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Laboratory and field ageing of SBS modified bitumen: Chemical properties and microstructural characterization



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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- Ageing trends of 19 years field aged unaged and laboratory aged bitumen.
- Gradual decrease of reactive oxygen penetration depth into the bulk material.
- Photooxidation causes major structural and chemical changes on the surface features.
- Fluorescence microscopy demonstrates fluorescing catana and peri phase.

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ABSTRACT

Styrene-butadiene-styrene (SBS) modified bitumen is a widely-used civil engineering material with a variety of applications. The properties and durability of bitumen greatly depend on its chemical composition. Due to its organic nature bitumen is highly prone to oxidation. The main cause of bitumen oxidation is the interplay of sunlight (photo-oxidation), atmospheric oxidation with reactive oxygen species (ROS), mechanical ageing and thermal oxidation. However, current standardized ageing methods, such as rolling thin film oven test (RTFOT) and pressure ageing vessel (PAV) do not include photo-oxidation and lack realistic ageing simulation. In this work, different laboratory aging procedures like PAV, RTFOT and UV radiation are applied to SBS modified binder. At the same time field aged bitumen with 19 years service in the road is analysed. The surface has been treated with UV radiation and ROS, resulting in deformation of surface microstructures and change in chemical composition. Since ageing mainly affects the surface of bitumen, a layer study on field aged bitumen samples was conducted to demonstrate ROS penetration depth. Fluorescence spectroscopy indicated that the ROS penetration mainly affected the first centimetres of the surface and a rapid decrease of ROS diffusion could be discovered. Fluorescence excitation-emission matrix (FEEM) results show that the overall fluorescence intensity decreases with ageing. The link between chemical and morphological change due to ageing could be given with fluorescence microscopy. The colloidal nature of bitumen exerts in the microstructural composition, which undergoes

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undergo a major chemical and morphological change with progressive ageing. We recorded the first fluorescence image of the typical surface microstructures with previously unattainable resolution with fluorescence microscopy, highlighting fluorescing Catana and Peri phase of the surface domains while Para phase exhibited less fluorescence intensity. The link between chemical and morphological change could be given with atomic force microscopy (AFM). Finally, AFM and fluorescence microscopy indicated that photo-oxidation promoted a gradual deformation of the chemically inhomogeneous surface structures toward shrink in size, deformation of the catana pattern and a drastic increase in microstructure height compared to neat bitumen, which encourages the importance of inclusion of atmospheric photo-oxidation to standardized bitumen testing methods.

1. Introduction

Bitumen, as obtained by crude oil fractional distillation, is a complex mixture of hydrocarbons with traces of metals and consists of a variety of complex organic molecules. Bitumen can be further subdivided into four fractions, with the aid of polarity chromatography i.e. Saturates, Aromatics, Resins and Asphaltenes (SARA). Bitumen's chemical composition and its polymer content plays a crucial role for successful application and durability. Therefore, improving laboratory ageing methods and providing realistic ageing methods is a valuable social economic objective. Due to its mainly organic nature bitumen is highly susceptible to reactive oxygen species (ROS) and UV exposure. Contact of the surface with air or UV radiation can dramatically change the surface microstructure properties of bitumen. Ageing of bitumen can be recognized in the ratio of its SARA fractions [1-3], increase in its carbonyl and sulfoxide groups [4-6] increase in the surface roughness on the sub microscale [5,7,8] and changes in its overall fluorescence intensity [5] which significantly influences the mechanical properties of bitumen leading to changes in asphalt performance and embrittlement [9–12]. Overall, the ratio of SARA fractions and therefore the polarity gradient plays a crucial role in the colloidal nature of bitumen and thus influence microstructural composition. Short-term and long-term ageing of bitumen leads to changes in physicochemical and morphological properties. However, it is not fully understood yet how ageing changes the molecular and microstructural composition of bitumen and how deep ROS penetrate from the surface into the material over a specific time period and therefore studies on the ageing especially on the surface - layer by layer is necessary to understand the penetration depth of oxidants.

Several studies have been conducted to study linear dependencies on the ageing behaviour with Fourier Transform Infrared Spectroscopy (FTIR) [4,13,14], Dynamic Shear Rheometer (DSR) [15,16], Fluorescence Microscopy [17,18] and Atomic Force Microscopy (AFM) [5,19, 20]. While FTIR is mainly used to determine the carbonyl and sulfoxide increase during ageing, DSR provides mechanical bulk information on the viscoelastic behaviour of bitumen at medium or high temperatures. AFM captures the topography of bitumen on the microscale providing information on the surface roughness and surface microstructures. Studies conducted with fluorescence microscopy can determine the overall fluorescence [21,22]. Confocal Laser Scanning Microscopy (CLSM) has revealed the heterogeneity of bitumen surface and the existence of fluorescing centres in the range of 1–10 µm [21]. Fluorescence spectroscopy is suited to analyze aromatic and conjugated hydrocarbons due to their large π molecular orbital systems, which are capable to absorb and emit. A photon of lower energy is emitted than it is absorbed upon return from the excited to the ground electronic state. This phenomenon is almost exclusive to these classes of molecules [23]. Fluorescence spectroscopic studies of bitumen and its SARA fractions have provided a solid starting point to track fluorescent capable compounds. The characterization of each fraction of bitumen was successfully determined using fluorescence spectroscopy. The maximum of fluorescence emission for bitumen has been observed between 240 and 270 nm excitation wavelength. An additional second maximum has been observed at 360 nm excitation wavelength. Studies of FEEM performed on humic-like substances show similar maxima in the spectra observed

for bitumen [21]. Studies performed on various PAHs such as Naphthalene, Anthracene, Fluoranthene, Indenopyrene and Benzoperylene demonstrate that the emission depends on the ring number of the compound. As a general rule high ring number compounds appear at a longer wavelength and at least two or more aromatic rings in the condensed aromatic structure are needed to be present for an emission window that falls in the similar excitation and emission region as for bitumen [24]. Smaller condensed aromatic hydrocarbons such as naphthalene fall into the emission region of below 350 nm [25,26].

