

Document Version

Final published version

Citation (APA)

Pipintakos, G., Ching, H. Y. V., Mühlich, U., Soenen, H., Van Doorslaer, S., Sjövall, P., Varveri, A., Vande Velde, C., & Lu, X. (2021). Experimental Validation of the Dual-Oxidation Routes in Bituminous Binders. In H. Di Benedetto, H. Baaj, E. Chailleux, G. Tebaldi, C. Sauzéat, & S. Mangiafico (Eds.), *Proceedings of the RILEM International Symposium on Bituminous Materials* (pp. 903-909). (RILEM Bookseries; Vol. 27). Springer. https://doi.org/10.1007/978-3-030-46455-4_115

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Experimental Validation of the Dual-Oxidation Routes in Bituminous Binders



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Abstract Oxidative ageing in bituminous materials is considered to be one of the most important factors for distress types in road applications. The increasing interest in oxidative ageing has highlighted the need for a thorough understanding of the oxidation mechanisms at molecular level. This paper offers some insight in the validity of the proposed hypotheses about the oxidation routes of bitumen, the fast- and the slow-rate route, reflecting on previous studies. Fourier-Transform Infrared (FTIR) and Electron Paramagnetic Resonance (EPR) spectroscopy were utilised for this verification. To elucidate the uncertain formation of sulfoxides, an additional surface investigation with Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) was performed. The findings of the aforementioned techniques reveal the existence of the oxidation products reported previously and contribute to the understanding of the oxidation mechanisms. Overall, this research strengthens experimentally the hypotheses of the dual-oxidation routes of bitumen.

Keywords Oxidative ageing · Bitumen · FTIR · TOF-SIMS · EPR

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1 Introduction

Hitherto, various studies have demonstrated the link between oxidative ageing and alterations in physical and chemical properties, which eventually lead to cracking and raveling [1, 2]. Although considerable research has been devoted to the rheological consequences of oxidative ageing, less attention has been paid to the understanding and evidence of the oxidation routes at molecular scale. As articulated by various researchers two major oxidation routes may exist, namely the chemically distinct “fast-spurt” and the “slow/long-term” routes [3–6]. This idea has gained considerable support since a direct link with the asphalt production stages can be established. It appears that the initial increase of viscosity during production, transportation and compaction is controlled by the fast reaction whereas the long-term ageing during service life is attributed to a slow reaction [6].

Briefly, during the fast reaction path different products are produced with examples including hydroaromatic hydroperoxides and sulfoxides. However, as hydroperoxides might be thermally unstable they can also decompose to form free radicals, which can successively initiate the slower hydrocarbon reaction [3, 4]. Among the main products of the slow oxidation route are sulfoxides and carbonyls. Of pragmatic importance is the fact that upon sulfoxide formation during the slow reaction, alcohol chemical groups are also produced which strengthens the belief that the infrared absorption band (around 1100 cm^{-1}) of alcohols and sulfoxides may coincide [4, 7].

It appears that experimental validation of the above mechanisms has been confined primarily to sulfoxide and carbonyl formation. Considerable research has been devoted to the determination of these functional groups via chemical analysis such as FTIR [8–11]. So far, little attention has been paid to the proof of free radicals as well as to the alcohol formation that accompanies sulfoxides. These factors, if experimentally proven, could validate at least the fast oxidation route and establish the basis for the understanding of the slow reaction.

In this study, a number of uncertainties regarding the oxidation routes are addressed. An issue of obvious concern is the validation of the source of the increased sulfoxide indicator. To explore this aspect and unravel the possible overlap of sulfoxide and alcohol in an infrared spectrum, TOF-SIMS was utilised. The organic radical formation is finally investigated with EPR spectroscopy, underutilised for bitumen applications and appropriate for the identification of the free radicals. Links between the results of the three techniques under predefined oxidation time and temperature will finally confirm certain hypotheses of the oxidation routes.

Table 1 Properties of the binders

Material	Property	Binder		Test Method
		A	B	
Bitumen	Penetration 25 °C (0.1 mm)	16	189	EN1426
	Softening point (°C)	61.1	37.5	EN1427
	Viscosity 135 °C (mm ² /s)	1285	203	EN12595

2 Materials and Methods

2.1 Materials and Ageing Treatment

For the experimental part two bituminous binders were used as specified in Table 1, namely a hard binder A and a soft one, binder B. For a thorough investigation of the oxidation evolution of the two binders, modified thin film oven ageing (M-TFO) of approximately 1 mm thick layer was preferred for the FTIR and the TOF-SIMS measurements. That was not the case for the EPR measurements where binder films of thickness 3–5 mm were aged directly in polypropylene tubes in a ventilated oven. The temperature chosen (50 °C) was considered realistic in the framework of ageing simulations in order to accelerate the oxidation process and simultaneously capture and differentiate between the main oxidation routes. The ageing time intervals (0–2–5 and 8 days) were selected according to preliminary infrared findings for a prolonged ageing time (Fig. 1 [left]) using the same ageing treatment.

