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Effects of Laboratory Ageing on the Chemical Composition and High-Temperature Performance of Warm Mix Asphalt Binders

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Abstract: Warm asphalt mixtures can suffer from decreased short-term high-temperature performance; therefore, introducing additional modifiers can mitigate this risk. This study investigates the effects of a liquid organosilane warm mix additive (WMAd) and grade-bumping polyethylene-based additive added simultaneously to asphalt binders on their chemical composition and its relationship with performance characteristics. Previous studies found relationships between the formation of certain chemical species during bitumen ageing and the increase in their viscosity, stiffness and other performance characteristics—the present work intended to verify these relationships when the two mentioned additives are used. Two asphalt binders were investigated—a paving-grade 50/70 binder and a 45/80-55 polymer-modified bitumen. The chemical analysis was performed using Fourier-transform infrared (FTIR) spectroscopy in attenuated total reflectance mode and focused on the quantification of carbonyl, sulfoxide, polybutadiene and polystyrene structures in the asphalt binders subjected to laboratory short- and long-term ageing. Additionally, the relationships between asphalt binder performance and selected FTIR indices were evaluated using a dynamic shear rheometer. It was found that the investigated additives significantly affected the apparent contents of all evaluated chemical structures in the asphalt binders; however, these changes were not reflected in their performance evaluation.

Keywords: paving-grade bitumen; polymer-modified bitumen compaction aid; warm mix additive; FTIR; DSR

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1. Introduction

The popularization of warm mix asphalt (WMA) techniques is one of the means to decrease energy expenses and improve working conditions in the road construction industry. These techniques typically use additives or alterations in the production of asphalt mixtures to decrease their processing temperatures typically by 20 °C to 30 °C compared to the conventional asphalt paving processes. This reduction limits the energy expenditure to heat the constituents of the mixtures and decreases the fuming and volatilization of organic compounds [1–3].

To enable the production of WMA mixtures and the coating of aggregate mixtures with asphalt binders, sufficient mixture workability and compactibility must be provided at decreased temperatures by using special technical means. These include the utilization of proprietary techniques and additives (e.g., liquid and solid WMAd) [4–8], asphalt binder foaming using water and water-bearing additives [9–19] and bio-based fluxing agents [20–25], as well as the simultaneous use of different processes [19,26–31]. In recent years, techniques enabling the production of half-warm mix asphalt mixtures have also gained significant attention [32–34]. One of the added benefits of warm mix asphalt techniques is the possibility of extending the hauling distance of the mixture [35].

The decreased processing temperatures used in warm mix asphalt cause decreased ageing of asphalt binders compared to hot mix asphalt. This may lead to decreased high-temperature performance in the early service life of pavements produced with these methods, as indicated in laboratory studies [29,36–40], and confirmed in the field [41–43]. Additionally, it is also known that the ageing of asphalt binders may be affected by the use of certain additives (e.g., anti-stripping agents and liquid WMAds). These may slow down the ageing process, limiting the increase in asphalt binder stiffness resulting from technological and long-term ageing. This phenomenon was found to have a source in the antioxidative and dispersive action of these additives [44,45]. On the other hand, solid warm mix additives based on waxes, thanks to their distinct properties, may enhance high-temperature performance and aggregate–binder adhesion in warm mixtures [46–51]. Some synthetic waxes additionally slow down the formation of carbonyl compounds in asphalt binders, therefore decreasing the ageing-induced changes in their properties while preserving the high-temperature performance of the binder and asphalt mixture [39,52,53].

Certain characteristics of asphalt binders can be linked to the content and formation of carbonyl and sulfoxide species [44]. It was shown that ketone formation due to oxidative ageing is highly correlated to bitumen viscosity [54–56], having significant effects on the rheology of aged asphalt binders. The contents of carbonyls and sulfoxides also strongly correlate with increased stiffness of the binders, specifically when considered in terms of ageing [29,57–59]. Fourier-transform infrared (FTIR) spectroscopy used in these studies was found to be useful not only in the determination of ageing specific compounds [57–65] but also in the detecting and quantitative determination of certain polymers in asphalt binders [57,66–69].

Based on the presented state of the art, a study was conducted to investigate the effects of the simultaneous use of a new-generation liquid warm mix additive and a polyolefin additive used for improving the high-temperature performance of asphalt binders. This study focused on the apparent changes in the chemical composition of two asphalt binders—a paving-grade and polymer-modified bitumen. Additionally, relationships between the measured chemical indices obtained using the FTIR spectroscopic method and the high-temperature stiffness of the binders were investigated.

2. Materials and Methods

2.1. Materials

2.1.1. Asphalt Binders

The present study utilized two different asphalt binders: a 50/70 paving-grade bitumen and a 45/80-55 polymer-modified bitumen, both used locally in paving, e.g., wearing courses. The asphalt binders were obtained commercially from a local refinery (Orlen Asfalt, Płock, Poland), and their basic characterization is provided in Table 1.

Table 1. Properties of the asphalt binders used in this study.

Property	Unit of Measurement	Base Bitumen		Testing Method
		50/70	45/80-55	
Penetration at 25 °C	0.1 mm	64.6	61.5	EN 1426
Softening point	°C	49.9	59.44	EN 1427
Fraass breaking point	°C	−12.9	−16.5	EN 12593
Penetration index	-	−0.61	1.56	EN 12591
Performance grade	°C	64–22	70–28	AASHTO M 332
Dynamic viscosity at 135 °C	Pa·s	0.42	1.06	EN 13302

Both asphalt binders were characterized by comparable values of penetration, but because of the polymer modification present in the 45/80-55 polymer-modified bitumen, the remaining properties of the binders were significantly different. The 45/80-55 binder exhibited more preferable high- and low-temperature performance (represented by its performance grade), which also was reflected in its conventional properties of softening point and Fraass breaking point. The attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectra of these asphalt binders are presented in Figure 1. The spectra show distinct peaks associated with the presence of butadiene and styrene chemical groups in the 45/80-55 binder, which confirm the presence of a styrene–butadiene–styrene copolymer.