Humic-like substances exhibit strong and broad emission between 390 and 520 nm at excitation wavelengths at 250 and 360 nm which is coherent with the both maxima in the FEEM of bitumen [27]. Given the presence of humic-like substances in bitumen [28] FEEM data of humic-like substances can serve as a reference point to identify high molecular weight aromatic systems with various functional groups. Ozonolysis on humic-like substances revealed a decrease in the overall fluorescence intensity of these prominent maxima as observed in bitumen [29,30].

1.1. Photochemical oxidation

A variety of oxidation mechanisms have been proposed as nonphotochemical and photochemical sources of ROS [31,32]. Additionally, oxidation chambers with and without UV source have sometimes revealed a puzzling mismatch, given that oxygen and heat has long been assumed to be the only oxidation source of significance [14,33-35]. Studies suggest that Ozone and NOx to be the major contributor of significance [36]. However, the contribution of OH radicals is often underestimated. UV-B radiation leads to OH formation in the presence of humidity in atmospheric conditions. The reactivity of OH radicals originates from its oxidation potential which is 2.8 V (this makes it the second most reactive species next to fluorine atom) and therefore is significantly higher than Ozone and NO_x molecules bearing the potential to react with organic molecules, initiate and perform many radical oxidation reactions. Since the OH radical plays a key role in the troposphere and in day time chemistry it is the major contributor of bitumen oxidation [37,38].

Although photolysis of Ozone is the major source for the natural production mechanism of OH radical, it is not only limited to Ozone. The reaction of HO_2 radicals with NO represent an important source for the OH formation (1). Additionally, photolysis of HONO (which becomes relevant in polluted air (reactions on surfaces, e.g. aerosol particles) portrays another source for OH radicals [39].

$$HO_2 + NO \rightarrow OH + NO_2$$
 (1)

$$HONO + hv \rightarrow HO + NO$$
 (2)

The formation of OH radicals in laboratory simulated oxidation can be created with UV radiation in the UV-B range with wavelengths of below 320 nm or 410 nm by photolysis of Ozone.

$$O_3 + hv \ (\lambda < 320 \text{ nm}) \rightarrow O(^1D) + O_2(^1\Delta)$$
 (3)

$$O_3 + h\nu(\lambda < 410 \text{ nm}) \rightarrow O(^3P) + O_2(^1\sum)$$
 (4)

The excited Oxygen Atoms O(¹D) can be deactivated by collision



Fig. 1. Major factors initiating and continuing bitumen oxidation, including Ozone, NO_x and OH radical as the main oxidants. Loss of volatile organic compounds is inevitable.

partners M (e.g. N2, O2, H2O)

$$O(^{1}D) + M \rightarrow O(^{3}P) + M$$
(5)

However, part of the excited Oxygen Atoms (5-20%) react with the humidity presence in the atmosphere:

$$O(^{1}D) + H_{2}O \rightarrow OH + OH \tag{6}$$

OH initiated oxidation of aromatics and saturates aliphatic hydrocarbons were extensively studied [40]. It has been shown that aromatic compounds underwent primarily addition-elimination reactions. The influence of elevated NO_x concentrations has been studied by Berndt et al. [41] Oxidation with OH radicals in presence of NO_x and O₃ forms phenols from aromatic substances which then further yields in quinones. While phenols/quinones makes the majority of the yield, glyoxal, *cis*butenedial and *trans*-butenedial are also generated [41].

The influence of UV radiation on ageing includes: (i) highly reactive photochemical smog generated by UV radiation in presence of NOx and volatile organic compounds (VOCs) and (ii) direct absorption of UV photons by the molecules situated on the surface. The mechanism of the production of reactive gas by UV radiation was shown in Eqs. (1)–(6). in more detail. Therefore, it is vital to explore the atmosphere-bitumen interface in more detail. The atmosphere – road interface is illustrated in Fig. 1.

While photochemical oxidants lead to chemical reactions and oxidation of certain bitumen compounds and lower reactive compounds can even diffuse more into the bulk of the porous asphalt concrete, UV radiation attacks almost exclusively the outer surface molecules. Since bitumen as a black material bears enhanced light absorption capacity the absorption of UV-photons by the surface molecules plays a significant role in generation of radicals. Taking polymers as an example: aldehydes, ketones and carboxylic acids in polymer chains are created by photo-oxidation during photolysis [42]. Photooxidation reactions are initiated by the existence of chromophoric groups. Chain scission, cross linking, secondary oxidative reactions, chain propagation, chain branching and termination steps take place whereby free radicals play the main character [42]. Looking at bitumen composition, aromatics, resins and asphaltenes are chromophoric compounds while only the saturates fractions is non-chromophoric. Hence, free radicals and subsequent radical reactions are expected due to UV photon absorption which is in our case a maximum of quantum energy of 4.43 eV. On the one hand, the surface molecules experience splitting and formation of radicals, photochemical smog especially which possess lower reactivity than OH radicals diffuse deeper into the bulk material and may cause an oxidation gradient within the bulk decaying exponentially. Rather than

considering both mechanisms as disconnected from each other, their interplay in initiating and continuing oxidation phenomena is essential to conduct and model realistic field ageing. The interplay and interdependency of each oxidation mechanisms may be the following: harsh oxidation of the first layer due to direct UV radiation can cause drastic physicochemical changes resulting in changes in the mechanical properties and therefore cause cracking and rutting on the submicron scale and subsequent uncovering of the bulk material. This phenomenon is problematic for the material, since ROS as well as water soluble reactants (or water molecules which may also freeze in fine fissures during wintertime \rightarrow further deformation) can penetrate deeper and more importantly along the cracking routes and cause inhomogeneous ageing which will cause cracking induced deterioration. Therefore, a rather homogenous ageing gradient along the vertical axis is preferable.

