Research paper

Evaluating the effects of TiO_2 as a photocatalytic material in pavement engineering in terms of pollutant degradation and bitumen performance

Arne Chantrain [1,*], Seyed Reza Omranian [1], Navid Hashaminejad [1] and Cedric Vuye [1]

[1] University of Antwerp, Faculty of Applied Engineering, EMIB Research group, Groenenborgerlaan 171, B-2020 Antwerp, Belgium;

* Correspondence: arne.chantrain@student.uantwerpen.be

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Abstract: The World Health Organisation reported that approximately 91% of the world population lives in places with poor air quality conditions. Gaseous pollutants can cause severe cardiovascular and respiratory diseases and affect global warming. In order to reduce the negative effects of these pollutants, air-purifying techniques using photocatalytic materials have been explored. Titanium Dioxide (TiO_2) is known as a stable and economically interesting photocatalytic semiconductor with proven capabilities for degrading pollutants. Although TiO_2 has been investigated in the construction industry, no clear recommendation has been drawn. Asphalt pavements cover a large surface area (nationally/internationally) and are exposed to exhaust gasses which turn them into a great platform for air purifying purposes. This research evaluates the incorporation of TiO_2 into/onto asphalt pavements (AC6 with B50/70 bitumen) by evaluating the rate of soot degradation using Image Analysis. Furthermore, the effect of TiO_2 on the chemical and rheological properties of bitumens were studied employing Fourier Transform Infrared Microscopy (FTIR) and Dynamic Shear Rheometer (DSR). The results clearly showed the degradation of the soot after 14 days and no direct rheological effects of TiO_2 were observed based on the DSR test outcomes. The presence of TiO_2 could be verified using FTIR. However, no significant differences were observed in the bitumens carbonyl and sulfoxide bands as two well-known aging band indicators. To conclude, the TiO_2 application for 200 mg on the mixtures surface and 5% bitumen modification showed the optimal influence on the degradation of the pollutants, while exhibited no undesirable influence on the binder characteristics.

Keywords: Titanium Dioxide; asphalt pavement; air-purifying; bitumen modification; surface application.

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1. Introduction

The World Health Organisation (WHO, 2016) reported that approximately 91% of the world population lives in places with poor air quality conditions, where the level of pollutants exceeds the WHO air quality guidelines, both in urban and rural regions. Exposure to soot and a number of various gaseous pollutants, such as volatile organic compounds (VOC), can result in severe cardiovascular and respiratory diseases. It indicates an urgent need for effective crisis management and sophisticated plans in decision making in order to reduce the negative impacts of pollutants on the environment, and their (in)direct influence on global warming. For this reason, various environmental deadlines have already been proposed. In addition, multiple abatement technologies have been considered for air purifying purposes, including photocatalysis as a sustainable process for air remediation. These technologies are based on the principle of a semiconductor photocatalyst and light as the sole energy input [1].

Titanium Dioxide (TiO_2) is widely known as a stable and economically interesting photocatalytic semiconductor. It has already proven its capability of converting solar energy into chemical energy, and thus its capacity for degrading certain pollutants [1, 2]. In this respect, throughout photocatalytic reactions, harmful pollutants, such as Nitric Oxide (NO), can be degraded into HNO_3 [2, 3]. This stoichiometric reaction for NO can be seen underneath and can also be established for other pollutants such as Carbon monoxide (CO), certain VOCs, and Sulfur Dioxide (SO_2) [2-5]:

$$TiO_2 \rightarrow^{hv} h^+ + e^-$$
$$h^+ + OH^- \rightarrow OH^*$$
$$e^- + O_2 \rightarrow O_2^-$$
$$H^+ + O_2^- \rightarrow HO_2^*$$
$$NO + HO_2^* \rightarrow NO_2 + OH^*$$
$$NO_2 + OH^* \rightarrow HNO_3$$

Vehicles are one of the main sources of pollutant emissions. The large road surface area (±150 000 km in length in Belgium) and the vicinity of road pavements to the vehicle emissions, make asphalt pavements a very suitable and interesting surface to be considered for air purification purposes. In this regard, a TiO_2 photocatalyst can be applied into/onto the pavement, see Table 1, and the degraded material can be easily washed away by rainwater through the already existing drainage system. According to Wang et al. (2016), apart from the cost of the material and the application, no further investments are required [3].

TiO_2 has already been introduced in several industries including construction, e.g. paints, concrete paving blocks, and asphalt pavement (a test project run by the Belgian Road Research Centre, with unsatisfactory results [6, 7]). However, no well-established and proven asphalt pavement application procedure is available at this moment. In addition, the effects of wheel loads and traffic have not been studied in detail. Yet, it is crucial to develop deeper methodological insights into the most optimal and durable TiO_2 application technology, both in terms of photocatalytic air purification efficiency, as well as traffic durability (also referred to as immobilization) [6, 8-10].

Table 1. Benefits and drawbacks of TiO_2 application methods

	Benefits	Drawbacks
Spray Coating	• High Photocatalytic efficiency [11] • Application possible after construction [11]	• Influencing skid resistance [11] • Immobilization issues • Spray-solution only possible with dense asphalt types
Bitumen Modification	• Expected higher efficiency on long term • Lower impact on surface properties (e.g. skid resistance) [12]	• Lower photocatalytic efficiency [11] • Application only possible during construction • Possible chemical- and rheological effect on binder properties [13]
Volume Incorporation	• Expected higher efficiency on long term • Lower impact on surface properties (e.g.) skid resistance [14] • Can replace filler [14]	• Application only possible during construction • Possible chemical- and rheological reactions while mixing [13]

Various (laboratory) studies have been conducted covering multiple application methods and dosages of TiO_2 in pavement structures over the last few years, although they do not lead to clear recommendations. The three commonly used TiO_2 application techniques are (i) spray coating, (ii) bitumen modification, and (iii) volume incorporation. Every application method carries its own benefits and drawbacks as presented in Table 1. In the spray coating method, TiO_2 particles are deposited on the surface of the asphalt pavement. This method thus results in a large active photocatalytic surface in direct contact with the polluted environment, resulting in notable efficiency of degradation potential. Results obtained by Hassan et al. (2012) confirm this trend, where samples with different loadings of TiO_2 showed NO_x degradation ranging from 31 to 55%, depending on the TiO_2-loading. More recent studies by Wang et al. (2018), Hu et al. (2017), and Toro et al. (2016) confirm the possibility to degrade pollutants such as NO, hydrocarbons (HC), CO, and VOCs by TiO_2 spray coating. These experiments resulted in average reductions of 30% for NO, HC, and CO and varying efficiencies between 0-55% for VOCs. A remarkable aspect of VOC degradation (such as benzene, toluene, or p-xylene) is the emergence of photolabile side products (i.e. formaldehyde and acetaldehyde) [12, 15, 16].

The main scope of this research is to investigate the potential of nano-TiO_2 particles to degrade pollutants and their influence when incorporated into a binder. UV-ageing will be taken into account as well since this energy is necessary for photocatalyst activation. In addition, TiO_2 might (positively) affect the ageing of binders. Since this research focusses on three fundamentally different aspects and application types (i.e. surface coating and bitumen modification), three sub-objectives have been identified:

- To monitor the amount of soot degradation by TiO_2 surface application under UV-irradiation.
- To understand the extent to which TiO_2 affects the chemical-, rheological-, and physical properties when incorporated in a binder.
- To study their possible effects on binder ageing

2. Materials and Methods

In order to make a detailed recommendation for the sub-objectives, two different experimental procedures were set up. Firstly, the degradation efficiency of soot by TiO_2 surface application was evaluated. Secondly, several tests were conducted to evaluate the chemical- and rheological effects when incorporating TiO_2 in the binder and ageing by UV-irradiation. Both procedures, based on literature and standards, were discussed in this paragraph while also focussing on more general aspects such as the properties of Nano-TiO_2.

