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Testing and evaluation of the new polymer-modified binder compositions with improved resistance against thermo- and photo- oxidative aging

Abstract: The article presents the use of aging evaluation methods to assess new binders with improved aging resistance. A series of new compositions were subjected to RTFOT, PAV and UV Light accelerated aging and evaluated based on rheological analysis with DSR, FT-IR spectroscopy, alongside standard normative methods for binder evaluation. Furthermore, recent progress in development of standardized FT-IR testing method was taken into consideration in order to compare different aspects of semi quantitive infrared analysis of bitumens. Results of this study highlight the importance of long-term binder stabilization alongside the methods for testing and accurate evaluation of stabilizing efficiency of novel binder compositions, in order to enhance the commercial viability of new binders with significantly improved aging-resistance. Binders with modified composition show approximately 20% higher resistance to both RTFOT + PAV and RTFOT + UV aging, compared to the reference samples.

Keywords: improved aging resistance, photo-oxidative aging, polymer-modified bitumen, thermo-oxidative aging.

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1. INTRODUCTION

Currently many industry standards are used for evaluation and classification of binder's performance at the point of sale from the manufacturer, such as Ring and Ball Test, Penetration Test, Thermal Stability Test and various other tests of the rheological properties of the samples [1-2]. Results obtained at this stage provide an accurate and useful representation of the properties of a binder in its virgin state, referred to as an unaged material.

Recently however, both in literature on the subject and in the industry in general, an increasing focus is put upon aging characteristics of bituminous binders [3]. Aging of binders refers collectively to a change in chemical structure and physical properties of the material, caused both during the preparation of asphalt mixture and road construction – Short Term Aging (STA); along with changes observed during the rest of the service life of a pavement – Long Term Aging (LTA) [4]. Short-Term Aging is often simulated using Rolling Thin Film Oven Test (RTFOT), while the most common method for the Long-Term Aging found in the literature is Pressure Aging Vessel (PAV) method [5-6].

Changes in the chemistry of bitumen are usually attributed as a result of complex processes involving evaporation of volatile compounds, oxidation by oxygen in air, molecular rearrangements and condensation reactions [7-8]. One of the most commonly used models for the monitoring changes occurring as a result of aging is the analysis of SARA composition of bitumen – with the respective fractions being Saturates, Aromatics, Resins and Asphaltenes. Depending on the initial composition of analyzed bitumen, significant changes both in share of each fraction by weight and in chemical structure of species within fraction are observed, generally favouring the formation of asphaltenes and resins at the cost of aromatics and saturates as the aging continues [9]. It was found in the literature that both the combination of laboratory STA and LTA methods can somewhat accurately simulate degradation of bitumen in real-life field conditions [10].

In order to more accurately simulate field aging of bitumen, including various polymer modified bitumens, recent published research in the field has brought to light some new methods to complement the RTFOT and PAV testing. As an additional tool for in-depth analysis of changes that occur as a result of adverse conditions affecting the pavement during its lifetime, aging simulations that use increased concentrations of Reactive Oxygen Species (ROS) – ozone O_3 and nitrogen oxides NO_x – have been suggested [11]. Other simulations use UV light to reproduce the destructive effect of solar radiation on bituminous binders [12].

Light in the UV or visible range has been used to simulate bitumen weathering. Recent increase in attempts to standardize the testing procedure and combine multiple analytical methods aims to provide an accurate picture of changes occurring in binder as a result of an exposure to various bands of irradiance [13]. Light induced degradation in the presence of oxygen, known as photo-oxidation, was a topic of extensive research as a subject of polymer chemistry – with materials such as polystyrene, poly(vinyl chloride) and many butadiene based elastomers proven to undergo degradation when exposed to sunlight [14]. Comprehensive analysis of photo-induced changes in unmodified bitumen conducted by Werkovits et al. has proven formation of various carboxylic products, suggesting the oxidation mechanism beyond the scope of aging simulated with thermo-oxidative methods such as RTFOT and PAV [15]. Styrene butadiene styrene block copolymers themselves are also expected to show significant susceptibility towards UV-induced degradation, impacting the overall aging-resistance of polymer-modified bitumen [14], [16]. Some research in the field of UV degradation of polymer-modified bitumens has been already conducted, but the comprehensive mechanism that considers interactions between polymer and bitumen matrix, with their respective transformations as a result of photo-induced processes remains to be established [17-20].

It is widely accepted that various products of oxidation of binder should correspond to increased absorption in the carboxyl and carbonyl range (1600-1800 cm^{-1}) of the infrared spectrum [21-23]. Recent development of quantitive or semi-quantitive method for evaluation of aging in bitumens using FT-IR spectroscopy has pushed towards higher degree of standardization, with the aim to provide more accurate results and allow for better comparison of data between researchers [24-27]. It was identified that variables including a selection of an integration method for analyzed signals, limits for band integration, baseline correction method and various other post-processing of spectra can significantly decrease accuracy of the calculated data [28-30]. In the process of the selection of method for this experiment, findings in published work were considered, with the aim to select an approach that would accurately reflect observed oxidation without exceedingly increasing complexity of the analysis.

2. MATERIALS AND METHODS

2.1. MATERIALS

Four different modified binders, produced from the same crude oil source, were used as a basis for the study. Binders with improved aging (IA) resistance were prepared based on polymer modified bitumen (45/80-55 grade) and highly modified bitumen (45/80-80), which were also used as a reference for comparison of the aging properties. The binders were subjected to simulated aging, including the RTFOT and subsequent PAV or UV exposure, and all samples were analyzed before and after each aging stage – in accordance with procedures described in the Methods section.

