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Impact of UV–Vis light on the oxidation of bitumen in correlation to solar spectral irradiance data

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ABSTRACT

The ageing behavior of bitumen is a complex phenomenon which is tackled by many studies in the laboratory and on the field. While ageing parameters like temperature, moisture, reactive gasses or UV light have been utilized in the laboratory, the impact of visible light has not been addressed yet. Thus, this study investigates the impact of UV–visible light in the range of 365–770 nm on the oxidation behavior of bitumen. Furthermore, a correlation to solar spectral data was conducted, which should link the ageing experiments run in the lab to the conditions on earth's surface. FTIR spectroscopy on the sample surfaces was conducted to determine the extent of ageing. The results show that when considering solar spectral data, blue light in the range of 405 nm contributes significantly towards oxidation of bitumen. Additionally, an unexpected, characteristic oxidation profile shows higher oxidation levels around light in the blue (405 nm) and green (525 nm) wavelength ranges. This provides first evidence on how visible light can cause significant oxidation for bitumen in asphalt pavements. The obtained knowledge can be used to better understand which parameters contribute towards the ageing process in the field and to provide suitable solutions for laboratory ageing.

1. Introduction

The increasing demand to understand the ageing behavior of bitumen is a concerning matter for many researchers and applicants around the world. Since bitumen is classified as an organic material, it is the composite in an asphalt pavement that is most prone to oxidation or ageing. However, oxidation or ageing can be induced by many different parameters like temperature, reactive gasses, moisture, UV light or a combination of them. Before diving into these parameters, it is important to note that bitumen ageing is usually divided into two sections: short-term (STA) and long-term ageing (LTA). STA reflects the ageing a bituminous material undergoes during production of an asphalt mixture, transportation, laying and compaction of a road pavement. This process is simulated in the laboratory by the Rolling Thin Film Oven Test (RTFOT) according to the EN 12607-1 [1] or the ASSHTO T240-13 [2]. This procedure merely induces thermal oxidation for a short duration. LTA on the other hand is a much more complex phenomenon, as it implies the ageing behavior of a bituminous material during its service life, where many of the above-mentioned parameters need to be considered. The most common way to simulate this is the Pressure Ageing Vessel (PAV) test, which is performed according to the EN 14679 [3] or the ASSHTO R28-12 [4]. The PAV ages bitumen at an elevated temperature between 90 and 110 °C and a pressure of 2.1 MPa. Hence, the driving force and parameter addressed in this LTA simulation is temperature in combination with pressure. Its impact on ageing of bitumen has been covered extensively by researchers throughout the last decades [5]. Following the findings from the SHARP Reports in the 90′s, various test conditions using different temperatures have led to the conclusion that an increase in temperature combined with high pressure leads to a significant increase in oxidation. However, Petersen et al. [5] indicate a certain threshold for a sufficient ageing temperature at around 100 °C that should not be exceeded. Above these temperatures, molecular interactions could potentially change and other reactions can occur, which cannot be found out in the field.

In addition to temperature and pressure, researchers have considered other parameters that can have an impact on ageing. The recent application of reactive oxygen species (ROS), which resembles a combination of ozone and nitrogen oxides, have shown to induces significant oxidation at temperatures and pressure that resemble field conditions [6,7]. These gases can be present in small traces in the troposphere near the

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pavement surface, since e.g. nitrogen oxides are produces by car engines. Even at temperatures around 60–80 °C ROS can easily oxidize hydrocarbons, such as bitumen at the pavement surface.

Another parameter that has also been addressed in the last years is the implementation of water or moisture, which has also been combined with UV light or oxygen. Recent work by Ma et al. [8] presents an overview of possible reactions on oxygen and moisture and tackles fundamental questions in a comprehensive review. They provide suggestions to consider a combination of various effects such as sorption, diffusion and clustering, as these all can contribute to the ageing mechanism. Thus, this suggests that a combination of such ageing parameters should be considered when addressing and understanding field ageing and the mechanism involved. Other researchers, such as Qian et al. [9] have performed practical work and coupled UV ageing experiments at 365 nm and 390 nm of short-term aged bitumen with exposure to water, acid or salt, while Carcía et al.[10] have performed UV experiments under controlled moisture and temperature conditions. Crucho et al. [11] have exposed asphalt mixture samples to UV-B radiation (280–315 nm) which were stored in water. Since chemical analysis of the binders was not always conducted, it is not clear which contribution of ageing comes from the UV light and from water or moisture. Furthermore, such a detailed ageing mechanism of bitumen is not fully understood yet. Some conclusion of these works merely state that a decreasing wavelength induces a higher oxidation. This highlights that many parameters contribute to ageing in reality. However, before combining them, they should all be understood individually. Thus, one last, but very important parameter, will be addressed: the impact of light. While it is quite obvious that sun light is shining onto our road surfaces, its practical implementation is a challenging task. The most common way researchers have achieved this implementation is by the usage of UV lamps. Li et al. [12] have performed ageing experiments on unaged bitumen using UV light in the range of 290–390 nm. Their results showed that an incorporation of oxygen and formation of functional groups could be found in all wavelength ranges investigated. However, 360 nm showed the most significant oxidation. Other researchers have utilized UV in the range between 340 and 365 nm on unmodified and polymer modified binders [13-16]. Mouillet et al. [17] have reported the effect of UV radiation on styrene–butadienestyrene (SBS) polymers, as it breaks the C═C double bonds and also leads to an increasing formation of ketones, which is a typical sign for bitumen ageing. Thus, the overall conclusion taken is that the photo-energy in combination with atmospheric oxygen can trigger significant oxidation. While UV light exhibits the highest photo-energy, lower parts of the visible spectrum also show significant contribution to oxidation on the surface of bitumen. A first indicator was given by a laboratory study that investigated the storage conditions of bitumen samples that were analyzed with spectroscopy. These samples were stored for up to 20 days under standard laboratory glass lid at daylight. Attenuated Total Reflection-Fourier Transform Infrared (ATR-FTIR) spectroscopy of the sample surfaces revealed that significant oxidation was observed when samples were left in the light for more than one day after preparation [18]. As the samples were stored inside the laboratory and were covered with a normal borosilicate glass, UV radiation was blocked and did not reach the sample surface. Nonetheless, light within the visible range must have had a significant impact on the oxidation on the materials surface, which is well detectable with ATR-FTIR spectroscopy. While these experiments were performed on unaged bitumen, the question can be raised whether the short-term aged bitumen, which reflects the materials state after a road is paved, also shows such a drastic oxidation behavior. Furthermore, previous studies did not investigate whether certain ranges of the visible light are inducing more oxidation than others. This becomes important as we have not touched on a crucial environmental parameter yet, the impact of the earth's atmosphere on the absorption of light. It is common knowledge, that earth's atmosphere absorbs certain wavelengths more than other. This is nicely displayed by the normalized spectral solar irradiance data obtained from Hulstrom et al. [19] which is replotted in the range 300–800 nm in Fig. 1[1]. Herein, one can see that below 500 nm, the spectral irradiance is much lower, meaning that e.g. UV light is more absorbed by our atmosphere than blue, green or red light. This results in a lower intensity or spectral irradiance in the lower parts of the visible and UV spectral range. Therefore, when bitumen in the field is exposed to sun light, only a fraction of it contains UV light at the range of 300–390 nm, while blue and green light is present in much higher intensities. If visible light also causes oxidation, and its availability on earth is much greater than UV light, it should and cannot be neglected when considering photo-oxidation.

The data shown in Fig. 1 was generated using a BRITE Monte Carlo radiative transfer code and have been adopted by the National Aeronautics and Space Administration (NASA) and American Society of Testing and Materials (ASTM) and many others when taking the impact of solar irradiance into consideration. A prime example is the research field of solar panel development, which makes use of such data sets when designing new solar panel materials. Hence, it can and should be applicable for the research field of road engineering as well. The practical implementation would therefore need to consider not only the possible impact of visible light on the oxidation behaviour of bitumen but also adjust the percentages to match the respective irradiance values of the wavelengths from actual solar spectral irradiance present on earth's surface.

Thus, the goal of this study is to determine the significance or the impact of different ranges of visible light on the oxidation of bitumen is when ultimately considering conditions on earth's surface. In order to better understand this phenomenon, STA bitumen samples are exposed to small, well-defined wavelength windows produced by 15 LEDs which are in the range of 365–770 nm. Before adjusting the parameters to match the solar spectral irradiance profile on earth's surface, various tests were carried out to address the ageing setup used and the oxidation behavior of the material investigated. FTIR spectroscopy was used to measure the degree of oxidation via the formation of functional groups such as carbonyls and sulfoxides. Additionally, the result will show, whether certain wavelengths induce more oxidation than others, which would indicate that bitumen is more susceptible to certain ranges on visible light due to its complex molecular composition.