2.1. Properties of Nano-TiO_2

The abovementioned experiments both use the Evonik P25 TiO_2 for which the characteristics can be seen in Table 2.

Table 2. Technical properties of Evonik P25 TiO_2 [13, 17]

Properties	Results
Appearance	White powder
Specific Surface Area (m²/g)	35 – 65
Particle size (nm)	23 - 28
Loss on Drying 105°C, 2h (%)	≤ 1,5
Purity (%)	≥ 99,5
pH-value, in 4% dispersion	3,5 – 4,5
Crystal form	80% Anatase, 20% rutile

2.2. Surface application

2.2.1. Asphalt samples

The efficiency of TiO_2 was studied based on the changes in degradation of deposited soot particles on the surface of asphalt samples. To improve the contrast between the asphalt sample and these dark soot particles, a red-coloured asphalt (AC6 with B50/70 bitumen, designed for bicycle paths) was chosen and provided by COLAS Belgium. Large samples of 18x50x5 cm were made using the plate compactor method, according to EN 12697-33/2019, which were then cut to samples of 5x5x5 cm.

2.2.2. Photocatalyst coating

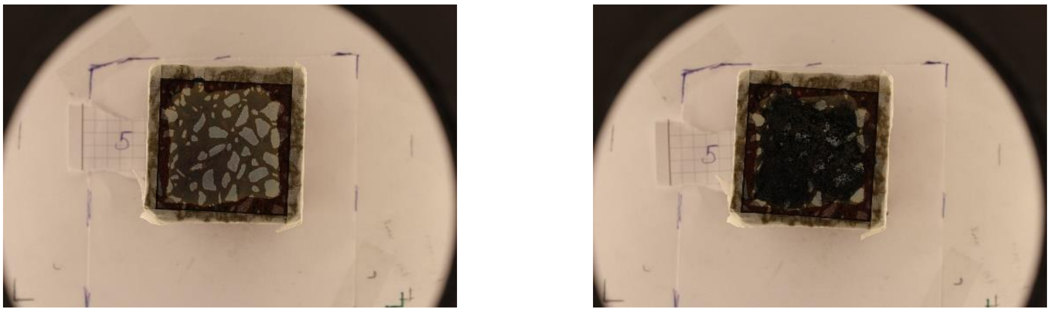
Initially, a suspension of methanol and TiO_2/soot was prepared for surface application. Three different amounts of Evonik P25 TiO_2 were mixed with 2 ml of methanol (Merck). These mixtures were suspended for 1 h by sonication and afterwards, 200 µl was drop-casted on top of the asphalt surfaces resulting in a coverage of ±0,08 l/m² for each sample. The asphalt samples were then dried at room temperature for 2 h and subsequently overnight at 80°C [17].

Similar procedures were adopted to prepare a soot suspension (Printex-U, Evonik) with different percentages. Afterwards, the solvent was drop-casted on top of the asphalt sample, which had already been treated with the TiO_2 suspension. The samples were again dried for 2 h at room temperature and 80°C overnight [17]. The various combinations of soot- and TiO_2 quantities lead to the following samples:

Table 3. Division of samples for soot degradation experiment.

Sample	TiO2 (mg)	Soot (mg)
T100/S2	100	2
T150/S2	150	2
T200/S5	200	5
T150/S5	150	5
T200/S8	200	8
T100/S8	100	8
T150/S5	150	5
T200/S2	200	2
T150/S8	150	8
T150/S5	150	5
T100/S5	100	5

Figures 1a and 1b show the images on day 0 with TiO_2 and with- and without soot application, respectively.



(**a**) (**b**)

Figure 1. Pictures of the asphalt samples taken inside the standardized photobox at day 0: (**a**) T200/S8 with only TiO_2 applied; (**b**) T200/S8 with TiO_2 and soot applied on the surface.

2.2.3. Soot degradation

In order to evaluate the soot degradation, a similar procedure performed by Van Hal et al. (2019), was adopted [17]. After the sample preparation, the asphalt cubes were placed in a custom made box with full-time UV-B irradiation of 10 W/m² as shown in Figure 2a. Pictures were taken in a standardized photobox, Figure 2b, excluding external light and direct illumination. A Canon EOS 500D camera was positioned 18 cm above the samples and the digital images were taken in manual mode (iso 200, aperture f8 and focal exposure 1:5) at maximal resolution (5184x3456) at 72 dpi [10, 17].

(**a**) (**b**)

Figure 2. The figures above show the sample treatment and photobox: (**a**) Custom made box with fulltime UV-irradiation; (**b**) Standardized photobox by DuEL-research group.

Every picture is afterwards analysed using "Matlab Image Processing Toolbox", following a Matlab script to capture the greyscale values for every picture. By converting the image into grey scale values it is possible to evaluate the soot degradation since dark soot can vanish and the white TiO_2 can become visible. Due to a lot of irrelevant background, the pictures were firstly cropped manually so only the surface was visible. Subsequently, the images were processed by Matlab and converted into greyscale for which a histogram could be constructed by counting every pixel and plotting them in the corresponding pixel value (0 = complete black; 255 = clear white).

In order to obtain an insight into soot degradation and the time necessary for such reactions, pictures were taken and analysed at 0, 1, 4, 7, 14, 28 and 56 days. In addition, a picture was taken without any soot added on top on day 0 as a reference for each sample.

2.3. Bitumen Modification

To evaluate the extent to which TiO_2 bitumen modification affects the rheological- and chemical properties of asphalt binders, several tests were conducted. Firstly, a Total B50/70 binder was mixed, with 0, 1, 3 and 5% TiO_2 by weight of binder, for 30 min. with the Low-Shear Mixer (350 RPM). These samples were poured into a custom-made silicone mould of ± 1 mm and placed under UV-irradiation at 10 W/m² [13].

2.3.1. FTIR

Fourier Transform Infrared Microscopy (FTIR) was carried out at 0, 1, 3, 7, 14, 28, 42 and 56 days to detect any changes in chemical composition. The Thermo Scientific Nicolet iS10 Fourier Transform Infrared spectrometer (Waltham, MA, USA) was equipped with an Attenuated Total Reflectance (ATR) fixture and a Smart Orbit Sampling Accessory. The average spectra were obtained after the acquisition of the spectra, 32 repetitive scans in the range 400 cm^{-1} to 4000 cm^{-1} with a resolution of 4 cm^{-1} were performed. At least four replicants of every sample were cut out and placed with their surface on the diamond [13].

In order to improve the contact between the bitumen sample and the diamond, additional experiments were conducted. The binder samples, already exposed to UV-irradiation, were heated and evenly mixed, subsequently drops were cast on the FTIR-diamond, and these samples were tested on 0, 28 and 56 days.

2.3.2. DSR

A Dynamic Shear Rheometer (DSR) test was carried out to evaluate the viscoelastic behaviour of the binders after TiO_2 incorporation. The DSR used in this study was an Anton Paar MCR 500 (Graz, Austria). The frequency sweep test was conducted based on EN 14770:2012 Standard procedures. According to the standard, temperatures fluctuate from 0 to 40°C, and 40 to 80°C, for 8 mm and 25 mm plate geometries, respectively. This frequency sweep was repeated at several temperatures (increments of 10°C) on two replicates per binder sample. The data were further analysed using the RHEA™ software (v2.0, Abatech, Blooming Glen, PA, USA) [13].