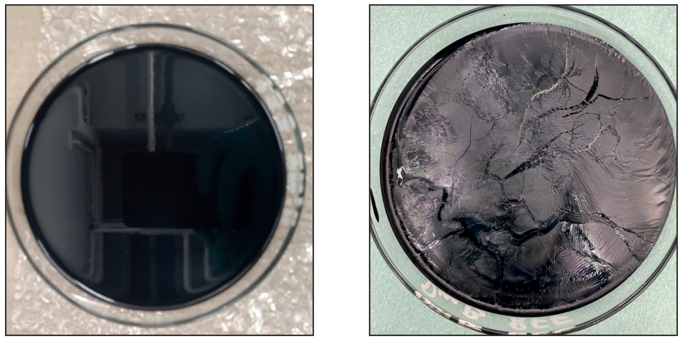
2.2. METHODS

2.2.1. RTFOT and PAV aging

The standardized Rolling Thin Film Oven Testing (RTFOT) and Pressure Aging Vessel (PAV) were used to simulate the STA and LTA respectively. RTFOT was conducted according to EN 12607-1 at the temperature of 163°C for 75 minutes [31]. PAV testing was performed at 100°C for 20 hours, at the pressure of 2.1 MPa according to EN 14769:2023 [32].

2.2.2. UV aging procedure

As of yet, there is no standardized procedure for the light aging of the bitumen. The conditions vary somewhat between researches, with the consensus that chosen wavelengths should correspond the blue and ultraviolet ranges of solar spectrum, responsible for photo-oxidative aging [13]. In this experiment, samples of bitumen after RTFOT of 50.0 g ± 0.5 g were poured on circular plates with a diameter of 15 cm. The temperature of the asphalt was such that it allowed for the warm mixture to spread evenly on the dish. The Atlas UV 2000 chamber was used to simulate UV aging, and each sample was exposed to the monochromatic 340nm light, with the irradiance of 0.7 W/m^2 for 7 days, and the temperature set at 60°C. Fig. 1 illustrates the surface of the prepared sample of 45/80-55 grade bitumen before and after UV aging.



a) b)

Fig. 1. Comparison of 45/80-55 grade binder: a) before aging, b) after UV aging

2.2.3. Standardized testing of bitumen properties

All unaged bitumen samples were subjected to assessment required by the PN-EN 14023:2010 normative classification [2], a Polish standard, based on the European norm. The Ball and Ring Test for the softening point was conducted according to PN-EN 1427:2007 [33], and the Penetration Test according to PN-EN 1426:2007 standard [34]. Storage stability of binders was assessed based on PN-EN 13399 [35]. Elastic recovery was measured at the temperature of 25°C, according to PN-EN 13398 [36].

2.2.4. Fourier-Transform Infrared Spectroscopy

All spectra used in the study have been registered using Perkin-Elmer Spectrum Two FT-IR spectrometer with ATR diamond crystal, at resolution of 4 cm^{-1} and four scans in the range from 4000 to 450 cm^{-1}. The binder sample has been applied directly onto the crystal, and pressed down with the pressure screw. Baseline correction was performed for the post-processing of the spectra using a set point approach. The selected points were set to 3100 cm^{-1}, 1753 cm^{-1}, 930 cm^{-1} and 660 cm^{-1}, similar to a method proposed by Porot et al. [37]. This approach was found to work well for low- and medium-intensity carbonyl signals. In the high intensity signals, registered directly from the surface of the samples after exposure to UV-light, the baseline had to be adjusted to account for the increase in width of the carboxyl signal. Spectra used for calculation of the carbonyl indices were used without further normalization.

For the integration of bands, a baseline approach was chosen. The tangential approach was briefly tested, but results obtained with this method suggest a larger variation of calculated indices, in agreement with the literature [38]. For the integration limits of each band, it was found beneficial to work upon set-boundary system, as opposed to manual selection of limits of each signal. A couple sets of integration limits for carbonyl band found in published work were considered, with the 1722-1678 cm^{-1} range being chosen as providing accurate results while limiting the interference from various modifiers present in bitumens, with absorption peaks in close proximity to analyzed bandwidth. Initial analysis was conducted upon the sulfoxide range, but it was later rejected because of significant interference from other components introduced to the binder upon modification. Similar to many other sources, carbonyl index was calculated as a ratio of carbonyl area to the reference range [39]. The aliphatic range of $-CH_2$ and $-CH_3$ bending vibrations at 1518 cm^{-1} to 1330 cm^{-1} was selected based upon literature and used without further modification [37]. To summarize, equation (1) was utilized to calculate the carbonyl index used to assess bitumen aging:

$$I_{C=O} = \frac{A_{C=O\ (1722\text{–}1678)}}{A_{ref\ (1518\text{–}1330)}}, \quad (1)$$

where:

$I_{C=O}$ – carbonyl index,

$A_{C=O}$ – area under the curve of carbonyl range,

A_{ref} – area under the curve of reference range.

The difference of carbonyl index, between the aged sample and the unaged bitumen of the same grade was calculated using (2):

$$\Delta I_{C=O} = I_{C=O\ (aged)} - I_{C=O\ (unaged)}. \quad (2)$$

2.2.5. DSR analysis

Rheology of all bitumen samples selected for the experiment was analyzed according to the PN-EN 14770:2012 [40] standard using Anton Paar Physica MCR 101 dynamic shear rheometer (DSR). The parallel plate setup was used, with the 25 mm diameter shearing plates and the gap of 1 mm. The complex shear modulus G^* and phase angle δ were measured, for each sample before and after aging, at temperatures of 10°C, 25°C, 60°C and 80°C at a constant oscillation speed of 10 rad/s. The ranges of applied deformations were determined taking into account the stiffness of the tested materials, in a way that allows tests to be carried out in the linear range of viscoelasticity of binders.