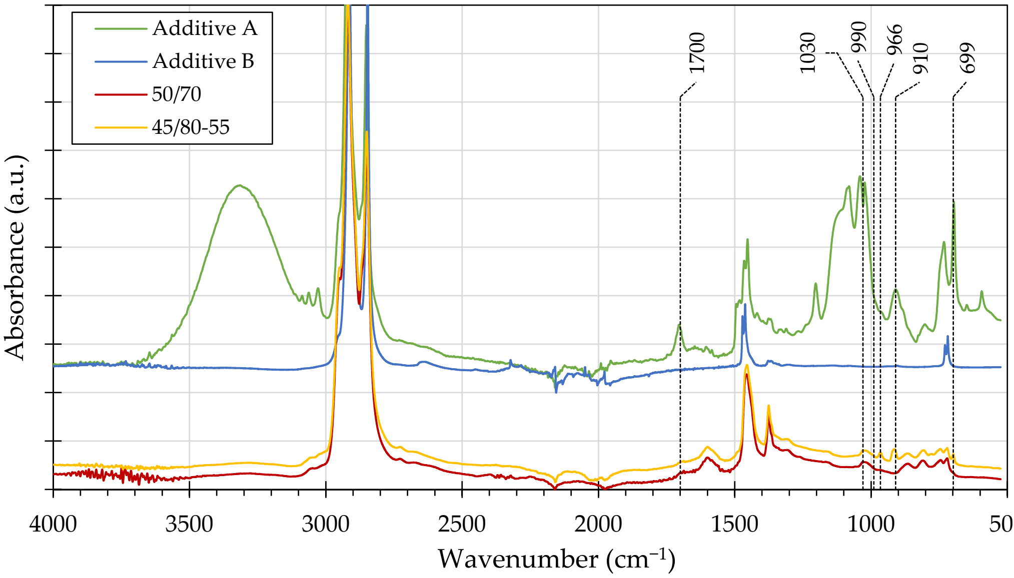

Figure 1. ATR-FTIR spectrograms of the additives and asphalt binders used in this study (normalized and then shifted for clarity).

2.1.2. Additives

The present study evaluated the effects of the simultaneous use of two asphalt binder additives:

- additive A: ZycoTherm (Zydex Ind., Morrisville, North Carolina, United States), a liquid organosilane WMA additive, used for decreasing production and paving temperatures of asphalt mixtures [70];
- additive B: Titan 7205 (Honeywell, Charlotte, North Carolina, United States), a solid polyethylene wax pelletized additive used for grade bumping of paving-grade and polymer-modified asphalt binders [71].

The properties of the additives are presented in Table 2. Figure 1 presents the FTIR spectra. The photographs of additive A can be found in Figure 2a and additive B is shown in Figure 2b.

Table 2. Characterization of the additives used in this study.

Property	Unit of Measurement	Additive A	Additive B
Form	-	viscous liquid	solid pellets, 2–3 mm in dia.
Colour	-	yellow	white
Density	g/cm^3	1.01	0,93
Viscosity at 20 °C	Pa·s	0.12	-
Typical dosing range (by wt. of asphalt binder)	%	0.1–0.15	0.5–1


(**a**) (**b**)

Figure 2. Photographs of the additives used in this study: (**a**) additive A and (**b**) additive B.

As shown in Figure 1, additive A is a complex substance, composed of many compounds, which is reflected in its spectrogram. It should be noted that the FTIR spectrum of this additive displayed prominent peaks in the 1700 cm^{-1}, 1030 cm^{-1}, 966 cm^{-1} and 699 cm^{-1} wavenumbers. The first two wavenumbers are also used in asphalt binders for the identification of carbonyl and sulfoxide structures produced in the oxidation reactions in bitumen, while the two latter ones are associated with polystyrene and polybutadiene structures. The additive B was identified as a form of polyethylene.

2.2. Methods

The investigation involved subjecting the blends of asphalt binders and the investigated additives to short-term and long-term laboratory ageing performed using the rolling thin-film oven (RTFOT, EN 12607-1) and the pressure ageing vessel (PAV, EN 14769), respectively.

The experiment was designed with a three-level, full factorial approach to evaluate the combined effects of both additives on the properties of the two asphalt binders. The investigated dosing ranges of these additives included the following:

- additive A: 0.00%, 0.15%, and 0.30%;
- additive B: 0.0%, 1.0%, and 2.0%.

The implemented design for both asphalt binders enabled the evaluation of linear, quadratic and interaction terms (as shown in Equation (1)) related to the effects of the investigated additives. The experiments were conducted with 3 replicates.

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_1^2 + \beta_4 X_2^2 + \beta_5 X_1 X_2 \quad (1)$$

The effects of the additives under investigation were evaluated by Fourier-transform infrared spectroscopy using the attenuated total reflectance (ATR-FTIR) method. The Thermo-Scientific Nicolet iS 5 FTIR Spectrometer (Waltham, MA, USA) and the PIKE Technologies GladiATR (Madison, WI, USA) attenuated total reflectance accessory with a diamond window were used. The changes in the chemical structure of the asphalt binders were evaluated using structural and chemical indices characterizing the relative changes in the amounts of compounds associated with oxidative ageing (sulfoxide and carbonyl indices) and the presence of the elastomeric modifier (polybutadiene and polystyrene index). These indices were calculated as a function of the areas under the peaks in the spectrograms, specific to excitation in particular bonds present in the molecules. The method for calculating structural indices was based on comparing the absorption bands, which were of interest, to those remaining invariant in the experiment. For this invariant reference, different values can typically be chosen, including a reference absorption band [72], a group of absorption bands [73] or the sum of all evaluated peaks [57] in the spectrum. In this method, the areas of absorption bands (peaks) of interest are compared to those reference values, and the structural indices are computed. An analysis of different reference values (peaks and groups of peaks) was conducted to evaluate their variability in the experimental data (Table 3). It was found that the sum of all peaks had the smallest relative variability with a coefficient of variance of 1.01%. Therefore, this value was used for calculating the structural indices as shown in Table 4.

Table 3. Analysis of the selected peaks in obtained ATR-FTIR spectra for the variability of their areas.

Structural Group	Peak Wave Number (cm^{-1})	Mean (-)	Max–Min (-)	Standard Deviation (-)	Coefficient of Variance (%)
Aliphatic	1460 [72]	6.691	0.797	0.196	2.93
Sum of peaks	2000-600 [73]	10.587	1.370	0.363	12.93
Sum of peaks	2953-699 * [57]	50.520	1.868	0.512	1.01

* evaluated peaks: $A_{(2953, 2923, 2862)}$, A_{1700}, A_{1600}, A_{1460}, A_{1376}, A_{1310}, A_{1030}, A_{990}, A_{966}, A_{910}, A_{864}, A_{814}, A_{743}, A_{724} and A_{699},.

Table 4. Structural indices used in the evaluation of bituminous binders [57,62,67–69,74].