DSR samples were produced for 8 mm and 25 mm geometries, according to the standard, and were evaluated at two different time-intervals, namely 0 and 7 days. Furthermore at every time-interval two different percentages of TiO_2, 0% and 5%, were tested.

3. Results and discussion

This section will graphically and analytically show all the relevant data gathered by the various experiments and discuss them individually while also referring to the already existing literature and tests. The first subsection will focus on the soot degradation experiment while the second elaborates on the FTIR and DSR outcomes.

3.1. Soot degradation

Figures 3, 5 and 7 show all the data obtained by analysing the photographs with Matlab. As mentioned in the previous section, 11 different samples were evaluated but only the two most relevant samples and one intermediate sample are presented in this paper. These two samples are the specimens with the maximum and minimum expectations for soot degradation, 200 and 100 mg of TiO_2 covered by 2 and 8 mg soot, respectively. The third sample is an intermediate sample with 150 mg TiO_2 and 5 mg soot. The x-axis represents the pixel values (0=completely black; 255=clear white) and the y-axis shows the number of pixels that were counted for every pixel value.

Besides the graph, the picture for each time interval is presented for visual understanding of the soot degradation process as shown in Figures 4, 6 and 8.

When looking at these histograms and photographs underneath, it is clear to state that soot degradation by TiO_2 surface application on asphalt samples and activation by UV-irradiation is possible. The surface of every sample after 56 days is significantly "cleaned" compared to the first day and also the graphs show a shift in peak to lighter areas or a decline in peak for the darker areas, confirming this trend. Although no exact stoichiometric reaction is available, it is expected that the organic soot and carbon is oxidized and converted into CO_2, H_2O and mineral acids, which can be seen in the preliminary stoichiometric equation underneath [18].

$$organic + O_2 \xrightarrow{TiO_2} CO_2 + H_2O + mineral\ acids \qquad (airborne\ pollutants)$$

$$C + O_2 \xrightarrow{TiO_2} CO_2 \qquad (deposited\ pollutants)$$

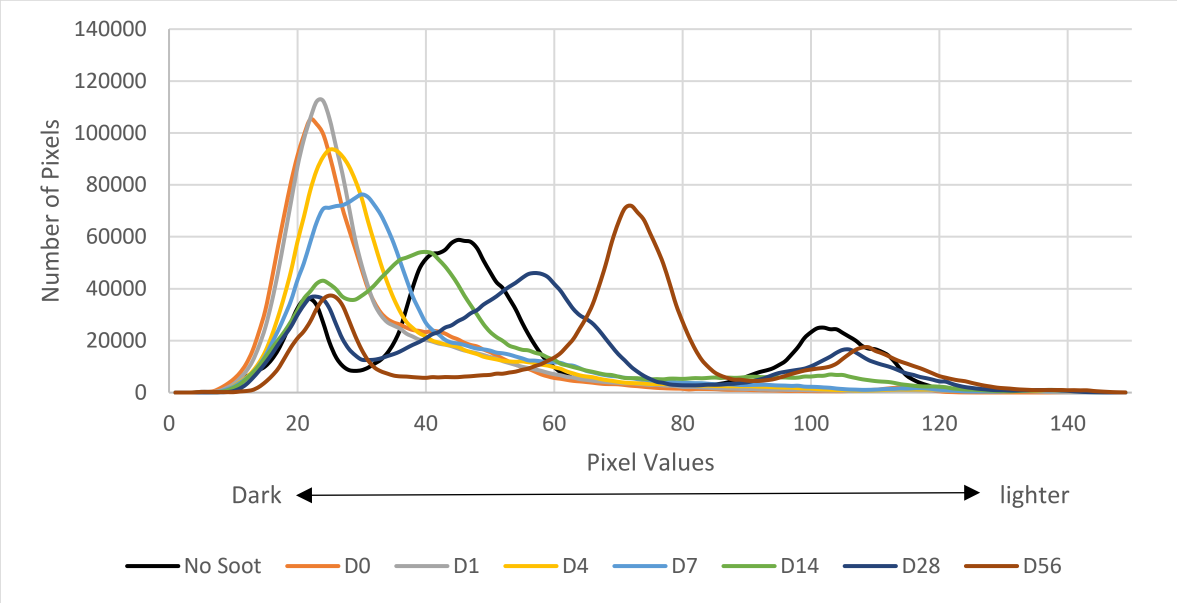


Figure 3. Histograms of the T200/S2 sample showing the soot degradation from D0 to D56.

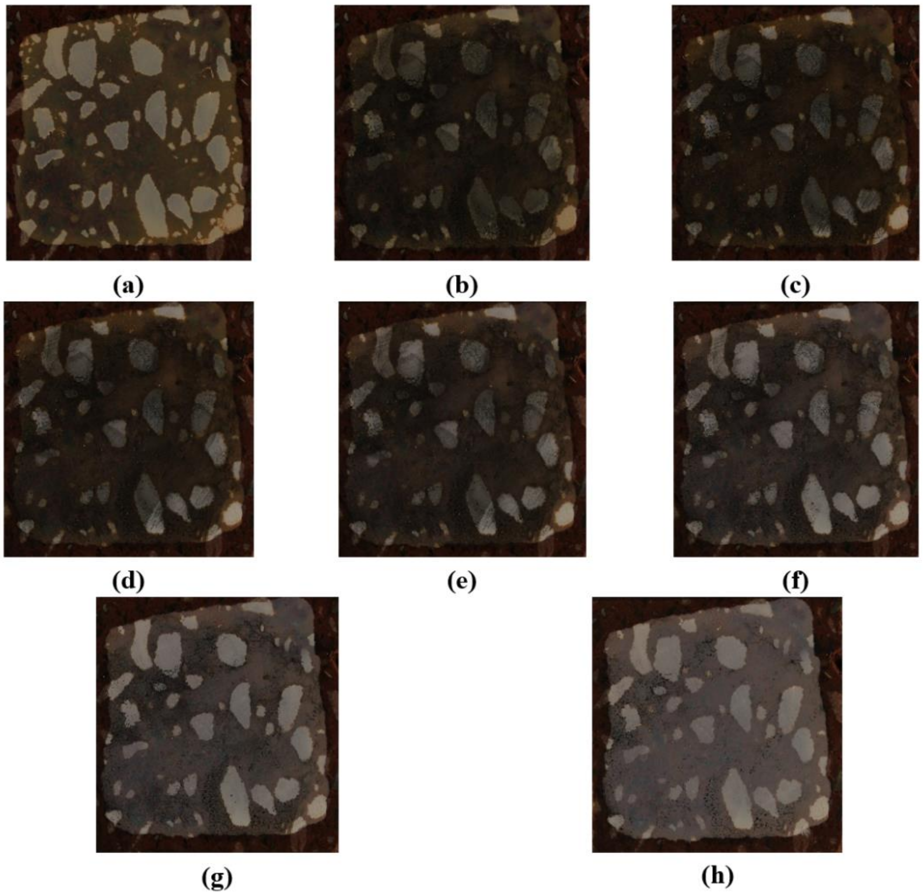


Figure 4. Comparison for each image of the asphalt surface for sample T200/S2: (a) No Soot; (b) Day 0; (c) Day 1; (d) Day 4; (e) Day 7; (f) Day 14; (g) Day 28; (h) Day 56.