Specific aging indices based on Complex Modulus G^* and Phase Shift Angle δ were used to analyze the aging of binders after individual aging stages – Complex Modulus Aging Index (3) and Phase Angle Aging Index (4):

$$CMAI = \frac{G^*_{aged}}{G^*_{unaged}}, \quad (3)$$

$$PAI = \frac{\delta_{aged}}{\delta_{unaged}}. \quad (4)$$

3. RESULTS AND DISCUSSION

3.1. COMPARISON OF BINDERS BEFORE AGING

The alternative binder compositions, evaluated in this study, are composed with the improved aging performance in mind. While aging resistance of novel compositions is a focus of the study, presented binders should perform at least as well as commercially sold modified bitumen. With that in mind, the comparison of normative parameters between reference binder and the IA variant before aging is provided.

To accurately represent improved aging properties of IA (improved aging) compositions they should be compared to bitumen of the same normative classification, in this case based upon PN-EN 14023 standard [2]. Parameters for all unaged bitumens presented in this study are compared in Table 1.

Both reference and IA samples are well within the classification range, 45/80-55 and 45/80-80 respectively. The IA compositions shown meet all the normative requirements for modified binders used in road construction and, as such, could be used as a direct replacement for both standard and commercial grade modified bitumens.

Similarly, the main rheological parameters of shear modulus and phase angle of unaged bitumen samples, in the function of temperature, are shown in Fig. 2. Both standard and improved aging compositions follow the same temperature curve in the change of shear modulus and phase angle, regardless of the augmented compositions of binders. As such, monitoring of the impact of aging on the changes in these parameters can provide valuable information on aging susceptibility of evaluated compositions.

Table 1. Normative parameters of binder samples before aging

Tested properties	Type of bitumen			
	45/80-55 REF	45/80-55 IA	45/80-80 REF	45/80-80 IA
Classification according to PN-EN 14023	45/80-55		45/80-80	
Penetration at 25°C [0.1 mm]	61	62	53	59
Softening point [°C]	66.4	61.6	91	90.5
Elastic recovery at 25°C [%]	90	86	93	86
Storage stability test Softening point difference [°C]	0.4 Top: 70.6 Bottom: 70.2	1.0 Top: 67.2 Bottom: 68.2	0.0 Top: 93.0 Bottom: 93.0	0.0 Top: 93.5 Bottom: 93.5
Storage stability test Penetration difference [0.1 mm]	0 Top: 65 Bottom: 65	0 Top: 69 Bottom: 69	−1 Top: 58 Bottom: 59	−1 Top: 64 Bottom: 65

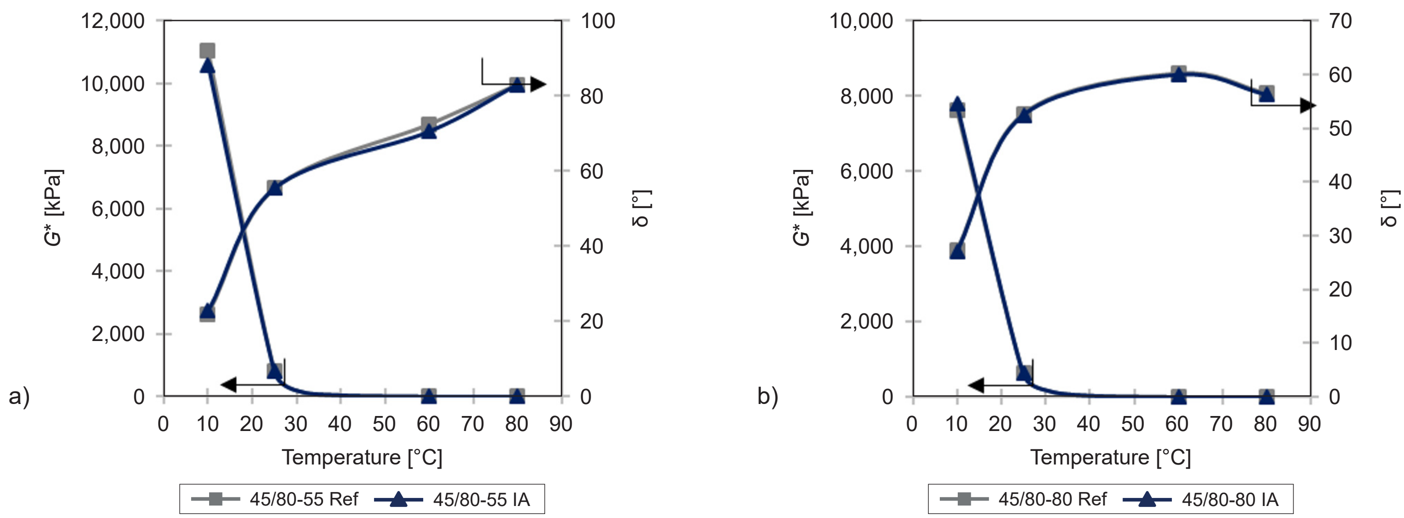


Fig. 2. Shear modulus and phase angle for unaged bitumens: a) 45/80-55, b) 45/80-80

3.2. AGING IMPACT ON BITUMEN

3.2.1. DSR analysis

As a primary method for evaluation of physical properties after aging DSR rheological approach was chosen. Binder aging was monitored using the *CMAI* and *PAI* indicators, and the results for each type of binder at different stages of aging are shown in Fig. 3.