In this study, the general goal is to understand the surface and diffusion properties of bitumen and to correlate its chemical nature and ageing behaviour with its microscopic properties. For this purpose, the heavily field aged bitumen (19 years service life) has been examined to recognize oxidation dependencies. Moreover, standardized laboratory aged bitumen (PAV and RTFOT) are compared to field aged bitumen. In order to gain an understanding of UV ageing, a corresponding study is carried out with a special UV photochemical ageing setup.

The scope of this paper is to track ageing via fluorescence spectroscopy and see whether ageing changes the excitation and emission maxima and whether certain patterns are visible throughout the fluorescence excitation emission matrices and provide information on the degradation of the aromatic and the resin compounds. FEEM of bitumen facilitates to picture the shifts of maxima induced by ageing. Moreover, ageing is mainly affecting the surface. Therefore, a layer study is conducted on the field aged samples to provide information on the penetration depth of reactive oxygen species. Since bitumen is a complex material and is rather a colourful mixture of various chemical compounds it is challenging and yet interesting to unravel the puzzle of how ageing affects the bitumen material and its microstructure. Hence, with fluorescence spectroscopy one cannot assign certain bitumen molecules to distinctive excitation or emission maxima, but one can only interpret certain groups of molecules.

The mechanical properties of asphalt composites are evaluated via the multi-scale material modelling method, where the arrangement of microstructures play a vital role in predicting asphalt performance as a holistic system [9,43]. Therefore, assessment of microstructural changes in bitumen is crucial. The final goal of the present work is to provide a better understanding of the surface phenomena evoked by ageing. Hence, to further investigate the evolution of microstructures and changes in the surface chemical characteristics of various phases, direct photooxidation was conducted. The surface changes were tracked with fluorescence microscopy and AFM.

2. Materials and testing

2.1. Materials and material ageing

Around 25% of all bitumen used in Germany and in Austria are modified (preferably with styrene-butadiene-styrene (SBS))[44]. Almost all surfaces courses in both countries consist of SBS modified bitumen which are more prone to aging, especially the first layer. Hence for this study SBS bitumen was used, which was available from a 19 years field aged highway. Polymer modified (3 wt% SBS content) bitumen 45/80-65 according to Austrian Standard (ÖNORM B 3613, 2018) with a penetration grade of 54 mm/10 and a softening point ring and ball of 79.2 °C was chosen as the virgin material for laboratory aging [45–47]. Two very similar bitumen (also modified with SBS) of the same penetration grade from two different manufacturers (BP and Shell) were used for asphalt paving 19 years ago and used to evaluate field aging.

Table 1

Overview of ageing conditions.

-	-		
Sample description	Ageing procedure	Ageing time	Ageing conditions
V1	Virgin	_	-
PAV 1	$1 \times PAV$	1200 min	100 °C, 2.1 MPa
PAV 2	$2 \times PAV$	2400 min	100 °C, 2.1 MPa
PAV 3	$3 \times PAV$	3600 min	100 °C, 2.1 MPa
111	$1 \times \text{RTFOT} \text{ and } 1 \times$	75 min and	163 °C and 100 °C,
	PAV	1200 min	2.1 MPa



Fig. 2. Photochemical oxidation set-up with a bitumen sample.

2.2. Standard ageing methods

Repetitive ageing was conducted on the bitumen with PAV and RTFOT according to EN 12607-1 and EN 14769 [48,49]. The different ageing conditions are presented in Table 1.

Standardized laboratory aging procedures are available to simulate thermal oxidation focusing on mechanical changes in the asphalt binder. These procedures are Rolling Thin Film Oven Test (RTFOT) which simulates short term aging during asphalt production and Pressure Aging Vessel (PAV) which simulates long term aging during service conditions [48,49]. Both procedures are applying elevated temperatures combined with a defined air supply and have been commonly used in the asphalt industry for many years. More details on the mechanical changes of asphalt binders due to thermal aging were presented in a previous



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paper^[5].

2.3. Photoexposure

The photo-oxidation of the bitumen surface was carried out in a photochemical reaction cell and is shown in Fig. 2 to examine the effects of photochemical influence. A Lumatec Superlite I 05 with UV-B and UV-A components was used as the UV source. The spectrum emitted by the UV lamp and the intensity are shown in Fig. 3.

Three sample sets were prepared on glass slides with a 5 mm thickness and kept in sealed boxes upon UV irradiation. The samples were placed directly under irradiation to maximize the surface area of sample exposed. Samples were irradiated for 30, 60, 2160 and 2880 min in a photochemical reactor equipped with a Lumatec Superlite I 05 UV source which provides a spectral shape similar to that of natural sunlight in the wavelength region of 280-730 nm, the most important wavelengths for environmental photoreactions. All samples were analysed within 2 h to eliminate dynamic changes with the bulk material. The ageing conditions are summarized in Table 2.

For the microscopic study the unaged bitumen is illuminated for twelve hours in the photochemical reaction cell with air supply containing humidity. The resulting mixture of OH radicals, O3 and NOx reacts intensively with the bitumen surface. A change in the chemistry and structures of the bitumen can be observed both with AFM and with fluorescence microscopy. A change due to a possible temperature development is excluded by infrared (IR) cut-off filters, which were implemented between the light source and the inlet to the photochemical reaction chamber. The samples were analyzed within 1-2 h, sufficient enough for microstructure formation after sample preparation and short enough to eliminate exchange with bulk material.

2.4. Field ageing

Field aged samples (19 years service life) from the highway L3080 between Nordhausen and Sangerhausen (Germany) were provided. The top layers of drill cores with a diameter of 15 cm were cut into 1 cm thick layers, extracted separately and combined as groups of 5. Fig. 4 shows the procedure described for drill cores 1-5, in which the top layers are summarized as BK1-5 S1. The overview of representative bitumen samples from the sampling section is provided in Table 3, while

Table 2		
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С	ver	view	of	ageing	conditions.