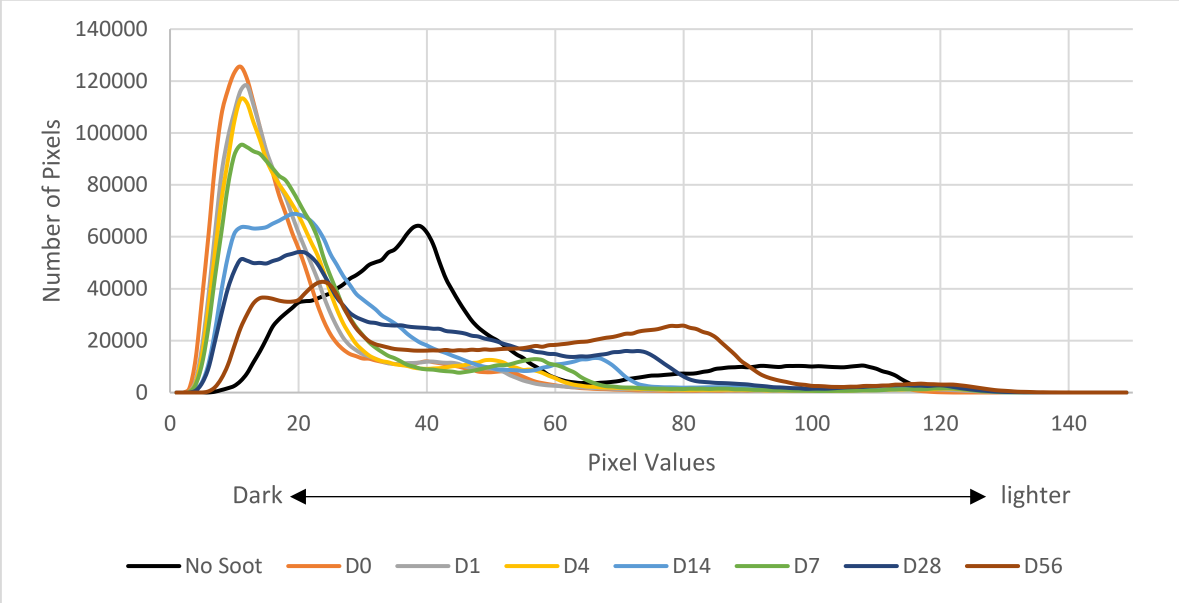


Figure 5. Histograms of the T100/S8 sample showing the soot degradation from D0 to D56.

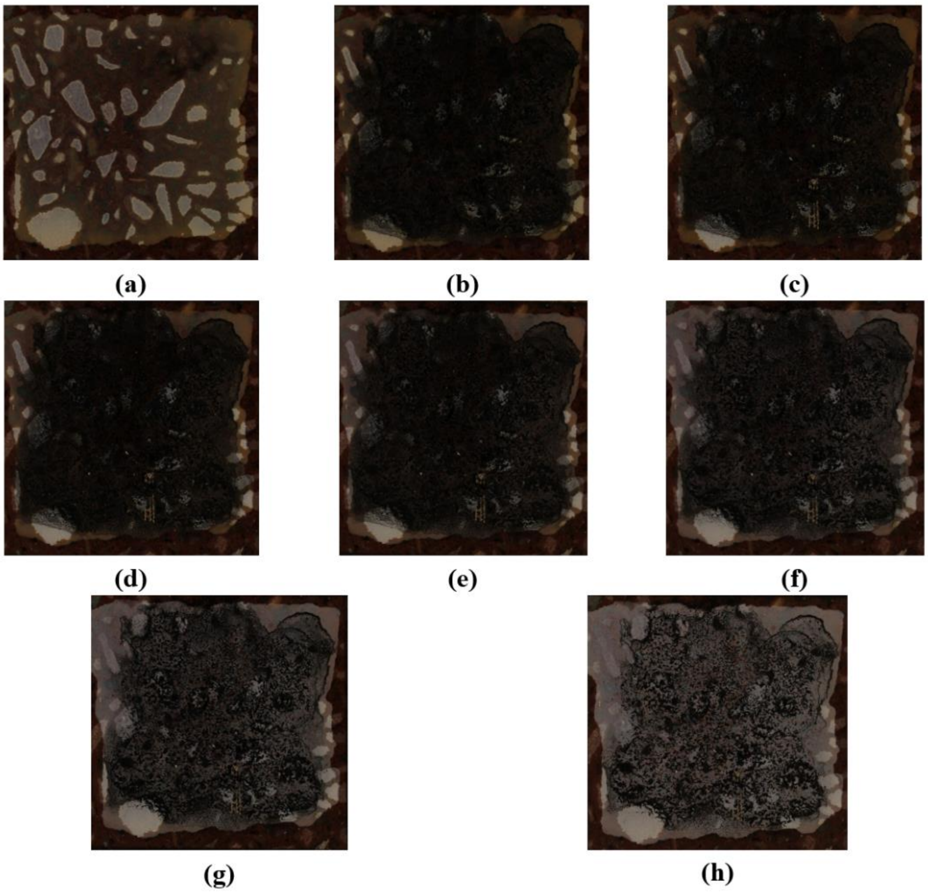


Figure 6. Comparison for each image of the asphalt surface for sample T100/S8: (a) No Soot; (b) Day 0; (c) Day 1; (d) Day 4; (e) Day 7; (f) Day 14; (g) Day 28; (h) Day 56.

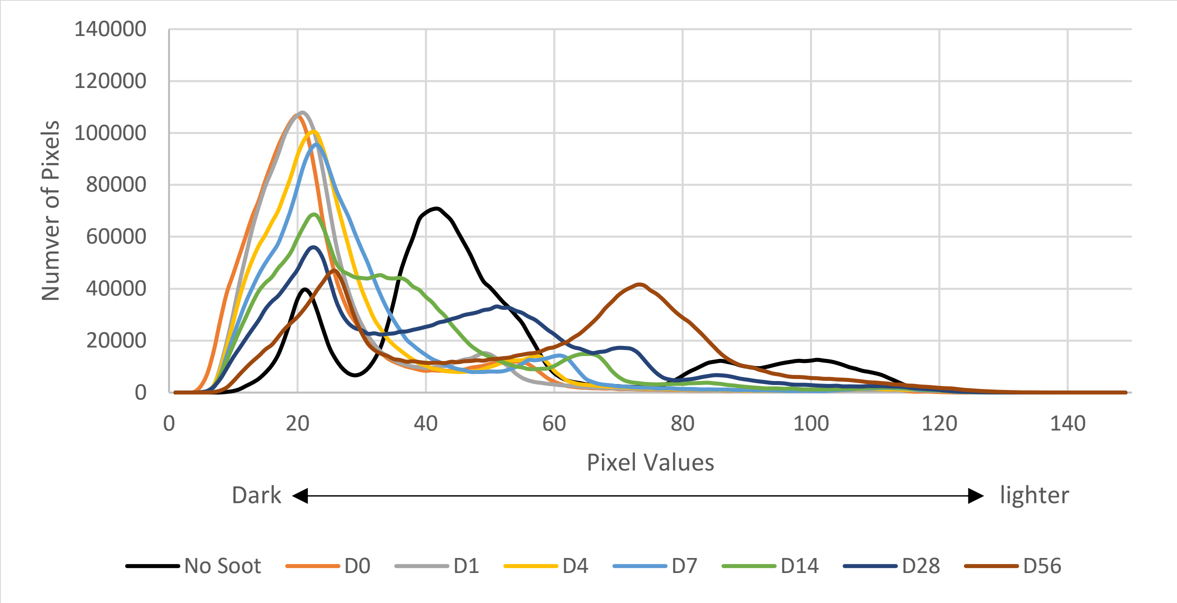


Figure 7. Histograms of the T150/S5 sample showing the soot degradation from D0 to D56.

