the binder and additive contribute to it.

Similarly, correspondence between the amount of DLTDP added and the increase of I_{CO} was observed, regardless of the binder type. Moreover, there was a significant increase at 1738 cm^{-1} (C = O stretching groups) due to the addition of DLTDP (especially for binders with 6% and 10% of DLTDP) which may disturb the evaluation of the carbonyl functional groups formed. In other words, the quantification of carbonyl

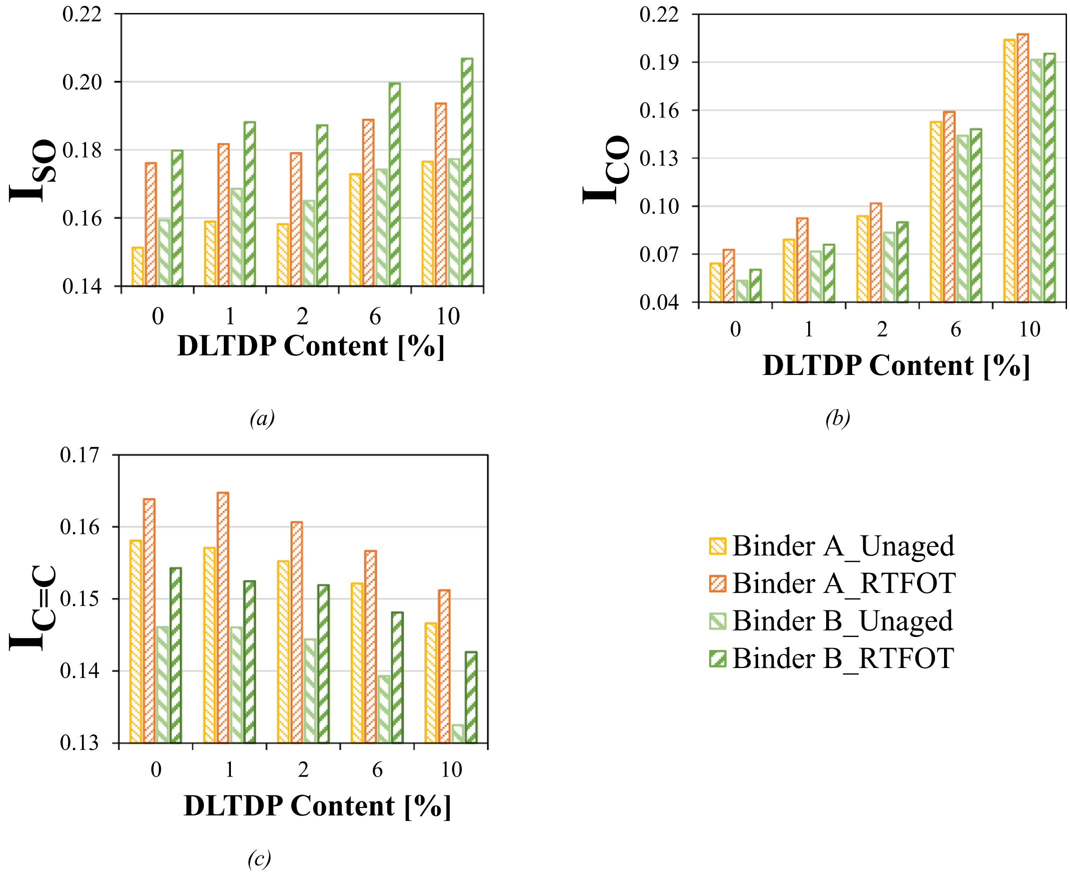


Fig. 7. Functional indices for different binders and contents of DLTDP added: (a) I_{SO};(b) $I_{CO,}$ and (c) $I_{C=C.}$

functional groups may be biased by band appearing at the region usually adopted for calculation of I_{CO}.

Aromatics index ($I_{C=C}$) have been also selected in this study to evaluate the effect of DLTDP on the chemical composition of asphalt binders since some studies indicated the aromatisation as one of the aging mechanism of asphalt binders [2,64–65]. According to Fig. 7 (c), the addition of DLTDP led to a reduction of $I_{C=C,}$ especially for percentages equal to or higher than 2% added. Given the effect of DLTDP on $I_{C=C}$, it is not possible to confirm that this index can correctly quantify the aging of the asphalt binders modified with this additive.

3.1.3. DLTDP: Optimal content

As previously mentioned, the minimum value of RAI was selected as a criterion parameter for determination of the optimal dosage. Fig. 8 (a) shows the variation of RAI according to the content of additive added to the asphalt binders (A and B).

As shown in Fig. 8 (a), the addition of DLTDP affected the RAI values of each binder (A and B) differently. Consequently, each binder resulted in a specific second-degree polynomial function, which was used to determine the optimal content of DLTDP. The optimal content obtained for binders A and B were equal to 6.3% and 1.6%, respectively.

For binder A, the content equal to 6.0% was adopted to facilitate the weighting of the additive and also considering that the values of RAI observed for at the content of 6.0% and 6.3% were both equal to 2.18. For binder B an optimal content of 1.0% was adopted, since this content resulted in the lowest value of RAI.

The feasibility of employing FTIR aging indices of optimal content of DLTDP was also assessed. Therefore, the development of SAI, CAI, and ArAI due to the addition of DLTDP (to both binders) is presented in Fig. 8 (b), (c), and (d), respectively.

Among the FTIR aging indices versus DLTDP content curves, SAI led to polynomial regression curves with similar trends observed for the RAI curves, and, consequently to similar values of optimal content for binder A (6.71%) and binder B (1%). Analogously, ArAI polynomial regression curves followed the same trend as the observed for RAI curves and optimal contents (6.68% and 1.0% for binder A and B, respectively). However, the correlation coefficient (R^2) found for the curve of binder A was low. On the other hand, the CAI was not adequate as the addition of DLTDP may interfere in the quantification of the carbonyl functional groups. Finally, given the similarity between RAI and SAI curves (Fig. 8 (a) and (b)) it can be assumed that SAI could be also be used cautiously as a tool for the selection of the optimal content of DLTDP additive for the asphalt binders A and B.

3.1.4. Furfural: Rheological characterization

The complex modulus master curves (Fig. 9 (a) and (b)) showed the schematic comparison of binders with different contents of furfural and aging conditions.

As illustrated in Fig. 9 (a) and (b), adding furfural softens the unaged binders, A and B. However, the overlapping of RTFOT master curves may indicate that the addition of furfural was not able to soften none of the aged asphalt binders.

The effect of different contents of furfural on the rutting resistance (@ 58 °C) and continuous performance high-temperature grade of the studied asphalt binders are shown in Fig. 10 (a) and (b).