The lower value of the *CMAI* Index, the better the resistance to aging of the binder at a given temperature. In the case of the *PAI* Index, higher values indicate a lower degree of aging of the asphalt. The *CMAI* values determine the degree of stiffness and the hardening of the binder after various degrees of aging. *PAI* results indicate the degree of loss of elasticity of the binder. The results of aging indices for 45/80-80 grade highly modified bitumen are shown in Fig. 4.

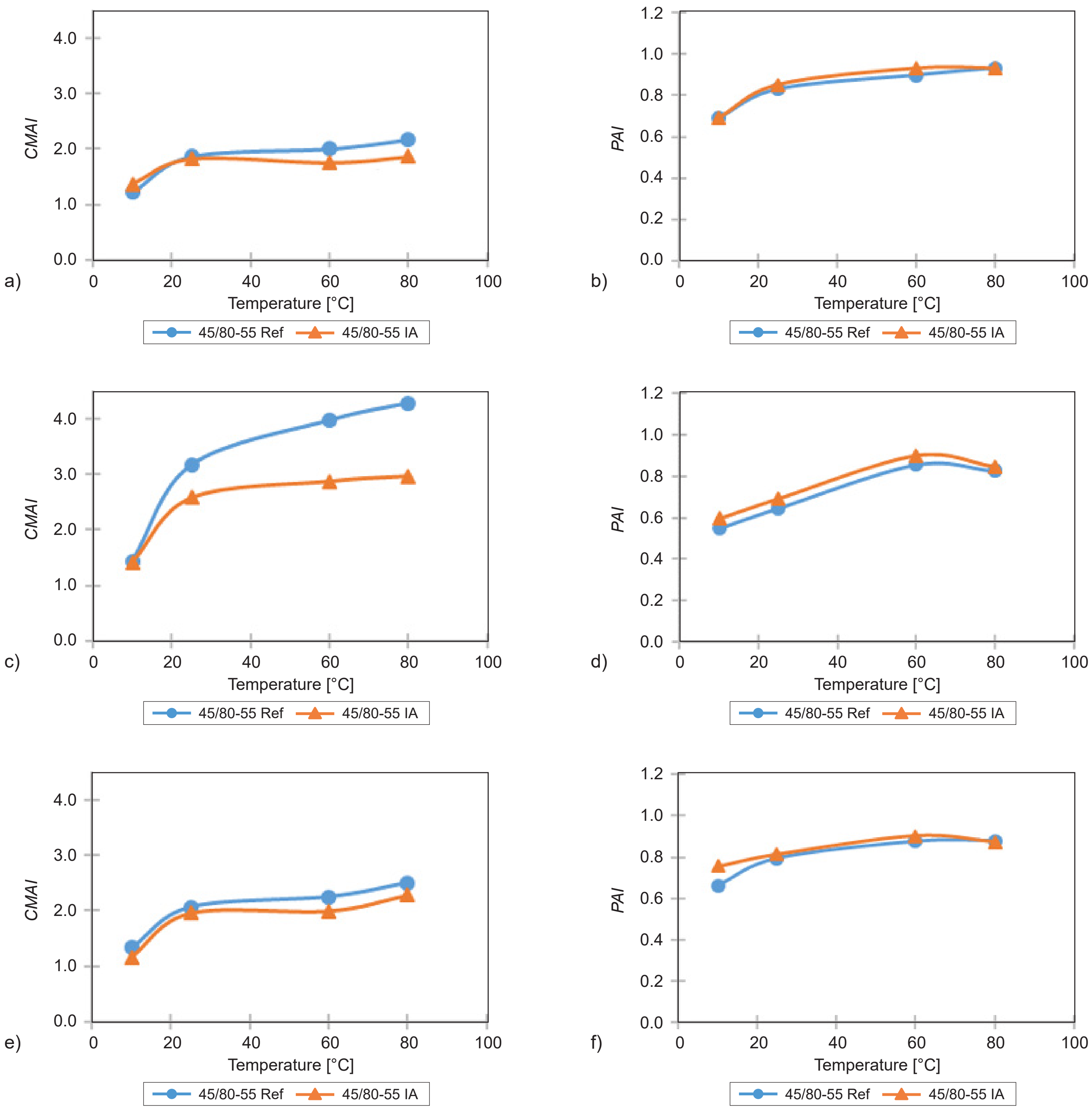


Fig. 3. *CMAI* and *PAI* indicators for 45/80-55 grade bitumens: a) *CMAI* 45/80-55 after RTFOT, b) *PAI* 45/80-55 after RTFOT, c) *CMAI* 45/80-55 after RTFOT + PAV, d) *PAI* 45/80-55 after RTFOT + PAV, e) *CMAI* 45/80-55 after RTFOT + PAV, f) *PAI* 45/80-55 after RTFOT + UV