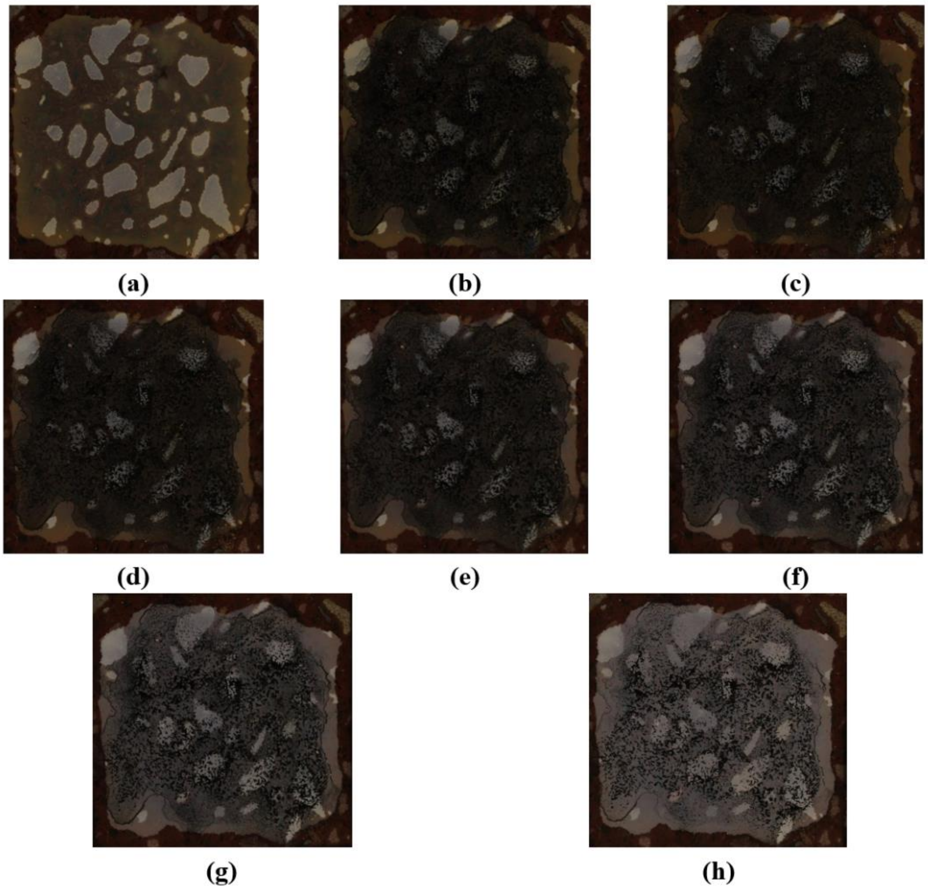


Figure 8. Comparison for each image of the asphalt surface for sample T150/S5: (a) No Soot; (b) Day 0; (c) Day 1; (d) Day 4; (e) Day 7; (f) Day 14; (g) Day 28; (h) Day 56.

The general progress, for every sample, showed that no significant degradation should be expected during the first time intervals until day seven. After seven days, some samples already had some substantial degradation while clear changes in the spectrum could only be observed after day 14 for all the samples. After day 14, the curve of every histogram kept declining and shifted more to the right, meaning further degradation of the soot particles and therefore successful results. Even though some soot residue is still left on the asphalt surface, there is some clear degradation and the results are similar to various other papers published concerning soot degradation in general. Van Hal et al. (2019) published results where soot degradation on glass slides is evaluated and some similar amount of residue is still left after 65 days [17]. In another study by Smits et al. (2013) soot residues are found on the surface of the cementitious material as well [10].

Although the trend in soot degradation is comparable with the studies mentioned in the previous paragraph, some remarkable differences can be observed as well. The most important difference is the speed of degradation which is considerably higher in the studies by Smits et al. (2013) and also Van Hal et al. (2019) achieved some clear degradation after already a few days. They respectively reported approximately 60% of soot degradation during the first 48 hours and some significant changes after 120 hours [10, 17]. Although it varies for some different dosages, the results in this section showed considerable degradation can be observed during the second week of the experimental process. During the first time intervals (Day 1, 4) some small shifts- and decrease of peaks can be observed but will remain rather negligible. After 7 days it is possible to detect some substantial degradation for a couple of samples. However, the largest changes become visible after 14 days, which is relatively slow compared to the other studies. The reason for this slower degradation may be due to the differences in soot- and TiO_2 dosages and perhaps reactions with the base materials such as binder and mixture. Although the study by Van Hal et al. (2019) uses a similar amount of TiO_2, soot levels are almost half or even four times less [17]. The same reason can be concluded for the study by Smits et al. (2013) where TiO_2 dosages are noticeably higher and soot dosages considerably lower, resulting in an obvious increase in degradation efficiency [10]. The dosages used in these tests are significantly higher compared to some realistic values (± 2,5 $\mu g/m^2$ on the highway of Antwerp according to the "Vlaamse Milieumaatschappij") and therefore even more positive results are expected in real life. Unfortunately the scale was accurate until 1 mg and therefore it wasn't possible to follow these realistic values and a comparison between larger values was opted.

Some remarkable observations can be made from Figure 3. Several histograms, i.e. day 28 and 56, shift over the reference histogram ("No-Soot"), resulting in a more clear surface compared to the initial surface, and therefore a degradation >100%. Certainly when looking at Figure 4, which shows some soot residue, 100% degradation seems unlikely and therefore results should be interpreted carefully. When comparing the first- (a) and last picture (h) of figures 4, 6 and 8, a change in colour of TiO_2 can be observed, becoming more greyish, which might be the reason for this shift of histograms. Although a lot of changes for TiO_2 surface properties have been identified after UV-irradiation, i.e. changes in roughness, microhardness, resistance to thermal degradation etc. [19], changes in colour have not been studied elaborately. A couple of reasons for this change in colour could be due to the reactions between TiO_2 and asphalt surfaces or binders. Another possibility is a change in colour due to colour properties such as absorption and scattering which could be affected by defects in TiO_2 energy states. Photons with energy levels less than the band gap of TiO_2 could be absorbed and affect the colour of TiO_2 [20]. A different reason, which needs some further investigation, is the change in colour due to the presence of deposited soot particles on the surface.

Some additional remarks can be made for the analysis technique since it is very difficult to convert this graphical data into analytical data. First of all, the problem mentioned above, the graphs shifting beyond the zero-sample, make it very difficult to use the area underneath the histogram to define the soot degradation. This would result in >100% degradation, which is impossible and, when looking at Figure 4, also not the case. Secondly, no photographs of the samples were taken before adding TiO_2, making a comparison using formulas based on the original state [17] impossible as well.

In order to improve future results, following remarks are suggested when repeating the experiment. It is important to include more "zero-samples" or control samples to improve the interpretation of the results. Taking pictures before adding TiO_2 is one of the improvements but adding more samples with no soot, no TiO_2, only TiO_2, … and analysing them at all time intervals will be very valuable as well. Also, the application of TiO_2 and soot should be handled more carefully in order to guarantee clean and similar coverage over the surface for every sample.