As depicted in Fig. 10 (a) and (b), the addition of furfural reduced the rutting parameters of both unaged binders. On the other hand, the softening response was not followed by RTFOT aged binders (A and B). The reduction of the rutting parameter of unaged binder is not in line with the results presented in the other two studies on furfural [24,30]. However, in Omairey et al., [27] a 12.5% reduction in the initial shear modulus was observed after the addition of 2% furfural in 60 penetration grade asphalt. This indicates that furfural can also act as a softener of asphalt binders. A possible explanation for the controversies found in

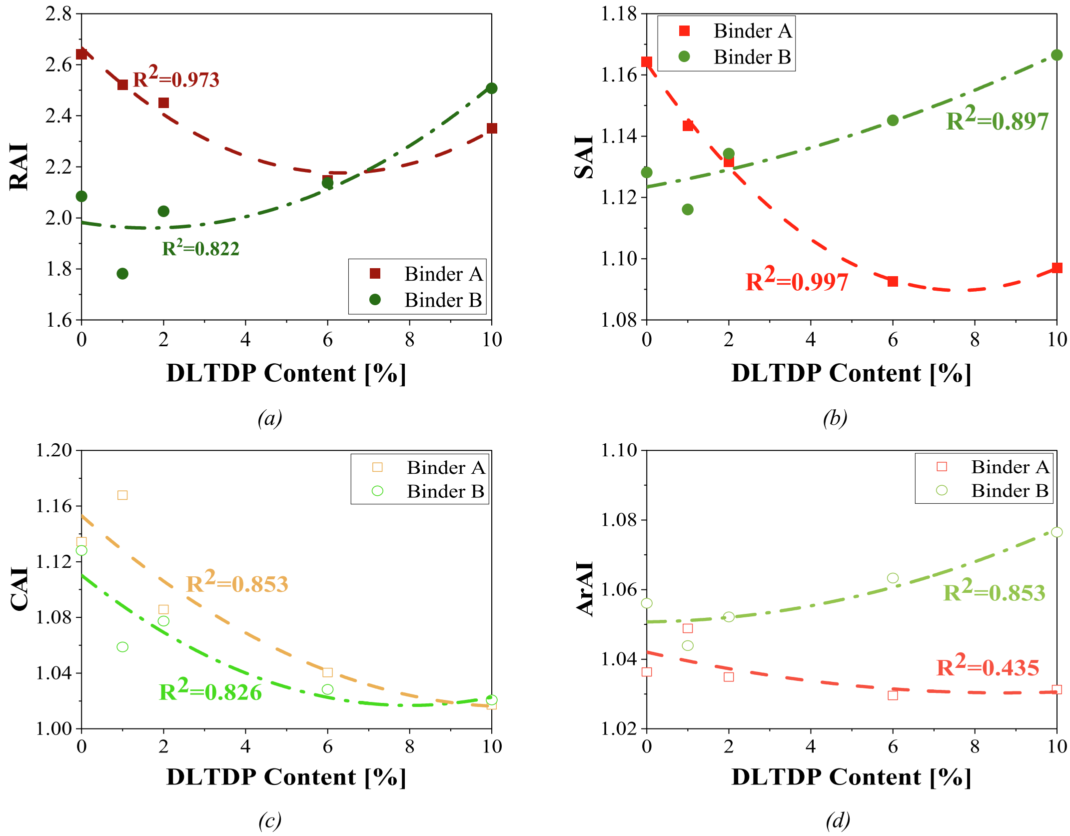


Fig. 8. Aging indices of binders with different contents of DLTDP. (a) RAI; (b) SAI; (c) CAI; and (d) ArAI.

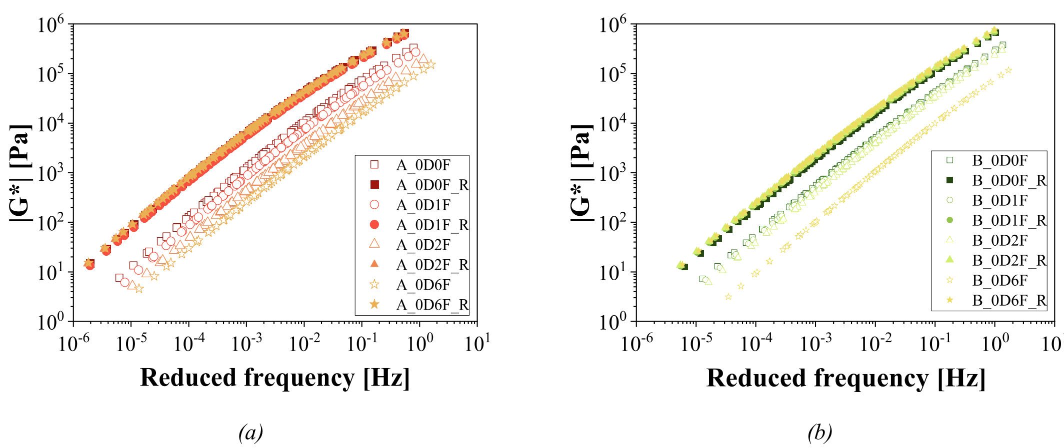


Fig. 9. |G*| master curves of asphalt binders (A and B) modified with different contents of furfural. (a) binder A (unaged and RTFOT aged condition); (b) binder B (unaged and RTFOT aged condition).

published studies lies in the fact that some studies have considered the addition of furfural in asphalt binder in the presence of an acid (catalyst agent). In these circumstances, the interaction between additive and phenol derivatives (present in the binder) increases the stiffness of the binder [66].

Meanwhile, in the present study, the addition of furfural without the presence of a catalyst agent was chosen to determine the function of the pure additive and also reduce impracticability in the production of asphalt mixtures carried out in the field. Once this practice would require special handling and safety precautions. Therefore, as furfural is a liquid at room temperature, it is expected that the addition of this additive to an unaged asphalt binder will result in a decrease in its stiffness.

Based on the values of the rutting parameter and the Superpave specification, the outcomes of the addition of furfural on the continuous high PG were determined (Fig. 10 (b)). In general, the furfural reduced the high continuous PG of both binders. It is worthy of mention that this reduction was mainly due to the reduction of the rutting parameter of the unaged binders.

3.1.5. *Furfural: Chemical characterization*

FTIR analysis was performed on both binders (A and B) modified with different contents of furfural (Fig. 11 and Fig. 12). Fig. 13 depicts the IR spectrum of the pure furfural, which is used to identify the additive in the spectra of the modified binder.