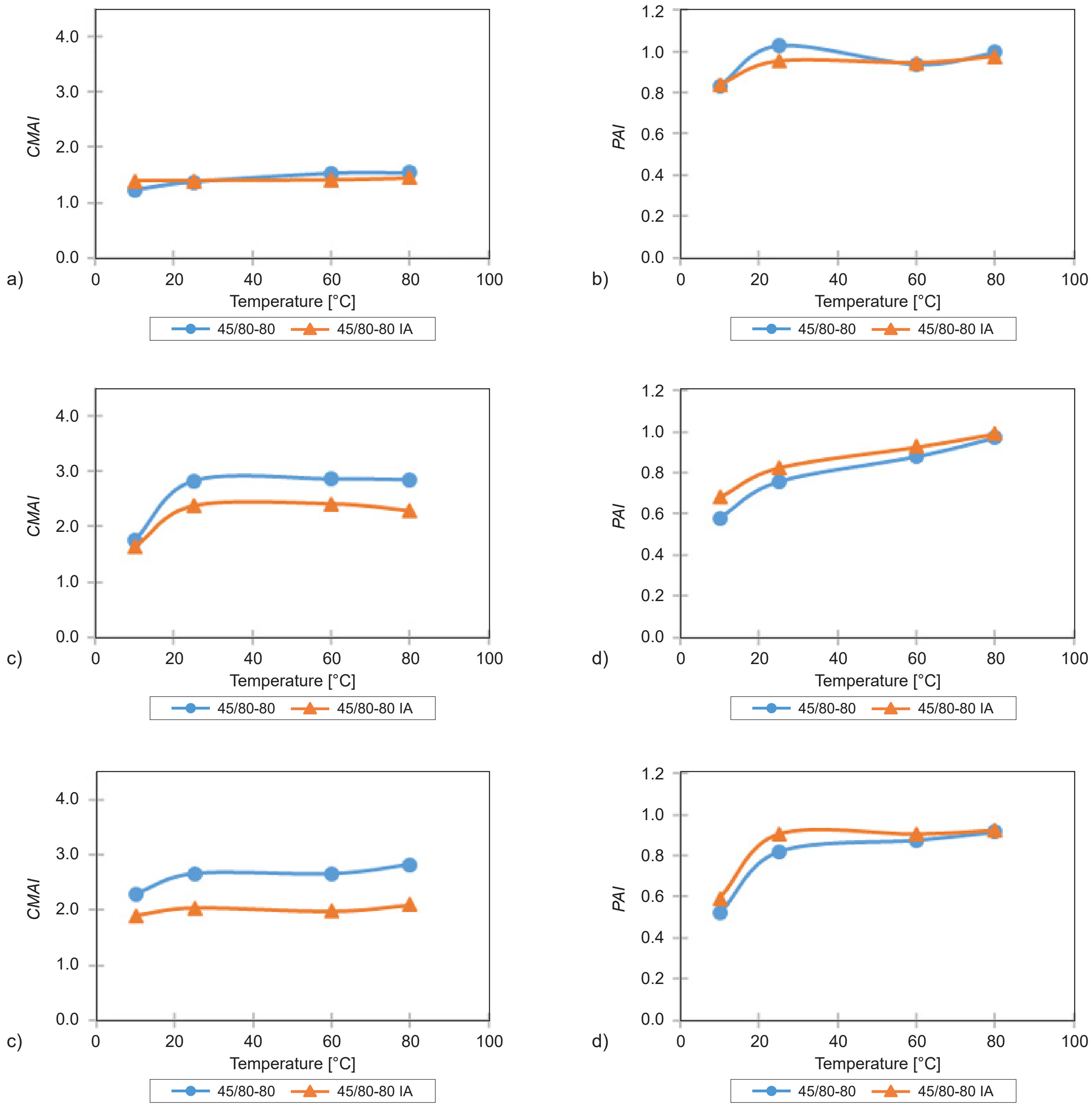


Fig. 4. *CMAI* and *PAI* indicators for 45/80-80 grade bitumens: a) *CMAI* 45/80-80 after RTFOT, b) *PAI* 45/80-80 after RTFOT, c) *CMAI* 45/80-80 after RTFOT + PAV, d) PAI 45/80-80 after RTFOT + PAV, e) *CMAI* 45/80-80 after RTFOT + PAV, f) *PAI* 45/80-80 after RTFOT + PAV

For both modified and highly modified asphalts, no clear differences are observed in *CMAI* and *PAI* indices after RTFOT. IA binders show a slight improvement in *CMAI* and *PAI* values at higher temperatures 60°C, 80°C etc., as shown in Fig. 3a-3b, Fig. 4a-4b. IA binders have significantly increased resistance against long-term aging by thermo-oxidation (RTFOT + PAV). In the case of the 45/80-55 IA asphalt, we observe a minor improvement in the range of 20-30% compared to the 45/80-55 reference sample (Fig. 3c-3d). For the resistance against photo-induced oxidation (RTFOT + UV), the comparison of *CMAI* indicator between the reference and IA binders of the 45/80-55 grade (Fig. 3e) shows lower values for the IA variant in the whole temperature range, suggesting visible improvement of the aging resistance in these conditions. In the case of highly modified asphalts, IA binders show significant improvement in aging resistance. An improvement in *CMAI* in the range of 16-20% is observed for temperatures of 25-80°C after RTFOT + PAV aging (Fig. 4c-4d). The effect of improved photo-oxidation resistance (RTFOT + UV) is estimated at 17-25% (Fig. 4e-4f).

3.2.2. FT-IR analysis

FT-IR spectroscopy was used to track the changes in the chemical structure of binders, as a consequence of accelerated aging. Figs. 5 and 6 compare spectral range from 2000 cm^{-1} to 650 cm^{-1} after each stage of aging, for the 45/80-55 and 45/80-80 reference bitumens respectively. This is where most important bands of IR absorption in bitumen are present, including the characteristic signals of carbonyl vibrations (at 1700 cm^{-1}), stretching vibration of aromatic rings (at 1600 cm^{-1}) and the signal for sulfoxides (at 1030 cm^{-1}). Signals attributed to the presence of polymers introduced to the material during modification were identified at the 699 cm^{-1} for bending the C-H vibration of the phenyl group in the styrene block, 966 cm^{-1} for the C–H bond in the trans-polybutadiene segment alongside 910 cm^{-1}, and 994 cm^{-1} for the terminal double bond attributed to the polybutadiene segment as a result of 1.2-addition of butadiene during polymerization.