3.2. Bitumen modification

3.2.1. FTIR

Below, all relevant results obtained by the FTIR are presented to evaluate the chemical effect of TiO_2 incorporation in binders as well as the effect of the UV-ageing. First of all, the effect of ageing will be discussed using the ICO and ISO, carbonyl and sulfoxide indices, see Figure 9 and 10. Lastly, the influence of TiO_2 on the chemical composition will be discussed and seen in Figure 12 and 13.

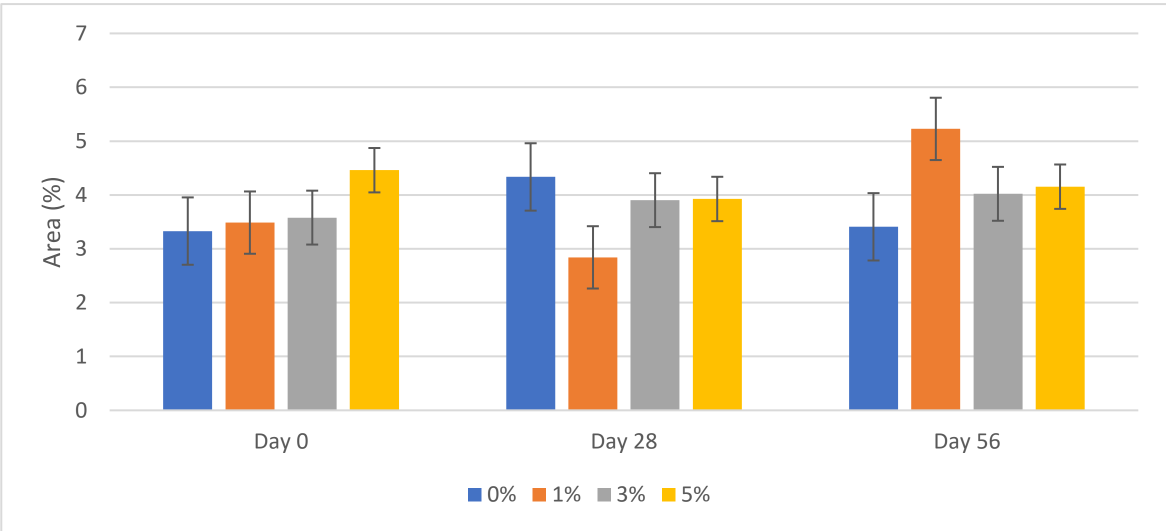


Figure 9. Evaluation of ICO-Area for every bitumen sample using FTIR.

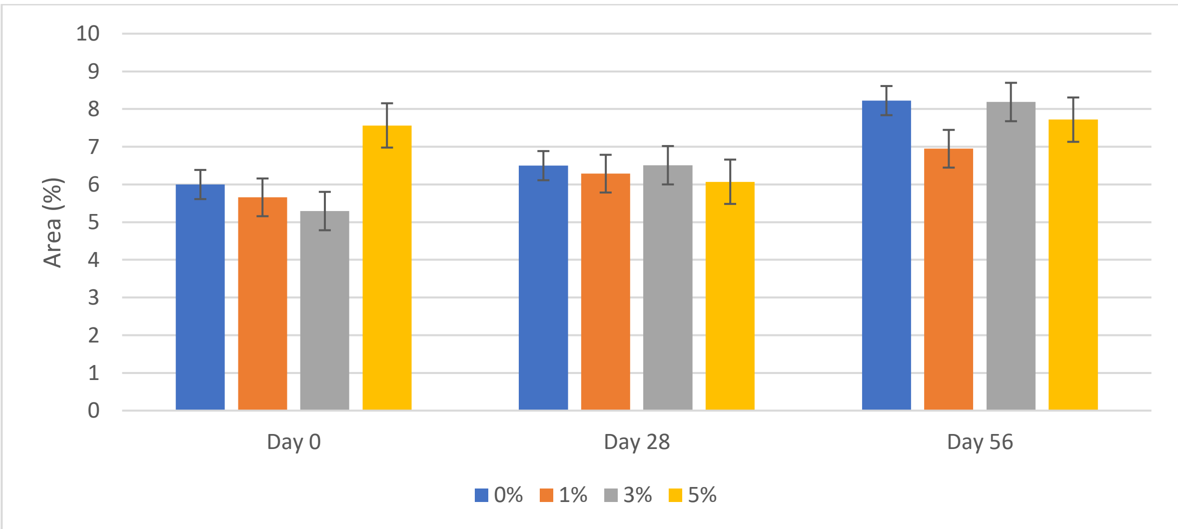


Figure 10. Evaluation of ISO-Area for every bitumen sample using FTIR.

Carbonyl and sulfoxide indices are situated between wavelengths 1655-1760 cm^{-1} and 986-1047 cm^{-1}, respectively. Both indices are related to ageing and the general hypothesis, following the literature, should be an increase for both parameters proportional with ageing [13, 21-24]. Figure 9 is inconclusive and shows no increase for the carbonyl index, as the value varies around the same level after 28 and 56 days of ageing. Figure 10, the sulfoxide index, shows a slight increase for every percentage, except 5%. Although there is a small increase, this does not match the expected trend which can be found in literature and seen in Figure 11, which shows two graphs, comparing the carbonyl- and sulfoxide indices for three different types of binder [24]. These samples are aged using the rolling thin film oven test (RTFOT), simulating short-term ageing, and subsequently conditioned with a pressure ageing vessel (PAV), in order to simulate the long term ageing. It is clear that the increase of both parameters is a lot higher compared to the results above and this trend is confirmed by Yaseen et al. (2020) [23].

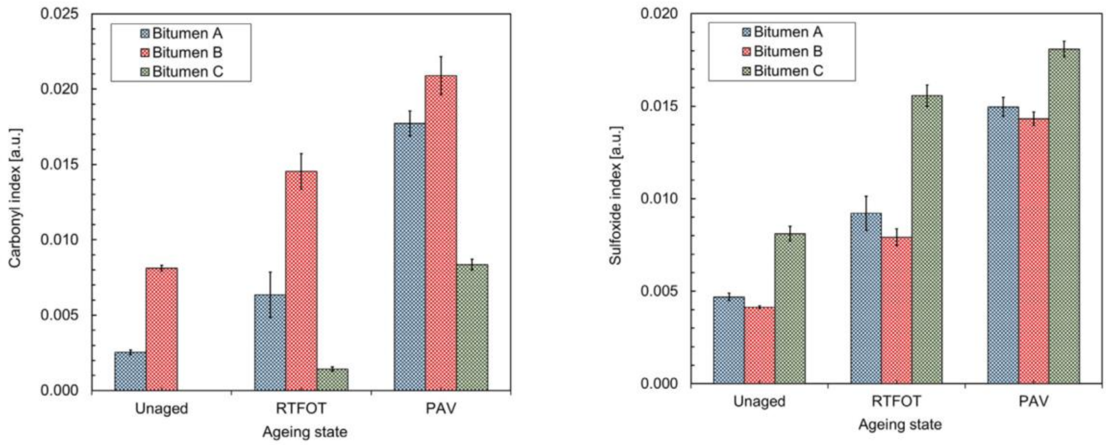


Figure 11. Effect of ageing on the (a) carbonyl- and (b) sulfoxide indices [24].