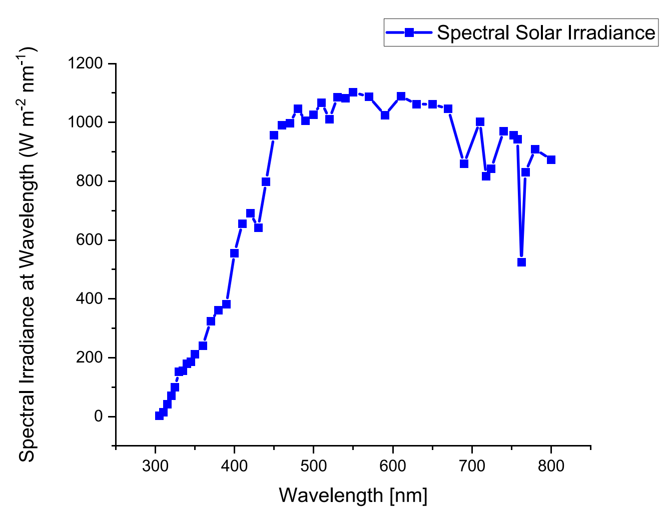

Fig. 1. Spectral solar irradiance data in the range between 300 and 800 nm (using data from[19]).

[1] The perceive values for intermediate values (e.g. 365nm) are obtained by interpolation, which is recommended by the authors.

2. Materials and methods

2.1. Materials and sample preparation

In this study, a short-term-aged (STA), non-modified 70/100 penetration graded binder (PG 58–28) was used. The unaged base bitumen has a needle penetration value of 84 [0.1 mm] and a softening point of 45.8 °C. The justification for the usage of a STA binder was based on the thought that the binder used in this study should have the same ageing level as a bitumen after production of a road pavement or a sealing membrane, which in this case is after short-term ageing. Therefore, a Rolling Thin Film Oven Test (RTFOT) was performed according to the European standard EN 12607-1 [1]. For sample preparation, a small quantity (~1 g) of the RTFOT aged binder was applied onto a metal spoon and heated up over a hot gun turret (see Fig. 2 (A)) for a duration of 30–60 s. During this short period of time, a thermometer was used to stir and homogenize the sample continuously and monitor the temperature. Once the binder has reached 140 °C (good workability), the thermometer was used to scoop small bitumen droplets from the spoon and apply them onto a small piece of silicone foil, as shown in the middle of Fig. 2 (B). The resulting samples were immediately placed in a crystallization dish, covered with a metal lid (see Fig. 2 (C)) and stored in a dark, climatized room before being exposed to the light ageing procedure. The precise number of samples prepared will be elaborated later.

2.2. Light ageing

The goal of the light ageing procedure was to expose STA bitumen to small, well-defined wavelength windows produced by 15 different LEDs in the range of 365–770 nm and see how much oxidation is caused by the respective wavelengths. An overview with the overall test program and preliminary tests conducted is shown in Fig. 3. Before conducting such experiments, certain preliminary tests were necessary to ensure that the ageing induced comes solely from the light itself. This contained the adjustment of ageing durations to equalize the power of the 15 different LEDs, testing the impact of surface temperature induced by the LEDs as well as the impact of the objective used in this study.

After these preliminary tests, three different ageing test programs were conducted. The first and second ageing test program varied exposure time and LED intensities to investigate the oxidation behaviour of the STA bitumen. These tests provided the necessary basis for the third and final ageing test program, where the LED intensity and ageing duration are adjusted to mimic a normalized intensity profile of the solar irradiance found on the surface of the earth. This study intends to provide first evidence on how much visible light impacts bitumen ageing on the field.

2.2.1. Ageing setup

The light ageing procedure was performed using an optical microscopic setup from Nikon as shown schematically in Fig. 4. It consists of a Nikon flexible column stand, a motorized Märzhäuser stage (X. Y. Z), a Nikon DS-Fi3 camera, an 5x CFI TU Plan objective (BD 5x, N.A. 0.150, W.D., 18.0 mm), a full reflective mirror in the filter cube and a LED light source, which resembles the most important part of the setup, since it was responsible for the ageing or oxidation induced on the bitumen surface. It is important to note that all measurements were carried out in a dark, climatized room. The ageing chamber was also covered with a non-transparent material, which prevented any outside light to reach the sample. Thus, the bitumen sample was merely exposed to the light coming from the respective LED.

The light source used was a pE-4000-Universal LED, which contains 15 different LEDs ranging from 365 to 770 nm. These wavelengths cover the entire range of visible light as well as some parts of the UV-A and infrared. Especially the 365 nm was crucial, since many experiments in the previously mentioned literature were carried out at said wavelength. The perceived wavelengths, the spectral window (Full with half maximum – FWHM) and nominal power of the LEDs are given in Table 1. It is important to note that these data, especially the power of the LEDs, were recorded by coupling the microscopic setup with an optical spectrometer via an integrated sphere. A key factor in these power measurements was that they were conducted at the focal plane of the respective objective as well as using a full reflective aluminum mirror in the filter cube. Hence, the same procedure was followed when exposing the bitumen samples to the 15 different LEDs as demonstrated on the left side of Fig. 4, which allowed a correlation to the power data provided in Table 1.

The fully reflective aluminum mirror of the filter cube shows an overall constant reflection rate of 90 % across the entire wavelength range from 300 to 800 nm (see Fig. 5). Hence, it can be assumed that the reflection of the mirror for all 15 LEDs is nearly the same.

All these components were mandatory to correlate all LEDs' powers with each other in order to age the bitumen samples. Furthermore, the microscopic setup allowed a precise sample handling and ensured that each bitumen sample exposed to the light of different wavelengths was in the exact same position (focal plane) as shown on the left side of Fig. 4.

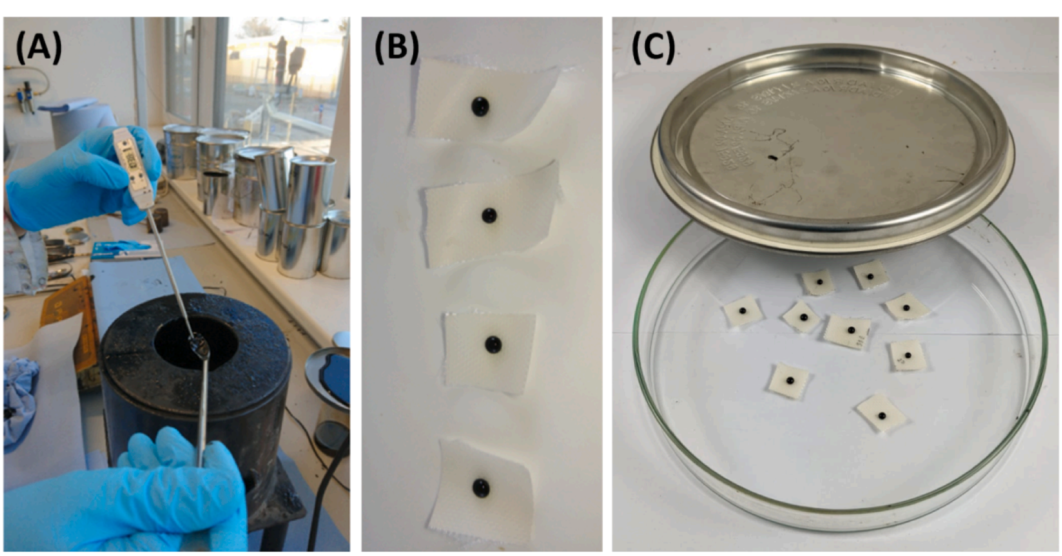

Fig. 2. Sample preparation using a metal spoon and thermometer (A) the resulting samples (B) and their storage (C).

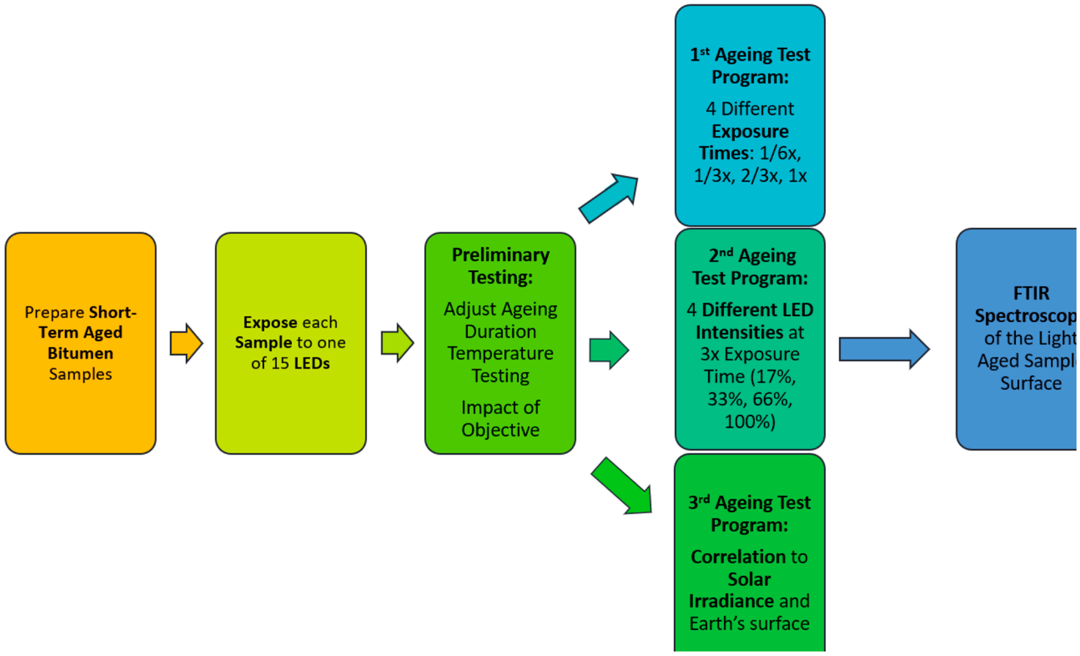

Fig. 3. Overview of the test program.

