II MIĘDZYNARODOWA KONFERENCJA - Nowoczesne nawierzchnie drogowe - recykling i dekarbonizacja
Warsaw, 22 - 23 October 2025
MRP'25 II INTERNATIONAL CONFERENCE - Modern road pavements - recycling and decarbonization
INSTYTUT BADAWCZY DRÓG I MOSTÓW
ROAD AND BRIDGE RESEARCH INSTITUTE
1955 - 2025

Assessment of Polymer-Modified Bituminous Binders with Enhanced Resistance to Thermooxidative and Ozone Aging

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INTRODUCTION

- The aim of the study is to prepare and evaluate polymer modified bitumen (PMB) binders with improved resistance to both short- and long-term aging.
- Aging simulations include standardized thermooxdiative aging with RTFOT and PAV, alongside ozone aging conducted in the environmental chamber.
- Aged binders were evaluated against unaged samples using standardized tests and compared with the normative requirements for bituminous binders. The rheological properties after each stage of aging were analyzed using DSR rheometer.
- Chemical changes in analyzed binders were studied using FT-IR spectroscopy. Findings in recent literature were incorporated into the calculation of carbonyl index.

MATERIALS AND METHODS

- Binders with improved aging (IA) resistance were prepared based upon commercially available bitumen grades, which were used as a baseline for comparison.
  - 45/80-55 grade modified bitumen
  - 45/80-80 grade highly modified bitumen
- RTFOT was conducted upon all samples according to EN 12607-1 at the temperature of 163°C for 75 minutes. PAV testing was performed at 100°C for 20 hours, at the pressure of 2,1MPa according to EN14769:2023.
- Rheological properties of binder were measured according to PN-EN 14770:2012. Specific aging indices based on Complex Modulus (G*) and Phase Shift Angle (δ) were calculated:

$$\text{Complex Modulus Aging Index (CMAI)} = \frac{G^*_{aged}}{G^*_{unaged}}$$

$$\text{Phase Angle Aging Index (PAI)} = \frac{\delta_{aged}}{\delta_{unaged}}$$

- Change in absorption in the infrared spectrum as a result of photooxidation was estimated using relative intensity of the carbonyl absorption band (~1700cm^{-1}):

$$I_{C=O} = \frac{A_{C=O\ (1722-1678)}}{A_{ref\ (1518-1330)}}, \qquad \Delta I_{C=O} = I_{C=O\ (aged)} - I_{C=O\ (unaged)}$$

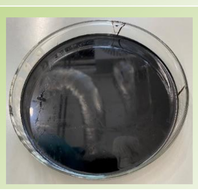
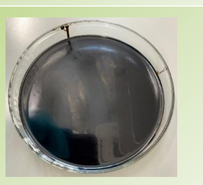
OZONE AGING

- Samples of bitumen after RTFOT of 50.0g +/- 0.5g were poured on circular plates with a diameter of 15 cm.
- The ozone simulation was conducted using ANSEROS Ozone Testing Chamber, at 10.0ppm of O_3 for 72 hours at the temperature of 60°C.
- Considering that the chamber generates ozone from air using electric discharge generator, a non-negligible amount of various nitrogen oxides (NO_x) is likely present. The exact concentration of NO_x was not measured during the experiment, but it is about 10 times lower than O_3 concentration similar that in other experiments with comparable setups.
- Since the process occurs directly on the surface, thickness of the sample will affect the degree of degradation in the homogenized material.

Fig 1. Ozone chamber used in experiment

Fig 2. Bitumen samples in the ozone chamber

Surfaces of reference and IA compositions after RTFOT + O_3 aging

50/70	45/80-55 REF	45/80-55 IA	45/80-80 REF	45/80-80 IA
				

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AGING RESISTANCE AND IMPACT OF OZONE

Impact of different aging methods on reference binders:

- Comparison of reference binders with different polymer content: a) unmodified (50/70), b) modified (45/80-55) and c) highly modified (45/80-80) binders:

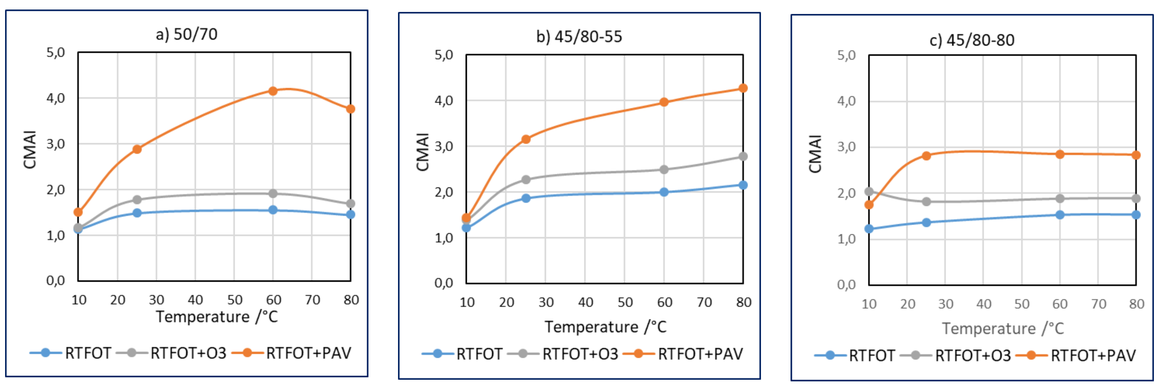
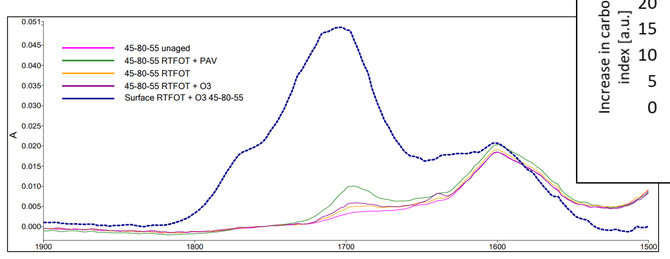


Figure 3 a-c: CMAI indicators for the reference binders after each stage of aging

- The FT-IR analysis allowed for monitoring the increasing degree of oxidation as aging progressed. Calculated carbonyl index allows for semi-quantitive measurement of degree of oxidation in bitumens:

Figure 4: FT-IR spectra of 45/80-55 binder, 1900-1500cm^{-1}



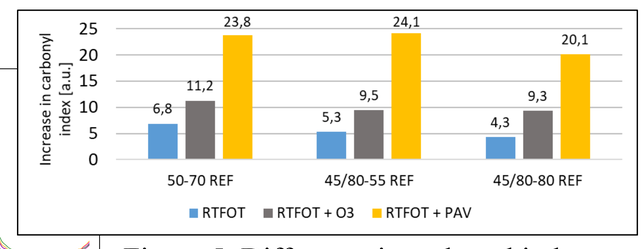


Figure 5: Difference in carbonyl index after each stage of aging in each binder grade

Analysis of new compositions with improved aging resistance (IA):

- Aging resistance of modified compositions of 45/80-55 and 45/80-80 binders were tested against the reference samples, using DSR and FT-IR analysis:

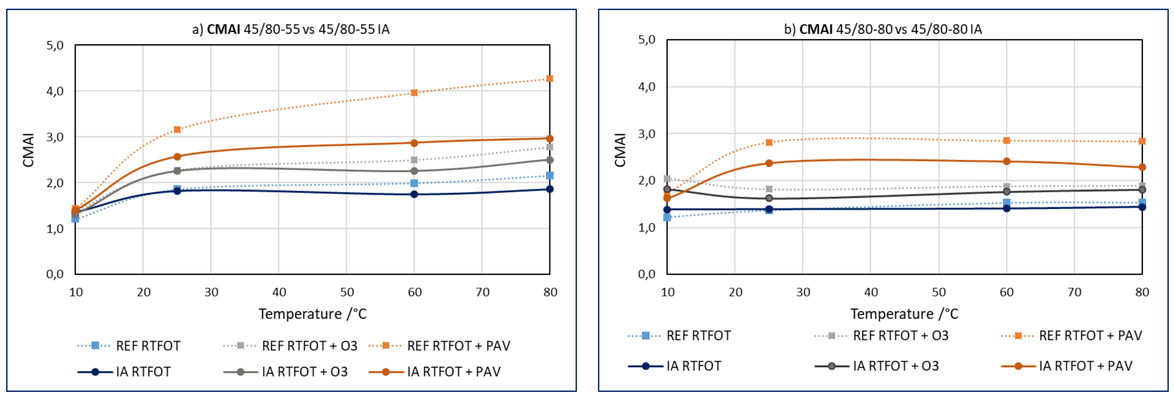


Figure 6 a-b: Comparison of CMAI indicator of reference and IA binders, after each stage of aging

- The IA compositions show significant improvement in terms of CMAI index, at all the three aging stages in the whole temperature range.

CONCLUSIONS

- The impact of ozone, alongside other reactive oxygen species, on analyzed binders resulted in consistent oxidation of binders in the study, with resulting impact of both rheological properties and carbonyl index of about 25% that of PAV procedure.
- FT-IR analysis revealed the progressing oxidation in bitumens, both in case of modified and unmodified binders. The calculation of carbonyl index using the semi-quantitive approach allowed for accurate modeling of the evolution of carbonyl band and was found complementary to DSR analysis.
- Improved aging compositions allowed for about 20% improvement in terms of change of rheological properties after aging, in both in case of modified and highly modified binder. The obtained effect of improved aging resistance of IA binders requires further research and confirmation on asphalt-mineral mixtures, as well as in real operating conditions.