Structural Index	Bond	Characteristic Peak Wave Number (cm^{-1})	Structural Index Expression:
Sulfoxide	S=O, stretching	1030	$I_{S=O} = \frac{A_{1030}}{\sum A_{all}}$
Carbonyl	C=O, stretching	1700	$I_{C=O} = \frac{A_{1700}}{\sum A_{all}}$
Polybutadiene	C-H, oop bending of trans-alkene	966	$I_{PB} = \frac{A_{966}}{\sum A_{all}}$
Polystyrene	C-H, oop bending in monoakrylated aromatic	699	$I_{PS} = \frac{A_{699}}{\sum A_{all}}$

$\Sigma A_{all} = A_{(2953, 2923, 2862)} + A_{1700} + A_{1600} + A_{1460} + A_{1376} + A_{1310} + A_{1030} + A_{990} + A_{966} + A_{910} + A_{864} + A_{814} + A_{743} + A_{724} + A_{699}$; oop—out of plane.

In addition to the FTIR testing of the asphalt binders, their high-temperature performance was evaluated before and after RTFOT ageing. The values of high-temperature stiffness (G*/sin(δ)), as defined in AASHTO M320 and AASHTO T315, measured at 64 °C and 70 °C in the case of the 50/70- and 45/80-55-based binders, respectively, are presented, and the non-recoverable creep compliance (AASHTO T 350) measured at 58 °C and 64 °C in case of 50/70 and 45/80-55 is shown.

A simple handling procedure for the samples was employed in this study. The bitumen samples were heated at 140 °C for three hours in closed containers, mixed with the appropriate additives and homogenized for their uniform distribution. Homogenization was achieved through blending for 15 min using a low-shear mixer at ca. 2000 rpm and at a sustained temperature of 140 °C. The testing was conducted directly after the necessary processing (e.g., ageing). The material for the FTIR measurements was poured into 100 mm diameter and 75 mm high metal containers, and the samples were obtained after cooling by scraping the material from an approx. 5 mm depth under the asphalt surface with a metal spatula. The material was then transferred to the ATR crystal heated to 30 °C. The samples for the rheological measurements were prepared by pouring them into silicone moulds.

3. Results

3.1. Carbonyl and Sulfoxide Indices

The following section investigates the relative changes in the $I_{C=O}$ and $I_{S=O}$ indices relative to the non-aged reference binders (without additives). The corresponding statistical models approximating the values of the indices and their regression coefficients are evaluated in the provided tables.

Figure 3 presents changes in the values of the carbonyl index as a function of the investigated additives' (additive A and B) content, and Table 5 shows the statistical analysis of these effects.

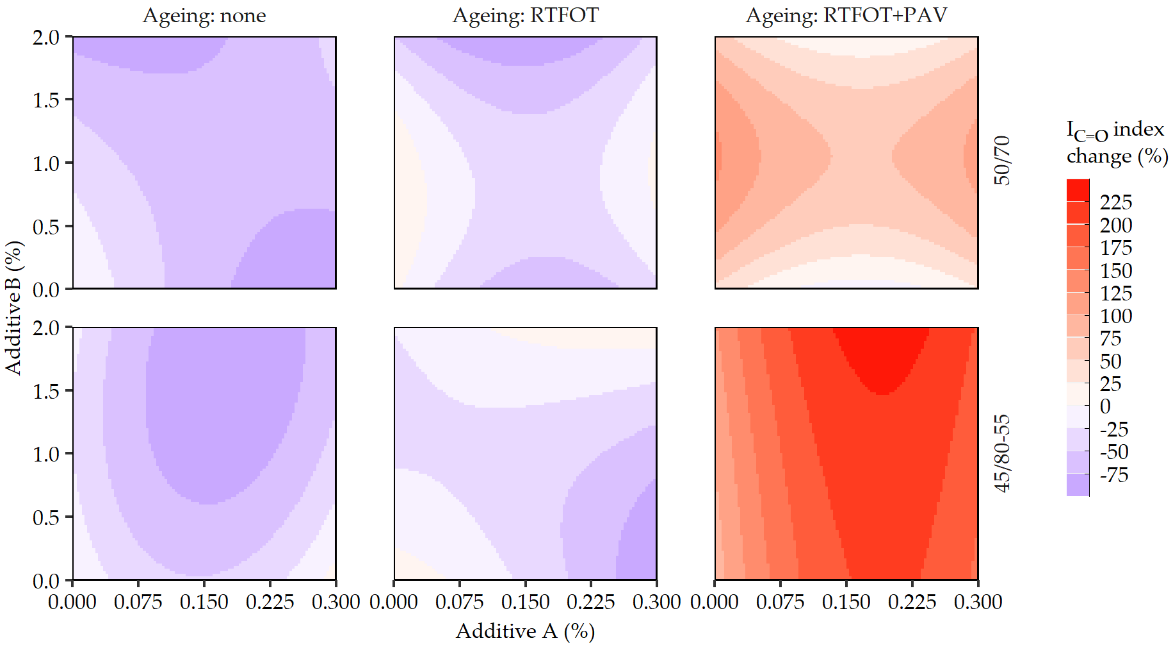

Figure 3. Surface plots of the changes in the carbonyl index in 50/70 and 45/80-55 asphalt binders in response to the investigated additives and laboratory ageing.

Table 5. A summary of the statistical models approximating the values of the carbonyl index measured in the 50/70 and 45/80-55 asphalt binders.

$I_{C=O}$ Effect:	Ageing: None 50/70	Ageing: None 45/80-55	Ageing: RTFOT 50/70	Ageing: RTFOT 45/80-55	Ageing: RTFOT+PAV 50/70	Ageing: RTFOT+PAV 45/80-55
Intercept	0.003 ***	0.001 ***	0.003 ***	0.002 ***	0.004 ***	0.003 ***
Additive A	−0.020 ***	−0.008 ***	−0.021 ***	−0.001 ***	−0.018 ***	0.021 ***
Additive B	−0.002 ***	−0.0003 ***	0.001 ***	−0.001 ***	0.004 ***	0.0002 *
(Additive A)^2	0.030 ***	0.035 ***	0.059 ***	−0.013 ***	0.053 ***	−0.053 ***
(Additive B)^2	0.00004 **	0.0002 ***	−0.001 ***	0.0003 ***	−0.002 ***	0.00002
A:B interaction	0.008 ***	−0.002 ***	0.002 ***	0.004 ***	−0.0001	−0.0003
Observations	27	27	27	27	27	27
R^2	0.999	0.999	0.998	0.997	0.997	0.989
Adjusted R^2	0.999	0.998	0.998	0.996	0.996	0.986

Note: *—$p \leq 0.05$; **—$p \leq 0.01$; ***—$p \leq 0.001$.