	Sample	Ageing time	Ageing conditions
UV 130 minbatch reactor, UV radiation, NOx, O3, OFUV 260 minbatch reactor, UV radiation, NOx, O3, OFUV 32160 minbatch reactor, UV radiation, NOx, O3, OFUV 42880 minbatch reactor, UV radiation, NOx, O3, OF	UV 1	30 min	batch reactor, UV radiation, NO_x , O_3 , OH -
	UV 2	60 min	batch reactor, UV radiation, NO_x , O_3 , OH -
	UV 3	2160 min	batch reactor, UV radiation, NO_x , O_3 , OH -
	UV 4	2880 min	batch reactor, UV radiation, NO_x , O_3 , OH -



OPTICAL OUTPUT

Spectrum		Power	Power Density	
UVB	280-320 nm	500 mW	2,500 mW/cm ²	
UVA	320-400 nm	4,500 mW	22,500 mW/cm ²	
Violet	400-420 nm	2,000 mW	10,000 mW/cm ²	
Blue	400-500 nm	8,000 mW	40,000 mW/cm ²	
UVA-Violet	320-420 nm	6,500 mW	32,500 mW/cm ²	
UVA-Blue	320-500 nm	12,500 mW	62,500 mW/cm ²	

Fig. 3. Lumatec Superlite I 05 UV/VIS-Lamp specifications. Reproduced with permissions from Lumatec GmbH [52].



Fig. 4. Separation of drill cores in layers.

Table 3

Overview of representative 19 years field aged bitumen samples from the sampling section.

Sample	Information
BK1-5_S1 BK1-5_S2	Layer 1 (first centimetre) of drill core $1 - 5$ Layer 2 (second centimetre) of drill core $1-5$
BK1-5_S3	Layer 3 (third centimetre) of drill core 1–5
BK56–60_S1 BK56–60_S2	Layer 1 (first centimetre) of drill core 56–60 Layer 2 (second centimetre) of drill core 56–60
BK56-60_S3	Layer 3 (third centimetre) of drill core 56–60



Fig. 5. Highway L3080 immediately after the cores were taken from the highway. The sampling clusters (5 samples) are clearly visible on the road surface.

drill cores BK1–5 represents the bitumen from Shell and BK56–60 represents the bitumen from BP which were used during construction 17 years ago. Six different clusters of drill cores are included in this study. Fig. 5 shows the testing field with typical visible drill core sampling features. The extraction of bitumen was performed using tetrachloroethylene according to EN 12697-3 [53].

2.5. Spectroscopic testing

2.5.1. Fluorescence spectroscopy

In this study, a fluorescence spectrometer (FSP920) from Edinburgh Instruments was used. The setup is equipped with a XE900 xenon arc lamp, which delivers high-intensity radiation with a broad spectrum. A very narrow selection of the spectral bandwidth is guaranteed by the construction of double Czerny-Turner monochromators (type TMS300). The detector is a S900 single photon photomultiplier (type R928). FEEM was carried out with the spectrometer. Fluorescence emission mappings of selected bitumen were performed for a range of 240-520 nm excitation at an emission window of 400-700 nm, with wavelength increments of 5 nm. A cut-off filter at 390 nm was employed. Three representative testing samples were prepared for each ageing state and layers of drill cores. To prepare the samples, bitumen was heated to 120 $^{\circ}$ C for 5 min. During the heating process the sample was stirred to ensure a minimum temperature gradient within the sample. The homogenized samples were poured into silicone moulds and were covered with an objective slide. The samples were then cooled to room temperature with 10 °C per hour cooling rate and fluorescence spectra were recorded. In order to exclude the oxidative influence on the sample

Table 4

Measurement parameter for fluorescence excitation scans and fluorescence excitation emission matrices.

Measurement parameter	FEEM	Excitation scan
Excitation wavelength (nm)	230-500	240-500
Emission wavelength (nm)	400-700	520
Step size (nm)	5	1
Repeats of scans and cycle	1 imes 1	3 imes 3
Dwell time (s)	0,5	0,5
Iris (%)	100	100
Filter (nm)	395	495
Scan slit (nm)	2	2
Fixed/Offset slit (nm)	2	2

Table 5

Parameters for fluorescence microscopy studies.

Microscope unit	Specifications and parameters
Objective	Plan Fluor 100x
Numerical aperture	0.9
Epifluorescence unit with filter	465–495 nm
Dichroic mirror	505 nm
Emission filter	515–555 nm
Light source	100 W metal-halide
Illumination time	700 ms

surface, the sample chamber was continuously flushed with N₂ current, which limited the oxygen uptake of the sample. Excitation scans at variable excitation, fixed detection wavelength were chosen as the measurement method. The same detection wavelength was chosen for the excitation scans, 525 nm, and the spectral range of 200-500 nm excitation wavelength was recorded. It is important for the recording to use a 340 nm filter in order to avoid a signal of the second diffraction order of the Rayleigh line at 207.5 nm on the detector. A total of nine spectra were recorded per measurement and were summarized as an average spectrum for all three representative samples of each ageing state and drill core layers. Additionally, FEEM were recorded for a complete determination of the fluorescence profile. Its pathway is crucial to understand the degradation pattern of bitumen fluorescence signature upon laboratory and field ageing. The measurement parameters are provided in Table 4. The recorded excitation spectra and FEEM were analyzed using Origin Pro, Version2020 9.7, (OriginLab, Northampton, MA, USA). Overall Fluorescence intensity was calculated using MATLAB version 9.9.0.1467703 (R2020b). Natick, Massachusetts: The MathWorks Inc.