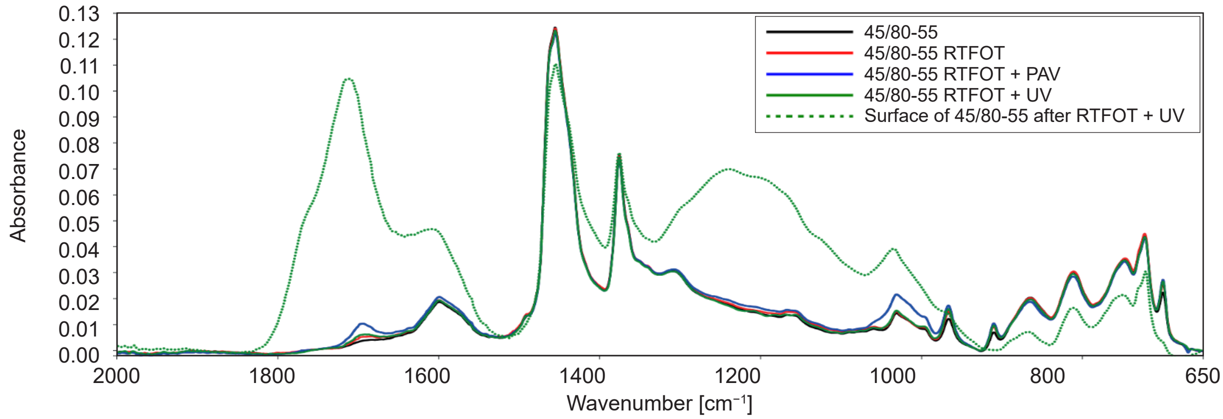


Fig. 5. FT-IR spectra of the 45/80-55 reference binder at different aging stages

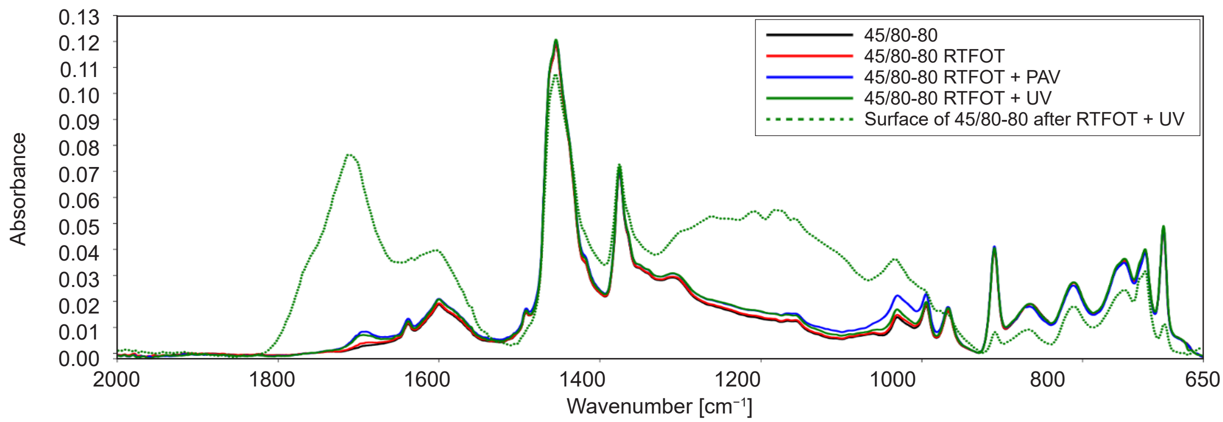


Fig. 6. FT-IR spectra of the 45/80-80 reference binder at different aging stages

The two spectra of the surface of binders after the UV irradiance are shown in order to qualitatively assess the main differences between the thermo- and photo-oxidative aging but should not be directly compared to the other spectra as they are obtained by a different procedure. The results were compared to the recent literature study on the light induced degradation of the thin-film layer by Werkovits et al. [15] and found to closely correspond to the progressive oxidation of the bitumen matrix described by the authors.

The carbonyl signal from the surface after UV exposure is orders of magnitude more intensive than homogenized sample, where it is reduced by mixing with the unexposed bitumen below the surface of the material after aging procedure. This is expected and agrees with the hypothesis that UV degradation is generally a surface-based phenomenon. The other notable observation is the significant decrease in the intensity of polymer-specific signals at 699 cm^{-1}, 910 cm^{-1}, 960 cm^{-1} and 995 cm^{-1} in both 45/80-55 and 45/80-80 bitumens. It could suggest that UV aging of bitumen could have a significant impact on the polymer modifier, either by direct degradation of polymer chains or by inducing physical changes in the morphology of polymer-bitumen network. Up to date work on the degradation of modified bitumen suggests that polymer plays a major role in these processes [16]. More detailed analysis of this interaction would be a promising subject for further studies, with the potential to combine both chemical analyses using spectroscopic and NMR methods alongside analysis of changes in morphology using microscopy.