Analysis of the plots presented in Figure 3 shows both similarities and distinctions between the effects of the evaluated additives depending on the type of base asphalt binder. It can be clearly seen that both additives resulted in a decrease in the carbonyl index in non-aged and RTFOT-aged binders. On the other hand, after PAV ageing, a significant rise in this parameter was observed when the additives were present in the binders—particularly in the case of the 45/80-55 PMB.

The lowest values of the carbonyl index in the 50/70 binder before ageing were observed when the additives were used separately, at the maximum dosing (0.3% and 2% of additives A and B, respectively). After short- and long-term ageing, the lowest values were observed when 0.15% of additive A was used alone and in conjunction with 2% of additive B. Intermediate values were seen when the additives were used simultaneously in the mid-range of dosing (0.15% and 1%). High values of $I_{C=O}$ were associated with high dosages of additive B.

In the case of the 45/80-55 polymer-modified binder, the effects of the additives were much more varied in different ageing statesof the binders. Before ageing, the lowest values of the carbonyl index were observed when simultaneously 0.15% of additive A and 2% of additive B were used. After RTFOT ageing, it was the maximum dosing of additive A alone which yielded this minimum. After the PAV ageing on the other hand, any combination of the additives resulted in an increase in the values of the carbonyl index, specifically when both additives were present in high dosages.

The summary of the statistical models (Table 5) shows that both additives had significant effects on the measured changes in the carbonyl index ($p \leq 0.05$). In the case of the RTFOT+PAV aged binders, the interaction effect was not confirmed to be statistically significant.

Figure 4 presents changes in the values of the sulfoxide index as a function of the investigated additives' (additive A and B) content and Table 6 shows the statistical analysis of these effects.

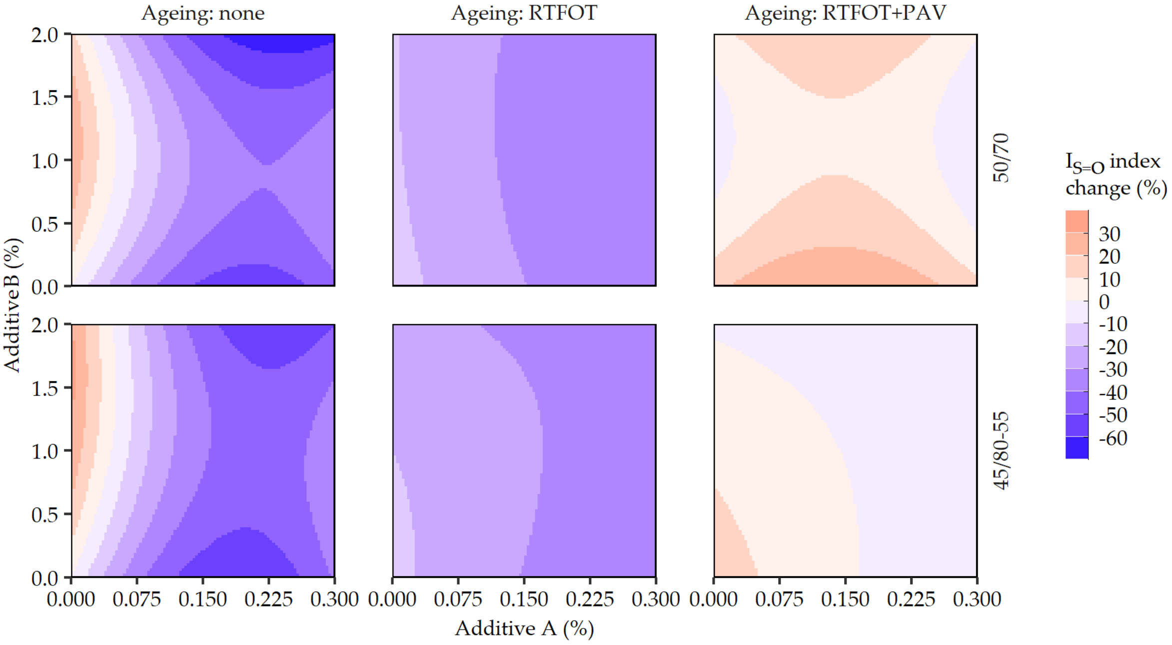

Figure 4. Surface plots of the changes in the sulfoxide index in 50/70 and 45/80-55 asphalt binders in response to the investigated additives and laboratory ageing.

Table 6. A summary of the statistical analysis (analysis of variance) on the investigated additives' effects on the values of the sulfoxide index measured in the 50/70 and 45/80-55 asphalt binders.

$I_{S=O}$	**Ageing: none**		**Ageing: RTFOT**		**Ageing: RTFOT+PAV**	
Effect:	**50/70**	**45/80-55**	**50/70**	**45/80-55**	**50/70**	**45/80-55**
Intercept	0.008 ***	0.008 ***	0.005 ***	0.005 ***	0.007 ***	0.007 ***
Additive A	−0.046 ***	−0.049 ***	−0.008 ***	−0.006 ***	0.011 ***	−0.006 ***
Additive B	0.001 ***	0.001 ***	−0.0003 **	−0.0001	−0.002 ***	−0.0003 **
(Additive A)^2	0.105 ***	0.120 ***	0.016 ***	0.005 **	−0.041 ***	0.004 ʻ
(Additive B)^2	−0.001 ***	−0.0003 ***	0.0001 ʻ	−0.0001 *	0.001 ***	−0.0001 ʻ
A:B interaction	0.0004 *	−0.001 ***	0.0004*	0.002 ***	−0.00004	0.002 ***
Observations	27	27	27	27	27	27
R^2	0.998	0.998	0.962	0.966	0.962	0.938
Adjusted R^2	0.998	0.997	0.953	0.958	0.954	0.923

Note: ʻ—$p \leq 0.1$; *—$p \leq 0.05$; **—$p \leq 0.01$; ***—$p \leq 0.001$.

The effects of the additives on the sulfoxide indices were similar in both binders before ageing and after the short-term RTFOT ageing procedure. In general, the addition of additive A resulted in a decrease in the sulfoxide index although, in the non-aged asphalt binders, this effect was the largest in magnitude. The use of additive B on its own caused large increases in this index before ageing, but this effect was limited by the increasing concentration of additive A. After the RTFOT ageing, additive B had only minor effects on this index.

After long-term PAV ageing of the 50/70 asphalt binders, the largest decrease in the sulfoxide indices was observed when additive B was set at 1% with additive A at

0% or 0.3%. Otherwise, the index increased significantly when 0.15% of additive A was used. In the case of the 45/80-55 asphalt binder, the decreases in the sulfoxide index were mainly associated with high dosing of additive A although additive B also contributed constructively to these effects.