2.5.2. Fluorescence microscopy

Revealing the presence of auto-fluorescent molecules such as aromatics and resins, and assignment to surface structures is enabled by fluorescence microscopy. While fluorescing centres are attributed to aromatics and resins, asphaltenes do not exhibit fluorescence in the selected excitation and emission window and therefore are not captured in this study. Saturates are not capable of fluorescence due to their aliphatic nature and absence of conjugated double bonds. Fluorescing microstructures were resolved before and after photochemical ageing

Table 6

Fluorescence emission of the maxima located at 265 nm and calculated sum fluorescence emission from FEEM maps using MATLAB. Fluorescence emission at maximum band and sum fluorescence emission decreases gradually with progressive ageing.

Sample	Fluorescence emission at maxima (cps)	Sum fluorescence emission (cps)
Unaged PAV 1 PAV 2 PAV 3 111 (RTFOT&PAV)	$\begin{array}{c} 2.80 \cdot 10^4 \\ 2.75 \cdot 10^4 \\ 1.75 \cdot 10^4 \\ 1.54 \cdot 10^4 \\ 8.5 \cdot 10^3 \end{array}$	$\begin{array}{l} 2.91 \cdot 10^7 \ (s=0.2) \\ 6.13 \cdot 10^7 \ (s=0.5) \\ 2.62 \cdot 10^7 \ (s=0.1) \\ 1.61 \cdot 10^6 \ (s=0.1) \\ 1.92 \cdot 10^6 \ (s=0.1) \end{array}$

using a Nikon Eclipse Ci-L instrument. Equipped with a Nikon colourdigital camera DS-Fi3. The Nikon software NIS Elements BR was used for image acquisition. Selected measurement parameters are shown in Table 5. The spatial resolution of fluorescence microscopy is limited to 286 nm due to the Abbe diffraction limit.

2.5.3. Atomic force microscopy (AFM)

AFM measurements were carried out using a WITec Alpha 300RSA+ instrument. The images were acquired using the tapping mode with silicone nitride AFM probes with a resonance frequency in the range of 75 kHz and a spring constant k at 2.8 N/m. A piezo stage (P-527-K081) is implemented in the used WITec instrument. A lateral resolution down to 1 nm and depth resolution of below 0.3 nm can be achieved with this set up.

3. Results and discussion

The main objective of this paper is to track successive ageing with various testing methods with regards to trends in morphology and shifts in chemical composition. The goal is to extend the existing standardized ageing methods (PAV and RTFOT) towards implementation of UV radiation and photochemical smog in order to achieve a more realistic ageing trend. While RTFOT simulates the short-term ageing, PAV simulates the long-term ageing, the impact of UV radiation is missing. In particular UV ageing leads to cleavage of covalent bonds, triggers photochemical reactions and generates ROS in gas phase. From materials and atmospheric science, it is known that reactive oxygen species and UV radiation play a crucial role on the oxidation of organic materials [54]. UV studies on SBS modified bitumen exist, however there are

no scientific studies dealing with the photochemical smog and its influence on SBS modified bitumen [13,55]. We have gone well beyond with a controlled photochemical chamber experiment as well as depicting 3D FEEM to elucidate shifts in chemical composition and tracking the deformation trends of the surface due to progressive UV including photochemical ageing. The findings of this study aim to bring existing standardized laboratory ageing closer to a more meaningful and realistic ageing behaviour that exist in the field.

3.1. Conventional PAV and RTFOT ageing

We find evidence of decrease in overall fluorescence emission in all aged samples. The unaged binder shows the sum fluorescence emission from the FEEM recordings with $2.91 \cdot 10^7$ (s = 0,2) counts per second. Increase of ageing duration drives an overall gradual decrease in the sum fluorescence emission. The maxima of all samples show a decrease of the maximum band located at 265 nm, as shown in Table 6 and emphasizes the combinatory ageing method 111 (RTFOT&PAV) exhibits greater ageing effects than PAV 3.

Excitation spectra of bitumen, as presented in Fig. 6, are similar to those in the literature for bitumen and humic-like substances [21], characterized by two peak emissions located at about 265 nm and 295 nm excitation wavelength [56]. Additional maxima around 332, 446 and 480 nm are also observed. Bitumen spectra contain thousands of chemical compounds. The quantification of the underlying differences on a compound-by-compound level is not attempted here, but rather using the combined effects of similar molecules to identify the changes of interest. The excitation spectra demonstrate the decrease of the maxima depending on the ageing state.

Unaged bitumen exhibits the highest intensity of fluorescence emission $(2.8 \cdot 10^4$ counts per second) and heavily aged field samples exhibit the lowest emission with $1.45 \cdot 10^4$ counts per second. The absolute fluorescence intensities show a gradual decrease within the ageing methods for all maxima. Studies have shown that the high number of aromatic rings are responsible for fluorescence emission at longer excitation wavelengths [26]. Hence, maxima located at about 265 nm and 295 nm excitation are assigned to one aromatic ring systems. The broad maximum at 332 nm is assigned to aromatic systems with two rings, while the maxima located at 446 and 480 nm represent perylene- and tetracene-like aromatic systems representing more than 4 aromatic rings. Overall, a strong decrease in small aromatic structures is observed due to ageing, while structures with more than two aromatic ring systems declined but not to the same extent. Fluorescence spectra



Fig. 6. Excitation spectra of unaged and various aged bitumen exhibiting major variations in absolute and relative fluorescence intensity. All spectra were recorded from 3 sample sets and show good repeatability and reproducibility.