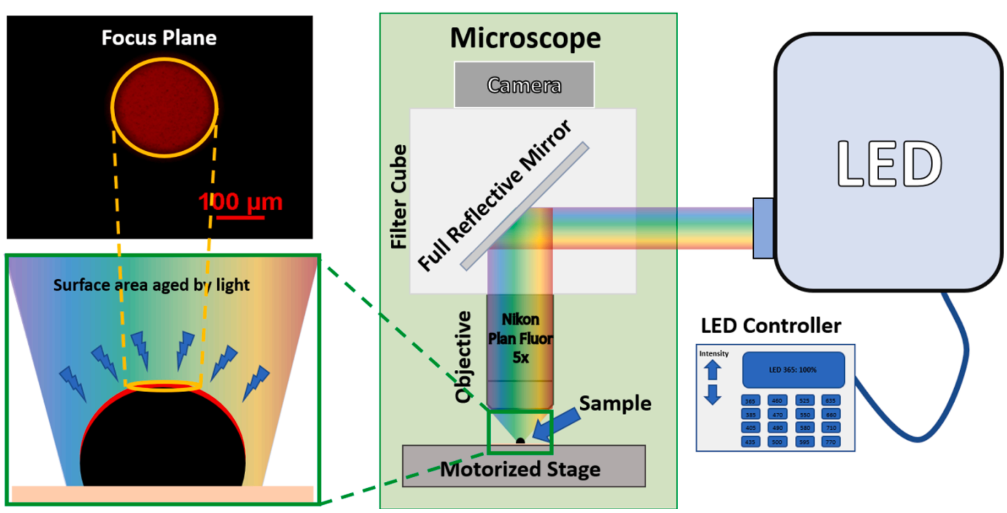

Fig. 4. Schematic drawing of the light ageing setup.

Table 1
Technical data from the pE-400 Universal LED light source used for light ageing.

Wavelength [nm]	FWHM [nm]	Power [mW]
365	12.91	33.65
385	10.65	107.88
405	16.09	55.53
435	13.38	26.26
460	17.61	127.17
470	22.9	48.02
790	25.55	38.38
500	24.72	13.32
525	28.32	10.24
550/580	84.47	77.67
595	14.27	12.58
635	17.05	57.4
660	21.42	96.94
740	40.84	44.48
770	28.08	25.53

2.2.2. *Influence of the ageing setup, time and surface temperature*

Since the light ageing procedure is performed on small bitumen droplets merely the samples surface is oxidized. In order to ensure that the oxidized surface is also investigated spectroscopically after ageing, a precise protocol was followed when performing these experiments. This involved carefully conducted sample preparation and storage as well as minimal exposure to light during sample mounting (stored in the dark and only exposed to 635 nm at 20 % intensity for a maximum of 10–30 of seconds for bringing the sample in the focal plane). Each light exposure was timed using a computer software. For each LED applied two replicate experiments were conducted.

2.2.2.1. Adjustment of ageing duration for equalisation of different LEDs power. In order to compare the LEDs with each other, a certain adjustment was necessary, since they all have different characteristic power (energy per time) values, which are listed in Table 1 and Table 2, respectively. Hence, to ensure that each sample is exposed to the same

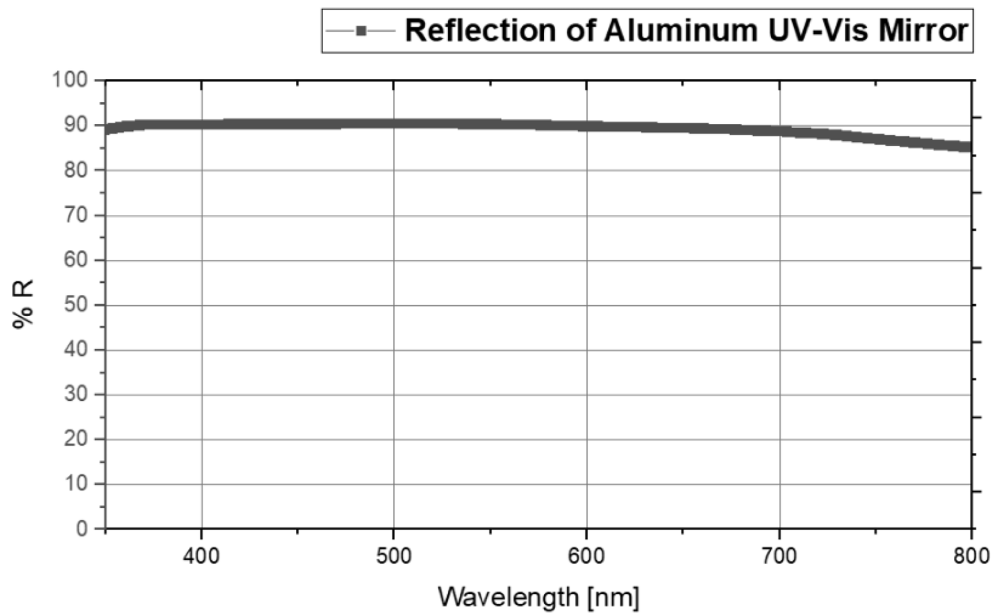

Fig. 5. Reflection spectrum of the aluminium mirror inside the microscopic epi unit.

Table 2
Overview of the adjusted exposure times for each LED used for the ageing experiments.

Wavelength [nm]	Power [mW]	Adjusted Exposure time [mins]
365	33.65	15.0
385	107.88	4.8
405	55.53	9.0
435	26.26	19.2
460	127.17	4.0
470	48.02	10.5
490	38.38	13.2
500	13.32	37.9
525	10.24	49.3
550/580	77.67	6.6
595	12.58	40.1
635	57.4	8.8
660	96.94	5.1
740	44.48	11.3
770	25.53	19.8

amount of total energy over time coming from each LED, the overall power was adjusted by varying the exposure time. This means that bitumen samples exposed to a strong LED (e.g. 460 nm with a power of 127.17 mW) were exposed for a much shorter time compared to a weak LED (e.g. 525 nm with a power of 10.24 mW). Overall, this should induce similar level of total energy (mW*min) per bitumen sample after the light ageing procedure. The calculations were benchmarked on the 365 nm LED (33.65 mW) and an ageing duration of 15 min, which results in a total energy per ageing duration value of 505 mW*min. Hence, in these 15 min the bitumen sample will be exposed to ~ 505 mW. Using this benchmark, Eq. (1) was used to determine how long each sample needs to be exposed to the other 14 LEDs until they have been subjected to such a total energy (505 mW*min). An overview of the respective adjusted ageing durations per LED can be found in Table 2.

$$AgeingDuration[min] = \frac{505[mW*min]}{LEDPower[mW]} \quad (1)$$

2.2.2.2. Impact of temperature on the sample surface. A crucial parameter that can have an effect on the oxidation of bitumen is temperature on the sample surface. It is well known that temperature alone can induce thermal ageing on bitumen [5], which is the most common method to long-term age bituminous materials (e.g. PAV or oven ageing procedures). Since the energy of the photons is absorbed by the black material, it can heat up the surface, which can again induce thermal ageing when reaching higher temperatures (approx. + 60 °C). Therefore, a thermal sensor was fixed on top of a bitumen sample as shown in Fig. 6.

Each LEDs impact on the surface temperature was measured for 5 min after reaching a constant temperature value. The measured values are documented in Table 5, which will be addressed in the results.

2.2.2.3. Impact of the objective. One last factor to consider in the ageing setup is the transmission curve or profile of the objective used for focusing the light. There are two reasons why a 5x objective was used: at first, an objective is needed to focus the sample in the focal plane and make it comparable to the power measurements in Table 1. The other reason is that the 5x objective provided a large enough illumination cone to cover the entire bitumen sample with light, which is also schematically shown on the left bottom side in Fig. 4. However, as the objective is made from a glass with a high refractive index, it could lead to higher

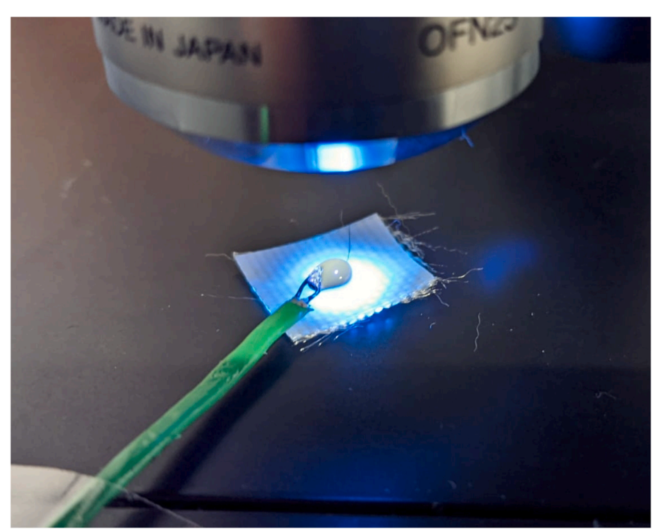

Fig. 6. Temperature sensor on top of the bitumen sample.

absorption of light in certain wavelength domains, especially at the lower end of the visible spectrum. Furthermore, a contrary phenomenon of increasing oxidation can occur due to the focusing and bundling of the light because of the objective. To determine the impact of these two effects, an experimental study without an objective was conducted and compared to the results with the 5x objective. For the practical implementation, bitumen samples were again placed under the microscope and focused on the focal plane with the 5x objective using the 635 nm LED at 20 % intensity. Afterwards, the objective revolver was swapped to an empty position (no objective mounted) and the samples was left to be exposed at the maximum exposure time shown in Table 2. This will show the impact of the objective in regards to its characteristic transmission curve and also whether focusing the light will increase the oxidation rate or induce a different ageing mechanism (e.g. faster oxidation of carbonyls compared to sulfoxides, which can happen when harsh ageing conditions are applied).