The results of statistical analyses provided in Table 6 show that in all cases, both additives contributed to the changes in the values of the sulfoxide index observed in both binders. The interaction between the additives was not proven to be statistically significant only in the case of the 50/70 paving-grade bitumen after PAV ageing.

Table 7 shows the values of carbonyl and sulfoxide indices and their changes at the corners and centerpoint of the experimental plan to evaluate the magnitudes of the described effects directly using measured data.

Table 7. Quantitative changes in the carbonyl and sulfoxide index values in the 50/70 and 45/80-55 asphalt binders due to the use of additives and different ageing protocols.

Asphalt Binder	**Additive (%)**		**$I_{C=O}$**			**$I_{S=O}$**		
	A	**B**	**Non-Aged**	**RTFOT**	**RTFOT+PAV**	**Non-Aged**	**RTFOT**	**RTFOT+PAV**
50/70	0.0	0.0	0.0018	0.0027 (50%)	0.0037 (106%)	0.0043	0.005 (16%)	0.0069 (60%)
	0.0	2.0	0.0004 (−78%)	0.0013 (−28%)	0.0041 (128%)	0.0067 (56%)	0.0048 (12%)	0.0062 (44%)
	0.3	0.0	0.0002 (−89%)	0.0018 (0%)	0.0032 (78%)	0.0035 (−19%)	0.0039 (−9%)	0.0067 (56%)
	0.3	2.0	0.0017 (−6%)	0.0015 (−17%)	0.0036 (100%)	0.0027 (−37%)	0.004 (−7%)	0.0059 (37%)
	0.15	1.0	0.0007 (−61%)	0.0016 (−11%)	0.0045 (150%)	0.0035 (−19%)	0.0039 (−9%)	0.0064 (49%)
45/80−55	0.0	0.0	0.0020	0.0022 (10%)	0.0031 (55%)	0.0047	0.0051 (9%)	0.0071 (51%)
	0.0	2.0	0.0014 (−30%)	0.0013 (−35%)	0.0036 (80%)	0.0081 (72%)	0.0045 (−4%)	0.006 (28%)
	0.3	0.0	0.0019 (−5%)	0.0002 (−90%)	0.0045 (125%)	0.0039 (−17%)	0.0037 (−21%)	0.0056 (19%)
	0.3	2.0	0.0006 (−70%)	0.0018 (−10%)	0.0049 (145%)	0.0035 (−26%)	0.0042 (−11%)	0.0059 (26%)
	0.15	1.0	0.0003 (−85%)	0.0012 (−40%)	0.0052 (160%)	0.0033 (−30%)	0.0043 (−9%)	0.0061 (30%)

In the case of asphalt binders without additives, increases in both indices were seen as the ageing procedures were conducted. In the case of the reference 50/70 binder, the changes in $I_{C=O}$ were comparable after RTFOT and PAV ageing, while the $I_{S=O}$ index changed the most after the PAV procedure. In the 45/80-55 polymer-modified asphalt binder, there were only minor changes in the carbonyl and sulfoxide indices due to RTFOT ageing, while the biggest changes in both indices were observed after PAV ageing. This could be linked to the presence of the SBS polymer and its inhibiting effects on the formation of these oxidation products, as reported by Lu and Isaacson [66].

Here, it can be clearly seen that the application of the additives with the 50/70 asphalt binder resulted in a decrease in the carbonyl and sulfoxide indices in most cases. The exceptions were the $I_{C=O}$ values in two of the RTFOT+PAV-aged binder blends (one where 2% additive B was used alone and in the centerpoint) and the $I_{S=O}$ values of the non-aged 50/70 binder with 2% of additive B. Similar results were observed in the case of the 45/80-55 asphalt binder, with the only difference being that all RTFOT+PAV-aged blends were characterized by increased carbonyl indices.

3.2. Polybutadiene and Polystyrene Indices

The following section presents the relative changes in the polybutadiene and polystyrene indices in polymer-modified asphalt binders, relative to the non-aged reference binders (PMB without additives). The corresponding statistical models approximating the values of the indices, and their regression coefficients are evaluated in the provided tables.

Figures 5 and 6 present the values of the polybutadiene index and polystyrene indices, respectively, and their changes in the 45/80-55 asphalt binder as a function of the amount of the investigated additives, while Table 8 shows the statistical analysis of these effects.

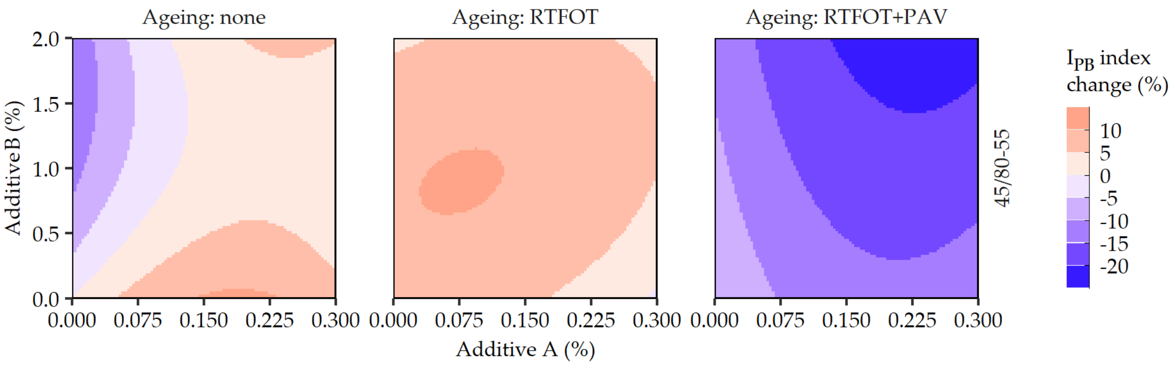

Figure 5. Surface plots of the changes in polybutadiene index values in the 45/80-55 asphalt binder in response to the investigated additives and laboratory ageing.