2.2 Spectroscopic Techniques

FTIR

The FTIR analysis was performed with a Thermo Scientific Nicolet iS10 FTIR spectrometer equipped with an Attenuated Total Reflectance (ATR) fixture and a Smart Orbit Sampling Accessory. At least three replicas were measured per ageing time interval in order to ensure repeatability, while the collected spectrum ranged from 400 cm⁻¹ to 4000 cm⁻¹ with a resolution of 4 cm⁻¹.

EPR

Spectra of aged and unaged bitumen samples were recorded with a Bruker Elexsys E680 spectrometer fitted with an ER 4102ST TE₁₀₂ mode resonator at ~9.75 GHz (X-band). Customised 2 mL polypropylene Eppendorf tubes were used as sample holders ensuring that the total material quantity did not overfill the cavity. Preliminary power saturation measurements were performed to select the appropriate power level of 0.5 mW in order to avoid saturation effects. Two replicas were measured per ageing interval under constant instrumental settings: center field = 341 mT, sweep width

= 20 mT, number of sweeps = 2, resolution = 2048 points, modulation amplitude = 0.1 mT and modulation frequency = 100 kHz. The signal intensity was finally processed based on the peak-to-trough distance and normalised by the sample mass.

TOF-SIMS

TOF-SIMS analysis was conducted in a TOF-SIMSIV instrument (IONTOF GmbH, Germany) using 25 keV Bi^{3+} primary ions and low-energy electron flooding for charge compensation. The bitumen samples were deposited on silicon wafer substrates and subsequently allowed to cool according to a special protocol [12]. The analysis was carried out at a sample temperature of $-80\text{ }^{\circ}\text{C}$ over analysis areas of $200\text{ }\mu\text{m} \times 200\text{ }\mu\text{m}$. Positive and negative ion spectra were acquired at three locations of each sample, with the instrument optimised for high mass resolution.

3 Results and Discussion

Semi-quantitative methods for analyzing the FTIR spectrum can be useful for identifying and characterising the evolution of specific oxidation products such as sulfoxides [8–11]. Consistent with previous studies, this study demonstrated an initial rapid increase of sulfoxides followed by a constant rate formation, (Fig. 1 [right]), which can be attributed to the fast and slow oxidation route respectively [3, 4]. As shown in Fig. 1 [left], binder A has almost completed the fast reaction path at about 5 days, whereas binder B reached this transition point at about 2 days. Additionally, the sulfoxide intensity, analyzed with a widely accepted quantitative method [8], documented that binder A suffered from a harsher oxidation effect, under the predefined ageing conditions, compared to binder B.

From the previous analysis, it becomes apparent that at 8 days of controlled ageing the slow oxidation route has been initiated for both binders. For a fair comparison of the two binders the formation of free radicals, reported simultaneously with the

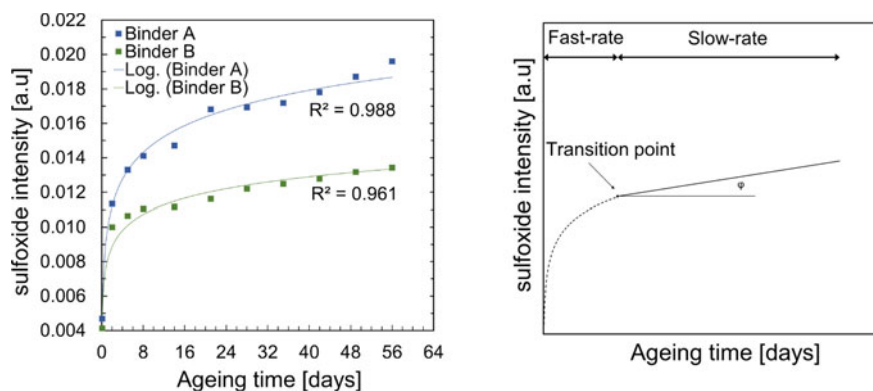


Fig. 1. Evolution of the sulfoxide intensity via FTIR [left] and indicative reaction phases [right]

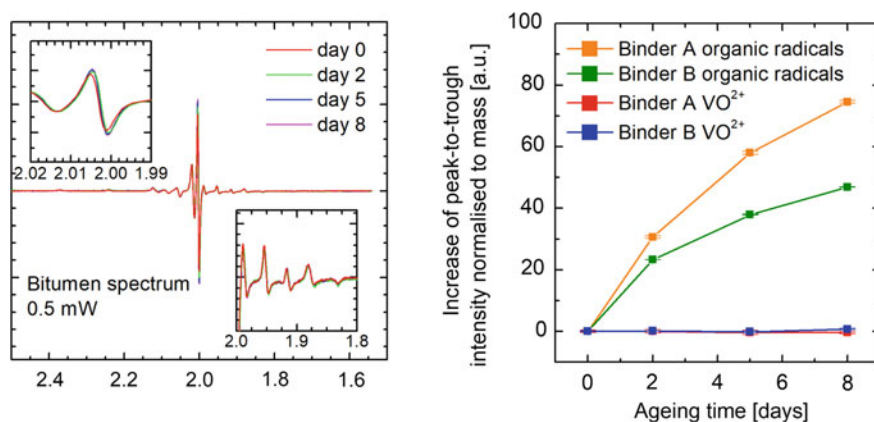


Fig. 2. Example of X-band EPR spectra with the insets showing expansions of selected regions of organic radicals (top) and vanadyl ions (bottom) [left] and evolution of these signals [right]