Homogenized samples after each stage of aging vary in the intensity of the carbonyl, aromatic and sulfoxide bands. The minor increase of absorbance in the wide range of 1500 cm^{-1} to 1100 cm^{-1} was attributed in the literature to various vibrational modes of the main oxidation products [15]. The carbonyl range, from 1720 cm^{-1} to 1660 cm^{-1}, for each of the analyzed samples is shown in detail in Fig. 7.

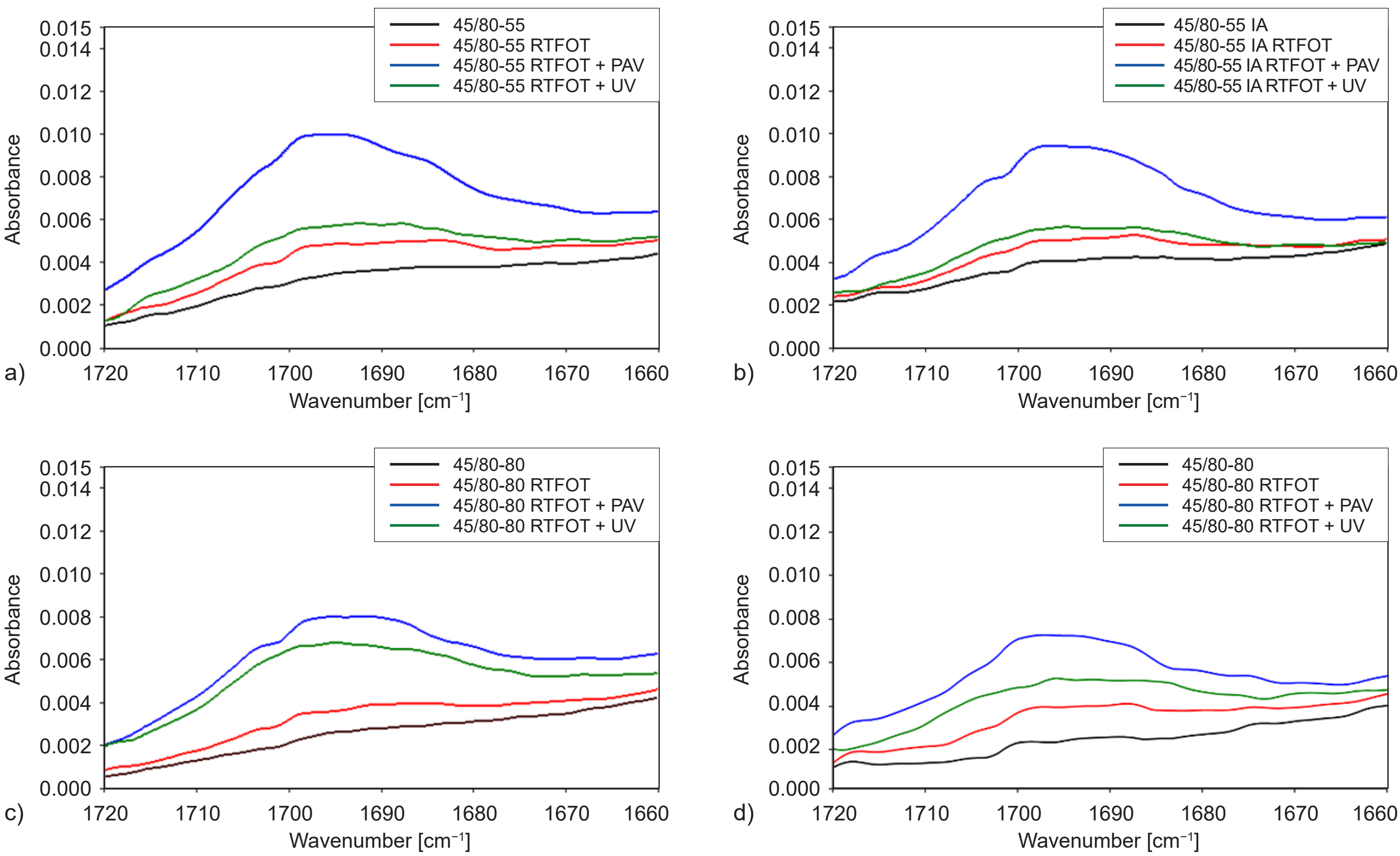


Fig. 7. Change in carbonyl (1720 cm^{-1} to 1660 cm^{-1}) range of each analyzed binder: a) 45/80-55 Ref, b) 45/80-55 IA, c) 45/80-80 Ref, d) 45/80-80 IA

For all analyzed binders, absorbance in the carbonyl range visibly increases at each step of accelerated aging procedure. The increase in carbonyl band follows a set trend, with the lowest relative absorption in the unaged state, and noticeable increase of the carbonyl signal by RTFOT and subsequently either PAV simulation or ultraviolet exposure. In the conditions of the experiment, the increase by RTFOT + PAV is higher than RTFOT + UV in each case. In order to semi-quantitively assess the increase in carbonyl band presence in the aged samples, carbonyl index of each aging state is calculated according to eq. 1. The differences between the carbonyl index (2) at each aging state and the index of the unaged binder are shown in Fig. 8.