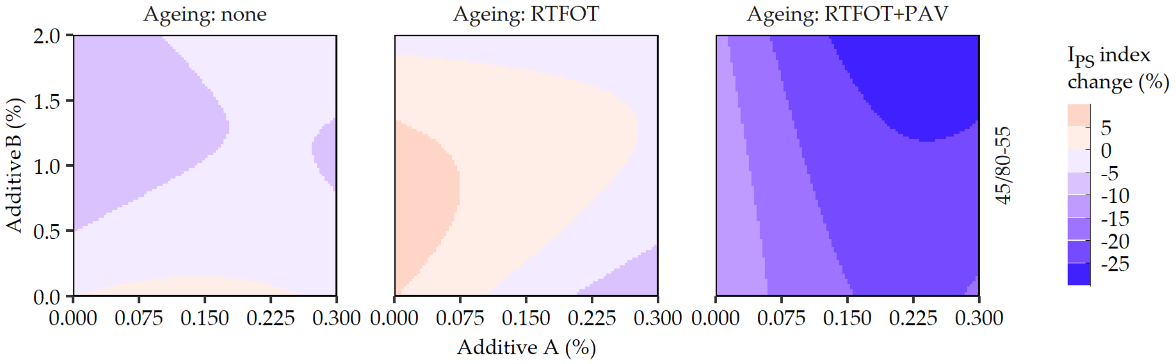

Figure 6. Surface plots of the changes in polystyrene index values in the 45/80-55 asphalt binder in response to the investigated additives and laboratory ageing.

Table 8. A summary of the statistical analysis (analysis of variance) on the investigated additives' effects on the values of the polybutadiene index measured in the 45/80-55 asphalt binder.

PMB Indices		**I_{PB} (45/80-55)**			**I_{PS} (45/80-55)**	
Effect:	**Ageing: None**	**Ageing: RTFOT**	**Ageing: RTFOT+PAV**	**Ageing: None**	**Ageing: RTFOT**	**Ageing: RTFOT+PAV**
Intercept	0.004 ***	0.004 ***	0.003 ***	0.002 ***	0.002 ***	0.002 ***
Additive A	0.004 ***	0.00002	−0.003 ***	0.0004	−0.001 ***	−0.002 ***
Additive B	−0.001 ***	0.0002 ***	−0.0001 *	−0.0003 ***	0.0002 ***	−0.00002
(Additive A)^2	−0.009 ***	−0.004 **	0.008 ***	−0.002 *	0.001	0.005 ***
(Additive B)^2	0.0001 ***	−0.0001 ***	0.00001	0.0001 ***	−0.0001 ***	−0.00002
A:B interaction	0.001 ***	0.001 ***	−0.0002 ’	0.0003 ***	0.0004 ***	−0.0002 *
Observations	27	27	27	27	27	27
R^2	0.954	0.856	0.922	0.821	0.894	0.960
Adjusted R^2	0.943	0.822	0.903	0.778	0.869	0.950

Note: ’—$p \leq 0.1$; *—$p \leq 0.05$; **—$p \leq 0.01$; ***—$p \leq 0.001$.

As it is presented in the plots in Figure 5, the additives altered the measured values of the polybutadiene index to a lesser extent than was seen in the case of the carbonyl and sulfoxide indices. The largest effects of the additives were observed in the non-aged binder and after the PAV ageing. Before ageing, additive A caused a substantial increase in the I_{PB} index value, while additive B decreased it to some extent. After RTFOT ageing, both additives had far less impact on this index. The PAV ageing significantly changed the way the additives affected the values of the polybutadiene index. The use of both additives caused a decrease in the index after long-term ageing, which was largest when both additives were used at the highest concentrations simultaneously.

The effects of the investigated additives on the polystyrene index were similar to those on the polybutadiene index as shown in Figure 6. Also in this case, the additives changed the measured values of the polystyrene index, but to a lesser extent than in the case of the carbonyl and sulfoxide indices. The magnitude of these effects was similar in all ageing states of the 45/80-55 PMB asphalt binder, but their character differed significantly, as was seen in the I_{PB} values. Before ageing, additive B decreased moderately the index value, while additive A increased it slightly. After RTFOT ageing, both additives decreased the I_{PS} values at their higher concentrations. The PAV ageing, again, significantly changed the way the additives affected the values of the index. Simultaneous use of additives A and B caused a decrease in this index, which was largest when both additives were used at 0.3% and 2% concentrations, respectively.

The statistical analysis, whose summary is provided in Table 8, has shown that in all cases, the additives significantly affected the values of the polybutadiene and polystyrene indices ($p \leq 0.05$).

The values of polybutadiene and polystyrene indices for the five selected nodes of the experimental plan (at the corners and centerpoint) are presented in Table 9. The subsequent ageing stages of the 45/80-55 asphalt binder without the additives caused only minor changes in the mentioned indices, with a small increase after RTFOT ageing and a decrease after the PAV procedure. The effects of the additives on these indices were smaller than it was in the case of the carbonyl and sulfoxide indices. In general, the investigated additives caused minor decreases (not exceeding −20%) in both indices, with the exception of non-aged binders with high contents of additive A, where 9% and 12% increases were observed.

Table 9. Quantitative changes in the polybutadiene and polystyrene index values in the 45/80-55 asphalt binder due to the use of additives after different ageing protocols.

Asphalt Binder	Additive (%)		I_{PB}			I_{PS}		
	A	B	Non-Aged	RTFOT	RTFOT+PAV	Non-Aged	RTFOT	RTFOT+PAV
45/80-55	0.0	0.0	0.0034	0.0038 (12%)	0.0033 (−3%)	0.0022	0.0023 (5%)	0.0020 (−9%)
	0.0	2.0	0.0028 (−18%)	0.0037 (9%)	0.0032 (−6%)	0.0019 (−14%)	0.0021 (−5%)	0.0019 (−14%)
	0.3	0.0	0.0038 (12%)	0.0035 (3%)	0.0031 (−9%)	0.0022 (0%)	0.002 (−9%)	0.0018 (−18%)
	0.3	2.0	0.0037 (9%)	0.0037 (9%)	0.0027 (−21%)	0.0021 (−5%)	0.0021 (−5%)	0.0016 (−27%)
	0.15	1.0	0.0034 (0%)	0.0039 (15%)	0.0029 (−15%)	0.0020 (−9%)	0.0022 (0%)	0.0017 (−23%)

3.3. Relationships between Asphalt Binder Performance and Carbonyl and Sulfoxide Indices

The measurements of high-temperature stiffness ($G^*/\sin(\delta)$), non-recovery compliance ($J_{nr\ 3.2\ kPa}$) and percent recovery (R) taken before and after RTFOT ageing of the investigated binders were used to evaluate the relationships between the measured changes in chemical indices and the high-temperature performance of the asphalt binders.

As indicated in the introduction, it is typically assumed that the changes in the high-temperature characteristics of asphalt binders that have undergone oxidative ageing correlate well with the formation of carbonyl and sulfoxide species.