Both binders showed several new bands after their blending with

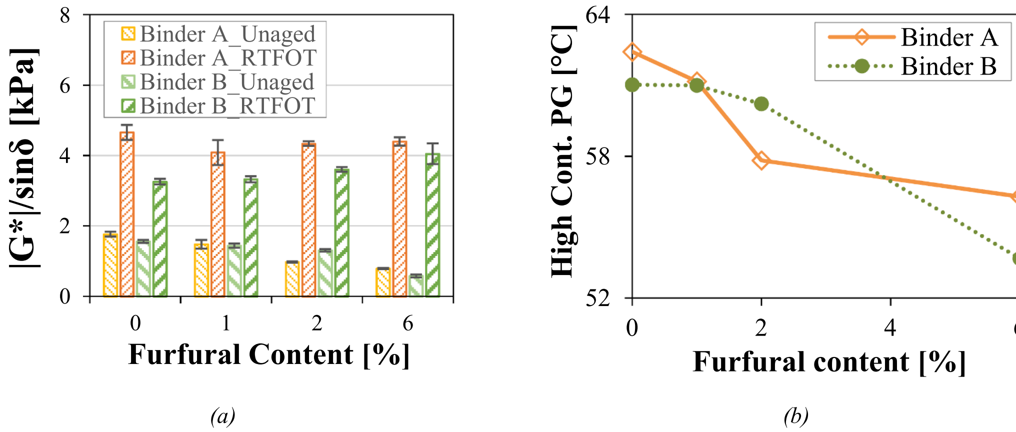


Fig. 10. (a) Rutting parameter of asphalt binders modified with furfural; (b) Effect of furfural on the continuous PG.

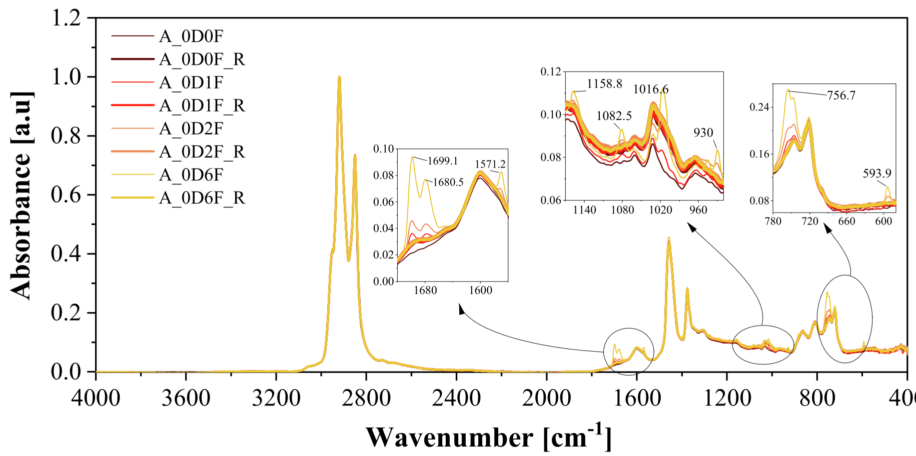


Fig. 11. FTIR spectra of binder A modified with different contents of furfural.

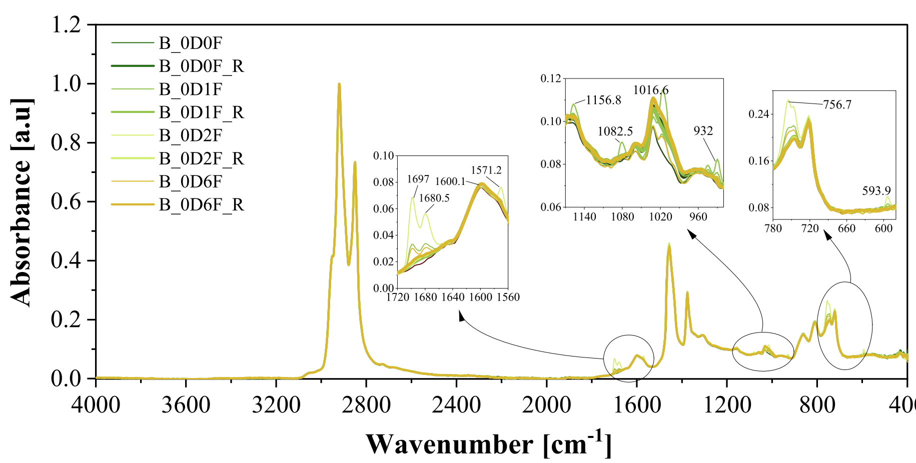


Fig. 12. FTIR spectra of binder B modified with different contents of furfural.

furfural. The main bands can be found at (1720–1660 cm^{-1}), (1580–1560 cm^{-1}), and (780–720 cm^{-1}) which were also observed in the spectrum of the furfural. However, an overlapping of absorbance spectra of the RTFOT aged (represented by the thick lines) was observed for both binders, regardless of the initial furfural content. This may indicate a complete degradation/ evaporation of furfural during the RTFOT aging procedure. This seems reasonable, since the RTFOT aging procedure was performed at 163 °C which is higher than the boiling point of furfural (161.7 °C).

As for DLTDP, functional groups indices (I_{CO}, I_{SO}, and $I_{C=C}$) were calculated to evaluate the effect of furfural on the binder's chemical composition and aging resistance. The results are given in Fig. 14 (a)-(c).

As depicted in Fig. 14 (a)-(c), the increase of the content of furfural added was followed by an increase in all functional group indices (I_{CO}, I_{SO}, and $I_{C=C}$) for unaged binders (A and B). This result was expected since the bands were observed in the carbonyl, aromatics, and sulfoxide

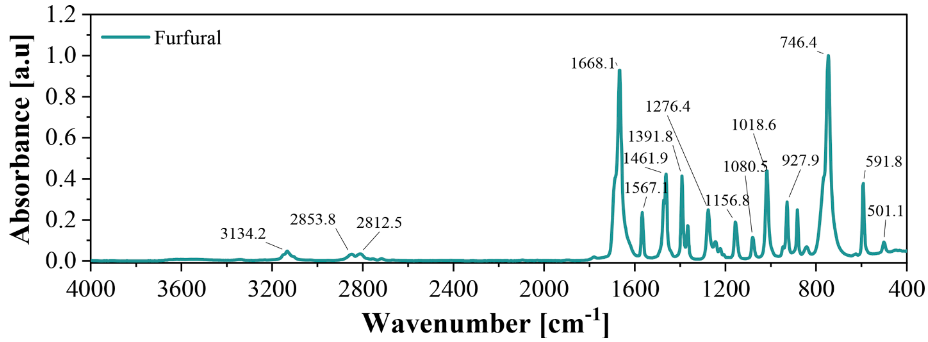


Fig. 13. FTIR spectra of furfural.