sulfoxide during the spurt, was investigated in this time-frame. Fig. 2 [left] shows the time dependent evolution of the EPR spectrum of a typical binder sample and signals from organic radicals ($\text{RO}^\cdot$, $\text{OH}^\cdot$) and a vanadyl species (VO^{2+}). Comparing regions where there was only a VO^{2+} contribution (around $g = 1.9536$) with the corresponding organic radical regions (around $g = 2.0016$) reveals clear trends for the radical evolution (insets) [13].

What is striking about the data in Fig. 2 [right] is that the intensity of the organic radicals is constantly increasing for both binders, within the time-frame of the fast route, whereas VO^{2+} species appear to remain steady. The successive increments of the organic radicals, as oxidation evolved, imply that indeed the expected radical formation is evident during the fast-rate route. A comparison of the two binders indicates that the relative increase of organic radical intensity of binder A was almost doubled in comparison with binder B. On the other hand, the vanadyl signal intensities of the two binders remained unchanged, something which could be further associated with the vanadium content and used as a marker for the origin of crude oil.

Having supported experimentally to some extent certain hypotheses for the mechanisms of the fast oxidation route articulated previously, a TOF-SIMS analysis for the changes of the chemical compounds upon ageing was considered crucial. Being motivated by the negligible change of the infrared spectrum during oxidation in the area $3000\text{--}3500\text{ cm}^{-1}$ related with various oxygen-containing compounds and the rise of the peak around 1100 cm^{-1} assigned to alcohol and sulfoxide appearance, a further exploration was performed based on previous studies [12].

It is assumed that at 8 days under the given ageing conditions both binders are in the slow reaction path. Thus, according to the underlying mechanisms sulfoxides and multifunctional alcohols as well as carbonyls are produced. The FTIR spectrum confirms partially the former and validates the latter. The results of the TOF-SIMS surface analysis unravel the riddle for the oxidation products of the fast

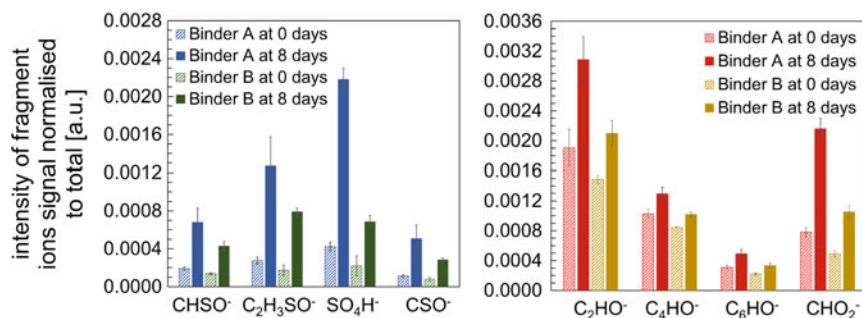


Fig. 3. Intensity of SO_x-containing [left] and HO_x-containing compounds via TOF-SIMS [right]

oxidation route. The findings were analyzed based on normalised signal intensity and categorised in SO_x-containing, Fig. 3 [left], and HO_x-containing fragments Fig. 3 [right].

It can be seen from the intensity of the fragments with the generic formula RSO_x that indeed the formation of sulfoxide-related compounds is evident also with this technique. When it comes to the HO_x-containing fragments, the preliminary observations with the infrared spectrum along with the rise of these compounds, indicates eventually to be alcohol-related. Moreover, the oxidation effect of binder A is significantly stronger than binder B, which is in agreement with the FTIR results. It is also worth mentioning that the amount of nitro-compound fragments was increased during oxidation, in contrast to the organic ions without heteroatoms and the ones containing S and N without oxygen which remained unchanged. In the future, this exploratory study will be exploited for the quantification of different fragments formed during the ageing process.

4 Conclusions

In this investigation the mechanisms of the dual-oxidation routes of bitumen were validated experimentally. The results from FTIR supported the existence of two oxidation paths, a fast- and a slow-rate and the rapid sulfoxide formation during the fast path. EPR measurements during the fast oxidation route confirmed that organic radicals are produced and can be associated with the initiation of the slow oxidation route. This study established also a quantitative framework for detecting sulfoxide and alcohol compounds in the slow reaction path. Taken together, the findings of the FTIR and TOF-SIMS spectrometry indicated that sulfoxides, carbonyls and other oxygen-containing compounds, with high probability to be alcohols, are formed during the slow oxidation route. Overall, the insights gained from this study may be particularly interesting for improving our understanding for the underlying oxidation mechanisms which subsequently can be incorporated in the bitumen characterisation by means of the intensity of the ageing products.

Acknowledgments The authors gratefully acknowledge support from Nynas AB, and the E.U. for HYVC's H2020-MSCA-IF (grant number 792946, iSPY).

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