Figures 7 and 8 present how the high-temperature performance and the measured FTIR chemical indices of the individual asphalt binders changed with short-term ageing. In the case of the performance characteristics shown in Figure 7, it can be seen that, although the additives caused some changes in the high-temperature properties of both asphalt binders, these changes were mostly consistent through the ageing process, regardless of the additives used. This can be particularly seen in case of the high-temperature stiffness (Figure 7a), but also in case of the non-recoverable creep compliance (Figure 7b) and percent recovery from the multiple stress creep recovery(MSCR) test (Figure 7c). This can be inferred based on the fact that, in most cases, the lines connecting respective points on the plots are roughly parallel, meaning that the changes in the measured properties due to the RTFOT ageing were comparable in magnitude. The only major exception was the 45/80-55 asphalt binder with 0.3% additive A, which exhibited a decrease in the percent recovery after RTFOT.

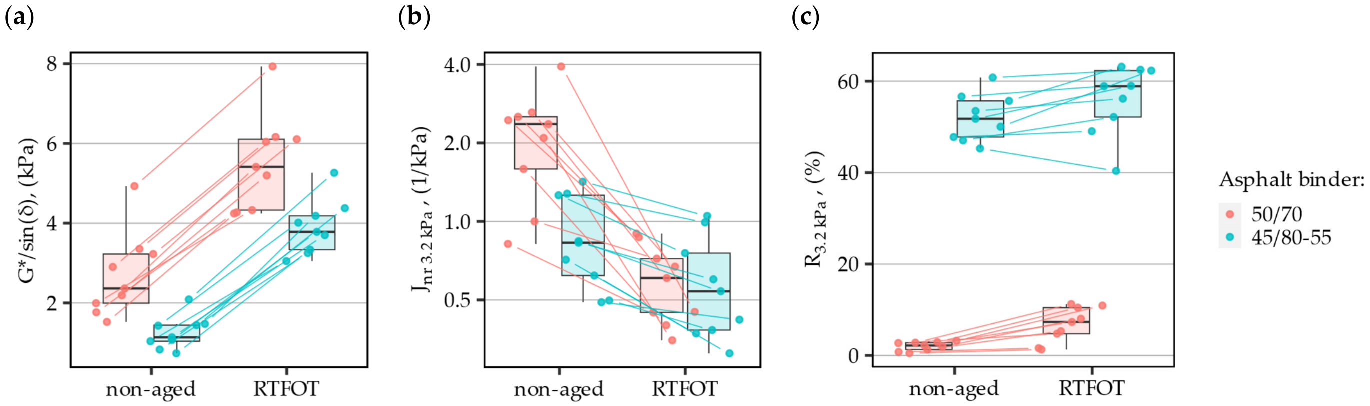

Figure 7. Changes in the high-temperature performance of the investigated binders due to RTFOT ageing: (**a**) high-temperature stiffness G*/sin(δ), (**b**) non-recoverable creep compliance $J_{nr\ 3.2\ kPa}$ and (**c**) percent recovery R in the MSCR test.

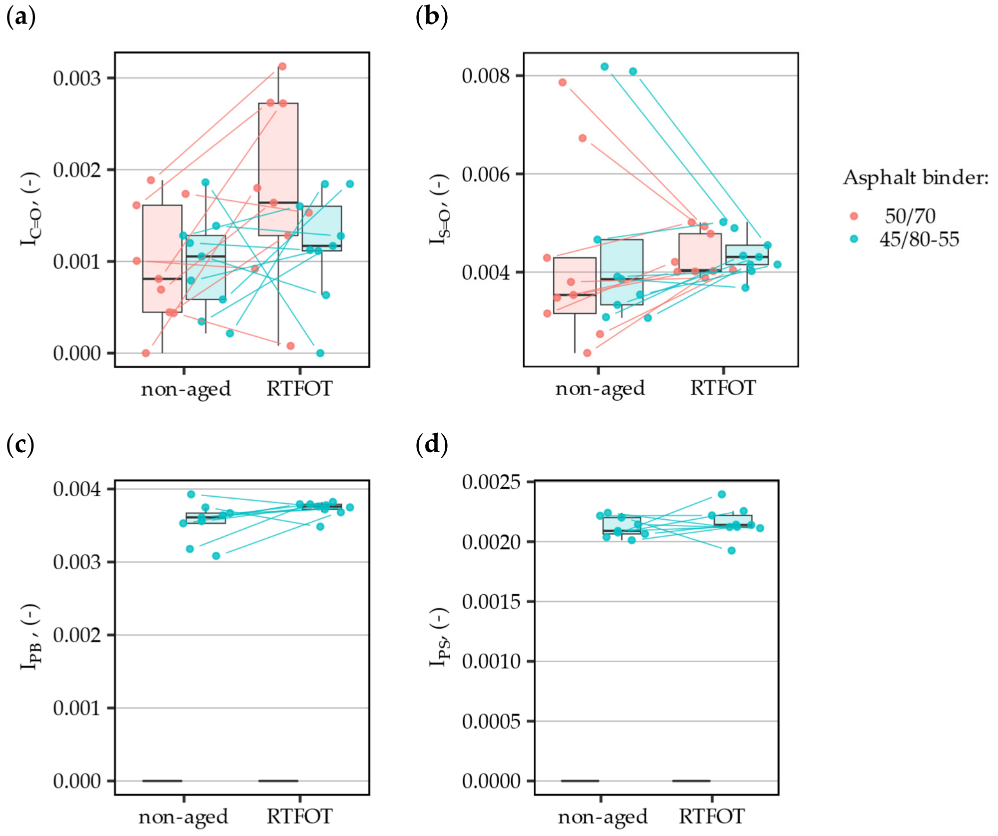

Figure 8. Changes in the FTIR chemical indices of the investigated binders due to RTFOT ageing: (**a**) carbonyl index $I_{C=O}$, (**b**) sulfoxide index $I_{S=O}$, (**c**) polybutadiene index I_{PB} and (**d**) polystyrene index I_{PS}.

Different results can be observed in Figure 8 showing the trajectories of the changes in the FTIR chemical indices. The values of carbonyl (Figure 8a) and sulfoxide (Figure 8b) indices were highly affected by the additives, resulting either in their increases or decreases before the RTFOT ageing and due to it.

The four outlying values that can be observed in the $I_{S=O}$ plot (in the 0.006 and 0.008 range) correspond to the values of sulfoxide indices of non-aged binders with 1% and 2% additive B. Additionally, very strong effects of additive A in quenching the $I_{S=O}$ values can be observed. Had it not been for these highlighted values, a strong correlation between the high-temperature stiffness and $I_{S=O}$ index would have been observed.

Regarding the I_{PB} (Figure 8c) and I_{PS} (Figure 8d) indices measured in the 45/80-55 binders, it can be seen that their variability in the presence of the additives was significantly lower compared to the other indices. Nevertheless, the direction of changes in the polybutadiene and polystyrene indices also differed significantly with different contents of the additives.