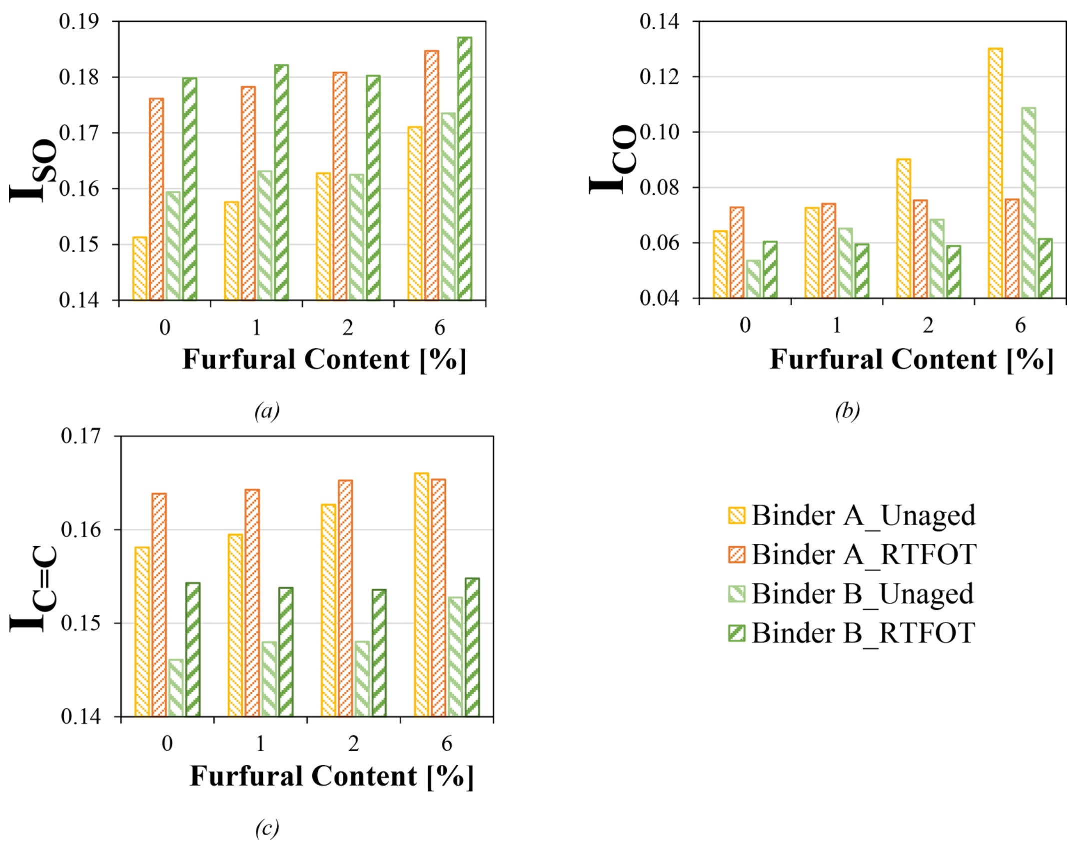


Fig. 14. Functional indices for different binders and contents of furfural added. (a) I_{SO};(b) $I_{CO,}$ and (c) $I_{C=C}$.

bands region, after the blending of the asphalt binders with furfural.

In addition, the I_{CO} and $I_{C=C}$ of the RTFOT aged binders were not affected by the content of the furfural added, which confirmed the evaporation during RTFOT. The increase of I_{SO} for aged binder due to the addition of furfural indicated that a certain amount of furfural interacted with asphalt binders generating sulfoxides. From the findings, it can be assumed that the determination of FTIR indices was biased by the addition of furfural, especially when unaged binders were considered.

3.1.6. Furfural: Optimal content

Three different contents of furfural were added to asphalt binders (A and B) to determine the optimal content of this chemical compound. Fig. 15 (a) displays the values of RAI for various contents of furfural added to both binders.

Regardless of the type of binder, the increase in the content of furfural led to an increase in the short-term aging index. It should be considered that the increase of RAI was depending on the type of asphalt binder type and furfural content. Given the harmful and negative effect of furfural on the short-term aging resistance of both binders (A and B), it was considered the minimum content mentioned in the literature. Still, since there might be beneficial effects in combination with DLTDP, furfural was further considered in this study. In this regard, an optimal content of 1.5% (wt% of unmodified binder) was adopted for both binders since it was the minimum content mentioned in the literature review [24].

In addition, the polynomial curves related to FTIR indices (SAI, CAI, and ArAI) indicated that the addition of furfural would increase the aging resistance of the asphalt binders. However, the decrease of the FTIR aging indices (due to the addition of furfural) was related primarily to the increase of the denominator (binder in the unaged condition), and not by the decrease of the numerator. Therefore, the analysis of the aging resistance of asphalt binder from the FTIR aging indices may lead to biased results and thus, wrong conclusions.

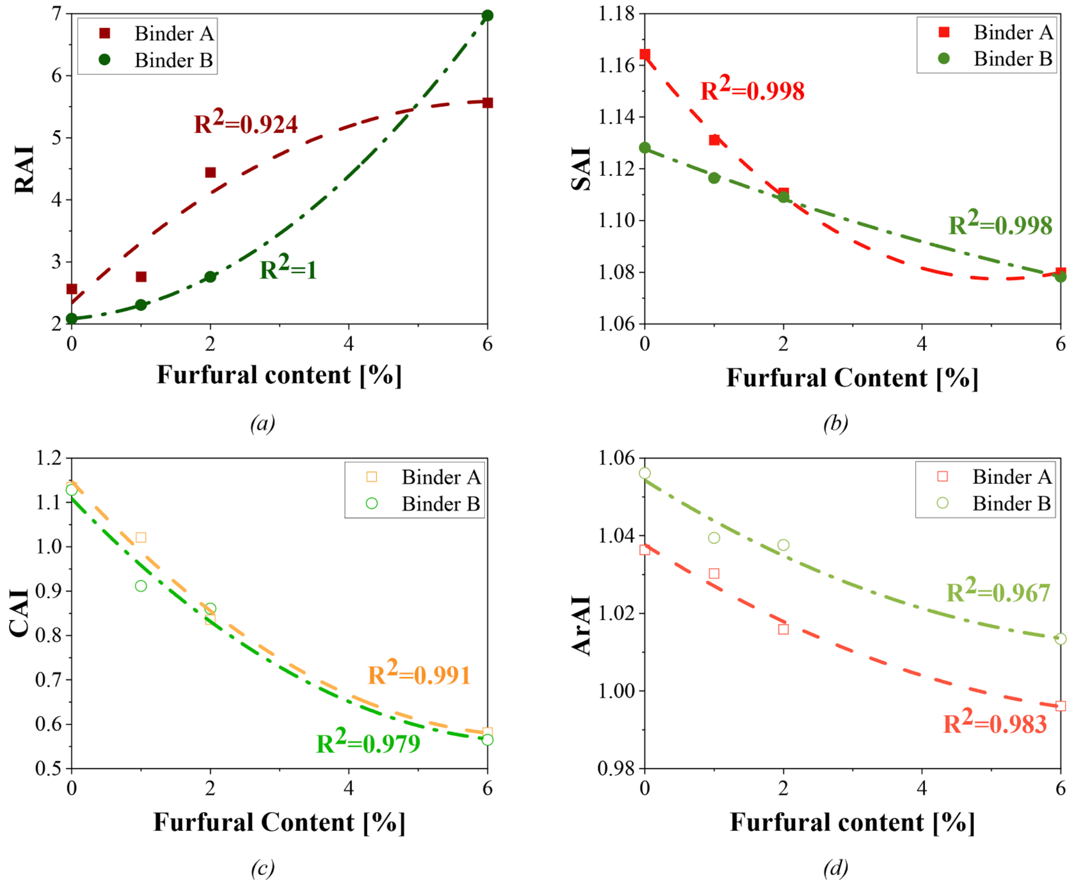


Fig. 15. Aging indices of binders with different contents of furfural: (a) RAI; (b) SAI; (c) CAI; and (d) ArAI.