2.2.3. First and second ageing test programm: Determination of oxidation rate caused by visible light at different ageing durations and LED intensities

After conducting all preliminary tests involving the adjustment of ageing durations per LED to reach an overall similar level of total energy exposed onto the bitumen surface as well as the determination of impact factors such as temperature and objective, the oxidation behavior induced by light was tested. This was done by application of two different ageing test programs with various ageing durations (1/6x, 1/3x, 2/3x, and 1x) and different LED intensities (0.17 %, 0.33 %, 0.66 % and 100 %). The reason for varying these two parameters was to see how they affect the oxidation rate (linear or logarithmic) and if time and LED intensity can be linked[2]. The precise exposure times in adjustment to the LEDs' characteristic powers are shown in Table 3. Testing these two parameters is a crucial step for later comparison to solar spectral intensities, were an adjustment of the LEDs power was necessary to reflect conditions on earth's surface.

2.2.4. Third and final ageing test Program: Correlation to solar irradiance and Earth's surface

The final goal of this study is to correlate the intensity profile and exposure time of the LEDs to match a normalized solar spectrum of the earth's surface. Thus, certain adjustments to the LEDs' intensities and ageing duration need to be done to reflect the conditions on earth or the pavement surface. This should reveal information how visible light impacts oxidation of bitumen in the field.

Table 4 shows the resulting adjusted intensity for each LED used in the ageing experiments, when considering solar spectral irradiance data from Hulstrom et al. [19]. Thus, the final part of this study contained a measurement series at the maximum measurement time (1x) and a simultaneous adjustment of the LEDs intensity. While the maximum measurement time negates the difference in the characteristic power of each led, the reduction of the intensity was made to mimic the solar spectral intensity profile. These samples indicate the level of oxidation caused by visible light in the range of 365–770 nm and will reveal which wavelengths induce significant oxidation of the material on our road surfaces.

Table 3
Overview of the four adjusted different ageing durations in regards to the time adjustments for respective wavelength.

Wavelength [nm]	1/6x Exposure time [mins]	1/3 × Exposure time [mins]	2/3x Exposure time [mins]	1x Exposure time [mins]
365	2.5	5.0	10.0	15.0
385	0.8	1.6	3.2	4.8
405	1.5	3.0	6.0	9.0
435	3.2	6.4	12.8	19.2
460	0.7	1.3	2.6	4.0
470	1.8	3.5	7.0	10.5
490	2.2	4.4	8.8	13.2
500	6.3	12.6	25.3	37.9
525	8.2	16.4	32.9	49.3
550/580	1.1	2.2	4.4	6.6
595	6.7	13.4	26.7	40.1
635	1.5	3.0	6.0	8.8
660	0.9	1.8	3.6	5.1
740	1.9	3.8	7.6	11.3
770	3.3	6.6	13.2	19.8

2.3. Analysis methods – Attenuated total reflection Fourier-Transformation infrared (ATR-FTIR) spectroscopy

After exposing each bitumen sample to the respective wavelength for the precisely defined ageing duration, they were analyzed with ATR-FTIR spectroscopy. The reason for using such a spectroscopic technique can be justified by the depth of penetration of the technique. ATR-FTIR spectroscopy makes use of infrared light in the range of 25.000–2.500 nm (4000–400 cm^{-1}) which can penetrate up to a couple of microns into the material. Hence, it only investigates the sample surface. Since ageing caused by light also takes place at the very surface of the material (as highlighted by the red area in Fig. 4 and Fig. 7), an investigation with such a method seems fitting.

All FTIR spectra were recorded in attenuated total reflection (ATR) geometry on a diamond crystal using a Bruker Alpha II, which is equipped with an DTGS detector. Special care was taken when applying the sample onto the ATR crystal, as the aged surface should be brought in direct contact with it (see Fig. 7). Furthermore, a reference bitumen in short-term aged state was measured. This provides the possibility to evaluate the increase in the formation of oxidation products like ketones and sulfoxides due to the influence of the different wavelengths.

Each spectrum was recorded from 680 to 4000 cm^{-1} at a resolution of 4 cm^{-1} and 24 scans. Each light aged sample was measured with four repeats, resulting in four spectra per sample and 8 spectra per ageing state, as two ageing repetitions were conducted per LED and ageing duration. Prior to each analysis, the crystal was cleaned with a bitumen solvent (limonene) and a well evaporable alcohol (isopropanol) before a background of the empty ATR crystal was recorded. Once the background was recorded, the sample was applied within a time window of 1 min and the 4 spectra per sample were recorded. Spectral data evaluation was carried using the attached software OPUS. All spectra were

Table 4
Overview of the final ageing test program with correlation to solar spectral irradiance.

Wavelength [nm]	Spectral Irradiance at Wavelength [$Wm^{-2}nm^{-1}$]	Adjusted LED Intensity [%]	Ageing Duration [mins]
365	282.25	25.6	15.0
385	372.05	33.8	4.8
405	606.15	55.0	9.0
435	720.2	65.3	19.2
460	990.8	89.9	4.0
470	998	90.5	10.5
490	1005.1	91.2	13.2
500	1026.7	93.2	37.9
525	1048.2	95.1	49.3
550/580	1102.2	100.0	6.6
595	1040.425	94.4	40.1
635	1062.1	96.4	8.8
660	1053.95	95.6	5.1
740	971	88.1	11.3
770	830.7	75.4	19.8

[2] The LEDs intensity could be lowered manually from 0 to 100 %. However, the lamp manufacturer told us to verify the linearity in correlation to our experiments.

Table 5
Overview of the temperature on the bitumen surface induced by the respective LED and its power.

Wavelength [nm]	Power [mW]	Temperature on Bitumen Surface [°C]
365	33.65	32.2
385	107.88	40.5
405	55.53	37.2
435	26.26	28.4
460	127.17	40.2
470	48.02	29.6
490	38.38	26.4
500	13.32	27.2
525	10.24	27.2
550/580	77.67	34.2
595	12.58	26.1
635	57.4	28.4
660	96.94	31.1
740	44.48	27.7
770	25.53	26.2

normalized between 3200 and 2800 cm^{-1}, which focuses on the main aliphatic band at 2920 cm^{-1}. Full base line integration was carried out using the following ranges for the functional groups:

- Carbonyls (AI_{CO}): 1660–1800 cm^{-1}
- Sulfoxides (AI_{SO}): 1079–984 cm^{-1}
- Reference aliphatic band (AI_{CH3}): 1525–1350 cm^{-1}

The resulting integrational values were evaluated according to Eq. (2). This involved standard statistical evaluation with mean and standard deviation of the 8 spectra per ageing state, which are shown in the form of an ageing index (AI_{FTIR}) throughout the results section.

$$AI_{FTIR} = \frac{AI_{CO} + AI_{SO}}{AI_{CH_3}} \quad (2)$$

The results will show both, normalized spectra of the respective bitumen samples and the ageing indices, which will be plotted versus the different wavelengths used in the ageing experiments. However, since most ageing test programs contained many spectra, merely the most significant and different spectra are shown.

3. Results and discussion

3.1. Influence of the ageing Setup, time and surface temperature

3.1.1. Adjustment of the ageing durations

Fig. 8 displays the FTIR spectra (fingerprint region) of all STA samples after being exposed to ~ 505 mW*min of the respective LED. Since the spectra were normalized at the main aliphatic band at 2920 cm^{-1}, and the most significant changes are occurring at the fingerprint region, merely a section between 1800 and 680 cm^{-1} is shown. The spectra are separated into four sections, with increasing wavelength ranges from (A)–(D), which should enable better comparison. In addition to the spectra, the respective ageing indices were plotted in Fig. 9. Herein, the oxidation caused by the respective wavelengths of the LEDs can be seen by the amount of carbonyls (at 1700 cm^{-1}) and sulfoxides (at 1030 cm^{-1}) formed during its exposure time to the LEDs.

Before diving into the specific results of each wavelength, an overall statement should be made: Photon of a lower wavelength exhibits higher energy due to its inverse proportionality and should in theory induce more oxidation of the bitumen. Hence, a continuous gradient from lower wavelengths to higher wavelengths should be observable across the ageing indices. However, as clearly seen in the summarized ageing indices in Fig. 9, this is not the case. Starting off at range of 365–435 nm (Spectra (A) in Fig. 8), which possess the highest energy, one can see that this is the light region, where the most significant changes occurred. Interestingly, beside 365 nm, which exhibits the highest energy of all wavelengths, 405 nm showed the second highest formation rate of these oxidized functional groups, whereas 385 nm was significantly below that. This could indicate that certain molecular groups in bitumen are more prone to oxidize at 405 nm compared to 385 nm, even though 365 nm exhibits a higher energy. Another possible explanation could be that the 405 nm LED induced a lot more heat on the sample surface than the 385 nm, which will be discussed in the next chapter.