Fig. 7. Penetration depth study with fluorescence spectroscopy. Absolute and relative fluorescence spectra for field aged drill core samples for the cluster of drill cores BK1_5, and BK56_60 for each layer S1 (uppermost layer), S2 (second layer) and S3 (third layer) are presented demonstrating the penetration depth of ROS. An ageing trend with a rapid decrease in oxidation gradient with increasing layer depth is observed.

normalized to the highest emission band (one aromatic ring systems) demonstrate the change in composition in relation to small aromatic compounds. While a relative decrease in higher aromatic structures is shown for all PAV aged samples, RTFOT and PAV ageing represents an exception to this trend and shows an even higher emission intensity at longer wavelengths than PAV 1 aged samples however still presents a significant lower emission than unaged samples. The decrease of intensity for small aromatic compounds might be caused either by the breakdown of small aromatic compounds or as well the quenching effect by the resin and asphaltene molecules that might cause a further decrease in fluorescence emission of small aromatic structures [57]. In

Table 7

Fluorescence emission of the maxima located at 265 nm and calculated sum fluorescence emission from FEEM maps using MATLAB. Fluorescence emission at maximum band and sum fluorescence emission increases gradually with increasing layer depth.

Sample	Fluorescence emission at maxima (cps)	Sum fluorescence emission (cps)
BK_1-5_S1 BK_1-5_S2 BK_1-5_S3 BK_56-60_S1 BK_56-60_S2 BK_56-60_S3	$\begin{array}{c} 1.27 \cdot 10^3 \\ 2.82 \cdot 10^3 \\ 4.01 \cdot 10^3 \\ 5.34 \cdot 10^2 \\ 1.79 \cdot 10^3 \\ 2.16 \cdot 10^3 \end{array}$	$\begin{array}{l} 7.10\cdot 10^4 \ (\mathrm{s}=0.2) \\ 1.31\cdot 10^5 \ (\mathrm{s}=0.1) \\ 1.62\cdot 10^5 \ (\mathrm{s}=0.3) \\ 8.31\cdot 10^4 \ (\mathrm{s}=0.1) \\ 1.22\cdot 10^5 \ (\mathrm{s}=0.3) \\ 1.43\cdot 10^5 \ (\mathrm{s}=0.1) \end{array}$

general, quenching effect mainly affects the fluorescence emission by small aromatic molecules that overlap with the excitation of larger aromatic compounds [58].

3.2. Layers study

The highest impact of atmospheric ageing is seen on the first centimetre of the individual layers of the field aged samples with the lowest sum fluorescence emission $(7.10 \cdot 10^4 \text{ (s} = 0.2) \text{ and } 8.31 \cdot 10^4 \text{ (s} = 0.1)$ counts per second) for the uppermost layer (first cm) for both drill cores which are BK_1-5_S1 and BK_56-60_S1 as seen in Fig. 2. The second layer of the field aged samples BK_1-5_S2 and BK_56-60_S2 exhibit a strong increase in fluorescence intensity for both sample clusters $(1.31 \cdot 10^5 \text{ (s} = 0.2) \text{ and } 1.22 \cdot 10^5 \text{ (s} = 0.3) \text{ counts per second}$, while the third layers BK_1-5_S3 BK_56-60_S3 exhibit the highest fluorescence $(1.62 \cdot 10^5 \text{ (s} = 0.1)\text{ and } 1.43 \cdot 10^5 \text{ (s} = 0.3) \text{ counts per second}$. It is important to note, that the difference between the first and the second layers is significantly higher than the layers below, which indicates the diffusion of ROS is highly limited to the first centimetres. This can be explained with the ROS availability on the uppermost layers, while the diffusion of the ROS into the material is hindered with increasing layer thickness and hardening of the binder. The penetration depth of ROS may also vary depending on the porosity and viscosity of the asphalt mixture (increase of void and increase of binder surface and therefore high ROS accessibility). The sharp increase in fluorescence with

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Table 8

Calculated sum fluorescence emission from FEEM maps using MATLAB. Sum fluorescence emission decreases gradually with progressive photoexposure.

Sample	Sum fluorescence emission (cps)
UV 1 (30 min)	$7.52 \cdot 10^4 \ (s = 0.1)$
UV 2 (60 min)	$5.82 \cdot 10^4$ (s = 0.2)
UV 3 (2160 min)	$5.55 \cdot 10^4$ (s = 0.1)
UV 4 (2880 min)	$4.82 \cdot 10^4 (s = 0.3)$

increasing layer depth is represented in Fig. 7. The normalized spectra show a relative increase in fluorescence emission range of >300 nm values in all stages consistent with degradation, meaning preferentially breaking down higher molecular asphaltene compounds resulting in lower aromatic ring structures. However, the sum fluorescence is still lower than the initial fluorescence emission (Table 7).

While an overall trend in fluorescence emission is observed with progressive ageing, reabsorption and matrix effects due to high analyte concentration still remain a challenge in fluorescence spectroscopy of bitumen samples. To shed more light on these effects, extensive studies are needed.

3.3. Photo-oxidative ageing study

As shown in Table 8, within the first 30 min of photodegradation, overall fluorescence emission has decreased by approximately three orders of magnitude of the initial fluorescence in all samples. In contrast, the following 30 min did not decrease the fluorescence emission to the same extent (additional \sim 5,5%). The rate of fluorescence emission loss

due to photocatalytic oxidation was lower over the time period being oxidized. By 2160 min and 2880 min of UV exposure fluorescence emission still decreased by approximately 6,7% compared with initial conditions (Table 3). However, there was little to no measurable change (<10%) in fluorescence emission following irradiation in all samples.

Significant changes on bitumen surface due to photoexposure is observed as seen in Fig. 8. Fluorescing centres in the range of below 10 μ m are visible throughout the ageing process. Interestingly, a fluorescing network appears after 48 h UV exposure and becomes bigger and richer in contrast with the time being oxidized.