3.2. Phase II: Evaluation of the effect of the compound additives on the PG grade

Based on the optimal contents of DLTDP and furfural determined in phase I, the recipes for the anti-aging compound additives (referred to as C1 and C2) were determined. The anti-aging additives, C1 and C2, were added to asphalt binders, A and B, respectively. Consequently, the synergistic effect of the combined effect of these two compound additives on the performance grade of the asphalt binders was evaluated in phase II. In addition, binder A was selected to verify if furfural has evaporated during RTFOT aging, as conjectured in phase I. Thus, it was also considered the addition of only DLTDP to asphalt binder A.

3.2.1. Viscosity

In Fig. 16 the viscosity-temperature chart for binders at unaged condition measured at three different temperatures (135 °C, 155 °C, and 165 °C) is displayed.

As expected, the increase in the temperature led to the decrease of viscosity of unmodified and modified binders. In addition, the viscosity at 135 °C of all binders was below the limit of 3 Pa·s constrained by Superpave specification indicating that all the binders fulfilled the minimum workability criterium. Also, the addition of compounds C1 and C2, reduced the viscosity of binders A and B, respectively. Consequently, the mixing and compaction temperatures of modified binders (A_C1 and B_C2) may be lower than the obtained for their respective unmodified binders. Thus, this reduction of viscosity may reduce the

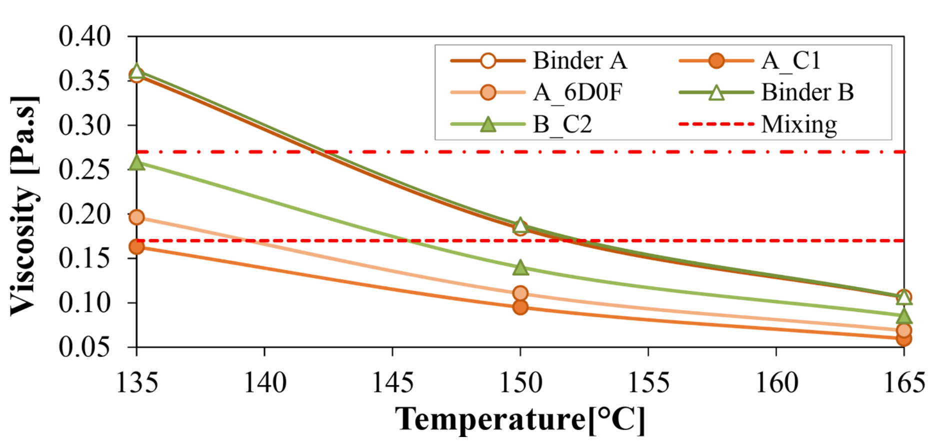


Fig. 16. Effect of anti-aging additives on the viscosity of the asphalt binders.

energy consumption during mixing and compaction of the mixtures. It is important to notice that the viscosity values of the A_C1 binder were lower than the values observed for binder A_6D0F. This finding is expected since furfural is presented as a liquid at room temperature.

3.2.2. High-temperature PG

The complex modulus and phase angle master curves of unmodified and modified asphalt binders (A and B), at different aging conditions, are shown in Fig. 17 (a) to (d).

According to Fig. 17 (a) and (c), the addition of anti-aging additives (C1, DLTDP and C2) resulted in the softening of unaged asphalt binders (A and B). This finding is expected, given the effect of those additives on the viscosity of both asphalt binders. The same softening effect was extended to the RTFOT aged samples indicating that the studied anti-ageing additives have high potential to be employed as softeners of asphalt binders. Regarding the phase angle master curves, the modified asphalt binders showed higher values of phase angle when compared with the unmodified binders (A and B), regardless of the aging condition. This finding indicated that the modified binders were less elastic (more viscous) than unmodified asphalt binders.

In addition, the data obtained from the frequency sweep test (at 1.59 Hz) allowed the determination of the rutting parameter. This parameter is considered in Superpave to determine the high PG temperatures of asphalt binders. In that matter, the benchmarks for rutting parameters equal to or higher than 1.0 kPa and 2.2 kPa are adopted for unaged and RTFOT aged, respectively. The rutting parameters of the binders studied (at different aging conditions) are presented in Fig. 18 (a)-(d).

As shown in Fig. 18 (a)-(d), both unmodified binders (A and B) presented a high PG temperature of at least 58 °C. On the other hand, the addition of anti-aging additives (C1 and DLTDP) into binder A reduced its high PG temperature to 46 °C. Similarly, the modification of binder B by the addition of anti-aging additive C2 led to a reduction of the high PG temperature to 52 °C. In summary, the addition of anti-aging additives (DLTP and C1 in binder A and C2 in Binder B) to asphalt binders led to a decrease in the rutting resistance and high PG temperatures of the studied binders.

3.2.3. Intermediate temperature PG

The complex modulus and phase angle master curves of unmodified and modified asphalt binders (A and B), at unaged and RTFOT + PAV aged conditions, are shown in Fig. 19 (a)-(d).

As can be witnessed in Fig. 19 (a) and (b), the unaged modified binders presented lower values of complex modulus and higher values of phase angle when compared to the values observed for unmodified binders. However, the difference between the values of |G*| observed for unmodified and modified binders is narrowed at values high of frequencies (low temperatures) indicating that at low temperatures the softening effect of the modified binders is not significant.

Regarding the RTFOT + PAV, a downward shift in |G*| master curves and upward shift in δ curves for modified binders (A_C1_P and A_6D0F_P) was observed when comparing it to unmodified binder A. Moreover, the difference between the |G*| and δ master curves for A_C1_P and A_6D0F_P is not pronounced, revealing that the softening effect of furfural is partially annulled after RTFOT + PAV aging due to the evaporation of furfural. In the case of binder B, the modification did not impact the |G*| and δ master curves significantly when comparing it to unmodified binder B, both at RTFOT + PAV aged conditions.

As performed for the rutting parameter, the |G*| and δ recorded during the frequency sweep test (at a frequency equal to 1.59 Hz) were used to calculate the Superpave fatigue parameters, presented in Fig. 20 (a)-(d). According to Superpave specification, this parameter is limited to 5.000 kPa as the criterion of performance of RTFOT + PAV aged binders, at intermediate temperatures.