The explanation for this observation might be the preparation of these specific samples. Firstly some tests were performed where the surface of the bitumen was placed on the FTIR-diamond but contact and workability of this method decreased significantly. Secondly, hot bitumen samples were mixed and drop cast on top of the FTIR-diamond to improve contact. It is proven that only the upper layers of bitumen absorb UV radiation and thus this technique resulted in a loss of "ageing-information" [25]. Therefore no conclusive answer concerning UV-ageing of carbonyl and sulfoxide indices can be proposed. A different reason could be UV-ageing itself which is less significant compared to ageing with RTFOT and PAV [25, 26]. A combined technique of UV-irradiation and RTFOT/PAV might deliver some better results. Although this observation is inconclusive about ageing of carbonyl and sulfoxide indices, it gives rise to the assumption that no new functionalities in sulfoxide- or carbonyl-related groups are introduced due to the incorporation of TiO_2 [13]. Since TiO_2 is mixed with the full binder, it should be distributed over the whole sample and therefore this conclusion won't be affected by the mixing of the binder.

When evaluating the influence of TiO_2 in asphalt binders, clear changes can be observed. Figures 12 and 13 clearly show changes related to the incorporation of TiO_2. First of all, differences can be distinguished in the spectrum of Figure 12 which can be linked to TiO_2. When evaluating wavelengths between 0 and ±700 cm^{-1} an increase in total area is seen when adding a higher percentage of TiO_2. This trend can be seen for day 0, day 28 and day 56, and is due to the Ti-O-Ti stretching at 657 cm^{-1} and vibration of Ti-O-O at 590 cm^{-1} [13, 21, 22]. Subsequently, these values are plotted for every percentage and time interval in Figure 13 and show a quasi-linear trend with R^2=0,9347 (day 0). This linear trend has been reported by Rocha Segundo et al. (2020) as well, although this study was a lot more precise with R^2=0,9999 [13].

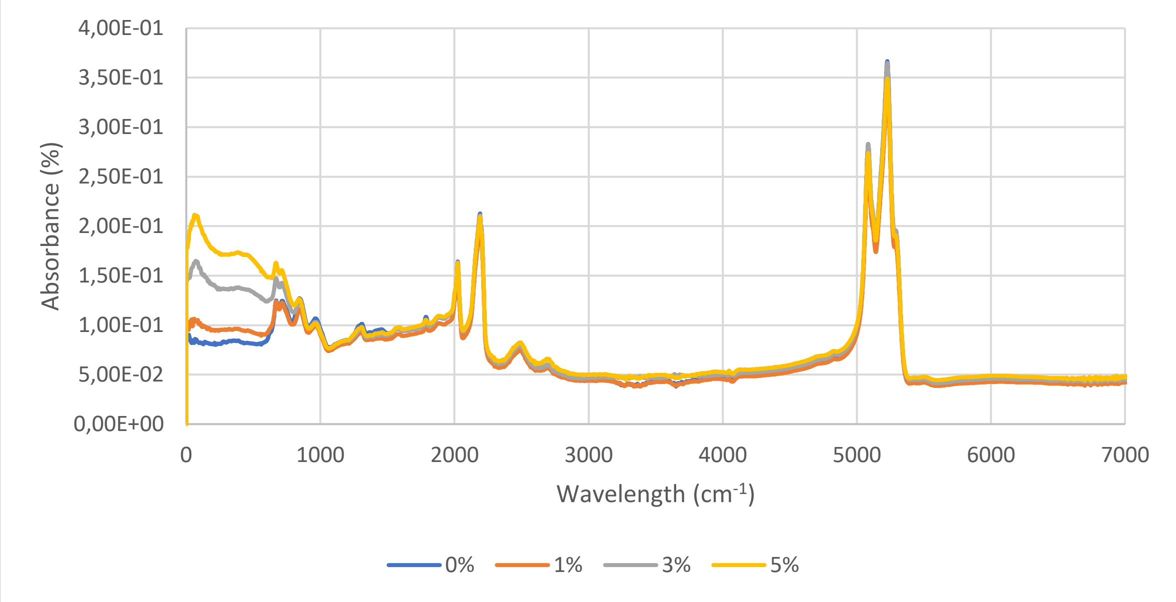


Figure 12. FTIR spectrum for all TiO2 percentages at day 0.

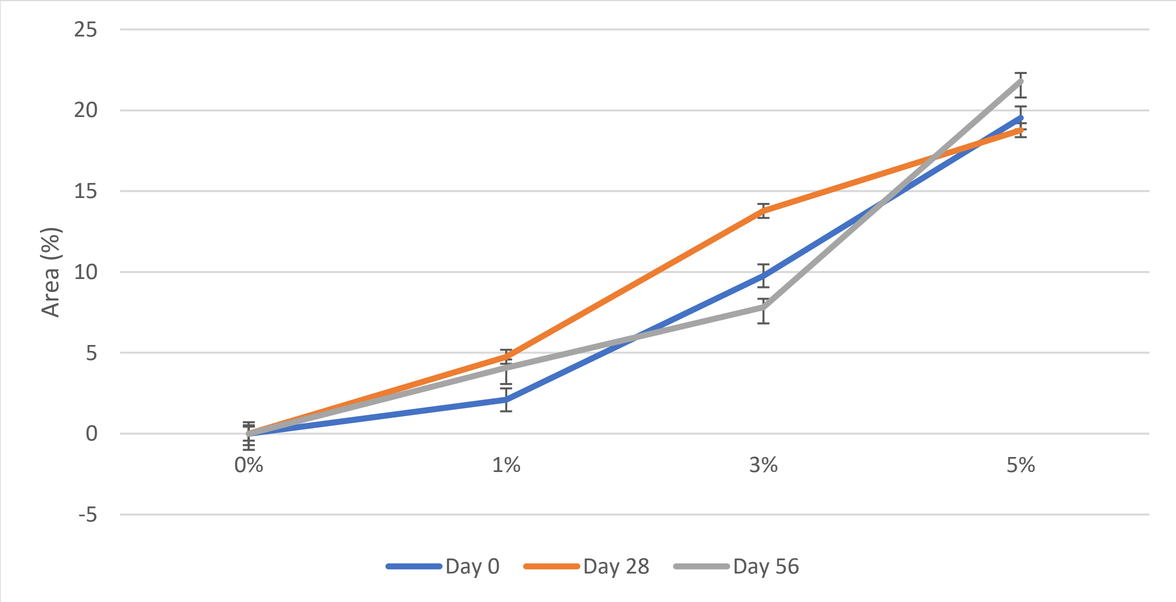


Figure 13. Evaluation of TiO_2-Area for every bitumen sample using FTIR.

Results by the FTIR prove the influence of TiO_2 on the chemical structure of the binder. Although some specific changes can be seen, the direct influence on the rheological parameters should be examined further before drawing any conclusions. Various tests such as DSR (master curve and black diagram), penetration and softening point, dynamic viscosity, LAS test, MSCR etc. test are suggested, to obtain a thorough insight into the effect of chemical/physical changes.

3.2.2. DSR

This section discusses the outcome of the DSR test, more specifically the master curve and black space diagram, as shown in Figure 14 and 15. As mentioned, two different percentages of TiO_2 (0% and 5%) have been evaluated at two different time intervals and for each sample two replicates are tested.

The complex modulus (G*) was plotted on the y-axis and the frequency was plotted on the x-axis.