Going towards higher wavelength ranges, once again an interesting observation can be made: while 435 nm and 460 nm induced a similar amount of oxidized functional groups, 470–500 nm is again significantly below them. However, 525 nm exhibits a local maximum, which is not in line with the initial assumption that photons with higher energy produce a higher number of oxidized products. This indicates again that bitumen is more susceptible to photons in certain ranges on visible light due to its molecular composition. From 525 nm onwards (until 770 nm) an overall continuous decrease in carbonyls and sulfoxide formation can be observed, which is in line with the assumption of energy dependent oxidation.

Since these measurements provided unexpected results, preliminary tests of the surface temperatures as well as further testing at various ageing durations and different light (LED) intensities were carried out to see the rate of formation of carbonyls and sulfoxides in correlation to each wavelength.

3.1.2. Temperature

Before going further into results of different ageing durations and LED intensities, another important preliminary parameter needs to be addressed: Temperature on the sample surface. One possible explanation for a higher oxidation rate at 405 nm or 525 nm could be that the temperature induced is significantly above all the other LEDs. However,

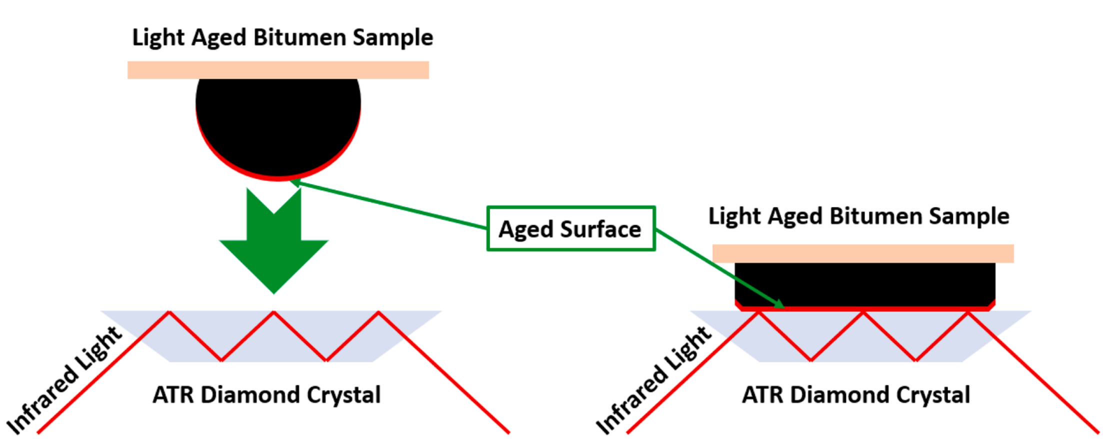

Fig. 7. Schematic drawing of an FTIR measurement, that ensures that the aged surface is in contact with the ATR crystal.

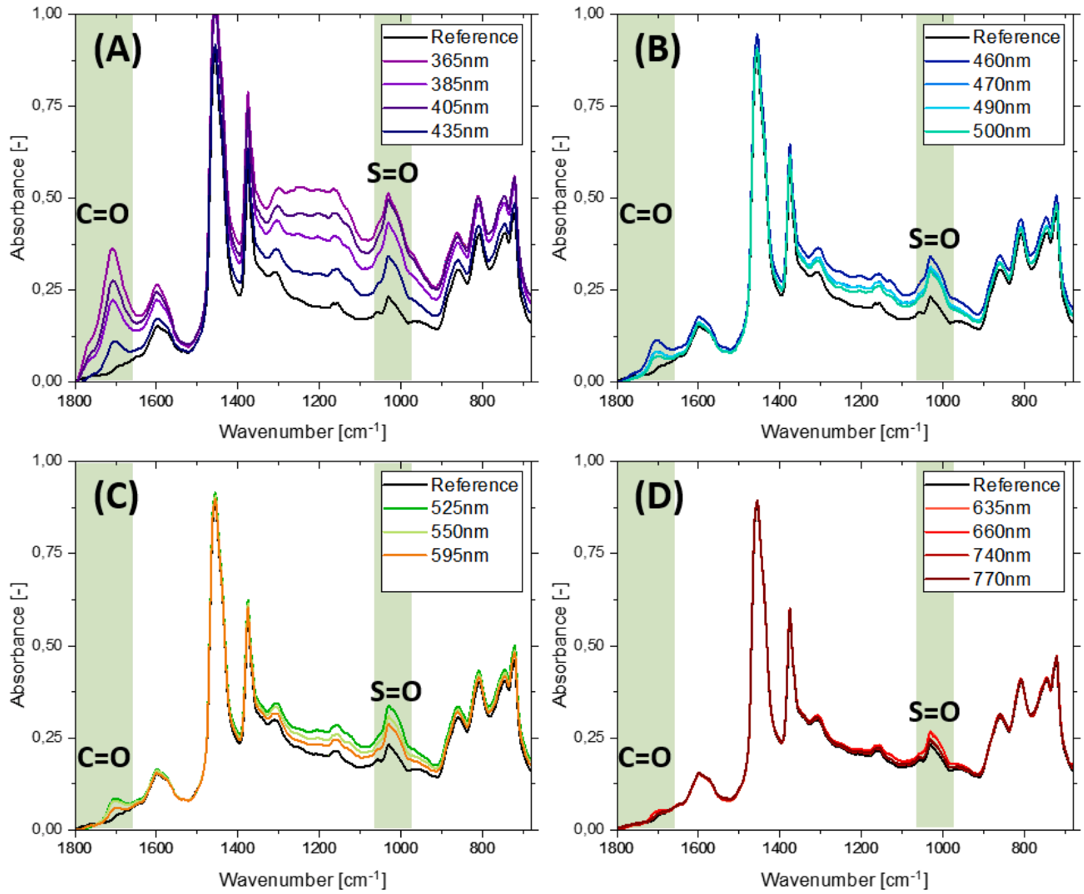

Fig. 8. FTIR spectra of the fingerprint region of all light aged samples in the range of (A) 365–435 nm, (B) 460–500 nm, (C), 525–595 nm and (D) 635–770 nm.

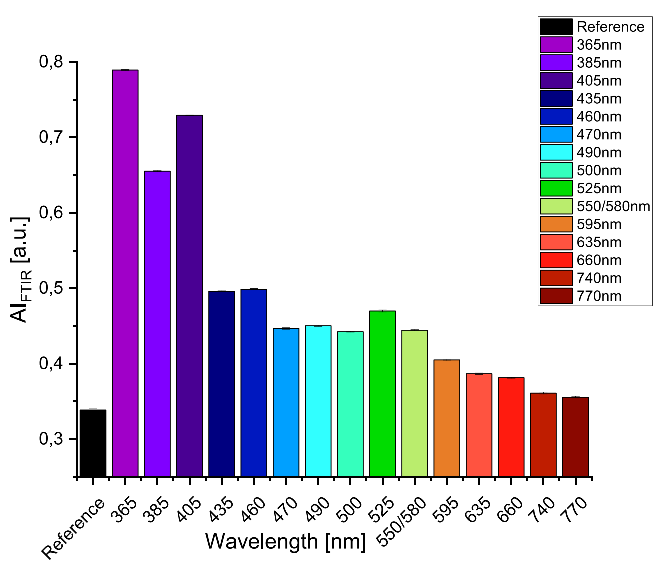

Fig. 9. FTIR ageing indices from all light aged samples with adjusted exposure times to equalize power per sample.

when taking a look at the results of the temperature measurements on the sample surfaces in Table 5, it can clearly be observed that this is not the case. The results show that a maximum temperature of 40.5 °C was measured from the 385 nm LED. When taking a closer look at Table 5, it can be seen that the temperature is linked to the respective LEDs power, meaning that LEDs with higher power values caused higher temperatures on the sample surfaces. However, the overall impact of temperature can be considered as insignificant in terms of thermal oxidation alone, as they do not exceed 41 °C.

3.1.3. Impact of the obective

The last parameter investigated prior to the ageing test programs was the impact of the objective on the oxidation rate in regards to the 15 LEDs. This intends to show what impact focusing light by an objective has. As stated earlier, two possible effects can occur: loss in light intensity due to the objectives transmission curve or increase in oxidation due to focusing of the light. Fig. 10 shows the resulting ageing indices of the samples that were light aged without an objective. While the overall number of carbonyls and sulfoxides formed is a lot lower compared to with the 5x objective used, the overall trend of the ageing indices remains the same. Again, 405 and 525 nm show a discontinuous trend in the expected ageing gradient when considering the energy of the respective photons.

In order to address the two points of concern, being the characteristic transmission curve of the objective as well as the impact of focusing the light onto a sample surface, an ageing index comparison was deemed useful. Table 6 shows such a comparison, where the ratio of the ageing indices from Fig. 9 to Fig. 10 are given. Looking at the values, it is obvious that the transmission curve of the objective plays a less important role, since the ageing indices received from the ageing procedures with the 5x objective are significantly higher in the lower wavelength range. This means that the objective does not reduce the lights intensity significantly or that the focusing effect of the light outweighs the transmission profile to such an extent. Hence, it can be said that focusing the light has a more significant effect in the range between 365 and 405 nm and the slowly falling off towards a ratio of 1, where both ageing indices approach the same value independent from the usage of an objective.