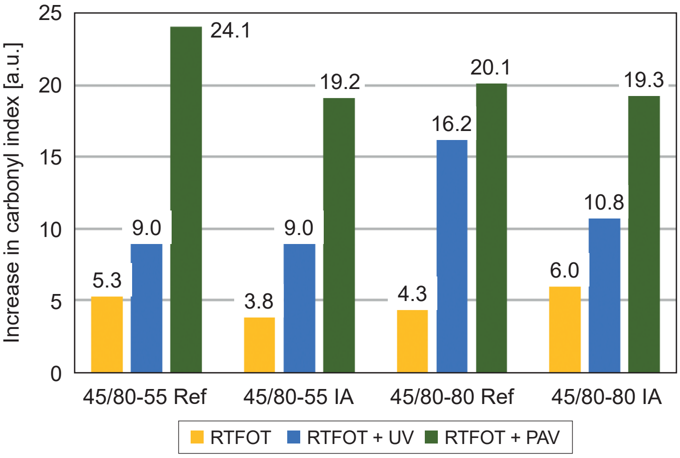


Fig. 8. Increase of carbonyl index by aging stages of tested compositions

Change in carbonyl index after short-term aging, simulated with the RTFOT procedure, suggests similar degree of oxidation at that stage for all analyzed bitumens. This observation is consistent with literature studies, with most authors suggesting a lesser degree of oxidation in RTFOT than during standard PAV procedure [3]. The IA composition is considered to have similar performance as the reference binder against the short-term aging simulated with RTFOT.

Employing the standard PAV procedure after the RTFOT has yielded an additional increase in the carbonyl index, equivalent to about three or four times the increase observed during RTFOT. The increased oxidation during PAV, as compared to RTFOT, is directly attributed to the oxidative character of this aging simulation. The change in carbonyl index of the 45/80-55 reference binder is noticeably higher than the 45/80-80 reference binder, yet both IA variants undergo the same degree of oxidation during RTFOT + PAV aging. With the main difference between compositions being the amount of polymer introduced during modification, it might suggest the better stabilizing efficiency in the tested IA variant of the 45/80-55 grade bitumen.

After the RTFOT + UV aging there was a major difference observed in the carbonyl index between the 45/80-55 and the 45/80-80 type binders, with the 45/80-80 IA variant demonstrating significantly lesser susceptibility to oxidization. The major difference between bitumens of different types provides the insight into the difference between thermo- and photo-oxidative aging, where significantly increased concentration of SBS-type polymer in the latter grade translates to increased degree of oxidation. It is thought to be compelling evidence that the exposure to the UV light can degrade and oxidize the modifying polymer itself or at least introduce ample change to the mechanism of the interaction between the polymeric network and the bituminous matrix. These changes have crucial impact on many parameters of both modified and highly modified binders, and underline the necessity for effective stabilization of these binders, achieved to some extent within the showcased IA compositions analyzed.

4. CONCLUSIONS

The aging resistance of four distinct binder compositions was evaluated independently using two methods, including study of rheological properties with DSR, alongside the FT-IR analysis of the absorption in carbonyl band representative of the oxidation during bitumen aging. Results obtained using both techniques were found to agree with each other and allowed for the quantitive evaluation of the resistance against aging of each IA composition. The standard RTFOT and PAV aging simulations were used to study the behaviour of each material during aging. In addition to these methods, the short-term aged samples were subjected to UV light, representative of the impact of sunlight during the service-life of the pavement. The following conclusions were put forward as a result of conducted experiments:

1. FT-IR analysis is a promising method for evaluation of the chemical changes occurring in binders as a consequence of aging, although more standardization is necessary to ensure repeatability and allow for better

comparison of data. The FT-IR results were complementary to the analysis of binders using DSR method.

2. There is a difference in susceptibility to long term aging, by RTFOT + PAV and RTFOT + UV, especially in polymer-modified binders with different concentrations of polymer.
3. Highly modified bitumens, with about twice the polymer content, had undergone higher degradation under UV aging. The amount of polymer in asphalt binder introduced during modification can significantly affect the susceptibility to photooxidative degradation.
4. The IA compositions have undergone lesser increase in the carbonyl index in case of 45/80-80 samples as well as shown better rheological properties – of about 20% improvement in both grades, suggesting their higher resistance against both thermos-oxidative and photo-oxidative aging.
5. The obtained effect of improved aging resistance of IA binders requires further research and confirmation on asphalt-mineral mixtures, as well as long-term evaluation on test pavement sections in real operating conditions.

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Badania i ocena nowych, modyfikowanych polimerami kompozycji asfaltowych o zwiększonej odporności na starzenie termo- i fotooksydacyjne

Streszczenie: Artykuł opisuje zastosowanie metod oceny stopnia degradacji asfaltów na przykładzie opracowanych kompozycji o zwiększonej odporności na starzenie. Seria badawcza nowych lepiszczy została poddana symulacjom przyspieszonego starzenia RTFOT, PAV oraz starzeniu z wykorzystaniem światła UV. Próbki na każdym etapie starzenia przeanalizowano za pomocą DSR, spektroskopii w podczerwieni FT-IR oraz normowych parametrów asfaltów. Ponadto w pracy uwzględniono dotychczasowe postępy w opracowywaniu standaryzowanej metody pomiarów metodą FT-IR oraz zaproponowano wnioski dotyczące wybranych aspektów półilościowej analizy lepiszczy za pomocą spektroskopii w podczerwieni. Przedstawione wyniki podkreślają znaczenie efektywnego doboru metod oceny odporności na starzenie lepiszczy, w celu skutecznego opracowywania asfaltów o niższej podatności na degradację. Otrzymane lepiszcza o zmodyfikowanej kompozycji wskazują o około 20% wyższą odporność na starzenie zarówno RTFOT + PAV, oraz RTFOT + UV, w stosunku do próbek referencyjnych.

Słowa kluczowe: asfalty modyfikowane polimerami, starzenie fotooksydacyjne, starzenie termooksydacyjne, ulepszona odporność na starzenie.