The analysis above shows that the investigated additives did not affect the evolution of the high-temperature performance of the binders in the course of RTFOT ageing, but the opposite was found regarding the FTIR chemical indices.

To further evaluate these findings, a correlation analysis was conducted. Tables 10 and 11 present correlation matrices of the performance properties and FTIR chemical indices of 50/70 and 45/80-55 asphalt binders, respectively.

Table 10. Correlation matrix of the performance parameters and FTIR chemical indices calculated for the 50/70-based asphalt binders before and after RTFOT.

	Pearson Correlation Coefficient R: 50/70				
	G*/sin(δ)	**$J_{nr\ 3.2\ kPa}$**	**$R_{3.2\ kPa}$**	**$I_{S=O}$**	**$I_{C=O}$**
G*/sin(δ)	1	−0.62 **	0.85 ***	0.22	0.29
$J_{nr\ 3.2\ kPa}$	−0.62 **	1	−0.59 **	−0.28	−0.4 ′
$R_{3.2\ kPa}$	0.85 ***	−0.59 **	1	0.16	0.44 ′
$I_{S=O}$	0.22	−0.28	0.16	1	0.24
$I_{C=O}$	0.29	−0.4 ′	0.44 ′	0.24	1

Note: ′—$p \leq 0.1$; **—$p \leq 0.01$; ***—$p \leq 0.001$.

Table 11. Correlation matrix of the performance parameters and FTIR chemical indices calculated for the 45/80-55-based asphalt binders before and after RTFOT.

	Pearson Correlation Coefficient R: 45/80-55						
	G*/sin(δ)	**$J_{nr\ 3.2\ kPa}$**	**$R_{3.2\ kPa}$**	**$I_{S=O}$**	**$I_{C=O}$**	**I_{PB}**	**I_{PS}**
G*/sin(δ)	1	−0.65 **	0.56 *	0.03	0.24	0.27	0.12
$J_{nr\ 3.2\ kPa}$	−0.65 **	1	−0.82 ***	−0.16	−0.06	0.02	−0.03
$R_{3.2\ kPa}$	0.56 *	−0.82 ***	1	0.35	0.41 ′	−0.08	0.11
$I_{S=O}$	0.03	−0.16	0.35	1	0.36	−0.77 ***	−0.19
$I_{C=O}$	0.24	−0.06	0.41′	0.36	1	0.06	0.38
I_{PB}	0.27	0.02	−0.08	−0.77 ***	0.06	1	0.63 **
I_{PS}	0.12	−0.03	0.11	−0.19	0.38	0.63**	1

Note: ′—$p \leq 0.1$; *—$p \leq 0.05$; **—$p \leq 0.01$; ***—$p \leq 0.001$.

It can be firmly stated that, in the conducted experiments, the correlation between the FTIR indices and the high-temperature performance of the binders was weak ($r \leq 0.44$), and in none of the cases, the statistical significance of the relationship was confirmed ($p > 0.05$). Such an outcome may be attributed to the major effects of the additives on the FTIR indices shown in the previous section and, at the same time, their low impact on the rheological properties of the binders.

4. Discussion

This study has shown that the use of the investigated additives significantly affected the FTIR absorption bands associated with the carbonyl and sulfoxide structures forming in neat asphalt binders due to oxidative ageing (RTFOT and PAV). These values of the carbonyl and sulfoxide indices measuring relative changes in the contents of these species generally decreased after the introduction of both additives in neat asphalt binders and after RTFOT, by as much as 89%. After PAV ageing, the carbonyl and sulfoxide indices increased in most blends and the magnitude of this increase was generally related to the amount of the additives. On the other hand, in reference binders without additives, these indices gradually increased with the induced oxidative stress.

The additives had far smaller effects on the measurements of the polybutadiene and polystyrene structural indices.

Provided that even before laboratory ageing significant changes were seen in all structural indices, it can be concluded that the additives influenced the measurements based on the evaluated FTIR spectral bands. It should be noted that the FTIR spectrum of additive A is characterized by substantial absorption peaks in the carbonyl and sulfoxide bands, while additive B (identified as a form of polyethylene) may degrade due to oxidation to ketones, carboxylic acids and esters [75]. These effects may contribute to the effects seen in the carboxyl and sulfoxide spectral bands.

It was also assessed that the apparent changes in the chemical composition of the asphalt binders after oxidative (RTFOT) ageing were not followed by the changes in the rheological performance of the binders in high temperatures. These discrepancies in the changes in the high-temperature performance and apparent changes in chemical composition as a result of oxidative ageing measured by the FTIR indices may be the cause of the lack of correlations between the measured performance parameters and FTIR indices.

5. Conclusions

The present paper investigated the effects of two additives (ZycoTherm—liquid, warm mix additive; Titan 7205—solid, high-temperature-improving additive) used simultaneously, on the contents of carbonyl, sulfoxide, polybutadiene and polystyrene FTIR chemical indices in a 50/70 paving-grade bitumen and 45/80-55 polymer-modified bitumen. Additionally, the high-temperature performance of the asphalt binders was assessed using a direct shear rheometer, and relationships between these characteristics were evaluated. The major findings of this study include the following:

- The simultaneous use of both additives significantly decreased the FTIR indices related to carbonyl species in the asphalt binders before and after RTFOT ageing; the decrease amounted up to 90% in relation to the levels seen in non-aged binders without additives; and these effects were far less pronounced after PAV ageing.
- The sulfoxide FTIR indices in non-aged binders were affected to a similar extent (a decrease of up to 37% in relation to the levels seen in non-aged binders without additives), but the driving factor in this change was the ZycoTherm warm mix additive; the values of this $I_{S=O}$ index after PAV ageing were less affected; and the Titan 7205 significantly increased the $I_{S=O}$ index in both non-aged binders when used alone (up to 72% increase).
- The changes in the polybutadiene and polystyrene indices in the polymer-modified bitumen did not exceed 27%; small increases and decreases (up to ±15%) of these indices were seen in non-aged and RTFOT aged binders; and after PAV ageing, both I_{PB} and I_{PS} indices clearly decreased when more of the additives were used.
- Although the additives clearly affected the high-temperature performance of both asphalt binders, the evolution of these rheological properties due to RTFOT ageing was not affected despite their significant effects on the FTIR indices.

Based on these findings, it can be concluded that estimation of the rheological performance based on known relationships with carbonyl and sulfoxide contents may not be reliable in the case of asphalt binders containing these investigated additives.

Further studies should be conducted to evaluate the performance of these additives and their effects on performance and FTIR responses in the scope of more severe ageing protocols.

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