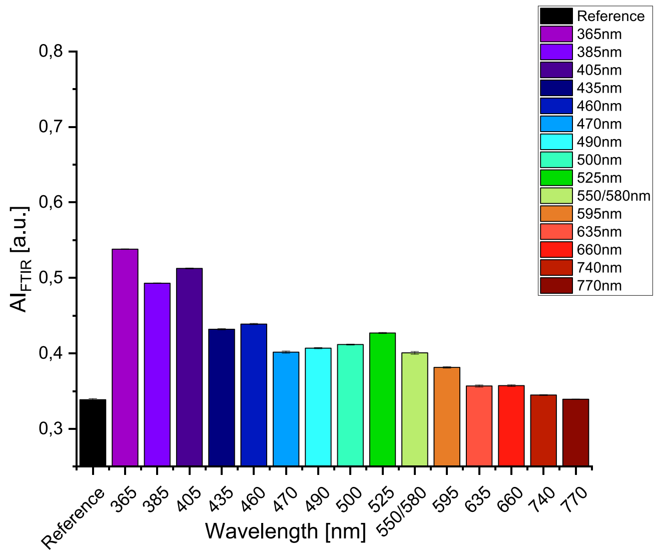

Fig. 10. FTIR ageing indices from light ageing using no objective.

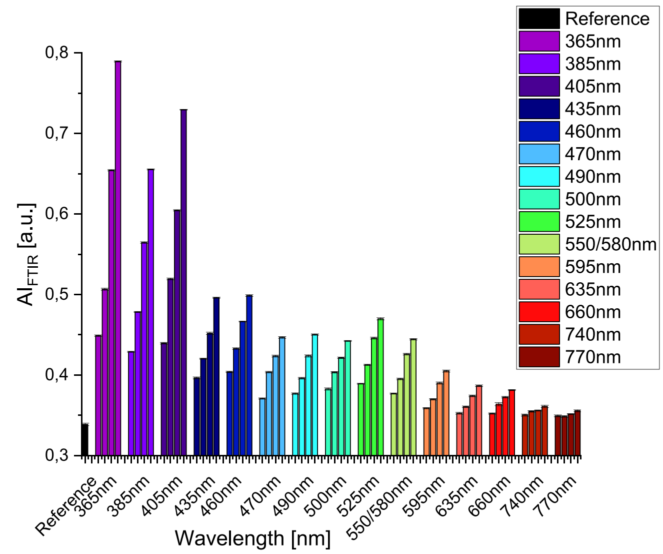

Fig. 11. FTIR ageing indices of the first ageing test program with the variation of ageing duration.

Table 6
Ageing index ratio between 5x objective and no objective.

Wavelength [nm]	Ageing Index Ratio
365	1,47
385	1,33
405	1,42
435	1,15
460	1,14
470	1,11
490	1,11
500	1,07
525	1,10
550/580	1,11
595	1,06
635	1,08
660	1,07
740	1,08
770	1,05

Thus, it can be concluded that the impact of the objective would mainly affect 365–405 nm, but is difficult to consider in a calculation since the overall power values without an objective cannot be measured with a spectrometer, as it requires the focusing of the light on a focal plane in order to determine the power values via an integrated sphere measurement (as it has been performed for the initial power value determination of each LED which is listed in Table 1). Therefore, the ageing test programs were conducted using an objective.

3.2. First ageing test program: Determination of oxidation by visible light caused by different ageing durations

Since the preliminary testing with the adjustment of the ageing duration to equalize the overall total energy on the bitumen surface has shown interesting results, further investigations on the impact of each LED was sought after. This was followed up by a variation of ageing duration, which shows at which rate these oxidized species were formed and whether the wavelength has an impact or not. Therefore, the previously mentioned ageing duration was set to a factor of 1x, and three additional ageing durations (1/6x, 1/3x, and 2/3x) were added.

Since the total amount of FTIR spectra (4 different ageing durations × 15 LEDs) would be rather confusing, merely the resulting ageing indices are displayed in Fig. 11. When comparing them to the trends in Fig. 9, the same pattern can be seen for all reduced ageing durations. This again indicates that bitumen is more susceptible to certain ranges on visible light due to its molecular composition. Interestingly, the rate at which carbonyls and sulfoxides are forming seems to follow a linear trend. To confirm this assumption, all four ageing indices per wavelength were plotted and a linear fit was made, which is shown in Table 7.

When taking a closer look at the values from Table 7, it can be seen that that a linear function fits well across the data from the LEDs. Merely at lower wavelengths (740 and 770 nm), where the overall oxidation was little, the function falls below an R^2 of 0.95. As these wavelengths did not contribute much to the oxidation of bitumen, their non-linear behaviour can be neglected.

The slopes in Table 7 indicate at which rate carbonyls and sulfoxides form and confirm the previous assumption that 365 nm and 405 nm exhibit the highest formation rates, followed by 385 m.

While the ageing indices as well as their linear fit provide a useful overview of the materials oxidation rate, they have a certain disadvantage, as no actual spectral data is shown. Hence, one cannot judge whether other ageing effects occur like the formation of additional functional groups. Since the total number of spectra is too high, a specific set of four different wavelengths (365, 405, 525 and 635 nm) were selected and are plotted in Fig. 12.

Looking at the spectra from 365 nm (A) and 405 nm (B) in Fig. 12, it can be seen that beside the drastic formation of carbonyls and sulfoxides, an overall major increase in the entire fingerprint region is observable, especially between the range of 1350–900 cm^{-1}. Such an increase has

Table 7
Linear correlation of all ageing indices received after variation of the ageing duration.

Wavelength	Linear Function	Slope	R^2
365	y = 0.138x + 0.3755	0.138	0.9989
385	y = 0.0899x + 0.3858	0.090	0.9996
405	y = 0.1113x + 0.3923	0.111	0.9905
435	y = 0.0387x + 0.3783	0.037	0.9946
460	y = 0.0368x + 0.3907	0.037	0.9868
470	y = 0.0281x + 0.3656	0.028	0.9386
490	y = 0.0289x + 0.3649	0.029	0.9955
500	y = 0.0227x + 0.3757	0.023	0.9758
525	y = 0.0318x + 0.3777	0.032	0.9841
550	y = 0.027x + 0.3667	0.027	0.9819
595	y = 0.0185x + 0.351	0.018	0.9932
635	y = 0.0136x + 0.3465	0.014	0.9981
660	y = 0.011x + 0.3498	0.011	0.9542
740	y = 0.0038x + 0.3495	0.004	0.9186
770	y = 0.0027x + 0.347	0.003	0.8982

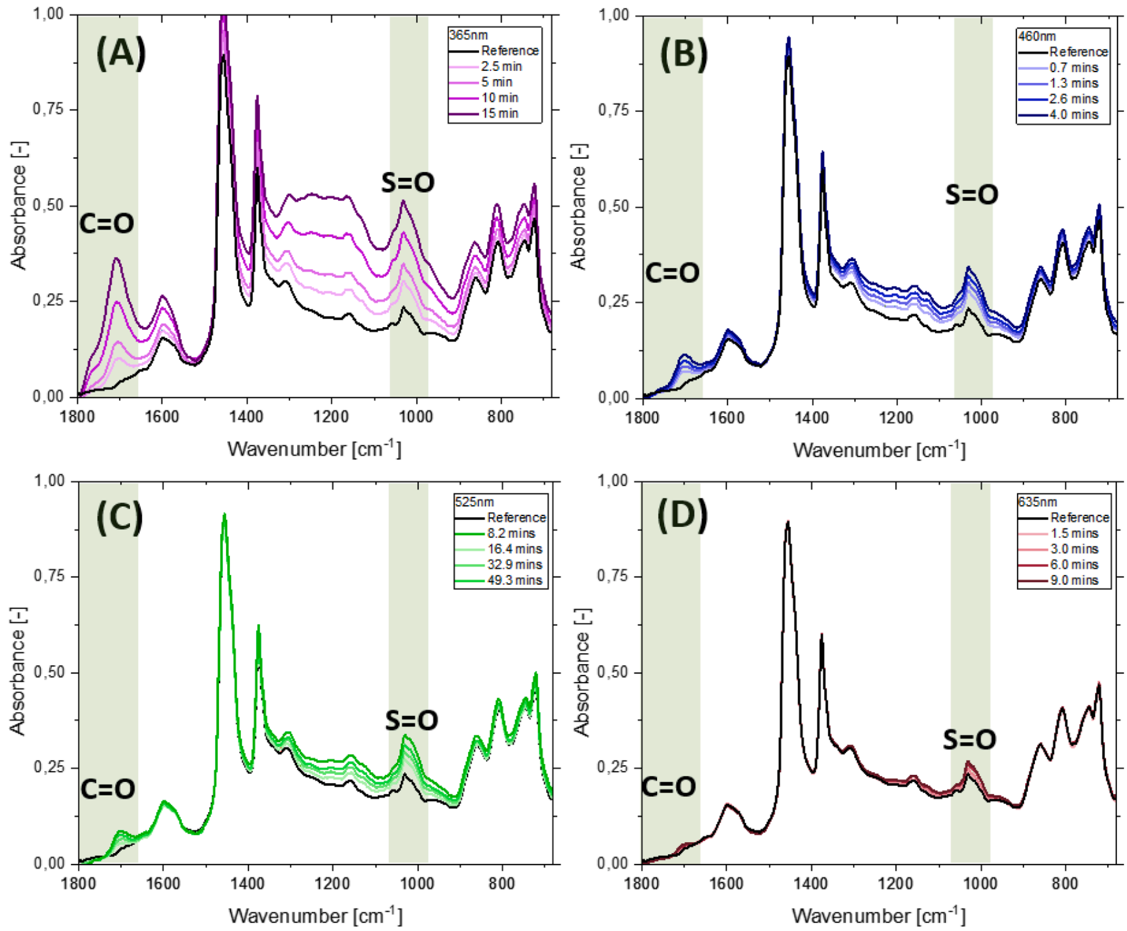

Fig. 12. FTIR spectra of the samples aged at 365, 405, 525 and 635 nm at the four different ageing duration.

never been reported before. However, it was previously assumed that this can be attributed to an increase in the materials overall polarity which occurs during ageing [20,21]. Thus, the surface of the material must be in a strongly oxidized condition that exhibits an extreme shift towards higher polarity. Future investigations by doing SARA analysis could reveal whether this assumption holds true.