Based on Fig. 20 (c) and (d), the intermediate temperature observed

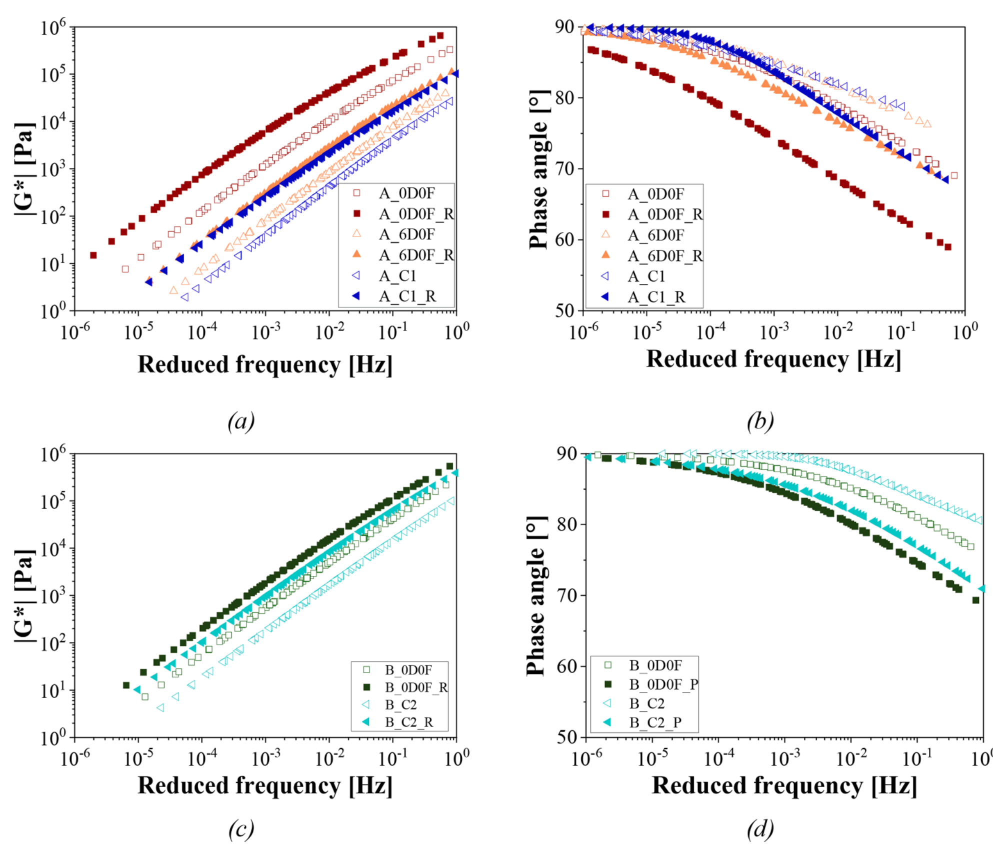


Fig. 17. Master curves of asphalt binder at unaged and RTFOT aged condition (and their respective modified binders with different anti-aging additives). (a) |G*| master curves (binder A); (b) δ master curves (binder A); (c) |G*| master curves (binder B); (d) δ master curves (Binder B).

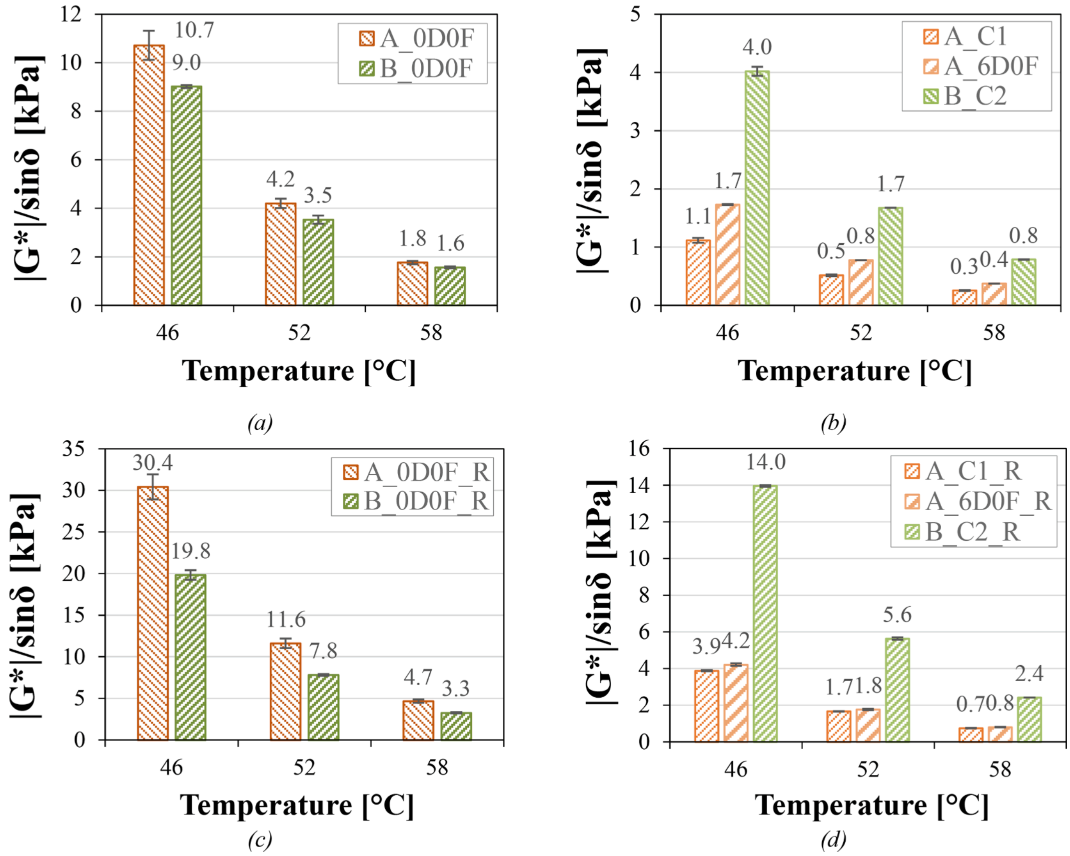


Fig. 18. Rutting parameter of asphalt binders (and their respective modified binders with different anti-aging additives): (a) Unaged unmodified binders; (b) Unaged modified binders; (c) RTFOT aged unmodified binders; (d) RTFOT aged modified binders.

for the unmodified binder A (16 °C) was lower than the temperature registered for binder B (22 °C). The finding indicated that binder B may be more susceptible to fatigue than binder A. However, the addition of only 2.5% C2 to binder B culminated in the increase in its fatigue resistance.

The addition of 6% DLTDP and 7.5% C2 to binder A improved the performance grade at an intermediate temperature significantly. Given the above, it can be hypothesized that the studied additives may be beneficial to the fatigue resistance of the asphalt binders considered in this study.

3.2.4. Low temperature PG

The average values of S and m-value calculated from BBR test at 60 s of loading time at three different temperatures (−18 °C, −24 °C and −30 °C) are presented in Fig. 21 (a) and (b), respectively.