This effect can be due to agglomeration effects on the surface which increases due to ageing, as well as evaporation of volatile fluorescing compounds due to UV/VIS light absorption. Fluorescing particulate structures and growing network structures exhibit increased fluorescence. As shown in previous studies fluorescing centers were observed in unmodified bitumen and were interpreted as originating from asphaltenes [21]. It is well known that SBS modified bitumen forms a two-phase morphology with spherical domains or strings of increased SBS content, especially in roof bitumen with increased polymer content [59]. In this study, such domains and strings are not visible for the unaged bitumen, therefore a good polymer miscibility is assumed. However, the growing network structure due to progressive UV ageing has never been observed before. As SBS exhibits fluorescence and is susceptible to UV radiation, the network structure may originate from the polymer degradation which further results in deterioration of the bitumen properties such as elastic recovery, cracking resistance at and rutting resistance [60]. Nevertheless, to assess the role of polymer in building the network structure a control experiment with the same bitumen composition except the polymer modification is proposed for future experiments.



Fig. 8. Fluorescence microscopy images of bitumen surface affected by UV irradiation.

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Fig. 9. FEEM for all bitumen samples show the same overall trend.

3.4. Fluorescence excitation emission matrices (FEEM)

FEEM reveal similar characteristic features as reported before [21, 61]. The gradual excitation and emission shift is similar, yet unique und distinct for each ageing method. This suggests formation of different oxidation pathways and intermediate products, although we cannot supply direct reaction-mechanisms here. However, it is known that pressure and temperature induce different changes in the molecular composition than oxidative agents that are created during photo-exposure. While pressure and thermal oxidation induce similar bulk properties as short- and long-term ageing on the field, the absence of UV light classifies this approach as a rather unrealistic ageing method when compared to real field ageing trends. Three main trends and features are visible along the ageing pathway, which are the following: (a) overall sum emission decreases at emission at high excitation (>340 nm) high

emission (>500 nm) area, suggesting a breakdown of high molecular weight compounds. (b) the second strongest distinct maximum located to the highest maximum area at excitation between 290 and 330 nm and emission window between 475 and 625 nm declines with progressive ageing suggesting a breakdown of small aromatic molecules and as well as reabsorption by molecules in this specific emission window. Aromatic compounds of high molecular weight such as PAH or humic-like substances show peak fluorescence emission at higher wavelengths (400–520 nm). Increasing molecular weight and aromaticity shift the emission of the fluorescing molecules toward the longer wavelengths. Aromatic compounds of less than two aromatic rings are expected below 350 nm excitation. While the overall fluorescence emission decreases with ageing, the relative intensity of the emissions behaves differently with regards to the ageing method. The broad emission between 295 and 330 nm excitation region (area 2 in Fig. 9) decreases significantly for



Fig. 10. Maximum fluorescence area becomes narrower for all ageing methods.

heavily aged samples. In contrast, emissions at higher wavelength (area 1 in Fig. 9) decrease with same fashion for PAV and UV ageing methods, with the exception of the combinatory aged sample PAV + RTFOT. UV ageing demonstrates the most effective degradation for area 1 and 2. However if the UV penetrates the surface for longer than 36 h the FEEM exhibits a strong shift towards longer emission and excitation wavelengths, indicating formation of higher molecular compounds with an

increased aromatic π -system. A look at the fluorescence microscope images in Fig. 8 shows a network structure with high and low fluorescing areas. Earlier studies on bitumen with ESEM show similar network structures which exhibit a string like network highly correlated to the network structure observed in this study [9,62–64]. Since ESEM uses high electron voltage to picture the surface, a destruction of the sample surface is assumed. UV radiation also causes absorption that subsequently may cause heat. A rough temperature measurement during the UV treatment of 36 h showed an increase of 1 °C at the sample surface. Obviously, this increase is seemingly too low to cause dramatic changes in bitumen and other factors such as degradation of volatiles ROS susceptible molecules on the surface or agglomeration and loss of volatile compounds has to be considered. To elucidate this effect in more detail a surface experiment on a thin film bitumen is performed in Section 3.5.

Focusing on the maximum emission area (Fig. 10), shifts of the emission wavelength to shorter values for all aged samples is observed meaning an increase of smaller aromatic systems. These interactions were shown to cause a blue shift of almost 20 nm of emission for PAV ageing compared to the unaged bitumen. Field aged sample exhibits both blue and red shift. Overall emission as well excitation maxima occur within a relatively narrow range. UV ageing shows the highest shifts towards longer wavelengths, demonstrating the formation of high molecular compounds with a higher number of aromatic ring systems or agglomerates. As a general observation the excitation and emission window of high fluorescing area becomes narrower, while blue shift dominates for field and PAV ageing. PAV ageing lacks the red shift and UV ageing does not exhibit blue shift. All observations from ageing where UV is involved reveal a significant red shift of the maxima. The excitation maxima shift towards higher excitation wavelength. A significant loss of FEEM area at lower wavelength side is visible.

Significant decline in emission >290 nm and significant shift of excitation as well as emission is observed. PAV ageing results in blue shift (increase of small aromatic ring systems), UV ageing in red shift (increase of large aromatic systems), and field ageing shows both effects.

3.5. UV Impact on surface properties

A combined look into AFM and fluorescence microscopy on bitumen surface shows that the aromatics and resins play an important role in bitumen microstructure. The distinct microstructures (catana phase or bee structure and peri phase) exhibit high fluorescence emission whereas the surrounding para phase is comparatively low in fluorescence, due to an elevated content of asphaltenes and/or saturates. It is important to note, that the ripples and the ridges of the catana phase exhibit major variations. Interestingly, this observation contradicts the idea that microstructures only consist of asphaltenes and suggests aromatic and resin structures to be the present as well and to contribute to



Fig. 11. Fluorescence microscopy and AFM images before and after atmospheric photooxidative treatment. The ageing period is twelve hours. Significant changes in surface microstructures, namely the catana, peri and para phase is visible. Oxidation leads to higher contrast in fluorescence indicating agglomeration and break-down of the para phase.



Fig. 12. Fluorescence images of the bitumen surface after UV irradiation at different sample locations. Fluorescing molecules mainly in the catana and peri phase, para phase is relatively dark.