Coming back to the range between 1800 and 1600 cm^{-1}, a shoulder around 1750 cm^{-1} is visible, which corresponds to the presence of carboxylic acids [22]. As they resemble another end of an oxidation product of organic molecules, their presence is completely reasonable. Another interesting observation is that at the highest ageing level, the formation of ketones at 1700 cm^{-1} is increasing to such an extent that it even surpasses the aromatic band's intensity at 1600 cm^{-1}. This indicates that an oxidation process at 365 nm or even at 405 nm induces a harsh oxidation leading to a rapid formation of ketones. It needs to be kept in mind that the samples were only aged and investigated on the surface, as ATR-FTIR spectroscopy merely captures the top micrometres of the material. Nonetheless, this ageing level was achieved within 10–15 min using roughly 505 mW*min of total energy from 365 nm or 405 nm.

Coming to the spectra of the 525 nm aged samples, as displayed in (C) in Fig. 12, again a continuous increase in oxidation can be observed with extended ageing duration. However, no drastic formation of carbonyls and sulfoxides as well as a lower increase in the range between 1350 and 900 cm^{-1} can be seen here. This is even further reduced, when looking at the spectra of the 635 nm aged samples ((D) in Fig. 12). Exposure to such a wavelength merely induces a slight increase in ketones at 1700 cm^{-1} and (compared to the increase of the ketones) a slightly higher formation rate of sulfoxides at 1030 cm^{-1}, which was previously reported [18].

Overall it can be concluded that by varying the ageing duration an overall linear oxidation rate can be observed, especially for wavelengths below 740 nm. Due to this linear trend, the overall adjustment of the ageing durations to equalize the energy exposure per bitumen sample can also be justified. However, to reflect conditions on earth's surface, the LEDs intensity profile needs further testing, which will be shown in the next chapter below.

3.3. Second ageing test program: Determination of oxidation by visible light caused by different LED intensities

Since the variation of ageing duration has shown an overall linear trend, the same questions can be asked in regards to the LEDs' intensity profiles. Each LEDs intensity can be manually adjusted between 0 and 100 %. However, a concern was expressed whether all LEDs power profiles show a linear behaviour. Thus, similar to the variation of ageing durations, a reduction of the respective LEDs intensities was tested. Again, three additional intensity steps (17 %, 33 % and 66 %) were chosen, which also reflects the steps from the ageing duration variation. Once again, as the number of spectra is rather large, merely the ageing indices as well as the determination of linear functions and ageing rates are shown in Fig. 13 and Table 8.

Similar to the results from the first ageing test program, the previously displayed trends could be observed in regards to the two functional groups that have formed upon ageing. Addressing the oxidation behaviour with the linear function an overall good accordance up to 770 nm can be seen. Merely, 770 nm shows once again a R^2 value below 0.95, which once again can be neglected due to the overall low level of

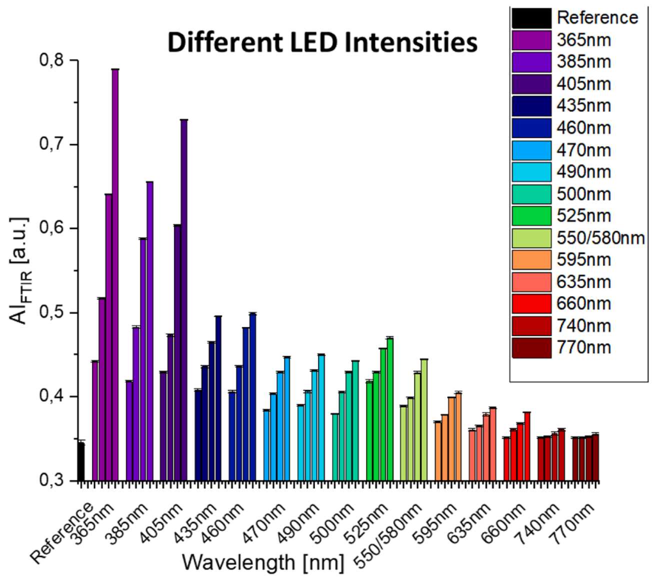

Fig. 13. FTIR ageing indices of the first ageing test program with the variation of the LEDs intensities.

Table 8
Linear correlation of all ageing indices received after variation of the LEDs intensities.

Wavelength	Linear Function	Slope	R^2
365	y = 0.137x + 0.3749	0.137	0.999
385	y = 0.0947x + 0.3823	0.095	0.983
405	y = 0.1221x + 0.3606	0.122	0.997
435	y = 0.0389x + 0.3805	0.039	0.951
460	y = 0.0373x + 0.3951	0.037	0.945
470	y = 0.0249x + 0.3752	0.025	0.977
490	y = 0.024x + 0.3805	0.024	0.990
500	y = 0.0241x + 0.3751	0.024	0.930
525	y = 0.0213x + 0.4091	0.021	0.973
550	y = 0.0231x + 0.3777	0.023	0.984
595	y = 0.0146x + 0.3644	0.014	0.948
635	y = 0.0108x + 0.3555	0.011	0.987
660	y = 0.0113x + 0.3472	0.011	0.977
740	y = 0.0039x + 0.3489	0.004	0.975
770	y = 0.0016x + 0.3501	0.002	0.850

oxidation that occurred at such high wavelengths.

Comparing the oxidation rates from the first (Table 7) and second (Table 8) ageing trial, an overall good accordance can be seen, reaching a maximum discrepancy of 10 % in the lower wavelength range, which is the area of interest, as it contributes the most to ageing. However, this variation can be expected from such a large number of ageing experiments, as precise recreation of sample homogeneity is not possible and was tried as best as humanly possible.

Fig. 14 shows once more spectra of the samples with the most significant (and insignificant) changes due to variation of the LEDs' intensities. Similar to Fig. 12, the same phenomena can be seen for the two lower wavelengths (365 nm - (A) and 405 nm - (B) in Fig. 12). High content of carbonyls at 1700 cm^{-1} and sulfoxides at 1030 cm^{-1} as well as an overall increase in the region between 1350 and 900 cm^{-1} is observable. The shoulder assigned to the carboxylic acid is also visible [22].

The spectra from 525 nm ((C) in Fig. 14) shows a slightly higher level after being exposed for 49.3 min at 17 % LED intensity, compared to the respective counterpart (8.2 mins at 100 % LED intensity) from the first ageing test program (Fig. 12). This indicates that even though the linearity for this LED is given, it follows a slightly different profile compared to the variation of ageing durations. While this does not have a very significant impact on the third and final ageing test program, since no significant intensity reduction of the LED at 525 nm was necessary, it emphasized the necessity for conducting such an ageing trial with variation of the LEDs' intensities.

Coming to the last series of spectra (aged at 635 nm), which are shown in (D) in Fig. 14), again no significant oxidation can be seen. Little formation of ketones at 1700 cm^{-1} as well as slightly higher formation of sulfoxides at 1030 cm^{-1} can be observed.

Overall, the second ageing test program revealed that the LEDs' intensities are well in line with the variation of the ageing duration, especially in the lower wavelength region, and will enable the final correlation to solar spectral irradiance data. However, these test programs were necessary, as it turns out that some LEDs (e.g. 525 nm) do follow a different linear trend when comparing intensity profile to ageing duration.

3.4. Third ageing test program: Correlation to solar irradiance and Earth's surface

In order to understand the impact of visible light on the oxidation of bitumen, the respective conditions on our earth's surface need to be considered and mimicked as best as possible. As described earlier, not all wavelengths are reaching the earth's surface with the same intensity. Especially light with higher energy and lower wavelength are more absorbed by our atmosphere. Thus, the solar spectral irradiance data shown in Fig. 1 was considered for these experiments (see Table 4), which mainly impacts the LEDs below 500 nm. An overview of the results from this third and final ageing test program is shown in form of the ageing indices on the right-hand side of Fig. 15. These indices give first indication to how surface oxidation of bitumen under atmospheric conditions would look like in regards to the respective wavelengths. Thus, it can be concluded that 405 nm exhibited the highest oxidation potential of all visible light wavelengths when considering the impact of earth's atmosphere. Additionally, it can be seen that the wavelength region around 400 nm (from 365 nm to 460 nm) induced the most oxidation. Merely 435 nm seemed to fall below the rest in this range, which again indicates that specific molecular components in bitumen are reacting more to wavelengths like 405 nm, compared to 435 nm.