According to Fig. 21 (a) and (b), the Superpave limits were fulfilled only for the temperature equal to −18 °C, in the case of unmodified binders (A and B). On the other hand, the modified binders (A_6D0F_P, A_C1_P, and B_C2_P) met the Superpave requirements at a temperature equal to −30 °C, −24 °C, and −24 °C, respectively. This finding indicates that the addition of the anti-aging additives improved the low-temperature performance of binders (A and B). For instance, the addition of 6% of DLTDP and 7.5% of C1 to binder A resulted in the drop of the continuous grading temperature equal to 9.8 °C and 6.0 °C, respectively. The greater drop observed for binder A_6D0D_P when compared to A_C1_ P is due to the jeopardized effect of furfural on the increase of the stiffness of the binder after the PAV aging procedure, as shown in Fig. 20 (d). For binder B, the addition of 2.5% of C2 resulted in a reduction equal to 2.2 °C.

Based on the BBR results it can be hypothesized that the addition of the anti-aging additive resulted in a decrease of S values and increase of m-value indicating that the modified binders may be less susceptible to low temperature cracking due to thermal stress than the unmodified binders, especially when 6% of DLTDP was added to binder A.

3.2.5. PG grading and continuous PG

The performance grades (full and continuous), the difference between continuous low PG and continuous high PG and aging indices (RAI and FAI) of the binders evaluated in phase II of this study were shown in Table 6.

For binders A and B, a decline of the high-temperature performance due to the addition of the additives (C1, DLTDP and C2) was observed. This was followed by an improvement in intermediate and low-temperature range due to the modification of the material. Moreover, the addition of the anti-aging additives reduced the difference between the low and high continuous PG which indicates no anti-aging improvement due to the addition of the additives.

The addition of the compound formed by DLTDP and furfural led to a softening at high and low temperatures. However, the softening effect at high temperatures was stronger than at low temperatures. Thus, the continuous PG span (difference between upper and lower PG) was reduced due to the modifications of both asphalt binders (A and B).

In general (with exception of A_6D0F binder) the addition of additive increased RAI and FAI. However, the increase of the aging indices was related primarily to the decrease of the denominator (binder in the unaged condition), and not by the increase of the numerator. In other words, the addition of anti-aging additives (especially for compounds with furfural) to unaged binders culminated in the strong reduction of the stiffness and increase of phase angle of the binders, leading to lower values of the denominator. Those findings may indicate that RAI and FAI indices are not adequate to express the aging resistance of the asphalt binders studied in this study.

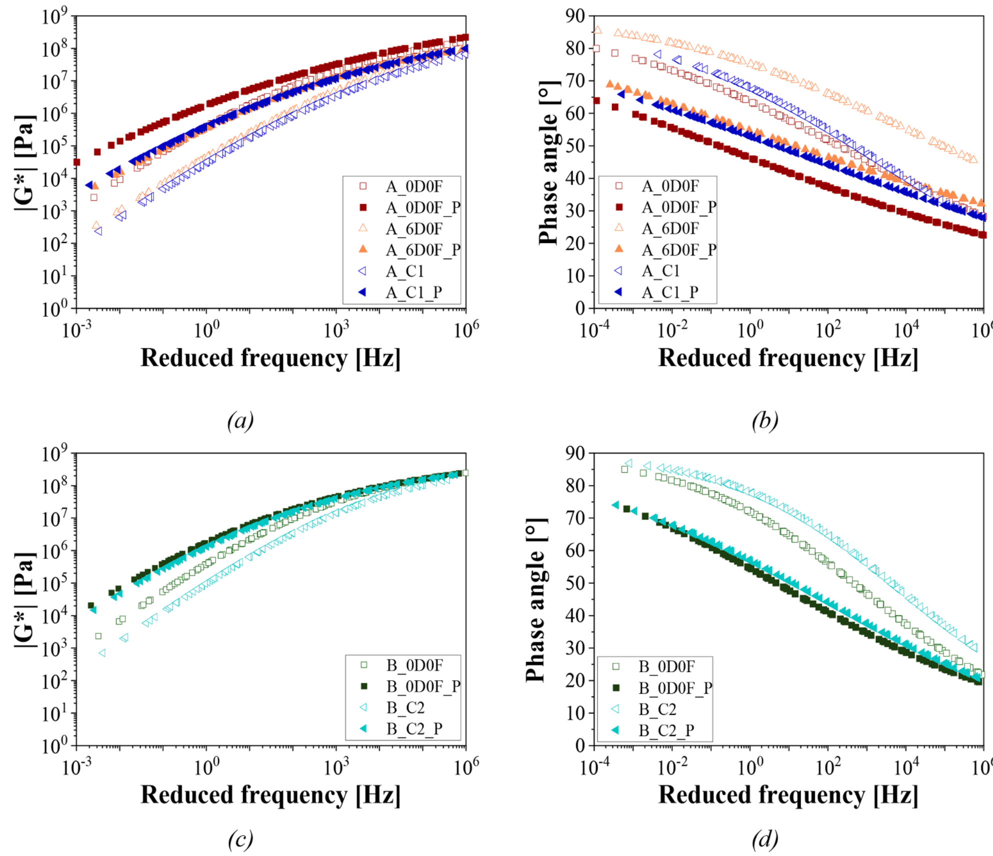


Fig. 19. Master curves of asphalt binder at unaged and RTFOT + PAV aged condition (and their respective modified binders with different anti-aging additives) . (a) |G*| master curves (binder A); (b) δ master curves (binder A); (c) |G*| master curves (binder B); (d) δ master curves (Binder B).