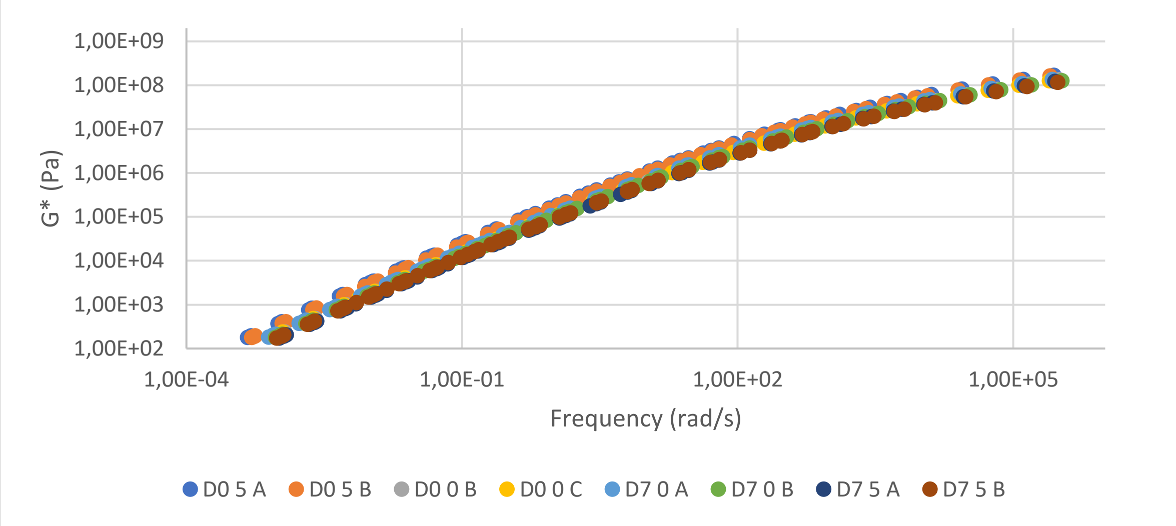


Figure 14. Master curve with frequency sweep in this study.

The DSR results clearly show no critical changes by adding 5% TiO_2 or by UV-ageing the sample over 7 days. There is some small difference between most of the samples and the samples of 5% at day zero but this variation is negligible and probably due to some human errors during the tests since these samples were tested first (i.e. bad trim, poor preparation). Although it seems that UV-ageing doesn't affect the viscoelastic behaviour of the binder, a more careful interpretation is necessary. Just as mentioned for the FTIR above, these samples are mixed first before tested and therefore a lot of information concerning the ageing disappears, since only the surface of the sample is aged.

When comparing these results with previous studies, similar results can be found for the same percentages of TiO_2. Zhang et al. (2021) reported only small and insignificant changes in phase angle and complex modulus by incorporating TiO_2 [27]. Furthermore, this study shows, even though there are some small changes, the gradient of the curve won't be affected, which is of great importance [27]. This result is confirmed by Rocha Segundo et al. (2020) who also reported no evidence for a noticeable effect in viscoelastic behaviour by the addition of TiO_2 up to 10% [13]. At last, Noor et al. (2018) also reported only a slight increase in phase angle for asphalt with 10% TiO_2 confirming all these observations and studies [28].

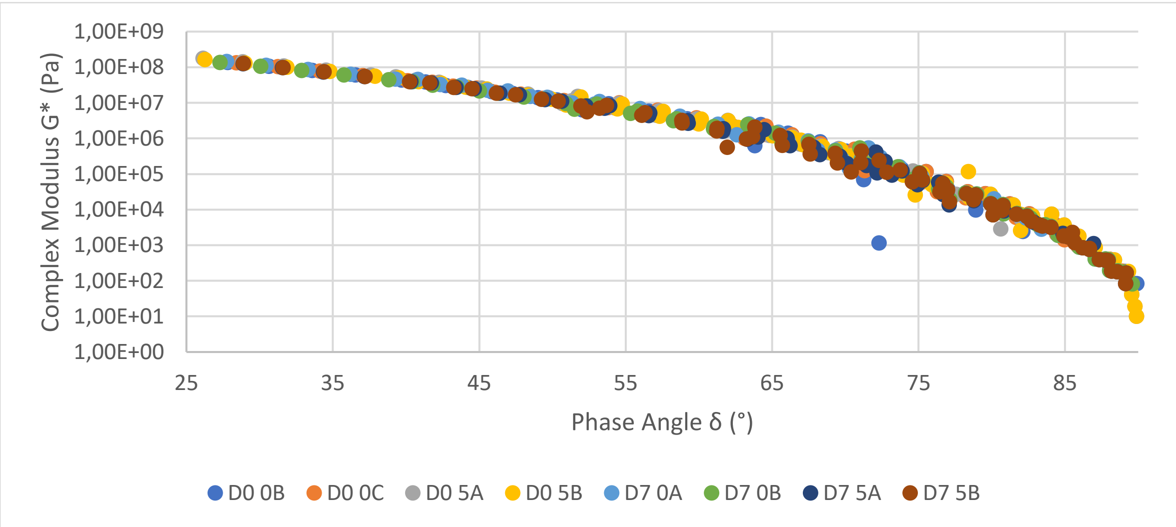


Figure 15. Black Space Diagram in this study.

All the abovementioned trends are also confirmed by the Black Space Diagram, seen in Figure 15. It is quite clear that all the samples, except for a few measurements, follow the same gradient and result in the same rheological behaviour. The B50/70 shows a simple viscoelastic behaviour with the phase angle gradually approaching the viscous asymptote of 90° at elevated temperatures and a conventional black diagram curve [13].These results also confirm that, on first sight, the incorporation of TiO_2 has only limited, to none, influence on the rheological parameters of bitumen. Rocha Segundo et al. (2020) confirm the trend, following the black diagram, as well and state that the addition of TiO_2 has a small, rather insignificant, effect on the viscoelasticity of the binder [13].

5. Conclusions and recommendations for further research

A lot of tests have been evaluated and therefore a lot of conclusions can be made based on the results while also recommending some improvements for further experiments.

First of all, and most important, it is clear that TiO_2 is capable to degrade soot over a relatively short period of time. Although the dosages were rather high, compared to realistic values, degradation is visible for every single sample and can be proven by the graphs as well as by comparing several images. In order to refine future experiments, a lot of improvements can be made, such as improving the photobox to make sure the background can be eliminated easily. Also the boundaries of the sample itself can be improved by using bright tape for example. When using a bright colour, the peak referring to this colour can be removed and won't be taken into account when evaluating the samples. Furthermore, an expansion of samples is necessary to obtain a thorough insight into the degradation of soot samples. Not only an expansion of test samples is necessary, but an expansion in control samples is crucial as well, i.e. samples with no surface coating, only soot, only TiO_2, ... Some further examinations in regard to the change of colour of TiO_2, are suggested as well (e.g. rinsing of the sample to check whether the change is due to the deposition of soot particles).

Secondly, it is shown, using FTIR, that the incorporation of TiO_2 does not affect carbonyl and sulfoxide indices. The influence of UV-ageing on these parameters is evaluated but a conclusion cannot be made due to a loss of information when mixing the binder. For future experiments, thin-film samples should be used, instead of a homemade silicon mould, and this should be aged under UV-light at a higher temperature (e.g. 50°C) in order to guarantee workability on the FTIR. The influence of TiO_2 can be observed at wavelengths beneath 1000 cm^{-1} and a quasi-linear trend can be distinguished. Although this trend could be observed, the actual rheological effect needs some further examination.

At last, some limited rheological tests have been evaluated using DSR. These results show no impact of TiO_2 on the rheological behaviour of this specific binder. For this experiment, thin films have to be used as well in the future, to guarantee the ageing over the whole sample, so no information gets lost when mixing the sample. Also, a more detailed approach should be expected when preparing the samples to limit the differences between samples due to inaccuracies when trimming etc.

To conclude, it is clear that TiO_2 can have an important role in air-purifying roads since degradation is clearly observed while chemical- and rheological parameters are relatively unaffected.

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