The left-hand side of Fig. 15 shows the associated spectra from the ageing procedures conducted at 365, 405, 550 and 635 nm. It should be noted that this figure does not show the spectrum of 525 nm (which was usually selected) due to the fact that the correlation between ageing duration and LED intensity did not match well (and should therefore be treated with more care). From these spectra it is clearly visible that 405 nm induced the highest formation of carbonyls and sulfoxides, when considering the conditions from the solar spectra irradiance data. By comparing the spectra of the next two wavelengths (365 nm and 550 nm), something highly interesting can be observed. While 365 nm induced a higher formation of ketones, 550 nm exhibited a higher sulfoxide content. This indicates that the formation of these two products is dependent on the wavelength or energy of the photon. With higher energy or lower wavelength, a formation of ketones is promoted, which is turned around with increasing wavelength or lower energy, where it favours the formation of sulfoxides. Thus, the energy of the photon seems to play a crucial role in the oxidation mechanism of bitumen and should be considered when simulating field ageing in the laboratory. Furthermore, when closely looking at the sulfoxide band (highlighted in the second red box on the left-hand side in Fig. 15), another interesting phenomenon can be seen: A clear difference in the bands shape at 1030 cm^{-1} can be seen when comparing all four spectra. It seems that the sulfoxide band of the 550 nm and 635 nm aged samples exhibit a shoulder which is located around 1015 cm^{-1}. This band or shoulder does not appear in the spectra of the 365 and 405 nm samples, where only a rather sharp band at 1030 cm^{-1} is visible. This provides evidence that either another chemical species is interfering with the usual sulfoxide band at 1030 cm^{-1} or that some sort of shift occurs due

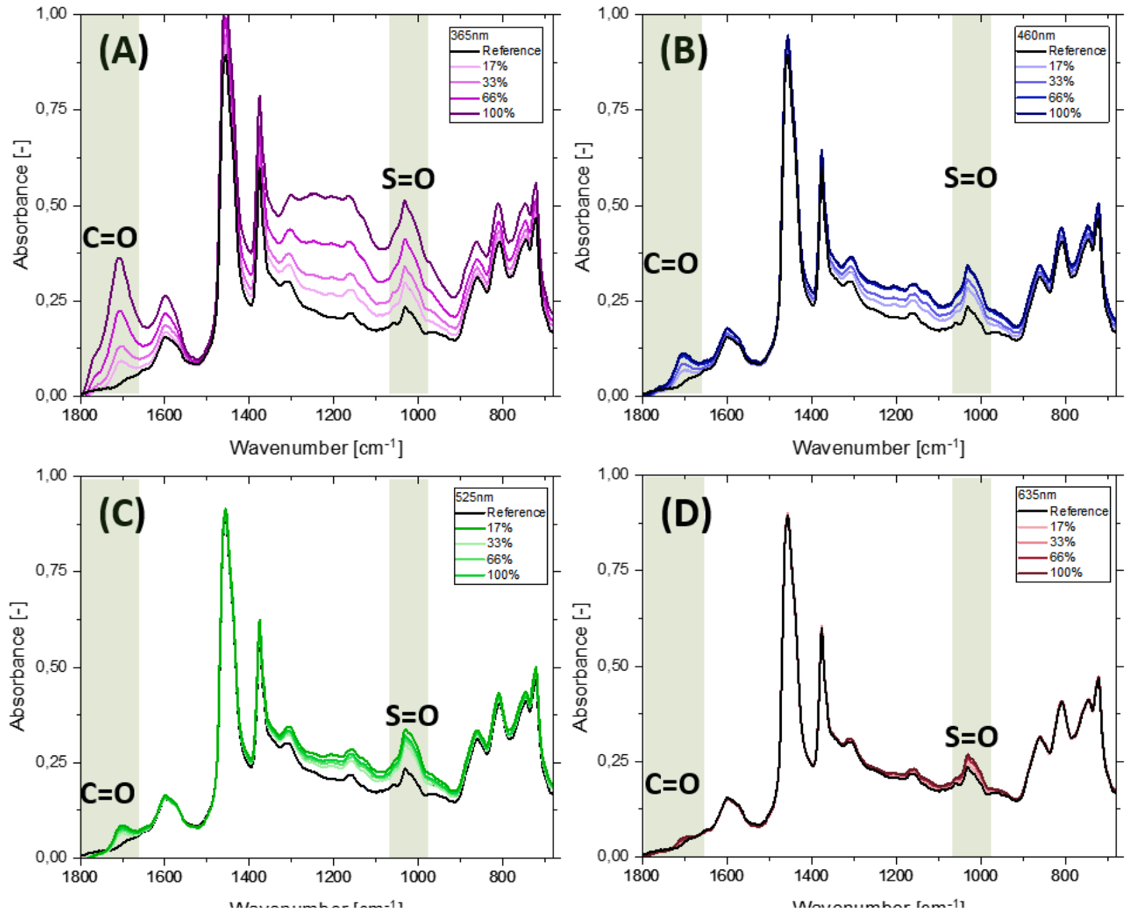

Fig. 14. FTIR spectra of the samples aged at 365, 405, 525 and 635 nm at the four different LED intensities.

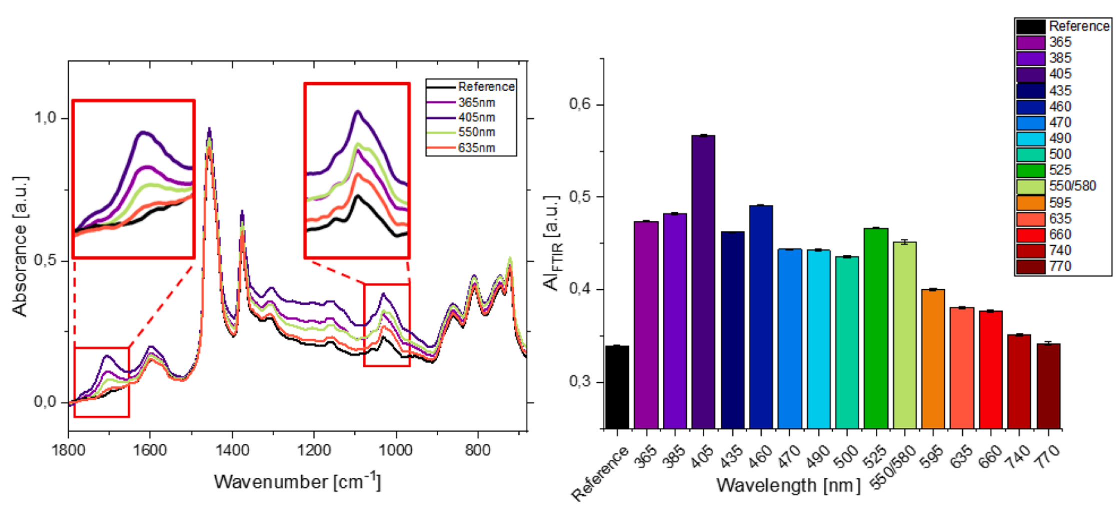

Fig. 15. FTIR Spectra of four different LEDs (left) and FTIR ageing indices of all 15 LEDs (right).

to changes in chemical surrounding of the sulfoxide. However, no precise assignment of this band can be made yet and needs further investigation.

4. Conclusions and outlook

This study has investigated the impact of visible light on the oxidation behavior of short-term aged (STA) bitumen. Various ageing experiments have been conducted with 15 different LEDs ranging from 365 to 770 nm. ATR-FTIR spectroscopy was used to determine the degree of oxidation of the sample surface caused by the respective wavelength ranges by summarizing the two functional groups (carbonyls and sulfoxides) which are formed upon ageing.

The results show that when STA bitumen is exposed to ~ 505 mW*min of the respective LED an unexpected, characteristic oxidation profile (local maxima at 365, 405, 460 and 525 nm) can be observed. This indicates that bitumen is more susceptible to certain ranges on visible light due to its molecular composition. However, no specific molecular groups are found yet, which can explain this oxidation behavior.

Correlation to solar spectral irradiance data (condition on earth's surface) revealed that visible light in the range of 365–460 nm and furthermore around 525–550 nm show a higher oxidation rate than their surrounding wavelength ranges and need to be considered for simulating field ageing.

A closer look at the resulting FTIR spectra revealed that a photo-energy specific interaction with bitumen occurs as photons with higher energy induce a higher formation of carbonyls, while photons with lower energy support the formation of sulfoxides. The ratio at which carbonyls and sulfoxides are formed is a crucial piece of information when looking into the bitumen ageing mechanism and the goal to realistically simulate it in the laboratory.

Overall, these findings provide spectroscopic insight on how significant visible light for bitumen ageing is. Future work will focus on comparison to conventional laboratory ageing like the PAV, which will reveal whether the mechanism of photo-oxidation differs from thermal ageing. Furthermore, larger quantities of bitumen will be aged with the respective wavelengths which will enable additional chemical and rheological analysis. Ultimately, the results obtained can also be used to address the design and implementation of antioxidants or light absorbing materials and will help us to better understand field ageing and its simulation in the laboratory.

CRediT authorship contribution statement

Johannes Mirwald: Conceptualization, Methodology, Investigation, Formal analysis, Validation, Data curation, Writing – original draft, Visualization. **Drilon Nura:** Investigation. **Lukas Eberhardsteiner:** Resources, Funding acquisition, Writing – review & editing. **Bernhard Hofko:** Resources, Supervision, Project administration, 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.

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