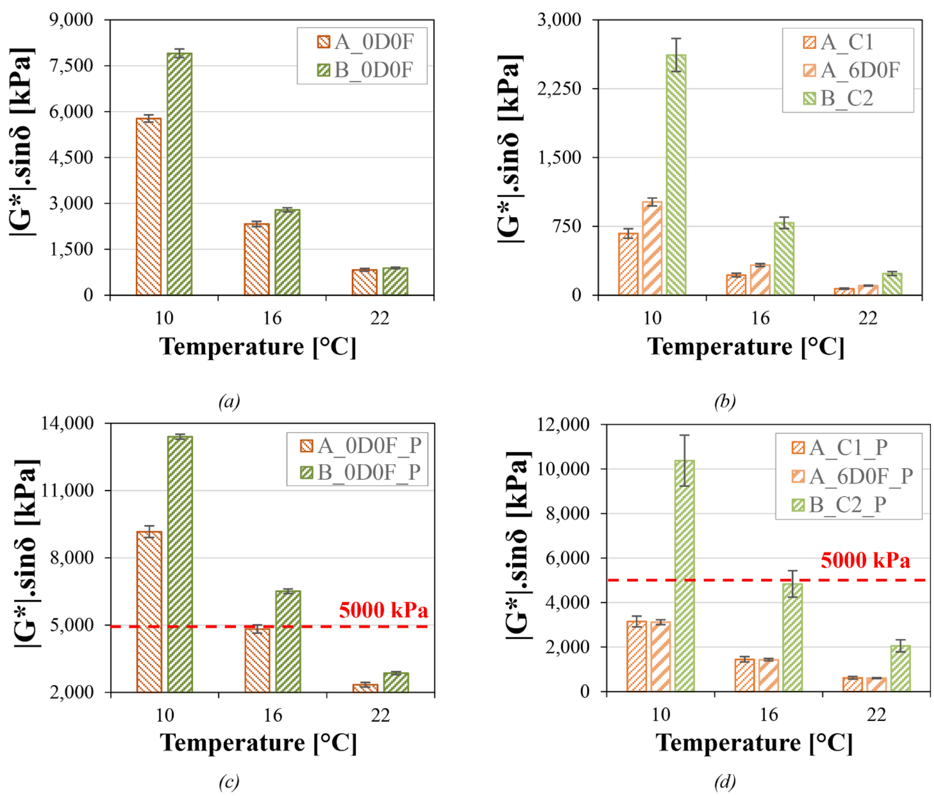
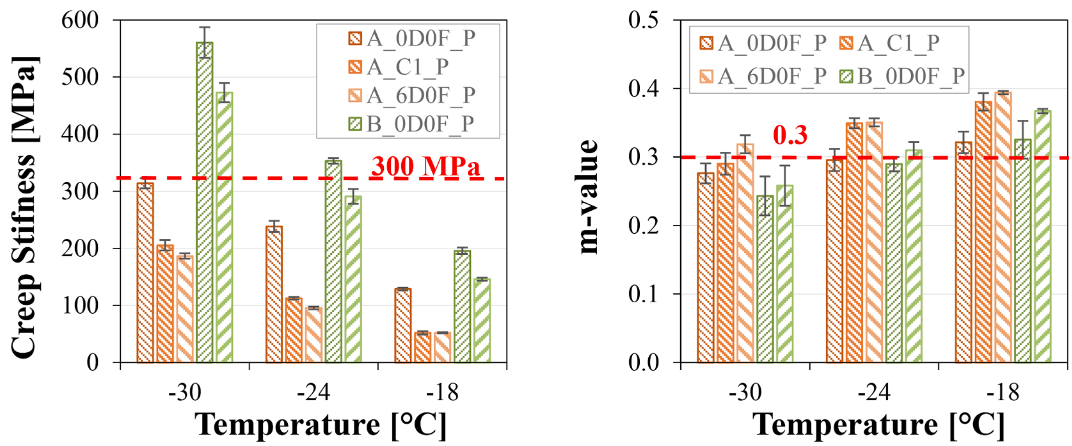


Fig. 20. Fatigue parameter of asphalt binders (and their respective modified binders with different anti-aging additives): (a) Unaged unmodified binders; (b) Unaged modified binders; (c) RTFOT + PAV aged unmodified binders; (d) RTFOT + PAV aged modified binders.



(a) *(b)*

Fig. 21. BBR results (a) S; (b) m-value.

Table 6
PG grading and aging indices of binders studied in phase II.

Parameter	Condition	Specification	PG				
			A_0D0F	**A_C1**	**A_6D0F**	**B_0D0F**	**B_C2**
Viscosity	unaged	<=3 Pa.s	OK	OK	OK	OK	OK
|G|*/sinδ	Unaged	>=1 kPa at 1.59 Hz	58	46	46	58	52
|G|*/sinδ	RTFOT	>=2.2 kPa at 1.59 Hz	58	46	46	58	58
Upper PG			58	46	46	58	52
|G|*.sinδ	PAV	<=5000 kPa at 1.59 Hz	16	7	7	19	16
Intermediate PG			16	7	7	19	16
S	PAV	<=300 MPa at 60 sec	−34	−46	−46	−28	−34
m-value	PAV	>=0.3 at 60 sec	−28	−34	−40	−28	−34
Lower PG			−28	−34	−40	−28	−34
PG			58–28	46–34	46–40	58–28	52–34
Continuous PG			62.4–33.0	46.9–39.0	50.1–42.8	61.0–32.2	56.1–34.4
RAI (@ 46 °C)			2.8	3.5	2.4	2.2	3.5
FAI (@ 22 °C)			2.8	8.8	5.8	3.2	8.7
Difference between cont. low and cont. high PG			95.4	85.9	92.9	93.2	90.5

4. Summary and conclusions

This study looked into the impact of two different anti-aging additives (furfural and DLTDP) on the rheological and chemical composition of two types of asphalt binders. It was divided into two phases. The initial phase aimed to provide a methodology for dosing of an anti-aging compound (composed of DLTDP and furfural). In the second phase, the effect of the addition of this compound on the performance grade of the binders was evaluated. The main findings and conclusions are as follows:

4.1. Phase I: Determination of optimal dosage

- The addition of DLTDP had a jeopardizing effect on the rutting resistance of asphalt binders studied. The softening magnitude was asphalt binder type and DLTDP content dependent. Also, the addition of this additive affected the chemical composition of both asphalt binders which may bias the quantification of FTIR functional indices.
- As observed in the DLTDP case, the addition of furfural resulted in the softening of both binders at unaged conditions. On the other hand, the softening effect was not observed after the RTFOT aging procedure.
- The similarity between furfural modified and unmodified binder (after RTFOT) indicated the evaporation of the additive during the RTFOT procedure, which can be explained by the fact that the standard aging temperature (163 °C) is higher than the boiling point of furfural (161.7 °C).
- The optimal content of DLTDP was asphalt binder type dependent. For furfural, the minimum value reported in the literature was considered.

4.2. Phase II: Evaluation of the effect of the compound additives on the PG grade

- The addition of the additives considered in phase II (C1, C2, or DLTDP) reduced the rutting resistance and improved the fatigue and thermal cracking resistance of the studied binders.
- The reduction of continuous PG span after the addition of the additives indicated the inferior performance of the modified binders when compared to unmodified ones despite the improvement of the intermediate and low-temperature performance.

Thus, it can be concluded that the combined use of furfural and DLTDP provides a softening of the binders in the upper and lower temperature regions. However, since the span of the continuous PG shrinks due to a stronger softening effect at high temperatures and short-term aging than for low temperatures and long-term aging, the use of this combination of additives as an anti-aging agent could not be proven by this study.

Moreover, further research considering a wider range of asphalt binder types (originated from different sources and refining processes), microscope techniques, statistical analysis, and the use of different methods (such as crossover frequency and Glover-Rowe) to better explore the rheological data is needed to validate and better understand the mechanism and interaction between the studied additives and asphalt binders.

CRediT authorship contribution statement

Ingrid Camargo: Conceptualization, Methodology, Formal analysis, Validation, Writing – original draft, Investigation, Project administration. **Bernhard Hofko:** Conceptualization, Supervision, Resources, Project administration, Funding acquisition, Writing – review & editing. **Johannes Mirwald:** 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.

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