Fig. 13. AFM images after ageing: amplitude, phase and topography images. Catana phase is still visible, however its typical bee structure is deteriorated. The maximum height of the catana phase is 537.8 nm.

the structural set-up of the catana phases.

Subsequently, the study was expanded and bitumen surface was subjected to UV radiation (Fig. 11). Results show that UV radiation leads to a higher contrast between the microstructure (catana and peri phase) and para phase, which indicates agglomeration of the fluorescence centers and thus also confirms the theoretical assumptions, namely increasing amount of higher polar material with increasing ageing and a steeper polarity gradient between the microstructure and the matrix phase. Thus, these changes in chemical composition lead to colloid formation as a result of ageing [9,65–67].

The alteration of surface properties is crucial for multi-scale modelling and thus material stiffness and elasticity/brittleness. The change in surface composition is sufficient to explain the changes in physicochemical behaviour upon ageing due to the multi-scale model. As shown in Figs. 8 and 11 UV radiation as well as the hereby generated OH radicals, Ozone and NO_x gases react with the surface on the microlevel. It is shown that UV radiation and photochemical smog induce changes on all surface phases. The fluorescence emission of the para phase decreases significantly, suggesting that UV and photochemical smog attack mainly the para phase. However, catana and peri phases also undergo alterations induced by the UV treatment with remaining fluorescence emission but exhibiting major variations in shape and size as shown in Fig. 12.

As a result of ageing, the particulate microstructures shrink in size and gradually lose their catana pattern but show a drastic increase in height differences from less than 10 nm (Fig. 11) to more than 500 nm (Fig. 13). AFM amplitude, phase and topography images demonstrate the deformation of the catana structure due to photooxidative treatment.

While the focus of our study was on the optical properties of bitumen, changes on the surface microstructures are also important to understand the impact of UV irradiation on the surface structures on the micro-level [68]. As a result of the photo-oxidation, structural changes of the surface are observed. It is noteworthy that the substructures show differences in fluorescence and the catana structures also differ chemically from their surroundings. Thus, the chemical heterogeneity and the deformation of the microstructures will play an important role in the multi-scale modelling and result in changes in the mechanical properties. The surface after photochemical ageing shows increased domain formation and agglomeration of the fluorescence centers and thus also confirms the theoretical assumptions with regard to the colloid formation as a result of ageing [66]. The para phase lost its fluorescence capability indicating a breakdown of the auto-fluorescing molecules that react with photochemical smog and is affected by UV light. While aliphatics are not capable of fluorescence, and asphaltenes exhibit fluorescence at longer emission wavelength, and aromatics are not as reactive as resins, resins are identified as the main candidates for the para phase.

Our findings show that aromatics and resin structures are found mainly on the microstructures, namely the catana and peri-phase. While the SBS content in this bitumen is between 2% and 3%, its contribution to the fluorescence image should vanish/decrease drastically after 12 h of UV treatment, since SBS is hyper-susceptible to UV radiation. Therefore, aromatic and resin compounds are suggested to be the main contributor to fluorescing catana and peri phases. Earlier studies on pure bitumen also demonstrated fluorescing centres coherent with the shape and size of the microstructures [21].

4. Conclusions

Standardized bitumen laboratory ageing such as PAV and RTFOT addresses solely mechanical and thermal stress, while UV and photochemical smog is neglected. It is known that UV and photochemical oxidants (NOx, Ozone and especially OH radicals) exhibit a different ageing kinetics and therefore result in different shifts in chemical composition due to ageing. OH radicals are known to be powerful oxidizing agents generated in the atmosphere under the impact of UV radiation below 310 nm, but are completely neglected in PAV and RTFOT testing methods. Here we demonstrate the power of UV and photochemical ageing and highlight the importance of implementing these factors into the existing standardized testing methods. Last but not least on 19 years field aged samples we demonstrate the oxidation gradient. With FEEM we have demonstrated that photochemical ageing results in unique shifts in chemical composition different than in PAV and RTFOT ageing. Furthermore, the changes in surface morphology due to progressive UV and photochemical ageing are observed with fluorescence microscopy which is powerful tool for the chemical identification of surface structures, chemical segregation and phase agglomeration phenomena due to oxidation in bitumen. While AFM monitors the three-dimensional topography of the bitumen surface, fluorescence microscopy also allows a direct observation of the surface chemistry. Catana structures dispersed in the peri phase are typically characterized by AFM, but were here for the first time identified by fluorescence microscopy showing the presence of aromatic and resin compounds. Photo-ageing of the surface evolves the microstructures which are distinctly chemically different from their surrounding peri phase. Aromatics and resins show a shrink in the lateral size of the microstructures, while the height increased drastically from about 10-530 nm. A growing network structure due to progressive photooxidation is observed, possibly due to the UV susceptibility of SBS. Layer study from field aged binders show the penetration of ROS into the bulk material where a gradual decrease of ageing could be discovered. Overall, the observed oxidation gradient, chemical features of the surface microstructure and the link to the bulk chemistry provides opportunities for future studies and extension of the standardized testing methods (PAV and RTFOT) for a more realistic ageing and highly encourages the inclusion of surface chemistry for future studies since oxidation initiates on the surface and further paves the way to diffusion of oxidants of various sources into the bulk chemistry.

CRediT authorship contribution statement

Ayse Nur Koyun: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Project administration, Supervision, Validation, Visualization, Writing - original draft, editing. Johannes Büchner: Provided the field and laboratory aged samples, determined the penetration grade of the bitumen and reviewed and edited the draft. Michael P. Wistuba: Funding acquisition, Project administration, Resources, Writing - review & editing. Hinrich Grothe: Funding acquisition, Project administration, Resources, 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.

Data availability

The data that support the findings of this study are available from the authors on reasonable request (see author contributions for specific data sets).

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.colsurfa.2021.126856.

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